RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 13 1 MAY 1987

Observation of a low-energy infrared anomoly in superconducting $La_{1.85}Sr_{0.15}CuO_4$

Z. Schlesinger, R. T. Collins, and M. W. Shafer
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 16 March 1987)

We have studied the infrared reflectively of normal and superconducting $La_{2-x}Sr_xCuO_4$ up to 4000 cm^{-1}. For $0.05 \lesssim x \lesssim 0.2$ a pronounced drop in reflectivity near 500 cm^{-1} (60 meV) is observed. Both the size of the decrease and the extent of the frequency range over which the reflectivity is small suggest a possible electronic origin for this behavior, e.g., a plasma edge or interband excitation threshold. Coincident with this reflectivity drop is a strong optic-phonon mode. For compositions outside the range in which high T_c occurs these features become much weaker, suggesting a possible relationship between these modes and the composition dependence of T_c in this system.

Since the discovery of superconductivity in 1911, the value of the highest known superconducting transition temperature (T_c) has increased gradually, reaching a plateau at 23 K in 1973.[1] Recently, Bednorz and Müller[2,3] discovered a new class of superconducting systems in which dramatically higher T_c's have been observed by a number of groups,[4–8] most recently up to 90 K.[9] Prior to these discoveries, the possibility of obtaining high T_c's with an ordinary phonon-coupling mechanism was regarded as impossible. Consequently, these recent results have stimulated renewed interest in the possibility that these high T_c's arise from nonphonon interactions,[10–12] e.g., plasmon or exciton mechanisms.

In this Rapid Communication we report the observation of a dramatic drop in reflectivity occurring in resonance with a strong optic phonon in the high-T_c superconductor $La_{2-x}Sr_xCuO_4$. This infrared behavior is very unusual even for an oxide superconductor,[13–15] and may be indicative of a low-lying electronic mode. For compositions outside the range in which high T_c occurs this resonant complex becomes much weaker, suggesting a connection with the superconductivity.

Our sintered samples of $La_{2-x}Sr_xCuO_4$ with x ranging from 0 to 0.25 were prepared from nitrate solutions which were converted to oxides and reacted by solid-state reaction. The samples were pressed into pellets, annealed, and polished. The samples are quite dense, and in most cases we obtain a mirrorlike finish. Infrared spectra at temperatures from 300 to 10 K were obtained using scanning and Michelson interferometers. With each system the reflectivity was studied with nominally unpolarized radiation incident at approximately 45°. Figure 1 shows the ratio of the reflectivity in the superconducting state to the normal state in the region of the gap for a sample with $x=0.15$ ($T_c \simeq 35$ K). The size of the gap is consistent with previous measurements.[16] Details of the temperature and frequency dependences in this region will be published elsewhere.

In Fig. 2 we show the reflectivity spectrum for the same sample at room temperature referenced to a gold mirror. The gross features of this spectrum do not change appreciably between 300 and 10 K. Above 600 cm^{-1} the reflectivity is quite low ($\sim$25%) and remains so up to 4000 cm^{-1} in our measurements. Also shown is a Drude reflectivity, calculated using the Hagen-Rubens relation with our measured value of $\rho = 1.5\times10^{-3}$ Ω cm, and assuming a carrier concentration of order 2×10^{21} cm^{-3} and a mass of order unity. The measured spectrum does not follow the Drude curve in any appreciable region. At low frequencies ($\omega \leq 250$ cm^{-1}) the reflectivity is significantly lower than the Drude value, suggesting the existence of a strong low frequency infrared active mode.

As a guide to the eye, a dashed line has been drawn through the data from 300 to 600 cm^{-1}. The deviations from this line represent a Lorentz oscillator contribution to the dielectric function $\varepsilon(\omega)$ which we interpret as a Cu-O optic phonon. A very similar optic-phonon signature has been observed in the fluctuating valence com-

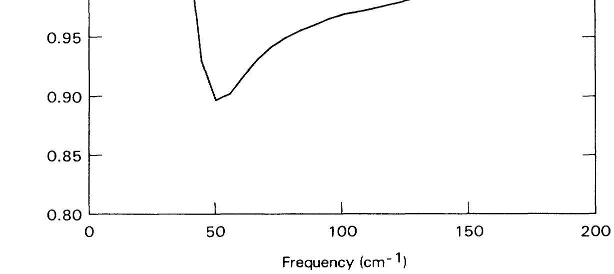

FIG. 1. The ratio of the superconducting (13 K) to normal (36 K) reflectivity of $La_{1.85}Sr_{0.15}CuO_4$ is shown. The superconductor becomes highly reflecting below the gap frequency of about 40 cm^{-1}.

