and superconductivity could both be determined at the same temperatures with two different techniques, namely, Mössbauer effect and mutual inductance.

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Ginzburg-Landau Approach to $L \neq 0$ Pairing*

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By comparing the predictions of the weak-coupling BCS theory with a general Ginzburg-Landau approach, we show that the weak-coupling model may give a qualitatively incorrect description of pairing with $L \neq 0$. Specific examples of the errors the weak-coupling model leads to are described for d- and p-wave pairing. In the latter case the general Ginzburg-Landau approach has structure enough to account for the current discrepancies between the weak-coupling predictions and the observed behavior of the low-temperature transition in liquid He_3.

We wish to point out that the weak-coupling BCS theory lacks sufficient structure to give a general description of the transition to a paired state with any pair angular momentum L other than $L=0$.[1] The possibility of a failure of the weak-coupling model has been raised by the work of Anderson and Brinkman,[2] whose strong-coupling analysis of p-wave pairing leads to an equilibrium state differing drastically from the predictions of the weak-coupling model, and whose properties appear to be more in accord with those of the low-temperature A phase of liquid He_3.[3] It remains to be seen whether the particular expansion of Ref. 2 will fully account for the observed behavior of He_3, but regardless of the ultimate success of that model, it is important to emphasize, at a time when increasingly elaborate applications of the weak-coupling model to $L \neq 0$ pairing are being made or contemplated, that the weak-coupling approach may well give a misleading and quite possibly seriously incorrect description of the transition when $L \neq 0$.

To see why the weak-coupling model is unreliable when $L \neq 0$ (as well as why the difficulty does not arrive for s-wave pairing), one need only compare the weak-coupling form for the free energy near T_c with the general Ginzburg-Landau form.[4] We assume that T is close enough to T_c for the pairing to be in a state characterized by a definite value of L, determined by the most attractive component of the effective pairing interaction. The order parameter is then a complex scalar function of $\hat{k}$, $\Delta_0(\hat{k})$, for even L, and a 2×2 matrix of the form $\vec{\Delta}(\hat{k}) \cdot \vec{\sigma}(i\sigma_y)$, for odd L,

where Δ_0 or the vector $\vec{\Delta}$ are linear combinations of spherical harmonics of degree L.[5] Just below the transition temperature, one must retain terms up to fourth order in the order parameter, not only to stabilize the free energy, *but also to resolve, at least in part, the highly degenerate set of order parameters that become possible at T_c when $L \neq 0$.*

In the weak-coupling model the free energy f_0 has the form

$$f_0 = \int \frac{d\hat{k}}{4\pi}\left[\alpha_0 \begin{Bmatrix} |\Delta_0|^2 \\ \mathrm{Tr}(\Delta^\dagger\Delta) \end{Bmatrix} + \beta_0 \begin{Bmatrix} |\Delta_0|^4 \\ \mathrm{Tr}(\Delta^\dagger\Delta)^2 \end{Bmatrix}\right], \quad (1)$$

where the upper line is for L even, and the lower line for L odd. A more general expansion yields a form with the same quadratic term but in which, except for $L=0$, the quartic term is characterized not by one, but by many independent parameters. We illustrate some of the consequences of this for the theories of d-wave and p-wave pairing.

For $L=2$ the order parameter has the form $\Delta_0 = \sum_{\mu\nu} B_{\mu\nu}\hat{k}_\mu\hat{k}_\nu$, where B is a symmetric complex matrix with zero trace. Because the free energy must be invariant under rotations and gauge transformations, the second-order term must be proportional to $\mathrm{Tr}(B^\dagger B)$. However, there are three linearly independent fourth-order terms,[6] so that f has the general form

$$f = \alpha\,\mathrm{Tr}(B^\dagger B) + \beta_1|\mathrm{Tr}(B^2)|^2 + \beta_2[\mathrm{Tr}(B^\dagger B)]^2 + \beta_3\,\mathrm{Tr}[B^2(B^\dagger)^2]. \quad (2)$$

The weak coupling form (1) corresponds to the special case $\beta_2 = 2\beta_1$, $\beta_3 = 0$.

