

Upper Critical Field of a $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ Single Crystal: Interaction between Superconductivity and Antiferromagnetic Order in Copper Oxides

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The temperature dependence of the anisotropic upper critical magnetic field, $H_{c2}(T)$, has been determined resistively in antiferromagnetic $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ single crystals. We observe the first evidence in high- T_c copper oxides for the interaction between superconductivity and antiferromagnetic ordering of rare-earth ions; estimates of the exchange coupling $J \approx 0.1$ eV and the Ginzburg-Landau coherence lengths $\xi_{ab} = 79$ Å and $\xi_c = 14.7$ Å are obtained. In both $\text{Nd}_{1.84}\text{Ce}_{0.16}\text{CuO}_{4-y}$ and $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$, the H_{c2} data above T_N can be described by $H_{c2}(T)/H_{c2}^0 = (1 - T/T_c)^{1.6}$.

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The recent discovery of high-temperature superconductivity in the $L_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($L = \text{Pr, Nd, Sm, and Eu}$; $x \approx 0.15$)^{1,2} and $L_{2-x}\text{Th}_x\text{CuO}_{4-y}$ ($L = \text{Pr, Nd, and Sm}$; $x \approx 0.15$)²⁻⁴ compounds has demonstrated that superconductivity can occur by electron doping into an insulating parent compound, here $L_2\text{CuO}_4$. The nature of the charge carriers in the electron-doped compounds has not yet been resolved. Measurements of the Hall^{1,5} and Seebeck⁶ coefficients of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ suggest that the charge carriers are electrons, an interpretation corroborated by x-ray absorption spectroscopy (XAS).⁷ However, photoemission spectroscopy⁸ does not provide evidence for Cu 3d hole filling by Ce; furthermore, no clear evidence for the formation of Cu^{1+} could be found from electron-energy-loss spectroscopy (EELS).⁹ The EELS study and another XAS study¹⁰ on $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ indicate the presence of holes in the O 2p band.

The elucidation of intrinsic superconducting properties can be complicated by the presence of magnetic rare-earth ions. At least two of the electrons-doped compounds ($L = \text{Nd}$ and Sm) exhibit the coexistence of superconductivity and antiferromagnetic order of the rare-earth ions at low temperatures.¹¹ In this Letter, we present evidence from $H_{c2}(T)$ measurements on a $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ single crystal for the interaction of superconductivity and rare-earth magnetic order, the first observation of such behavior in the high- T_c copper oxides. We show that consideration of rare-earth magnetism enables the correct determination of intrinsic parameters, particularly the Ginzburg-Landau coherence lengths. We also note the absence of appreciable dissipative or fluctuation contributions to the resistive transitions and observe a scaling behavior of H_{c2} near T_c .

Single crystals of $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ were grown from a CuO-rich composition of the starting materials. A mixture of Sm_2O_3 (99.99% pure), CeO_2 (99.99% pure), and CuO (99.999% pure) in the molar ratio 37.6:320, respectively, was heated slowly to 1300°C in

air. After a 1-2-h soak at 1300°C, the temperature was lowered at a rate of 10°C h⁻¹ down to 1000°C and then cooled to room temperature by shutting off the furnace. Single crystals in the form of thin platelets were mechanically removed from the flux. X-ray-diffraction analysis confirmed the Nd_2CuO_4 structure with the c axis perpendicular to the largest face of the platelets. To induce superconductivity, the crystals were annealed at 950°C in flowing helium for 14 h and then quickly cooled to room temperature over a period of 1-2 h. Low-frequency electrical resistivity measurements were performed using a four-lead ac resistance bridge; dc magnetic-susceptibility data were taken using a SQUID susceptometer (SHE corporation).

