

Optical properties of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$: Evidence for strong electron-phonon and electron-electron interactions

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The optical properties of the high- T_c superconductor $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ have been measured over the far-infrared through ultraviolet frequency range at temperatures between 4 and 300 K. The frequency-dependent conductivity shows strong vibrational features in the far infrared (240, 355, and 495 cm^{-1}) and two electronic transitions in the infrared (3500 $\text{cm}^{-1}/0.44$ eV and 10500 $\text{cm}^{-1}/1.3$ eV). The measurements are interpreted within a model of strongly correlated electrons interacting strongly with vibrational modes.

In this Brief Report we describe the optical properties of the high- T_c superconductor $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. Our measurements, made at temperatures between 4 and 300 K, span the frequency range between the far infrared and the ultraviolet. We find that the frequency-dependent conductivity (obtained by the Kramers-Kronig analysis of reflectance) shows strong vibrational features in the far infrared (240, 355, and 495 cm^{-1}) and two electronic transitions in the infrared (3500 $\text{cm}^{-1}/0.44$ eV and 10500 $\text{cm}^{-1}/1.3$ eV). The oscillator strength of the vibrational frequencies rules out an interpretation in terms of ordinary optical phonons, whereas the energy of the low-lying electronic transition is inconsistent with a single-particle picture of the electronic band structure.

Most previous optical studies¹⁻⁴ of this material have been far-infrared investigations of the energy gap in the superconducting state; for example, we have recently presented evidence that the gap is close to the BCS value.⁴ At least three higher-frequency measurements have been reported. From vibrational spectroscopy on powdered samples, Stavola, Cava, and Rietman⁵ concluded that the Peierls transition which takes place in La_2CuO_4 is suppressed by doping with Sr. A minimum seen in room-temperature reflectance measurements by Tajima *et al.*⁶ at 6700 $\text{cm}^{-1}/0.83$ eV was interpreted as the conduction-electron plasma frequency; this yielded a very small value (1 eV) for the free-electron bandwidth. Finally, Schlesinger, Collins, and Shafer⁷ interpreted a decrease in reflectivity (increase in absorptivity) at 450 $\text{cm}^{-1}/0.06$ eV as an "electronic excitation" related to the superconductivity of the material.

Samples of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ were prepared by previously described⁴ ceramic techniques. The samples were single phase with the midpoint of a 1.6-K-wide superconducting transition at 40.3 K but with an incomplete Meissner effect. The room-temperature conductivity was approximately 40 $\Omega^{-1}\text{cm}^{-1}$, at the low end of the reported range for this material. However, where we can make comparisons^{6,7} our optical spectra are in accord with those reported elsewhere.

The optical measurements were made as near-normal

incidence reflection on polished sample surfaces. The far-infrared was measured at McMaster University using a custom-built Michelson interferometer and 0.3-K Ge bolometer; the mid-infrared at the University of Florida with an IBM/Bruker interferometer; and the near-infrared, visible and ultraviolet at the University of Florida with a Perkin-Elmer grating monochromator. Following the measurements the sample was coated with a metal overlayer, Pb at McMaster University and Al at the University of Florida, in order to provide a reference reflectance. On account of the granular nature of the surface, this coating made important quantitative changes in the absolute value of the reflectance, particularly at higher frequencies.

Figure 1 shows the reflectance at 4 and 300 K. Except for frequencies below 200 cm^{-1} , where effects of superconductivity are seen,⁴ the data at 70 K are extremely close to that at 4 K. Warming to 300 K gives a decrease in the mid-infrared reflectance.

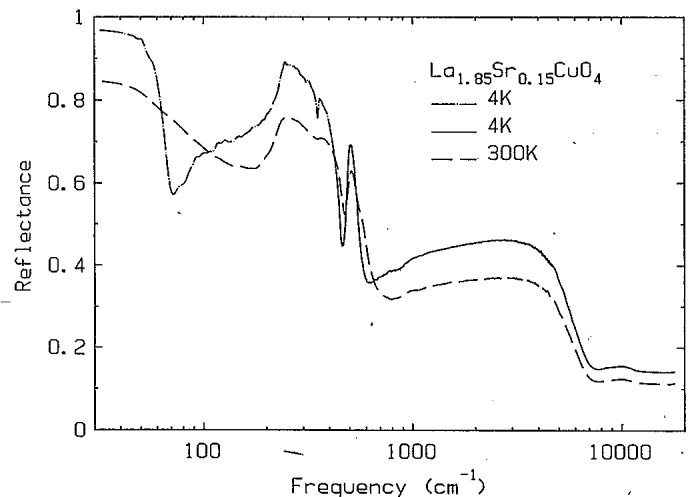


FIG. 1. Reflectance of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ at 4 and 300 K. Note the logarithmic frequency scale. The data below 400 cm^{-1} are from Ref. 4.

