Phenomenological theory of unconventional superconductivity

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This article is a review of recent developments in the phenomenological description of unconventional superconductivity. Starting with the BCS theory of superconductivity with anisotropic Cooper pairing, the authors explain the group-theoretical derivation of the generalized Ginzburg-Landau theory for unconventional superconductivity. This is used to classify the possible superconducting states in a system with given crystal symmetry, including strong-coupling effects and spin-orbit interaction. On the basis of the BCS theory the unusual low-temperature properties and the (resonant) impurity scattering effects are discussed for superconductors with anisotropic pairing. Using the Ginzburg-Landau theory, the authors study several bulk properties of such superconductors: spontaneous lattice distortion, upper critical magnetic field, splitting of a phase transition due to uniaxial stress. Two possible mechanisms for ultrasound absorption are discussed: collective modes and damping by domain-wall motion. The boundary conditions for the Ginzburg-Landau theory are derived from a correlation function formulation and by group-theoretical methods. They are applied to a study of the Josephson and proximity effects if unconventional superconductors are involved there. The magnetic properties of superconductors that break time-reversal symmetry are analyzed. Examples of current and magnetic-field distributions close to inhomogeneities of the superconducting order parameter are given and their physical origin is discussed. Vortices in a superconductor with a multicomponent order parameter can exhibit various topological structures. As examples the authors show fractional vortices on domain walls and nonaxial vortices in the bulk. Furthermore, the problem of the possible coexistence of a superconducting and a magnetically ordered phase in an unconventional superconductor is analyzed. The combination of two order parameters that are almost degenerate in their critical temperature is considered with respect to the phase-transition behavior and effects on the lower and upper critical fields. Because heavy-fermion superconductors—which are possible realizations of unconventional superconductivity—have been the main motivation for the phenomenological studies presented here, the authors compare the theoretical results with the experimental facts and data. In particular, they emphasize the intriguing features of the compound UPt_3 and consider in detail the alloy $U_{1-x}Th_xBe_{13}$.

CONTENTS

I. INTRODUCTION

In the last decade great achievements in the field of superconductivity have reopened an intense and exciting discussion of this phenomenon in condensed-matter physics. Superconductivity, once called one of the best understood many-body problems in physics, became again a problem full of questions, mystery, and challenge. This new era was initiated when in heavy-fermion materials—a class of materials close to magnetic instabilities—astonishingly superconductivity was discovered, first in $CeCu_2Si_2$ by Steglich *et al.* (1979), then in UBe_{13} (Ott *et al.*, 1983) and UPt_3, (Stewart *et al.*, 1984). In 1986 the general public also became aware of the new developments when Bednorz and Müller (1986) opened the era of high-T_c (or CuO) superconductors by their discovery of superconductivity in $(La,Sr)_2CuO_4$. There followed an intense investigation of the class of copper-oxide materials, which led to further discoveries of superconducting systems, one exceeding the other in their critical temperatures: the Y-Ba-Cu-O system (Wu *et al.*, 1987), the Bi-Sr-Ca-Cu-O system (Maeda *et al.*, 1988), and the Tl-Ca-Ba-Cu-O system (Sheng and Hermann, 1988). These new superconductors exhibit unconventional properties, the heavy fermions much more significantly than the Cu superconductors. For the latter the ordinary BCS theory seems to fit most of the features of the superconducting state. A great effort in experiment as well as in theory has been stimulated and is still going on. Even if there is a difference of more than two orders of magnitude between the T_c's of the two classes, they share the common feature of being systems of strongly correlated electrons.

Another class of recently discovered superconducting materials are the so-called organic superconductors. The first superconducting compound, $(TMTSF)_2PF_6$, was reported in 1980 by Jérome *et al.* Further investigations led to various compounds of the type $(BEDT\text{-}TTF)_2ReO_4$ (Parkin *et al.*, 1983) with higher transition temperatures, actually reaching 12.8 K (Kini *et al.*, 1990). The most intriguing aspect of this class of superconductors is the fact that in the normal state they are low-dimensional conductors.

In this article we shall concentrate on the heavy-fermion superconductors, since they show the most significant differences from conventional superconductors. Heavy fermions are compounds containing rare-earth or actinide ions whose f-shell electrons are strongly correlated. These f electrons determine the properties of quasiparticles at the Fermi level, giving rise to a large effective mass, observed in an extremely large γ factor of the linear part in the low-temperature specific heat, and at the same time a similarly enhanced Pauli spin susceptibility $\chi(0)$. Hence the characteristic temperature is also quite small: $T_F \sim 10-50$ K. When we consider the superconducting members of this group of materials—the transition temperature is in the range of $0.5 \sim 1$ K (see Table XIII)—a measurement of the ratio $(C_s - C_n)/C_n$ at T_c gives in all compounds a value of the order of one. This suggests that the superconductivity is produced mainly by the heavy quasiparticles. It was argued, using the picture of the BCS theory of superconductivity, that these quasiparticles with f characters would have difficulty forming ordinary s-wave Cooper pairs due to the strong Coulomb repulsion. To avoid a large overlap of the wave functions of the paired particles, the system would rather choose an anisotropic channel, like a p-wave spin triplet or a d-wave spin singlet state, to form pairs, as is done in superfluid ^3He (p-wave spin triplet pairing).

In many respects the analogy with ^3He is a good guide for the interpretation of experimental results in the heavy-fermion superconductors. The first experimental support for the idea of anisotropic pairing was found in the observation by Ott *et al.* (1984) of the T^3 law in the specific heat of UBe_{13}. It is a property of superconductivity due to anisotropic pairing that the gap in the quasiparticle excitation spectrum can have points of zeros or lines of zeros. These yield an excitation spectrum that gives rise to power laws in the low-temperature behavior of various physical quantities instead of the exponential behavior expected for conventional superconductivity. This idea has gained further support as such power laws have been measured in other quantities, such as ultrasonic attenuation, NMR relaxation rate, thermal conductivity, and London penetration depth. Furthermore, the pronounced peak in ultrasonic attenuation observed immediately below T_c in UBe_{13} (Golding *et al.*, 1985) confirmed the similarity to ^3He, which shows this feature too. At least in conventional superconductors the sound attenuation decreases rapidly below the transition temperature. The discovery of double transitions in $(U_{1-x}Th_x)Be_{13}$ by Ott *et al.* (1985) and in UPt_3 by Fisher *et al.* (1989) has a natural place in this picture, since it allows for the existence of several superconducting phases with different symmetry, a well-known feature of ^3He, where we find different phases, the so-called A, A', and B phases.

Thus it became common to speak of *anisotropic superconductivity* in heavy-fermion compounds. This term is applicable in a rotationally invariant system, but becomes ambiguous if the rotational symmetry is reduced due to the presence of a crystal field. Therefore we shall avoid this name in this article and use instead the term *unconventional superconductor,* which will include all superconducting states with any deviation from the ordinary BCS type of pairing state. It will become clear later that this corresponds to a classification according to the symmetries broken by the superconducting state. In this respect a superconductor is *conventional* if it breaks only the U(1) gauge symmetry.

Even if the analogy between superfluid ^3He and heavy-fermion superconductors provides a rather fruitful basis for understanding the latter, it should not be pushed too far. There are important differences between these two systems—to mention only one, the presence of a crystal field. Furthermore, in heavy-fermion superconductors charged particles are paired instead of neutral atoms as in ^3He. The strong correlation effects and the spin-orbit interaction in heavy-fermion systems may also change the picture. Throughout this article we shall point out these differences wherever they are important.

For the superfluidity of ^3He the responsible mechanism could be identified. Spin fluctuations play a major part in the potential which produces the anisotropic pairing (for a review, see Leggett, 1975). In heavy-fermion materials, the problem turns out to be much more complicated, since for most systems a simple Fermi-liquid theory is not sufficient to describe their normal-state properties. At present no satisfactory explanation for their superconductivity has been given. On the other hand, problems in the identification of the symmetry of the superconducting phase have motivated a widespread effort at working out the properties of unconventional superconductors on the level of phenomenological theories, applying the idea of the Ginzburg-Landau theory. This type of theory based on group theory allows us to describe the specific properties of each system in a simple way, without a detailed knowledge of the microscopic background. The main purpose of the present article is to review these recent theoretical developments and their application to the heavy-fermion superconductors. For general aspects of the heavy fermions and their superconductivity various reviews are available—in theory by Varma (1985), Lee *et al.* (1986), Gor'kov (1987), and Fulde *et al.* (1988), and in experiment by Stewart (1984), de Visser *et al.* (1987), Ott (1987a, 1987b), Rauchschwalbe (1987), Fisk *et al.* (1988), and Grewe and Steglich (1989).

We give here a short outline of this article:

In Sec. II we develop the phenomenological theory (Ginzburg-Landau theory) of unconventional superconductivity using the concept of the Landau theory for the second-order phase transitions. For that purpose we briefly review the BCS theory of superconductivity with anisotropic pairing, to introduce the symmetry properties of the order parameter. The order parameters will be characterized by irreducible representations of the symmetry group of the Hamiltonian. The relevant symmetry group is specified and the action of the group elements on the order parameter is described there. To determine stable superconducting states, we examine the Ginzburg-Landau free energy constructed as an expansion in the order-parameter space of each representation. The resulting symmetry classification of superconducting states and the generalized Ginzburg-Landau free energy will be the starting point of the analysis in the following sections.

In Sec. III we discuss bulk properties of the unconventional superconductors. As a first point we consider the power-law behaviors mentioned above and analyze the effects of impurity scattering using typical examples of a spherically symmetric system. As a next point, phenomena associated with the phase transitions are discussed using the Ginzburg-Landau formulation. We consider first spontaneous crystal lattice deformation due to the breakdown of the crystal symmetry by the superconducting order parameter. Conversely, if the symmetry of the crystal is externally lowered, a splitting of the transition may occur for order parameters that originally belong to a multidimensional irreducible representation. Next we look at the anisotropy of the upper critical field $\mathbf{H}_{c2}$. Finally, we consider a possible mechanism for the ultrasonic attenuation peaks close to T_c: the existence of collective modes and the domain-wall damping mechanism.

In Sec. IV we turn to problems connected with the boundary of a superconductor. In an unconventional superconductor the order parameter is strongly influenced by the boundary, in contrast to an ordinary *s*-wave superconductor. After a derivation of the boundary condition by the correlation function method, we discuss the corresponding formulation in the Ginzburg-Landau theory on the basis of group-theoretical arguments. As an extension of vital experimental importance, we consider the problems of the Josephson effect and the proximity effect.

The breakdown of time-reversal symmetry at a second-order phase transition is a general feature of materials with magnetic ordering. Among the unconventional superconducting states are several that likewise are not invariant under time-reversal operation. We shall indicate how magnetic behaviors occur in these systems. In particular, we concern ourselves with magnetic properties associated with inhomogeneous structures of the superconducting phase.

Vortices are magnetic properties of unconventional as well as conventional superconductors. However, the vortices in an unconventional superconductor can show various structures. We explain the possibility of fractionally quantized vortices and stable nonaxial vortices for a superconducting phase with multicomponent order parameter. The discussion of magnetic properties in Sec. V is completed by an analysis of the possible coexistence of superconductivity and antiferromagnetism.

In Secs. II–V we restrict our analysis to a single representation in order-parameter space. However, such a decoupling of a single representation is not always allowed. Section VI is devoted to the special phase-transition behavior and the lower and upper critical fields of two representations that have only slightly different transition temperatures.

In this review we try to describe some of the basic phenomena expected for unconventional superconductors and at the same time illustrate them by typical simple examples. To this end we conclude with a discussion of experimental results on heavy-fermion systems in the light of the theories developed in this article (Sec. VII).

The theories presented here were developed mainly to describe effects in heavy-fermion superconductors. Nevertheless, the general aspects of these theories may also be applicable to the class of CuO or organic superconductors. Regardless of the microscopic mechanism causing the superconducting instability, which may be essentially different in these classes, the concept of the Ginzburg-Landau theories is based only on very general properties of second-order superconducting transitions. It is our hope that many of the phenomena discussed in this article might offer possible tests for the unconventional nature of the superconductivity.

II. CLASSIFICATION OF THE SUPERCONDUCTING STATES

A. BCS theory of anisotropic superconductivity

In 1957 Bardeen, Cooper, and Schrieffer proposed their theory of superconductivity as the first successful explanation for the microscopic origin of this phenomenon (Bardeen Cooper and Schrieffer, 1957). Their theory is based mainly on the discovery that the degenerate state of a normal Fermi gas is unstable if an attractive potential between the fermions is present (Cooper, 1956). The stable ground state is a coherent state in which the electrons are combined into pairs (so-called Cooper pairs), but with a rather large extension compared with the spacing between electrons in the gas and with a vanishing total momentum. Effectively, it is a pairing in momentum space rather than in real space. The potential has its origin in electron-phonon coupling, which yields an attractive region in a thin layer near the Fermi surface in the momentum space. It has been found that the only attractive channel of this potential is the isotropic channel which leads to electron pairs with a relative s-wave symmetry (spin singlet configuration). Most of the known superconductors can be described in a convincing manner by this theory.

The electron-phonon interaction may not be the only possible mechanism to obtain an attractive potential. Other interactions could favor anisotropic pairing, with spin triplet configurations too. Anderson and Morel (1961) and Balian and Werthamer (1963) examined this general type of superconductivity. At the beginning of the sixties a more academic problem, it later became important in the theory of superfluid ^{3}He, in which a spin-fluctuation mechanism is assumed to be responsible for the creation of p-wave (spin triplet) pairs (for a review see Anderson and Brinkman, 1975, or Leggett, 1975). We briefly review here this generalized BCS theory, focusing our attention mainly on the symmetry properties of the superconducting states as the basis of our further studies.

Let us consider a pairing potential in momentum space which leads to the effective Hamiltonian

$$\mathcal{H}=\sum_{\mathbf{k},s}\varepsilon(\mathbf{k})a^{\dagger}_{\mathbf{k}s}a_{\mathbf{k}s}+\frac{1}{2}\sum_{\mathbf{k},\mathbf{k}',s_1,s_2,s_3,s_4}V_{s_1s_2s_3s_4}(\mathbf{k},\mathbf{k}')a^{\dagger}_{-\mathbf{k}s_1}a^{\dagger}_{\mathbf{k}s_2}a_{\mathbf{k}'s_3}a_{-\mathbf{k}'s_4}\ , \tag{2.1}$$

where $\varepsilon(\mathbf{k})$ is the band energy measured relative to the chemical potential μ. The quantity $V_{s_1s_2s_3s_4}(\mathbf{k},\mathbf{k}')$ denotes the matrix element

$$\langle -\mathbf{k},s_1;\mathbf{k},s_2|\hat{V}|-\mathbf{k}',s_4;\mathbf{k}',s_3\rangle$$

[note that V has the following symmetries: $V_{s_1s_2s_3s_4}(\mathbf{k},\mathbf{k}')=-V_{s_2s_1s_3s_4}(-\mathbf{k},\mathbf{k}')=-V_{s_1s_2s_4s_3}(\mathbf{k},-\mathbf{k}')=V_{s_4s_3s_2s_1}(\mathbf{k}',\mathbf{k})$]. The operator $\hat{V}$ is a general effective electron-electron interaction which is attractive in a small range near the Fermi surface [where $-\varepsilon_c\le\varepsilon(\mathbf{k})\le\varepsilon_c$; ε_c is the cutoff energy]. Its physical origin will not be discussed here. In the presence of this attractive potential, the degenerate Fermi gas is unstable.

The Hamiltonian in Eq. (2.1) needs to be treated as a many-body problem. It can be treated in a reasonable way by a mean-field approach. We define a mean field, which is often called a pair potential (we shall later also name it a "gap function"),

$$\begin{aligned}\Delta_{ss'}(\mathbf{k})&=-\sum_{\mathbf{k}',s_3,s_4}V_{s'ss_3s_4}(\mathbf{k},\mathbf{k}')\langle a_{\mathbf{k}'s_3}a_{-\mathbf{k}'s_4}\rangle\ ,\\ \Delta^{*}_{ss'}(-\mathbf{k})&=\sum_{\mathbf{k}'s_1,s_2}V_{s_1s_2s's}(\mathbf{k}',\mathbf{k})\langle a^{\dagger}_{-\mathbf{k}'s_1}a^{\dagger}_{\mathbf{k}'s_2}\rangle\ .\end{aligned} \tag{2.2}$$

The brackets $\langle A\rangle$ denote the expectation value $\mathrm{tr}[\exp(-\beta\mathcal{H})A]/\mathrm{tr}[\exp(-\beta\mathcal{H})]$. We replace the two operators $a^{(\dagger)}_{\mathbf{k}s}a^{(\dagger)}_{-\mathbf{k}s'}$ in Eq. (2.1) by $\langle a^{(\dagger)}_{\mathbf{k}s}a^{(\dagger)}_{-\mathbf{k}s'}\rangle+(a^{(\dagger)}_{\mathbf{k}s}a^{(\dagger)}_{-\mathbf{k}s'}-\langle a^{(\dagger)}_{\mathbf{k}s}a^{(\dagger)}_{-\mathbf{k}s'}\rangle)$. The term in the brackets ( ) is interpreted as the fluctuations of the operator around its mean-field value. If these fluctuations are considered to be small compared with the mean-field value, we can neglect them in orders higher than one, so that $\mathcal{H}$ can be approached by a one-particle Hamiltonian,

$$\tilde{\mathcal{H}}=\sum_{\mathbf{k},s}\varepsilon(\mathbf{k})a^{\dagger}_{\mathbf{k}s}a_{\mathbf{k}s}+\frac{1}{2}\sum_{\mathbf{k},s_1,s_2}[\Delta_{s_1s_2}(\mathbf{k})a^{\dagger}_{\mathbf{k}s_1}a^{\dagger}_{-\mathbf{k}s_2}-\Delta^{*}_{s_1s_2}(-\mathbf{k})a_{-\mathbf{k}s_1}a_{\mathbf{k}s_2}]\ . \tag{2.3}$$

Here we also omitted one term containing only the mean field but no operators, since it gives only a contribution to the ground-state energy. This effective one-particle Hamiltonian is easy to diagonalize in order to find its eigenvalues and the corresponding eigenoperators $\alpha^{\dagger}_a(\alpha_b)$ with the property $\partial_t\alpha^{\dagger}_a=i[\tilde{\mathcal{H}},\alpha^{\dagger}_a]=E_a\alpha^{\dagger}_a$ and $\partial_t\alpha_b=i[\tilde{\mathcal{H}},\alpha_b]=-E_b\alpha_b$. They can be obtained by a (unitary) Bogoliubov (or canonical) transformation,

$$a_{\mathbf{k}s}=\sum_{s'}(u_{\mathbf{k}ss'}\alpha_{\mathbf{k}s'}+v_{\mathbf{k}ss'}\alpha^{\dagger}_{-\mathbf{k}s'})\ . \tag{2.4}$$

The new operators $\alpha^{(\dagger)}_{\mathbf{k}s}$ satisfy the anticommutation relations of fermions and generate the elementary excitations (Bogoliubov quasiparticles) of the system. The use of a four-component notation $[\mathbf{a}_{\mathbf{k}}=(a_{\mathbf{k}\uparrow},a_{\mathbf{k}\downarrow},a^{\dagger}_{-\mathbf{k}\uparrow},a^{\dagger}_{-\mathbf{k}\downarrow})$ and $\boldsymbol{\alpha}_{\mathbf{k}}=(\alpha_{\mathbf{k}\uparrow},\alpha_{\mathbf{k}\downarrow},\alpha^{\dagger}_{-\mathbf{k}\uparrow},\alpha^{\dagger}_{-\mathbf{k}\downarrow})]$ leads to a more compact formulation of Eq. (2.4): $\mathbf{a}_{\mathbf{k}}=U_{\mathbf{k}}\boldsymbol{\alpha}_{\mathbf{k}}$ with

$$U_{\mathbf{k}}=\begin{pmatrix}\hat{u}_{\mathbf{k}} & \hat{v}_{\mathbf{k}}\\ \hat{v}^{*}_{-\mathbf{k}} & \hat{u}^{*}_{-\mathbf{k}}\end{pmatrix}\ \text{and}\ U_{\mathbf{k}}U^{\dagger}_{\mathbf{k}}=1\ , \tag{2.5}$$

where the second equation is the unitarity condition of the transformation. The 2×2 matrices $\hat{u}_{\mathbf{k}}$ and $\hat{v}_{\mathbf{k}}$ are defined by Eq. (2.4). Using this formalism, we can write diagonalization of $\tilde{\mathcal{H}}$ as

$$\hat{E}_{\mathbf{k}}=U^{\dagger}_{\mathbf{k}}\hat{\mathcal{E}}_{\mathbf{k}}U_{\mathbf{k}} \tag{2.6}$$

where we used the 4×4 matrices

$$\hat{E}_{\mathbf{k}}=\begin{pmatrix}E_{\mathbf{k}+} & 0 & 0 & 0\\ 0 & E_{\mathbf{k}-} & 0 & 0\\ 0 & 0 & -E_{-\mathbf{k}+} & 0\\ 0 & 0 & 0 & -E_{-\mathbf{k}-}\end{pmatrix} \tag{2.7}$$

and

$$\hat{\mathcal{E}}_{\mathbf{k}}=\begin{bmatrix} \varepsilon(\mathbf{k})\hat{\sigma}_0 & \hat{\Delta}(\mathbf{k}) \\ -\hat{\Delta}^*(-\mathbf{k}) & -\varepsilon(\mathbf{k})\hat{\sigma}_0 \end{bmatrix} . \quad (2.8)$$

The diagonal elements of $\hat{E}_{\mathbf{k}}$ correspond to the excitation spectrum of the system, and $\hat{\mathcal{E}}_{\mathbf{k}}$ is the representation of $\mathcal{H}$, where $\hat{\sigma}_0$ is the 2×2 unit matrix and $\hat{\Delta}(\mathbf{k})$ the matrix defined in Eq. (2.2). To find the transformation $U_{\mathbf{k}}^{\dagger}$ in the general case we need more insight into the structure of $\hat{\Delta}(\mathbf{k})$. From Eq. (2.2) or (2.3) it is clear that $\hat{\Delta}(\mathbf{k})$ must have the symmetry of a pairing wave function in $\mathbf{k}$ space. The antisymmetric nature of a fermion wave function requires therefore

$$\hat{\Delta}(\mathbf{k})=-\hat{\Delta}^{T}(-\mathbf{k}) . \quad (2.9)$$

For singlet pairing the effective pairing potential $\hat{\Delta}$ has to be an even function $\mathbf{k}$. Therefore $\hat{\Delta}(\mathbf{k})$ is an antisymmetric matrix which can be described by a single even function $\psi(\mathbf{k})$,

$$\hat{\Delta}(\mathbf{k})=i\hat{\sigma}_y\psi(\mathbf{k})=\begin{bmatrix} 0 & \psi(\mathbf{k}) \\ -\psi(\mathbf{k}) & 0 \end{bmatrix} . \quad (2.10)$$

On the other hand, triplet pairing requires odd $\mathbf{k}$ dependence. The matrix is symmetric and, by following the notation of Balian and Werthamer (1963), can be parametrized by an odd vectorial function $\mathbf{d}(\mathbf{k})$,

$$\hat{\Delta}(\mathbf{k})=i(\mathbf{d}(\mathbf{k})\cdot\hat{\boldsymbol{\sigma}})\hat{\sigma}_y =\begin{bmatrix} -d_x(\mathbf{k})+id_y(\mathbf{k}) & d_z(\mathbf{k}) \\ d_z(\mathbf{k}) & d_x(\mathbf{k})+id_y(\mathbf{k}) \end{bmatrix} . \quad (2.11)$$

We use $\hat{\boldsymbol{\sigma}}$ to denote the Pauli matrices. This notation is particularly practical because under spin rotation operation $\mathbf{d}$ transforms like a three-dimensional vector under rotation. Other transformation properties are also easier to handle in this notation than in the matrix form, as will be seen towards the end of this section (Table I). For these $\hat{\Delta}$ matrices we distinguish two types. A matrix $\hat{\Delta}(\mathbf{k})$ is called *unitary* if the product $\hat{\Delta}\hat{\Delta}^{\dagger}$ is proportional to the unit matrix $\hat{\sigma}_0$; otherwise it is called *nonunitary*. Clearly, only triplet pairing matrices can be nonunitary:

$$\hat{\Delta}\hat{\Delta}^{\dagger}=|\mathbf{d}|^2\hat{\sigma}_0+\mathbf{q}\cdot\hat{\boldsymbol{\sigma}} \quad (2.12)$$

with $\mathbf{q}=i(\mathbf{d}\times\mathbf{d}^*)$, which is only finite for $\mathbf{d}(\mathbf{k})\neq\mathbf{d}^*(\mathbf{k})$, i.e., according to Table I, $\mathbf{d}(\mathbf{k})$ is not invariant under time reversal. The physical interpretation of $\mathbf{q}(\mathbf{k})$ is of special interest because it denotes a net spin average $\mathrm{tr}[\hat{\Delta}(\mathbf{k})^{\dagger}\hat{\boldsymbol{\sigma}}\hat{\Delta}(\mathbf{k})]$ of the pairing state for $\mathbf{k}$. From that one should not simply conclude that the total spin average [the average of $\mathbf{q}(\mathbf{k})$ over the whole Fermi surface] is finite. In many cases its average over the Fermi surface is zero. The meaning of a finite vector $\mathbf{q}(\mathbf{k})$ is more that the structure of the pair correlation is different for up- and down-spins in different directions of $\mathbf{k}$. Clearly, this can only occur if time-reversal symmetry is broken. However, we shall see in Sec. V that in some cases this can give rise to a finite net magnetic moment associated with Cooper pairs, which can couple to a magnetic field. This effect is well known for the (nonunitary) A phase of superfluid ^{3}He.

The solution of Eq. (2.6) is different for the two types of $\hat{\Delta}$ matrices. In the case of a unitary $\hat{\Delta}(\mathbf{k})$ the Bogoliubov transformation matrices have a rather simple form,

$$\hat{u}_{\mathbf{k}}=\frac{[E_{\mathbf{k}}+\varepsilon(\mathbf{k})]\hat{\sigma}_0}{\{[E_{\mathbf{k}}+\varepsilon(\mathbf{k})]^2+\frac{1}{2}\mathrm{tr}\hat{\Delta}\hat{\Delta}^{\dagger}(\mathbf{k})\}^{1/2}} ,$$
$$\hat{v}_{\mathbf{k}}=\frac{-\hat{\Delta}(\mathbf{k})}{\{[E_{\mathbf{k}}+\varepsilon(\mathbf{k})]^2+\frac{1}{2}\mathrm{tr}\hat{\Delta}\hat{\Delta}^{\dagger}(\mathbf{k})\}^{1/2}} , \quad (2.13)$$

where $E_{\mathbf{k}+}=E_{\mathbf{k}-}=E_{\mathbf{k}}=[\varepsilon^2(\mathbf{k})+\frac{1}{2}\mathrm{tr}\hat{\Delta}\hat{\Delta}^{\dagger}(\mathbf{k})]^{1/2}$ is the energy spectrum of the elementary excitations with a gap $[\frac{1}{2}\mathrm{tr}\hat{\Delta}\hat{\Delta}^{\dagger}(\mathbf{k})]^{1/2}$ depending on $\mathbf{k}$. Since $E_{\mathbf{k}+}=E_{\mathbf{k}-}$ the excitation spectrum is twofold degenerate.

For a nonunitary $\hat{\Delta}(\mathbf{k})$ the transformation matrices are more complicated:

$$\hat{u}_{\mathbf{k}}=Q\left[\left[\frac{E_{\mathbf{k}+}+\varepsilon(\mathbf{k})}{E_{\mathbf{k}+}}\right]^{1/2}(|\mathbf{q}|\hat{\sigma}_0+\mathbf{q}\cdot\hat{\boldsymbol{\sigma}})(\hat{\sigma}_0+\hat{\sigma}_z)+\left[\frac{E_{\mathbf{k}-}+\varepsilon(\mathbf{k})}{E_{\mathbf{k}-}}\right]^{1/2}(|\mathbf{q}|\hat{\sigma}_0-\mathbf{q}\cdot\hat{\boldsymbol{\sigma}})(\hat{\sigma}_0-\hat{\sigma}_z)\right]$$
$$\hat{v}_{\mathbf{k}}=-iQ\left[\frac{1}{\sqrt{E_{\mathbf{k}+}[E_{\mathbf{k}+}+\varepsilon(\mathbf{k})]}}[|\mathbf{q}|\mathbf{d}-i(\mathbf{d}\times\mathbf{q})]\cdot\hat{\boldsymbol{\sigma}}\hat{\sigma}_y(\hat{\sigma}_0+\hat{\sigma}_z)+\frac{1}{\sqrt{E_{\mathbf{k}-}[E_{\mathbf{k}-}+\varepsilon(\mathbf{k})]}}[|\mathbf{q}|\mathbf{d}+i(\mathbf{d}\times\mathbf{q})]\cdot\hat{\boldsymbol{\sigma}}\hat{\sigma}_y(\hat{\sigma}_0-\hat{\sigma}_z)\right] \quad (2.14)$$

where

$$Q^{-2}=8|\mathbf{q}|(|\mathbf{q}|+q_z)$$

and

$$E_{\mathbf{k}\pm}=\sqrt{\varepsilon(\mathbf{k})^2+|\mathbf{d}(\mathbf{k})|^2\pm|\mathbf{q}(\mathbf{k})|} .$$

The degeneracy of the excitation energy is lifted because the value of $\mathbf{q}(\mathbf{k})$ is finite. Thus there are two $\mathbf{k}$-dependent gaps $|\mathbf{d}(\mathbf{k})|^2\pm|\mathbf{d}(\mathbf{k})\times\mathbf{d}^*(\mathbf{k})|$ in the energy spectrum. This split in the excitation energy can be understood as a consequence of the reduction of symmetry through the loss of time-reversal symmetry. (For a detailed calculation of these transformation matrices see Appendix A.)

From these results we can derive the self-consistency equation for the mean-field potential in Eq. (2.2), using the fact that $a_{ks}^{(\dagger)}$ is a Fermi operator:

$$\Delta_{ss'}(\mathbf{k})=-\sum_{\mathbf{k}',s_3,s_4} V_{s'ss_3s_4}(\mathbf{k},\mathbf{k}')\mathcal{F}_{s_3s_4}(\mathbf{k}',\beta) \qquad (2.15)$$

where in the case of a unitary pairing state

$$\hat{\mathcal{F}}(\mathbf{k},\beta)=\frac{\hat{\Delta}(\mathbf{k})}{2E_{\mathbf{k}}}\tanh\left[\frac{\beta E_{\mathbf{k}}}{2}\right] \qquad (2.16)$$

and in the case of nonunitary pairing states

$$\hat{\mathcal{F}}(\mathbf{k},\beta)=\left[\frac{1}{2E_{\mathbf{k}+}}\left[\mathbf{d}+\frac{\mathbf{q}\times\mathbf{d}}{|\mathbf{q}|}\right]\tanh\left[\frac{\beta E_{\mathbf{k}+}}{2}\right]+\frac{1}{2E_{\mathbf{k}-}}\left[\mathbf{d}-\frac{\mathbf{q}\times\mathbf{d}}{|\mathbf{q}|}\right]\tanh\left[\frac{\beta E_{\mathbf{k}-}}{2}\right]\right]i\hat{\sigma}\hat{\sigma}_y\ . \qquad (2.17)$$

The variable β denotes $(k_BT)^{-1}$. These equations determine the temperature dependence of $\hat{\Delta}(\mathbf{k})$ and the critical temperature T_c. At temperatures very close to T_c the gap function is very small, so that a linearization of the self-consistency (or gap) equation is allowed:

$$v\Delta_{s_1s_2}(\mathbf{k})=-\sum_{s_3s_4}\langle V_{s_2s_1s_3s_4}(\mathbf{k},\mathbf{k}')\Delta_{s_3s_4}(\mathbf{k}')\rangle_{\mathbf{k}'}\ , \qquad (2.18)$$

where

$$\frac{1}{v}=N(0)\int_0^{\varepsilon_c}d\varepsilon\frac{\tanh\left[\frac{\beta_c\varepsilon(k)}{2}\right]}{\varepsilon(\mathbf{k}}=\ln(1.14\beta_c\varepsilon_c) \qquad (2.19)$$

gives the weak-coupling definition of v and $\langle\ \rangle_{\mathbf{k}}$ denotes the average over the Fermi surface with the density of states $N(0)$. Equation (2.18) is an eigenvalue equation for $\hat{\Delta}(\mathbf{k})$. The largest eigenvalue v defines the superconducting instability, the real T_c, and the form of the ordered state, $\hat{\Delta}(\mathbf{k})$. For the solution of Eq. (2.18) we need the precise form of the pairing potential $\hat{V}$. Certain information about these solutions, however, can be obtained even without a detailed knowledge of $\hat{V}$, as will be studied in the next section. The important instrument for this purpose is group theory, making use of the symmetry properties of Eq. (2.18).

The Hamiltonian in Eq. (2.1) has a certain symmetry represented by a group $\mathcal{G}$. This group consists of the point group G of the crystal lattice symmetry, the spin-rotation symmetry group SU(2), the time-reversal symmetry group $\mathcal{K}$, and the gauge symmetry group U(1).

The behavior of $\hat{\Delta}(\mathbf{k})$ under transformation by the elements of $\mathcal{G}$ is determined by the invariance condition of $\tilde{\mathcal{H}}$. An element g of the point group G acts only on the $\mathbf{k}$-vector,

$$ga_{\mathbf{k},s}^{\dagger}=a_{\hat{D}_{(G)}^{(-)}(g)\mathbf{k},s}^{\dagger}\rightarrow g\hat{\Delta}(\mathbf{k})=\hat{\Delta}(\hat{D}_{(G)}^{(-)}(g)(\mathbf{k}))\ , \qquad (2.20)$$

where $\hat{D}_{(G)}^{(-)}(g)$ is the three-dimensional representation of G in the $\mathbf{k}$-space. The SU(2) spin-rotation group transforms the matrix space of $\hat{\Delta}(\mathbf{k})$ as $[g\in \mathrm{SU}(2)]$

$$ga_{\mathbf{k},s}^{\dagger}=\sum_{s'}D_{(S)}(g)_{s,s'}a_{\mathbf{k},s'}^{\dagger}\rightarrow g\hat{\Delta}(\mathbf{k})=\hat{D}_{(S)}^{\tau}(g)\hat{\Delta}(\mathbf{k})\hat{D}_{(S)}(g)\ . \qquad (2.21)$$

The 2×2 matrix $\hat{D}_{(S)}$ is the representation of SU(2) in the spin-$\frac{1}{2}$ space (the symbol $\hat{D}^{\tau}$ denotes the transposition of the matrix $\hat{D}$). The time-reversal $K\in\mathcal{K}$ leads to

$$Ka_{\mathbf{k},s}^{\dagger}=\sum_{s'}(-i\sigma_y)_{s,s'}a_{-\mathbf{k},s'}\rightarrow K\hat{\Delta}(\mathbf{k})=\hat{D}_{\mathcal{K}}^{\tau}\hat{\Delta}(-\mathbf{k})\hat{D}_{\mathcal{K}}=\hat{\sigma}_y\hat{\Delta}^*(-\mathbf{k})\hat{\sigma}_y\ , \qquad (2.22)$$

where $\hat{D}_{\mathcal{K}}=-i\hat{\sigma}_yC$ with C as an operator that changes the sign of the $\mathbf{k}$-vector and a state $|\phi\rangle$ to $|\phi\rangle^{\dagger}$, i.e., $C\hat{\Delta}(\mathbf{k})C=\hat{\Delta}^*(-\mathbf{k})$. Finally, the application of an element Φ of U(1) is a multiplication of a phase factor,

$$\Phi a_{\mathbf{k},s}^{\dagger}=e^{i\phi/2}a_{\mathbf{k},s}^{\dagger}\rightarrow\Phi\hat{\Delta}(\mathbf{k})=e^{i\phi}\Delta(\mathbf{k})\ . \qquad (2.23)$$

As already suggested above, it is more convenient to express these transformation properties for the functions $\psi(\mathbf{k})$ and $\mathbf{d}(\mathbf{k})$ in the notation given in Eqs. (2.10) and (2.11). The transformation rules are shown in Table I. Clearly, the symmetry properties of a paring state can be more easily recognized in this form, so that this notation is preferable whenever one wishes to consider symmetry properties of a superconducting state.

Finally, we should like to point out one case of symmetry reduction that will be of special interest in the next section, namely, that caused by the presence of strong spin-orbit coupling. For strong spin-orbit coupling the point-group transformation of $\mathbf{k}$ and the spin transformations can no longer be treated independently. The spins have to be considered as "frozen" in the lattice. Therefore the spin-rotation group is "absorbed" by the point group G. Any symmetry operation on the crystal lattice has also to be followed by the spins. Thus the transformation properties of the triplet states are changed in the following way. Under a point-group transformation g the gap function transforms as

$$g\mathbf{d}(\mathbf{k})=\hat{D}_{(G)}^{(+)}(g)\mathbf{d}(\hat{D}_{(G)}^{(-)}(g)\mathbf{k})\ , \qquad (2.24)$$

where $\hat{D}_{(G)}^{(\pm)}(g)$ is the representation in three-dimensional space with positive (spin-space) or negative ($\mathbf{k}$-space) inversion operation, respectively.

TABLE I. Symmetry transformation properties of the gap functions $\psi(\mathbf{k})$ (even parity) and $\mathbf{d}(\mathbf{k})$ (odd parity) without spin-orbit coupling.

Transformation	Even parity	Odd parity
Fermion exchange	$\psi(\mathbf{k})=\psi(-\mathbf{k})$	$\mathbf{d}(\mathbf{k})=-\mathbf{d}(-\mathbf{k})$
Point group	$g\psi(\mathbf{k})=\psi(\hat{D}_{(G)}^{(-)}(g)\mathbf{k})$	$g\mathbf{d}(\mathbf{k})=\mathbf{d}(\hat{D}_{(G)}^{(-)}(g)\mathbf{k})$
Spin rotation	$g\psi(\mathbf{k})=\psi(\mathbf{k})$	$g\mathbf{d}(\mathbf{k})=\hat{D}_{(G)}^{(+)}(g)\mathbf{d}(\mathbf{k})$
Time reversal	$K\psi(\mathbf{k})=\psi^*(-\mathbf{k})$	$K\mathbf{d}(\mathbf{k})=-\mathbf{d}^*(-\mathbf{k})$
U(1) gauge	$\Phi\psi(\mathbf{k})=e^{i\phi}\psi(\mathbf{k})$	$\Phi\mathbf{d}(\mathbf{k})=e^{i\phi}\mathbf{d}(\mathbf{k})$

B. Symmetry classification and the generalized Ginzburg-Landau theory

We pointed out in the Introduction that we are dealing in this article with special superconducting systems in which the origin of the superconducting phase transition is still obscure. This means that we are not able to give the specific form of the basic Hamiltonian [Eq. (2.1)] which was discussed on a more general level in the previous section. On the other hand, we also discussed there the symmetry properties of this Hamiltonian and of the mean-field $\hat{\Delta}$ (gap function) with the motivation that it would be helpful in gaining some insight into the superconducting phase of the system. It is the purpose of this and several further sections to exploit these symmetry properties by means of group-theoretical techniques in order to explain several very intriguing features of unconventional superconductors.

Since we are mainly interested in explaining the properties of the heavy-fermion superconductors, mentioned in the Introduction, we want to concentrate especially on their symmetry properties as a basis for further studies. The three most prominent superconducting materials among them are $CeCu_2Si_2$, UBe_{13}, and UPt_3, and we shall restrict our discussion to the corresponding three crystal lattice symmetries represented by their point groups, D_{4h}, (tetragonal), O_h (cubic), and D_{6h} (hexagonal), respectively. Furthermore, these compounds contain heavy ions, Ce or U. Hence, in addition to the crystal field, the spin-orbit interaction (which is proportional to the square of the nuclear charge number) may play an important part in the Hamiltonian, including the pairing interaction, as was emphasized by Anderson (1984).

First of all, we have to be aware that the single-particle states are affected by spin-orbit coupling, since they cannot be eigenstates of the spin operator anymore. However, they can be labeled rather similarly as *pseudo-spin*-states,

$$|\mathbf{k},\alpha\rangle = c^{\dagger}_{\mathbf{k}\alpha}|0\rangle \ , \tag{2.25}$$

using α as the pseudo-spin-index. These states are superpositions of spinor states. Their field operator can be written as

$$\Psi^{\dagger}_{\alpha}(\mathbf{r}) = \sum_{\mathbf{k},s} \chi_{\mathbf{k},\alpha s}(\mathbf{r})|s\rangle e^{i\mathbf{k}\cdot\mathbf{r}} c^{\dagger}_{\mathbf{k}\alpha} \ , \tag{2.26}$$

where $\chi_{\mathbf{k},\alpha s}(\mathbf{r})$ is a function periodic in the crystal space. The pseudo-spin-state is generated from a spin eigenstate by turning on the spin-orbit interaction adiabatically. This leads to a one-to-one correspondence between the original spin state and this pseudo-spin-state (let us define $\uparrow \to \alpha$ and $\downarrow \to \beta$). Hence the transformation properties under the symmetry group $\mathcal{G} = G \times \mathcal{K} \times U(1)$ must be formally identical, with the restriction, of course, that spin space and orbit space do not transform separately.

Cooper pairs in such a system are composed of two particles belonging to energetically degenerate states and combining to a total of zero momentum. For even-parity pairing, the pseudo-spin-state $|\mathbf{k},\alpha\rangle$ is paired with its time-reversed state $K|\mathbf{k},\alpha\rangle = |-\mathbf{k},\beta\rangle$. In the case of odd-parity pairing, four degenerate states can be involved: $|\mathbf{k},\alpha\rangle$, $K|\mathbf{k},\alpha\rangle = |-\mathbf{k},\beta\rangle$, $\mathcal{I}|\mathbf{k},\alpha\rangle = |-\mathbf{k},\alpha\rangle$, and $K\mathcal{I}|\mathbf{k},\alpha\rangle = |\mathbf{k},\beta\rangle$. In this case the parity $\mathcal{I}$ has to be a symmetry of the system (all systems we consider contain $\mathcal{I}$). Since the pseudospin and the spin are symmetrically closely related, the even-parity states correspond to (pseudospin) singlet states and the odd-parity to (pseudospin) triplet states, as we introduced them in the previous section. That we are dealing with pseudo-spin-states rather than with ordinary spin states leads to some important effects, if we consider the junction between two materials of different strength in the spin-orbit coupling, as will be a matter of discussion in Sec. IV. Here, however, we shall not further emphasize this point.

A first step towards finding the stable superconducting state (the form of the gap function) is the solution of the linearized gap equation [Eq. (2.18)], which has the form of an eigenvalue equation. The largest eigenvalue gives us the transition temperatures (the first occurring instability of the normal state if we scan the temperature downwards) and the eigenfunction space of $\hat{\Delta}(\mathbf{k})$. We shall now use the well-known property of an eigenvalue problem, that the eigenfunction spaces for every single eigenvalue form a basis of an irreducible representation of the symmetry group of the equation. For example, in the hydrogen atom the eigenstates of the electron for each energy eigenvalue are basis functions of the irreducible representation belonging to the symmetry group generated by the angular momentum operator $\mathbf{L}$ (total rotational symmetry) and the Pauli-Lenz vector $\frac{1}{2}(\mathbf{P}\times\mathbf{L}+\mathbf{L}\times\mathbf{P})$, both of which are conserved quantities of the corresponding Hamiltonian. On this basis we can classify the possible gap-function spaces of Eq. (2.18) with respect to their symmetry behavior, as being the basis of the irreducibile representations of $\mathcal{G}$.

Let us first explain the procedure, how to obtain such basis functions, in a rotationaly symmetric system with the group $G = SO(3) \times \mathcal{I}$, neglecting both the spin-orbit interaction and the crystal field. In this system the representations of the symmetry group are

$$\mathcal{D}(\mathcal{G}) = \mathcal{D}_{(l)} \otimes \mathcal{D}_{(S)} \otimes \mathcal{D}_{(\mathcal{K})} \otimes \mathcal{D}_{(\Phi)} \ , \tag{2.27}$$

where $D_{(l)}$ denotes the $\mathbf{k}$-space representation and $\mathcal{D}_{(S)}$ the spin-space representation of G. The indices l and S have, in the case of particle pairing, the physical meaning of relative angular momentum and total spin, respectively. $\mathcal{D}_{(\mathcal{K})}$ and $\mathcal{D}_{(\Phi)}$ are the representation of time-reversal and U(1) gauge symmetry, respectively. The product $\mathcal{D}_{(\mathcal{K})} \otimes \mathcal{D}_{(\Phi)}$ represents the transformations Φ and $K\Phi$. These transformations conserve the function space of the two other representations, $\mathcal{D}_{(l)} \otimes \mathcal{D}_{(S)}$. Hence the eigenvalues can be labeled S and l and the eigenfunctions can be expressed by spherical harmonics $Y_{lm}(\mathbf{k})$ for $\mathcal{D}_{(l)}$ and the spin functions $\chi_s(0,0)$ for $\mathcal{D}_{(S=0)}$ and $\chi_t(1,s_z)$ or $\{\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}\}$ for $\mathcal{D}_{(S=1)}$ [$\chi_t(1,+1) = -\hat{\mathbf{x}} + i\hat{\mathbf{y}}$, $\chi_t(1,-1) = \hat{\mathbf{x}} + i\hat{\mathbf{y}}$ and $\chi_t(1,0) = \sqrt{2}\,\hat{\mathbf{z}}$]. In this sense the representations of time-reversal and U(1) gauge symmetry may be neglected. The eigenfunctions to the eigenvalue $T_c(l,S)$ can be written in the form

$$\hat{\Delta}(\mathbf{k})=\begin{cases}\sum_m c_m Y_{lm}(\hat{\mathbf{k}})i\hat{\sigma}_y & \text{singlet} \quad (l=\text{even}) ,\\ \sum_{m,\hat{\mathbf{n}}=\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}} c_{m\hat{\mathbf{n}}} Y_{lm}(\hat{\mathbf{k}})i(\hat{\boldsymbol{\sigma}}\cdot\hat{\mathbf{n}})\hat{\sigma}_y & \text{triplet} \quad (l=\text{odd}) ,\end{cases} \tag{2.28}$$

where the c_m and $c_{m\hat{\mathbf{n}}}$ are complex numbers. These eigenfunction spaces have the dimensions $2l+1$ for a singlet and $3(2l+1)$ for a triplet. In this case the eigenfunctions are unique, because each representation has only one set of basis functions, which just corresponds to the eigenfunctions. This is not in general the case.

If we introduce spin-orbit coupling the symmetry of the system is lowered (**k**-and spin-space do not transform independently), and these eigenfunction spaces split into subspaces with different eigenvalues. To obtain the new eigenfunction classes we have to decompose the representation product (Kronecker product) of **k**- and spin-space,

$$\mathcal{D}_{(l)}\otimes\mathcal{D}_{(0)}=\mathcal{D}_{(l)} \quad \text{singlet} \quad (l=\text{even}) ,$$
$$\mathcal{D}_{(l)}\otimes\mathcal{D}_{(1)}=\mathcal{D}_{(l-1)}\oplus\mathcal{D}_{(l)}\oplus\mathcal{D}_{(l+1)} \quad \text{triplet} \quad (l=\text{odd}) , \tag{2.29}$$

where l, even or odd, also denotes the behavior under the parity $\mathcal{I}$. The basis functions of the new representations can be derived by the Clebsch-Gordan formalism and the new eigenvalues can be labeled by the total angular momentum. However, one total angular momentum J [representation $\mathcal{D}_{(J)}$] has in most cases several sets of basis functions obtained from the Clebsch-Gordan procedure. These sets are in general mixed together by $\hat{V}$ and are not the true eigenfunctions. On the level of this symmetry consideration the eigenfunction spaces can only be specified in classes $[\mathcal{D}_{(J)}]$ according to their symmetry behavior. Their concrete form, however, cannot be found without detailed knowledge of $\hat{V}$.

We now turn the crystal field on. Again the symmetry is lowered from a continuous rotation group with an infinite number of irreducible representations to a discrete point group with only a few representations. Hence only a few classes of eigenfunction spaces exist. In the case of the cubic group O_h there are 10 classes corresponding to the representations $\Gamma_1^\pm$, $\Gamma_2^\pm$ (1D), $\Gamma_3^\pm$ (2D) and $\Gamma_4^\pm$, $\Gamma_5^\pm$ (3D) ($\pm$ denotes the property under parity). For the hexagonal symmetry group D_{6h} we have 12 representations $\Gamma_1^\pm$ $\Gamma_2^\pm$, $\Gamma_3^\pm$, $\Gamma_4^\pm$ (1D) and $\Gamma_5^\pm$, $\Gamma_6^\pm$ (2D), and for tetragonal symmetry D_{4h} 10 representations $\Gamma_1^\pm$, $\Gamma_2^\pm$, $\Gamma_3^\pm$, $\Gamma_4^\pm$ (1D) and $\Gamma_5^\pm$ (2D). We shall use for the representations this notation, which is found for example in the table book of Koster *et al.* (1963).

Thus we have reached the stage where we can classify the eigenfunctions of Eq. (2.18) with respect to the representations of their symmetry groups which are listed above. A list of all classes is given in Tables II–IV, each with a representative set of basis functions $\hat{\Delta}(\Gamma,m;\mathbf{k})$. The chosen basis functions are projections of the $\mathcal{D}_{(J)}$ with small J on the space of the crystal field representations. This type of gap function is therefore often called *s*-, *p*-, or *d*-wave, etc., according to its **k**-space symmetry [$\hat{\Delta}(\alpha\mathbf{k})=\alpha^l\hat{\Delta}(\mathbf{k})$ with $l=0,1,2,\ldots$, respectively]. One exception is the totally symmetric, nonconstant basis function, which is often labeled as "extended *s*-wave." However, this nomenclature should not be confused with the effective form of the eigenfunctions, which in the crystal field can be any superposition with large-J contributions.

Among the representations Γ there is one that contains the eigenfunctions with the largest eigenvalue T_c. We assume that this $T_c(\Gamma)$ is much larger than the T_c's of all the other representations. Hence the stable superconducting state immediately below T_c is described by a linear combination of the basis functions $\hat{\Delta}(\Gamma,m;\mathbf{k})$ of the corresponding eigenfunction space:

$$\hat{\Delta}(\mathbf{k})=\sum_m \eta(\Gamma,m)\hat{\Delta}(\Gamma,m;\mathbf{k}) , \tag{2.30}$$

where the $\eta(\Gamma,m)$ are complex numbers. As a solution

TABLE II. (a) Even-parity basis gap functions $\hat{\Delta}(\Gamma,m;\mathbf{k})=i\hat{\sigma}_y\psi(\Gamma,m;\mathbf{k})$ and (b) odd-parity basis gap functions $\hat{\Delta}(\Gamma,m;\mathbf{k})=i[\hat{\boldsymbol{\sigma}}\cdot\mathbf{d}(\Gamma,m;\mathbf{k})]\hat{\sigma}_y$ for the cubic lattice symmetry (O_h).

Irreducible representation Γ	Basis functions
	(a)
Γ_1^+	$\psi(\Gamma_1^+;\mathbf{k})=1,\ k_x^2+k_y^2+k_z^2$
Γ_2^+	$\psi(\Gamma_2^+;\mathbf{k})=(k_x^2-k_y^2)(k_y^2-k_z^2)(k_z^2-k_x^2)$
Γ_3^+	$\psi(\Gamma_3^+,1;\mathbf{k})=2k_z^2-k_x^2-k_y^2$ $\psi(\Gamma_3^+,2;\mathbf{k})=\sqrt{3}(k_x^2-k_y^2)$
Γ_4^+	$\psi(\Gamma_4^+,1;\mathbf{k})=k_yk_z(k_y^2-k_z^2)$ $\psi(\Gamma_4^+,2;\mathbf{k})=k_zk_x(k_z^2-k_x^2)$ $\psi(\Gamma_4^+,3;\mathbf{k})=k_xk_y(k_x^2-k_y^2)$
Γ_5^+	$\psi(\Gamma_5^+,1;\mathbf{k})=k_yk_z$ $\psi(\Gamma_5^+,2;\mathbf{k})=k_zk_x$ $\psi(\Gamma_5^+,3;\mathbf{k})=k_xk_y$
	(b)
Γ_1^-	$\mathbf{d}(\Gamma_1^-;\mathbf{k})=\hat{\mathbf{x}}k_x+\hat{\mathbf{y}}k_y+\hat{\mathbf{z}}k_z$
Γ_2^-	$\mathbf{d}(\Gamma_2^-;\mathbf{k})=\hat{\mathbf{x}}k_x(k_z^2-k_y^2)+\hat{\mathbf{y}}k_y(k_x^2-k_z^2)$ $+\hat{\mathbf{z}}k_z(k_y^2-k_x^2)$
Γ_3^-	$\mathbf{d}(\Gamma_3^-,1;\mathbf{k})=2\hat{\mathbf{z}}k_z-\hat{\mathbf{x}}k_x-\hat{\mathbf{y}}k_y$ $\mathbf{d}(\Gamma_3^-,2;\mathbf{k})=\sqrt{3}(\hat{\mathbf{x}}k_x-\hat{\mathbf{y}}k_y)$
Γ_4^-	$\mathbf{d}(\Gamma_4^-,1;\mathbf{k})=\hat{\mathbf{y}}k_z-\hat{\mathbf{z}}k_y$ $\mathbf{d}(\Gamma_4^-,2;\mathbf{k})=\hat{\mathbf{z}}k_x-\hat{\mathbf{x}}k_z$ $\mathbf{d}(\Gamma_4^-,3;\mathbf{k})=\hat{\mathbf{x}}k_y-\hat{\mathbf{y}}k_x$
Γ_5^-	$\mathbf{d}(\Gamma_5^-,1;\mathbf{k})=\hat{\mathbf{y}}k_z+\hat{\mathbf{z}}k_y$ $\mathbf{d}(\Gamma_5^-,2;\mathbf{k})=\hat{\mathbf{z}}k_x+\hat{\mathbf{x}}k_z$ $\mathbf{d}(\Gamma_5^-,3;\mathbf{k})=\hat{\mathbf{x}}k_y+\hat{\mathbf{y}}k_x$

TABLE III. (a) Even-parity basis gap functions $\hat{\Delta}(\Gamma,m;\mathbf{k})=i\hat{\sigma}_y\psi(\Gamma,m;\mathbf{k})$ and (b) odd-parity basis gap functions $\hat{\Delta}(\Gamma,m;\mathbf{k})=i[\hat{\boldsymbol{\sigma}}\cdot\mathbf{d}(\Gamma,m;\mathbf{k})]\hat{\sigma}_y$ for the hexagonal lattice symmetry (D_{6h}).

