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Thermal properties of single-crystal $La_2CuO_{4-\Delta}$

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We report measurements of the thermal conductivity, Raman spectrum, magnetic susceptibility, and specific heat of a single crystal of $La_2CuO_{4-\Delta}$ from room temperature down to 10 K. We observe a sharp kink in the heat conductivity near 250 K in the [001] direction and a broader anomaly in the range 130–200 K in the [110] direction. These features have been correlated, in terms of a strongly temperature-dependent phonon-magnon scattering mechanism, with changes in the magnetic structure as identified through susceptibility studies. These results differ substantially from experiments on sintered samples, which show a thermal conductivity more reminiscent of a tunneling system. It is suggested that the amorphouslike behavior of the sintered materials is an artifact of their rather poor crystalline nature, which masks the intrinsic effects associated with the single crystal as reported here.

Two years have passed since the first discoveries of superconductivity in ceramic oxides.[1] A question yet to be answered is whether the electron pairing which results in superconductivity is due to "standard" phonon mediation or another more exotic mechanism. Among the alternatives, electronic attraction via magnetic interactions has been suggested.[2,3] Indeed, it has been shown that superconductivity in the lanthanum-based materials seems to be intimately related to the magnetic state of the system.[4–6] Many other measurements[7–13] favor a strong electron-phonon interaction which could possibly produce the high transition temperatures of these compounds. Pure La_2CuO_4 is a semiconductor rather than a superconductor, but shares many similarities with its superconducting offspring, $La_{1.85}(Ba,Sr)_{0.15}CuO_4$. Study of single crystals eliminates problems such as grain boundaries, crystallite size effects, etc., which have significantly complicated the interpretation of data taken on sintered samples.

Here we report measurements of the thermal conductivity, specific heat, magnetic susceptibility, and Raman spectra of bulk single crystals of $La_2CuO_{4-\Delta}$ as a function of temperature. The magnetic properties of the crystals were characterized by temperature-dependent susceptibility, and the phonon properties by temperature-dependent Raman scattering and specific heat. Information gleaned from these can provide an explanation for our thermal conductivity results, in which both phonons and magnetic effects evidently play important roles.

The single crystal used in this study was fabricated at the MIT Crystal Physics Laboratory.[14] The inset to Fig. 1 is a schematic diagram indicating the crystal structure of the $La_2CuO_{4-\Delta}$ system. In the present (tetragonal) notation, the [001] axis of the orthorhombic structure is perpendicular to the copper-oxygen planes, and the [110] axis lies along the diagonal within a copper-oxygen plane. Spins localized on the copper sites exhibit three-

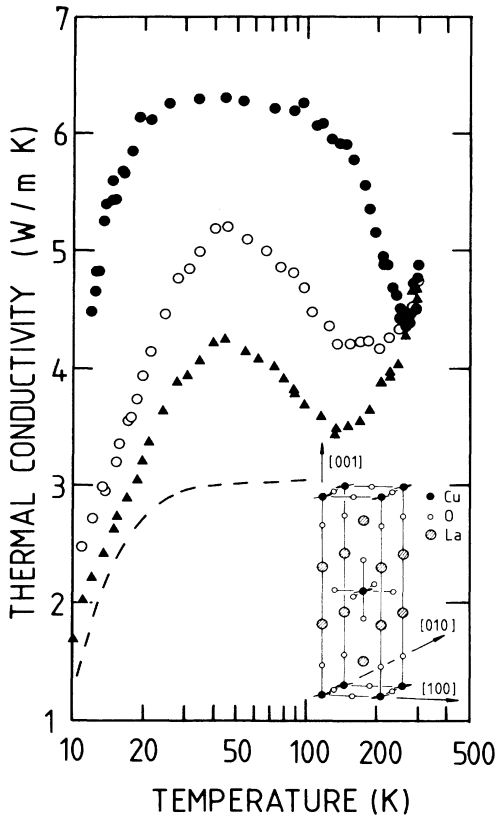

FIG. 1. Thermal conductivity of single-crystal $La_2CuO_{4-\Delta}$ for the heat flow $Q//[001]$ (top, closed circles), $Q//[221]$ (middle, open circles) and $Q//[110]$ (bottom, triangles). The dashed line represents results of Nunez-Regueiro *et al.* (Ref. 17) on a sintered sample. The inset shows a schematic diagram of $La_2CuO_{4-\Delta}$ in terms of the tetragonal coordinate system used in this paper.

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dimensional antiferromagnetic order below 300 K and 2D antiferromagnetic order above this temperature.[4] These moments are aligned with their axes almost parallel to the [110] axis, though there is a slight[15] out-of-plane antiferromagnetic canting. The [001] and [110] crystallographic axes were identified via Laue backscattering. The observed Laue patterns compare well with computer-generated Laue patterns calculated from the expected crystal structure of $La_2CuO_{4-\Delta}$, but exhibit strong evidence of twinning between the [110] and [1$\bar{1}$0] planes. The Laue patterns were taken from all sides of our crystal in order to verify its homogeneity and integrity.

