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Analysis of Thermodynamic and Transport Properties
of $La_{2-x}M_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ Superconductors

by

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Anisotropic Ginzburg-Landau theory for coupled s-wave and d-wave order parameters is used to analyze the unique thermodynamic and transport properties of the new La$_{2-x}$(Ba,Sr)$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_{7-\delta}$ superconductors. This simple phenomenological approach is used to explain the prevalence of the large Sommerfeld coefficients of the specific heat, the existence of multiple specific heat anomalies, the ultrasonic attenuation peak, and model the anisotropic critical field data as observed in oriented samples.

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multiple specific heat anomalies, the ultrasonic
attenuation peak, and model the anisotropic critical
field data as observed in oriented samples.

Following the discovery by Bednorz and Müller [1] of "high-
temperature" superconductivity in the rare-earth copper oxides,
there have been numerous investigations of the anisotropic
electronic [2,3] and magnetic [3-7] properties of these materials.
It is now well recognized that any successful theory of
superconductivity for the high-T_c oxides must include the quasi-two-
dimensional nature of the Cu-O planes; the theory must provide, in
addition, for a coupling between the planes [8,9]. One of the best
known theories of the new superconductors is the resonating-valence-
bond (RVB) model of Anderson [10] which describes the onset of
superconductivity as a Bose condensation of quasi-particle pairs
within a large-U Hubbard model. It has been shown by Kotliar [11]
and Inui, et al [12] that the superconducting order parameter of
this model possesses s-wave and d-wave components, the latter being
favored at large U and near half-filling. At low temperatures the
mixed (s+d)-state is favored, similar to that found in the heavy-
fermion superconductor $U_{1-x}Th_xBe_{13}$ [13-15]. It is interesting to
note that the low-temperature behavior of the penetration depth,
$\lambda(T)$ [16], the large Sommerfeld coefficients of the specific heat, γ
[17,18], the enhancement of the sound velocity and ultrasonic
attenuation [19,20], and the thermopowers [17] of the
$La_{2-x}(Sr,Ba)_xCuO_4$ (called 214) and $YBa_2Cu_3O_{7-\delta}$ (called 123)

materials are very similar to the heavy-fermion systems. This leads us to believe, as has been suggested on the basis of high-resolution X-ray scattering experiments, [21] that s- and d-wave coupling may exist in the high-T_c superconductors.

Model

In this work we apply anisotropic Ginzburg-Landau (GL) theory [22], previously extended by us to include coupled s-wave and d-wave superconducting order parameters [23], to qualitatively analyze the single-crystal and oriented-film data on the 214- and 123-materials. In particular we think that the large Sommerfeld coefficients $\gamma \sim 5$ mJ/mol K^2 [4,24,25] and 9 mJ/mol K^2 [18,20] for the 40 K and 90 K superconductors, respectively, the anomalous peak in the ultrasonic attenuation at $T \sim 0.9\ T_c$ [19,20], the upturn in the $Hc_2(T)$ curve [6,7], and the anisotropy in the magnetic properties of these materials can be explained in the context of coupled (s+d)-wave states. A brief investigation of the (s+d)-wave state on a square lattice has been reported previously [26] and will be compared with the full three-dimensional results. We are aware that the limitations on any mean-field-theory description of the high-T_c materials, namely the Brout condition, due to critical fluctuations is very restrictive [27]; however, the qualitative agreement of the GL thoery with experiment deserves mention.

As is done in the GL-theory for a single even-parity order parameter, we write the free energy density difference between the superconducting state and the normal state as an expansion in even powers of the complex gap function $\Delta(\vec{k})$, which is related to the anomalous thermal average $<c_{\vec{k}\uparrow} c_{-\vec{k}\downarrow}>$ of the microscopic theory [28], where $c_{\vec{k}\uparrow}$ is the electron annihilation operator with wave vector $\vec{k}$ and spin $\uparrow$. However, for the multiple-order parameter case we must expand $\Delta(\vec{k})$ as a linear combination of the angular momentum basis functions $\{Y_j(\hat{k})\}$,

