



STRUCTURAL AND ELECTRONIC ANISOTROPY IN POLYCRYSTALLINE COMPACTIONS OF THE HIGH- T_c SUPERCONDUCTOR
 $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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X-ray diffraction studies show that simple cold-pressing of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ polycrystalline compactions, as practiced by numerous researchers, leads to very large microstructural anisotropy, with the crystallographic c axis preferentially oriented parallel to the axis of pressing. As shown by variable-temperature resistivity and thermoelectric power measurements, the direction of greatest metallic character at temperatures above the superconducting transition temperature is that perpendicular to the pressing direction, i.e., that parallel to the direction in which the $(\text{CuO})_n$ sheets and chains are preferentially oriented. Both $\rho(T)$ and $S(T)$ are only weakly temperature-dependent, with the transition to the superconducting state taking place in both measurements over a slightly narrower temperature range in the perpendicular direction. Above T_c , the $S(T)$ data are positive and give no obvious evidence for phonon-drag or precursor phenomena. A tentative analysis using a Hubbard/Heikes approach yields an average copper oxidation state in good agreement with experiment.

1. Introduction

The recent advent of mixed-metal oxides such as $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Ln = lanthanide) having superconducting transition temperatures in excess of 90 K^{1-5} has stimulated intense excitement and activity in the scientific community. Key questions concern the relationship between charge transport/charge transport mechanism(s) and crystal and electronic structure. Since the vast majority of physical measurements to date have been performed on polycrystalline compactions (of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$), further questions of general relevance to all low-dimensional superconductors and metals arise concerning how single crystal charge transport properties are modulated by the poorly understood nature of the polycrystal microstructure. In this communication we report studies of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ which reveal very large and heretofore unrecognized microstructural anisotropy in simple cold-pressed polycrystalline compactions of this high- T_c superconductor. We report the magnitude and temperature dependence of the accompanying anisotropy in electrical conductivity and thermoelectric power. These data also represent, to our knowledge, some of the first detailed charge transport information for a $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic where $\text{Ln} \neq \text{Y}$.

2. Experimental

Polycrystalline samples of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ were prepared from mixtures of the metal oxides heated to 930°C following the general synthetic procedure that has been described previously.⁶ The dark blue powder that was obtained was then cold-pressed (8-10 tons on a ring press) into circular disks (1 cm diameter, 3-5 mm thickness). The disks were reheated to 930°C in an oxygen atmosphere, slowly cooled to 550°C , and then quenched in air. Rectangular specimens of dimensions $3 \times 5 \times 3 \text{ mm}$ were cut from the disks with a high speed diamond-tipped circular blade. X-ray diffraction patterns were obtained on a Rigaku Geigerflex instrument using Ni-filtered $\text{CuK}\alpha$ radiation. Experiments were performed with the incident beam scattered from specimen faces which were parallel or perpendicular to the direction of the pressing axis.

Four-probe resistivity measurements were performed on the above samples with $60 \mu\text{m}$ gold wire contacts held in place with gold paste. Pairs of sample specimens were cut from the same pressed disk and mounted so that current flow was parallel to the pressing direction in one sample and perpendicular in the other. Reproducibility between different pairs of specimens was within experimental error. Resistivity data were acquired and processed on a computer-automated transport system using ac measurement techniques described elsewhere.^{7,8} Thermoelectric power (TEP) measurements were performed on

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the above specimens using a slow ac technique (10^{-2} Hz) and thermal gradients of 2 K.⁸ A conventional sample geometry was employed with gold wire contacts. Data acquisition and analysis utilized the aforementioned automated system.

