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Electronic anisotropy in single-crystal La_2CuO_4

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We have measured resistivity ρ components both parallel and perpendicular to the Cu-O planes in single-crystalline La_2CuO_4 . Substantial anisotropy, reaching values as large as 10^3 , is observed in the resistivity. The temperature dependence of ρ , together with Hall effect and thermoelectric power measurements, suggests hopping conduction between localized states at low temperatures, with diffusive transport at higher temperatures. These results are in contradistinction to previous reports.

The crystal structure of the compound La_2CuO_4 , which consists of layers of Cu-O and La-O planes, suggests that crystallographic anisotropy could play an important role in determining the physical properties of this material¹ and related superconducting compounds in which divalent atoms are substituted for La. Indeed, the magnetic susceptibility of La_2CuO_4 has been found¹ to vary by a factor of 3 depending upon the magnetic field direction with respect to the planar structure. However, recent measurements² of the electrical resistivity surprisingly showed little evidence for anisotropic transport. The temperature dependence of the resistivity found in that study follows a $\ln\rho \propto T^{-1/4}$ variation between roughly 300–10 K. Such behavior is characteristic of conduction by variable-range hopping.³ In this Rapid Communication, we report electrical resistivity components of single crystalline La_2CuO_4 both parallel and perpendicular to the Cu-O planes. Contrary to earlier reports,² we find that the resistivity is highly anisotropic and that the temperature dependence is not that of simple, uncorrelated variable-range hopping and also not that expected⁴ of a resonating-valence-bond state which has been suggested⁵ as a mechanism for superconductivity in La_2CuO_4 -based materials.

La_2CuO_4 crystals ($\sim 1 \times 1 \times 0.1 \text{ cm}^3$) were grown from a PbO-based flux. Lattice constants were determined by the eight-position Hamilton technique⁶ using ten reflections with $29^\circ < \theta < 37^\circ$. These x-ray measurements indicated the orthorhombically distorted K_2NiF_4 structure at room temperature with lattice constants $a = 5.358 \pm 0.002 \text{ \AA}$, $b = 13.181 \pm 0.007 \text{ \AA}$, and $c = 5.403 \pm 0.002 \text{ \AA}$ (volume = 379.26 \AA^3). Wet chemical analyses gave a composition of $\text{La}_{1.75}\text{CuO}_{4.3}$ plus ~ 2 at. % Pb for the crystals studied. The presence of Pb and excess oxygen may be associated in part with PbO flux at the sample surface; however, this cannot account for all the oxygen excess.

The electrical resistivity was determined on specimens with well-defined geometry by both the Montgomery method⁷ and a standard four-terminal configuration. Electrical connection to the crystals was made by pressing indium-coated fine copper wires into indium pads on the sample. The contact arrangements used are shown in Fig. 1. For the Montgomery configuration [Fig. 1(a)], current and voltage probes extend along sample edges containing the Cu-O planes. The electrical *resistance*, defined as the

ratio of voltage produced per applied current, was measured with the current parallel and subsequently perpendicular to the Cu-O planes. The resistance versus temperature determined in this way is displayed in Fig. 2.

These data have been analyzed using the procedure described in Ref. 7 to evaluate the *resistivity* parallel (ρ_{\parallel}) and perpendicular (ρ_{\perp}) to the Cu-O planes. (Because our crystals are twinned in the Cu-O plane, we have assumed isotropic resistivities in those planes and, therefore, use loosely the terminology "single crystal.") Results of this analysis are shown in Fig. 3 and values of ρ_{\parallel} and ρ_{\perp} at selected temperatures are given in Table I for one specimen. Several crystals from two different batches were measured and values of ρ_{\parallel} and ρ_{\perp} agreed with those given in Table I within a factor of 2. To check for possible artifacts introduced by the analysis procedure, the resistivity parallel to the Cu-O planes was measured directly using the lead configuration shown in Fig. 1(b). For highly anisotropic conduction, current and voltage contacts ideally

