Substitution of Ga for Cu in $R Ba_2Cu_{3-x}Ga_xO_{7-y}$ systems (R = Yb, Er, Y, Dy, Gd, Eu, and Nd)

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We have investigated the effect of Ga doping on the structure, oxygen content, and superconducting transition temperature T_c of $R Ba_2Cu_{3-x}Ga_xO_{7-y}$ (R = Yb, Er, Y, Dy, Gd, Eu, and Nd, and x = 0, 0.05, 0.1, 0.15, 0.2, and 0.3). We observed that in these systems, the superconducting T_c, the melting point, and the critical Ga concentration $x_{O\text{-}T}$ at which the samples undergo an orthorhombic-tetragonal transition, are all rare-earth-ion size dependent. The results suggest that the decrease of density of states $N(E_F)$ and/or the localization of the carriers, which is likely related to a Mott transition due to Ga substitution, are the possible origins for the suppression of superconductivity and the observed metal-semiconductor transition.

I. INTRODUCTION

The effect of the metallic elements M (M=V, Fe, Co, Ga, Al, Ni, and Zn) substitution for copper of the $YBa_2Cu_3O_{7-y}$ has been widely investigated.[1-13] It was found in general that the nominally trivalent magnetic (Fe and Co) and nonmagnetic (Ga and Al) dopants substitute on the Cu(1) sites in the Cu-O chains, whereas nominally divalent (Ni and Zn) dopants go onto the Cu(2) sites in the Cu-O_2 planes.[2,6,8,13] However, there are also existing data to indicate that at higher concentrations Fe goes to both Cu(1) and Cu(2) sites,[6] and that Zn does not substitute appreciably into the Cu(2) site.[11,12] All the substitutions result in the reduction of T_c, but with very different rates. The most pronounced effects are the 13 K/atom % for Zn substitution on the plane site,[1,10] and the 5 K/atom % for Co substitution on the chain site.[6,10]

The substitution of Cu ions by Ga in the $YBa_2Cu_3O_{7-y}$, with a closed-shell ($3d^{10}$) electronic state, has been studied in detail.[1-4,10-13] Neutron-diffraction[2] and NMR[11-13] studies suggest the preferential occupation of Ga is the Cu(1) sites and the substitution promotes the presence of an orthorhombic-tetragonal (O-T) structure transition.[1-4,10-13] Doping with Ga leads to a decrease in T_c, and yields significant deviations from the linear "metal-like" temperature dependence of the normal-state resistivity[1-4] at high Ga concentration.

On the other hand, our recent investigation of the superconducting behavior of the $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ (R=Yb, Er, Y, Dy, Gd, Eu, Sm, and Nd) systems has demonstrated that the superconducting transition temperature T_c decreases monotonically with increasing Pr concentration x, and at a constant Pr concentration, T_c decreases approximately linearly with increasing radius of the R ions.[14-17] Meanwhile, the magnetic ordering temperatures T_N of Pr ions in these systems (x = 0.5–1.0) were observed to decrease monotonically with increasing R concentration. At a constant x, T_N is R-ion size dependent.[18] These results were qualitatively interpreted in terms of the hybridization between the local states of Pr ion and the valence-band states of the CuO_2 planes.[14-18] A similar rare-earth-ion size effect was observed in the Ga-doped[19] [on the Cu(1) sites] $R Ba_2Cu_{3-x}Ga_xO_{7-y}$ systems. In order to gain more insight into the mechanism responsible for the observed results, we have carried out detailed studies of the Ga-substituted $R Ba_2Cu_{3-x}Ga_xO_{7-y}$ systems (R = Yb, Er, Y, Dy, Gd, Eu, and Nd with x = 0–0.3) regard the problems of phase segregation, the change of oxygen content, and the superconducting transition.

