Anomalous Temperature Dependence of the Upper Critical Magnetic Field in Bi-Sr-Cu-O

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$H_{c2}(T)$ has been measured for thin BSCO films over a larger combined range of magnetic field and reduced temperature than for any other superconductor. $H_{c2}(T)$ diverged anomalously as the temperature decreased: At the lowest temperature, it was 5 times that expected for a conventional superconductor. Such a strong divergence cannot be explained by any conventional model.

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The coherence length ξ is one of the characteristic parameters of a superconductor. It is a difficult quantity to measure directly, however, and it is thus often calculated from the expression $H_{c2}(0)=\Phi_0/2\pi\xi^2$, where $H_{c2}(0)$ is the upper critical magnetic field measured near $T=0$, and Φ_0 is the magnetic flux quantum. For low temperature superconductors, the measurement of $H_{c2}(T)$ is not particularly difficult because its full extent lies within reach of the magnetic fields (say, 15 T) which may be generated at several laboratories. By contrast, measurements of $H_{c2}(T)$ for the high temperature superconductors (HTS) have been limited to temperatures near T_c because H_{c2} in these materials rapidly exceeds accessible laboratory magnetic fields when the temperature is reduced to only nine-tenths of T_c. Thus the values of ξ calculated from such data require either a large extrapolation to $T=0$ K using a presumed functional form for H_{c2} or calculation of $H_{c2}(0)$ from the slope $(dH_{c2}/dT)_{T_c}$ using the Werthamer-Helfand-Hohenberg (WHH) expression [1] $H_{c2}(0)=0.7T_c(dH_{c2}/dT)_{T_c}$. If, for some reason, H_{c2} should depart from the expected theoretical behavior, then this procedure could be subject to unanticipated error.

To further compound the uncertainty in obtaining ξ for HTS materials, the superconductive transitions are generally broadened in an applied magnetic field [2-7] which introduces ambiguity in choosing H_{c2}. However, magnetization measurements [8] yielded the expected linear behavior of H_{c2} near T_c from which $H_{c2}(0)$ has been calculated using the WHH expression. The magnetization results are more reliable because there is less ambiguity in defining H_{c2} than in the former case. The anomalous upturn in $H_{c2}(T)$ has even been seen in a polycrystalline sample of the cubic, non-copper-oxide material $Ba_{1-x}K_xBiO_3$ [3]. Measurements of $R(T)$ in a magnetic field on crystals [2,3] and thin films of $La_{2-x}Sr_xCuO_4$ [9] showed an upward curving $H_{c2}(T)$ for the field oriented parallel to the c axis. Even though some of the most striking curves in Ref. [9] came from $R(T,H)$ data which did not broaden appreciably, this odd result was explained as being caused by flux motion [10]. The same authors performed similar measurements on the $Nd_{2-x}Ce_xCuO_4$ [11] system and obtained rather conventional $H_{c2}(T)$ results. However, the authors used the $R=0$ and $R=\frac{1}{2}R_{\text{normal}}$ criteria for defining $H_{c2}(T)$, which are susceptible to the effects of flux dynamics. If one uses an $R=90\% R_{\text{normal}}$ criterion then this $H_{c2}(T)$ curve also curves upward. Similar studies [12,13] on $Sm_{1.85}Ce_{0.15}CuO_{4-y}$ show relatively narrow superconducting transitions which do not significantly broaden in an applied magnetic field for H parallel to the c axis. The $H_{c2}(T)$ curve which was extracted from these data also shows an unconventional upward curvature extending down to temperatures as low as 1 K (corresponding fields of 4-7 T).

In this Letter we report the first $H_{c2}(T)$ data on a high-quality thin film of $Bi_2Sr_2CuO_y$. The measurements extend over the largest combined range of reduced temperature, $t=T/T_c$ (minimum $t=0.005$), and magnetic field (fields as high as 35 T) for any superconductor to date. We observed a striking divergence in $H_{c2}(T)$ as T approached zero. We find that such a divergence cannot be rationalized by any of the conventional or unconventional models for the behavior of superconductors in a magnetic field and thus requires the development of a new physical theory. Similar results have been observed in overdoped $Tl_2Ba_2CuO_6$ thin films by Mackenzie *et al.* [14].

