Effects of Doping Mn on Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4} System

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Abstract—Nd\textsubscript{1.85}Ce\textsubscript{0.15}Cu\textsubscript{1-x}Mn\textsubscript{x}O\textsubscript{4} samples with doping level up to 20\% have been synthesized by solid-state reaction method. The influence of Mn on their normal-state transport, crystal structure, superconductivity and magnetic properties has been investigated. For the samples with \(x\geq 0.03\), magnetization under zero-field cooling indicates that the magnetic state changes from ferromagnetic to paramagnetic at \(T=100\) K, which can be explained with the interaction between \(\text{Mn}^{4+}\) and \(\text{Mn}^{3+}\). The electrical resistivity \(\rho\) of samples increases with Mn doping. For the samples with doping level lower than 0.20, \(\rho\) initially increases with the decrease of temperature, i.e., \(\frac{\rho}{dT}>0\), and then shows superconductivity transition at \(T\approx 20\) K. The results suggest the coexistence of superconductivity and ferromagnetic ordering in Mn doped Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4}.

Index Terms—Crystal structure transition, magnetic properties, Mn doping.

1. Introduction

Since the discovery of high-\(T_c\) superconductors (HTSC), element substitution is proved to be very useful method in understanding unconventional superconductivity and the anomalous normal state behavior\([1]\). Nearly all the HTSC discovered up to date are cuprates; thus, Cu is thought to be of prime importance as superconductivity is supposed to reside primarily in the CuO\(_2\) planes. For Cu-site substitutions in high-\(T_c\) cuprates, the 3d metals are of importance due to their similar outer orbital structure and close ionic sizes to that of Cu. Although the effect of non-magnetic impurities has been intensively studied in hole-doped systems, as \(\text{La}_{2-x}\text{Sr}_{x}\text{CuO}_4\) (LSCO)\([2,3]\), the doping effect of Mn on Nd\textsubscript{2-x}Ce\textsubscript{x}CuO\textsubscript{3} (NCCO) has not been studied intensively. NCCO has many other features in magnetic and superconducting properties distinguishing itself from the hole-doped analog, therefore, the study on the doping effect of Mn on Nd\textsubscript{1.85}Ce\textsubscript{0.15}Cu\textsubscript{1-x}Mn\textsubscript{x}O\textsubscript{4} is of particular interests. It is well known that Mn doping causes a series of interesting phenomena in LSCO\([4,5]\), for example, the superconductivity coexisting with ferromagnetism which was originated from the \(\text{Mn}^{4+}\)-O-\(\text{Mn}^{4+}\) superexchange interaction in mixed-valence Mn doped \(\text{La}_{1.85(4/3)}\text{Sr}_{0.15(4/3)}\text{Cu}_{1-x}\text{Mn}_x\text{O}_4\) \((x=0.06)\)\([6,7]\). This manifests the unique effect of Mn substitution for Cu on the magnetic and electrical properties of LSCO. Since NCCO is regarded as an electron-doped analog of LSCO, it would be interesting to investigate the doping effect of Mn on NCCO.

In this paper, a series of Mn doped samples of Nd\textsubscript{1.85}Ce\textsubscript{0.15}Cu\textsubscript{1-x}Mn\textsubscript{x}O\textsubscript{4} have been synthesized. The Mn doping effects on crystal structure, magnetic, electrical properties and superconductivity of this system were studied and compared with the doping behavior of its analog LSCO.

2. Experimental Details

Samples of Nd\textsubscript{1.85}Ce\textsubscript{0.15}Cu\textsubscript{1-x}Mn\textsubscript{x}O\textsubscript{4} \((x=0, 0.01, 0.03, 0.05, 0.07, 0.09, \text{ and } 0.20)\) were prepared by solid-state reaction method from high purity oxides: Nd\textsubscript{2}O\textsubscript{3} 99.95\%, CeO\textsubscript{2} 99.99\%, CuO 99.9\%, MnO\textsubscript{2} 99.5\%. Stoichiometric amounts of oxides were well mixed by long-time grinding, and the mixture was calcinated at 950 °C for 24 h in air. After regrinding, they were pressed into pellets by 10 M\(p\) then sintered at 1050 °C for 20 h in air. After sintering, all of the samples were quenched from 1050 °C to room temperature in air. Finally, the samples were annealed at 900 °C for 10 h in the flowing Ar and were quenched to room temperature.

