

High-field measurements on the high- T_c superconductors $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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We have measured the superconductive properties of the high- T_c superconductors $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in magnetic fields up to 25 T. Conservative estimates of the critical field at $T=0$ yield, respectively, 45 ± 5 and 200 ± 25 T. The slope (dB_{c2}/dT) near T_c for the Y-Ba-Cu-O compound is about twice as large as in La-Sr-Cu-O. For both compounds the magnetoresistivity indicates a large anisotropy of the critical field. The Sommerfeld parameter γ is estimated to be, respectively, 7 and 16 $\text{mJ}(\text{moleCu})^{-1}\text{K}^{-2}$, which indicates that the higher T_c of Y-Ba-Cu-O, when compared with La-Sr-Cu-O, might be due primarily to an increased density of states at the Fermi level.

Recent measurements on the new class of high- T_c superconductors indicate that these high T_c 's are accompanied by unprecedented high values for the critical field. Orlando *et al.*¹ have shown that at least a fraction of the La-Sr-Cu-O compound is still superconducting at 45 T and at 4.2 K. Uchida *et al.*² have measured the resistance of this material in magnetic fields up to 33 T. Up to the highest field they find no deviation from a linear behavior characterized by $(dB_{c2}/dT)_{T_c} \approx 2$ T/K. [Throughout this article we will determine the critical field $B_c(T)$ at the point where the resistance is half the normal-state resistance, extrapolated from the linear behavior above T_c .] Uchida *et al.* extrapolate their data to zero temperature, which gives an upper limit for the critical field of 60 T. In general, low-field measurements on $\text{La}(\text{Sr},\text{Ba})\text{CuO}$ (Refs. 3–6) yield a somewhat smaller slope, and consequently a lower extrapolation to zero temperature.

The first experiments on multiphase Y-Ba-Cu-O samples showed a slope $(dB_{c2}/dT)_{T_c}$ in the range of 1.2 to 1.8 T/K, and extrapolations to zero temperature between 75 and 120 T,^{7–11} where we again restrict ourselves to the midpoint data. Estimates based on the onset data, however, show that a considerably higher critical field may be obtained for homogeneous single-phase material.⁷

These rather low values for the slope are at first somewhat puzzling. Cava *et al.*¹² have calculated the Sommerfeld parameter γ for the Y-Ba-Cu-O compound, based on a slope of 1.3 T/K. They find a surprisingly small value $\gamma = 3\text{--}5$ $\text{mJ}(\text{moleCu})^{-1}\text{K}^{-2}$. This seemed to indicate that the density of electronic states at the Fermi level is even lower than in $\text{La}(\text{Sr},\text{Ba})\text{CuO}$. The high critical temperature of Y-Ba-Cu-O, compared with $\text{La}(\text{Sr},\text{Ba})\text{CuO}$, therefore raises the question whether yet another mechanism is responsible for its superconductivity.

The purpose of the present study is to compare the superconductive properties of both materials in dc magnetic fields up to 25 T. We will compare the results on high-quality single-phase samples with the standard Werthamer, Helfand, and Hohenberg (WHH) theory¹³ of type-II superconductivity, and discuss its implications for the spin-orbit interaction and density of states in these materials.

We prepared our La-Sr-Cu-O samples similarly to Ref. 14. The Y-Ba-Cu-O samples were made from the appropriate mixtures of the oxides Y_2O_3 , CuO, and the carbonate BaCO_3 , which were fired in air at approximately 900 °C for at least 40 h, with four intermediate grindings. The thoroughly mixed powders were pressed into pellets at a pressure of 6 kbar. The pellets were annealed for 20 h in air at 925 °C. A second annealing in pure oxygen was found to improve the superconductive properties. Characterization of the Y-Ba-Cu-O samples was done with x-ray diffraction, magnetization, and resistivity measurements. The x-ray spectra confirmed a homogeneous composition with an orthorhombic crystal structure in agreement with the data of Cava *et al.*¹² Upon cooling of the samples in a magnetic field of 0.105 mT, a Meissner effect of about 60% of the ideal value was observed. When the sample was cooled to 20 K before the field was applied, the diamagnetic shielding was even larger than expected for the ideal diamagnetic case, as a result of the porous nature of these ceramic samples.

