Soft-Phonon Behavior and Transport in Single-Crystal La_2CuO_4

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Using a flux technique, we have grown sizable single crystals of $La_{2-x}Sr_xCuO_4$. With x rays and neutrons we have studied both the static and dynamic aspects of the tetragonal-to-orthorhombic structural phase transition; classic soft-phonon behavior is observed at the $(\frac{1}{2},\frac{1}{2},0)$ zone boundary involving rotations of CuO_6 octahedra. The pure and lightly doped single crystals show hopping conductivity, $\ln\rho \sim (T_0/T)^{1/4}$, indicating that the electronic states at the Fermi energy are localized.

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The quarternary compound $La_{2-x}Sr_xCuO_4$ and related materials exhibit dramatic behavior with structural, antiferromagnetic, metal-insulator, and superconducting transitions.[1-3] The underlying physics and chemistry of these materials are manifestly quite rich and complex. Indeed, the explicit pairing mechanism responsible for the high-temperature superconductivity is still a matter of speculation.[4,5] To date, the vast majority of measurements reported on these materials have been on polycrystalline ceramics and thin films. Clearly, growth and characterization of high-quality single crystals are essential.

In this Letter we report our initial results on the growth and electronic properties of single-crystal $La_{2-x}Sr_xCuO_4$ together with x-ray and neutron scattering measurements of the static and dynamic behavior accompanying the tetragonal-to-orthorhombic (T-O) structural transition. Single crystals as large as 0.3 cm^3 in volume have been grown with use of a flux technique. From the sharpness of the second-order T-O transition and the agreement between x-ray and neutron measurements, we conclude that the single crystals are macroscopically quite homogeneous. These materials all exhibit hopping-conductivity behavior, $\ln\rho \sim (T_0/T)^{1/4}$, indicating that the electronic states at the Fermi energy are localized.[6] There is no signature of the T-O transition in the resistivity; this argues against any simple electronic mechanism for the transition.[5] Inelastic-neutron-scattering measurements reveal prototypical soft-mode behavior at the T-O transition; the condensed phonon mode remains soft down to low temperatures. We discuss first the crystal growth.

Because of its high peritectic melting temperature of 1640 K, it is very difficult to grow single-crystal La_2CuO_4 from stoichiometric melts. Therefore, we have investigated various flux growth techniques to lower the temperature at which the material can be grown. We have found that $Li_4B_2O_5$ at approximately 50 mol% of the melt with stoichiometric $La_{2-x}Sr_xCuO_4$ crystallizes the K_2NiF_4 phase at a satisfactorily low temperature. Accordingly, with the use of La_2O_3, CuO, $SrCO_3$, Li_2CO_3, and B_2O_3 as starting materials, a large crucible with a melt of 50 mol% $La_{2-x}Sr_xCuO_4$ and 50 mol% $Li_4B_2O_5$ was seeded with a Pt wire at $\simeq 1425$ K. With very low cooling and pulling rates, platelike crystals as large as $15\times20\times1$ mm^3 could be obtained; the *c* axis is in the narrow growth direction. Comparison with T-O transition temperatures and transport data in the ceramics suggests that the amount of Sr incorporated into the single crystal is an order of magnitude less than that in the melt. Some Li^+ from the flux is probably also incorporated into the single crystals. However, both transport and structural data suggest that the amount of Li in our crystals is small.

Neutron-scattering experiments were performed on the H7 triple-axis spectrometer at the Brookhaven National Laboratory high-flux beam reactor. A variety of spectrometer configurations were used in order to optimize each individual measurement. X-ray measurements were carried out at the Massachusetts Institute of Technology with use of a triple-axis spectrometer with perfect Si monochromator and analyzer. Samples of $La_{2-x}Sr_xCuO_4$ with $x=0$, 0.02, and 0.05 were studied.