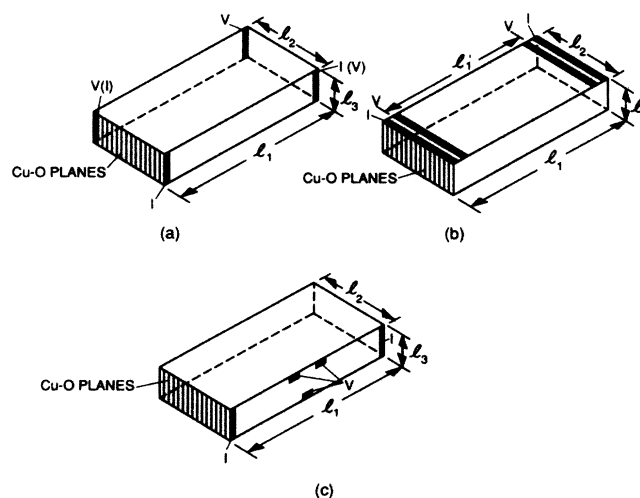


FIG. 1. Contact configurations used to measure the electrical resistivity of La_2CuO_4 using (a) the Montgomery method, (b) the conventional four-terminal method, and (c) the Hall constant. Relevant dimensions are (a) $l_1 = 0.222 \text{ cm}$, $l_2 = 0.016 \text{ cm}$, $l_3 = 0.061 \text{ cm}$; (b) $l_1 = 0.305 \text{ cm}$, $l'_1 = 0.161 \text{ cm}$, $l_2 = 0.034 \text{ cm}$, $l_3 = 0.045 \text{ cm}$; and (c) $l_1 = 0.265 \text{ cm}$, $l_2 = 0.016 \text{ cm}$, $l_3 = 0.036 \text{ cm}$.

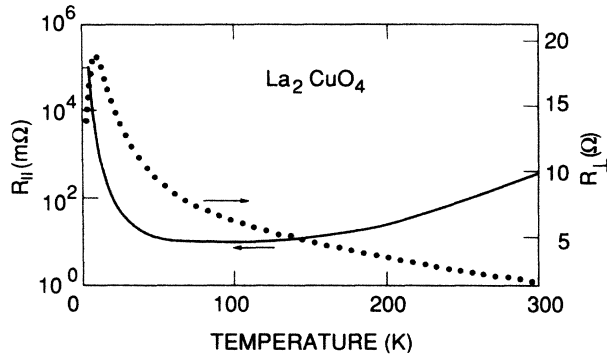


FIG. 2. Electrical resistance of La_2CuO_4 measured parallel (R_{\parallel}) and perpendicular (R_{\perp}) to the Cu-O planes with the contact configuration shown in Fig. 1(a).

should extend around the perimeter of the sample; however, because of the small sample dimensions, this configuration could not be achieved. In spite of this experimental difficulty, resistivity values obtained using the configuration in Fig. 1(b) are in reassuringly good agreement with those determined by the Montgomery method (see Table I for a comparison). We point out the importance of a proper analysis of the measurements and the distinction between resistance and resistivity in a highly anisotropic sample. For example, $R_{\parallel}(300)/R_{\parallel}(77) \approx 31$ but $\rho_{\parallel}(300)/\rho_{\parallel}(77) \approx 1.6$; further, there is a peak in R_{\perp} at low temperatures but no peak in ρ_{\perp} .

The Hall effect was measured using the contact configuration shown in Fig. 1(c). At room temperature the measured Hall constant $R_H = 1.15 \times 10^{-9} \text{ } \Omega \text{ cm/G}$ (positive) leads to a hole carrier concentration in the Cu-O plane of

$$n = 1/R_H e c = 5.44 \times 10^{19} / \text{cm}^3 \quad (1)$$

within the framework of a single carrier description. Only a weak temperature dependence has been observed between 300 and 60 K; below this temperature reliable data

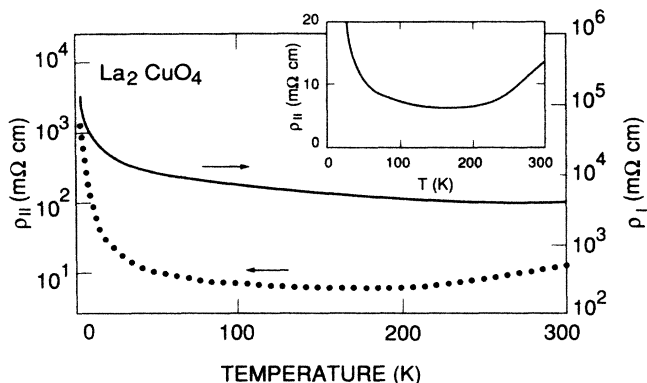


FIG. 3. Electrical resistivity of La_2CuO_4 , deduced from the resistance data of Fig. 2 using the Montgomery method, parallel (ρ_{\parallel}) and perpendicular (ρ_{\perp}) to the Cu-O planes. Note the difference in magnitude of the two vertical scales. The inset shows the high-temperature part of the parallel resistivity on a linear scale.

