Localization and interaction effects during superconductor-insulator transition of $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+d}$

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An extensive study has been made of the resistivity of superconducting and semiconducting samples of the $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+d}$ system. The effect of changing the Gd concentration and the annealing conditions is found to be a gradual change in the normal-state resistivity measured at 280 K (ρ_n). With the increase in ρ_n, T_c is depressed. The form of the T_c depression is found to be consistent with a theory of localization and interaction effects on the superconductivity. In the insulator regime, however, the resistivity is due to variable-range hopping (VRH), the dimensionality of which changes from two to three as the ρ_n increases away from the superconductor-insulator boundary. The observation of the two-dimensional VRH behavior in juxtaposition with the superconductivity is in qualitative agreement with a theoretical model that considers the competition between superconductivity and localization in a disordered system. When $\rho_n > 1$ Ω cm, the resistivity variation is found to be dominated by multiphonon-assisted hopping.

A characteristic feature of copper oxide superconductors is the transition to the insulator phase with the decrease in the carrier concentration.[1-3] In the insulator phase a large gap exists in the electron energy spectrum due to a strong on-site Coulomb repulsion at the copper sites ($U \sim 8$ eV). The conductivity however is dominated by variable-range hopping (VRH) because the electronic states at the Fermi level are localized. Recent neutron-diffraction study of magnetic excitations in the nonmetallic La_2CuO_4 suggest that the superconductivity, the magnetism, and the insulator state have a common origin in the Coulomb interaction between the valence electrons.[4] From this standpoint a study of the superconductor-insulator transition through transport measurements is of fundamental interest because it enhances our understanding of superconductivity[5] and more significantly, it helps identify the connection between the superconductor and the insulator state. Most of the work to date that addresses related issues has been carried out on the La-Sr-Cu-O system.[6-8] The resistivity studies of the $La_{2-x}Sr_xCuO_4$ system with $0.02 \geq x \geq 0.1$ are of particular interest in view of the fact that they provide three useful hints: (i) The resistivity variation in the temperature range 0.3–10 K, changes from a functional form that describes hopping in a system of electrons with long-range Coulomb interactions to VRH in three dimensions as the carrier concentration is increased; (ii) there exists a correlation between T_c and the normal-state resistivity; and (iii) the normal-state transport depends on the mode of hole doping. In order to get more insight of these issues we have chosen the $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+d}$ system with two characteristic Cu-O layers and a $T_c \sim 73$ K. This system has the advantage that the oxygen stoichiometry is stable and the Cu-O planes which are responsible for the conductivity are devoid of complications. The fact that the crystal structure is modulated does not appear to influence the superconductivity of the system.[9] Another crucial advantage is the electronic structure remains unchanged during the superconductor-insulator transition.[10] This makes the interpretation of the resistivity results during the crossover less ambiguous. With these considerations we have studied the effect of doping and annealing conditions on T_c and the normal-state resistivity of $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+d}$ for $0 \leq x \leq 1$. Powder x-ray-diffraction patterns were recorded, primarily to check the purity of the samples, but also to study the variation of lattice parameters. The principal effect of varying the annealing conditions is found to be a gradual change in the resistivity measured at 280 K (ρ_n) along with the usually noted change in the carrier concentration. A decrease in the hole concentration results in increase of ρ_n and a fall in T_c. The correlation of T_c with ρ_n, besides the carrier concentration, is found to be of considerable significance on account of the fact that the form of the relation between T_c and ρ_n is in accordance with the suppression of the superconductivity by an apparent enhancement of the Coulomb interaction. Near the superconductor-insulator boundary we observe the superconductivity in conjunction with the variable-range hopping in two dimensions, which agrees qualitatively with a theoretical model that considers the competition between superconductivity and the localization. In the insulating regime the data displays a clear crossover from two-dimensional (2D) to three-dimensional (3D) VRH, with increasing normal-state resistivity.

