

## Infrared study of anisotropy in single-crystal $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

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We have made infrared reflectivity measurements on single crystals of  $\text{La}_2\text{CuO}_4$  and  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$  with the infrared radiation polarized parallel and perpendicular to the copper-oxygen planes. In  $\text{La}_2\text{CuO}_4$  we observe nearly insulating spectra, from which we easily identify the dominant in-plane and out-of-plane infrared-active phonons. When  $\text{La}_2\text{CuO}_4$  is doped with Sr, we observe a dramatic increase in the electronic contribution to the  $a$ - $b$  plane conductivity, which tends to screen the in-plane phonons. In contrast, the out-of-plane response is essentially unchanged by doping. This leads to a conductivity anisotropy which we estimate to be at least 50 to 1 for our  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$  crystal. Our observations on single crystals resolve some of the controversies which have arisen over the interpretation of reflectivity measurements on polycrystalline samples.

The discoveries of superconductivity at temperatures above 30 K in  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  (Ref. 1) and 90 K in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (Ref. 2) have triggered unprecedented research into the normal-state and superconducting properties of the oxide superconductors. Of particular interest are the anisotropies in their electronic properties which exist by virtue of the layered nature of the materials. A characterization and understanding of these anisotropies is important because of their potential significance to the mechanism of high  $T_c$ , and also because of the way in which anisotropies have complicated the interpretation of measurements on polycrystalline samples. In particular, this has been true of the infrared reflectivity studies of the finite frequency conductivity [ $\sigma(\omega)$ ], where such exotic electronic excitations as "phase" phonons<sup>3-5</sup> and excitons<sup>4,5</sup> have been inferred from polycrystalline measurements and related to the mechanism of superconductivity. Controversies over the analysis of polycrystalline spectra (and especially over the existence of these excitations)<sup>3-9</sup> point to the need for infrared studies of single-crystal samples.

In this paper we present polarized normal-state reflectivity measurements on large single crystals of  $\text{La}_2\text{CuO}_4$  and  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . Reflectivity spectra were collected with the incident radiation polarized either parallel ( $a$ - $b$  plane) or perpendicular ( $c$  axis) to the Cu-O planes. In  $\text{La}_2\text{CuO}_4$  both polarizations yield nearly insulating spectra which are dominated by infrared-active phonons. These spectra allow us to easily identify the principal infrared-active [transverse optical (TO)] phonons in the  $\text{La}_2\text{CuO}_4$ -based high- $T_c$  superconductors. The addition of Sr to  $\text{La}_2\text{CuO}_4$  leaves the  $c$ -axis spectrum virtually unchanged, while the  $a$ - $b$  plane response becomes that of a conductor. From these measurements, we estimate a room-temperature conductivity anisotropy for our  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$  crystal of greater than 50 to 1, parallel and perpendicular to the  $a$ - $b$  plane, respectively. The results of the present study demonstrate that many of the unusual properties of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , which were inferred from polycrystalline spectra, were artifacts of the large conductivity anisotropy of this material.

The single crystals studied here were grown from Cu-O rich melts cooled from 1300°C. The  $\text{La}_2\text{CuO}_4$  crystals were orthorhombic at room temperature while the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  crystals were tetragonal and had a nominal Sr composition of  $x=0.08$  as measured by ion microprobe. The dimensions of the crystals were typically greater than 10 mm along the  $a$  and  $b$  axis and from 2-5 mm along the  $c$  axis.<sup>10</sup> Measurements of the susceptibility of the crystals did not show a superconducting transition at temperatures above 4.2 K. In the doped crystal this may have been due to the low Sr content or to disorder-induced scattering. In general, it has been difficult to produce large superconducting crystals of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . Susceptibility measurements revealed that the  $\text{La}_2\text{CuO}_4$  crystal is antiferromagnetic at temperatures below  $T_n \approx 280$  K. The crystals were cut perpendicular to the  $a$ - $b$  plane and polished to prepare them for the reflectivity measurements. Room-temperature reflectivity measurements were made at near-normal incidence with a scanning Fourier transform interferometer at frequencies from 40 to 4000  $\text{cm}^{-1}$ . Wire-grid polarizers covering this frequency range were aligned parallel or perpendicular to the  $c$  axis to obtain the  $c$ -axis and  $a$ - $b$  plane responses, respectively. The absolute reflectivities were obtained by ratioing the signal from the sample to the signal from a Au or Al mirror.