In the weak-coupling case it can be shown[7] that the free energy assumes its minimum for any B of the form $B = \lambda(B_1 + iB_2)$, where the B_i are real symmetric traceless matrices restricted only by the orthonormality condition $\mathrm{Tr}(B_iB_j) = \delta_{ij}$, and the parameter λ is determined by minimizing f_0 for fixed B_i. The result is a highly degenerate family of order parameters. If one adhered to the weak-coupling model, the next step would be to investigate the sixth-order term (proportional to $\int d\hat{k}|\Delta_0|^6$) to determine the splitting of this degeneracy. This is simply incorrect. The degeneracy is split in fourth order by the term in β_3. Even should β_3 be small, there is no reason for it to vanish identically, and the splitting it produces will be more important than that given by the sixth-order terms just below T_c.

For $L=1$ the matrix Δ is of the form $\sum_{\mu\nu}\sigma_\mu A_{\mu\nu}\times\hat{k}_\nu(i\sigma_y)$, where A is a general complex matrix. If we neglect the weak dipolar interactions,[8] then the underlying Hamiltonian is invariant under rotations in spin space alone, or in k space alone. For the free energy to have this invariance (together with gauge invariance) the second-order term must be proportional to $\mathrm{Tr}(AA^\dagger)$, but there are five linearly independent fourth-order terms consistent with these requirements, giving a free energy of the form

$$f = \alpha\,\mathrm{Tr}(AA^\dagger) + \beta_1|\mathrm{Tr}(A\tilde{A})|^2 + \beta_2[\mathrm{Tr}(AA^\dagger)]^2 + \beta_3\,\mathrm{Tr}[(A\tilde{A})(A\tilde{A})^*] + \beta_4\,\mathrm{Tr}[(AA^\dagger)^2] + \beta_5\,\mathrm{Tr}[(AA^\dagger)(AA^\dagger)^*]. \quad (3)$$

The weak-coupling form (1) corresponds to the special case $-\beta_5 = \beta_4 = \beta_3 = \beta_2 = -2\beta_1$.

When the parameters in (3) have the weak-coupling form, one can prove that f_0 is minimized by real A (yielding Δ proportional to a unitary matrix). The weak-coupling free energy is stationary only when $A\tilde{A}$ is proportional to a one-, two-, or three-dimensional projection operator, the two- and three-dimensional cases being referred to as Anderson-Morel or Balian-Werthamer gaps, respectively. The weak-coupling free energy is always lowest for the three-dimensional projection operator[9] and highest for the one-dimensional one.

In the general case a full analysis of (3) proves more difficult. If one restricts oneself to trial Δ proportional to unitary matrices[10] then f is stationary only for $AA^\dagger$ proportional to one-, two-, or three-dimensional projections. Now, however, the three-dimensional case is most favorable only if

$$\beta_3 + 4(\beta_4 + \beta_5) > 3(\beta_1 + |\beta_1 + \beta_3|). \quad (4)$$

Otherwise the one-dimensional case is most favorable.[11]

Should the inequality (4) be reversed, the nature of the paired state is radically altered. The energy gap $\mathrm{Tr}(\Delta^\dagger\Delta)$, for example, changes from a constant to an anisotropic gap with nodes, yielding a much broader anomaly in the zero-sound attenuation.[12]

In the presence of a magnetic field $\vec{H}$ the invariants that are linear and quadratic in H, to leading order in A have the form[13]

$$i\sum\epsilon_{\mu\nu\lambda}H_\mu(AA^\dagger)_{\nu\lambda},\ \sum H_\mu(AA^\dagger)_{\mu\nu}H_\nu. \quad (5)$$

Close to T_c the term quadratic in H suppresses the Balian-Werthamer type of solution, leading to a diagonal matrix Δ (if the z axis is taken along $\vec{H}$). The quartic terms in f are proportional to