Samples of $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+d}$ with $0 \leq x \leq 1$ were prepared by solid-state reaction of appropriate quantities of well-mixed metal oxides and carbonates which were reacted at 850 °C for 72 h. The reacted materials were pulverized and cold pressed into pellets which were sintered and annealed in air or oxygen in the temperature range 860–910 °C. One set of air-annealed samples is further annealed in nitrogen at 650° C. A second set of samples is quenched in liquid nitrogen. The powder x-ray diffraction patterns were recorded at room temperature using an INEL-120 x-ray diffractometer with the Cu $K\alpha$ radiation. Four-probe dc resistivity data of rectangular slab samples were collected in the temperature range 4.2–300 K. ac susceptibility measurements were performed using a home-built system. T_c represents the temperature corresponding to a sample resistivity less than 1 $\mu\Omega$ cm and also the temperature at which the real part of the ac susceptibility departs from its normal-state value. The number of holes per subcell has been estimated by assuming a trivalent state for bismuth. The oxygen content has been determined by reducing the samples in 5 vol % H_2-N_2 environment and monitoring the resulting weight loss. The effective Cu-O charge has been determined by iodometric titration.[11]

The powder x-ray-diffraction data establishes that for Gd concentrations $x < 0.8$ the samples are single phase. However, above this concentration an additional peak around $2\theta = 28.6°$ appears with a relative intensity of 5% at its maximum, which is due to Gd_2O_3. All prominent peaks have been indexed assuming a subcell with an orthorhombic symmetry. The difference between a and b cell parameters is small, but increases with x. This may be the reason for the splitting of the 200 reflection which is apparent only for $x > 0.7$. The a and b parameters increase whereas the c parameter decreases almost linearly with x. The decrease in c with increasing x is considered to signify the substitution of a smaller Gd ion at the Ca site.

Some representative plots demonstrating the effect of annealing on the superconducting transition of Gd-substituted samples is shown in Fig. 1(a). A conspicuous feature is the metal-like variation of the resistivity above the superconductivity on set. This evidently is at variance with the semiconductorlike behavior observed invariably in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ systems when T_c is reduced. In superconductors this has a fundamental significance owing to the fact that the variation would indicate the character of the interaction among the charge carriers that are competing with the superconductivity.[12] It is apparent from Fig. 1(a) that the transition width increases with the depression in T_c. Such broadening of the superconducting transition often signifies the presence of macroscopic inhomogeneities as well as secondary phases arising from inadequate material processing. The x-ray pattern of the present samples, however, do not indicate the presence of secondary phases. The ac susceptibility transition, shown in Fig. 1(b), that characterizes the bulk of the sample also agrees well with the resistivity T_c.[13] Therefore, we suspect that the 110-K phase sheath often found on the 73-K phase grains of the bismuth system is responsible to some degree for the observed broadening.[14]

The transition temperature measured as a function of Gd concentration (x) and the annealing conditions are summarized in Fig. 2(a). For all annealing conditions the highest values of T_c are found for $x = 0$. Apart from the nitrogen-annealed samples, the variation of T_c with doping falls into a region $x < 0.35$ for which T_c is insensitive to substitution followed by a second region $x > 0.35$ where T_c decreases rapidly to zero. For nitrogen-annealed samples the T_c decreases linearly with x through the range $0 \leq x \leq 0.45$.

The correlation of T_c with the number of holes per subcell is shown in Fig. 2(b). The hole concentration is evaluated using the effective Cu-O oxidation state (p) as well as the oxygen stoichiometry ($8+d$). The error in the determination of p, using a well-established double-titration technique, is ± 0.02.[11] Unfortunately the accuracy in the determination of the oxygen stoichiometry using thermogravimetry is affected by a chemical reaction between the sample and the platinum crucible of the thermobalance. The possibility of incomplete reduction of the sample also exists. These factors contribute to the scatter of the points shown in Fig. 2(b). It is clear that at low hole concentrations T_c rises rapidly and reaches a maximum value of 81.3 K before decreasing at higher concentrations. This characteristic feature of high-T_c superconductors has been related to the density of states at the Fermi level $[N(E_F)]$. The photoemission spectroscopy studies indicate that the intensity of the absorption corresponding to O $1s \rightarrow 2p$ excitation in $YBa_2Cu_3O_y$, for $6.26 \leq y \leq 6.9$ and in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+d}$, for $O \leq x \leq 1$ increases (decreases) with the increase (decrease) in the hole concentration.[15–17] This combined with the observation that the energy of the absorption edge does not shift is considered as an evidence for the creation of impuritylike O $2p$ states in the correlation gap as a result of hole doping.

