Evidence for anisotropic pairing in $YBa_2Cu_3O_{7-\delta}$ from the Landau theory of fluctuation specific heat

James F. Annett, Mohit Randeria, and S. R. Renn
Department of Physics and Material Research Laboratory, University of Illinois, 1110 W. Green St., Urbana, Illinois 61801
(Received 19 April 1988)

Recently, Inderees *et al.* have observed inverse-square-root behavior of specific heat of $YBa_2Cu_3O_{7-\delta}$ near T_c corresponding to Gaussian fluctuations. We analyze their results using the most general Landau theories of superconductivity that are consistent with either orthorhombic or tetragonal crystal symmetry. In particular, we calculate the amplitude ratio C_+/C_-, where $C(T)=C_\pm|T-T_c|^{-1/2}$ and the coefficients C_+ and C_- are associated with the behavior of $C(T)$ above and below T_c, respectively. We conclude that the value of the amplitude ratio observed experimentally is inconsistent with ordinary *s*-wave pairing. For an orthorhombic crystal only triplet superconductivity is possible. Assuming tetragonal symmetry we find that either triplet pairing or some *d*-wave singlet states are allowed. The latter must have an order parameter transforming like d_{xz}, d_{yz}. This singlet case lies within the experimental bounds only if the anisotropic gradient terms satisfy certain conditions, which we discuss in terms of microscopic models.

I. INTRODUCTION

Recently Salamon and co-workers[1,2] have measured the specific heat of the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ close to T_c. They observe, in addition to the usual mean-field discontinuity, a correction proportional to $|t|^{-1/2}$ where $t\equiv(T-T_c)/T_c$. Such a temperature dependence is a general consequence of Gaussian fluctuations of the order parameter in a Landau theory in three dimensions. In ordinary bulk superconductors these effects are negligible; however, they become observable in $YBa_2Cu_3O_{7-\delta}$ because of the very short coherence length ($\xi_0\sim 10$ Å). Inderhees *et al.* have compared their results to the predictions of the Gaussian fluctuation theory for the $O(n)$ symmetric Ginzburg-Landau free-energy functional in *d* dimensions. The standard result[3] for the specific heat of this model, near T_c, is $C(T)=C_{MF}(T)+C_G(T)$ where C_{MF} is the mean-field contribution exhibiting a discontinuity and $C_G=C_\pm|t|^{-2+d/2}$ are the Gaussian fluctuation corrections above and below T_c, respectively. In particular, the amplitude ratio C_+/C_- is $n/2^{d/2}$ for this model.[4] For more general Ginzburg-Landau theories it is convenient to think of this amplitude ratio as defining an effective order-parameter dimensionality n_{eff} by $n_{eff}=2^{d/2}C_+/C_-$. Now the major conclusions of Inderhees *et al.* are that (a) $YBa_2Cu_3O_{7-\delta}$ exhibits three-dimensional superconductivity and (b) the effective dimensionality n_{eff} is bounded by $5<n_{eff}<9$. Indeed, for the best sample they found $6<n_{eff}<8$. Such a large value of n_{eff} is surprising since it is inconsistent with the simplest Landau theory, corresponding to *s*-wave pairing, as for example in the usual Bardeen-Cooper-Schrieffer theory, which has a single complex order parameter (i.e., $n=2$).

We have analyzed this experimental result in terms of the most general Landau theories consistent with singlet or triplet pairing in either an orthorhombic or tetragonal lattice. We show below that while the amplitude ratio C_+/C_- is not in general universal in the Gaussian fluctuation regime, its measured value severely constrains the form of the allowed order parameter. In particular, ordinary *s*-wave pairing cannot agree with the experimental data. Indeed for orthorhombic lattices only triplet pairing with negligible spin-orbit coupling is consistent with the experiment. For tetragonal symmetry we find both singlet and triplet states which are allowed. The singlet states have a (d_{xz},d_{yz})-type order parameter. Furthermore, these states only fall within the experimental bounds provided the anisotropic gradient terms satisfy certain conditions, which we shall discuss below.

It is important to stress that these results are completely general and do not depend on the microscopic theory of the superconductivity, the form of the Landau theory being entirely a consequence of the crystal symmetry. The only significant assumptions we are making are first, the neglect of accidental degeneracies or further symmetries which might be present due to the microscopic mechanism for superconductivity.[5] Second, we shall assume that the experimental data do indeed correspond to Gaussian fluctuation effects; i.e., we assume that the observed $C(T)$ divergences are not due to critical fluctuations, which would imply non-Gaussian exponents. This is reasonable since the Ginzburg region[3] where critical effects are important would be outside the experimental range of $|t|>3\times10^{-3}$ assuming a coherence volume $\xi_0^3\geq 10^3$ Å^3 [taking the discontinuity in $C_{MF}(T)$ as 14 mJ/cm^{3}K (Ref. 1)].

The rest of the paper is organized as follows. In Sec. II we briefly review a standard method for classifying the possible superconducting order parameters in the presence of crystalline anisotropy and for obtaining the corresponding Landau theory. In Sec. III we show how to compute the C_+/C_- amplitude ratio for an arbitrary Ginzburg-Landau free energy. In Sec. IV we discuss superconductors with orthohombic symmetry. Here we show that the only case which allows $n_{eff}>2$ is triplet pairing without spin-orbit coupling. In Sec. V we analyze the case of tetragonal symmetry. We find that the only allowed singlet superconductor has "d-wave" pairing and requires certain special anisotropic stiffness coefficients in order to have a large enough C_+/C_-. We then list those triplet superconductors consistent with tetragonal symmetry which permit sufficiently large C_+/C_-. In Sec. VI we discuss, within a simple class of models, the angular dependence of the anisotropic gap function which could result in the enhanced stiffness coefficients required for the "d-wave" singlet case discussed above. Finally, in Sec. VII, we conclude with some comments on the evidence for anisotropic superconductivity from other experiments and summarize our results.