II. EXPERIMENTAL

All the samples of $R Ba_2Cu_{3-x}Ga_xO_{7-y}$ (R = Yb, Er, Y, Dy, Gd, Eu, and Nd) with nominal composition x = 0, 0.05, 0.1, 0.15, 0.2, and 0.3 were synthesized using solid-state reaction method. Stoichiometric powders of high purity ($\geq$99.99%) R_2O_3, $BaCO_3$, CuO, and Ga_2O_3 were well mixed, ground, calcined in air at 910 °C for 24 h. The resultant samples were reground and pressed into regular bars and sintered at 930 °C for 50 h in flowing oxygen, cooled in 5 h to 680 °C, maintained for 10 h, then cooled in 3 h to 400 °C, maintained for 10 h, then slowly cooled to room temperature. These samples were then treated again with the same procedure. Using the above processes, we obtained hard, dense pellets which exhibit good intergranular conductivity and yields reproducible results.[20]

Inductively coupled plasma-atomic emission spectroscopy (ICP/AES) was utilized to determine the stoichiometric ratio of metal ions after the last sintering process. The results showed that all the samples keep the initial stoichiometry within the experimental error (±5%). X-ray diffraction (XRD) data at room temperature were taken for all samples. Differential temperature analysis (DTA) and thermogravimetric analysis (TGA) were carried out using a MAC-Science thermal analysis system for studying the phase formation and estimating the variation of oxygen content in the samples. Oxygen content of the annealed samples was determined by the iodometric analysis[21] with an accuracy of ±0.03. Resistivity measurements were carried out using a standard four-probe method. The T_c values, determined by the magnetization measurements using a Quantum Design

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SQUID magnetometer, are consistent with those obtained from electrical measurements.

III. RESULTS AND DISCUSSION

X-ray powder diffraction analysis showed that all the samples are essentially single-123 phase within experimental error.[19] All samples, including those that possibly exhibit phase separation based on DTA results, showed the trend towards a tetragonal symmetry, indicating the successful substitution of gallium ion. As Ga content x increased to a critical value, $x_{O\text{-}T}$, the structural transition from orthorhombic-to-tetragonal symmetry (O-T) took place. It is noted that the $x_{O\text{-}T}$ shifts to lower value with increasing radius of the rare-earth ions (Table I). This result strongly suggests that the orthorhombic distortion (oxygen ordering) in the Cu-O chain plane depends on the R ions, although the R ions are located far from the Cu-O chain.

The DTA curves of $R\,Ba_2Cu_{3-x}Ga_xO_{7-y}$ systems with $0 \le x \le 0.3$ are shown in Fig. 1 for R = Nd (a), Eu (b), Dy (c), and Er (d). The sharp peaks in DTA curves are related to the melting temperatures of the compounds and can be used to identify the phase purity of the compounds. The single peak in DTA curve observed in the samples with R = Nd, Eu, and Dy, whose ion radii are relatively larger, indicates they are single phase [Figs. 1(a)–1(c)]. In contrast, multiphase samples are usually found, showing multimelting temperatures in DTA, in those systems with smaller ionic radius rare earth, e.g., R = Er and $x > 0.1$ [Fig. 1(d)], R = Y and $x > 0.15$, although XRD showed no impurity peaks. Figure 2 displays the DTA data of $R\,Ba_2Cu_{2.9}Ga_{0.1}O_{7-y}$ (R = Er, Y, Dy, Eu, and Nd) samples. Figure 3 summarizes the DTA peak positions of the system with various Ga contents x as a function of the ionic radius of R. It is clearly shown that at a constant Ga content x the melting point shifts to higher value with increasing R-ion radius. One can conclude that among these Ga-doped systems, $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ has the highest thermal stability and is less affected by the Ga doping.

The low solid solubility ($x < 0.15$) in $YBa_2Cu_{3-x}Ga_xO_{7-y}$ can be attributed to the incompatibility of the $YBa_2Cu_3O_{7-y}$ with $YGaO_3$ whose perovskite phase can only be synthesized under high pressure (45 kbar) and high temperature (1000 °C).[22] A similar requirement is also appropriate for R = Eu, Gd-Lu, which also have a relatively small R-ion radius. On the other hand, other $RGaO_3$ with R = La, Pr, Nd, and Sm can be synthesized at 1 atm. These results are consistent with our previous work on $PrBa_2Cu_{3-x}Ga_xO_{7-y}$ which shows a single phase from x = 0–0.9.[20]

We also measured the oxygen content using the standard iodometric titration technique. Figure 4 shows the oxygen content $(7-y)$ vs Ga concentration x for various $R\,Ba_2Cu_{3-x}Ga_xO_{7-y}$ systems. We observed that (1) small Ga doping (x = 0.05) decreases oxygen content $(7-y)$; and as x increases, $(7-y)$ slightly increases for all $R\,Ba_2Cu_{3-x}Ga_xO_{7-y}$ samples; (2) R-ion size does not obviously affect oxygen content, although the $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ system has the lowest $(7-y)$ values among these systems.

