Superconducting and semiconducting properties of the $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$ system

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X-ray-diffraction, electrical resistivity, and dc susceptibility measurements have been used to investigate the $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$ system for different values of x in the range $0 \le x \le 1$. There were no impurity phases detected from the diffraction patterns, which indicates that the Ga atoms are incorporated in the crystalline structure. The lattice parameter c of the orthorhombic cell decreases with increasing Ga concentration since the size of the Ga^{3+} ion is smaller than that of the Ca^{2+} ion it replaces. Samples with $x \le 0.6$ are metallic and have a superconducting transition with a temperature of the midpoint of the transition that is independent of x for $0 \le x \le 0.6$. There is a semiconducting behavior for $0.7 \le x \le 1.0$. A thermally activated conduction process takes place in the low-temperature region of the samples with $0.7 \le x \le 0.9$. In $Bi_2Sr_2GaCu_2O_y$ for which $x = 1.0$ the thermally activated conduction process exists only for temperatures above 170 K. For lower temperatures the conduction is governed by a three-dimensional variable-range hopping process. The most probable jump distance and the average hopping energy at 10 K are 27 Å and 1 meV, respectively.

I. INTRODUCTION

The superconducting bismuth cuprates of the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+1}$ ($n = 1,2,3$) are characterized by complex layered structures, which differ in the stacking sequence of perovskite and rocksalt layers along the crystallographic c axis and a superconducting transition temperature (T_c), which increases with n from 10 to 110 K. There has been considerable interest in studying the properties of the second member of the series ($n = 2$) in which the divalent calcium ion is replaced by a trivalent rare-earth or yttrium ions.[1-3] Such a substitution is found to change the carrier concentration continuously while maintaining the crystal structure. The electrical properties also change drastically, and with a high concentration of yttrium or rare-earth elements, an insulating rather than a superconducting behavior is observed.

Almost all the substitutions at the divalent calcium-ion site have been made with the trivalent magnetic elements. Interestingly, Ummat, Nkum, and Datars[4] recently reported that Ga, which is also a trivalent element but nonmagnetic, can be substituted for Ca in the $Bi_{1.4}Pb_{0.6}Sr_2Ca_{2-x}Ga_xCu_3O_y$ system. It was concluded from the identification of CaO by x-ray diffraction that Ga replaces Ca in the compound. The high-T_c phase with a T_c of 104–107 K for this compound existed for $x \le 0.3$. The volume fraction of the 2:2:1:2 phase with a T_c between 65 and 70 K was largest for $x = 0.5$ and dropped to a very small value for $x = 1.0$ and remained small up to $x = 2.0$. It is interesting to extend this work and study the effect of the substitution of Ga in the compound without lead and which does not contain the 2:2:2:3 phase. Thus, in this work, a systematic study of the effect of Ga substitution for Ca in $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$ is reported. The compounds are metallic superconductors for $x \le 0.6$ and have semiconductorlike behavior for $0.7 \le x \le 1.0$. There is a variable-range hopping associated with semiconducting properties[5,6] in the sample without Ca.

II. EXPERIMENTAL DETAILS

Samples of the nominal composition $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$ with $0 \le x \le 1.0$ were prepared by the conventional solid-state reaction method. High-purity (99.999%) powders of Bi_2O_3, $SrCO_3$, $CaCO_3$, Ga_2O_3, and CuO were mixed in the appropriate amounts and ground well in an agate mortar. Samples with nine different values of x were prepared. The mixtures were calcined at 800 °C for 12 h and cooled with the furnace turned off. The resulting mixtures were ground well and pressed into pellets of 9 mm diameter and 1.1 mm thick under a pressure of 4 tons/cm^2. The pellets were sintered at 845 °C for 72 h with one intermediate pressing. The samples were then cooled with the furnace turned off.