It is convenient to discuss the results for the normal-state resistivity in regimes specified by the resistivity at 280 K (ρ_n). Samples with $\rho_n < 0.012$ Ω cm become superconducting. An interesting observation for these samples, as shown in Fig. 3, is the suppression of T_c with the increase in ρ_n. Similar behavior with increasing sheet resistance is well known in homogeneous thin-film superconductors[18] and is independent of the material studied.[19] Since the normal-state resistivity is a measure of the disorder, the depression of T_c with increasing ρ_n is considered to be related to the localization. A theoretical treatment of such an effect in high-temperature superconductors is yet to emerge. However, it is well known in conventional superconductors that, in the weak disorder regime, static and nonmagnetic disorder have little effect on T_c because they do not destroy time-reversal symmetry.[20] At the same time it is also known that the

Coulomb interaction effect is enchanced with disorder.[21] This has been taken into consideration for two-dimensional superconductors. Within the mean-field approximation it has been shown that T_c is depressed by the increasing sheet resistance due to an increase in the Coulomb interaction.[22] The result of the perturbation theory is

$$\ln\left[\frac{T_c}{T_{c0}}\right] = -\frac{(g_1-3g')N(0)}{4\pi\varepsilon_F\tau_0}\left[\ln\left[5.5\frac{\xi_0}{l}\frac{T_{c0}}{T_c}\right]\right]^2 - \frac{(g_1+g')N(0)}{4\pi\varepsilon_F\tau_0}\left[\ln\left[5.5\frac{\xi_0}{l}\frac{T_{c0}}{T_c}\right]\right]^3 . \quad (1)$$