Thermogravimetric analysis (TGA) is also utilized to estimate the effect of Ga doping on the oxygen content. Each specimen was heated up to 900 °C at a rate of 10 °C/min in vacuum or flowing argon to estimate the amount of oxygen removed from the sample and was heated under oxygen or air to estimate the amount of oxygen added to the samples. We observed qualitatively that, for each R, less weight loss for samples at higher x, implying that Ga doping is beneficial in keeping oxygen. The TGA results, which are similar to the TGA observations on Co-, Fe-, and Al-doped $YBa_2Cu_3O_{7-y}$,[5,6] are consistent with the titration data (only for Ga concentration, $x > 0.05$). This data, giving the fact that the amount of oxygen removed from the compound slightly decreases with increasing the dopant x, support that these trivalent ions (Al, Fe, Co, and Ga) are residing in the chain sites and are in agreement with x-ray data.[6,19]

Figure 5 shows the ZFC $M(T)$ data for R = Y (a), Dy (b), Nd (c), and of both ZFC and FC for R = Eu (d) at different Ga content x. The magnetically determined $T_{c,\mathrm{mag}}$ are estimated by linearly extrapolating the increasing (near T_c) diamagnetic $M(T)$ curve to M = 0, and the values are in good agreement with those deduced from resistivity measurements.[19] Since a small field of 1×10^{-3} Tesla was applied for measuring $M(T)$, the ergodic limit points separating reversible and irreversible trajectories were close to M = 0 [Fig. 5(d)]. As can be seen in Fig. 5, the $T_{c,\mathrm{mag}}$ decreases with increasing Ga content x. Paramagnetic behavior for R = Er, Dy, and Nd is often seen in the $M(T)$ curves at higher Ga concentration where superconductivity is weakened [e.g., Figs. 5(b) and 5(c)]. The $M(T)$ curves were plotted in Fig. 6 to compare the effect on $T_{c,\mathrm{mag}}$ for the same percentage of Ga substitution (x = 0.1) in different systems. At the same Ga

TABLE I. The structures of $R\,Ba_2Cu_{3-x}Ga_xO_{7-y}$ systems at various x ("O" orthorhombic, "T" tetragonal).

	r_{ion} (pm)	x = 0	x = 0.05	x = 0.1	x = 0.15	x = 0.2	x = 0.3
$YbBa_2Cu_{3-x}Ga_xO_{7-y}$	85.8	O	O	O	O	O	O
$ErBa_2Cu_{3-x}Ga_xO_{7-y}$	88.1	O	O	O	O →	T	T
$YBa_2Cu_{3-x}Ga_xO_{7-y}$	89.3	O	O	O →	T	T	T
$DyBa_2Cu_{3-x}Ga_xO_{7-y}$	90.8	O	O →	T	T	T	T
$EuBa_2Cu_{3-x}Ga_xO_{7-y}$	95.0	O →	T	T	T	T	T
$NdBa_2Cu_{3-x}Ga_xO_{7-y}$	99.5	O →	T	T	T	T	T

