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Temperature dependence of the far-infrared reflectivity spectrum of the high-T_c superconductor $YBa_2Cu_3O_{7-y}$

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The far-infrared spectrum of $YBa_2Cu_3O_{7-y}$ shows features not typical of a conventional superconductor. Besides rich phonon structure superimposed on a Drude-like tail, we find two regions of enhanced reflectivity below T_c. They begin at temperature-independent edges and each appears to be associated with a phononlike peak. These results could indicate temperature-independent energy gaps at 150 and 255 cm^{-1} or could be evidence of internal pair excitations strongly coupled to lattice modes. Also present are features suggestive of lattice modes which soften below T_c.

Very recently there has been intense interest in the family of layered perovskite high-T_c superconductors of composition $RBa_2Cu_3O_{7-y}$, where R represents a transition-metal or rare-earth ion[1-4] and y is a number less than 1. Knowledge of the elementary excitations, especially those with energies comparable to the superconducting transition temperature, and their dependence upon temperature is essential to a full understanding of these materials. The possible existence of a gap, its location, and temperature dependence would provide information on whether the superconducting properties stem from the usual electron-phonon coupling mechanism or from some new interaction.[5-9] We have focused our attention on $YBa_2Cu_3O_{7-y}$ whose transition temperature is about 91 K. We have measured the far-infrared (FIR) reflectivity from 20 to 4000 cm^{-1} as a function of temperature and computed the optical constants.

The material was prepared from $Y(NO_3)_3 \cdot 6H_2O$, BaO, and CuO powders, preheated for 4 h at 400 °C, ground and fired at 960 °C in oxygen flow for 10 h, reground and fired again as before. X-ray measurements indicate the powder to be single-phase orthorombic. Careful measurements on a good single crystal gave $a = 3.842$ Å, $b = 3.866$ Å, and $c = 11.654$ Å, in good agreement with previous work.[10] The resultant black powder was then pressed into a disk of 1.27 cm diameter and sintered at 960 °C for 10 h and allowed to cool slowly to room temperature in flowing oxygen. The surfaces of the sample were very smooth and well suited for FIR measurements. Polishing the sample surface did not affect the reflection spectra. Resistance measurements on the same sintered material gave a superconducting transition with a midpoint temperature of 91.5 K and a width (10% to 90%) of 1.8 K. The resistivity just above the transition was 1.4 mΩ cm.

The far-infrared reflectivity measurements near normal incidence were made using a Bruker 113 V Fourier spectrophotometer. The samples were held in a helium cryostat. Reference spectra were taken using a highly reflecting reference mirror and sample spectra measured at a number of temperatures using a room-temperature detector. We estimate the relative precision of the reflectance to be at least 0.1% at all temperatures; because of the possibility of systematic errors due to several effects related to the sample geometry, the relative accuracy of the reflectance is no better than 3%.

The reflectivity spectrum at all temperatures consists of a smooth, Drude-like decrease over which are superimposed a number of temperature-dependent features. Reflectivity decreases from 0.70 at 50 cm^{-1} to 0.10 at 3000 cm^{-1}; fitting the data to the Drude model yields $\sigma_0 = 30\ (\Omega\,cm)^{-1}$ and scattering time $\tau = 2.3 \times 10^{-15}$ sec. The value of σ_0 is not consistent with the measured dc resistivity of 1.4 mΩ cm; this is not surprising in view of the granular nature of the material.

Figure 1 shows the reflectivity at several temperatures over the full spectral region in which the temperature-

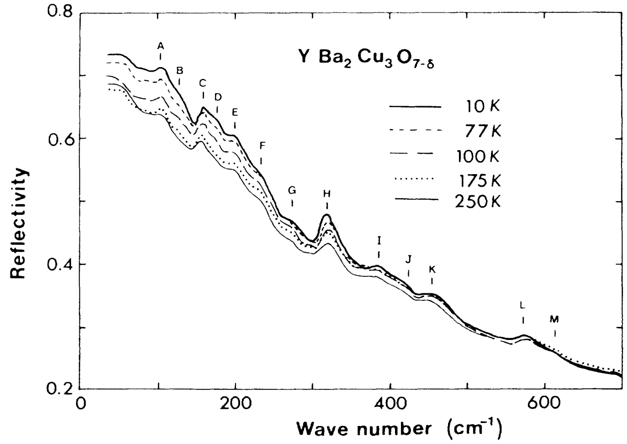

FIG. 1. Reflectivity spectrum of $YBa_2Cu_3O_{7-y}$ in the low-energy region. δ in the figures is the same as y in the text. A number of temperature-dependent features are superimposed over a Drude-like decrease with increasing energy. Features are labeled for future reference.