Our results for all three samples are quite similar. We therefore discuss in detail here only the data for La_2CuO_4. As has already been discussed extensively elsewhere,[2] La_2CuO_4 exhibits a tetragonal (space-group *I4/mmm*) to orthorhombic (space-group *Cmca*) displacive structural transition at temperatures as high as $\simeq 533$ K. There are two equivalent displacement wave vectors $\{\mathbf{q}_x\} \equiv \frac{1}{2}(1,\pm1,0)$, and the distortions are predominantly staggered rotations in the *x-y* plane perpendicular to $\{\mathbf{q}_x\}$. The structural transition temperature itself depends sensitively on the stoichiometry of the ma-

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terial. In our La_2CuO_4 crystals, the T-O transition occurs at 432 ± 1 K. For simplicity we use tetragonal crystallographic nomenclature. Below $T_c = 423$ K, we observe at a relative intensity level of 10^{-5} or greater only those additional reflections $(h/2,k/2,l)$ predicted for the orthorhombic *Cmca* space group. We show in Fig. 1 the integrated intensity of the $(\frac{3}{2},\frac{3}{2},2)$ superlattice reflection as a function of temperature. It is evident that the crystal exhibits a sharp, apparently second-order, phase transition. As shown in Fig. 1, the intensity data are well described by a single power law $I \simeq (423 - T)^{0.55 \pm 0.08}$, and since the intensity scales as the square of the order parameter, this gives $\beta = 0.275 \pm 0.04$. This transition should be in the universality class of the 3D *XY* model with fourfold anisotropy for which one expects asymptotically $\beta = 0.35$. We do not regard this disagreement as significant since the corrections to scaling should be large and the measurements do not extend very close to T_c.

Using Landau theory, we expect that near T_c the orthorhombic strain $a-b$ should scale like the square of the order parameter; equivalently $a-b$ should scale linearly with the superlattice intensity. We have measured the strain precisely using x rays on a separate La_2CuO_4 crystal cut from the same boule as that used in the neutron measurements. These data are also shown in Fig. 1; to compare the two sets of data, only the vertical scale has been adjusted. It is evident that the two measurements agree very well. It should be noted that the x rays probe only the outer 6 μm of the crystal. The data in Fig. 1 thence show that these crystals are quite homogeneous. As indicated in Fig. 1 there is a weak tail above $T_c = 423$ K. Indeed, a very weak but sharp "central peak"[7,8] at the superlattice position persists up to at least 500 K.

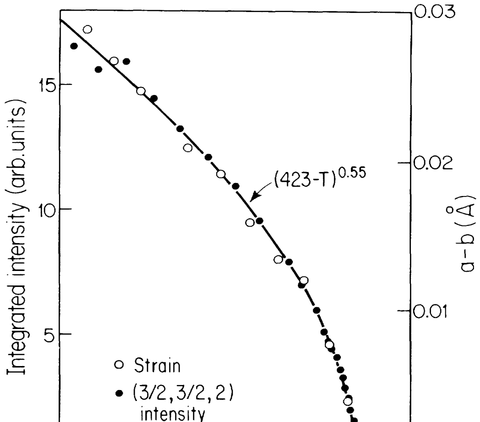

FIG. 1. $(\frac{3}{2},\frac{3}{2},2)$ superlattice peak intensity in La_2CuO_4 measured with neutrons, together with the orthorhombic strain, $a-b$, measured with x rays in a separate crystal from the same boule. The vertical scales have been adjusted to agree on average. The solid line is the best-fit power law as discussed in the text. The room-temperature orthorhombic lattice constants are 5.386, 5.350, and 13.145 Å.

We have carried out an extensive study of the low-lying phonon modes. In this Letter we present results for the $(\zeta,\zeta,0)$ direction; these are the most important since the T-O instability[2] occurs at the *X* point, $(\frac{1}{2},\frac{1}{2},0)$. Similar but more limited data have been obtained in the $(\frac{1}{2},\frac{1}{2},\xi)$ direction. The crystal was mounted with the $(1,\bar{1},0)$ axis vertical. The dispersion relations for the lowest-energy phonons accessible in this plane are shown in Fig. 2. Most of the measurements were made at $\simeq 423$ K; however, except for the soft mode near $(\frac{1}{2},\frac{1}{2},0)$ the phonon energies are only weakly temperature dependent. We note first that the TA and LA modes exhibit conventional behavior with no evidence for the breathing-mode instability predicted near the *X* point.[4] Instead, we observe a low-lying optical mode at $\simeq 11$ meV which exhibits classical soft-mode behavior at the *X* point at $T_c = 423$ K.