Figures 1 and 2 present measured reflectivity spectra (solid lines) for the  $\text{La}_2\text{CuO}_4$  and  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$  samples. Part (a) of each figure gives the reflectivity for the incident electric field parallel to the  $c$  axis while (b) is for polarization along the  $a$ - $b$  plane. The spectra have been fit to a model dielectric function of the form

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega} + \sum_n \frac{\omega_{pn}^2}{(\omega_n^2 - \omega^2) - i\Gamma_n\omega}, \quad (1)$$

where the second term on the right-hand side is the usual Drude term with plasma frequency  $\omega_p$  and damping  $\Gamma$ . The terms in the summation correspond to optical-phonon modes (or, in principle, other excitations) with  $\omega_{pn}$ ,  $\omega_n$ , and  $\Gamma_n$  giving the strength, frequency, and damping of the

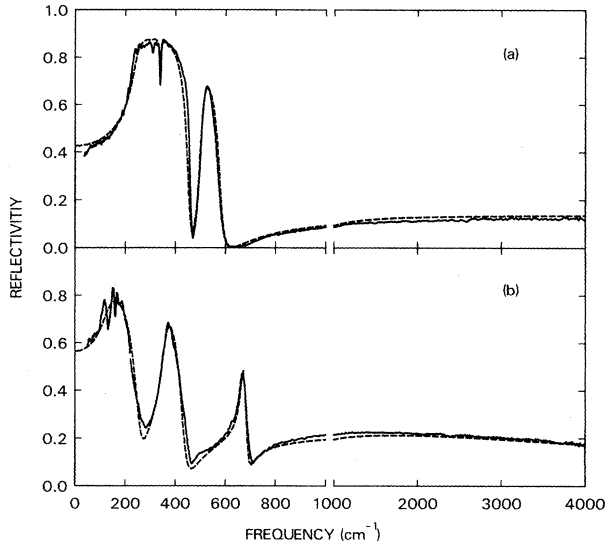


FIG. 1. Room-temperature reflectivity for the (a)  $c$  axis and (b)  $a$ - $b$  plane of  $\text{La}_2\text{CuO}_4$ . The solid lines are the measured spectra. The dashed lines are fits to the spectra. Both polarizations give nearly insulating spectra.

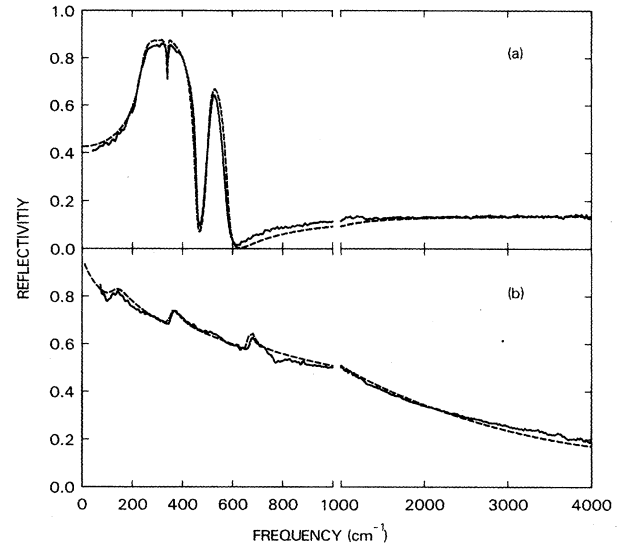


FIG. 2. Room-temperature reflectivity spectra for the (a)  $c$  axis and (b)  $a$ - $b$  plane of a  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$  crystal. The solid lines are measured spectra. The dashed lines are fits. The  $c$ -axis spectrum is nearly insulating and virtually the same as observed for  $\text{La}_2\text{CuO}_4$ , while the  $a$ - $b$  plane response is conducting.

mode, respectively. The fits have been included as dashed lines while the phonon parameters obtained from the fits are given in Table I. Kramers-Kronig analyses have also been applied to the spectra yielding virtually the same parameters as obtained from the fits.

