Correlation of dopant-induced optical transitions with superconductivity in $La_{2-x}Sr_xCuO_{4-\delta}$

S. Etemad, D. E. Aspnes, M. K. Kelly, R. Thompson, J.-M. Tarascon, and G. W. Hull

Bell Communications Research, Red Bank, New Jersey 07701

Optical data for a series of $La_{2-x}Sr_xCuO_{4-\delta}$ solid solutions from $x = 0$ to $x = 0.30$ reveal several structures, including a relatively intense, dopant-induced absorption band around 0.5 eV whose oscillator strength tracks the Meissner effect and T_c measured on the same set of samples. The dopant-induced optical-transition–superconductivity correlation strongly supports an electronically driven superconductivity mechanism mediated by the 0.5-eV excitation.

The discovery of superconductivity at unexpected high temperatures in copper-containing perovskite materials has focused much attention on the physical properties of this class of compounds,[1] and has stimulated extensive theoretical efforts to identify the relevant superconductivity mechanism(s) involved. Suggested explanations presently range from models based on Bardeen-Cooper-Schrieffer (BCS) theory,[2] including two-band generalizations,[3] to Cooper pairing mediated by excitons,[4,5] or plasmons,[6] and to fundamentally different proposals involving resonating valence-bond states.[7,8] A central factor is the nature of the excitation involved: Is it vibrational (phonons) as in the classical BCS theory, or electronic?

Superconductivity-mediating electronic excitations should also manifest themselves in the optical response of the material. The signature of these excitations would be correlation with superconductivity-related phenomena, such as the Meissner effect and the critical temperature T_c, as they vary with some physical parameter, such as doping. Since the series of compounds $La_{2-x}Sr_xCuO_{4-\delta}$ are semiconductors for $x < 0.01$, superconductors for $0.03 < x < 0.30$, and metallic conductors for $x \geq 0.30$, they provide a unique opportunity to establish this correlation and moreover to distinguish superconductivity-correlated behavior from simple doping dependences.

In this paper we report the results of a systematic investigation of the optical responses of 10 solid solutions of $La_{2-x}Sr_xCuO_{4-\delta}$ from $x = 0$ to $x = 0.30$ over the spectral range from 0.3 to 5.8 eV. Our results reveal four identifiable optical structures: a relatively strong rise in reflectivity R caused by an absorption band around 0.5 eV whose room-temperature oscillator strength tracks T_c and the fractional ideal diamagnetism (Meissner effect); a relatively weak structure in the imaginary part of the dielectric function ϵ_2 at ~2.0 eV that monotonically weakens and vanishes with increasing x consistent with a simple doping dependence; and weak and strong features in ϵ_2 at 2.7 and above 5.5 eV, respectively, that are essentially independent of x as expected from typical band-structure behavior.

The samples used in this work were sintered, pressed pellets prepared from 99.999% pure La_2O_3, CuO, and $SrCO_3$ as described previously.[9] They were polished on a glass plate with a suspension of 0.05 μm alumina abrasive in methanol, then were finish lapped for about 2 min using the same suspension on a single sheet of lens paper. When both procedures were followed, ellipsometric spectra (which are strongly affected by microscopic surface quality but relatively unaffected by macroscopic pits and voids) were consistently reproducible to 5%. Examination of the finished pellets in a polarizing metallographic microscope revealed that they consisted of randomly oriented, anisotropic grains of characteristic dimension of the order of 20 μm interspersed with randomly sized voids that covered roughly 10–15% of the total surface area. After polishing, the samples were usually measured immediately and then stored in a dry atmosphere to preserve their surfaces.

