Critical-Field Enhancement and Reduced Dimensionality in Superconducting Layer Compounds

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A strong upward curvature in $H_{c2\parallel}$ and a temperature-dependent critical-field anisotropy are observed in $2H$-TaS_2 intercalated with methylamine. This is characteristic of dimensional crossover in Josephson-coupled superconducting layers and is confirmed by a dramatic reduction of the coherence length perpendicular to the layers. Critical fields greater than 213 kG are observed.

Layer-structure compounds[1] such as $NbSe_2$, TaS_2, and $TaSe_2$ are very anisotropic metals and exhibit a wide variety of electronic phase transitions both in the pure-crystal phase as well as in those produced by doping[2,3] or intercalation.[4,5] In pure form all of these compounds show transitions to a charge-density-wave phase.[6] Pure $2H$-$NbSe_2$ is the best superconductor with a transition temperature of 7.2 K. The anisotropy of the upper critical field has been studied extensively[7-9] and compared to models based on anisotropic Ginsburg-Landau (GL) theory. Pure $2H$-TaS_2 has a T_c of 0.8 K and is more anisotropic than $2H$-$NbSe_2$ although both would be considered as three-dimensional superconductors with large anisotropies. Intercalation of $2H$-TaS_2 with organic molecules has been found to increase both the superconducting transition temperature[5] and upper-critical-field anisotropy.[10,11]

In this paper we present new observations on the extreme superconducting critical-field anisotropy observed in $2H$-TaS_2 intercalated with methylamine (MeA) and dimethylamine (DMA). A temperature-dependent critical-field anisotropy and a strong upward curvature of $H_{c2\parallel}$ is observed at all measured temperatures below T_c. This is the behavior predicted by theories for two-dimensional Josephson-coupled superconductors.

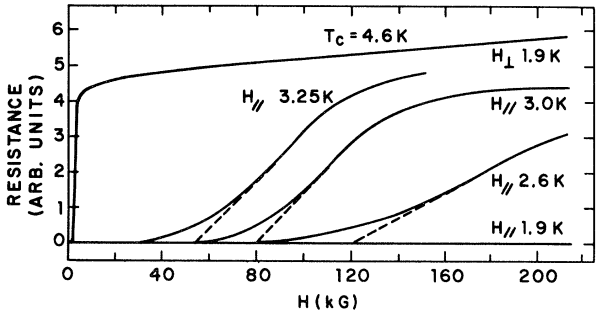

FIG. 1. Resistive transitions induced by applied magnetic fields at selected temperatures. $H_{c2\parallel}$ has been determined from intercept of dashed lines.

Previous measurements on critical-field anisotropies in layer crystals and intercalated layer crystals generally show a temperature-independent anisotropy. At reduced temperatures of 0.8 and below the present experimental data indicate a linear dependence of the critical-field anisotropy on $T_c - T$ and the coherence length perpendicular to the layers also falls much more rapidly than predicted by GL theory. The value of $H_{c2\parallel}$ exceeds the experimental limit of 213 kG at ~2 K and is greater than the paramagnetic limit of 96.7 kG = $18.6T_c$ by more than a factor of 2 with $T_c = 5.2$ K.

The critical fields have been determined by measuring the resistive transitions induced by the applied field as shown in Fig. 1. The upper critical fields $H_{c2\parallel}$ grow rapidly at low temperature and data for several different samples is shown in Fig. 2(a). The corresponding values of $H_{c2\perp}$ increase as shown in Fig. 2(b), but less rapidly so that the upper-critical-field anisotropy $H_{c2\parallel}/H_{c2\perp}$ rises as a linear function of $T_c - T$ as shown in Fig. 3.

A fit to the angular dependence of the critical field can be used to determine the ratio of the coherence lengths perpendicular and parallel to the layers. The ratio $\xi_\parallel/\xi_\perp$ has been determined to be ~6 for pure[3] $2H$-TaS_2, ~25 for $2H$-TaS_2 + $(\text{pyridine})_{1/2}$ (Refs. 10,11) and ~37 for $2H$-TaS_2 + $(\text{aniline})_{3/4}$.[10] In the first two cases the ratio was temperature independent corresponding to a temperature-independent critical-field anisotropy. In the case of $2H$-TaS_2 + $(\text{aniline})_{3/4}$ the anisotropy was temperature independent down to 1.7 K with an increase in anisotropy observed below this temperature for one specimen. For the present specimens the ratio $\xi_\parallel/\xi_\perp$ is temperature dependent over the entire range and reaches a value of 80 at ~2 K and >100 at lower temperatures based on a linear extrapolation of the critical-field anisotropy.

