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Effect of Ga substitution on the superconducting properties of the electron-doped system: Nd-Ce-Cu-O

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We are reporting on results of dc magnetization measurements of the new electron-doped $Nd_{2-x}Ce_xCu_{1-y}Ga_yO_4$ superconductors. The effect of Ga^{3+} on T_c is similar to that of Ce^{4+}, although the extra electron of the former comes from the Cu-O planes. For example, for $x=0.12$ the undoped compound ($y=0$) is not superconducting; but by the addition of Ga ($y=0.03$), the material becomes superconducting at $T_c=20$ K, and the Meissner fraction and the critical current density are improved compared to $Nd_{1.85}Ce_{0.15}CuO_4$. The irreversibility line $T_{irr}(H)$ for doped and undoped samples scales with the applied field as H^p, with $p \simeq 0.6$, but for the Ga-doped sample it is pushed to higher temperatures.

Since the discovery of high-temperature superconductivity[1] in $La_{2-x}Sr_xCuO_4$ it has become a common belief that holes located in Cu-O planes which are the charge carriers here as well as in $YBa_2Cu_3O_7$ system, are essential for superconductivity. The holes or missing electrons are obtained by substitution of a divalent ion such as Sr^{2+} or Ba^{2+} for trivalent La, and for this reason these superconductors are called "*p*-type." The recent discovery[2] of the electron-doped ("*n*-type") superconductors added fresh fuel to controversies about the mechanism of superconductivity in copper oxide compounds. Electron superconductors are obtained in $R_{2-x}Ce_xCuO_{4-\delta}$ ($R=$Nd, Sm, Pr) when tetravalent Ce is partially substituted for trivalent *R*. The largest Meissner signal and highest $T_c=22$ K were observed in $Nd_{2-x}Ce_xCu_{4-\delta}$ for $x=0.15$ and $\delta=0.04$. Superconductivity was observed in a very limited Ce concentration range.[3] Below $x=0.14$ and above $x=0.18$ superconductivity disappears.

La-Sr-Cu-O and Nd-Ce-Cu-O have similar tetragonal crystal structures. The only difference between them is that in Nd-Ce-Cu-O each Cu ion is bonded to four oxygen atoms in sheets of Cu-O squares, whereas the Cu in La-Sr-Cu-O is surrounded by an octahedral arrangement of six oxygen atoms.

At this stage the resistivity of ceramic *n*-type samples exhibits semiconductor behavior and no pressure effect on T_c was found,[4] in remarkable contrast to the *p*-type superconductors in which T_c increases with increasing pressure. Due to a complex microstructure or compositional inhomogeneities in the material, zero resistance is difficult to achieve, and both the volume Meissner fraction (MF) and the shielding branch, even when measured at low applied fields, are small and do not exceed 20%–25% of the ideal $-\frac{1}{4}\pi$ value. In single crystals[5] the resistivity shows a metallic temperature dependence in both *ab* and *c* directions, but the MF is only 25%. On the other hand, magnetoresistance measurements show that this system exhibits significant anisotropy of the critical field, H_{c_2}, with respect to the *c* axis. $H_{c_2}(0)$ values of 6.7 and 137 T were estimated for the *c* axis and basal plane, respectively.[5]

In the present paper we present the first study of the effect of Ga substitution on superconductivity of the *n*-type superconductors. Since Ga is always trivalent, its substitution for divalent Cu provides a second source of electron doping. We find in general that in $Nd_{2-x}Ce_xCu_{1-y}Ga_yO_{4-\delta}$, the sum $x+y$ affects T_c qualitatively the way Ce^{4+} does alone in $Nd_{2-x}Ce_xCuO_4$, where electrons are donated only from outside the Cu-O planes. Our major finding concerning these Ga-doped samples is that in those materials which are not superconducting ($x<0.14$) the addition of Ga makes them superconducting. Moreover, for ceramic samples with $x+y=0.15$ and $x<0.13$, zero resistance is obtained and the superconducting features are improved. The Meissner and shielding values increase significantly, indicating the existence of a perfect bulk superconductor. The critical current density J_c is also increased by an order of magnitude. On the other hand, the temperature T_{irr}, which is defined as the temperature at which the reversible and irreversible branches separate, is field dependent and scales with the applied field as $H^{0.6}$ for both Ga-doped and undoped materials.