Shown in the inset of Fig. 1(a) is the temperature dependence of the electrical resistivity in the basal plane for a $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ single crystal, in zero applied magnetic field. The resistivity ρ exhibits metallic behavior and has values of 1 mΩ cm at room temperature and 380 μΩ cm just above T_c . The $\rho(T)$ behavior below 150 K, which is qualitatively different from that of hole-doped superconductors, is reminiscent of ordinary metals, and is similar to that recently reported for a $\text{Nd}_{1.84}\text{Ce}_{0.16}\text{CuO}_{4-y}$ single crystal.⁶ The superconducting transition temperature T_c , defined throughout this work as the temperature at which ρ drops to 50% of its extrapolated normal-state value, is 11.4 K, while the 10%-90% transition width is 2.7 K. Magnetization data were taken on the same single crystal cooled in a field of 50 G applied along the basal plane in order to minimize demagnetization corrections. A Meissner fraction of more than 43% is observed which demonstrates that the sample is a bulk superconductor.

Shown in Fig. 1 are the resistive-transition curves in magnetic fields H applied perpendicular and parallel to the c axis. There is a striking parallel shift of the transition curves to lower temperatures for both H directions; the transition widths remain essentially constant as in conventional type-II superconductors. Unlike other

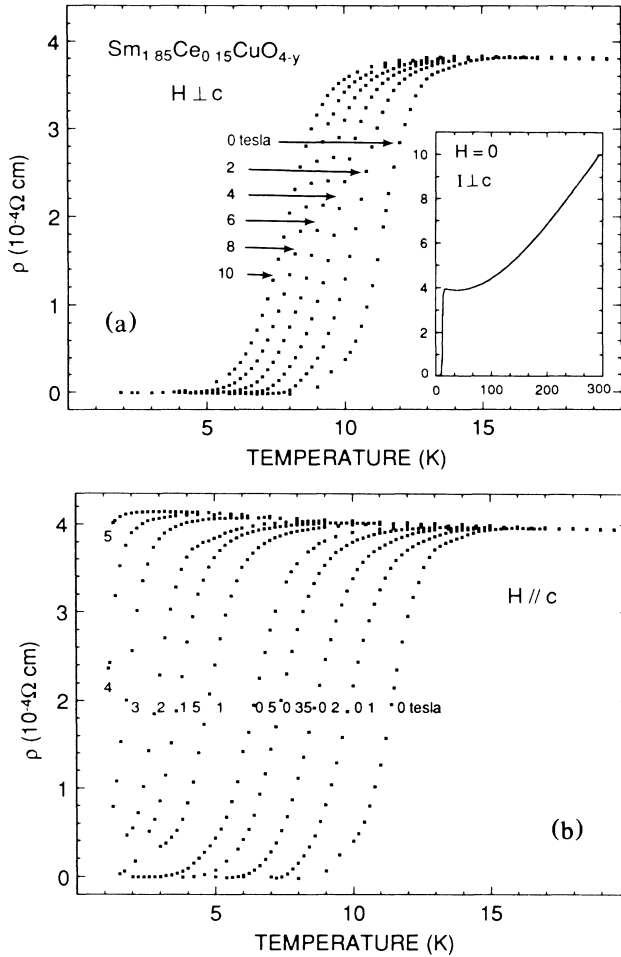


FIG. 1. Electrical resistivity ρ as a function of temperature T for a $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ single crystal in applied magnetic fields up to 10 T (a) perpendicular and (b) parallel to the c axis. Inset: $\rho(T)$ in the (a,b) plane for $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$.

high- T_c cuprates where the determination of H_{c2} is complicated by extensive field-induced broadening of the resistive transitions, possibly due to dissipative flux motion¹² or to fluctuation effects,¹³ in this case H_{c2} is well defined.

The $H_{c2}(T)$ curves obtained from the $\rho(T,H)$ data are displayed in Fig. 2 for the two orientations and reveal a large anisotropy with H_{c2} largest for H perpendicular to c , typical of the layered compounds. The shapes of these curves remain unchanged if T_c is defined from the 90% or 10% instead of the 50% drop in resistivity. For $\mathbf{H} \perp \mathbf{c}$, the H_{c2} curve exhibits a slight upward curvature near T_c ; the initial slope ($-dH_{c2}/dT$) estimated by ignoring such curvature is 3.6 T/K. For $\mathbf{H} \parallel \mathbf{c}$, $H_{c2}(T)$ presents a positive curvature throughout the whole temperature range and the initial slope ($-dH_{c2}/dT$) estimated from the data below 11 K is 0.1 T/K. The rapid increase of H_{c2} below 5 K for $\mathbf{H} \parallel \mathbf{c}$ can be explained in terms of magnetic ordering of Sm^{3+} ions and is dis-

