RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 16 1 DECEMBER 1987

Infrared anisotropy of $La_{1.85}Sr_{0.15}CuO_{4-y}$

G. L. Doll, J. Steinbeck, G. Dresselhaus, and M. S. Dresselhaus
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

A. J. Strauss and H. J. Zeiger
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173

(Received 3 September 1987)

By calculating the infrared reflectance $R(\omega)$ for a collection of randomly oriented crystallites, we fit the reflectance of polycrystalline $La_{1.85}Sr_{0.15}CuO_{4-y}$. From this calculation, the normal state of $La_{1.85}Sr_{0.15}CuO_{4-y}$ is found to be metallic in the Cu—O planes and nonmetallic out-of-plane. The deconvolution of $R(\omega)$ into $R_{\parallel}$ and $R_{\perp}$ allows the anisotropy of the system to be examined and provides a method by which infrared measurements of polycrystalline materials can be interpreted.

The discovery of high-temperature superconductivity in $La_{1.85}Ba_{0.15}CuO_{4-y}$ (Ref. 1) and subsequently in $YBa_2Cu_3O_{7-y}$ (Ref. 2) has resulted in an enormous amount of research into the physical properties of these systems. Most reported measurements have been performed on pressed and sintered powder samples which possess considerable inhomogeneity, and random orientations of anisotropic material. Therefore, the variable quality of the samples tends to render interpretation of the data difficult and often inconsistent between different research groups.

In this work, we have investigated the effect of randomly oriented crystallites on the ir reflectance spectrum of $La_{1.85}Sr_{0.15}CuO_{4-y}$. Results of this analysis indicate that consideration of the crystal anisotropy is necessary in order to obtain meaningful results from the ir spectra of polycrystalline specimens.

One of the major problems in interpreting the optical data for the high-T_c copper oxides has been taking account of the random orientations of the anisotropic material comprising the pressed powders. Orenstein *et al.*[3] recognized this problem and concluded that the dependence of the reflectance $R(\omega)$ on crystal orientation is described approximately by the relation $R(\omega) \sim R_{\parallel} + (R_{\perp} - R_{\parallel})\sin^2\theta$, where θ is the angle between the electric field vector and the c axis, and $R_{\parallel}$ and $R_{\perp}$ are the normal incidence reflectivities for $\theta = 0$ and $\pi/2$, respectively. In their model $R_{\parallel}$ was assigned a frequency-independent value, supposedly characteristic of the insulating, out-of-plane direction as predicted by band-structure calculations.[4,5] Although the possibility of ir structure in $R_{\parallel}$ was not addressed, we find it is precisely this structure that appears in the ir spectra of $La_{2-x}Sr_xCuO_{4-y}$.

Recently, Bassat, Odier, and Gervais[6] studied the reflectance of La_2NiO_{4-y}, which is structurally similar to $La_{1.85}Sr_{0.15}CuO_{4-y}$. At room temperature both compounds have the K_2NiF_4 tetragonal layered perovskite structure. In addition, the La_2NiO_{4-y} system is known to possess oxygen vacancies and mixed-valence states of Ni and O, which are also characteristic of Cu and O in superconducting $La_{1.85}Sr_{0.15}CuO_{4-y}$. By means of polarized reflectance studies on large single crystals of La_2NiO_{4-y}, Bassat *et al.* observed a significant optical anisotropy. They found that the spectrum associated with the Ni—O planes ($\mathbf{E}\perp\hat{\mathbf{c}}$) exhibited a Drude-like conductivity characteristic of metals, while the spectrum with the orthogonal polarization ($\mathbf{E}\parallel\hat{\mathbf{c}}$) was nonmetallic and rich in phonon structure. (In this work we have defined the $\hat{\mathbf{c}}$ axis to be normal to the Cu-O planes.) Because of their work with single-crystal La_2NiO_{4-y}, we are in a better position to interpret the ir spectra of polycrystalline $La_{1.85}Sr_{0.15}CuO_{4-y}$.