Representative scans at the point (3.05/2,3.05/2,2) at several temperatures are shown in Fig. 3. It is evident that the mode, which is broad above T_c, softens and becomes overdamped as the temperature is decreased. At the position $(\frac{3}{2},\frac{3}{2},2)$ there is also a sharp $E = 0$ central peak which grows in intensity as T_c is approached. Closely similar behavior is seen at the analogous phase transitions in $SrTiO_3$ and $LaAlO_3$, although there are some differences in detail.[7,8] This "central peak" aspect of the transformation requires further study. By using compatibility relations obtained from Weber's calculations[4] and from measured phonon intensities, we con-

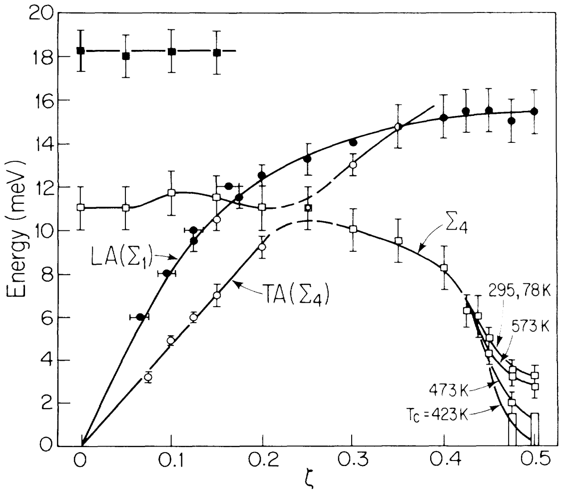

FIG. 2. Phonon dispersion curves in the $(\zeta,\zeta,0)$ direction in La_2CuO_4. The mode labeling is from Ref. 4. The dispersion curves are only weakly temperature dependent, except near $(\frac{1}{2},\frac{1}{2},0)$ as indicated. The solid lines are visual guides.

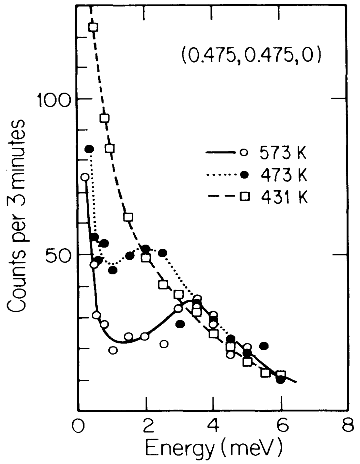

FIG. 3. Scans at (3.05/2,3.05/2,2) corresponding to (0.475,0.475,0) at various temperatures. The lines are visual guides.

clude that the soft mode is the Σ_4 optical-phonon mode whose eigenvector corresponds closely to the displacements observed in the orthorhombic phase.[2] As indicated in Fig. 2, below T_c the soft mode becomes underdamped with the orthorhombic-zone-center $(\frac{3}{2},\frac{3}{2},2)$ energy increasing to $\simeq 3.2$ meV. The soft mode has the same symmetry as the TA mode and, hence, should exhibit anticrossing behavior[4]; the coupling must, however, be weak since any consequent splitting is below our resolution. Similar soft-mode behavior is found in the Sr-doped crystals.

None of the crystals studied with neutrons is metallic, as a result of localization effects; their electronic transport properties are, nonetheless, illuminating. Plotted in Fig. 4 are four-probe resistivity data for four samples. The first is a ceramic of pure La_2CuO_4 which had been annealed in Ar at 675 K for 30 min. It should be noted that this same ceramic on oxygenation had zero resistance at 38 K. The second and third are single crystals of La_2CuO_4 grown from melts with different $Li_4B_2O_5$ and La_2CuO_4 ratios. One of these (triangles) is from the same boule as the crystal used for the neutron-scattering studies. The last is the same crystal of $La_{1.98}Sr_{0.02}CuO_4$ studied with neutrons; for this sample, the resistivity was measured along both the (100) and (001) directions.