3. Results and Discussion

Figure 1 shows X-ray diffraction patterns

and below the superconducting transition temperature. Resistivity data parallel to and perpendicular to the pressing axis are shown for a typical sample in Figure 2. Above T_c , it can be seen that the magnitude of the resistivity in the perpendicular direction is ca. 50% that in the parallel direction. That the direction of lowest specimen resistance (perpendicular to the pressing axis) is perpendicular to the preferential orientation of the crystallite c axis is

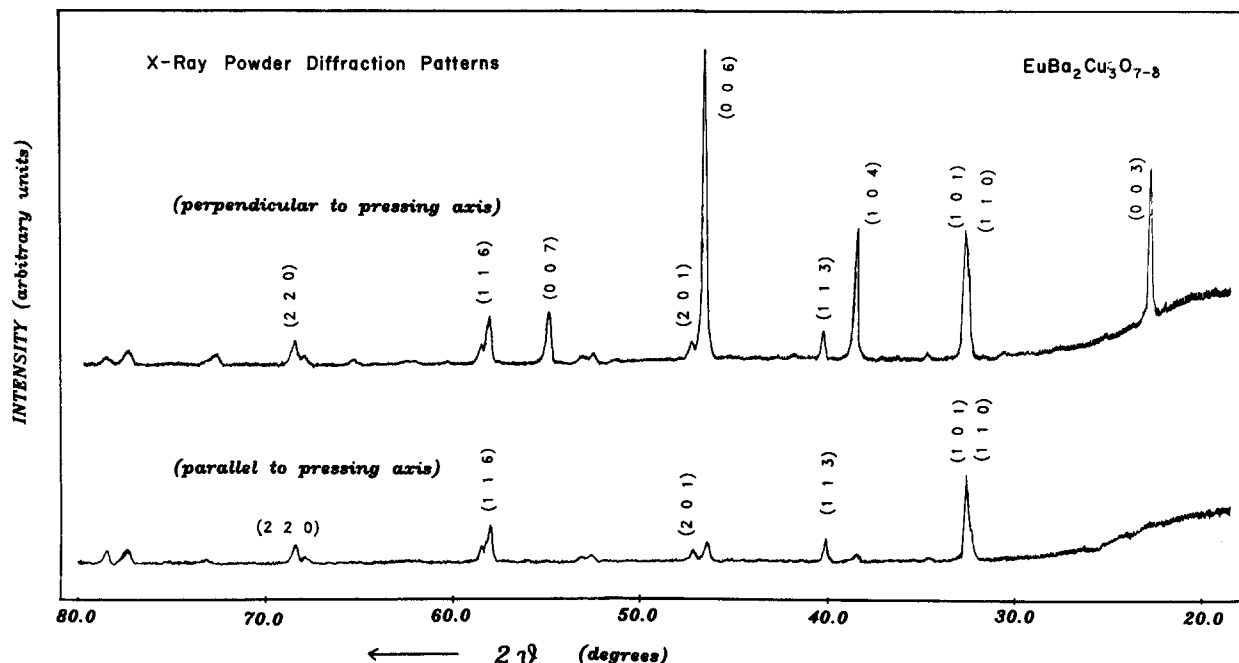


Fig. 1. X-ray diffraction patterns of a cold pressed polycrystalline $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample recorded on faces perpendicular to (top) and parallel to (bottom) the pressing axis. The diffraction lines are indexed according to an orthorhombic cell with lattice parameters $a = 3.820$ Å, $b = 3.884$ Å, and $c = 11.681$ Å.

of cold-pressed polycrystalline $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compactions with the incident beam scattering off faces perpendicular to and parallel to the pressing axis. The basic pattern can be indexed in an orthorhombic cell with lattice parameters $a = 3.820$, $b = 3.884$, and $c = 11.681$ Å.^{9,10,11} Particularly noteworthy is the dramatic enhancement in the intensity of the (001) reflections for the sample face perpendicular to the pressing axis. In contrast, the (001) reflections have virtually disappeared for the sample face parallel to the pressing direction. These results strongly suggest that almost complete crystallite orientation can occur by simply cold-pressing the powder samples. This is consistent with the plate-like character of the microstructure with the c axis perpendicular to the plate planes. A more quantitative analysis of these data is in progress.