The samples with nominal compositions $Nd_{2-x}Ce_xCu_{1-y}Ga_yO_{4-\delta}$ were prepared by solid-state reaction technique. Prescribed amounts of Nd_2O_3, CeO_2, Ga_2O_3, and CuO were mixed and pressed into pellets and preheated at 1000 °C for about 20 h in air. The products were cooled to room temperature, reground, and fired again to 1100 °C for 24 h and then furnace cooled to ambient temperature. To produce the superconductivity, samples were annealed at 950 °C for 13 h under a reducing atmosphere of flowing Ar, and then quenched to room temperature in the same atmosphere. X-ray-diffraction measurements indicate that all samples are single phase and the lines are indexed on the basis of tetragonal structure (T' phase).[2]

The dc susceptibility measurements on solid ceramic pieces were carried out in a commercial SHE superconducting quantum interference device magnetometer and in a 155 PAR vibrating sample magnetometer in various fields 3 Oe $< H <$ 15 kOe as a function of temperature in the range of 4.2–30 K. The magnetization was measured by two different procedures: (a) The sample was zero-field cooled (ZFC) to 4.2 K, a field H was applied, and the magnetization of the shielding branch was measured as a function of temperature. (b) The sample was field cooled (FC) from above T_c in a field H and the Meissner branch was measured. In all measurements demagnetization corrections are negligible ($<2\%$).

Although Ga^{3+} and Cu^{2+} are similar in size (0.62 and 0.69 Å, respectively) their mutual substitution in rare-earth and transition metal oxides is limited. In $YBa_2Cu_3O_7$, Ga is incorporated into the compound, at least below 5 at.%; for higher concentrations extra phases were found.[6] Due to the low solubility of Ga, the doping level in the present paper is limited to 5 at.%. Three different Ga-doped systems were investigated:

(i) $Nd_{1.85}Ce_{0.15}Cu_{1-y}Ga_yO_{4-\delta}$. Ga was doped up to 5 at.% into a system where the optimal Ce concentration ($x=0.15$) is constant. To insure uniformity of Ce concentration, a mixture of appropriate proportions of Nd_2O_3 and CeO_2 was prepared. This mixture was divided into several parts and to each part different concentrations of CuO and Ga_2O_3 were added. All the samples mentioned here were prepared together at the same time under the same conditions described above. No detectable changes in the lattice parameters are observed for samples where $y=0.00$ and $y \leq 0.02$. The unit-cell lattice constants are $a=3.941$ Å and $c=12.04$ Å, in fair agreement with data published already.[2,7] This system was examined by a scanning electron microscope. Its composition was found to be uniform from grain to grain and the pictures show smooth and uniform surfaces. There were no detectable additional phases (except for $y=0.03$) and the chemical composition was confirmed.

The FC magnetization curves measured at 20 Oe for $Nd_{1.85}Ce_{0.15}Cu_{1-y}O_4$ are exhibited in Fig. 1. No subtraction of the paramagnetic contribution of Nd^{3+} was made. One definitely observes the decrease in T_c with increasing Ga content up to $y=0.02$. $T_c=21(1)$, 19(1), and 16(1) K for $y=0.00$, 0.01, and 0.02, respectively. The MF values for these samples are 12%–17% at 4.1 K. For $y=0.03$ one of our samples did not show any diamagnetic signal and the data presented in Fig. 1 (measured on a second sample) indicate very poor bulk superconductivity.

Ga has one more valence electron than Cu. In other words, by doping Ga into a system with constant Ce concentration, we increase the electron concentration. Indeed, our experiments reveal that the addition of Ga is equivalent to an increase of Ce concentration and T_c is sensitive only to electron concentration regardless of its source. This result is notably different from the one seen in La-Sr-Cu-O, where substitution of Ga on the Cu site severely reduces T_c. T_c decreases linearly with Ga and the system ceases to be superconducting with only 2.2 at.% doping.[8]

(ii) $Nd_{1.85}Ce_{0.15}Cu_{1-y}O_{4-\delta}$. To prove that the decrease in T_c and the disappearance of superconductivity mentioned above are due to Ga addition and are not a result of Cu deficiency, the $Nd_{1.85}Ce_{0.15}Cu_{1-y}O_4$ system up to $y=0.04$ was prepared. Figure 2 shows that for $y=0.04$ the compound is superconducting, $T_c=17$ K, and the MF is $\sim 15\%$. Although Cu concentration is smaller than those described in Fig. 1, superconductivity is retained. X-ray measurements indicate a single-phase material with $a=3.943$ Å and $c=12.05$ Å. There are two possible ways to explain this result: (1) The stoichiometry of the superconducting phase remains $Nd_{1.85}Ce_{0.15}CuO_4$, and an undetectable extra phase of Nd (Ce) oxide is present in the material. (2) Superconductivity survives for Cu deficiency up to 4 at.%, and T_c remains nearly constant. The oxygen content is expected to decrease and the Nd-Ce-Cu-O system behaves in this respect like Y-Ba-Cu-O systems.[9]