The resistivity data are plotted as $\ln\rho$ vs $T^{-1/4}$ in order to illustrate that for each sample the resistivity varies as $\exp(T_0/T)^{1/4}$ over a wide temperature range. Such strict adherence to the variable-range-hopping prediction is quite rare.[6] For all of the samples, we find T_0 between 2×10^6 and 6×10^6 K. The fact that the T_0 for the ceramic is quite similar to that for the single crystals is striking; this suggests that the larger measured resistivity for the ceramic originates in grain-boundary effects. These materials thus all exhibit strong effects of disorder in their resistivity. In the La_2CuO_4 single crystals, both oxygen vacancies and Li impurities provide the disorder; indeed, as may be seen from Fig. 4, the addition of 1% Sr has little additional effect on the resistivity. It should also be noted that the resistivity is not highly anisotropic. The inset of Fig. 4 shows the resistance of a sample from the same melt as that used for the phonon measurements. There is no indication of the structural transition in the resistivity. This, together with the strong evidence for localization of states near E_F, appears to rule out Fermi-surface mechanisms for the soft-phonon behavior.

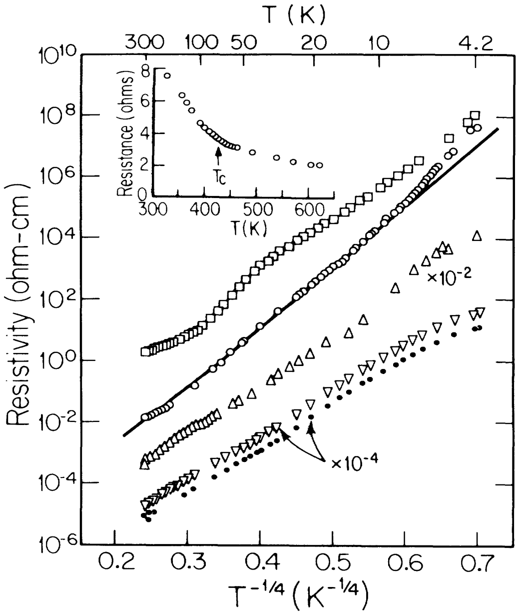

FIG. 4. $\ln\rho$ vs $T^{-1/4}$ for deoxygenated ceramic La_2CuO_4 (squares), single-crystal La_2CuO_4 (open circles and triangles), and single crystal with $\simeq 2$ mol% Sr (inverted triangles, *a* axis; solid circles, *c* axis). The solid line is the result of a least-squares fit between 10 and 100 K with $T_0=6\times10^6$ K. Note that all the single-crystal data superimpose. Inset: variation of the resistance in the vicinity of the T-O transition in La_2CuO_4.

In summary, we have found interesting transport, structural, and lattice-dynamical behavior in pure and Sr-doped La_2CuO_4. It is, of course, not clear at this stage how these results relate to the high-temperature superconductivity. Specifically, current band-structure calculations suggest that the T-O soft mode should couple weakly to the conduction electrons since it only modulates the in-plane Cu-O transfer integral in second order. Nevertheless, it is striking that these compounds, like the *A*15's, exhibit dramatic soft-phonon behavior.[9] Further, Sr doping levels which eliminate the T-O transition and presumably, the attendant phonon softening, also remove the superconductivity. Clearly, further theoretical work on the role of the phonons as well as isotope-effect experiments on this system are very important.

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Note added.—Since the submission of this paper, a partial isotope effect has indeed been observed[10] as we anticipated. New two-dimensional magnetic phenomena are also observed in our crystals.[11] Finally, we have confirmed that the soft-mode behavior as shown in Fig. 2 and the $T^{-1/4}$ behavior of Fig. 4 also occur in crystals of La_2CuO_4 grown in a CuO flux, thus verifying their universality.

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