Irreducible representation Γ	Basis functions
	(a)
Γ_1^+	$\psi(\Gamma_1^+;\mathbf{k})=1,\ k_x^2+k_y^2,\ k_z^2$
Γ_2^+	$\psi(\Gamma_2^+;\mathbf{k})=k_xk_y(k_x^2-3k_y^2)(k_y^2-3k_x^2)$
Γ_3^+	$\psi(\Gamma_3^+;\mathbf{k})=k_zk_x(k_x^2-3k_y^2)$
Γ_4^+	$\psi(\Gamma_4^+;\mathbf{k})=k_zk_y(k_y^2-3k_x^2)$
Γ_5^+	$\psi(\Gamma_5^+,1;\mathbf{k})=k_xk_z$
	$\psi(\Gamma_5^+,2;\mathbf{k})=k_yk_z$
Γ_6^+	$\psi(\Gamma_6^+,1;\mathbf{k})=k_x^2-k_y^2$
	$\psi(\Gamma_6^+,2;\mathbf{k})=2k_xk_y$
	(b)
Γ_1^-	$\mathbf{d}(\Gamma_1^-;\mathbf{k})=\hat{\mathbf{x}}k_x+\hat{\mathbf{y}}k_y,\hat{\mathbf{z}}k_z$
Γ_2^-	$\mathbf{d}(\Gamma_2^-;\mathbf{k})=\hat{\mathbf{x}}k_y-\hat{\mathbf{y}}k_x$
Γ_3^-	$\mathbf{d}(\Gamma_3^-;\mathbf{k})=\hat{\mathbf{z}}k_x(k_x^2-3k_y^2),$
	$k_z[(k_x^2-k_y^2)\hat{\mathbf{x}}-2k_xk_y\hat{\mathbf{y}}]$
Γ_4^-	$\mathbf{d}(\Gamma_4^-;\mathbf{k})=\hat{\mathbf{z}}k_y(k_y^2-3k_x^2),$
	$k_z[(k_y^2-k_x^2)\hat{\mathbf{y}}-2k_xk_y\hat{\mathbf{x}}]$
Γ_5^-	$\mathbf{d}(\Gamma_5^-,1;\mathbf{k})=\hat{\mathbf{x}}k_z,\hat{\mathbf{z}}k_x$
	$\mathbf{d}(\Gamma_5^-,2;\mathbf{k})=\hat{\mathbf{y}}k_z,\hat{\mathbf{z}}k_y$
Γ_6^-	$\mathbf{d}(\Gamma_6^-,1;\mathbf{k})=\hat{\mathbf{x}}k_x-\hat{\mathbf{y}}k_y$
	$\mathbf{d}(\Gamma_6^-,2;\mathbf{k})=\hat{\mathbf{x}}k_y-\hat{\mathbf{y}}k_x$

of the linearized gap equation any linear combination in Eq. (2.30) is allowed. As we are going beyond this linear approach only a finite number of combinations can satisfy the (nonlinear) gap equation. We could perform this step by an expansion of the gap equation with respect to the gap function, assuming $\hat{\Delta}$ to be small if the temperature is very close to the instability point. To perform the

TABLE IV. (a) Even-parity basis gap functions $\hat{\Delta}(\Gamma,m;\mathbf{k})=i\hat{\sigma}_y\psi(\Gamma,m;\mathbf{k})$ and (b) odd-parity basis gap functions $\hat{\Delta}(\Gamma,m;\mathbf{k})=i[\hat{\boldsymbol{\sigma}}\cdot\mathbf{d}(\Gamma,m;\mathbf{k})]\hat{\sigma}_y$ for the tetragonal lattice symmetry (D_{4h}).

Irreducible representation Γ	Basis function
	(a)
Γ_1^+	$\psi(\Gamma_1^+;\mathbf{k})=1,\ k_x^2+k_y^2,\ k_z^2$
Γ_2^+	$\psi(\Gamma_2^+;\mathbf{k})=k_xk_y(k_x^2-k_y^2)$
Γ_3^+	$\psi(\Gamma_3^+;\mathbf{k})=k_x^2-k_y^2$
Γ_4^+	$\psi(\Gamma_4^+;\mathbf{k})=k_xk_y$
Γ_5^+	$\psi(\Gamma_5^+,1;\mathbf{k})=k_xk_z$
	$\psi(\Gamma_5^+,2;\mathbf{k})=k_yk_z$
	(b)
Γ_1^-	$\mathbf{d}(\Gamma_1^-;\mathbf{k})=\hat{\mathbf{x}}k_x+\hat{\mathbf{y}}k_y,\ \hat{\mathbf{z}}k_z$
Γ_2^-	$\mathbf{d}(\Gamma_2^-;\mathbf{k})=\hat{\mathbf{x}}k_y-\hat{\mathbf{y}}k_x$
Γ_3^-	$\mathbf{d}(\Gamma_3^-;\mathbf{k})=\hat{\mathbf{x}}k_x-\hat{\mathbf{y}}k_x$
Γ_4^-	$\mathbf{d}(\Gamma_4^-;\mathbf{k})=\hat{\mathbf{x}}k_y+\hat{\mathbf{y}}k_x$
Γ_5^-	$\mathbf{d}(\Gamma_5^-,1;\mathbf{k})=\hat{\mathbf{x}}k_z,\ \hat{\mathbf{z}}k_x$
	$\mathbf{d}(\Gamma_5^-,2;\mathbf{k})=\hat{\mathbf{y}}k_z,\ \hat{\mathbf{z}}k_y$

resulting $\mathbf{k}$ and spin-sums we had to use simplifications like a spherical Fermi surface or particle-hole symmetry, as well as a simple form for the interaction potential with $\varepsilon_c/k_BT_c\gg1$ [see Eqs. (2.18) and (2.19)]. This is known as the "weak-coupling" limit. However, for systems with strong-coupling effects we have to tackle this problem in a more general way.

One possible way of describing second-order phase transitions like the superconducting transition is to apply the relevant phenomenological Landau theory. The concept of the Landau theory is based on the fact that the equilibrium of a macroscopic system usually has a lower symmetry at low temperatures than at high temperatures. The high-temperature symmetry corresponds to that of the microscopic structure of the system, which is expressed in the Hamiltonian. The breakdown of this symmetry is introduced by a macroscopic order parameter, which vanishes for high temperatures but starts to be finite below a certain critical temperature. It is possible to analyze the rules of this symmetry breakdown purely by group-theoretical arguments. However, for a physical description of the system it is more convenient to use the formulation of the Landau theory, expanding the free energy F with respect to the order parameter close to the transition point.

As we have seen in the previous section, the gap function as the mean field in the Hamiltonian is an appropriate quantity to describe the superconducting state in terms of its symmetry properties. This symmetry is the same as that of the pair wave function $\langle a_{\mathbf{k}s}^{\dagger}a_{-\mathbf{k}s'}^{\dagger}\rangle$ and can be described by a set $\{\eta(\Gamma,m)\}$ [Eq. (2.30)]. We shall use the set of $\eta(\Gamma,m)$ as the order parameter that describes the system. Restricting the description to one representation Γ, we construct the free energy as an expansion in these $\eta(\Gamma,m)$. They transform like coordinates in the basis function space $\{\hat{\Delta}(\Gamma,m;\mathbf{k})\}$. The time reversal acts on them as $\eta\to\eta^*$ and the gauge transformation by a multiplication of all components with the same phase factor $\eta\to\eta e^{i\phi}$.

Since the free energy originates from the Hamiltonian, it has the same symmetry as $\mathcal{H}$. The free energy as a function of the order parameter has to be a scalar under all symmetry transformations. To maintain U(1) gauge and time-reversal symmetry only real even-order products of $\eta(\Gamma,m)$ can occur in the expansion of F. To ensure invariance under the point-group transformation it is convenient to use the Clebsch-Gordan formalism for the construction of the invariant terms. We have to decompose the products $\Gamma^*\otimes\Gamma$ for the second-order terms and $\Gamma^*\otimes\Gamma\otimes\Gamma^*\otimes\Gamma$ for the fourth-order terms in $\eta(\Gamma,m)$ and $\eta^*(\Gamma,m)$ and so on. In the decomposition we keep only the terms that are invariant, namely, those which belong to the trivial representation Γ_1^+ of the point group.[1] These invariant terms are introduced in

[1]This decomposition is very easily carried out by using any group-theory table book (for example, Koster *et al.*, 1963).

the free energy, each with a coefficient β_i. Terminating the expansion at fourth order, we find that the free energy has the form

$$F_\Gamma(T,\eta)=F_0(T)+V\left[A_\Gamma(T)\sum_m|\eta(\Gamma,m)|^2+f_\Gamma(\eta^4)\right], \quad (2.31)$$

where $F_0(T)$ is the free energy of the normal state of the system (with volume V). The second-order term has a simple, isotropic form. Its coefficient is of the form $A_\Gamma(T)=a'[T/T_c(\Gamma)-1]$. The symbol $f_\Gamma(\eta^4)$ denotes all fourth-order terms of $\eta(\Gamma,m)$ invariant under the symmetry group $\mathcal{G}$. They are listed in Table V(a)–(c) for the different representations of the point groups. These fourth-order terms are required to be positive definite $[f_\Gamma(\eta^4)>0]$ in order to maintain the overall stability of the free energy (the coefficients β_i have to satisfy special conditions). Above $T_c(\Gamma)$ with $A_\Gamma>0$ the second-order terms are also positive definite, so that the minimum of the free energy is realized for the vanishing order parameter $\eta(\Gamma,m)$. However, at $T_c(\Gamma)$ A_Γ changes sign, producing a minimal free energy for finite $\eta(\Gamma,m)$ for $T<T_c$. The latter minimum points of F determine the symmetry of the stable superconducting state below $T_c(\Gamma)$.

The superconducting system is characterized by several parameters β_i, the coefficients in the fourth-order terms [Table V(a)–(c)]. These parameters can be calculated in the weak-coupling limit as mentioned above. However, strong-coupling effects may change them considerably. It is an advantage of the Landau formulation that we can take these unknown strong-coupling effects into account by introducing only very few parameters (here maximally three under the restriction of only one irreducible representation). So we consider the β_i parameters as undetermined, material-dependent constants.

TABLE V. Fourth-order invariant terms in (a) the cubic symmetry O_h, (b) the hexagonal symmetry D_{6h}, and (c) the tetragonal symmetry D_{4h}. The coefficients β_i are material-dependent constants.

Γ	Fourth-order terms $f_\Gamma(\eta^4)$
	(a)
$\Gamma_{1,2}^{\pm}$	$\beta_1|\eta|^4$
$\Gamma_3^{\pm}$	$\beta_1(|\eta_1|^2+|\eta_2|^2)^2+\beta_2(\eta_1^*\eta_2-\eta_1\eta_2^*)^2$
$\Gamma_{4,5}^{\pm}$	$\beta_1(|\eta_1|^2+|\eta_2|^2+|\eta_3|^2)^2+\beta_2|\eta_1^2+\eta_2^2+\eta_3^2|^2+\beta_3(|\eta_1|^2|\eta_2|^2+|\eta_2|^2|\eta_3|^2+|\eta_3|^2|\eta_1|^2)$
	(b)
$\Gamma_{1,2,3,4}^{\pm}$	$\beta_1|\eta|^4$
$\Gamma_{5,6}^{\pm}$	$\beta_1(|\eta_1|^2+|\eta_2|^2)^2+\beta_2(\eta_1^*\eta_2-\eta_1\eta_2^*)^2$
	(c)
$\Gamma_{1,2,3,4}^{\pm}$	$\beta_1|\eta|^4$
$\Gamma_5^{\pm}$	$\beta_1(|\eta_1|^2+|\eta_2|^2)^2+\beta_2(\eta_1^*\eta_2-\eta_1\eta_2^*)^2+\beta_3|\eta_1|^2|\eta_2|^2$

On this basis one obtains all possible stable superconducting phases in a system, including crystal field, spin-orbit coupling, and strong-coupling effects, by a simple minimization of the free energy below $T_c(\Gamma)$ (Volovik and Gor'kov, 1984, 1985; Blount, 1985; Ueda and Rice, 1985a, 1985b).[2] In Table VI(a)–(c) we give a complete list of all these states specifying their dependence on the parameters β_i. Many of these states are degenerate. Due to the presence of the crystal field and the spin-orbit coupling this degeneracy must be discrete [apart from the U(1) gauge freedom]. In most cases the fourth-order terms are sufficient to generate this discrete degeneracy. However, in some cases even sixth-order terms have to be included in the free-energy expansion, because a spurious continuous degeneracy appears if only terms up to fourth order are taken into account. Examples of these are the two-dimensional representations of $O_h,\Gamma_3^{\pm}$, and of $D_{6h},\Gamma_5^{\pm}$, and $\Gamma_6^{\pm}$, for the choice of the coefficient $\beta_2>0$. The corresponding sixth-order terms which lift the degeneracy are

$$\gamma_1(|\eta_1|^2+|\eta_2|^2)^3+\gamma_2(|\eta_1|^2+|\eta_2|^2)|\eta_1^2+\eta_2^2|^2+\gamma_3|\eta_1|^2|3\eta_2^2-\eta_1^2|^2 \quad (2.32)$$

for the $\Gamma_3^{\pm}$-representation of O_h, and

$$\gamma_1(|\eta_1|^2+|\eta_2|^2)^3+\gamma_2(|\eta_1|^2+|\eta_2|^2)|\eta_1^2+\eta_2^2|^2+\gamma_3(|\eta_1|^2-|\eta_2|^2)\{(|\eta_1|^2-|\eta_2|^2)^2-3(\eta_1^*\eta_2+\eta_1\eta_2^*)^2\} \quad (2.33)$$

for both the $\Gamma_5^{\pm}$-and the $\Gamma_6^{\pm}$-representation of D_{6h}. Depending on the sign of the coefficient γ_3, either the state $(\eta_1,\eta_2)=(1,0)$ $(\gamma_3<0)$ or the state $(\eta_1,\eta_2)=(0,1)$ $(\gamma_3>0)$ is stabilized in both cases.

The important point in this classification of superconducting states is not the specific form of the order parameter (or the gap function) $\hat{\Delta}(\mathbf{k})$, but its symmetry. At the transition several symmetries of the system can be broken. One is of course the U(1) gauge symmetry causing the superconducting state, since our order parameter is complex. Some states also break the point group, yielding a symmetry corresponding to a subgroup of G. This subgroup is defined as the largest point group to leave the energy spectrum $E_{\mathbf{k}}$, defined in the previous section, invariant. It corresponds to the point group given under

[2]A classification of possible superconducting states neglecting spin-orbit coupling has been given by Ozaki, Machida, and Ohmi (1985, 1986a). In this case the order-parameter spaces of odd-parity pairing states are larger and the minimization of the corresponding free-energy expansion is in general difficult. These authors used the group-theoretical methods of the subordination scheme of symmetry groups in the second-order phase transition to find the so-called "inert" states. We shall not consider this method in this article.

TABLE VI. (a) Stable superconducting states of the representations Γ_i^+ (even parity) and Γ_i^- (odd parity) in the point group G for given relations between the coefficients β_i of the fourth-order terms: (a) for the cubic point group O_h; (b) for the hexagonal point group D_{6h}; (c) for the tetragonal point group D_{4h}. Columns: (i) degeneracy; (ii) structure of the zeros in the gap of the quasiparticle excitation spectrum, (L) lines, (P) points, and (–) none; (iii) symmetry $G'(\Gamma)$ of the state; G' is the largest subgroup of G in which the quasiparticle excitation spectrum $E(\mathbf{k})$ is totally symmetric (basis function of the trivial representation Γ_1) and Γ denotes the representation of the gap function in this subgroup. The states marked by an asterisk are pure states with no admixture of order parameters belonging to other representations: $\omega=\exp(i2\pi/3)$.

Γ	β_i	$\psi(\mathbf{k})/\mathbf{d}(\mathbf{k})$	(i)	(ii)	(iii)
		(a)			
Γ_1^+	–	$1,\ k_x^2+k_y^2+k_z^2$	1	–	$O_h(\Gamma_1^+)^*$
Γ_2^+	–	$(k_x^2-k_y^2)(k_y^2-k_z^2)(k_z^2-k_x^2)$	1	L	$O_h(\Gamma_2^+)^*$
Γ_3^+	$\beta_2<0$	$k_x^2-k_y^2$	3	L	$D_{4h}(\Gamma_3^+)^*$
		$2k_z^2-k_x^2-k_y^2$	3	–	$D_{4h}(\Gamma_1^+)$
	$\beta_2>0$	$k_x^2+\omega k_y^2+\omega^2 k_z^2$	2	P	$O_h(\Gamma_3^+)^*$
Γ_4^+	$\beta_3<0<\beta_2$	$k_y k_z(k_y^2-k_z^2)+\omega k_z k_x(k_z^2-k_x^2)+\omega^2 k_x k_y(k_x^2-k_y^2)$	8	P	$D_{3d}(\Gamma_3^+)$
	$\beta_2,\beta_3<0$	$k_y k_z(k_y^2-k_z^2)+k_z k_x(k_z^2-k_x^2)+k_x k_y(k_x^2-k_y^2)$	4	L	$D_{3d}(\Gamma_2^+)$
	$4\beta_2<\beta_3,\ \beta_3>0$	$k_y k_z(k_y^2-k_z^2)$	3	L	$D_{4h}(\Gamma_2^+)^*$
	$0<\beta_3<4\beta_2$	$k_y k_z(k_y^2-k_z^2)+ik_z k_x(k_z^2-k_x^2)$	6	L	$D_{4h}(\Gamma_5^+)$
Γ_5^+	$\beta_3<0<\beta_2$	$k_y k_z+\omega k_z k_x+\omega^2 k_x k_y$	8	P	$D_{3d}(\Gamma_3^+)$
	$\beta_2,\beta_3<0$	$k_y k_z+k_z k_x+k_x k_y$	4	–	$D_{3d}(\Gamma_1^+)$
	$4\beta_2<\beta_3,\ \beta_3>0$	$k_y k_z$	3	L	$D_{4h}(\Gamma_4^+)^*$
	$0<\beta_3<4\beta_2$	$k_y k_z+ik_x k_z$	6	L	$D_{4h}(\Gamma_5^+)$
Γ_1^-	–	$\hat{\mathbf{x}}k_x+\hat{\mathbf{y}}k_y+\hat{\mathbf{z}}k_z$	1	–	$O_h(\Gamma_1^-)^*$
Γ_2^-	–	$\hat{\mathbf{x}}k_x(k_z^2-k_y^2)+\hat{\mathbf{y}}k_y(k_x^2-k_z^2)+\hat{\mathbf{z}}k_z(k_y^2-k_x^2)$	1	P	$O_h(\Gamma_2^-)^*$
Γ_3^-	$\beta_2<0$	$\hat{\mathbf{x}}k_x-\hat{\mathbf{y}}k_y$	3	P	$D_{4h}(\Gamma_3^-)^*$
		$2\hat{\mathbf{z}}k_z-\hat{\mathbf{x}}k_x-\hat{\mathbf{y}}k_y$	3	–	$D_{4h}(\Gamma_1^-)$
	$\beta_2>0$	$\hat{\mathbf{x}}k_x+\omega\hat{\mathbf{y}}k_y+\omega^2\hat{\mathbf{z}}k_z$	2	P	$O_h(\Gamma_3^-)^*$
Γ_4^-	$\beta_3<0<\beta_2$	$\hat{\mathbf{x}}(\omega k_y-\omega^2 k_z)+\hat{\mathbf{y}}(k_z-\omega k_x)+\hat{\mathbf{z}}(\omega^2 k_x-k_y)$	8	P	$D_{3d}(\Gamma_3^-)$
	$\beta_2,\beta_3<0$	$\hat{\mathbf{x}}(k_y-k_z)+\hat{\mathbf{y}}(k_z-k_x)+\hat{\mathbf{z}}(k_x-k_y)$	4	P	$D_{3d}(\Gamma_2^-)$
	$4\beta_2<\beta_3,\ \beta_3>0$	$\hat{\mathbf{y}}k_z-\hat{\mathbf{z}}k_y$	3	P	$D_{4h}(\Gamma_2^-)^*$
	$0<\beta_3<4\beta_2$	$\hat{\mathbf{x}}(k_y+ik_z)-(\hat{\mathbf{y}}+i\hat{\mathbf{z}})k_x$	6	P	$D_{4h}(\Gamma_5^-)$
Γ_5^-	$\beta_3<0<\beta_2$	$\hat{\mathbf{x}}(\omega k_y+\omega^2 k_z)+\hat{\mathbf{y}}(k_z+\omega k_x)+\hat{\mathbf{z}}(\omega^2 k_x+k_y)$	8	P	$D_{3d}(\Gamma_3^-)$
	$\beta_2,\beta_3<0$	$\hat{\mathbf{x}}(k_y+k_z)+\hat{\mathbf{y}}(k_z+k_x)+\hat{\mathbf{z}}(k_x+k_y)$	4	–	$D_{3d}(\Gamma_1^-)$
	$4\beta_2<\beta_3,\ \beta_3>0$	$\hat{\mathbf{y}}k_z+\hat{\mathbf{z}}k_y$	3	P	$D_{4h}(\Gamma_4^-)^*$
	$0<\beta_3<4\beta_2$	$\hat{\mathbf{x}}(k_y+ik_z)+(\hat{\mathbf{y}}+i\hat{\mathbf{z}})k_x$	6	P	$D_{4h}(\Gamma_5^-)$
		(b)			
Γ_1^+	–	$1,k_x^2+k_y^2,k_z^2$	1	–	$D_{6h}(\Gamma_1^+)^*$
Γ_2^+	–	$k_x k_y(k_x^2-3k_y^2)(k_y^2-3k_x^2)$	1	L	$D_{6h}(\Gamma_2^+)^*$
Γ_3^+	–	$k_z k_x(k_x^2-3k_y^2)$	1	L	$D_{6h}(\Gamma_3^+)^*$
Γ_4^+	–	$k_z k_x(k_y^2-3k_x^2)$	1	L	$D_{6h}(\Gamma_4^+)^*$
Γ_5^+	$\beta_2<0$	$k_x k_z$	3	L	$D_{2h}(\Gamma_2^+)$
		$k_y k_z$	3	L	$D_{2h}(\Gamma_4^+)$
	$\beta_2>0$	$k_z(k_x+ik_y)$	2	L	$D_{6h}(\Gamma_5^+)^*$
Γ_6^+	$\beta_2<0$	$k_x^2-k_y^2$	3	–	$D_{2h}(\Gamma_1^+)$
		$k_x k_y$	3	L	$D_{2h}(\Gamma_3^+)$
	$\beta_2>0$	$(k_x+ik_y)^2$	2	P	$D_{6h}(\Gamma_6^+)^*$
Γ_1^-	–	$\hat{\mathbf{x}}k_x+\hat{\mathbf{y}}k_y,\hat{\mathbf{z}}k_z$	1	P	$D_{6h}(\Gamma_1^-)^*$
Γ_2^-	–	$\hat{\mathbf{x}}k_x-\hat{\mathbf{y}}k_x$	1	P	$D_{6h}(\Gamma_2^-)^*$
Γ_3^-	–	$\hat{\mathbf{z}}k_x(k_x^2-3k_y^2),\ k_z[(k_x^2-k_y^2)\hat{\mathbf{x}}-2k_x k_y\hat{\mathbf{y}}]$	1	P	$D_{6h}(\Gamma_3^-)^*$
Γ_4^-	–	$\hat{\mathbf{z}}k_y(k_y^2-3k_x^2),\ k_z[(k_y^2-k_x^2)\hat{\mathbf{y}}-2k_x k_y\hat{\mathbf{x}}]$	1	P	$D_{6h}(\Gamma_4^-)^*$
Γ_5^-	$\beta_2<0$	$\hat{\mathbf{x}}k_z,\ \hat{\mathbf{z}}k_x$	3	–	$D_{2h}(\Gamma_2^-)$
		$\hat{\mathbf{y}}k_z,\ \hat{\mathbf{z}}k_y$	3	P	$D_{2h}(\Gamma_4^-)$
	$\beta_2>0$	$\hat{\mathbf{z}}(k_x+ik_y),\ k_z(\hat{\mathbf{x}}+i\hat{\mathbf{y}})$	2	P	$D_{6h}(\Gamma_5^-)^*$

TABLE VI. (*Continued*).

Γ	β_i	$\psi(\mathbf{k})/\mathbf{d}(\mathbf{k})$	(i)	(ii)	(iii)
Γ_6^-	$\beta_2<0$	$\hat{\mathbf{x}}k_x-\hat{\mathbf{y}}k_y$	3	–	$D_{2h}(\Gamma_1^-)$
		$\hat{\mathbf{x}}k_y+\hat{\mathbf{y}}k_x$	3	P	$D_{2h}(\Gamma_3^-)$
	$\beta_2>0$	$(\hat{\mathbf{x}}+i\hat{\mathbf{y}})(k_x+ik_y)$	2	P	$D_{6h}(\Gamma_6^-)^*$
		(c)			
Γ_1^+	–	$1,k_x^2+k_y^2,k_z^2$	1	–	$D_{4h}(\Gamma_1^+)^*$
Γ_2^+	–	$k_xk_y(k_x^2-k_y^2)$	1	L	$D_{4h}(\Gamma_2^+)^*$
Γ_3^+	–	$k_x^2-k_y^2$	1	L	$D_{4h}(\Gamma_3^+)^*$
Γ_4^+	–	k_xk_y	1	L	$D_{4h}(\Gamma_4^+)^*$
Γ_5^+	$4\beta_2>\beta_3,\ \beta_2>0$	$k_z(k_x+ik_y)$	2	L	$D_{4h}(\Gamma_5^+)^*$
	$\beta_2,\beta_3<0$	$k_z(k_x+k_y)$	2	L	$D_{2h}(\Gamma_2^+)$
	$4\beta_2<\beta_3,\ \beta_3>0$	k_xk_z	2	L	$D_{2h}(\Gamma_2^+)$
Γ_1^-	–	$\hat{\mathbf{x}}k_x+\hat{\mathbf{y}}k_y,\ \hat{\mathbf{z}}k_z$	1	–	$D_{4h}(\Gamma_1^-)^*$
Γ_2^-	–	$\hat{\mathbf{x}}k_y-\hat{\mathbf{y}}k_x$	1	P	$D_{4h}(\Gamma_2^-)^*$
Γ_3^-	–	$\hat{\mathbf{x}}k_x-\hat{\mathbf{y}}k_y$	1	P	$D_{4h}(\Gamma_3^-)^*$
Γ_4^-	–	$\hat{\mathbf{x}}k_y+\hat{\mathbf{y}}k_x$	1	P	$D_{4h}(\Gamma_4^-)^*$
Γ_5^-	$4\beta_2>\beta_3,\ \beta_2>0$	$\hat{\mathbf{z}}(k_x+ik_y),\ k_z(\hat{\mathbf{x}}+i\hat{\mathbf{y}})$	2	P	$D_{4h}(\Gamma_5^-)^*$
	$\beta_2,\beta_3<0$	$\hat{\mathbf{z}}(k_x+k_y),\ k_z(\hat{\mathbf{x}}+\hat{\mathbf{y}})$	2	P	$D_{2h}(\Gamma_2^-)$
	$4\beta_2<\beta_3,\ \beta_3>0$	$\hat{\mathbf{z}}k_x,\ \hat{\mathbf{x}}k_z$	2	P	$D_{2h}(\Gamma_2^-)$

column c in Table VI(a)–(c). Furthermore, time-reversal symmetry can also be lost. In this case the state is intrinsically complex and cannot be transformed to a real state by the application of a U(1) gauge transformation. We shall see below that the symmetry breakdown of the point group or time-reversal symmetry leads to various physical effects, that are unknown in conventional superconductors, which only break the U(1) gauge symmetry.

It is found that the classified states can have line or point nodes of zeros in the gap (column a of Table VI). This fact is important for the low-temperature behavior of various thermodynamic quantities, as will be discussed in the next section. It can be proved that odd-parity states in general do not generate line nodes if spin-orbit coupling is present (Blount, 1985). Only some special basis functions have line nodes in the above classification (see Table VI). If we consider a superposition of several such basis functions due to spin-orbit coupling these line nodes are removed. The zero nodes listed in Table VI correspond to the general symmetry properties of the state and may differ from that of the special examples given for $\hat{\Delta}(\mathbf{k})$, which may have more nodes due to their simple form (see Volovik and Gor'kov, 1984, 1985).

Considering the superconducting states classified, the question arises whether they really can be "pure" states, belonging to only one irreducibile representation for all temperatures below T_c. Even if we assume that the transition temperature of the dominant representation is much higher than all the others, there is the possibility of finding a small admixture of basis functions of other irreducible representations in the solution of the gap equation at all temperatures below T_c. This was already mentioned by Leggett (1975) and Wojtanowski and Wölfle (1986) in the case of continuous space symmetry and confirmed by Monien *et al.* (1986a, 1986b) for point-group symmetry. Such an admixture with other representations can be caused by the breakdown of the point-group symmetry below T_c, because this changes the symmetry properties of the gap equation. We can write the gap equation in the form

$$\Delta_{s_1s_2}(\mathbf{k})=-\sum_{\mathbf{k}',s_3s_4}\tilde{V}_{s_2s_1s_3s_4}(\mathbf{k},\mathbf{k}')\Delta_{s_3s_4}(\mathbf{k}')\ , \qquad (2.34)$$

where

$$\tilde{V}_{s_1s_2s_3s_4}(\mathbf{k},\mathbf{k}')=V_{s_1s_2s_3s_4}(\mathbf{k},\mathbf{k}')\tanh(E_{\mathbf{k}'}/2k_BT)/2E_{\mathbf{k}'} .$$

Since the gap function enters in the excitation spectrum $E_{\mathbf{k}}$, below T_c the function $\tilde{V}$ has the symmetry of $\mathrm{tr}(\hat{\Delta}^\dagger\hat{\Delta})(\mathbf{k})$. If $\tilde{V}$ has a lower symmetry than the original one, the gap function $\hat{\Delta}(\mathbf{k})$ is no longer an eigenfunction in general. The problem of which gap functions $\hat{\Delta}'(\mathbf{k})$ of other representations can mix with the original $\hat{\Delta}(\mathbf{k})$ is determined by the existence condition of matrix elements of the form

$$\sum_{\mathbf{k},\mathbf{k}',s_1,s_2,s_3,s_4}\Delta_{s_1s_2}(\mathbf{k})\tilde{V}_{s_1s_2s_3s_4}(\mathbf{k},\mathbf{k}')\Delta'_{s_3s_4}(\mathbf{k}')\ . \qquad (2.35)$$

This matrix element can be finite only if both gap functions belong to the same representation of the point group where $\tilde{V}$ is invariant. Therefore the possibility of such an admixture is determined by the following necessary conditions:

(1) The gap function $\hat{\Delta}(\mathbf{k})$ breaks the point-group symmetry G. The new point group G' is defined to be the

largest subgroup of G in which $E_{\mathbf{k}}$ is an invariant function of $\mathbf{k}$.

(2) The basis function $\hat{\Delta}'(\mathbf{k})$ belongs to the same irreducible representation of G' as $\hat{\Delta}(\mathbf{k})$.

We consider three examples of the cubic point group:

- The gap function $\psi(\mathbf{k})=k_x^2+\omega k_y^2+\omega^2 k_z^2$ has no admixture because it does not lower the point-group symmetry.
- The gap function $\psi(\mathbf{k})=k_z k_y$ breaks the point-group symmetry ($O_h \rightarrow D_{4h}$), but there exists no other gap function that belong to the same representation (Γ_4^+) of D_{4h}. Therefore no admixture appears.
- The gap function $\psi(\mathbf{k})=2k_z^2-k_x^2-k_y^2$ $[D_{4h}(\Gamma_1^+)]$ satisfies both conditions and is mixed with the basis function of Γ_1^+ of O_h.

The relation of the admixture varies with the temperature. Close to the transition point where $\hat{\Delta}(\mathbf{k})$ has the temperature dependence $(T_c-T)^{1/2}$, the admixed $\hat{\Delta}'(\mathbf{k})$ is proportional to $(T_c-T)^{3/2}$ (we call it a "driven" order parameter). This result can be found by constructing the Landau free energy of both representations including the mixing terms. We shall touch on this point in Sec. VI, where we discuss the combination of different representations. In Table VI, states that are pure below T_c are marked with a star.

The Ginzburg-Landau theory of superconductivity, as an extension of the simple phase-transition theory, also takes into account the spatial variation of the order parameter and includes the gauge-invariant coupling of the order parameter to the magnetic field. This formulation is well known for the conventional case, where it was used as a very good description of the superconducting state even before the microscopic theory was developed. It is a simple procedure to extend the free energies above to complete Ginzburg-Landau theories of unconventional superconductors. The construction of these lowest-order coupling terms is similar to that for the homogeneous terms. We have to combine the gradient $\mathbf{D}=\nabla-2ie\mathbf{A}/c$ with the order parameter $\eta(\Gamma,m)$ into invariant second-order terms ($\mathbf{A}$ is the vector potential). These terms are obtained by decomposition of the product,

$$\mathcal{D}^*_{(D)}\otimes\Gamma^*\otimes\mathcal{D}_{(D)}\otimes\Gamma \; . \qquad (2.36)$$

The representation of $\mathbf{D}$ is denoted by $\mathcal{D}_{(D)}$. Again only the invariant Γ_1^+ component enters in the free-energy expansion. In the point-group symmetries under consideration, $\mathcal{D}_{(D)}$ is Γ_4^- for O_h with the basis $\{D_x,D_y,D_z\}$, $\Gamma_2^-\oplus\Gamma_5^-$ for D_{6h} with the basis $\{D_z\}\oplus\{D_x,D_y\}$, and $\Gamma_2^-\oplus\Gamma_5^-$ for D_{4h} with the basis $\{D_z\}\oplus\{D_x,D_y\}$. In Table VII(a)–(c) the gradient terms are listed. With these terms additional parameters K_i are introduced in the free energy. In the strong-coupling limit they are material constants undetermined by this theory, similarly to the β_i parameters.

Finally, adding the magnetic-field energy term, we obtain the complete Ginzburg-Landau theory:

TABLE VII. Gradient terms of (a) the cubic symmetry O_h, (b) the hexagonal symmetry D_{6h}, and (c) the tetragonal symmetry D_{4h}. The coefficients K_i (mass tensors) are material-dependent constants.

Γ	Gradient terms
	(a)
$\Gamma_{1,2}^{\pm}$	$K_1[\lvert D_x\eta\rvert^2+\lvert D_y\eta\rvert^2+\lvert D_z\eta\rvert^2]$
$\Gamma_3^{\pm}$	$K_1[\lvert D_x\eta_1\rvert^2+\lvert D_y\eta_1\rvert^2+\lvert D_z\eta_1\rvert^2+\lvert D_x\eta_2\rvert^2+\lvert D_y\eta_2\rvert^2+\lvert D_z\eta_2\rvert^2]$
	$+K_2[2(\lvert D_z\eta_2\rvert^2-\lvert D_z\eta_1\rvert^2)-(\lvert D_x\eta_2\rvert^2-\lvert D_x\eta_1\rvert^2)-(\lvert D_y\eta_2\rvert^2-\lvert D_y\eta_1\rvert^2)$
	$+\sqrt{3}\{(D_x\eta_1)(D_x\eta_2)^*-(D_y\eta_1)(D_y\eta_2)^*+\text{c.c.}\}]$
$\Gamma_{4,5}^{+}$	$K_1[\lvert D_x\eta_1\rvert^2+\lvert D_y\eta_2\rvert^2+\lvert D_z\eta_3\rvert^2]$
	$+K_2[\lvert D_x\eta_2\rvert^2+\lvert D_x\eta_3\rvert^2+\lvert D_y\eta_1\rvert^2+\lvert D_y\eta_3\rvert^2+\lvert D_z\eta_1\rvert^2+\lvert D_z\eta_2\rvert^2]$
	$+K_3[(D_x\eta_1)^*(D_y\eta_2)+(D_y\eta_2)^*(D_z\eta_3)+(D_z\eta_3)^*(D_x\eta_1)+\text{c.c.}]$
	$+K_4[(D_x\eta_2)^*(D_y\eta_1)+(D_y\eta_3)^*(D_z\eta_2)+(D_x\eta_3)^*(D_z\eta_1)+\text{c.c.}]$
	(b)
$\Gamma_{1,2,3,4}^{\pm}$	$K_1(\lvert D_x\eta\rvert^2+\lvert D_y\eta\rvert^2)+K_2\lvert D_z\eta\rvert^2$
$\Gamma_{5,6}^{\pm}$	$K_1\lvert D_x\eta_1+D_y\eta_2\rvert^2+K_2\lvert D_x\eta_2-D_y\eta_1\rvert^2$
	$+K_3\{\lvert D_x\eta_1-D_y\eta_2\rvert^2+\lvert D_x\eta_2+D_y\eta_1\rvert^2\}+K_4[\lvert D_z\eta_1\rvert^2+\lvert D_z\eta_2\rvert^2]$
	(c)
$\Gamma_{1,2,3,4}^{\pm}$	$K_1(\lvert D_x\eta\rvert^2+\lvert D_y\eta\rvert^2)+K_2\lvert D_z\eta\rvert^2$
$\Gamma_5^{\pm}$	$K_1[\lvert D_x\eta_1\rvert^2+\lvert D_y\eta_2\rvert^2]+K_2[\lvert D_x\eta_2\rvert^2+\lvert D_y\eta_1\rvert^2]$
	$+K_3[(D_x\eta_1)^*(D_y\eta_2)+\text{c.c.}]+K_4[(D_x\eta_2)^*(D_y\eta_1)+\text{c.c.}]$
	$+K_5[\lvert D_z\eta_1\rvert^2+\lvert D_z\eta_2\rvert^2]$

$$F=F_0+\int \left[F_{\text{homogeneous}}+F_{\text{gradient}}+\frac{\mathbf{B}^2}{8\pi}\right]d^3x \; . \tag{2.37}$$

These generalized Ginzburg-Landau theories describe the phenomenology of unconventional superconductors, close to T_c, disregarding fluctuation effects.

III. BULK PROPERTIES OF UNCONVENTIONAL SUPERCONDUCTORS

A. Low-temperature properties

1. Power-law behaviors

In a conventional s-wave superconductor the order parameter is totally rotationally symmetric. Therefore the low-energy excitations have a gap except for the case of a gapless superconductor with magnetic impurities. For the s-wave state there is moreover no low-lying collective mode, since in the case of charged particles the collective density fluctuations are nothing but plasma modes. The existence of the gap in the excitation spectrum naturally leads to the exponential temperature dependence of various physical quantities, such as the specific heat, relaxation rate of nuclear magnetic resonance (NMR), and Knight shift. On the other hand, in an unconventional superconductor the order parameter can have point or line zeros. Due to the excitations across these points or lines, the excitation spectrum starts from zero energy.

The density of states of the quasiparticles is defined by

$$\rho(\omega)=\sum_{k,\pm}\delta(\omega-E_{k\pm}) \; , \tag{3.1}$$

where $E_{k\pm}$ is the quasiparticle energy given in Sec. II.A. In this section we shall restrict ourselves to the case of unitary states, $E_{k\pm}=E_k$.

Let us consider several typical examples. In an ordinary s-wave superconductor the density of states is

$$\rho(\omega)=\begin{cases} 0 \quad (\omega<\Delta_0) \; , \\ N(0)\omega/\sqrt{\omega^2-\Delta_0^2} \quad (\omega>\Delta_0) \; , \end{cases} \tag{3.2}$$

where $N(0)$ is the density of states at the Fermi energy in the normal phase and Δ_0 is the magnitude of the gap function. The density of states has a gap of Δ_0 and it diverges at $\omega=\Delta_0$.

Now we turn to examples of the p-wave states in rotationally symmetric space. In ^{3}He two superfluid phases exist under different pressures. The low-pressure B phase is the so called Balian-Werthamer (BW) state of p-wave pairing and the high-pressure A phase is the so-called Anderson-Brinkman-Morel (ABM or axial) state. The gap function in the BW state,

$$\Delta_{ss'}(\mathbf{k})=\Delta_0\begin{bmatrix} -\hat{k}_x+i\hat{k}_y & \hat{k}_z \\ \hat{k}_z & \hat{k}_x+i\hat{k}_y \end{bmatrix} \; , \tag{3.3}$$

has a constant product $\Delta\Delta^\dagger=\Delta_0^2$. Thus the density of states has the same form as the ordinary s-wave state. Consequently the equilibrium thermodynamic properties of the BW state and the s-wave state are identical. This should not be misunderstood that all their properties are identical. Nonequilibrium properties of the BW state like spin susceptibility exhibit certain differences from those of the BCS state.

On the other hand, the gap becomes zero at two points in the ABM or axial state, where the gap function has the form

$$\Delta_{ss'}(\mathbf{k})=\Delta_0\begin{bmatrix} \hat{k}_x+i\hat{k}_y & 0 \\ 0 & \hat{k}_x+i\hat{k}_y \end{bmatrix} \; . \tag{3.4}$$

Here the density of states is given by

$$\rho(\omega)=N(0)\frac{1}{2}\frac{\Delta_0}{\omega}\left\{\frac{\omega}{\Delta_0}+\frac{1}{2}\left[\left[\frac{\omega}{\Delta_0}\right]^2-1\right] \times\log\frac{\omega+|\Delta_0|}{|\omega-|\Delta_0||}\right\} \; . \tag{3.5}$$

It varies as ω^2 at low energies and has a logarithmic divergence at $\omega=\Delta_0$.

The third example of the p-wave state is the polar state (not realized in ^{3}He), where the gap function is

$$\Delta_{ss'}(\mathbf{k})=\Delta_0\begin{bmatrix} \hat{k}_z & 0 \\ 0 & \hat{k}_z \end{bmatrix} \; . \tag{3.6}$$

Obviously the gap has line zeros on the equator. For the density of states we obtain

$$\rho(\omega)=\begin{cases} N(0)\frac{\pi}{2}\frac{\omega}{\Delta_0} \quad (\omega<\Delta_0) \; , \\ N(0)\frac{\omega}{\Delta_0}\arcsin\frac{\Delta_0}{\omega} \quad (\omega>\Delta_0) \; . \end{cases} \tag{3.7}$$

It has a form linear in ω for low energies ($\omega<\Delta_0$) and is finite at $\omega=\Delta_0$.

The three states of p-wave pairing considered here are representative examples offered in order to discuss the density of states of quasiparticles in unconventional superconductors. The important point is that the generic form of $\rho(\omega)$ at low energies depends solely on the topology of the gap zeros.[3] If they are line zeros, then $\rho(\omega)\propto\omega$, and if they are point zeros, then $\rho(\omega)\propto\omega^2$. The difference in the energy dependence of $\rho(\omega)$ is reflected in the temperature dependence of various physical quantities at low temperatures. As a first example we consider the specific heat. At low temperatures where the T dependence of the order parameter can be neglected, the specific heat is given by

[3] A generalization to the case of a multiband Fermi surface is discussed by Volovik (1989) and Vasil'chenko and Sokol (1989).

$$C=\frac{2}{T}\int_0^\infty dE\,\rho(E)E^2\left[-\frac{df}{dE}\right]\quad (T\ll T_c)\;, \tag{3.8}$$

where $f(E)$ is the Fermi distribution function. Therefore it is obvious that the T dependence of the specific heat depends on the topology of the gap structure in the following way:

$$C\propto\begin{cases}T & \text{gapless}\;,\\ T^2 & \text{line zeros}\;,\\ T^3 & \text{point zeros}\;.\end{cases} \tag{3.9}$$

Another example is the NMR relaxation rate, which is given by (Moriya, 1963)

$$1/T_1=\gamma_N^2 A_{\rm hf}^2 k_B T\sum_{\mathbf{q}}{\rm Im}\chi^{-+}(\mathbf{q},\omega_0)/\omega_0\;, \tag{3.10}$$

where ω_0 is the nuclear resonance frequency, γ_N the gyromagnetic ratio of the nuclear spin, $A_{\rm hf}$ the hyperfine coupling constant, and $\chi^{-+}(\mathbf{q},\omega)$ the dynamical susceptibility transverse to the magnetic field at the nucleus. It is straightforward to extend the standard BCS result (Hebel and Slichter, 1959) to include the unconventional case,

$$\frac{T_{1N}}{T_1}=\frac{2}{N(0)^2}\int_0^\infty dE\,\rho(E)\rho(E+\omega_0)\left[1-\frac{\langle\Delta_{\uparrow\downarrow}(\hat{\mathbf{k}})\rangle}{E}\frac{\langle\Delta^*_{\downarrow\uparrow}(\hat{\mathbf{k}})\rangle}{E+\omega_0}\right]\left[-\frac{df}{dE}\right]\;, \tag{3.11}$$

where $1/T_{1N}$ is the relaxation rate in the normal state and $\langle\Delta_{\uparrow\downarrow}(\hat{\mathbf{k}})\rangle$ denotes the average of the order parameter on the Fermi surface. This average vanishes for the unconventional superconductors, which belong to other representations than Γ_1^+. The resonance frequency is generally small compared with energy scales of electrons. Therefore we may take the limit of $\omega_0\rightarrow 0$ if the integral converges. However, for the s-wave or the BW state, the integral diverges logarithmically if ω_0 is set equal to zero. For superconducting states with point or line zeros, the integral converges and the temperature dependence of $1/T_1$ at low temperatures is given as

$$1/T_1\propto\begin{cases}T & \text{gapless}\;,\\ T^3 & \text{line zeros}\;,\\ T^5 & \text{point zeros}\;.\end{cases} \tag{3.12}$$

One remark is in order here. As mentioned in Sec. II.B, in heavy-fermion systems that have ions with heavy mass like Ce or U, spin-orbit coupling should also be important for the Cooper pairs (Anderson, 1984). An important consequence of group theory is that, with spin-orbit coupling, line zeros are not allowed for odd-parity superconductors (Volovik and Gor'kov, 1984, 1985; Blount, 1985; Ueda and Rice, 1985a, 1985b). Blount, in particular, gave a general proof of this. Therefore at very low temperatures pure samples should obey power laws corresponding to the point zeros when they are odd-parity superconductors.

Various power-law behaviors are reported in heavy-fermion materials for many properties, including the specific heat and the NMR relaxation rate discussed here. We shall say more about these experimental results in Sec. VII. The accumulated body of data from this type of experiment indicates clearly that there are many low-lying excitations associated with nodes of gap functions in heavy-fermion superconductors. However, in some cases there is no consistency about the gap structures among the results for different quantities experimentally observed, if we assume exponents for a pure material. One possible explanation for this kind of inconsistency is that the temperature range experimentally accessible is not yet sufficiently low to derive the genuine exponents. Another, probably more plausible, explanation is that this discrepancy can be resolved when we include the effect of impurity scatterings, which is the subject of the next section.

The power-law behaviors discussed here are a manifestation of the anisotropy of the gap function of unconventional superconducting states. However, these power laws give information only about the generic form of the gap function. Recently another experimental method was proposed to determine the wave-vector dependence of the gap function directly, namely, Andreev scattering (Bruder, 1990). The idea is to use a point contact to inject electrons into the normal part of a normal/superconductor (NS) junction. An electron with wave vector $\mathbf{k}$ and kinetic energy E (above the Fermi energy), such that $E<\Delta(\mathbf{k})$, cannot be simply transmitted to the superconductor but will be Andreev reflected (Andreev, 1964). This means that the electron, together with another electron of the normal Fermi sea, will enter the superconductor as a Cooper pair and a hole-like quasiparticle will be reflected along the path of the incoming electron. Andreev scattering has been seen in experiments involving silver/lead interfaces (Bozhko *et al*, 1982; Benistant *et al.*, 1983), in which the magnitude of the gap function could be determined from the energy dependence of the Andreev reflection coefficient. What is required for the purpose of identifying unconventional superconductors is an angle-resolved version of these experiments, i.e., a measurement of the directional dependence of the differential conductivity of an NS junction where S is a candidate for unconventional superconductivity. Although a satisfactory solution for the problem of collimating and focusing the reflected holes has not yet been found, the experiment has the potential advantage that it couples to the $\mathbf{k}$ dependence of the gap function in a very direct way.

2. Effect of impurities

It is well known that nonmagnetic impurities in *s*-wave superconductors do not change the thermodynamic properties (Anderson's theorem, 1959). Only paramagnetic impurities act as depairing centers. On the other hand, the depairing effect of nonmagnetic impurities on unconventional states was already recognized in the early work of Balian and Werthamer (1963). In addition to the suppression of T_c, impurities will also modify the low-temperature properties. For the BW state, Buchholtz and Zwicknagl (1981) discussed the change in density of quasiparticle states due to a magnetic field, impurities, and a surface and showed that the response to these perturbations are quite different from those of conventional superconductors. In this section we shall consider the effect of impurities on unconventional superconducting states.

The most natural framework in which to discuss the effect of impurity scattering on superconductivity is the Abrikosov-Gor'kov theory (Abrikosov and Gor'kov, 1960; see also Skalski *et al.*, 1964, and Maki, 1969). The essential properties of the impurity scattering may be seen in the simple example of *s*-wave scattering. It is convenient to simplify the calculation by neglecting spin-orbit coupling.

In the Abrikosov-Gor'kov theory, the gap function is given by

$$\Delta_{ss}(\mathbf{k})=-T\sum_{\mathbf{k}'\omega_n} V(\mathbf{k},\mathbf{k}')F_{ss'}(\mathbf{k}',i\omega_n) \ , \qquad (3.13)$$

where F is the anomalous Green's function (see Appendix B). In this formalism the gap function can be considered as the (anomalous) self-energy due to the pairing potential. Impurity scattering gives additional contributions to the self-energy. First, we treat this problem in the Born approximation (Gor'kov and Kalugin, 1985; Ueda and Rice, 1985b). One contribution to the self-energy is of the normal type, Fig. 1(a),

$$\Sigma^{(1)}(i\omega_n)=n_{\mathrm{i}}u^2\sum_{\mathbf{k}'}G(\mathbf{k}',i\omega_n) \ , \qquad (3.14)$$

where n_{i} is the impurity concentration and u characterizes the *s*-wave scattering potential $[G_{s,s'}(\mathbf{k},i\omega_n)=G(\mathbf{k},i\omega_n)\delta_{s,s'}]$. There is also a contribution of the anomalous type, Fig. 1(b),

$$\Sigma^{(2)}_{ss'}(i\omega_n)=n_i u^2\sum_{\mathbf{k}'}F_{ss'}(\mathbf{k}',i\omega_n) \ . \qquad (3.15)$$

In the case of nonmagnetic impurities in *s*-wave superconductors, Anderson's theorem manifests itself in the following fact. For the *s*-wave state $\Sigma^{(1)}$ is simply proportional to $i\omega_n$ and $\Sigma^{(2)}$ is proportional to Δ, and their proportionality constants are the same under the assumption of a constant density of states near the Fermi energy. Therefore the effect of impurity scattering can be taken as a simple renormalization of the energy scale without any influence on thermodynamic properties. In contrast,

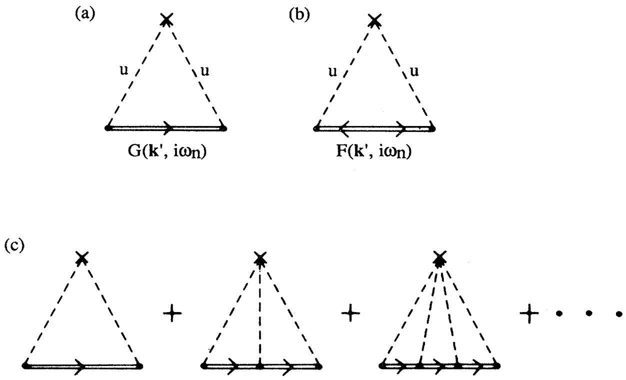

FIG. 1. The two types of self-energies of impurity scattering: normal and anomalous. In the Born approximation the normal-type self-energy is expressed by the diagram (a) and the anomalous one by (b). In the *T*-matrix approximation, multiple-scattering processes (c) are also taken into account.

for any unconventional state $\Sigma^{(2)}$ is zero, since the summation in Eq. (3.15) vanishes. Therefore simple scaling no longer works in this case. Generally, a difference between the two proportionality constants leads to depairing effects.

With the self-energies due to impurity scattering, the Gor'kov equations for the Green's functions (Appendix B) are modified as

$$[i\omega_n-\varepsilon(\mathbf{k})-\Sigma^{(1)}(i\omega_n)]G(\mathbf{k},i\omega_n)] \\ -\Sigma_{s'}\Delta_{ss'}(\mathbf{k})F^{\dagger}_{s's}(\mathbf{k},i\omega_n)=1 \qquad (3.16)$$

$$[i\omega_n+\varepsilon(\mathbf{k})+\Sigma^{(1)}(-i\omega_n)]F^{\dagger}_{ss'}(\mathbf{k},i\omega_n) \\ -\Delta^{\dagger}_{ss'}(\mathbf{k})G(\mathbf{k},i\omega_n)=0 \ . \qquad (3.17)$$

For the unitary states they are easy to solve:

$$G(\mathbf{k},i\omega_n)=\frac{i\tilde{\omega}_n+\varepsilon(\mathbf{k})}{(i\tilde{\omega}_n)^2-\varepsilon(\mathbf{k})^2-\Delta(\mathbf{k})\Delta^{\dagger}(\mathbf{k})} \qquad (3.18)$$

$$F^{\dagger}_{ss'}(\mathbf{k},i\omega_n)=\frac{+\Delta^{\dagger}_{ss'}(\mathbf{k})}{(i\tilde{\omega}_n)^2-\varepsilon(\mathbf{k})^2-\Delta(\mathbf{k})\Delta^{\dagger}(\mathbf{k})} \ , \qquad (3.19)$$

where $i\tilde{\omega}_n=i\omega_n-\Sigma^{(1)}(i\omega_n)$. By substituting Eqs. (3.18) and (3.19) into Eqs. (3.13) and (3.14), we obtain self-consistency equations for $\Delta_{ss'}(\mathbf{k})$ and $\Sigma^{(1)}(i\omega_n)$. We show the self-consistency equations for the BW, ABM, and polar states as typical examples in a rotationally invariant system:

(a) BW state:

$$1=\pi N(0)\bar{V}k_BT\sum_n\frac{1}{\sqrt{\tilde{\omega}_n^2+\Delta_0^2}} \ , \qquad (3.20)$$

$$\tilde{\omega}_n=\omega_n+\Gamma\frac{\tilde{\omega}_n}{\sqrt{\tilde{\omega}_n^2+\Delta_0^2}} \ . \qquad (3.21)$$

(b) ABM state:

$$1=\frac{3}{2}\pi N(0)\bar{V}k_BT\sum_n\frac{1}{2\Delta_0}\left\{\frac{\tilde{\omega}_n}{\Delta_0}-\left[1-\left(\frac{\tilde{\omega}_n}{\Delta_0}\right)^2\right]\frac{i}{2}\log\frac{i\tilde{\omega}_n-\Delta_0}{i\tilde{\omega}_n+\Delta_0}\right\} \tag{3.22}$$

$$\tilde{\omega}_n=\omega_n-\Gamma\frac{i}{2}\frac{\tilde{\omega}_n}{\Delta_0}\log\frac{i\tilde{\omega}_n-\Delta_0}{i\tilde{\omega}_n+\Delta_0}\ . \tag{3.23}$$

(c) Polar state:

$$1=\frac{3}{2}\pi N(0)\tilde{V}k_BT\sum_n\frac{1}{\Delta_0}\left\{\left[1+\left(\frac{\tilde{\omega}_n}{\Delta_0}\right)^2\right]^{1/2}-\left(\frac{\tilde{\omega}_n}{\Delta_0}\right)^2\log\frac{\Delta_0+\sqrt{\tilde{\omega}_n^2+\Delta_0^2}}{\tilde{\omega}_n}\right\} \tag{3.24}$$

$$\tilde{\omega}_n=\omega_n+\Gamma\frac{\tilde{\omega}_n}{\Delta_0}\log\frac{\Delta_0+\sqrt{\tilde{\omega}_n^2+\Delta_0^2}}{\tilde{\omega}_n}\ . \tag{3.25}$$

In the above expressions $\tilde{V}$ is the strength of the pairing interaction defined by $V(\mathbf{k},\mathbf{k}')=3\tilde{V}\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}'$ (rotationally symmetric form) and $\Gamma=\pi n_i N(0)u^2$ is the strength of the impurity scattering, i.e., half of the scattering rate, $\Gamma=1/2\tau_N$. Equations (3.20) and (3.21) have the same form as for magnetic impurities in an ordinary s-wave superconductor.