Optical data were obtained at room temperature by spectroreflectometry from 0.3 to 3.0 eV and by spectroellipsometry from 1.5 to 5.8 eV. The spectroellipsometer is described in detail elsewhere.[10] In principle, ellipsometry directly yields both real and imaginary parts of the complex dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$. Averaging artifacts due to the optical anisotropy of the grains substantially affected the zero offset (but not the optical structure) of ϵ_2 for small ϵ_2. Consequently, we did not attempt to interpret our absolute values of ϵ_2 in terms of absorption coefficients. However, ϵ_1 is not significantly affected by optical anisotropy, so we consider our ϵ_1 results to be accurate to within 10%. Our reflectance measurements were done with a $\frac{1}{3}$-m monochromator in conjunction with black-body radiation sources and a sensitive pyroelectric detector. With appropriate reflective and CaF_2 optics, we obtained reflectance data from 0.3 to 3.0 eV with different combinations of gratings and filters. The effect of void scattering on the reflectance data was corrected by coating the samples with gold and using them as references and by scaling the results to match reflectance spectra calculated from the ellipsometrically determined ϵ data. The good overlap agreement between corrected and calculated spectra justified this procedure. Meissner-effect data were obtained using a superconducting quantum interference device (SQUID) magnetometer in a magnetic field of 30 Oe operating down to 4.2 K.

Figure 1 summarizes the compositional dependence of the reflectance of six representative $La_{2-x}Sr_xCuO_{4-\delta}$ samples. The logarithmic presentation of the energy scale is to emphasize the low-energy part of the spectra. The curves for $x = 0$ and $x = 0.30$ are repeated in both panels to aid the comparison. The extension of the reflectivity result from 0.3 eV down to 0.1 eV for the $x = 0.15$ sample is obtained elsewhere[11] and is similar to the result reported
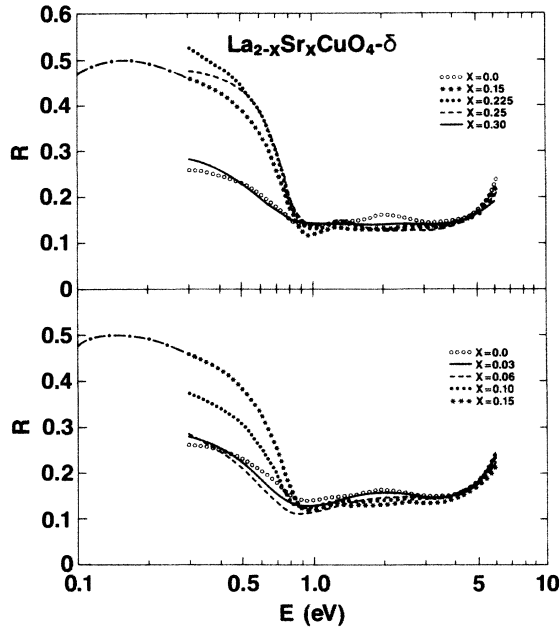
FIG. 1. Reflectances of $La_{2-x}Sr_xCuO_{4-\delta}$ samples for various x from 0.00 to 0.30 eV. Measured reflectances below 1.5 eV are scaled to match reflectances above 1.5 eV, which are calculated from ellipsometric data.
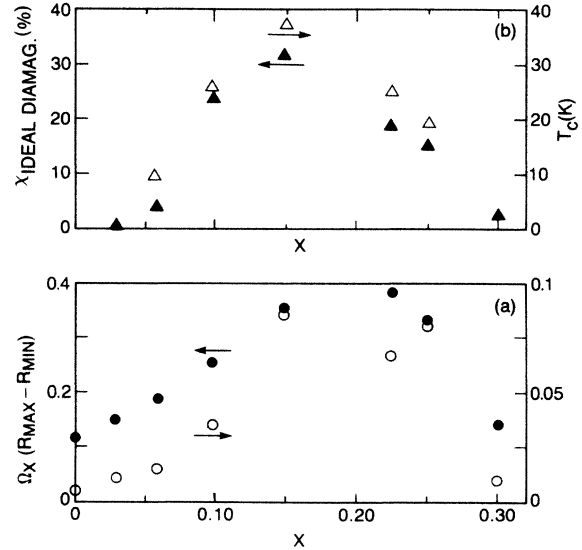

FIG. 2. (a) Variation with x of Ω_x, defined as the difference between the maximum and the minimum in reflectance spectra of Fig. 1 from 0.3 to 0.9 eV, for two successive treatments of the samples. Open circles: after annealing; closed circles: after re-polishing. The effect of optical scattering has been minimized only for the closed-circle data which were obtained by using the same surface coated with gold as reference. (b) Variation with x of the superconducting transition temperature (open triangles) and fractional ideal diamagnetism (closed triangles) for the same samples.

