Upward curvature of H_{c2} in high-T_c superconductors: Possible evidence for s-d pairing

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A mechanism is proposed to explain the upward curvature of the plot of thermodynamic H_{c2} versus temperature in the high-T_c superconductors, as observed in dc magnetization measurements. If a multicomponent order parameter is assumed, the internal degrees of freedom of this parameter change along the $H_{c2}(T)$ curve. In a superconductor with s-d mixing, a pure d wave at low fields will turn into a superposition of s and d at high fields, with a corresponding change in slope of H_{c2}. In a pure d-wave superconductor belonging to a two-dimensional representation, an orthorhombic distortion can produce the curvature. At low fields the slope of the curve is dominated by coupling to the orthorhombic distortion; at high fields the coupling of the supercurrent to the field is more important. Thus the curvature in $H_{c2}(T)$ can be interpreted as evidence for d-wave pairing or for a mixture of s and d. The consequences of these two possibilities for other experiments are discussed. In particular, the mixed s and d picture can be reconciled with penetration-depth measurements, and therefore seems favored.

I. INTRODUCTION

A fundamental issue that bridges microscopic theory and experimental phenomenology of high-T_c superconductors is the symmetry of the pairing state. A number of investigators have proposed on theoretical grounds that d-wave pairing occurs,[1] but there is presently no real consensus on this.[2] A second intriguing possibility is that a mixture of s- and d-wave pairing occurs. In mean-field theory, exact calculations[3] and variational calculations,[4] it appears that a d wave is slightly lower in energy, and at T_c there would be no mixing, but at lower temperatures a superposition of s- and d-wave states could have the lowest energy. Experimental evidence for anisotropic pairing is the nonexponential temperature dependence of the Knight shift at low temperature.[5] On the other hand, the experimental temperature dependence of $\lambda(T)$ at low temperature seems to indicate a gap function without nodes, as in ordinary s-wave BCS theory.[6] In the heavy-fermion materials, the temperature dependence of thermodynamic and transport properties at low temperature has been very helpful in establishing the unconventional nature of the pairing. In high-T_c systems, disentangling electronic and phononic contributions to these quantities has made progress more difficult.

Because of this unsettled situation, it is important to identify experiments that can reliably distinguish between one-component and multiple-component superconductivity in the high-T_c materials. In this paper, I propose that the shape of the upper-critical-field curves can shed light on this question. In particular, the upward curvature of H_{c2} versus temperature plots are adduced as evidence for multicomponent behavior. Upward curvature near the critical temperature in $H_{c2}(T)$ has been observed in both La-Sr-Cu-O and Y-Ba-Cu-O.[7,8] These are ac determinations of H_{c2} and the curvature has been convincingly attributed to the onset of reversible behavior due to flux motion,[9] which implies that it is not a thermodynamic property that is being measured. However, when H_{c2} is taken from reversible dc magnetization measurements on single crystals,[10] the upward curvature is still present, at least in Y-Ba-Cu-O. This method leaves the sample in equilibrium, so the curvature is truly a thermodynamic property. The theory proposed here of the dc measurements, which involves d-wave pairing, is complementary to the flux creep theory of the ac measurements. The apparent inconsistency with the penetration depth measurements will be discussed in detail in the following.

The curved shape of the H_{c2} curve near T_c can occur in layered superconductors.[11] This is usually understood as a dimensional crossover when H is parallel to the layers. Proximity effects can also produce curvature when H is perpendicular to the layers,[12] but this appears always to be a rather small effect. In Y-Ba-Cu-O very substantial curvature is observed for both directions of field relative to the CuO_2 planes. It also occurs in the heavy-fermion systems UPt_3 (Ref. 13) and URu_2Si_2 (Ref. 14). Since these materials are thought to be unconventional superconductors, this is suggestive. A theory of the effect in these materials has recently been proposed.[15,16]

I consider two possibilities for the superconducting state of the high-T_c materials: a mixed s- and d-wave state where both s and d components belong to a one-dimensional representation, i.e., each is characterized by a single complex order parameter; and a two-dimensional d-wave state characterized by a two-component complex vector. In both cases the symmetry breaking is described by four real numbers rather than two, as in ordinary s-wave BCS theory. I also qualitatively investigate the

consequences of these two possibilities for penetration depth and specific-heat measurements. Based on this analysis it appears that only the s- and d-wave mixing picture is consistent with present data. It is also pointed to by microscopic considerations.

