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Metal-insulator transition and superconductivity in $Y_1Ba_2Cu_3O_{7-x}$

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The oxygen concentration in the $Y_1Ba_2Cu_3O_{7-x}$ superconducting compound has been changed by subjecting it to rapid quenching from temperatures in the range 500–1000 °C. The lower oxygen concentration destroys the superconductivity, causes removal of the orthorhombic distortion in the perovskite structure and results in a metal-insulator (*M-I*) transition. The presence of variable range hopping conductivity and thermopower in the insulating regime strongly suggests that the *M-I* transition is of Anderson type. The results in general are understood in terms of the relative overlap between d_{z^2} and $d_{x^2-y^2}$ components of the e_g band of the octahedrally coordinated copper atoms.

An understanding of electron-transport properties and electronic structure of $Y_1Ba_2Cu_3O_{7-x}$ oxygen-defect perovskites is gaining considerable importance because of the interesting superconducting nature of these compounds.[1-4] It has been generally observed that the superconducting transition temperature T_c, the transition width, and the extent of orthorhombic distortion of the material are highly sensitive to the concentration of oxygen in the sintering environment.[3] The amount of oxygen available during sintering and cool down establishes the oxygen vacancy concentration in the perovskite lattice. A systematic analysis of the effects of a gradual change in the oxygen concentration of $Y_1Ba_2Cu_3O_{7-x}$ on its electron transport properties, crystal structure, and superconducting transition temperature, which would facilitate understanding the origin of high T_c in these compounds, is highly desired. This communication reports results of such a study conducted on a series of $Y_1Ba_2Cu_3O_{7-x}$ bulk samples prepared by slow cooling from the sintering temperature and by rapid quenching from temperatures in the range 500–1000 °C. These quenching treatments lead to a gradual decrease in the oxygen concentration and also to an orthorhombic-to-tetragonal phase transformation. Electrical resistivity and thermoelectric power measurements in the composition/structure space show superconducting, normal metallic, and insulating behaviors.

Samples of $Y_1Ba_2Cu_3O_{7-x}$ were prepared by mixing stoichiometric proportions of $BaCO_3$, Y_2O_3, and CuO followed by heating the mixture of 950 °C for 24 h. The mixture was reground and cold pressed into pellets 2.5 cm diam. and 0.3 cm thick. The pellets were given a final heat treatment at 950 °C for 24 h in a flowing oxygen ambient. The heat treatment was followed by cool down to room temperature over a period of 2 h. The oxygen ambient was maintained during the cool down. X-ray diffraction analysis confirmed that the samples, thus prepared, were single phase with an orthorhombic perovskite unit cell ($a=3.821$ Å, $b=3.901$ Å, $c=11.698$ Å). The samples for electrical resistivity and thermopower measurements were in the form of $0.3\times0.3\times0.8$ cm^3 bars cut from the pellets. Electrical resistivity measurements in the temperature range of 77 to 400 K were carried out in a four-point probe configuration with 0.5-mm-diam. copper wires as current and voltage leads. These contacts were made by first drilling four holes (0.6 mm diam.) in the sample and then inserting the copper wires. Intimate electrical contact between the wires and the sample was provided by using silver paint. Thermopower of the samples was measured by employing the constant-ΔT method.[5] A pair of thin copper-Constantan thermocouples was embedded at the two ends of the sample. The latter was mounted on a small Teflon wedge such that one end of it was in intimate thermal contact with a copper cold finger or heater assembly. At the start of the measurement, both the junctions were at 77 K. The temperature of the cold block was then slowly increased, thus creating a temperature gradient along the length of the sample. The response of two thermocouples was amplified and then plotted on an *x-y* recorder. Accuracy in the measurement of ΔT was ± 1 K. The voltage developed across the copper wires of the thermocouples, which is the thermo emf of the sample, was measured with a Keithley nanovoltmeter (model 181) and recorded against the average temperature of the sample.

Oxygen deficiency in the samples was created by quenching a number of superconducting bars from temperatures in the range 500–1000 °C on a thick copper plate. The lattice parameters of the as-prepared and quenched samples were measured by x-ray powder diffraction analysis. A high-purity polycrystalline silicon powder mixed with the sample was used as a standard for x-ray diffraction measurements.