II. LANDAU THEORY AND POINT-GROUP SYMMETRIES

We begin our discussion with a brief review of Landau theories for superconductors in the presence of crystalline anisotropy. Such a program has been pursued in detail in the context of heavy-fermion systems by a number of authors[6–8] and recently a classification of the possible phases of the high-temperature superconductors has been given by Sigrist and Rice.[9] The order parameter for superconductivity is given by the pairing matrix $F_{\alpha\beta}(\mathbf{k}) = \langle c_\alpha(\mathbf{k}) c_\beta(-\mathbf{k})\rangle$, where $\mathbf{k}$ lies on what is, in general, a multisheeted nonspherical Fermi surface and where α,β are spin indices (or pseudospin indices in the presence of spin-orbit coupling). It is usual to also introduce $A_0(\mathbf{k})$ and $\mathbf{A}(\mathbf{k})$, where

$$F_{\alpha\beta} = -i(A_0(\mathbf{k})I + \mathbf{A}(\mathbf{k})\cdot\sigma)\sigma_y. \qquad (1)$$

With this definition $A_0(\mathbf{k})$ transforms as a scalar under rotations and $\mathbf{A}(\mathbf{k})$ transforms as a vector. Now, the group classification of phases is possible because close to T_c the gap equation can be linearized, giving a matrix equation from which the transition temperature is determined by the highest eigenvalue.[6] The order parameter at T_c must therefore transform according to an irreducible representation of the relevant symmetry group. (This property can also be inferred directly from the Landau theory without any microscopic knowledge of the order parameter, since in any Ginzburg-Landau free energy the quadratic term has the general form $\alpha_{mn}A_m^* A_n$ and the transition temperature is determined by the first negative eigenvalue of the matrix α_{mn}.) Singlet and triplet states can now be distinguished by parity; since $A_0(\mathbf{k})$ and $\mathbf{A}(\mathbf{k})$ are even and odd under spatial inversion, respectively, we can assume that for crystals with an inversion symmetry either $A_0(\mathbf{k})$ or $\mathbf{A}(\mathbf{k})$ but not both will become unstable at the transition.

The above implies that close to T_c, the ony significant thermal fluctuations are of the form

$$A_0(\mathbf{k}) = \sum_m \eta_m \psi_m^\Gamma(\mathbf{k}) \qquad (2)$$

for singlet superconductors, and

$$\mathbf{A}(\mathbf{k}) = \sum_m \eta_m \boldsymbol{\psi}_m^\Gamma(\mathbf{k}) \qquad (3)$$

for triplets, where $\psi_m^\Gamma(\mathbf{k})$ and $\boldsymbol{\psi}_m^\Gamma(\mathbf{k})$ are sets of modes corresponding to irreducible representation Γ of the symmetry group. For singlet superconductors the symmetry group will be $G\times T\times \mathrm{U}(1)$, where G is the point group, T is time reversal, and U(1) is gauge symmetry. For triplet superconductors the group is either $G\times T\times\mathrm{U}(1)$ if there is significant spin-orbit interaction, or else $G\times T\times \mathrm{U}(1)\times \mathrm{O}(3)$ if there is no spin-orbit interaction. In this latter case the unstable modes will have the following form:[6]

$$[\mathbf{A}(\mathbf{k})]_\mu = \sum_{\mu m} \eta_{\mu m}\psi_m^\Gamma(\mathbf{k}) \qquad (4)$$

for $\mu = 1,\ldots,3$. Therefore, for the purposes of constructing a classical partition function, one may write the Ginzburg-Landau free-energy functional, or coarse-grained effective Hamiltonian, $H[\eta]$, as a functional of $\eta_m(\mathbf{r})$ or $\eta_{\mu m}(\mathbf{r})$ which are to be treated as slowly varying. Near the transition one may, therefore, expand $H[\eta]$ in the form

$$H[\eta]/T = \int d^d r [\tfrac{1}{2}K_{ijab}\partial_i\eta_a^*\partial_j\eta_b - \alpha\eta_a^*\eta_a + \sum_i \beta_i R_i(\eta)] , \qquad (5)$$

where $R_i(\eta)$ denote a maximal set of invariant quartic polynomials and T_{ijnl} are the stiffness coefficients. Explicit expressions for the free energies consistent with orthorhombic and tetragonal crystal symmetries have been given by Volovik and Gorkov, and by Ozaki, Machida, and Ohmi,[8] which we shall consider in turn below. We shall also make use of the group-theoretic classification for the possible order parameters of the high-temperature superconductors by Sigrist and Rice.[9]

III. THE AMPLITUDE RATIO C_+/C_-

In this section we will obtain a general expression for the Gaussian fluctuation contribution to the specific heat for an arbitrary Ginzburg-Landau free-energy functional of the type considered above. Let η_a, $a=1,\ldots,n$ be an n-component real order parameter. To compute the Gaussian fluctuations, it is necessary to expand the effective Hamiltonian to quadratic order in deviations $\eta_a(\mathbf{r})$ from its minimum. Above T_c this is trivial; below T_c one expands around the broken symmetry state. It is convenient to write the result in terms of the Fourier-transformed variables:

$$H[\eta]/T = \tfrac{1}{2}\sum_{\mathbf{q}} \eta_a^*(\mathbf{q})[q^2 K_{ab}(\hat{q}) + |t|M_{ab}^{\pm}]\eta_b(\mathbf{q}) , \qquad (6)$$

where $t\equiv(T-T_c)/T_c$, $\hat{q}$ is a unit vector in the $\mathbf{q}$ direction, summation over repeated indices is assumed, and an irrelevant additive constant is dropped. Here $K(\hat{q})$ is the stiffness matrix, which in general is anisotropic, and $M^{\pm}$ is the mass matrix above and below the transition, respectively.

The free energy F of the system is given by the functional integral

$$\exp(-F/T) = \int D\eta_a^*(\mathbf{q})D\eta_a(\mathbf{q})\exp(-H[\eta]/T) . \qquad (7)$$

We thus obtain

$$F = F_0^{\pm} + \frac{T}{2}\int \frac{d^dq}{(2\pi)^d} \mathrm{Tr}\ln[q^2K(\hat{q}) + |t|M^{\pm}] . \quad (8)$$

The $t^{-2+d/2}$ singularity in the specific heat due to Gaussian fluctuations is then found from

$$C(t) = \frac{1}{2}\int \frac{d^dq}{(2\pi)^d} \mathrm{Tr}\{[q^2K(\hat{q}) + |t|M^{(\pm)}]^{-1}M^{(\pm)}\}^2 . \quad (9)$$

Let $\lambda_a^{(\pm)}(\hat{q})$, $a=1,\ldots,n$ be the eigenvalues[10] of $K^{-1}(\hat{q})M^{(\pm)}$, respectively. The amplitude ratio of interest, in $d=3$ dimensions, is given by

$$\frac{C_+}{C_-} = \frac{\int d\Omega_q \sum_{a=1}^{n}[\lambda_a^{(+)}(\hat{q})]^{3/2}}{\int d\Omega_q \sum_{a=1}^{n}[\lambda_a^{(-)}(\hat{q})]^{3/2}} . \quad (10)$$

For the simplest case of an n-component Ginzburg-Landau theory with the full $O(n)$ symmetry, both K and M^+ are proportional to the $(n\times n)$ unit matrix, and M^- is a projector along the broken symmetry direction (with magnitude twice the eigenvalue of M^+). This immediately leads to the result stated earlier, that for the $O(n)$ model $C_+/C_- = n/(2)^{3/2}$.