The three sets of equations reduce to the same set of equations when they are linearized. The transition temperature obtained by the linearized equation decreases as a function of Γ in the same way as in ordinary gapless superconductors with magnetic impurities.

In this formalism the density of states of quasiparticles is given by

$$\rho(\omega)=N(0)\frac{1}{\Gamma}\mathrm{Im}[i\tilde{\omega}_n]|_{i\omega_n=\omega+i\delta}\ . \tag{3.26}$$

In Fig. 2(a) we show the density of states for the BW state. For a weak impurity scattering, there is a gap in the density of states given by

$$\omega_g=\Delta_0[1-(\Gamma/\Delta_0)^{2/3}]^{3/2}\ . \tag{3.27}$$

When $\Gamma/\Delta_0\geq 1$ the system is in a gapless regime. This behavior in the BW state is the same as for the usual paramagnetic impurity effect in an s-wave superconductor. The density of states for the ABM state is shown in Fig. 2(b). The density of states at low energies is given by

$$\rho(\omega)=\begin{cases}N(0)\left(\dfrac{\omega}{\Delta_0}\right)^2\left[1-\dfrac{\pi}{2}\left(\dfrac{\Gamma}{\Delta_0}\right)\right]^{-3} & (\Gamma/\Delta_0<2/\pi)\ ,\\[2ex] N(0)\dfrac{\Delta_0}{\Gamma}\cot\dfrac{\Delta_0}{\Gamma} & (\Gamma/\Delta_0>2/\pi)\ .\end{cases} \tag{3.28}$$

The most remarkable result is obtained for the polar state [Fig. 2(c)]. In this case, when there are impurities, zero-energy excitations always exist and their density of states at the Fermi level is given by

$$\rho(0)=N(0)\Delta_0/\Gamma\sinh(\Gamma/\Delta_0)\ . \tag{3.29}$$

The main conclusion of the Born approximation is that the most serious effect would be on any polar state, i.e., a state with line zeros, since in this case the low-temperature behavior is modified by any concentration of impurities. In contrast, a state with point zeros has a critical concentration before an essential modification of the power laws sets in. Although the analysis was carried through only for the simplest forms of p-wave states, the results depend merely on the generic form of the density of states and therefore should be applicable with slight modification to any state with the same generic form.

In a single-site Kondo problem, resistivity becomes a constant at $T=0$ after a logarithmic increase. The constant corresponds to the phase shift of $\pi/2$, the unitary limit. In many heavy-fermion systems, resistivity increases as temperature is lowered, reaches a maximum, and then decreases rapidly. The value of the resistivity at the maximum, in many cases, is consistent with the value of the unitarity limit. Therefore it would not be surprising if scatterers in heavy-fermion systems had large phase shifts, as Pethick and Pines (1986) pointed out. To treat scattering with a large phase shift, the Born approximation is not sufficient, and multiple scattering processes should be included.

Multiple scattering of electrons by magnetic impurities in ordinary superconductors was studied by Shiba (1968), using a T-matrix approximation. He found that there exists a localized excited state around a classical impurity spin, which at finite concentration forms an impurity band. For the investigation of the impurity effect in the BW states mentioned before, Buchholtz and Zwicknagl also employed the T-matrix approximation, as did

Schmitt-Rink, Miyake, and Varma (1986) and Hirschfeld, Vollhardt, and Wölfle (1986), independently, in studying the consequences of resonant impurity scattering in heavy-fermion systems.

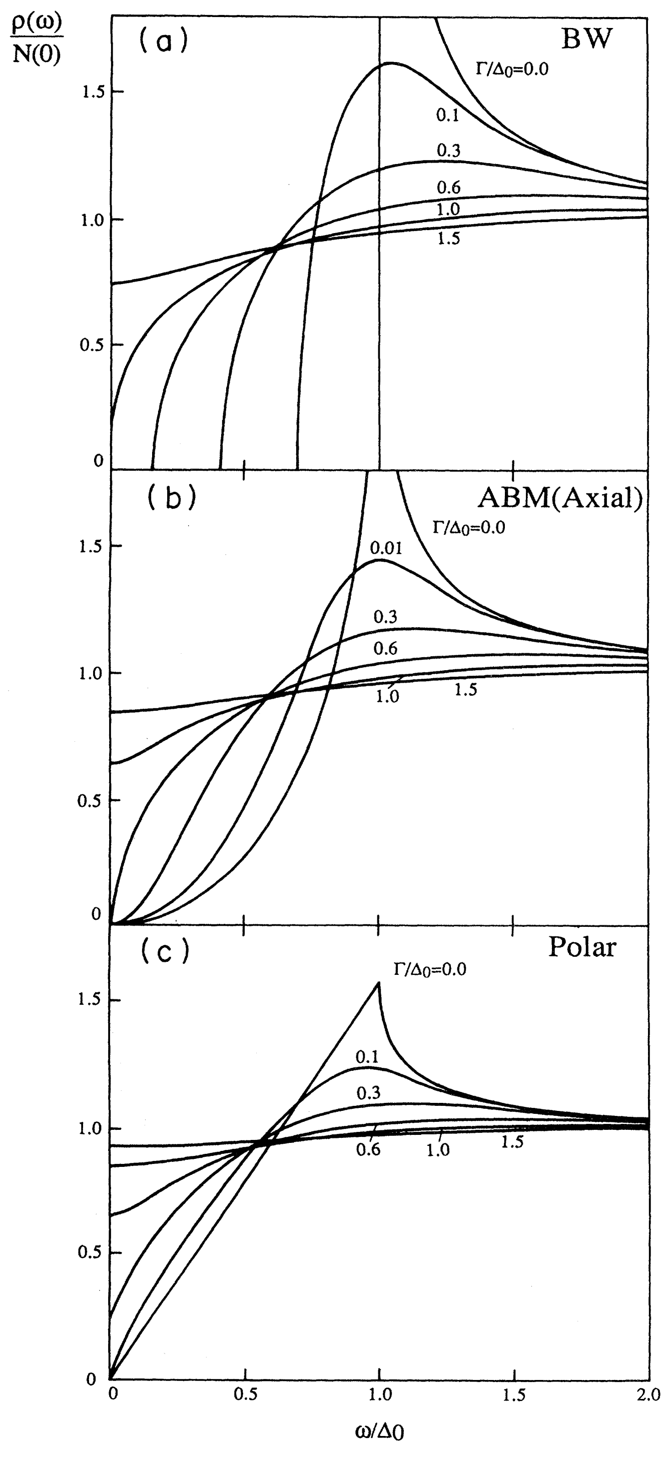

FIG. 2. Density of states of quasiparticles obtained by the Born approximation: (a) for the BW state; (b) for the ABM state; (c) for the polar state (Ueda and Rice, 1985b).

In the T-matrix approximation the self-energy due to impurity scattering is given by [Fig. 1(c)]

$$\Sigma^{(1)}(i\omega_n)=n_i u^2\sum_{\mathbf{k}} G(\mathbf{k},i\omega_n)\Big/\left[1-u\sum_{\mathbf{k}} G(\mathbf{k},i\omega_n)\right] . \tag{3.30}$$

A self-consistent theory is obtained by using the odd part of the self-energy, $[\Sigma^{(1)}(i\omega_n)-\Sigma^{(1)}(-i\omega_n)]/2$, in Eqs. (3.16) and (3.17). The even part of the self-energy, $[\Sigma^{(1)}(i\omega_n)+\Sigma^{(1)}(-i\omega_n)]/2$, is just a shift of the chemical potential and can be neglected. In this theory impurity scattering is characterized by two parameters. One is the phase shift defined by

$$\tan\delta=-\pi u N(0) , \tag{3.31}$$

and the second is the scattering rate $\Gamma=1/2\tau_N\sin^2\delta$ in the unitarity limit $\delta=\pi/2$.

Schmitt-Rink *et al.* and Hirschfeld *et al.* assume that in a Kondo lattice each magnetic ion leads to a phase shift of conduction electrons $\delta=\pi/2$. However, the net effect is zero because of the periodicity; the resistivity of a periodic system is zero at zero temperature. Therefore a nonmagnetic ion in such a lattice would appear to offer a phase shift $\pi/2$ with respect to the background. With this assumption, the impurity scattering is characterized again by a single parameter Γ. Figure 3 shows the calculated density of quasiparticle states for a polar state for various scattering potentials, setting as the pair-breaking parameter $\Gamma/\Delta_0=0.01$. At low energies there is a resonance peak and at higher energies the density of states is almost identical to its value without impurities ($\cot\delta\to\infty$). The same statement can be made for the ABM (axial) state. In both cases the width of the resonance peak increases as Γ/Δ_0 gets larger.

From the density of quasiparticle states, we can immediately see the effect of resonant impurity scatterings on specific heat. At very low temperatures ($T/T_c<0.1$) it shows a small T-linear specific heat due to the appearance of the resonance, while at elevated temperatures it follows closely the power law expected without impurites (Hirschfeld *et al.*, 1986, 1988; Miyake, 1986; Ott *et al.*, 1987). Similarly, the NMR relaxation rate shows a Korringa-like behavior at very low temperatures and follows a power law for the pure case at higher temperatures (Hirschfeld *et al.*, 1988).

The situation is very different for transport properties in heavy-fermion superconductors. For these quantities the Born approximation is inadequate not only quantitatively but also qualitatively. As an example we consider thermal conductivity κ. In a simple kinematic theory it is given by $\kappa=\frac{1}{3}v_F^2\tau C$. In the Born approximation, it can be shown that the product of the relaxation time $\tau(\omega)$ and the density of states $\rho(\omega)$ is almost energy independent (Coffey *et al.*, 1985; Pethick and Pines, 1986). In this result, the modification of $\rho(\omega)$ discussed in this section is neglected, which gives only a minor change when the impurity concentration is small. Therefore the thermal conductivity in the Born approximation is almost linear in T and the coefficient remains the same order as its normal-state value, which contradicts the experimentally observed T^2 behaviors. Pethick and Pines proposed that the discrepancy may be resolved when the resonant nature of the impurity scattering in the unitarity limit is taken into account.

Calculations of the thermal conductivity using the T-matrix approximation were carried out independently by Schmitt-Rink, Miyake, and Varma (1986) and Hirschfeld, Vollhardt, and Wölfle (1986). Their results may be summarized as follows. At very low temperatures, κ/T goes to a finite value due to the appearance of the low energy resonance. At higher temperatures, in a wide temperature range, κ follows a T^2 law for the case of line zeros and a T^3 law for the point zeros. This result means that the product of $\tau(\omega)$ and $\rho(\omega)$ shows almost the same behavior as $\tau_N\rho(\omega)$ where τ_N is the scattering rate in the normal state. This fact cannot be understood by the Born approximation, as we discussed before. It should also be mentioned that vertex corrections to the thermal resistivity are discussed by Hirschfeld, Wölfle, and Einzel (1988).

The T-matrix approximation is also applied to the study of ultrasonic attenuation in heavy fermions (Hirschfeld *et al.*, 1986; Schmitt-Rink *et al.*, 1986). The temperature dependence of the sound attenuation depends on its polarization and propagation direction. Miyake (1986) and Schmitt-Rink *et al.* (1986) have concluded that the assumption of a state with line zeros, together with a scattering in the unitarity limit, leads to results consistent with the experimental observations in UPt_3, $CeCu_2Si_2$, and UBe_{13}.

An anomalous temperature dependence of the London penetration depth in UBe_{13} was reported by Gross *et al.* (1986); $\lambda(T)-\lambda(0)$ follows a T^2 law. These authors analyzed the temperature dependence by the Born approximation and concluded that the behavior is consistent with an energy gap with point nodes. Recently, Choi and Muzikar (1988,1989b) developed a theory of the superfluid density tensor which determines the penetration depth. They treated the impurity scattering by the T-matrix approximation and pointed out the possibility that impurity scattering enhances the anisotropy of the density tensor. Turning to the electromagnetic properties, the electromagnetic absorption in unconventional superconductors was studied by Hirschfeld *et al.* (1989). They found a new structure at $\omega\sim\Delta_0$ associated with transitions into the resonance state.

In summary, impurities modify the power laws, especially at low temperatures. The consequences of resonant scattering in unconventional superconductors for specific heat, thermal conductivity, ultrasonic attenuation, NMR relaxation rate, and electromagnetic absorption have been examined by several authors, as we have seen in this section. In particular, Miyake (1987) and Schmitt-Rink *et al.* (1986) have pointed out that the experimentally observed power laws are more consistent with line zeros than with point zeros. However, to draw a definite conclusion about the gap structure we need further experiments that are directly related to the symmetry of the order parameter.

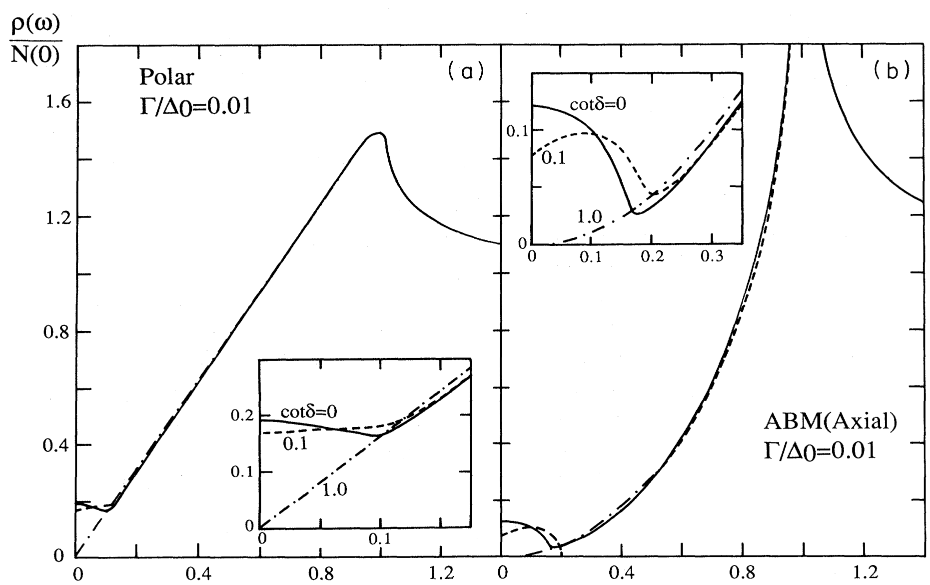

FIG. 3. The density of states of the polar and the ABM states obtained by the T-matrix approximation for a pair-breaking parameter of $\Gamma/\Delta_0=0.01$ and different values of the phase shift. The inserts illustrate the resonance peaks in the low-energy, gapless region (Hirschfeld *et al.*, 1986).

B. Phenomena associated with the phase transition

One purpose of the study of phenomenological theories of the superconducting phase transitions is to identify the symmetry of the superconducting phase in heavy-fermion compounds or at least to establish the assumption of unconventional superconductivity. As we mentioned above, one very important feature of the phase transition of unconventional superconductors is the eventual breakdown of various symmetries, such as the crystal point group and time-reversal symmetry, as well as the U(1) gauge symmetry. It is expected that such loss of symmetry will be manifested in several observable phenomena, even if it might not be so drastic as the occurrence of superconductivity itself. In the case of the breakdown of point-group symmetry, one effect is the spontaneous deformation of the lattice (Joynt and Rice, 1985; Ozaki, 1986). On the other hand, an externally produced lowering of the crystal symmetry eventually causes a splitting of the superconductivity phase transition for a superconductor described by a multicomponent order parameter (Sigrist *et al.*, 1987a, 1987b; Volovik, 1989). Effects related to the breakdown of time-reversal symmetry are also very interesting. However, their discussion is postponed to Sec. V. The superconducting state can also affect the propagation of ultrasound in these systems. A multicomponent order parameter allows various couplings to the ultrasound waves. Via damping in superconductivity domain walls (Joynt *et al.*, 1986) or by exciting collective modes (Hirashima and Namaizawa, 1985, Monien *et al.*, 1986a, 1986b; Wölfle, 1986) an explanation of the experimentally observed ultrasonic attenuation peaks may be possible. Another proposed approach to confirming unconventional superconductivity is to investigate the unconventional direction dependence of the upper critical magnetic field H_{c2} (Gor'kov, 1984; Burlachkov, 1985; Machida *et al.*, 1985).

1. Spontanous crystal lattice deformation

The spatial symmetry of the superconducting phase is manifested in its quasiparticle excitation spectrum $E_{\mathbf{k}}$ or, especially, in the term $\mathrm{tr}[\hat{\Delta}^{\dagger}(\mathbf{k})\hat{\Delta}(\mathbf{k})]$. Joynt and Rice (1985) examined the question of whether there is an observable effect, similar to magneto striction, connected with lowering of the spatial symmetry in $E_{\mathbf{k}}$. How can a coupling between the superconducting order parameter and the crystal lattice be imagined? The basic idea becomes obvious when we write the condensation energy (energy gain with respect to the normal state if the system undergoes a superconducting transition) at $T=0$ in the form

$$E_c=-\frac{1}{4}\sum_{\mathbf{k}}\delta(\varepsilon(\mathbf{k})-\mu)\,\mathrm{tr}[\hat{\Delta}^{\dagger}(\mathbf{k})\hat{\Delta}(\mathbf{k})] , \qquad (3.32)$$

where $\sum_{\mathbf{k}}\delta(\varepsilon(\mathbf{k})-\mu)$ is the (normal-state) density of states at the Fermi surface. It is reasonable to assume that a superconducting system with an anisotropic $\hat{\Delta}(\mathbf{k})$ maximizes its condensation energy by an enhancement of the density of states in the directions along which the gap is larger and by a decrease along the directions of a small gap. This increase in the density of states can be produced by a change of the crystal lattice. The coupling between lattice deformation (strain) and the band energy can be approximated in lowest order by

$$\varepsilon(\mathbf{k}\epsilon)=\varepsilon(\mathbf{k})+\sum_{i,j}\Lambda_{ij}\epsilon_{ij}k_ik_j , \qquad (3.33)$$

where ϵ_{ij} is the strain tensor and Λ_{ij} a coupling tensor. The form of Λ_{ij} depends on the symmetry of the original lattice structure. Therefore the minimization of Eq. (3.32) with respect to ϵ_{ij}, together with the elastic energy $\frac{1}{2}\sum_{i,j,l,m}c_{ijlm}\epsilon_{ij}\epsilon_{lm}$ of the lattice, leads to the description of the deformation.

In order to treat this effect close to the transition temperature, Ozaki (1986) has introduced a formulation of the strain–order-parameter coupling on the basis of group theory. Following this formulation we add to the Ginzburg-Landau free energy F, given in Sec. II, (a) terms that couple the order parameter η, in second order, to the strain tensor ϵ, in first order, and (b) the elastic energy of the crystal lattice. The restriction for the construction of these terms is again only that they be invariant under all symmetry transformations of the system:

$$F_{\Gamma,\mathrm{strain}}(\eta,\epsilon)=-\sum_{\gamma,m}C(\gamma)\mathcal{V}(\gamma,m;\eta)\epsilon(\gamma,m)+\frac{1}{2}\sum_{\gamma,m}B(\gamma)\epsilon(\gamma,m)^2 . \qquad (3.34)$$

The sum goes over all representations γ, which are components of the decomposition of $\Gamma^*\otimes\Gamma$, and their basis functions labeled by m. The symbol $\epsilon(\gamma,m)$ denotes a combination of ϵ-tensor elements and has the symmetry property of the basis function m in the representation γ of the original point group: $\epsilon(\gamma,m)=\sum_{i,j}\chi_{ij}\epsilon_{ij}$ (see Table VIII). Similarly, $\mathcal{V}(\gamma,m;\eta)$ is the bilinear form of $\eta(\Gamma,m)$ with the symmetry of the basis function (γ,m) (see Table IX). The coupling constants $C(\gamma)$ and the elastic constants $B(\gamma)$ are real numbers characterizing the system.

With these additional terms it is possible to describe the behavior of the lattice by minimization of F with respect to $\epsilon(\gamma,m)$. Clearly, the order parameter is affected by the presence of this coupling. We shall, however, neglect this minor effect now and use in the following example only the "bare" order parameter calculated without the coupling terms in Eq. (3.34). Let us consider the superconducting phase $\psi(\mathbf{k})=\eta k_xk_y[\eta=(0,0,\eta)$ with $|\eta|^2=-A(T)/4(\beta_1+\beta_2)]$ in the representation Γ_5^+ of the cubic point group O_h. Inserting this in Eq. (3.34) and minimizing with respect to $\epsilon(\gamma,m)$, we find

$$\epsilon(\Gamma_1^+)=\frac{C(\Gamma_1^+)|\eta|^2}{B(\Gamma_1^+)} ,\qquad \epsilon(\Gamma_3^+,1)=\frac{2C(\Gamma_3^+)|\eta|^2}{B(\Gamma_3^+)} . \qquad (3.35)$$

All other components $\epsilon(\gamma,m)$ are zero. The first term corresponds to a uniform change of the volume, but the second to an anisotropic deformation. In notation that is easier to understand it is

$$\epsilon_{xx}=\epsilon_{yy}=2\left[\frac{C(\Gamma_1^+)}{B(\Gamma_1^+)}-\frac{\sqrt{2}C(\Gamma_3^+)}{B(\Gamma_3^+)}\right]\frac{|\eta|^2}{2\sqrt{3}},$$
$$\epsilon_{zz}=2\left[\frac{C(\Gamma_1^+)}{2B(\Gamma_1^+)}+\frac{\sqrt{2}C(\Gamma_3^+)}{B(\Gamma_3^+)}\right]\frac{|\eta|^2}{\sqrt{3}}, \tag{3.36}$$

This result describes a deformation of the cubic lattice to a tetragonal symmetry D_{4h} with the fourfold axis parallel to the z direction. The resultant symmetry corresponds to the symmetry of the excitation energy $E_{\mathbf{k}}$ (the gap maxima lie in the x-y plane along the diagonals, whereas in the z direction there is a minimum). Therefore the column "symmetry" in Table VI shows just the lattice symmetry produced by the superconducting transition. In the region close to T_c the temperature dependence of the strain tensor is proportional to $|\eta|^2(T)\sim|T-T_c|$. For $T=0$ Joynt and Rice (1985) gave an estimate for the magnitude of this deformation using experimental data about the dependence of T_c on uniform pressure: $\epsilon(\Gamma_1^+)\sim10^{-6}$ and $\epsilon(\Gamma_3^+,1)\sim10^{-7}$. Since this is a very small effect, it may not be detected by x-ray experiments. One possible way to observe it may be to measure the macroscopic deformation of a single crystal. However, for this purpose it is required that the whole sample choose only one among the degenerate superconducting phases. Otherwise the creation of many domains would destroy this macroscopic effect.

TABLE VIII. Strain tensor combinations as basis functions of the representations of the point group G: (a) for the cubic point group O_h where the coefficients of the elastic energy in Eq. (3.34) have the following relations to the elastic tensor c_{ijkl}: $B(\Gamma_1^+)=c_{11}+2c_{12}$, $B(\Gamma_3^+)=c_{11}-c_{12}$, $B(\Gamma_5^+)=c_{44}/4$; (b) for the hexagonal point group D_{6h} with $B(\Gamma_1^+,1)=[(c_{11}+c_{12})c_{33}-c_{13}^2]/(c_{11}+c_{12}+c_{33}-2c_{13})$, $B(\Gamma_1^+,2)=(c_{11}-c_{13})^2/(c_{11}+c_{12}+c_{33}-2c_{13})$, $B(\Gamma_5^+)=c_{44}/2$, $B(\Gamma_6^+)=(c_{11}-c_{12})$, and $a=(c_{11}+c_{12}-c_{13})/(c_{13}-c_{33})$; (c) for the tetragonal point group D_{4h} with $B(\Gamma_1^+,1)=[(c_{11}+c_{12})c_{33}-c_{13}^2]/(c_{11}+c_{12}+c_{33}-2c_{13})$, $B(\Gamma_1^+,2)=(c_{33}-c_{13})^2/(c_{11}+c_{12}+c_{33}-2c_{13})$, $B(\Gamma_3^+)=c_{11}-c_{12}$, $B(\Gamma_4^+)=c_{66}/2$, $B(\Gamma_5^+)=c_{44}/2$, and $a=(c_{11}+c_{12}-c_{13})/(c_{13}-c_{33})$.

	(a)
$\epsilon(\Gamma_1^+)$	$\frac{1}{\sqrt{3}}(\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz})$
$\epsilon(\Gamma_3^+,1)$	$\frac{1}{\sqrt{6}}(2\epsilon_{zz}-\epsilon_{xx}-\epsilon_{yy})$
$\epsilon(\Gamma_3^+,2)$	$\frac{1}{\sqrt{2}}(\epsilon_{xx}-\epsilon_{yy})$
$\epsilon(\Gamma_5^+,1)$	$\sqrt{2}\epsilon_{yz}$
$\epsilon(\Gamma_5^+,2)$	$\sqrt{2}\epsilon_{zx}$
$\epsilon(\Gamma_5^+,3)$	$\sqrt{2}\epsilon_{xy}$
	(b)
$\epsilon(\Gamma_1^+,1)$	$\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz}$
$\epsilon(\Gamma_1^+,2)$	$a(\epsilon_{xx}+\epsilon_{yy})+\epsilon_{zz}$
$\epsilon(\Gamma_5^+,1)$	$\sqrt{2}\epsilon_{xz}$
$\epsilon(\Gamma_5^+,2)$	$\sqrt{2}\epsilon_{yz}$
$\epsilon(\Gamma_6^+,1)$	$\frac{1}{\sqrt{2}}(\epsilon_{xx}-\epsilon_{yy})$
$\epsilon(\Gamma_6^+,2)$	$\sqrt{2}\epsilon_{xy}$
	(c)
$\epsilon(\Gamma_1^+,1)$	$\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz}$
$\epsilon(\Gamma_1^+,2)$	$a(\epsilon_{xx}+\epsilon_{yy})+\epsilon_{zz}$
$\epsilon(\Gamma_3^+)$	$\frac{1}{\sqrt{2}}(\epsilon_{xx}-\epsilon_{yy})$
$\epsilon(\Gamma_4^+)$	$\sqrt{2}\epsilon_{xy}$
$\epsilon(\Gamma_5^+,1)$	$\sqrt{2}\epsilon_{xz}$
$\epsilon(\Gamma_5^+,2)$	$\sqrt{2}\epsilon_{yz}$

TABLE IX. Bilinear forms of the order parameters in Γ corresponding to the basis functions of the irreducible representations of (a) O_h, (b) D_{6h}, and (c) D_{4h}, constructed by the decomposition of $\Gamma\otimes\Gamma$.

Representation	Bilinear forms
	(a)
$\Gamma_{1,2}^{\pm}$	$\mathcal{V}(\Gamma_1^+)=\lvert\eta\rvert^2$
Γ_3^{+}	$\mathcal{V}(\Gamma_1^+)=\lvert\eta_1\rvert^2+\lvert\eta_2\rvert^2$
	$\mathcal{V}(\Gamma_3^+,1)=\lvert\eta_1\rvert^2-\lvert\eta_2\rvert^2$
	$\mathcal{V}(\Gamma_3^+,2)=\eta_1^*\eta_2+\eta_1\eta_2^*$
$\Gamma_{4,5}^{\pm}$	$\mathcal{V}(\Gamma_1^+)=\lvert\eta_1\rvert^2+\lvert\eta_2\rvert^2+\lvert\eta_3\rvert^2$
	$\mathcal{V}(\Gamma_3^+,1)=2\lvert\eta_3\rvert^2-\lvert\eta_1\rvert^2-\lvert\eta_2\rvert^2$
	$\mathcal{V}(\Gamma_3^+,2)=\sqrt{3}(\lvert\eta_1\rvert^2-\lvert\eta_2\rvert^2)$
	$\mathcal{V}(\Gamma_5^+,1)=\eta_2^*\eta_3+\eta_2\eta_3^*$
	$\mathcal{V}(\Gamma_5^+,2)=\eta_3^*\eta_1+\eta_3\eta_1^*$
	$\mathcal{V}(\Gamma_5^+,3)=\eta_1^*\eta_2+\eta_1\eta_2^*$
	(b)
$\Gamma_{1,2,3,4}^{\pm}$	$\mathcal{V}(\Gamma_1^+,m)=\lvert\eta\rvert^2$
$\Gamma_{5,6}^{\pm}$	$\mathcal{V}(\Gamma_1^+,m)=\lvert\eta_1\rvert^2+\lvert\eta_2\rvert^2$
	$\mathcal{V}(\Gamma_6^+,1)=\lvert\eta_1\rvert^2-\lvert\eta_2\rvert^2$
	$\mathcal{V}(\Gamma_6^+,2)=\eta_1^*\eta_2+\eta_1\eta_2^*$
	(c)
$\Gamma_{1,2,3,4}^{\pm}$	$\mathcal{V}(\Gamma_1^+,m)=\lvert\eta\rvert^2$
$\Gamma_5^{\pm}$	$\mathcal{V}(\Gamma_1^+,m)=\lvert\eta_1\rvert^2+\lvert\eta_2\rvert^2$
	$\mathcal{V}(\Gamma_3^+)=\lvert\eta_1\rvert^2-\lvert\eta_2\rvert^2$
	$\mathcal{V}(\Gamma_4^+)=\eta_1^*\eta_2+\eta_1\eta_2^*$

2. Splitting of the phase transition

Another aspect of the superconducting phase transition including multicomponent order parameters occurs if the symmetry of the crystal lattice is externally lowered, e.g., by the application of uniaxial stress. Remembering the argument for the effect explained in the previous section, we notice that uniaxial deformation of the lattice could support or suppress certain components of the order parameter due to an anisotropic change of the density of states. In the group-theoretical view, this appears as a lifting of degeneracy when the symmetry of the system is lowered, since in most cases the originally degenerate states no longer belong to one single irreducible representation of the new symmetry. The gap functions then have, in principle, to be classified with respect to the new symmetry.

Therefore the application of uniaxial stress to a crystal lattice yields a slight difference of the transition temperatures among the originally degenerate basis gap functions of a multidimensional representation. This problem may be conveniently treated by using the group-theoretical formalism introduced in Sec. II. To illustate this effect we consider here the example of the two-dimensional representation Γ_3^+ of the cubic group O_h.

First we analyze the case of uniaxial stress along the z axis. The cubic lattice is transformed into a tetragonal one. The strain tensor (Table VIII) has therefore a finite component $\epsilon(\Gamma_3^+,1)$, since ϵ_{zz} is different from $\epsilon_{xx}=\epsilon_{yy}$ and also $\epsilon(\Gamma_1^+)$, if the volume is changed. The coupling to the order parameter [Eq. (3.34)] leads to a correction of the second-order terms in the Ginzburg-Landau energy,

$$\begin{aligned}&[A(T)+C(\Gamma_1^+)\epsilon(\Gamma_1^+)+C(\Gamma_3^+)\epsilon(\Gamma_3^+,1)]|\eta_1|^2\\&\quad+[A(T)+C(\Gamma_1^+)\epsilon(\Gamma_1^+)-C(\Gamma_3^+)\epsilon(\Gamma_3^+,1)]|\eta_2|^2\\&\qquad=A_1(T)|\eta_1|^2+A_2(T)|\eta_2|^2\ ,\end{aligned}\tag{3.37}$$

with $A_i(T)=a'(T_i/T_c)(T/T_i-1)$. The new transition temperatures T_i are determined by the zero of the prefactors of $|\eta_i|^2$,

$$\begin{aligned}T_1&\approx T_c\left[1-\frac{1}{a'}[C(\Gamma_1^+)\epsilon(\Gamma_1^+)+C(\Gamma_3^+)\epsilon(\Gamma_3^+,1)]\right]\ ,\\T_2&\approx T_c\left[1-\frac{1}{a'}[C(\Gamma_1^+)\epsilon(\Gamma_1^+)-C(\Gamma_3^+)\epsilon(\Gamma_3^+,1)]\right]\ .\end{aligned}\tag{3.38}$$

The uniform deformation $\epsilon(\Gamma_1^+)$ produces simply a shift of the transition temperature. However, the component $\epsilon(\Gamma_3^+,1)$ yields a split of T_c. Note, that for a volume conserving deformation, an enhancement of the superconducting transition temperature takes place. The lift of degeneracy is explained by the fact that the two-dimensional cubic representation Γ_3^+ splits in tetragonal symmetry into $\Gamma_1^+\oplus\Gamma_3^+$ of D_{4h} (both 1D). We proceed further in the analysis of the Ginzburg-Landau free energy (for the fourth-order terms see Table V in Sec. II) assuming that $C(\Gamma_3^+)<0$ $(T_1>T_2)$ (the treatment of the case $T_1<T_2$ is exactly analogous),

$$\begin{aligned}F=&A_1(T)|\eta_1|^2+A_2(T)|\eta_2|^2+\beta_1(|\eta_1|^2+|\eta_2|^2)^2\\&-4\beta_2|\eta_1|^2|\eta_2|^2\sin^2(\Delta\phi)\ ,\end{aligned}\tag{3.39}$$

where we use the parametrization $\eta_j=|\eta_j|e^{i\phi_j}$ and $\Delta\phi=\phi_1-\phi_2$. Since only the last term contains the relative phase $\Delta\phi$, the minimization condition implies for $\beta_2>0$ $\sin\Delta\phi=\pm1$ and for $\beta_2<0$ $\sin\Delta\phi=0$. Immediately below T_1 the phase

$$|\eta_1|^2=-\frac{A_1(T)}{2\beta_1}\quad\text{and}\quad\eta_2=0\tag{3.40}$$

appears with the nondegenerate gap function $\psi(\mathbf{k})=\eta_1(2k_z^2-k_x^2-k_y^2)/\sqrt{6}$ having the symmetry $D_{4h}(\Gamma_1^+)$. This phase breaks only the U(1) gauge symmetry. Inserting this $|\eta_1|^2$ in F the effective Ginzburg-Landau theory for η_2, we obtain

$$\begin{aligned}\tilde{F}=F_0+&\left[A_2(T)-\left[1-\frac{2\beta_2}{\beta_1}\sin^2\Delta\phi\right]A_1(T)\right]|\eta_2|^2\\&+\beta_1|\eta_2|^4\ .\end{aligned}\tag{3.41}$$

The second-order term of η_2 is renormalized by the presence of the finite order parameter η_1, so that its transition point is not situated at T_2, but is determined by the zero of the total prefactor of $|\eta_2|^2$. It is obvious that this expression remains positive for all temperatures if $\sin\Delta\phi=0$ $(\beta_2<0)$. In that case Eq. (3.40) is the stable phase for all temperatures below T_1. On the other hand, for $\sin\Delta\phi=\pm1$ $(\beta_2>0)$ an additional instability occurs at

$$T_0=T_2\frac{1-G}{1-G\dfrac{T_2}{T_1}}\quad\text{with } G=1-\frac{2\beta_2}{\beta_1}\ .\tag{3.42}$$

Below T_0 the free energy in Eq. (3.39) has to be minimized for both components η_j,

$$\begin{aligned}|\eta_1|^2&=\frac{[A_2(T)-A_1(T)]-2\beta_2A_2(T)}{8\beta_2(\beta_1-\beta_2)}\ ,\\|\eta_2|^2&=\frac{-[A_2(T)-A_1(T)]-2\beta_2A_1(T)}{8\beta_2(\beta_1-\beta_2)}\ .\end{aligned}\tag{3.43}$$

This new phase is twofold degenerate and has the symmetry $D_{2h}(\Gamma_1^+)$, $\psi(\mathbf{k})=a(T)k_z^2+b(T)k_x^2+b^*(T)k_y^2$. The transition to this phase is continuous, i.e., of second order, and breaks the time-reversal $[\psi^*(\mathbf{k})\neq\psi(\mathbf{k})]$ and the point-group symmetry. This analysis shows that uniaxial stress can split a superconducting phase transition, generating two superconducting phases different in symmetry. It is also clear that such an effect can only take place for multicomponent order parameters.

Successive second-order phase transitions could be observed, for example, in the specific heat $C(T)$ measurements. Each transition is accompanied by a discontinuity of $C(T)$. The specific heat is given by

$$C(T)=-T\frac{\partial^2F}{\partial T^2}\ .\tag{3.44}$$

In our example the first transition leads to

$$\Delta C_1=\frac{a'^2}{2\beta_1T_c^2}T_1\tag{3.45}$$

and the second

$$\Delta C_2=\frac{a'^2T_0}{2(\beta_1-\beta_2)T_c^2}-\Delta C_1\frac{T_0}{T_1}\ .\tag{3.46}$$

Comparing the two we find

$$\frac{\Delta C_2}{\Delta C_1}=\frac{\beta_2}{\beta_1-\beta_2}\frac{T_0}{T_1} . \tag{3.47}$$

This ratio can be of the order of unity when we assume that the coefficients β_1 and β_2 are of the same order. Only the splitting of the transitions is proportional to the strain ϵ, but the magnitude of the discontinuities of $C(T)$ at the transitions is mainly determined by the four-order terms in Eq. (3.39) and is therefore almost independent of the strain ϵ. Hence measurements of the specific-heat discontinuities could give a relation among the coefficients β_i (Sigrist *et al.*, 1987; Hess *et al.*, 1989; Machida *et al.*, 1989).

Stress along the [1,1,1] direction produces a rhombohedral deformation of the cubic lattice with the point group D_{3d}. However, no splitting of T_c is expected in the Γ_3^+ representation of O_h, because it is compatible with the two-dimensional representation Γ_3^+ of D_{3d}. Therefore both basis states are still degenerate.

In the same way one finds a large variety of transitions between different superconducting phases for the three-dimensional representations $\Gamma_{4,5}^+$ of O_h in a deformed cubic lattice. Even first-order transitions can occur among different superconducting phases (Sigrist *et al.*, 1987).

In the hexagonal system (D_{6h}) the two-dimensional representations $\Gamma_5^\pm$ and $\Gamma_6^\pm$ split by the application of uniaxial stress in any direction in the basal plane. The behavior is exactly the same as in the cubic representation Γ_3^+ analyzed above.

The property of the two-dimensional representation $\Gamma_5^\pm$ in the tetragonal group D_{4h} is similar. Orthorhombic deformation by uniaxial stress along the [1,0,0] or [1,1,0] direction leads to a splitting of T_c. There are two different types of additional second-order transitions (crystal-symmetry and time-reversal breaking) possible, depending on the coefficients β_i of the fourth-order terms of the Ginzburg-Landau free energy (Volovik, 1989).

Even if the degeneracy of T_c is lifted, regions may be found in the β_i space where additional transitions are suppressed, as we also discussed in the example above. Thus a negative result in such an experiment still cannot rule out unconventional superconductivity. On the other hand, the occurrence of more than one superconducting transition is strong evidence of unconventional superconductivity, since in a conventional superconductor only one superconducting phase exists. Only the possibility of an additional breakdown of symmetry, as allowed by a multicomponent order parameter, could produce further transitions inside the superconducting phase. With regard to this see also Sec. VII.C, where we discussed the double transition observed in UPt_3.

3. The upper critical field H_{c2}

A further typical effect of unconventional (multicomponent) superconductivity is connected with the upper critical field H_{c2}. In several theoretical studies it has been proposed that the anisotropy of H_{c2} be considered in order to prove unconventional superconductivity in the heavy-fermion systems (Gor'kov, 1984; Burlachkov, 1985; Machida *et al.*, 1985). In conventional superconductors the angular dependence of H_{c2} is restricted to the anisotropy produced by the mass tensor (the coefficients K_i of the gradient terms). No anisotropy is expected in the basal plane of a tetragonal or hexagonal system and none at all in a cubic system. A multicomponent order parameter, however, can produce anisotropy even in some of these cases.

To illustrate this we consider the example of the two-dimensional representation Γ_5^+ in a tetragonal system with a magnetic field in the basal (x-y) plane: $\mathbf{H}=(H\cos\theta, H\sin\theta, 0)$. The Ginzburg-Landau free energy is given in Sec. II. The procedure for calculating H_{c2} is exactly the same as in conventional superconductors (see, for example, de Gennes, 1966). If the external field is close to H_{c2} the order parameter is assumed to be small. Therefore the Ginzburg-Landau equation, obtained by variation with respect to η_1 and η_2, can be linearized:

$$\begin{aligned}&(K_1D_x^2+K_2D_y^2+K_5D_z^2)\eta_1\\&\qquad+(K_3D_xD_y+K_4D_yD_x)\eta_2=A(T)\eta_1\\&(K_2D_x^2+K_1D_y^2+K_5D_z^2)\eta_2\\&\qquad+(K_3D_yD_x+K_4D_xD_y)\eta_1=A(T)\eta_2 ,\end{aligned} \tag{3.48}$$

with $\mathbf{D}=\nabla-i(2e/c)\mathbf{A}$. These equations have the form of a two-component Schrödinger equation with an external magnetic field, where $A(T)$ corresponds to the energy eigenvalue, the "Landau levels." In the considered case the most convenient form for the vector potential is $\mathbf{A}=\mathbf{A}(z)=Hz(\sin\theta,-\cos\theta,0)$, because then we can assume homogeneity in x and y directions. The superconducting instability is given by the smallest eigenvalue of the equation [$A(T)=-\omega_c/2$ with ω_c as the cyclotron frequency],

$$\begin{aligned}&\left[\frac{2e}{c}Hz\right]^2\{(K_1\sin^2\theta+K_2\cos^2\theta)\eta_1\\&\qquad+[(K_3+K_4)\sin\theta\cos\theta]\eta_2\}-K_5\partial_z^2\eta_1=-A(T)\eta_1\\&\left[\frac{2e}{c}Hz\right]^2\{(K_2\sin^2\theta+K_1\cos^2\theta)\eta_2\\&\qquad+[(K_3+K_4)\sin\theta\cos\theta]\eta_1\}-K_5\partial_z^2\eta_2=-A(T)\eta_2 .\end{aligned} \tag{3.49}$$

Therefore, by a diagonalization of the equation, we derive the maximal magnetic field below which a finite order parameter can exist:

$$H_{c2}(\theta)=-A(T)\frac{c}{e}\left\{2K_5(K_1+K_2)\left[1-\left\{1-\frac{K_1^2+K_2^2-(K_3+K_4)^2}{(K_1+K_2)^2}f(\theta)-\frac{K_1K_2}{(K_1+K_2)^2}g(\theta)\right\}^{1/2}\right]\right\}^{-1/2} \tag{3.50}$$

where $f(\theta)=\sin^2(2\theta)$ and $g(\theta)=4(\cos^4\theta+\sin^4\theta)$. The upper critical field is in general angular-dependent, and its anisotropy factor

$$\frac{H_{c2}(\pi/4)}{H_{c2}(0)}=\left[\frac{K_1+K_2-|K_1-K_2|}{K_1+K_2-(K_3+K_4)}\right]^{1/2} \tag{3.51}$$

can be rather large. It has to be mentioned that the values K_i obtained in the weak-coupling limit assuming a spherical Fermi surface lead to an isotropic H_{c2} field (K_1:K_2:K_3:K_4=3:1:1:1; Machida *et al.*, 1985). Similar results are found in the case of cubic symmetry for all multidimensional representations. The hexagonal system, however, has no anisotropy in the basal plane. This case corresponds to the above calculation when we require additionally that the coefficients K_i satisfy the condition $K_1=K_2+K_3+K_4$ (Burlachkov, 1985).

Another interesting feature of the superconducting state at H_{c2} can be studied if we consider a magnetic field parallel to the high-symmetry axis (z axis) in a tetragonal or hexagonal system $[H=(0,0,H)]$. This case has been investigated recently by Zhitomirskii (1989) and Sundaram and Joynt (1989). It is convenient to introduce a pair of operators $\Pi_\pm=(D_x\pm iD_y)q/\sqrt{2}$ with $q^2=c/2eH$ and the commutation relation $[\Pi_-,\Pi_+]=1$. Substituting $\Pi_\pm$ into Eq. (3.48), replacing the order parameter by $\eta_\pm=(\eta_x\pm i\eta_y)/\sqrt{2}$, and omitting D_z (the system is homogeneous along the z axis), we obtain

$$\begin{aligned}(\tilde{K}_1\Pi_+\Pi_-+\tilde{K}_2\Pi_-\Pi_+)\eta_+ &+(\tilde{K}_3\Pi_+^2+\tilde{K}_4\Pi_-^2)\eta_-=-\frac{c}{eH}A(T)\eta_+\\ (\tilde{K}_4\Pi_+^2+\tilde{K}_3\Pi_-^2)\eta_+ &+(\tilde{K}_1\Pi_-\Pi_++\tilde{K}_2\Pi_+\Pi_-)\eta_-=-\frac{c}{eH}A(T)\eta_-\end{aligned} \tag{3.52}$$

with $\tilde{K}_1=K_1+K_2+K_3-K_4$, $\tilde{K}_2=K_1+K_2-K_3+K_4$, $\tilde{K}_3=K_1-K_2+K_3-K_4$, and $\tilde{K}_4=K_1-K_2-K_3-K_4$. The symbols Π_+ and Π_- can be considered as creation and annihilation operators, respectively, in an occupation number representation:

$$\Pi_+|n\rangle=\sqrt{n+1}|n+1\rangle \quad\text{and}\quad \Pi_-|n\rangle=\sqrt{n}\,|n-1\rangle\ . \tag{3.53}$$

Therefore we expand the order parameters $\eta_\pm$ in this representation space: $\eta_\pm=\sum_{n=0}^{\infty}a_{n\pm}|n\rangle$. With Eq. (3.52) this leads to an infinite linear equation system, whose lowest eigenvalue has to be determined. However, in the case of a hexagonal system ($\tilde{K}_4=0$) it can easily be decoupled, since the space $\{|n\rangle\}$ breaks into small, disjoint subspaces: $\{\eta_-,\eta_+\}=\{|n\rangle,|n+2\rangle\}$.

The two possible ground states are (I) $(\eta_-,\eta_+)=(0,a_{0+}|0\rangle)$ and (II) $(\eta_-,\eta_+)=(a_{0-}|0\rangle, a_{2+}|2\rangle)$. The lowest eigenvalues in these subspaces give again the corresponding upper critical fields,

$$\begin{aligned}H_{c2}^{\mathrm{I}}(T)&=-A(T)\frac{c}{e\tilde{K}_2}\ ,\\ H_{c2}^{\mathrm{II}}(T)&=-A(T)\frac{2c}{e}[3(\tilde{K}_1+\tilde{K}_2)\\ &\qquad-\sqrt{(\tilde{K}_1+3\tilde{K}_2)^2+8\tilde{K}_3^2}]^{-1}\ .\end{aligned} \tag{3.54}$$

Depending on the coefficients K_i, the field H_{c2}^{I} or H_{c2}^{II} is the relevant (higher) upper critical field. Thus two types of high-field superconducting states are possible. The vortices corresponding to state (I) are axial and yield a conventional hexagonal vortex lattice, as expected, along the symmetric axis (z axis) of a hexagonal system. On the other side, state (II) breaks axial symmetry and its vortex lattice need not be hexagonal.

Finally we should mention that the symmetry of the order parameter induced by the field need not be the same as that of the zero-field parameter. Therefore phase transitions can occur if the applied magnetic field is decreased. At the same time, a change of the vortex lattice is also expected (Joynt, 1988; Volovik, 1988). An application of this example will be considered in Sec. VII.C to explain experimental results in UPt_3.

4. Collective modes

One of the special properties of unconventional superconductors is the existence of collective modes with small frequencies. Such modes have been clearly observed in superfluid ^{3}He by ultrasonic attenuation; see Wölfle (1978). Observation of a sound attenuation peak near T_c in UBe_{13} (Golding *et al.*, 1985) and in UPt_3 (Müller *et al.*, 1986) have stimulated the investigation of the collective modes in unconventional superconductors.

In the conventional s-wave pairing state, the important collective modes are longitudinal collective modes (zero sound) in the neutral Fermi gas and the plasma modes in the charged case (Anderson, 1958). Therefore for conventional s-wave superconductivity the collective modes are important theoretically from the point of view of gauge invariance but have little relevance to experiments. In unconventional superconductors, on the other hand, there can be several low-energy collective modes due to multicomponent order parameters.

The pairing interaction, Eq. (2.1), can be generalized as

$$\mathcal{H}_{\text{pair}}=\frac{1}{2}\sum_{\mathbf{q}}\sum_{\mathbf{k}\mathbf{k}'}\sum_{s_1s_2s_3s_4}V_{s_1s_2s_3s_4}(\mathbf{k},\mathbf{k}')a^\dagger_{\mathbf{q}/2-\mathbf{k}s_1}a^\dagger_{\mathbf{q}/2+\mathbf{k}s_2}a_{\mathbf{q}/2+\mathbf{k}'s_3}a_{\mathbf{q}/2-\mathbf{k}'s_4} \tag{3.55}$$

to include the finite total momentum $\mathbf{q}$ of the Cooper pairs. It reduces to Eq. (2.1) when only the $\mathbf{q}=0$ terms are retained. Once the linearized gap equation in Sec. II is solved, the matrix element of the interaction is expressed by the basis gap functions $\Delta_{s_1 s_2}(\Gamma,m;\hat{\mathbf{k}})$ as

$$V_{s_1 s_2 s_3 s_4}(\mathbf{k},\mathbf{k}') = \sum_{\Gamma} V(\Gamma) \sum_{m} \Delta_{s_2 s_1}(\Gamma,m;\hat{\mathbf{k}}) \Delta^{*}_{s_3 s_4}(\Gamma,m;\hat{\mathbf{k}}') , \quad (3.56)$$

where $V(\Gamma)$ is the coupling constant for an irreducible representation Γ.

We define field operators for Cooper pairs,

$$\Psi_m(\mathbf{q}) = \sum_{s_1 s_2} \Delta^{*}_{s_1 s_2}(\Gamma,m;\hat{\mathbf{k}}) a_{\mathbf{q}/2+\mathbf{k}_{s_1}} a_{\mathbf{q}/2-\mathbf{k}_{s_2}} \quad (3.57)$$

$$\Psi^{\dagger}_m(\mathbf{q}) = \sum_{s_1 s_2} \Delta_{s_1 s_2}(\Gamma,m;\hat{\mathbf{k}}) a^{\dagger}_{\mathbf{q}/2-\mathbf{k}_{s_2}} a^{\dagger}_{\mathbf{q}/2+\mathbf{k}_{s_1}} \ . \quad (3.58)$$

With the field operators the interaction Hamiltonian can be expressed as

$$\mathcal{H}_{\text{pair}} = \tfrac{1}{2} \sum_{\mathbf{q}} \sum_{\Gamma} V(\Gamma) \sum_{m} \Psi^{\dagger}_m(\mathbf{q}) \Psi_m(\mathbf{q}) \ . \quad (3.59)$$

The gap function $\Delta_{s_1 s_2}(\mathbf{k})$ is given by the average of the field operators,

$$\Delta_{s_1 s_2}(\mathbf{k}) = -\sum_{\Gamma} V(\Gamma) \sum_{m} \Delta_{s_1 s_2}(\Gamma,m;\hat{\mathbf{k}}) \langle \Psi_m(\mathbf{q}=\mathbf{0}) \rangle \ . \quad (3.60)$$

Collective modes are essentially the oscillatory motion of the order parameter around its equilibrium value. Some of them can couple with charge and spin-density fluctuations. Therefore it is necessary to consider the fluctuations of the order parameter around the expectation value, Eq. (3.60), and the charge and spin-density fluctuations simultaneously. This can be done by solving the equation of motion for the field operators using the random-phase approximation in the presence of external perturbation, for example in the presence of electromagnetic fields. In the charged case the Coulomb interaction has to be taken into account in addition to the pairing interaction. Thus we obtain a set of linear coupled equations whose eigenvalues give frequencies of the collective modes. An alternative method is the kinetic equation formalism developed by Wölfle (1978).

The collective modes in triplet p-wave states in a neutral Fermi gas have been investigated extensively in connection with ^{3}He. These modes consist of vibrations of the internal structure of the order parameter, with frequencies of the order of the amplitude of the order parameter Δ_0. One typical example is the real and imaginary "squashing modes" in the BW state. The name comes from the fact that they describe an oscillatory motion in which the amplitude of the order parameter is squashed in its real and imaginary parts. Another example is the "clapping modes" in the ABM phase. The orbital part of the order parameter in the ABM state is characterized by a set of two unit vectors $\mathbf{n}_1$ and $\mathbf{n}_2$ [in Eq. (3.3) $\mathbf{n}_1=\hat{\mathbf{x}}$ and $\mathbf{n}_2=\hat{\mathbf{y}}$]. The clapping modes describe a relative oscillation of the two unit vectors about the equilibrium configuration $\mathbf{n}_1 \perp \mathbf{n}_2$ within the plane spanned by these vectors. Experiments on sound attenuation in superfluid phases of ^{3}He were successfully analyzed by the absorption mechanism due to these collective modes. This fact was taken as an important support for the identification of the ^{3}He-A and ^{3}He-B phases as the ABM and the BW states of triplet pairing, respectively.

Hirashima and Namaizawa investigated collective modes in triplet p-wave superconductivity (charged Fermi gas) (1985, 1987; for d-wave pairing, 1988). They investigated the collective modes in four possible phases: polar, ABM, planar, and BW phases. An essential modification in the charged case is again that the zero sounds of the neutral case are lifted up to plasmons. The other collective modes remain unchanged in the long-wavelength limit. The forms of the collective modes and their frequencies are found in Hirashima and Namaizawa (1987).

Another essential difference between the superfluid and superconductors is that the relevant symmetry for a superconductor is discrete, while it is the continuous SO(3) for the superfluid. Therefore there is no Goldstone mode in a superconducting state in a crystal lattice with spin-orbit coupling and all collective modes have finite frequencies. In most cases their frequencies are comparable to the order-parameter amplitude Δ_0 (Monien *et al.*, 1986a, 1986b).

It is not yet clear whether the sound attenuation peaks observed in UBe_{13} and UPt_3 are due to collective modes. We shall discuss this point in Sec. VII. In the following we discuss another mechanism of sound attenuation due to domain-wall damping.