The phase identification of the samples was carried out by recording x-ray-diffraction patterns in the 2θ range 10°–50° at room temperature with a Nicolet powder diffractometer using Cu $K\alpha$ radiation. The resistivity measurements were made in zero magnetic field with the standard four-probe technique on rectangularly shaped samples. Contacts were made with silver paste and annealed at 600 °C for 20 min. The contact resistance was less than 2 Ω. The samples were mounted on a probe with double jackets. He gas in the sample space facilitated good thermal equilibrium and avoided moisture condensation. Current of about 1 mA was usually used for the metallic samples, whereas for the semiconducting samples current ~50 μA was used to avoid Joule heating. The temperature was monitored with carbon glass and platinum resistance thermometers. The dc susceptibility measurements were made with a Quantum Design superconducting quantum interference device magnetometer in an applied magnetic field of 25 G.

III. RESULTS AND DISCUSSIONS

The range of composition $0 \leq x \leq 1.0$ is explored. No impurity phases are detected from the x-ray pattern of the samples even for the sample with $x=1.0$. This indicates that the Ga^{3+} ions are incorporated into the crystalline structure. Figure 1 shows the x-ray-diffraction patterns of the $Bi_2Sr_2CaCu_2O_y$ ($x=0$) and $Bi_2Sr_2GaCu_2O_y$ ($x=1.0$) samples. The reflections of all the samples are indexed according to the orthorhombic type of unit cell. The lattice parameters of the $Bi_2Sr_2GaCu_2O_y$ sample are $a=5.43$ Å, $b=5.39$ Å, and $c=24.48$ Å. The values of a and b are almost the same for the whole range of x, while the c parameter decreases with increasing Ga concentration. The lattice parameters of $Bi_2Sr_2CaCu_2O_y$ are $a=5.41$ Å, $b=5.38$ Å, and $c=30.68$ Å. The decrease in c with increasing Ga concentration results from the smaller size of the Ga^{3+} ion (0.62 Å) compared with that of the Ca^{2+} ion (1.00 Å) it replaces. A similar variation in the lattice parameter c has been observed in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$.[7]

Figure 2 shows the temperature dependence of the electrical resistivity of the samples. Samples with $x \leq 0.5$ are superconducting and show metallic behavior ($\rho=\rho_0+\rho_1 T$) in the normal state with the resistivity going to zero below the transition. Figure 2(a) shows that the temperature at which the resistivity goes to zero ($T_c^{\rho=0}$) decreases gradually with the increase of gallium concentration (x), while the temperature of the onset of the superconductivity remains almost constant. The temperature of the midpoint of the transition [$T_c(50\%)$] does not change with x with a value of 76 ± 1 K for $0.1 \leq x \leq 0.5$. This value is 2 K lower than for the sample without Ga. It must be noted that all the resistivity measurements were made in zero magnetic field. The effect of the Earth's magnetic field on the measurements is negligible. Therefore the suppression of $T_c^{\rho=0}$ is not due to flux motion, but rather due to the substitution of Ga.

There is a superconducting transition in the sample with $x=0.6$, as shown in Fig. 2(b), but the resistivity does not go to zero even at 5 K. This indicates that not all the sample is superconducting for large x. As the gallium concentration increases beyond $x=0.6$, the samples show a semiconducting behavior. Samples with $x=0.7$ and 0.9 show metallic behavior in the high-temperature ($T>70$ K for $x=0.7$ and $T>88$ K for $x=0.9$) and a semiconducting behavior in the low-temperature region with the resistivity increasing as the temperature is decreased. A shallow minimum (ρ_{min}) separates these regions in these samples. The appearance of ρ_{min} has been