Corrections to this result due to electromagnetic terms in the free energy have been investigated by Goldenfeld and Pethick.[11] They find, however, that the extra contribution to C_+/C_- is smaller by a factor of κ^{-d}, and thus is negligible for the high-temperature superconductors which have an Abrikosov parameter $\kappa \sim 50$.

IV. ORTHORHOMBIC SUPERCONDUCTORS

$YBa_2Cu_3O_{7-\delta}$ has an orthorhombic (D_{2h}) crystal structure and thus we first analyze order parameters consistent with this symmetry. For singlet pairing and also for triplet pairing in the presence of large spin-orbit coupling, the only allowed representations are one dimensional (see, e.g., Sigrist and Rice[9]). In each case, the effective number of order components is two, giving $C_+/C_- = 2/2^{3/2}$, which is incompatible with the experimental results.

We are thus forced to turn to the case of triplet pairing ($S=1$) without spin-orbit coupling. Here again the p-wave order parameter breaks up into three one-dimensional representations (Γ_2^-, Γ_3^-, Γ_4^-, or B_{2u}, B_{1u}, B_{3u}) due to the low crystalline symmetry (using the notation of Sigrist and Rice or of Tinkham,[12] respectively). However, in each case the existence of three independent spin degrees of freedom, as well as the phase, leads to an order parameter with six (real) components. Thus, as shown below, one can obtain amplitude ratios corresponding to a maximum value of $n_{\mathrm{eff}} = 6$.

The Landau theories, and thus the C_+/C_- calculations, for the three cases of interest are formally identical, so we shall give the results only for the Γ_3^- representation. As described in Sec. II above, the order parameter is represented by $A_\mu(\mathbf{k}) = \eta_{\mu,3}k_z$ (the other two representations have k_z replaced by k_x and k_y, respectively). The corresponding Ginzburg-Landau free-energy functional is[8]

$$H[\eta]/T = -\alpha\eta_{\mu,3}\eta_{\mu,3}^* + \beta_1\eta_{\mu,3}\eta_{\mu,3}^*\eta_{\nu,3}\eta_{\nu,3}^* + \beta_2\eta_{\mu,3}\eta_{\mu,3}\eta_{\nu,3}^*\eta_{\nu,3}^* + \frac{1}{2m}\partial_i\eta_{\mu,3}\partial_i\eta_{\mu,3}^* . \quad (11)$$

For $-1 < b \equiv \beta_2/\beta_1 < 0$, the free-energy minimum below T_c is $\eta_{\mu,3} = \Delta_0(1,0,0)$ with $\Delta_0^2 = \alpha/2(\beta_1+\beta_2)$. Expanding about this minimum to find the mass matrix $M^{(-)}$ and using the formalism of Sec. III, we find

$$C_+/C_- = \frac{6(1-|b|)^{3/2}}{(2)^{3/2}[(1-|b|)^{3/2}+2|b|^{3/2}]} \quad (-1<b<0) . \quad (12)$$

On the other hand, for $b \equiv \beta_2/\beta_1 > 0$, the free-energy minimum below T_c is $\eta_{\mu,3} = \Delta_0(1/\sqrt{2})(1,i,0)$ with $\Delta_0^2 = \alpha/2\beta_1$. In this case the amplitude ratio is given by

$$C_+/C_- = \frac{6}{(2)^{3/2}(1+2b^{3/2})} \quad (b>0) . \quad (13)$$

We find that, in both the phases, C_+/C_- is nonuniversal, with $0 \le n_{\mathrm{eff}} \le 6$, depending on the ratio $b = \beta_2/\beta_1$ of the quartic coefficients. Note that in the Gaussian fluctuation regime, one does not in general expect universal amplitude ratios, in contrast to the critical region.[13] C_+/C_- takes its maximum value, corresponding to an $n_{\mathrm{eff}} = 6$ for $b=0$, where the Landau theory has full $O(6)$ symmetry and $M^{(-)}$ has five zero eigenvalues for the Goldstone modes. For $b \ne 0$, in both phases, two of these modes acquire a nonzero mass, contribute to C_-, and hence reduce the amplitude ratio. Indeed, this is quite generally true, in any case where the stiffness matrix is proportional to the $n\times n$ unit matrix then C_+/C_- is bounded above by $n/2^{d/2}$.

V. TETRAGONAL SUPERCONDUCTORS

We now turn to the case of tetragonal superconductors with D_{4h} symmetry. The motivation for this, in the present context, is the following. While the 1:2:3 superconductor has orthorhombic symmetry, the amount by which it deviates from tetragonality is small ($\delta a/a \sim 0.02$). In fact a large class of the proposed microscopic mechanisms relies on pairing within the CuO_2 planes which are very close to tetragonality. One can crudely estimate the splitting δT_c in the transition temperatures of two representations derived from a single tetragonal representation under the orthrohombic distortion as $\delta T_c \sim |B(\partial T_c/\partial p)(\delta a/a)|$. Using the measured values of these parameters,[14] we find $\delta T_c/T_c \sim 0.03$. If $\delta T_c/T_c \ll t$, where t is in the reduced temperature range over which the Gaussian fluctuations are seen, then one would expect to see a transition corresponding to a representation of the tetragonal group. We have been unable to determine conclusively whether transition should have tetragonal or orthorhombic symmetry since our crude estimate puts $\delta T_c/T_c$ inside the experimental range $(0.003<t<0.05)$. In any case, it does not rule out the possibility of the tetragonal phases.

A. Singlet pairing

Let us first look at singlet pairing. The only irreducible representation of D_{4h} which is not one dimensional (and therefore has more than two real components) is Γ_5^+ (or E_g). The "d-wave" order parameter has two complex ($\equiv$four real) components (η_x, η_y). The corresponding Ginzburg-Landau free-energy functional is given by[8]

$$H[\eta]/T = \frac{1}{2m_1'}(|\partial_x\eta_x|^2+|\partial_y\eta_y|^2)+\frac{1}{2m_1''}(|\partial_y\eta_x|^2+|\partial_x\eta_y|^2)+\frac{1}{2m_2}(|\partial_z\eta_x|^2+|\partial_z\eta_y|^2)$$
$$+\frac{1}{4m_3'}(\partial_x\eta_y\partial_y\eta_x^*+\text{c.c.})+\frac{1}{4m_3''}(\partial_x\eta_x\partial_y\eta_y^*+\text{c.c.})+V(\eta)\,, \tag{14}$$

where

$$V(\eta) = -a\eta_i\eta_i^*+\beta_1(\eta_i\eta_i^*)^2+\beta_2|\eta_i\eta_i|^2+\beta_3(|\eta_x|^4+|\eta_y|^4)\,. \tag{15}$$

Notice that for a particular choice of parameters, namely, $m_1'=m_1''=m_2$; $(m_3')^{-1}=(m_3'')^{-1}=0$, so that the stiffness matrix is proportional to the unit matrix, and $\beta_2=\beta_3=0$, we recover the O(4) model. One might then be tempted to conclude (in analogy with the results of Sec. IV) that the maximum attainable C_+/C_- ratio is that corresponding to $n_{\text{eff}}=4$. This is not correct, as we shall now show. The basic point is that, while the additional quartic terms always lower the amplitude ratio from its value for the pure $O(n)$ symmetric theory, the anisotropic stiffness terms can, and do, increase n_{eff}.