TABLE I. Resistivity parameters of La_2CuO_4 at selected temperatures.

T (K)	ρ_{\parallel} (m Ω cm)	ρ_{\perp} (Ω cm)	$\rho_{\perp}/\rho_{\parallel}$
300	14.1 ^a	4.2 ^a	298
	8.0 ^b		
77	8.6 ^a	9.1 ^a	1058
	4.3 ^b		
4	1230 ^a	119 ^a	96

^aMontgomery method.

^bStandard four-contact method.

have not been obtained because of large magnetoresistance and heating problems. However, at liquid-helium temperatures, we could estimate an upper limit for the Hall coefficient $R_H < 10^{-8} \text{ } \Omega \text{ cm/G}$.

In Fig. 4 we show the thermoelectric power S of La_2CuO_4 measured with a temperature gradient parallel to the Cu-O planes. At high temperatures S approaches a large, positive value consistent with a small number of holelike carriers responsible for entropy transport. Below about 50 K, S is proportional to the square root of temperature, as shown in the inset.

The small number of carriers estimated from Hall-effect measurements indicates that only approximately 0.5% of the available Cu sites are occupied by carriers (holes). The observed large thermopower also indicates conduction by a small number of carriers. Using the value for the carrier concentration given in Eq. (1) and the standard expressions

$$\sigma = ne^2 l / m v_F, \quad v_F = h(3\pi^2 n)^{1/3} / m, \quad (2)$$

where σ is the conductivity and v_F is the Fermi velocity, we estimate the room-temperature mean free path l to be 6.3 Å, a value comparable to the lattice constant a_0 . Perpendicular to the Cu-O planes the mean free path is ap-

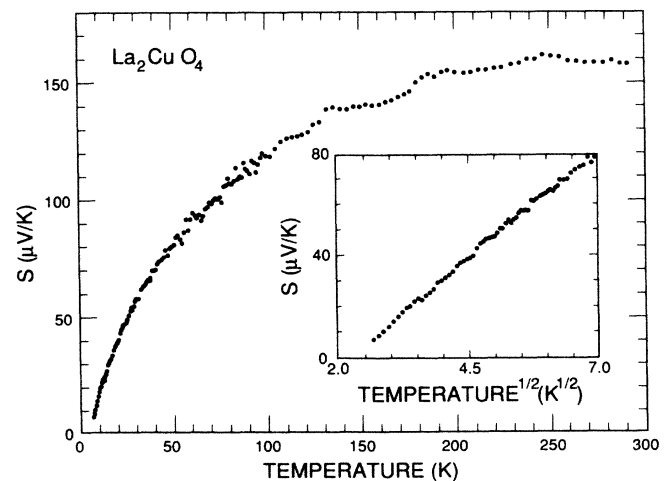


FIG. 4. The thermoelectric power S vs temperature measured in the Cu-O plane of La_2CuO_4 . The inset shows a linear variation of S with $T^{1/2}$ for $T \lesssim 50$ K.

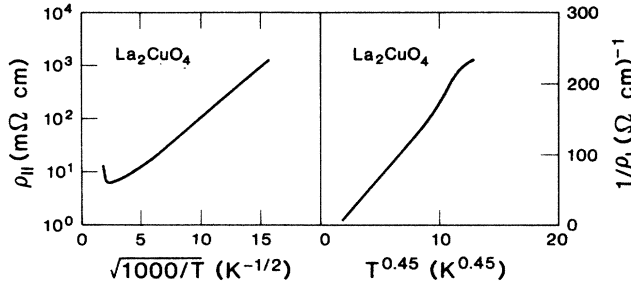


FIG. 5. Resistivity parallel to the Cu-O planes (ρ_{\parallel}) vs $\sqrt{1000/T}$ (left panel) and inverse resistivity perpendicular to the Cu-O planes ($1/\rho_{\perp}$) vs $T^{0.45}$ (right panel) for La_2CuO_4 .

proximately two orders of magnitude smaller than a_0 at room temperature if we assume the same number of carriers in this direction.