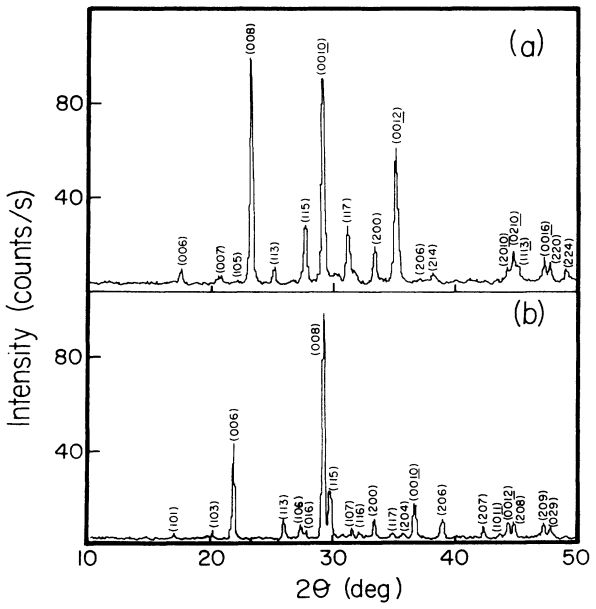

FIG. 1. X-ray-diffraction patterns of (a) $Bi_2Sr_2CaCu_2O_y$ and (b) $Bi_2Sr_2GaCu_2O_y$ recorded at room temperature.

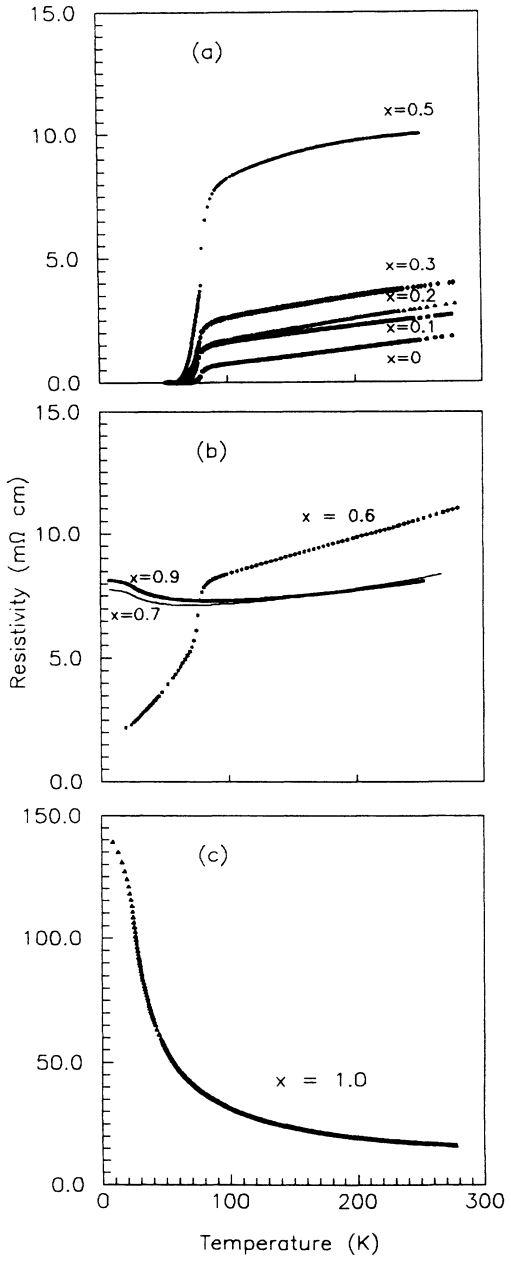

FIG. 2. Temperature dependence of the electrical resistivities of the $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$ samples. Sample with $x=1$ shows a semiconducting behavior.

observed in $Bi_2Sr_2Ca_{1-x}Y_2Cu_2O_y$ (Ref. 7) and $La_{2-x}Sr_xCuO$.[8] The $x=1.0$ sample shows a semiconducting behavior over the whole temperature range of measurement. The absence of a minimum in this sample suggests that ρ_{min} occurs at a relatively higher temperature (>300 K).