The free energy of Eq. (14) has three inert phases: $\eta=\eta(1,0)$ (for $\beta_3<0, 2\beta_2<-\beta_3$), $\eta=\eta(1,1)$ (for $\beta_3>0, \beta_2<0$), and $\eta=\eta(1,i)$ (for $\beta_2>0, 2\beta_2>-\beta_3$), with the domains over which they represent free-energy minima shown in parentheses. In addition, the quartic coefficients must satisfy the stability conditions: $\beta_1>0$, $\beta_1+\beta_2+\beta_3/2>0$, $\beta_1+\beta_2+\beta_3>0$, and $\beta_1+\beta_3/2>0$.

For arbitrary Ginzburg-Landau coefficients, calculation of C_+/C_- [using Eq. (10)] requires numerical integration since the eigenvalues of $K^{-1}(\hat{q})M^{(\pm)}$ have nontrivial dependence on $\hat{q}$. However, several limiting cases can be worked out analytically.

First, consider the case when $m_1'=m_1''$; $(m_3')^{-1}=(m_3'')^{-1}=0$, so that the stiffness matrix is diagonal. For arbitrary values of the quartic coefficients in the $(\beta_2/\beta_1, \beta_3/\beta_1)$ plane, i.e., for all the three phases, we find (see Fig. 1) that $0\le C_+/C_-\le 4/2^{3/2}$. The maximum value, corresponding to $n_{\text{eff}}=4$, is obtained at $(\beta_2/\beta_1, \beta_3/\beta_1)=(0,0)$ when the free energy has full O(4) symmetry. Away from the origin, the amplitude ratio decreases as some the Goldstone modes acquire a mass. The minimum value (zero) is obtained on the instability lines. These results are analogous to those obtained in Sec. V for the orthorhombic phases.

We now turn to the effect of anisotropic gradient terms on C_+/C_-. The stiffness matrix $K(\hat{q})$ is no longer diagonal. It is convenient to rescale lengths in the (x,y) plane, and along the z axis, so as to choose $[(m_1')^{-1}+(m_1'')^{-1}]/2=1$ and $(m_2)^{-1}=1$, respectively. Then $K(\hat{q})$ is characterized by two parameters:[15]

$$c_1\equiv[(m_1')^{-1}-(m_1'')^{-1}]/2$$

and

$$c_3\equiv[(m_3')^{-1}+(m_3'')^{-1}]/4.$$

Now K develops a zero eigenvalue (signaling an instability of the system) when $c_1^2(\hat{q}_x^2-\hat{q}_y^2)^2+4c_3^2(\hat{q}_x\hat{q}_y)^2=1$, which will occur for some $\hat{q}$ when $c_1=1$ or $c_3=1$. Since the eigenvalues of $K^{-1}M$ determine the amplitude ratio, one might expect problems when the stiffness matrix becomes noninvertible.

To simplify the discussion, we set $\beta_2=\beta_3=0$ since we understand the role of these quartic coefficients will be to increase C_-. Actually we take a limit that approaches the origin from one of the three phases. For the (1,0) phase, we have plotted the contours of constant n_{eff} in the (c_3, c_1) plane in Fig. 2. We find that $n_{\text{eff}}\ge 4$ and takes its maximum value at $(c_3, c_1)=(1,0)$. Doing the C_+/C_- integrals analytically, as $c_3\to 1$ along the c_3 axis, we find that both C_+ and C_- diverge with a finite ratio corresponding to $n_{\text{eff}}=4\sqrt{2}$. Similar results are obtained for the (1,1) and $(1,i)$ phases, with again $n_{\text{eff}}\le 4\sqrt{2}$, although the contours of n_{eff} are different in each case; see Figs. 3 and 4.

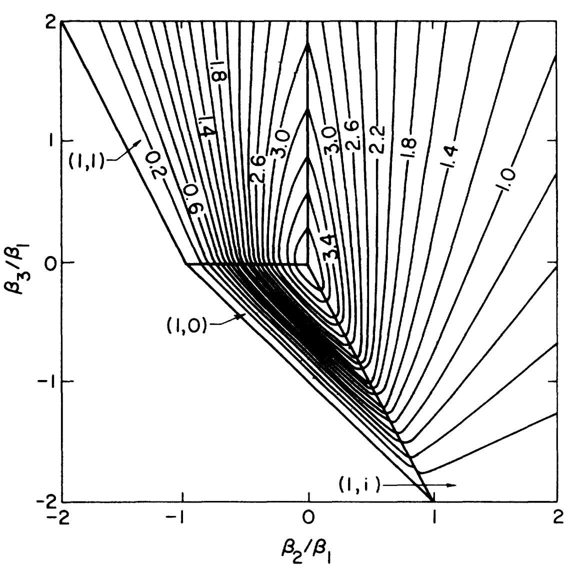

FIG. 1. Effective order-parameter dimensionality n_{eff} for the singlet tetragonal Γ_5^+ phases as a function of Ginzburg-Landau parameters β_2/β_1 and β_3/β_1 of Eq. (15). Here we set $c_1\equiv[(m_1')^{-1}-(m_1'')^{-1}]/2=0$ and $c_3\equiv[(m_3')^{-1}+(m_3'')^{-1}]/4=0$. Note that n_{eff} attains its maximum value of 4 at the origin and tends to zero at the instability lines.