$(\int d\hat{k}/4\pi - \langle\rangle)$

$$\beta_3(|\langle\Delta_\uparrow^2\rangle|^2 + |\langle\Delta_\downarrow^2\rangle|^2) + (\beta_2+\beta_4)(\langle|\Delta_\uparrow|^2\rangle^2 + \langle|\Delta_\downarrow|^2\rangle^2) + (4\beta_1+2\beta_3)|\langle\Delta_\uparrow\Delta_\downarrow\rangle|^2 + 2(\beta_2+\beta_5)\langle|\Delta_\uparrow|^2\rangle\langle|\Delta_\downarrow|^2\rangle + 2(\beta_4+\beta_5)|\langle\Delta_\uparrow\Delta_\downarrow{}^*\rangle|^2. \quad (6)$$

In the weak-coupling case the first two terms become proportional to $\langle|\Delta_\uparrow|^4 + |\Delta_\downarrow|^4\rangle$, and the last three, which couple $\Delta_\uparrow$ and $\Delta_\downarrow$, all vanish. Thus the conclusion of Ambegaokar and Mermin[3] that the spin-up and spin-down populations pair independently in a strong enough field is an artifact of the weak-coupling model, and their description of the phase boundaries near T_c in strong fields must be modified as follows:

The highest transition remains one in which only a single-spin population pairs, with a phase boundary of the form $T_1(H) = T_c + K_1 H$. If one assumes that the second diagonal component of Δ appears via a second-order transition, then the second phase boundary has the form $T_2(H) = T_c + K_2 H$, but, in contrast to the weak-coupling case, $K_2 \neq -K_1$.[14] The splitting of the phase boundary remains linear in H, but is no longer symmetric about a line of constant T. There is some evidence that this is the case in He_3.[15]

It also follows from (5) that the deviation of the zero-field susceptibility from its normal-state form is proportional to $(AA^\dagger)_{zz}$. If $AA^\dagger$ is a three-dimensional projection, this cannot vanish, resulting in a major disparity between the weak-coupling model and the experimental observation that the susceptibility appears unchanged in the "A" phase,[16] suggesting that the coefficients in (3) are such as to stabilize a solution with $AA^\dagger$ one or two dimensional.

We were provoked into extending our investigation of the Ginzburg-Landau theory of $L \neq 0$ pairing beyond its weak-coupling form by a talk on the spin-fluctuation hypothesis at Cornell University by P. W. Anderson. We have since had some useful correspondence with W. F. Brinkman, who also called to our attention an error in an earlier version of the manuscript. We have had continual help and advice from V. Ambegaokar, and many valuable conversations with M. E. Fisher, J. Serene, and P. Wölfle.

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[1]We use the term "weak coupling" in a somewhat different sense from its use in the theory of superconducting metals. To derive the coefficients in the free-energy expansion (or, equivalently, in the gap equation) one must expand the anomalous part of the irreducible self-energy to third order in Δ. A weak-coupling model takes this expansion from $\Sigma = (\delta\Sigma/\delta G)_0 \delta G$, where the subscript 0 indicates evaluation in the normal state, and δG is the deviation of the propagator from its normal state form, taken to third order in Δ to determine the fourth-order free energy. A full third-order expansion, however, also includes third-order contributions from the terms $(1/n)(\delta^n\Sigma/\delta G^n)_0(\delta G)^n$, for $n=2$ and 3. These are the terms that give the additional structure in the free energy when $L \neq 0$.

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[4]We consider only a spatially uniform system in its "classical" critical region.

[5]We assume the energy dependence of Δ is of negligible importance, so that we are not describing a strong-coupling theory in the sense that the term is used in metals physics.

[6]Another fourth-order invariant, $\mathrm{Tr}[(B^\dagger B)^2]$, is linearly dependent on the three given in Eq. (2), because of the relation $|\mathrm{Tr}(B^2)|^2 + 2[\mathrm{Tr}(B^\dagger B)]^2 = 2 \times \mathrm{Tr}[B^\dagger B)^2] + 4\,\mathrm{Tr}(B^{\dagger 2} B^2)$ that any symmetric traceless 3×3 matrix must satisfy. With the aid of this identity it is straightforward to show that the weak-coupling free energy (1) has the form (2) with $\beta_3 = 0$, from which the features of the best weak-coupling Δ_0 follow directly.