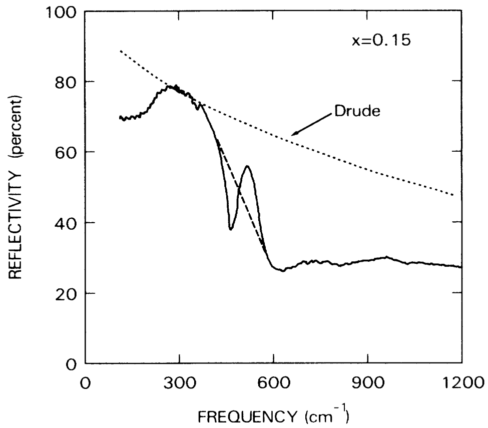

FIG. 2. The reflectivity of $La_{1.85}Sr_{0.15}CuO_4$ referenced to a gold mirror is shown as a function of frequency up to 1200 cm^{-1}. The dots show a calculated Drude absorptivity for our measured resistivity ($\rho \simeq 1.5 \times 10^{-3}$ Ω cm). The dashed line is a guide to the eye included to help separate the Lorentz oscillator (phonon) contribution and the reflectivity drop both occurring near 500 cm^{-1}. The overall scale of the vertical axis has an uncertainty of about 10%.

pound $CePd_3$.[17] An approximate mode frequency of $\simeq 490$ cm^{-1} is given by the crossing between the data and dashed line. Essentially coincident with this phonon frequency there is a substantial drop in the reflectivity from about 70% at 300 cm^{-1} to $\sim$25% at 600 cm^{-1}. The reflectivity remains near this low value up to 4000 cm^{-1}. The large size of the reflectivity drop and the extent of the frequency range over which the reflectivity is small strongly suggest an electronic origin for this behavior.

A pronounced decrease in the reflectivity of a metal is usually associated with a plasma edge or an interband absorption threshold,[18] but typically these occur at much higher energies than the reflectivity drop in Fig. 1. One interesting exception is $CePd_3$, in which a sudden drop in reflectivity from about 97% to 90% occurring near 100 cm^{-1} has been described using a very low-energy ($\sim$6-meV) interband scattering channel model.[17] It is not clear, however, if such a model is appropriate to describe the much larger reflectivity drop (to $\sim$25%) observed in our system.

To get such a large drop in reflectivity a plasma edge, i.e., a zero crossing of the real part of $\varepsilon(\omega)$, may be required. As a point of reference we note that the frequency of our observed reflectivity drop is about an order of magnitude below the free carrier plasma frequency estimated for $n \simeq 2 \times 10^{21}$ and an effective mass of order unity. (In $La_{2-x}Sr_xCuO_4$ the effective mass may be much heavier.) The frequency of a plasma edge can be dependent on carrier density, as in a free-electron metal, or it can be determined by an interband excitation threshold which drives $\mathrm{Re}(\varepsilon(\omega))$ through zero, as occurs, for example, in Ag.[18] An interesting class of models in which low-frequency plasmons occur are those in which more than one band is partially occupied. In a two-band theory Lee and Ihm have associated high T_c with the coincidence of the hole plasmon frequency and the relevant optic phonon.[19] The