The resistive transition was measured in a variable-temperature cryostat. In a magnetic field, the temperature was regulated with a capacitance thermometer, which was calibrated in zero field against a germanium resistor. The resistance was determined with a standard four-probe technique, with the leads glued to the sample using carbon black paint. The current density was kept below 5×10^{-3} Acm^{-2} , to avoid Ohmic heating or exceeding the critical current density.

Measurements were done in a 15-T Bitter magnet, and for the higher fields in a 25-T hybrid magnet system. Most data were taken at a constant temperature, while sweeping the field. As a check, some points were taken in a fixed field, while varying the temperature.

In zero field, the 10%–90% width of the resistive transition for our best La-Sr-Cu-O and Y-Ba-Cu-O samples was 3 and 1.4 K, respectively. The resistive transitions become significantly broader in an applied magnetic field. Measurements in high magnetic fields prove to be especially useful to ascertain the homogeneity of the superconductive properties. Samples with a different composition or with a different annealing procedure often showed a

clearly resolved shoulder in the resistive transition. With increasing magnetic field this shoulder was found to develop into a steplike structure, while the steep portions of both steps shifted only gradually to lower temperatures. This proves that these samples consist of two phases with different critical temperatures. Our further analysis only concerns those samples which had a steep monotonic resistive transition up to the highest field.

In Fig. 1 we show the resistive transitions of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-\delta}$ sample for magnetic fields up to 14.5 T. In all fields we find a monotonic decrease of the resistance. However, the tail extending to low temperatures is still a remnant of possible inhomogeneities or of anisotropic effects.^{1,2,6,7} In these materials with a strong two-dimensional nature, we may expect a significantly different field effect on crystallites with their planes parallel or perpendicular to the field. By taking the midpoint data (shown in the inset of Fig. 1) as the critical field, we therefore underestimate the critical fields that may be obtained for single crystals with the field parallel to the a - b (Cu-O) planes.

The slope dB_{c2}/dT found for the $R=0$ critical-field data is roughly 2.5 times smaller than the slope for the onset data. It seems very unlikely that this large difference in slope is due to inhomogeneity of the critical temperature. We therefore propose that the relatively large transition width in a magnetic field does not originate from inhomogeneities, but from the anisotropy of the critical field.

The data can be qualitatively understood with the following simple model. Assume that the upper critical field $B_{c1}(T)$ is equal to the onset field $B_0(T)$ where the resistance first drops below the normal-state resistance. The zero-resistance state is then realized at the field B' where the first percolation path between superconducting grains is established. We further assume that the critical field $B_c(\theta)$ of a crystallite with its a - b plane tilted over an angle θ with respect to the applied field is given by

Tinkham's formula.¹⁵ If B' becomes less than $B_c(\theta)$ for more than about 25% of the grains, percolating superconducting paths will begin to form. It can easily be shown that the field B' at which the resistance first becomes zero must be intermediate between the perpendicular critical field $B_{c\perp} = B_c(\theta = 90^\circ)$ and the parallel critical field $B_{c\parallel}$, and varies linearly with temperature. From the numerical calculation based on the data for B' and B_0 we estimate that the ratio $B_{c\perp}/B_{c\parallel}$ is of the order 4–5 for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. Recently Hidaka *et al.*¹⁶ have indeed reported an upper-critical-field anisotropy of 5 for single crystals of the related $\text{La}_{1-x}\text{Ba}_x\text{CuO}_4$ compound.

This rather large anisotropy indicates that possible applications depend strongly on the ability to orient the crystallites with respect to the field. In thin epitaxially grown films one might be able to reach large critical fields at $T=0$. However, for wires with randomly oriented grains, the critical field at $T=0$ could be limited to a much smaller value. At magnetic fields close to this limit the current is of a percolation type, and the resulting critical current density could be quite low.

A characteristic feature of these materials is also the relatively strong effect of a field as low as 2 T. For fields above 5 T the relative effect is much smaller, and the critical temperature varies to a very good approximation linearly with the field. There are several mechanisms which may cause this upward curvature of the critical field versus temperature plot close to T_c . For example, one might think of the sample as an array of weakly coupled grains which is very sensitive for low fields. However, we think that the most plausible reason is that the critical temperature of the grains has a statistical distribution centered around 33 K, and with a half width of the order of 5 K. A numerical calculation, based on the simple percolation model discussed above, indeed shows that such a statistical distribution can readily explain the rounding close to T_c .