earlier[12] on that single composition. The result of primary importance is that the oscillator strength of the feature characterized by the relatively sharp rise in R below 0.9 eV increases nonlinearly with x, reaches a maximum, and then decreases. We note that the onset of this rise in R is pinned at 0.9 eV and does not move with the dopant concentration, a behavior that suggests the rise in R is due to an absorption band. The Kramers-Kronig analysis of R data over a wider spectral range for a single composition,[12] as well as this set of samples,[11] shows that this rise in R is indeed due to a strong, relatively narrow absorption band of full width at half maximum (FWHM) ~ 0.5 eV situated at 0.5 eV.

The variation of oscillator strength Ω_x of the 0.3–0.9 eV feature with x is shown explicitly in Fig. 2(a) after annealing in oxygen (open circles) and after repolishing (closed circles) to obtain the spectra shown in Fig. 1. Here Ω_x is defined as the difference between the maximum value of R at 0.3 eV and the minimum value, which changes with x but lies in the range 0.7–0.9 eV. While the absolute magnitude of Ω_x varies somewhat with sample history, its dependence on x always has the form shown in Fig. 2(a). We note that annealing tends to eliminate the rise in R for $x = 0.0$ and to decrease the magnitude of R by roughening up the shiny polished surfaces. The presence of a finite Ω_x for the nominal $x = 0.0$ sample may be due to incidental doping caused by oxygen deficiency. In Fig. 2(b) we plot the corresponding variation of the fraction of ideal diamagnetism at 4.2 K (Meissner effect) measured on the same set of samples, as well as their superconductivity transition temperatures defined as the point where the slope of χ_{dia} vs temperature breaks sharply as χ_{dia} vanishes. These results are similar

to those reported earlier,[13] and they are intended to quantify "superconductivity" of the samples used in these optical studies. It is clear that the strength of the reflectance structure is closely correlated with "superconductivity."

The rise in reflectance with decreasing energy below 0.9 eV was first reported for the single composition $x = 0.09$ by Tajima and co-workers[14] and interpreted as a plasma excitation. In parallel with our study, detailed analysis of the reflectance from a single concentration $La_{1.85}Sr_{0.15}CuO_{4-\delta}$ have shown that the rise in reflectance is due to the presence of a broad absorption band in the range 0.5–1 eV (Refs. 12 and 15). However, in neither case were range of compositions considered, nor were they correlated with the superconducting properties of the sample. What distinguishes our findings regarding this dopant-induced band is that its strength Ω_x follows closely T_c and the dc Meissner effect as the dopant concentration is changed continuously to cover the full range corresponding to the appearance and disappearance of superconductivity.