Figure 1 shows results of electrical resistivity measurements in the temperature range 77–400 K, on a slow cooled sample (a) and a series of rapidly quenched samples. The slow cooled sample shows the characteristic metallic temperature coefficient of resistance (3.23×10^{-4} K^{-1} at 300 K) with onset of superconductivity T_c at 93 K and a complete zero resistance state at 89 K. The samples quenched from 500, 600, and 700 °C also show metallic conduction. However, their resistivity increases with the quenching temperature. Moreover, the quenching has a marked effect on the superconducting transition temperature of the samples. A gradual destruction of superconductivity is observed with the increasing quenching temperatures. The T_c and the change in the resistance be-

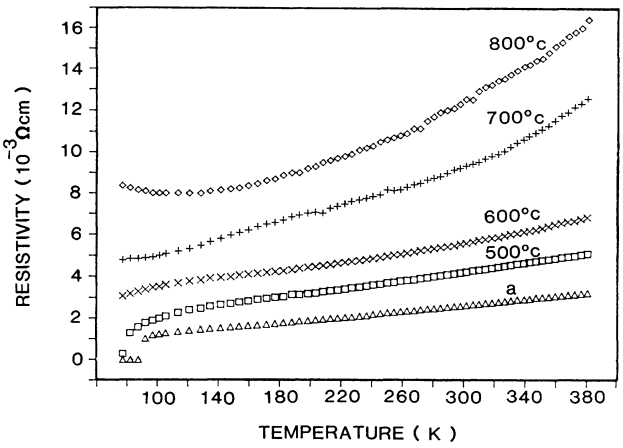

FIG. 1. Electrical resistivity vs temperature for a normally cooled sample (marked *a*) and samples quenched from temperatures in the range 500–800 °C. The quenching temperatures have been marked for each curve.

tween the T_c and the lowest temperature of measurement are 86 K and 20%, and 79 K and 4%, for the samples quenched from 500 and 600 °C, respectively. The sample quenched from 700 °C did not show any indications of the onset of a superconducting state down to 77 K. On increasing the quenching temperature further to 800 °C, the resistivity in the temperature range shows an upturn with decreasing temperature. This insulatorlike behavior in the resistivity is dominant in samples quenched from 900 °C and above. To facilitate the understanding of the resistivity in terms of the electron transport mechanism in insulating and semiconducting systems, we have plotted the conductivity of some high-temperature quenched samples as a function of $1/T$ in Fig. 2. Clearly the range of quenching temperature between 900–950 °C, which results in conductivity between 15 to 40 $\Omega^{-1}\text{cm}^{-1}$, marks a metal-insulator transition in this system. The conductivity of the samples in the insulator side of the transition shows the characteristic thermally activated conduction. However, the activation energy, even for the sample with the maximum room-temperature resistivity (quenched from 1000 °C), remains temperature dependent up to fairly high temperatures. This behavior indicates a phonon-assisted quantum-mechanical tunneling of the charge carriers in localized states at the Fermi energy or the so-called variable range hopping.[6] Under a flat band approximation, following Ambagaokar, Halperin, and Langer[7] the conductivity due to variable range hopping can be expressed as

$$\sigma=\sigma_0\exp[-(T_0/T)^{1/4}] , \quad (1)$$

where

$$T_0=\frac{16\alpha^3}{k\rho_0} ,$$

and α, ρ_0, and k are the decay constant of the localized state, the density of states at E_F, and the Boltzmann constant, respectively. In Fig. 3 we have plotted the conductivity data for the samples quenched from 975 and 1000 °C as a function of $T^{-1/4}$. Indeed, the conductivity shows a well-defined $T^{-1/4}$ dependence over a temperature range that becomes wider with the increasing quenching temperature.

Results of thermoelectric power (S) measurements relative to copper on a slow cooled, superconducting sample and on three samples quenched from 700, 975, and 1000 °C are shown in Fig. 4. Due to a large error in measuring ΔT at the initiation of the temperature gradient across the sample, thermoelectric power (TEP) measurements were not carried out between 77 and 85 K. The thermopower of the slow-cooled, superconducting sample (*a*) is $\sim 8\ \mu$V/deg at 120 K and it remains virtually insensitive to temperature between 120 and 400 K. Below 120 K the thermopower first shows a slow decrease and then drops precipitously to zero at ~ 90 K. As expected, the absolute TEP of the sample in the superconducting state is zero. The thermopower of the quenched samples increases with the quenching temperature. As

