Field-Dependent Diamagnetic Transition in Magnetic Superconductor $Sm_{1.85}Ce_{0.15}CuO_{4-y}$

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The magnetic penetration depth of single crystal $Sm_{1.85}Ce_{0.15}CuO_{4-y}$ was measured down to 0.4 K in dc fields up to 7 kOe. For insulating Sm_2CuO_4, Sm^{3+} spins order at the Néel temperature, $T_N = 6$ K, independent of the applied field. Superconducting $Sm_{1.85}Ce_{0.15}CuO_{4-y}$ ($T_c \approx 23$ K) shows a sharp increase in diamagnetic screening below $T^*(H)$ which varied from 4.0 K ($H = 0$) to 0.5 K ($H = 7$ kOe) for a field along the c axis. If the field was aligned parallel to the conducting planes, T^* remained unchanged. The unusual field dependence of T^* indicates a spin-freezing transition that dramatically increases the superfluid density.

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The coexistence of magnetism and superconductivity has been studied in many materials [1–4]. $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (NCCO) [5,6] and $Sm_{1.85}Ce_{0.15}CuO_{4-y}$ (SCCO) [7,8] are widely studied electron-doped copper oxides in which rare-earth magnetic ordering coexists with superconductivity. Heat capacity measurements have shown peaks at $T_N(Nd^{3+}) \approx 1.2$ K [9] and $T_N(Sm^{3+}) \approx 5$ K [10,11], respectively. Neutron scattering confirmed that insulating Sm_2CuO_4 exhibits Sm^{3+} antiferromagnetism below $T_{N,Sm} \approx 6$ K on top of the high temperature Néel ordering of the Cu spins (at $T_{N,Cu} \sim 270$ K). Within each plane Sm^{3+} spins are ferromagnetically aligned along the c axis, but with their direction alternating from one plane to the next [8]. In this Letter, we report measurements of the magnetic penetration depth in SCCO for magnetic fields applied perpendicular and parallel to the conducting ab plane. A sharp increase in diamagnetic screening is observed upon cooling below a temperature T^* which is slightly less than the ordering temperature for Sm^{3+} spins. T^* is rapidly suppressed by a c-axis magnetic field. The unusual field dependence of T^* indicates a spin-freezing transition of Cu^{2+}, which in turn enhances the superconductivity.

Single crystals of SCCO were prepared using a directional flux growth technique [12]. Penetration depth measurements were performed with a 12 MHz tunnel oscillator used previously in several studies [13,14]. A dc field up to 7 kOe could be applied along $h_{ac}(t)$ and up to 800 Oe perpendicular to $h_{ac}(t)$. The oscillator frequency shift is proportional to the sample magnetic susceptibility, χ_m, with a sensitivity of $4\pi\Delta\chi_m \approx 10^{-7}$ for typical high-T_c crystals ($1 \times 1 \times 0.05$ mm^3). In the superconducting state $-4\pi\chi_m = [1 - (2\lambda/d)\tanh(d/2\lambda)]$, where λ is the penetration depth and d is the effective sample dimension [14].

For a reference, we first measured an insulating Sm_2CuO_4 single crystal which exhibited Sm^{3+} antiferromagnetism below $T_{N,Sm} \approx 6$ K. Figure 1 shows the frequency shift and the susceptibility for both ac and dc magnetic fields applied along the c axis. $T_{N,Sm}$ is insensitive to the applied dc field. The susceptibility below 4.5 K is field sensitive, showing an upturn below 2 K that is suppressed by a c-axis field. The origin of this upturn is not yet understood, but neutron scattering data in NCCO have shown a similar upturn below T_N [15].