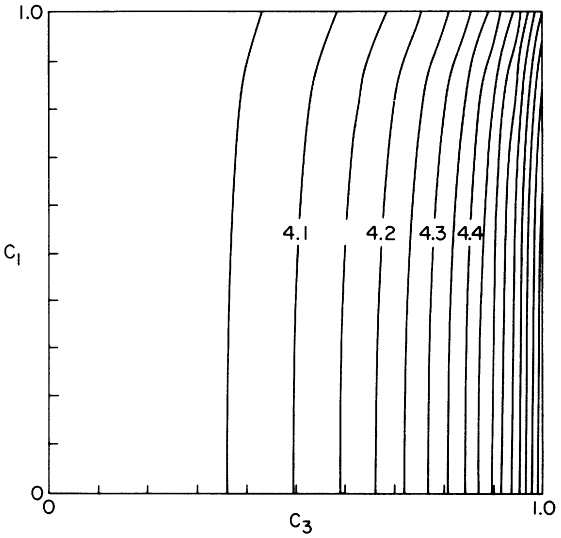

FIG. 2. Effective order-parameter dimensionality, n_{eff} for the singlet tetragonal Γ_5^+ (1,0) phase, as a function of Ginzburg-Landau parameters of Eq. (14): $c_1 \equiv [(m_1')^{-1} - (m_1'')^{-1}]/2$ and $c_3 \equiv [(m_3')^{-1} + (m_3'')^{-1}]/4$. Here we set $\beta_2 = \beta_3 = 0$. n_{eff} approaches a maximum value of $4\sqrt{2} = 5.65$ at $(c_3, c_1) = (1,0)$.

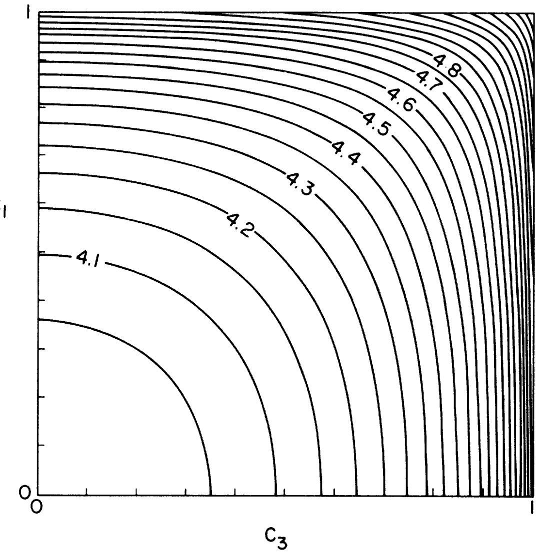

FIG. 4. As for Fig. 2, but for the Γ_5^+ $(1,i)$ phase. Here $n_{\text{eff}} = 4\sqrt{2}$ on the lines $c_1 = 1$ and $c_3 = 1$.

Thus although the order parameter corresponding to the tetragonal Γ_5 representation has four real components, the n_{eff} can be larger than four, and, in fact, we obtain the bound $n_{\text{eff}} \leq 4\sqrt{2} = 5.65$. The largest n_{eff} obtained here is close to, but below, the experimental lower bound on the best sample. This, however, is the only singlet superconductor which can possibly have $n_{\text{eff}} > 2$.

The upper bound occurs, as shown above, only when the anisotropic gradient terms are such as to give near vanishing eigenvalues for the stiffness matrix. In the following section, we discuss, within the simple class of microscopic models, a possible mechanism for obtaining such anisotropic gradient terms. In the remainder of this section, we list, for completeness, the triplet tetragonal superconductors which are consistent with observed amplitude ratio.

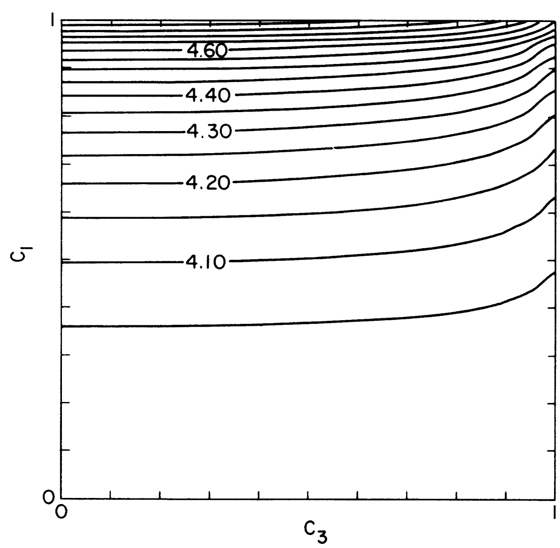

FIG. 3. As for Fig. 2, but for the $\Gamma_5^+(1,1)$ phase. Here n_{eff} is $4\sqrt{2}$ at $(c_3, c_1) = (0,1)$.

B. Triplet pairing

For the case of strong spin-orbit scattering the only odd-parity irreducible representation of the tetragonal group which has more than two order-parameter components is Γ_5^- (or E_u). The C_+/C_- analysis is identical to the one presented above for Γ_5^+.

When spin-orbit coupling is weak, the tetragonal triplet superconductors correspond to the two-dimensional Γ_5^- (or E_u) representation and the one-dimensional Γ_2^- (or A_{2u}) representation. The order parameter in the latter case has six [=1(orbital) ×3(spin)×2(phase)] real components and the free energy is the same as Eq. (11). The C_+/C_- analysis for the Γ_2^- case then parallels the one given in Sec. IV.

The order parameter transforming under the Γ_5^- representation has twelve real components. The free-energy functional given by Ozaki *et al.*[8] has seven allowed quartic invariants, in addition to anisotropic gradient terms. There are eight inert states, as discussed by Ozaki *et al.*, and a separate C_+/C_- analysis would be required for each one. The large number of Ginzburg-Landau parameters does not make a very detailed study worthwhile; however, the following remarks can be made under quite general grounds. In the absence of anisotropic stiffness coefficients [i.e., when the stiffness matrix K has full O(12) symmetry after appropriate rescaling of lengths] $n_{\text{eff}} \leq 12$. Also, $n_{\text{eff}} \to 0$ at the instability boundaries in β_i parameter space (as in Fig. 1); therefore n_{eff} can have any value between 0 and 12. Thus, certainly there are regions of parameter space which will be consistent with the experimental bounds $5 < n_{\text{eff}} < 9$.

VI. PARTICLE-HOLE SYMMETRY AND ANISOTROPIC STIFFNESS CONSTANTS

In Sec. V A we found that the only singlet states which could give $n_{\rm eff} > 2$ were the tetragonal Γ_5 phases, and that this required certain highly anisotropic stiffness coefficients. It is clear that one requires some microscopic analysis to determine the plausibility of achieving such large C_+/C_- values for any of these phases. In this section we will argue that the Γ_5 phases of the simplest models of copper oxide superconductors have an additional (particle-hole) symmetry[10,16] which leads to the required anisotropic stiffness constants.