II. MIXED s- AND d-WAVE

First, a mixture of an s-wave and a d-wave state is presented. The s-wave state belongs to the Γ_1 representation of the tetragonal point group, with basis function, e.g., $\cos k_x+\cos k_y$, and a d-wave state belonging to the Γ_3 representation with basis function, e.g., $\cos k_x-\cos k_y$. Both Γ_1 and Γ_3 are one-dimensional representations. For a complete discussion of the possible symmetries of the gap function, see the treatment of Sigrist and Rice,[17] whose notation I follow, except that I consider only even, spin-singlet representations. The complete gap would have the form

$$\psi(\mathbf{k})=\psi_d(\cos k_x-\cos k_y)+\psi_s(\cos k_x+\cos k_y)\ .$$

The Γ_3 representation is indicated by most theoretical work on the strong-coupling Hubbard model of the high-T_c materials. It is very important to note that in the large-U limit of this model, *the* Γ_1 *state is very nearly degenerate with the* Γ_3 *state* because at half-filling an SU(2) symmetry exists in the space of projected wave functions.[18] It is therefore natural to assume that the doped system will show some admixture of Γ_1 with the dominant Γ_3 state.

I now compute H_{c2} for the s-d case. The first step is to construct the quadratic part of the free energy. For the gradient terms this is not quite trivial. The operators

$$p_x=-i\frac{\partial}{\partial x}+\frac{2e}{\hbar c}A_x \quad \text{and} \quad p_y=-i\frac{\partial}{\partial y}+\frac{2e}{\hbar c}A_y$$

belong to the Γ_5 representation. (Here $\mathbf{A}$ is the vector potential.) Because the decomposition

$$\Gamma_1\times\Gamma_3\times\Gamma_5\times\Gamma_5=\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4$$

contains the identity representation once, there must be precisely one term quadratic in the p_i and linear in ψ_s and ψ_d that is invariant under the point group. Adding this term to the usual Ginzburg-Landau terms yields the full quadratic free-energy density. Taking $\mathbf{H}=H\hat{\mathbf{z}}$, we find

$$\begin{aligned}F_2=&\alpha_s(T-T_s)|\psi_s|^2+\alpha_d(T-T_d)|\psi_d|^2\\&+K_s(|p_x\psi_s|^2+|p_y\psi_s|^2)+K_d(|p_x\psi_d|^2+|p_y\psi_d|^2)\\&+K_{sd}(p_x\psi_s p_x^*\psi_d^*-p_y\psi_s p_y^*\psi_d^*+\text{c.c.})\ .\end{aligned}$$

Thus, rather remarkably, although there is no coupling of s and d to quadratic order in the absence of a field, the field does produce such a coupling, and therefore the mixing of s and d, while not affecting T_c, does definitely influence the upper critical field [or $T_c(H)$]. We will assume, following the microscopic considerations already given, that $T_d>T_s$. Hence $T_d=T_c$, the zero-field critical temperature.

To determine H_{c2}, we must minimize the total free energy; the phase boundary $H_{c2}(T)$ is the curve along which the minimum condensation free energy $\gamma=\int d^3x\,F_2(H,T)$ vanishes. To carry this out, it is convenient to define the creation and annihilation operators

$$p_+=(l/\sqrt{2})(p_x+ip_y) \quad \text{and} \quad p_-=(l/\sqrt{2})(p_x-ip_y)\ ,$$

which satisfy the commutation relation $[p_-,p_+]=1$. Here l is the magnetic length: $l^2=\hbar c/2eH$. The equations $\delta\gamma/\delta\psi_s^*=0$ and $\delta\gamma/\delta\psi_d^*=0$ then give

$$\begin{aligned}&\alpha_s l^2(T-T_s)\psi_s+K_s(2p_+p_-+1)\psi_s\\&\qquad+K_{sd}(p_+^2+p_-^2)\psi_d=0\ ,\\&\alpha_d l^2(T-T_d)\psi_d+K_d(2p_+p_-+1)\psi_d\\&\qquad+K_{sd}(p_+^2+p_-^2)\psi_s=0\ .\end{aligned}$$