The  $a$ - $b$  plane and  $c$ -axis reflectivity spectra for  $\text{La}_2\text{CuO}_4$  are essentially those of insulators. The principal features in the spectra are due to infrared-active phonons. Neglecting a small orthorhombic distortion,  $\text{La}_2\text{CuO}_4$  has the  $\text{K}_2\text{NiF}_4$  structure (space group  $D_{4h}^{17}$ ) and should have seven infrared-allowed phonons; four polarized along the  $a$ - $b$  plane ( $E_u$  modes) and three polarized along the  $c$  axis ( $A_{2u}$  modes).<sup>11</sup> All of the  $c$ -axis modes are accounted for and three strong  $a$ - $b$  plane modes are present in Fig. 1. We also observe fine structure in Fig. 1(b) at  $\approx 150\text{ cm}^{-1}$  which is probably associated with zone-boundary acoustic modes that become allowed as a result of the orthorhom-

bic distortion that doubles the unit cell. The eigenvectors of the various modes have been discussed in studies of other layered perovskites.<sup>11</sup> In Table I we have also included the TO phonon parameters for the isostructural compound  $\text{La}_2\text{NiO}_4$  taken from the work of Gervais *et al.*<sup>12</sup> In their study they resolve the fourth  $a$ - $b$  plane mode at  $224\text{ cm}^{-1}$ , but do not observe the  $\approx 340\text{-cm}^{-1}$   $c$ -axis mode or the fine structure present in our orthorhombic  $\text{La}_2\text{CuO}_4$  crystal. The most notable differences between the  $\text{La}_2\text{CuO}_4$  and  $\text{La}_2\text{NiO}_4$  spectra are in the lowest-energy  $a$ - $b$  plane and  $c$ -axis modes. These phonons, which involve motion of the O octahedra against their La cage,<sup>11</sup> are of particular interest because they are related to the ferroelectric modes of cubic perovskites. From Table I it appears that the strength of the  $134\text{-cm}^{-1}$   $\text{La}_2\text{CuO}_4$  phonon is nearly twice as large as its  $\text{La}_2\text{NiO}_4$  counterpart.

TABLE I. Frequencies, strengths, and dampings of the infrared-active (TO) phonons of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  obtained from the fits to spectra in Figs. 1 and 2, and for  $\text{La}_2\text{NiO}_4$  taken from Ref. 12.

	$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$			$\text{La}_2\text{NiO}_4$		
	$\omega_n$ ( $\text{cm}^{-1}$ )	$\omega_{pn}$ ( $\text{cm}^{-1}$ )	$\Gamma_n$ ( $\text{cm}^{-1}$ )	$\omega_n$ ( $\text{cm}^{-1}$ )	$\omega_{pn}$ ( $\text{cm}^{-1}$ )	$\Gamma_n$ ( $\text{cm}^{-1}$ )
$E \parallel c$	242	1000	30	275	1050	39
	342	92	4			
	501	304	20	503	260	26
		$\epsilon_\infty = 4.75$			$\epsilon_\infty = 5.2$	
$E \perp c$	132	790	52	151	344	13
				224	224	70
	358	552	28	351	628	45
	667	410	16	656	383	32
		$\epsilon_\infty = 5.5$			$\epsilon_\infty = 5.6$	