The $Bi_2Sr_2CuO_y$ system is an excellent choice for studying $H_{c2}(T)$ of a copper-oxide superconductor. It has a comparatively simple structure (no chains, one CuO layer). Also the superconducting properties are easily modified by varying the Bi-Sr ratio. T_c is relatively low and thus the superconducting transitions are not significantly broadened in a magnetic field (flux dynamic broadening effects are small). Furthermore, $H_{c2}(T)$ is within laboratory reach over a very broad range of temperatures.

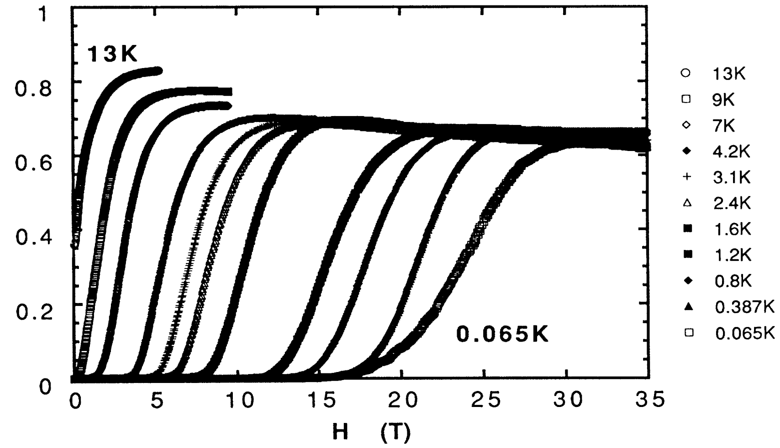

FIG. 1. Resistance R as a function of magnetic field H at several temperatures T. The temperatures decrease monotonically from 13 K (far left-hand curve) to 65 mK (far right-hand curve).

The superconducting phases of the $Bi_2Sr_2CuO_y$ system are actually Sr deficient [15–17]. While bulk superconducting samples (both "single crystals" and polycrystalline) have been studied [15–17], they are difficult to prepare in pure form owing to the tendency to also generate the stoichiometric compound $Bi_2Sr_2CuO_y$, which is a monoclinic insulating phase [16,17]. Superconducting films were successfully made using atomic, layer-by-layer, molecular-beam evaporation (ALL MBE) [18] where the chemical composition is carefully controlled. Films approximately 1000 Å thick of $Bi_2Sr_2CuO_y$ were grown on $SrTiO_3$ substrates and subsequently patterned into a geometry suitable for resistance measurements.

The resistive transition of the film in zero magnetic field indicated that the superconductive transition began at a temperature of 19 K and extended down to 12 K where the transition was complete. When the magnetoresistance was measured, the film was oriented with its c axis parallel to the applied field. The resistance was measured using a standard, four-probe ac (excitation frequency: 100 kHz, applied current: 0.4 μA) technique as the magnetic field was pulsed from zero to 35 T. The magnetic field reached its maximum value 70 ms after pulse initiation, and it subsequently decayed to zero in 800 ms. Data were recorded during both periods to check for errors due to thermal drifts caused by heating or for error signals induced by transient effects. The measured resistance was essentially the same in both cases, indicating that these effects were not significant. Measurements were made at temperatures as low as 1.6 K in a pumped ^{4}He cryostat. The sample was then transferred into another cryostat which contained a plastic dilution refrigerator in which the sample could be cooled down to 65 mK.

Figure 1 shows a series of $R(H,T)$ curves for temperatures varying from 13 K down to 65 mK. These curves indicate that the transition widths are relatively insensitive to the applied field strength and that the quenched, normal state resistance increases below $T_c(H=0)$. We define H_{c2} for each curve as the magnetic field where the extrapolated normal state resistance and the tangent of the transition meet (Fig. 2 inset). Because the transition is not significantly broadened by the magnetic field, we have shown that any choice of position on the $R(H,T)$ curve defines $H_{c2}(T)$ curves with essentially the same shape.

