

INFRARED PROPERTIES OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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We review recent experimental data on the infrared properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramics and single crystals. Kramers-Kronig analysis shows that the normal state far-infrared optical conductivity is dominated by a Drude response from free carriers with a plasma frequency of the order of 1.0 eV and a relaxation rate of .037 eV (300 cm^{-1}) at 100 K. A strong mid-infrared band centered between 0.2 and 0.5 eV is seen in all the samples. Below the superconducting transition temperature the far-infrared conductivity is depressed below 400 cm^{-1} but this is not a true energy gap since there remains, even in the best oriented crystal samples, a residual absorption.

1. INTRODUCTION

Since the discovery of high temperature superconductivity the infrared properties of the new materials have been a subject of much interest. If they are ordinary BCS superconductors then far-infrared spectroscopy can be used to determine the energy gap. Holstein phonon absorption should be observable above the gap frequency if the pairing is via the conventional electron-phonon mechanism.

The far-infrared properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ were interpreted initially in complete analogy with simple BCS superconductors where the signature of the energy gap is an edge in reflectance. Very low values of the $2\Delta/k_B T_c$ parameter between 1.6 to 3.5 were estimated from this criterion.(1-4) It soon became apparent that the analogy with simple BCS metals was invalid and that the optical properties of the new ceramics were dominated by the dispersion caused by strong phonons.(5) Instead of being a superconducting gap the reflectance edge at low frequency resulted from the premature zero crossing of the real part of the dielectric function caused by a strong low-lying phonon at 250 cm^{-1} .

In view of these difficulties with the raw reflectance data it is important to perform Kramers-Kronig transformations on the reflectance or to fit the reflectance to a physically reasonable model of the optical conductivity. Recent work both on ceramics and oriented crystals and films has considerably clarified the underlying optical properties of the new superconductors, particularly $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the normal state. Below the superconducting transition the situation is more uncertain and a true energy gap has not been found.

In the following paper we will review this work with an emphasis on recent results of the McMaster - Uni-

versity of Florida group. Three processes dominate the infrared spectrum in the normal state: the Drude response of the charge carriers in the far infrared, the absorption by optic phonons, and the broad mid infrared absorption centred between 0.2 and 0.5 eV.

There has been some confusion in the literature about the mid-infrared absorption. The first reports on polycrystalline ceramic specimens described a broad band centered at 0.5 eV in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (6-8) and 0.37 eV in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (9) whose height followed the concentration of dopant, Sr in the case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and oxygen in the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The undoped insulating parent compounds did not show this absorption. A similar absorption is present in the earlier perovskite superconductors, doped SrTiO_3 (10) and $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ (11)

Recently, a number of authors, (12-14) working on single crystals and oriented films, have termed this mid-infrared response Drude absorption. We will show that this interpretation is inconsistent with the temperature dependence of both the far infrared conductivity and the four-probe dc conductivity. The mid-infrared absorption has also been called an "exciton" or "charge transfer" absorption but since the exact nature of the physical process responsible is not known we will use the term mid-infrared band. This broad band is centered in the mid-infrared in contrast to the narrower Drude absorption centered on zero frequency. It is also incorrect to refer to it as "the 0.5 eV band" since it only occurs at this energy in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ceramics.

1. REFLECTANCE SPECTRA OF $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

Figure 1 shows the reflectance of a high quality ceramic sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The surface has not been polished and is highly textured: X-ray powder diffraction and scanning electron microscopy show a

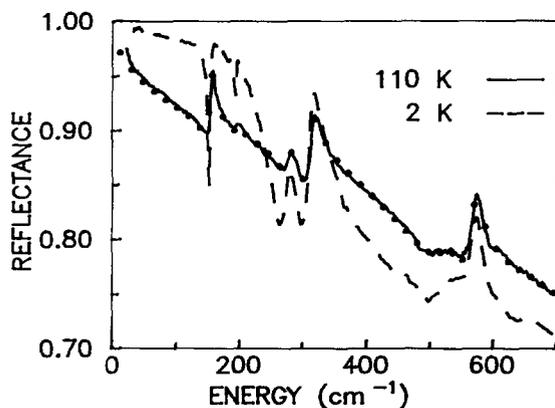


Figure 1. Reflectance of a sample of ab plane textured ceramic $YBa_2Cu_3O_{7-\delta}$. The dotted curve is a fit with six Lorentz oscillators and a Drude term plus a mid-infrared absorption.

surface composed mainly of $10 \mu\text{m}$ plate-like grains with c-axis orientation normal to the surface. Single reflection geometry near normal incidence was used and at the end of the experiment the sample was coated in situ with a metal film to correct for geometrical effects caused by surface imperfections. This final step is extremely important since surface roughness can lead to a substantial artificial absorption that imparts a false, low conductivity Drude-like reflectance on the spectrum.