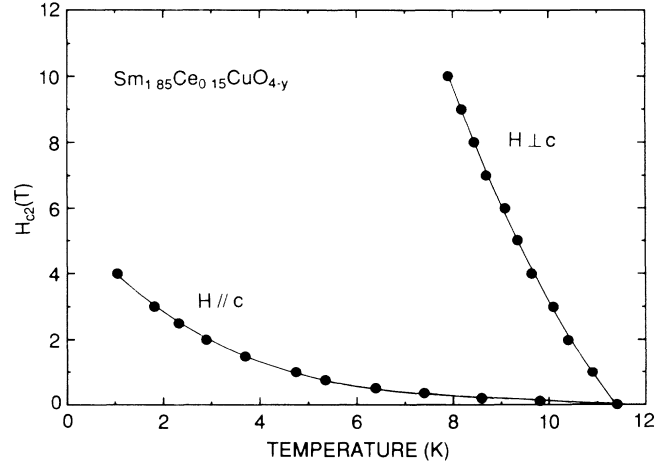


FIG. 2. Upper critical magnetic field $H_{c2}(T)$ determined from $\rho(T,H)$ measurements for applied magnetic fields $\mathbf{H} \parallel \mathbf{c}$ and $\mathbf{H} \perp \mathbf{c}$. Solid lines are guides to the eye.

cussed below. For $\mathbf{H} \perp \mathbf{c}$, the steep slope of $H_{c2}(T)$ and the higher temperatures imply that paramagnetic effects are small, and the weak-coupling formula¹⁴

$$H_{c2}(0) = -0.69T_c(dH_{c2}/dT)_{T=T_c}$$

can be used to estimate $H_{c2}(0) \approx 28.2$ T. For $\mathbf{H} \parallel \mathbf{c}$, we use the extrapolated value $H_{c2}(0) = 5.23$ T, which will be justified later in the text. The Ginzburg-Landau coherence lengths deduced from these $H_{c2}(0)$ values are $\xi_{ab} = 79$ Å and $\xi_c = 14.7$ Å. The anisotropy factor is about 5 and results in an effective-mass ratio $m_c/m_{ab} \approx 29$. This intrinsic anisotropy is smaller than found in Ref. 6; the large factor (~ 21) determined in that study is most likely an artifact of the magnetic pair-breaking contribution of the Nd^{3+} ions, similar to that of the Sm^{3+} ions discussed below. Of notable importance is the large value of the coherence length within the Cu-O planes which increases the pinning energy according to the scaling theory of Anderson and Kim¹⁵ and could account for the parallel-shift behavior of the resistive transitions. Corresponding values of ξ_{ab} in hole-doped copper-oxide superconductors range typically between 13 and 40 Å. Positive curvatures in $H_{c2}(T)$ curves have been widely reported in high- T_c cuprates and generally accounted for by flux-creep dissipation or fluctuation effects; however, these effects are generally accompanied by resistive broadening not observed here. Inhomogeneity in rare-earth or oxygen content may be a factor; an interesting possibility is that the curvature is due to superconducting dimensional crossover¹⁶ where upward curvatures are reported not only for H perpendicular but also parallel to the c axis.¹⁷ A recently proposed mechanism for the upward curvature in H_{c2} involves a mixing of order-parameter components.¹⁸

In Fig. 3(a), normalized H_{c2} data for $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ (this work) and $\text{Nd}_{1.84}\text{Ce}_{0.16}\text{CuO}_{4-y}$ (Ref. 6)