dependent features occur. These features are labeled A–M for future reference. The steep increase in reflectance observed by Bonn *et al.*[5] below 100 cm^{-1} which they described as "plasmonlike" does not appear in our spectra. We suggest that this feature and probably another similar one observed by them in the related material $La_{1.85}Sr_{0.25}CuO_4$, are not associated with superconductivity. We propose instead that these features may be due to excess carriers introduced by impurities or other defects.

The temperature dependence of the reflectivity $R(T)$ in the spectral region below 300 cm^{-1} is shown in more detail in Fig. 2. Because the temperature dependence of the reflectivity above T_c is much less dramatic than that below T_c (as will be demonstrated below), we have plotted $R(T)-R(100\text{ K})$ in Fig. 2. Despite the poor signal-to-noise ratio, we can make the following observations. It is clear that $R(90\text{ K})$ differs from $R(100\text{ K})$ by a constant amount. At least six distinct features (A,B,C,D,E,F) rapidly become more prominent, however, as the temperature decreases further. Careful examination and comparison with Fig. 1 reveals that it is the shoulders B and F which increase in strength significantly; the strengths of the other features increase only slightly. Below 55 K, the structures change much less rapidly.

In Fig. 3(a) we summarize the three different temperature dependences exhibited by the strengths of the features observed in Fig. 1. The strength of peak K decreases smoothly with increased temperature in the manner expected of a lattice mode. This behavior is also seen for features A, G, I, J, L, and M. The strength of the very strong peak H also decreases with increasing temperature, but there is a distinct break around 90 K. Finally, the shoulder B is seen to disappear quite abruptly on crossing T_c; similar behavior is shown by shoulder F. It is more difficult to characterize unambiguously the temperature dependences of features C, D, and E; they overlap and tend to "smear out" with increasing temperature.

In Fig. 3(b) we summarize the temperature dependences of the characteristic energies of the same three features described above. We see a gradual shift in wave number of peak K, in the manner expected for an ordinary lattice mode. The shift for the strong peak H however is unusual because the characteristic energy first increases by about 1 cm^{-1} from 10 to 100 K and then decreases again as room temperature is approached. The shoulders B and F do not show any energy shift; neither do the dips in reflectivity, located at slightly higher wave number, from which they rise. Their locations stay fixed as a function of temperature; only the strengths of the shoulders vary.

We observe then that the temperature-dependent structures can be grouped into three distinct classes according to their variation with temperature. First, there is peak K (445 cm^{-1}) whose strength and energy vary smoothly with temperature. There are a number of weak features whose temperature dependence appears similar to that of peak K. Second, there is the very strong peak H (317 cm^{-1}) which varies differently above and below the superconducting critical temperature. Finally, there are two distinct features which turn on quite suddenly below T_c; they are the shoulders B (130 to 150 cm^{-1}) and F (240 to 255 cm^{-1}), each of which has a peak riding on top (A and E, respectively).

In discussing the rich infrared spectrum of this material, we leave aside the peaks I, K, and L, noting that they behave like ordinary phonons, a conclusion confirmed by Raman scattering measurements.[11] We note also that the anomalous behavior of the strong phononlike structure H is suggestive of an incipient structural phase transition which may or may not be associated with the superconducting transition; this anomalous behavior is also confirmed in the same Raman measurements.