Recently another phenomenon related to the collective modes has been studied, namely, electromagnetic absorption. Hirschfeld *et al.* (1989) studied the contribution of the collective modes to the electromagnetic absorption for the BW phase. Their conclusion is that the collective modes of the order parameter contribute significantly to the power absorption at frequencies well below the quasiparticle gap edge of $2\Delta_0$; however, at the same time, they pointed out that it is also sensitive to impurity scattering and will be broadened when $\tau_N \Delta_0 < 1$.

5. Ultrasonic attenuation due to domain walls

Anisotropic superconductors with multicomponent order parameter can bear domains of different discretely degenerate superconducting states. These domains are separated by walls, regions where the order parameter is converted from one to another stable states (see Sec. V). Due to the discrete degeneracy of the superconducting states, the extension of these domain walls cannot be large, because the order parameter is strongly pinned to its stable bulk states due to its anisotropy energy (described by the fourth-order terms in the Ginzburg-

Landau free energy). Therefore the order parameter has to overcome a certain energy barrier to pass from one state to the other. The competition between this energy barrier and the rigidity of the order parameter determines a finite width in space for this conversion, so that a well-localized domain wall is created. The existence of such domain walls has led to the proposal that they could give a contribution to the unconventionally large ultrasound absorption mentioned before (Joynt, Rice, and Ueda, 1986). We shall base our explanation of this mechanism on the work done by Truell and Elbaum, who considered attenuation of sound due to planar defects in solids (Truell and Elbaum, 1962).

A domain wall lowers locally the condensation energy of the superconducting state, i.e., a certain energy expense ε_0 per unit area has to be invested for their creation (see Sec. V). Therefore, to keep the total energy small, they may be fixed at pinning centers where the superconducting condensation energy is lowered anyway, e.g., due to the presence of impurity atoms or crystal lattice defects. Fixed by these pinning centers, the domain wall behaves like an elastic membrane trying to be as flat as possible (equilibrium position). We assume that the average distance between pinning centers is L. Therefore, for a reference example, we consider a domain wall pinned at the corners of a square with side length L. For small deviations ζ from its equilibrium position in the plane we find an energy increase

$$\frac{\varepsilon_0}{2}\int[\nabla_{x,y}\zeta(x,y)]^2 dS \tag{3.61}$$

with $\nabla_{x,y}$ as the gradient in the x-y plane. The integral goes over the square.

We now consider the coupling mechanism between the superconducting domain wall and the sound waves. We assume that the wavelength of the sound is much larger than the average size a of the domains. Therefore the strain ϵ_{ij} induced by the sound is practically homogeneous over the range of several domains. With this assumption we can write the energy density due to lattice deformation as

$$\begin{aligned} f=&\frac{1}{2}\sum_{\gamma,m}B(\gamma)\epsilon^2(\gamma,m) \\ &+\frac{1}{aL^2}\sum_{\gamma,m}\Delta\mathcal{V}(\gamma,m;\lambda)_{i,j}\epsilon(\gamma,m)\int\zeta dS \\ &+\frac{\varepsilon_0}{2aL^2}\int[\nabla_{x,y}\zeta(x,y)]^2 dS \end{aligned} \tag{3.62}$$

The symbols $\epsilon(\gamma,m)$, $B(\gamma)$, $C(\gamma)$, and $\mathcal{V}(\gamma,m;\lambda)$ have been introduced in Sec. III.B.1. To get the average contribution of the domain walls to the energy density we have to take energies concerning the domain wall per unit area (L^{-2}) and to multiply them by a factor a^2/a^3, the ratio of the surface region to the volume of the domain. The second term describes the coupling. Since the strain ϵ can couple differently to the superconducting phase in different domains, it induces an energy-density difference between the domains i and j given by $\sum_{\gamma,m}\Delta\mathcal{V}(\gamma,m;\lambda)_{i,j}\epsilon(\gamma,m)$ with

$$\Delta\mathcal{V}(\gamma,m;\lambda)=C(\gamma)[\mathcal{V}(\gamma,m;\lambda)|_i-\mathcal{V}(\gamma,m;\lambda)|_j] . \tag{3.63}$$

The bilinear form $\mathcal{V}(\gamma,m;\lambda)|_i$ is evaluated in the superconducting phase i. Note that $\Delta\mathcal{V}(\Gamma_1^+)$ is always zero. The coupling term between domain wall and strain is determined by the change of energy if the domain wall is deformed.

The sound attenuation due to the domain walls can be calculated starting with the equation of motion in terms of strain ϵ_{ij} and stress σ_{ij},

$$\frac{\partial^2\sigma_{ij}}{\partial x_j^2}=\rho\frac{\partial^2}{\partial t^2}\epsilon_{ij} \quad \text{and} \quad \sigma_{ij}=\frac{\partial f}{\partial\epsilon_{ij}} , \tag{3.64}$$

where ρ is the mass density. For simplicity we consider a longitudinal sound wave along the z axis; $\sigma=\sigma_{zz}$ and $\epsilon=\epsilon_{zz}$. The relation between ϵ_{zz} and σ_{zz} is given by

$$\epsilon=\frac{\sigma}{B}-\frac{1}{BL^2a}\sum_{\gamma,m}\Delta\mathcal{V}(\gamma,m;\lambda)_{i,j}b(\gamma,m)\int\zeta dS , \tag{3.65}$$

where $b(\gamma,m)=\epsilon(\gamma,m)/\epsilon_{zz}$ is a constant. Note that the second term is small compared to σ/B. We now need an equation of motion for ζ. To consider the return of the deviated wall to its equilibrium position we neglect the kinetic energy of the wall, assuming that the movement is characterized by overdamping (relaxational motion). Thus the equation of motion of ζ has the form

$$\Upsilon\frac{\partial}{\partial t}\zeta(x,y;t)=-\frac{\delta f}{\delta\zeta} . \tag{3.66}$$

Finally we obtain the following system of coupled equations:

$$\begin{aligned} &\partial_z^2\sigma-\frac{1}{v_0^2}\frac{\partial^2}{\partial t^2}\sigma=-\frac{1}{av_0^2}\frac{\partial^2}{\partial t^2}\left[\int\zeta dS\right] \\ &\qquad\qquad\times\sum_{\gamma,m}\Delta\mathcal{V}(\gamma,m;\lambda)_{i,j}b(\gamma,m) \\ &\varepsilon_0\nabla_{x,y}^2\zeta-\Upsilon\frac{\partial\zeta}{\partial t}=\frac{\sigma}{B}\sum_{\gamma,m}\Delta\mathcal{V}(\gamma,m;\lambda)_{i,j}b(\gamma,m) \end{aligned} \tag{3.67}$$

where $v_0=\sqrt{B/\rho}$ is the sound velocity. The deviation ζ does not directly depend on z. To solve this system we introduce the ansatz

$$\sigma(z,t)=\sigma_0 e^{-\alpha z}\exp i\omega\left[t-\frac{z}{v}\right] . \tag{3.68}$$

Here α is the absorption coefficient and v the effective sound velocity. Using only the lowest-frequency mode for the deviation ζ, we find

$$\alpha(\omega)=\frac{4}{\pi^2 a \Upsilon \rho v_0^3}\frac{\omega^2}{\omega^2+\omega_1^2}\left[\sum_{\gamma,m}\Delta\mathcal{V}(\gamma,m;\lambda)_{i,j}b(\gamma,m)\right]^2 ,$$
$$v(\omega)=v_0\left[1-\frac{4\omega_1}{\pi^2 a \Upsilon \rho v_0^3}\frac{1}{\omega^2+\omega_1^2}\left[\sum_{\gamma,m}\Delta\mathcal{V}(\gamma,m;\lambda)_{i,j}b(\gamma,m)\right]^2\right] , \quad (3.69)$$

with the lowest mode frequency $\omega_1=\pi^2\varepsilon_0/\Upsilon L^2$ for the square. Ultarsonic attenuation occurs if the energy-density difference $[\Delta\mathcal{V}(\gamma,m;\lambda)_{ij}b(\gamma,m)]$ induced by the sound wave is finite. At the same time the sound velocity is renormalized $v<v_0$.

As an example we consider the superconducting phase in the cubic representation Γ_5^+ with the three degenerate states $[D_{4h}(\Gamma_4^+)]$,

$$\psi_1(\mathbf{k})=\lambda k_y k_z, \quad \psi_2(\mathbf{k})=\lambda k_z k_x, \quad \text{and} \quad \psi_3(\mathbf{k})=\lambda k_x k_y . \quad (3.70)$$

For longitudinal sound waves along the z axis, only the strain component ϵ_{zz} and thus $b(\Gamma_1^+)=1/\sqrt{3}$ and $b(\Gamma_3^+,1)=2/\sqrt{6}$ are finite. With the bilinear forms in Table IX we obtain

$$\Delta\mathcal{V}(\Gamma_3^+,1)_{i,j}=\begin{cases}3C(\Gamma_3^+)|\lambda|^2 & i=3 \text{ and } j=1,2 ,\\ 0 & i=1 \text{ and } j=2 .\end{cases} \quad (3.71)$$

Therefore the absorption coefficient α has the form

$$\alpha(\omega)=\frac{4}{\pi^2 a \Upsilon \rho v_0^3}\frac{\omega^2}{\omega^2+\omega_1^2}[3C(\Gamma_3^+)|\lambda|^2]^2 , \quad (3.72)$$

and a similar expression can be derived for the sound velocity.

To show the temperature dependence of α we assume that the only T-dependent quantities are the order parameter ($|\lambda|\propto|T-T_c|^{1/2}$) and the domain-wall energy ($\varepsilon_0\propto|T-T_c|^{3/2}$, see Sec. V):

$$\alpha(\omega,T)\propto\frac{\omega^2}{\omega^2+\tilde{\omega}_1^2|T-T_c|^3}|T-T_c|^2 , \quad (3.73)$$

where $\tilde{\omega}_1$ is the constant in the lowest mode frequency ω_1 after extraction of the temperature dependence. From this equation we see that α has a peak immediately below the transition and decreases like $|T-T_c|^{-1}$ for lower temperatures. This behavior is modified if other quantities such as Υ are temperature-dependent. The frequency dependence of α for a fixed temperature is quadratic in the low-frequency region ($\tilde{\omega}|T-T_c|^{3/2}\gg\omega$) and becomes constant in the high-frequency limit.

IV. BOUNDARY CONDITIONS AND INTERFACE EFFECTS

In this section we turn away from bulk properties to problems related with the boundary of a superconductor. It is well known that a conventional s-wave superconductor is not affected by the presence of an interface to a nonconducting medium. The situation is essentially different for most of the non-s-wave superconductors. Anisotropic superconductivity is strongly influenced by a boundary within the range of its coherence length. This was first noticed by Ambegaokar *et al.* (1974) for the p-wave superfluid ^{3}He. They found that the internal angular momentum of the Cooper pairs always turns perpendicular to the vessel wall confining the fluid. Considering the Cooper pairs as rotating quasimolecules, this is a very natural result. A similar effect is also expected in anisotropic superconductors. However, there the situation is slightly different. The rotational symmetry SO(3) is reduced to a discrete point-group symmetry of the crystal, and spin-orbit coupling destroys the independence of orbit and spin degrees of freedom. The latter, especially, yields a "magnetically active" boundary, which is able to produce spin scattering processes (Millis *et al.*, 1988). The Cooper pair angular momentum is no longer a good quantum number and therefore cannot be used to described the boundary conditions. Nevertheless, for the derivation of appropriate boundary conditions we shall essentially follow the method given by Ambegaokar *et al.* (1974). If we consider the reduction of symmetry by the boundary, group theory turns out to be a very powerful instrument in this field too.

Related problems occur in the study of the proximity effect or the Josephson effect. These are more related to the direct observations. Because of different behavior under time-reversal symmetry, no Josephson coupling between singlet and triplet superconducting phases is expected in lowest order. This type of effect has been suggested as a proof of triplet superconductivity in heavy-fermion systems (Pals *et al.*, 1977). However, it has been shown that this effect may be less significant than initially expected if strong-orbit coupling is present (Fenton, 1985a, 1985b; Sauls *et al.*, 1985; Geshkenbein and Larkin, 1986).

A. Boundary conditions of an unconventional superconductor

1. Correlation function formulation

The interface of a superconductor with an insulator or with the vacuum is a region where scattering of quasiparticles due to total reflection determines the behavior of the order parameter. Its influence on the superconducting state depends on the interference of the incident and the reflected Cooper pair wave function. For isotropic wave functions no effect is expected. Anisotropy of the pair wave function, however, can lead to drastic effects.

In the analysis below of this interference problem we restrict ourselves to the weak-coupling limit and follow essentially the treatment of Ambegaokar *et al.* (1974). For this purpose we briefly introduce the correlation function formalism for unconventional superconductors, developed by de Gennes (1966) for the case of conventional superconductivity (see also Lüders and Usadel, 1971). This formulation is very useful for studying a superconducting state if it is inhomogeneous in space. The starting point for this description is the linearized gap equation for a spatially varying gap function written in a Green's-function formalism (see Appendix B),

$$\Delta_{s_1s_2}(\mathbf{k},\mathbf{q})=-k_BT\sum_n \sum_{\substack{\mathbf{k}',\mathbf{k}'',\mathbf{q}'\\ s_3,s_4,s_5,s_6}} V_{s_2s_1s_3s_4}(\mathbf{k},\mathbf{k}')G^0_{s_3s_5}\left[\mathbf{k}'+\frac{\mathbf{q}}{2},\mathbf{k}''+\frac{\mathbf{q}'}{2};i\omega_n\right] \times G^0_{s_4s_6}\left[-\mathbf{k}'+\frac{\mathbf{q}}{2},-\mathbf{k}''+\frac{\mathbf{q}'}{2};-i\omega_n\right]\Delta_{s_5s_6}(\mathbf{k}'',\mathbf{q}') \ . \tag{4.1}$$

The pairing interaction is assumed to be homogeneous. As we did earlier in Sec. III.B, we write $V_{s_1s_2s_3s_4}(\mathbf{k},\mathbf{k}')$ in spectral form, using the basis gap function of the homogeneous linearized gap equation (Sec. II),

$$V_{s_1s_2s_3s_4}(\mathbf{k},\mathbf{k}')=\sum_\Gamma V(\Gamma)\sum_m \Delta_{s_2s_1}(\Gamma,m;\hat{\mathbf{k}})\Delta^+_{s_3s_4}(\Gamma,m;\hat{\mathbf{k}}') \ , \tag{4.2}$$

where $\hat{\mathbf{k}}$ denotes $\mathbf{k}/k_F$ and the potential is restricted to the Fermi surface. We shall restrict ourselves to the components of the dominant representation and write its basis functions in the shorthand notation $\hat{\Delta}(\Gamma,m;\mathbf{k})=\hat{\Delta}_{(m)}(\mathbf{k})$ and $V(\Gamma)=-V$ in further equations. In principle this restriction is allowed only in the homogeneous region of a superconductor, where the full crystal symmetry applies, as we shall point out below. Changing to the $\mathbf{r}$ space, introducing the combination

$$\hat{\Delta}(\hat{\mathbf{k}},\mathbf{r})=\sum_m \eta_m(\mathbf{r})\hat{\Delta}_{(m)}(\hat{\mathbf{k}}) \ , \tag{4.3}$$

and using the orthonormality condition of $\hat{\Delta}_{(m)}(\mathbf{k})$, we obtain a nonlocal relation between the components of the order parameter (coordinates) η_m:

$$\eta_i(\mathbf{r})=\sum_j \int d^3\mathbf{r}'\,K_{ij}(\mathbf{r},\mathbf{r}')\eta_j(\mathbf{r}') \ , \tag{4.4}$$

where the kernel has the form

$$K_{ij}(\mathbf{r},\mathbf{r}')=Vk_BT\sum_{\omega_n,s_1,s_2,s_3,s_4}\left\{\left[\hat{\Delta}^+_{(i)}\left[\frac{\nabla_r-\nabla_{r_1}}{2ik_F}\right]\right]_{s_1s_2}\left[\hat{\Delta}_{(j)}\left[\frac{\nabla_{r_1'}-\nabla_{r'}}{2ik_F}\right]\right]_{s_3s_4} G^0_{s_1s_3}(\mathbf{r},\mathbf{r}';i\omega_n)G^0_{s_2s_4}(\mathbf{r}_1,\mathbf{r}_1';-i\omega_n)\right\}_{\substack{\mathbf{r}_1\to\mathbf{r}\\ \mathbf{r}_1'\to\mathbf{r}'}} \ . \tag{4.5}$$

This kernel may be understood as the probability amplitude of a Cooper pair to propagate from a point $\mathbf{r}'$ to a point $\mathbf{r}$. The Green's function $G^0_{ss'}(\mathbf{r},\mathbf{r}';i\omega_n)$ is the normal-state Green's function, which will include spin-orbit coupling (s indicates pseudo spin). It may be represented by

$$G^0_{ss'}(\mathbf{r},\mathbf{r}';i\omega_n)=\sum_\nu \frac{\phi^*_{\nu s}(\mathbf{r})\phi_{\nu s'}(\mathbf{r}')}{i\omega_n-\varepsilon_\nu}\delta_{ss'} \ , \tag{4.6}$$

with the single quasiparticle wave function defined by $\mathcal{H}_0\phi_{\nu s}(\mathbf{r})=\varepsilon_\nu\phi_{\nu s}(\mathbf{r})$ ($\mathcal{H}_0$ is the single-particle part of the Hamiltonian). Equation (4.6) then leads to the following form of the kernel:

$$K_{ij}(\mathbf{r},\mathbf{r}')=Vk_BT\sum_{\omega_n}\sum_{\mu,\nu}\frac{\mathrm{tr}\left\langle \nu\left|\hat{\Delta}^+_{(i)}\left[\frac{m_e}{2k_F}\mathbf{J}(\mathbf{r})\right]\right|\mu\right\rangle\left\langle\mu\left|\hat{\Delta}_{(j)}\left[\frac{m_e}{2k_F}\mathbf{J}(\mathbf{r}')\right]\right|\nu\right\rangle}{(i\omega_n-\varepsilon_\nu)(-i\omega_n-\varepsilon_\mu)} \ , \tag{4.7}$$

where

$$\langle \nu|\hat{\Delta}((m_e/2k_F)\mathbf{J}(\mathbf{r}))|\mu\rangle_{ss'}=\{\Delta_{ss'}[(\nabla_{\mathbf{r}}-\nabla_{\mathbf{r}_1})/2ik_F]\phi^*_{\nu s}(\mathbf{r})\phi_{\mu s'}(\mathbf{r}_1)\}_{\mathbf{r}_1\to\mathbf{r}} \ .$$

Thus $\mathbf{J}(\mathbf{r})$ is the current operator (m_e is the electron mass). Rewriting the denominator (for $\omega_n>0$) as

$$\frac{1}{(i\omega_n-\varepsilon_\nu)(-i\omega_n-\varepsilon_\mu)}=i\int_0^\infty dt\frac{e^{-(|\omega_n|-i\varepsilon_\nu)t}}{i\omega_n-\varepsilon_\nu}e^{i(\varepsilon_\mu-\varepsilon_\nu)t}\ , \tag{4.8}$$

we can change Eq. (4.7) to the form

$$K_{ij}(\mathbf{r},\mathbf{r}')=\frac{Vk_bT}{2}\sum_{\omega_n}\int_0^\infty dt\int d\varepsilon\, i\frac{e^{-(|\omega_n-i\varepsilon)t}}{i\omega_n-\varepsilon}\sum_\nu\left\langle\nu\left|\mathrm{tr}\hat{\Delta}^+_{(i)}\left[\frac{m_e}{2k_F}\mathbf{J}(\mathbf{r})\right]\hat{\Delta}_{(j)}\left[\frac{m_e}{2k_F}\mathbf{J}(\mathbf{r}',t)\right]\right|\nu\right\rangle\delta(\varepsilon-\varepsilon_\nu)\ . \tag{4.9}$$

The correlation function $\sum_\nu\langle\nu|\mathrm{tr}\hat{\Delta}^+_{(i)}\hat{\Delta}_{(j)}|\nu\rangle\delta(\varepsilon-\varepsilon_\nu)$ can be replaced by the average value $N(0)\overline{\langle\nu|\mathrm{tr}\hat{\Delta}^+_{(i)}\hat{\Delta}_{(j)}|\nu\rangle}_{\varepsilon_\nu=0}$, since only a small energy range at the Fermi energy ($\varepsilon=0$) is relevant in this problem. Furthermore, it can be shown that $\overline{\langle\nu|\mathrm{tr}\hat{\Delta}^+_{(i)}\hat{\Delta}_{(j)}|\nu\rangle}_{\varepsilon_\nu=0}$ may be replaced by the classical average $\langle\mathrm{tr}\hat{\Delta}^+_{(i)}\hat{\Delta}_{(j)}\rangle$ for particles at the Fermi surface. This is possible because only the slow varying (classical) parts of the particle wave function contribute to the kernel $K_{ij}(\mathbf{r},\mathbf{r}')$ (for a detailed analysis see, for example, Lüders and Usadel, 1971):

$$K_{ij}(\mathbf{r},\mathbf{r}')=N(0)\pi k_BT\sum_{\omega_n}\int_0^\infty dt\, e^{-2|\omega_n|t}\left\langle\mathrm{tr}\hat{\Delta}^+_{(i)}\left[\frac{m_e}{2k_F}\mathbf{J}(\mathbf{r})\right]\hat{\Delta}_{(j)}\left[\frac{m_e}{2k_F}\mathbf{J}(\mathbf{r}',t)\right]\right\rangle_{E_F,\text{classical}}\ . \tag{4.10}$$

The symmetry properties of the kernel become immediately clear in this formulation, since the transformation properties of the gap function are well known.

In the homogeneous case, K_{ij} depends only on the differences $\mathbf{r}-\mathbf{r}'$: $K_{ij}(\mathbf{r},\mathbf{r}')=K_{ij}(\mathbf{r}-\mathbf{r}')$. Following de Gennes (1964, 1966) in the pure-metal limit we obtain

$$\begin{aligned}K_{ij}(\mathbf{r}-\mathbf{r}')&=\frac{VN(0)k_BT}{2v_F}\sum_{\omega_n}\frac{\mathrm{tr}\left[\hat{\Delta}^+_{(i)}\left[\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\right]\hat{\Delta}_{(j)}\left[\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\right]\right]}{|\mathbf{r}-\mathbf{r}'|^2}\exp\left[-\frac{2|\omega_n||\mathbf{r}-\mathbf{r}'|}{v_F}\right]\\&=\frac{VN(0)k_BT}{2v_F}\frac{\mathrm{tr}\left[\hat{\Delta}^+_{(i)}\left[\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\right]\hat{\Delta}_{(j)}\left[\frac{\mathbf{r}-\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\right]\right]}{|\mathbf{r}-\mathbf{r}'|^2}\frac{1}{\sinh(2\pi|\mathbf{r}-\mathbf{r}'|k_BT/v_F)}\ ,\end{aligned} \tag{4.11}$$

where v_F is the Fermi velocity. We see immediately that $K_{ij}(\mathbf{r}-\mathbf{r}')=K^*_{ji}(\mathbf{r}-\mathbf{r}')=K_{ij}(\mathbf{r}'-\mathbf{r})$.

Let us now turn to the surface scattering problem. In this consideration we restrict ourselves to a planar specularly reflecting surface as the boundary of a superconducting half-space. In that geometry the order parameter $\eta_m(\mathbf{r})$ depends only on $r=\mathbf{n}\cdot\mathbf{r}$ and is homogeneous parallel to the boundary ($\mathbf{n}$ is the unit vector normal to the surface). Close to the surface the kernel consists of two parts, a direct (K^d) and a reflected (K^r) component. As becomes clear in Fig. 4, we can formally replace the reflected part by a direct kernel with the reference point $\tilde{\mathbf{r}}'$, which is the mirror image of $\mathbf{r}'$ with respect to the boundary,

$$\begin{aligned}\eta_i(\mathbf{r})&=\int_{\text{h.s.}}[K^d_{ij}(\mathbf{r},\mathbf{r}')+K^r_{ij}(\mathbf{r},\mathbf{r}')]\eta_j(\mathbf{r}')d^3r'\\&=\int_{\text{h.s.}}[K^d_{ij}(\mathbf{r},\mathbf{r}')+\chi_jK^d_{ij}(\mathbf{r},\tilde{\mathbf{r}}')]\eta_j(\mathbf{r}')d^3r'\ ,\end{aligned} \tag{4.12}$$

where "h.s." denotes the integral over the superconducting half-space. For $K^d_{ij}(\mathbf{r},\mathbf{r}')$, Eq. (4.11) can be inserted. The coefficient χ_j describes the scattering property of the basis order parameter $\hat{\Delta}_{(j)}(\mathbf{k})$. In the simplest case it can be derived from Eq. (4.10) that χ_j is $+1$ if $\hat{\Delta}_{(j)}(\mathbf{k})$ is even under a reflection at the boundary and -1 if it is odd. The reflection at the boundary is defined by $\mathbf{k}\to\mathbf{k}-2(\mathbf{n}\cdot\mathbf{k})\mathbf{n}$. We call this transformation $\mathcal{P}(\mathbf{n})$ parity. Because of spin-orbit coupling, the spin is also transformed by the reflection (spin scattering). The distinction with respect to even- and odd-parity functions is appropriate, since off-diagonal elements K_{ij} do not exist in Eq. (4.12) if $\hat{\Delta}_{(i)}$ and $\hat{\Delta}_{(j)}$ have different parity $\mathcal{P}(\mathbf{n})$:

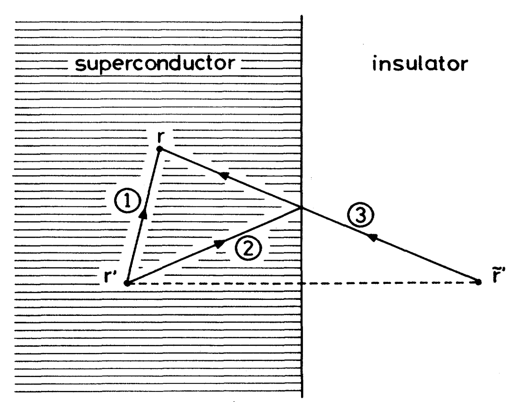

FIG. 4. Geometry of the scattering at a specularly reflecting surface. The kernel between $\mathbf{r}'$ and $\mathbf{r}$ has two contributions: one direct via 1 and one reflected via 2. The reflected path can formally be replaced by a direct path 3, where the starting point $\tilde{\mathbf{r}}'$ lies in the insulating region and is the mirror image of $\mathbf{r}'$.

$$\int K_{ij}(R,r-r')\eta_j(r')d^2Rdr'$$
$$=\int K_{ij}(-R,r-r')\eta_j(r')d^2Rdr'$$
$$=\int K_{ij}(R,r'-r)\eta_j(r')d^2Rdr'$$
$$=-\int K_{ij}(R,r-r')\eta_j(r')d^2Rdr'=0\ , \qquad (4.13)$$

with $\mathbf{R}=\mathbf{n}\times(\mathbf{r}-\mathbf{r}')$ and $r-r'=\mathbf{n}\cdot(\mathbf{r}-\mathbf{r}')$. Therefore the diagonalization of K_{ij}—since it is Hermitian, this is always possible—always yields basis functions with well-defined parity $\mathcal{P}(\mathbf{n})$.[4] Using Eqs. (4.11) and (4.12) in diagonalized form, it can be easily seen that $\eta_i(\mathbf{r})$ keeps the bulk value if $\chi_i=+1$, but is forced to zero if $\chi_i=-1$ at the boundary. In the former case specular reflection leads to constructive, in the latter case to destructive interference.

As an example, we examine the order parameter belonging to the two-dimensional representation Γ_5^+ in the tetragonal point group D_{4h}. The basis functions are

$$\hat{\Delta}_{(1)}(\mathbf{k})=i\hat{\sigma}_y k_x k_z \quad \text{and} \quad \hat{\Delta}_{(2)}(\mathbf{k})=i\hat{\sigma}_y k_y k_z\ . \qquad (4.14)$$

If the surface normal vector $\mathbf{n}$ points along [1,0,0], this basis [Eq. (4.14)] is just the correct basis to diagonalize the kernel leading to $\chi_1=-1$ and $\chi_2=+1$. Thus $\eta_1(x)$ is suppressed towards the boundary, whereas $\eta_2(x)$ remains constant in this lowest-order approach. On the other hand, for $\mathbf{n}=(1,1,0)$ the following basis is appropriate:

$$\hat{\Delta}_{(1)}(\mathbf{k})=i\hat{\sigma}_y\frac{k_z(k_x+k_y)}{\sqrt{2}}$$

and (4.15)

$$\hat{\Delta}_{(2)}(\mathbf{k})=i\hat{\sigma}_y\frac{k_z(k_x-k_y)}{\sqrt{2}}\ .$$

The coefficient $\eta_1(\mathbf{r}\cdot\mathbf{n})$ in the new basis is stressed to zero, since $\mathcal{P}(\mathbf{n})\hat{\Delta}_{(1)}(\mathbf{k})=-\hat{\Delta}_{(1)}(\mathbf{k})$, and $\eta_2(\mathbf{r}\cdot\mathbf{n})$ remains constant because $\mathcal{P}(\mathbf{n})\hat{\Delta}_{(2)}(\mathbf{k})=\hat{\Delta}_{(2)}(\mathbf{k})$. For a surface perpendicular to the z direction, both basis functions have negative parity $\mathcal{P}$. Thus both components are suppressed there.

2. Boundary conditions in the Ginzburg-Landau formulation

The linearized gap equation in the form of Eq. (4.4) is the basis for the microscopic derivation of the second-order terms in the Ginzburg-Landau free-energy expansion (Gor'kov, 1959). Excluding the gradient and fourth- and higher-order terms, we find that the corresponding part of the Ginzburg-Landau equation is

$$\eta_i(\mathbf{r})=\sum_j\int K_{ij}(\mathbf{r},\mathbf{r}')d^3r'\eta_j(\mathbf{r})$$
$$=\sum_j Q_{ij}(\mathbf{r})\eta_j(\mathbf{r})\ . \qquad (4.16)$$

This is the local limit of Eq. (4.4), assuming that the variation of η is slow compared to the range ξ_0 of the kernel $[\xi_0 \ll \xi(T)]$. In the homogeneous region, Q_{ij} is always diagonal and proportional to the unit matrix for one single representation. However, close to the boundary these second-order terms do not have the same form, since the kernel is changed due to quasiparticle scattering. To add these boundary corrections in their most general form to the Ginzburg-Landau functional, we shall again use a group-theoretical method. The boundary lowers locally the spatial symmetry of the system. The remaining symmetry group $\mathcal{G}'$ is a subgroup of the bulk symmetry group $\mathcal{G}$, which we represent further simply by the corresponding point groups G (G'). This means that we can add further terms to the Ginzburg-Landau free energy which are invariant under this lower symmetry G' and are restricted to the boundary. We need not extend these terms to higher than second order, since the second-order terms will describe the essential effects of the boundary as did the linearized gap equation in the previous section.

A convenient way to find the invariant terms is to derive the coupling terms of the order parameter to the normal vector $\mathbf{n}$ of the surface in a manner similar to that used in Sec. III.B for the strain tensor (Gor'kov, 1987). Since the normal vector $\mathbf{n}$ (written in the crystal lattice basis) belongs to the vector representation $\mathcal{D}_{(G)}$ (Γ_4^- for O_h; $\Gamma_2^-\oplus\Gamma_5^-$ for D_{4h} and D_{6h}), we can derive these terms by the decomposition of

$$\mathcal{D}_{(G)}^{\otimes m}\otimes\Gamma^*\otimes\Gamma\ , \qquad (4.17)$$

where Γ is the representation of the order parameter. Because the vector representation has negative parity, the exponent m has to be an even integer ($\mathcal{D}^{\otimes m}=D\otimes D\otimes\cdots\otimes D$, m times). In Table X a list of these terms is given. Their restriction to the surface is represented by a δ function located there. The real extension is of the order of ξ_0, which is negligibly small compared to the length scale $\xi(T)$ in the Ginzburg-Landau regime close to T_c. We should mention that invariant terms of the form

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[4] In general $\hat{\Delta}_{(j)}(\mathbf{k})$ is not restricted to the space of the basis functions of the representation Γ under the transformation $\mathbf{k}\to\mathbf{k}-2(\mathbf{n}\cdot\mathbf{k})\mathbf{n}$. Therefore in principle the restriction to one representation, as done for Eq. (4.4), is not justified, since kernel matrix elements between different representations can occur, leading to admixtures of other order parameters close to the surface, even if their critical temperature is far below the dominant $T_c(\Gamma)$. These admixtures are required to generate gap functions that have a clearly defined parity $\mathcal{P}(\mathbf{n})$. Consequently, this corresponds to a classification of states with respect to the direction of their total angular momentum (see Ambegaokar *et al.*, 1974). If the angular momentum is parallel to $\mathbf{n}$, the $\mathcal{P}(\mathbf{n})$ parity is $+1$, and if it is perpendicular it is -1. We shall not go into this problem further here, because the main features we want to consider later can be understood in the restricted version.

$$\mathcal{D}_{(G)}^{\otimes m}\otimes\Gamma^*\otimes\Gamma'+\text{c.c.} \tag{4.18}$$

also exist, combining two different representations, and these can lead to admixtures of other representations (see footnote 4). However, for simplicity, we neglect them in further considerations without loss of the main surface properties we want to describe. To complete the boundary conditions we have to consider the variation of the Ginzburg-Landau free energy with respect to the vector potential. There we find the condition $\mathbf{n}\times(\mathbf{B}-\mathbf{H}_{\text{ext}})|_{\text{sf}}=0$, which is also known from the conventional Ginzburg-Landau theory ($\mathbf{H}_{\text{ext}}$ is the external magnetic field; however, we shall concentrate on the case of zero field). This condition is obtained from variational minimization if we add the term $-(1/4\pi)\int d^3r\,\mathbf{H}_{\text{ext}}\cdot\mathbf{B}$ to the free energy.

Let us now consider the example of the previous section—the two-dimensional representation of D_{4h}. The surface free energy has the form

$$F_{\text{sf}}=\{[g_1(n_x^2+n_y^2)+g_2n_z^2](|\eta_1|^2+|\eta_2|^2)+g_3(n_x^2-n_y^2)(|\eta_1|^2-|\eta_2|^2)+g_4n_xn_y(\eta_1^*\eta_2+\eta_1\eta_2^*)\}\delta[\mathbf{n}\cdot(\mathbf{r}-\mathbf{r}_0)]\ , \tag{4.19}$$

where $\mathbf{r}_0$ is a point on the boundary. It is easy to see that the choice of coefficients $g_1=g_3=g_4/2>0$ and $g_1\approx a'\xi_0>0$ reproduces the result for specular scattering, already seen in the previous section [a' has the dimension of energy per volume and is defined by the second-order coefficient $A(T)=a'(T/T_c-1)$; ξ_0 takes the spatial extension of the kernel K into account]. For a surface perpendicular to $\mathbf{n}=(1,0,0)$ we find

$$F_{\text{sf}}=2g_1|\eta_1|^2\delta(x)\ . \tag{4.20}$$

The component η_1 is suppressed at the surface. To give an approximate solution of the boundary problem in the Ginzburg-Landau region we consider a superconductor with the homogeneous phase $\hat{\Delta}(\mathbf{k})=i\hat{\sigma}_yk_z(k_x\pm ik_y)\eta_0(T)$. The magnitude of η_0 derived from the minimization of the corresponding free energy (Sec. II.A) is

$$|\eta_0(T)|^2=\frac{-A(T)}{4(\beta_1-\beta_2)+\beta_3} \tag{4.21}$$

with the free-energy density

$$f_0=A(T)|\eta_0(T)|^2\ . \tag{4.22}$$

TABLE X. Surface terms of the Ginzburg-Landau theories in (a) cubic symmetry, where n is the surface normal vector and g_i are real constants describing the surface properties, (b) hexagonal symmetry, and (c) tetragonal symmetry.

Irreducible representation Γ	$F_{\text{SF}}(\mathbf{n};\eta)$
	(a)
$\Gamma_1^\pm$	$g_1\lvert\eta\rvert^2$
$\Gamma_2^\pm$	$[g_1+g_2\{(n_x^2-n_y^2)(n_y^2-n_z^2)(n_z^2-n_x^2)\}^2]\lvert\eta\rvert^2$
$\Gamma_3^\pm$	$g_1(\lvert\eta_1\rvert^2+\lvert\eta_2\rvert^2)+g_2[(2n_z^2-n_x^2-n_y^2)(\lvert\eta_2\rvert^2-\lvert\eta_1\rvert^2)+3(n_x^2-n_y^2)(\eta_1^*\eta_2+\eta_1\eta_2^*)]$
$\Gamma_{4,5}^\pm$	$g_1(\lvert\eta_1\rvert^2+\lvert\eta_2\rvert^2+\lvert\eta_3\rvert^2)$ $+g_2[n_x^2(2\lvert\eta_1\rvert^2-\lvert\eta_2\rvert^2-\lvert\eta_3\rvert^2)+n_y^2(2\lvert\eta_2\rvert^2-\lvert\eta_1\rvert^2-\lvert\eta_3\rvert^2)+n_z^2(2\lvert\eta_3\rvert^2-\lvert\eta_1\rvert^2-\lvert\eta_2\rvert^2)]$ $+g_3[n_yn_z(\eta_2^*\eta_3+\eta_2\eta_3^*)+n_zn_x(\eta_3^*\eta_1+\eta_3\eta_1^*)+n_xn_y(\eta_1^*\eta_2+\eta_1\eta_2^*)]$
	(b)
$\Gamma_1^\pm$	$[g_1(n_x^2+n_y^2)+g_2n_z^2]\lvert\eta\rvert^2$
$\Gamma_2^\pm$	$[g_1(n_x^2+n_y^2)+g_2n_z^2+g_3(n_xn_y(n_x^2-3n_y^2)(n_y^2-3n_x^2))^2]\lvert\eta\rvert^2$
$\Gamma_3^\pm$	$[g_1(n_x^2+n_y^2)+g_2n_z^2+g_3(n_xn_y(n_x^2-3n_y^2))^2]\lvert\eta\rvert^2$
$\Gamma_4^\pm$	$[g_1(n_x^2+n_y^2)+g_2n_z^2+g_3(n_yn_z(n_y^2-3n_x^2))^2]\lvert\eta\rvert^2$
$\Gamma_{5,6}^\pm$	$[g_1(n_x^2+n_y^2)+g_2n_z^2](\lvert\eta_1\rvert^2+\lvert\eta_2\rvert^2)$ $+g_3[(n_x^2-n_y^2)(\lvert\eta_1\rvert^2-\lvert\eta_2\rvert^2)+2n_xn_y(\eta_1^*\eta_2+\eta_1\eta_2^*)]$
	(c)
$\Gamma_1^\pm$	$[g_1(n_x^2+n_y^2)+g_2n_z^2]\lvert\eta\rvert^2$
$\Gamma_2^\pm$	$[g_1(n_x^2+n_y^2)+g_2n_z^2+g_3(n_xn_y(n_x^2-n_y^2))^2]\lvert\eta\rvert^2$
$\Gamma_3^\pm$	$[g_1(n_x^2+n_y^2)+g_2n_z^2+g_3(n_x^2-n_y^2)^2]\lvert\eta\rvert^2$
$\Gamma_4^\pm$	$[g_1(n_x^2+n_y^2)+g_2n_z^2+g_3n_x^2n_y^2]\lvert\eta\rvert^2$
$\Gamma_5^\pm$	$[g_1(n_x^2+n_y^2)+g_2n_z^2](\lvert\eta_1\rvert^2+\lvert\eta_2\rvert^2)$ $+g_3(n_x^2-n_y^2)(\lvert\eta_1\rvert^2-\lvert\eta_2\rvert^2)+g_4n_xn_y(\eta_1^*\eta_2+\eta_1\eta_2^*)$

Approximating η_2 by $i|\eta_0|$=const and varying the free energy with respect to $|\eta_1(x)|$, including the gradient terms (Table VII), we obtain the differential equation

$$\partial_x^2|\eta_1|+\frac{2\beta_1}{K_1}|\eta_1|(|\eta_0|^2-|\eta_1|^2)=0 . \tag{4.23}$$

With the surface terms we find the boundary conditions

$$[-K_1\partial_x|\eta_1|+2g_1|\eta_1|]_{x=0}=0 ,$$
$$\left[-K_1|\eta_1|\left[\partial_x\phi_1-\frac{2e}{c}A_x\right]\right]\Bigg|_{x=0}=0 . \tag{4.24}$$

We parametrized the order parameter $\eta_j=|\eta_j|\exp(i\phi_j)$ and separated it into a real and an imaginary part. The second equation corresponds to the natural condition—well known from the conventional Ginzburg-Landau theory—that no supercurrent is allowed to flow perpendicular to the surface (for the complete expression of the current see Sec. V.A). The first equation together with Eq. (4.23) gives the analytic solution

$$|\eta_{1(x)}|=|\eta_0|\tanh\left[\frac{x-x_0}{\sqrt{2}\tilde{\xi}}\right]$$

and (4.25)

$$x_0=\frac{\tilde{\xi}}{\sqrt{2}}\sinh^{-1}\left[\frac{K_1}{\sqrt{2}\tilde{\xi}g_1}\right] ,$$

with $\tilde{\xi}^{-2}(T)=2\beta_1|\eta_0(T)|^2/K_1$ as the coherence length in the x direction. This result is restricted to the range $|x|\gg\xi_0$.[5] In this analysis $|\eta_1(0)|$ is finite and can be connected with an extrapolation length b defined by $\partial_x|\eta_1(0)|=|\eta_1(0)|/b$, which leads to $b\approx K_1/2g_1\approx K_1/2a'\xi_0$. The length b is of the order ξ_0 and therefore negligibly small compared with $\tilde{\xi}(T)$.

To calculate the surface energy F_s per unit area we insert Eq. (4.25) in the free energy. By a partial integration and using Eqs. (4.23) and (4.24), we find

$$F_s=\int_0^\infty(f-f_0)dx=\beta_1\int_0^\infty(|\eta_0|^4-|\eta_1|^4)dx$$
$$=\tfrac{2}{3}\beta_1\tilde{\xi}|\eta_0|^4 . \tag{4.26}$$

Generally the surface energy is proportional to $|\eta_0(T)|^3\sim|T-T_c|^{3/2}$, whereas the bulk energy has a quadratic temperature dependence $|T-T_c|^2$. This different T dependence is due to the fact that the region of reduced condensation energy at the surface is confined within a length $\tilde{\xi}\sim|\eta_0|^{-1}$, which changes with temperature as $|T-T_c|^{-1/2}$.

This solution does not take into account that the two order-parameter components are coupled by the fourth-order terms $(2\beta_1-4\beta_2+\beta_3)|\eta_1|^2|\eta_2|^2$ for $\Delta\phi=\pm\pi/2$. Hence in general the component η_2 also varies at the surface. Roughly we can say that its modulus is lowered if $(2\beta_1-4\beta_2+\beta_3)<0$ and enhanced if $(2\beta_1-4\beta_2+\beta_3)>0$. The analytic solution of the complete problem is more complicated. However, the given solution is a good approach under the condition $|2\beta_1-4\beta_2+\beta_3|\ll2\beta_1$ [note that $-2\beta_1<2\beta_1-4\beta_2+\beta_3<2\beta_1$ is required for the stability of the state in Eq. (4.21)].

Considering the direction $\mathbf{n}=(1,1,0)/\sqrt{2}$, it is useful to diagonalize the bilinear form in Eq. (4.19) by

$$\eta_1'=\frac{1}{\sqrt{2}}(\eta_1+\eta_2) \text{ and } \eta_2'=\frac{1}{\sqrt{2}}(\eta_1-\eta_2) . \tag{4.27}$$

This yields the basis gap functions

$$\hat{\Delta}'_{(1)}(\mathbf{k})=i\hat{\sigma}_yk_z(k_x+k_y)/\sqrt{2}$$

and

$$\hat{\Delta}'_{(2)}(\mathbf{k})=i\hat{\sigma}_yk_z(k_x-k_y)/\sqrt{2} ,$$

which are the states classified by the parity operation $\mathcal{P}(\mathbf{n})$ in the previous section. The component η_1' is suppressed, and η_2' has similar properties to those of η_2 above. Finally, in the case of $\mathbf{n}=(0,0,1)$, the surface term treats both components equally, reconfirming the earlier result. These last two examples can be treated similarly to the first case. However, one has to keep in mind that in unconventional superconductors the coherence length $\tilde{\xi}(\mathbf{n})$ is in general direction-dependent.

As we have seen, the group-theoretical treatment is appropriate for analyzing the problem of specularly reflecting surfaces. It is, however, more general, since it is based only on the symmetry properties of the surface. Hence this formulation can be used for all surfaces with scattering properties that do not further lower its symmetry. This is the case if the scattering behavior is homogeneous parallel to the surface, considered on a length scale ξ_0. Therefore diffuse scattering may also be included. The phenomenological parameters g_i depend on the quality of the surface and describe the scattering of the Cooper pairs off the surface.

In the A phase of superfluid ^{3}He the geometry of the confining vessel has a significant influence on the superfluid phase. At the wall the angular momentum is aligned parallel to the surface normal vector $\mathbf{n}$. Since the direction of the angular momentum is continuously degenerate, the bulk phase is determined by the shape of the surface. A similar effect is not expected in anisotropic superconductors. The degeneracy of the superconducting phases is discrete, and therefore a certain phase is fixed in the bulk region. Thus no defect, and so no surface, can have a long-range influence except just at the phase transition. Additionally, in the case of heavy-fermion superconductors, the range of the surface influence is rather short, because the zero-temperature coherence length ξ_0 is of the order of 10× the lattice constant, so no essential effect on the superconducting phase is expected except for very thin films. On the other

[5]In the range $|x|\le\xi_0$ the spatial extension of the kernel $K_{ij}(\mathbf{r},\mathbf{r}')$ in Eq. (4.4) has to be taken into account. Hence a nonlocal problem has to be solved.

hand, we shall see in Sec. V that the boundary conditions derived here can lead to magnetic effects if the superconducting phase breaks time-reversal symmetry.

B. Josephson and proximity effects

In the previous section we analyzed a completely reflecting interface. An experimentally more interesting situation, however, is a partially transparent interface of a superconductor with a normal metal or with another superconductor. The former configuration leads to a penetration of Cooper pairs from the superconducting to the normal region, even if the normal metal has a much weaker or vanishing pairing interaction. This is the *proximity effect* (de Gennes, 1964). The latter leads to the *Josephson effect,* a macroscopic visualization of the coherence of the superconducting state via the current flow through the interface (Josephson, 1962). Both effects have been studied for unconventional superconductors. It was suggested that very significant properties should occur if the pairing interaction favored on one side of the interface a singlet but on the other a triplet pairing state. Since the two pairing states transform differently under time reversal—the triplet state is even and the singlet state is odd—it was concluded that no Josephson coupling could occur between them in lowest order, at least if the interface were not magnetic. This means that the matrix element $T_{ss'}(\mathbf{k},\mathbf{k}')$ in the tunneling Hamiltonian,

$$\mathcal{H}_T = \sum_{\mathbf{k},\mathbf{k}',s,s'} [T_{ss'}(\mathbf{k},\mathbf{k}') a^{(1)\dagger}_{\mathbf{k}s} a^{(2)}_{\mathbf{k}'s'} + T^*_{ss'}(\mathbf{k},\mathbf{k}') a^{(2)\dagger}_{\mathbf{k}'s'} a^{(1)}_{\mathbf{k}s}] , \quad (4.28)$$

where $a^{(i)}_{\mathbf{k}s}$ is a quasiparticle operator labeled by $i=1,2$ for the two sides of the interface, is invariant under time reversal and spin rotation ($T_{ss'} \sim \delta_{ss'}$) (Pals, van Haeringen, and van Maaren, 1977). Thus in the ac Josephson effect the frequency $\omega = 2\ \mathrm{eV}/\hbar$ should not be observed, but rather $\omega = 4\ \mathrm{eV}/\hbar$ due to higher-order effects, which are not forbidden by time-reversal symmetry. It was proposed that this very clear result be used as a test for the parity of an unknown superconducting phase by a connection with a well-known *s*-wave (singlet) superconductor. In contrast to the experiments examined in Sec. III to determine the spatial symmetry of the pairing state (excluding parity), this effect could give information about the parity of the unconventional superconducting phase.

Heavy-fermion superconductors seem to be good candidates for this test. However, strong spin-orbit interaction in these materials makes this method less significant. Several authors have revised the results of Pals *et al.*, proving that in the presence of spin-orbit interaction an ordinary (ac) Josephson effect is not excluded (Fenton, 1985a; Sauls, Zhou, and Anderson, 1985; Geshkenbein and Larkin, 1986; Millis, Rainer, and Sauls, 1988). The key point is that the materials on either side of the interface are very dissimilar with respect to spin-orbit coupling. We consider an interface separating a heavy-fermion compound with strong spin-orbit coupling and a light electron metal, which is an *s*-wave superconductor with very weak spin-orbit coupling. Spin-orbit coupling yields a superposition of different spinor states, so the quasiparticles are not eigenstates of the spin, but can be labeled as pseudospin states, as mentioned in Sec. II. Consequently, passing through the interface, the quasiparticles have to convert between two different spinor-state combinations. Due to the difference of spin-orbit coupling, the tunneling Hamiltonian $\mathcal{H}_I$ [Eq. (4.28)] produces spin flips. Thus $T_{ss'}$ is no longer spin independent. Since this spin-flip tunneling is generated by the superposition of spinor states under strong spin-orbit coupling, its order of magnitude is the same as for non-spin-flip tunneling (Geshkenbein and Larkin, 1986).[6] However, the absolute magnitude of the tunneling matrix is also determined by the transmission rate of the interface. The large effective-mass mismatch leads to a rather small rate. Considering the solution of the Schrödinger equation for a free particle under the assumption of a sudden change of its effective mass at the interface, we obtain a transmission rate $|T| \approx 4m_e/m_{hF} \approx 10^{-2}$ (Fenton, 1985a).

1. Josephson effect

In this section we concern ourselves with the Josephson effect in unconventional superconducting phases, especially for the case of unequal parity on the two sides of the interface. The coupling mechanism explained above can be very easily formulated for a Josephson junction by the assumption of a "magnetically active" interface, i.e., an interface that is able to produce spin flips due to different spin-orbit coupling on either side (Millis, Rainer, and Sauls, 1988). The corresponding tunneling Hamiltonian [Eq. (4.28)] has a matrix of the general form

$$\hat{T}(\mathbf{k},\mathbf{k}') = T_0(\mathbf{k},\mathbf{k}')\hat{\sigma}_0 + \mathbf{T}(\mathbf{k},\mathbf{k}')\cdot\hat{\boldsymbol{\sigma}} . \quad (4.29)$$

The second term produces transitions between different spin states. The invariance of $\mathcal{H}_T$ under time reversal gives the following relations for the four components of the tunneling matrix:

[6]Fenton has shown that even with non-spin-flip tunneling, a coupling of even- and odd-parity superconductivity can be found. This effect is due to the local breakdown of parity because of the spatial variation of the unconventional superconductivity order parameter at the interface. The order of magnitude is T_c/T_F (~ 0.1 for heavy-fermion compounds) compared to the equal-parity coupling (Fenton, 1985a, 1985b).

$$T_0(\mathbf{k},\mathbf{k}')=T_0^*(-\mathbf{k},-\mathbf{k}') ,$$
$$\mathbf{T}(\mathbf{k},\mathbf{k}')=-\mathbf{T}^*(-\mathbf{k},-\mathbf{k}') . \tag{4.30}$$

Following the Ambegaokar-Baratoff formulation of the Josephson current, in which one considers $j=e\partial\langle N_i\rangle/\partial t=e\partial\sum_{\mathbf{k}s}\langle a_{\mathbf{k}s}^{(i)+}a_{\mathbf{k}s}^{(i)}\rangle/\partial t=-ie\langle[N_i,\mathcal{H}_T]\rangle$, we obtain in the lowest order of the perturbation theory the following form expressed in terms of anomalous Green's functions:

$$j=2ek_BT\,\mathrm{Im}\sum_{\omega_n}\sum_{\mathbf{k},\mathbf{k}'}\mathrm{tr}[\hat{F}_{(1)}^{\dagger}(\mathbf{k},i\omega_n)\hat{T}(\mathbf{k},\mathbf{k}')\hat{F}_{(2)}(\mathbf{k}',i\omega_n)\hat{T}^{\tau}(-\mathbf{k},-\mathbf{k}')] , \tag{4.31}$$

where we have neglected the normal-current component (Ambegaokar and Baratoff, 1963). The symbol $\hat{T}^{\tau}$ denotes the transposed matrix. Note that time-reversal symmetry leads to the relation $\hat{T}^{\tau}(-\mathbf{k},-\mathbf{k}')=T_0^*(\mathbf{k},\mathbf{k}')\hat{\sigma}_0+\hat{\sigma}_y\hat{\sigma}\mathbf{T}^*(\mathbf{k},\mathbf{k}')\hat{\sigma}_y$. The anomalous Green's function $F(\mathbf{k},i\omega_n)$ is given in Appendix B.

We assume that side (1) is a singlet superconductor describes by a scalar function $\psi(\mathbf{k})$ and side (2) a triplet superconductor with a vectorial gap function $\mathbf{d}(\mathbf{k})$ according to Eqs. (2.10) and (2.11). For unitary states, therefore, the Josephson current has the form

$$j_{st}=2ek_BT\,\mathrm{Im}\sum_{\omega_n}\sum_{\mathbf{k},\mathbf{k}'}\frac{\psi^*(\mathbf{k})\mathbf{d}(\mathbf{k}')\cdot\mathbf{W}(\mathbf{k},\mathbf{k}')}{(\omega_n^2+E_{(1)\mathbf{k}}^2)(\omega_n^2+E_{(2)\mathbf{k}'}^2)} \tag{4.32}$$

with

$$\mathbf{W}(\mathbf{k},\mathbf{k}')=(T_0\mathbf{T}^*+T_0^*\mathbf{T}+i\mathbf{T}^*\times\mathbf{T})(\mathbf{k},\mathbf{k}') . \tag{4.33}$$

The current depends on the relative phase $\Delta\phi=\phi(1)-\phi(2)$ between the two superconductors, but also on the relative phase between the matrix elements in $T_{ss'}$, represented by ϕ_T $[j\sim\sin(\phi_T+\Delta\phi)]$. In a similar way the Josephson current between two states of equal parity can be obtained:

$$j_{ss}=2ek_BT\,\mathrm{Im}\sum_{\omega_n}\sum_{\mathbf{k},\mathbf{k}'}\frac{\psi_{(1)}^*(\mathbf{k})\psi_{(2)}(\mathbf{k}')W_0(\mathbf{k},\mathbf{k}')}{(\omega_n^2+E_{(1)\mathbf{k}}^2)(\omega_n^2+E_{(2)\mathbf{k}'}^2)} \tag{4.34}$$

with

$$W_0(\mathbf{k},\mathbf{k}')=[|T_0|^2+|\mathbf{T}|^2](\mathbf{k},\mathbf{k}') \tag{4.35}$$

for singlet-singlet coupling and

$$j_{tt}=2ek_BT\,\mathrm{Im}\sum_{\omega_n}\sum_{\mathbf{k},\mathbf{k}'}\frac{\mathbf{d}_{(1)}^*(\mathbf{k})\cdot\mathbf{d}_{(2)}(\mathbf{k}')W_0(\mathbf{k},\mathbf{k}')+i[\mathbf{d}_{(1)}^*(\mathbf{k})\times\mathbf{d}_{(2)}(\mathbf{k}')]\cdot\mathbf{W}(\mathbf{k},\mathbf{k}')}{(\omega_n^2+E_{(1)\mathbf{k}}^2)(\omega_n^2+E_{(2)\mathbf{k}'}^2)} \tag{4.36}$$

for triplet-triplet coupling. In contrast to j_{st}, these latter two currents still remain finite if we remove the spin-flip part $(\mathbf{T}\cdot\hat{\sigma})$ from the tunneling Hamiltonian.