Prior to cutting, the longest side of the sample was approximately ($\pm 4°$) along the [221] axis. We measured the thermal conductivity along that direction first. The sample then was cut in a parallelepiped of approximate dimensions $5\times7\times2$ mm^3, with the [001] and [110] axes parallel, within 3°, to the two longer dimensions. The thermal conductivity was measured in both the [001] and [110] crystal directions, i.e., both parallel and perpendicular to the copper magnetic-moment direction, using a steady-state technique, the details of which are described elsewhere.[8] The specific heat of our sample was measured from 10–300 K using a technique due to Fagaly and Bohn.[16] Susceptibility measurements were carried out at Michigan State University on the same sample that was used for the thermal measurements using a SHE Corporation susceptometer in vertical magnetic fields. The sample was oriented in the field with an accuracy of $\pm 7°$. The sample was cooled from room temperature to 5 K, both in zero field and in the maximum available field of 0.7 T. The data were taken during the subsequent warmups; both cooling cycles gave the same susceptibility to within the accuracy of the measurement. At 5 and 300 K the field dependence of the magnetic moment was studied for both field directions. Though we deliberately searched for hysteresis in these field sweeps we found none. Finally, Raman spectra were taken using 4880-Å and 5145-Å Ar^+ laser radiation in a classical backscattering configuration. The spectra were taken on a [100] polished face, with the incident and backscattered light polarized parallel to each other and to the tetragonal [001] axis.

Figure 1 shows the thermal conductivity of a single crystal of $La_2CuO_{4-\Delta}$ between 10 and 300 K in the [001], [110], and [221] directions. The latter is consistent with the values obtained along the principal axes. Also shown are results on sintered samples of $La_2CuO_{4-\Delta}$ (Ref. 17) in the same temperature range. In contrast with "low-T_c" metallic superconductors, in which most of the heat in the normal state is carried by electrons, high-T_c superconductors conduct heat mainly via lattice vibrations.[7–10] In single-crystal $La_2CuO_{4-\Delta}$, where the electrical resistivity is about 10^{-2} Ω m at room temperature,[18] we can use the Wiedemann-Franz law to verify that the electronic heat conduction contributes less than 2% to what we measure. We see no evidence for the conduction of heat by magnons: the peak in the thermal conductivity is close to 0.1 times the Debye temperature of the phonons. Furthermore, we measured the thermal conductivity at 300, 220, 130, and 110 K as a function of applied magnetic field up to 2 T (heat flow in [001] direction and field in [001] or [110] or [1$\bar{1}$0] directions, and heat flow in [110] direction and field in [001] or [110] or [1$\bar{1}$0] directions) and observed no field dependence to within about 0.1%. Were magnons the majority heat carriers, a strong field dependence should certainly have been observed.

We see in Fig. 1 that the single-crystal specimen has a higher thermal conductivity than the sintered version. Whereas the sintered specimen shows a plateau in the thermal conductivity above 30 K, which Nunez-Regueiro *et al.*[17] attribute to tunneling systems, the thermal conductivity of the single crystal in the [110] direction has a peak near 40 K in addition to a broad minimum which occurs between 130 and 200 K. The thermal conductivity in the [001] direction, in contrast, has a sharp minimum near 250 K. The 40-K peak indicates that the sample does indeed display crystalline character with respect to heat transport, but the additional rise in $\kappa(T)$ at higher temperatures is quite unusual. "Phonon absorption" such as that which occurs near 130 K in the [110] direction and at 250 K in the [001] direction has been observed in several charge-density-wave (CDW) and spin-density-wave (SDW) systems[19–21] and is accounted for by scattering of phonons by spins (or pseudospins in the case of CDW). It has been shown[4] that oxygen-deficient $La_2CuO_{4-\Delta}$ undergoes a transition to a three dimensionally ordered antiferromagnetic structure below room temperature. Our susceptibility results confirm this observation. We observe that χ shows a rather sharp maximum of 6×10^{-7} emu/g at 250 K for magnetic field along the [001] direction, perpendicular to the spin axis, with a plateau region at 3.7×10^{-7}emu/g from 200 down to 50 K. For magnetic field in the spin axis [110] direction, the maximum in χ occurs at 3.5×10^{-7} emu/g and 250 K, but is much broader, exhibiting a tail which extends down to 120 K; from 50 to 100 K, we find $\chi\simeq2.7\times10^{-7}$ emu/g. Thus the sharpness and broadness of the dips in the thermal conductivity in the [001] and [110] directions, respectively, are reproduced in the susceptibility data as well.

The zone-center Raman-active A_{1g} phonons at 430 cm^{-1} and 228 cm^{-1} were examined for temperatures extending from room temperature to $\sim$8 K. While these out-of-plane modes were found to slightly harden (the Raman frequency shifting about 2 cm^{-1} to higher values) and the Raman widths to narrow by about 14% at low temperature, no anomalous temperature dependence of either line was observed. To our knowledge, no anomalous temperature dependence of the Raman-active phonon modes of pure $La_2CuO_{4-\Delta}$ has been observed on other single-crystal samples.

The specific heat is shown in Fig. 2; we observe Debye-type behavior throughout the temperature range, with a T^3 behavior below 30 K. A small anomaly is perhaps evident at 150 K, but it is within the experimental error.