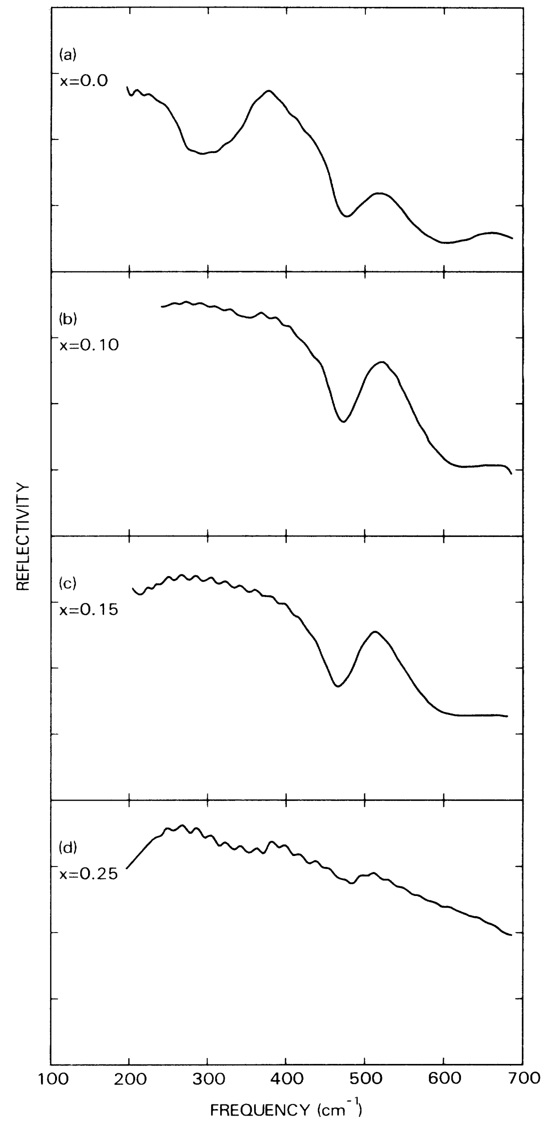

FIG. 3. Reflectivity spectra are shown for Sr concentrations of (a) $x=0.0$; (b) $x=0.10$; (c) $x=0.15$; and (d) $x=0.25$. For each curve full scale is approximately 100%.

effect of anisotropy on the plasma edge in this system, and on the relationship between the plasma edge and the longitudinal plasmon mode, is a potentially important question that we do not address here.[20] In this low-frequency range a plasma oscillation need not be strictly electronic, but may include sympathetic lattice motion as well. In a highly polaronic system the distinction between lattice and electronic modes can become blurred. In this frequency range a very strong polar phonon can exhibit a plasmalike edge which is almost indistinguishable from an ordinary electronic plasma edge. The apparent coincidence of the optic phonon (at 490 cm^{-1}) and the reflectivity drop in our data is intriguing; however, we do not at present know to what extent the modes responsible for these features may be coupled, or pinned to the same frequency.

In Fig. 3 we explore the composition dependence of the unusual infrared behavior exhibited in Fig. 2. In Fig. 3(a) the reflectivity of a pure ($x=0$) sample (not superconducting) is shown. This sample is a poor conductor ($\rho \simeq 200$ mΩ cm) and, thus, in the absence of appreciable electronic screening it is not surprising that optic phonons show up strongly in this spectrum.[17] The samples in Figs. 3(b) and 3(c) are in the intermediate composition range in which high-T_c superconductivity occurs ($x=0.10$, $T_c \simeq 25$ K and $x=0.15$, $T_c \simeq 35$ K, respectively). Both show the unusual drop in reflectivity resonant with a strong optic phonon as in Fig. 2. At room temperature these samples have roughly two orders of magnitude higher conductivity than the pure sample in Fig. 3(a) and thus should screen much more effectively. However, in this regard one must be careful since the large reflectivity drop at ~ 500 cm^{-1} indicates that we do not really understand finite frequency screening in this composition range. In Fig. 3(d) the reflectivity spectrum for a sample with $x=0.25$ (not superconducting) is shown. It exhibits a gradual, mostly structureless decrease in R with only weak, presumably well screened, phonon features. This observed composition dependence partially coincides with that for high T_c, suggesting that the unusual infrared features in Figs. 3(b) and 3(c) may be associated with the high-temperature superconductivity in this system. The attainment of high T_c by coupling to such energetic modes is attractive because it does not require extremely strong coupling. For example, for $\omega_0=60$ meV and $T_c=35$ K, one obtains $\lambda \simeq \frac{1}{2}$ with a Coulomb pseudopotential of $\mu=0.1$.[21]

Recently, Sulewski *et al.*[22] have reported a strong structure in $\alpha_{tr}^2F(\omega)$ peaked around 2.8 meV based on their observation of Holstein-like structure[23,24] in a low-frequency infrared measurement of the ratio of the superconducting-to-normal reflectivities of $La_{2-x}Sr_xCuO_4$. We have attempted a similar study at higher frequencies and observed weak (1%) structures near 500 cm^{-1} which are suggestive of Holstein steps. We cannot be confident of the interpretation of these low-temperature features, however, because of additional spectral changes occurring above T_c associated with small changes in the strong infrared features in the spectrum in this frequency range. (This problem is not present in Pb because the coupling occurs in the acoustic-phonon region where there are no infrared active modes.)

