Excitonic Absorption and Superconductivity in $YBa_2Cu_3O_{7-y}$

K. Kamarás,[a] C. D. Porter, M. G. Doss, S. L. Herr, and D. B. Tanner
Department of Physics, University of Florida, Gainesville, Florida 32611

and

D. A. Bonn, J. E. Greedan, A. H. O'Reilly, C. V. Stager, and T. Timusk
Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

(Received 19 June 1987)

Optical and neutron-diffraction studies of superconducting and nonsuperconducting samples of $YBa_2Cu_3O_{7-y}$ are described. Superconducting samples, with $y \approx 0.1$, showed two strong electronic transitions, at 3000 cm^{-1} (0.37 eV) and at 20000 cm^{-1} (2.5 eV), which are interpreted as charge-transfer bands (i.e., excitons). Nonsuperconducting samples, with $y \approx 0.8$ (prepared by heating of superconducting samples in vacuum to deplete the oxygen content), did not show these features. Our measurements support an excitonic mechanism for the superconductivity in high-T_c copper oxide compounds.

PACS numbers: 74.70.Ya, 71.35.+z, 71.45.Gm, 78.20.Ci

In this Letter we describe the optical and structural properties of the high-T_c superconductor $YBa_2Cu_3O_{7-y}$. Our optical measurements, made at temperatures between 4 and 300 K, span the frequency range between the far infrared and the ultraviolet. We studied samples with $y \simeq 0.1$, which were superconducting, and samples with $y \simeq 0.8$, which were not. The structure of the $y \simeq 0.8$ sample is found to be tetragonal, in contrast to the orthorhombic structure of the $y \simeq 0.1$, superconducting sample.

For the superconducting samples, the frequency-dependent conductivity (obtained by Kramers-Kronig analysis of reflectance) is decidedly non-Drude in form, consisting of two broad bands. These bands are interpreted as arising from charge-transfer transitions (i.e., excitons) and are evidence for strong electron-electron interactions in the material.[1,2] Their presence appears to rule out single-particle pictures of the electronic structure. The nonsuperconducting (or "dead") sample did not show these electronic absorptions.

Only limited optical studies of this material have been previously presented. Our far-infrared study[3] focused on the the energy gap in the superconducting state, presenting evidence that the gap is close to the BCS value, $2\Delta/kT_c \approx 3.5$. Three other far-infrared measurements[4] have been reported. The room-temperature infrared reflectance has been reported by Orenstein *et al.*[5] The closely related compound $La_{2-x}Sr_xCuO_4$ has been studied by a number of investigators.[5-10]

The preparation, crystal structure, and magnetic properties of $YBa_2Cu_3O_{6.9}$ have been described previously.[11] This material has $T_c = 93$ K and a Meissner fraction close to unity. $YBa_2Cu_3O_{6.2}$ was prepared by heating a sample of nominal composition $YBa_2Cu_3O_7$ in a 10^{-2}-Torr vacuum at 540 ± 10 °C for 12 h. The oxygen content was determined by the weight changes during reoxidation at 400 °C, and during subsequent reduction in H_2 at 1000 °C. The composition of the vacuum-reduced material was $y = 0.80 \pm 0.06$. The x-ray powder diffraction pattern of the vacuum-reduced compound was indexed on a tetragonal cell with $a = 3.865(1)$ Å and $c = 11.790(1)$ Å. Magnetic-susceptibility data were obtained in an applied field of 30 Oe by cooling the sample from room temperature in a PAR vibrating sample magnetometer. The sample remained weakly paramagnetic down to 4 K. Thus, this treatment effectively kills the superconductivity.

Neutron-powder-diffraction data were collected at the McMaster Nuclear Reactor, and refinement was carried out as described previously.[11] Solution of the structure was carried out in *P4/mmm* space group, which is a supergroup of *Pmmm*, the space group for orthorhombic $YBa_2Cu_3O_7$. In *P4/mmm* the sites $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2})$, which are distinct in orthorhombic symmetry, are now equivalent. Refinement proceeded smoothly to the positional and thermal parameters given in Table I. The refinement showed that the oxygen deficiency was associated with the O(1) $[(\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2})]$ site.