We associate the dips in the heat conduction with the magnetic transition in the lattice. A qualitative explanation of this behavior is the following: above the Néel temperature, the system exhibits no staggered magnetic moment,[4] and the disordered spins will scatter heat-carrying phonons at a rate which is essentially temperature independent, as Slack has proposed[22] for CoF_2. In this

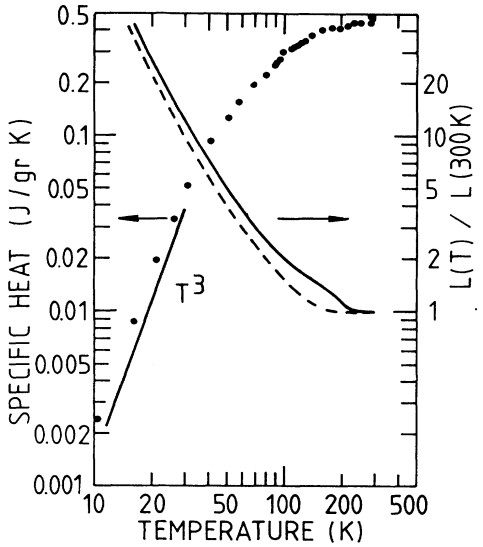

FIG. 2. Specific heat (left ordinate) of single-crystal $La_2CuO_{4-\Delta}$. The solid line indicates a T^3 dependence. The right ordinate shows the phonon mean free path L vs temperature, normalized to its value at 300 K, L is derived from thermal conductivity and specific-heat data for two directions of heat flow: $Q \| [001]$ (top, full line), and $Q \| [110]$ (bottom, dashed line). L (300 K) $\simeq$ 10 nm for each direction of Q.

paramagnetic state, the scattering by disordered spins will compete with phonon-phonon umklapp processes in determining the thermal resistance. Using the model of Roufosse and Klemens,[23] we estimate the umklapp-limited thermal conductivity of $La_2CuO_{4-\Delta}$ at the Debye temperature to be approximately 10 $W m^{-1} K^{-1}$, about twice as high as the observed value. Thus we assume that above the Néel temperature, the dominant scatterers of phonons are the disordered spins. Since the phonon-disordered spin scattering rate is essentially temperature and frequency independent, while the phonon density is still increasing (see Fig. 2), one would expect that the thermal conductivity above T_N will *rise* as the temperature increases, until finally being cut off by umklapp processes at some higher temperature (i.e., above 300 K). On the other hand, as one cools below T_N, the number of disordered spins decreases, and the phonon-spin scattering time will scale with the magnetic order parameter, which increases with decreasing temperature. Thus one expects that cooling below T_N will also cause the heat conduction to *rise*. In this picture, then, the minimum in the thermal conductivity is correlated with the ordering temperature. The comparative sharpness and broadness of the thermal conductivity minima in the [001] and [110] directions simply reflect the nature of the magnetic ordering in each antiferromagnetic sublattice. The widths in the thermal conductivity are correlated with the comparable widths in the susceptibility for fields in those two directions.

As a test of this hypothesis, we analyze our data using the kinetic expression for the thermal conductivity: $\kappa = \frac{1}{3} C_L v L$, where C_L is the lattice specific heat per unit volume, v is the phonon group velocity, and L the phonon mean free path. Detailed information on the phonon velocities for all three polarizations and propagation directions does not exist. However, neutron scattering results[24] indicate that there is little anisotropy, at least for the longitudinal modes. Transverse modes, being on the average slower, carry most of the heat, and we assume that they also show little anisotropy. We can thus use the average phonon velocity of $v = 4 \times 10^5$ $m s^{-1}$ (Ref. 24) and our experimental data for κ and C_L to calculate L from this formula. The results are shown in Fig. 2. We see that, indeed, in the magnetically disordered state, the mean free path is constant at approximately 10 nm for both propagation directions, which is on the order of the magnetic correlation length at this temperature.[4] As the sample is cooled below T_N, the mean free path rises as the magnetic lattice orders. The sharper magnetic transition in the [001] direction causes L to increase more rapidly in this direction than the [110] direction.

In conclusion, we have measured the thermal conductivity, specific heat, Raman scattering, and susceptibility of a single crystal of $La_2CuO_{4-\Delta}$ from room temperature down to 10 K. The specific heat shows Debye-type behavior with a T^3 dependence below 30 K. The thermal conductivity for a single crystal exhibits a peak at 40 K and an anomalous minimum at higher temperature. The latter anomaly has been correlated with a magnetic order-disorder transition in this material, and a model in which the heat-carrying phonons are scattered predominantly by spin waves is shown to be in accord with the results. This is strong support for a model in which the lattice modes in $La_2CuO_{4-\Delta}$ interact strongly with magnetic spin waves. The thermal conductivity of a single crystal also differs substantially from the conductivity measured on sintered samples, which was more reminiscent of a tunneling system.[17] It is suggested that the amorphouslike behavior of the sintered materials is an artifact of their rather poor crystalline nature, which masks the intrinsic effects reported here.

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