The resistivity-temperature behavior of the $x=0.7$ and 0.9 samples is similar to those observed in earlier polycrystalline samples of $YBa_2Cu_3O_y$. Such results were not confirmed with experiments done on single crystals. The behavior of the polycrystalline samples was found to result from oxygen deficiency.[9,10] A key parameter determining the properties of $YBa_2Cu_3O_y$ is its oxygen content. Metallic behavior and superconductivity are observed at high oxygen concentrations, while for low oxygen concentrations $YBa_2Cu_3O_y$ is a semiconductor. The 2:2:1:2 Bi-based system used in this study, however, has the advantage that the oxygen stoichiometry is stable and does not change much when the material is doped with other atoms. Another crucial advantage is that the electronic structure remains unchanged[11] during the superconductor-insulator transition. This makes the interpretation of the resistivity results in the region of the crossover less ambiguous. We therefore do not expect to have the problem that existed with polycrystalline $YBa_2Cu_3O_y$.

It has been observed that for disordered systems superconductivity disappears in the vicinity of the metal-insulator transition. For a pair wave function $\psi=\psi_0 e^{-i\phi}$, superconductivity may be destroyed by reducing the amplitude (ψ_0) or by destroying the phase coherence (ϕ). These two modes manifest themselves differently. In the case of phase breaking, T_c (onset of superconductivity) remains unchanged,[12,13] but the current-carrying capacity disappears and the transition width increases until the material has no region of zero resistivity. In the case of amplitude reduction, the temperature of onset of superconductivity remains well defined and decreases.[14,15] The data of Fig. 2(a) shows that T_c (onset of superconductivity) is almost constant, while the transition width increases with increasing Ga concentration. This suggests that the substitution of gallium suppresses superconductivity in $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$ by destroying the phase coherence.

The semiconducting behavior of the ρ-vs-T curve of $Bi_2Sr_2GaCu_2O_y$ ($x=1.0$) follows the equation

$$\rho=\rho_0\exp[(T_0/T)^n] , \quad (1)$$

where T_0 and n are constants. The value of the exponent n determines the nature of the conduction mechanism in the semiconducting sample. The resistivity at temperatures below 170 K can be described well with $n=\frac{1}{4}$, as shown in Fig. 3(a). A plot of $\ln\rho$ vs T^{-1} in the same temperature range is shown in Fig. 3(b), which shows that the resistivity data in this region cannot be fit to a simple thermally activated behavior. Thus there is strong evidence that the conduction in this region is governed by a phonon-assisted three-dimensional (3D) variable-range hopping (VRH).

Hopping conductivity in $Bi_2Sr_2GaCu_2O_y$ implies that the electronic states are localized at the Fermi level by disorder. The localization length can be deduced from the knowledge of T_0 and the density of states. The value of T_0 obtained from the fit is 7790 K. In the 3D VRH, the parameter T_0 depends on the localization length a and the density of states at the Fermi level $N(E_F)$ according to

$$T_0=16/[kN(E_F)a^3] , \quad (2)$$

where k is the Boltzmann's constant. The preexponential factor ρ_0 in Eq. (1) depends on T, a, and $N(E_F)$, but a definite theoretical approach is still a matter of dispute and various models have been proposed.[16–19] Among other simplifying assumptions, Mott considers $N(E_F)$ as energy independent and obtains[5,17]