Kramers-Kronig analysis of the reflectance shows that there are plasmonlike or longitudinal optical phononlike zeros in the real part of the dielectric function at 70, 460, and 570 cm^{-1} , along with a near zero at 5000 cm^{-1} . As discussed in our earlier paper for the case of the 70- cm^{-1} feature, these zeros are the reason that there are deep minima in the reflectance near these frequencies.⁴ Thus, for example, the reflectance drop between 300 and 600 cm^{-1} is *not* an absorption edge, as was suggested in Ref. 7, but is instead due to the 570- cm^{-1} zero crossing of the real part of the dielectric function. Except for the 495- cm^{-1} vibrational feature, the absorption hardly changes through this region.

The frequency-dependent conductivity $\sigma_1(\omega)$, which governs the absorption, is shown in Fig. 2. The electronic part of the spectrum is decidedly non-Drude-like, with a broad peak at 3500 $\text{cm}^{-1}/0.44$ eV and a weaker maximum at 10500 $\text{cm}^{-1}/1.3$ eV. This feature is more significant than it appears in Fig. 2; the log scale really compresses it. At low frequencies, the conductivity is dominated by a vibrational feature at 240 cm^{-1} ; weaker peaks are seen at 355 and 495 cm^{-1} . Finally, we note that the low-frequency conductivity, which at 300 K is about 200 $\Omega^{-1}\text{cm}^{-1}$, is a little larger than the normal-state dc conductivity.

A key to interpreting these measurements is the oscillator strength of the various peaks. The strong vibrational features are too intense to be ordinary optical phonons, whereas the low-lying electronic peak has too little oscillator strength to be attributed to nearly free carriers.⁸ Figure 3 shows the partial oscillator strength sum rule as applied to our data. This quantity is

$$S(\omega) \equiv f \frac{N_{\text{eff}}}{M} Z^2 = \frac{2m_e}{\pi n_u e^2} \int_0^\omega \sigma_1(\omega') d\omega', \quad (1)$$

where m_e (e) is the electronic mass (charge), and n_u is the number of formula units per unit volume. The factor f is the volume fraction of conducting material in the inhomogeneous sample, included because our $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$

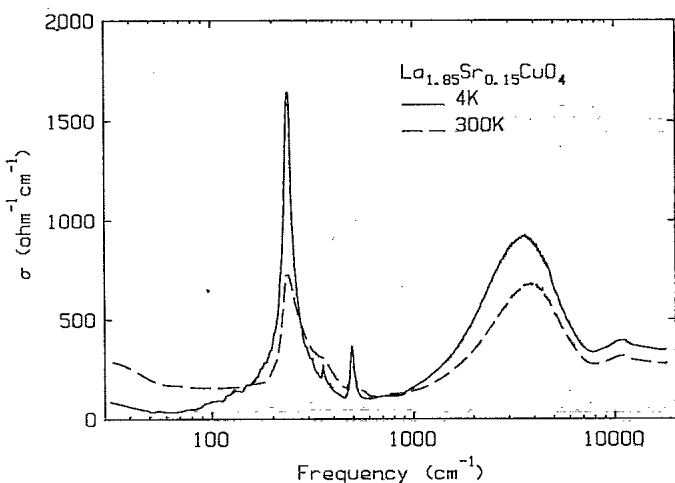


FIG. 2. The frequency-dependent conductivity of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, at 4 and 300 K, as determined by Kramers-Kronig analysis of the reflectance.

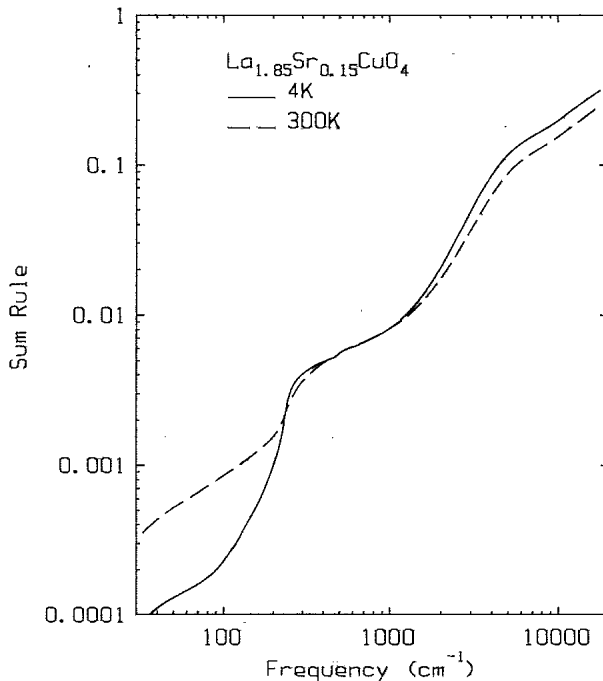


FIG. 3. The partial oscillator strength sum rule for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ at 4 and 300 K.

