Electronic and Magnetic Properties of Electron-doped Superconductor, Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$

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Temperature-dependent magnetization ($M(T)$) and specific heat ($C_p(T)$) measurements were carried out on single crystal Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ ($T_c = 16.5$ K). The magnetic anisotropy in the static susceptibility, $\chi = M/H$, is apparent not only in its magnitude but also in its temperature dependence, with $\chi_\perp$ for $\mathbf{H} \perp \mathbf{c}$ larger than $\chi_\parallel$ for $\mathbf{H} \parallel \mathbf{c}$. For both field orientations, $\chi$ does not follow the Curie-Weiss behavior due to the small energy gap of the $J = 7/2$ multiplet above the $J = 5/2$ ground-state multiplet. However, with increasing temperature, $\chi_\parallel(T)$ exhibits a broad minimum near 100 K and then a slow increase while $\chi_\perp(T)$ shows a monotonic decrease. A sharp peak in $C_p(T)$ at 4.7 K manifests an antiferromagnetic ordering. The electronic contribution, $\gamma$, to $C_p(T)$ is estimated to be $\gamma = 103.2$ (7) mJ/mole-Sm$^{-2}$K$^2$. The entropy associated with the magnetic ordering is much smaller than $R \ln 2$, where $R$ is the gas constant, which is usually expected for the doublet ground state of Sm$^{3+}$. The unusual magnetic and electronic properties evident in $M(T)$ and $C_p(T)$ are probably due to a strong anisotropic interaction between conduction electrons and localized electrons at Sm$^{3+}$ sites.

74.25.Bt, 74.25.Ha, 75.30.Gw, 74.72.Jt

I. INTRODUCTION

After the discovery of high-temperature superconductivity in copper-oxide compounds $^{[1]}$, a new class of superconducting compounds was found with the formula Ln$_{2-x}$M$_x$CuO$_4$ where Ln stands for Pr, Nd, Sm, and Eu, and M for Ce and Th $^{[2]}$. These compounds have become the subjects of an intense study due to their peculiar physical properties, which are different from the high-temperature superconductors of cuprates. The Ln$_2$CuO$_4$ parent compounds crystallize in a tetragonal “T-phase” structure containing CuO$_2$ planes in which the copper ions are surrounded by a square planar arrangement of oxygen ions, in contrast to the La$_2$CuO$_4$ parent compound which forms an orthorhombic “T-phase” structure at low temperature (below $\approx 500$ K) containing CuO$_2$ planes in which copper ions are surrounded by an octahedral arrangement of oxygen ions. Ln$_{2-x}$M$_x$CuO$_4$ (M = Ce or Th) compounds have electrons as a charge carrier in forming superconducting electron pairs, contrast to the related La$_{2-x}$M$_x$CuO$_4$ (M = Sr or Ba) compounds containing holes as a charge carrier. The electron-doped compounds have the pressure dependence of $T_c$ variation with negative $\partial \ln T_c/\partial P$, where $P$ is pressure, while the hole-doped ones have positive $\partial \ln T_c/\partial P$. Antiferromagnetic (AFM) ordering of the rare-earth ions in Ln$_2$CuO$_4$ has been found for Ln = Nd ($T_N \approx 1.7$ K), Sm ($T_N \approx 5.9$ K), and Gd ($T_N \approx 6.6$ K) while no magnetic ordering for Ln = Pr and Eu. The AFM ordering temperatures for Ln = Nd and Sm are lowered by substituting electron donor element (Ce$^{4+}$ or Th$^{4+}$ ions) for Ln$^{3+}$ ions. The superconductivity appears at the narrow range of electron doping near $x = 0.15$ with $T_c > T_N$ and co-exists with the AFM state below $T_N$. The AFM transition nature is studied in terms of magnetization and specific heat measurements $^{[3,4]}$. The entropy estimation associated magnetic ordering in Sm$_2$CuO$_4$ confirms the doublet ground state, expected by crystalline electric field splitting $^{[5]}$. However, the electronic contribution to specific heat, $\gamma \approx 82$ mJ/mole-Sm$^{-2}$K$^2$, in Sm$_2$CuO$_4$ is found to be much larger than the ones of other compounds. The large value of $\gamma$ is suspected to be due to the existence of magnetic correlation much above the $T_N$, making the evaluation of $\gamma$ uncertain, but not understood clearly yet.