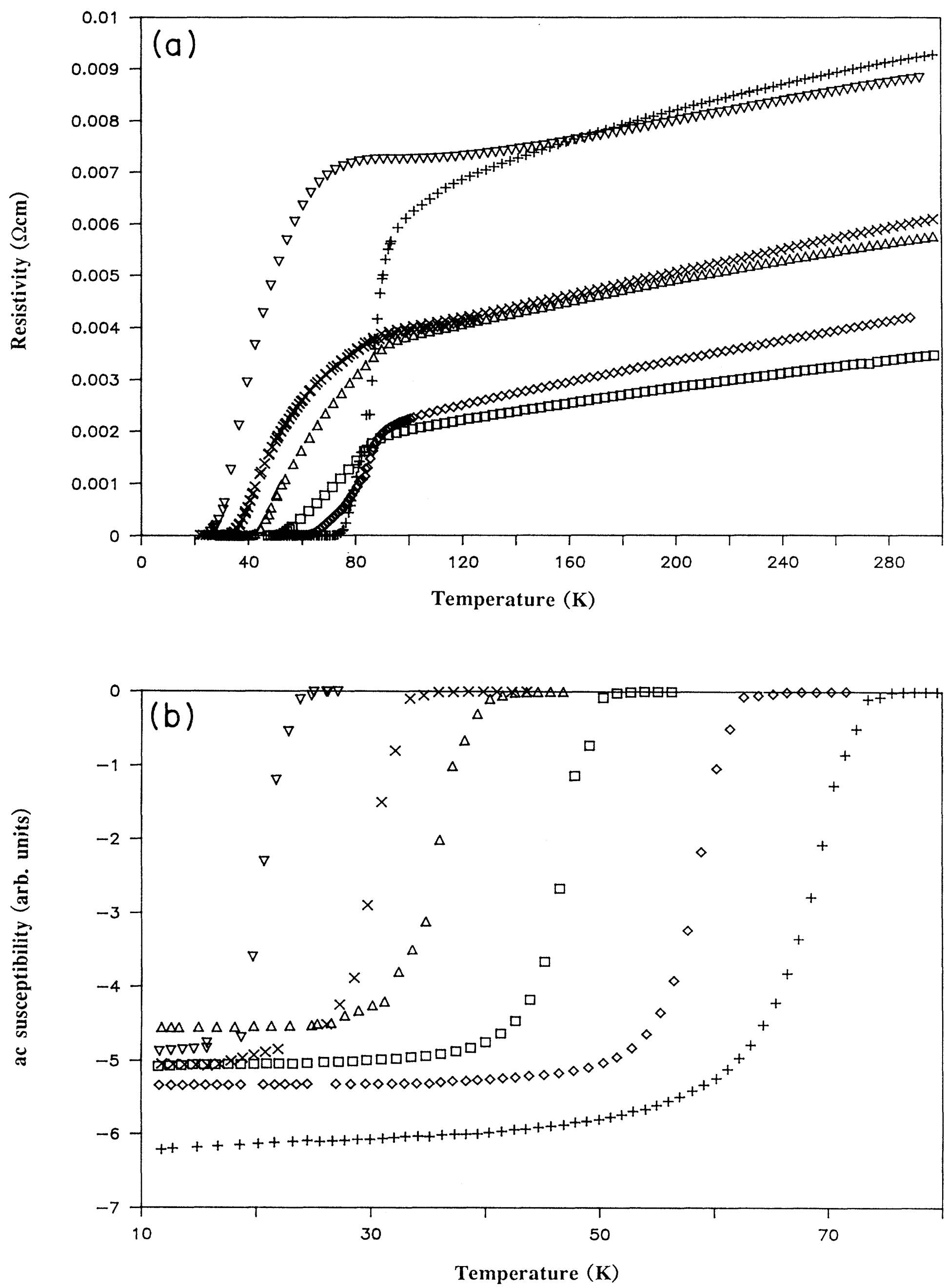

FIG. 1. (a) Resistivity and (b) ac susceptibility variation of $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+d}$ samples [(+): $x=0$, quenched in liquid nitrogen; (◇): $x=0.4$, annealed in oxygen; (□): $x=0.45$, annealed in air; (△): $x=0.4$, quenched in liquid nitrogen; (×): $x=0.5$, annealed in air; and (▽): $x=0.45$, quenched in liquid nitrogen]. The curve with the symbol (+) is scaled up by a factor of 4.

In this equation $g' \ll 1$ and the sheet resistance $R = \pi / e^2 \varepsilon_F \tau_0$. The first term is due to the reduction in the density of states and the second term is a (vertex) correction to electron-electron interaction. In order to compare our results with the theory we have taken $\xi(0) = 20$ Å and the ratio $\xi_0 / l \sim 7.2$.[23] The value of $g_1 N(0)$ is taken as unity. It may be noted that the quality of fit, as shown in Fig. 3, is satisfactory in spite of the fact that the sheet resistance required by the theory has been taken to be the measured resistivity at 280 K (ρ_n). In the present study this is justified on the basis that the thickness of the Cu-O layer remains constant and the resistivity only increases because of the increase in the disorder.

