Comparative Study of Superconducting Energy Gaps in Oriented Films and Polycrystalline Bulk Samples of Y-Ba-Cu-O

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We have made a study of infrared reflectivity from an epitaxial film of $Y_1Ba_2Cu_3O_{7-x}$ in which the c axis is primarily oriented perpendicular to the film surface and from bulk polycrystalline samples with no orientation. In the oriented film the region of enhanced reflectivity associated with the superconducting energy gap extends to 400 cm^{-1} (50 meV) compared with only 200 cm^{-1} in the bulk material. We estimate the energy gap for the film to be $2\Delta = (4.7 \pm 1.2)kT_c$, a value which is consistent with recent tunneling measurements and with strong-coupling superconductivity.

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The recent discoveries of layered superconducting oxides with critical temperatures (T_c) of approximately 40 K [1] and 90 K,[2] have generated a great deal of interest in these materials. Since the crystal structures of these compounds are highly anisotropic, their electronic and superconducting properties may be expected to depend on crystal orientation. Fundamental questions regarding these anisotropies and their relationship to the mechanism of high-temperature superconductivity make it desirable to study oriented samples.

In this Letter we report a comparison of infrared-reflectivity measurements made on an epitaxial film and on polycrystalline bulk samples of the $\simeq 90$ K superconductor $Y_1Ba_2Cu_3O_{7-x}$. The individual crystallites making up the film were primarily oriented with their c axis perpendicular to the film surface. As a result, infrared measurements on the film are expected to be more sensitive to the properties of the a-b (Cu-O) plane than measurements on polycrystalline samples. The reflectivity from the film is found to be in good agreement with the dc conductivity. The region of enhanced reflectivity associated with the superconducting energy gap extends to nearly 400 cm^{-1} yielding an estimate for the gap $[(4.7 \pm 1.2)kT_c]$ in reasonable agreement with tunneling results and strong-coupling BCS superconductivity. In contrast, the estimated gap in the unoriented bulk samples is nearly a factor of 2 smaller. Also, the low-frequency, normal-state reflectivity from the bulk samples is considerably smaller than for the film. Anisotropies in the dc conductivity and in the superconducting gap may be responsible for the differences between the unoriented bulk samples and epitaxial film.

The thin-film samples were grown on $SrTiO_3$ substrates with a 1-2-3 ratio of Y-Ba-Cu, as described elsewhere.[3] The films were approximately 1 μm thick and were composed of individual crystallites with characteristic lateral dimensions of approximately 10 μm. X-ray and TEM studies indicated that the films were single phase with the c axis of the individual crystallites oriented primarily perpendicular to the film surface. The films exhibited sharp resistive and diamagnetic transitions at 90 K with transition widths of $\simeq 1.5$ K. One multiphase and two single-phase polycrystalline bulk samples were studied. The preparation of these samples has also been previously discussed.[4] The single-phase samples were prepared with the 1-2-3 composition and exhibited sharp superconducting transitions at $\simeq 90$ K. In the multiphase sample the onset of the resistive transition occurred at 90 K, but the transition was not complete until approximately 60 K.

Infrared-reflectivity measurements were made for frequencies from 50–4000 cm^{-1} with a scanning interferometer. The infrared radiation was incident on the sample at approximately 45° and was nominally unpolarized. Scattering from the rough surfaces of the bulk samples caused a rapid decrease in the reflectivity with increasing frequency. Absolute reflectivities for these samples were obtained by first measuring the sample reflectivity and then evaporating Au onto the sample surface and again measuring the reflectivity to obtain a reference.

Figure 1 gives the room-temperature reflectivity from the thin film and from one of the single-phase polycrystalline bulk samples. We obtain a good fit (solid line) to the epitaxial-film reflectivity with a classical Drude model with a resistivity $\rho = 1.0$ m Ω cm, which is approximately the measured room-temperature dc resistivity for the film (carrier concentration $n = 3.0 \times 10^{21}$ cm^{-3}, mass $m^* = 1$, and $\epsilon_\infty = 4$). For the polycrystalline bulk sample, the Drude model does not provide a good fit to the reflectivity, and the reflectivity is much smaller than for the film, although the measured dc conductivities for the film and bulk are nearly the same. Structure associated with infrared active phonons is visible in the spectrum at approximately 150, 300, and 570 cm^{-1}. Some structure at 300 cm^{-1} is also visible in the epitaxial-film spectrum.