In poorer quality and untextured samples the absolute value of the reflectance is lower and the low frequency phonon structure is broader. Taking the absolute reflectance at, say, 600 cm^{-1} as a sample quality measure one finds values ranging from above the 73 % shown here down to 10 % for oxygen deficient tetragonal samples. The other rare earth substitutions give similar spectra with some shifts in the phonon frequencies.⁽¹⁵⁾

The details of the reflectance spectra are subject to sample-to-sample variation and highlight the danger of trying to associate particular features in the reflectance spectrum with the superconductor's energy gap. Figure 2 shows the conductivity obtained by Kramers-Kronig transformation of the data shown in reflectance in fig 1. The complex structure in reflectance has become intelligible: only six sharp phonon peaks and a smooth background remain. In the superconducting state, shown as a dashed curve, the overall conductivity is depressed at low frequencies but no sharp gap structure can be seen.

Crystals grown by a flux technique have very large smooth ab plane surfaces which can yield even better quality spectra than oriented ceramics. Fig. 3 shows the reflectance of a mosaic of crystals. The most striking

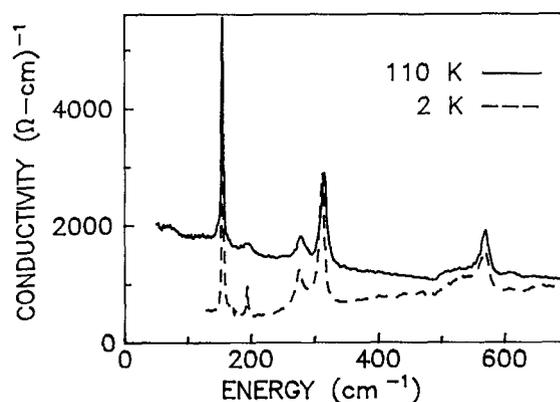


Figure 2. The frequency dependent conductivity of a textured ceramic sample $YBa_2Cu_3O_{7-\delta}$. A region of depressed conductivity appears in the far infrared with the onset of superconductivity. The rising conductivity towards low frequencies in the normal state is due to free carriers with a relaxation time of the order of 300 cm^{-1} .

ing feature is the nearly total absence of the phonon structure in this very highly conducting sample. There are no phonon-like features larger than the 0.5 % uncertainty of this reflectance spectrum.

3. THE DRUDE ABSORPTION

The dotted curve in figure 3 is a fit to the reflectance by a model that uses a high frequency dielectric constant of 10, a Drude term with a plasma frequency of 1.3 eV and a damping constant of 300 cm^{-1} (0.037 eV), and a mid-infrared band with center frequency of 0.23 eV, width 0.56 eV, plasma frequency 3.25 eV. The dc conductivity measured with a four-probe technique was $6000 (\Omega \text{ cm})^{-1}$ in fairly good agreement with the far-infrared conductivity at low frequency. Similar parameters fit the oriented ceramic sample although the plasma frequency in the ceramic is 0.78 eV. This low value may be the result of reduced electron density near the ceramic surface or contributions from unoriented grains.

The amplitude of the Drude conductivity is strongly temperature dependent. The inset in fig. 4 shows the 100 cm^{-1} optical conductivity, plotted as resistivity, as a function of temperature of the textured sample. It follows the familiar linear variation of dc resistance with temperature seen in high T_c superconductors.

