Magnetic Ordering of Sm in Sm_2CuO_4

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Long-range antiferromagnetic order of the Sm ions in Sm_2CuO_4 is observed via neutron diffraction at $T_N = 5.95$ K. The magnetic structure consists of ferromagnetic sheets *within* the *a-b* planes, with the spins in alternate sheets aligned antiparallel. This spin structure and spin direction are completely different from those observed in any other copper-oxide superconductor system. The temperature dependence of the upper critical field H_{c2} for the superconductor $Sm_{1.85}Ce_{0.15}CuO_4$ ($T_c = 23.5$ K) shows a sudden increase in H_{c2} at $T/T_c \sim 0.7$, but this anomaly cannot be attributed to the Sm magnetic ordering. No anomaly in H_{c2} is observed at the T_N for Sm.

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The discovery of superconductivity in a new class of copper-oxide systems, $R_{2-x}Ce_xCuO_4$ (R = Nd, Pr, Sm) [1], has attracted considerable interest since these are the only copper-oxide systems known to date that carry electrons as the charge carriers. In addition to their transport properties, these materials and their parent insulating compounds R_2CuO_4 exhibit a variety of interesting magnetic behavior involving both the rare earth and copper spins [2–11]. Two members of these electron-doped systems (Nd,Sm) [2,3] have displayed a coexistence of rare-earth magnetic order and superconductivity, providing an interesting situation to study the interplay between the two cooperative phenomena, particularly since there is no clear separation between the magnetic and superconducting subsystems. It is therefore of central concern to elucidate the magnetic properties in these systems and the relationship between the magnetism and superconductivity.

Neutron diffraction, magnetic susceptibility, and specific heat measurements have been carried out previously to investigate the magnetic properties of the R_2CuO_4 compounds [2–11]. The Cu spins in these materials order at relatively high temperatures ($\sim$280 K) in a simple antiferromagnetic arrangement with the Cu moments lying in the *a-b* plane [4–9]. The rare-earth ordering in the Nd_2CuO_4 compound is particularly interesting since it is found that the ordered Cu sublattice exhibits a substantial coupling to the Nd sublattice, thereby inducing the ordering of Nd ions [3]. As for the related Pr_2CuO_4 compounds, it has been suggested that a small Pr moment is induced [6] similar to that found in Nd_2CuO_4, while crystal-field [8] and magnetization [10] measurements have suggested the absence of an ordered moment due to crystal-field quenching. In this Letter we present the results from neutron diffraction on the nature of the Sm ordering in the Sm_2CuO_4 compound, and elucidate the possible relationship of this ordering to the anomalies observed in the H_{c2} phase boundary of the superconductor $Sm_{2-x}Ce_xCuO_4$.

Sm_2CuO_4 has the same basic crystal structure as Nd_2CuO_4 and Pr_2CuO_4, which is tetragonal $I4/mmm$ (T' phase) with lattice parameters $a = 3.917$ Å and $c = 11.95$ Å at 200 K. The neutron measurements were quite difficult to do because of the very high neutron absorption for Sm. To minimize these absorption effects, a thin platelike high-quality single crystal of Sm_2CuO_4 weighing 66 mg was used, which is the same crystal used in our earlier studies of the Cu ordering [9]. Its growth and preparation techniques can be found in the literature [9,12]. Unpolarized neutron diffraction data were taken with a wavelength of 2.358 Å on the BT-2 and BT-6 triple-axis spectrometers with a pyrolytic graphite (PG)(002) monochromator and a PG filter for suppressing higher-order wavelength contaminations. The angular collimations used were 60′ before the monochromator, and 60′-40′ before and after the sample, respectively. The crystal was mounted in the $(h,0,l)$ scattering plane and enclosed in a ^{3}He cryostat.