The invariance of the tunneling Hamiltonian under spatial transformation that leaves the interface invariant leads to the transformation property

$$gT_0(\mathbf{k},\mathbf{k}')=T_0[\hat{D}^{(-)}(g)\mathbf{k},\hat{D}^{(-)}(g)\mathbf{k}'] ,$$
$$g\mathbf{T}(\mathbf{k},\mathbf{k}')=\hat{D}^{(+)}(g)\mathbf{T}[\hat{D}^{(-)}(g)\mathbf{k},\hat{D}^{(-)}(g)\mathbf{k}'] . \tag{4.37}$$

The matrices $\hat{D}^{(\pm)}(g)$ are the vector transformation matrices for axial and polar vectors, respectively (see also Sec. II.A). Consequently $W_0(\mathbf{k},\mathbf{k}')$ and $\mathbf{W}(\mathbf{k},\mathbf{k}')$ transform in the same way. There are twice as many restrictions on the allowed transformations as are described in Sec. IV.A, since the orientation of the crystal axis of both sides of the interface enters in the problem. Thus two interface normal vectors $\mathbf{n}_1$ [side (1)] and $\mathbf{n}_2$ [side (2)] determine the symmetry of the interface, where $\mathbf{n}_1$ and $\mathbf{n}_2$ are defined with respect to the corresponding crystal lattice bases. Obviously, the current j is invariant under these transformations, since the vector $\mathbf{d}$ transforms like $\mathbf{T}$.

Such symmetry properties give once more the basis for a group-theoretical treatment in the framework of the Ginzburg-Landau theory, similar to the boundary conditions (Geshkenbein and Larkin, 1986; Yip *et al.*, 1990). The superconducting phases in the two media (1) and (2) obey the equilibrium conditions given by the free energies $F_{(1)}$ and $F_{(2)}$, respectively. Tunneling and reflection of the quasiparticles are properties of the interface. The reflection leads to boundary terms separately in (1) and (2), as given in Sec. IV.A. The tunneling, however, produces a connection of the two sides, introduced here by coupling terms which are invariant under all spatial transformations g mentioned before, under time-reversal and gauge symmetry. In general, the crystal symmetry in mediums (1) and (2) is different, as are the corresponding point groups G_1 and G_2, respectively. With the normal vectors $\mathbf{n}_1$ and $\mathbf{n}_2$ in the corresponding crystal lattice basis, these terms can be written in the form

$$f_{\text{coupling}}(\Gamma^{(1)},\Gamma^{(2)}) = \left[\left[T^* \sum_m \Phi(\Gamma^{(1)},m;\mathbf{n}_1)\eta^*(\Gamma^{(1)},m) \right] \left[T' \sum_{m'} \Phi(\Gamma^{(2)},m';\mathbf{n}_2)\eta(\Gamma^{(2)},m') \right] + \text{c.c.} \right]_{\text{interface}} . \tag{4.38}$$

In this equation $\Phi(\Gamma^{(i)},m;\mathbf{n}_i)$ is a function of $\mathbf{n}_i$ with the symmetry of the basis function $(\Gamma^{(i)},m)$ in the group G_i. In Table XI we give a list of the simplest possible functions Φ with the correct symmetry for the point groups O_h, D_{6h}, and D_{4h}. The coupling constants T and T' are complex numbers representing the tunneling properties. According to Eqs. (4.32)–4.36), they should be taken to be equal for even-even-parity junctions and may be chosen to be different for other junctions, in order to include the effect of a finite relative phase in the tunneling matrix possible for odd-even and odd-odd-parity junctions. With this combination, the f_{coupling} is invariant under all spatial transformations separately in sides (1) and (2), and under a parity transformation of the whole system. It is clearly invariant under U(1) gauge transformations. Time-reversal invariance is ensured with the transformation condition $KT=T^*$. In the case of odd parity, these terms have been given by Geshkenbein and Larkin (1986). Higher-order coupling terms, where the order parameters occur in fourth or higher-order combinations, are here neglected since they correspond to higher-order couplings in the perturbation by $\mathcal{H}_T$, proportional to $|\hat{T}|^N$ with $N \geq 4$.

By variation of the free energy with these interface terms, boundary conditions are found which couple the order parameters of the two sides. As an example we consider the configuration $G_1=G_2=D_{4h}$ and $\Gamma^{(1)}=\Gamma_5^-$, $\Gamma^{(2)}=\Gamma_5^+$ with the general form of the free energy

$$F = \int d^3r [f_{(1)} + f_{\text{sf}(1)}(\mathbf{n}_1) + f_{(2)} + f_{\text{sf}(2)}(\mathbf{n}_2) + f_{\text{coupling}}(\mathbf{n}_1,\mathbf{n}_2)] ,$$

where $f_{\text{sf}(i)}$ are the surface terms on each side of the interface (Sec. IV.A) and

$$f_{\text{coupling}} = [T^* T'(n_{1y}\eta_1^{(1)*} - n_{1x}\eta_2^{(1)*})n_{2z} \times (n_{2x}\eta_1^{(2)} + n_{2y}\eta_2^{(2)}) + \text{c.c.}]_{\text{interface}} . \tag{4.39}$$

TABLE XI. Symmetry basis function $\Phi(\mathbf{n})$ of an interface (Josephson junction) in (a) cubic symmetry, where $\mathbf{n}$ is the surface normal vector of the interface in the basis of the crystal lattice, (b) hexagonal symmetry, and (c) tetragonal symmetry.

Irreducible representation Γ	$\Phi(\Gamma,m;\mathbf{n})$
	(a)
Γ_1^+	$\Phi(\Gamma_1^+;\mathbf{n})=1$
Γ_2^+	$\Phi(\Gamma_2^+;\mathbf{n})=(n_x^2-n_y^2)(n_y^2-n_z^2)(n_z^2-n_x^2)$
Γ_3^+	$\Phi(\Gamma_3^+,1;\mathbf{n})=2n_z^2-n_x^2-n_y^2$
	$\Phi(\Gamma_3^+,2;\mathbf{n})=\sqrt{3}(n_x^2-n_y^2)$
Γ_4^+	$\Phi(\Gamma_4^+,1;\mathbf{n})=n_y n_z(n_y^2-n_z^2)$
	$\Phi(\Gamma_4^+,2;\mathbf{n})=n_z n_x(n_z^2-n_x^2)$
	$\Phi(\Gamma_4^+,3;\mathbf{n})=n_x n_y(n_x^2-n_y^2)$
Γ_5^+	$\Phi(\Gamma_5^+,1;\mathbf{n})=n_y n_z$
	$\Phi(\Gamma_5^+,2;\mathbf{n})=n_z n_x$
	$\Phi(\Gamma_5^+,3;\mathbf{n})=n_x n_y$
Γ_1^-	$\Phi(\Gamma_1^-;\mathbf{n})=n_x n_y n_z(n_x^2-n_y^2)(n_y^2-n_z^2)(n_z^2-n_x^2)$
Γ_2^-	$\Phi(\Gamma_2^-;\mathbf{n})=n_x n_y n_z$
Γ_3^-	$\Phi(\Gamma_3^-,1;\mathbf{n})=\sqrt{3}n_x n_y n_z(n_x^2-n_y^2)$
	$\Phi(\Gamma_3^-,2;\mathbf{n})=n_x n_y n_z(2n_z^2-n_x^2-n_y^2)$
Γ_4^-	$\Phi(\Gamma_4^-,1;\mathbf{n})=n_x$
	$\Phi(\Gamma_4^-,2;\mathbf{n})=n_y$
	$\Phi(\Gamma_4^-,3;\mathbf{n})=n_z$
Γ_5^-	$\Phi(\Gamma_5^-,1;\mathbf{n})=n_x(n_y^2-n_z^2)$
	$\Phi(\Gamma_5^-,2;\mathbf{n})=n_y(n_z^2-n_x^2)$
	$\Phi(\Gamma_5^-,3;\mathbf{n})=n_z(n_x^2-n_y^2)$
	(b)
Γ_1^+	$\Phi(\Gamma_1^+;\mathbf{n})=1$
Γ_2^+	$\Phi(\Gamma_2^+;\mathbf{n})=n_x n_y(n_x^2-3n_y^2)(n_y^2-3n_x^2)$
Γ_3^+	$\Phi(\Gamma_3^+;\mathbf{n})=n_z n_x(n_x^2-3n_y^2)$
Γ_4^+	$\Phi(\Gamma_4^+;\mathbf{n})=n_z n_y(n_y^2-3n_x^2)$
Γ_5^+	$\Phi(\Gamma_5^+,1;\mathbf{n})=n_x n_z$
	$\Phi(\Gamma_5^+,2;\mathbf{n})=n_y n_z$
Γ_6^+	$\Phi(\Gamma_6^+,1;\mathbf{n})=n_x^2-n_y^2$
	$\Phi(\Gamma_6^+,2;\mathbf{n})=2n_x n_y$
Γ_1^-	$\Phi(\Gamma_1^-;\mathbf{n})=n_x n_y n_z(n_x^2-3n_y^2)(n_y^2-3n_x^2)$
Γ_2^-	$\Phi(\Gamma_2^-;\mathbf{n})=n_z$
Γ_3^-	$\Phi(\Gamma_3^-;\mathbf{n})=n_x(n_x^2-3n_y^2)$
Γ_4^-	$\Phi(\Gamma_4^-;\mathbf{n})=n_y(n_y^2-3n_x^2)$
Γ_5^-	$\Phi(\Gamma_5^-,1;\mathbf{n})=n_y$
	$\Phi(\Gamma_5^-,2;\mathbf{n})=-n_x$
Γ_6^-	$\Phi(\Gamma_6^-,1;\mathbf{n})=2n_x n_y n_z$
	$\Phi(\Gamma_6^-,2;\mathbf{n})=-(n_x^2-n_y^2)n_z$
	(c)
Γ_1^+	$\Phi(\Gamma_1^+;\mathbf{n})=1$
Γ_2^+	$\Phi(\Gamma_2^+;\mathbf{n})=n_x n_y(n_x^2-n_y^2)$
Γ_3^+	$\Phi(\Gamma_3^+;\mathbf{n})=n_x^2-n_y^2$
Γ_4^+	$\Phi(\Gamma_4^+;\mathbf{n})=n_x n_y$
Γ_5^+	$\Phi(\Gamma_5^+,1;\mathbf{n})=n_x n_z$
	$\Phi(\Gamma_5^+,2;\mathbf{n})=n_y n_z$
Γ_1^-	$\Phi(\Gamma_1^-;\mathbf{n})=n_x n_y n_z(n_x^2-n_y^2)$
Γ_2^-	$\Phi(\Gamma_2^-;\mathbf{n})=n_z$
Γ_3^-	$\Phi(\Gamma_3^-;\mathbf{n})=n_x n_y n_z$
Γ_4^-	$\Phi(\Gamma_4^-;\mathbf{n})=n_z(n_x^2-n_y^2)$
Γ_5^-	$\Phi(\Gamma_5^-,1;\mathbf{n})=n_y$
	$\Phi(\Gamma_5^-,2;\mathbf{n})=-n_x$

Before performing the variation of F, it is convenient to diagonalize the bilinear surface terms $f_{sf(1)}$ and $f_{sf(2)}$ (see Sec. IV.A). For simplicity we fix $\mathbf{n}_1=(1,0,0)$, leaving the basis in (1) unchanged, whereas $\mathbf{n}_2$ will be arbitrary, with

$$\eta_1'^{(2)}=(n_{2x}\eta_1^{(2)}+n_{2y}\eta_2^{(2)})/\sqrt{n_{2x}^2+n_{2y}^2}$$

and

$$\eta_2'^{(2)}=(-n_{2y}\eta_1^{(2)}+n_{2x}\eta_2^{(2)})/\sqrt{n_{2x}^2+n_{2y}^2}$$

[diagonalizing Eq. (4.19) with $g_1=g_3=g_4/2$]. In the new basis the variation of F with respect to $\eta_j^{(l)}$ leads to the boundary conditions

$$\begin{aligned}
\partial_x\eta_1^{(1)}&=\frac{1}{b_1^{(1)}}\eta_1^{(1)} ,\\
\partial_x\eta_2^{(1)}&=-\frac{T^*T'}{2K_2^{(1)}}n_{2z}\sqrt{n_{2x}^2+n_{2y}^2}\,\eta_1'^{(2)} ,\\
\mathbf{n}_2\cdot\nabla\eta_1'^{(2)}&=\frac{1}{b_1^{(2)}(\mathbf{n}_2)}\eta_1'^{(2)}\\
&\quad+\frac{T'^*T}{2\tilde{K}(\mathbf{n}_2)}n_{2z}\sqrt{n_{2x}^2+n_{2y}^2}\,\eta_2^{(1)} ,\\
\mathbf{n}_2\cdot\nabla\eta_2'^{(2)}&=\frac{1}{b_2^{(2)}(\mathbf{n}_2)}\eta_2'^{(2)} .
\end{aligned} \tag{4.40}$$

All equations are restricted to the interface. The gradients are taken with respect to the basis of the crystal lattice (1) or (2), respectively. Terms containing the extrapolation lengths $b_j^{(l)}$ describe the reflection property of the interface (Sec. IV.A.2), while the others describe the transfer property [$\tilde{K}(\mathbf{n}_2)$ is a combination of coefficients $K_i^{(2)}$ in the free energy $f_{(2)}$ depending on $\mathbf{n}_2$]. These terms exhibit their physical interpretion if we introduce the order parameter in the form $\eta_j^{(l)}=|\eta_j^{(l)}|\exp i\phi_j(l)$ and separate them into real and imaginary parts. From the first two equations [connected with side (1)] we obtain ($T^*T'=|\tilde{T}|^2e^{i\phi_T}$)

$$\begin{aligned}
\partial_x|\eta_1^{(1)}|&=\frac{1}{b_1^{(1)}}|\eta_1^{(1)}| ,\\
\partial_x|\eta_2^{(1)}|&=-\frac{|\tilde{T}|^2}{2K_2^{(1)}}n_{2z}\sqrt{n_{2x}^2+n_{2y}^2}\,|\eta_1'^{(2)}|\\
&\quad\times\cos[\phi_T+\phi_1(2)-\phi_2(1)] ,\\
|\eta_1^{(1)}|\partial_x\phi_1(1)&=0 ,\\
|\eta_2^{(1)}|\partial_x\phi_2(1)&=-\frac{|\tilde{T}|^2}{2K_2^{(1)}}n_{2z}\sqrt{n_{2x}^2+n_{2y}^2}\,|\eta_1'^{(2)}|\\
&\quad\times\sin[\phi_T+\phi_1(2)-\phi_2(1)] .
\end{aligned} \tag{4.41}$$

The other two equations lead to similar expressions as boundary conditions belonging to side (2). The imaginary part [the third and fourth equations of Eq. (4.41)] can be combined into an expression for the current density at the interface,

$$\begin{aligned}
j&=\frac{e}{c}[K_1|\eta_1^{(1)}|^2\partial_x\phi_1(1)+K_2|\eta_2^{(1)}|^2\partial_x\phi_2(1)]\\
&=\frac{e}{2c}|\tilde{T}|^2n_{2z}\sqrt{n_{2x}^2+n_{2y}^2}\,|\eta_1'^{(2)}|\,|\eta_2^{(1)}|\\
&\quad\times\sin[\phi_T+\phi_1(2)-\phi_2(1)] .
\end{aligned} \tag{4.42}$$

The real part [the first and second equations of Eq. (4.41)] is the effective boundary condition for the superconductor on side (1). Solving the Ginzburg-Landau equations and these interface equations of both sides self-consistently, as a one-dimensional problem, we obtain the characteristics of the current j versus the phase difference at the interface. In that calculation it has to be taken into account that the order parameter in the bulk region is also suppressed by a finite current density. In general, for good coupled (1D) superconductors, the characteristics deviate considerably from the simple form $j=j_m\sin(\phi_T+\Delta\phi)$ (Baratoff, Blackburn, and Schwartz, 1970).

However, let us now consider the case of very weakly coupled superconductors ($b_j^{(l)}\ll 2K/|\tilde{T}|^2$). Then the boundary conditions are dominated by the reflection terms. The tunneling terms can be neglected for the calculation of the order parameters at the interface, and the current j is small enough not to affect the order parameters. Thus the result of an almost totally reflecting boundary is appropriate for the problem. In our example $|\eta_2^{(1)}|$ keeps its bulk value $|\eta_0^{(1)}|$. For $|\eta_1'^{(2)}|$, however, a reduction is found at the interface. Regarding Eq. (4.25) we estimate $|\eta_1'^{(2)}|\approx|\eta_0^{(2)}|b_1^{(2)}(\mathbf{n}_2)/\sqrt{2}\tilde{\xi}_1^{(2)}(\mathbf{n}_2)$, where $\tilde{\xi}_1^{(2)}(\mathbf{n}_2)$ is the coherence length of $\eta_1'^{(2)}$ along the direction $\mathbf{n}_2$. Thus the Josephson current has the form

$$j=j_m\sin[\phi_T+\phi_1(2)-\phi_2(1)] \tag{4.43}$$

with

$$j_m=\frac{e}{2c}|\tilde{T}|^2|n_{2z}|\sqrt{n_{2x}^2+n_{2y}^2}\,|\eta_0^{(1)}||\eta_0^{(2)}|\times\frac{b_1^{(2)}(\mathbf{n}_2)}{\sqrt{2}\tilde{\xi}^{(2)}(\mathbf{n}_2)} \tag{4.44}$$

as the critical current of the junction. Since not only $|\eta_0^{(l)}|$ but also $\tilde{\xi}$ is temperature dependent, the increase of $j_m\propto|T-T_c|^\alpha$ is determined by whether and how the coupled order parameters are suppressed at the interface. Obviously, the fact that the interface reflection properties can lead to a drastic suppression of some of the order parameters in the coupling region can reduce the Josephson current considerably. We see also from Eq. (4.44) that j_m strongly depends on the orientation of the crystal axis relative to the interface, reflecting the symmetry of the superconducting state. This can lead to an anisotropy in j_m with lower symmetry than the crystal structure. However, the observation of this property is difficult. In addition to the problem of preparing optimal and equivalent junctions for different directions, a junction that connects only to a single domain of the superconducting phase is required. For the case of a connection to many domains, the averaged angular dependence has just the symmetry of the crystal, and all information about the symmetry of the order parameter is lost.

The phase difference $\Delta\phi=\phi_1(2)-\phi_2(1)$ determines the current with a 2π periodicity and leads to an ac frequency $\omega=2$ eV/$\hbar$, as in conventional Josephson junctions. However, the phase difference, where the current vanishes, does not necessarily correspond to the zero value or π value of $\Delta\phi$, but to some value $-\phi_T$, which is determined by the tunneling matrix (Geshkenbein and Larkin, 1986). This fact could also be noticed in the microscopic expressions for j.

2. Proximity effect

The theoretical study of the mutual proximity of the superconducting states between two superconductors of different parity led to the conclusion that their order parameters might suppress each other strongly (Scharnberg, Fay, and Schopohl, 1978; Fenton, 1980). A superconductor with an attractive triplet channel is not likely to be attractive in any singlet channel and vice versa. Based on this idea several experiments have been suggested to test the parity of the heavy-fermion superconductors.

Millis (1985) considered an arrangement in which a thin film (thickness a) of an s-wave superconductor is placed on a bulk heavy-fermion superconductor (Fig. 5). The bulk critical temperature (T_c^0) of the s-wave superconductor is supposed to be smaller than that of the bulk heavy-fermion superconductor (T_c^b). The measurement of the superconducting order parameter on the film surface (point M) opposite to the interface by a tunneling effect gives information about the parity of the superconducting state of the bulk material. This arrangement can easily be studied as a one-dimensional problem in the Ginzburg-Landau approach. The behavior of the system is mainly determined by the boundary conditions at the interface. However, we do not go into details here, since the treatment is very similar to that of the Josephson-junction problem.

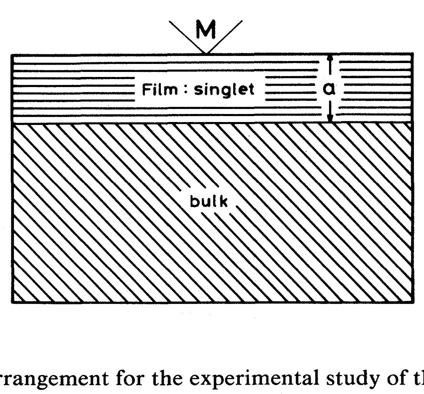

FIG. 5. Arrangement for the experimental study of the proximity effect between an unconventional *bulk* superconductor and a conventional s-wave superconducting film (Millis, 1985).

If the bulk superconductor has s-wave symmetry, it will also induce a finite, detectable superconducting order parameter in the film via the proximity effect. Immediately below the bulk transition temperature T_c^b, the film order parameter behaves as $|\eta_{\text{film}}(T)| \sim |\eta_{\text{bulk}}(T)|/\xi_{\text{bulk}}(T) \sim (1-T/T_c^b)^{3/2}$ that is, as a "driven" order parameter. Below T_c^0 the order parameter η_{film} "has its own life" and is then essentially proportional to $(1-T/T_c^0)^{1/2}$.

In the case of an odd-parity (triplet) superconductor in the bulk, it is assumed that a driven s-wave order parameter in the film is absent or only very small, because the effect of a magnetically active interface, which is able to convert even- and odd-parity states, is considered to be negligibly small in this picture. Therefore the effective boundary condition for a thin film would have the form

$$\partial_x \eta_{\text{film}} + \frac{1}{b}\eta_{\text{film}}|_{\text{interface}} = 0 \,, \tag{4.45}$$

acting suppressively for η_{film} at the interface. The extrapolation length b is determined by the tunneling and reflection properties of the interface and by the properties of the bulk superconductor (the effective coherence length of the s-wave order parameter in the bulk, etc.). With this boundary condition the transition temperature of a film of thickness a is reduced compared to T_c^0, as may be easily calculated in the Ginzburg-Landau formulation,

$$\tilde{T}_c = T_c \left[1 - \frac{\xi_0^2}{a^2} r(b/a) \right] , \tag{4.46}$$

with ξ_0 as the zero-temperature coherence length of the film superconductor ($\propto l^{1/2}$ for the dirty limit, where l is equal to the mean free path of the film) and r a function of the ratio b/a with $r \to \pi/2$ for $b \ll a$. For temperatures larger than $\tilde{T}_c$ the s-wave order parameter detected at the M would essentially be zero. From these two qualitatively different behaviors one could distinguish experimentally whether even- or odd-parity superconductivity were present in the bulk superconductor.

A similar arrangement was studied by Ashauer *et al.* (1986). Taking the opposite approach, they assumed $T_c^0 \geq T_c^b$ and calculated the effective transition temperature of the film (at the point M) in the presence of different bulk phases. They found a significant difference in the film transition temperature depending on whether singlet or triplet superconductivity was present in the bulk. Their result for the temperature-a-phase diagram is plotted in Fig. 6(a) for a clean and in Fig. 6(b) for a dirty film [by renormalization of the film thickness by the transmission rate T of the interface ($\bar{a}=a/T$)]. It is remarkable that the reduction of the s-wave superconductivity of the film by a triplet bulk superconductor is quantitatively almost the same as by a normal (nonsuperconducting) metal. Thus their effective extrapolation length [Eq. (4.45)] has to be almost equal. Obviously, for an experiment, good films of a thickness a of the order $\xi_0 T$ or smaller are required, where ξ_0 is the coherence length of the s-wave superconductor. Therefore a large mass mismatch, mentioned initially, could suppress T strongly, so that this experiment is rather difficult to realize with heavy-fermion superconductors.

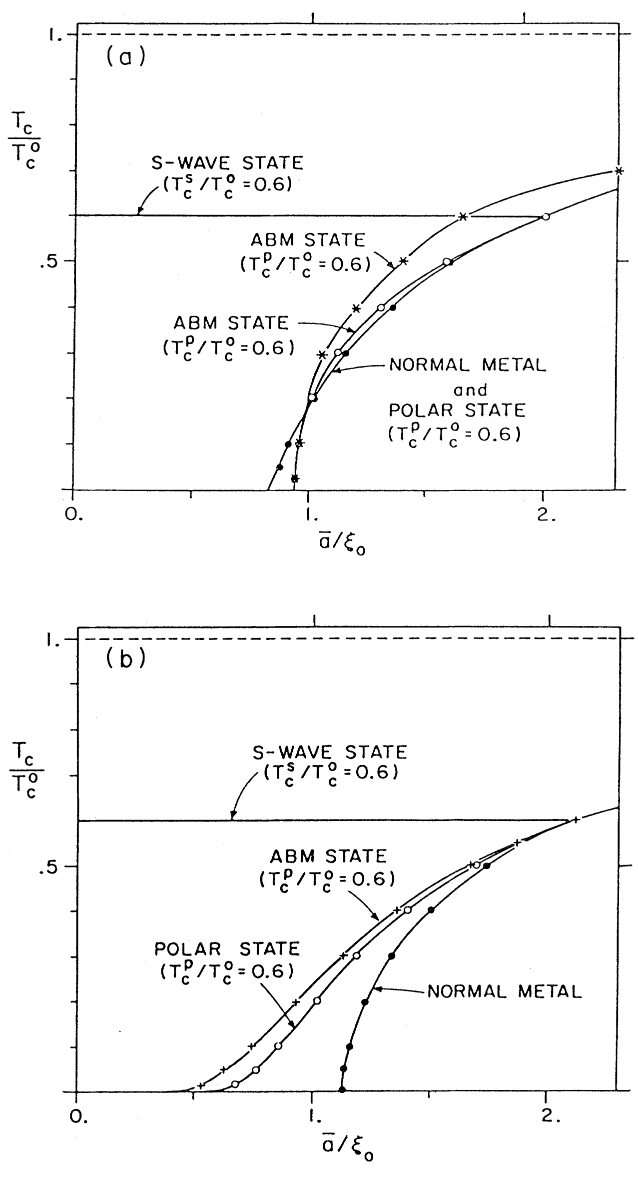

FIG. 6. Critical temperatures T_c of clean and dirty films (thickness a) in proximity contact with various bulk materials (different types of p-wave superconductors, normal-metal, and s-wave superconductors with smaller T_c^s). The critical temperature is defined by the vanishing of the s-wave order parameter in the film. T_c^0 and T_c^p are the unperturbed transition temperatures of the film and the p-wave superconductors, respectively; ξ_0 is the coherence length of the s-wave superconductor, and $\bar{a}=a/(1-R)$ is an adjusted thickness which includes the effect of reflections at the interface: (a) clean thin film; (b) a dirty film. From Ashauer, Kieslemann, and Rainer, 1986.

V. MAGNETIC PROPERTIES OF UNCONVENTIONAL SUPERCONDUCTORS

Listing the possible superconducting phases in Sec. **II**, we found that most of them break not only U(1) gauge symmetry but also additional symmetries. In this section we concern ourselves mainly with phases that break time-reversal symmetry. The violation of time-reversal invariance is in general a property of magnetic systems. Indeed, it is found that these superconducting phases breaking time-reversal symmetry have magnetic properties too (Volovik and Gor'kov, 1984; Blount, 1985; Ueda and Rice, 1985a). A first demonstration of these properties was given by Volovik and Gor'kov (1985), who analyzed the current and magnetic-field distribution close to a domain wall in such a superconducting phase. The occurrence of magnetic fields in these superconductors is associated with the spatial variation of the superconducting order parameter. Such fields are completely absent in the homogeneous bulk region. We shall show in this section that they can have two different origins: (a) a tensorial response of the supercurrent to the spatial variation of the phase of the order parameter, and (b) an intrinsic magnetic moment due to spin polarization (triplet) and the relative angular momentum of the Cooper pairs.

Another magnetic structure of a superconductor is the vortex, a line defect in the superconducting phase, which includes a filament of magnetic flux. For topological reasons, in conventional superconductors only vortices with a flux quantum $\Phi_0 = n \times hc/2|e|$ can exist, induced by a winding of the order parameter phase around a line. Since anisotropic superconductors with multicomponent order parameters can have more than one phase factor, several structures of vortices are topologically possible. It will be shown that even vortices with fractional flux quanta can occur as energetically stable structures.

Another aspect of the magnetic properties of anisotropic superconductivity arises if the superconducting state forms in the presence of magnetic ordering in the system. The question arises under which conditions this coexistence is favored.

A. Magnetic properties of inhomogeneous structures

Clearly, only multicomponent superconductors can yield time-reversal-breaking (complex) states. These states are transformed by the time-reversal operation into another state, which is not simply related to the original one by a U(1) gauge transformation ($K\hat{\Delta} \neq \hat{\Delta} e^{i\phi}$). They can produce unconventional magnetic behavior, which is, however, compatible with the general properties of a superconductor. To illustrate this fact we concentrate, as in some previous sections, on the simplest nontrivial example of an anisotropic superconductor with a time-reversal-breaking state, whose order parameter is in the 2D representation $\Gamma_5^{\pm}$ of the tetragonal symmetry D_{4h}. It includes most of the interesting effects of an unconventional superconductor. The free energy has the form

$$F=\int d^3r' \Bigg[A(T)(|\eta_1|^2+|\eta_2|^2)+\beta_1(|\eta_1|^2+|\eta_2|^2)^2+\beta_2(\eta_1^*\eta_2-\eta_1\eta_2^*)^2+\beta_3|\eta_1|^2|\eta_2|^2$$
$$+K_1(|D_x\eta_1|^2+|D_y\eta_2|^2)+K_2(|D_y\eta_1|^2+|D_x\eta_2|^2)$$
$$+K_3[(D_x\eta_1)^*(D_y\eta_2)+(D_x\eta_1)(D_y\eta_2)^*]+K_4[(D_x\eta_2)^*(D_y\eta_1)+(D_x\eta_2)(D_y\eta_1)^*]$$
$$+K_5(|D_z\eta_1|^2+|D_z\eta_2|^2)+\frac{1}{8\pi}\mathbf{B}^2\Bigg] \tag{5.1}$$

as determined in Sec. II.B ($\mathbf{D}=\nabla-2ie\,\mathbf{A}/c$). For the coefficients β_i in the range $\beta_2>0$ and $\beta_3<4\beta_2$ $[4(\beta_1-\beta_2)+\beta_3>0]$, the time-reversal-breaking, twofold-degenerate bulk phase $[D_{4h}(\Gamma_5^+)]$

$$(\eta_1,\eta_2)=\eta_0(1,\pm i)$$

with

$$|\eta_0|^2=\frac{-A(T)}{4(\beta_1-\beta_2)+\beta_3} \tag{5.2}$$

minimizes the free energy in the homogeneous region. This state has a bulk energy density

$$f=\frac{-A^2(T)}{4(\beta_1-\beta_2)+\beta_3}=-\frac{H_c^2}{8\pi}\ , \tag{5.3}$$

which determines $H_c(T)$, the thermodynamic critical magnetic field. To introduce a length scale of the magnetic field (Meissner effect), we consider the London equation obtained by variation of F with respect to the vector potential. From this equation the London penetration depth λ in the basal plane along the main axis is found to be

$$\lambda^2(T)=\frac{c^2}{8\pi(2e)^2(K_1+K_2)|\eta_0|^2}\ . \tag{5.4}$$

Note that the effective London penetration depth is anisotropic in this system, depending on the direction of the field and the boundary.

Further, using the conventional relation for the "Ginzburg-Landau parameter" κ,

$$\kappa=\frac{\lambda}{\xi}=\sqrt{2}\frac{2|e|}{c}H_c\lambda^2 =\frac{c}{2e}\frac{\sqrt{4(\beta_1-\beta_2)+\beta_3}}{\sqrt{4\pi}(K_1+K_2)}\ , \tag{5.5}$$

we define the basal plane "coherence length"

$$\xi^2=\frac{4\pi}{H_c^2(T)}(K_1+K_2)|\eta_0|^2\ . \tag{5.6}$$

The effective coherence length is also anisotropic and depends on the components of the order parameter. These quantities are the basis for a dimensionless formulation of the Ginzburg-Landau function [Eq. (5.1)], which is appropriate for studies of inhomogeneous structures of the superconducting state. We define

$$\mathbf{r}'=\xi\mathbf{r},\ \mathbf{A}(\mathbf{r}')=\sqrt{2}H_c\lambda\mathbf{a}(\mathbf{r})\ ,$$
$$\mathbf{B}(\mathbf{r}')=\nabla_{\mathbf{r}'}\times\mathbf{A}(\mathbf{r}')=\sqrt{2}H_c\kappa\mathbf{b}(\mathbf{r})\ ,$$

with $\mathbf{b}(\mathbf{r})=\nabla_{\mathbf{r}}\times\mathbf{a}(\mathbf{r})$ and the order parameter $(\eta_1,\eta_2)=|\eta_0|(u,v)$. Then

$$F=\frac{1}{4\pi}H_c^2\xi^3\int d^3r\Bigg[-\tfrac{1}{2}(|u|^2+|v|^2)+(\tfrac{1}{8}+\tfrac{1}{2}\tilde{\beta}_2)(|u|^2+|v|^2)^2+\tfrac{1}{2}\tilde{\beta}_2(u^*v-uv^*)^2$$
$$-\frac{\tilde{\beta}_3}{8}(|u|^2-|v|^2)^2+k_1(|d_xu|^2+|d_yv|^2)+k_2(|d_yu|^2+d_xv|^2)$$
$$+\tilde{k}[(d_xu)^*(d_yv)+(d_xv)^*(d_yu)+\text{c.c.}]+\Delta\tilde{k}[(d_xu)^*(d_yv)-(d_xv)^*(d_yu)+\text{c.c.}]$$
$$+k_5(|d_zu|^2+|d_zv|^2)+\kappa^2\mathbf{b}^2\Bigg]\ , \tag{5.7}$$

where the coefficients are renormalized as $\tilde{\beta}_i=\beta_i/[4(\beta_1-\beta_2)+\beta_3]$, $k_i=K_i/(K_1+K_2)$ (that is, $k_1+k_2=1$) and the gradients $\mathbf{d}=\nabla_{\mathbf{r}}-i\mathbf{a}$ (the charge e is taken to be positive here). Furthermore, we combined the k_3 and k_4 terms so that $\tilde{k}=(k_3+k_4)/2$ and $\Delta\tilde{k}=(k_3-k_4)/2$. Note that, in the weak-coupling limit, $\Delta\mathbf{k}$ is vanishing (see, for example, Machida, Ohmi, and Ozaki, 1985). In this formulation we see that the form of this Ginzburg-Landau theory depends effectively on eight parameters (in the simplest case a conventional superconductor has only one parameter, i.e., κ).

The complicated gradient terms lead to an unconventional supercurrent density, which is defined by $\mathbf{j}=\nabla\times\mathbf{b}(=-\partial f/2\kappa^2\partial\mathbf{a})$. For $\mathbf{j}$ in the x-y plane we find

$$j_x = \frac{1}{\kappa^2}\mathrm{Im}[k_1 u^* \partial_x u + k_2 v^* \partial_x v + \tilde{k}(u^* \partial_y v + v^* \partial_y u) + \Delta\tilde{k}(u^* \partial_y v - v^* \partial_y u)] - \frac{1}{\kappa^2}\mathrm{Re}[(k_1|u|^2 + k_2|v|^2)a_x + \tilde{k}u^* v a_y] ,$$

$$j_y = \frac{1}{\kappa^2}\mathrm{Im}[k_2 u^* \partial_y u + k_1 v^* \partial_y v + \tilde{k}(u^* \partial_x v + v^* \partial_x u) - \Delta\tilde{k}(u^* \partial_x v - v^* \partial_x u)] - \frac{1}{\kappa^2}\mathrm{Re}[(k_1|v|^2 + k_2|u|^2)a_y + \tilde{k}u^* v a_x] . \tag{5.8}$$

The terms proportional to $\mathrm{Im}u^*(\nabla - i\mathbf{a})u$ and $\mathrm{Im}v^*(\nabla - i\mathbf{a})v$ are familiar from conventional superconductivity. However, the terms with the coefficients $\tilde{k}$ and $\Delta\tilde{k}$ contain gradients perpendicular to the current direction. This is a consequence of the multicomponent structure of the order parameter, as we shall discuss in more detail below. The z component in this system has a conventional form and is not tensorially coupled with the other components due to its special symmetry property in a tetragonal lattice.

1. Domain walls

The easiest way to examine the effect of the unconventional current expression is to consider a domain wall between two degenerate states of a superconductor (Volovik and Gor'kov, 1985; Sigrist *et al.*, 1989). We shall use this section also to give some insight into the structure of a domain wall in an unconventional superconductor. For the superconducting phase $D_{4h}(\Gamma_5^{\pm})$ two types of domains are possible, represented by $(u,v)=(1,+i)$ and $(1,-i)$. To analyze the structure of the domain wall between these two states it is convenient to reduce the problem to one spatial dimension in the following geometry:

$$(u,v) = \begin{cases} (1,-i) \text{ or } \gamma = -\pi/2 & \text{for } x \to -\infty , \\ (1,+i) \text{ or } \gamma = +\pi/2 & \text{for } x \to +\infty , \end{cases} \tag{5.9}$$

where we have assumed homogeneity in the y and z directions ($u = |u|e^{i\phi}$, $v = |v|e^{i\chi}$ and $\gamma = \phi - \chi$).

The first step in the study of the domain-wall structure is to classify it according to its symmetry properties. We define the symmetry group $\tilde{\mathcal{G}}$ by taking all group elements out of $\mathcal{G} = G \times \mathcal{K} \times \mathrm{U}(1)$, which leaves the boundary conditions in Eq. (5.9) invariant,

$$\tilde{\mathcal{G}} = \{E, KC_{2x}e^{i\pi}, C_{2y}, KC_{2z}e^{i\pi}, \sigma_z e^{i\pi}, \sigma_x e^{i\pi}, K\sigma_y, KI\} , \tag{5.10}$$

This group is isomorphic to the point group D_{2h} ($=\{E, C_{2x}, C_{2y}, C_{2z}, I, \sigma_y, \sigma_x, \sigma_z\}$). Since E and $\sigma_z e^{i\pi}$ ($\sim I$) act in the same way on the order parameter, only even-parity irreducible representations of D_{2h} need be used for the classification. Due to the finite values of the order parameter in the boundary conditions, the order parameter itself is not appropriate for the classification, but the following functions are: $\delta u(x) = u(x) - 1$ and $\delta v(x) = v(x) - v_0(x)$ with $v_0(x) = i\tanh(\alpha x)$ ($\alpha > 0$ real), so that $\delta u(\pm\infty) = \delta v(\pm\infty) = 0$. The following types of basic domain-wall structures are possible:

Γ_1^+:	δu: real, even	δv: imaginary, odd
Γ_2^+:	δu: imaginary, even	δv: real, odd
Γ_3^+:	δu: imaginary, odd	δv: real, even
Γ_4^+:	δu: real, odd	δv: imaginary, even.

(5.11)

Let us now derive the specific structure of the domain wall from the Ginzburg-Landau theory. Even if the problem is only one dimensional, the solution of the corresponding Ginzburg-Landau equations is difficult, since the variation of F leads to at least six coupled nonlinear differential equations (four for the order parameters and two for a_x and a_y), if we neglect the vector-potential component a_z by reason of its symmetry. Under special conditions, however, an approximate result can be obtained.

In the case (I) $\tilde{\beta}_2 \ll 1$ it is reasonable to set $|u| \approx |v|$. If there is no imbalance in the Josephson phase between the two sides (see Sec. IV), the current through the domain wall has to vanish,

$$\kappa^2 j_x = k_1|u|^2(\partial_x\phi - a_x) + k_2|v|^2(\partial_x\chi - a_x) - 2\tilde{k}|u|\,|v|a_y\cos(\chi - \phi) = 0 . \tag{5.12}$$

At the same time, this equation corresponds to the London equation of the a_x component restricted to one dimension. If we neglect the vector potential for the moment, the following two differential equations result from the variation of F with respect to $|u|$ ($=|v|$), ϕ and χ, using Eq. (5.12) to eliminate one equation:

$$\partial_x^2|u| + |u| - |u|^3(1 + 4\tilde{\beta}_2\cos^2\gamma) = 0$$
$$|u|^2\partial_x^2\gamma + 2|u|(\partial_x u)(\partial_x\gamma) + \frac{\tilde{\beta}_2}{k_1 k_2}|u|^4\sin(2\gamma) = 0 , \tag{5.13}$$

with the boundary conditions $|u|(\pm\infty) = 1$ and $\gamma(\pm\infty) = \pm\pi/2(\gamma = \chi - \phi)$. These equations are approximately solved by

$$|u|(x) = 1 - \frac{2\tilde{\beta}_2}{\cosh^2(\sqrt{2}x/\tilde{\xi})} + O(\tilde{\beta}_2^2)$$
$$\gamma(x) = \mathrm{arcsinh}[\tanh(\sqrt{2}x/\tilde{\xi})] + O(\tilde{\beta}_2^2) , \tag{5.14}$$

where $\tilde{\xi} = \sqrt{k_1 k_2/\tilde{\beta}_2}$ is the length scale (thickness) of the domain wall [this length scale must not be confused with that introduced in Eq. (5.6)]. The order parameter is slightly suppressed in the center of the wall, and the relative phase has a continuous kink solution. The energy of this wall per unit length is given by

$$\varepsilon_0=\frac{H_c^2\xi}{4\pi}\int dx(f(x)-f_0)$$
$$=\frac{H_c^2\xi}{4\pi}4\sqrt{2\tilde{\beta}_2k_1k_2}+O(\tilde{\beta}_2^{3/2}) , \quad (5.15)$$

where $f_0=-\frac{1}{2}$ is the dimensionless bulk energy density of the superconductor. The temperature dependence of ε_0 is proportional to $|T-T_c|^{3/2}$ close to T_c for the same reason as at the surface (see Sec. IV).

If we consider the case (II) $\tilde{\beta}_2\gg 1$ another domain wall structure occurs. The simplest approximate solution of the Ginzburg-Landau equations is given by

$$u(x)=1 \quad v(x)=i\tanh\left[\frac{x\sqrt{2}}{\tilde{\xi}'}\right] , \quad (5.16)$$

with $\tilde{\xi}'=4\sqrt{k_2/(1+4\tilde{\beta}_2-\tilde{\beta}_3)}$ and the domain-wall energy

$$\varepsilon_0'=\frac{H_c^2\xi}{6\pi}\sqrt{2k_2(1+4\tilde{\beta}_2-\tilde{\beta}_3)} . \quad (5.17)$$

This solution is a good approach for $1-4\tilde{\beta}_2+\tilde{\beta}_3\ll 1$ and $k_2<k_1$.

Comparing these two solutions with the symmetry classification given above, we find that domain wall (II) corresponds to the Γ_1^+ representation, whereas domain wall (I) belongs to a combination of Γ_1^+ and Γ_3^+: $\Gamma_1^+\oplus\Gamma_3^+$. It can be shown that there is a continuous transition between the two types of domain walls, depending on the coefficients β_2, β_3 as well as on k_i. Clearly, the symmetry of domain wall (II) is higher than that of (I) which is twofold degenerate due to the different behavior of the two representations under symmetry transformation. This degeneracy can be easily understood in the following way: the relative phase γ going from $-\pi/2$ to $+\pi/2$ can pass through 0 or through π. Both are solutions with the same energy ε_0. For domain wall (II) this type of degeneracy cannot occur, since the relative phase changes discontinuously in the center of the wall. Other representations than Γ_1^+ and Γ_3^+ are not realized as stable domain walls within the region $\tilde{\beta}_2>0$, $4\tilde{\beta}_2>\tilde{\beta}_3$ and assuming the above given boundary conditions.

The symmetry group of domain walls in an arbitrary direction is usually isomorphic to a subgroup of $\tilde{\mathcal{G}}$ (one exception is the domain wall lying in the x-y plane, which has a symmetry group larger than $\tilde{\mathcal{G}}$, i.e., D_{4h}; $\tilde{\mathcal{G}}$ is isomorphic to a subgroup therein). If the normal axis of the domain wall lies in the x-y plane, the subgroup is mostly isomorphic to $C_{2h}(z)$, whose trivial representation Γ_1^+ is compatible with both Γ_1^+ and Γ_3^+ of D_{2h}. Thus there cannot be any symmetry distinction between two domain-wall structures of the types (I) and (II) nor, therefore, any transition between them. Furthermore, the degeneracy for the case $\tilde{\beta}_2\ll 1$ is lost. However, this lifting of degeneracy may be small compared to the domain-wall energy. This twofold degeneracy is exactly established only if the domain wall is parallel to the x, y, xy or $(-x)y$ axis.

Our original aim was to consider the magnetic properties of these domain walls. Hence we must now treat the variational equations (London equations) for the vector potential. The only component we need to consider is a_y, since a_x has already been dealt with in Eq. (5.12):

$$\partial_x^2a_y-\frac{1}{\kappa^2}(k_1|v|^2+k_2|u|^2)a_y+j_y'=0 \quad (5.18)$$

where the second term is the diamagnetic current induced by a magnetic field, and j_y' is the current driven by the spatial variation of the order parameter in the domain wall. This j_y' is calculated from Eq. (5.8) to be

$$\mathrm{Im}[\tilde{k}(u^*d_xv+v^*d_xu)+\Delta\tilde{k}(u^*d_xv-v^*d_xu)]/\kappa^2 .$$

Using Eq. (5.12), we derive the functions $j_y'(x)$,

$$j_y^{(\mathrm{I})}=\frac{\sqrt{2}}{\kappa^2\tilde{\xi}}[\tilde{k}k_1k_2(k_1-k_2)-\Delta\tilde{k}]\frac{1}{\cosh^2(\sqrt{2}x/\tilde{\xi})} \quad (5.19)$$

for domain wall (I) and

$$j_y^{(\mathrm{II})}=\frac{\sqrt{2}}{2\kappa^2\tilde{\xi}'}(\tilde{k}-\Delta\tilde{k})\frac{1}{\cosh^2(\sqrt{2}x/\tilde{\xi}')} \quad (5.20)$$

for (II). In both cases there is a current peaked in the center of the wall and flowing parallel to the y axis. The origin of these spontaneous currents will be discussed more generally in the next section.

To see the behavior of the magnetic field induced by this current, we approximate j_y by $j_02\sqrt{2}\exp(-2\sqrt{2}|x|/\tilde{\xi})/(\kappa^2\tilde{\xi})$ [j_0 is chosen to give the same total current as the current expressions above where, for the domain wall (II), $\tilde{\xi}$ has to be replaced by $\tilde{\xi}'$] and set $k_1|u|^2+k_2|v|^2=1$ everywhere. Then the London equation can easily be solved, leading to a magnetic field

$$b_z(x)=j_0\frac{8}{8\kappa^2-\tilde{\xi}^2}(e^{-|x|/\kappa}-e^{-2\sqrt{2}|x|/\tilde{\xi}})\frac{x}{|x|} . \quad (5.21)$$

This field has opposite sign on the two sides of the domain wall and is screened towards the bulk region on a length scale κ (the London penetration depth in dimensionless units). The effective current, including the diamagnetic contributions, is given by $j_y=-\partial_xb_z$ and contains a peak in the center, as before, and additionally two wings of counter currents on both sides. Thus both the field and the current vanish on the average, and no net magnetization is associated with a domain wall. The maximum value reached locally by the field is $|B_z|\approx 8H_cj_0/\sqrt{2}\kappa(2\sqrt{2}\kappa+\tilde{\xi})$. The weak-coupling limit ($k_1=\frac{3}{4}$, $k_2=\tilde{k}=\frac{1}{4}$, $\Delta\tilde{k}=0$, $j_0\leq 1/8$) leads, for large κ, to a value well below the conventional lower critical magnetic field along the z axis: $H_{c1}=H_c\ln\kappa/\sqrt{2}\kappa$. The contribution of this magnetic field and the current to the domain-wall energy is small, of the order of κ^{-1} in the large-κ limit.

The solution of all six Ginzburg-Landau equations in a consistent way requires numerical calculation. In Fig. 7 the result is given for the small-$\tilde{\beta}_2$ limit, confirming the validity of the approximate solution.

Finally, we should like to mention that domain walls in time-reversal-conserving superconducting states can also yield magnetic properties. For example, the region $\tilde{\beta}_2,\tilde{\beta}_3<0$ with the twofold-degenerate bulk state $(u,v)\propto(1,\pm1)$ has similar domain walls between the two degenerate states. In the limit $|\tilde{\beta}_2|\ll 1$ these domain walls can break time-reversal symmetry locally and have similar magnetic properties to those described above. Due to the breakdown of time-reversal symmetry, the structure of the domain wall is twofold degenerate too.

2. Magnetization at the surface

The surface of a superconductor has properties similar in many respects to the domain wall (Sigrist *et al.*, 1989). The order parameter also varies spatially towards the surface in a range $\tilde{\xi}$, as already described in Sec. IV. We consider the example of a surface perpendicular to the x axis demonstrated there ($x>0$: superconductor and $x<0$: vacuum). The component $|u|$ is assumed to be stressed to zero as

$$|u(x)|=\tanh(\sqrt{2}x/\tilde{\xi}) \quad \text{and} \quad \chi-\phi=\pm\frac{\pi}{2}=\text{const} , \tag{5.22}$$

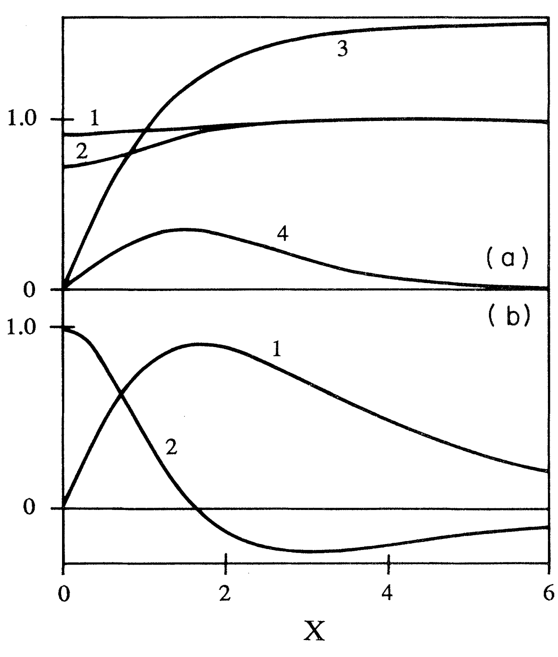

FIG. 7. Result of a self-consistent solution of the domain-wall problem for the parameters $\tilde{\beta}_2=0.1$, $\tilde{\beta}_3=-0.6$, $k_1=0.7$, $\tilde{k}=0.1$, and $\kappa=4$: (a) order parameter $(u,v)=\exp(i\phi)(|u|,|v|\exp(i\gamma))$: **1** $|u|$; **2** $|v|$; **3** γ; **4** $10\times\phi$. (b) magnetic field and current distribution: **1** $10^3\times b_z$; **2** $10^3\times j_y$ (Sigrist *et al.*, 1989).

with $\tilde{\xi}^2=16k_1/(1+4\tilde{\beta}_2-\tilde{\beta}_3)$, whereas $|v|$ is assumed to remain constant $(=1)$ (the same approach as in Sec. IV.A). The boundary condition in Eq. (4.24) prohibits a current perpendicular to the wall: $j_x=0$. Thus the London equation for a_y has the form

$$\frac{\partial^2}{\partial x^2}a_y-\frac{1}{\kappa^2}(k_1|v|^2+k_2|u|^2)a_y - \frac{\tilde{k}+\Delta\tilde{k}}{\kappa^2}|v|\frac{\partial}{\partial x}|u|\sin(\chi-\phi)=0 . \tag{5.23}$$

Substituting Eq. (5.22) in (5.23), we see that the last term denotes a supercurrent flowing parallel to the surface: $j_y=-(\tilde{k}+\Delta\tilde{k})\sqrt{2}\sin(\chi-\phi)/\kappa^2\tilde{\xi}\cosh^2(\sqrt{2}x/\tilde{\xi})$, similar to the domain wall. The induced magnetic field can be obtained by an approach analogous to that of Sec. V.A.1, replacing j_y by

$$-(\tilde{k}+\Delta\tilde{k})2\sqrt{2}\sin(\chi-\phi)\exp(-2\sqrt{2}|x|/\tilde{\xi})/\tilde{\xi}\kappa^2 .$$

Then the magnetic field is

$$b_z(x)=(\tilde{k}+\Delta\tilde{k})\frac{8}{8\kappa^2-\tilde{\xi}^2} \times(e^{-x/\kappa}-e^{-2\sqrt{2}x/\tilde{\xi}})\sin(\chi-\phi) , \tag{5.24}$$

where we take the external magnetic field to be zero. The maximal magnitude in real units is about the same as in the case of the domain wall. Because the sign of the magnetic field depends on the relative phase $(\chi-\phi)$, it is different in the two domains $(u,v)=(1,\pm i)$. Contrary to the case of the domain wall, there exists a finite net magnetization at the surface:

$$|M|\approx 4\sqrt{2}(\tilde{k}+\Delta\tilde{k})H_c/(2\sqrt{2}\kappa+\tilde{\xi})$$

per unit surface area. This has the consequence that a single domain superconductor has a finite, macroscopically observable magnetic moment due to the time-reversal-breaking state.

Even if the currents found at the surface and the domain wall seem to be rather unconventional, their origins are in some ways analogous to those of supercurrents in conventional superconductors. They are the response to a spatial variation of the phase of the order parameter. In a multicomponent order parameter $[\hat{\Delta}=\sum_j|\eta_j|\exp(i\phi_j)\hat{\Delta}_j]$, the behavior of this phase is determined by several variables, first of all by the phase of each component. However, the total phase is also clearly changed if the magnitude of the moduli $|\eta_j|$ of each component varies in a different way, and the value of the relative phase among them is somewhere between 0 and $\pm\pi$ (note that the latter is the condition for a time-reversal-breaking state). The multicomponent structure of the order parameter yields a tensorial behavior, so that currents can also be induced by gradients of the phase variation perpendicular to its direction.