Evidently the left-hand side is a Hermitian operator acting on the state (ψ_s,ψ_d). We need to find the lowest eigenvalue, which is a function of H and T, and set it equal to zero. We treat the problem in perturbation theory, assuming that $K_{sd}\ll K_s$ and $K_{sd}\ll K_d$. Then to zeroth order the ψ_s and ψ_d satisfy uncoupled harmonic-oscillator equations, and the ground states of the two are $|0\rangle_s$ and $|0\rangle_d$ in an occupation number representation, satisfying $p_-|0\rangle_s=0$ and $p_-|0\rangle_d=0$ with eigenvalues $\alpha_s l^2(T-T_s)+K_s$ and $\alpha_d l^2(T-T_d)+K_d$. These would give upper critical fields

$$H_{c2}=\frac{\alpha_s\hbar c}{2eK_s}(T_s-T)$$

and

$$H_{c2}=\frac{\alpha_d\hbar c}{2eK_d}(T_d-T)\ ,$$

of which the larger of the two would be the actually observed H_{c2}. These linear curves are in contradiction to experiment, so (in the context of this theory) we may conclude that $K_{sd}\neq 0$. To first order in K_{sd}, $|0\rangle_s$ couples only to $|2\rangle_d$ and $|0\rangle_d$ couples only to $|2\rangle_s$. The two lowest eigenvalues are given by

$$\tfrac{1}{2}[\alpha_d l^2(T-T_d)+K_d+\alpha_s l^2(T-T_s)+5K_s]-\tfrac{1}{2}\{[\alpha_d l^2(T-T_d)+K_d+\alpha_s l^2(T-T_s)+5K_s]^2+4K_{sd}^2\}^{1/2}$$

and a similar expression with $s\leftrightarrow d$. These eigenvalues are obtained by diagonalization in the two-dimensional subspace. This is justified if $K_d>K_s$. The upper-critical-field curves belonging to the two eigenvalues can cross at very high fields. I will not consider this possibility—the data would theoretically show a kink but are not sufficient to judge whether this occurs.

The H_{c2} equation obtained by setting the aforementioned eigenvalue to zero is most simply written in the form

$$[\alpha_d l^2(T-T_d)+K_d][5K_s+\alpha^2 l^2(T-T_s)]=K_{sd}^2 \ . \tag{1}$$

As $T\rightarrow T_c$, we find from this equation

$$H_{c2}=\frac{\alpha_d \hbar_c}{2eK_d}(T_d-T)\equiv s(T_d-T)$$

as before, reflecting the fact that there is no admixture of s wave as $H\rightarrow 0$ along the H_{c2} curve. For large H, the curve is also linear: $H_{c2}=s_z(T_s-T)$, where $s_z=\alpha_s\hbar_c/10eK_s$. If $\alpha_d/K_d \ll \alpha_s/K_s$, then we find upward curvature in H_{c2}. The high-field H_{c2} appears to extrapolate to a value of "T_c" that is less than the actual T_c. This corresponds to the actual observations. A least-squares fit to the experimental data of Ref. 10 is given in Fig. 1, which yields parameter values $s=0.019$ T/K, $s_z=1.92$ T/K, and $T_s=91.57$ K. The number of parameters is rather large and the curve does not have enough features to pin many of them down. The fit is intended mainly to demonstrate concretely that the theory contains the basic qualitative elements of the observations. There is particularly large error in the value of s, because there are not many points at low field. The surprising large ratio of s_z to s is discussed in the following.