Below the Néel temperature $T_N = 5.95$ K, a series of magnetic Bragg peaks were observed such as the one shown in Fig. 1 for the (1,0,1) peak. The figure illustrates a transverse scan of a (1,0,1) magnetic peak obtained by subtracting the data taken at a temperature $T = 8$ K from the data taken at $T = 2$ K, well below the Sm ordering temperature. The observed width is entirely due to instrumental resolution, and indicates that long-range antiferromagnetic order has developed. The fact that the Miller indices are integers signify that the magnetic unit cell is identical to the chemical unit cell, and the magnetic space group is $I4/m'mm$. The Sm spin configuration is also shown in Fig. 1, where two unit cells are drawn for clarity; the locations of the Cu ions are also indicated. The Sm spin configuration consists of ferromagnetic sheets *within* the *a-b* planes, with the spins in alternate sheets aligned antiparallel. This spin structure is completely different from those observed in the related

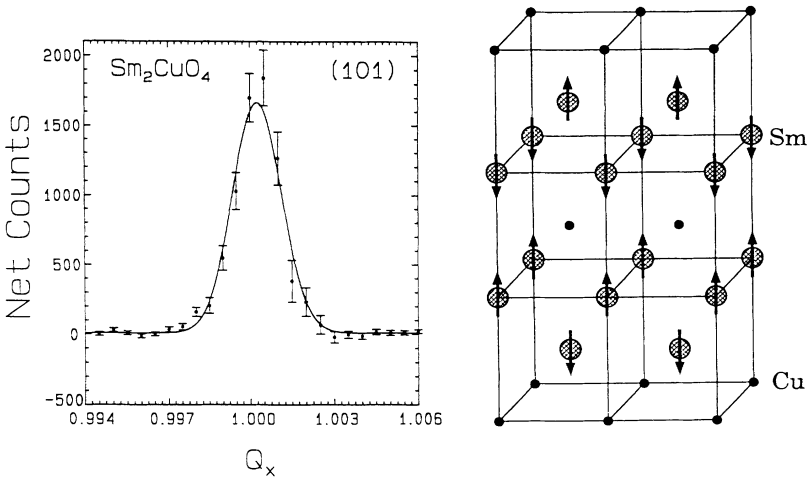

FIG. 1. Transverse scan of the (1,0,1) magnetic Bragg peak. The solid line is a fit by the Gaussian instrumental resolution function. The magnetic scattering was obtained by subtracting data taken at 8 K from the data taken at $T\sim 2$ K. The Sm spin structure is also shown, and consists of ferromagnetic sheets *within* the *a-b* planes, with the spin direction along the *c* axis and spins in alternate layers aligned antiparallel. The positions of the Cu ions, whose spins have already ordered at 280 K, are also indicated.

Nd_2CuO_4 and Pr_2CuO_4, and in fact, the ferromagnetic sheets of rare-earth ions in the *a-b* planes are not found in any other copper-oxide superconductor systems [13].

The magnetic intensity for a simple collinear magnetic structure is given by [14]

$$I_M = C\left(\frac{re^2}{2mc^2}\right)^2 \langle\mu_z\rangle^2 [f(\mathbf{K})]^2 \langle 1-(\hat{\mathbf{K}}\cdot\hat{\mathbf{M}})^2\rangle |F_M|^2 A_K ,$$

where the quantity in large parenthesis is the neutron-electron coupling constant (-0.27×10^{-12} cm), $\langle\mu_z\rangle$ is the thermal average of the aligned Sm magnetic moment, $f(\mathbf{K})$ is the magnetic form factor, F_M is the magnetic structure factor, A_K is the absorption factor, $\hat{\mathbf{K}}$ and $\hat{\mathbf{M}}$ are unit vectors in the direction of the reciprocal-lattice vector $\mathbf{K}$ and the spin direction, respectively, and the orientation factor $\langle 1-(\hat{\mathbf{K}}\cdot\hat{\mathbf{M}})^2\rangle$ must be calculated for all possible domains. The absence of any (0,0,*l*) magnetic peaks indicates that the Sm spin direction is along the *c* axis, which is perpendicular to the Cu spin directions that have already ordered at 280 K [9]. By comparing the integrated intensities of magnetic and nuclear peaks, we obtain an ordered Sm moment at 2 K of $(0.37\pm0.03)\mu_B$, where the error bar is statistical in origin only. We remark that due to the large absorption b_{Sm} is strongly wavelength dependent; we have used $b_{Sm}=0.17\times10^{-12}$ cm to obtain this value, but a revised value of μ_z may be appropriate if a better value of b_{Sm} at this wavelength becomes available.

