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INFRARED STUDIES OF HIGH Tc SUPERCONDUCTORS

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The infrared properties of the high temperature superconductors are dominated by the strong temperature dependent absorption of the free carriers at low frequency and a temperature independent midinfrared band. Dramatic changes in reflectance do occur as the material becomes superconducting but these changes cannot be used to determine the energy gap, since as a result of the development of the superconducting condensate, changes in the real part of the dielectric function dominate. Also, since the relaxation rate of the free carriers is of the order of 200 cm^{-1} at 100 K the materials are near the clean limit below this temperature and we do not expect to see structure at the energy of the superconducting gap. The reflectance edge observed in many experiments at 450 cm^{-1} is caused by the onset of the midinfrared absorption which has the character of a direct particle-hole excitation rather than the Holstein scattering of the free carriers.

1. INTRODUCTION

In ordinary superconductors[1] infrared spectroscopy has been very successful in establishing the existence of the energy gap and, under increased sensitivity, also able to show that phonons are strongly coupled to the electrons.[2] The high temperature superconductors have for several reasons resisted attempts to yield either clear evidence of a gap or a spectrum of excitations coupled to the charge carriers.[3] First, because of the very short coherence length the materials are probably close to the clean limit at low temperature making the gap structure weak. Secondly there are strong electronic absorption bands in the very region where one might expect to see the gap structure which dominate the optical conductivity and tend to hide any weak contribution of the free carriers.

In the early work on untextured ceramics the superposition of the low conductivity c axis response with the higher ab plane conductivity led to further complexity. With the availability of textured samples,[4] single crystals[5] and oriented films[6] the situation has clarified. In the following we will review some of this recent work.

2. LOW FREQUENCY DRUDE RESPONSE

The simplest model for the optical properties of a free carrier system is the Drude model where:

$$4\pi\sigma(\omega) = \omega_p^2\tau/(1+(\omega\tau)^2)$$

where ω_p is the plasma frequency and $1/\tau$ the scattering rate of the carriers. Both quantities can in principle be determined from the frequency dependent infrared conductivity and compared with the dc conductivity determined from a four-probe resistance measurement.

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This analysis applied to the normal state infrared properties shows that the oxide materials have a very conventional Drude response.[4] Like the dc conductivity, the magnitude of the optical conductivity is temperature dependant with an accurately linear variation with temperature and an intercept at zero temperature of less than 100 $\mu\Omega$ cm. In this it tracks the behavior of four-probe dc resistivity very closely. The scattering rate in the normal state in the best samples is of the order of 1.3 - 2 kT_c. The magnitude of the plasma frequency is in agreement with the value found from muon spin resonance.

In the superconducting state the optical response of the carriers follows London electrodynamics where the conductivity consists of a delta function at zero frequency and the real part of epsilon depends quadratically on temperature. The slope can be analysed to give a plasma frequency which agrees to within 20 independent measurements in the normal state.[7] In contrast, in the ordinary dirty limit materials only a portion $\Delta\tau$ of the conductivity is removed from under the Drude curve.[8]

The scattering rate at low temperature in the superconducting state cannot be measured directly because of the high critical fields required to drive the material normal. In the samples with the highest conductivity the linear resistivity appears to extrapolate to zero within a few $\mu\Omega$ cm. Is it reasonable to speculate that this linear variation will continue below T_c as well?

The Bloch-Grünheisen (BG) resistivity extrapolates not to zero resistivity but to a value that is negative. The resistivity of the high T_c materials in contrast seems to extrapolate to zero. In good samples the resistivity at T_c is of the order of 60 $\mu\Omega$ cm and the intercept $\pm$ 2 $\mu\Omega$ cm. It has been argued that the zero intercept is the result of a compensation of the negative intercept expected for ordinary (BG) resistivity by residual impurity scattering. We find this unlikely. It is more reasonable to assume that the linear variation continues to low temperatures and is not caused by a Debye spectrum of phonons plus just the right amount of residual resistance but by some unknown low frequency scattering process.