$$\Delta(\vec{k}) = \sum_{j=0}^{2} \eta_j(k)\ Y_j(\hat{k}) = \sum_{j=0}^{2} \Delta_j(k)\ \exp(i\theta_j)Y_j(\hat{k})\ , \tag{1}$$

where Y_0, Y_1 and Y_2 are analogous to the s, $d_{x^2-y^2}$ and d_{z^2} atomic orbitals. Y_0 and Y_2 both belong to the A_{1g} irreducible representations of the D_{4h} (tetragonal) and the D_{2h} (orthorhombic) point groups, while Y_1 degenerates from a B_{1g} to an A_{1g} representation in going over from D_{4h}- to D_{2h}-symmetry. The consequence of this is to induce some low-angular-momentum s-$d_{x^2-y^2}$- coupling as described below. Generating the invariant terms of the free-energy density, as previously described [29], we can write the free-energy difference between the superconducting and normal state for a tetragonal lattice as

$$F_s - F_n = \int d^3r\ [\ _{sq} + \ _T + \ _{GS} + \ _{GT} + b^2/(8/\pi)]\ , \tag{2a}$$

$$L \cdot \ _{sq} = \sum_{j=0}^{1} (\alpha_j\Delta_j^2 + \beta_j\Delta_j^4) + \Delta_0^2\Delta_1^2\ (\gamma_1 + \delta_1\ \cos2\theta_1)\ , \tag{2b}$$

$$\mathcal{F}_T = \alpha_2\Delta_2^2 + \beta_2\Delta_2^4 + \Delta_0^2\Delta_2^2(\gamma_2+\delta_2\cos2\theta_2)$$
$$+ \Delta_0\Delta_2\cos\theta_2 \, (\lambda_2 + \mu_{20}\Delta_0^2 + \mu_{22}\Delta_2^2) \quad , \tag{2c}$$

$$\mathcal{F}_{GS} = \sum_{j=0}^{1} |\alpha_j|\xi_{jp}^2[|D_x\eta_j|^2 + |D_y\eta_j|^2]$$
$$+ M_{01}[(D_x\eta_0)(D_x\eta_1)^* - (D_y\eta_0)(D_y\eta_1)^* + cc] \quad , \tag{2d}$$

$$\mathcal{F}_{GT} = \sum_{j=0}^{2} |\alpha_j|\xi_{jz}^2|D_z\eta_j|^2 + |\alpha_2|\xi_{2p}^2[|D_x\eta_2|^2 + |D_y\eta_2|^2]$$
$$+ \sum_{j=0}^{1} M_{j2}[(D_x\eta_j)(D_x\eta_2)^* + (-1)^j(D_y\eta_j)(D_y\eta_2)^* + cc]$$
$$+ M_z[(D_z\eta_0)(D_z\eta_2)^* + cc] \quad . \tag{2e}$$

Here we define the coherence lengths, $\xi_{j\ell}$, as $\xi_{j\ell}^2 = \hbar^2/[2m_{j\ell}|\alpha_j|]$, $\alpha_j = A_j(T-T_j)$, where j refers to the species and ℓ the orientation (p refers to the xy-plane), as is done in GL-theory for axial symmetry. The gauge-invariant differential operators are defined as $D_\zeta = (\partial/\partial\zeta - i\phi_{inv}A_\zeta)$ ($\zeta = x,y,z$), with vector potential $\vec{A}$ and $\phi_{inv} = 2\pi/\phi_0$, $\phi_0 = hc/(2e)$) being the flux quantum. The coupling terms in the gradient expressions are characterized by reciprocal effective masses, $M_{ij} = \hbar^2/4m_{ij}$. The phase angles θ_1 and θ_2 are taken relative to θ_0, the phase of η_0, thus ensuring the gauge invariance of Eq. (2). We use $b^2/8\pi$ to represent the internal magnetic field energy density.