In Fig. 2 ratios of the superconducting (15 K) to normal (98 K) reflectivities for the three types of samples

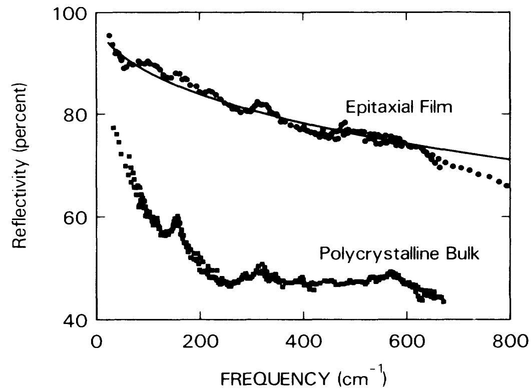

FIG. 1. Absolute reflectivities at room temperature from the epitaxial film of $Y_1Ba_2Cu_3O_{7-x}$ and from a single-phase, polycrystalline bulk sample of $Y_1Ba_2Cu_3O_{7-x}$. The solid line is the calculated reflectivity for the film with use of a classical Drude model.

studied are shown. In an ideal BCS superconductor this ratio should increase to a maximum at 2Δ, and then approach unity at higher frequencies. Figure 2(a) gives the ratio for the multiphase bulk sample. The region of enhanced reflectivity due to the superconducting gap appears to extend to about 100 cm^{-1} although differences between the superconducting and normal reflectivities exist up to frequencies of 550 cm^{-1}. Conclusions about the properties of the 1-2-3 phase of Y-Ba-Cu-O cannot be drawn from this sample, because of the possibility that more than one superconducting phase is present. Ratios for the two single-phase bulk samples are given in Fig. 2(b). The increased reflectivity due to the superconducting gap extends to $\simeq 200$ cm^{-1}. Sharp line structure is present in the ratio at 150 cm^{-1}, between 200 and 350 cm^{-1}, and at 570 cm^{-1}. We attribute this structure to infrared-active phonons, since phonon modes at approximately these frequencies could be seen in the absolute reflectivity (Fig. 1). Because of the complicated nature of the ratio, it is difficult to determine the size of the gap. A reasonable estimate is $2\Delta \simeq 170$ cm^{-1} (21 meV) $= 2.7kT_c$. Figure 2(c) shows the superconducting-to-normal ratio for the epitaxial film. In this ratio, the enhanced reflectivity due to the gap extends to nearly 400 cm^{-1} indicating a gap which is nearly twice as large as obtained from the unaligned bulk samples. In addition, the phonon modes are smaller relative to the gap signal than in the bulk samples. The increase in reflectivity in the gap region is about a factor of 3 smaller than for the single-phase bulk samples. This is consistent with the larger absolute reflectivity of the film (Fig. 1) although none of the samples becomes completely reflecting in the superconducting state, indicating that there are regions in each sample which do not become superconducting. We crudely estimate the superconducting gap for this sample to be 300 ± 75 cm^{-1} (37 ± 9 meV) $\simeq (4.7 \pm 1.2)kT_c$. Recent tunneling measurements on single-phase $Y_1Ba_2Cu_3O_{7-x}$ have given gaps of $2\Delta = 36.0$–40.0 meV $\simeq 4.8kT_c$.[5-7] The estimated gap from the thin film is consistent with this while that obtained on the unoriented bulk samples is considerably smaller. The observation of a gap which is consistent with tunneling is significant, since previous infrared studies of both $Y_1Ba_2Cu_3O_{7-x}$ [5,8,9] and of the related high-T_c superconductor $La_{2-x}Sr_xCuO_4$ [10] have typically given gaps nearly a factor of 2 smaller than the gaps determined from tunneling measurements[5,6,7,11]