We now turn to the other direction, H in the a-b plane. We take $\mathbf{H}=H\hat{\mathbf{x}}$; then ψ_s and ψ_d can be taken independent of x. The free energy density becomes

$$F_2=\alpha_s(T-T_s)|\psi_s|^2+\alpha_d(T-T_d)|\psi_d|^2+K_s|p_y\psi_s|^2+K_{sz}|p_z\psi_s|^2+K_d|p_y\psi_d|^2+K_{dz}|p_z\psi_d|^2-K_{sd}(p_y\psi_s p_y^*\psi_d^*+\text{c.c.}) \ .$$

This can be solved in a fashion analogous to the preceding case. Define annihilation and creation operators

$$a_s=l(K_{sz}/4K_s)^{1/4}[p_z+i(K_s/K_{sz})^{1/2}p_y] \ ,$$

$$a_s^\dagger=l(K_{sz}/4K_s)^{1/4}[p_z-i(K_s/K_{sz})^{1/2}p_y] \ ,$$

and similarly for a_d and $a_d^\dagger$. $|0\rangle_s$ and $|0\rangle_d$ are defined by $a_s|0\rangle_s=a_d|0\rangle_d=0$, and so on. This case differs from the preceding one in that

$${}_s\langle 0|0\rangle_d=\frac{(K_sK_d/K_{sz}K_{dz})^{1/8}\sqrt{2}}{[(K_s/K_{sz})^{1/2}+(K_d/K_{dz})^{1/2}]^{1/2}}<1$$

rather than $|0\rangle_s$ and $|0\rangle_d$ having the same functional form. We abbreviate this as ${}_s\langle 0|0\rangle_d=c$. The variational equations for this case are

$$\alpha_s l^2(T-T_s)\psi_s+\sqrt{K_sK_{sz}}(2a_s^\dagger a_s+1)\psi_s+\tfrac{1}{2}K_{sd}\sqrt{K_{dz}/K_d}(a_d-a_d^\dagger)^2\psi_d=0 \ ,$$

$$\alpha_d l^2(T-T_d)\psi_d+\sqrt{K_dK_{dz}}(2a_d^\dagger a_d+1)\psi_d+\tfrac{1}{2}K_{sd}\sqrt{K_{sz}/K_s}(a_s-a_s^\dagger)^2\psi_s=0 \ .$$

In the first approximation, this problem may be solved in the lowest Landau level alone, the space spanned by $\{|0\rangle_s,|0\rangle_d\}$. The secular equation for these two levels is

$$\begin{vmatrix} \alpha_s l^2(T-T_s)+\sqrt{K_sK_{sz}}, & -cK_{sd}\sqrt{K_{dz}/K_d} \\ -cK_{sd}\sqrt{K_{sz}/K_s}, & \alpha_d l^2(T-T_d)+\sqrt{K_dK_{dz}} \end{vmatrix}=0 \ .$$

This leads to a critical-field equation similar to that given above for $\mathbf{H}=H\hat{\mathbf{z}}$:

$$[\alpha_d l^2(T-T_d)+\sqrt{K_dK_{dz}}][\alpha_s l^2(T-T_s)+\sqrt{K_sK_{sz}}]=K_{sd}^2c^2\sqrt{K_{dz}K_{sz}/K_dK_s} \ . \tag{2}$$

As

$$T\rightarrow T_d, \quad H_{c2}=\frac{\alpha_d\hbar c}{2e\sqrt{K_dK_{sz}}}(T_d-T)=s_d(T_d-T) \ .$$

Again there is no s admixture in this limit. For large H, $H_{c2}=s_x(T_s-T)$, where for small K_{sd}

$$s_x=\frac{\hbar c}{2e}\alpha_s/\sqrt{K_sK_{sz}} \ .$$

In Fig. 1, experimental data from Ref. 10 for H_{c2} with H in the a-b plane is plotted together with $H_{c2}(T)$ from Eq. (2). The least-squares fit determines the parameters: $s_d=0.128$ T/K, $s_x=14.3$ T/K, and $T_s=91.44$ K, with s_d particularly inaccurate. Again the ratio of high-field to low-field slopes is very large.