For a comparison with the WHH theory, we have plot-

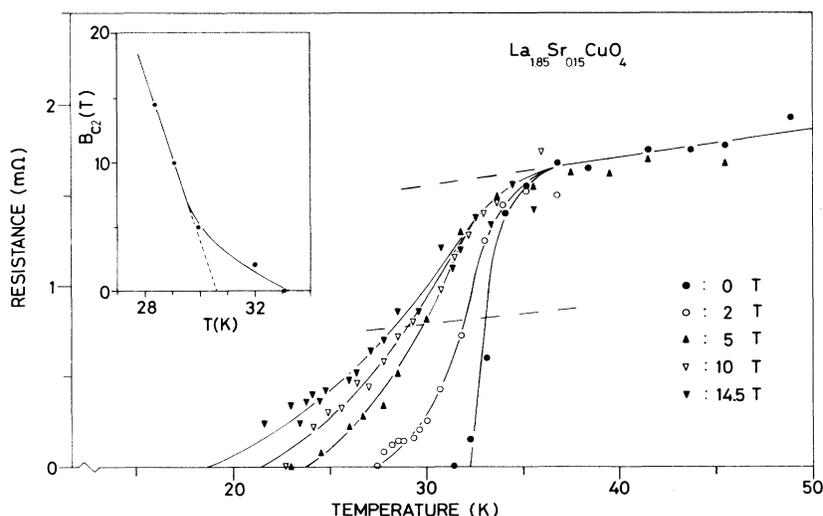


FIG. 1. Resistive transitions of a $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ sample as a function of temperature, for different values of the magnetic field. The inset shows the critical field B_{c2} taken at 50% of the extrapolated normal-state resistance, as a function of temperature, $dB_{c2}/dT = 2.2$ T/K.

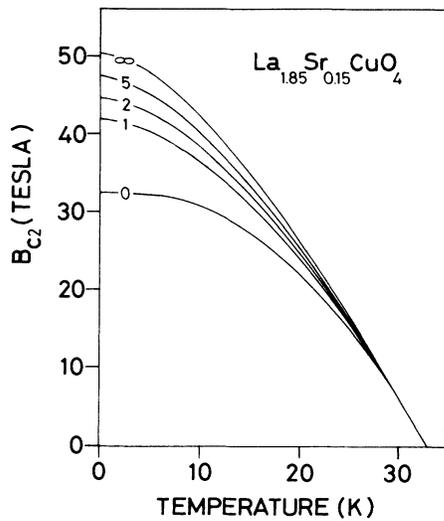


FIG. 2. Calculation of the temperature-dependent critical magnetic field of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, according to the Werthamer, Helfand, and Hohenberg theory, for different values of the spin-orbit coupling parameter λ_{so} (see text).

ted the midpoint critical-field data in the inset in Fig. 1. From the high-field part of this curve we deduce a value $(dB_{c2}/dT)_{T_c} = 2.2$ T/K. This slope is in good agreement with the results of Orlando *et al.*¹ and Capone, Hinks, Jorgensen, and Zhang.⁶

In Fig. 2 we show the critical field at various temperatures calculated for different values of the spin-orbit coupling parameter λ_{so} , according to the standard WHH theory. Experimental data up to magnetic fields of 33 T

(Refs. 1 and 2) show no deviation from linear behavior, therefore, the calculations shown in Fig. 2 indicate that $\lambda_{\text{so}} \geq 5$. From the experimental accuracy we estimate an absolute lower limit for the spin-orbit coupling parameter $\lambda_{\text{so}} \geq 2$. This value is unexpectedly high. If we evaluate the spin-orbit scattering time τ_{so} given by $\tau_{\text{so}} = \hbar / 3\pi k_B T_c \lambda_{\text{so}}$, we find $\tau_{\text{so}} \approx 10^{-14}$ s, which is of the same order of magnitude as the total inelastic scattering time τ_s . From the Abrikosov Gor'kov relation¹⁷ $\tau_{\text{so}} = \tau_s (\alpha Z)^4$, one expects a much smaller ratio $\tau_{\text{so}}/\tau_s \approx 2 \times 10^{-3}$. For Z we substituted the atomic number of Cu, α is the fine-structure constant $\alpha = e^2/\hbar c$. If we assume a Fermi velocity⁵ $v_F \approx 10^7$ cm/s, then the spin-orbit scattering length, corresponding to $\lambda_{\text{so}} \approx 5$, would be of the order of the lattice periodicity. A similar discrepancy with the Abrikosov-Gor'kov result is found for some of the A -15 superconductors.¹⁸