Doping with Ce^{4+} leads to a semiconductor with a slightly reduced $T_{N,Sm}$ [16]. Subsequent oxygen reduction yields the electron-doped superconductor SCCO with $T_c \approx 23$ K [12,16]. Figure 2 shows the frequency shift in superconducting SCCO for both ac field orientations. $h_{ac}(t)$ applied along the c axis generates ab-plane supercurrents. In this case the resonator senses the ab-plane penetration depth λ_{ab} as shown by the bottom curve. The expanded region below 6 K shows a drop in frequency

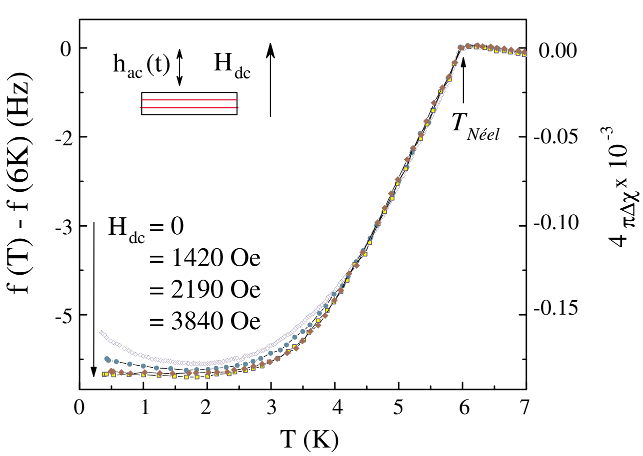

FIG. 1 (color online). Frequency shift and susceptibility of insulating Sm_2CuO_4. ac and dc fields are parallel to the c axis. T_N is independent of H_{dc} but the upturn beginning near 4.5 K is suppressed by the field.

below $T^* \approx 4$ K corresponding to *enhanced diamagnetism*. T^* ranged from 4–4.3 K depending upon the sample. Only samples with $T_c > 20$ K showed the drop in frequency at T^*. Two crystals with $T_c \approx 16$ K showed only a slight break at 4 K. The extra frequency shift of ≈ 100 Hz is much larger than the change observed in Fig. 1. The top curve in Fig. 2 shows the frequency shift with $h_{ac}(t)$ along the *ab* plane. In this orientation the signal is dominated by very weak interplane supercurrents, and the sample is almost magnetically transparent. Demagnetization corrections are negligible in this orientation and using $-4\pi\chi_m = [1 - (2\lambda_C/d)\tanh(d/2\lambda_C)]$, we estimate the *c*-axis penetration depth, $\lambda_C(0) \approx 400$ μm. The inset shows that the diamagnetic transition at T^* is also observed for this orientation.

The drop in frequency below T^* corresponds to $\Delta\lambda_{ab} = \lambda_{ab}(T^*) - \lambda_{ab}$ (0.35 K) = 1 μm. For comparison, reversible magnetization measurements on aligned powders of SCCO yielded $\lambda_{ab}(0) \approx 0.46$ μm [17] while $\lambda_{ab}(0) \approx 0.2$–0.3 μm in the related compounds, $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ (PCCO) [18] and NCCO [19]. λ_{ab} may be larger in SCCO than in NCCO and PCCO due to spin fluctuations above the magnetic ordering temperature [20]. From the top inset of Fig. 2 we estimate that $\Delta\lambda_C = \lambda_C(T^*) - \lambda_C\,(0.35\,\text{K}) \approx 60\,\mu$m, although $\tanh(d/2\lambda_C)$ correction to susceptibility rounds the transition at T^* considerably.

The diamagnetic enhancements shown in Fig. 2 cannot arise from the additive contribution of the Sm^{3+} spin susceptibility. Using data from the insulating state, Fig. 1, we estimate $\chi^{\parallel}_{\text{spin}}(T_N) - \chi^{\parallel}_{\text{spin}}(0.4\text{ K}) \approx 1.4\times 10^{-4}$, which would correspond to a drop in frequency of 3.5 Hz for the sample in Fig. 2. This estimated shift is much smaller than the measured 120 Hz shown in the lower inset of Fig. 2. In addition, for our superconducting crystals, $\chi^{\parallel}_{\text{spin}}$ is shielded by supercurrents to within a surface layer of order λ_{ab}, rendering any additive spin contribution unobservably small. For $h_{ac}(t)$ along the *ab* plane, the field penetrates most of the sample and would excite the bulk spin susceptibility $\chi^{\perp}_{\text{spin}}$. However, $\chi^{\perp}_{\text{spin}}$ is nearly temperature independent while the upper inset of Fig. 2 shows a 20 Hz drop in frequency. Misalignment of the sample axes could mix contributions from λ_C and λ_{ab}. We estimate the maximum error from misalignment to be 0.2 Hz, which is far smaller than the drop shown in Fig. 2. The drop in frequency is also far too large to be explained by any plausible amount of magnetostriction.