In this study, we have examined the effects of optical anisotropy in the limits of small and large crystallite dimensions relative to the wavelength of the incident light. For wavelengths much smaller than the crystallite dimension ($\lambda \ll d$), $R(\omega)$ is obtained by averaging over crystallite orientation, while the effective medium approximation[7] is applied in the small crystallite limit ($\lambda \gg d$).

In the case of $\lambda \ll d$, we consider light to be incident on a crystallite in the medium at an angle θ with the $\hat{\mathbf{c}}$ axis. Furthermore, we allow for two orthogonal polarizations of light in a plane whose normal is defined to be the Poynting vector of the incident radiation ($\mathbf{S}$). For simplicity, we assign one polarization to be coplanar with the $\hat{\mathbf{c}}$ axis ($\mathbf{E}_{\parallel}$) and the other polarization as $\mathbf{E}_{\perp} = \mathbf{S} \times \mathbf{E}_{\parallel}$. Projecting the dielectric tensor of the crystallite onto the polarization plane, the dielectric functions for both polarizations are easily calculated. Since the dielectric tensor is diagonal and $\epsilon_{xx} = \epsilon_{yy}$ for tetragonal symmetry, the dielectric functions are

$$\epsilon_{\perp}(\omega) = \epsilon_{xx}(\omega)\cos^2\theta + \epsilon_{zz}(\omega)\sin^2\theta \ , \tag{1}$$

$$\epsilon_{\parallel}(\omega) = \epsilon_{xx}(\omega) \ . \tag{2}$$

For $\lambda \ll d$ the reflectance of an aggregate of randomly oriented crystallites is then found by integrating Eqs. (1) and (2) over θ:

$$R(\omega) = \frac{1}{\pi}\int_0^{\pi/2} \left\{ \left| \frac{1-\sqrt{\epsilon_{\perp}(\omega)}}{1+\sqrt{\epsilon_{\perp}(\omega)}} \right|^2 + \left| \frac{1-\sqrt{\epsilon_{\parallel}(\omega)}}{1+\sqrt{\epsilon_{\parallel}(\omega)}} \right|^2 \right\} d\theta \ . \tag{3}$$

For $\lambda \gg d$, we calculate the reflectance via the effective-medium approximation (EMA). Restricting ourselves to the simplest case of a two-component medium consisting of spherical grains, in which the dielectric functions of the components take on the anisotropic values of our system, the effective dielectric function of the medium is found to be[8]

$$\epsilon_{\mathrm{EMA}}(\omega)=\frac{1}{4}\left[\epsilon_{\perp}(\omega)\pm\sqrt{\epsilon_{\perp}^{2}(\omega)+8\epsilon_{\perp}(\omega)\epsilon_{\parallel}(\omega)}\right] . \qquad (4)$$

From the tetragonal symmetry, we have assumed the volume fractions of ϵ_a and ϵ_b to be $\frac{2}{3}$ and $\frac{1}{3}$, respectively. $R(\omega)$ (for near-normal incidence) is then calculated in the usual way.[9]

The ir reflectance spectra of single-crystal La_2NiO_{4-y} for $\mathbf{E}\parallel\hat{\mathbf{c}}$ and $\mathbf{E}\perp\hat{\mathbf{c}}$ obtained by Bassat *et al.*[6] are shown in Fig. 1(a) as the dashed and solid lines, respectively. The strong anisotropy is immediately apparent. Of particular importance are the reststrahlen bands of the $\mathbf{E}\parallel\hat{\mathbf{c}}$ polarization. In view of the similarities between La_2NiO_{4-y} and $La_{1.85}Sr_{0.15}CuO_{4-y}$, it is not unreasonable to expect a similar contribution from $\mathbf{E}\parallel\hat{\mathbf{c}}$ to appear in the spectrum of $La_{1.85}Sr_{0.15}CuO_{4-y}$. Bassat *et al.* fit their reflectance data for La_2NiO_{4-y} by applying the factorized form of the dielectric function[10]