Samples with $\rho_n > 0.012$ Ω cm show semiconducting

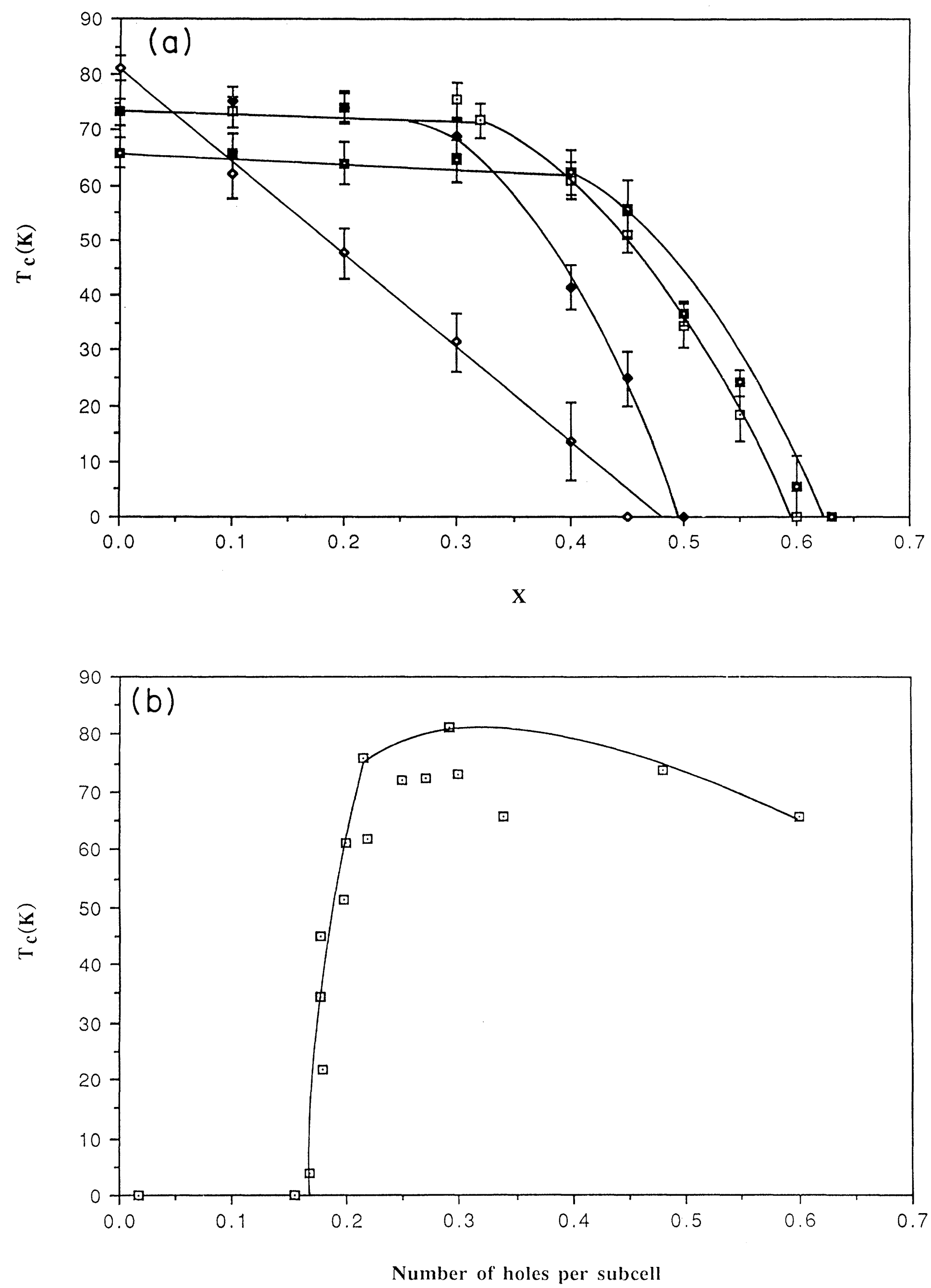

FIG. 2. (a) Variation of T_c with x for samples of $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+d}$ [(□): air annealed; (■): oxygen annealed; (◇): liquid-nitrogen quenched; and (◆): nitrogen annealed]. The error bars indicate the transition width corresponding to 10% and 90% drop in resistivity. (b) Variation of T_c with the number of holes per subcell. The solid lines are a guide to the eye.