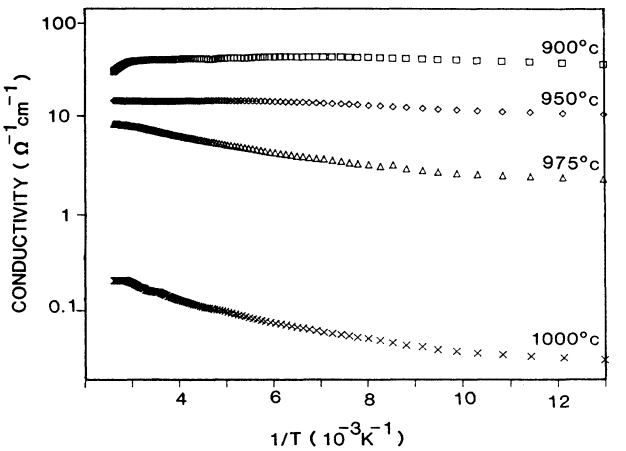

FIG. 2. Electrical conductivity vs reciprocal temperature for samples quenched from temperatures in the range 900–1000 °C.

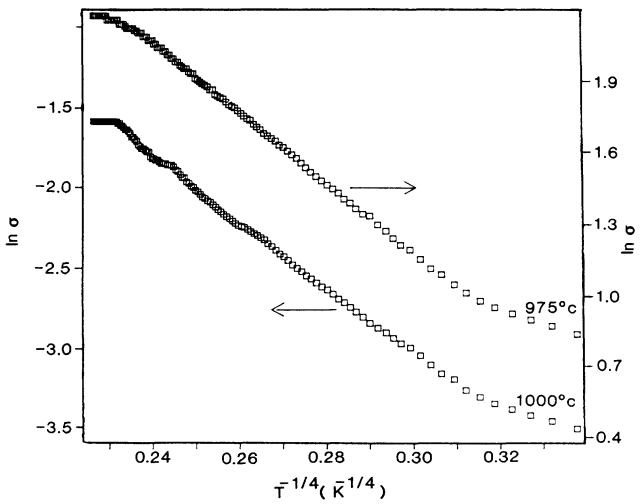

FIG. 3. Electrical conductivity of the samples quenched from 975–1000 °C has been plotted against $T^{-1/4}$.

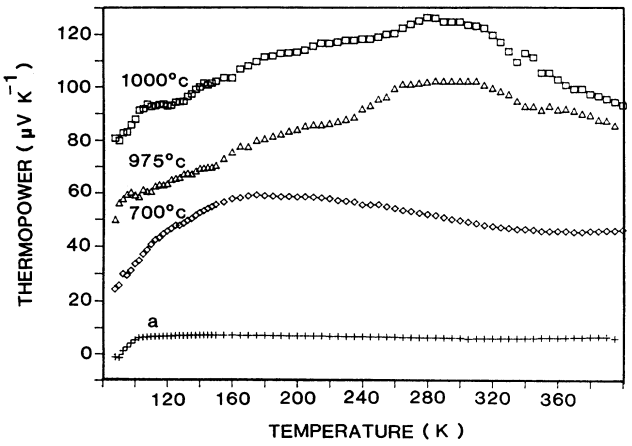

FIG. 4. Thermoelectric power relative to copper of a normally cooled sample (marked *a*) of $Y_1Ba_2Cu_3O_{7-x}$. The figure also shows TEP of samples quenched from 700, 975, and 1000 °C.

seen from Fig. 4, three regions of behavior of the TEP can be identified with the increasing temperature. These are a slow rise, a broad hump, and a decrease at the upper end of the temperature scale.

Finally, in Fig. 5 we show results of lattice parameter measurements on the slow cooled and quenched samples. In the normally cooled sample (*a*) the orthorhombic distortion ($b-a$) is 0.08 Å. The extent of the orthorhombic distortion diminishes on increasing the quenching temperature. These changes in the *a* and *b* lattice parameters are accompanied by a progressive expansion of the lattice along the *c* axis. Within the accuracy of our measurements, the samples quenched at and above 800 °C are essentially tetragonal. Since some copper atoms in this perovskite structure have an octahedral coordination, the observed equalization of the *a* and *b* axes and the expansion along the *c* axis, have the net effect of enlarging the crystal field splitting of the d_{z^2} and $d_{x^2-y^2}$ components of e_g band of the Cu atoms. The orthorhombic-to-tetragonal phase change in $Y_1Ba_2Cu_3O_{7-x}$ as a function of temperature has been reported recently by some other groups.[8,9]

