Electrical and magnetic properties of the metallic $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ superconductor

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Received 8 October 1990

Samples of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ with $x=0.13, 0.15$ and 0.17 have been prepared under N_2 and He atmospheres at various temperatures. AC electrical resistance $R(T)$ measurements reveals a metallic behavior in the normal state resistance for the $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ sample which was annealed in the He atmosphere at 1000°C . A superconducting transition occurs at 24 K with the mid-point transition temperature $T_c(50\%)=19\text{ K}$ and a superconducting transition width $\Delta T_c(T_c(90\%)-T_c(10\%))=9\text{ K}$. DC magnetization measurement reveals bulk superconductivity in the sample. Powder X-ray diffraction patterns indicate a single-phase $\text{Nd}_2\text{CuO}_{4-y}$ structure in this sample. The lattice parameters deduced from the diffraction peaks yield the values of $a=3.950\pm0.002\text{ \AA}$ and $c=12.067\pm0.009\text{ \AA}$, respectively.

The recent discovery of the occurrence of superconductivity in the $\text{R}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ ($\text{R}=\text{Pr}, \text{Nd}, \text{Sm}$ and Eu) [1,2] and $\text{R}_{2-x}\text{Th}_x\text{CuO}_{4-y}$ ($\text{R}=\text{Pr}, \text{Nd}$ and Sm) [2–4] compounds with transition temperature up to 24 K has attracted a lot of research interest. Hall measurements [1,5] on $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ indicate that the charge carriers are electrons. However, electron-energy-loss (EELS) study indicates the presence of holes in the O 2p band in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$. One interesting property of the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ system is the temperature dependence characteristic of the normal state resistivity, semiconducting-like behavior, $d\rho(T)/dT<0$, were observed in the polycrystalline superconducting samples. However, for $x\geq0.18$, superconductivity disappears and the resistivity exhibits a typical metallic behavior with $d\rho(T)/dT>0$. Many experimental and theoretical studies have been based on these results. In this paper, we report our results on the polycrystalline samples of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ with $x=0.13, 0.15$ and 0.17 and show that metallic superconductor exists for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$. DC magnetization measurements reveal bulk superconductivity in such samples.

The samples used in this study were prepared by solid-state reaction from high purity Nd_2O_3 , CeO_2 and CuO powders. Stoichiometric mixtures of these

powders were ground thoroughly and heated in air at 900°C for 20 h and removed from the furnace and quenched in air to room temperature, reground and fired in air at 900°C for another 20 h and quenched to room temperature. The resulting powders were then pressed into pellets and fired in air at 1100°C for 18 h and quenched to room temperature. The pellets were then sintered in flowing He or N_2 at 1000°C or 850°C for 18 h and furnace cooled to room temperature in He or N_2 flow. AC electrical resistance $R(T)$ measurements on bar-shaped samples were performed with four-wire technique using a Linear Research Model LR 400 AC resistance bridge operating at a frequency of 16 Hz with platinum and germanium thermometers as the temperature sensors. DC magnetization measurements were performed using Quantum Design MPMS SQUID magnetometer in various fields.

Shown in fig. 1 are the normalized AC electrical resistance $R(T)/R(280\text{ K})$ as a function of temperature T curves for various of x of $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ samples which were annealed in He at 850°C and in N_2 at 1000°C . The temperature dependence of the resistance behaviors is inconsistent with what have been reported [1,7]. For the He-annealed (at 850°C) samples, $R(T)/R(280\text{ K})$ increases as the temperature cools from room temper-

Fig. 1. Normalized electrical resistance $R(T)/R(280\text{ K})$ as a function of temperature T curves for $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ with $x=0.13, 0.15$ and 0.17 . (a) for samples annealed in He at 850°C . (b) for samples annealed in N_2 at 1000°C .

ature, and becomes more metallic as x increases. A superconducting transition occurs at 22 K for all values of x . The zero resistance occurs at 12 K and 9 K for $x=0.13$ and for $x=0.15$, respectively. For $x=0.17$, the transition is not complete down to 4.5 K . The $R(T)/R(280\text{ K})$ vs T behavior for the N_2 -annealed samples shows similar characteristics.

For the samples annealed in He atmosphere at 1000°C , the $R(T)/R(280\text{ K})$ vs T behaves quite differently. As shown in fig. 2, where $R(T)/R(280\text{ K})$ for $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ with $x=0.13, 0.15$ and 0.17 are plotted as a function of temperature T . For $x=0.13$, the resistance exhibits semiconducting-like behavior in the normal state and superconducting transition occurs at 23 K . However, the $R(T)/R(280\text{ K})$ vs T curves for $x=0.15$ and $x=0.17$ show typical metallic behaviors in the normal state. For $x=0.15$, $(R)T$ decreases linearly as temperature T decreases from room temperature to above 100 K . Below 100 K , $R(T)$ still decreases with decreasing T but the de-