One consequence of the tetragonal symmetry observed in the $y = 0.8$ sample is that the Cu-O chains which characterize the orthorhombic, superconducting $YBa_2Cu_3O_7$ are nonexistent. Also, the *c* axis of the tetragonal phase is 0.10 Å larger than the 11.69-Å *c* axis of the orthorhombic phase.

The interatomic distances are given in Table II and compared with those from the orthorhombic, superconducting phase (given in square brackets). The most significant difference appears to be that the oxygen O(2) atom which connects the Cu(1) and the Cu(2) atoms in the planes moves toward the CU(1) atoms in the tetragonal phase. All of the other distances in the copper-oxygen network remain essentially constant.

TABLE I. Atomic positions, isotropic temperature factors, and agreement indices for $YBa_2Cu_3O_{6.2}$ at 298 K.

	x	y	z	B (Å^2)
Y	0	0	0	0.46(8)
Ba	0	0	0.3065(3)	0.69(9)
Cu(1)	1/2	1/2	1/2	0.77(9)
Cu(2)	1/2	1/2	0.1406(3)	0.76(6)
O(1)[a]	1/2	0	1/2	1.6(1.0)
O(2)	1/2	1/2	0.3484(4)	1.6(1)
O(3)	1/2	0	0.1208(2)	0.61(5)
Weighted profile R	0.050	a	3.8620(3) Å	
Nuclear R	0.044	b	11.7883(13) Å	
Profile R	0.036	Volume	175.82(3) Å	
Expected R	0.019			
Number of degrees of freedom	951			
Number of Bragg reflections	136			

[a] O(1) occupancy refined to 0.24(3).

The optical measurements were made as near-normal-incidence specular reflection on freshly polished sample surfaces. We used benzene or alcohol to make the polishing slurry; when the water was used a strong hydroxyl signature was seen in the infrared spectra. Following the measurements, the sample was coated with a metal overlayer and the reflectance of the coated surface was measured to obtain a reference spectrum. On account of the granular nature of the surface, this coating made important quantitative changes in the reflectance, particularly at higher frequencies.

Figure 1 shows representative normal-state reflectance data for superconducting ($y=0.1$) and nonsuperconducting ($y=0.8$) samples. *Note the logarithmic frequency scale.* The $y=0.1$ data were taken at 105 K, whereas the $y=0.8$ data were at 300 K; however, neither sample showed strong temperature dependence. For the $y=0.1$ sample, the most significant effect is below T_c, where the superconducting energy gap is observed.[3] With increasing temperature there is also a small ($\approx 2\%$) decrease in the mid-infrared reflectance combined with a loss of intensity of the vibrational features.

There are three vibrational doublets in the far infrared, at 151 and 191 cm^{-1}; 279 and 310 cm^{-1}; and 548 and 609 cm^{-1}. A broad high-reflectance region occurs in the mid-infrared, with a plasma edge giving a minimum at about 15000 cm^{-1} (1.9 eV). A second broad band is centered at 20000 cm^{-1} (2.5 eV). On account of the logarithmic scale, this upper band does not appear very significant. In reality, it is both broad, with a width of 8000 cm^{-1} (1 eV), and strong, with an oscillator strength of about 80% of the lower-frequency band. (The oscillator-strength estimate comes from our Kramers-Kronig analysis.)

TABLE II. Selected interatomic distances (in angstroms) 298 K for $YBa_2Cu_3O_{6.2}$. Values for $YBa_2Cu_3O_{6.9}$ are given in square brackets (Ref. 11).