(iii) $Nd_{2-x}Ce_xCu_{1-y}Ga_yO_{4-\delta}$, $x+y=0.15$. The most striking phenomena were observed for Ce content lower than the optimal value of $x=0.15$. These samples without Ga doping are not superconducting.[2-4] Since T_c is very sensitive to electron concentration regardless of its source (see Fig. 1), decreasing Ce^{4+} content may be compensated for by adding Ga^{3+} to the Cu site. Figure 2 shows that compounds with $x \leq 0.13$ and $y \geq 0.02$ are indeed superconducting with $T_c=20$ K, and surprisingly their MF in-

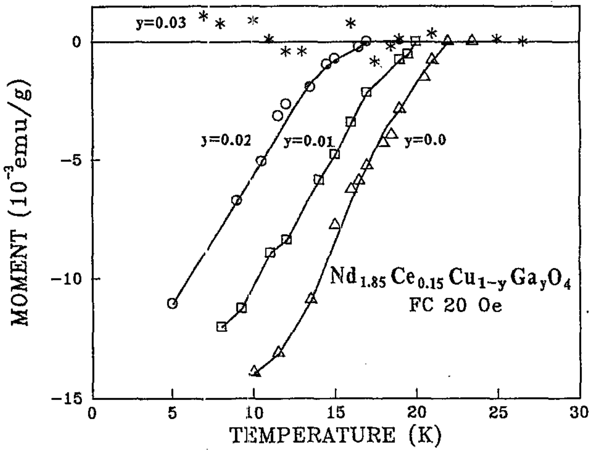

FIG. 1. Temperature dependence of the Meissner signal at 20 Oe for $Nd_{1.85}Ce_{0.15}Cu_{1-y}Ga_yO_4$.

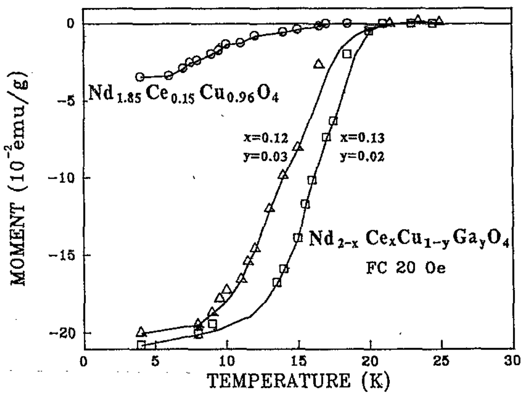

FIG. 2. Temperature dependence of the Meissner signal at 20 Oe for $Nd_{2-x}Ce_xCu_{1-y}Ga_yO_4$ ($x+y=0.15$) and for Nd-Ce-Cu-O with copper deficiency.

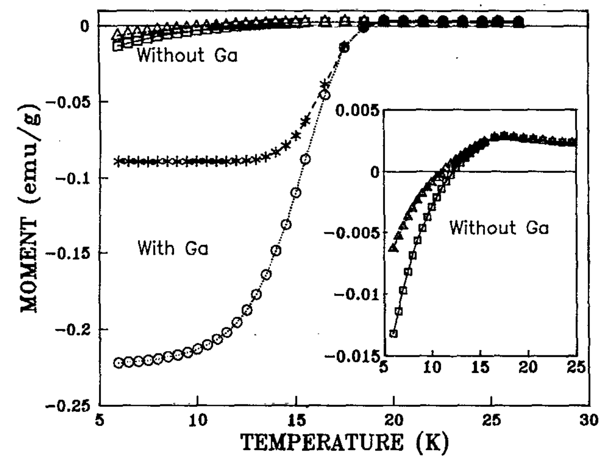

FIG. 3. ZFC and FC magnetization curves for Nd-Ce-Cu-O (without Ga) and Nd-Ce-Cu-Ga-O (with Ga) at 50 Oe. The inset shows the data for Nd-Ce-Cu-O in an extended scale.