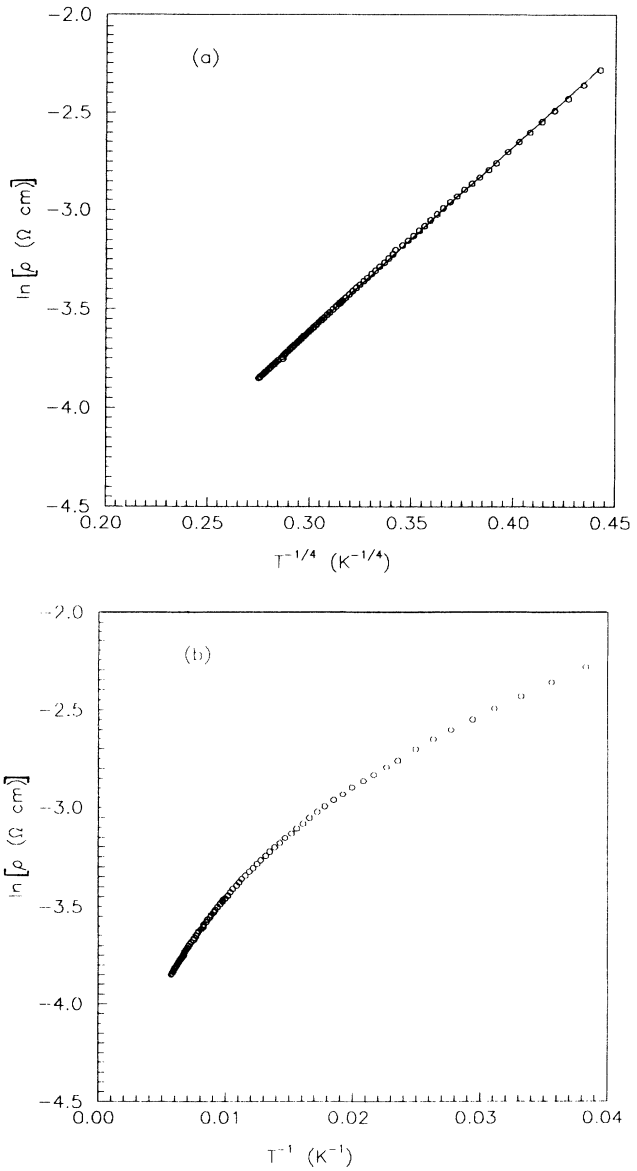

FIG. 3. Logarithm of the low-temperature ($T<170$ K) resistivity of $Bi_2Sr_2GaCu_2O_y$ (a) as a function of $T^{-1/4}$ and (b) as function of T^{-1}. The linear fit in (a) indicates variable-range hopping conduction in this region.

$$\rho_0(T)=(10/\nu e^2)[kT/aN(E_F)]^{1/2}\ , \tag{3}$$

where ν is the phonon frequency and e is the electronic charge. Ortuno and Pollak,[19] on the other hand, assume that $N(E_F)$ depends on energy exponentially and obtain

$$\rho_0(T)=(kT)^{0.42}/[1.7e^2\nu N(E_F)^{0.58}a^{0.74}]\ . \tag{4}$$

Thus, by assuming a value for ν, it is possible to evaluate a and $N(E_F)$ by using Eq. (2) with either Eq. (3) or (4).

With $\nu=10^{13}$ s^{-1}, Mott's model gives $a=4.3$ Å and $N(E_F)=3.0\times10^{23}$ eV^{-1} cm^{-3} at $T=10$ K. The Ortuno-Pollak model yields a value of a of 53 Å, which is unreasonable since it is larger than the order of magnitude of the largest cell dimension ($\sim$20 Å). The density of states obtained is 1.6×10^{20} eV^{-1}cm^{-3}, which is in agreement with values obtained for other Bi-based systems.[17] The value of $N(E_F)$ obtained from Mott's model is a little higher than the reported values. Thus neither of these models give very reasonable values of a and $N(E_F)$, probably because of the inadequate approximation for the density-of-states distribution.

Alternatively, we follow the commonly used procedure of assuming a value of $N(E_F)$ and calculating a from Eq. (2). Assuming $N(E_F)\sim10^{22}$ eV^{-1}cm^{-3} (in agreement with previously reported values for Bi-based systems[20]), a value of 13 Å is obtained, which is a reasonable estimate. If it were much smaller, then it would be of the order of the interatomic spacing and the density of states would be unphysically high. On the other hand, if a were much larger than this estimate, the density of states would be unusually small.