In fitting Eq. (1) to this mode we made no attempt to separate the contributions from the phonons which become allowed because of the orthorhombic distortion. Also, in our fits to the  $\text{La}_2\text{NiO}_4$  spectra of Ref. 12, we require a greater strength for the lowest-frequency  $a$ - $b$  plane mode than that given in Table I. Preliminary analysis indicates that making these two corrections will bring the strengths and frequencies of the phonons into better agreement. The lowest-frequency  $c$ -axis modes in  $\text{La}_2\text{CuO}_4$  and  $\text{La}_2\text{NiO}_4$  have the same strengths but differ in frequency by considerably more than expected for the mass substitution, suggesting that La-O bond strengths are quite different in the two materials. The frequencies and strengths of the rest of the infrared-allowed phonons are in very good agreement. Grevais *et al.*<sup>12</sup> have also published polarization-dependent spectra for  $\text{La}_2\text{CuO}_4$ , but a comparison of their results to the results of the present study would not be meaningful because of the high degree of misorientation in their sample. Orenstein *et al.* have presented reflectivity spectra for a crystal of  $\text{La}_2\text{CuO}_4$ .<sup>13</sup> These measurements had a low-frequency cutoff of  $\approx 400\text{ cm}^{-1}$  and did not cover the entire frequency range of the infrared-active phonons. In the region of overlap their spectra are in reasonable agreement with those in Fig. 1. Tajima *et al.*<sup>14</sup> have obtained reflectivity spectra for the  $a$ - $b$  plane of  $\text{La}_2\text{CuO}_4$  and  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . Their  $a$ - $b$  plane phonon frequencies of 150, 360, and  $680\text{ cm}^{-1}$  are close to those presented here and in the  $\text{La}_2\text{NiO}_4$  data of Ref. 12.

We note that the  $a$ - $b$  plane reflectivity of  $\text{La}_2\text{CuO}_4$  gradually drops at higher frequencies, indicating the presence of a broad peak in the conductivity near  $4000\text{ cm}^{-1}$ . Such a mode has been included in the fit in Fig. 1(b) ( $\omega_p = 4000\text{ cm}^{-1}$ ,  $\omega_{pn} = 6400\text{ cm}^{-1}$ ,  $\Gamma_n = 6000\text{ cm}^{-1}$ ). Orenstein *et al.*<sup>13</sup> have also observed this feature in the  $a$ - $b$  plane of their  $\text{La}_2\text{CuO}_4$  crystals. The mode was not visible in the spectra of Tajima *et al.*<sup>14</sup> In the crystal studied here, the presence or absence of the peak depended upon the method used to polish the sample; hence it is not clear if it is intrinsic to  $\text{La}_2\text{CuO}_4$ .

Our measurements on single-crystal  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$  yield a spectrum for  $c$ -axis polarization which is virtually identical to the  $\text{La}_2\text{CuO}_4$   $c$ -axis spectrum as is evident in Figs. 1(a) and 2(a), where the same fit has been plotted for both crystals. This result is in marked contrast to reports, based on the analysis of polycrystalline  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , that the  $\approx 240\text{-cm}^{-1}$   $c$ -axis phonon increases dramatically in strength with increasing Sr composition for  $0 < x < 0.15$ .<sup>4</sup> These observations led to the identification of the  $240\text{-cm}^{-1}$  mode as a "phase" phonon, involving both lattice and electronic degrees of freedom.<sup>3,4</sup> From our single-crystal study it is clear that the strength of the mode is insensitive to Sr concentration (the mode is also present in  $\text{La}_2\text{NiO}_4$  at approximately the same strength). The  $c$ -axis spectra do not show any evidence of a metallic contribution down to the lowest frequency studied ( $40\text{ cm}^{-1}$ ), from which we place an upper bound on the  $c$ -axis dc conductivity of  $\sigma_{dc} \leq 6\ (\Omega\text{ cm})^{-1}$ .