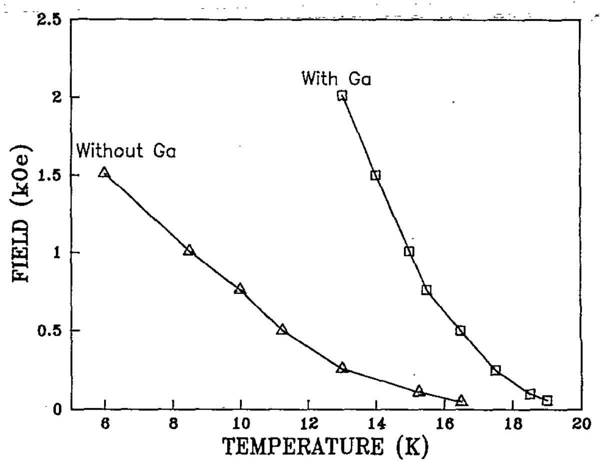

FIG. 4. The irreversible temperature T_{irr} as a function of the applied field for Nd-Ce-Cu-O and Nd-Ce-Cu-Ga-O (with Ga).

creases by a factor of 4. From the magnitude of the diamagnetic moment and assuming that the samples have a density of ~7 gr/cm^3, we deduce (without correcting for the demagnetization factor) an MF at 4.2 K of approximately 80% for the samples with $x+y=0.15$. This value is remarkable for a ceramic material and much higher than the MF of 25% obtained in undoped single crystals.[5]

Using the standard four-point method we measured the electrical resistivity of $Nd_{1.85}Ce_{0.15}CuO_4$ and $Nd_{1.88}Ce_{0.12}Cu_{0.97}Ga_{0.03}O_{4-\delta}$. Both samples were measured together under the same conditions. Their resistivity exhibits semiconductor behavior: Their resistance ratios for the normal-state resistivity $R(300\text{ K})/R(25\text{ K})$ are 1.3 and 0.9, respectively. For Nd-Ce-Cu-O the superconducting transition is broadened so that zero resistance is never observed even down to 4.2 K. On the other hand, for Nd-Ce-Cu-Ga-O the superconducting transition is much sharper and zero resistance (dc voltage drop less than 1 nV over ~3-mm length) is reached at 12 K. This is consistent with the large MF observed for Nd-Ce-Cu-Ga-O (Fig. 2).

We also investigated the reversible and irreversible magnetization properties of Nd-Ce-Cu-O and Nd-Ce-Cu-Ga-O. Examples of the low-temperature magnetization in both FC and ZFC modes with a magnetic field of 50 Oe are shown in Fig. 3. Note once again the significant increases in the shielding curve and the MF for Nd-Ce-Cu-Ga-O. The inset shows the ZFC and FC obtained for Nd-Ce-Cu-O on an extended scale. The magnetic irreversibility which characterizes all type-II superconductors is exhibited here too. Above a field-dependent temperature, T_{irr}, where FC and ZFC branches coincide, is the reversible region. The field dependence of T_{irr} is shown in the form of a field-temperature phase diagram in Fig. 4. From the linearity of $\log_{10}(1-t)$ vs $\log_{10}H$ plot, where $t=T_{irr}(H)/T_c$, we obtain a slope of 0.60(3) ($T_c=19.5$ K) and 0.55(5) ($T_c=17.5$ K) for Nd-Ce-Cu-Ga-O and Nd-Ce-Cu-O, respectively. Note that for both samples T_{irr} scales with the applied field as $H^{0.6}$, in good agreement with the $\frac{2}{3}$ power law found in La-Sr-Cu-O.[10] The irreversibility line for Nd-Ce-Cu-O is shifted to a relatively lower temperature. For example, for $H=1.5$ kOe the irreversibility temperature for Nd-Ce-Cu-Ga-O is 8 K higher (see Fig. 4). This implies that the activation energy needed for a vortex to overcome the pinning barrier is lower for Nd-Ce-Cu-O than for Nd-Ce-Cu-Ga-O. There is a strong correlation between the exact temperature dependence of the irreversibility line and the MF in high-T_c superconductors. According to the picture proposed in the framework of the trapped flux model,[11,12] the MF at low temperatures reflects the amount of flux which is trapped at the irreversibility line during the cooling process, and it is well known that more flux will be trapped if trapping occurs at lower temperatures. In Nd-Ce-Cu-O the small MF is not a result of extensive flux pinning, since the shielding signal is small too. The small diamagnetic signal found in Nd-Ce-Cu-O is probably connected with inhomogeneities in oxygen distribution and vacancies. The oxygen-poor regions are much smaller than the oxygen-rich regions.