Y-O(3)	2.397(1)	[2.400(1)]
Ba-O(1)	2.990(2)	[2.911(4)]
Ba-O(2)	2.7732(9)	[2.753(1)]
Ba-O(3)	2.919(3)	[2.945(7)]
Cu(1)-O(1)	1.931(3)	[1.945(2)]
Cu(2)-O(2)	1.800(4)	[1.827(5)]
Cu(2)-O(2)	2.437(5)	[2.332(5)]
Cu(2)-O(3)	1.9453(4)	[1.947(1)]

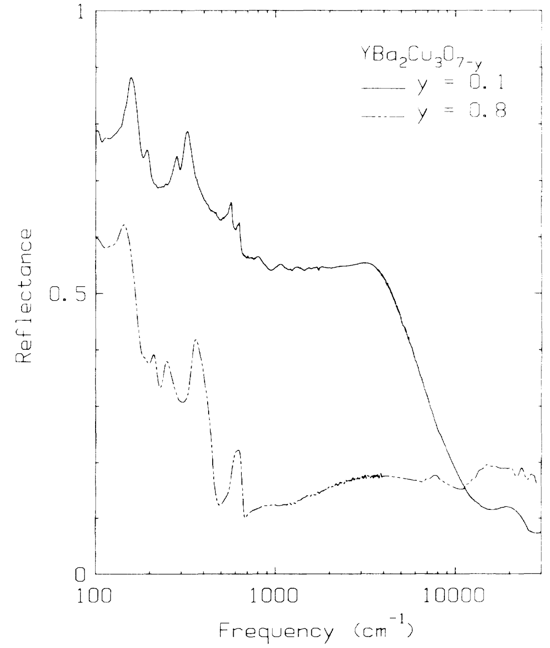

FIG. 1. Reflectance of superconducting $YBa_2Cu_3O_{6.9}$ (at 105 K) and of nonsuperconducting $YBa_2Cu_3O_{6.2}$ (at 300 K). Note the logarithmic frequency scale.

Our results are qualitatively in agreement with those of Orenstein *et al.*[5] We find, however, about twice as large a mid-infrared reflectance and a much sharper plasma edge. We attribute most of this difference to our having overcoated the sample with a metal so as to correct for the rough surfaces; our uncorrected spectra resemble theirs. However, we have also observed some sample-to-sample variation in the sharpness of the plasma edge.

The infrared reflectance of the dead sample ($y=0.8$) is substantially smaller than that of the superconducting sample, with the plasma edge absent. The surfaces of this sample were quite poor, leading to low signal-to-noise ratio at high frequencies. Little temperature dependence was observed; in particular, the reflectance did not change in any way on cooling through the 90-K region. Vibrational features are observed at $\simeq 104$, 114, 211, 351, and 626 cm^{-1}. As shown by their relatively low reflectance maxima, the oscillator strength of these features is smaller than those in the $y=0.1$ sample.

We used Kramers-Kronig analysis to determine the frequency-dependent conductivity, $\sigma_1(\omega)$, which is shown in Fig. 2. For the superconductor ($y=0.1$), the electronic part of the spectrum has a broad peak at 3000 cm^{-1} (0.37 eV). The conductivity of the dead sample ($y=0.8$) is strikingly different from that of the superconducting sample. The 3000-cm^{-1} (0.37-eV) band is absent from this specimen. Instead, there is a slowly rising conductivity, with a suggestion of a high-lying electronic peak above 16000 cm^{-1} (2 eV).

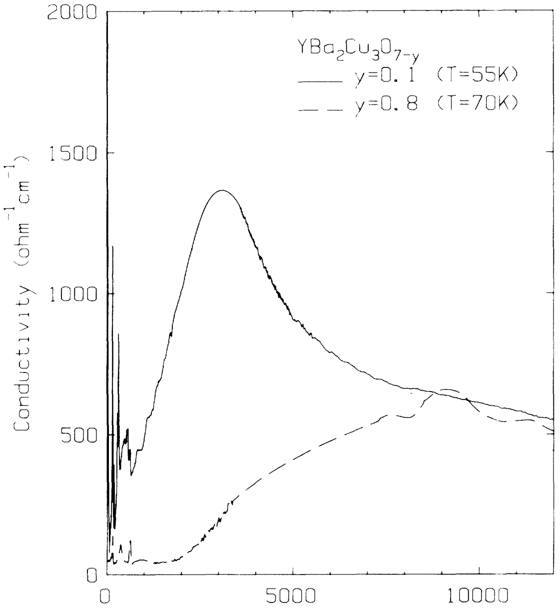

FIG. 2. The frequency-dependent conductivity of superconducting $YBa_2Cu_3O_{6.9}$ at 55 K and of nonsuperconducting $YBa_2Cu_3O_{6.2}$ at 70 K, as determined by Kramers-Kronig analysis of the reflectance.