The ellipsometrically determined ϵ responses of $La_{2-x}Sr_xCuO_4$ for $x = 0.00$, 0.15, and 0.30 are shown in Fig. 3(a). On this scale, the spectra are relatively featureless, with ϵ showing typical oxide-dispersion behavior. The relatively flat spectral dependence of ϵ_2 throughout the accessible spectral range suggests a broad distribution of weak transitions analogous to charge-transfer excitations in other transition-metal oxides. We assign the rise in ϵ_2 above 5 eV to transitions from the upper Cu $3d$–O $2p$ complex to La $4f$ levels on the basis of published
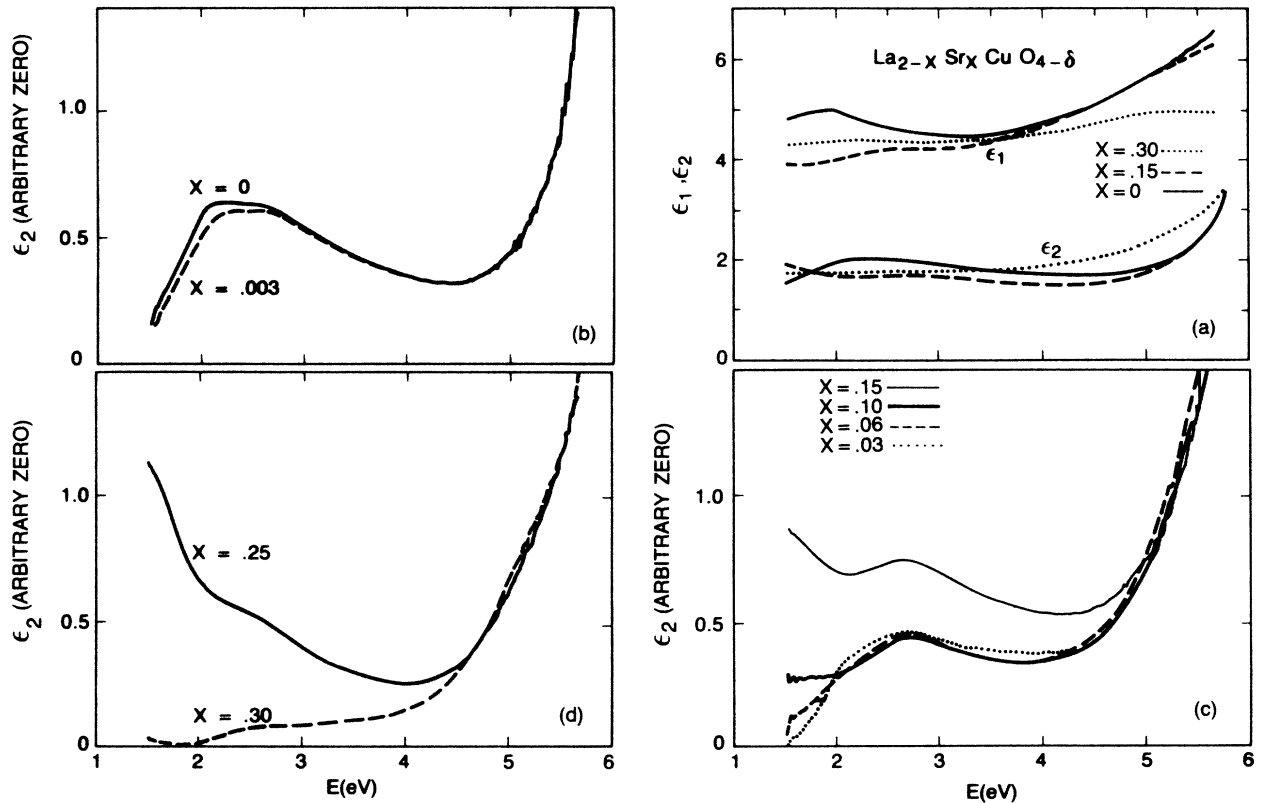
FIG. 3. Ellipsometrically measured ϵ spectra for $x = 0.00$, 0.15, and 0.30. (b)-(d): ϵ_2 spectra on expanded vertical scales without regard to zero offset. The structure in ϵ_2 at ~ 2 eV is the only feature in our spectral range that is affected in the initial stage of doping of La_2CuO_4.

band-structure calculations.[16,17] While ϵ_2 appears to be relatively independent of x for these three compositions, the significant reduction in ϵ_1 above 5 eV for $x = 0.30$ indicates a corresponding reduction in ϵ_2 at higher energies for this doping. Extrapolation of the ϵ_1 data to longer wavelengths shows that the contributions to the infrared dielectric constant from electronic transitions above 1.5 eV are about 4.5, in agreement with the value previously determined from reflectance measurements.[15,12]

Further information is obtained by displaying the ϵ_2 data on expanded vertical scales without regard to their zero values, as shown in Figs. 3(b)-3(d). Figure 3(b) emphasizes ϵ_2 spectra for low x in the energy range 1.5 to 4.0 eV, showing that the 2-3-eV peak can be resolved into two components at 2.0 and 2.7 eV, respectively. Of all features, the 2.0 eV structure is the only one noticeably affected by Sr doping for low x and is the most likely candidate for the onset of the interband absorption in pure La_2CuO_4. The effects of further increases in Sr doping is shown in Fig. 3(c), which reveals that the 2.0-eV peak continues to decrease with increasing x and finally disappears altogether for $x = 0.10$. The oscillator strength of this feature may be shifting into the 0.5-eV band in a

manner analogous to that observed for solitons in polyacetylene.[18] In contrast, the 2.7 and above -5.5-eV structures remain for all x. Thus the 0.5-eV structure coexists with band-structure-like transitions that are essentially independent of x as well as features that vary continuously with doping.