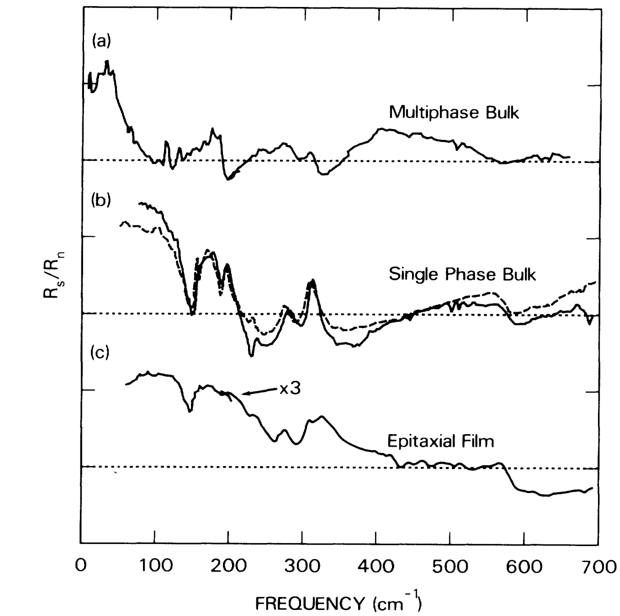

FIG. 2. Ratio of the superconducting (temperature $=15$ K) to normal (temperature $=98$ K) reflectivities for (a) a multiphase polycrystalline bulk sample, (b) two single-phase polycrystalline bulk samples, and (c) the oriented film of $Y_1Ba_2Cu_3O_{7-x}$. The dotted lines correspond to ratios of 1. Spacings between tics on the verticle axis are 0.1 (corresponding to 10% changes in the ratio).

We have also studied the temperature dependence of the superconducting-to-normal ratios. Surprisingly, no evidence for a reduction of the gap is observed even quite close to T_c (within 2 K) for either the epitaxial film or bulk samples. The ratios at different temperatures are essentially multiples of one another. This apparent lack of temperature dependence in the gap is not understood.

We have modeled the normal and superconducting reflectivities in the presence of infrared-active phonons to determine why the phonons give rise to structure in the ratios in Fig. 2. This is illustrated in Fig. 3 where the calculated ratios of the superconducting to normal reflectivity with (dashed line) and without (dotted line) phonons are shown along with the measured ratio (solid line) for one of the single-phase bulk samples. The calculation assumes a Drude conductivity of 5.0 m Ω cm (the approximate conductivity which fits the bulk

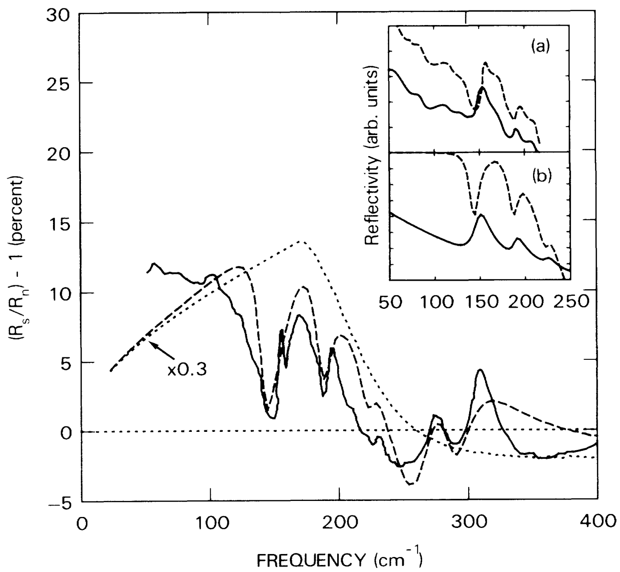

FIG. 3. Ratios of superconducting to normal reflectivities. The solid line is measured. The dotted line is calculated by assuming that the zero-temperature Mattis-Bardeen relation applies in the superconducting state and that the normal state is described by a Drude conductivity of 5 m Ω cm. In the dashed line phonon modes at 148, 190, 225, 270, and 300 cm^{-1} have been included in the calculation. (The feature at 160 cm^{-1} is an artifact of the beam splitter.) Inset: (a) Measured and (b) calculated absolute reflectivities in the frequency range of the 148-cm^{-1} phonon in both the normal (solid line) and superconducting (dashed line) states.