Single crystals of $2H$-TaS_2 were produced by

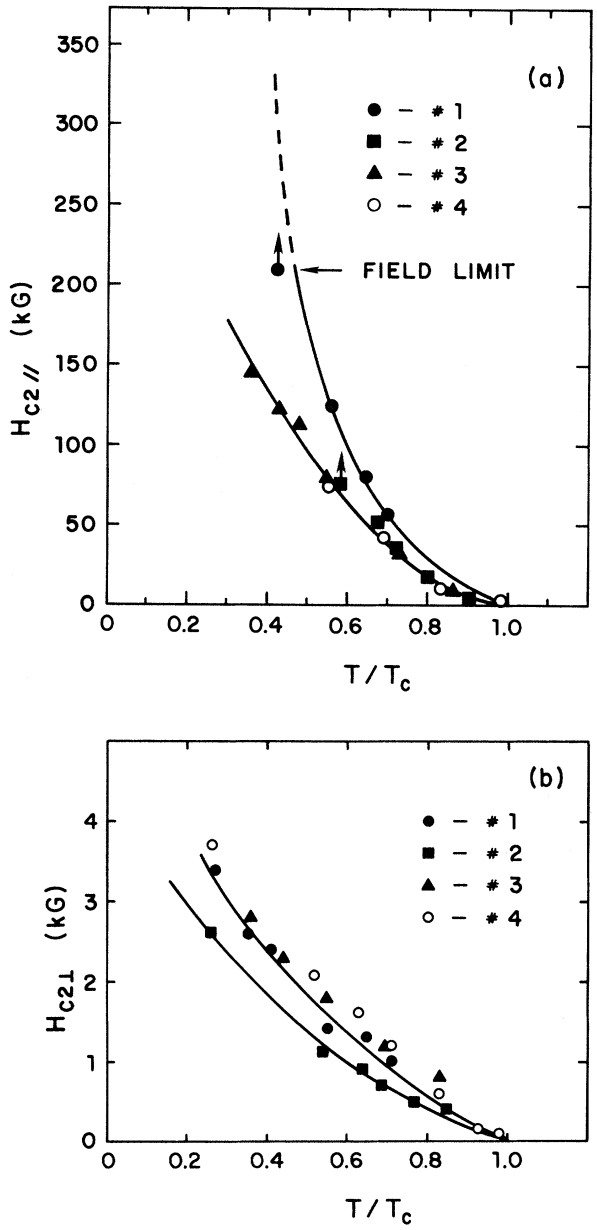

FIG. 2. Upper critical fields (a) $H_{c2\parallel}$, (b) $H_{c2\perp}$ as a function of T/T_c. T_c's for the samples are 4.6 K (No. 1), 4.2 K (No. 2), 3.6 K (No. 3), and 4.1 K (No. 4). Points with arrows are zero resistance at field limit. Dashed line indicates extrapolation based on linear dependence observed in Fig. 3 and the value of $H_{c2\perp}$.

annealing single crystals of $4Hb$-TaS_2 grown by the iodine-vapor transport method. The residual resistance ratios of the pure crystals were ~200 and the existence of well-defined de Haas-Shubnikov oscillations[12] confirmed the high perfection of the crystals. Intercalation was carried out at room temperature for 1 to 6 h. After intercalation the residual resistance ratios were in the range 6–10 and the resistivity just above T_c was measured to be $\rho = 7\times10^{-4}$ Ω cm. The crystals intercalated with MeA show T_c's in the range 3.8–5.2 K and are quite sensitive to temperature cycling which can change the quality and T_c of a given specimen. All specimens show the strong increase in anisotropy at low temperature and exhibit the same qualitative behavior.