In conclusion, we observe an abrupt drop in reflectivity near 500 cm^{-1} ($\simeq 60$ meV), which indicates the existence of an unusually low-lying plasmalike edge and/or an unusually low energy electronic excitation. In resonance with this electronic feature is a strong optic phonon. Observed composition dependence suggests a possible connection between these features and the high-temperature superconductivity in this system.

It is a pleasure to acknowledge very valuable conversations with D. H. Lee, R. L. Greene, P. M. Horn, D. J. Scalapino, L. J. Sham, A. J. Sievers, J. C. Tsang, and A. R. Williams. We thank T. Penney for sharing his low-temperature resistivity measurements with us prior to publication.

[1] J. R. Gavaler, Appl. Phys. Lett. **23**, 480 (1973); L. R. Testardi, H. H. Wernick, and W. A. Royer, Solid State Commun. **15**, 1 (1974).

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

[3] J. G. Bednorz, M. Takashige, and K. A. Müller, Europhys. Lett. **3**, 379 (1987).

[4] S. Uchida, R. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Lett. (to be published).

[5] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).

[6] Z. X. Zhao, L. Q. Chen, C. G. Cui, Y. Z. Huang, J. X. Liu, G. H. Chen, S. L. Li, S. Q. Guo, and Y. Y. He (unpublished).

[7] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).

[8] J. M. Tarascon, L. H. Greene, W. R. McKinnon, G. W. Hull, and T. H. Geballe, Science (to be published).

[9] M. K. Wu, J. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987); P. H. Hor, L. Gao, R. L. Meng, Z. J. Huang, Y. Q. Wang, K. Forster, J. Vassilious, C. W. Chu, M. K. Wu, J. R. Ashburn, and C. J. Torng, *ibid.* **58**, 911 (1987).

[10] W. A. Little, Phys. Rev. **134**, A1416 (1964); H. Frolich, J. Phys. C **1**, 544 (1968).

[11] D. Allender, J. Bray, and J. Bardeen, Phys. Rev. B **7**, 1020 (1975).

[12] J. Ruvalds, Adv. Phys. **30**, 677 (1981); M. Grabowski and L. J. Sham, Phys. Rev. B **29**, 6132 (1984).

[13] M. L. Cohen, *Superconductivity,* edited by R. D. Parks (Marcel Dekker, New York, 1969), Chap. 12.

[14] A. S. Burker, Jr., in *Optical Properties and Electronic Structure of Metals and Alloys,* edited by F. Abeles (North-Holland, Amsterdam, 1966).

[15] F. Tajima, S. Uchida, A. Masaki, H. Takagi, K. Kitazawa, S. Tanoka, and A. Katsui, Phys. Rev. B **32**, 6302 (1985).

[16] Z. Schlesinger, R. L. Greene, J. G. Bedorz, and K. A. Müller, Phys. Rev. B **35**, 5334 (1987); P. E. Sulewski, H. J. Sievers, R. A. Buhrman, J. M. Tarascon, and L. H. Greene (unpublished); U. Walter, M. S. Sherwin, A. Stacy, R. L. Richards, and H. Zettl, Phys. Rev. B **35**, 5327 (1987).

[17] F. E. Pinkerton, B. C. Webb, A. J. Sievers, J. W. Wilkins, and L. J. Sham, Phys. Rev. B **30**, 3068 (1984).

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

[19] D. H. Lee and J. Ihm, Solid State Commun. (to be published).

[20] V. Z. Kresin (unpublished); J. Ruvalds (unpublished).

[21] D. J. Scalapino (private communication).

[22] P. E. Sulewski, A. J. Sievers, R. A. Buhrman, J. M. Tarascon, and L. H. Greene (unpublished).

[23] R. R. Joyce and P. L. Richards, Phys. Rev. Lett. **24**, 1007 (1970); G. Brandli and A. J. Sievers, Phys. Rev. B **5**, 3550 (1972).

[24] P. B. Allen, Phys. Rev. B **3**, 305 (1971); J. C. Swihart and W. Shaw, Physica **55**, 678 (1971).