samples consist of randomly oriented grains, each of which we assume to be highly conducting in two directions and nonconducting in the third. Within the effective medium theory, it is possible to show⁹ that this situation is equivalent to a composite consisting of $\frac{1}{3}$ insulator and $\frac{2}{3}$ conductor (implying that the conductor is well above percolation). The remaining quantities are N_{eff} , the number of effective carriers or oscillators per formula unit; Z , the charge associated with the carrier or oscillator (in units of e); and M , the effective mass of the carrier or reduced mass of the oscillator (in units of m_e). The lower limit of integration is extended to zero by assuming constant conductivity between zero and the beginning of the data. Thus, the zero-frequency delta function in the response of the superconductor is omitted from $S(\omega)$.

If each Sr removes one free carrier, then $N_{\text{eff}} = 0.85$ and with $f = 0.66$, the sum rule should saturate at $S = 0.56$. As shown in Fig. 3, the low-lying peak accounts for only about half of this value. This deficit could arise from any one of three causes. First, the effective mass of the carriers could be $M = 2m_e$; this, however, disagrees with band-structure calculations.¹⁰ Second, the number of carriers could be smaller than given by the composition, perhaps because of partial gapping of the Fermi surface from a charge-density-wave (CDW) distortion. However, in the case of a CDW distortion it is expected that transitions across the Peierls gap would exhaust the sum rule for the conduction electrons; i.e., there would be no higher-lying (1.3 eV) band.

The third explanation, which we favor, is that the electrons suffer from strong electron correlation effects.^{11,12} A strong on-site repulsion U would prohibit double occupancy of sites and lead to an insulating ground state for

La_2CuO_4 . Doping would produce holes in the lower Hubbard band; the carrier concentration would equal the number of dopant ions, about 1.6×10^{21} for 15% Sr. This number is in agreement with plasma-frequency⁶ and Hall¹³ measurements. In a strong Coulomb picture there are typically two electronic excitations, a high-energy one at U , the effective on-site interaction energy, and a lower one at V , the effective near-neighbor or long-range interaction energy. In our data, these would be, respectively, the peaks at $10500 \text{ cm}^{-1}/1.3 \text{ eV}$ and $3500 \text{ cm}^{-1}/0.44 \text{ eV}$. A related picture of the electronic structure has been presented by Varma, Schmitt-Rink, and Abrahams¹² who predict a strong low-energy peak at 0.5 eV , very close to where we observe it.

The oscillator strength of the vibrational features is extremely high. As shown in Fig. 3, $S(\omega)$ increases by approximately 0.005 on going through the 240 cm^{-1} peak and by 0.001 at the 495 cm^{-1} peak. If we use the reduced mass of Cu-O, $M = 23500m_e$, Eq. (1) with $N_{\text{eff}} = 1$ yields for the strongest mode a charge $Z = 13e$. (Alternatively, taking $Z = e$, we obtain $M = 130m_e$.) For the weaker mode we find either $Z = 6e$ or $M = 660m_e$.

Clearly, these modes are *electronic* in origin. We propose that they are due to the "dimer charge oscillation" or "phase-phonon" mechanism used by Rice¹⁴ to understand the optical spectra of organic charge-transfer salts. In the case of the La-Sr-CuO system, the modes in question would be the symmetric vibrational modes of the distorted Cu-O octahedra. According to this model, breathing or symmetric-stretching modes become infrared active when they are strongly coupled to the electronic density. Essen-

tially, the infrared radiation modulates the charge density on a site or in a bond; in turn, the bond lengths follow the local charge density. Antisymmetric linear combinations of the symmetric stretching modes give high-infrared conductivities at renormalized vibrational frequencies. The frequency decreases and the intensity of the mode are both governed by the strength of the electron-phonon coupling. We note that Weber¹⁵ calculates just such a decrease of zone-boundary breathing mode frequencies due to electron-phonon coupling.

For the Rice mechanism to act there must be differences in electron density among the sites, due either to CDW formation from electron-phonon interaction or to Coulomb-driven localization of the electrons on specific sites. In the organics, it is in the salts with strong Coulomb interaction that the effect is strongest. A fit of the Rice model to our data will be reported elsewhere.

In summary, the optical properties of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ are consistent neither with a free-electron picture for the conduction electrons nor with the vibrational features being simple optical phonons. The data suggest that the electrons are strongly interacting—among themselves and with the vibrational modes.

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nance, a number of factors argue against this interpretation. (i) This resonance becomes very broad at high metal concentrations. (ii) Well above percolation (the case for our samples), most of the oscillator strength should be in the dc-conductivity mode. (iii) In a percolating system above percolation, vibrational lines are first distorted and then swamped by the conducting background. See, K. D. Cummings, J. C. Garland, and D. B. Tanner, *Phys. Rev. B* **30**, 4170 (1984). Our data do not display any of these characteristics.

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