For superconductivity, experimental determination of the order-parameter symmetry of n-type cuprate superconductors is critical in establishing an unified understanding of the mechanism of superconducting pairing in cuprates. Recent experiments suggest that the dominant symmetry of the order parameter is of $d$-wave type $^{[6,7]}$. In addition, the role of rare-earth magnetic mo-
ment interacting with $d$-wave superconducting system of electrons opens up a new area of theoretical and experimental studies. So far only Nd$_{2-x}$Ce$_x$CuO$_4$–$\delta$ was extensively studied in which relatively weak moments strongly influence the temperature dependence of the penetration depth \cite{8}, which helps to identify the order-parameter symmetry. It is interesting to investigate the electronic and magnetic properties in normal state of electron doped Sm$_{1.85}$Ce$_{0.15}$CuO$_4$–$\delta$ by specific heat measurements. Temperature dependent magnetization in the normal state is also necessary to study the specific heat data because the crystalline electric field effects significantly affect the magnetic properties of Sm$^{3+}$ ion, causing magnetic anisotropy both in magnitude and temperature dependence of magnetization. In this paper, the specific heat and magnetization data are represented to study the normal state properties of superconducting Sm$_{1.85}$Ce$_{0.15}$CuO$_4$–$\delta$ compounds.

**II. EXPERIMENTAL DETAILS**

Superconducting single crystals of Sm$_{1.85}$Ce$_{0.15}$CuO$_4$–$\delta$ have been grown by a flux-based technique. A batch of about 40 g is prepared by mixing and grinding powders of Sm$_2$O$_3$ (99.9%), CeO$_2$ (99.99%), and CuO (99.99%) in the molar ratio of (2-x):(2x):(7.2~13.4), respectively. The powders were pre-baked at 800–950 °C (for Sm$_2$O$_3$ and CeO$_2$) or at 400–600 °C (for CuO) to remove some volatile impurities. The mixed batch needs to be sintered at 900 °C and ground several times. It was soaked at 1000 °C for 10–20 hours and heated to 1210 °C in air (300 °C/h). After a short soak for 1–3 h, the temperature was lowered to 1000 °C at a rate of 5–12 °C/h, and then to room temperature. As-grown crystals with typical size of $\sim 1.5 \times 1 \times 0.03$ mm$^3$ were synthesized by this procedure. Superconductivity was induced by annealing and quenching in inert gas; the initial raising rate of temperature was 5–10 °C/min (300–600 °C/h), and the soak time at 880 °C was 16 hours. The quenching needs to be done within 30 minutes to preserve the high-temperature structure.

The as-grown single crystals of Sm$_{1.85}$Ce$_{0.15}$CuO$_4$–$\delta$ are confirmed to be of the single phase of the Sm$_2$CuO$_4$ structure by measurements of powder x-ray diffraction of pulverized single crystals. The impurity phases of Cu$_2$O and Sm$_2$O$_3$, which are often found in polycrystalline samples, are not detected in the diffraction pattern. Temperature dependent static magnetization was measured by using a 7-Tesla Quantum Design superconducting quantum interference device magnetometer (SQUID). The field cooled (FCW) and zero-field-cooled (ZFC) data in the superconducting state were obtained on warming after the magnet was quenched. The specific heat measurements down to 1.2 K were made on the grown single crystal, using a time constant method (relaxation method) technically described in detail elsewhere \cite{10}.

**III. RESULTS AND DISCUSSION**

FIG. 1. Superconducting state volume magnetization $M$ in an applied field $H = 10$ G versus temperature of single crystal Sm$_{1.85}$Ce$_{0.15}$CuO$_4$–$\delta$ for (a) $H \parallel c$ and (b) $H \perp c$: zero-field-cooled (ZFC) (dark circles) and field-cooled (FCW) (open circles) data taken on warming as shown.

The magnetization versus temperature ($M$($T$)) data in Fig. 1(a) and 1(b) show the flux expulsion (FCW) and magnetic shielding (ZFC) effects for $H \parallel c$ and $H \perp c$ in a Sm$_{1.85}$Ce$_{0.15}$CuO$_4$–$\delta$ crystal for an external magnetic field $H = 10$ G, respectively. The plots show typical superconducting diamagnetic signal for both field orientations, indicating bulk superconductivity. The much higher values of $M$($T$) for $H \parallel c$ than $H \perp c$ is due to the demagnetization field inside the sample, which is not corrected for actual real field for the measurements. The superconducting transition temperature, $T_c$, is found to be 16.5 K, the temperature at which more than 1% of superconducting volume fraction appears. It is noted that the superconductivity in Nd$_{2-x}$Ce$_x$CuO$_4$–$\delta$ appears only both in the very limited Ce concentration range of $x \approx 0.15$ and in the reduced oxygen content of $\delta \approx 0.07$ \cite{9}. The superconducting properties of Sm$_{1.85}$Ce$_{0.15}$CuO$_4$–$\delta$ single crystal are quite similar to the ones of bulk Nd$_{2-x}$Ce$_x$CuO$_4$–$\delta$ samples, indicating the apparent oxygen deficiency in our sample. In addition, the observed $T_c \approx 16.5$ K and the broad superconducting transition in the magnetization in low magnetic...
fields is often found in the bulk Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ samples, due to the partial occupancy of apical oxygen in $T$-phase structure [11]. It should be noted that, recently, the microwave surface resistance measurement, which depends neither on electric percolation nature nor on magnetic shielding current, shows that the real $T_c$, clearly higher than the $T_c$ determined above, exists without measurable bulk Meissner effect in Sm$_{2-y}$Ce$_y$CuO$_{4-\delta}$ compounds [12]. So the $T_c$, which is determined in this study, is believed to be lower bound of real $T_c$.