Figure 2 shows the temperature dependence of the (1,0,1) magnetic Bragg peak intensity, and reveals a Néel temperature of $T_N=5.95\pm0.05$ K, in very good agreement with specific heat and magnetic susceptibility data [10]. Note from the equation that this intensity is proportional to $\langle\mu_z\rangle^2$, where μ_z is the ordered (sublattice) moment. Since the magnetic and nuclear Bragg peaks are coincident, the magnetic intensity data were obtained by subtracting the nuclear scattering (270000 counts in the figure), plus a small contribution from "background," from the observed intensities. The sharpness of this phase transition indicates that there is no coupling between the Sm and Cu spins, which is not surprising since the spin directions are orthogonal and the magnetic structures are different. This contrasts with the behavior observed in the related Nd_2CuO_4 system, where the magnetic structures and spin directions are the same, and strong coupling is observed [3]. We remark that below 1 K the intensity of this (1,0,1) peak once again increases in intensity in a continuous fashion, and the nature of this low-tem-

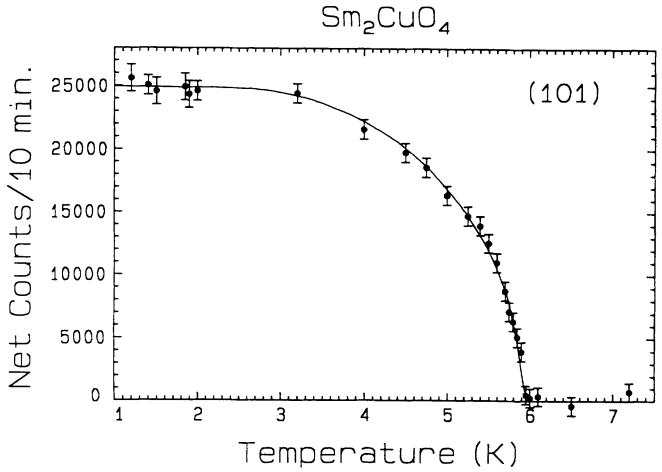

FIG. 2. Temperature dependence of (1,0,1) magnetic Bragg peak intensity, revealing a Néel temperature $T_N=5.95$ K. The solid line is a guide to the eye.

perature transition will be a subject of a separate study.

It is important to note that the Sm ordering temperature of 5.95 K is relatively high, and if one scales T_N from the isostructural Gd_2CuO_4 compound ($T_N=6.5$ K [15], $\mu=7\mu_B$), then the Sm ordering temperature would be expected to be 2 orders of magnitude lower than observed if the interactions were purely dipolar in nature. Thus it is clear that the dominant interaction between the Sm spins is exchange, and that this exchange interaction must be mediated through the copper-oxygen layers. Hence, if the usual theories of superconductivity were invoked, one would expect that the spin depairing in the paramagnetic state would destroy any chances for the formation of a superconducting state. Moreover, because the spin structure is ferromagnetic in the *a-b* plane, in the ordered state the exchange field will not average to zero over the scale of the superconducting coherence length.

In addition to the general effects of the Sm spins on the superconducting state, we should expect a change in the nature of the magnetic-superconducting interaction at the Néel temperature. In the paramagnetic state the Cu-O planes contain a mirror symmetry (*m*), while in the ordered state the Cu-O layer includes an antimirror plane (*m'*) which the superconducting wave functions must accommodate. Indeed, it recently has been reported from measurements of the temperature dependence of the upper critical field on $Sm_{1.85}Ce_{0.15}CuO_4$ ($T_c=11.4$ K) that H_{c2} displays an anomalous rate of increase at $T/T_c\simeq0.5$, which is just in the vicinity of the Sm ordering temperature $T_N=4.9$ K in the doped system [11]. Because of the proximity of this anomaly to T_N it was natural to conclude that this effect was caused by Sm antiferromagnetic ordering. Our own measurements on $Sm_{1.85}Ce_{0.15}CuO_4$ single crystals reveal a similar anomaly as shown in Fig. 3. The top portion of the graph shows the temperature dependence of the resistivity as a function of field, where we note that the superconducting transition remains sharp and well defined in an applied field. Taking the midpoint as the definition of T_c, the bottom portion of the figure shows a ln-ln plot, where $H_{c2}(0)=44.12$ kOe is the extrapolated value from the fit. A clear break in the data is found at $T/T_c\simeq0.7$, but since $T_c=23.5$ K for this sample, this anomaly occurs at 17 K (and $H\sim5$ kOe) and clearly cannot be attributed to the Sm magnetic ordering. Similar results have also been obtained in other samples, and we find that this anomaly occurs for $T/T_c\simeq0.5$–0.7. We have also observed an upward curvature for H_{c2} in the $Nd_{1.85}Ce_{0.15}CuO_4$ system, and we have plotted in the inset some of our data for comparison [16]. We believe this anomaly could originate from flux-creep effects, or oxygen inhomogeneities in the sample.

