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Normal-state resistivity of the high-T_c compound $Y_1Ba_2Cu_3O_{7-\delta}$

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The resistivity of $Y_1Ba_2Cu_3O_{7-\delta}$ has been measured in an oxygen atmosphere from 90 to 800 K. Above 300 K, the slope of the resistivity versus temperature curve increases from its initial constant value. Around 625 K an anomaly occurs and resistivity remains essentially constant with increasing temperature and becomes hysteretic during cooling. We correlate the data above 500 K with the gain and loss of oxygen observed by thermogravimetric analysis. Such an explanation is consistent with recent density-of-states calculations.

Numerous workers have measured the low-temperature resistance of pressed, calcined, polycrystalline compound of the 1:2:3 90-K superconductor $Y_1Ba_2Cu_3O_{7-\delta}$ (Ref. 1) and a few workers have investigated the high-temperature electron transport properties of these materials.[2] Many of these papers report nearly identical results: The resistivity is relatively large, about 250 $\mu\Omega$ cm just above T_c and is linear with temperature with a slope $d\rho/dT = 1.7$–2.5 $\mu\Omega$ cm/K. Large variability of results from different laboratories are cited, which probably results from differing densities and oxygen contents of the various samples.

Many theoretical papers[3-5] have utilized the linear temperature dependence of the resistivity to speculate on the mechanisms of superconductivity in these high-temperature superconducting ceramics. In this paper we have extended these measurements above room temperature in order to discover where the linear relationship breaks down, the mechanisms which give rise to this behavior, and the possible implications of this phenomenon to superconductivity.

Two samples of $Y_1Ba_2Cu_3O_{7-\delta}$ were used in this study. The samples are part of a single batch made at Naval Research Laboratory by Toth *et al.*,[6] pieces of which have undergone extensive characterization by neutron diffraction, x-ray analysis, electron microscopy, etc.[7] Every care has been taken to assure that these samples are typical. Nevertheless, we realize that the differences in grain boundaries, oxygen content, twins, etc. may occur from laboratory to laboratory. The resistivity was measured by the four-probe technique. Four gold strips, 200 nm thick, were sputtered on $\frac{1}{2}$ in. diameter $Y_1Ba_2Cu_3O_{7-\delta}$ disks. Gold wires, 5 mils in diameter, were connected to the gold strips by mechanical pressure. The specimen was then placed inside a furnace and slowly heated up in a constant oxygen flow. The rate of change of temperature was about 1–2 °C/min.

Figure 1 displays the temperature (T) dependence of the resistivity (ρ) of sample 1 as it is heated up from 77 to 800 K. The superconducting transition occurs at 90 K and is quite sharp, with a transition width less than 1 K. We observed a spike a fraction of a degree after the onset of the transition, a remnant of which is barely noticeable on the drawing. We observed the well-known low-temperature linear temperature dependence of the resistivity which, for this sample, has a slope $d\rho/dT \approx 4$ $\mu\Omega$ cm/K. Above 300 K the slope begins to increase with increasing temperature. The value of resistivity-temperature slope at 400 K is $d\rho/dT \approx 17$ $\mu\Omega$ cm/K for sample 1. Between 575 and 675 K, an anomaly is noted: The resistivity becomes practically independent of temperature. Above 700 K, the resistivity rapidly increases with increasing temperature.

As long as the temperature remains less than 500 K, the heating and cooling curves are identical. Whenever the sample is cycled above about 525 K, the ρ vs T curves become hysteretic, and the initial resistivity at room temperature is no longer identical to the room-temperature resistivity at the end of the cycle. The orthorhombic to tetragonal phase transition (at ~940 K) was never approached in these experiments.