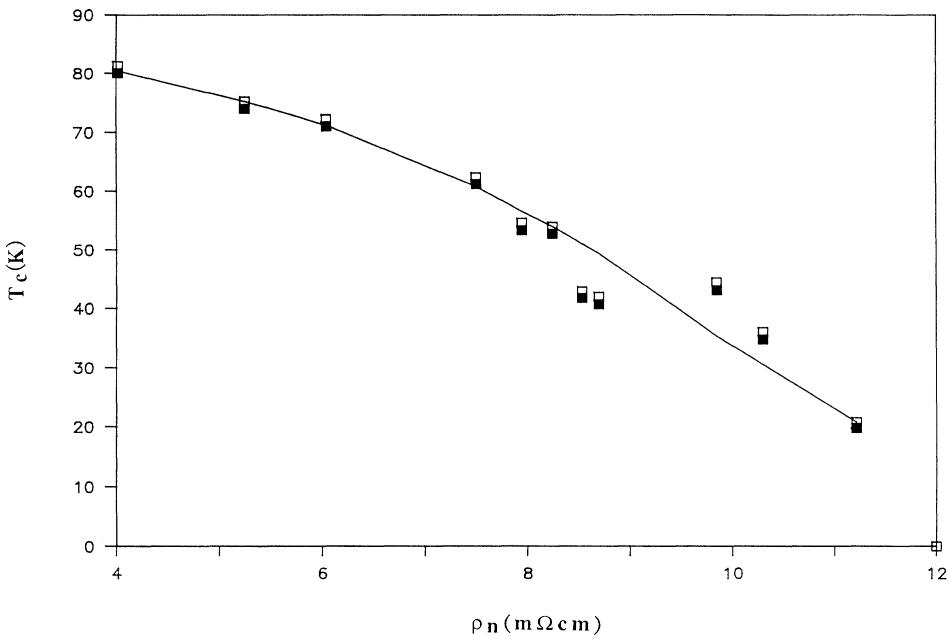

FIG. 3. Variation of T_c with ρ_n (normal-state resistivity at 280 K) [T_c obtained from (□) resistivity and (■) ac susceptibility]. The solid line is a fit to Eq. (1) in the text.

behavior. A feature that signifies the superconductor-to-insulator crossover is depicted in Fig. 4, where the resistivity of the oxygen and air-annealed samples of $Bi_2Sr_2Ca_{0.4}Gd_{0.6}Cu_2O_{8+d}$ are plotted. The results are interesting, in that as the temperature is decreased the system passes through the regions dominated by metallic ($300 > T > 120$ K), semiconducting ($120 > T > 20$ K), and superconducting behavior ($T < 20$ K). In the semiconducting regime ($120 > T > 20$ K) the resistivity fits well to the exponential form

$$\rho(T)=\rho(0)\exp(T_0/T)^m \ . \tag{2}$$

The value of m in the equation is found to be $\frac{1}{3}$, which is expected for two-dimensional variable-range hopping (VRH).[24] In fact, all samples ($0.012 < \rho n < 0.1$ Ω cm) that are near the superconductor-insulator boundary have $m=\frac{1}{3}$. The observation of superconductivity in an essentially localized system gives credence to a theoretical model that examines the intrinsic competition between superconductivity and localization.[25] According to this theory superconductivity is observed in an otherwise localized system when $N(E_F)\Delta\alpha^{-d} > 1$. Physically this means that even though states are localized over an energy scale of $[N(E_F)\alpha^{-d}]^{-1}$, if it is smaller than Δ (the energy gap) then the Josephson tunneling between the localized superconducting regions thus formed stabilize the superconducting state as the overall ground state. In this regard, since the localization length near the boundary in the insulator side is larger than the typical coherence length the electrons effectively behave as the extended particles. Therefore superconductivity is observed.