The phase content and the lattice parameters were determined by powder X-ray diffraction (XRD) using Cu-K\(_\alpha\) radiation. Electrical resistivity of the samples was measured by a conventional dc four-probe method using a physical property measurement system (PPMS, quantum design). The dc magnetic susceptibility was measured using a commercial SQUID magnetometer (MPMS, quantum design).
3. Results and Discussion

The XRD patterns of the Nd$_{1.85}$Ce$_{0.15}$Cu$_{1-x}$Mn$_x$O$_4$ are shown in Fig. 1 (a). On the basis of powder XRD analyses, nearly single-phase Nd$_{1.85}$Ce$_{0.15}$Cu$_{1-x}$Mn$_x$O$_4$ has been obtained, especially for the samples with the compositions of $x$<0.09, although very small amount of impurity phases are detected for the samples of $x$=0.13 and $x$=0.20. Within the limit of calculation error, the Nd$_{1.85}$Ce$_{0.15}$Cu$_{1-x}$Mn$_x$O$_4$ phase can be well indexed by a tetragonal unit cell with $a$=0.397 and $c$=1.17 nm. As shown in Fig. 1 (b), the detailed values of the lattice parameter $a$ and $c$ obtained from Rietveld refinements reveal that there are anomalous changes in Nd$_{1.85}$Ce$_{0.15}$Cu$_{1-x}$Mn$_x$O$_4$ system. With the increase of Mn doping content, $a$ and $c$ increase firstly up to a maximum level when $x$=0.13. Previous experimental results have shown that the lattice parameters of NCCO doped by 3$d$ metals (Fe, Co, Ni and Zn, etc.) are monotonously increased or decreased, such anomalous changes of lattice parameters in NCCO have not been reported yet. Here, our experimental results show that such anomalous changes of lattice parameters in Mn-doped NCCO system, which imply the influence of the substitution Cu by Mn on the microstructure of NCCO, are very different from those of other 3$d$ metals.

Fig. 1. Powder XRD patterns for all the samples at room temperature and lattice parameters of different doping levels: (a) XRD patterns for Nd$_{1.85}$Ce$_{0.15}$Cu$_{1-x}$Mn$_x$O$_4$ samples with a variety of doping levels, and (b) variation of lattice parameters with Mn content, $x$.

Fig. 2 shows the susceptibility for the Nd$_{1.85}$Ce$_{0.15}$Cu$_{1-x}$Mn$_x$O$_4$ samples in field of 10 Oe after the zero field-cooling process. Superconductivity transitions are observed in the Mn concentration range of $x$≤0.05. A diamagnetic contribution to the magnetization appears in the region where the superconducting transition temperatures are expected to be. With the increase of temperature from 20 K, the magnetization drops, crossing zero at about 50 K, then decreases gradually as a PM behavior. From the $M$-$T$ curve of the sample $x$=0.03, it is evident that the sample has a superconductivity transitions at about 20 K.

Fig. 2. Temperature dependence of magnetic moment for Nd$_{1.85}$Ce$_{0.15}$Cu$_{1-x}$Mn$_x$O$_4$ samples in the zero-field-cooling process in an applied field of 10 Oe.

Brief qualitative characterization of the magnetometry data by noting the following circumstance is concluded. The indicated features of the $M$-$T$ curves are due specifically to the introduction of manganese.

At $T$>$T_c$, the magnetization falls off monotonically with the increase of temperature, as in the case of Curie-Weiss paramagnetism. A detailed analysis of the temperature dependence is done for samples with low Mn content 0.3≤$x$≤0.7 in the temperature interval 100 K≤$T$≤300 K. It is assumed that the other contributions to the magnetization in this temperature interval are independent of $T$, as follows:

$$M(T) = \left( \frac{C}{T - \Theta} \right) H + M_0 \tag{1}$$

where $\Theta$ is the characteristic temperature, $C$ and $M_0$ are constants. Equation (1) can well describe the behavior of the samples with a positive $\Theta$ varying from −3 K to −10 K. The fitting between the (1) and the experimental data is given in Fig. 3. The negative $\Theta$ means that the interaction of the local moments is antiferromagnetic.