Many of the early critical field measurements of the HTS have been questioned because the $R(T)$ curves broaden significantly in a magnetic field due to flux dynamics. Roesler *et al.* [19] have performed tunneling measurements on $Ba_{1-x}K_xBiO_3$ films in magnetic fields and were able to extract the Pauli-limited $H_{c2}(T)$ curve. They also measured $R(T,H)$ for the same sample. They concluded that $H_{c2}(T)$ defined by the $R(H,T)$ curve corresponded to the one obtained from tunneling if the former was defined near the "top" of the transiton. Therefore, in this work, $H_{c2}(T)$ is defined as shown in the inset of

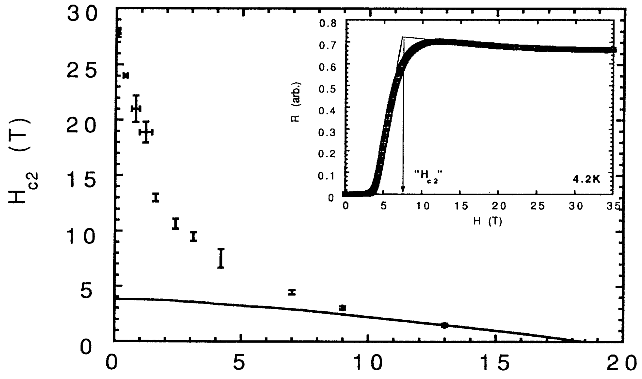

FIG. 2. Upper critical magnetic field $H_{c2}(T)$ data derived from Fig. 1. Solid curve: WHH theory. Inset: Demonstration of construction used to define H_{c2} from a measured $R(H)$ curve.

Fig. 2 which yields values that are virtually identical to a 10% resistance drop criterion.

Figure 2 displays the $H_{c2}(T)$ data extracted from the $R(H,T)$ data shown in Fig. 1. The conventional WHH curve, matched at $dH_{c2}(T_c)/dT$, is shown for comparison. That slope is estimated to be 0.29 T/K so that $H_{c2}(0)$ is calculated to be 3.8 T. This value of $H_{c2}(0)$ corresponds to a coherence length of ~55 Å in the *a-b* plane.

The curves measured here have several features in common with measurements on the Nd-Ce-Cu-O [11] and Sm-Ce-Cu-O [12,13] systems in that the transition widths are relatively insensitive to the applied field strength and the quenched, normal state resistance increases below the zero-field transition temperature. Dalichaouch *et al.* [12] compared the rather classical critical field behavior for the $Nd_{1.84}Ce_{0.16}CuO_{4-y}$ system reported by Hikata and Suzuki [11] with the divergent behavior for H_{c2} they observed in $Sm_{1.85}Ce_{0.15}CuO_{4-y}$. Magnetic susceptibility measurements showed that the Sm^{3+} ions order antiferromagnetically at about $0.6T_c$, which is the temperature below which the normalized $H_{c2}(T)$ data for the Nd and Sm compounds were no longer coincident. The authors thus proposed that the anomaly in $H_{c2}(T)$ for the latter was due to an interaction between the rare-earth magnetic moments and the superconducting charge carriers. Such coupling has been known to cause deviations from conventional $H_{c2}(T)$ behavior in the RMo_6X_8 (R = rare earth and X = S, Se) and in the RRh_4B_4 systems [20]. Since there are no magnetic rare-earth ions in the Bi-Sr-Cu-O system studied by us, however, this argument does not apply. There is evidence that uncompensated copper spins due to underoxygenated material may antiferromagnetically order in the YBCO system [21]. It is therefore possible that such ordering occurs in this system too, which could perhaps account for the anomaly.

Han *et al.* [13] subsequently analyzed the same data presented in Ref. [12] using the Ginzburg-Landau fluctuation theory for layered superconductors developed by Ullah and Dorsey [22,23]. Upon this reanalysis, the divergence in H_{c2} vanished, and they extracted an $H_{c2}(T)$ curve which matched the WHH curve. Such an analysis is inappropriate in our case because our data fall outside the range of the theory [24].

The WHH theory predicts the well-known shape for conventional superconductors in either the dirty or clean limits and includes spin and spin orbit effects [1]. When applied to HTS, however, the WHH model fails to account for the anomalous shape of $H_{c2}(T)$.