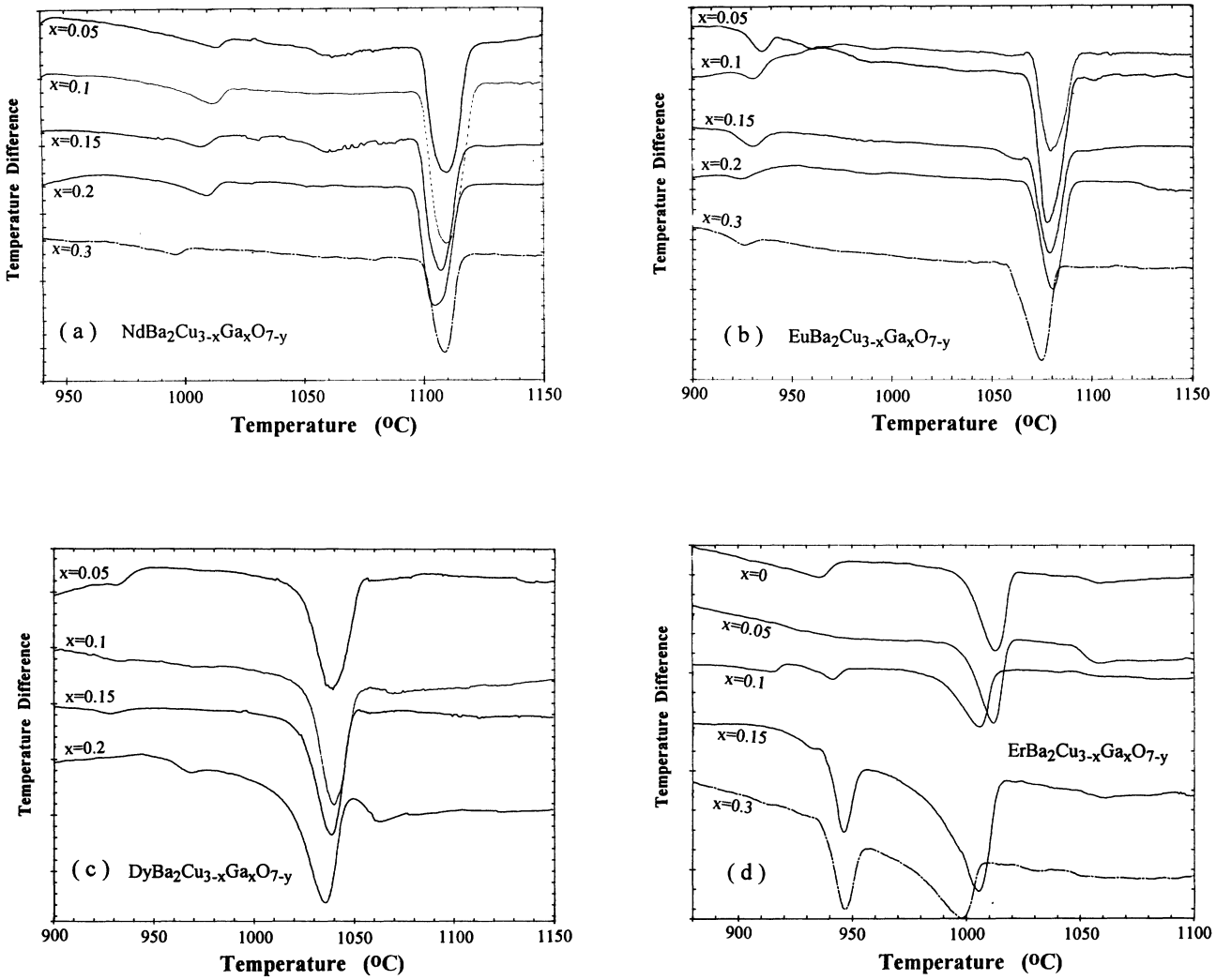

FIG. 1. DTA curves of $R Ba_2Cu_{3-x}Ga_xO_{7-y}$ for R = Nd (a), Eu (b), Dy (c), and Er (d).

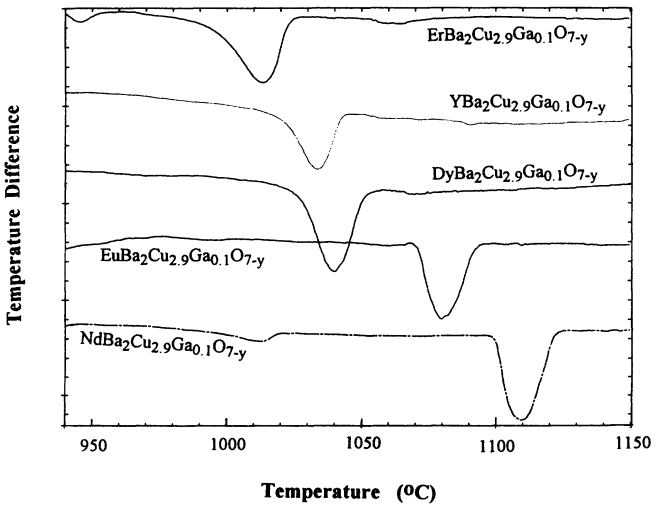

FIG. 2. DTA curves of $R Ba_2Cu_{2.9}Ga_{0.1}O_{7-y}$ (R = Yb, Er, Y, Dy, Gd, Eu, and Nd).