Equation (2) has been subdivided into terms arising from a two-dimensional analysis of the square xy-planes, $\mathcal{F}_{sq}$ and $\mathcal{F}_{GS}$, and the additional terms required to analyze tetragonal systems, $\mathcal{F}_T$ and $\mathcal{F}_{GT}$. Reduction of the symmetry to an orthorhombic point group adds an additional term of the form $\Delta_0\Delta_1\cos\theta_1$ to Eq. (2c) and destroys the axial symmetry of the gradient terms. In light of the smallness of the orthorhombic distortion and prevalence of twinning in the copper oxide superconductors [30], we assume the $\Delta_0\Delta_1$ term to act as a perturbation on the free energy of the tetragonal lattice and ignore the effect of reduced symmetry on the gradient terms. It is interesting to note that the two d-wave states above do not couple directly to each other up to order $\ell = 2$ of the relative orbital angular momentum of the Cooper pairs.

Results

We have performed a full minimization of the free energy with respect to the Δ_i's, θ_i's and the vector potential $\vec{A}$ to obtain a self-consistent picture of the thermodynamics and spatial variation of the order parameters which reproduces the dominant features of the single-crystal data of the high-T_c oxides. Even though many parameters appear in Eq. (2), we understand the basic physics in simple qualitative terms. The simplest scenario is that of the

coexistence of a highly anisotropic $d_{x^2-y^2}$-state, Δ_1, responsible for the quasi-two-dimensional character of these materials, with a nearly isotropic, mixed $(s+d_{z^2})$-state, possibly characterizing the "holon"-pair hopping wihtin the RVB picture [31]. As determined by Kotliar [11], the transition temperature, T_1, of the d-state is higher than that of the mixed state. A schematic picture of the relative magnitudes of the order parameters is given in Fig. 1. The relative phases are $\theta_1 - \pi/2$ and $\theta_2 - \pi$ near the transition temperatures. The small amount of $\Delta - \Delta_0 + \Delta_2$ state persisting above the onset temperature, $\bar{T}$, is a consequence of the small perturbation to Eq. (2) caused by a shift from tetragonal to orthorhombic symmetry. Perhaps in a naive way, this may be viewed as adding the three-dimensional character necessary for the onset of superconductivity [9]. The existence of d-wave states, consequently gapless superconductivity, would explain the large observed Sommerfeld coefficients, while the multiple transitions of these states would explain the two specific heat anomalies observed near T_c [32,33].

We feel that the peak in the ultrasound attenuation results from the oscillations of the relative phases θ_1 and θ_2 about their equilibrium values $\theta_1^0 - \pi/2$ and $\theta_2^0 - \pi$, as suggested by Kumar and Wolfle [13] in a different context. Defining $\omega_j^2 - \partial \mathcal{H}_L/\partial \theta_j^2$ (j = 1,2), where $\mathcal{H}_L - \mathcal{H}_{sq} + \mathcal{H}_T$, the oscillation frequencies are given by

$$\omega_1^2 - 4\Delta_0^2\Delta_1^2\delta_1 \quad , \tag{3a}$$

and

$$\omega_2^2 - \Delta_0\Delta_2(\lambda_2 - 8\Delta_0\Delta_2\delta_2 + \mu_{20}\Delta_0^2 + \mu_{22}\Delta_2^2) \quad . \tag{3b}$$

There will be a sharp onset of these oscillations at $\bar{T}$ which will correspond to the attenuation peak at $T - 0.9\,T_c$.

We next consider the variation of the upper critical field, H_{c2} with orientation and temperature. Using a straightforward variational approach on the linearized form of Eq. (2), we have derived the differential GL equations, the full details of which will be presented elsewhere. For the sake of simplicity we assume a $(s+d_{z^2})$-wave mixed state with $\Delta_0 - \Delta_2 - \Delta_m$ and $\xi_{0p} - \xi_{2p} - \xi_{\parallel m}$ and write differential equations for fields parallel, $H^{\parallel}$, and perpendicular, $H^{\perp}$ to the xy-plane. For $H^{\parallel} - (H,0,0)$ and $\vec{A} - (0,-zH,0)$, we have,

$$\Delta_m - (\xi_m\phi_{inv}Hz)^2\,\Delta_m + \xi_m^2(d^2\Delta_m/dz^2) - 0 \quad , \tag{4a}$$

$$\Delta_1 - (\xi_{1p}\phi_{inv}Hz)^2\,\Delta_1 + \xi_{1z}^2(d^2\Delta_1/dz^2) - 0 \quad . \tag{4b}$$