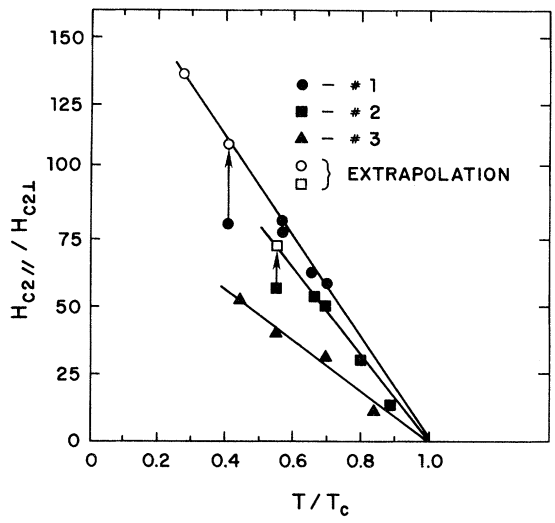

FIG. 3. Upper-critical-field anisotropy, $H_{c2\parallel}/H_{c2\perp}$, plotted as a function of reduced temperature. Open points represent extrapolated points because of limitations in the experimental field.

The anisotropic GL theory is generally valid only close to T_c where $\xi_\perp(T)$ is much larger than the layer separation S. A more appropriate theory for a layered superconductor is that of Lawrence and Doniach[13] (LD) in which the layered material is considered to be a stack of two-dimensional superconductors coupled through Josephson tunneling between the layers. Klemm, Luther, and Beasley[14] (KLB) found that the LD equations predict the existence of a temperature $T^* < T_c$ for which $H_{c2\parallel}$ becomes infinite. This condition is defined by the relation $\xi(T^*) = S/\sqrt{2}$. The physical interpretation given to this condition is that for this value of $\xi_\perp$ the normal cores of the vortices can fit between the layers and thus orbital effects are removed as a method for quenching superconductivity. For $T < T^*$, the Josephson-coupled character of the layer materials should be prominent.

KLB have extended the LD model to include the effects of Pauli paramagnetism and spin-orbit scattering. Orbital effects, Pauli paramagnetism, and spin-orbit scattering all affect the behavior of

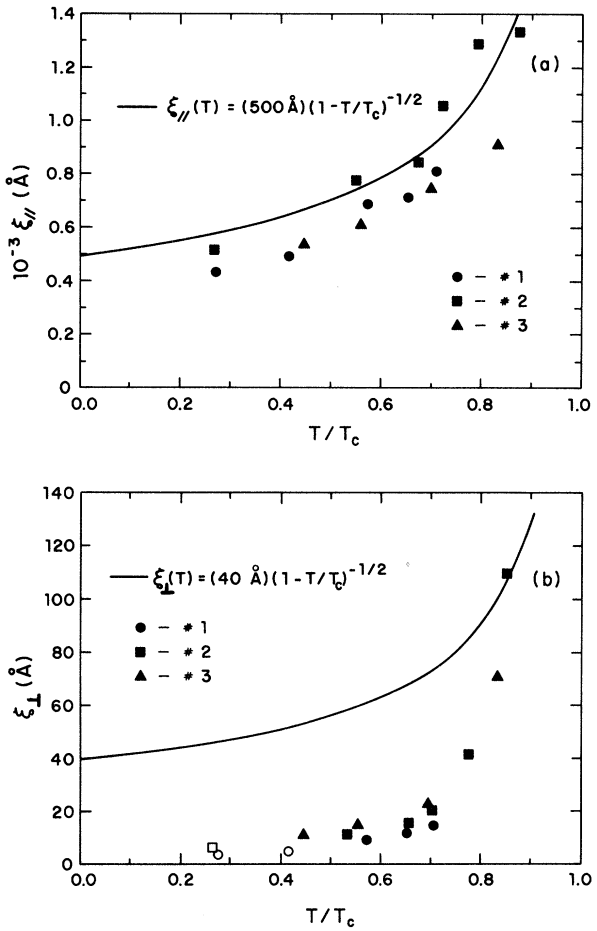

FIG. 4. Temperature dependence of coherence lengths estimated from Eqs. (1) and (2). Solid lines represent GL temperature dependence. (a) $\xi_{\parallel}$ follows GL fairly closely. (b) $\xi_{\perp}$ decreases more rapidly than GL and approaches layer spacing below 2 K. Open points are based on extrapolation from Fig. 3.