The five fitted parameters s, s_zs_d, s_x, and T_x, together with $T_d=92.5$ K, are not enough to determine the nine parameters appearing in the free energy. Nevertheless, some statements can be made. The low-field slopes s and s_d satisfy the relation $s/s_d=\sqrt{K_{dz}/K_d}$, and we find $K_{dz}/K_d=0.023$. At high field, assuming that the slope is dominated by the s-wave component, one finds an ap-

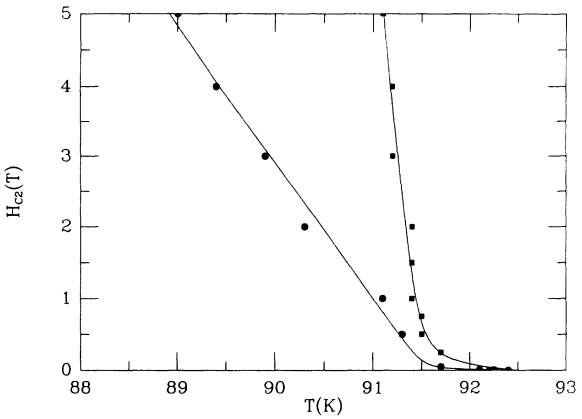

FIG. 1. Thermodynamic upper-critical field vs temperature for Y-Ba-Cu-O. The circles (squares) are data for H along (perpendicular to) the c axis, taken from Ref. 8. The solid curves are theoretical, as described in the text.

proximate relation $s_z/s_x \approx \sqrt{K_{sz}/K_s}$, so that $K_{sz}/K_z \approx 0.017$. These are essentially effective-mass ratios and only confirm once more the very large crystalline anisotropy. T_s is given as 91.57 and 91.44 from the two curves—this discrepancy is within the experimental error. As a whole, the difference between T_s and T_c is a good measure of the difference between the tendencies to s- and d-wave superconductivity. A good experimental test of the s-d mixing hypothesis would be to measure the offset between the actual T_c and the "T_c" extrapolated from the high-field curve as a function of doping. At zero doping, s and d are degenerate, so the offset should increase as the doping level increases.

The most striking aspect of the data is the very large change in slope from low to high fields. If we again assume that this represents a crossover from d to s, this would imply that the d coherence lengths are about ten times greater than the very short s coherence lengths of about 16 Å (a-b plane) and 3 Å (c axis).[10] Such a crossover picture is dictated by the rather linear behavior of H_{c2} at high fields. The Ginzburg-Landau theory does not suggest any explanation for the mismatch of d and s coherence lengths given in the a-b plane by $K_d/\alpha_d T_c$ and $K_s/\alpha_s T_c$, respectively. The coherence length that is usually quoted would be identified here with the s coherence length and is anomalously short, as is well known. The d coherence length, greater than 100 Å, has a more conventional magnitude.

III. TWO-DIMENSIONAL PURE d-WAVE STATE

Second, I consider the two-dimensional Γ_5 representation with basis functions, e.g., $\sin k_z \sin k_x$ and $\sin k_z \sin k_y$. This is most analogous to states that have been proposed for UPt_3 and URu_2Si_2. Since these systems are known to be multicomponent superconductors and also have upward curvature in their critical fields, they form a natural basis for comparison. However, the mechanism that gives upward curvature in H_{c2} is rather different in the s-d mixing and in the Γ_5 cases, as we shall see.

We must again construct the invariant free energy. The gradient operators $\{p_x, p_y\}$ belong to Γ_5, so gradient terms in the free energy will transform as $\Gamma_5 \times \Gamma_5 \times \Gamma_5 \times \Gamma_5$, whose decomposition is $4(\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4)$. Only the $4\Gamma_1$ terms are admissible invariants. To be consistent with Ref. 19, I choose a notation in which these are proportional to K_1, K_2, K_3, and K_5. The quadratic free-energy density for an arbitrary field direction is[15,20]

$$F_2 = \alpha_0(T-T_0)\boldsymbol{\psi}\cdot\boldsymbol{\psi}^* + \sum_{ij}(K_1 p_i\psi_j p_i^*\psi_j^* + K_2 p_i\psi_i p_j^*\psi_j^* + K_3 p_i\psi_j p_j^*\psi_i^*) + K_4\sum_i |p_z\psi_i|^2 + K_5\sum_i |p_i\psi_i|^2 + \delta(|\psi_x|^2 - |\psi_y|^2).$$

Here the indices i and j run over the Cartesian components x and y of the basal plane. $\boldsymbol{\psi}$ has two complex components: $\boldsymbol{\psi}=(\psi_x,\psi_y)$. A small correction proportional to δ has been added to take into account the orthorhombic distortion. This shifts the critical temperature: $T_c = T_0 + |\delta|/\alpha_0$. One should note that similar results would be obtained from some other multicomponent forms, including p wave.