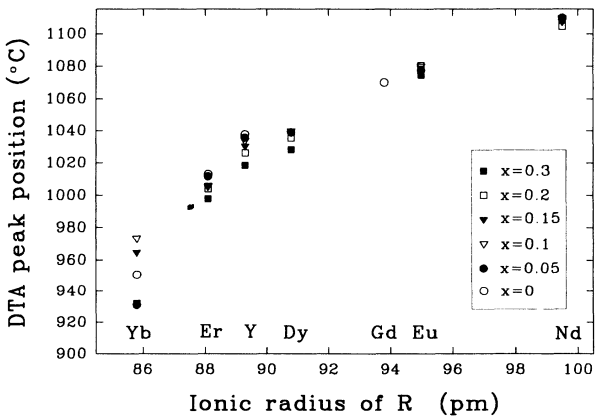

FIG. 3. DTA peak positions of $R Ba_2Cu_{3-x}Ga_xO_{7-y}$ systems as a function of the ionic radius of R at various Ga content x.

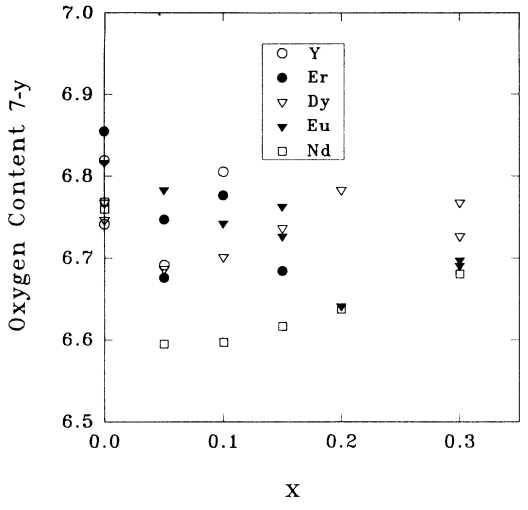

FIG. 4. Oxygen content $(7-y)$ vs Ga concentration x for various $R\mathrm{Ba_2Cu_{3-x}Ga_xO_{7-y}}$ systems.

concentration, $x=0.1$, for instance, the suppression of superconductivity is remarkable for $\mathrm{NdBa_2Cu_{2.9}Ga_{0.1}O_{7-y}}$, and almost undetectable for $\mathrm{YbBa_2Cu_{2.9}Ga_{0.1}O_{7-y}}$. The dependences of $T_{c,\mathrm{mag}}$ on Ga content are displayed in Fig. 7. $T_{c,\mathrm{mag}}$ decreases approximately linearly with Ga substitution for all the studied $R\mathrm{Ba_2Cu_{3-x}Ga_xO_{7-y}}$ systems (R=Yb, Er, Y, Dy, Gd, Eu, and Nd). Consistent results are also obtained from the resistivity measurements as shown in Fig. 8 which displays both $T_{c,\mathrm{mag}}$ and $T_{c,\mathrm{mid}}$ (defined as the midpoint of the resistivity transition), as a function of R^{3+}-ion radius. These data show that T_c decreases nearly linearly with increasing R^{3+}-ion radius when x keeps constant. However, the T_c suppression rates, dT_c/dx, are quite different for different $R\mathrm{Ba_2Cu_{3-x}Ga_xO_{7-y}}$ systems. For example, at the same Ga concentration, $x=0.15$, $T_{c,\mathrm{mag}}=20$ K for R=Nd and 89 K for R=Yb, respectively (Fig. 7). This indicates that Ga is extremely effective in suppressing the superconductivity for R=Nd but less effective for R=Yb.