Lee and Read[4] have postulated that the linear temperature relationship of the resistivity below room temperature can be explained by electron-electron scattering in a two-dimensional square lattice whose bands are nearly half-filled. They derived the equation for the low-temperature electron-electron scattering time as

$$1/\tau_{e-e} = \alpha k_B T/\hbar \ , \tag{1}$$

where α is proportional to the electron-electron interaction strength squared. Ignoring directional and energy

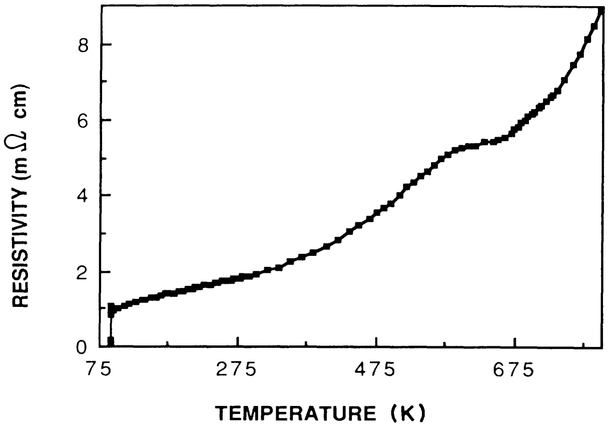

FIG. 1. Resistivity vs temperature curve for sample 1 during heating.

variation, the resistivity is given by

$$\rho=[N(E_F)e^2v_F^2]^{-1}(1/\tau) \ , \tag{2}$$

where $N(E_F)$ is the density of states at the Fermi level, and v_F is the Fermi velocity.

An alternate explanation, by Allen, Pickett, and Krakauer,[5] is that the electron-phonon scattering dominates, and the linear T dependence of the resistivity is a result of the high-temperature limit of the electron-phonon scattering lifetime $\tau_{e\text{-ph}}$,

$$1/\tau_{e\text{-ph}}=2\pi\lambda k_BT/\hbar \ , \tag{3}$$

where λ is the electron-phonon interaction constant. This formula applies for $T>\Theta_D$, where Θ_D is the Debye temperature. Besides the two theories singled out, many others flourish. In applying any of these theories, we ignore the effects of scattering at grain boundaries due to the fact that the mean free path of the electrons is much less than the grain size in these materials.[8] The measured resistivity of the polycrystalline samples represents an average[9] of the three principal directions of the orthorhombic crystal.

The increase in the slope $d\rho/dT$ above 300 K can be interpreted as a turn-on of the electron-phonon interaction which may dominate when the sample temperature exceeds the Debye temperature. Inderhees, Salamon, Friedmann, and Ginzberg[10] have fitted the lattice contribution of the heat capacity to a Debye specific heat with $\Theta_D\approx 440$ K. Below 300 K the Lee-Reed mechanism may dominate.

In Fig. 2, heating and cooling curves between room temperature and 800 K are shown for sample 2. The similarity of Fig. 2 to Fig. 1 demonstrates that the same physical mechanisms governing the electrical resistivity are present in both samples, even though sample 2 possesses higher resistivity (and by implication, to all 1:2:3 compounds with relatively high oxygen content). To avoid cluttering the figure, the cooling curve of sample 1 is not shown, but it strongly resembles the cooling curve of Fig. 2. The resistance anomaly in the heating curve of Fig. 2 is even more pronounced than in Fig. 1: The resistivity actually *decreases* as the temperature is increased around 675 K. The cooling curve of sample 2 contains no such anomaly, nor does the cooling curve of sample 1 display one. The temperature cycle was repeated several times on the same specimen, and the resistivity anomaly was reproducible. As shown in Fig. 2, the final room temperature resistivity upon cooling is less than the initial resistivity. As a matter of fact the final resistivity might be higher or lower than the initial value depending on the prior history of heat treatment and O_2 content.

A simple explanation of these phenomena is offered by combining the experimental thermogravimetric analysis (TGA) of $Y_1Ba_2Cu_3O_{7-\delta}$ with Eq. (2). Figure 3(b) (inset) shows the heating and cooling TGA curves of $Y_1Ba_2Cu_3O_{6.79}$ in O_2 at a rate of 1 °C/min obtained by Steinfink *et al.*[11] It is seen that O_2 content does not change until 225 °C, and the oxygen uptake during the warming curve *increases* around 325 °C. The cooling curve shows that the O_2 content of $Y_1Ba_2Cu_3O_{7-\delta}$ increases monotonically with decreasing temperature from 900 °C (where $\delta\sim 0.94$) to room temperature (where $\delta\sim 0.18$).