I now compute H_{c2} for this two-dimensional case.

Case 1: $\mathbf{H}=H\hat{\mathbf{z}}$. Now $[p_x,p_y]=-i/l^2$, where $l^2=\hbar c/2eH$. F_2 simplifies to

$$F_2 = \alpha_0(T-T_0)\boldsymbol{\psi}\cdot\boldsymbol{\psi}^* + \delta(|\psi_x|^2-|\psi_y|^2) + K(|p_x\psi_x|^2+|p_y\psi_y|^2) + K_1(p_x\psi_y p_x^*\psi_y^* + p_y\psi_x p_y^*\psi_x^*)$$
$$+ K_2(p_x\psi_x p_y^*\psi_y^* + p_y\psi_y p_x^*\psi_x^*) + K_3(p_x\psi_y p_y^*\psi_x^* + p_y\psi_x p_x^*\psi_y^*),$$

where $K = K_1+K_2+K_3+K_5$. We minimize this in two stages, a simple generalization of the Abrikosov procedure. First,[21] define $\psi_\pm = (1/\sqrt{2})(\psi_x \pm i\psi_y)$ and $p_\pm = (1/\sqrt{2})(p_x \pm ip_y)$. Then choose ψ_+ and ψ_- in the lowest Landau level: $p_-\psi_+ = p_-\psi_- = 0$. This leads to a total free energy

$$\gamma = \int d^3x[\alpha_0(T-T_0)(|\psi_+|^2+|\psi_-|^2) + \delta(\psi_+\psi_- + \psi_+^*\psi_-^*) + (K_5+K_1+K_3)|\psi_+|^2/l^2 + (K_5+K_1+K_2)|\psi_-|^2/l^2].$$

Second, diagonalize the quadratic form and set the lowest eigenvalue (which is a function of H and T) equal to zero, yielding $H_{c2}(T)$:

$$\alpha_0(T-T_0)+\frac{eH}{\hbar c}(K+K_1)-\left[\left[\frac{eH}{\hbar c}(K_3-K_2)\right]^2+\delta^2\right]^{1/2}=0\ . \tag{3}$$

As a function of H and T, this is essentially the same as (1). At T_c, we find a slope $-dH_{c2}/dT|_{T_c}=s'=\alpha_0\hbar c/e(K+K_1)$. This crosses over to the larger value

$$-dH_{c2}/dT\rightarrow\alpha_0\hbar c/e(K+K_1-|K_2-K_3|)=s_z'\ ,$$

when $H\gg\hbar c\delta/e|K_2-K_3|$. Hence $H_{c2}(T)$ shows upward curvature in this case as well, but only if $\delta\neq 0$—it is a consequence of the orthorhombic distortion. When δ is small, the curved portion is pushed closer to T_c. Since Eq. (3) has the same form as Eq. (1), the fit to the data is the same, and the same values are obtained for the parameters: $s'=0.019$ T/K, $s_z'=1.92$ T/K, and $|\delta/\alpha_0|=0.96$ K.

Case 2: $\mathbf{H}=H\hat{\mathbf{x}}$, $\mathbf{A}=-z\hat{\mathbf{y}}$. Now we choose ψ uniform in x, obtaining

$$\int d^3x[\alpha_0(T-T_0)\boldsymbol{\psi}\cdot\boldsymbol{\psi}^*+\delta(|\psi_x|^2-|\psi_y|^2)+K|p_y\psi_y|^2+K_1|p_y\psi_x|^2+K_4(|p_z\psi_x|^2+|p_z\psi_y|^2)]\ .$$