$$\frac{\epsilon(\omega)}{\epsilon_\infty}=\prod_j\frac{\Omega_{j,\mathrm{LO}}^2-\omega^2\pm i\omega\gamma_{j,\mathrm{LO}}}{\Omega_{j,\mathrm{TO}}^2-\omega^2\pm i\omega\gamma_{j,\mathrm{TO}}}-\frac{\Omega_p^2}{\omega(\omega-i\gamma_p)} , \qquad (5)$$

where Ω_j and γ_j represent the LO and TO phonon frequencies and damping factors, respectively. The second term on the right-hand side is the Drude expression. Using the fitting parameters for $\epsilon(\omega)$ reported by Bassat *et al.*, we have calculated $R(\omega)$ for a randomly oriented sample of La_2NiO_{4-y} in the small and large crystallite limits as described above. The resulting spectra are plotted as solid and dashed lines in Fig. 1(b) for $\lambda \ll d$ and $\lambda \gg d$, respectively. Both spectra are qualitatively similar to published spectra for $La_{1.85}Sr_{0.15}CuO_{4-y}$.[11,12] The ir reflectance spectra of a polycrystalline La_2NiO_4 sample has been reported by Gervais, Odier, and Nigar.[13] While their data are qualitatively similar to the calculated reflectances shown in Fig. 1(b), there are significant differences. However, we believe these differences are probably attributable to factors such as smaller crystallite dimensions and uncompensated surface roughness and do not necessarily reflect upon the applicability of our analysis to estimate the effects of anisotropy on the ir spectra of the copper oxides.

A $La_{1.85}Sr_{0.15}CuO_{4-y}$ pellet prepared by conventional ceramic techniques was used in this study. The crystallite size has not been determined. The onset of superconductivity occurred at 40 K for a bar-shaped sample prepared in the same run. Polishing the pellet with 0.3-μm alumina powder in spectroscopic grade methanol produced a shiny surface which is critical for reflectance measurements. The sample was found to be hygroscopic and was therefore handled in a dry environment. $R(\omega)$ was measured with near-normal incident light over the spectral range of 400 to 4800 cm^{-1} at $T=298$ K. The spectrum is in good agreement with published data.[14]

Our interpretation of the reflectance of $La_{1.85}Sr_{0.15}CuO_{4-y}$ in the small and large crystallite limits is examined in Figs. 2(a) and 2(b). The fits to the data are displayed in Fig. 2(b). In the spectral region studied, both models describe the data well. Values of the parameters used to

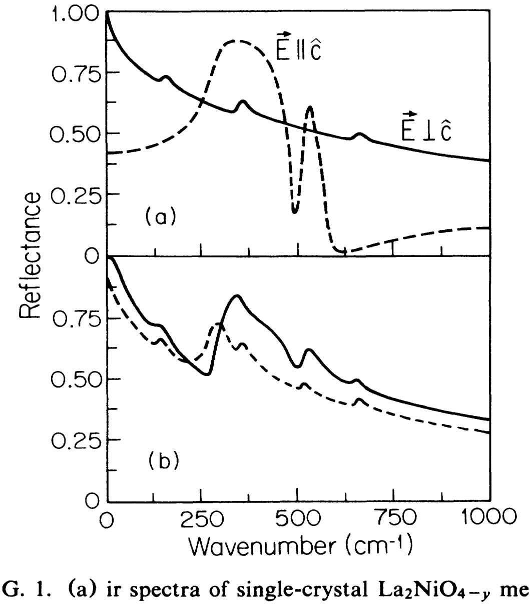

FIG. 1. (a) ir spectra of single-crystal La_2NiO_{4-y} measured by Bassat *et al.* for $\mathbf{E}\parallel\hat{\mathbf{c}}$ and $\mathbf{E}\perp\hat{\mathbf{c}}$ polarizations (Ref. 6). (b) The reflectance of a randomly oriented collection of La_2NiO_{4-y} crystallites calculated for small ($\lambda \gg d$, dashed line) and large ($\lambda \ll d$, solid line) crystallites.

