Temperature dependence of the phonon structure in the high-temperature superconductor Bi$_2$Sr$_2$CaCu$_2$O$_8$ studied by infrared reflectance spectroscopy

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(Received 30 November 1990)

We have investigated a ceramic sample of the high-temperature superconductor Bi$_2$Sr$_2$CaCu$_2$O$_8$ ($T_c = 85$ K) by infrared and visible reflectance spectroscopy at several temperatures both below and above the superconducting transition. We find that the temperature variation in the vibrational region is associated with minima or antiresonance features of the optical conductivity, instead of maxima, indicating strong Fano-type electron-phonon interaction and implying that the phonon structure in the infrared is strongly affected by the *ab*-plane response.

Vibrational spectroscopy has been intensively used to study high-temperature superconductors since their discovery.[1] In the widely studied RBa$_2$Cu$_3$O$_{7-\delta}$ materials, two types of anomalous temperature dependence of vibrational lines have been found around T_c. One is a softening of some lines, which has been explained in the framework of a strong-coupling model by Zeyher and Zwicknagl.[2] The other is a sudden increase in the linewidth when going from the superconducting to the normal state.[3,4] This latter effect has been attributed to coupling of the vibrations to the metallic electrons, causing an anomalous broadening in the normal state but disappearing when the electrons condense into the superfluid below T_c. In both cases, the measurements were performed on ceramic samples and the phonons seen in the infrared spectra were assumed to be those polarized along the c axis of the crystal, because the *ab*-plane phonons are strongly screened by the free carriers. For reasons which we do not understand, the temperature dependence of the c-axis phonons in *crystalline* YBa$_2$Cu$_3$O$_{7-\delta}$ materials is considerably less than in ceramic samples.[5,6]

While numerous Raman studies[7–9] have been performed on the bismuth superconductors, infrared measurements are scarce. In crystals, due to their extreme thinness, only *ab*-plane spectra have been taken so far;[10] these show no sharp phonon lines on account of the screening by the conducting electrons. The infrared spectrum of a 2:2:1:2 ceramic at room temperature has been reported by Piro *et al.*[11] while Popovic *et al.*,[12] in a study of the analogous compound Bi$_2$(Sr$_{1-x}$Ca$_x$)$_2$CuO$_6$, have observed a line at 490 cm^{-1} which shows an appreciable blue shift between 10 and 300 K. We have investigated the temperature dependence of the infrared spectra of Bi$_2$Sr$_2$CaCu$_2$O$_8$ ceramic samples on a finer temperature scale to see if we can find a similar effect in the phonon spectrum.

Bi$_2$Sr$_2$CaCu$_2$O$_8$ ceramic samples were prepared from Bi$_2$O$_3$, SrCO$_3$, CaCO$_3$, and CuO according to the procedures described in Ref. 13. The sample investigated

had a superconducting transition temperature of $T_c = 85$ K, as determined by measurement of the dc susceptibility, and about 30% Meissner effect. Reflectance spectra in the infrared region (160–5000 cm^{-1}) were measured with a Bruker FTS 113v spectrometer equipped with a specular reflectance insert whereas a home-made spectrometer based on a Perkin-Elmer grating monochromator was used from the near infrared to the ultraviolet (2000–20 000 cm^{-1}). Low temperature measurements were performed in the infrared range using a continuous flow He cryostat. Due to diffuse scattering from the grainy surface of the sample, spectra taken against a standard reference mirror are strongly distorted, especially at higher frequencies. Therefore, all our spectra presented here are normalized to the same sample coated by a 2000-Å thick Al layer.[14] The optical conductivity was calculated from the reflectance by Kramers-Kronig analysis. We used room temperature data above 5000 cm^{-1} as high-frequency extension at all temperatures; this is justified by the negligible temperature dependence of the reflectance between 2000 and 5000 cm^{-1}, and has practically no effect on the conductivity below 1000 cm^{-1}. At low frequencies a metallic extrapolation $\mathcal{R} = 1 - A\sqrt{\omega}$ was applied in the normal state, while below T_c the reflectance was made to approach unity by the formula $\mathcal{R} = 1 - B\omega^4$.