In the following we will treat λ_{so} as a free parameter within the WHH theory. Assuming $\lambda_{\text{so}} \approx 2-5$, we find for the extrapolated midpoint critical field at zero temperature $B_{c2}(0) = 45 \pm 5$ T for the LaSr compound. The parallel critical field $B_{c\parallel}$ at $T=0$ is approximately 65 T, close to the paramagnetic Clogston limit. For polycrystalline samples the zero-resistance state will be realized for magnetic fields below 25–30 T.

The Sommerfeld parameter γ can be estimated from the simple relation $\gamma = 2.2 \times 10^{-4} \rho_n^{-1} (-dB_{c2}/dT)_{T_c}$. If we assume $\rho_n \approx 400$ Ωcm (Ref. 5), we obtain $\gamma \approx 7$ mJ(moleCu)⁻¹K⁻², in good agreement with the results of Batlogg *et al.*⁴

Let us now turn to a discussion of the results on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. In Fig. 3 we have plotted the resistive transitions of a representative good-quality sample in magnetic fields up to 25 T. Again we find a relatively

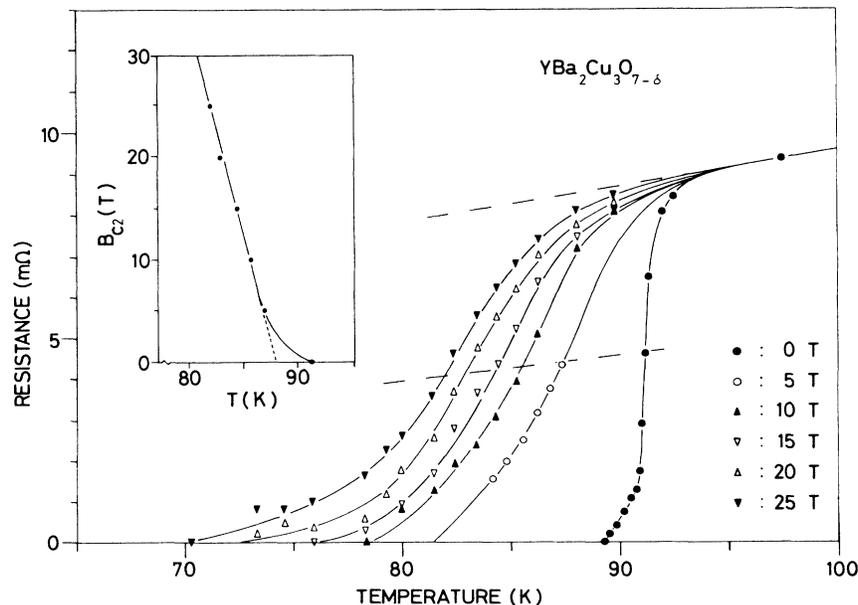


FIG. 3. Resistive transitions of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as a function of temperature, for different values of the magnetic field. The inset shows the critical field B_{c2} , taken at 50% of the extrapolated normal-state resistance, as a function of temperature, $dB_{c2}/dT = 4.2$ T/K.

strong effect of a small field. For magnetic fields above 5 T we observe a nearly linear shift of the transition towards lower temperatures. In the original publication, Wu *et al.*⁹ showed that the resistive tail of their multiphase samples extended down to 40 K, in fields as low as 5.7 T. Subsequent work by Sun *et al.*¹⁰ also observed zero resistance at the rather low temperature of 42 K in a magnetic field of 8 T. In contrast, we find that the zero-resistance state is established at 70 K in the maximum field of 25 T. This strongly suggests that the superconducting phase in the Y-Ba-Cu-O system indeed consists of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, as proposed by Cava *et al.*¹² The zero-resistance state at liquid-nitrogen temperature was observed for fields below 15 T. This already proves some practical applicability even with the not well optimized samples made in our laboratory.