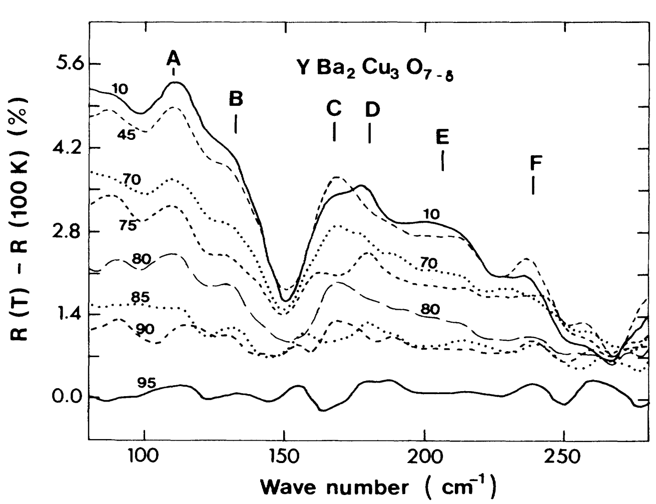

FIG. 2. Reflectivity difference spectrum $R(T)-R(100\text{ K})$ of $YBa_2Cu_3O_{7-y}$ below 300 cm^{-1} at several temperatures.

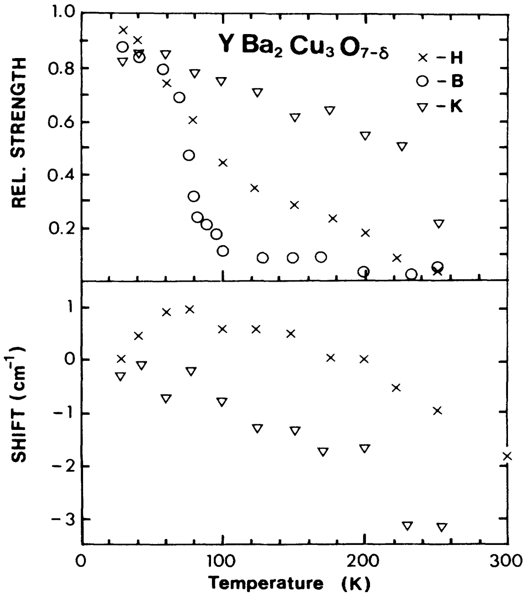

FIG. 3. Temperature dependence of the relative strength $[R(T)-R(10\text{ K})]/[R(10\text{ K})-R(100\text{ K})]$ and the shifts of the characteristic energy of three of the spectral features identified by letter in Fig. 1.

We concentrate on the features that appear below 90 K and are therefore obviously connected with superconductivity. It is readily apparent that the usual behavior expected of a BCS superconductor, namely a single, temperature-dependent edge appearing at the energy gap followed by a rise in reflectivity at lower wave numbers,[7,9] is not present. We find instead two structures whose shapes superficially resemble gap edges with rising reflectivity shoulders. However, these edges are temperature independent. Moreover, the rise in reflectivity, even at the lowest temperatures, is very small compared to that expected in a BCS-type superconductor. Each of these structures has a phononlike peak associated with it; the peak appears about 50 cm^{-1} below the edge. The phononlike peaks are already present above T_c and grow monotonically with decreasing temperature.

If these two structures appearing in the superconducting state are identified with quasiparticle excitations across energy gaps, the edges at 150 and 255 cm^{-1} (19 and 32 mV) would correspond to $2\langle\Delta\rangle/k_B T_c$ of 2.5 and 4.2 respectively; simple BCS theory predicts 3.5. Recent tunneling measurements on films of this material indicate that sometimes gaplike features can be seen, but at much higher energies.[12] There are arguments why infrared and tunneling measurements could differ, the most convincing being that tunneling probes within a coherence length (about 20 Å)[13] of the surface, as compared to the much larger infrared penetration length which probes the bulk material. One could also make an argument that the features observed are not the actual energy gap (or gaps) of the superconductor. The infrared electric field could couple to the internal structure of pairs[14] formed by charged quasiparticles located near lattice sites in the central Cu-O plane. The fact that the edge structures both are located about 50 cm^{-1} above a strong phononlike peak would indicate a strong coupling of these excitations to lattice modes. It is clear that much theoretical work is required to clarify the nature of the elementary excitations and to calculate the electromagnetic response of the various proposed new mechanisms for superconductivity.[15]

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