Typical $M(H)$ isotherm data for Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ are shown in Fig. 2(a) for $H \parallel c$ and 2(b) for $H \perp c$ at several different temperatures for 0 G $\leq H \leq$ 70 kG. For both field orientations, the magnetization is linear in the whole applied field range for temperature above 50 K and at 5 K in the $H >$ 10 kG below which superconducting signals appear. It is noted that the nonlinear behavior of magnetization, leading to a saturation of the Sm$^{3+}$ magnetic moments, is not observed even at $T = 5$ K and $H = 70$ kG. The magnetic moment at this temperature and field is found to be 0.031 $\mu_B$/Sm$^{3+}$ and 0.027 $\mu_B$/Sm$^{3+}$ for $H \perp c$ and $H \parallel c$, respectively. Those values are much smaller than the theoretically expected value of 0.845 $\mu_B$/Sm$^{3+}$ for Hund’s isolated Sm$^{3+}$ ion, $^6H_5/2$.

Fig. 2 shows the temperature-dependent magnetic susceptibility, $\chi(T)$, for Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ with $H = 5$ kG perpendicular and parallel to $c$-axis and their powder average for $5$ K $\leq T \leq$ 350 K. The large anisotropy in $\chi(T)$ between $H \perp c$ and $H \parallel c$ is quite clear and the temperature dependence for both field orientations clearly deviate from the typical Curie-Weiss behavior. In addition, the temperature dependences of $\chi(T)$ for both field orientations is also significantly different: with increasing temperature, $\chi || (T)$ for $H \parallel c$ shows a broad local minimum around 100 K and a slow increase whereas $\chi \perp (T)$ for $H \perp c$ shows a monotonic decrease. The similar $\chi(T)$ of non-Curie-Weiss behavior is found in the magnetization of Sm$^{3+}$ ions and ascribed to the comparable size of $J$ multiplet to the $k_B T$ in Sm$^{3+}$ ions Hund’s ground state of $J = 5/2$ [8]. Thus, van Vleck contribution due to the higher level of $J = 7/2$ should be considered to account for the observed susceptibility. The observed magnetic susceptibility is described according to the standard formula of

$$\chi(T) = N_A \left[ \frac{\mu^2_{eff}}{3k_B(T - \Theta)} + \frac{20\mu_B^2}{7k_B\Delta E} \right]$$  \hspace{1cm} (1)

where the first term is a Curie-Weiss contribution from the $J = 5/2$ ground state multiplet, and the second one is a temperature independent van Vleck susceptibility due to coupling of the $J = 5/2$ ground state multiplet with the $J = 7/2$ multiplet at an average energy $k_B \Delta E$ above ground state. The best fits for the data of $H \parallel c$, $H \perp c$, and powder average are plotted by solid lines as shown in the Fig. 3. The fitting results are unsatisfactory for both field orientations but apparently quite good for the powder-average case. From the fitting results of the powder average data, the splitting $\Delta E$, the effective moment $\mu_{eff}$, and the Curie-Weiss temperature $\Theta$ are extracted to be 466 K, 0.36 $\mu_B$, and -6.4 K, respectively. The value of $\Delta E$ is smaller than the of Sm$_3$CuO$_4$, ($\approx$ 1150 K) [8], which is probably due to the doping of electrons by Ce$^{4+}$ ion and the interaction between the localized and the doped electrons.