Similarly, for $H^{\perp} - (0,0,H)$ and $\vec{A} - (0,xH,0)$, we have

$$(\alpha_m-\lambda_2)\Delta_m - (\alpha_m\xi_m^2+2M_{02})(\phi_{inv}Hx)^2\Delta_m + (\alpha_m\xi_m^2+2M_{01})(d^2\Delta_m/dx^2) - 0,$$

$$\tag{4c}$$

$$\Delta_1 - (\xi_{1p}\phi_{inv}Hx)^2 \Delta_1 + \xi_{1p}^2(d^2\Delta_1/dx^2) = 0 \quad . \tag{4d}$$

These equations are decoupled and can readily be solved for H_{c2} within the harmonic oscillator approximation to yield

$$H_{c2}^{\parallel} = (\phi_{inv}\xi_{1p}\xi_{1z})^{-1} \quad , \quad H_{c2}^{\perp} = (\phi_{inv}\xi_{1p}^2)^{-1}$$

$$H_{c2} = (1 - \lambda_2/\alpha_m)[\phi_{inv}(\xi_m^2 + 2M_{02}/\alpha_m)]^{-1} \quad . \tag{5}$$

Figure 2 gives the variation of the critical fields with temperature for $\xi_{1z} < \xi_m < \xi_{1p}$. For $H^{\parallel}$ the upper critical field is always determined by the smallest coherence length $\xi_{1z}(0\ K) \sim 7$Å. For $H^{\perp}$ the upper critical field becomes the larger between H_{c2} and H_{c2} as given above. This may explain the discrepancy in the reported 0 K values of the in-plane coherence length ($\xi_{1p}(0) \sim 34$Å, $\xi_m(0) \sim 22$Å), as well as the kink in the H_{c2} data.

The variation of the lower critical field, H_{c1}, with orientation and temperture for the mixed state can be approximated by the expression $H_{c1} = (\Phi_0/4\pi \lambda_{eff}^2)\ln (\kappa_{eff})$ [34], which is valid for large values of the GL-parameter, $\kappa_{eff} = \lambda_{eff}/\xi_{eff}$. For this case the variation of the internal field occurs mainly in a region where the order parameters exhibit their maximum values. One can therefore obtain the penetration depth, λ_{eff}, by casting the current relations into the form of the London equation, $\vec{\nabla} \times \vec{b} = - \lambda_{eff}^{-2}\vec{A}$. The results for $H_{c1}^{\parallel}$ and $H_{c1}^{\perp}$ are,

$$H_{c1}^{\parallel}: \quad \lambda_{\parallel}^{-2} = 2\lambda_m^{-2} + \lambda_{1z}^{-2} + \lambda_z^{-2} \tag{6a}$$

$$H_{c1}^{\perp}: \quad \lambda_{\perp}^{-2} = 2\lambda_m^{-2} + \lambda_{1p}^{-2} + \lambda_p^{-2} \quad , \tag{6b}$$

where the same assumptions on Δ_0 and Δ_2 were made as for the calculation of H_{c2}. At tempertaures near $T_c = T_1$ the lower critical field should behave as λ_1^{-2} since it is proportional to the square of the order parameter. Consequently the anisotropy of H_{c1} should go as the square of the anisotropy of H_{c2}. At lower temperatures the influence of the coupling terms λ_p^{-2} and λ_z^{-2} makes predictions more difficult. The anticipated behavior of H_{c1} for several values of the coupling terms is given in Fig. 3. We are at present not aware of any single-crystal H_{c1} studies over the entire temperature range $0 - T_c$.

Summary

We have analyzed the thermodynamic, magnetic and ultrasound attenuation data on oriented samples of the high-T_c superconductors within the context of anisotropic Ginzburg-Landau theory for coupled, even-parity superconducting states. We are able to present a consistent interpretation of the data in terms of the coexistence of a quasi-two-dimensional d-wave state, with critical temperature $T_1 = T_c$ and a more isotropic mixed (s+d)-wave state with critical tempertaure $T_m < T_c$. We predict the possibility of a "kink" in the temperature dependence of the lower critical field near $0 \cdot 9T_c$, which should be tested by experiments on single crystals.