reflectivity at 100 K) for the normal state, and a zero-temperature Mattis-Bardeen conductivity[12] with $2\Delta = 170$ cm^{-1} in the superconducting state. Phonon modes were modeled as Lorentz oscillators with frequencies 148, 190, 225, 270, and 300 cm^{-1}, strengths of 400, 215, 120, 340, and 360 cm^{-1}, respectively, and dampings of 12.0 cm^{-1}. The calculated phonon structure reproduces the experimentally observed features quite well. Phonons become visible in the ratio because the electronic screening of the phonons changes at the superconducting transition causing changes in the size and shape of the phonon features. The inset to Fig. 3 illustrates this for the 148-cm^{-1} phonon mode. Here the (a) calculated and (b) measured absolute reflectivities in the frequency range of this phonon are given for both the normal (solid lines) and superconducting (dashed lines) states. The measured spectrum exhibits a characteristic change in the shape of the phonon feature (from an increase in reflectivity on the high-energy side of the phonon to a decrease in reflectivity on the low-energy side) which is reproduced by the calculation. The phonon-related feature at 570 cm^{-1} cannot be explained in the same way. This mode appears to become visible in the ratio because of a shift in the energy of the phonon at the superconducting transition, providing some evidence for electronic coupling to this mode.

Anisotropies in the electronic and superconducting properties of $Y_1Ba_2Cu_3O_{7-x}$ can explain some of the differences we observe between the epitaxial film and unoriented bulk samples. The layered natures of $Y_1Ba_2Cu_3O_{7-x}$ and of $La_{2-x}Sr_xCuO_4$ are expected to give rise to a nearly two-dimensional band structure in which the effective mass, and hence resistivity, along the *c* axis is large relative to the mass and resistivity along the *a*-*b* (Cu-O) plane.[13] Measurements made on single crystals of $La_{2-x}Sr_xCuO_4$ have given a 20:1 anisotropy for the conductivity in these two directions.[14] An infrared reflectivity study of a single crystal of the related compound La_2NiO_4 showed essentially metallic reflectivity when the radiation was incident along the *c* axis, but exhibited a lower-conductivity spectrum with large phonon features when the radiation was polarized along the *c* axis.[15] Anisotropies in the critical currents and fields of $Y_1Ba_2Cu_3O_{7-x}$ have also been observed.[16] In the present study we would expect reflectivity from the epitaxial thin film to be primarily determined by the higher-conductivity *a*-*b* plane since the incident radiation is primarily polarized perpendicular to the *c* axis, while the unoriented bulk samples would contain roughly equivalent contributions from both low- and high-conductivity directions. This could account for the overall smaller (and non-Drude-type) reflectivity observed for the bulk material in Fig. 1. Also, electronic screening of the phonons would be less effective along the lower-conductivity *c* axis giving rise to larger phonon features in the unoriented bulk samples. The structure due to phonon modes which is observed in the thin film could actually be due to small unoriented regions present in the film. Anisotropies in the superconducting gap itself may explain the different apparent sizes of the gap in the unoriented bulk samples and epitaxial films. Further studies of oriented samples and single crystals should clarify the degree to which anisotropy is responsible for the differences between the epitaxial films and bulk samples.

Bonn *et al.*[8] have recently reported reflectivity measurements on polycrystalline bulk samples of $Y_1Ba_2Cu_3O_{7-x}$. The change in reflectivity which they observe when the sample passes through the superconducting transition is most consistent with our results for the multiphase bulk sample. We find it difficult to reconcile their data with the gap value of 200 cm^{-1}, which they obtain from a Kramers-Kronig transform. Thomas *et al.*[9] have also made a reflectivity study of bulk polycrystalline samples and obtain reasonable agreement with the single-phase data presented here [Fig. 2(b)].

In summary, we have made infrared-reflectivity measurements on an oriented thin film of the 90-K superconductor $Y_1Ba_2Cu_3O_{7-x}$ and have compared the results to measurements on polycrystalline bulk samples of the same material. The reflectivity from the film is in reasonable agreement with the dc conductivity, and we find a superconducting energy gap for the film $[2\Delta \simeq 4.7 \pm 1.2) kT_c]$ which is consistent with recent tunneling measurements of the superconducting energy gap and with strong-coupling BCS superconductivity. In contrast the reflectivity from the bulk samples suggests a considerably smaller superconducting energy gap.

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