A particularly interesting feature in Fig. 3 is that the susceptibility for $H \parallel c$ reaches a minimum and then in-
creases slowly as the temperature increases still further, which is similar to the one in Sm due to the small interval between $J = 5/2$ and $J = 7/2$ multiplets. This minimum susceptibility behavior is not observed for $H \perp c$ and powder averaged one, which show monotonic decrease with increasing temperature. One of the possible scenarios for this remarkable anisotropy is that the splitting of $J$ multiplets has angular dependence. It is conjectured that this can be caused by the non-negligible anisotropic hybridization of conduction electrons with the localized Sm$^{4+}$ ions and its angular dependence. The heavy electronic behavior of Sm$_2$CuO$_4$ compound is manifested by the relatively large $\gamma$ ($\approx 82$ mJ/mole-Sm-K$^2$) value, which is the electronic specific contribution. The large value of $\gamma$ is also found in the electron doped Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ in this study in specific heat measurements (see below).

$C_p(T)$ measurements. Thus, the observed transition in Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ is also of AF nature and the $T_N$ is shifted to lower temperature with charge carrier (electrons) being doped.

In order to separate the magnetic and nonmagnetic contribution to $C_p$, the data for $10 K \leq T \leq 18 K$ is fitted to the equation

$$C_p^{\text{NM}}(T) = \gamma T + \beta T^3,$$

(2)

where the linear and the cubic terms correspond to the electronic and lattice contributions to the specific heat, respectively. The $C_p^{\text{NM}}(T)$ for $10 K \leq T \leq 18 K$ from Fig. 4(a) is plotted again with $C_p^{\text{NM}}(T)/T$ versus $T^2$ in Fig. 4(b) together with the fitting values (solid line), which shows nice agreement between the data and Equation (2). It is found that $\gamma = 191.0 (7)$ mJ/mole-K$^2$ and $\beta = 1.3 (1)$ mJ/mole-K$^4$, yielding the Debye temperature $\Theta_D \approx 219 K$ from the relation of $\Theta_D \propto (n/\beta)^{1/3}$, where $n$ is the number of atoms in a formula unit. Although the above equation for the specific heat is valid for temperatures below $\Theta_D/50$ in usual metal, the equation quite often works well for temperatures below $\Theta_D/10$ within an error of few percent, which is satisfied in our temperature range [4].

**FIG. 4.** (a) Specific heat $C_p$ versus temperature $T$ of single crystal Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ for $1.5 K \leq T \leq 19.0 K$. (b) $C_p$ versus $T^2$.

The temperature dependent specific heat, $C_p(T)$, for Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ is plotted in Fig. 4(a). Clear evidence of a phase transition in Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ is given by the sharp peak at $T = 4.7 K$ and the superconducting transition is seen near $T_c \approx 16.5 K$ as a slight jump of $C_p$, which is consistent with the $T_c$ from low field magnetization. The data at $T = 5.7 K$, which is level off the measured data, is not understood yet and probably sample dependent (or measurement error). It was shown that a phase transition in Sm$_2$CuO$_4$ at $T \approx 6 K$ is attributed to AFM transition from the $M(T)$ and $C_p(T)$ measurements. Thus, the observed transition in Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ is also of AF nature and the $T_N$ is shifted to lower temperature with charge carrier (electrons) being doped.

**FIG. 5.** Magnetic specific heat ($C_p^{\text{mag}}$) versus temperature $T$ of singel crystal Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$, $C_p^{\text{mag}} = C_p - C_p^{\text{NM}}$ ($= \gamma T + \beta T^3$) (see text). Inset: entropy associated with the magnetic transition versus temperature.

The observed value of $\gamma = 103.2 (7)$ mJ/mole-Sm-K$^2$ is significantly larger than those found in other Ln$_2$CuO$_4$ compounds, $0 \pm 10$ mJ/mole-Nd-K$^2$ for Ln = Nd, $1.3 \pm 0.1$ mJ/mole-Pr-K$^2$ for Ln = Pr [5]. For Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ compound, which has highest superconducting transition temperature among electron doped superconductors, the value of $\gamma$ is enhanced to be $\approx 29$ mJ/mole-Nd-K$^2$ [4]. It is natural to judge that the enhanced $\gamma$ is due to the doped electrons. Even for Sm$_2$CuO$_4$, the $\gamma$ value was previously found to be exceptionally large ($\approx 82$ mJ/mole-Sm-K$^2$) [4]. It was speculated that the effects of magnetic correlation exist well above $T_N \approx 5.9 K$, thereby making accurate determination of $\gamma$ difficult. However, our estimated $\gamma$ for
Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ is still quite large even though $T_N$ is now lowered to be 4.7 K. However, it is not clear now what is the origin of the large value of $\gamma$ in the superconducting state.