In contrast to the  $c$  axis, the  $a$ - $b$  plane reflectivity of  $\text{La}_2\text{CuO}_4$  changes significantly when it is doped with Sr. A conducting  $a$ - $b$  plane spectrum is observed for

$\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$  in Fig. 2(b). The amplitudes of the phonon features are significantly reduced by the screening of the free carriers. We have fit the  $a$ - $b$  plane reflectivity to a heavily damped Drude term [ $\omega_p = 10800\text{ cm}^{-1}$ ,  $\Gamma = 6500\text{ cm}^{-1}$ , yielding  $\sigma_{dc} \approx 300\ (\Omega\text{ cm})^{-1}$ ] plus three Lorentz oscillators to represent the phonons. The phonon strengths and dampings used in the fit were the same as those obtained from the  $a$ - $b$  plane reflectivity of  $\text{La}_2\text{CuO}_4$ . From these fits, we place a lower bound of 50 to 1 on the dc conductivity anisotropy in this crystal. Measurements of dc resistivities have given values of 30 to 1 and 50 to 1 for the conductivity anisotropy at room temperature in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (Ref. 15) and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (Ref. 16), respectively, while considerably larger anisotropies have recently been reported for  $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_x\text{Cu}_2\text{O}_{8-y}$ .<sup>17</sup>

Several workers have attempted to determine the finite-frequency conductivity of the high- $T_c$  superconductors by applying a Kramers-Kronig analysis to reflectivity spectra of polycrystalline  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (Refs. 3 and 4) and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (Ref. 5). The real part of the conductivity obtained in this manner appears to be strongly peaked near 0.3 to 0.5 eV. The peak was taken as evidence for an electronic excitation, and identification of the peak as a charge transfer exciton was proposed.<sup>5</sup> An effective-medium analysis of polycrystalline samples also led to the conclusion that a strong electronic mode was present in the superconductors.<sup>6</sup> In this case the mode was associated with the  $c$  axis. Despite some ambiguities which still exist in our understanding of the  $a$ - $b$  plane conductivity (as discussed below), we do not find this peak in our measurements on the  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$  sample. Although a high-energy mode such as that seen in the  $\text{La}_2\text{CuO}_4$  spectra of Fig. 1 could be hidden within the  $a$ - $b$  plane conductivity, the measurements on  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  crystals presented here and by Tajima *et al.*,<sup>14</sup> and similar studies of crystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (Ref. 18), make it clear that the  $a$ - $b$  plane conductivity is not dominated by a peak near 0.5 eV. Similarly, we find no evidence for an electronic feature in the  $c$ -axis spectra. We have previously presented an alternative analysis of the polycrystalline reflectivity in which we suggested that the peak in  $\sigma(\omega)$  (and also the "phase" phonon discussed above) is an artifact of the extreme anisotropy of the layered oxide superconductors.<sup>7</sup>

Although we are able to fit the  $a$ - $b$  plane reflectivity in our  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  single crystal to a Drude-like form [Fig. 2(b)], the question which remains to be answered is whether any true deviations from Drude behavior exist in the single-crystal spectra, and, if so, the significance of such deviations. A complete understanding of transport in the  $a$ - $b$  plane will require connecting the ac conductivity to the highly temperature-dependent dc conductivity. Establishing such a connection may uncover non-Drude behavior at low frequencies which could be modeled, for example, by a frequency-dependent mass and scattering rate as is observed in heavy-fermion systems.<sup>19,20</sup> The changes in reflectivity which indicate non-Drude behavior can be quite subtle, and our single-crystal samples still are not sufficiently large to allow us to determine whether such deviations are significant. Temperature-dependent infrared measurements on larger well-characterized crystals

should significantly improve our understanding of the electronic character of the layered oxide superconductors.

To summarize, we have made polarized reflectivity measurements on single-crystal  $\text{La}_2\text{CuO}_4$  and  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$ . Reflectivity spectra characteristic of insulators are found for polarizations both parallel and perpendicular to the  $a$ - $b$  plane of  $\text{La}_2\text{CuO}_4$ . The addition of Sr leaves the low-conductivity  $c$  axis unchanged, while the

$a$ - $b$  plane response becomes conducting. We estimate the conductivity anisotropy, parallel and perpendicular to the  $a$ - $b$  plane, to be greater than 50 to 1 at room temperature in our  $\text{La}_{1.92}\text{Sr}_{0.08}\text{CuO}_4$  crystal. A comparison of the properties of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  reported in this single-crystal study to the wide variation in properties determined from studies of polycrystalline samples underscores the importance of single-crystal measurements.

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