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Figure Captions

Figure 1. Schematic temperature dependence of the superconducting order parameters, where Δ_m is for the mixed (s+d)-state and Δ_1 for the pure $d_{x^2-y^2}$-state. T_1 and $T = a = T_m$ are the critical temperatures of the mixed and pure states, respectively, and $T = b = \tilde{T}$ is the onset temperature.

Figure 2. Schematic temperature dependence of the upper critical field, H_{c2}. The dashed curves are not experimentally observable. $H^{\parallel}_{c2}$ is the field parallel to the ab-plane, and H_{c2} is the field parallel to c-axis. $T = a = T_m$ and $T = b = \tilde{T}$.

Figure 3. Schematic temperature dependence of the lower critical field, H_{c1}. The dashed curves represent the effect of the coupling terms λ_p^{-2} and λ_z^{-2}. $T = a = T_m$ and $T = b = \tilde{T}$.
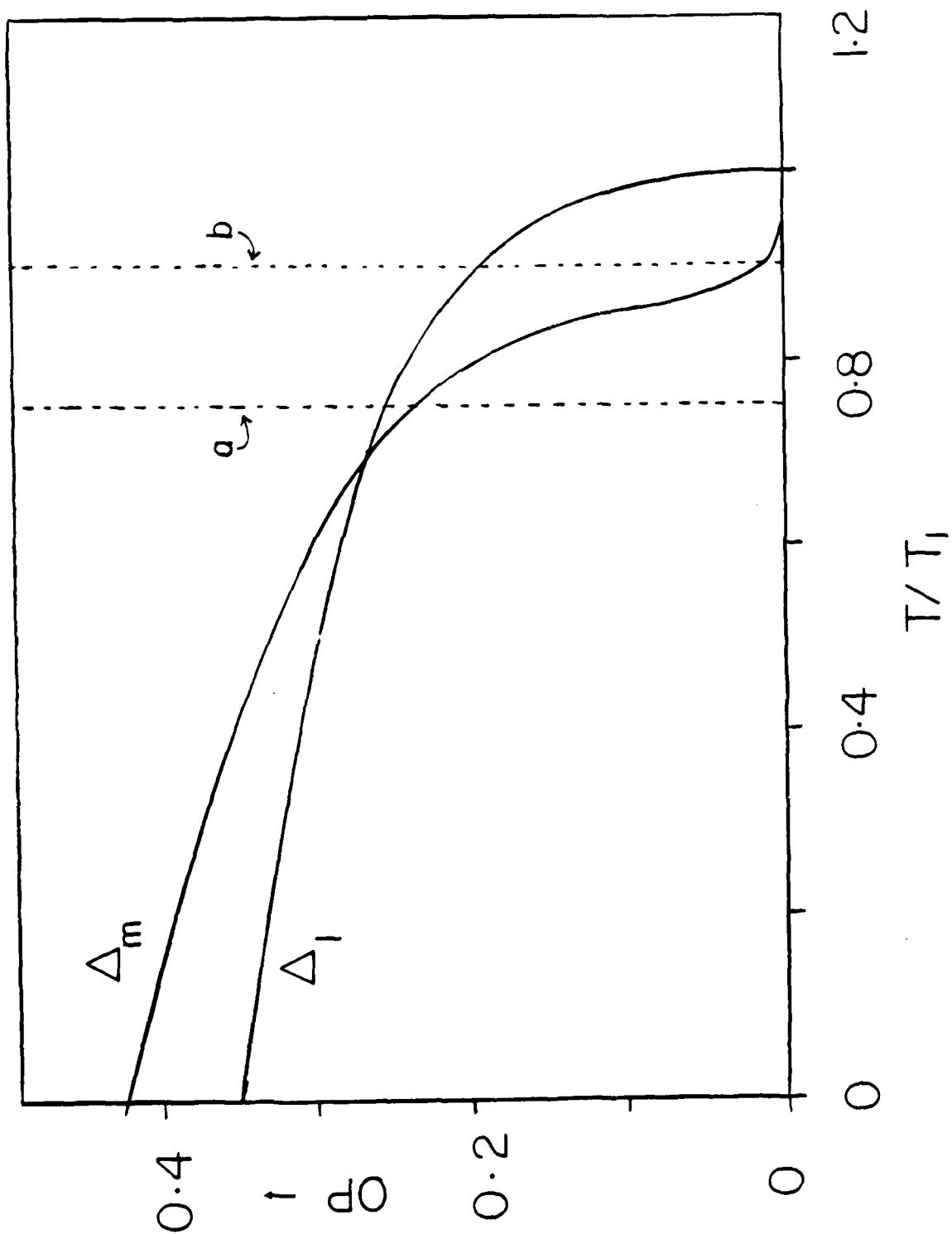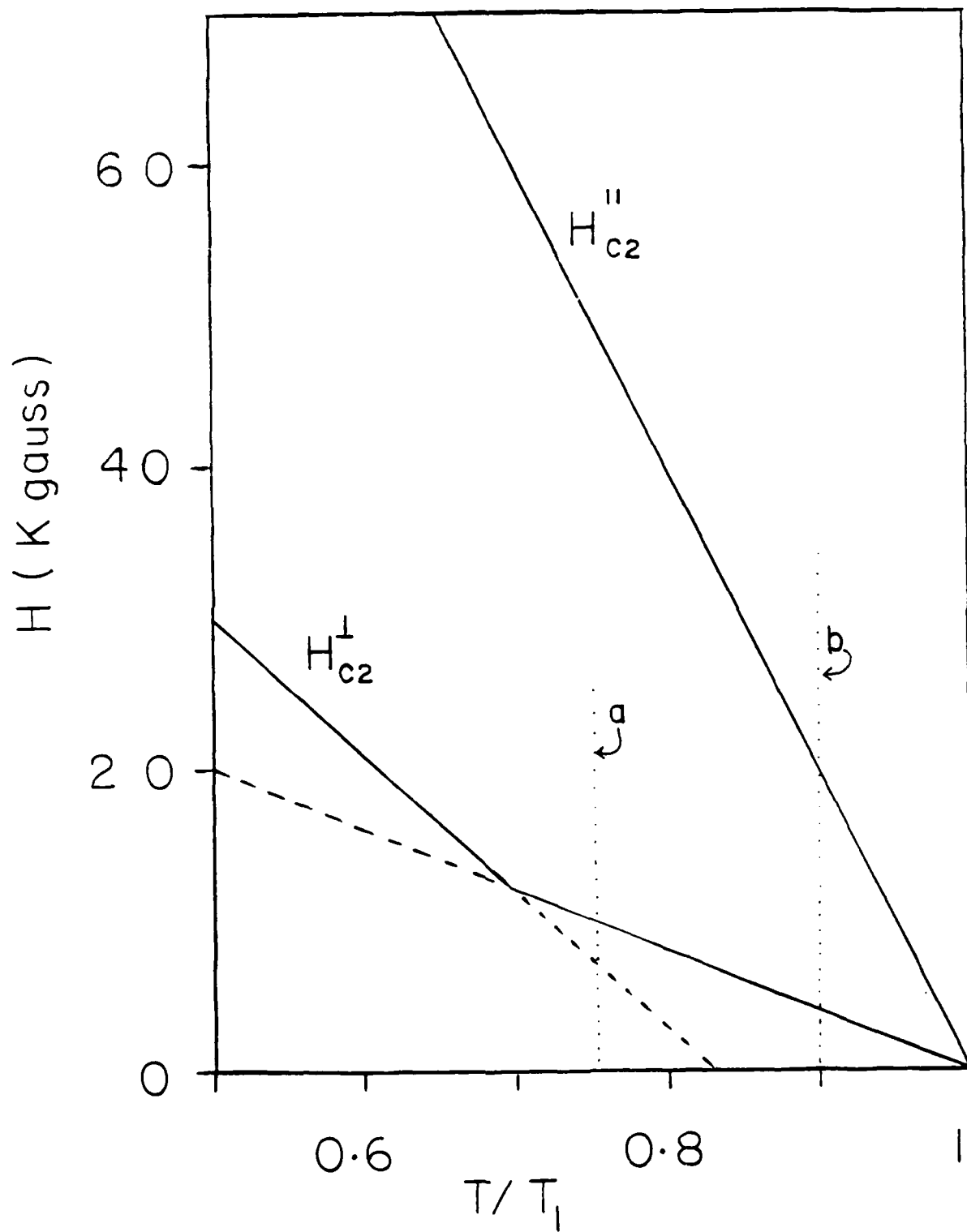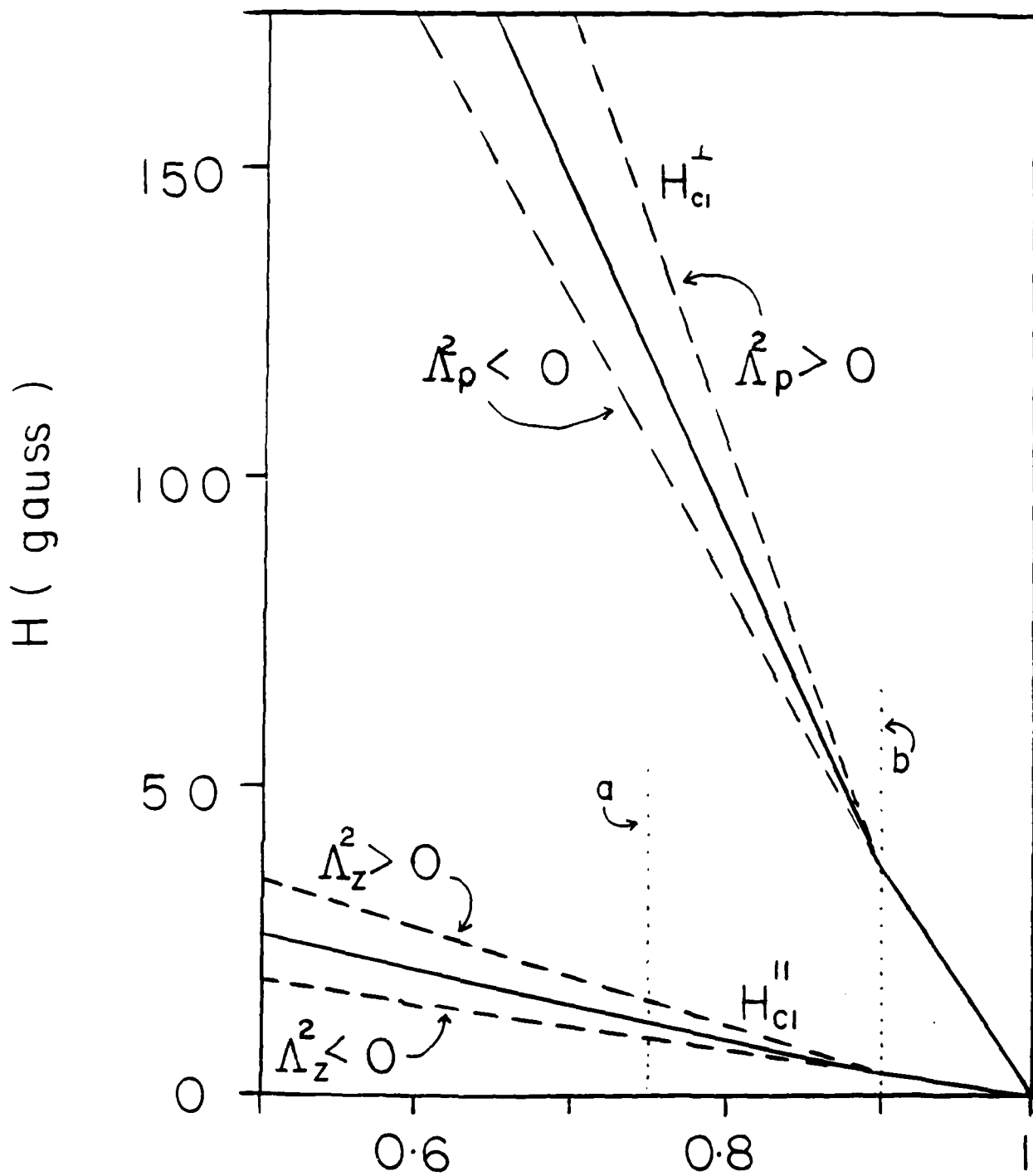
Fig 1

Fig. 2

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