For simplicity let us consider the model electronic Hamiltonian on a tetragonal bravais lattice:

$$H = \sum_{\langle i,j\rangle,\sigma} t_{ij} C_{i\sigma}^{\dagger} C_{j\sigma} + \sum_{i,j,l,n} V_{ijln} C_{i\uparrow}^{\dagger} C_{j\uparrow}^{\dagger} C_{l\uparrow} C_{n\downarrow} , \quad (16)$$

where $t_{ij} = t$ if i,j are nearest-neighbor intraplanar sites, $t_{ij} = t_\perp$ for nearest-neighbor interplanar sites, and $t_{ij} = 0$ otherwise. We have also introduced Wannier basis matrix elements V_{ijln} which correspond to some attractive singlet potential. By assuming that only nearest-neighbor hopping occurs in the single-particle Hamiltonian we are only considering models with a single square Fermi surface.

Now consider the linearized gap equation associated with the above model:

$$\omega \psi_n(\mathbf{k}) = -\int dS_{k'} n(\hat{\mathbf{k}}') V(\mathbf{k},\mathbf{k}') \psi_n(\mathbf{k}') , \quad (17)$$

where the integration is over the Fermi surface of the above model, $n(\hat{k}) dS_k$ is the number of states per unit energy in a k-space shell with energy thickness ω_c and of area dS_k centered around k on the Fermi surface, and where

$$V(\mathbf{k},\mathbf{k}') = N^{-2} \sum_{n,n'} \sum_{m,m'} \exp[-i\mathbf{k}(\mathbf{R}_n - \mathbf{R}_{n'}) + i\mathbf{k}'(\mathbf{R}_{m'} - \mathbf{R}_m)] V_{nn'mm'} . \quad (18)$$

The transition temperature is, in the weak-coupling limit related to the largest eigenvalue ω by $T_c = 1.14\omega_c \times \exp(-1/\omega)$. At half-filling the square-shaped Fermi surface of the above model becomes perfectly nested as $t_\perp \to 0$. Furthermore, in the limit of tightly bound atomic orbitals the matrix elements V_{ijln} for $i \neq n$ or $j \neq l$ will be negligibly small. In the simultaneous limit when the band is half filled, $t_\perp \to 0$ and when the above matrix elements vanish (which we shall call the "particle-hole symmetric" limit following Sigrist and Rice[9]), the linearized gap equation acquires an additional symmetry[9,16] not associated with the point group D_{4h}. Consider the reciprocal lattice translation T defined by $T\psi(\mathbf{k}) = \psi(\mathbf{k}+\mathbf{Q})$, where $\mathbf{Q} = \pi/a(1,1,0)$ and where $\psi(\mathbf{k}+\mathbf{G}) = \psi(\mathbf{k})$ for any reciprocal lattice vector. The operation IT, where I is the inversion operator, flips edges and leaves the square-shaped Fermi surface invariant (see Fig. 5). To see that IT is, in fact, a symmetry of the linearized gap equation in the above limit, observe that $V(\mathbf{k}+\mathbf{Q},\mathbf{k}'+\mathbf{Q}) = V(\mathbf{k},\mathbf{k}')$. Therefore, the relevant symmetry group in the particle-hole symmetric limit is the direct product $D_{4h} \times (E, IT)$. The basis functions ψ_n^Γ can, therefore, be classified according to whether they are even or odd under IT. For an even

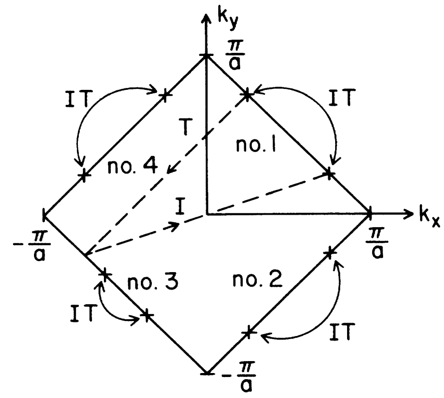

FIG. 5. The particle-hole symmetry IT on a square Fermi surface, where I is inversion and T is translation by (π/a) (1,1).

basis (class I in the notation of Ref. 12) one has a basis vector $\boldsymbol{\psi}(\mathbf{k}) \parallel \mathbf{v}(\mathbf{k})$ whereas for an odd basis (class II) $\boldsymbol{\psi}(\mathbf{k}) \perp \mathbf{v}(\mathbf{k})$ (see Fig. 6). As we shall see the absence of mixing between the even and odd basis functions causes the Γ_5 phases to be extremely anisotropic.

To understand the nature of this anisotropy, we will calculate m_1' m_1'', m_3', and m_3''. This will be done by comparing the expression for the supercurrent obtained from the Ginzburg-Landau theory with that obtained with the

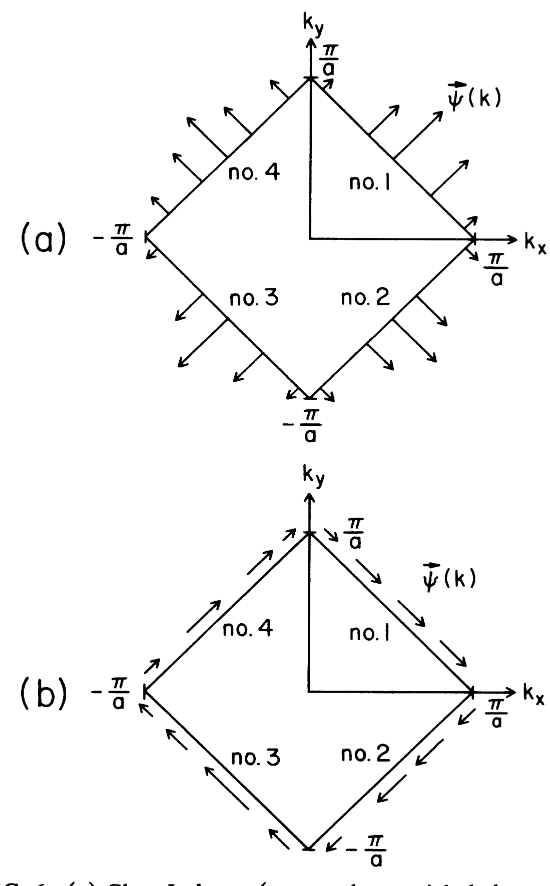

FIG. 6. (a) Class-I phases (even under particle-hole symmetry) have $\boldsymbol{\psi}(\mathbf{k}) \parallel \mathbf{v}(\mathbf{k})$. (b) Class-II phase (odd under particle-hole symmetry) have $\boldsymbol{\psi}(\mathbf{k}) \perp \mathbf{v}(\mathbf{k})$.