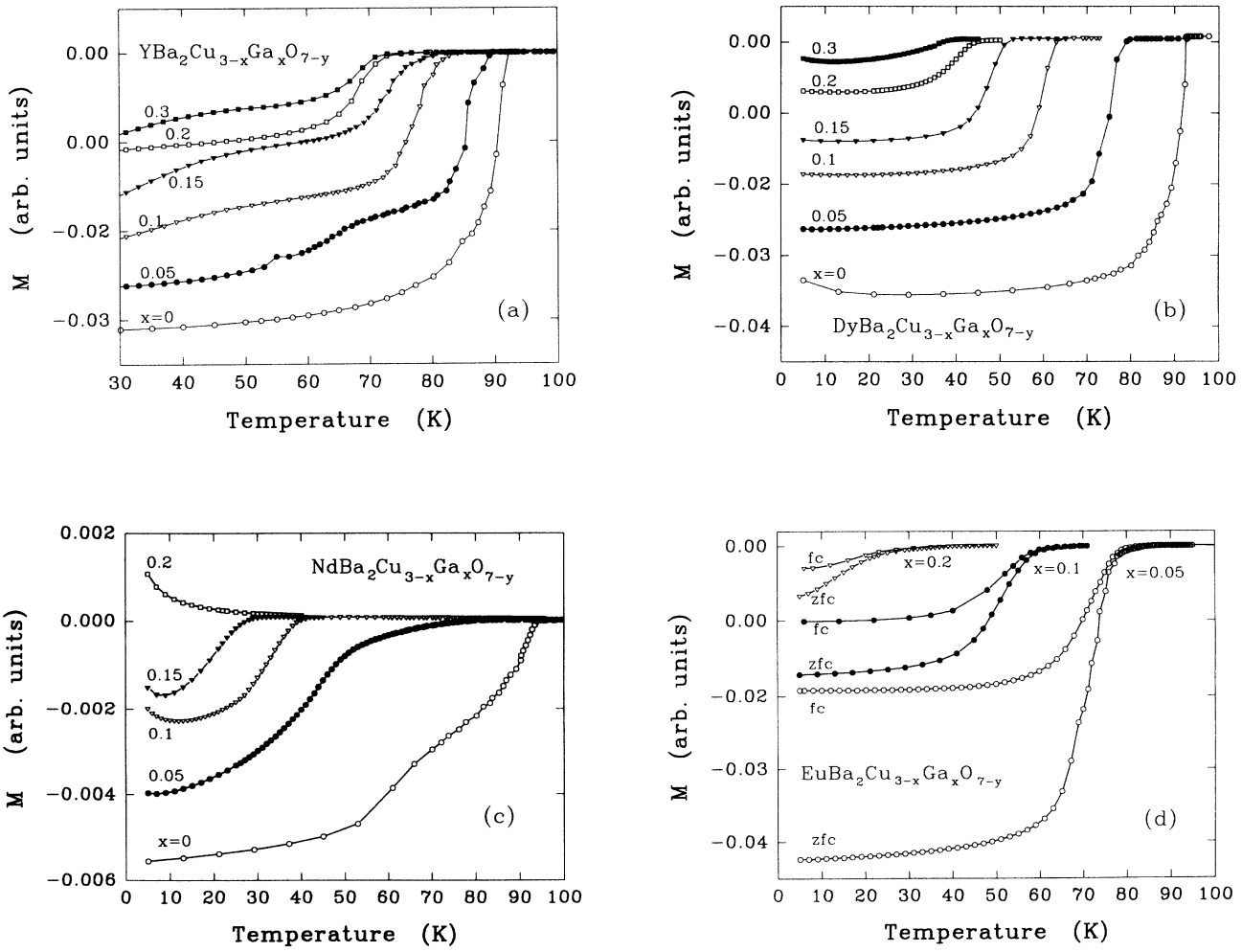

FIG. 5. Magnetization vs temperature for $R\mathrm{Ba_2Cu_{3-x}Ga_xO_{7-y}}$, R=Y (a), Dy (b), Nd (c) [with zero-field cooling (ZFC)], and Eu (d) [with both ZFC and FC (field cooling)].