In the vicinity of the Néel temperature T_N for Sm, on the other hand, we observe *no* anomaly in the upper critical field. Hence there is no substantial effect of the rare-earth ordering on H_{c2}, while conventional theories [17] based on a BCS mechanism would predict a substantial

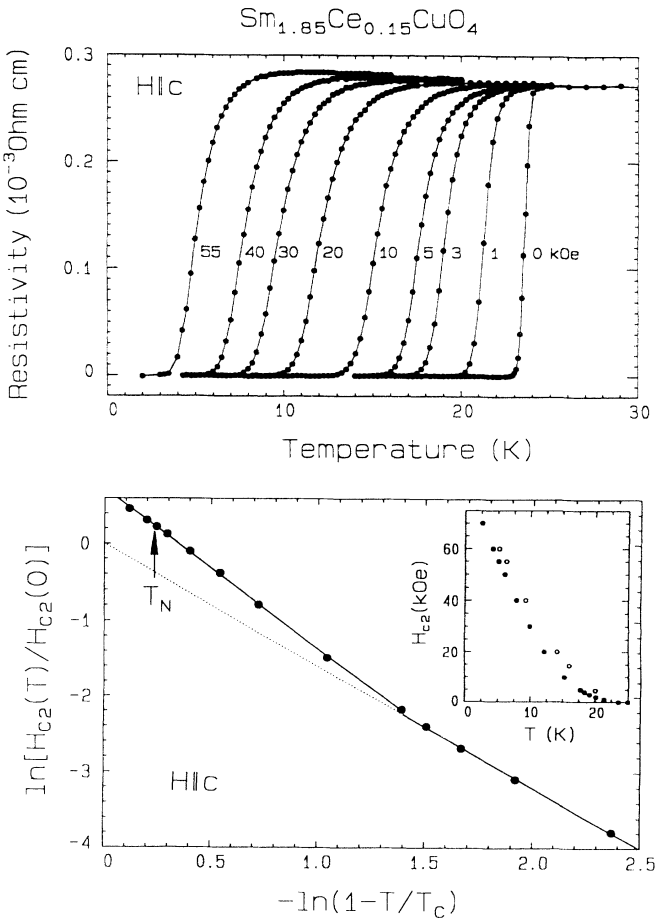

FIG. 3. Top: Temperature dependence of the resistivity of a $Sm_{1.85}Ce_{0.15}CuO_4$ single crystal ($T_c=23.5$ K) for a series of fields applied along the *c* axis. Note that the transition remains sharp in a field. Bottom: Field dependence of T_c (midpoint) shown in a plot of $\ln[H_{c2}(T)/H_{c2}(0)]$ vs $-\ln(1-T/T_c)$. The solid lines are the least-squares fits to the data. The sudden rise in H_{c2} occurs at ~17 K and $H_{c2}\sim5$ kG, while *no* anomaly is observed at the Néel temperature for $Sm_{1.85}Ce_{0.15}CuO_4$ ($T_N=4.9$ K [11]). Inset: Comparison of the H_{c2} data for the present Sm system (solid circles) with the $Nd_{1.85}Ce_{0.15}CuO_4$ system (open circles, $T_c=25.2$ K), where similar upward curvature behavior has been observed.

effect which in fact was thought to have been observed [11]. Indeed, it is our view that these electron-doped materials should not be superconducting at all if conventional pair-breaking effects associated with the rare-earth ions were present, irrespective of the effects of possible Cu magnetic moments in the superconducting state. Finally, we note that since the Sm system consists of alternate superconducting and ferromagnetic layers, the superconducting order parameter requires a change of sign in adjacent layers. This "π-phase" model [18] is predicted to substantially affect the superconducting state below the magnetic ordering temperature, and should give rise to a number of anomalies in the superconducting proper-

ties including a nonmonotonic field dependence to the critical current along the c axis. It will be particularly interesting to determine how or if the ordering of the Sm ions influences properties of the superconducting state other than H_{c2}.

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