linear response analysis of the microscopic Hamiltonian [Eq. (16)]. We begin with the Ginzburg-Landau theory: In the presence of a slowly varying static vector potential, the supercurrent is

$$J_i = -\frac{\delta H[\eta;A]}{\delta A_i} = -k_B T e_*^2 K_{ijab}\eta_a^* \eta_b A_j , \tag{19}$$

where $e_* = 2e$. We have omitted terms[17,18] involving the gradients of the η_l's by supposing that we have constrained η to be spatialy uniform. Now according to the linear response analysis of the microscopic theory (again assuming that η is constained to be spatially uniform), $J_i = -(e^2/m) n_{ij}^s A_j$, where m is an arbitrary mass chosen to be the bare electron mass, and where the superfluid density tensor, n_{ij}^s, is given by

$$n_{ij}^s = \frac{7}{2}\zeta(3)\frac{m}{\pi^2 k_B^2 T_c^2}\int \frac{dS_k}{(2\pi)^3 v(\mathbf{k})} v_i(\mathbf{k}) v_j(\mathbf{k}) \,|\Delta(\mathbf{k}k)|^2 . \tag{20}$$

In the above expression, the integration is over the Fermi surface, $v_i(k)$ are components of the Fermi velocity $\mathbf{v}_F(\mathbf{k})$, $v(\mathbf{k}) = |\mathbf{v}_F(\mathbf{k})|$, and $\Delta(\mathbf{k})$ is the quasiparticle excitation gap given by

$$\Delta(k) = -\int dS_{k'} n(\mathbf{k}') V(\mathbf{k},\mathbf{k}') F_{\uparrow\downarrow}(\mathbf{k}') = \omega A_0(\mathbf{k}) . \tag{21}$$

In the above expression for n_{ij}^s in the Ginzburg-Landau regime we are neglecting strong-coupling corrections.[19]

Now comparing the above two expressions for the supercurrent, one obtains the desired parameters of the Ginzburg-Landau theory:

$$\frac{1}{2m_1''} = c_0 \int \frac{dS_k}{(2\pi)^3 v(\mathbf{k})} v_x^2(\mathbf{k}) \,|\psi_y(\mathbf{k})|^2 , \tag{22}$$

$$\frac{1}{2m_1'} = c_0 \int \frac{dS_k}{(2\pi)^3 v(\mathbf{k})} v_y^2(\mathbf{k}) \,|\psi_y(\mathbf{k})|^2 , \tag{23}$$

and

$$\frac{1}{8}\left[\frac{1}{m_3'} + \frac{1}{m_3''}\right] = c_0 \int \frac{dS_k}{(2\pi)^3 v(\mathbf{k})} \times v_x(\mathbf{k}) v_y(\mathbf{k}) \psi_x(\mathbf{k}) \psi_y^*(\mathbf{k}) , \tag{24}$$

where the constant

$$c_0 = \frac{7}{4}\zeta(3)\frac{\omega^2 \omega_c^2}{\pi^2 (k_B T_c)^3} .$$

For class-I superconductors where $\boldsymbol{\psi}(\mathbf{k}) = \mathbf{v}(\mathbf{k})$, the above results give $(m_1'')^{-1} = (m_1')^{-1} = [(m_3')^{-1} + (m_3'')^{-1}]/4$ whereas for class-II superconductors one obtains

$$(m_1')^{-1} = (m_1)^{-1} = -[(m_3')^{-1} + (m_3'')^{-1}]/4 .$$

In either case the stiffness matrix has a zero eigenvalue and the amplitude ratio achieves its maximum value of $4\sqrt{2} = 5.65$ in the (1,0) and $(1,i)$ phases.

Of course corrections to the particle-hole symmetric limit, either in the form of next-nearest-neighbor hopping, or interplanar hopping or nonvanishing matrix elements V_{ijln} ($i \neq n$ or $j \neq l$) will cause the order parameter stiffness matrix to be nonsingular hence reducing the amplitude ratio from its upper bound.

VII. DISCUSSION

We shall now compare our results with evidence for or against anisotropic superconductivity in $YBa_2Cu_3O_{7-\delta}$ inferred from other experiments. The first observation of which we are aware supporting anisotropic pairing is the small orthorhombic strain anomaly at T_c reported by Horn *et al.*[14] The presence of this strain anomaly, and the absence of any corresponding volume anomaly would imply anisotropy of the order parameter in the a-b plane.[20] This experimental result has recently been considered theoretically by Volovik[21] assuming a singlet state belonging to the tetragonal group. He finds that the state which couples most strongly to the strain is the (1,0) phase of the Γ_5 representation, although the other possible states also couple to the strain and so the order parameter cannot be definitely determined.

It has been argued that Josephson effects are forbidden or at least weak between singlet and triplet superconductors.[22] This would imply singlet superconductivity in $YBa_2Cu_3O_{7-\delta}$.[23] Unfortunately the situation is not so clear in the presence of spin-orbit coupling when the only distinction between singlet and triplet states is parity under inversion. Because inversion symmetry is broken by the tunnel junction Josephson effects may in fact occur.[24] Indeed, Josephson tunneling has been observed between Nb and UBe_{13}.[25]

Strong arguments against anisotropic superconductivity in $YBa_2Cu_3O_{7-\delta}$ have been presented by Harshman *et al.*,[26] who find the low-temperature dependence of the penetration depth to be inconsistent with nodes in the gap function. We would like to make two comments about this. First, the gap structure depends both on the order-parameter symmetry and on the Fermi surface topology. For example, the Anderson-Brinkman-Morel type triplet states that have nodes on the k_z axis for a spherical Fermi surface could be nodeless on a Fermi surface like that of $YBa_2Cu_3O_{7-\delta}$ which is open in the k_z direction.[27] Second, the group theory analysis of the order parameter and the Ginzburg-Landau theory are valid only close to T_c. Away from T_c the nonlinear gap equation can mix states of differing symmetry,[28] and thus may alter the gap nodal structure. This comment would also apply to all other measurements of the low-temperature gap function such as optical reflectivity, Raman scattering, tunneling nuclear quadrupole resonance and low-temperature heat-capacity measurements, some of which appear to show a nonvanishing gap, while others report evidence for gaplessness.

Triplet superconductivity is not unreasonable in $YBa_2Cu_3O_{7-\delta}$ given the noncoexistence of antiferromagnetism and superconductivity. In fact a number of authors have proposed triplet pairing mechanisms.[29] As far as we are aware the Γ_5^+ singlet phases have not been predicted by any theoretical model to date.

To summarize our results, we have found the following.

(1) The amplitude ration C_+/C_- in the Gaussian fluc-

tuation regime is nonuniversal. However its large measured value puts severe constraints on the form of the superconducting order parameter. In particular, all the allowed order parameters are anisotropic.