The most probable jump distance R and the average hopping energy ΔW at a temperature T is determined from the relations[13,21]

$$R(T)=\{4.13\times10^3a/[N(E_F)T]\}^{1/4} \tag{5}$$

and

$$\Delta W=(3/4\pi)/[R^3N(E_F)]\ . \tag{6}$$

Using $N(E_F)\sim10^{22}$ eV^{-1}cm^{-3} and $a=13$ Å, we obtain $R=27$ Å and $\Delta W\sim1$ meV at $T=10$ K. The hopping conditions $R\gg a$ and $\Delta W\gg kT$ are therefore satisfied.

At temperatures higher than 170 K for the $x=1.0$ sample, the carriers are thermally activated from localized states near the Fermi level to nonlocalized states. The ρ-T dependence is described by

$$\rho=\rho_1\exp(T_1/T)\ , \tag{7}$$

as shown in Fig. 4, with $\rho_1=10.5\times10^{-3}$ Ω cm and $T_1=123$ K. According to Mott,[21]

$$\rho_1=\hbar l/Ae^2 \tag{8}$$

and

$$kT_1=(E_c-E_L)\ , \tag{9}$$

where l is the inelastic diffusion length, A is a constant of the order of 0.1, and E_c and E_F are, respectively, the energy values of the mobility edge and the Fermi level. From Fig. 4 and Eqs. (8) and (9), values of

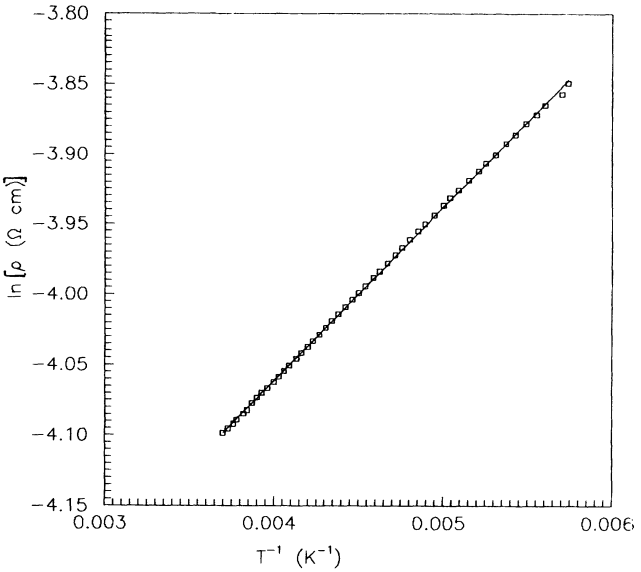

FIG. 4. Logarithm of the high-temperature ($T>170$ K) resistivity of $Bi_2Sr_2GaCu_2O_y$ as a function of T^{-1}

$E_c-E_L=0.01$ eV and $l=25$ Å.

The low-temperature resistivity data for the samples with $x=0.7$ and 0.9 are found to be best fit with Eq. (7), as shown in Fig. 5. Thus, in the low-temperature region where the ρ-T curves show semiconducting behavior, carriers are thermally activated. This is quite different from the $Bi_2Sr_2Ca_{1-x}M_xCu_2O_Y$ (M=Y or a rare-earth element) samples in which conduction in samples with similar behavior ($\rho_{\min}$) is found to be governed by variable-range hopping. While the conduction in the semiconducting samples of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ and the rare-earth-doped systems is governed by variable-range hopping in the low-temperature region, changing from