For values of ρ_n between 0.1 and ~1 Ω cm the data at high temperatures fit to Eq. (2) equally well with $m=\frac{1}{3}$ or $\frac{1}{4}$, whereas at low temperatures the value of $m=\frac{1}{4}$ is preferred. When ρ_n is above 1 Ω cm, the resistivity data fit well to $m=\frac{1}{4}$. This value implies an onset of the 3D VRH behavior owing to the commencement of hopping between the CuO_2 planes. An example of it, observed in nitrogen-annealed $Bi_2Sr_2Ca_{0.4}Gd_{0.6}Cu_2O_{8+d}$ and $Bi_2Sr_2Ca_{0.2}Gd_{0.8}Cu_2O_{8+d}$, is shown in Fig. 5. It is evident that resistivity of the latter displays different slopes in high- and low-temperature regimes. Such an observation is not uncommon in copper oxide superconductors. For example, the resistivity measurements on the $La_{1.98}Sr_{0.02}CuO_4$ samples in the temperature range 0.1–3 K (Ref. 7) and that of 4.2–300 K (Ref. 4) gave two different values of T_0. Despite this support, we realize that the above observation does not comply with the theory of variable-range hopping, applicable to the shallow impurity states at liquid-helium temperatures in the amorphous semiconductors. In fact, it has been argued that the resistivity variation of the form represented by Eq. (2), often observed at high temperatures in various semiconductors, cannot be attributed to VRH because the hopping-rate calculation presumes involvement of only a single acoustic phonon, whereas a more accurate theory for the conductivity at high temperatures in noncrystalline solids would consider a multiphonon jump rate process.[26] This process also manifests in an $\exp(T_0/T)^{1/4}$ form and contributes appreciably when T_0 is of the order of 10^7–10^{10} K. Since the number of phonons that assist the jump rate increase with increasing temperature the model also expects a change in the slope, as shown in Fig. 5.

A salient feature of the above data in the insulator regime is the observation of the 2D to 3D crossover, ex-

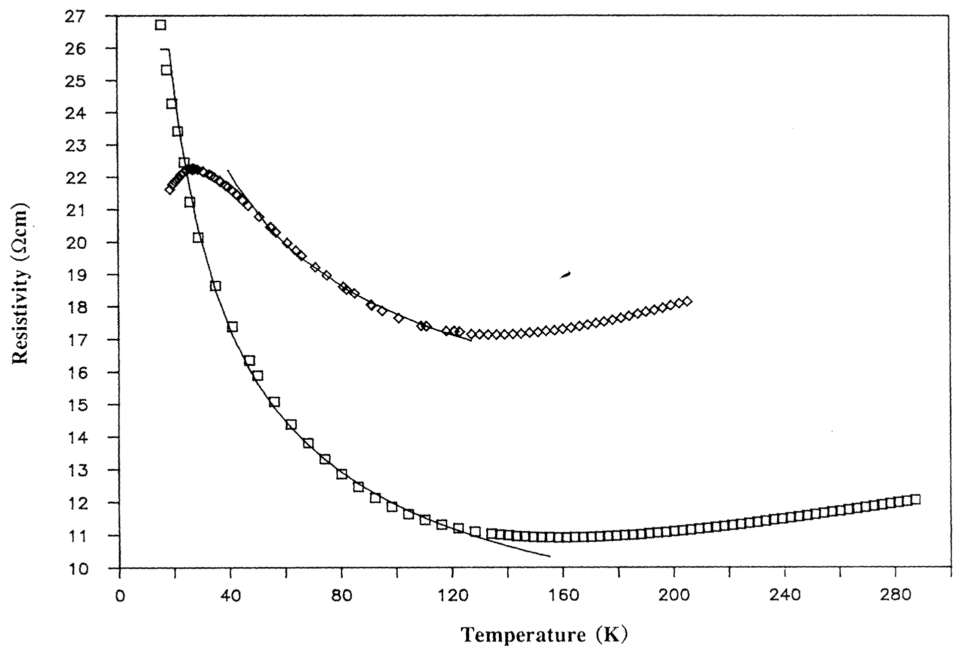

FIG. 4. Resistivity variation of oxygen- (◇) and air- (□) annealed $Bi_2Sr_2Ca_{0.4}Gd_{0.6}Cu_2O_{8+d}$. The data of the oxygen-annealed sample is scaled up by a factor of 2. The solid curves are a fit to VRH in two dimensions.

pected for these highly anisotropic materials. Since the inelastic-scattering length determines the dimensionality of the VRH, it is evident that the crossover takes place when the in-plane and out-of-plane inelastic-scattering lengths become comparable. Analysis of our data for a number of samples with increasing normal-state resistivity suggests that we are in the VRH regime when $\rho_n \sim 0.1$ Ω cm ($T_0 \sim 10^3$ K) and enter into the multiphonon-assisted hopping regime when $\rho_n > 1$ Ω cm ($T_0 \sim 10^7$ K).