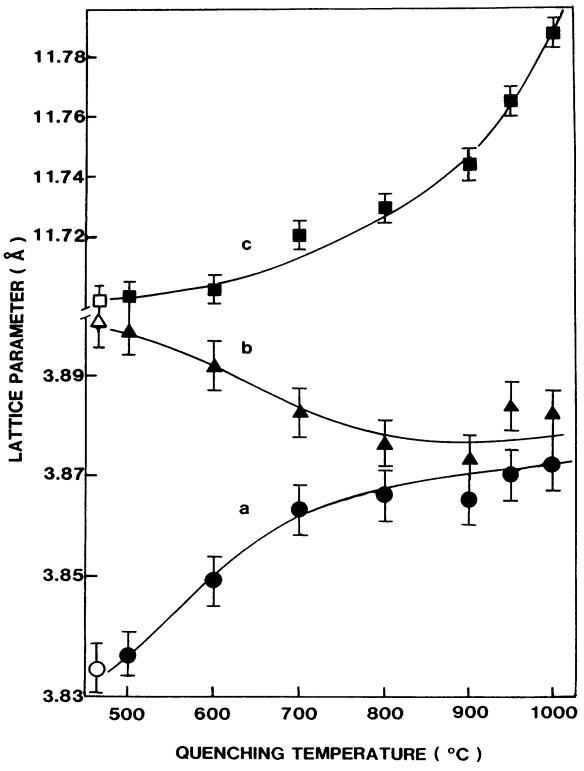

FIG. 5. *a*, *b*, and *c* axis lattice parameters of $Y_1Ba_2Cu_3O_{7-x}$ compound as a function of quenching temperature. Open symbols are for normally cooled sample.

A gradual metal-insulator transition (*M-I*) has been observed by several workers[10-12] in the alkali and alkaline earth doped transition-metal oxides. The *M-I* transition is of the Anderson type in which the random distribution of the dopants and rare-earth ions causes sufficient disorder to localize the states in the impurity band and the transition-metal *d* band. Although, the effect of removal of oxygen on the electron transport properties of $Y_1Ba_2Cu_3O_{7-x}$ in our case is similar to that of decreasing the dopant concentration in systems mentioned above,[10-12] it also causes a structural phase transformation in the present case. Provost, Sheder, Michel, and Raveau[13] have studied the effect of oxygen deficiency on the electron transport behavior of a tetragonal perovskite of the type $Ba_3La_3Cu_6O_{14+y}$. Their data show a gradual transition from strong localization to quasimetallic behavior with increasing *y*. The authors have interpreted their results in terms of a varying degree of localization in the Cu $3d$–O $2p$ hybridized band. Although the system under present investigation shows a phase change from orthorhombic-to-tetragonal symmetry along with the transition to an insulating state, it appears that the effect of the phase change is only to increase the separation between d_{z^2} and $d_{x^2-y^2}$ components of the $3d$ band, which must be overlapping in the metallic state. The *M-I* transition is essentially decided by the Anderson localization. Putting an upper limit on the density of states at which delocalization occurs as 10^{21} cm^{-3}eV^{-1}, the slope of σ vs $T^{-1/4}$ curve for the sample quenched from 975 °C gives the extent of the localized state ($1/\alpha$) as $\cong 16$ Å. At this juncture, it is fair to state that the carriers in state with $\alpha^{-1} \sim 16$ Å or larger are not likely to lead to deformation of the lattice and consequent small polaron formation.[14]

The functional dependence of the thermopower in the variable range hopping regime for an energy dependent density of states can be expressed as[15]

$$S = \frac{1}{2} k^2 T_0 T^{1/2} \left(\frac{d \ln N}{dE} \right)_{E=E_F} , \qquad (2)$$

where T_0 is the same as defined in Eqs. (1). If the density of states at E_F is not a rapidly varying function of the temperature, the TEP is expected to show a $T^{1/2}$ dependence. The increase in the thermopower with temperature up to 290 K for samples quenched from 975 and 1000 °C is in agreement with the variable range hopping theory. The drop in the thermopower above ~ 300 K suggest exci-

tation to a mobility edge.