4. THE OPTICALLY ACTIVE PHONONS

The two lowest frequency phonons seen in the textured sample narrow dramatically in the superconducting state. The peak at 195 cm^{-1} for example changes from 9.6 to 2.7 cm^{-1} in width. This can be explained in terms of the existence of an energy gap with $2\Delta \geq 195$

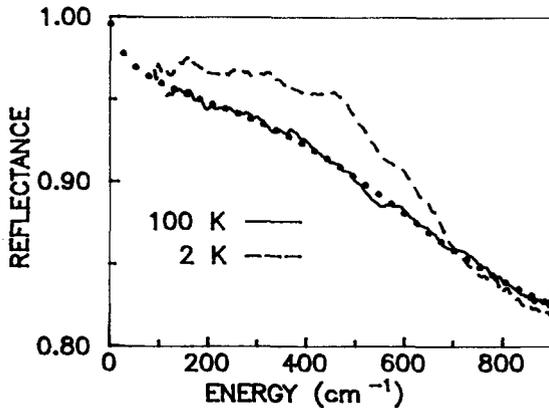


Figure 3. Reflectance of a mosaic of single crystals of $YBa_2Cu_3O_{7-\delta}$ in the normal state (solid curve) and the superconducting state (dashed curve). The dotted curve is a fit with a Drude term plus a mid-infrared absorption. Note that in this absolute reflectance curve a finite absorption remains in the superconducting state. There is no evidence of a true gap.

cm^{-1} . Phonons with energy less than 2Δ are unable to break pairs and can propagate without scattering. In this picture we attribute most of the width in the normal state to the electron-phonon interaction. This narrowing of the two low-lying phonons is evidence for the existence of an energy gap: using this criterion we can place the gap between the frequency of the phonon that narrows at 195 cm^{-1} and the lowest one that does not at 314 cm^{-1} giving a range of $2.98 \leq 2\Delta/k_B T_c \leq 4.80$.

The lowest phonon we observe, at 155 cm^{-1} , has an unusually large strength parameter, $S = 31$, much too strong to be caused by simple, optically active phonons that have $S \approx 2$. It resembles the very strong line in $La_{2-x}Sr_xCuO_4$ at 250 cm^{-1} .(5, 7)

5. THE MID-INFRARED ABSORPTION

The mid-infrared conductivity of a textured ceramic sample is shown in figure 4 at two temperatures. There is relatively little temperature dependence at high frequencies. The mid-infrared band in polished ceramics samples of $YBa_2Cu_3O_{7-\delta}$ tends to peak at 0.37 eV (3000 cm^{-1})(9) whereas in the textured samples and single crystals the peak occurs at 0.25 eV (2000 cm^{-1}). This upward shift of the peak in the untextured ceramics may be due to anisotropy, as pointed out by Orenstein.(16)

Attempts have been made to fit the mid-infrared spectral region with a single very broad Drude absorption centered at zero frequency with a width parameter of the the order of 0.6 eV and a magnitude be-

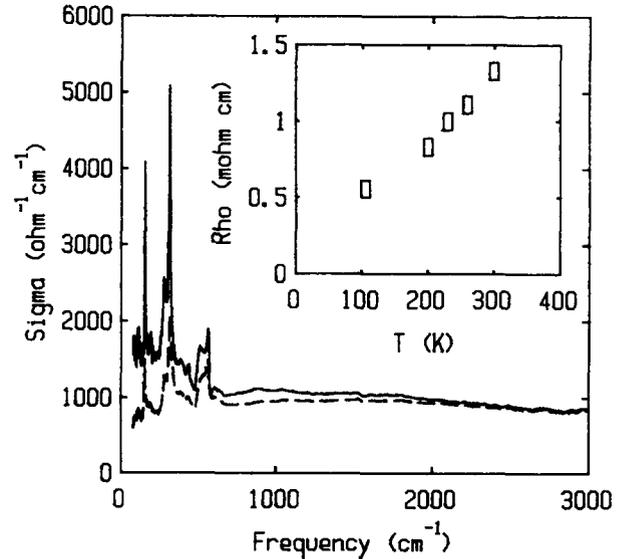


Figure 4. Mid-infrared conductivity of textured $YBa_2Cu_3O_{7-\delta}$ at 105 K , solid line and 300 K , dashed line. While the low frequency Drude absorption is temperature dependent, the band in the mid-infrared is relatively temperature independent. The inset shows the temperature dependence of the optical conductivity measured at 100 cm^{-1} .

tween $1500\text{ }(\Omega\text{ cm})^{-1}$ and $2000\text{ }(\Omega\text{ cm})^{-1}$. Such a fit is only possible at room temperature where, by coincidence, the Drude conductivity happens to match the mid-infrared strength and makes the combination superficially resemble a single Drude term with a very large relaxation rate. At 100 K the dc and far-infrared conductivities have increased, making the fit to a single Drude term impossible. A separate, narrower Drude absorption is needed for a consistent fit at both room temperature and at 100 K .