In the weak-coupling limit the gradient terms of a Ginzburg-Landau theory of a multicomponent order parameter can be written in the form

$$F_G=\frac{C}{4}\sum_{j,l,m,n}\left[\int d^3R\, K_{jl}(\mathbf{R})R_mR_n\right]\times\left[\left[\partial_m-\frac{2ie}{c}A_m(\mathbf{r})\right]\eta_j(\mathbf{r})\right]^*\times\left[\left[\partial_n-\frac{2ie}{c}A_n(\mathbf{r})\right]\eta_l(\mathbf{r})\right], \quad (5.25)$$

which can be derived from Eq. (4.4) by assuming a slow variation of the order parameter $[\xi(T)\gg\xi_0]$ and gauge invariance (see, for example, Abrikosov, Gor'kov, and Dzyaloshinski, 1963). The kernel has the structure

$$K_{jl}(\mathbf{R})=f(|\mathbf{R}|)\,\mathrm{tr}[\hat\Delta_j^+(\mathbf{R})\hat\Delta_l(\mathbf{R})], \quad (5.26)$$

as given in Eq. (4.9). The constant C is chosen to give the correct units. From this equation the supercurrent can be calculated by the derivative with respect to the vector potential $(\mathbf{J}=-c\partial F_G/\partial\mathbf{A})$,

$$\mathbf{J}(\mathbf{r})=Ce\,\mathrm{Im}\int d^3R\, f(|R|)\mathbf{R}\,\mathrm{tr}\left[\hat\Delta^+(\mathbf{r};\mathbf{R})\left[\nabla_r-\frac{2ie}{c}\mathbf{A}\right]\hat\Delta(\mathbf{r};\mathbf{R})\right]\cdot\mathbf{R}\,. \quad (5.27)$$

We now introduce $\hat\Delta(\mathbf{r};\mathbf{R})=\sum_j\eta_j(\mathbf{r})\hat\Delta_j(\mathbf{R})$. For our discussion of the current induced by the phase variation, we neglect the diamagnetic currents, the part that depends on the vector potential.

Let us consider the case of a planar surface. It is convenient to characterize the spatial variation of the order parameter at the surface by separating it into components, which are classified by the parity $\mathcal{P}(\mathbf{n})$ (reflection at the boundary, which is represented by the normal vector $\mathbf{n}$): even components are assumed to be constant and odd components are suppressed at the boundary (see Sec. IV). This assumption allows us to write a simple expression for the final result without losing the general content. Therefore we decompose the order parameter,

$$\hat\Delta(\mathbf{r};\mathbf{R})=\hat\Delta_e(\mathbf{R})+\hat\Delta_o(\mathbf{n}\cdot\mathbf{r};\mathbf{R})=\hat\Delta_e(\mathbf{R})+\sum_j\hat\Delta_o^{(j)}(\mathbf{R})\eta_j(\mathbf{n}\cdot\mathbf{r})\,, \quad (5.28)$$

where the indices e and o denote "even" and "odd," respectively. If we choose the basis gap function to be orthogonalized {also with $\int d^3R\,(\mathbf{n}\cdot\mathbf{R})^2\mathrm{tr}[\hat\Delta^{+(i)}(\mathbf{R})\hat\Delta^{(j)}(\mathbf{R})]\propto\delta_{ij}$}, it is easy to see that there is no current perpendicular to the surface: $\mathbf{n}\cdot\mathbf{J}=0$. On the other hand, we find for the currents parallel to the surface

$$\begin{aligned}\mathbf{J}_\parallel&=\mathbf{J}-\mathbf{n}(\mathbf{n}\cdot\mathbf{J})\\&=\mathbf{n}\times Ce\,\mathrm{Im}\int d^3R\, f(|\mathbf{R}|)(\mathbf{R}\times\mathbf{n})(\mathbf{n}\cdot\mathbf{R})\mathrm{tr}[\hat\Delta^+(\mathbf{n}\cdot\mathbf{r};\mathbf{R})\partial_n\hat\Delta(\mathbf{n}\cdot\mathbf{r};\mathbf{R})]\,.\end{aligned} \quad (5.29)$$

By making use of Eq. (5.28) and by partial integration we obtain

$$\mathbf{J}_\parallel=-\mathbf{n}\times\frac{iCe}{2}\int d^3R\, f(|\mathbf{R}|)(\mathbf{n}\cdot\mathbf{R})^2(\mathbf{R}\times\nabla_\mathbf{R})\,\mathrm{tr}[\hat\Delta_e^+(\mathbf{R})\partial_n\hat\Delta_o(\mathbf{n}\cdot\mathbf{r};\mathbf{R})-\hat\Delta_e(\mathbf{R})\partial_n\hat\Delta_o^+(\mathbf{n}\cdot\mathbf{r};\mathbf{R})]\,. \quad (5.30)$$

This can be reduced to the form

$$\mathbf{J}_\parallel=-\nabla_r\times Ce\,\mathrm{Im}\int d^3R\, f(|\mathbf{R}|)(\mathbf{n}\cdot\mathbf{R})^2\mathrm{tr}\{[\mathcal{P}(\mathbf{n})\hat\Delta^+(\mathbf{n}\cdot\mathbf{r};\mathbf{R})](\mathbf{R}\times\nabla_\mathbf{R})\hat\Delta(\mathbf{n}\cdot\mathbf{r};\mathbf{R})\}\,, \quad (5.31)$$

using the fact that the operator $\mathbf{n}\times(\mathbf{R}\times\nabla_\mathbf{R})$ changes the $\mathcal{P}(\mathbf{n})$ parity of a function $\hat\Delta_{e,o}(\mathbf{R})$. The expression $\mathcal{P}(\mathbf{n})\hat\Delta^+(\mathbf{n}\cdot\mathbf{r};\mathbf{R})$ is defined as $\hat\Delta^+[\mathbf{n}\cdot\mathbf{r};R-2\mathbf{n}(\mathbf{n}\cdot\mathbf{R})]$. From this final equation we can very easily obtain the magnetic field, using the Maxwell equation $4\pi\mathbf{J}(\mathbf{r})/c=\nabla_r\times\mathbf{B}(\mathbf{r})$. Since the diamagnetic current was excluded from our discussion, in this expression the magnetic field is finite and constant in the bulk region. Therefore, inserting the bulk-state gap function into the formula for the magnetic field, we obtain a criterion for the existence, magnitude, and direction of a local magnetization at the surface with the normal vector $\mathbf{n}$. Clearly, the result is that a time-reversal-invariant state $[\psi^*(\mathbf{R})=\psi(\mathbf{R})$ or $d^*(\mathbf{R})=\mathbf{d}(\mathbf{R})]$ produces no such magnetization, since for these states the expression $\mathrm{Im}[\hat\Delta^+(\mathbf{R}\times\nabla_\mathbf{R})\hat\Delta]$ vanishes.

Applying this formula to our example ($\Gamma_5^\pm$ of D_{4h}) for both even- and odd-parity states, we find a finite magnetization along the z axis, with the same sign as for any normal vector in the x-y plane for a fixed bulk state. However, for $\mathbf{n}$ parallel to the z axis, all currents are vanishing. Similarly, the time-reversal-breaking state $O_h(\Gamma_3^+)$ generates a current for any direction of the surface except for $\mathbf{n}$ parallel to the main axis (Bares, 1988). In this case, however, the magnetization has different directions for differently oriented surfaces. Consequently, this phase need not yield a finite magnetization for a single domain sample, in contrast to the former example.

Since the behavior of the surface and the domain wall are analogous, these results can also be transferred to the domain wall with the only difference that the sign of the current and the field can depend on the choice of some parameters (in our example on the ratio k_1/k_2). More precisely, the current direction depends on whether the even- or the odd-parity $\mathcal{P}(\mathbf{n})$ components of the order parameter are varying more strongly in the domain wall.

The weak-coupling approach in our example requires k_3 and k_4 to be equal, leading to $\Delta\tilde{k}=0$. Beyond this limit these two coefficients are in general different. It can be shown that their difference, due to particle-hole asymmetry, is smaller by a factor of the order of $(T_c/T_F)^2$ than the weak-coupling coefficients [in conventional superconductors T_c/T_F is very small, $\sim 10^{-4}$, but for heavy-fermion superconductors it is considerably larger, ~ 0.1; (Serene and Rainer, 1983)].[7] Therefore this term has to be discussed separately, since it is not included in Eq. (5.25),

$$\Delta\tilde{k}[(d_x u)^*(d_y v)-(d_y u)^*(d_x v)+\text{c.c.},] ,$$

$$\Delta\tilde{k}=\tfrac{1}{2}(k_3-k_4) . \qquad (5.32)$$

Even if it looks rather similar to the $\tilde{k}$ term in Eq. (5.7), it has essentially different properties in generating spontaneous currents and magnetic fields. It does not contribute at all to the diamagnetic current for the Meissner effect. In a time-reversal-breaking superconducting state, any inhomogeneity of the order parameter, even without spatial variation of the phase of the order parameter—all $|\eta_j|$ have the same spatial dependence and the phases ϕ_j are constant—leads to a current and a local magnetization. To understand the origin of this gradient term we consider a planar inhomogeneity. We now take the opposite approach to that used earlier. Starting with the induced magnetic field, we show that it leads to that kind of gradient term. Neglecting all screening effects, as above, we write for the magnetic field

$$\mathbf{B}(\mathbf{r})=e\pi\int d^3R\, g(|\mathbf{R}|)\,\mathrm{tr}\left[\hat{\Delta}^+(\mathbf{n}\cdot\mathbf{r};\mathbf{R})\left[\frac{1}{i}(\mathbf{R}\times\nabla_{\mathbf{R}})+\hat{\sigma}\right]\hat{\Delta}(\mathbf{n}\cdot\mathbf{r};\mathbf{R})\right] , \qquad (5.33)$$

where $g(|\mathbf{R}|)$ is a function that includes strong-coupling effects. Obviously this expression is related to an intrinsic magnetic moment of the superconducting phase described by the operator

$$\hat{\mathbf{m}}(\mathbf{R})=\frac{1}{i}(\mathbf{R}\times\nabla_{\mathbf{R}})+\hat{\sigma} , \qquad (5.34)$$

which is composed of the relative angular momentum and the spin polarization of the Cooper pairs (Leggett, 1975). In this formulation we neglect corrections due to spin-orbit coupling. Considering this magnetic moment, Volovik and Gor'kov classified the time-reversal-breaking states to be "ferro- or antiferromagnetic" by the following natural definition:

$$\langle \mathrm{tr}[\hat{\Delta}^+(\mathbf{R})\hat{\mathbf{m}}(\mathbf{R})\hat{\Delta}(\mathbf{R})]\rangle=\begin{cases}0, & \text{antiferromagnetic,}\\ \text{finite,} & \text{ferromagnetic,}\end{cases} \qquad (5.35)$$

where $\langle\ \rangle$ denotes the average over the direction of $\mathbf{R}$. Obviously, the magnetic field in Eq. (5.33) is only finite for ferromagnetic states. Our example considered above $[D_{4h}(\Gamma_5^\pm)]$ is a ferromagnetic state in that sense. On the other hand, the cubic state $O_h(\Gamma_3^\pm)$ is an antiferromagnetic one. The total list of the classified ferromagnetic states is $D_{3d}(\Gamma_3^\pm)$, $D_{4h}(\Gamma_5^\pm)$, $D_{6h}(\Gamma_5^\pm)$, $D_{6h}(\Gamma_6^\pm)$; the only antiferromagnetic state is $O_h(\Gamma_3^\pm)$.

The finite ferromagnetic moments do not occur macroscopically in the bulk region of a superconductor due to complete screening by diamagnetic currents. However, inhomogeneities of the superconducting state can produce a local occurrence of magnetic field, especially if the screening length is large compared to the characteristic length scale of the inhomogeneity (mostly the coherence length). Then the screening of the spatially modulated magnetic moment cannot be perfect.

What is the physical basis for the gradient term in Eq. (5.32)? Clearly, we can include the magnetic moment of the superconducting state in the Ginzburg-Landau theory by a Zeeman term,

$$\begin{aligned}F_Z&=-4\pi e\int d^3x\, d^3R\,[\nabla_{\mathbf{r}}\times\mathbf{A}(\mathbf{r})]g(|\mathbf{R}|)\\&\quad\times\mathrm{tr}[\hat{\Delta}^+(\mathbf{r};\mathbf{R})\hat{\mathbf{m}}(\mathbf{R})\hat{\Delta}(\mathbf{r};\mathbf{R})]\\&=-C\int d^3x[\nabla_{\mathbf{r}}\times\mathbf{A}(\mathbf{r})]\langle\mathbf{m}(\mathbf{r})\rangle ,\end{aligned} \qquad (5.36)$$

which is finite only for a ferromagnetic superconducting phase. This term does not produce additional boundary conditions, since the magnetic moment turns parallel to the normal vector $\mathbf{n}$ at the surface (see footnote 4),

$$\int_{\mathrm{sf}}[\mathbf{A}(\mathbf{r})\times\langle\mathbf{m}(\mathbf{r})\rangle]\cdot\mathbf{n}d^2S_{\mathbf{r}}=0 . \qquad (5.37)$$

Therefore Eq. (5.36) is equivalent to

$$F_Z=-C\int d^3x\ \mathbf{A}(\mathbf{r})[\nabla_{\mathbf{r}}\times\langle\mathbf{m}(\mathbf{r})\rangle] , \qquad (5.38)$$

which leads straightforwardly to Eq. (5.33) for the magnetic field. However, this term can also be expressed by

[7]It should be noted that in the weak-coupling limit impurity scattering effects can also lead to a finite $\Delta\tilde{k}$, close to the scattering center (Choi and Muzikar, 1989a). This can be understood if we consider the change of the kernel $K_{ij}(\mathbf{r},\mathbf{r}')$ around an impurity (see Sec. V.A.3). This effect can be important in the dirty limit.

$$F=-4\pi e \,\mathrm{Im}\int d^3r \int d^3R\, g(|\mathbf{R}|)\,\mathrm{tr}([\mathbf{D}\hat{\Delta}(\mathbf{r};\mathbf{R})]^+[\hat{\mathbf{m}}(\mathbf{R})\times[\mathbf{D}\hat{\Delta}(\mathbf{r};\mathbf{R})]\})\ , \tag{5.39}$$

which corresponds to a gradient term of the Ginzburg-Landau free energy ($\mathbf{D}=\nabla-2ie\,\mathbf{A}/c$). Therefore the Zeeman term can be transformed to an equivalent gradient term, which is included in the group-theoretical derivation given in Sec. II.B, since it is one of the invariant terms. It is clear that this type of gradient term exists only for "ferromagnetic" states. For "antiferromagnetic" states all magnetic properties are due only to the tensor character of the gradient terms and the corresponding currents.

A very simple criterion for the possible existence of a ferromagnetic state in an order-parameter representation Γ can be derived by considering Eq. (5.36). Since $\nabla\times\mathbf{A}$ transforms according to the vector representation $\mathcal{D}_{(G)}$, and the magnetic moment is a bilinear form of the order parameter, the existence of such a term requires that the decomposition of $\mathcal{D}_{(G)}\otimes\Gamma^*\otimes\Gamma$ contain the representation Γ_1^+.

3. The magnetic effect of impurities or lattice defects

From the previous discussion it is clear that an inhomogeneity of the superconducting phase at an impurity or a defect of the crystal lattice—where the order parameter is slightly suppressed within a length scale ξ—can produce a local magnetization (Gor'kov, 1987). This was analyzed quasiclassically by Choi and Muzikar (1989a), based on an earlier work of Rainer and Vuorio (1977), who considered the influence of small scattering centers on superfluid ^{3}He [another treatment of the problem was offered by Mineev (1989)]. We shall here consider the Ginzburg-Landau approach to this problem, which is only valid in the region of a slow variation of the order parameter. Therefore, for regions very close to the scattering center, we refer the reader to the abovementioned authors.

We have seen in Sec. IV.A that a kernel $K_{ij}(\mathbf{r},\mathbf{r}')$, relating the order-parameter component η_i at the point $\mathbf{r}$ to η_j at $\mathbf{r}'$, can be expressed by a correlation function of classical particles [Eq. (4.10)]. Therefore the kernel in the presence of a scattering center at $\mathbf{r}_0$ can easily be calculated using this classical picture for the correlation function. For a kernel between $\mathbf{r}$ and $\mathbf{r}'$ in the vicinity of $\mathbf{r}_0$ we have to include the path via the scattering center ($\mathbf{r}'\to\mathbf{r}_0\to\mathbf{r}$), as well as the shadow effect if the scattering center lies on the line between $\mathbf{r}$ and $\mathbf{r}'$ $[(\mathbf{r}'-\mathbf{r}_0)\cdot(\mathbf{r}_0-\mathbf{r})=|\mathbf{r}'-\mathbf{r}_0|\,|\mathbf{r}_0-\mathbf{r}|]$. The classical correlation function then leads to the following additional contribution to the homogeneous kernel in Eq. (4.11) (see Rainer and Vuorio, 1977):

$$K_{ij}^{\mathrm{scatt}}(\mathbf{r},\mathbf{r}')=\frac{VN(0)k_BT}{2v_F}\,\frac{\mathrm{tr}\left[\hat{\Delta}^+_{(i)}\left[\frac{\mathbf{r}_0-\mathbf{r}}{|\mathbf{r}_0-\mathbf{r}|}\right]\hat{\Delta}_{(J)}\left[\frac{\mathbf{r}'-\mathbf{r}_0}{|\mathbf{r}'-\mathbf{r}_0|}\right]\right]}{|\mathbf{r}_0-\mathbf{r}|^2|\mathbf{r}'-\mathbf{r}_0|^2}$$
$$\times\left[\frac{d\sigma}{d\Omega}\left[\frac{\mathbf{r}_0-\mathbf{r}}{|\mathbf{r}_0-\mathbf{r}|},\frac{r'-\mathbf{r}_0}{|\mathbf{r}'-\mathbf{r}_0|}\right]-\delta\left[\frac{\mathbf{r}_0-\mathbf{r}}{|\mathbf{r}_0-\mathbf{r}|}-\frac{\mathbf{r}'-\mathbf{r}_0}{|\mathbf{r}'-\mathbf{r}_0|}\right]\sigma\left[\frac{\mathbf{r}_0-\mathbf{r}}{|\mathbf{r}_0-\mathbf{r}|}\right]\right]\frac{1}{\sinh(2\pi k_BT(|\mathbf{r}_0-\mathbf{r}|+|\mathbf{r}'-\mathbf{r}_0|)/v_F)} \tag{5.40}$$

where $d\sigma(\hat{\mathbf{r}},\hat{\mathbf{r}}')/d\Omega$ is the differential cross section $[\sigma(\hat{\mathbf{r}})=\int d\Omega' d\sigma(\hat{\mathbf{r}},\hat{\mathbf{r}}')/d\Omega]$. This formula contains both the scattering (first cross-section term) and the shadow scattering (second cross-section term). To include the effect of this scattering center in the Ginzburg-Landau theory we can use this kernel in the local limit at T close to T_c,

$$\frac{N(0)}{2}\sum_{i,j}\int d^3r\,d^3r'\,\eta_i^*(\mathbf{r})K_{ij}^{\mathrm{scatt}}(\mathbf{r},\mathbf{r}')\eta_j(\mathbf{r}')\to\frac{N(0)}{2}\sum_{i,j}\frac{\tilde{\sigma}}{\xi_0^2}\,\frac{\xi_0^2e^{-|\mathbf{r}|/\xi_0}}{4\pi|\mathbf{r}|^2}\eta_i^*(\mathbf{r})Q_{ij}\eta_j(\mathbf{r})\ , \tag{5.41}$$

where we take $\mathbf{r}_0$, the scattering center, at the origin and $\xi_0=v_F/2\pi k_BT_c$ (Rainer and Vuorio, 1977).[8] The influence of a scattering center is characterized by a cross section $\tilde{\sigma}$ and the matrix Q_{ij} [generally of the order $O(1)$], which are defined as

$$\tilde{\sigma}Q_{ij}\left[\frac{\mathbf{r}}{|\mathbf{r}|}\right]=\int d\Omega_{r'}\mathrm{tr}\left[\hat{\Delta}^+_{(i)}\left[\frac{\mathbf{r}}{|\mathbf{r}|}\right]\hat{\Delta}_{(j)}\left[\frac{\mathbf{r}'}{|\mathbf{r}'|}\right]\right]\left[\frac{d\sigma}{d\Omega}\left[\frac{\mathbf{r}}{|\mathbf{r}|},\frac{\mathbf{r}'}{|\mathbf{r}'|}\right]-\delta\left[\frac{\mathbf{r}}{|\mathbf{r}|}-\frac{\mathbf{r}'}{|\mathbf{r}'|}\right]\sigma\left[\frac{\mathbf{r}}{|\mathbf{r}|}\right]\right]\ . \tag{5.42}$$

[8]In the next order of the local limit, second-order gradient terms of the form $\sum_{i,j,\alpha,\beta}\tilde{Q}_{ij}(D_\alpha\eta_i)^*M_{\alpha\beta}(D_\beta\eta_j)$ can be derived. So, on the basis of the weak-coupling limit, generally several additional terms can occur which are not present in the bulk. However, we neglect them here, since they give no contribution in the perturbative approach used below.

In the limit of slow variation of the order parameter $[\xi(T) \gg \xi_0]$, we can neglect the spatial extension of this kernel and write it in the form

$$F_{\text{scatt}} = \frac{N(0)}{2} \sum_{i,j} \int d^3r\, \eta_i^*(\mathbf{r}) S_{ij} \eta_j(\mathbf{r}) \xi_0^3 \delta(\mathbf{r}) , \tag{5.43}$$

with $S_{ij} = \sigma V Q_{ij} / \xi_0^2$, which is very small, under the reasonable assumption that $\sigma \ll \xi_0^2$ (for Q_{ij} we take its angular average). Thus it is possible to analyze the effect of this scattering term perturbatively.

To fix the idea let us turn back to our example $[D_{4h}(\Gamma_5^{\pm})]$. We introduce for simplicity a symmetric scattering term

$$F_{\text{scatt}} = \frac{H_c^2 \xi^3}{4\pi} \int d^3r\, S[|u(\mathbf{r})|^2 + |v(\mathbf{r})|^2] \delta(\mathbf{r}) , \tag{5.44}$$

with $S = (\sigma/\xi_0^2)[\xi_0/\xi(T)]^3 Q T_c / 2|T - T_c| \propto |T - T_c|^{1/2}$ in dimensionless quantities. To calculate the distortion of the order parameter in first order of S, we expand u and v: $u = u_0 + u'$ and $v = v_0 + v'$, where u_0 and v_0 are the homogeneous order parameter components. Only the moduli of the order parameter are affected by this scattering term, so the Ginzburg-Landau equation can be linearized in $|u'|$ and $|v'|$,

$$\begin{aligned} &(k_1 \partial_x^2 + k_2 \partial_y^2 + k_5 \partial_z^2 - B)|u'| + (\tilde{k} \partial_x \partial_y - B')|v'| = S\delta(\mathbf{r}) , \\ &(k_2 \partial_x^2 + k_1 \partial_y^2 + k_5 \partial_z^2 - B)|v'| + (\tilde{k} \partial_x \partial_y - B')|u'| = S\delta(\mathbf{r}) , \end{aligned} \tag{5.45}$$

where $B = (1 + 4\tilde{\beta}_2 - \tilde{\beta}_3)/2 > \frac{1}{2}$ and $B' = (1 - 4\tilde{\beta}_2 + \tilde{\beta}_3)/2 < \frac{1}{2}$. Transforming these equations into the Fourier space and solving them algebraically, we obtain

$$\begin{aligned} |\tilde{u}'(\mathbf{q})| &= \frac{-S(B - B' + k_2 q_x^2 + k_1 q_y^2 + k_5 q_z^2 - \tilde{k} q_x q_y)}{(B + k_1 q_x^2 + k_2 q_y^2 + k_5 q_z^2)(B + k_2 q_x^2 + k_1 q_y^2 + k_5 q_z^2) - (B' + \tilde{k} q_x q_y)^2} , \\ |\tilde{v}'(\mathbf{q})| &= \frac{-S(B - B' + k_1 q_x^2 + k_2 q_y^2 + k_5 q_z^2 - \tilde{k} q_x q_y)}{(B + k_1 q_x^2 + k_2 q_y^2 + k_5 q_z^2)(B + k_2 q_x^2 + k_1 q_y^2 + k_5 q_z^2) - (B' + \tilde{k} q_x q_y)^2} . \end{aligned} \tag{5.46}$$

The essential form of this solution is $\sim(\tilde{B} + kq^2)^{-1}$, which means in real space a $|\mathbf{r}|^{-1}$ dependence for a region $|\mathbf{r}| < \xi(T)$ and an expon ntial behavior for large $|\mathbf{r}|$ $[> \xi(T)]$.[9]

In order to analyze the current induced by this distorted order parameter, we consider $\mathbf{j}$ in the lowest finite order in u' and v'. Obviously, the z component always vanishes. For the two other components we obtain

$$j_{x(y)}(\mathbf{r}) = \tilde{k}_\kappa^2 \partial_{y(x)}[|v'(\mathbf{r})| - |u'(\mathbf{r})|] \sin(\chi - \phi) \tag{5.47}$$

from the $\tilde{k}$ term and

$$j_{x(y)}(\mathbf{r}) = +(-)\frac{\Delta\tilde{k}}{\kappa^2} \partial_{y(x)}[|v'(\mathbf{r})| + |u'(\mathbf{r})|] \sin(\chi - \phi) \tag{5.48}$$

as the $\Delta\tilde{k}$ contribution. From these current expressions we can calculate the magnetic field by the Biot-Savart formula,

$$\begin{aligned} \mathbf{b}(\mathbf{r}) &= \frac{1}{4\pi} \int d^3r' \frac{(\mathbf{r} - \mathbf{r}') \times \mathbf{j}(\mathbf{r}')}{|\mathbf{x} - \mathbf{x}'|^3} \\ &= i \int \frac{d^3q}{(2\pi)^3} \frac{\mathbf{q} \times \tilde{\mathbf{j}}(\mathbf{q})}{|\mathbf{q}|^2} e^{i\mathbf{q}\cdot\mathbf{r}} . \end{aligned} \tag{5.49}$$

Let us consider the magnetic field at $\mathbf{x} = 0$. We simplify the solution Eq. (5.44) by neglecting the coupling terms between the two components, i.e., the terms with $\tilde{k}$ and B'. In doing so we obtain an estimate of $\mathbf{b}(0)$ in the limit $k_1, k_2 \to \frac{1}{2}$,

$$b_z(0) \approx -\frac{\tilde{k}S}{2\pi^2} \kappa^2 (k_1 - k_2) \frac{\xi(T)}{\xi_0} \sin(\chi - \phi) . \tag{5.50}$$

The factor $\xi(T)/\xi_0$ appears due to a cutoff at the inverse length ξ_0^{-1}, since we neglected the extension of the kernel in Eq. (5.41). The magnetic field and its sign strongly depend on the difference between k_1 and k_2, similarly to the domain-wall magnetization. The current around the scattering center is induced by the different spatial variation of the two components. This difference in the variation is determined by the parameters k_1 and k_2. If these coefficients are equal, the distortion is rotationally symmetric around the z axis. Then no currents or magnetic fields occur due to the term in Eq. (5.47).

On the other hand, the magnetic field induced by the current in Eq. (5.48) does not lead to such a k_1-k_2 depen-

[9]A more detailed study of the distortion of the order parameter around a scattering center was given by Rainer and Vuorio (1977) and Choi and Muzikar (1989a, 1990) on the basis of the quasiclassical approach.

dence. We obtain in that case approximately

$$b_z(0)\approx\frac{\Delta\tilde{k}S}{\pi^2\kappa^2}\frac{\xi(T)}{\xi_0}\sin(\chi-\phi) \ . \tag{5.51}$$

As pointed out before, the magnetic field produced by this term has its origin in the screening defect of the intrinsic magnetic moment varying in space around the impurity. Any distortion of the order parameter leads to a finite current distribution at the impurity.

For this ferromagnetic superconducting phase we find a local magnetization around an impurity. In a similar way, antiferromagnetic phases can generate a magnetic field at such scattering centers. However, in this case the intrinsic magnetic moment is vanishing and gives no contribution, as pointed out earlier. Furthermore, the field $\mathbf{b}(\mathbf{r}=0)$ vanishes for a totally symmetric scattering center, since no direction is specified in an antiferromagnetic system. The field is situated around the impurity in a complex pattern, obeying the symmetry properties of the superconducting state.

In all cases the magnetic field cancels itself as can be seen in

$$\int d^3r\,\mathbf{b}(\mathbf{r})=i\int\frac{d^3q}{(2\pi)^3}\frac{\mathbf{q}\times\mathbf{j}(\mathbf{q})}{|\mathbf{q}|^2}\delta(\mathbf{q})=0 \ , \tag{5.52}$$

where we used Eq. (5.49). This canceling takes place on a length scale ξ, so diamagnetic currents do not participate strongly in this effect if the Ginzburg-Landau parameter κ is much larger than 1. Choi and Muzikar (1990) discussed whether there might be cases in which this canceling is not complete, leading to a net magnetic moment. Then the diamagnetic currents, which could be neglected up to now, would have to be taken into account in order to screen this moment. However, this is only the case if the long-distance recovery of the distorted order parameter is not exponential but like $|\mathbf{r}|^{-1}$, as easily can be found from Eq. (5.52). Such a long-range behavior is only possible for continuous ("soft") modes of the order parameter. In a system with crystalline structure, however, no such modes exist that could couple to the scattering center.

In real units the magnetic field obtained for our example is

$$B_z(0)\approx\left\{\begin{matrix}-\frac{1}{2}\tilde{k}(k_1-k_2)\\ \Delta\tilde{k}\end{matrix}\right\}\sqrt{2}\frac{\sigma}{\xi_0^2}Q\frac{H_c(T)}{\kappa}\sin(\chi-\phi) \ . \tag{5.53}$$

The temperature dependence of $\mathbf{B}$ is linear, as for the thermodynamic critical field in the Ginzburg-Landau limit. To estimate the order of magnitude of the field in a specific system, we can assume that the cross section is of the order of the atomic radius squared and H_c/κ can be approached by the measured lower critical field. However, the magnitude of the magnetic field induced from a region very close to the impurity may be several times larger, at least in the case of a ferromagnetic superconducting phase (see Choi and Muzikar, 1989a, 1990; Mineev, 1989). We shall discuss in Sec. VII how this occurrence of local magnetization at impurities or crystal lattice defects can give an explanation for detected internal magnetic fields in a heavy-fermion superconductor.

B. Vortices

In this section we are concerned with a more familiar magnetic property of superconductors, the existence of vortices. A vortex is a line defect in the superconducting phase and can be energetically stabilized by an externally applied magnetic field. Its structure is described by a singularity of the order-parameter phase, which winds around the line by an integer times 2π, and determines a topological charge. This charge is physically manifested by the existence of magnetic flux in this line, exactly one flux quantum ($hc/2e$) per unit winding of the phase. In fact, the single-winding vortex, containing one flux quantum, is energetically the most stable. For conventional or one-component superconductors, this vortex is the only form to carry magnetic field in the bulk region. A multicomponent order parameter, however, can yield various types of vortex structures, since from the topological point of view each component separately can produce a vortex by winding its phase around a line. This problem has been very intensively investigated for superfluid ^{3}He (see, for a review, Salomaa and Volovik, 1987). The results found there, however, cannot simply be transferred to the case of the superconducting phases, since unconventional vortex structures in ^{3}He are strongly related to the complete rotational symmetry of the system. For very weak spin-orbit coupling, even in a system with a crystal field, a certain kind of nonsingular, coreless vortex is possible, rather similar to those found in ^{3}He. This type of vortex corresponds to a continuous spin texture around a center line (Burlachkov and Kopnin, 1986). However, when a strong spin-orbit interaction is included, the superconducting states have no continuous degeneracy, so that these types of structure are no longer stable. Nevertheless, even under these circumstances an unconventional superconducting phase can produce vortex structures deviating essentially from the well-known conventional vortex. Vortices for unconventional superconductors have been investigated mainly for time-reversal-breaking superconducting states, because the connection between magnetic flux lines and intrinsic magnetic properties is an attractive field in which to find new effects.

1. Fractionally quantized vortices

Each component of a multicomponent superconductor can produce independently a topologically stable vortex with its own topological charge (Volovik and Gor'kov, 1984). From the point of view of energy, however, the behavior of the other components has to be strongly correlated. If the phase of only one component is winding around a line, it transforms the superconducting state in the whole system by varying the relative phase(s) with the other component(s). Since the superconducting state is not continuously degenerate with respect to such a change, this structure leads to an increase of the energy density in almost the whole system and is therefore not at all favorable. This can only be avoided by a winding in all components of the order parameter to conserve the energetically stable superconducting state, at least at a distance far from the vortex core ($\gg \tilde{\xi}$). Thus it seems rather unlikely that stable "one-component vortices" will be found. However, in a special environment they can exist, i.e., on a domain wall that preexists in the superconductor (Sigrist, Rice, and Ueda, 1989; Izyumov and Laptev, 1990).

To fix our ideas, let us consider again the example examined in the previous section: a domain wall lying in the yz plane. As we have mentioned there, the structure of the domain wall is twofold degenerate for the parameters $\tilde{\beta}_2 \ll 1$, since the relative phase $\gamma = \chi - \phi$ has two possible ways to move (continuously) from $-\pi/2$ to $+\pi/2$, by passing through 0 or π. These two structures, present in the same domain wall, have to be separated by a line defect, an analog to the Bloch line in a ferromagnet. Obviously, this line corresponds to a winding of the phase of one component, since the relative phase γ takes continuously the values $-\pi/2 \to 0 \to +\pi/2 \to \pi \to 3\pi/2 = -\pi/2$, going around the line. The variation of the phase takes place mainly in the domain wall, which absorbs all energetically unfavorable long-range effects of this winding. Hence the distortion of the order parameter is effectively concentrated in a small region of length scale $\tilde{\xi}$, similar to a conventional vortex.

The flux carried by this line defect can easily be calculated by considering the integral

$$\oint_{\wp} (\nabla\phi - \mathbf{a})ds = \oint_{\wp} \nabla\phi ds - \Phi(\wp) \tag{5.54}$$

on a special path $\wp$, which we choose rectangular, partially parallel and partially perpendicular to the domain wall. The parallel parts of $\wp$ may be so distant from the wall that they do not give any contribution to the integral. The perpendicular parts cross the wall far enough from the line defect that the domain-wall structure is completely recovered. Using the condition that the current component $j_x = 0$ in a stable domain wall [Eq. (5.12)], we obtain

$$\partial_x\phi - a_x = -\frac{k_2|v|^2}{k_1|u|^2 + k_2|v|^2}\partial_x\gamma + \frac{\tilde{k}|u||v|}{k_1|u|^2+k_2|v|^2} a_y \cos\gamma , \tag{5.55}$$

which inserted in Eq. (5.54) leads to the flux quantization

$$\Phi = \Phi_0(n + k_2) + O\left[\frac{\tilde{k}^2\tilde{\xi}}{\kappa}\right] , \tag{5.56}$$

where we again made use of the approach $|u| \approx |v|$. The symbol Φ_0 denotes a standard flux quantum (in dimensionless units 2π), which corresponds to the total topological charge if both phases are winding. The number n is an integer counting the simultaneous winding of both components. The last term is comparatively small due to the fact that a_y is of the order $\tilde{k}/\kappa$ and $\cos\gamma$ only contributes in a range $\tilde{\xi}$ at the domain wall. The smallest possible flux quanta are $\Phi \approx \pm k_1\Phi_0, \pm k_2\Phi_0$, smaller than the standard flux quantum, since $0 < k_1, k_2 < 1$ and so they are fractional flux quanta.[10]

In a certain limit the energy of the line can be estimated as for the Abrikosov vortex, taking mainly the magnetic field and the kinetic energy of the circular currents into account, but neglecting the core energy. The latter is very small compared to the former two if $\kappa \gg \tilde{\xi} \approx 1$. This neglect is even more justified in the case under consideration, since only the component with the winding phase has to vanish in the center of the line defect. Hence no normal conducting core is present, in contrast to conventional vortices.

Three length scales enter this problem, the London penetration depth κ, the length scale of the domain wall $\tilde{\xi}$, and the coherence length of the order parameter $\xi \approx 1$ (in the x-y plane). Assuming the limit $\kappa \gg \tilde{\xi} \gg \xi$, we consider a line defect located at $\mathbf{r}=0$ and directed along the z axis, carrying a magnetic flux $\Phi = \Phi_0 k_2 = 2\pi k_2$. Let us fix the gauge so that only the phase χ of the component v is winding, whereas ϕ is set to zero everywhere. Thus we can write the free energy F in units $H_c^2\xi^2/4\pi$ per unit length along the z axis outside the core region ($|u| = |v| = 1$),

$$F = \int d^2r \{2\tilde{\beta}_2\cos^2\chi + k_1[a_x^2 + (\partial_y\chi - a_y)^2] + k_2[a_y^2 + (\partial_x\chi - a_x)^2] + \kappa^2\mathbf{b}^2\} , \tag{5.57}$$

where we subtracted the bulk energy density -0.5 in the integrand. For simplicity we neglected the terms that lead to the domain-wall current, $\tilde{k} = \Delta\tilde{k} = 0$.

This functional can be rewritten as

$$F = \int d^2r[\kappa^2(\mathbf{b}^2 + \kappa^2\mathbf{j}^2) + 2\tilde{\beta}_2\cos^2\chi + k_1k_2(\nabla\chi)^2] , \tag{5.58}$$

where $\mathbf{j}$ is the current derived from Eq. (5.57) by $\mathbf{j} = -\partial F/2\kappa^2\partial\mathbf{a}$. The symbol ∇ denotes here the $2D$ gradient in the x-y plane.

The magnetic-field part can be estimated in the same

[10] A change of direction of the domain wall leads to a change in the fractional flux quanta. The flux quanta are $\Phi(\mathbf{n}) = k(\mathbf{n})\Phi_0$, $[1-k(\mathbf{n})]\Phi_0$ with $k(\mathbf{n}) = k_1(k_2 - k_1) \times [(\mathbf{n}\times\hat{\mathbf{z}})\cdot\hat{\mathbf{x}}/|\mathbf{n}\times\hat{\mathbf{z}}|]^2$, where $\mathbf{n}$ is the normal vector of the wall. In our example we obtain half-quantized vortices for the wall with the normal vector $\mathbf{n} = (\pm1, \pm1, 0)$. Note, however, that the domain walls in arbitrary directions need not be degenerate, as mentioned above.

way as in conventional vortices (see, for example, de Gennes, 1966),

$$\varepsilon_1=\frac{\Phi^2}{2\pi}\ln\frac{\kappa}{\xi}\ , \qquad (5.59)$$

where ξ is the radius of the core.

To estimate the contribution of the phase χ we have to consider its variational equation derived from F,

$$\frac{1}{r}\partial_r(r\partial_r\chi)+\frac{1}{r^2}\partial_\theta^2\chi+\frac{1}{\tilde{\xi}^2}\sin(2\chi)=0 \qquad (5.60)$$

in polar coordinates. For large r this differential equation is solved by the domain-wall kink solution (see Sec. V.A.1). For small $r(\ll\tilde{\xi}=\sqrt{k_1k_2/\beta_2})$, the second term is dominant and bears asymptotically the solution $\chi=\theta$. Since in the intermediate region a simple solution is not available, we give an upper limit to the energy contribution of χ by taking this latter solution in the range $\xi<r<\tilde{\xi}$ and the domain-wall kink solution in the range $r>\tilde{\xi}$. The dominant term in the integral Eq. (5.58) (integral range $r>\xi$) is contained in the gradient term: $(\partial_\theta\chi)^2/r^2$. Subtracting the domain-wall energy and neglecting smaller contributions, we obtain the total vortex energy

$$\varepsilon\le 2\pi k_2\left[k_2\ln\left[\frac{\kappa}{\xi}\right]+k_1\ln\left[\frac{\tilde{\xi}}{\xi}\right]\right] \qquad (5.61)$$

and the critical field, the lowest external field which stabilizes this line defect,

$$\tilde{h}=\frac{\varepsilon}{2\kappa^2\Phi}=\frac{1}{2\kappa^2}\left[k_2\ln\left[\frac{\kappa}{\xi}\right]+k_1\ln\left[\frac{\tilde{\xi}}{\xi}\right]\right]$$
$$<\frac{1}{2\kappa^2}\ln\left[\frac{\kappa}{\xi}\right]=h_{c1}\ , \qquad (5.62)$$

which is generally smaller than the bulk lower critical field h_{c1} if we assume that the extension of the core region for both cases is about the same.

Two neighboring line defects on a domain wall have in general different flux quanta and critical fields. The sum of their flux is an integer number of Φ_0. This fact is easily understood by considering the relative phase that winds oppositely around the two lines. However, the sum of their line energies is smaller than that of one conventional vortex including the same finite flux. The difference is given by $\Delta\varepsilon=-4\pi k_1k_2\ln(\kappa/\tilde{\xi})$. Therefore a pair of such line defects can be produced by the decay of a bulk vortex (one flux quantum) into two fractional vortices. Then domain walls would act as very strong pinning regions for vortices.

These considerations can also be extended to domain walls whose structure is only nearly degenerate, i.e., to domain walls with arbitrary direction mentioned in Sec. V.A. A line defect—also in this case a fractional vortex—separates two domain-wall structures with different energy per unit area. Therefore a force is acting on the line defect supporting a movement that enlarges the low-energy domain wall. The movement of such line defects is one way to convert a domain wall with higher energy into one with lower energy. If the difference between the two energies per unit area is small, the decay of a bulk vortex can take place even on the domain wall with the lower energy per area. Between the two fractional vortices generated, an energetically more expensive portion of the domain wall is created, supported by the gain of vortex line energy. In this case, too, the domain wall acts as a strong pinning region for bulk vortices.

2. Bulk vortices

As we have already pointed out, in the bulk region there is no chance of generating an energetically stable fractional vortex. From this fact we should not jump to the conclusion that the structure of a bulk vortex has to be axial as in conventional superconductors. Indeed, it has been found in numerical calculations that under certain conditions bulk vortices can yield a nonaxial structure, even if the phases of all components are winding (Schenstrom *et al.*, 1989; Tokuyasu, Hess, and Sauls, 1990).[11] These calculations have been performed for the two-component time-reversal-breaking superconductor $D_{6h}(\Gamma_5^+)$ in a hexagonal lattice, which is very similar to our example. In that case the system makes use of the possibility that each component can form its singularity spatially separated. In doing so it can avoid generating a normal core region, i.e., a zero of the total order parameter, because each component vanishes at a different line. The displacement of the singularities was found to be small, of the order of the coherence length ξ. Clearly, this separation can be also rather large under extreme conditions, e.g., for a very low energy barrier between degenerate superconducting phases, a case analyzed by Izyumov and Laptev (1990). Then the distance between the two singularities is of the order $\tilde{\xi}$, the length scale of the domain wall, which is a measure for the barrier energy.

The splitting of the core leads to a configuration in which a different state occurs in the center of the vortex than in the surrounding region, which is similar to the time-reversed state. This structure can be roughly interpreted as a splitting of the conventional vortex into two fractional vortices by creating domain walls connecting the two centers (Fig. 8). If the spatial separation of the two fractional vortices is small compared to the length scale of the magnetic field (London penetration depth), this effect costs mainly core energy.

There are other important aspects of these multicomponent vortices associated with the breakdown of time reversal in the original bulk superconducting phase

[11]Note that the possible existence of nonaxial vortices was indicated in Sec. III.B.3 when we considered the upper critical field H_{c2}.

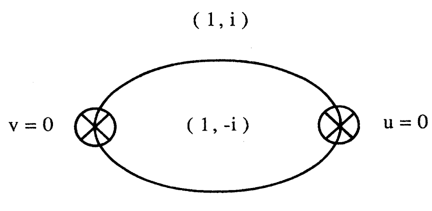

FIG. 8. Schematic structure of a split bulk vortex in a two-component superconductor with a bulk phase of the type $(1,+i)$. Between the two singular lines, marked by ⊗, the time-reversed state $(1,-i)$ occurs. The two connecting lines mark the region of energy loss due to the change of the relative phase (structure similar to a domain wall).

(Tokuyasu, Hess, and Sauls, 1990). As we explained in Sec. V.A, the spatial variation of the order parameter can lead to a local magnetization in a time-reversal-breaking superconductor. Considering vortices parallel to the magnetization axis (in hexagonal and tetragonal symmetry the z axis), it was found that the line energy of a vortex depends on the sign of its magnetic flux, whether it is parallel or antiparallel to the magnetization direction. This points clearly to a coupling of the external magnetic field to the intrinsic magnetization, as is confirmed by the dependence of this effect on the magnitude and sign of the parameters $\tilde{k}$ and $\Delta\tilde{k}$. The difference in the line energy (and critical field) is also accompanied by a certain difference in the vortex symmetry (nonaxial symmetry). On the basis of this fact, Tokuyasu and co-workers proposed the measurement of the critical magnetic field in a single domain sample for magnetic fields parallel and antiparallel to the z axis of the system as a test for unconventional superconductivity with a time-reversal-breaking superconducting state, especially for the heavy-fermion compound UPt_3.

The anisotropic symmetry of the vortex core extends to larger distances in the magnetic field and current distribution. In the case of an anisotropic magnetic-field shape, the orientation angle of this structure is involved as an additional degree of freedom in the problem of creating a vortex lattice. In particular, there is the possibility of frustration if the symmetry of the magnetic field is not compatible with the symmetry of the vortex lattice. As an example, Tokuyasu and co-workers examined triangular vortices in a triangular lattice. They suggested that, due to frustration, a change of the lattice structure should take place from a triangular to a hexagonal or to a honeycomb lattice if the density of vortices reaches a critical value (see Fig. 16 below). Such structure modifications could yield several unconventional phase transitions in the superconducting mixed state depending on the external magnetic field. We shall take up this point in Sec. VII.C as a possible explanation of experimental data in UPt_3.

C. Coexistence of antiferromagnetism and superconductivity

In some heavy-fermion superconductors the superconductivity occurs in the presence of antiferromagnetism. In this section we consider phenomena in which the two different kinds of order parameter coexist. We start from a microscopic derivation of the coupling term between the two order parameters by a weak-coupling theory. This enables us to discuss what constitutes favorable conditions for the coexistence. In the presence of antiferromagnetic ordering, the symmetry is lowered from the original symmetry group $\mathcal{G}$ to a subgroup $\mathcal{G}'$. If an irreducible representation in $\mathcal{G}$ is multidimensional, in general it splits into lower-dimensional representations of $\mathcal{G}'$ with different critical temperatures, another example of the splitting of the phase transition studied in Sec. III.B.

To derive the coupling term by a weak-coupling theory, we first note that the lowest-order coupling term is a biquadratic form of the two order parameters. Therefore we may start from the magnetic part of the free energy (Ueda and Konno, 1988; Konno and Ueda, 1989). The magnetic free energy in second order can be written as

$$F_M^{(2)}=\frac{1}{2}\sum_{i,j} M_i[(\chi^{-1})_{ij}-I\delta_{ij}]M_j \ , \tag{5.63}$$

where $M_i(i=x,y,z)$ is the staggered magnetization, χ_{ij} is the staggered susceptibility in the superconducting state, and I is the interaction constant responsible for the antiferromagnetism. The coupling term is obtained by expanding the susceptibility in terms of the superconducting order parameter as

$$[\delta(\chi^{-1})]_{ij}=-\sum_{i',j'}(\chi^{-1})_{ii'}\delta\chi_{i'j'}(\chi^{-1})_{j'j} \ , \tag{5.64}$$

where $\delta\chi_{ij}$ is the change of the susceptibility due to the superconducting order parameter. When we use a staggered magnetic field defined as

$$M_i=\sum_j \chi_{ij}B_j \ , \tag{5.65}$$

the coupling term has the form

$$F_{\Delta M}=-\frac{1}{2}\sum_{i,j} B_i\delta\chi_{ij}B_j \ . \tag{5.66}$$

Hence the problem is reduced to a calculation of the staggered susceptibility

$$\chi_{ij}=\int_0^\beta d\tau\langle s_i(\mathbf{Q},\tau)s_j(-\mathbf{Q},0)\rangle \tag{5.67}$$

with

$$s_j(\mathbf{Q})=\sum_{\mathbf{k}} c^\dagger_{\mathbf{k}+\mathbf{Q}\alpha}(\sigma_j)_{\alpha\beta}c_{\mathbf{k}\beta} \ , \tag{5.68}$$

where the contribution of the orbital moment is neglected for simplicity. The susceptibility can be expressed by the Green's functions

$$\chi_{ij}=k_B T\sum_{i\omega_n}\sum_{\alpha\alpha'\beta\beta'}\sum_{\mathbf{k}}[-(\sigma_i)_{\alpha\beta}(\sigma_j)_{\alpha'\beta'}G_{\beta'\alpha}(\mathbf{k}+\mathbf{Q},i\omega_n)G_{\beta\alpha'}(\mathbf{k},i\omega_n)+(\sigma_i)_{\alpha\beta}(\sigma_j)_{\alpha'\beta'}F^{\dagger}_{\alpha'\alpha}(\mathbf{k}+\mathbf{Q},i\omega_n)F_{\beta\beta'}(\mathbf{k},i\omega_n)] . \tag{5.69}$$

Since we need to calculate the susceptibility up to the second order of the superconducting order parameter, we use the following expansion form for the Green's functions, easily derived from the results in Appendix B,

$$G_{\alpha\beta}(\mathbf{k},i\omega_n)=\frac{\delta_{\alpha\beta}}{i\omega_n-\varepsilon(\mathbf{k})}+\frac{\sum_{\gamma}\Delta_{\alpha\gamma}\Delta^{\dagger}_{\gamma\beta}}{[i\omega_n-\varepsilon(\mathbf{k})][\omega_n^2+\varepsilon(\mathbf{k})^2]} , \tag{5.70}$$

$$F_{\alpha\beta}(\mathbf{k},i\omega_n)=\frac{\Delta_{\alpha\beta}(\mathbf{k})}{\omega_n^2+\varepsilon(\mathbf{k})^2} , \tag{5.71}$$

$$F^{\dagger}_{\alpha\beta}(\mathbf{k},i\omega_n Z)=-\frac{\Delta^{\dagger}_{\alpha\beta}(\mathbf{k})}{\omega_n^2+\varepsilon(\mathbf{k})^2} . \tag{5.72}$$

After frequency summation in the expression for the susceptibility, the coupling term is obtained as

$$F_{\Delta M}=(\gamma_1+\gamma_2)\langle\psi(\mathbf{k})\psi^*(\mathbf{k})+d(\mathbf{k})\cdot\mathbf{d}^*(k)\rangle\mathbf{B}\cdot\mathbf{B}+\bar{\gamma}_2\langle\psi(\mathbf{k})\psi^*(\mathbf{k}+\mathbf{Q})\rangle\mathbf{B}\cdot\mathbf{B}$$
$$+\bar{\gamma}_2\langle[\mathbf{d}(\mathbf{k})\cdot\mathbf{B}][\mathbf{d}^*(\mathbf{k}+\mathbf{Q})\cdot\mathbf{B}]-[\mathbf{d}(\mathbf{k})\times\mathbf{B}]\cdot[\mathbf{d}^*(\mathbf{k}+\mathbf{Q})\times\mathbf{B}]\rangle , \tag{5.73}$$

where $\langle\ \rangle$ denotes the average on the Fermi surface. For the gap function we have used the parametrization introduced in Eqs. (2.10) and (2.11). The coefficients are given by

$$\gamma_1=\tfrac{1}{2}\sum_{\mathbf{k}}\frac{1}{\varepsilon(\mathbf{k}+\mathbf{Q})-\varepsilon(\mathbf{k})}\frac{\partial}{\partial\varepsilon(\mathbf{k})}\left[\frac{1}{\varepsilon(\mathbf{k})}\tanh\frac{\beta\varepsilon(\mathbf{k})}{2}\right] , \tag{5.74}$$

$$\gamma_2=\sum_{\mathbf{k}}\frac{1}{\varepsilon(\mathbf{k}+\mathbf{Q})^2-\varepsilon(\mathbf{k})^2}\frac{1}{\varepsilon(\mathbf{k})}\tanh\frac{\beta\varepsilon(\mathbf{k})}{2} , \tag{5.75}$$

where an energy cutoff is assumed for $\varepsilon(\mathbf{k})$ in γ_i and $\bar{\gamma}_2$ is defined by the same equation as γ_2 with an additional cutoff for $\varepsilon(\mathbf{k}+\mathbf{Q})$.[12]

From the expression we see that the coupling coefficients are of the order of $N(0)/T_F^2$ where $N(0)$ is the density of states at the Fermi energy. These coefficients are expected to be positive (repulsive) for most cases (Kato, Machida, and Ozaki, 1987; Konno and Ueda, 1989; Ozaki and Machida, 1989) and are assumed to be positive in the following discussions even though there is no rigorous proof for that. By the coupling term the superconducting transition temperature is shifted by a factor of the order of $(B/T_F)^2$. Since the effective Fermi temperature for heavy-fermion materials is of the order of 10 K, the effect can be large. Coexistence is reported for UPt_3 (Aeppli *et al.*, 1988) and URu_2Si_2 (Palstra *et al.*, 1985; Schlabitz *et al.*, 1986). The magnitudes of the antiferromagnetic moments are extremely small, 0.02 μ_B for UPt_3 A(Aeppli *et al.*, 1988), and 0.03 μ_B for URu_2Si_2 (Broholm *et al.*, 1987). It is natural to assume that the smallness of the ordered moment makes the coexistence possible and that the superconducting transition will be suppressed when the moment becomes larger.

Furthermore, the compatibility of superconductivity and antiferromagnetism depends on the translational symmetry of the superconducting order parameter under **Q**. For a singlet (even-parity) state, it is relatively favorable to coexistence if the translational symmetry is odd $[\psi(\mathbf{k}+\mathbf{Q})=-\psi(\mathbf{k})]$ (Kato, Machida, and Ozaki, 1987; Ozaki and Machida, 1989). On the other hand, if the translational symmetry is even (mixed), the state is classified as unfavorable (intermediate) for coexistence. In the absence of spin-orbit coupling, a triplet state is always favorable to coexistence when the relative orientation of the **d** and **B** are fixed in an appropriate way, if it has a pure (not mixed) translational symmetry: $\mathbf{d}\parallel\mathbf{B}$ for odd translational symmetry, $\mathbf{d}(\mathbf{k}+\mathbf{Q})=-\mathbf{d}(\mathbf{k})$; and $\mathbf{d}\perp\mathbf{B}$ for even translational symmetry, $\mathbf{d}(\mathbf{k}+\mathbf{Q})=\mathbf{d}(\mathbf{k})$. A triplet state is also classified as intermediate for coexistence if its translational symmetry is mixed. When there is a spin-orbit coupling, the odd-parity states are in most cases intermediate, since the freedom of rotation of the **d** vector is limited by the spin-orbit coupling. It should be mentioned that once the spin-orbit interaction is included there can be additional terms in the coupling term which break the rotational symmetry of the spin space. In summary, an unconventional superconducting state, generally speaking, can be more favorable to coexistence than the conventional *s*-wave state. The compatibility de-

[12]We thank H. Fukuyama for this simpler form of γ_2 compared with Konno and Ueda (1989).

pends on the translational symmetry of the order parameter. This type of classification, including the translational property, is found in Putikka and Joynt (1988), and Konno and Ueda (1989), and Ozaki and Machida (1989).