If this picture is correct the scattering rate at very low temperatures could be very small. In terms of the slope of the resistivity the scattering rate is given by:[9]

$$1/\tau = 2\pi\lambda kT.$$

With $1/\tau = 1.3kT$ we get $\lambda = 0.2$. Such a low value of λ means that the coupling of the carriers to modes that scatter them at low frequency is weak and spectroscopic evidence in the form of a strong Holstein sideband can be expected. This is unlike the situation in conventional strong coupling materials such as lead where this effect has been observed.[2]

There is no evidence in the optical data of anomalous low lying modes that couple strongly to the electrons as for example in the organic superconductors where there is a large discrepancy between the low frequency infrared conductivity and the dc conductivity, a difference attributed to low-lying pinned charge density waves.[10] Similarly, in the heavy Fermion systems the conduction electrons are strongly coupled to low-lying magnetic excitations. This coupling can be identified in the infrared spectrum as a low frequency structure.[11]

3. THE MIDINFRARED BAND

A common feature of all the oxide superconductors is a region of sharply decreasing reflectance in the midinfrared. This decidedly non-Drude behavior starts in the 300 to 400 cm^{-1} region. Kramers Kronig analysis shows that a strong absorption band with a sharp onset having an oscillator strength of the order of one electron per formula unit is responsible for the absorption.

Fig 1. shows this midinfrared band as observed by four different groups. The absorption can best be seen in the superconducting state when the Drude band that overlaps the midinfrared band at low frequencies has been shifted to zero frequency. However, recent measurements on high quality films trace the onset of absorption at 450 cm^{-1} all the way up to

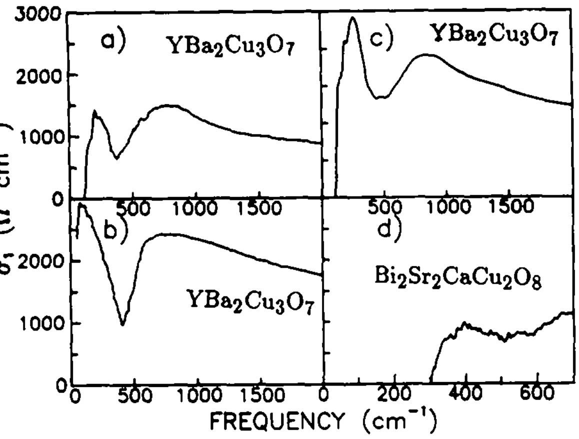

Figure 1
The midinfrared band, data from four groups. a) Thin film produced by laser ablation by the Siemens/Regensburg group. b) Another laser processed film from the Bellcore/Florida collaboration. c) A single crystal of $YBa_2Cu_3O_7$ from AT&T. d) $Bi_2Sr_2CaCu_2O_8$crystal from McMaster. In all cases there is temperature independent absorption in the midinfrared of the order of 1500 (Ω cm$)^{-1}$ in amplitude. The gap-like onset of the absorption has the superficial appearance of a superconducting gap but the gap is also present in the normal state.

room temperature.[7] Another way of resolving the midinfrared band is to study samples with depressed T_c. The Drude contribution is depressed in such samples relative to the midinfrared band and the two can be clearly resolved even at high temperature.[5]

There is overall agreement on the shape of midinfrared conductivity at low temperature.[6,7,12] A strong double peaked absorption is seen with an onset at about 150 cm^{-1} in $YBa_2Cu_3O_7$ and 300 cm^{-1} in $Bi_2Sr_2CaCu_2O_8$.[13] The absorption peaks around 1000 cm^{-1} and has a broad tail towards the near infrared. Recent measurements on samples with varying oxygen content show that the band shape is variable. In very low T_c materials the band is weak and centered at 5000 cm^{-1}. As the oxygen content is increased the peak at 1000 cm^{-1} becomes more dominant, reaching a conductivity of 2500 (Ω cm$)^{-1}$ in the best crystals.[12]

At room temperature, in most samples, the midinfrared band cannot be resolved from the Drude contribution at low frequency. As a result the sum of the two bands can be fit by a single Drude band with an apparent plasma frequency of the order of 3 eV and a very high damping of 0.5 eV (4000 cm^{-1}) or higher. Such a free carrier model is not consistent with the known temperature variation of the spectra since the midinfrared band is temperature independent whereas the low frequency band tracks the dc conductivity. This along with the unphysically large scattering rate needed for this model rules out the simple free electron picture for the midinfrared band.