creasing rate becomes smaller. The resistance ratio $R(280\text{ K})/R(25\text{ K})$ for this sample is 1.4 , which is smaller than that for the single crystal sample with the applied current along the ab plane [8]. The superconducting onset temperature is 24 K and the midpoint transition temperature $T_c(50\%)$ is 19 K and the transition width $\Delta T_c(T_c(90\%) - T_c(10\%))$ is about 9 K . Zero resistance is obtained at 13 K . The feature of $R(T)$ during the superconducting transition and the broadness of ΔT_c indicate the possibility of compositional (e.g., oxygen) inhomogeneities in the sample. Powder X-ray diffraction patterns reveal a single-phase Nd_2CuO_4 -type tetragonal structure in such sample. The lattice parameters obtained from the diffraction peaks are $a=3.950 \pm 0.002\text{ \AA}$ and $c=12.067 \pm 0.009\text{ \AA}$, respectively. This temperature-dependent characteristic in resistivity is similar to that reported for the single crystalline $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ samples with the applied current in the ab plane [8] and indicates that the positive slope [$d\rho(T)/dT > 0$] above T_c is an intrinsic property of the polycrystalline sample, and it is highly possible that the conducting carriers are along the ab plane for this compound. One possible explanation for the $R(T)$ behavior above the superconducting transition, as proposed in ref. [7], is when Ce is introduced to donate electron carriers in the Cu-O plane, both Kondo effect and superconductivity occur. The Kondo effect comes from the antiferromagnetic coupling between the conduction electrons and the localized Nd^{3+} moments and gives an $\alpha \ln(T)$ term contribution to the resistivity. So the total resistivity is the sum of the contribution from the s-f exchange interactions between the conduction electrons and Nd^{3+} local moments, and the contribution from phonon scattering, which gives a linear dependence in $R(T)$, and the contribution of the residue resistivity γ . So $\rho(T)$ can be expressed in terms of $\rho(T) = \alpha \ln(T) + \beta T + \gamma$. This explains the $R(T)$ behavior in the normal state for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$. For $x=0.17$, $R(T)$ also decreases with decreasing T and a superconducting transition occurs at 23 K , however, the transition is still incomplete down to 4.2 K .

The oxygen contents of the $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ samples prepared under N_2 or He atmospheres were determined by an iodometric titration technique. For the N_2 -annealed sample, the obtained value of y is

Fig. 2. Normalized electrical resistance $R(T)/R(280\text{ K})$ as a function of temperature T curves for the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ samples annealed in He at 1000°C with $x=0.13$, 0.15 and 0.17 .

0.03 ± 0.01 . While for the He-annealed samples, the estimated values of y are 0.05 ± 0.01 (annealed at 1000°C) and 0.07 ± 0.015 (annealed at 850°C). These values of y obtained here are consistent with those reported previous by others for the superconducting samples which were annealed under the reducing atmosphere [5]. The uncertainty of the y values in each case reported here are due to the scattering of the data obtained from several iodometric titration experiments for samples from the same pellet and reveals the inhomogeneity of the oxygen content in the samples.

Figure 3 shows the Meissner and the shielding effects for the He-annealed $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ samples with $x=0.13$, 0.15 and 0.17 . These curves were obtained by first cooling the samples to 4.2 K in zero field, warmed up the samples in a field of 20 G to 30 K (shielding effect) and cooled down in a field of 20 G (Meissner effect). Both Meissner and shielding curves indicate the onsets of the superconducting transition at 23 K for $x=0.13$ and 0.15 and at 19 K for $x=0.17$, which is inconsistent with the results of the AC electrical resistance measurements.

Fig. 3. Magnetization vs temperature for the $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ samples annealed in He at 1000°C with $x=0.13$, 0.15 and 0.17 . The upper curves are the field cooling curves in a field of 20 G and the lower curves are the shielding curves.

Fig. 4. The inverse magnetic susceptibility as a function of temperature T for the $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ sample annealed in He at 1000°C with an applied field of 5 kG.

An estimate from the Meissner curves indicates the Meissner fraction of 19% for $x=0.13$ and 10% for $x=0.15$, respectively. If one includes the sample demagnetization factor and porosity in the samples, the actual values of the Meissner fraction should be larger. Which indicates bulk superconductivity in the samples.

Displayed in fig. 4 is the inverse magnetic susceptibility χ^{-1} as a function of temperature T for the He-annealed (at 1000°C) $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ sample in an applied magnetic field of 5 kG. The behavior is similar to that previously reported for the $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ superconductor which shows a semiconducting-like behavior in the normal state resistance [7]. Above ~ 60 K, the curve follows a Curie-Weiss with a value of effective moment $\mu_{\text{eff}} = 3.547 \mu_B$. Below 60 K, a reduction in the magnetic moment is observed. A behavior typical of Nd^{3+} ions with a crystalline electric field moment reduction below ~ 60 K.

In conclusion, we show that metallic superconductor exists for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$ polycrystalline sample. X-ray diffraction patterns indicate a single-phase $\text{Nd}_2\text{CuO}_{4-y}$ type tetragonal structure and DC

magnetization measurements reveal bulk superconductivity in such a sample. This work was supported by the ROC National Science Council under Grant No. NSC 79-0208-M002-39.

References

- [1] T. Tokura, H. Takagi and S. Uchida, *Nature* 337 (1989) 345.
- [2] J.T. Markert, E.A. Early, T. Bjørnholm, S. Ghamaty, B.W. Lee, J.J. Neumeier, R.D. Price and M.B. Maple, *Physica C* 158 (1989) 178.
- [3] J.T. Markert and M.B. Maple, *Solid State Commun.* 70 (1989) 145.
- [4] E.A. Early, N.Y. Ayoub, J. Beille, J.T. Markert and M.B. Maple, *Physica C* 160 (1989) 320.
- [5] H. Tagaki, S. Uchida and Y. Tokura, *Phys. Rev. Lett.* 62 (1989) 1197.
- [6] N. Nücker, P. Adelmann, M. Alexander, H. Romberg, S. Nakai, J. Fink, H. Rietschei, G. Roth, H. Schmidt and H. Spille, *Z. Phys. B* 75 (1989) 421.
- [7] For example, J.L. Peng, R.N. Shelton and H.B. Radorsky, *Phys. Rev. B* 41 (1990) 187.
- [8] J.-M. Tarascon, E. Wang, L.H. Greene, B.G. Bagley, G.W. Hull, S.M. D'Egido, P.F. Miceli, Z.Z. Wang, T.W. Jing, J. Clayhold, D. Brawner and N.P. Ong, *Phys. Rev. B* 40 (1989) 4494.