Figure 1 shows the reflectance and optical conductivity (from Kramers-Kronig analysis) of our sample at room temperature in the whole measured range. The intense electronic background is apparent, with a plasmalike edge at about 10 000 cm^{-1} (1.2 eV). The high-frequency part of the spectrum is very similar to that found in crystals and reflects the contribution of both free and bound electrons as discussed in Ref. 10. At low frequencies, however, there is definitely vibrational structure present.

Figure 2 shows reflectance spectra at seven temperatures between 20 and 300 K. The principal effect of temperature is to change the electronic background absorption in the far infrared. No change is apparent in the phonon structure within experimental error, because of
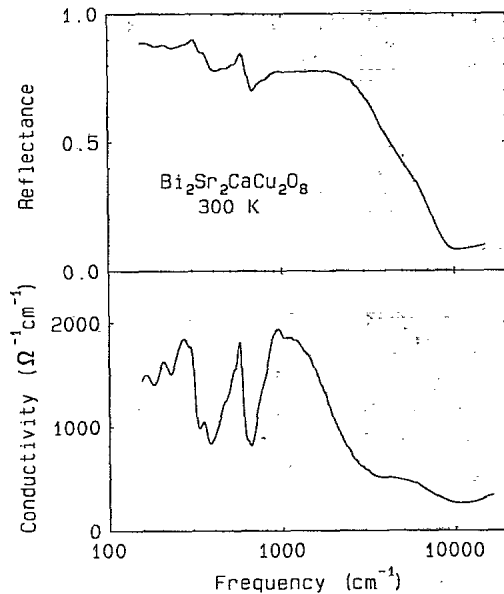
FIG. 1. Reflectance and optical conductivity vs frequency for a $Bi_2Sr_2CaCu_2O_8$ sample at room temperature. Note the logarithmic frequency scale.

FIG. 2. Reflectance of $Bi_2Sr_2CaCu_2O_8$ at seven temperatures. The curves in the inset have been shifted along the vertical axis for clarity. Temperatures from top to bottom of the main figure are 20, 50, 100, 150, 200, 250, and 300 K.

FIG. 3. Upper panel: optical conductivity (in Ω^{-1} cm^{-1}) vs frequency of $Bi_2Sr_2CaCu_2O_8$ at three temperatures. The vertical bars indicate the location of four A_g and one B_{1g} Raman modes. Lower panel: difference between the conductivity at several normal-state temperatures and the 20-K conductivity.

the very large linewidths.

The phonon lines are more evident in the optical conductivity, as shown in Fig. 3(a). The conductivity maxima shift down in the normal state with decreasing temperature, but do not soften further on going from normal to superconducting. Attempts to analyze the spectra by Drude-Lorentz fits to the reflectance[14] using independent oscillators gave frequencies and linewidths for all modes essentially constant below T_c, and both the frequencies and the linewidths increasing with temperature above T_c. Peak positions at 300 K are 260, 294, 349, 447, 515, and 563 cm^{-1}. The validity of such a simple approach is,
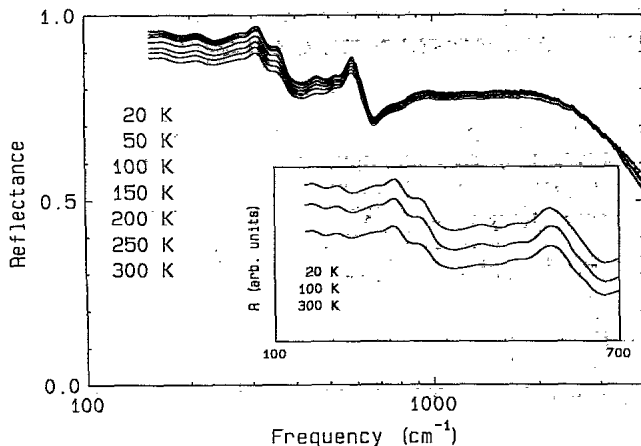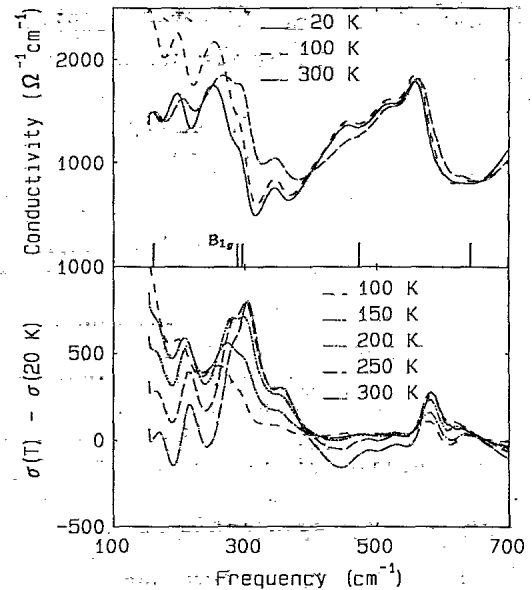
however, to be questioned for a number of reasons, which we will now discuss.