The contribution of magnetic correlation to the measured $C_p(T)$ is calculated as $C_p^{mag}(T) = C_p(T) - C_p^{NM}(T)$, where the extrapolation of $C_p^{NM}(T)$ for low temperature with the constants determined above is used, and is plotted in Fig. 3. The entropy associated with the magnetic transition is calculated from the $C_p^{mag}(T)$ and its temperature dependence is plotted in the inset of Fig. 3. The magnetic entropy saturates rapidly above $T_N$ to be $\approx 4.1$ J/kmole, indicating that the transition is driven by localized electrons. However, the accumulated entropy is clearly smaller than 1.85 $R$ $\ln 2$, where $R$ is gas constant, which is the usual value of a doublet ground state of Sm$^{3+}$. It was reported by [10] that the magnetic entropy associated with a magnetic transition is significantly reduced if the magnetic transition is due to itinerant heavy fermionic electrons in analogy to a BCS-type transition. Thus, the reduced entropy can be explained by the fact that itinerant electrons with heavy effective mass are involved in the transition. This explanation is also consistent with the anisotropic temperature-dependent behavior of magnetization and the enhanced electronic specific heat contribution.

IV. SUMMARY

The single crystal of superconducting Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ compounds is studied in terms of magnetization and specific heat measurements. The largest difference in susceptibility, so far reported, between $H \parallel c$ and $H \perp c$ is found and the temperature dependencies for both field orientations do not follow the Curie-Weiss behavior due to the small energy gap of $J = 7/2$ multiplet above $J = 5/2$ ground state. With increasing temperature, the $\chi_\parallel(T)$ for $H \parallel c$ exhibits a broad local minimum around $T = 100$ K and a slow increase while the $\chi_\perp(T)$ for $H \perp c$ shows a monotonic decrease. The specific heat data show a sharp peak at $T = 4.7$ K, which is of AF transition. The estimated $\gamma$ value of electronic contribution is enhanced with electron doping and clearly larger than the ones reported so far. The entropy associated magnetic transition is obviously smaller than the expected one of a doublet ground state. Although the peculiar features found in this paper in Sm$_{1.85}$Ce$_{0.15}$CuO$_{4-\delta}$ seem to be related with the conduction electrons which is strongly interacting with the localized electrons, more study not only in experiments but also in theory should be done to understand the magnetic and electronic properties and, further, the mechanism of superconductivity in electron doped superconductors.

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B 64, 189 (1986).
[2] Y. Tokura, H. Takagi, and S. Uchida, Nature 337, 345 (1989).
[3] C. Murayama, N. Mori, S. Yomo, H. Takagi, S. Uchida, and Y. Tokura, Nature 339, 293 (1989).
[4] S. Ghamaty, B. W. Lee, J. T. Markert, E. A. Early, T. Bjørnholm, C. L. Seaman, and M. B. Maple, Physica C 160, 217 (1989).
[5] C. L. Seaman, N. Y. Ayoub, T. Bjørnholm, E. A. Early, S. Ghamaty, B. W. Lee, J. T. Markert, J. J. Neumeier, P. K. Tsai, and M. B. Maple, Physica C 159, 391 (1989).
[6] V. Nekvasil, Physica C 170, 469 (1990).
[7] J. D. Kokales, P. Fournier, L. V. Mercaldo, V. Talanov, R. L. Greene, and S. M. Anlage, cond-mat/0002301.
[8] R. Prozorov, R. W. Giannetta, P. Fournier, and R. L. Greene, cond-mat/0002301.
[9] C. C. Tsuei, and J. R. Kirtley, Phys. Rev. Lett. 85, 182 (2000).
[10] G. R. Stewart, Rev. Sci. Instrum. 54, 1 (1983).
[11] P. G. Radaelli, J. D. Jorgensen, A. J. Schultz, J. L. Peng, and R. L. Greene, Phys. Rev. B 49, 15322 (1994).
[12] H. A. Blackstead, R. F. Jardim, P. Beeli, D. B. Pulling, and A. K. Heilman, Phys. Rev. B 57, 3683 (1998).
[13] A. H. Morrish, The Physical Principles of Magnetism, (Wiley, New York, 1965), p. 56.
[14] B. K. Cho, R. A. Gordon, C. D. W. Jones, F. J. DiSalvo, J. S. Kim, and G. R. Stewart, Phys. Rev. B 57, 15191 (1998).
[15] M. F. Hundley, J. D. Thompson, S-W. Cheong, Z. Fisk, and S. B. Oseroff, Physica C 158, 102 (1989).
[16] G. R. Stewart, Rev. Mod. Phys. 56, 755 (1984).