In an untwinned crystal δ has a definite sign, but in a twinned sample δ will change sign across the boundary. I work out the twinned case since this is important experimentally. The sign of δ does not matter for $\mathbf{H}=H\hat{\mathbf{z}}$, because H_{c2} depended only on δ^2, but here it has an effect and the differently oriented twins have different H_{c2} values. Choosing ψ_x and ψ_y in the lowest Landau level, we now find $H_{c2}(T)$ to be straight in one twin and piecewise straight in the other. This is rather similar to UPt_3.[15,16]

$$\text{twin 1: } H_{c2}(T)=\frac{\hbar c}{2e\sqrt{K_4}}\cdot\max\left[\frac{\delta-\alpha_0(T-T_0)}{\sqrt{K}},\frac{-\delta-\alpha_0(T-T_0)}{\sqrt{K_1}}\right]\ ,$$

$$\text{twin 2: } H_{c2}(T)=-\hbar c[\delta+\alpha_0(T-T_0)]/2e\sqrt{K_1K_4}\ .$$

In the first case the crossover is determined by the anisotropy parameter δ.

Case 3: $\mathbf{H}$ in an arbitrary direction in the basal plane. The phase boundary may be obtained following the second part of the procedure for Case 1. There will always be curvature in $H_{c2}(T)$ as long as $\mathbf{H}$ is not along a crystal axis. In the experiment of Ref. 10 the field direction is not known. The result for a 45° orientation is that the two curves for the twins collapse on to a single one. The curve is once more essentially as in Eq. (1), specifically

$$[\alpha_0 l^2(T-T_0)+2\sqrt{K_3K_4}][\alpha_0 l^2(T-T_0)+2\sqrt{KK_4}]=\delta^2\ ,$$

which gives a low-field slope

$$s_d'=-\left.\frac{dH_{c2}}{dT}\right|_{T=T_c}=\alpha_0\hbar c/2e\sqrt{KK_4}\ ,$$

and a high-field slope

$$s_x'=\alpha_0\hbar c/2e(\sqrt{KK_4}-\sqrt{K_1K_4})\ .$$

This quadratic equation for H can be solved and gives the same curves as we obtained in Sec. II. The high-field curve extrapolates back to T_0. Again the fit to the data is as in Fig. 1.

It is evident that if H is in the basal plane, the measured curve will depend on experimental details. An ideal resistance measurement would always give the highest H_{c2} and the curvature would depend strongly on direction. This does seem to be observed in some presently existing data.[22] A magnetization measurement may measure an average H_{c2}. This would always show some curvature but not necessarily large anisotropy, since the average phase boundary would tend to lie near the 45° value. For $\mathbf{H}$ neither perpendicular nor parallel to the basal plane, no exact solution exists, though some variational calculations have been carried out for similar problems.[23]

The physical mechanism underlying the unusual shape of the H_{c2} curve for the pure d-wave curve is very simple. At high fields the internal orientation (in ψ space) is determined by its relationship to the field direction. If $\mathbf{H}=H\hat{\mathbf{z}}$, then the angular momentum of the Cooper pair (in the direction $\psi\times\psi^*$) will tend to align or antialign (depending on the sign of K_2-K_3) with the field. The slope of the curve is determined by the energy of the coupling of the angular momentum to the field. At very low fields, on the other hand, the coupling to the orthorhombic distortion locks the direction of ψ into one of the crystal axes of the basal plane, and ψ no longer has a definite angular momentum, leading to a quite different coupling. When $\mathbf{H}$ is in the basal plane, a similar phenomenon is at work. Here the coupling of the field is to the direction of ψ itself. ψ tends to point either perpendicular or parallel to $\mathbf{H}$ at high fields (depending on the sign of K_2+K_3). At low fields, the crossover to a regime where the direction of ψ is dominated by δ again takes place. Very near T_c, the small anisotropy can play an important role, because small energies are involved.