At the temperature 25 K≤$T$≤100 K, it becomes obvious that the magnetization of the samples with $x$=0.03, 0.05 and $x$=0.07 contains nonmagnetic contributions with a peculiar temperature dependence. We have attempted to separate this contribution $M'(T)$ from the experimental data $M(T)$ by subtracting the paramagnetic component determined previously, as follows:

$$M'(T) = M(T) - \left( \frac{C}{T - \Theta} \right) H \tag{2}$$
The obtained $M'(T)$ results are plotted in Fig. 4. The temperature behavior of the contributions $M^*$ suggests that the nonparamagnetic contribution to the total magnetization is related to ferromagnetic ordering. From Fig. 4, the Curie temperature $T^C$ is estimated. The high temperature part of the $M'$ curve is matched to a dependence of the form. Using the effective field theories for temperatures near $T^C (T^C−T)^{1/2}$, the $T^C$ of the samples with $x=0.03$, 0.05 and $x=0.07$ are fitted as about 100 K, 99.5 K and 60 K, respectively.

The above-mentioned magnetic phenomena can be explained by the scenario described below. As revealed by the ESR spectra in LSCO\textsuperscript{13}, the distribution of Mn ions in NCCO is inhomogeneous microscopically and there are two kinds of steric states of Mn ions in the CuO$_2$ planes. One corresponds to the randomly distributed and isolated Mn ions which are in paramagnetic state, and the other corresponds to the Mn ions which have other Mn ions in their neighborhood and form clusters. These clusters exhibit ferromagnetism because the superexchange interaction through Mn$^{3+}$-O-Mn$^{3+}$ is ferromagnetic. The superexchange interaction through pds hybridization causes the AF correlation between the Cu$^{2+}$ spins. Superexchange of the two states of Mn ions in the CuO$_2$ planes is reasonable. As we know, both the NCCO and the Nd$_{2-x}$Ce$_x$MnO$_3$ (NCMO)\textsuperscript{16} have the same K$_2$NiF$_4$ structure and can exist independently. When prepared by the conventional solid-state reaction method, it is much possible for the NCMO to exist independently in the NCCO, so the Mn-O-Mn and Cu-O-Cu can exist in the same planes. Thus perhaps the superconductivity coexists with ferromagnetism in mixed-valence Mn doped Nd$_{1.85}$Ce$_{0.15}$Cu$_{1-x}$Mn$_x$O$_4$.

Fig. 5 shows the temperature dependence of resistivity for $0 \leq x \leq 0.20$. For $x=0$, the $\rho$ decreases abruptly at 20 K, manifesting the occurrence of superconductivity. For $x=0.20$, the $\rho$ increases gradually with the decrease of temperature. On the other hand, for samples with $0 \leq x \leq 0.07$, the $\rho$ increases gradually with the decrease of temperature, and then drops at about 20 K and decreases suddenly with further cooling, which show a broadened superconducting transition. The resistivity of normal state increases with the increase of Mn content. The relation of the onset superconducting transition $T_c(x)$ (the temperature at which $\rho$ begins decreasing) with the doping level $x$ is presented in Fig. 6.
localization of carriers\textsuperscript{[17][18]}. To analyze the variety of localization of carriers systemically, we redraw the $\rho - T$ curve with log $(1/T)$ dependence (see Fig. 7), which shows straight line fitting for all these curves, as expected from the localization of carriers. This suggests that the suppression of $T_c$ may also be related with the localization of carriers.

Fig. 7. Dependence of resistivity on log$(1/T)$ for Nd\textsubscript{1.85}Ce\textsubscript{0.15}Cu\textsubscript{1-x}MnO\textsubscript{4} samples in the region 20 K$<T<$300 K.

4. Conclusions

In summary, Nd\textsubscript{1.85}Ce\textsubscript{0.15}Cu\textsubscript{1-x}MnO\textsubscript{4} with manganese concentrations $x = 0, 0.01, 0.03, 0.05, 0.07, 0.13,$ and 0.20 was synthesized by conventional solid-phase technique. The resistive and magnetic measurements of samples are performed. It is assumed that the ions of the 3d impurity occupy copper positions in the two dimensional conducting planes. The samples with $x \leq 0.07$ exhibited superconductivity at low temperatures. The temperature $T_c$ of the start of the transition to superconductivity has an unusually weak dependence on $x$ which is practically the same as the typical value of $T_c$ in optimally doped NCCO ceramics. The results of the magnetic measurements indicate that ferromagnetic correlation between Mn$^{3+}$ and Mn$^{4+}$ coexists with the superconductivity. A logarithmic contribution to resistivity has been observed and well fitted as $\rho(x, T) = C \text{log}(1/T)$ in normal state, which suggests the localization of carriers in Nd\textsubscript{1.85}Ce\textsubscript{0.15}Cu\textsubscript{1-x}MnO\textsubscript{4}.

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