(2) For orthorhombic (D_{2h}) symmetry, the only case in which one obtains more than two effective order-parameter components is that of triplet p-wave pairing with weak spin-orbit coupling. The three allowed representations are (Γ_2^-, Γ_3^-, Γ_4^- or B_{2u}, B_{1u}, B_{3u}), and for each of them $n_{\rm eff}$ is a continuous function of the microscopic parameters bounded above by $n_{\rm eff} \leq 6$.

(3) For the tetragonal (D_{4h}) group, the only singlet superconductor which can have $n_{\rm eff} > 2$ has a "d-wave" order parameter, transforming according to the Γ_5^+ (or E) representation. In this case $n_{\rm eff}$ is bounded above by 5.65; however, $n_{\rm eff} > 4$ requires that certain anisotropic stiffness constants satisfy rather stringent conditions. We have shown that within a class of simple models such anisotropic gradient terms are indeed possible.

(4) There are three possibilities for triplet superconductivity in the tetragonal case consistent with the measured C_+/C_-. For strong spin-orbit coupling the Γ_5^+ (or E_g) representation [discussed in paragraph (3)] is allowed. For weak spin-orbit coupling the possible representations are Γ_2^- [discussed in paragraph (2)] and Γ_5^- or E_u. The latter has a 12-component order parameter and would have regions of allowed parameter space consistent with the experimental data.

ACKNOWLEDGMENTS

The authors would like to acknowledge a number of important conversations with E. Fradkin, N. Goldenfeld, A. J. Leggett, C. Pethick, D. Pines, and M. Salamon. This work has been supported by U.S. National Science Foundation (NSF) Grants No. DMR86-12860, and No. DMR84-15063 and by the John D. MacArthur and Catherine T. MacArthur Foundation, Grant No. 0-6-40129.

---

[1]S. E. Inderhees, M. B. Salamon, N. Goldenfeld, J. P. Rice, B. G. Pazol, D. M. Ginsberg, J. Z. Liu, and G. W. Crabtree, Phys. Rev. Lett. **60**, 1178 (1988).

[2]D. M. Ginsberg, S. E. Inderhees, M. B. Salamon, N. Goldenfeld, J. P. Rice, and B. G. Pazol (unpublished).

[3]S. K. Ma, *Modern Theory of Critical Phenomena* (Benjamin/Cummings, Reading, MA, 1976), pp. 72–102.

[4]This result corrects an error appearing in Eq. 3.59 of Ref. 3.

[5]For example an order parameter with SU(2) symmetry has been proposed by E. Dagotto, E. Fradkin, and A. Moreo (unpublished).

[6]K. Ueda and T. M. Rice, Phys. Rev. B **31**, 7114 (1985).

[7]E. I. Blount, Phys. Rev. B **32**, 2935 (1985); G. E. Volovik and L. P. Gorkov, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 550 (1984) [JETP Lett. **39**, 674 (1984)]; M. Ozaki, K. Machida, and T. Ohmi, Prog. Theor. Phys. **74**, 221 (1985).

[8]G. E. Volovik and L. P. Gorkov Zh. Eksp. Teor. Fiz. **88**, 1412 (1985) [Sov. Phys. JETP **61**, 843 (1985)]. M. Ozaki, K. Machida, and T. Ohmi, Prog. Theor. Phys. **75**, 442 (1986).

[9]M. Sigrist and T. M. Rice, Z. Phys. B **68**, 9 (1987).

[10]For Hermitian matrices K and M, with K nonsingular, the eigenvalues of $K^{-1}M$ are real, even though the latter is not necessarily Hermitian. Equivalently, C_+/C_- can be expressed in terms of the eigenvalues of the (manifestly Hermitian) matrix $K^{-1/2}MK^{-1/2}$.

[11]N. Goldenfeld and C. Pethick (private communication).

[12]M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964).

[13]This nonuniversality has also been noted recently by P. Muzikar (unpublished).

[14]We use a bulk modulus $B \simeq 2\times 10^3$ kbar [D. J. Bishop *et al.*, Phys. Rev. B 36, 2408 (1987)], $\partial T_c/\partial p \simeq 0.07$ K/kbar [J. E. Schirber *et al.*, Phys. Rev. B **35**, 8709 (1987)], and an orthorhombic distortion $\delta a/a \simeq 0.02$ [P. M. Horn *et al.*, Phys. Rev. Lett. **59**, 2772 (1987)].

[15]$K(\hat{q})$ does not depend on the combination $(m_3'^{-1} - m_3''^{-1})$ since the last two gradient terms in the free energy of Eq. (14) differ by only a total divergence.

[16]M. Ozaki and K. Machida (unpublished); M. Kato and K. Machida Phys. Rev. B **37**, 1510 (1988); M. Kato, K. Machida, and M. Ozaki, Jpn. J. Appl. Phys. **26**, Suppl. 26-3, 1245 (1987).

[17]A. J. Millis, Phys. Rev. B **35**, 151 (1987); F. Gross, B. S. Chandrasekhar, D. Einzel, K. Andres, P. J. Hirschfeld, H. R. Ott, J. Beauers, Z. Fisk, and J. L. Smith, Z. Phys. B **64**, 175 (1986).

[18]These terms are required in order to obtain a gauge-invariant J_i and to insure charge conservation. However, for the purposes of calculating the stiffness parameters we are free to hold our order parameter η fixed. For the derivation of the current in the absence of such a constraint see Ref. 17.

[19]J. W. Serene and D. Rainer, Phys. Rev. B **17**, 2901 (1978).

[20]R. Joynt and T. M. Rice, Phys. Rev. B **32**, 6074 (1985).

[21]G. E. Volovik (unpublished).

[22]J. A. Pals, W. van Haeringen, and M. H. van Maaren, Phys. Rev. B **15**, 2592 (1977).

[23]J. S. Tasi, Y. Kubo, and J. Tabuchi, Phys. Rev. Lett. **58**, 1979 (1987).

[24]E. W. Fenton, Solid State Commun. **54**, 709 (1985); A. Millis, D. Rainer, and J. A. Sauls, this issue Phys. Rev. B **38**, 4504 (1988).

[25]E. L. Wolf *et al.*, Physica B **135**, 65 (1985).

[26]D. R. Harshman *et al.*, Phys. Rev. B **36**, 2386 (1987).

[27]J. Yu, S. Massida, A. J. Freeman, and D. D. Koelling, Phys. Lett. A **122**, 198 (1987).

[28]H. Monien, K. Scharnberg, L. Tewordt, and N. Schopohl, Phys. Rev. B **34**, 3487 (1986).

[29]K. S. Bedell and D. Pines (unpublished); G. Chen and W. A. Goddard III, Science **239**, 899 (1988); P. de Gennes (unpublished).