[7]The solution was discovered by V. J. Emery (private communication). We derived it by exploiting the identity given in note 6, above, and it has been found independently by G. Barton and M. A. Moore, to be published.

[8]They must ultimately be considered as a perturbation that further reduces the degeneracy of the equilibrium state.

[9]This was first proved by Balian and Werthamer, Ref. 3.

[10]A unitary gap matrix implies no spontaneous magnetization in the paired phase, but no spontaneous magnetization implies only that $AA^\dagger$ is real [see Eq. (5)]. Outside of the weak-coupling model, the unitary assumption should be viewed with suspicion.

[11]We are grateful to W. F. Brinkman for telling us of an observation of P. W. Anderson on the best unitary

gap in the one-dimensional case.

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[13]These were derived by Ambegaokar and Mermin (Ref. 3) from the weak-coupling model, but to leading order in A the deficiencies of that model that we are concerned with do not arise. Within the calculation of Ref. 3, the existence of the term linear in H depends on a violation of "particle-hole symmetry" and a second quadratic term $H^2\,\mathrm{Tr}(AA^\dagger)$ is found to be negligibly small.

[14]For some values of the coefficients the second second-order phase boundary is suppressed completely.

[15]R. C. Richardson, private communication. Measurements of the ratio of the slopes of the split phase boundary and of the specific-heat discontinuities would be of great value in reducing the range of possible coefficients in the p-wave free energy.

[16]This difficulty was first pointed out by A. J. Leggett, and motivated the Anderson-Brinkman hypothesis that spin fluctuations play an important role.

$Al_{10}V$: An Einstein Solid

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Low-temperature specific-heat and electrical-resistivity measurements show that the intermetallic compound $Al_{10}V$ has a local soft mode of characteristic temperature 22°K. The behavior is well described by an Einstein model. The number of such modes, taken together with x-ray evidence, indicates that the mode is associated with a loose Al atom occupying a large hole in the $Al_{10}V$ structure. This and other peculiarities of the structure provide evidence of important bonding effects.

Truly localized vibrational modes are unusual in solids because of strong interatomic coupling; in this Letter we present experimental evidence for the existence of sharply defined local modes in the intermetallic compound $Al_{10}V$ that are well-described by an Einstein[1] model with a characteristic temperature of 22°K. To the best of our knowledge this is the lowest such characteristic temperature to have been found in a metal.

Samples of $Al_{10}V$ were prepared by arc melting 99.9+%-purity vanadium and 99.999+%-purity aluminum under an argon atmosphere; flat-bottomed buttons of weight 1 g were made for specific-heat measurements, and cast rods of 3 mm diameter and 30 mm length for electrical-resistivity measurements. After homogenization at 665°C for 80 h all samples were better than 95% single phase. Specific-heat measurements were performed on two samples, numbers 1 and 2; the vibrational specific heat of sample 2 had the same functional temperature dependence as 1 but was 15% smaller in magnitude. Samples number 3 and 4 were used for the electrical-resistivity measurements.

The measured low-temperature specific heat and electrical resistivity of our samples are shown in Figs. 1 and 2; in order to provide a yardstick we have included data for the compound Al_9Co_2, whose behavior is typical of all the other aluminum-rich aluminum–transition-metal intermetallics that we have investigated.[2] The extraordinary behavior of $Al_{10}V$ is immediately apparent, with the temperature dependences being 2 to 3 orders of magnitude greater than those for Al_9Co_2. Such a rapid increase with temperature indicates the presence of a low-lying vibrational mode, and our specific-heat data are well-fitted by the Einstein formula

$$C = C_E + \gamma T, \qquad C_E = 3N_I k_B \left(\frac{\Theta_E}{T}\right)^2 \frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T)-1]^2}, \tag{1}$$

with an Einstein temperature Θ_E of 22 ± 2°K, and a density of local (three-dimensional) oscillators N_I equivalent to 0.11 ± 0.03 per $Al_{10}V$ formula unit. The Einstein formula is an extremely sensitive function of Θ, so that although we are uncertain