An extension of the free carrier picture of the midinfrared band is the idea that the band is the result of strong frequency dependent scattering, very much like the Holstein absorption due to phonons in ordinary superconductors.[2] Unlike the Holstein absorption which shifts up in frequency by 2Δ the midinfrared band does not change shape or position when the materials become superconducting. Furthermore strong coupling of the carriers to excitations in the 400 - 500 cm^{-1} region would lead to a strongly coupled non linear dc resistivity with a large λ in contrast with what is actually observed: linear, weakly coupled resistivity.

The most viable explanation of the midinfrared band at this time is that it is an electronic particle-hole band. Its strength is of electronic magnitude and the fact that it does not change on entry to the superconducting state means that carriers other than the ones that are responsible for charge transport are involved. One possibility is that the band is of polaronic origin but the fact that the position in $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$ is so different speaks against this picture: one would expect the phonon spectra in the two systems to be very similar and any phonon sideband of the mode at the origin to also be similar in shape.

The very inertness of the midinfrared band when the materials become superconducting suggests the presence of a surface layer of a foreign phase with a low-lying electronic band. This possibility cannot be ruled out at the present time but seems unlikely in view of

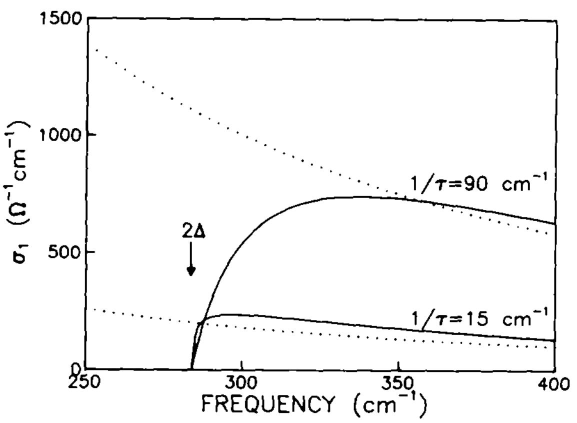

FIGURE 2
The calculated conductivity for a BCS superconductor for various ratios of scattering rate to the gap 2Δ. As the material approaches the clean limit the structure at 2Δ that denotes the superconducting gap becomes weaker. In the clean limit no gap structure appears in the optical constants.

the universal presence of the band in the spectra reported in a large class of materials.[3]

4. THE SUPERCONDUCTING GAP

One of the primary aims of the study of the infrared properties of the new superconductors has been the establishment of the energy gap. Unfortunately very little progress has been made. The features shown in Fig. 1 at low temperature have widely been associated with the gap but since they are present in the normal state as well as in the superconducting state they clearly do not represent a superconducting gap in the conventional sense.

The magnitude of the conductivity changes expected to occur at the gap frequency of the high T_c materials are shown in Fig. 2 where the optical conductivity of a superconductor with $2\Delta/kT_c = 4.5$ ($2\Delta = 284$ cm^{-1}) and $T_c = 91$ K is shown for two values of the scattering rate of electrons, $1/\tau$, according to a formula due to Leplae.[14]

It is clear that if the low temperature scattering rate is of the order of 15 cm^{-1} or larger a step in the conductivity could be seen at the gap frequency. Recent experiments show that no such feature appears in the 200 - 600 cm^{-1} region. Either the scattering rate is smaller than we estimated or else the gap is very large. Another possibility is that the gap has a large degree of anisotropy in the ab plane and is completely smeared over a range of frequencies of the order of a few hundred cm^{-1}.

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