The penetration depth measured in a resonator is enhanced by the susceptibility of magnetic ions: $\lambda_{\text{meas}} = \lambda\mu^{1/2}_{\text{spin}} = \lambda(1 + 4\pi\chi_{\text{spin}})^{1/2}$, where λ is the penetration depth that would exist in their absence [21,22]. This effect explains the upturn in λ_{ab} observed in NCCO, where the Nd^{3+} moments are large and remain paramagnetic to much lower temperatures [23]. For SCCO, this effect would give $\lambda_{ab}(T_N) - \lambda_{ab}(0.4\text{ K}) \approx 10^{-3}\lambda_{ab}(T_N)$ which is far too small to account for the drop in frequency observed. A somewhat similar situation was observed in $ErNi_2B_2C$ [3]. Those authors also concluded that the drop in λ at $T_{\text{Néel}} = 6$ K could not be attributed to the $\mu^{1/2}_{\text{spin}}$ factor.

Penetration depth [24] and Josephson critical current measurements [25] in $SmRh_4B_4$ have shown enhanced superfluid density below T_N, consistent with theories of *s*-wave, antiferromagnetic superconductors [26,27]. The situation is likely to be quite different in SCCO.

Figure 3 shows the effect of a static magnetic field H_{dc} on λ_{ab}. Both $h_{ac}(t)$ and H_{dc} were applied along the *c* axis. In marked contrast to the insulating phase, T^* in the

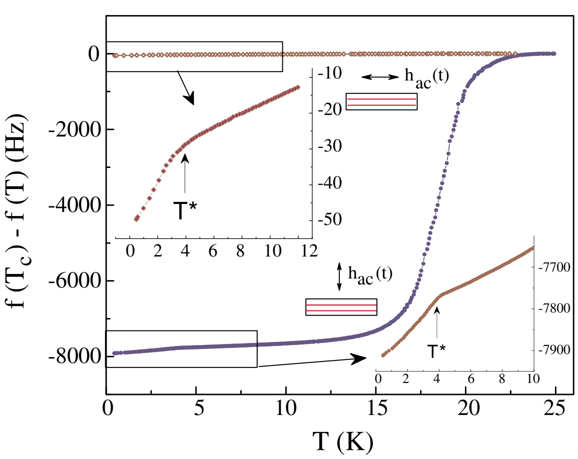

FIG. 2 (color online). Frequency shift versus temperature for an ac field parallel to *ab* planes (top) and parallel to the *c* axis (bottom). The insets magnify the regions near T^* where enhanced diamagnetism occurs.

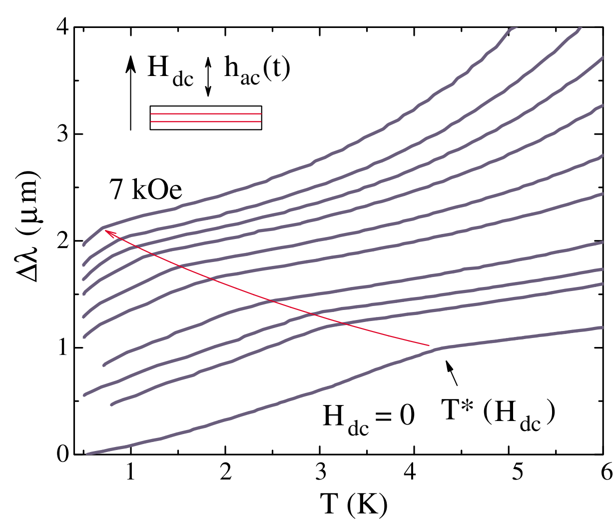

FIG. 3 (color online). Change in penetration depth with both ac and dc fields along the *c* axis, for values of H_{dc} ranging from 0 to 7 kOe. The line through the data plots indicates T^* as a function of H_{dc}. The curves are offset due to Campbell penetration depth, $\lambda^2 = \lambda^2_{\text{Campbell}} + \lambda^2_{\text{London}}$.