In summary we have found that in the $Bi_2Sr_2Ca_{1-x}Gd_xCu_2O_{8+d}$ system, the normal-state resis-

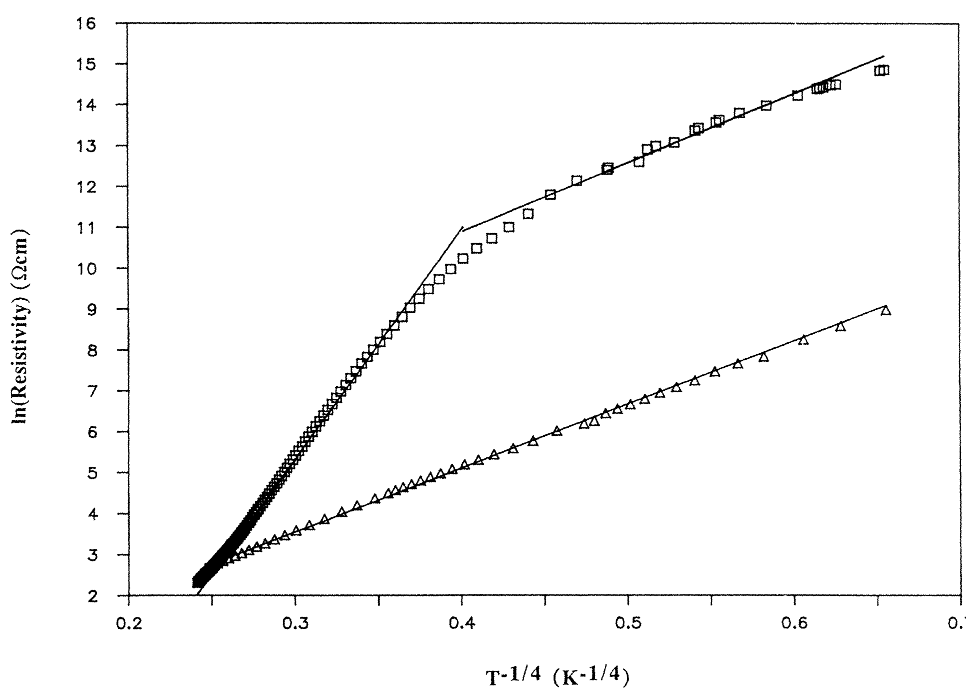

FIG. 5. Logarithm of resistivity as a function of $T^{-1/4}$ of nitrogen-annealed $Bi_2Sr_2Ca_{0.4}Gd_{0.6}Cu_2O_{8+d}$ (△) and $Bi_2Sr_2Ca_{0.2}Gd_{0.8}Cu_2O_{8+d}$ (□). The curve with the symbol (△) is scaled up by a factor of 10. The solid curves are a fit to VRH in three dimensions.

tivity (ρ_n) increases with decreasing hole concentration. The suppression of T_c with increasing ρ_n agrees well with a theory that is originally envisaged for 2D conventional superconductors. The satisfactory agreement between the theory and the data implies that the depletion of the carriers induces disorder, which in turn enhances the Coulomb interaction between the electrons. Since the Gd substitution at the Ca site cannot cause spatial disorder in the CuO_2 planes we speculate that the disorder envisaged here pertains to the randomness in the energy of the electronic levels involved in the current transport. In the insulator regime, with the increase in ρ_n, we find that the resistivity changes from 2D to 3D VRH and the $\exp(T_0/T)^{1/4}$ behavior observed in highly resistive samples agrees well with the multiphonon-assisted hopping between two well localized sites.

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