The lower panel of Fig. 3 shows the difference between the conductivity at several normal-state temperatures and that of the superconducting state (20 K), generated from the Kramers-Kronig results. At low frequencies (below 300 cm^{-1}) the extra conductivity is caused by the free carriers, showing a typical Drude-like broadening with increasing temperature.[15] Above that, however, considerable temperature variation is associated with the minima, rather than the maxima, of conductivity. (This effect is most notable in the 400–600-cm^{-1} region, where a number of conductivity maxima appear, yet the difference curves remain essentially flat.)

The oscillator fit results given here differ only slightly from those of Piro et al.,[11] due partly to diffuse scattering effects in their spectra (which decreases the reflectance level and the resolution and also tends to give higher peak frequencies), and partly to the broadening which renders the weaker lines almost unobservable at room temperature. The latter authors assign all their peaks to in-plane vibrations, assuming preferred orientation of the grains normal to the c axis. While preferred orientation is indeed most probable in this material, it also results in high electronic absorption and consequent shielding of the in-plane modes as mentioned above. Phonon lines found in highly oriented $YBa_2Cu_3O_{7-\delta}$ ceramics[16] have been identified in single-crystal polarized studies as c-axis modes,[5] whose assignment is now well established.[17] Therefore we expect A_u and B_{2u} vibrations to show up strongly, near their Raman-active Davydov counterparts of A_g and B_{1g} symmetry. Cardona et al.,[7] in oriented polycrystals, found the B_{1g} mode at 282 cm^{-1}. Although there exists some controversy regarding

the space group assignment and the number of both expected and observed A_g modes,[7-9] the existence of four strong Raman peaks of this symmetry, at around 160, 290, 470, and 630 cm^{-1}, has been proven. We show the position of these five modes in Fig. 3. Surprisingly, they also tend to line up with the dips rather than the peaks in conductivity.

Given the existence of a strong midinfrared electronic absorption in all copper-oxide superconductors[15] and by analogy to the direct electron-phonon interaction in quasi-$1d$ organic conductors that have a low-lying charge-transfer excitation,[18] we view the vibrational structure of our spectra as containing a strong antiresonance at 630 cm^{-1} and possibly another one at around 300 cm^{-1}. Such strong electron-vibration coupling has been discussed previously.[19,20] In the model of Rice[18] the coupling can manifest itself in either strong resonances or antiresonances, depending on the position of the phonon relative to the electronic excitation energy. The highest phonon feature around 600 cm^{-1} definitely shows a Fano-type asymmetry, indicating that the electronic band is centered at lower frequency. Finally, in the organic conductors, the charge-transfer excitation is polarized along the stacking direction while the vibrational motions are in the molecular planes and thus nearly orthogonal to the stack. Thus it is possible in principle to have coupling of c-axis displacements to ab-plane electronic features.

Anomalous phonon strengths possibly related to coupling effects have been earlier found[16,21] in $YBa_2Cu_3O_{7-\delta}$ in the form of resonances of low-frequency phonons. The mechanism of such a coupling is difficult to understand, especially since it is totally absent in films and crystals normal to the c axis, but shows up even in highly oriented ceramics. In $Bi_2Sr_2CaCu_2O_8$ the measurements presented here show that the temperature dependence of phonon features is associated with minima or antiresonance features of the optical conductivity. This result indicates a strong Fano-type electron-phonon interaction and suggests that the ab-plane response affects the observed vibrational spectrum in some way. At this point we do not attempt a specific fit, because the anisotropy of the electronic band is totally unknown and because this picture may also be complicated by the presence of other phases in the ceramic material. What we want to stress is that because of these effects, classical oscillator fits—which give maxima in the conductivity—may not be appropriate for determining phonon parameters in this compound.

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