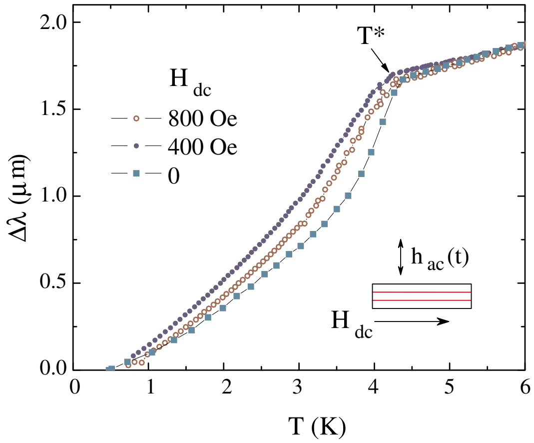

FIG. 4 (color online). $\Delta\lambda(T)$ for the ac field still along the c axis but H_{dc} along ab planes. T^* is unchanged by the magnetic field.

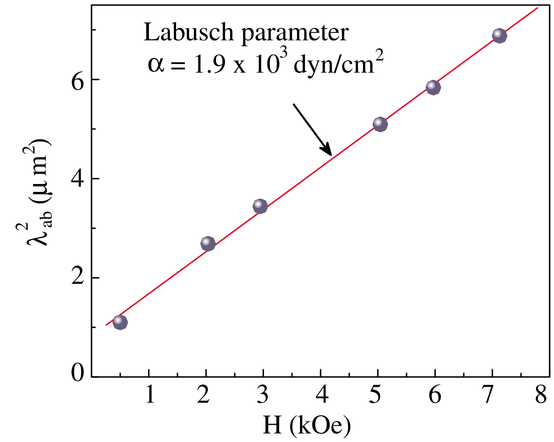

FIG. 5 (color online). Square of the penetration depth versus applied field at $T = 0.5$ K.

superconductor drops rapidly with field, reaching 0.6 K for $H = 0.7$ T. Figure 4 shows the effect of orienting H_{dc} parallel to the conducting planes, but maintaining $h_{ac}(t)$ along the c axis. The large drop in λ_{ab} remains, and T^* is unchanged.

The field dependence of λ_{ab} is plotted in Fig. 5, where data at $T = 0.5$ K have been taken directly from Fig. 3. The plot shows classic vortex behavior in which $\lambda^2(H) = \lambda^2_{\rm London} + \phi_0 H/(4\pi\alpha)$. The second term on the right is the square of the Campbell [28] pinning depth where α is the Labusch [29] pinning constant. $\lambda^2(H, T = 0.5 \text{ K})$ is linear in H and thus dominated by vortex motion with a pinning constant of $\alpha = 1.9 \times 10^3$ dyn/cm^2, a value roughly 3 orders of magnitude smaller than observed in typical $YBa_2Cu_3O_{7-y}$ crystals [30]. This weak pinning is consistent with recent magneto-optical measurements performed on similar SCCO samples [31] and may result from the spin polarization in the vortex core. In $DySo_6S_8$ ($T_c = 1.6$ K, $T_N = 0.4$ K), for example, Dy spins apparently assume an antiferromagnetic alignment outside the vortex core and a spin-flop orientation inside [32]. Most important, Fig. 5 demonstrates that the response below T^* still derives from superconductivity and not from spins located in possibly nonsuperconducting regions.

The most striking feature of the data is the strong field dependence of T^*, taken from Fig. 3 and plotted in Fig. 6. For an antiferromagnet with $T_N(H = 0) = 6$ K, a 0.7 T field might reduce T_N by 0.1 K at most [33]. Random field effects, possibly from Ce-induced disorder, can increase the field dependence [34]. However, heat capacity measurements in semiconducting $Sm_{1.85}Ce_{0.15}CuO_4$ showed that the peak appearing at $T_{N,\rm Sm} \sim 5$ K [10,11] is insensitive to fields as large as 9 T [11], ruling out this scenario. A superconducting impurity phase would exhibit a strong field dependence, but any such phase would require a transition temperature of 4 K and a strong critical field anisotropy to explain the difference between Figs. 3 and 4. Finally, there is good evidence that the Sm-Sm exchange constant is unaffected by superconductivity in the layers. A careful study of T_N with various dopants showed that Ce doping was most effective in lowering T_N, but subsequent oxygen reduction, required for superconductivity, had a negligible effect [16]. It appears that another ingredient beyond the Sm spins is required to explain Fig. 6.