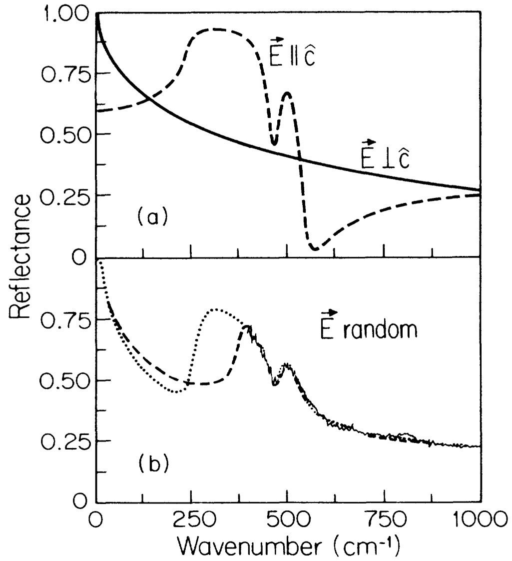

FIG. 2. (a) Calculated ir anisotropy in $La_{1.85}Sr_{0.15}CuO_{4-y}$ for the large crystallite limit ($\lambda \ll d$). Similar spectra are also obtained with the $\lambda \gg d$ calculation. (b) Measured $T=298$ K reflectance spectra of $La_{1.85}Sr_{0.15}CuO_{4-y}$ and the calculated reflectance spectra of randomly oriented crystallites for $\lambda \ll d$ (dotted line) and $\lambda \gg d$ (dashed line).

TABLE I. LO, TO phonon frequencies and plasma frequencies (Ω_p) for $\mathbf{E}\parallel\hat{\mathbf{c}}$ and $\mathbf{E}\perp\hat{\mathbf{c}}$ polarizations of La_2NiO_{4-y} from Bassat *et al.*, and the $\lambda \ll d$ and $\lambda \gg d$ calculations for $La_{1.85}Sr_{0.15}CuO_{4-y}$. The phonon widths ($\gamma_{j,M}$ where $j=1$, 2, and 3 and $M=$LO,TO) were not treated as adjustable parameters in the fitting, and were assigned to be $\gamma_{j,M}=30$ cm^{-1}.

	La_2NiO_{4-y}		$La_{1.85}Sr_{0.15}CuO_{4-y}$ $\lambda \ll d$		$La_{1.85}Sr_{0.15}CuO_{4-y}$ $\lambda \gg d$	
(cm^{-1})	$\mathbf{E}\parallel\hat{\mathbf{c}}$	$\mathbf{E}\perp\hat{\mathbf{c}}$	$E\parallel\hat{\mathbf{c}}$	$\mathbf{E}\perp\hat{\mathbf{c}}$	$\mathbf{E}\parallel\hat{\mathbf{c}}$	$\mathbf{E}\perp\hat{\mathbf{c}}$
$\Omega_{1,\mathrm{TO}}$	280	148	241[a]	⋯	385[a]	⋯
$\Omega_{1,\mathrm{LO}}$	487	193	460	⋯	469	⋯
$\Omega_{2,\mathrm{TO}}$	510	350	475	⋯	490	⋯
$\Omega_{2,\mathrm{LO}}$	575	390	550	⋯	605	⋯
$\Omega_{3,\mathrm{TO}}$	⋯	652	⋯	⋯	⋯	⋯
$\Omega_{3,\mathrm{LO}}$	⋯	662	⋯	⋯	⋯	⋯
Ω_p	0	3850	0	3850	0	3950
γ_p (cm^{-1})	⋯	⋯	⋯	7800	⋯	6500
ϵ_∞	⋯	⋯	12	3	12	3