The short mean free path, small carrier concentration, and large room-temperature thermoelectric power together suggest that the parallel resistivity shown in Fig. 3 is not due to band (i.e., metallic) conduction at high temperatures with a gradual crossover to semiconducting behavior at lower temperatures but more likely represents diffusive conduction at high temperatures and hopping between localized states at lower temperatures. The Einstein relation

$$\mu = eD/k_B T, \quad (3)$$

where μ is the mobility and D the diffusion constant, predicts the observed temperature variation of the parallel resistivity [$\rho_{\parallel} \propto T$ (Ref. 8) at high T , see Fig. 3, inset] assuming a weakly temperature-dependent diffusion constant. Below approximately 30 K the temperature dependence of ρ_{\parallel} is given by $\ln \rho_{\parallel} \propto T^{-1/2}$. See Fig. 5. For uncorrelated variable range hopping

$$\sigma \propto \exp[-(T_0/T)^{\alpha}], \quad (4)$$

where σ is the conductivity and $\alpha = \frac{1}{4}$ [$\frac{1}{3}$] for three-dimensional (3D) [two-dimensional (2D)] transport.³ Efros⁹ has argued that Coulomb correlations modify the exponent to $\alpha = \frac{1}{2}$ for 3D and 2D variable range hopping. The temperature dependence of the thermoelectric power (Fig. 4, inset) further supports this interpretation. In the case of variable range hopping, the thermoelectric power is predicted¹⁰ to vary as $S \propto \sqrt{T}$, as observed below 40 K. Therefore, the temperature variation of ρ_{\parallel} can be understood as arising from strongly correlated variable range hopping at low temperatures with a gradual transition to nearest-neighbor hopping and eventually to diffusive transport as the temperature is raised. One expects a progressive dimensional crossover as the average hopping distance $\langle R \rangle$ decreases with increasing temperatures. At low temperatures, where $\langle R \rangle$ is significantly larger than the lattice constants both in the Cu-O plane and perpendicular to the plane, the anisotropy is expected to be small; while at higher temperatures, where $\langle R \rangle$ approaches the nearest-neighbor distance, the anisotropic crystal struc-

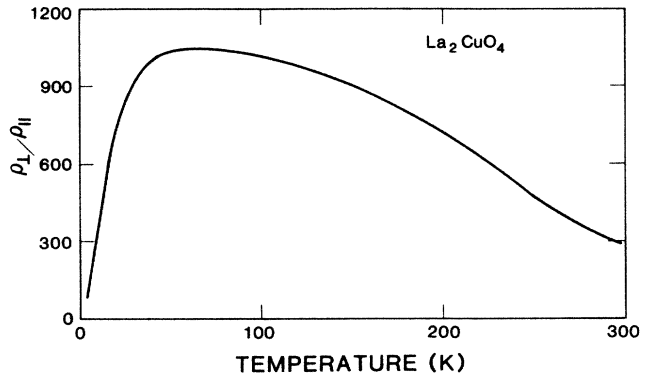


FIG. 6. The ratio of perpendicular to parallel resistivity in La_2CuO_4 as a function of temperature. Note that near 60 K ρ_{\perp} is over 1000 times larger than ρ_{\parallel} , but as $T \rightarrow 0$ the anisotropy approaches a small value.

ture plays a significant role and the hopping probability in the plane and perpendicular to the plane are different. This behavior is evident from the temperature dependence of the anisotropy $\rho_{\perp}/\rho_{\parallel}$ displayed in Fig. 6. The anisotropy is small in the variable range hopping (low-temperature) regime, approaches a maximum at $T \approx 60$ K, and then decreases slowly with increasing temperature. The broad minimum in ρ_{\parallel} represents a smooth crossover from nearest-neighbor hopping to diffusive transport at temperatures $k_B T$ comparable to the average energy difference between the nearest-neighbor energy levels.

Finally we discuss the results of Birgeneau *et al.*² who find $\ln \rho \propto (1/T)^{1/4}$ and a small anisotropy in a La_2CuO_4 crystal prepared from a $\text{Li}_4\text{B}_2\text{O}_5$ flux. Such an observation could arise from a relatively large Li impurity concentration or from a significantly different oxygen content in their crystals. Although the authors of Ref. 2 do not state explicitly the geometry of their lead configuration, we emphasize that careful attention to this matter and to a proper analysis of the measurement is essential. For example, the *resistance* parallel to the Cu-O planes (Fig. 2) at low temperatures behaves as $\ln R_{\parallel} \propto (1/T)^{1/4}$.

In conclusion, we find that electrical conduction in La_2CuO_4 is strongly anisotropic, with the resistivity in the Cu-O planes orders-of-magnitude smaller than that perpendicular to the Cu-O planes. Hall effect and thermoelectric power measurements suggest a small concentration of holelike carriers in the Cu-O plane. We interpret the temperature dependence of ρ_{\parallel} as a gradual crossover from variable range to nearest-neighbor hopping to diffusive transport as the temperature increases. Thermoelectric power data on the same specimens corroborate this interpretation.

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