In the presence of antiferromagnetic ordering, the symmetry group $\mathcal{G}'$ of the system is a subgroup of $\mathcal{G}$ containing all transformations which leave the antiferromagnetic wave vector $\mathbf{Q}$ and the magnetic moment invariant. The coupling term $F_{\Delta M}$ introduces this lower symmetry in the system of the superconducting order parameter. A general group-theoretical method for obtaining the subgroup $\mathcal{G}'$ and the coupling terms is described by Ozaki and Machida (1989).

The most important effect of the coupling term may be the possible lifting of degeneracy in a multidimensional irreducible representation, in certain cases. Let us consider an example with experimental relevance, UPt_3. This system has hexagonal-close-packed structure (hcp) with the space group $P6_3/mmc$, D_{6h}^4. According to the neutron-scattering experiments by Aeppli *et al.* (1988), the ordering vector is $\mathbf{Q}=\mathbf{b}_1/2$ where

$$\mathbf{b}_1=\left[\frac{4\pi}{\sqrt{3}a},0,0\right] . \tag{5.76}$$

The $\mathbf{Q}$ vector corresponds to the M point in the first Brillouin zone, and the direction of the moment is along $\mathbf{Q}$, $\mathbf{B}=(B,0,0)$.

We consider the two-dimensional irreducible representations of D_{6h}, namely, $\Gamma_5^{\pm}$ and $\Gamma_6^{\pm}$. For these order parameters the gap function is described by the two-component order parameter $\boldsymbol{\eta}=(\eta_1,\eta_2)$. Here it is assumed that, in the antiferromagnetic phase too, only Cooper pairs with total zero momentum are considered. The remaining symmetry of the system in the presence of antiferromagnetic long-range order is D_{2h}, an orthorhombic subgroup of the hexagonal point group D_{6h}. Therefore all irreducible representations in the presence of antiferromagnetic ordering are one-dimensional. The coupling term that introduces this lowering of the symmetry is described by a symmetric tensor Λ_{ij}.

$$F_{\Delta M}=\sum_{ij}\eta_i\Lambda_{ij}\eta_j . \tag{5.77}$$

The tensor Λ_{ij} is proportional to B^2 to satisfy the translational symmetry. In the weak-coupling theory, the explicit form of the coupling term is obtained from Eq. (5.73). As an example, let us consider an even-parity gap function, $\psi(\mathbf{k})=\eta_1\psi_1(\mathbf{k})+\eta_2\psi_2(\mathbf{k})$, where $\psi_1(\mathbf{k})$ and $\psi_2(\mathbf{k})$ are the basis functions. Then the coupling tensor is given by

$$\Lambda_{ij}=[(\gamma_1+\gamma_2)\langle\psi_i(\mathbf{k})\psi_i(\mathbf{k})\rangle\delta_{ij} + \bar{\gamma}_2\langle\psi_i(\mathbf{k})\psi_j(\mathbf{k}+\mathbf{Q})\rangle]B^2 . \tag{5.78}$$

A similar expression is obtained for the case of an odd-parity order parameter. If there is no spin-orbit coupling, the coupling term breaks rotational invariance of the spin space, as can be clearly seen from Eq. (5.73).

Diagonalization of the symmetric tensor Λ_{ij} leads to the simple form

$$F_{\Delta M}=[\gamma(|\eta_1|^2+|\eta_2|^2)+\gamma'(|\eta_1|^2-|\eta_2|^2)]B^2 , \tag{5.79}$$

where the first term expresses the shift of T_c on the average and the second term describes the splitting of the transition temperature. The structure of the free energy is exactly the same as that discussed for uniaxial stress in a cubic system (Sec. III.B.2). Actually, such a T_c splitting has been observed in UPt_3 experimentally (Fisher *et al.*, 1989), as will be discussed in Sec. VII. One of the important consequences of the lowering of symmetry in the magnetically ordered state is the appearance of anisotropy of H_{c2} in the basal plane. Machida and Ozaki (1989) and Hess *et al.* (1989) discussed the phenomena of T_c splitting based on this coupling term.

To include the effect of rotation of the antiferromagnetic moment, which may accompany the occurrence of superconductivity, we need additional degrees of freedom, $\mathbf{B}=(B_x,B_y,0)$. The rotation is assumed to be in the basal plane. In the presence of spin-orbit coupling, the two components B_x and B_y are not degenerate and hence have different antiferromagnetic transition temperatures. Note that B_x describes a longitudinal and B_y a transverse spin-density wave. The coupling term including the rotation of the antiferromagnetic moment is generalized as

$$\begin{aligned} F_{\Delta M}=&(\gamma_x B_x^2+\gamma_y B_y^2)(|\eta_1|^2+|\eta_2|^2)\\ &+(\gamma'_x B_x^2+\gamma'_y B_y^2)(|\eta_1|^2-|\eta_2|^2)\\ &+\gamma'' B_x B_y(\eta_1^*\eta_2+\eta_2^*\eta_1) . \end{aligned} \tag{5.80}$$

Microscopically, the last term originates from the spin-orbit coupling that we neglected in the derivation of Eq. (5.73). Blount *et al.* (1990) have introduced this coupling term to discuss the phase diagram of UPt_3 in the magnetic field (see also Sec. VII.C).

The second example is URu_2Si_2, which has a body-centered tetragonal structure, space group $I4/mmc$, D_{4h}^{17} (Palstra *et al.*, 1985; Schlabitz *et al.*, 1986). The antiferromagnetic vector of URu_2Si_2 is $\mathbf{Q}=(0,0,2\pi/c)$, corresponding to the Z point in the Brillouin zone, and the magnetic moment is parallel to the c axis (Broholm *et al.*, 1987). Therefore the symmetry of D_{4h} is not modified by the antiferromagnetism. Hence no qualitative change of transition behavior, except for the shift of T_c, is expected for URu_2Si_2.

VI. COMBINATION OF TWO ALMOST DEGENERATE ORDER PARAMETERS

In the previous sections we always supposed that one representation Γ of the point symmetry group is dominant, i.e., that it has a critical temperature far above those of the other representations. Consequently, the restriction of our discussion to one single representation seemed to be justified. However, as we mentioned already in Sec. II, this simple decoupling of the representations is not in every case correct. It is the purpose of this section to describe the typical phase-transition properties in a system where two representations are involved with almost equal transition temperatures. Additional phase transitions are possible, similar to the case of splitting of transitions discussed in Sec. III.B. However, the stability conditions of the superconducting states are in general much more complex than in that simple case. This type of consideration was first motivated by experimental data on thorium-doped UBe_{13}, which we shall study in Sec. VII.B in connection with experimental data on this material. We treat here an example of cubic lattice symmetry, a combination of the representations Γ_1^+ (1D) and Γ_5^+ (3D) of O_h (in subsequent notation we shall neglect the index $\pm$, supposing both representations to have the same parity). This example will later be referred to in interpreting some physical properties of the alloy $U_{1-x}Th_xBe_{13}$.

A. Phase transitions

If the transition temperatures of the gap functions of two irreducible representations are very close to each other, it is not possible to consider them independently. We have to extend the Ginzburg-Landau free energy to both representations, including also coupling terms between the order parameters,

$$F(\eta)=F_\Gamma(\eta(\Gamma,m))+F_{\Gamma'}(\eta(\Gamma',m)) +F_{\Gamma,\Gamma'}(\eta(\Gamma,m),\eta(\Gamma',m)) . \quad (6.1)$$

The coupling term $F_{\Gamma,\Gamma'}$ can be derived again by applying the condition that F is invariant under all symmetry transformations. The procedure is analogous to earlier cases. No second-order coupling terms exist, since the decomposition of $\Gamma\otimes\Gamma'$ never leads to scalar terms (Γ_1 components). The next higher order is four, where we have to decompose the four products

$$\begin{aligned}&\Gamma^*\otimes\Gamma\otimes\Gamma'^*\otimes\Gamma' ,\\ &\Gamma^*\otimes\Gamma^*\otimes\Gamma'\otimes\Gamma'+\text{c.c.} ,\\ &\Gamma^*\otimes\Gamma'\otimes\Gamma'^*\otimes\Gamma'+\text{c.c.} ,\\ &\Gamma^*\otimes\Gamma\otimes\Gamma^*\otimes\Gamma'+\text{c.c.} ,\end{aligned} \quad (6.2)$$

The asterisk again denotes the complex-conjugate order-parameter basis. Note that in these combinations the invariance under time reversal and U(1) gauge transformation is satisfied. In Table XII we give these fourth-order terms for the example $\Gamma=\Gamma_5$ (3D) and $\Gamma'=\Gamma_1$ (1D). A complete list of all terms of all combinations of representations in the cubic point group can be found in Sigrist and Rice (1989)[13] and for other point groups in Sahu, Langner, and George (1988).

It is convenient for further analysis to write the complete free energy in the parametrization $\eta(\Gamma_1)=|\eta|e^{i\phi}$ and $\eta(\Gamma_5,m)=|\eta_m|e^{i\phi_m}$, so that we obtain the free-energy density

$$\begin{aligned}f=&A_1(T)|\eta|^2+\beta_1|\eta|^4+A_5(T)(|\eta_1|^2+|\eta_2|^2+|\eta_3|^2)+\beta_1'(|\eta_1|^2+|\eta_2|^2+|\eta_3|^2)^2\\ &+\beta_2'[|\eta_1|^4+|\eta_2|^4+|\eta_3|^4+2|\eta_1|^2|\eta_2|^2\cos(2\phi_1-2\phi_2)+2|\eta_2|^2|\eta_3|^2\cos(2\phi_2-2\phi_3)+2|\eta_3|^2|\eta_1|^2\cos(2\phi_3-2\phi_1)]\\ &+\beta_3'(|\eta_1|^2|\eta_2|^2+|\eta_2|^2|\eta_3|^2+|\eta_3|^2|\eta_1|^2)+\theta_1|\eta|^2(|\eta_1|^2+|\eta_2|^2+|\eta_3|^2)\\ &+\theta_2|\eta|^2[|\eta_1|^2\cos(2\phi_1-2\phi)+|\eta_2|^2\cos(2\phi_2-2\phi)+|\eta_3|^2\cos(2\phi_3-2\phi)]\\ &+\theta_3|\eta||\eta_1||\eta_2||\eta_3|[\cos(\phi_3-\phi_2)\cos(\phi_1-\phi)+\cos(\phi_2-\phi_1)\cos(\phi_3-\phi)+\cos(\phi_1-\phi_3)\cos(\phi_2-\phi)] ,\end{aligned} \quad (6.3)$$

where β_i, β_i', and θ_i are real coefficients that are material dependent. The coefficients of the second-order terms are $A_i(T)=a'(T/T_i-1)[T_i=T_c(\Gamma_i)]$.

A general analysis of the phase transitions for all possible values of the coefficients is rather complicated in this system and even numerically hard to handle, since a large number of local minima of f make the search for the global minimum rather difficult. Therefore we restrict ourselves to some typical cases which allow simple analytic argumentation.

As we have seen in Sec. II.B, the superconducting states of the Γ_5 representation are determined by the relation between β_2' and β_3'. The different types of states are separated by lines in the β_2'-β_3' plane. However, if we include coupling terms to other representations, these lines are in general modified and the regions close to them are not at all simple to analyze. To avoid such complications we concentrate below on regions far from any original borderline in the β_2'-β_3' diagram.

As a first example let us consider the case $0\ll\beta_3'$ and $-4\beta_1'<4\beta_2'\ll\beta_3'$. With the assumption $T_5>T_1$, the stable superconducting state immediately below the onset of superconductivity at T_5 is clearly a single representation (SR) state,

$$|\eta_1|^2=\frac{-A_5(T)}{2(\beta_1'+\beta_2')} \quad \text{and} \quad \eta=\eta_2=\eta_3=0 , \quad (6.4)$$

[13]Note that these authors use for some coupling terms complex coefficients that are also supposed to transform under time-reversal symmetry to the complex conjugate (see also Sec. VII.B).

TABLE XII. Invariant coupling terms between the irreducible representations Γ_1 and Γ_5 of the cubic symmetry O_h.

Product	Invariant coupling terms	Coefficient
$\Gamma_1^*\otimes\Gamma_1\otimes\Gamma_5^*\otimes\Gamma_5$	$\lvert\eta^2\rvert(\lvert\eta_1\rvert^2+\lvert\eta_2\rvert^2+\lvert\eta_3\rvert^2)$	θ_1
$\Gamma_1^*\otimes\Gamma_1^*\otimes\Gamma_5\otimes\Gamma_5$	$\eta^{*2}(\eta_1^2+\eta_2^2+\eta_3^2)+\text{c.c.}$	θ_2
$\Gamma_1^*\otimes\Gamma_5\otimes\Gamma_5^*\otimes\Gamma_5$	$\eta^*(\eta_1^*\eta_2\eta_3+\eta_1\eta_2^*\eta_3+\eta_1\eta_2\eta_3^*)+\text{c.c.}$	θ_3
$\Gamma_1^*\otimes\Gamma_1\otimes\Gamma_1^*\otimes\Gamma_5$	No invariant term	–

which is threefold degenerate with the symmetry $D_{4h}(\Gamma_4)$ according to Table VI(a). This state is generally not stable for all lower temperatures. For example, an additional second-order (continuous) transition can occur at a certain lower temperature, say T_1', leading to a combined representation (CR) state where the Γ_1 order parameter also becomes finite,

$$|\eta_1|^2=\frac{A_1Q-2\beta_1A_5}{4\beta_1(\beta_1'+\beta_2')-Q^2},\quad \eta_2=\eta_3=0\ ,$$
$$|\eta|^2=\frac{A_5Q-2(\beta_1'+\beta_2')A_1}{4\beta_1(\beta_1'+\beta_2')-Q^2}\ , \tag{6.5}$$
$$\phi_1-\phi=\begin{cases}0,\pi, & \theta_2<0,\\ \frac{\pi}{2},\frac{3\pi}{2}, & \theta_2>0,\end{cases}$$

with $Q=\theta_1-|\theta_2|$. The transition point T_1' is determined as the temperature where $|\eta|^2$ vanishes in these equations. This corresponds to the zero of the effective second-order term of η obtained in f by inserting $|\eta_1|$ from Eq. (6.4):

$$T_1'=T_1\frac{1-G}{1-GT_1/T_5}$$
with (6.6)
$$G=\frac{Q}{2(\beta_1'+\beta_2')}\quad \Gamma_5\leftrightarrow\Gamma_1\oplus\Gamma_5\ .$$

This transition is defined for $Q<2(\beta_1'+\beta_2')$, and T_1' is enhanced compared with T_1 if Q is "attractive" (<0) and suppressed if Q is "repulsive" (>0). Obviously at this transition the point-group symmetry is broken, and for $\theta_2>0$ even time-reversal symmetry is lost [$C_{2h}(\Gamma_1)$ for $\theta_2<0$ and $D_{4h}(\Gamma_1\oplus\Gamma_4)$ for $\theta_2>0$, both sixfold degenerate].

A further transition is possible to the SR state of Γ_1,

$$|\eta|^2=\frac{-A_1(T)}{2\beta_1},\quad \eta_1=\eta_2=\eta_3=0\ , \tag{6.7}$$

with the transition point

$$T_5'=T_5\frac{1-G'}{1-G'T_5/T_1}$$
with (6.8)
$$G'=\frac{Q}{2\beta_1}\quad \Gamma_1\leftrightarrow\Gamma_1\oplus\Gamma_5$$

determined by the zero of the numerator of $|\eta_1|^2$ in Eq. (6.5). The transition can take place only under the assumption $Q>2\beta_1>0$. In that case the coupling between the two superconducting order parameters is repulsive, and because of $\beta_1<\beta_1'+\beta_2'$ the Γ_1 order parameter is able to suppress the Γ_5 order parameter. The CR state has the existence condition $T_1'>T_5'$, which can also be expressed as $Q^2<4\beta_1(\beta_1'+\beta_2')$. If all these conditions are fulfilled, we find three consecutive second-order transitions: normal state $\rightarrow$SR(Γ_5)$\rightarrow$CR($\Gamma_1\oplus\Gamma_5$)$\rightarrow$SR(Γ_1).

In the case $T_5'>T_1'$—for which the CR state cannot exist—a direct transition can take place between the SR(Γ_5) and the SR(Γ_1) states. Generally this transition is discontinuous, a *first-order transition*. The transition temperature $\tilde{T}$ is defined as the point where the free energies of both SR are equal,

$$F_{\Gamma_1}(\tilde{T})=-\frac{A_1^2(\tilde{T})}{4\beta_1}=F_{\Gamma_5}(\tilde{T})=-\frac{A_5^2(\tilde{T})}{4(\beta_1'+\beta_2')}\ . \tag{6.9}$$

For a physical solution ($T_5>\tilde{T}>0$) the condition $\beta_1'+\beta_2'>\beta_1$ is required. Then it leads to a transition series: normal state $\rightarrow$SR(Γ_5)$\rightarrow$SR(Γ_1).

In Figs. 9(a)–9(d) the qualitative phase diagram of the transitions is drawn for varying Q [Figs. 9(a) and 9(b)] and varying $2(\beta_1'+\beta_2')$ [Figs. 9(c) and 9(d)]. Regions where the SR(Γ_5) state is stable for all temperatures below T_5 can also be found in this phase diagram. Note that an examination of the opposite case $T_1>T_5$ leads to completely analogous conclusions.

In this example the conditions ($0\ll\beta_3'$ and $-4\beta_1'<4\beta_2'\ll\beta_3'$) have been chosen so that only coupling terms are involved which contain the two order parameters in the same order. The term with the coefficient θ_3, which is linear in the Γ_1 order parameter and in the third-order Γ_5 order parameter, gives no contribution, since it requires that all three components of the Γ_5 order parameter be finite, which is energetically rather unfavorable in this parameter range. To see the mode of operation of this type of coupling term (unequal order cou-

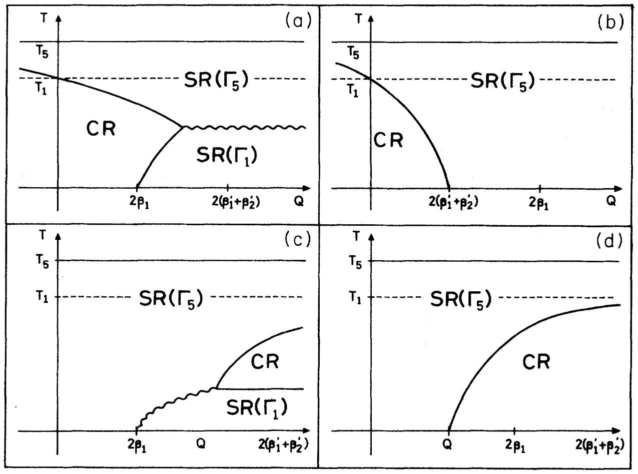

FIG. 9. Phase diagrams of additional phase transitions in the Ginzburg-Landau theory combining the two representations Γ_1 and Γ_5: T versus the coupling constant Q for (a) $\beta_1 < \beta_1' + \beta_2'$ and (b) $\beta_1 > \beta_1' + \beta_2'$; T versus the parameter $2(\beta_1'+\beta_2')$ for (c) $2\beta_1 < Q$ and (d) $2\beta_1 > Q$.

pling), we consider the case $0 > \beta_2', \beta_3'$ [also far from the borderlines in the β_2'-β_3' phase diagram, but additionally $\beta_1' > -(\beta_2' + \beta_3'/3)$], which leads to a state with $\eta_1 = \eta_2 = \eta_3 = \tilde{\eta}$ by minimization of $F_{\Gamma_5}[D_{3d}(\Gamma_1)$ according to Table VI(a)]. Making use of this form of the Γ_5 order parameter, we can write the free-energy density f [Eq. (6.3)] as

$$f(\eta,\tilde{\eta}) = A_1(T)|\eta|^2 + \beta_1|\eta|^4 + 3\{A_5(T)|\tilde{\eta}|^2 + [3(\beta_1'+\beta_2') + \beta_3']|\tilde{\eta}|^4\} + [\theta_1 + \theta_2\cos(2\tilde{\phi} - 2\phi)]|\eta|^2|\tilde{\eta}|^2 + 3\theta_3\cos(\tilde{\phi}-\phi)|\eta||\tilde{\eta}|^3 , \tag{6.10}$$

where we set $\phi_1 = \phi_2 = \phi_3 = \tilde{\phi}$. We assume for our discussion that the form of this Γ_5 order parameter is not changed for any temperature. For $T_5 > T_1$ we would expect that, in analogy with the former example, immediately below T_5 the SR(Γ_5) state would appear with

$$|\tilde{\eta}|^2 = \frac{-A_5(T)}{6(\beta_1'+\beta_2') + 2\beta_3'} . \tag{6.11}$$

However, this is prohibited by the θ_3 term, which leads to an admixture of the Γ_1 order parameter even if T_1 is very small compared with T_5. So we find for T close to T_5

$$|\eta| = \frac{\theta_3}{2A_1(T)}|\tilde{\eta}|^3 , \tag{6.12}$$

with the relative phase

$$\tilde{\phi} - \phi = \begin{cases} 0, & \theta_3 < 0, \\ \pi, & \theta_3 > 0. \end{cases}$$

The Γ_1 component increases proportionally to $|T - T_5|^{3/2}$, i.e., a "driven" order parameter. This CR state conserves time-reversal symmetry and is fourfold degenerate $[D_{3d}(\Gamma_1)]$. We have already discussed this effect in Sec. II.B, when we noted that not all states that are classified as SR are really pure SR states. According to the conditions for an admixture of another representation mentioned there, the actual Γ_5 state can mix with the Γ_1 representation, since it has the symmetry $D_{3d}(\Gamma_1)$, compatible with Γ_1. The CR state maintains the symmetry of the originally classified state (Monien *et al.*, 1986a, 1986b; Wojtanowski and Wölfle, 1986).

For lower temperatures an additional second-order phase transition can appear. The only symmetry that can be broken in our restricted free energy is time-reversal symmetry, by a change of the relative phase $\tilde{\phi} - \phi$. Obviously, this is favorable only if $\theta_2 > 0$, since both $\tilde{\phi} - \phi = 0$ and $= \pi$ minimize the θ_2 term for $\theta_2 < 0$. Differentiating the free energy with respect to the relative phase, we obtain the extremum condition

$$\sin(\tilde{\phi}-\phi)[4\theta_2|\eta|\cos(\tilde{\phi}-\phi) + \theta_3|\tilde{\eta}|] = 0 . \tag{6.13}$$

The expression in brackets gives a temperature-dependent solution for $\tilde{\phi} - \phi$ only if $|\theta_3|\tilde{\eta}|/4\theta_2|\eta|| \le 1$. Thus a continuous transition from a state with $\tilde{\phi} - \phi = 0$ or π takes place at the temperature T_0 with $|\theta_3|\,|\tilde{\eta}(T_0)| = 4\theta_2|\eta(T_0)|$. Obviously, for $\theta_2 < 0$ no such transition is possible.

Turning to the opposite case, $T_1 > T_5$, we obtain immediately below T_1 the SR (Γ_1) state [Eq. (6.7)]. This leads to an effective free energy for $\tilde{\eta}$ which contains, in addition to even-order terms, a third-order term of the form

$$3\theta_3\cos(\tilde{\phi}-\phi)\left[\frac{-A_1(T)}{2\beta_1}\right]^{1/2}|\tilde{\eta}|^3 . \tag{6.14}$$

This term can produce an instability to a CR state via a first-order transition if the coefficients in the free energy satisfy the relation

$$\theta_3^2 > 4(\theta_2 + |\theta_2|)[3(\beta_1'+\beta_2') + \beta_3'] . \tag{6.15}$$

Otherwise the transition is continuous. This condition can be derived by the minimization of the free energy with respect to $|\tilde{\eta}|$ for a given η at the transition point for the continuous transition from the SR(Γ_1) to the CR($\Gamma_1 \oplus \Gamma_5$) state $[A_5(T) - |\eta|^2(\theta_1 - |\theta_2|) = 0]$. If a finite $\tilde{\eta}$ minimizes the free energy, then a first-order transition has already taken place above this second-order transition point. The symmetry of the CR state is $D_{3d}(\Gamma_1)$ for $\theta_2 < 0$ and $D_{3d}(\Gamma_1 \oplus \Gamma_4)$ for $\theta_2 > 0$. In the latter case there is an additional continuous phase transition possible to the time-reversal-conserving state according to Eq. (6.13), but only if the first additional transition was of second order [Eq. (6.15) is not satisfied]. As in the former example, a series of three continuous transitions is possible here. A more detailed discussion of this example has been given by Lukjanchuk and Mineev (1989).

Finally we should like to mention that in general the treatment of first-order transitions in a multicomponent Landau theory is not simple. There is no obvious relation between the high- and the low-temperature states like the group-theoretical arguments available for second-order phase transitions. The search for the global minimum in a high-dimensional order-parameter space is then more or less a matter of trial and error, whether one uses analytical or numerical methods.

B. The critical magnetic fields

Having studied the homogeneous properties, we now consider effects on the upper critical and lower critical fields for a system with two almost degenerate order parameters. Let us first consider the upper critical field H_{c2}. Such an investigation has recently been carried out, including the order parameters of two representations, by Joynt (1990). Several other groups have also considered the problem of a single representation whose degeneracy is lifted by the presence of a magnetic ordering (Sec. V.C), as we shall discuss in Sec. VII.C. We have to extend our free-energy expression [Eq. (6.3)] by including the gradient terms. Apart from the coupling terms between the two representations we find them in Table VII(a). The coupling terms can again easily be derived by the decomposition of a Kronecker product $\Gamma_1^* \otimes \Gamma_5 \otimes \Gamma_4^* \otimes \Gamma_4 + \text{c.c.}$ $(=\Gamma_1 \oplus \Gamma_2 \oplus 2\Gamma_3 \oplus 3\Gamma_4 \oplus 4\Gamma_5)$, where Γ_4 is the representation of the gradient $\mathbf{D}=\nabla - 2e\,\mathbf{A}/c$. Only one term can be found in this example:

$$\tilde{K}[(D_x\eta)^*(D_y\eta_3+D_z\eta_2)+(D_y\eta)^*(D_z\eta_1+D_x\eta_3)+(D_z\eta)^*(D_x\eta_2+D_y\eta_1)+\text{c.c.}] \tag{6.16}$$

As an example, let us consider the critical field along one of the main axes, say, the z axis. We can perform the calculation as we did before in Sec. III.B for H_{c2}. By neglecting D_z and setting $\Pi_\pm = q(D_x \pm iD_y)/\sqrt{2}$ and $\eta_\pm = (\eta_i \pm i\eta_2)/\sqrt{2}$ $(q^2 = c/2eH)$, we obtain the linearized Ginzburg-Landau equations

$$K_1(\Pi_+\Pi_- + \Pi_-\Pi_+)\eta + \tilde{K}(\Pi_+^2+\Pi_-^2)\eta_3 = -A_1(T)q^2\eta \; , \tag{6.17}$$

$$K_2'(\Pi_+\Pi_- + \Pi_-\Pi_+)\eta_3 + \tilde{K}(\Pi_+^2+\Pi_-^2)\eta = -A_5(T)q^2\eta_3 \; ,$$

which are completely decoupled from the other two equations for η_+ and η_- [we use primed K coefficients for the Γ_5 representation analogous to Eq. (6.3)]. These latter two equations have exactly the same form as was given in Eq. (3.52) with $A(T)=A_5(T)$, so that their solution leads to a linear temperature dependence of the critical field,

$$H_{c2}^{(\pm)}(T) = -\frac{cA_5(T)}{eC(K_1',K_2',K_3',K_4')} \; , \tag{6.18}$$

where $C(K_1',K_2',K_3',K_4')$ is a constant depending on K_i' and is obtained from the lowest eigenvalue of an infinite matrix as we have seen before.

A more interesting problem is connected with the η-η_3 equation system, where the coupling term also enters. These equations, moreover, lead to the problem of finding the lowest eigenvalue in an infinite-dimensional system. However, a good insight into the properties of the solution can be obtained if we treat the problem in a perturbative way, assuming that the coupling term is very small $(\tilde{K} \ll K_1, K_2')$ (Joynt, 1990).

Starting with the zeroth order, we find two solutions (let us assume $T_5 > T_1$), which correspond to $\eta = |0\rangle$ and $\eta_3 = |0\rangle$, respectively, in the occupation number representation introduced in Sec. III.B,

$$H_{c2}^{(0)}(T) = -\frac{cA_5(T)}{2eK_2'} \; , \tag{6.19}$$

$$H_{c2}'^{(0)}(T) = -\frac{cA_1(T)}{2eK_1} \; , \tag{6.20}$$

where $H_{c2}^{(0)}$ represents the upper critical field (the lowest eigenvalue) immediately below T_5. If $K_1 < K_2'$, there is a crossing point of the $H_{c2}^{(0)}$ and $H_{c2}'^{(0)}$ line at some T' defined by $A_1(T')K_2' = A_5(T')K_1$. Below T', $H_{c2}'^{(0)}$ is the critical field.

Going to first-order perturbation, we write the two order parameters as linear combinations of the states $|0\rangle$ and $|2\rangle$. Diagonalizing the matrix in this subspace, we obtain corrections to our two former solutions $[(\eta,\eta_3)=(a_0|0\rangle, b_2|2\rangle)$ and $(\eta,\eta_3)=(a_2|2\rangle, b_0|0\rangle)$, respectively],

$$\begin{aligned} H_{c2}^{(1)} &= \frac{c}{e}A_1A_5[\{(5K_1A_5-K_2'A_1)^2+8\tilde{K}A_1A_5\}^{1/2}-5K_1A_5-K_2'A_1]^{-1} > H_{c2}^{(0)} \; , \\ H_{c2}'^{(1)} &= \frac{c}{e}A_1A_5[\{(K_1A_5-5K_2'A_1)^2+8\tilde{K}A_1A_5\}^{1/2}-K_1A_5-5K_2'A_1]^{-1} > H_{c2}'^{(0)} \; , \end{aligned} \tag{6.21}$$

where $H_{c2}^{(1)}$ is the upper critical field close to $T_c = T_5$ and $H_{c2}'^{(1)}$ occurs below a certain temperature T'. It can easily be seen that the sharp change of slope of H_{c2} between the two solutions exists in all orders of perturbation, because there is no finite matrix element between the two states $(\eta,\eta_3)=(|0\rangle,0)$ and $(\eta,\eta_3)=(0,|0\rangle)$ in any higher order of perturbation in the coupling term. This is different if the magnetic field is pointing along some arbitrary direction. Then all four components of the order parameter $(\eta,\eta_1,\eta_2,\eta_3)$ are coupled. In such a case a slope change in the critical field is mostly smooth.

We have three typical situations:

(a) $K_2'>C(K_1',K_2',K_3',K_4')$: the critical field goes linear as in Eq. (6.17), with the possibility of a change to H_{c2}' [as in Eq. (6.20)] if $K_1<C$ [Fig. 10(a)]; otherwise, see Fig. 10(b).

(b) $K_2'<C(K_1',K_2',K_3',K_4')$, K_1: the critical field is H_{c2} as in Eq. (6.20) without any kink [Fig. 10(b)].

(c) $K_1<K_2'<C(K_1',K_2',K_3',K_4')$: the critical field has a kink, as discussed above [Fig. 10(a)].

Finally we mention the possibility of a phase transition with decreasing field when the fourth-order terms in the free energy become important and favor a state with other symmetry than that induced by the magnetic field. This would, for example, be the case if we assumed situation (a) and the coefficient β_i with the condition $(4\beta_2<\beta_3, \beta_3>0)$. At high fields a state appears with two finite components of the Γ_5 order parameter (time-reversal-breaking), whereas for low fields a one-component state and, depending on the temperature and field, a finite Γ_1 order-parameter component is more favorable.

We turn now to the lower critical field H_{c1}, which is more closely related to the zero-field behavior of the system. The effect of an additional phase transition on this quantity is of special interest, since it allows a direct observation of an additional phase transition, as we shall show here, and will be compared with experimental data in Sec. VII (Kumar and Wölfle, 1987; Langner *et al.*, 1988; Hess *et al.*, 1989; Sigrist and Rice, 1989).

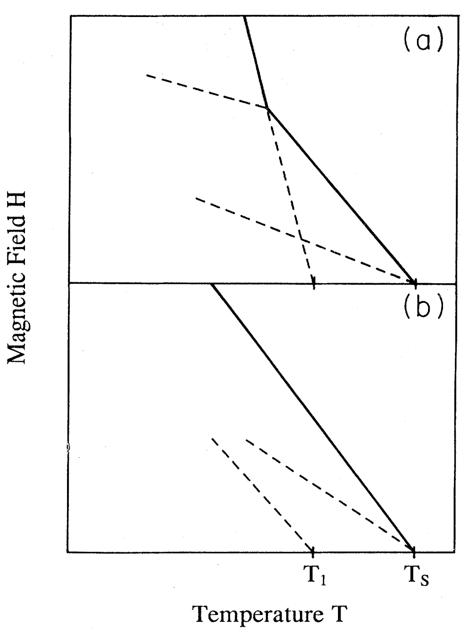

FIG. 10. Possible behaviors of the upper critical field H_{c2} in a superconductor with two almost degenerate order parameters: situation (a) a crossing of the lowest Landau levels leads to a kink and a change of the high-field superconducting state; situation (b) no crossing occurs.

In the limit of a London penetration depth very large compared with the coherence length of the order parameter, the main contribution to the line energy of a vortex comes from the magnetic field and the kinetic energy stored in the circulating supercurrent (Abrikosov limit). The structure of the core, whether there is one line or several split singularities as discussed in Sec. V, is not so important in this case. However, it is essential to take into account that the London penetration depth is not a scalar, but a tensor quantity in an unconventional superconductor. Thus the London equation has the general form

$$\nabla\times[\Lambda^2(\nabla\times\mathbf{H})]+\mathbf{H}=0\ , \tag{6.22}$$

where the tensor Λ^2 is defined as $\Lambda^2=c^2\hat{\rho}^{-1}/8\pi e^2$ with $\hat{\rho}$ as the superfluid density tensor, defined by the expression for the diamagnetic current $(\mathbf{J}_{\text{dia}}=2e^2\hat{\rho}\mathbf{A}/c^2)$. The equation for the field around a vortex is obtained from Eq. (6.22) by replacing the right-hand zero by $\Phi_0\mathbf{n}\delta(\mathbf{n}\times\mathbf{r})$ (where $\mathbf{n}$ is the direction of the external field and Φ_0 is a flux quantum). If the applied field $(\mathbf{n})$ is parallel to one of the main axes of Λ^2, the vortex line will also be parallel to $\mathbf{n}$. For an arbitrary $\mathbf{n}$, however, these directions need not coincide, as discussed in detail by Balatzkii *et al.* (1986; see also Gor'kov, 1987).

Consider the case of the CR phase, discussed in the previous section, $D_{4h}(\Gamma_1\oplus\Gamma_4)$. For this phase the tensor $\hat{\rho}$ has the rather simple form

$$\hat{\rho}=K_1(\hat{x}\hat{x}+\hat{y}\hat{y}+\hat{z}\hat{z})|\eta|^2 +[K_1'\hat{x}\hat{x}+K_2'(\hat{y}\hat{y}+\hat{z}\hat{z})]|\eta_1|^2\ , \tag{6.23}$$

with $\hat{i}\hat{j}$ denoting the tensor element ρ_{ij}. For this example the crystal axis is the main axis of the tensor, because there are no coupling terms between the order-parameter components. We choose $\mathbf{n}$ parallel to such an axis. Then the field calculated from the modified Eq. (6.22) is

$$\mathbf{H}=\mathbf{n}\frac{\Phi_0}{2\pi\lambda_\alpha\lambda_\beta}K_0(\sqrt{x_\alpha^2/\lambda_\alpha^2+x_\beta^2/\lambda_\beta^2})\ , \tag{6.24}$$

where $x_{\alpha(\beta)}$ denote the directions perpendicular to $\mathbf{n}$ having the corresponding London penetration depths $\lambda_{\alpha(\beta)}$ (K_0 is a modified Bessel function). This form becomes very simple if we choose $\mathbf{n}$ parallel to the x axis, because

$$\lambda_\alpha^2=\lambda_\beta^2=\lambda^2=\frac{c^2}{8\pi e^2}\frac{1}{K_1|\eta|^2+K_2'|\eta_1|^2} \tag{6.25}$$

leads to a completely axial vortex. The line energy is obtained in general from

$$\varepsilon=\frac{1}{8\pi}\int dx_\alpha dx_\beta[\mathbf{H}^2+(\nabla\times\mathbf{H})\Lambda^2(\nabla\times\mathbf{H})]\ , \tag{6.26}$$

where the integration is restricted to the region $\sqrt{(x_\alpha/\xi_\alpha)^2+(x_\beta/\xi_\beta)^2}>1$. Evaluating this integral in the usual way (see, for example, de Gennes, 1966), we find ($\mathbf{n}\|\hat{x}$)

$$H_{c1}=\frac{4\pi\varepsilon}{\Phi_0}=\frac{\Phi_0}{8\pi\lambda^2}\ln\kappa \;, \qquad (6.27)$$

with the Ginzburg-Landau parameter $\kappa=\lambda/\xi$ (for this case ξ also is constant in the y-z direction). To define ξ or κ directly, we may use Eq. (5.5).

Now let us consider the change of H_{c1} at the transition from the high-temperature phase $D_{4h}(\Gamma_4)$ to the low-temperature phase $D_{4h}(\Gamma_1\oplus\Gamma_4)$, the example given in the previous section. Using the equations for λ^2 and κ, we obtain a sharp change in the slope of H_{c1}, since λ decreasing due to the additional contribution of the Γ_1 order parameter to the superfluid density. The Ginzburg-Landau parameter drops rapidly from a constant value in the high-temperature phase down to a lower, almost constant value (Sigrist and Rice, 1989). Comparing the two slopes $H'_{c1}(=dH_{c1}/dT)$, above and below the second transition at T'_1, we find

$$\frac{H'_{c1}(T'_1-\delta)}{H'_{c1}(T'_1+\delta)}=\frac{\lambda'(T'_1-\delta)}{\lambda'(T'_1+\delta)}\left[1-\frac{1}{\ln\kappa}\right]+\frac{1}{\ln\kappa}>1 \;, \qquad (6.28)$$

where $\lambda'=d\lambda/dT$ and δ is an infinitesimal number. This ratio is larger than 1 in the large-κ limit where $\ln\kappa>1$ (κ taken at T'_1), if the London penetration depth is decreasing faster below the additional transition at T'_1 than above (Hess *et al.*, 1989). Comparing the ratio $\lambda'(T'_1-\delta)/\lambda'(T'_1+\delta)$ with the one of the specific heat $C(T'_1-\delta)/C(T'_1+\delta)$ we find that this condition is usually satisfied if the discontinuity of the specific heat ΔC is positive, provided that all coefficients K in the tensor $\hat{\rho}$ are of the same order of magnitude. This qualitative behavior is in agreement with experimental results found in several materials (see discussion in Sec. VII).

VII. ARE HEAVY-FERMION SUPERCONDUCTORS UNCONVENTIONAL SUPERCONDUCTORS?

In the previous sections we have developed a theory describing phenomena expected for unconventional superconductors, mainly based on the generalized Ginzburg-Landau theory. The character of this section is different. Here we examine the relevance of these theoretical studies to experiments on heavy-fermion superconductors. First we survey briefly the most important experimental observations in the three typical heavy-fermion superconductors, $CeCu_2Si_2$, UBe_{13}, and UPt_3. For more experimental details on heavy-fermion systems we refer the reader to reviews by Stewart (1984), de Visser, Menovsky, and Franse (1987), Ottt (1987a, 1987b), Rauchschwalbe (1987), and Grewe and Steglich (1989).

Further, we consider in more detail the two probably most exciting topics in heavy-fermion superconductors: In Sec. VII.B we discuss the peculiar phase diagram of thorium-doped UBe_{13}, and in Sec. VII.C we concern ourselves with the exotic T-H phase diagram of UPt_3. Both fields are still under intense discussion. Therefore the ideas discussed there are more hypothetical than established explanations of these phenomena. However, as will be seen, it is remarkable that the idea of unconventional superconductivity can reasonably account for various unusual behaviors that are hard to understand in the picture of conventional superconductivity. Therefore we believe that the concept of the unconventional superconductor is the most promising explanation for these unusual phenomena in heavy-fermion materials.

A. The three typical compounds

The most prominent heavy-fermion superconductors, $CeCu_2Si_2$, UBe_{13}, and UPt_3, also exhibit as heavy-fermion materials rather peculiar normal-state properties. At high temperatures their susceptibilities follow a Curie-Weiss law. In $CeCu_2Si_2$ the resistivity increases as the temperature is lowered and shows a maximum around 10 K (Stewart *et al.*, 1983). The resistivity of UBe_{13} shows a similar increase, with a narrow peak around 2.5 K (Ott *et al.*, 1983). The ratio of specific heat to temperature C/T in both materials reaches about 1J/mole K^2 at the superconducting transition temperature (Table XIII). These features are indications that the f electrons of the rare-earth or the actinide atoms can be regarded as almost localized at high temperatures, where they act as spin scattering centers, yielding what is known as the Kondo effect (an increase in resistivity). However, arranged in a lattice (called a Kondo or Anderson lattice), they form a quasiparticle band with a heavy effective particle mass ($m^*\sim 10^2 m_e$) below about 10 K. This temperature is considered as the characteristic temperature of the low-temperature region of the system, T_F, and is of the same order as the single-impurity Kondo temperature T_K in the three systems. Although the resistivity in UPt_3 decreases monotonically, inconsistent with this picture, the C/T also reaches a large value at T_c, indicating heavy quasiparticle bands. Thus UPt_3 may be considered as an f-electron Fermi liquid over a wider temperature range than the other two compounds.

At the transition point to superconductivity, the specific heat shows the usual discontinuity of a second-order phase transition. The ratio of the magnitude of the discontinuity to the normal-state specific heat is of the order of unity (Table XIII). This fact is the experimental evidence that heavy quasiparticles with an f-like character condense into Cooper pairs. When we take into account that the origin of the heavy mass is clearly the strong repulsive interactions among the f electrons, it is very natural to assume that the Cooper pairs avoid residual interactions among the quasiparticles by forming some anisotropic pairing state, as pointed out in the Introduction.

The slope of the critical magnetic field $-(dH_{c2}/dT)$ at T_c is remarkably large. One of the key questions concerning H_{c2} is the problem of Pauli limiting of H_{c2}. (As the magnetic field is increased, the normal state becomes energetically favored when the difference in the magnetic energy due to spin-state splitting exceeds the condensation energy.) The spin susceptibility in the superconducting state has to be smaller than or equal to that in the normal state. Considering two extreme cases, in a conventional pure superconductor the spin susceptibility is suppressed to zero at $T=0$, while in a special triplet state, called equal spin pairing, it is unaffected (see, for example, Leggett, 1975). Therefore the limiting of H_{c2} due to Pauli paramagnetization depends on the spin structure of the superconducting state. From an analysis of the upper critical field as a function of the temperature, Rauchschwalbe *et al.* (1985) suggested a singlet pairing for $CeCu_2Si_2$ and an unconventional state for UPt_3. The upper critical field of UBe_{13} can only with difficulty be fitted by a simple model of even-or odd-parity pairing. The peculiar structure of H_{c2} as a function of temperature led to the interpretation that there might be two phase transitions involved (see Rauchschwalbe, 1987). However, recent measurements show no indication of such an event in the lower critical field H_{c1} (Heffner *et al.*, 1990).

In an unconventional superconductor it is possible for the gap of the excitation spectrum to have points of zeros or lines of zeros in some special directions in the **k**-space. If such nodes exist in the gap, low-energy excitations are possible which lead to power-law behaviors of physical quantities, in contrast with the exponential temperature dependence in a conventional *s*-wave state (see Sec. III.A). The specific heat of UBe_{13} follows close to a T^3 law below T_c (Ott *et al.*, 1984). Subsequently, MacLaughlin *et al.* (1984) reported a T^3 law for the NMR relaxation rate with some deviation at very low temperatures. Power-law behaviors are also reported for the ultrasonic attenuation by Golding *et al.* (1985) and for the penetration depth by Einzel *et al.* (1986).

The temperature dependence of the specific heat in UPt_3 can be fitted by the relation $C/T=\gamma_0+\beta T$, as reported by Sulpice *et al.* (1986; see also Hasselbach *et al.*, 1989). However, the entropy balance is not satisfied with that expression and therefore the true dependence is not yet established in the low-temperature range $(0<T<T_c/5)$. The origin of the residual T linear specific heat is not yet clear. One possible explanation is the depairing effect due to impurities discussed in Sec. III.B.2. An alternative explanation is proposed by Burlachkov and Kopnin (1988), based on their finding a finite density of excitations in the domain-wall structure in the superconducting order parameter. The NMR relaxation rate $1/T_1$ varies in proportion to T^3 at low temperatures in this compound (Kohori *et al.*, 1988). For the ultrasonic attenuation, various power-law behaviors, depending on the frequency of the sounds, their propagation direction, and their polarization, are reported by

TABLE XIII. Experimental data collection.

	$CeCu_2Si_2$	UBe_{13}	UPt_3
Point group	D_{4h}	O_h	D_{6h}
T_c (K)	$\sim 0.6^{a,d}$	0.85^b	0.5^c
$\gamma(T>T_c)$ $(J/\mathrm{mol}\,K^2)$	1^a	1.1^b	0.45^c
$\Delta C/C_n(T_c)$	1.3^d	2.5^e	0.5^c
$-(dH_{c2}/dT)_{T_c}$ (kOe/K)	230^d	420^f	60 $(H\parallel c)^g$ 40 $(H\perp c)$
Power laws (T^n)			
Specific heat	$2-3^h$	3^e	$-^i$
NMR $1/T_1$	3^j	3^k	3^l
Ultrasound attenuation		Peak at T_c [m]	Peak at T_c [n]
Josephson[o]	Current with Al		No current with Al, Nb, UPt_3
Proximity[p]		Negative *s*-wave proximity	

[a]Steglich *et al.*, (1979).
[b]Ott *et al.* (1983).
[c]Stewart *et al.* (1984).
[d]Assmus *et al.* (1984).
[e]Ott *et al.* (1984).
[f]Maple *et al.* (1985).
[g]Chen *et al.* (1984).
[h]Steglich *et al.* (1984).
[i]$C/T=\gamma_0+\beta T$, Sulpice *et al.* (1986).
[j]Kitaoka *et al.* (1985).
[k]MacLaughlin *et al.* (1984).
[l]Kohori *et al.* (1988).
[m]Golding *et al.* (1985).
[n]Müller *et al.* (1986).
[o]Steglich *et al.* (1985).
[p]Han *et al.* (1986).

several authors (Bishop *et al.*, 1984; Müller *et al.*, 1986; Shivaram *et al.*, 1986).

The specific heat of $CeCu_2Si_2$ does not follow the exponential form of the BCS theory, but at the same time cannot be described by a specific power law over a wide range of temperature (the exponent varies in the range of $2<n<3$; Steglich *et al.*, 1984). The NMR relaxation rate $1/T_1$ in $CeCu_2Si_2$ obeys the T^3 law (Kitaoka *et al.*, 1985). In zero external field there is a deviation from the T^3 law at low temperatures, which Kitaoka *et al.* ascribed to paramagnetic impurities, noting that external magnetic fields suppress this deviation. The power laws reported for specific heat and NMR relaxation rate for the three typical heavy-fermion superconductors are summarized in Table XIII.

Although these power laws seem to point rather clearly towards superconductivity with anisotropic pairing, it has to be mentioned that the power laws are not in all cases consistent and do not lead to a clear decision of the topology of the gap zero nodes. For example, in UBe_{13} the power law with $n=3$ for the specific heat is compatible with point zeros, while $n=3$ for the relaxation rate favors line zeros in the gap. Furthermore, in the real low-temperature region ($T<0.1T_c$) measurements of the thermodynamic quantities could not be performed with good accuracy, mainly due to self-heating by nuclear processes in the material (^{235}U-decay).

The peak structure in ultrasound attenuation close to T_c, observed in UPt_3 and UBe_{13}, has been the motivation for studying collective modes in unconventional superconductors. The real mechanism explaining the attenuation peak is still under debate. As we discussed in Sec. III.B, the collective modes have finite frequencies in a crystal. However, Monien *et al.*, (1986a, 1986b) pointed out that if the spin-orbit coupling is not very strong there are modes with low frequencies which couple to the density fluctuations due to particle-hole asymmetry. In heavy-fermion systems this asymmetry can be large, and therefore they argued that these modes may be responsible for the peak. A detailed calculation including impurity scattering effects led to the conclusion that superconducting states with a nonspherically symmetric gap structure do yield ultrasound attenuation peaks (Monien *et al.*, 1987; Lenck *et al.*, 1988). The two essential mechanisms responsible for this effect had already been proposed earlier, first by Wölfle (1986), who emphasized that near T_c the dynamics of all non-Goldstone order-parameter components is purely relaxational and in this case critical slowing down of the relaxation time may lead to the attenuation peak, and secondly by Miyake and Varma (1986), who proposed a Landau-Khalatnikov mechanism. In this theory, too, critical slowing down of the relaxation time of fluctuations of the order-parameter amplitude gives rise to the attenuation peak near T_c. Finally, ultrasound damping, due to dissipative domain-wall motion, is also possible (Joynt *et al.*, 1986). This mechanism strongly depends on the symmetry of the (multicomponent) superconducting order parameter and could be used to determine its symmetry.

Recently, an alternative explanation has been offered by Coffey (1989). According to his picture the ultrasonic attenuation peak could also arise due only to the normal-state properties, or more explicitly, due to the large ratio m^*/m_e, and would not significantly depend on the Cooper pairing symmetry. Therefore this effect cannot simply be taken as a confirmation of unconventional superconductivity. On the other hand, we shall see in the next section that in the alloy $U_{0.97}Th_{0.03}Be_{13}$ two transitions occur, one with and the other without a peak, depending possibly on the quality of the transition. There this picture of a peak induced by the large effective mass might fail.

As pointed out in Sec. IV.B, the Josephson effect may be an informative probe of an unconventional superconductor. In a point contact of $CeCu_2Si_2$ with Al (a singlet *s*-wave superconductor), Steglich *et al.* (1985) observed a Josephson current with conventional behavior. Thus singlet superconductivity was claimed for this material. However, according to the arguments given in Sec. IV.B, in systems where spin-orbit coupling plays an important role, this experimental result does not exclude a triplet superconducting state. It is also still in doubt whether one should take a similar experiment for UPt_3 in point contact with Al and Nb, where no Josephson current could be found, as a clear indication for triplet pairing (Steglich *et al.*, 1985). As we saw in Sec. IV.B, the structure and symmetry of the interface plays an important role in the Josephson experiment. For an unconventional superconductor, the order parameter may be suppressed at the interface due to boundary effects. Moreover, the large mismatch between the effective masses of the heavy-fermion and the usual superconductor carriers can lead to very small tunneling rates. Hence it is extremely difficult to obtain decisive information purely from the properties of the tunneling effect.

In spite of this fact, a very significant experiment has been presented by Han *et al.* (1986). They investigated the Josephson effect in a contact between UBe_{13} and Ta. The latter is an *s*-wave superconductor with a higher critical temperature than the former and therefore, induces, for $T>T_c$ UBe_{13}, an *s*-wave order parameter in UBe_{13} in a small region around the contact. Between the induced and the Ta-superconducting state, a Josephson coupling is observed, i.e., a proximity-induced Josephson effect. With decreasing temperature the critical current is increasing and reaches a maximum at T_c of UBe_{13}. Below that critical temperature it is decreasing again. Because in experiments where UBe_{13} was replaced by the conventional superconductor Mo, the increase of the critical current was for all temperatures monotonic, it can be concluded that the *s*-wave order parameter induced by the proximity effect is suppressed due to the occurrence of the UBe_{13} order parameter. This pronounced negative *s*-wave proximity effect indicates that this order parameter might have odd parity (triplet superconductivity), as discussed for similar problems in Sec. IV.B.2.

B. The alloy $U_{1-x}Th_xBe_{13}$

Thorium-doped UBe_{13} has produced one of the most exciting fields in heavy-fermion superconductivity, in experiments as well as in theory. Thorium, even as a nonmagnetic impurity, should suppress superconductivity with increasing concentration, if the superconductor is anisotropic, as pointed out in Sec. III.A. It does so, but the decrease of the critical temperature is not monotonic, as can be seen in the experimental phase diagram (temperature versus Th concentration x) in Fig. 11(a). The transition temperature $T_c(x)$ has a sharp anomaly at $x_0 \approx 0.018$. An additional irregular point has been found very recently at $x_0' \approx 0.045$. Therefore the phase diagram may be divided into three regions, (I) for $0 < x < x_0$, (II) for $x_0 < x < x_0'$, and (III) for $x_0' < x$. Region (II) yields a special property. In specific-heat measurements an additional second-order transition below the onset of superconductivity has been discovered [Fig. 11(a); Ott *et al.*, 1985, 1986; Felder *et al.*, 1989].

The results of a series of experiments at this additional transition point ($T = T_0$) have given rise to controversy over the origin of this additional transition. From the fact that both transitions are strongly shifted to lower temperatures if an external field is applied, one can conclude that the lower transition is not a structural phase transition (Ott, 1987a, 1987b). On the one hand, measurements of the critical magnetic fields, especially H_{c1}, indicate clearly an increase in the superconducting condensation energy below this transition (Rauchschwalbe, 1987; Rauchschwalbe, Steglich, *et al.*, 1987; Heffner *et al.*, 1990). This fact suggests the interpretation that we have an additional superconducting transition (Volovik and Khmel'nitskii, 1984; Joynt, Rice, and Ueda, 1986; Kumar and Wölfle, 1987; Hirashima, 1988; Keller, Scharnberg, and Monien, 1988; Langner, Sahu, and George, 1988; Lukjanchuk and Mineev, 1988, 1989; Sigrist and Rice, 1989).

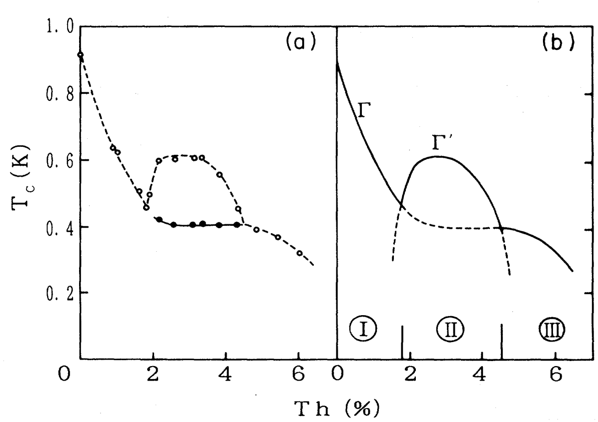

FIG. 11. Experimental and model phase diagram of $U_{1-x}Th_xBe_{13}$. (a) Phase diagram temperature versus Th concentration: ○, onset of superconductivity; ●, the additional second-order transition found in specific-heat measurements (Ott *et al.*, 1986; Felder *et al.*, 1989). (b) Model for the anomaly at x_0 and x_0': the transition temperatures of two superconducting states with different symmetry (Γ and Γ') are crossing at x_0 and x_0'.