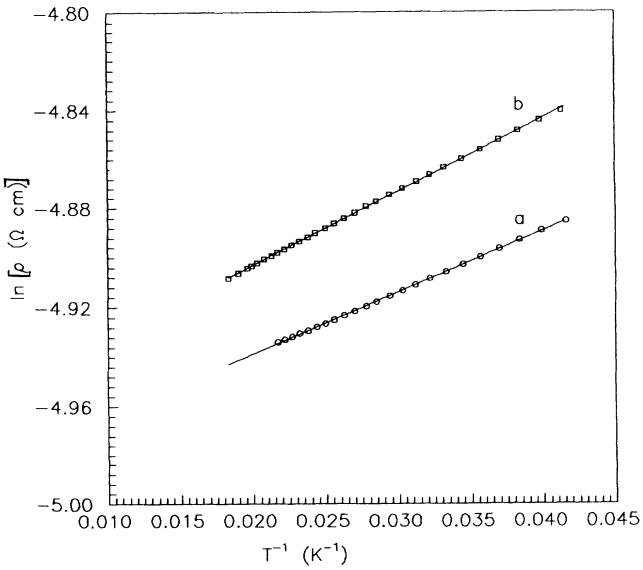

FIG. 5. Logarithm of the low-temperature resistivity of $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$ as a function of T^{-1} for (a) $x=0.7$ and (b) $x=0.9$.

2D to 3D variable-range hopping with increasing Y (or rare-earth element) concentration, it is observed that in the $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$ system the conduction mechanism in the semiconducting samples changes from thermally activated hopping to 3D variable-range hopping.

Figure 6 shows the temperature dependence of the dc susceptibility of some of the samples. The $x=0.3$ samples shows a sharp transition. The result of the $x=0.3$ samples shows some broadening, which is also evident in the resistivity measurements. Both samples have the same onset superconducting transition, in agreement with the resistivity measurements.

The comparison of the $Bi_{1.4}Pb_{0.6}Sr_2Ca_{2-x}Ga_xCu_3O_y$ series studied by Ummat, Nkum, and Datars[4] and $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$ shows that a small amount of Ga suppresses the transition temperature in both compounds by several degrees. The volume fraction of the superconducting phase is very small at $x=1$ in $Bi_{1.4}Pb_{0.6}Sr_2Ca_{2-x}Ga_xCu_3O_y$ and at $x=0.6$ in $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$. The remanent superconductivity in the $Bi_{1.4}Pb_{0.6}Sr_2Ca_{2-x}Ga_xCu_3O_y$ ($x \geq 1$) system may have been caused by a small amount of $Bi_{1.4}Pb_{0.6}Sr_2CaCu_2O_y$ in the material. Thus, in both cases, the superconductivity requires at least half of the total Ca and Ga ions to be Ca.

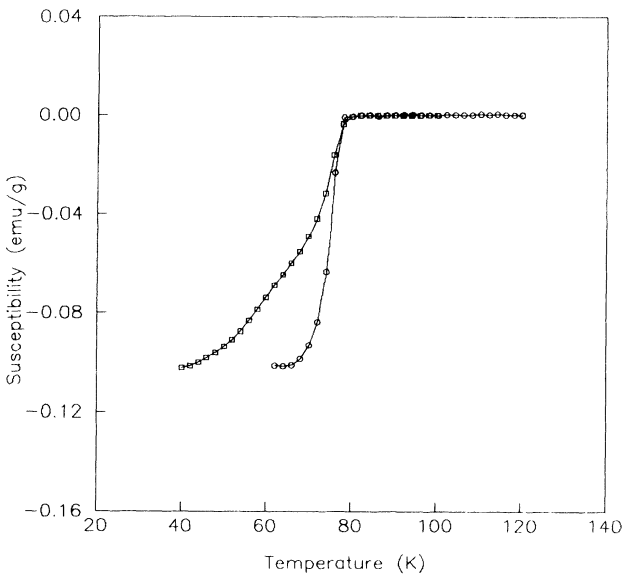

FIG. 6. Temperature dependence of dc susceptibility of $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$: $x=0$ (○) and $x=0.3$ (□).