In summary, we emphasize the discovery of a *positive correlation* between superconductivity and an intense, 0.5 eV dopant-induced absorption band in $La_{2-x}Sr_xCuO_{4-\delta}$. This result strongly supports a microscopic mechanism in which superconductivity is mediated by an electronic rather than a vibrational excitation, and should aid in developing detailed models of superconductivity in these materials.

Note added. After completion of this paper we found that Kamaras *et al.* have independently come to similar conclusions by comparing optical conductivity $\sigma(\omega)$ of superconducting and nonsuperconducting samples of $YBa_2Cu_3O_{7-y}$ system.[19] Our finding that the position of the rise in reflectivity is independent of dopant concentration corraborates their assignment of the peak in $\sigma(\omega)$ to a non-Drude absorption mechanism.

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

[2]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[3]D. H. Lee and J. Ihm, Solid State Commun. **62**, 811 (1987).

[4]C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Commun. **62**, 681 (1987).

[5]W. Y. Ching, Yongnian Xu, Guang-Lin Zhao, K. W. Wong, and F. Zandiehnadem, Phys. Rev. Lett. **59**, 1333 (1987).

[6]D. Pines, Can. J. Phys. **34**, 1379 (1959).

[7]P. W. Anderson, Science **235**, 1196 (1987).

[8]S. Kivelson, D. S. Rokhsar, and J. P. Sethna, Phys. Rev. B **35**, 8865 (1987).

[9]J. M. Tarascon, L. H. Greene, W. R. McKinnon, G. W. Hull, and T. H. Geballe, Science **235**, 1373 (1987).

[10]D. E. Aspnes and A. A. Studna, Appl. Opt. **14**, 220 (1975); Rev. Sci. Instrum. **43**, 291 (1978).

[11]S. L. Herr, C. D. Porter, D. B. Tanner, S. Etemad, D. E. Aspnes, M. K. Kelly, and J. M. Tarascon (unpublished).

[12]S. L. Herr, K. Kamaras, C. D. Porter, M. G. Doss, D. B. Tanner, D. A. Bonn, J. E. Greedan, C. V. Stager, and T. Timusk, Phys. Rev. B **36**, 733 (1987).

[13]R. B. van Dover, R. J. Cava, B. Batlogg, and E. A. Rietman, Phys. Rev. B **36**, (1987).

[13]It is not clear why χ_{dia} and T_c should track each other; however, as discussed in Ref. 9, it is suggestive of the presence of mixed phase. We note that in Ref. 13 it is shown that onset of superconductivity defined from the onset of decrease in resistivity is the same for all values of x. But for the values of x outside the optimum concentration range $0.1 < x < .3$ the transition is very broad. This could be the reason that why the T_c defined from a bulk measurement such as susceptibility appears to be lowered for these concentrations.

[14]S. Tajima, S. Uchida, S. Tanaka, S. Kanbe, K. Kitazawa, and K. Fueki, Jpn. J. Appl. Phys. **26**, L432 (1987).

[15]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).

[16]J. B. Goodenough, Prog. Solid State Chem. **5**, 145 (1971).

[17]L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987); J. Yu, A. J. Freeman, and J. -H. Xu, ibid. **58**, 1035 (1987).

[18]N. Suzuki, M. Ozaki, S. Etemad, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. Lett. **45**, 1209 (1980).

[19]K. Kamaras, C. D. Porter, M. G. Doss, S. L. Herr, D. B. Tanner, D. A. Bonn, J. E. Greedan, A. H. O'Reilly, C. V. Stager, and T. Timusk, Phys. Rev. Lett. **59**, 919 (1987).