The effect of the cold pressing on the $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ transport properties was examined by studying the conductivity and thermoelectric power as a function of temperature, both above

in agreement with other recent theoretical^{12,13} and experimental^{14,15} evidence that charge transport in the Ln-Y materials occurs primarily via the $(\text{CuO})_n$ sheets and/or chains perpendicular to c . It can also be seen in Figure 2 that both $\rho(T)_\parallel$ and $\rho(T)_\perp$ evidence slightly activated behavior ($d\rho/dT < 0$) prior to the onset of T_c . In the absence of other information, the *a priori* assignment of intrinsic activated behavior for such types of samples is unwarranted. For example, low-dimensional materials such as $\text{H}_2(\text{Pc})\text{I}$ ¹⁶ exhibit activated $\rho(T)$ for polycrystalline compactions^{17,18} and yet distinctly metallic $\rho(T)$, ($d\rho/dT > 0$) for single crystal measurements over the same temperature range.^{16,18} Thermoelectric power (*vide infra*), which is a zero-current measurement, is far less susceptible to such interparticle effects.^{18,19,20} For example, $S(T)$ data for single crystal and polycrystalline samples of $\text{H}_2(\text{Pc})\text{I}$ are nearly superimposable.^{18,19}

Charge transport parameters relating to the $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconducting transition are

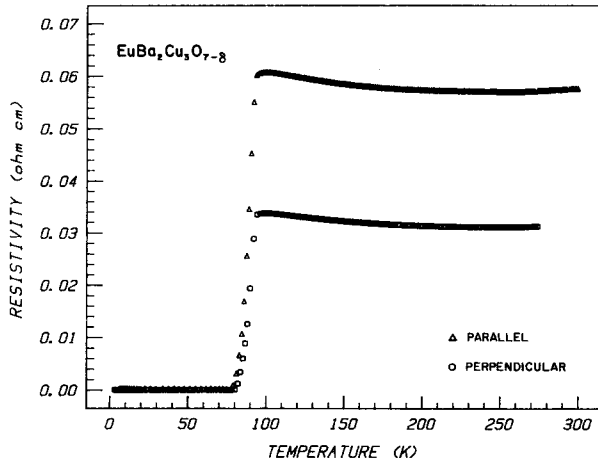


Fig. 2 Variable-temperature four-probe electrical resistivity data for a cold-pressed polycrystalline $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample measured with the current flow parallel to (top) and perpendicular to (bottom) the pressing axis.

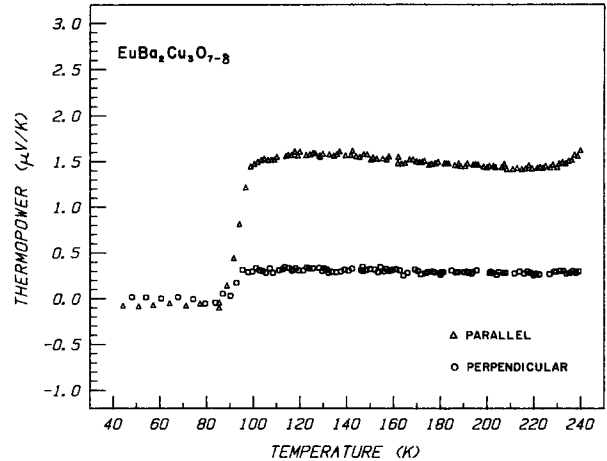


Fig. 3 Variable-temperature thermoelectric power data for a cold-pressed polycrystalline $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample measured in the direction parallel to (top) and perpendicular to (bottom) the pressing axis. Data are drawn relative to the thermopower of gold. Including a correction for gold above the transition would raise each plot by ca. $1 \mu\text{V/K}$ and introduce a very slight positive slope.

compiled in Table I. The present data are in reasonable agreement with the limited information available on similar materials,^{2,3} and variations in $\rho(T)$ values can be ascribed to slight differences in stoichiometry and sample processing procedures. An interesting feature of the present T_c data is the reproducible observation that the midpoint temperature and the temperature at which $\rho(T)=0$ is higher in the direction perpendicular to the pressing direction, i.e., parallel to the crystallite $(\text{CuO})_n$ planes/chains. In addition, the overall temperature range from onset to $\rho(T)=0$ is narrower in this same $(\text{CuO})_n$ direction.