The low-energy (0.37-eV) peak in the conductivity of the superconducting sample is not consistent with band-structure calculations,[12] which show the onset of interband transitions only above 2.5 eV. We attribute this peak to a charge-transfer band, or exciton,[1] brought on by Coulomb interactions among the charge carriers. If Coulomb repulsion is the dominant interaction, then the carriers will distribute themselves so as to minimize this repulsion. In the extreme (zero-bandwidth) limit the optical-absorption spectrum due to charge-transfer excitation can be qualitatively understood within the following Hamiltonian:

$$H_{ee}=U\sum_i n_{i\uparrow}n_{i\downarrow}+\tfrac{1}{2}\sum_i\sum_{j\neq i}V_{|i-j|}n_in_j, \qquad (1)$$

where n is the occupation number operator, U is the Coulomb energy suffered by two electrons on the same site, and $V_{|i-j|}$ is the energy cost of having one electron on site i and a second on j. The problem, one of distributing N electrons over M sites, has been solved by Hubbard[13] for the one-dimensional case. Generally, $U > V_1 > V_2$, etc., and the electrons are localized in a regular lattice of singly occupied and vacant sites. The details of this arrangement (which also occurs in the two-dimensional square lattice) depend on the relative values of the $V_{|i-j|}$ and N/M. For $N/M < 1$ there are two excited states involving a transfer of one electron to a neighboring site. The lower-energy one (at $\hbar\omega \simeq V_1$) consists of a transfer to a vacant site, whereas the higher-energy one (at $\hbar\omega \simeq U$) consists of a transfer to an already occupied site.

The oscillator strength of the vibrational features of the superconducting sample (better seen in Fig. 2 of Ref. 3) is extremely high. We have recently proposed[7] for the case of $La_{1.85}Sr_{0.15}CuO_4$ that this can be attributed to strong electron-vibrational coupling via the "dimer charge oscillation" or "phase-phonon" mechanism introduced by Rice.[14] The modes in question would be the symmetric vibrational modes of the Cu-O system which become infrared active when they are strongly coupled to the electronic density. Essentially, the infrared radiation modulates the charge density on a site or in a bond; in turn, the bond lengths follow the local charge density. For this mechanism to operate, there must be a variation in charge from site to site. Either a Peierls transition to a charge-density-wave ground state or a Coulomb-energy-driven localization of electrons on specific sites, as described above, can cause this variation.

Thus, there appears to be a close connection among five properties of $YBa_2Cu_3O_{7-y}$: the oxygen content, the existence of one-dimensional chains, the presence of the 3000-cm^{-1} (0.37-eV) peak in the infrared, very strong vibrational features, and superconductivity.

In this context, we wish to make the following points:

(1) An electronic peak in the infrared spectrum is a common feature of oxide superconductors, including[15] $BaPb_xBi_{1-x}O_3$ and[7] $La_{2-x}Sr_xCuO_4$. (2) The excitonic mechanism proposed by Little[16] and subsequently further developed both by Little and by Ginzburg and coworkers[17] can lead to high transition temperatures because exciton energies are so much higher than phonon energies. (3) In some theories,[16,17] the excitons involve different electrons than those responsible for the superconductivity. $YBa_2Cu_3O_{7-y}$ possesses two types of copper-oxygen layers: two-dimensional sheets and parallel one-dimensional chains. It is tempting to speculate that the superconductivity occurs on the sheets mediated by excitons on the chains. The difficulty with this notion is that there are no such obvious distinctions in $La_{2-x}Sr_xCuO_4$ or $BaPb_xBi_{1-x}O_3$. Furthermore, in other theories the same electrons are involved in the superconductivity and in the electronic absorption.[1] (4) If the superconductivity were due to extremely strong coupling to phonons, then the ratio $2\Delta/kT_c$ would be in the range 5–10 rather than the 3.5 value of BCS or weak-coupling theories.[18] Infrared absorption measurements[3,6] are consistent with $2\Delta/kT_c=3.5$–4, and thus inconsistent with strong coupling to phonons. (5) The excitonic mechanism gives $2\Delta/kT_c=3.5$; and thus is consistent with the infrared measurements. A mixture of electron-phonon and excitonic interactions also would yield the weak-coupling value for $2\Delta/kT_c$, even if the electron-phonon coupling were relatively strong.[18]