The inset to Fig. 6 shows a fit to the expression H (T) $= 0.64/T^* - 0.15$. Precisely this functional dependence was reported for the spin-freezing transition line of $\alpha -$ $Fe_{92}Zr_8$ [35]. In this frustrated Heisenberg ferromagnet, transverse spin components undergo a field-dependent spin-glass transition at T_{xy}, far below the temperature for longitudinal spin ordering. We conjecture that the boundary line in Fig. 6 represents a change in superfluid density caused by a similar spin-freezing transition. Of the e-doped superconductors measured (PCCO, NCCO, and SCCO), only SCCO shows a transition to enhanced

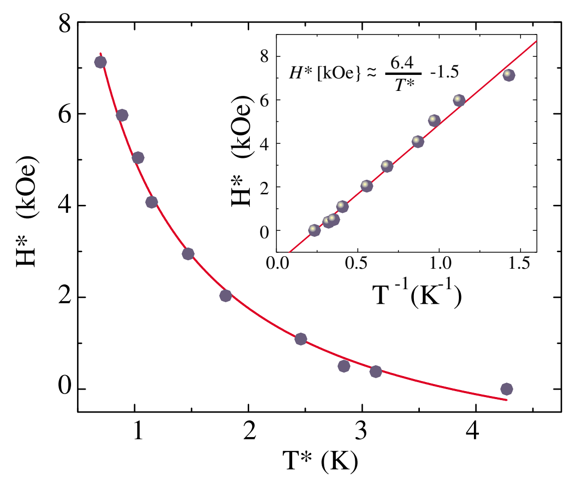

FIG. 6 (color online). Location of the diamagnetic transition $T^*(H)$ in the H-T plane. The inset shows the data plotted vs inverse temperature.

diamagnetism at low temperatures. This observation suggests that ordering of the Sm^{3+} spins changes the magnetic environment and initiates a freezing transition of the Cu^{2+} spins.

Spin freezing in conventional superconductors has been studied theoretically and leads to a strongly reduced thermal smearing in the density of states and in some cases the opening of a gap [20,36]. Evidence for spin freezing in e-doped cuprates has come from muon spin rotation measurements in overoxygenated $Nd_{1.85}Ce_{0.15}CuO_{4+y}$, where Cu^{2+} spins undergo a spin-glass transition at 4–5 K [37]. There is also evidence for a spin-glass region in the $Pr_{1-x}LaCe_xCuO_{4-y}$ [38]. While spin freezing has been extensively studied in the underdoped hole cuprates [39,40] this is the first evidence of its influence on the superfluid density in any superconductor, to our knowledge.

Two other experiments highlight the unusual influence of small fields on the Cu^{2+} spins. Neutron scattering showed no effect of a 7 T magnetic field on antiferromagnetic (AF) ordering of Cu in either insulating Nd_2CuO_4 or semiconducting $Nd_{1.85}Ce_{0.15}CuO_4$. However, c-axis fields as small as 2 T had a direct influence on AF ordering in superconducting NCCO [41,42]. The field sensitivity of NCCO has been advanced as evidence for competing antiferromagnetic and superconducting order within the SO(5) model for high temperature superconductivity [44]. Recent μSR measurements showed that even a 90 Oe c-axis field established Cu magnetic order in PCCO [43] and our measurements in SCCO demonstrate a nearly complete suppression of T^* in less than 1 T. By contrast, spin freezing in La-Sr-Cu-O was field independent up to 23 T [40]. Whether these very different field scales imply a fundamental distinction between hole and electron-doped cuprates is an important question.

In conclusion, superconducting $Sm_{1.85}Ce_{0.15}CuO_{4-y}$ shows a strong enhancement of diamagnetic screening below $T^* = 4$ K. T^* is rapidly suppressed with a c-axis field, suggesting a freezing transition for Cu^{2+} spins.

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