Figure 5 illustrates typical magnetic hysteresis curves at 4.2 K for Nd-Ce-Cu-O and Nd-Ce-Cu-Ga-O. Note that

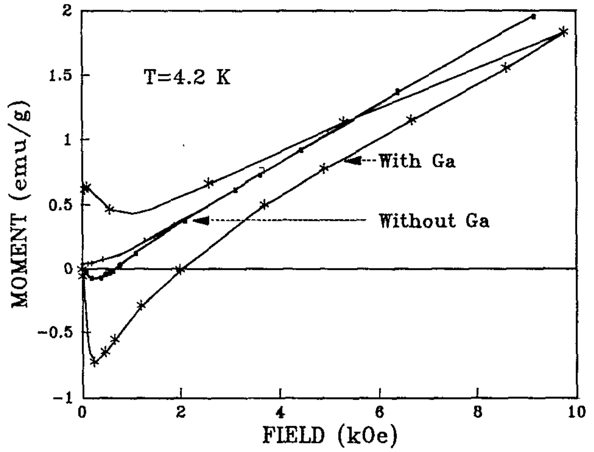

FIG. 5. Magnetic hysteresis curves at 4.2 K for Nd-Ce-Cu-O (without Ga) and Nd-Ce-Cu-Ga-O (with Ga).

these curves already show a significant reversible region at a relatively low applied field, $(H_r) = 1.5$ and 9.5 kOe for Nd-Ce-Cu-O and Nd-Ce-Cu-Ga-O, respectively. These fields are an order of magnitude smaller than those observed for Y-Ba-Cu-O (Refs. 11 and 13) and are consistent with the smaller J_c's (see below) which can be inferred from the Bean model. At 4.2 K, H_r matches the value obtained from the irreversibility line of the temperature-field phase diagram[14] shown in Fig. 4. Also note that due to the strong paramagnetic contribution of the Nd^{3+} ions, the magnetization values in Fig. 5 become positive at relatively low applied fields.

Values of the critical current density at 4.2 K were determined by using the Bean model, $J_c = 30\ M_{\text{rem}}/R$, where the remanent magnetization M_{rem} (in gauss) is taken from Fig. 5, and R $(= 10^{-4}$ cm) is a typical particle length scale. Note that for a ceramic sample the typical length scale is that of the grains, not the geometrical length scale, reflecting the break of intergrain links in the high-field limit of the hysteresis loop. This expression yields J_c of 1.3×10^5 A/cm^2 for Nd-Ce-Cu-Ga-O. The ratio between M_{rem} values obtained for Nd-Ce-Cu-Ga-O and Nd-Ce-Cu-O is approximatley 14:1 (see Fig. 5). This implies that for Nd-Ce-Cu-O J_c, is an order of magnitude lower.

We have also measured the temperature dependence of the remanent magnetization M_{rem} for Nd-Ce-Cu-O. M_{rem} was obtained by field cooling to 5 K, and then turning off the applied field. The temperature dependence of M_{rem} curves measured at different H always lie below the curves which represent the difference between ZFC-FC values measured under the same H, and have a minimum at 13.5 K regardless of the applied fields used in the FC process. This deviation, which is related to flux creep, will be discussed elsewhere.

In conclusion, we provide for the first time a new electron-doped system in which Ga is substituted for Cu and the additional electron comes from the Cu-O planes. Ga^{3+} has the same effect on T_c as Ce^{4+}; the two are interchangeable. We show here for the Nd-Ce-Cu-O system that ceramic specimens with Ce content between $x = 0.12$–0.14 (which are not superconducting) become superconducting by the addition of Ga, and superconducting properties such as MF and J_c are improved significantly compared to $Nd_{1.85}Ce_{0.15}CuO_4$. Magnetization measurements as a function of temperature and/or applied field reveal a reversibility region at modest fields even at low temperatures. It would be edifying to discover the source of improvement of the superconducting properties achieved in Nd-Ce-Cu-Ga-O. Further work on similar cation-doped systems is now being performed to resolve whether this intriguing result is an intrinsic property of the n-type superconductors, or whether the magnetic measurements reported here only reflect a systematic change in the intergranular coupling achieved by the addition of Ga. Finally it is worth mentioning that in both La-Sr-Cu-O and Nd-Ce-Cu-O systems, the highest T_c is obtained when $x = 0.15$, which means that the nature of the charge carriers in the n-type and p-type superconductors is similar. This observation might serve as a guideline for theories of electron-pairing that attempt to describe all copper oxide superconductivity by a single mechanism.

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