The anisotropic nature of the HTS suggests that reduced dimensionality could be the source of the anomaly. The two-dimensional nature of these systems has been treated theoretically assuming a cylindrical Fermi surface [25]. Performing a WHH type analysis for such a Fermi surface does not produce an anomalous $H_{c2}(T)$ curve. Schneider [26] studied a dirty limit, Ginzburg-Landau version of a mean-field model for quasi-two-dimensional superconductors to calculate $H_{c2}(T)$. This result calculates a correction to the linear slope, dH_{c2}/dT, near T_c and predicts upward bending deviations. This work however, is not relevant for temperatures far from T_c.

Work on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [27,28], α_t-(BEDT-TTF)$_2$I$_3$ [29], (SN)$_x$ [30-32], dichalcogenides [33,34], ZrSe$_2$(A$_x$ZrSe$_2$) [35], graphite intercalation compounds [36,37], and various multilayer systems (with H perpendicular to the film surface) [38-41] have revealed departures from WHH behavior at low temperatures and support the conjecture that reduced dimensionality is responsible for the anomalies.

Several groups [42-44] have calculated $H_{c2}(T)$ for the field perpendicular to the layers of superconducting superlattices. Figure 3 compares our data with two theoretical predictions. The curve labeled "superlattice" corresponds to the critical field line calculated by Takahashi and Tachiki [43] where we have scaled the published curve for $T_c = 18.5$ K and matched the measured value of H_{c2} at 4 K. This predicted curve is unable to model the divergent behavior observed by us.

Upward curvature in $H_{c2}(T)$ has been observed in heavy fermion systems such as UPt$_3$ [45,46]. Joynt [47] has suggested that an upward curvature in $H_{c2}(T)$ can occur in heavy fermion systems and applied his model specifically to YBCO, and suggested that this was evidence for *s-d* pairing. However, this model only accounts for curvature near T_c and is inadequate for the full temperature range of these data.

If electrons couple very strongly to the lattice then Bose particles (bipolarons) can form. Alexandrov has predicted divergent $H_{c2}(T)$ curves by treating bosons localizing in a random potential [48] where

$$H_{c2}(T) = H_d(1/t)^{3/2}\left[1 - t^{3/2} - \frac{Tn_L}{\gamma n}\beta(T/\gamma)\right]^{3/2}, \quad (1)$$

$$\beta(x) = \sum_{k=0}^{\infty} \frac{(-1)^k}{x+k},$$

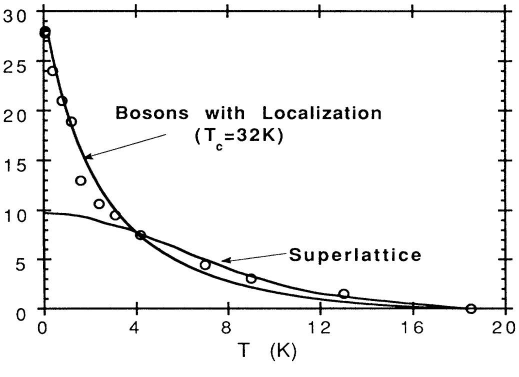

FIG. 3. Comparison of measured H_{c2} (○) data with a boson gas model and a superlattice model.

and $H_d = \phi_0/2\pi\xi_0^2$, $t = T/T_c$, n_L denotes concentration of localized states, n denotes concentration of boson states, and γ is the binding energy of a single random potential well. The curve labeled "bosons with localization" in Fig. 3 is a plot of this expression with $H_d = 2.8$ T, $n = n_L$, $\gamma = 4.5$ K, and $T_c = 32$ K. While the curve can be made to fit the data with these parameters, the fitted value of T_c is much too high compared with that obtained experimentally.

Finally, theoretical work which includes Landau quantization effects at high fields predicts divergent critical behavior at low temperatures [49]. Such behavior shows up as a precursor to the oscillatory and reentrant phenomena which are the true hallmarks of the model. While the quasi-two-dimensional nature and low carrier concentration typical of HTS systems make them ideal candidates for such a model, we must be careful in accepting until one observes H_{c2} oscillating as a function of temperature.

In conclusion, measurements of $H_{c2}(T)$ for single layer Bi-Sr-Cu-O reveal a startling divergence with decreasing temperature down to 65 mK and 30 T. This result cannot be explained by any conventional model which relies on magnetic ordering, local pairing mechanisms, or superlattice superconductivity.

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