The detailed mechanism for superconductivity in the high-T_c copper oxides is not at present known. We have discussed in this Letter only one of many possibilities. More generally, however, we believe that the occurrence of a strong electronic band in the infrared spectrum and its correlation with superconductivity provides evidence that the superconductivity of these materials is mediated by an electronic excitation.[10]

Research at the University of Florida was supported by the National Science Foundation—Solid State Chemistry—Grant No. DMR-84-16511, and by the U.S. Defense Advanced Research Projects Agency through a grant monitored by the U.S. Office of Naval Research. Research at McMaster University was supported by the Natural Sciences and Engineering Research Council of Canada, including infrastructure support for the Institute for Materials Research and the McMaster Nuclear Reactor. At McMaster University, we thank H. F. Gibbs and M. A. Crowe for assistance with thermal analysis and x-ray diffraction.

[a] Permanent address: Central Research Institute for Physics, P.O. Box 49, H-1525 Budapest, Hungary.

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

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

[3] D. A. Bonn, J. E. Greedan, C. V. Stager, T. Timusk, M. G. Doss, S. L. Herr, K. Kamarás, and D. B. Tanner, Phys. Rev. Lett. **58**, 2249 (1987).

[4] G. A. Thomas, H. K. Ng, A. J. Millis, R. H. Bhatt, R. J. Cava, E. A. Rietman, D. W. Johnson, G. P. Espinoza, and J. M. Vandenberg, Phys. Rev. B **36**, 846 (1987); L. Genzel, A. Wittlin, J. Kuhl, H. J. Mattausch, W. Bauhofer, and A. Simon, Solid State Commun. (to be published); J. M. Wrobel, S. Wang, S. Gygax, B. P. Clayman, and L. K. Peterson, Phys. Rev. B (to be published).

[5] Joseph 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).

[6] 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).

[7] S. L. Herr, K. Kamarás, 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); preliminary results reported by D. A. Bonn at the Meeting of the American Physical Society, New York, NY, March 1987 (unpublished).

[8] Setsuko Tajima, Shin-ichi Uchida, Soji Tanaka, Shinsaku Kanbe, Koichi Kitazawa, and Kazuo Fueki, Jpn. J. Appl. Phys. Part 2 **26**, L432 (1987).

[9] Z. Schlesinger, R. T. Collins, and M. W. Shafer, Phys. Rev. B **35**, 7332 (1987).

[10] Shortly after completion of this Letter we received a preprint by S. Etemad, D. E. Aspnes, M. K. Kelly, R. Thomspon, J.-M. Tarascon, and G. W. Hull (to be published) which reaches similar conclusions from a detailed study of Sr doping in $La_{2-x}Sr_xCuO_4$.

[11] J. E. Greedan, A. H. O'Reilly, and C. V. Stager, Phys. Rev. B **35**, 8770 (1987).

[12] S. Massidda, Jaejun Yu, A. J. Freeman, and D. D. Koelling, Phys. Lett. A **122**, 198 (1987); Jaejun Yu. S. Massidda, A. J. Freeman, and D. D. Koelling, Phys. Lett. A **122**, 203 (1987).

[13] J. Hubbard, Phys. Rev. B **17**, 494 (1978).

[14] M. J. Rice, Solid State Commun. **31**, 93 (1979).

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

[16] W. A. Little, Phys. Rev. **134**, A1416 (1964).

[17] V. L. Ginzburg, in *High Temperature Superconductivity*, edited by V. L. Ginzburg and D. A. Kirzhits (Consultants Bureau, New York, 1982).

[18] M. Schossmann, F. Marsiglio, and J. P. Carbotte, Phys. Rev. B (to be published).