[a] Estimated.

fit the data are compared with those of Bassat *et al.* for La_2NiO_{4-y} in Table I. No phonons were included in the fit to the data for the $\mathbf{E}\perp\hat{\mathbf{c}}$ contribution, as opposed to six used in the similar polarization study of La_2NiO_{4-y}. It is probable that ir-active phonons are present in the $\mathbf{E}\perp\hat{\mathbf{c}}$ polarization; however, their inclusion in this analysis is beyond the sensitivity and spectral range of our data. The $\mathbf{E}\parallel\hat{\mathbf{c}}$ phonon frequencies of the $La_{1.85}Sr_{0.15}CuO_{4-y}$ do not show significant disagreement except for the $\Omega_{1,\mathrm{TO}}$ mode. We display this mode as a fitting parameter only, and do not necessarily infer that it is a property of the system, since the frequency of this mode resides outside our spectral range. It is possible that additional phonons arising from Sr substitution for La are present in $R(\omega)$; however, this analysis will be pursued elsewhere. Quantitative evaluations of the ir phonon frequencies and plasma frequencies from polycrystalline samples require a larger spectral range than was available in the present work. Therefore, the values quoted in Table I may not be unique to the physical system. In Fig. 2(a) the calculated reflectances are shown for the two polarizations for the case of $\lambda \ll d$. These plots are qualitatively similar to the polarization study of single-crystal La_2NiO_{4-y} shown in Fig. 1(a).

Both La_2NiO_{4-y} and $La_{1.85}Sr_{0.15}CuO_{4-y}$ are decidedly anisotropic, exhibiting metallic behavior in the Cu—O planes ($\mathbf{E}\perp\hat{\mathbf{c}}$) and nonmetallic characteristics along the high-symmetry direction ($\mathbf{E}\parallel\hat{\mathbf{c}}$). The plasma frequencies (Ω_p) of the $\mathbf{E}\perp\hat{\mathbf{c}}$ components of both materials are nearly the same, indicating that the carrier mechanisms of the systems are similar. That is, the carriers in these materials probably arise from the mixed-valence states of the Ni and Cu and/or oxygen deficiencies, and Sr doping in the case of $La_{2-x}Sr_xCuO_{4-y}$ makes no significant contribution to the in-plane conductivity. The peak in the ir spectrum of $La_{1.85}Sr_{0.15}CuO_{4-y}$ near ~ 500 cm^{-1}, which has been identified[15] as a Cu—O basal plane phonon, is shown to be an out-of-plane Cu—O stretching mode, while the in-plane Cu—O breathing mode, which occurs[16] near 680 cm^{-1} in La_2CuO_4 is not found in our spectrum of $La_{1.85}Sr_{0.15}CuO_{4-y}$.

In our calculations, we have assumed that only two polarizations of the E field operate on the dielectric tensor, and that the tetragonal structure is free of symmetry-reducing distortions. A problem not addressed in this analysis is sample inhomogeneity, which should certainly be a consideration in any optical model. Another problem not addressed is the surface quality of our samples. Spectral features associated with microscopic voids and variations in the smoothness of the surface have not been considered. However, the ir region of the reflectivity spectrum is not affected as significantly by surface roughness as the higher-energy region,[17] and we believe our data are qualitatively correct.