On the other hand, Heffner and co-workers (1987, 1989) presented μSR data that point to the appearance of an additional internal magnetic field in the material below T_0. As very recent measurements indicate, this magnetic effect is clearly restricted to region (II) (Heffner *et al.*, 1990). This can be considered as support for the other interpretation of the additional transition, that at T_0 a SDW state occurs, coexisting with the superconducting state (Batlogg *et al.*, 1985; Kato *et al.*, 1987; Machida and Kato, 1987; Gulásci and Gulásci, 1989). This idea seems not unlikely, since in the compound URu_2Si_2 a similar situation was found, though with the opposite conditions, as mentioned earlier (the magnetic instability occurs at higher temperature than the superconduction one).

How we can find a consistent picture for these two seemingly contradictory experimental results? One attempt was recently presented by Gulásci and Gulásci (1989) to establish the latter proposal. Basing their arguments on the work of Psaltakis and Fenton (1983), they found that the occurrence of a spin-density wave state in a superconducting state produces an additional superconductivity order parameter, which breaks the translational symmetry [independently a similar idea based on group-theoretical arguments was presented by Ozaki and Machida (1989)]. It has been argued that this could be the origin of the increase in superconducting condensation energy in that model. On the other side, we have seen in Sec. V that unconventional superconductors that break time-reversal symmetry have rather pronounced magnetic properties. So the transition at T_0 could be interpreted as a superconducting transition that breaks time-reversal symmetry, producing internal magnetic fields in the superconducting state (Mineev, 1989; Sigrist and Rice, 1989).

We shall concentrate our attention in this section on the aspects of a phenomenological theory based purely on superconductivity transitions. The reader has to be aware that this field is still a matter of controversy and should not take the following considerations as uncontested.

1. A model for the phase diagram

Since the anomaly of $T_c(x)$ at $x_0 \approx 0.018$ is very sharp and cusplike, it has been proposed that it is the crossing point of transition temperatures belonging to superconducting states of different symmetry [Γ and Γ' in Fig. 11(b); Joynt, Rice, and Ueda, 1986; Kumar and Wölfle, 1987; Keller, Scharnberg, and Monien, 1988; Langner, Sahu, and George, 1988; Lukjanchuk and Mineev, 1988; Sigrist and Rice, 1989]. The other anomaly at x_0' can then be explained very naturally as a second crossing of the two lines [(I), (III): $T_c(\Gamma)>T_c(\Gamma')$; (II): $T_c(\Gamma)<T_c(\Gamma')$; see Fig. 11(b)]. Several experimental data can be considered as confirmation for the main point of the model, that in regions (I) and (II) different superconducting states appear at the onset of superconductivity. Such data are not yet available for phase (III).

Under uniform pressure the transition temperature $T_c(x)$ decreases, but the slope is different in the two regions,

$$\frac{\partial T_c(x)}{\partial P}\approx\begin{cases}0.022\ \text{K/Kbar}, & x<x_0\ ,\\ 0.07\ \text{K/kbar}, & x>x_0\ ,\end{cases} \tag{7.11}$$

where P is the pressure (Lambert, Dalichaouch, Maple, Smith, and Fisk, 1986). Due to this difference, the position x_0 of the anomaly is shifted: $x_0(P)\approx 0.018+1.7\times10^{-3}P$ (kbar) (Sigrist and Rice, 1989). In these experiments it has also been demonstrated that for pressures higher than 9 kbar regions (I) and (II) are separated by a nonsuperconducting region in the T-x phase diagram.

Further support for this model comes from the specific-heat measurements. There is an obvious contrast between the discontinuities of specific heat at the onset of superconductivity in the two regions (Ott *et al.*, 1985),

$$\frac{\Delta C}{T_c}\approx\begin{cases}1.56\ \text{Jmol}^{-1}\text{K}^{-1}, & x=0,0.017<x_0\ ,\\ 1.9\ \text{Jmol}^{-1}\text{K}^{-1}, & x=0.033>x_0\ .\end{cases} \tag{7.12}$$

As can easily be seen, in a weak-coupling theory this ratio $\Delta C/T_c$ should not be changed for a superconductor by a shift of T_c, so the change in this value may also suggest different superconducting states in the two regions.

A more significant, qualitative argument for this model was found in the ultrasound measurements. As mentioned earlier, pure UBe_{13} has a sharp ultrasonic attenuation peak located below the superconducting transition. Such a peak is completely missing at the upper transition for $x_0<x<x_0'$. However, a similar peak occurs at the second phase transition (Batlogg *et al.*, 1985; Bishop *et al.*, 1986).

In the model proposed, the critical temperatures, $T_c(\Gamma,x)$ and $T_c(\Gamma',x)$, of the two representations are of the same order of magnitude, at least in some regions of the phase diagram [Fig. 11(b)]. Thus the Ginzburg-Landau free-energy expansion of this system should include both representations, Γ and Γ', with their coupling terms. We have treated this type of theory already in Sec. VI and will here take that example (the combination of Γ_1 and Γ_5) as the basis for further considerations. In general the coefficients in this theory, especially in the coupling terms, may depend on the thorium concentration x. It is also not unlikely that in the doped materials time-reversal symmetry is lost with increasing thorium concentration, since these impurities destroy the inversion symmetry of the system, and furthermore the system $U_{1-x}Th_xBe_{13}$ may be close to a magnetic instability. To include these types of effects, Sigrist and Rice (1989) introduced coupling terms which implicitly assume breaking of time-reversal symmetry. It has to be emphasized that for very low concentrations of thorium such terms should disappear.

With regard to the example analyzed in Sec. VI, there are several possible ways to fit the phase diagram of $U_{1-x}Th_xBe_{13}$. Let us assume that the superconductivity in pure UBe_{13} belongs to the representation Γ_5 $(=\Gamma)$, producing a state with line or point nodes $[D_{4h}(\Gamma_4)]$ to reproduce the low-temperature data (see Sec. VII.A). Then the additional transition in region (II) can be inter-

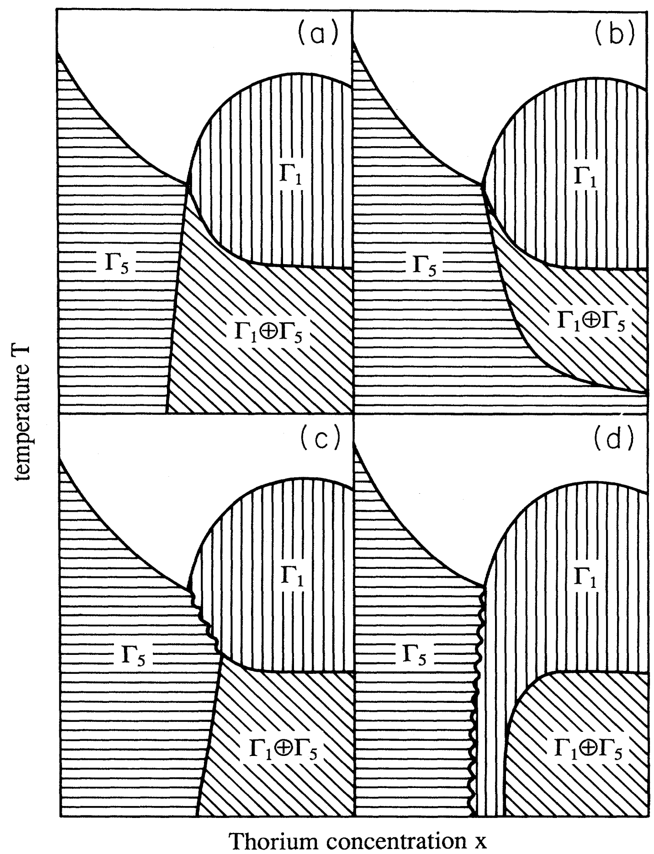

FIG. 12. Possible phase diagrams of $U_{1-x}Th_xBe_{13}$. Provided that the coupling parameter Q is decreasing monotonically with increasing x, several phase diagrams are possible (smooth lines correspond to second-order transitions): (a) $Q(x_0)<2\beta_1, 2(\beta_1'+\beta_2')$; (b) $2(\beta_1'+\beta_2')>Q(x_0)>2\beta_1$, $Q^2(x_0)<4\beta_1(\beta_1'+\beta_2')$; (c) $Q^2(x_0)>4\beta_1(\beta_1'+\beta_2')$, $\beta_1>\beta_1'+\beta_2'$; $x>x_0$ exists with $Q^2(x)\le 4\beta_1(\beta_1'+\beta_2')$ [the wavy line denotes a first-order transition between the two single representation (SR) states]; (d) $\beta_1<\beta_1'+\beta_2'$, two cases are possible: (1) $Q^2(x_0)<4\beta_1(\beta_1'+\beta_2')$, $2(\beta_1'+\beta_2')>Q(x_0)>2\beta_1$, $x>x_0$ exists with $Q(x)\le 2\beta_1$ [the wavy line corresponds to two closely neighboring second-order transitions confining a combined representation (CR) state]; (2) $Q^2(x_0)>4\beta_1(\beta_1'+\beta_2')$, $x>x_0$ exists with $Q^2(x)\le 4\beta_1(\beta_1'+\beta_2')$ and $Q(x)\le 2\beta_1$ (the wavy line corresponds to a first-order transition).

preted as the superconducting transition from the SR(Γ_1) state to the CR($\Gamma_1 \oplus \Gamma_5$) state, with $T_0 = T_5'$ [Eq. (6.8)]. However, there is a further transition possible in this model, which has to date no experimental reference. The corresponding transition line could be located in region (I) as well as in (II), but in both cases be strongly suppressed so that it was experimentally not observable [Figs. 12(a) and 12(b)]. The criterion for the location of the "leftover" line is given by the relation between Q and $2(\beta_1' + \beta_2')$ in Eq. (6.6). Due to the variation of the coefficients [e.g., $Q = Q(x)$; see Eqs. (6.5)–(6.8)], there may be some range of x where a first-order transition connects the two SR states [Fig. 12(c)] or where the SR(Γ_1) state is stable for all temperatures [Fig. 12(d)]. However, the main criterion for the form of the phase diagram is the existence condition for the CR state, $Q^2 < 4\beta_1' + \beta_2'$). Rough estimates for the coefficients of the free energy obtained from the specific-heat data favor the phase diagram in Fig. 12(a) or that in Fig. 12(d) ($\beta_1 < \beta_1' + \beta_2'$; Sigrist and Rice, 1989). The other crossing point x_0' can be discussed analogously.

2. Experiments at the second phase transition

The transition from the SR(Γ_1) to the CR($\Gamma_1 \oplus \Gamma_5$) state has physical properties that are in qualitative agreement with several experiments. First of all, it produces an increase in the superconductivity condensation energy. This is an essential point in explaining the experiment of Rauchschwalbe, Steglich, and co-workers [1987, recently reproduced and confirmed for various Th concentrations in region (II) by Heffner *et al.*, 1990]. The measurement of the lower critical field in the sample $U_{0.97}Th_{0.03}Be_{13}$ shows a significant change in $dH_{c1}(T)/dT$ at the second transition (Fig. 13). Apart from the correct temperature dependence of $H_{c1}(T)$ away

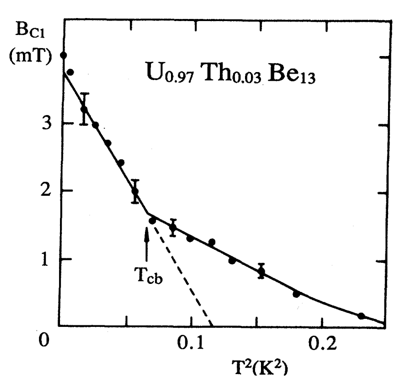

FIG. 13. Lower critical magnetic field B_{c1} in the alloy $U_{0.97}Th_{0.03}Be_{13}$ (second transition at T_{cb}) (Rauchschwalbe *et al.*, 1987a).

from the Ginzburg-Landau regime, this agrees completely with the analysis of H_{c1} at the additional transition given in Sec. VI. The change of κ upon passing through the transition point was estimated by Rauchschwalbe from his experimental data: $\kappa = 37 \pm 5$ above and $\kappa = 25 \pm 6$ well below T_0 for $x = 0.033$. Additionally, measurements of H_{c1} in region (I) show no similar indication for any additional phase transition (Heffner *et al.*, 1990).

As another example let us consider the ultrasound experiments done in the compound $U_{0.967}Th_{0.033}Be_{13}$, region (II) (Batlogg *et al.*, 1985; Bishop *et al.*, 1986). No effect is observed at the onset of superconductivity, as we mentioned above. However, below the transition at T_0 a sharp peak in the ultrasonic attenuation is found for longitudinal sound in both the [100] and the [111] direction. Since in our phase diagram the high-temperature phase belongs to a one-dimensional representation, neither collective modes nor the domain-wall damping mechanism (Sec. III.B) can produce any absorption, in agreement with the experimental result. At the second transition, however, both mechanisms can lead to an effect. It was pointed out by Hirashima (1988) that close to T_0 a softening of a collective mode occurs due to the presence of the second-order instability (neglecting the crystal-field effects). Similarly, Kumar and Wölfle (1987) proposed a coupling to the mode of the relative phase between the order parameters of the two representations.

Joynt *et al.* (1986) have shown that for a cubic system the domain-wall damping mechanism only leads to a coupling for both sound directions if the symmetry of the superconducting state is lower than tetragonal (this is never the case for an SR state in O_h). The sound waves have to induce a difference of the free-energy densities in different domains for both directions (see Sec. III.B). This is satisfied for the CR state $C_{2h}(\Gamma_1)$, but not for the time-reversal-breaking state $D_{4h}(\Gamma_1 \oplus \Gamma_4)$ (see Sec. VI).

Finally, the challenge for the model is to explain the magnetic properties of the low-temperature phase observed in μSR experiments (Heffner *et al.*, 1987, 1989, 1990). Measurement of the zero-field relaxation rate σ_{KT} shows a significant continuous increase of the internal magnetic field in region (II) below T_0 (Fig. 14). No similar effect is observed at the onset of superconductivity in this region or anywhere in region (I) and (III).

The zero-field relaxation rate is a measure of the magnitude of a randomly distributed internal magnetic field in a material. Such a field leads to the depolarization of the muon spin. The average polarization of the muon spin relative to its original direction behaves in time as

$$P(t) = \tfrac{1}{3}[1 + 2(1 - \sigma_{KT}^2 t^2)\exp(-\tfrac{1}{2}\sigma_{KT}^2 t^2)] , \qquad (7.13)$$

where σ_{KT}^2 is proportional to the second moment of the magnetic-field distribution function (see, for example, Schenck, 1985).

As we explained in Sec. V, a time-reversal-breaking superconducting state can produce a local internal magnet-

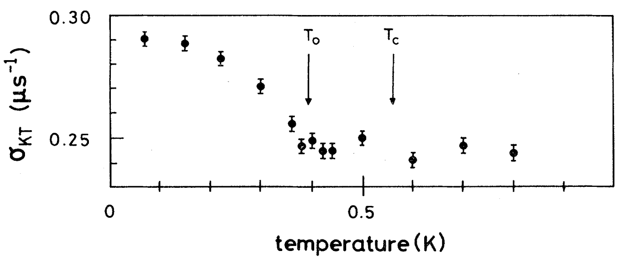

FIG. 14. Zero-field relaxation rate data for $U_{0.965}Th_{0.035}Be_{13}$ (Heffner *et al.*, 1989).

ic field around impurities. Its spatial average $\langle \mathbf{B} \rangle$ is vanishing and leads to no net magnetization of the material. In a sample where 3.5% of the U atoms are replaced by Th atoms, the average distance between the impurities is of the order of the lattice constant (where the unit-cell lattice constant $a \approx 14.5$ Å$\sim 10^{-1}\xi_0$), because every unit cell contains eight U atoms. Thus the magnetic field induced is present practically over the whole sample, with some random modulation. Moreover, a certain scattering of the muon trapping points due to the presence of impurities may lead to an additional randomness of the detected internal field distribution.

The time-reversal-breaking state $D_{4h}(\Gamma_1 \oplus \Gamma_4)$ in our example is antiferromagnetic according to the definition given in Sec. V.A, since it has a magnetization in the **k**-space as

$$\mathbf{m}(\mathbf{k}) \propto (\eta^* \eta_1 - \eta \eta_1^*) \begin{bmatrix} \hat{k}_y^2 - \hat{k}_z^2 \\ \hat{k}_x \hat{k}_y \\ \hat{k}_x \hat{k}_z \end{bmatrix} f(\mathbf{k}) , \qquad (7.14)$$

with zero average $\langle \mathbf{m}(\mathbf{k}) \rangle$ [$f(\mathbf{k})$ is totally symmetric in **k**]. However, we have seen before that η and η_1 usually vary differently in space leading to a current and field distribution whose magnitude is proportional to $|\eta(T)|\,|\eta_1(T)|$. Then the square root of the second moment of the magnetic field produced in the sample is proportional to the zero-field relaxation rate,

$$\sigma_{KT}(T) \propto |\eta(T)|\,|\eta_1(T)| \propto \sqrt{|T_0 - T|\,|T^* - T|} , \qquad (7.15)$$

where T^* is the "transition point" for the third transition, corresponding to T_1' in Eq. (6.6). The experimental data suggest that we take a negative value for T^*. This equation describes a continuous increase of σ_{KT}, like an order parameter, with its onset at T_0, which is in qualitative agreement with the experimental data (Fig. 14).

From a consideration of single-impurity case studied in Sec. V an estimate of the magnitude of the induced magnetic field cannot be given directly. That treatment, restricted to distances much larger than ξ_0, cannot be applied in this form in a regime where the impurities are closer to each other than ξ_0. However, considering the short-distance region ($k_F^{-1} < r < \xi_0$), Mineev estimated a magnetic field that could, very close to the impurity, reach a maximal value of the order $10G$ (for a ferromagnetic superconducting state). The experiments give a field spread width $\sim 1G$, which is in reasonable agreement with this estimate. Furthermore, with the assumption that the measured internal field comes from a field around the impurities, one would expect that σ_{KT} should be enhanced with increasing Th concentration. This fact is confirmed by the experimental data too.

A conclusion that certainly can be derived from these investigations is that the superconducting state for pure UBe_{13} does not break time-reversal symmetry. Otherwise, an effect on σ_{KT} should have been observed somewhere in region (I) of the phase diagram. The same is true for region (III). Concerning the phase diagram a further point may be concluded. Because the μSR experiments indicate no loss of time-reversal symmetry for both regions (I) and (III), in contrast to the low-temperature phase of region (II), the existence of phase-separation lines between them is indirectly proved.

The inconsistency in the present model, that the time-reversal-breaking phase has a spatial symmetry too high to satisfy the condition for coupling to the domain-wall damping mode, could be avoided by the assumption of time-reversal-breaking coupling terms mentioned above (Sigrist and Rice, 1989). Then all CR states would have orthorhombic symmetry.

An analogous argument can be applied to the combination of the two representations Γ_1 and Γ_4 of the cubic point group. For this example, however, ferromagnetic superconducting CR phases do exist, since the condition for such a state is satisfied by $\Gamma_1 \otimes \Gamma_4 = \Gamma_4$ (see Sec. V.A). The present experimental data do not permit a clear decision about the symmetry of the superconducting states in any of the phases occurring in this alloy.

In this phenomenological treatment we could not address the problem of why doping with thorium changes the system UBe_{13} in such a way. This behavior seems even more mysterious if we compare it with that of the La- or Lu-doped systems, which respond to increased doping with a monotonic suppression of superconductivity. Clearly, this is a problem related to the microscopic mechanism for superconductivity in this material, a problem that is beyond our scope here.

C. Unconventional superconductivity in UPt_3

Very recently UPt_3 has taken center stage as the most intensively discussed topic in the field of heavy-fermion superconductivity. The new experimental data seem to confirm that the superconductivity in this compound is not conventional. Even though the information from experiments is rather rich, no unambiguous identification of the symmetry of the superconducting state could be made to date, since a consistent picture covering all phenomena found in this material is still lacking. We give here a brief review of the actual situation in experiment and theory.

In neutron-scattering experiments, antiferromagnetic ordering has been discovered below a temperature $T_N \approx 5-6$ K with very small magnetic moments ($\sim 0.02\mu_B$/U atom) lying in the basal plane of the hexagonal crystal lattice of UPt_3 (see Sec. V.C; Aeppli *et al.*, 1988, 1989). When the material undergoes additionally a superconducting transition at $T_c = 0.5$ K, the two states coexist in a manner similar to that in URu_2Si_2.

Specific-heat measurements show a clear splitting of the superconducting transition by a value of ~ 60 mK at zero external field (Fisher *et al.*, 1989). The two observed transitions seem to have their origin in the superconductivity, as measurements of H_{c1} indicate by a significant change in the slope of this quantity (Taillefer, 1990). It was (previously) proposed that such a split could be produced by the coupling of the superconducting and the antiferromagnetic order parameters, causing a lifting of degeneracy in the superconducting order-parameter space due to lowering of symmetry in the magnetically ordered state (Joynt, 1988; Hess, Tokuyasu, and Sauls; 1989; Machida and Ozaki, 1989; Blount, Varma, and Aeppli, 1990; see Sec. V.C). In the case of hexagonal crystal symmetry, four two-dimensional irreducible representations are available, which have quite similar properties for this type of effect. To obtain two consecutive phase transitions it is required that the coefficients of the fourth-order terms in the Ginzburg-Landau theory [Table V(c)] both be positive, according to the treatment in Sec. III. Comparing that treatment with the experimental result for the ratio of the two discontinuities in specific heat, we obtain the relation $\beta_1 \approx 4\beta_2 - 5\beta_2$ for these coefficients, which is larger than the weak-coupling estimate $\beta_1 = 3\beta_2$ (Hess, Tokuyasu, and Sauls, 1989; Machida, Ozaki, and Ohmi, 1989; Schenstrom *et al.*, 1989).

From this point of view the low-temperature phase corresponds to the time-reversal-breaking states $D_{6h}(\Gamma_5^{\pm})$ or $D_{6h}(\Gamma_6^{\pm})$, which have in the background of antiferromagnetic ordering a lowered point-group symmetry, $D_{2h}(\Gamma_2^{\pm} \oplus \Gamma_4^{\pm})$ or $D_{2h}(\Gamma_1^{\pm} \oplus \Gamma_3^{\pm})$, respectively. The high-temperature state is real and has the symmetry $D_{2h}(\Gamma_2^{\pm})$ or $D_{2h}(\Gamma_1^{\pm})$ [see Table VI(c)].

Blount and co-workers (1990) additionally discussed the influence of the superconducting order parameter on the staggered magnetic moments in this model. They found a slight rotation of the staggered moment, because the presence of the superconducting state allows coupling between the longitudinal and the transverse parts of this moment (see Sec. VI.C). This rotation is also reported from experimental results (Aeppli *et al.*, 1989).

In experiments it is observed that the application of a magnetic field parallel to the basal plane leads to a narrowing of the transition split up to complete suppression at some critical value $H_{cr} \approx 5$ kG (see Fig. 15; Hasselbach, Taillefer, and Flouquet, 1989). At this point a clear kink in the upper critical field $H_{c2}(T)$ also occurs. This

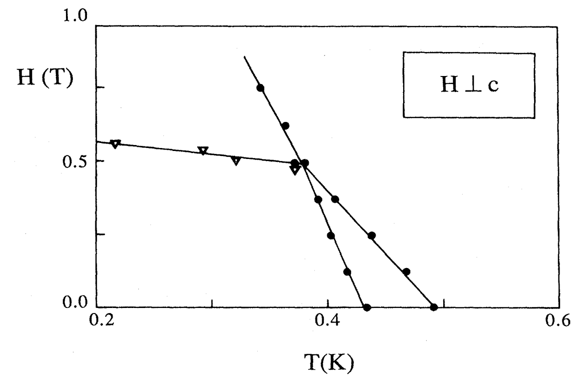

FIG. 15. Phase diagram of UPt_3 for a magnetic field in the basal plane (T vs H): ●, second-order transitions found in specific-heat measurements; △, the observed anomaly in the ultrasound absorption measurements (Hasselbach, Taillefer, and Flouquet, 1989).

kink is absent if the magnetic field is applied along the c axis.

This kink and the merging of the two transitions have been traced to a crossing of two $H_{c2}(T)$ lines each belonging to one of the split superconducting states (Hess, Tokuyasu, and Sauls, 1989; Machida, Ozaki, and Ohmi, 1989; Blount, Varma, and Aeppli, 1990; Joynt, Mineev, Volovik, and Zhitomirsky, 1990). The analysis is very similar to that presented at the end of Sec. VI for two almost degenerate representations. However, the antiferromagnetic state responsible for the splitting introduces an anisotropy in the behavior of the calculated H_{c2} lines. The two lines can only cross if the magnetic field is perpendicular to the antiferromagnetic moments. Fields in arbitrary directions mix the two split states in such a way that the kink changes to a smooth crossover and disappears completely if the field is parallel to the moments. Moreover, the additional degrees of freedom in the staggered moment introduced by Blount *et al.* (1990) do not solve this problem. One can speculate whether the anisotropy energy of the antiferromagnetic state might be small enough that the external field could align the magnetic moments perpendicular to the field for any direction (Machida, Ozaki, and Ohmi, 1989).

Two other ideas for ways to sidestep the anisotropy problem have been presented by Joynt *et al.* (1990):

(1) The experimental analysis of the antiferromagnetic ordering shows a domain structure with a very small size (~ 150 Å), which is comparable with the zero-temperature coherence length of the superconducting state ($\xi_0 \approx 50$ Å; Aeppli *et al.*, 1989). In the background of such a short-range modulated antiferromagnetic state, the first stable state to be realized by the two-component superconducting order parameter ($\Gamma_5^{\pm}$ or $\Gamma_6^{\pm}$) may be a glass state. This is a real state of the form $\eta = |\eta(\mathbf{r})| e^{i\alpha}[\cos\phi(\mathbf{r}), \sin\phi(\mathbf{r})]$, which varies randomly in the sample, taking advantage of the spatial fluctuations

of the coupled antiferromagnetic moments without a high expense of kinetic energy (gradient terms). It is assumed that for low temperatures the time-reversal-breaking state $D_{6h}(\Gamma_{5,6}^{\pm})$ is stable and homogeneous because it does not couple to the direction of the magnetic moments. The transition between the glass and the homogeneous state is claimed to be of weak first order. [A similar idea was earlier proposed in connection with the $U_{1-x}Th_xBe_{13}$-alloy (Volovik and Khmel'nitskii, 1984)].

(2) It is also possible to ignore the antiferromagnetic ordering and to assume that the transition temperature of the order parameters of two irreducible representations are close to each other, leading to the two observed transitions (similar to the model proposed for $U_{1-x}Th_xBe_{13}$ in the previous section).

Both proposals have the advantage that the anisotropy introduced by the magnetic ordering does not occur. However, very recently Taillefer (1990) discovered a peculiar anisotropy of H_{c2} in the basal plane. It is questionable whether this may be interpreted as a manifestation of the anisotropy appearing in the other theories.

Another class of experiments considers the high-field region of the *T-H* phase diagram of UPt_3. In ultrasound measurements an absorption peak has been observed for a magnetic field $H \sim 0.6 H_{c2}$ (~ 1.2 T), applied parallel to the *c* axis of the hexagonal crystal lattice (Qian *et al.*, 1987; Müller *et al.*, 1987). This may be an indication of a phase transition in the system. This effect has been confirmed for other field directions, including fields in the basal plane (Schenstrom *et al.*, 1989). Similar anomalies have been reported in the dissipation of the torsional oscillation of UPt_3 samples under high magnetic fields (Kleiman *et al.*, 1989).

The theoretical discussions of this phenomenon concentrate on fields parallel to the *c* axis. The first proposals, offered by Volovik (1988) and Joynt (1988), consider different superconducting states for the low- and high-field regions. In low fields the superconductor is in the London regime, where the state is determined by the bulk zero-field properties. Beyond this region the magnetic field determines which state is realized (see Sec. VI.B). At the transition between the two states in the intermediate-field region the vortex lattice symmetry can also be changed. However, the particular superconducting states proposed in the two treatises are controversial. Volovik's high-field state is the axial time-reversal-breaking $D_{6h}(\Gamma_5^{\pm})$ state [$\eta(1,\pm i)$, where $\pm$ depends on the sign of the applied field], which lead to a hexagonal vortex lattice. At low field the vortex lattice symmetry is broken, and the real state $\eta(1,0)$ or $\eta(0,1)$ is realized. In contrast, Joynt proposes a time-reversal-breaking high-field state $\boldsymbol{\eta}=\eta(1,ri)$ ($|r|<1$), which breaks the hexagonal symmetry, whereas for low fields the axial state is favorable, yielding a triangular vortex lattice. More recent investigations, discussed in Sec. III.B, show that there are two possible high-field solutions, an axial one yielding axial vortices arranged in a triangular lattice and an asymmetric one with nonaxial vortices in a distorted lattice (Sundaram and Joynt, 1989; Zhitomirskii, 1989). The latter phase is very similar to that considered by Joynt (1988).

Other possibilities for field-induced phase transitions have been suggested by Schenstrom *et al.* (1989) and have been worked out in detail by Tokuyasu *et al.* (1990). Unlike the idea mentioned above, in this picture the superconducting state as a background need not change essentially over the whole range of the magnetic field. It is assumed to be $D_{6h}(\Gamma_5^{+})$. In such a state unconventional nonaxial vortex structures can be more stable than axial ones, as we pointed out in Sec. V.B. In the actual system the magnetic-field distribution of the vortex has triangular symmetry, which may be, at least close to the core ($\sim 5-10\xi_0$), rather pronounced. Due to this fact the equilibrium state of the vortex lattice should also take into account the additional degree of freedom, the orientation of the vortex. For a field close to H_{c1} a triangular lattice is formed. With increasing density of the vortices in higher fields, their anisotropic structure becomes important in the arrangement of the lattice, leading in general to frustrations in a triangular lattice. Tokuyasu *et al.* proposed the change to be a honeycomb lattice or the conversion of a part of the vortices to axial symmetry ($\rightarrow$hexagonal) as a possible reaction of the system to avoid these frustrations (Fig. 16). In all models the change of the vortex lattice structure is considered to be the cause of the anomaly in the ultrasound absorption measured in the experiments. Such a change could additionally lead to an observable anomaly in the magnetization curve $M(H)$.

Summarizing this section, we can say that experimental facts clearly show that heavy-fermion superconduc-

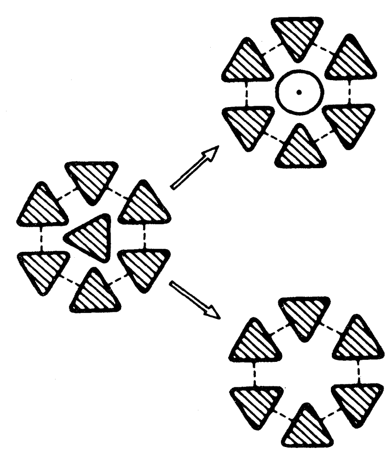

FIG. 16. The triangular lattice built of triangularly shaped vortices becomes frustrated when the density of vortices is large. To escape this frustration, two possible new vortex lattices can be formed: a honeycomb lattice or a hexagonal lattice also involving axial vortices (Tokuyasu *et al.*, 1990).

tivity is unconventional in many respects. Especially in the compounds UBe_{13} (and the related alloys) and UPt_3, the quality of evidence is so high that superconductivity due to a conventional s-wave pairing mechanism can be ruled out. Even with these very significant experimental data, no unambiguous statement can be given about the symmetry of the superconducting state realized in these materials. At least, it seems likely that some of the occurring superconducting states break time-reversal symmetry, yielding a series of unconventional magnetic effects. According to the argument presented in Sec. VII.B, the question of time-reversal-breaking states may have been solved for UBe_{13}. In the case of UPt_3, however, no decisive experiments to settle this problem are available to date. Neither have the experimental investigations yet led to a consensus about the microscopic origin of the superconducting instability. Many components seem to play an important role in these materials.

Surveying this article we find that the Ginzburg-Landau theories of anisotropic superconductivity contain a rich structure which could only partially be analyzed here. One essential feature, as we have seen, is the breakdown of various symmetries at the onset of superconductivity or at additional transitions. Especially in the case of multicomponent Ginzburg-Landau theories, several new topological structures are possible due to the presence of degenerate superconducting states. Domain walls and fractional and nonaxial vortices are only a few examples. These theories have been used to find explanations for several unconventional effects as well as to motivate new experiments, not only in heavy-fermion superconductors but also in other, e.g., high-T_c or organic superconductors.

The starting point for the formulation of these Ginzburg-Landau theories was a BCS-like theory of anisotropic Cooper pairing. This should not lead to the opinion that these theories are valid only within this background. The final formulation, as presented in Sec. II, is based on very general principles and is independent of the microscopic mechanisms producing superconductivity. The order parameter may be different from the pair wave or gap function in general; however, the structure of the Ginzburg-Landau theory describing an unconventional superconductor as a mean-field approach close to the phase transition should always be of the form discussed above.

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APPENDIX A: BOGOLIUBOV TRANSFORMATION FOR NONUNITARY GAP FUNCTIONS

In order to evaluate the unitary transformation $U_{\mathbf{k}}$, it is convenient to use a modification of Eq. (2.6), $U_{\mathbf{k}}\hat{E}_{\mathbf{k}}=\hat{\mathscr{E}}_{\mathbf{k}}U_{\mathbf{k}}$. In components of 2×2 matrices this equation can be written as

$$\hat{u}_{\mathbf{k}}(\hat{E}_{\mathbf{k}}-\varepsilon(\mathbf{k}))=-\hat{\Delta}(\mathbf{k})\hat{v}^*_{-\mathbf{k}}\ ,\qquad \hat{v}^*_{-\mathbf{k}}(\hat{E}_{\mathbf{k}}+\varepsilon(\mathbf{k}))=-\hat{\Delta}^+(\mathbf{k})\hat{u}_{\mathbf{k}} \tag{A1}$$

with

$$\hat{E}_{\mathbf{k}}=\begin{bmatrix} E_{\mathbf{k}+} & 0 \\ 0 & E_{\mathbf{k}-}\end{bmatrix} . \tag{A2}$$

We eliminate $\hat{v}^*_{-\mathbf{k}}$ in Eq. (2.15) and obtain

$$\hat{u}_{\mathbf{k}}(\hat{E}^2_{\mathbf{k}}-\varepsilon^2(\mathbf{k}))=\hat{\Delta}(\mathbf{k})\hat{\Delta}^+(\mathbf{k})\hat{u}_{\mathbf{k}} . \tag{A3}$$

If we assume a unitary $\hat{\Delta}(\mathbf{k})$, the solution is very simple. The excitation spectrum is $E_{\mathbf{k}\pm}=E_{\mathbf{k}}=[\varepsilon^2(\mathbf{k})+\frac{1}{2}\mathrm{tr}(\hat{\Delta}\hat{\Delta}^+)(\mathbf{k})]^{1/2}$. For $\hat{u}_{\mathbf{k}}$ any 2×2 matrix can be used. Profiting by this freedom we choose $\hat{u}_{\mathbf{k}}$ proportional to $\hat{\sigma}_0$. With Eq. (A1) and the unitary condition we obtain Eq. (2.13).

In the case of nonunitary superconducting states the solution of Eq. (A1) is not so simple, since the freedom of choice of $\hat{u}_{\mathbf{k}}$ in Eq. (A3) is lost if $\hat{\Delta}\hat{\Delta}^+$ is not proportional to the unit matrix. From this equation we obtain the following condition for $\hat{u}_{\mathbf{k}}$:

$$\hat{u}_{\mathbf{k}}|\mathbf{q}|\hat{\sigma}_z=\hat{\boldsymbol{\sigma}}\cdot\mathbf{q}\hat{u}_{\mathbf{k}} , \tag{A4}$$

where $\mathbf{q}$ denotes $i(\mathbf{d}\times\mathbf{d}^*)$. This equation can be solved by the ansatz

$$\hat{u}_{\mathbf{k}}=a(|\mathbf{q}|\hat{\sigma}_0+\mathbf{q}\cdot\hat{\boldsymbol{\sigma}})(\hat{\sigma}_0+\hat{\sigma}_z)+b(|\mathbf{q}|\hat{\sigma}_0-\mathbf{q}\cdot\hat{\boldsymbol{\sigma}})(\hat{\sigma}_0-\hat{\sigma}_z) . \tag{A5}$$

We choose the parameters a and b to be real. With Eq. (A1) we obtain for $\hat{v}_{\mathbf{k}}$

$$\hat{v}_{\mathbf{k}}=-\hat{\Delta}(\mathbf{k})\hat{u}^*_{\mathbf{k}}[\hat{E}_{\mathbf{k}}-\varepsilon(\mathbf{k})][\hat{E}^2_{\mathbf{k}}-\varepsilon^2(\mathbf{k})]^{-1} \tag{A6}$$

with

$$[\hat{E}_{\mathbf{k}}-\varepsilon(\mathbf{k})][\hat{E}_{\mathbf{k}}^2-\varepsilon^2(\mathbf{k})]^{-1}=\frac{[E_{\mathbf{k}+}+E_{\mathbf{k}-}+2\varepsilon(\mathbf{k})]\hat{\sigma}_0+(E_{\mathbf{k}+}-E_{\mathbf{k}-})\hat{\sigma}_z}{[E_{\mathbf{k}+}+\varepsilon(\mathbf{k})][E_{\mathbf{k}-}+\varepsilon(\mathbf{k})]} . \tag{A7}$$

Note that $\hat{u}_{\mathbf{k}}^*$ is related to $\hat{u}_{\mathbf{k}}$ via the Pauli-matrix identity $\hat{\boldsymbol{\sigma}}^*=-\hat{\sigma}_y\hat{\boldsymbol{\sigma}}\hat{\sigma}_y$. The Bogoliubov transformation has to satisfy the unitarity condition $\hat{u}_{\mathbf{k}}\hat{u}_{\mathbf{k}}^+ +\hat{v}_{\mathbf{k}}\hat{v}_{\mathbf{k}}^+=1$. This leads to the equations for a and b,

$$4|\mathbf{q}|(|\mathbf{q}|+q_z)\left[a^2\frac{2E_{\mathbf{k}+}}{E_{\mathbf{k}+}+\varepsilon(\mathbf{k})}+b^2\frac{2E_{\mathbf{k}-}}{E_{\mathbf{k}-}+\varepsilon(\mathbf{k})}\right]=1 ,$$
$$a^2\frac{2E_{\mathbf{k}+}}{E_{\mathbf{k}+}+\varepsilon(\mathbf{k})}-b^2\frac{2E_{\mathbf{k}-}}{E_{\mathbf{k}-}+\varepsilon(\mathbf{k})}=0 \tag{A8}$$

with the solution

$$a^2=\frac{E_{\mathbf{k}+}+\varepsilon(\mathbf{k})}{8E_{\mathbf{k}+}|\mathbf{q}|(|\mathbf{q}|+q_z)} ,$$
$$b^2=\frac{E_{\mathbf{k}-}+\varepsilon(\mathbf{k})}{8E_{\mathbf{k}-}|\mathbf{q}|(|\mathbf{q}|+q_x)} . \tag{A9}$$

Under the assumption that $\hat{u}_{\mathbf{k}}$ is a real matrix, the given solution is unique. If we insert a and b in Eqs. (A1) and (A3) and use the definition $\hat{\Delta}=i\hat{\boldsymbol{\sigma}}\cdot\mathbf{d}\hat{\sigma}_y$, we obtain the result in Eq. (2.14).

APPENDIX B: GREEN'S-FUNCTION FORMULATION OF UNCONVENTIONAL SUPERCONDUCTIVITY

The Green's-function formulation of the theory of superconductivity allows us to consider a much wider range of effects than the treatment given in Sec. II.A (Gor'kov, 1958). It is useful for the investigation of impurity scattering effects, but also gives a description of inhomogeneous situations and leads finally to the microscopic derivation of the Ginzburg-Landau theory of conventional s-wave-type superconductivity (Gor'kov, 1959). The extension of this formulation to non-s-wave superconductivity is straightforward. Since the derivation is essentially parallel to the conventional version found in several textbooks, we keep the derivations short here.

Let us first write the Hamiltonian introduced in Eq. (2.1) in a more general form in the momentum representation,

$$\begin{aligned}\mathcal{H}&=\mathcal{H}_0+\mathcal{H}_{\text{pair}}\\&=\sum_{\mathbf{k},\mathbf{k}',s,s'}\langle\mathbf{k}s|\mathcal{H}_0|\mathbf{k}'s'\rangle a_{\mathbf{k}_1s_1}^{\dagger}a_{\mathbf{k}_2s_2}+\frac{1}{2}\sum_{\substack{\mathbf{k},\mathbf{k}',\mathbf{q}\\s_1,s_2,s_3,s_4}}V_{s_1s_2s_3s_4}(\mathbf{k},\mathbf{k}')a_{(\mathbf{q}/2)-\mathbf{k},s_1}^{\dagger}a_{(\mathbf{q}/2)+\mathbf{k},s_2}^{\dagger}a_{(\mathbf{q}/2)+\mathbf{k}',s_3}a_{(\mathbf{q}/2)-\mathbf{k}',s_4} .\end{aligned} \tag{B1}$$

where $\mathcal{H}_0$ denotes the one-particle part of the Hamiltonian, including the effects of inhomogeneities like impurity or surface scattering. The pairing interaction is taken in a form which allows interaction between pairs of finite total momentum.

The finite-temperature Green's function in the imaginary-time momentum space is defined as

$$G_{ss'}(\mathbf{k},\mathbf{k}';\tau)=-\langle T_\tau\{a_{\mathbf{k}s}(\tau)a_{\mathbf{k}'s'}^{\dagger}(0)\}\rangle , \tag{B2}$$

and the anomalous Green's function as

$$F_{ss'}(\mathbf{k},\mathbf{k}';\tau)=\langle T_\tau\{a_{\mathbf{k}s}(\tau)a_{\mathbf{k}'s'}(0)\}\rangle,\quad F_{ss'}^{\dagger}(\mathbf{k},\mathbf{k}';\tau)=\langle T_\tau\{a_{\mathbf{k}'s'}^{\dagger}(\tau)a_{\mathbf{k}s}^{\dagger}(0)\}\rangle . \tag{B3}$$

The operator $a_{\mathbf{k}s}(\tau)$ denotes $\exp(\mathcal{H}\tau)a_{\mathbf{k}s}\exp(-\mathcal{H}\tau)$. The transformation of these Green's functions to the frequency momentum space leads to

$$\begin{aligned}G_{ss'}(\mathbf{k},\mathbf{k}';\tau)&=k_BT\sum_n G_{ss'}(\mathbf{k},\mathbf{k}';i\omega_n)e^{-i\omega_n\tau} ,\\F_{ss'}(\mathbf{k},\mathbf{k}';\tau)&=k_BT\sum_n F_{ss'}(\mathbf{k},\mathbf{k}';i\omega_n)e^{-i\omega_n\tau} ,\\F_{ss'}^{\dagger}(\mathbf{k},\mathbf{k}';\tau)&=k_BT\sum_n F_{ss'}^{\dagger}(\mathbf{k},\mathbf{k}';i\omega_n)e^{-i\omega_n\tau} ,\end{aligned} \tag{B4}$$

where ω_n is the Matsubara frequency for fermions $\pi k_BT(2n+1)$.

Using now the equation of motion for the Green's functions ($\partial a_{\mathbf{k}s}/\partial\tau=[\mathcal{H},a_{\mathbf{k}s}]$), we obtain the equation system (Gor'kov equations) for $G_{ss'}(\mathbf{k},\mathbf{k}';i\omega_n)$

$$\sum_{\mathbf{k}'',s''}\left[\langle \mathbf{k}s|i\omega_n-\mathcal{H}_0|\mathbf{k}''s''\rangle G_{s''s'}(\mathbf{k}'',\mathbf{k}';i\omega_n)-\sum_{\mathbf{q}''}\Delta_{ss''}(\mathbf{k}'',\mathbf{q}'')F^{\dagger}_{s''s'}\left[\frac{\mathbf{q}''}{2}-\mathbf{k}'',\mathbf{k}';i\omega_n\right]\delta_{\mathbf{q}''/2+\mathbf{k}'',\mathbf{k}}\right]=\delta_{\mathbf{k},\mathbf{k}'}\delta_{s,s'}\ , \tag{B5}$$

for $F^{\dagger}_{ss'}(\mathbf{k},\mathbf{k}';i\omega_n)$

$$\sum_{\mathbf{k}'',s''}\left[F^{\dagger}_{ss''}(\mathbf{k},\mathbf{k}'';i\omega_n)\langle \mathbf{k}''s''|i\omega_n+\mathcal{H}_0|\mathbf{k}'s'\rangle-\sum_{\mathbf{q}''}\Delta^{\dagger}_{s's''}(\mathbf{k}'',\mathbf{q}'')G_{s''s}\left[\frac{\mathbf{q}''}{2}+\mathbf{k}'',\mathbf{k};i\omega_n\right]\delta_{\mathbf{q}''/2-\mathbf{k}'',\mathbf{k}'}\right]=0\ , \tag{B6}$$

and for $F_{ss'}(\mathbf{k},\mathbf{k}';i\omega_n)$

$$\sum_{\mathbf{k}'',s''}\left[\langle \mathbf{k}s|i\omega_n-\mathcal{H}_0|\mathbf{k}''s''\rangle F_{s''s'}(\mathbf{k}'',\mathbf{k}';i\omega_n)-\sum_{\mathbf{q}''}\Delta_{ss''}(\mathbf{k}'',\mathbf{q}'')G_{s's''}\left[\mathbf{k}',\frac{\mathbf{q}''}{2}-\mathbf{k}'';-i\omega_n\right]\delta_{\mathbf{q}''/2+\mathbf{k}'',\mathbf{k}}\right]=0\ , \tag{B7}$$

where the four-operator term in the pairing Hamiltonian $\mathcal{H}_{\text{pair}}$ has been decoupled by the introduction of a mean field analogous to that in Sec. II.A. It is defined by

$$\begin{aligned}\Delta_{ss'}(\mathbf{k},\mathbf{q})&=-\sum_{\mathbf{k}',s_1,s_2}V_{s'ss_1s_2}(\mathbf{k},\mathbf{k}')\langle a_{\mathbf{q}/2+\mathbf{k}',s_1}a_{\mathbf{q}/2-\mathbf{k}',s_2}\rangle\\&=-k_BT\sum_n\sum_{\mathbf{k}',s_1,s_2}V_{s'ss_1s_2}(\mathbf{k},\mathbf{k}')F_{s_1s_2}\left[\frac{\mathbf{q}}{2}+\mathbf{k}',\frac{\mathbf{q}}{2}-\mathbf{k}';i\omega_n\right]\ .\end{aligned} \tag{B8}$$

Let us first consider a homogeneous system. In this case the two momenta in the argument of the Green's function $G_{ss'}(\mathbf{k},\mathbf{k}';i\omega_n)$ have to be equal ($\mathbf{k}=\mathbf{k}'$) and for the anomalous Green's function $F_{ss'}(\mathbf{k},\mathbf{k}')$ to be equal with opposite sign ($\mathbf{k}=-\mathbf{k}'$). Thus the mean field $\hat{\Delta}(\mathbf{k},\mathbf{q})$ in Eq. (B8) becomes independent of $\mathbf{q}$. The one-particle Hamiltonian is supposed to be diagonal in the momentum space (and for simplicity also in the spin space): $\langle \mathbf{k},s|\mathcal{H}_0|\mathbf{k}',s'\rangle=\varepsilon(\mathbf{k})\delta_{\mathbf{k},\mathbf{k}'}\delta_{s,s'}$. Therefore the Gor'kov equations can be written in a much simpler form,

$$[i\omega_n-\varepsilon(\mathbf{k})]G_{ss'}(\mathbf{k},i\omega_n)-\sum_{s''}\Delta_{ss''}(\mathbf{k})F^{\dagger}_{s''s'}(\mathbf{k},i\omega_n)=\delta_{ss'}\ , \tag{B9}$$

$$[i\omega_n+\varepsilon(\mathbf{k})]F^{\dagger}_{ss'}(\mathbf{k},i\omega_n)-\sum_{s''}\Delta^{\dagger}_{ss''}(\mathbf{k})G_{s''s'}(\mathbf{k},i\omega_n)=0\ , \tag{B10}$$

$$[i\omega_n-\varepsilon(\mathbf{k})]F_{ss'}(\mathbf{k},i\omega_n)-\sum_{s''}\Delta_{ss''}(\mathbf{k})G_{s's''}(-\mathbf{k},-i\omega_n)=0\ . \tag{B11}$$

Since the equations are not coupled in the momentum space, they can easily be solved. We find

$$\hat{G}(\mathbf{k},\omega)=-\frac{i\omega_n+\varepsilon(\mathbf{k})}{\omega_n^2+E_{\mathbf{k}}^2}\hat{\sigma}_0\quad\text{and}\quad\hat{F}(\mathbf{k},\omega)=\frac{\hat{\Delta}(\mathbf{k})}{\omega_n^2+E_{\mathbf{k}}^2} \tag{B12}$$

for singlet superconductivity and

$$\begin{aligned}\hat{G}(\mathbf{k},i\omega_n)&=\frac{[\omega_n^2+\varepsilon^2(\mathbf{k})+|\mathbf{d}(\mathbf{k})|^2)]\hat{\sigma}_0+\mathbf{q}\cdot\hat{\boldsymbol{\sigma}}}{(\omega_n^2+E_{\mathbf{k}+}^2)(\omega_n^2+E_{\mathbf{k}-}^2)}[i\omega_n+\varepsilon(\mathbf{k})]\ ,\\\hat{F}(\mathbf{k},i\omega_n)&=\frac{\{\omega_n^2+[\varepsilon^2(\mathbf{k})+|\mathbf{d}(\mathbf{k})|^2]\}\mathbf{d}(\mathbf{k})-i\mathbf{q}\times\mathbf{d}(\mathbf{k})}{(\omega_n^2+E_{\mathbf{k}+}^2)(\omega_n^2+E_{\mathbf{k}-}^2)}\cdot(i\hat{\boldsymbol{\sigma}}\hat{\sigma}_y)\end{aligned} \tag{B13}$$

for triplet superconductivity, where the case of nonunitary states ($\mathbf{d}^*\neq\mathbf{d}$) is included by $\mathbf{q}(\mathbf{k})=i\mathbf{d}(\mathbf{k})\times\mathbf{d}^*(\mathbf{k})$.

Inserting the solution for the anomalous Green's function in Eq. (B8) leads to the self-consistency equation for $\hat{\Delta}(\mathbf{k})$, which is exactly the gap equation as we found it in Eqs. (2.15)–(2.17) if the sum over all ω_n is performed.

For a general inhomogeneous system, the solution of the Gor'kov equations is much more complicated. Equation (B7) can be solved for the anomalous Green's function

$$F_{ss'}(\mathbf{k},\mathbf{k}';i\omega_n)=\sum_{\mathbf{k}'',\mathbf{q}'',s_1,s_2}\Delta_{s_1s_2}(\mathbf{k}'',\mathbf{q}'')G^0_{ss_1}\left[\mathbf{k},\frac{\mathbf{q}''}{2}+\mathbf{k}'';i\omega_n\right]G_{s's_2}\left[\mathbf{k}',\frac{\mathbf{q}''}{2}-\mathbf{k}'';-i\omega_n\right]\ , \tag{B14}$$

where $\hat{G}^0$ is the normal-state Green's function defined by

$$\sum_{\mathbf{k}'',s''}\langle \mathbf{k},s|i\omega_n-\mathcal{H}_0|\mathbf{k}'',s''\rangle G^0_{s''s'}(\mathbf{k}'',\mathbf{k}';i\omega_n)=\delta_{s,s'}\delta_{\mathbf{k},\mathbf{k}'}\ . \tag{B15}$$

We can substitute Eq. (B14) into Eq. (B5) to obtain an equation only for $\hat{G}$.

For temperatures close to $T_c, \hat{\Delta}$ is very small. Then $\hat{G}$ may be replaced by $\hat{G}^0$ in Eq. (B14). With this approximate anomalous Green's function we find the linearized gap equation

$$\Delta_{ss'}(\mathbf{k},\mathbf{q}) = -k_B T \sum_n \sum_{\mathbf{k}',\mathbf{k}'',\mathbf{q}'} \sum_{s_1 s_2 s_3 s_4} V_{s'ss_1s_2}(\mathbf{k},\mathbf{k}') G^0_{s_1s_3}\left[\frac{\mathbf{q}}{2}+\mathbf{k}', \frac{\mathbf{q}'}{2}+\mathbf{k}''; i\omega_n\right] \times G^0_{s_2s_4}\left[\frac{\mathbf{q}}{2}-\mathbf{k}', \frac{\mathbf{q}'}{2}-\mathbf{k}''; -i\omega_n\right]\Delta_{s_3s_4}(\mathbf{k}'',\mathbf{q}') , \tag{B16}$$

which we used in Sec. IV to develop the correlation function formalism. Further expansion in $\hat{\Delta}$ using the normal-state Green's function is the basis of the microscopic derivation for the higher-order terms of the Ginzburg-Landau theory.

Finally, let us consider the interpretation of $\mathbf{k}$ and $\mathbf{q}$ in $\hat{\Delta}(\mathbf{k},\mathbf{q})$. Introducing the field operator $\psi_s(\mathbf{r}) = \sum_{\mathbf{k}} a_{\mathbf{k}s} \exp(i\mathbf{kr})$, we can write the anomalous Green's function in the $\mathbf{r}$ space

$$F_{ss'}(\mathbf{r},\mathbf{r}';\tau) = -\langle T_\tau \psi_s(\mathbf{r},\tau)\psi_{s'}(\mathbf{r}')\rangle = \sum_{\mathbf{k},\mathbf{q}} F_{ss'}\left[\frac{\mathbf{q}}{2}+\mathbf{k}, \frac{\mathbf{q}}{2}-\mathbf{k}; \tau\right] e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} e^{i\mathbf{q}(\mathbf{r}+\mathbf{r}')/2} .$$

Obviously, $\mathbf{k}$ corresponds to the internal degree of freedom of the pairing state (symmetry of the pair wave function), whereas $\mathbf{q}$ is related to the motion of the center of mass $(\mathbf{r}+\mathbf{r}')/2$. From Eq. (B8) it becomes clear that $\mathbf{k}$ in $\hat{\Delta}(\mathbf{k},\mathbf{q})$ represents the internal degree of freedom of the gap function and $\mathbf{q}$ its spatial variation.

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