Thermoelectric power data both parallel to and perpendicular to the pressing direction are shown in Figure 3, plotted relative to gold.

Parameters relating to the superconducting transition are set out in Table I. Several features in the data are particularly noteworthy. First, the data above T_c again evidence a marked anisotropy, with the lowest (most metallic) $S(T)$ in the $(\text{CuO})_n$ direction. The widths of the $S(T)$ transitions and the anisotropy thereof are significantly diminished from the $\rho(T)$ data. This is consistent with the tendency of the zero-current TEP data to be less affected by interparticle effects. Above T_c , the data in both directions are positive, indicative of p-type carriers, and vary only weakly and monotonically with temperature. There is no

Table I. Superconducting Transition Data for $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Polycrystalline Compactions

Measurement	Orientation with Respect to Pressing Axis	T_c^{onset} (K)	mid T_c (K)	$\rho=0$ ($s=0$) T_c (K)	T_c^{onset} ρ ($\Omega \text{ cm}$)	T_c^{onset} S ($\mu\text{V/K}$)
$\rho(T)$	perpendicular	94.3	87.2	80.0	0.034	
	parallel	95.3	85.1	76.9	0.061	
$S(T)$	perpendicular	95.3	91.4	86.8		0.31 ^a
	parallel	96.6	90.1	85.4		1.21 ^a

^a $S(T)$ values relative to gold.

evidence in these data for the abrupt phonon-drag/precursor temperature dependencies reported in some $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ TEP investigations,²¹⁻²⁵ nor of $S(T) < 0$ reported in one study.²²

It is not clear at this stage whether there are fundamental differences in $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ transport processes, nor indeed whether a classical uncorrelated wide-band description is appropriate in either system. If the weak temperature dependence of $S(T)$ is associated with a regime in which (in the high temperature limit) the bandwidth is less than kT which is in turn less than the on-site Coulomb repulsion,²⁵⁻²⁷ then within the Hubbard model, a modified Heikes treatment²⁶⁻²⁹ leads to eq. (1)

$$S = - \frac{k}{|e|} \ln \frac{2(1-\rho)}{\rho} \quad (1)$$

where ρ here is the number of electrons per Cu site. From the data in Figure 3, this relationship leads to $\rho \approx 0.67$, or that the average Cu oxidation state is +2.33. Interestingly, this conclusion is supported by chemical analyses on similarly prepared materials which place δ between 0.1 and -0.19,³⁰ and ^{151}Eu Mössbauer data,³⁰ which clearly indicate that Eu is in the trivalent oxidation state. These considerations indicate that $0.60 < \rho < 0.75$, or that the average Cu oxidation state is in the range 2.26-2.40. Recent measurements of the $\text{Cu}^{+2}/\text{Cu}^{+3}$

ratio in various $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples place the Cu oxidation state in the same range.³¹

4. Conclusions

The present results on $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ show that substantial microstructural anisotropy is achieved in the simple types of polycrystalline $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compactions currently under investigation in numerous laboratories. This leads to significant sample anisotropy in both electrical conductivity and thermoelectric power (but less than under more drastic processing conditions³²), with the most "metallic" direction being that parallel to the direction in which the $(\text{CuO})_n$ sheets and chains are preferentially oriented (perpendicular to the pressing direction). Above T_c , both $\rho(T)$ and $S(T)$ exhibit rather weak temperature dependencies. While the exact nature of the transport mechanism remains unresolved, it is noteworthy that above T_c , a Hubbard/Heikes treatment of the nearly temperature-independent thermopower data yields a Cu oxidation state in good agreement with experiment. These results also raise the question of whether there may be subtle variations in $\text{LnBa}_2\text{Cu}_3\text{O}_{7-\delta}$ transport characteristics as a function of Ln. Further experiments are in progress to address these issues.

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