IV. DISCUSSION

There is no way to distinguish between the possibilities of s-d mixing and two-dimensional d wave on the basis of the H_{c2} data in Y-Ba-Cu-O. The only numerical distinction is that the high field extrapolated T_c should be the

same in the x and z direction for the pure d wave. Experimentally they are, in fact, close: 91.44 K and 91.57 K, respectively, which is within the fitting and experimental errors. The observations are therefore probably consistent with both models. There is a simple way that further experimentation could distinguish, however. Upward curvature for the two-dimensional case is produced only by the orthorhombic distortion, whereas the s and d order parameters are split apart even in the absence of such a distortion. For the tetragonal high-T_c materials, we expect no curvature in the H_{c2} plots for pure d and curvature for s-d mixing. Thus the question of the existence of curvature for tetragonal Bi-Sr-Ca-Cu-O is clearly very important for understanding the internal structure of the order parameter.[24] Experimentally, this is completely unclear at this time,[14] presumably again because of contributions to the resistance from the movement of flux.[25]

There is a second and very important difference between the $\Gamma_1-\Gamma_3$ mixing and the Γ_5 states. The fourth-order invariants for the $\Gamma_1-\Gamma_3$ states are:[3,26] $\beta_s|\psi_s|^4,\beta_d|\psi_d|^4,\beta|\psi_s\psi_d|^2$ and $\beta_{sd}(\psi_s^2\psi_d^{*2}+\text{c.c.})$. If $\beta_{sd}>0$, then the equilibrium ψ_s and ψ_d have a relative phase of $\pi/2$. The gap function would be

$$\psi(\mathbf{k})=|\psi_s|(\cos k_x+\cos k_y)+i|\psi_d|(\cos k_x-\cos k_y)\ .$$

$(|\psi(\mathbf{k})|^2)^{1/2}$, the energy gap, vanishes only at isolated points in the Brillouin zone. There will then be no nodes on the Fermi surface and an activated quasiparticle density. This would be consistent with penetration depth measurements, which indicate a very low density of quasiparticles at low temperatures.[6] The Γ_5 representation does not have this property, since in order to give an even representation, the basis functions must be odd under reflection in k_z, e.g., have the form k_zk_x,k_zk_y. Any gap constructed from functions of this kind must have nodes.

The Ginzburg-Landau theory of multicomponent superconductors in a magnetic field is generally quite rich. Unusual effects may be expected not only at the normal-superconducting phase boundary, but also in the $H-T$ plane as a whole, where transitions can occur between superconducting phases belonging to single representation of the point group, but having different orientations in the internal space.[19] These orientations depend on the direction of the external field, as we have seen, so the phase boundaries are expected to move as the direction of the field changes. This seems to be the case in UPt_3.[27] These boundaries can be detected in ultrasound or magnetization measurements at finite fields. At zero field, additional phase boundaries are also possible, and have probably recently been observed in the specific heat of UPt_3.[28]

The picture given here is based on the Ginzburg-Landau theory of BCS superconductors. In view of proposals that the usual picture of normal Fermi liquids breaks down in high-T_c materials, it is reasonable to question whether the Ginzburg-Landau theory is really valid in Y-Ba-Cu-O. In answer to this, it is important to distinguish two cases. If the normal state is a "spin liquid," i.e., breaks no symmetry of the Hamiltonian, the Ginzburg-Landau theory is justifiable on general grounds, even if the Gorkov derivation from microscopic theory would break down. If, on the other hand, the normal state breaks some subtle symmetry, such as parity,[29] then a full theory of the normal-superconducting phase boundary would need to include coupling of the superconducting order parameter to the order parameter of the "normal" state. This would be very analogous to the case of the antiferromagnetic heavy fermion superconductors, and could also produce unusual H_{c2} curves.

In summary, two physical ingredients are required to produce the unusual H_{c2} curves: an order parameter with internal degrees of freedom and a mechanism to split any possible degeneracy of these degrees of freedom. In the two-dimensional Γ_5 case the splitting is produced by an orthorhombic distortion. In the $\Gamma_1-\Gamma_3$ case, the two are nondegenerate at finite doping levels. Hence both can explain H_{c2}. However, based on overall phenomenology and microscopic theory, the $\Gamma_1-\Gamma_3$ s-d mixed phase is the most likely candidate for the actual superconducting state of Y-Ba-Cu-O.

The preceding discussion assumes that the upward curvature in H_{c2} is an intrinsic property of Y-Ba-Cu-O. Recent magnetization data on single untwinned crystals may indicate that this is not the case.[30] This would support the hypothesis that H_{c2} is strongly affected by twin boundaries.[31]

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