of $H_{c2\parallel}$ and for certain ranges of the parameters the combined effects can be expected to allow a dimensional crossover with an anomalous behavior of $H_{c2\parallel}$. A point-by-point estimate of $\xi_{\perp}$ and $\xi_{\parallel}$ as a function of temperature has been obtained by use of GL theory. The appropriate expressions are

$$H_{c2\perp}(T) = \frac{\varphi_0}{2\pi \xi_{\parallel}^{\,2}(T)} \tag{1}$$

and

$$H_{c2\parallel}(T) = \frac{\varphi_0}{2\pi \xi_{\parallel}(T)\xi_{\perp}(T)}, \tag{2}$$

where φ_0 is the flux quantum. The temperature dependence of coherence length predicted by the GL theory is given by

$$\xi(T) \sim \xi(0)\left[\frac{T_c}{(T_c - T)}\right]^{1/2}. \tag{3}$$

The values of $\xi_{\parallel}$ calculated at each temperature from Eq. (1) follow the temperature dependence of Eq. (3) fairly closely as shown in Fig. 4(a). In contrast the values of $\xi_{\perp}$ calculated from Eq. (1) and (2) and shown in Fig. 4(b) drop more rapidly than predicted by GL theory and become comparable to the 9.2-Å layer spacing below reduced temperatures of 0.5. This estimated behavior of $\xi_{\perp}$ clearly indicates a decoupling of the layers below $T/T_c = 0.8$.

The present data can be used to make rough estimates of the parameters KLB theory which depend on values determined for $dH_{c2\perp}/dT$ and $dH_{c2\parallel}/dT$. In all measurements so far made for intercalated layer structures an anomalous curvature near T_c has been observed. Comparisons of data and KLB theory by Prober *et al.*[10] neglect this curvature and extrapolate the lower-temperature linear portion of the anisotropy. The strong curvature of $H_{c2\parallel}$ over the entire temperature range in the present experiments makes this choice somewhat arbitrary. Neglecting the rapid curvature near T_c and extrapolating the slope with data points below $T/T_c \sim 0.8$ gives $dH_{c2\parallel}/dT = 114$ and $dH_{c2\perp}/dT = 0.45$. These numbers give values of $\xi_{\parallel}(0)$ and $\xi_{\perp}(0)$ of 418 and 3.2 Å, respectively. The corresponding coupling parameter[10] $r = 0.6$ and the paramagnetic parameter[10] $\alpha = 6$.

The lower limit on the spin-orbit scattering time can only be estimated using the mean free path calculated from the total resistivity of $\rho = 7 \times 10^{-4}\ \Omega$ cm measured just above T_c. This leads to a minimum value of the spin-orbit scattering parameter[10] $\tau_{s.o.}T_c \approx 0.002$. These values of the parameters correspond to curves in the family of theoretical curves calculated for $H_{c2\parallel}$ by KLB (see Figs. 8–10 of Ref. 14) which exhibit a relatively strong upward curvature. The value of T^* is near T_c and cannot be precisely located from the present data. These numbers are very favorable for dimensional crossover and extend the trend of consistency between theory and experiment established by Prober *et al.*[10]

The $2H$-TaS_2 + (DMA) crystals show the same temperature-dependent critical-field anisotropy as observed for $2H$-TaS_2 + $(MeA)_{1/2}$ and the analysis follows similar lines to that just presented. The relative anisotropy observed for $2H$-TaS_2 + $(pyridine)_{1/2}$, $(analine)_{3/4}$, and $(MeA)_{1/2}$ does not correlate directly with the layer spacings of ~12

Å, ~18 Å, and ~9 Å, respectively. This can result from differences in perfection of the intercalated crystals or from different effects of the organics on the Josephson tunneling probability and will require more extensive sample characterization.

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Observation of Strong Temperature Dependence and Direct-Transition Effects in Angle-Resolved X-Ray Photoelectron Spectra from the Valence Bands of Single-Crystal Tungsten

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Strong temperature dependence has been observed in angle-resolved x-ray photoelectron spectra from the tungstem valence bands, indicating the importance of phonon-assisted nondirect transitions in Brillouin-zone averaging. The spectral changes with direction at ambient temperature furthermore agree very well with the predictions of a direct-transition model assuming free-electron final-state dispersion and constant matrix elements. The direct and nondirect components in the temperature-dependent spectra are also determined.

Subsequent to the first observation that angle-resolved x-ray photoelectron spectra (XPS) from the valence bands of single-crystal materials exhibited significant changes in fine structure with emission direction,[1] a number of studies have been directed at the measurement and theoretical interpretation of such phenomena.[1-10] Two rather simple limiting models have been utilized in attempts to interpret the spectra:

(1) *A direct-transition (DT) model with free-electron dispersion in the final state.*[1,4,10]—In this model, as proposed by Baird, Wagner, and