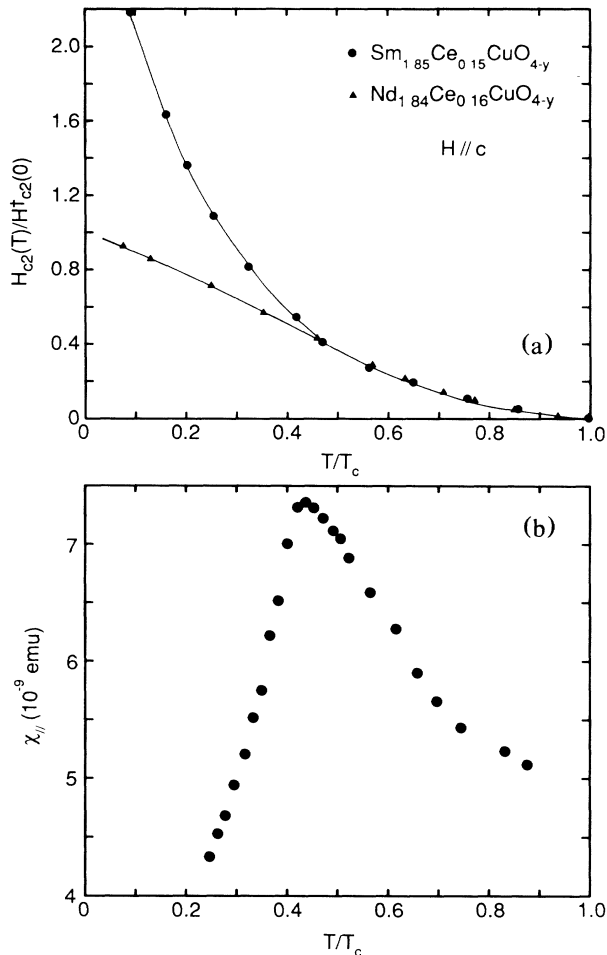


FIG. 3. (a) Normalized upper critical magnetic field $H_{c2}(T)/H_{c2}^{\dagger}(0)$ vs reduced temperature T/T_c for $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ (this work) and $\text{Nd}_{1.84}\text{Ce}_{0.16}\text{CuO}_{4-y}$ (Ref. 6) single crystals for $\mathbf{H} \parallel \mathbf{c}$, where $H_{c2}^{\dagger}(0)$ equals 1.83 and 7.0 T, respectively. (b) Magnetic susceptibility χ vs T/T_c for $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ single crystals measured in an applied magnetic field of 1 T parallel to the c axis.

single crystals are plotted versus reduced temperature T/T_c , for $\mathbf{H} \parallel \mathbf{c}$. Two outstanding features emerge from this plot. First, the normalized data for both systems scale with T/T_c for $T/T_c \gtrsim 0.5$, and consequently can be described with a single equation, i.e., $H_{c2}(T) = H_{c2}^{\dagger}(0)(1 - T/T_c)^{1.6}$ (see below). Second, there is a sudden departure of the $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ data from the behavior predicted by this scaling and followed by the $\text{Nd}_{1.84}\text{Ce}_{0.16}\text{CuO}_{4-y}$ data for $T/T_c \lesssim 0.5$. This increase in H_{c2} correlates with a sharp drop near $T_N = 4.9$ K in the static magnetic susceptibility for $\mathbf{H} \parallel \mathbf{c}$, shown in Fig. 3(b). Unequivocal evidence for bulk long-range antiferromagnetic ordering of the Sm^{3+} ions along the c axis near T_N has already been found in specific-heat and magnetic-susceptibility measurements on both single-crystal and polycrystalline specimens of Sm_2CuO_4 and superconducting $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$.^{11,19} This, along

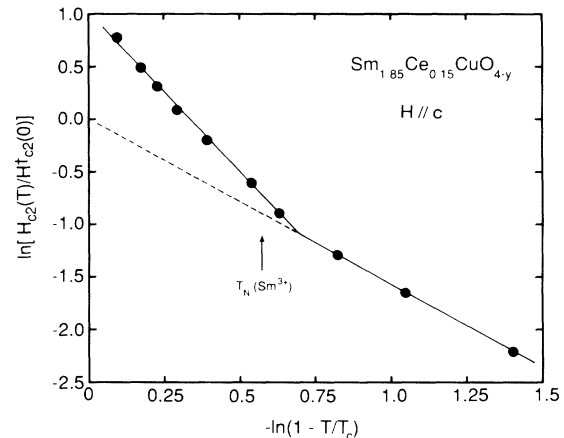


FIG. 4. $\ln[H_{c2}(T)/H_{c2}^{\dagger}(0)]$ vs $-\ln(1 - T/T_c)$ plot of the data in Fig. 3 for $\mathbf{H} \parallel \mathbf{c}$, where $H_{c2}^{\dagger}(0) = 1.83$ T. $T_N(\text{Sm}^{3+})$ refers to the peak in $\chi \parallel T$. Straight lines represent least-squares fits to the data.