As in the case of La-Sr-Cu-O, there is a large difference in slope $(dB_{c2}/dT)_{T_c}$ for the onset and for the $R=0$ data. From bulk-type measurements as the Meissner effect we estimate that the critical temperatures for the grains in our sample vary by at most 10%. This is confirmed by our tunneling measurements¹⁹ on different sections cut out of a sample from the same batch, which showed variations of the order parameter 2Δ within the same range. The broadening of the resistive transition can again be attributed to a strong anisotropy of the upper critical field, and can be reproduced with the simple model discussed above. For Y-Ba-Cu-O we find a similar anisotropy ratio $B_{c2\parallel}/B_{c2\perp} \approx 4-5$. Recent measurements on single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by Dinger, Worthington, Gallagher, and Sandstrom²⁰ of the lower critical field revealed an anisotropy $B_{c1\parallel}/B_{c1\perp} \approx 0.10$ and a value of $B_{c1\parallel} \approx 65$ mT. Total shielding of a magnetic field parallel to the CuO planes breaks down first because of the smaller value of the critical current density perpendicular to the a - b plane. In contrast, $B_{c2\parallel}$ is largest because it does not affect so strongly the supercurrents in the a - b plane.

The inset of Fig. 3 shows the midpoint critical-field values as a function of temperature. The slope $(dB_{c2}/dT)_{T_c}$ is 4.2 T/K. This value is considerably larger than previous results of multiphase Y-Ba-Cu-O samples, which varied between 1.2 and 1.8 T/K.⁷⁻¹¹ As in La-Sr-Cu-O we find at high fields no deviations from a straight line. In this case, however, this is not surprising since the range of the reduced temperature T/T_c covered is much less. In Fig. 4 we have plotted the calculations from the standard WHH theory for different values of the spin-orbit interaction parameter. As a rough estimate, we will assume that the spin-orbit interaction is basically the same as in La-Sr-Cu-O and that the parameter λ_{so} scales with T_c^{-1} . This yields $\lambda_{so} \approx 2$, and $B_{c2}(0) = 200 \pm 25$ T. The estimated parallel critical field $B_{c\parallel}$ is approximately

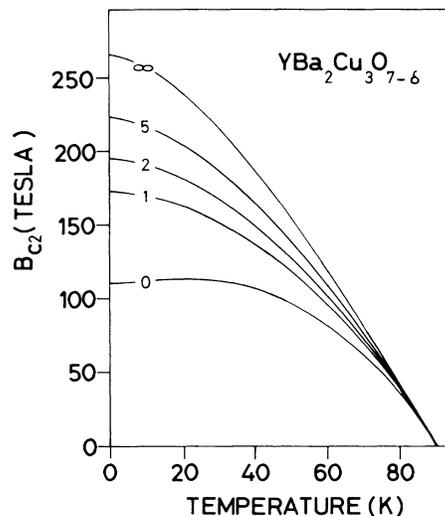


FIG. 4. Calculation of the temperature-dependent critical field of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, according to the Werthamer, Helfand, and Hohenberg theory, for different values of the spin-orbit coupling parameter λ_{so} (see text).

280 ± 40 T. The zero-resistance state at $T=0$ for polycrystalline material will be realized at magnetic fields below approximately 90 T.

Again, we can calculate the Sommerfeld parameter, which gives $\gamma = 16$ mJ(moleCu)⁻¹K⁻². This indicates that the density of states at the Fermi level is substantially higher than in La-Sr-Cu-O. It is tempting to assume that superconductivity in the known oxide superconductors: $\text{Ba}(\text{Pb,Bi})\text{O}_3$, $(\text{La,Sr})_2\text{CuO}_4$, $(\text{La,Ba})_2\text{CuO}_4$, and $M\text{Ba}_2\text{Cu}_3\text{O}_7$ (with $M = \text{Y}$, or a rare-earth element) originates from the same mechanism. The difference in critical temperature between these materials could be due mainly to a difference in the density of states at the Fermi level.

In conclusion, we find that the magnetoresistivity of the high- T_c superconductors $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ shows evidence for a strong spin-orbit interaction and a large anisotropy of the critical field. The density of states at the Fermi level for Y-Ba-Cu-O is about twice the value found for La-Sr-Cu-O.

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