We now assume that the density of states at the Fermi level $N(E_F)$ is proportional to $[1-\delta(T)]$, the temperature-dependent oxygen content determined by TGA. Massidda, Yu, Freeman, and Koelling,[12] in a local density band structure calculation, determined that $N(E_F)$ is 1.13 states/eV Cu atom for $\delta=0$, $N(E_F)=0.87$ states/eV Cu atom for $\delta=0.1$, $N(E_F)=0.52$ states/eV Cu atom for $\delta=0.2$. Combining Eq. (2) with either Eq. (1) or Eq. (3), we obtain

$$\rho=A[T/N(E_F)]=AT/[1-\delta(T)] \ , \tag{4}$$

where A is a constant. Figure 3(a) displays Eq. (4) using Steinfink *et al.*'s TGA data. Steinfink used a rate of heating and cooling equal to that used in our resistivity mea-

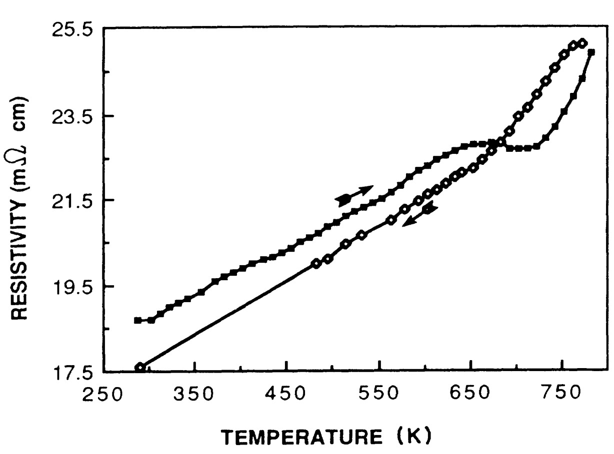

FIG. 2. Resistivity vs temperature curves for sample 2 during heating and cooling, displaying hysteretic behavior due to changes in the oxygen content.

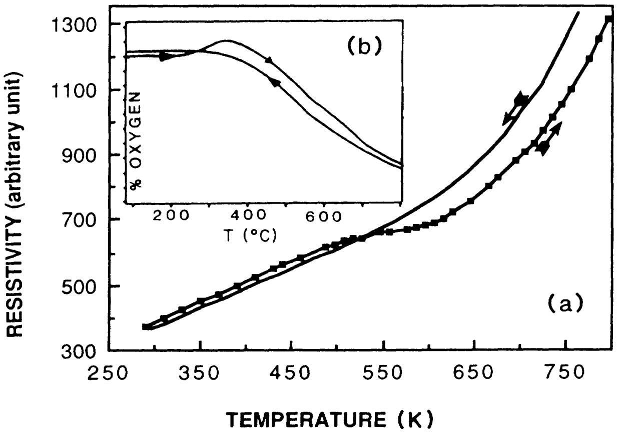

FIG. 3. (a) Graph of $T/[1-\delta(T)]$ vs T, which can be compared to Fig. 2 as explained in the text. (b) Oxygen content determined by thermogravimetric analysis under oxygen at a rate of 1 °C/min. Heating and cooling curves are shown. Data taken from Ref. 11 by permission of the authors.

surements. It reproduces all the features shown in Figs. 1 and 2, including the resistivity anomaly in the warming curve, the hysteresis in resistivity during temperature cycling, and the absence of the anomaly in the cooling curve. The rapid increase of resistivity above 700 K is due to oxygen loss.

The hysteresis observed at higher temperature in both TGA and resistivity data is most probably a kinetic effect which can be minimized by sweeping the temperature at a much slower rate. The small resistivity minimum at about 650 K might possibly be caused by ordering of oxygen atoms; however, the order-disorder transition temperature in flowing oxygen is about 1000 K. Even so, oxygen ordering can still play some part, but the maximum in oxygen uptake at 650 K appears to be the most probable cause.

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