The possibility that the mid-infrared band is due to a separate set of free carriers with an extremely short relaxation time can be ruled out from the lack of saturation of the dc resistance at high temperature.(17)

The mid-infrared absorption at room temperature is more peak-like in the polished ceramics than in the textured ceramics, epitaxial films and single crystals. This difference is probably caused by the suppression of the low frequency conductivity in the polished ceramic specimens to the order of $300\text{ }(\Omega\text{ cm})^{-1}$ or less by. Grains aligned with their c axis parallel to the plane of the sample can cause this poor low frequency conductivity.(16)

6. THE SUPERCONDUCTING STATE

The frequency scale of the gap-like depression of

conductivity seen in the textured ceramic sample is in rough agreement with the BCS weak coupling value of $2\Delta/k_B T_c = 3.5$ but differs from the Mattis Bardeen curve(18) expected for a conventional superconductor. There is residual absorption in the gap region, with the conductivity gradually rising in the 200 cm^{-1} region, whereas the onset of normal state conductivity occurs steeply in typical strong coupling superconductors such as lead.

Because of these deviations it is not possible to assign a value of the superconducting energy gap. We can make some estimates based on models. If the residual absorption is due to extreme gap anisotropy then an inspection of the calculated conductivity curves of Maekawa et al.(19) for d wave anisotropy shows that the gap occurs at a frequency where the conductivity has approached 80 % of the normal state value. For the curve shown in figure 2 this frequency is 300 cm^{-1} yielding a value of $2\Delta/k_B T_c \approx 5.2$. If on the other hand the presence of normal metal is responsible for the in-gap conductivity the gap could well be lower and indeed consistent with the weak coupling BCS value.

The observed conductivity is also consistent with Bose condensation models that predict no gap at all. The depressed conductivity below the superconducting transition would then be due to the freeze-out of the charged bosons that carry the transport current in the normal state. The oscillator strength of the Drude absorption is transferred to the delta function of the collective mode at zero frequency. Because the scattering rate of the carriers at the transition temperature happens to be close to $3.5 k_B T_c$ a broad depression of conductivity of this width results.

The crystal mosaic exhibits a very high reflectance in the superconducting state but the sample retains an absorption of the order of 3 %. The change in slope of the reflectance at 500 cm^{-1} in our crystal samples is due to a plasma edge associated with the large mid-infrared oscillator strength. This edge has been attributed to a superconducting energy gap(12). Obviously, since over 50 % of the normal state absorption remains even in the best crystals much further work is needed with far infrared techniques before any definitive statement can be made about even the the existence of an energy gap in the high temperature superconductors.

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REFERENCES

- (1) U. Walter et al. Phys. Rev. B35, (1987) 5327.
- (2) Z. Schlesinger et al. Phys. Rev. B35, (1987) 7232.
- (3) P.E. Sulewski et al. Phys. Rev. B35, (1987) 8829.
- (4) D.A. Bonn et al. Solid State Comm.62, (1987) 383.
- (5) D.A. Bonn et al. Phys. Rev. B35, (1987) 8843.
- (6) J. Orenstein et al. Phys. Rev. B36, (1987) 729.
- (7) S.L. Herr et al. Phys. Rev. B36, (1987) 733.
- (8) S. Etemad et al. Phys. Rev. B, submitted.
- (9) K. Kamarás et al. Phys. Rev. Lett. 59, (1987) 919.
- (10) A.S. Barker, Optical Properties and Electronic Structure of Metals and Alloys (North Holland, Amsterdam, 1965).
- (11) S. Tajima et al. Phys. Rev. B32, (1985) 6302.
- (12) Z. Schlesinger et al. Phys. Rev. Lett. 59, (1987) 1958.
- (13) I. Bozovic, et al. Phys. Rev. Lett. 59, (1987) 2219.
- (14) S. Tajima et al. Phys. Rev. submitted.
- (15) M. Cardona et al. Solid State Comm. 64,(1987) 727.
- (16) J. Orenstein and D.H. Rapkine, Phys. Rev. Lett. Comment, submitted.
- (17) M. Gurvitch and A.T. Fiory, Phys. Rev. Lett. 59 (1987) 1337.
- (18) D.C. Mattis and J. Bardeen, Phys. Rev. 111, (1958) 412.
- (19) S. Maekawa et al. Jpn. J. Appl. Phys. Lett. 26, (1987) L468.