with the fact that T_N in the $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ single crystal does not vary significantly with applied magnetic fields to 4 T, demonstrates that the peak in the magnetic susceptibility shown in Fig. 3(b) is associated with the antiferromagnetic ordering of Sm^{3+} ions along the c axis.

The effect of magnetic ordering on the upper critical field in $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ clearly indicates that there is a significant interaction between the rare-earth magnetic moments and the superconducting charge carriers. The $\sim 25\%$ decrease of the Néel temperature of the Sm^{3+} ions for 7.5% Ce doping in Sm_2CuO_4 , as found from specific-heat measurements,¹¹ is consistent with this observation. Additional evidence for the interaction between rare-earth magnetic ordering and superconductivity is presented in the \ln - \ln plot of Fig. 4, in which the normalized upper critical field, $H_{c2}(T)/H_{c2}^{\dagger}(0)$, is shown as a function of $1 - T/T_c$ for $\mathbf{H} \parallel \mathbf{c}$. The influence of the magnetic ordering associated with the Sm^{3+} ions on the superconducting state is evidenced by the distinct kink in the data near the Néel temperature. A least-squares fit of the data above 5.7 K yields a slope of 1.6 which is higher than that of the data for $\mathbf{H} \perp \mathbf{c}$, equal to 1.2 (not shown).

The spectacular effects of long-range antiferromagnetic order on superconductivity have been previously observed in the RMo_6X_8 ($X = \text{S}, \text{Se}$) and RRh_4B_4 systems.²⁰ For some compounds, such as ErMo_6S_8 and SmRh_4B_4 , H_{c2} increases below T_N , while for others, such as RMo_6S_8 for $R = \text{Tb}, \text{Dy}$, and Gd as well as NdRh_4B_4 , H_{c2} decreases below T_N . In the context of the multiple pair-breaking theory, the anomalous increase in H_{c2} for $\mathbf{H} \parallel \mathbf{c}$ in $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ can be explained in terms of a reduction of the magnetization and, in turn, of the exchange field associated with the Sm spins and a corresponding decrease in its pair-breaking effect on the

conduction-electron spins through the Zeeman interaction. We estimate the exchange coupling by first requiring the orbital critical field, $H_{c2}^*(T)$, to satisfy $H_{c2}^*(0) = H_{c2}(0)$, since the Sm^{3+} magnetization at $T=0$ will be zero for $\mathbf{H} \parallel \mathbf{c}$. [This consideration also justifies the choice of $H_{c2}(0)$ for $\mathbf{H} \parallel \mathbf{c}$ made earlier in the calculation of the coherence lengths.] We estimate $H_{c2}^*(T)$ with the form $H_{c2}^*(T) = H_{c2}^*(0)(1 - T/T_c)^\beta$. We may thus deduce²¹ the exchange field $H_J(T)$ due to the Sm^{3+} ions, which has a peak value at the Néel temperature of $H_J(T_N) \approx 90$ kOe (160 kOe), corresponding to an exchange coupling $J \approx 60$ meV (110 meV), for $\beta=2$ (1). This is about a factor of 4 greater than that observed in SmRh_4B_4 , and reflects a stronger rare-earth-conduction-electron coupling in the layered-copper-oxide compound.

In conclusion, we have demonstrated for the first time in high- T_c copper oxides that magnetic ordering of rare-earth ions affects superconductivity; the effect is appreciable in $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ although not yet observable in the $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds. This observation could be helpful in identifying the pairing mechanism in the family of electron-doped superconductors. Accounting for paramagnetic effects, we obtained values of the coherence lengths and anisotropy. We also noted the absence of dissipative or fluctuation effects and observed a scaling behavior of H_{c2} .

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