The consequences of this approach to the analysis of ir spectra are far reaching for the interpretations of optical data for the high-T_c copper oxides. With this method of analysis, there exists the possibility of optically examining the reported orthorhombic distortion of the copper oxides as the materials are cooled through their superconducting transition, although the deviation from tetragonal symmetry complicates the calculation. Investigations into the energy gap of the superconducting state usually include the examination of the normalized difference in the reflectances of the normal and superconducting states. The deconvolution of the $\mathbf{E}\parallel\hat{\mathbf{c}}$ and $\mathbf{E}\perp\hat{\mathbf{c}}$ contributions from $R(\omega)$ should provide an opportunity to reexamine the band gaps and to address the question of gap anisotropy more quantitatively. Moreover, information pertaining to the dimensionality of the superconducting state should be obtained, and the proposed Peierls distortion of La_2CuO_{4-y} critically examined. This analysis should also correctly identify the phonon modes in the ir spectra. According to our interpretation of the reflectance spectrum $La_{1.85}Sr_{0.15}CuO_{4-y}$ does not have an anomalously low plasma frequency or an unusually low-energy electronic excitation as has been previously reported.[14] Infrared structures in $R(\omega)$ are now identifiable as resulting from the anisotropy of the material. It is also expected that the anisotropy of $La_{1.85}Sr_{0.15}CuO_{4-y}$ should be considered in the analysis of Raman scattering measurements that have been performed on polycrystalline materials. Infrared and Raman measurements to investigate the carrier contribution and the phonon frequencies in the $La_{2-x}Sr_xCuO_{4-y}$ system, as a function of x and T, are currently underway and will be reported subsequently.

We wish to thank E. J. Delaney for preparing the $La_{1.85}Sr_{0.15}CuO_{4-y}$ pellet, and A. Chaiken, C. Schoen, and M. Siegel for valuable assistance and discussion. This work was supported at the Massachusetts Institute of Technology through National Science Foundation Materials Research Laboratories Program Grant No. DMR 84-18718 and at Lincoln Laboratory by the Department of the Air Force.

---

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] M. K. Wu, J. R. Ashburn, C. T. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Huang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3] J. Orenstein, G. A. Thomas, D. H. Rapkine, C. G. Bethea, B. F. Levine, R. J. Cava, E. A. Rietman, and D. W. Johnson, Jr., Phys. Rev. B **36**, 729 (1987).

[4] L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[5] J. Yu, A. J. Freeman and J.-H. Xu, Phys. Rev. Lett. **58**, 1035 (1987).

[6] J.-M. Bassat, P. Odier, and F. Gervais, Phys. Rev. B **35**, 7126 (1987).

[7] See , e.g., D. A. G. Bruggerman, Ann. Phys. (Leipzig) **24**, 636 (1935).

[8] G. L. Carr, S. Perkowitz, and D. B. Tanner, in *Infrared and Millimeter Waves,* edited by K. J. Button (Academic, New York, 1985), Vol. 13, p. 171.

[9] F. Wooten, *Optical Properties of Solids* (Academic, New York, 1972), p. 48.

[10] F. Gervais, in *Infrared and Millimeter Waves,* edited by K. J. Button (Academic, New York, 1983), Vol. 8, p. 306.

[11] D. A. Bonn, J. E. Greedan, C. V. Stager, T. Timusk, M. G. Doss, S. L. Herr, K. Kamarás, C. D. Porter, D. B. Tanner, J. M. Tarascon, W. R. McKinnon, and L. H. Greene, Phys. Rev. B **35**, 8843 (1987).

[12] D. A. Bonn, J. E. Greedan, C. V. Stager, and T. Timusk, Solid State Commun. **62**, 383 (1987).

[13] F. Gervais, P. Odier, and Y. Nigara, Solid State Commun. **56**, 371 (1985).

[14] Z. Schlesinger, R. T. Collins, and M. W. Shafer, Phys. Rev. B **35**, 7232 (1987).

[15] H. Sawada, Y. Saito, T. Iwazumi, R. Yoshizaki, Y. Abe, and E. Matsuura, Jpn. J. Appl. Phys. **26**, L426 (1987).

[16] P. Ganguly and C. N. R. Rao, J. Solid State Chem. **53**, 193 (1984).

[17] H. E. Bennett and J. O. Porteus, J. Opt. Soc. Am. **51**, 123 (1961).