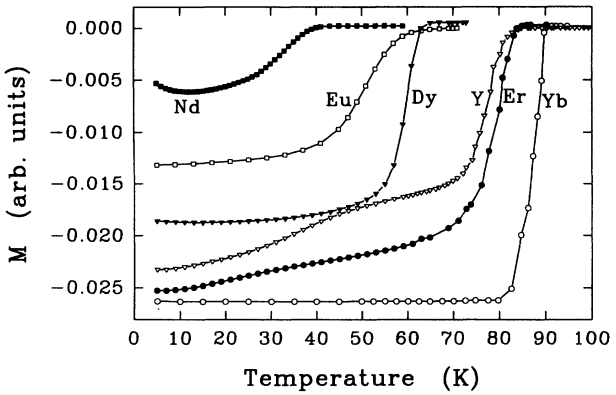

FIG. 6. Magnetization vs temperature for $R Ba_2Cu_{2.9}Ga_{0.1}O_{7-y}$ (R = Yb, Er, Y, Dy, Gd, Eu, and Nd).

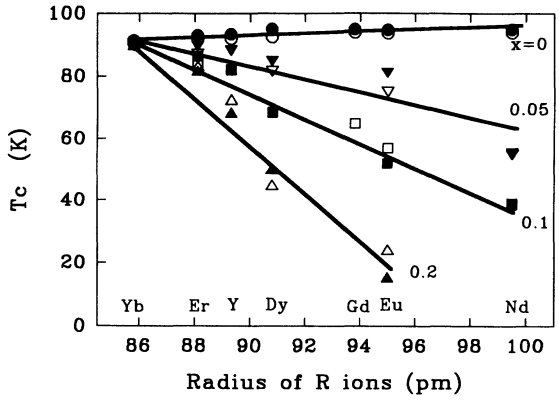

FIG. 8. $T_{c,mid}$ (solid symbols) and $T_{c,mag}$ (open symbols) as a function of R^{3+} ion radius in $R Ba_2Cu_{3-x}Ga_xO_{7-y}$ systems (R = Yb, Er, Y, Dy, Gd, Eu, and Nd) at various Ga content x.

To avoid complication due to the presence of multiple phases in the higher Ga concentration compounds (especially for those with R = Yb, Er, and Y), we compare the T_c suppressing rate of the doped compounds near $x = 0$. The experimental data of $[dT_{c,mag}/d(x/3)]_{x=0}$ are -0.1, -1.4, -2.6, -4.3, -7.8, -11.4, and -15.5 K/at. %, for R = Yb, Er, Y, Dy, Gd, Eu, and Nd, respectively.

The reduction of magnetic shielding fractions with increasing Ga concentration, x [Figs 5(a)–5(c)] gives an evidence for the reduction of fraction of superconducting materials or phase separation in samples with higher Ga concentration.

In an earlier paper[19] we showed that the normal-state resistivity increases dramatically in $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ with $x > 0.15$ and in $EuBa_2Cu_{3-x}Ga_xO_{7-y}$ with $x > 0.2$, indicating that the semiconducting behavior accompanies the destruction of superconductivity. Nevertheless, we found no direct correlation between this metal-semiconductor transition and the O-T structural transition.[19] We also do not find any direct correlation between T_c and the orthorhombic distortion (see Table I and Fig. 7). For example, the structure of $ErBa_2Cu_{2.8}Ga_{0.2}O_{7-y}$ becomes tetragonal (Table I) while its $T_{c,mid}$ remains as high as 81.5 K (see Fig. 8). These observations suggest that the origin of the T_c depression due to Ga substitution is not directly related to the O-T transition induced by Ga doping. The titration and TGA data indicate that the oxygen concentration is not substantially reduced by introducing Ga (Fig. 4). Therefore, the T_c suppression can neither be attributed to the change of oxygen stoichiometry by Ga. Due to the nonmagnetic nature of the Ga ion, the magnetic pair-breaking mechanism, as suggested for the Pr-doped RPrBCO systems,[23] is also unlikely to be responsible for the T_c depression.