IV. CONCLUSIONS

The substitution of Ga for Ca in the system $Bi_2Sr_2Ca_{1-x}Ga_xCu_2O_y$ is found to result in the decrease of the c parameter since the size of the Ga^{3+} ion is smaller than that of the Ca^{2+} ion it replaces. Samples with $x \leq 0.5$ are superconducting with the characteristic temperature of transition almost independent of x. Samples with $x \geq 0.7$ are nonsuperconducting. The $x=0.7$ and 0.9 samples have metallic behavior in the high-temperature region and semiconducting behavior in the low-temperature region. These two regions are separated by a shallow minimum. The $x=1.0$ sample has a semiconducting behavior over the whole temperature range of measurement. A thermally activated conduction process takes place in the low-temperature regions of the $x=0.7$ and 0.9 samples. In the $x=1.0$ sample, the conduction is governed by a three-dimensional variable-range hopping in the low-temperature region and by a thermally activated process in the high-temperature region.

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[1] A. Manthiram and J. B. Goodenough, Appl. Phys. Lett. **53**, 420 (1988).

[2] A. K. Ganguli, R. Nagarajan, K. S. Nanjundaswamy, and C. N. R. Rao, Mater. Res. Bull. **24**, 103 (1988).

[3] J. M. Tarascon, P. Barboux, G. W. Hull, R. Ramesh, L. H. Greene, M. Girond, M. S. Hegde, and W. R. McKinnon, Phys. Rev. B **39**, 4316 (1989).

[4] P. K. Ummat, R. K. Nkum, and W. R. Datars, Physica C **180**, 407 (1991).

[5] N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Materials*, 2nd ed. (Clarendon, Oxford, 1979).

[6] N. F. Mott and W. D. Twose, Adv. Phys. **10**, 107 (1967).

[7] P. Mandal, A. Poddar, and B. Ghosh, Phys. Rev. B **43**, 13 102 (1991).

[8] B. Ellman, H. M. Jaeger, D. P. Katz, T. F. Rosenbaum, A. S. Cooper, and G. P. Espinosa, Phys. Rev. B **39**, 9012 (1989).

[9] H. Oyanagi, H. Ihara, T. Matsubara, M. Tokumoto, T. Matsuchita, M. Hirabayashi, K. Murata, N. Tereda, T. Yao, H. Iwasaki, and Y. Kimura, Jpn. J. Appl. Phys. **26**, L1561 (1987).

[10] H. Takagi, S. Uchida, H. Iwabuchi, H. Eisaki, K. Kishio, K. Kitazawa, K. Fueki, and S. Tanaka, Physica B **148**, 349 (1987).

[11] A. Fujimori, Y. Tokura, H. Eisaki, H. Tagaki, and M. Sato, Phys. Rev. B **40**, 7303 (1989).

[12] A. E. White, R. C. Dynes, and J. P. Garno, Phys. Rev. B **33**, 3549 (1986).

[13] H. M. Jaeger, D. B. Haviland, A. M. Goldman, and B. G. Orr, Phys. Rev. B **34**, 4920 (1986).

[14] R. C. Dynes, A. E. Hite, J. M. Graybeal, and J. P. Garno, Phys. Rev. Lett. **57**, 2195 (1986).

[15] J. M. Graybeal and M. A. Beasley, Phys. Rev. B **29**, 4167 (1984).

[16]M. Pollak, in *Noncrystalline Semiconductors,* edited by M. Pollak (CRC, Boca Raton, FL, 1987), p. 121.
[17]P. Nagel, in *Amorphous Semiconductors,* edited by M. H. Brodsky (Springer, Berlin, 1985).
[18]W. Brenig, G. H. Doehler, and P. Woelfe, Z. Phys. **258**, 381 (1973).
[19]M. Ortuno and M. Pollak, Philos. Mag. B **47**, L93 (l1983).
[20]C. Paracchini, G. Calestani, and M. G. Fracesconi, Physica C **167**, 249 (1990), and references therein.
[21]N. F. Mott, *Conduction in Noncrystalline Materials* (Clarendon, Oxford, 1986).