In the realm of a semiclassical model with a single band, the thermopower of the superconducting sample and the samples in the metallic side of the transition can be expressed as[15]

$$S = -\frac{\pi^2}{3}\frac{k^2 T}{|e|}\frac{d(\ln\sigma)}{d(\ln E)_{E_F}} , \quad (3)$$

where notations have their usual meaning. In the absence of phonon-drag effects and magnetic interactions, the above expression predicts a linear increase in S with the increasing temperature. The temperature-independent thermopower of the superconducting sample as shown in Fig. 4 is clearly inconsistent with Eq. (3). A relatively high and temperature-independent thermopower has also been observed in the case of some metallic transition-metal salts,[11,12] quasi-one-dimensional conductors like tetracyanoquinodimethane[16] (TCNQ), and, more recently, in Sr- and Ba-doped La_2CuO_4.[17] Temperature-independent thermopower is expected in the narrow-band system when the thermal energy (kT) is larger than the band width. Such a model however, is inconsistent with the temperature dependence of the quenched samples. It appears that some yet unknown electron scattering processes are responsible for the observed behavior.

Finally, we briefly comment on the depression of T_c in the quenched samples. From the study of granular metals it is generally accepted that superconductivity disappears at the *M-I-* transition. The behavior of T_c in our samples is consistent with this prevailing view.[18,19] A direct comparison however, is premature knowing that the deliberately introduced inhomogeneity in the granular systems for the *M-I* transition to occur, makes it difficult to establish the depression of T_c as being one of the phenomena associated with electron localization. Clearly, the oxide superconductors provide interesting systems to study superconductivity and localization in three dimensions.

In conclusion, we have shown that electrical resistivity, thermopower, crystal structure, and T_c of the superconducting $Y_1Ba_2Cu_3O_{7-x}$ compound can be changed drastically by the removal of oxygen through some quenching treatments. The system undergoes an *M-I* transition at the higher loss of oxygen. Temperature dependence of both thermopower and resistivity suggest that the *M-I* transition is caused by Anderson localization. The depression of T_c with the increasing resistivity is consistent with the prevailing views of localization and superconductivity in three dimensions.

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[1]J. G. Bednorz and K. A. Müller, J. Phys. B **64**, 189 (1986).
[2]M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987).
[3]R. J. Cava *et al.*, Phys. Rev. Lett. **58**, 1676 (1987).
[4]P. Ganguly, A. K Raychaudhari, K. Sreedhar, and C. N. R. Rao, Pramana **27**, L229 (1987).
[5]R. R. Heikes and R. W. Ure, Jr., *Thermoelectricity: Science and Engineering* (Interscience, New York, 1961), p. 285.
[6]N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1974).
[7]V. Ambegaokar, B. E. Halperin, and J. S. Langer, Phys. Rev. B **8**, 3682 (1973).
[8]M. O. Eatough, D. S. Ginley, B. Morosin, and E. L. Venturini, Appl. Phys. Lett. **51**, 367 (1987).
[9]I. K. Schuller *et al.*, Solid State Commun. **63**, 385 (1987).
[10]N. F. Mott, Philos. Mag. **35**, 111 (1977).
[11]P. Dougier and A. Casalof, Solid State Chem. **2**, 396 (1970).
[12]M. Sayer, R. Chen, R. Fletcher, and A. Mansingh, J. Phys. C **8**, 2059 (1975).
[13]J. Provost, F. Shedar, C. Michel, and B. Raveau, Synth. Met. **4**, 157 (1981).
[14]D. Emin, Phys. Rev. Lett. **32**, 303 (1974).
[15]N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Material* (Oxford Univ. Press, Oxford, 1979), p. 52.
[16]P. M. Chaikin and G. Beni, Phys. Rev. B **13**, 647 (1976).
[17]J. R. Cooper, B. Alavi, L. W. Zhou, W. P. Beyermann, and G. Gruner, Phys. Rev. B **35**, 8794 (1987).
[18]G. Deutscher, A. Palevski, and R. Rosenbaum, in *Localization, Interaction and Transport Phenomena,* edited by B. Kramer, G. Bergmann, and Y. Bruynseraede (Springer-Verlag, Berlin, 1985), p. 108.
[19]R. C. Dynes and J. P. Garno, Phys. Rev. Lett. **46**, 137 (1981).