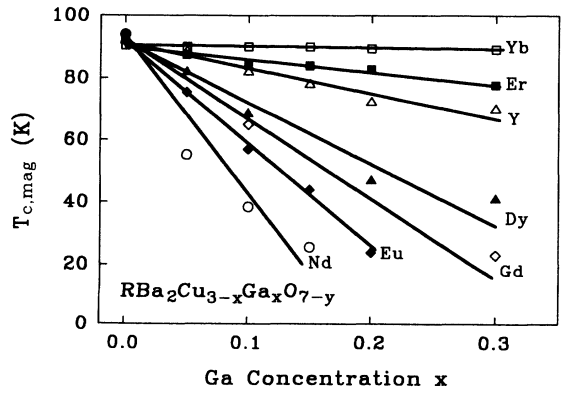

FIG. 7. $T_{c,mag}$ as a function of Ga concentration for $R Ba_2Cu_{3-x}Ga_xO_{7-y}$ systems R = Yb, Er, Y, Dy, Gd, Eu, and Nd).

On the basis of the observed results, we propose that the decrease in T_c by Ga substitution is likely due to a disordering effect and/or a decrease in the carrier density. Ga ($3d^{10}4s^24p^1$) atoms have completely filled $3d$ levels and no magnetic moment. The filled d orbital of Ga at the Cu(1) site diminishes the overlapping of the Ga d orbitals with the oxygen p orbitals (the radius of Ga^{3+} is only 0.62 Å). This result will severely harm the charge-transfer process, and thus reduce the effective carrier concentration in the Cu-O_2 planes leading to the decrease in the density of states at Fermi level $N(E_F)$. The trivalent Ga will not change the charge balance within the Cu-O chain but may significantly cause disorder and disturb the alignment of Cu ($3d_{x^2-y^2}$) and O ($2p_\sigma$) orbitals, resulting in the localization of mobile holes. This localization effect due to Ga doping can then account for the metal-insulator transition and simultaneously the destruction of superconductivity.[24]

The rare-earth-ion size effect on T_c due to Ga substitution in $R Ba_2Cu_{3-x}Ga_xO_{7-y}$ systems is not easy to understand, since the R ions locate far from the Cu(1) site occupied by Ga ions.

One possible interpretation is to treat the metal-semiconductor transition by Ga doping in terms of Mott transition.[25] Mott[26] supposed that impurities form a sublattice having a much larger period b than the host lattice. Bands formed by impurities are no more than half filled, thus the conductivity of impurity electrons would be of a metallic nature. However, the above conclusion leaves certain difficulty, since the single-electron approximation breaks down in the case of a narrow band. Mott

estimated the interaction energy U of two electrons of opposite spins located on the same site and found $U=e^2/a$, where a is the characteristic size of the electron wave functions. In the narrow-band case the bandwidth V_b is much less than U. Suppose b is infinitely large. Then the electron energy equals either E_0 or E_0+U, depending on whether or not there is another electron on the site, where E_0 is the electron energy corresponding to the state of only one electron on the impurity site. At a finite value of b, both levels (E_0 and E_0+U) spread into bands whose width is of order $I(b)$. The bandwidth $I(b)$ increases with increasing number of impurities ($1/b$). The number of states in each of these bands equals the number of lattice (impurity) sites. The lower band will become filled and the upper band empty. Thus, if the number of impurities is small, $I(b)\ll U$ our material is insulating. With decreasing b (increasing the number of impurities) a certain b_{cr} (critical point of b) is reached at which two bands become to overlap and the width of the forbidden gap vanishes, then the system goes into a metallic state (Mott transition).[26]

For most of superconducting copper oxides it seems to be true that doping a parent compound which has an insulating ground state, with suitable dopants leads to a conducting normal state and superconductivity at elevated temperature.[25] In our case we consider the compound $R\,Ba_2Cu_{3-x}Ga_xO_{7-y}$ with high Ga concentration, x, as a parent compound which is insulating and not superconducting. As increasing the copper concentrations it goes to a conducting normal state and superconducting (Mott transition).

The rare-earth-ion size effect on T_c observed in this work could then be ascribed to the ion size effect on the b_{cr} in Mott transition. This means that the value of U or explicit form of $I(b)$, or both of them are rare-earth-ion size dependent.[26]

ACKNOWLEDGMENTS

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