Gap States in HTSC by Infrared Spectroscopy

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Recent infrared reflectance spectroscopy on high quality crystals of a number of HTSC systems shows that *all* have finite conductivity in the frequency region of the superconducting gap. Results on untwinned YBCO from a number of laboratories show that this absorption is not due to experimental problems or sample-to-sample variations. Other materials also show absorption features in the gap region in the form of peaks. We discuss these results in terms of recent ideas of the effect of impurities in d-wave superconductors.

KEY WORDS: Superconductivity, gap, infrared, d-wave

1. INTRODUCTION

The observation of the superconducting gap by infrared spectroscopy has been a goal from the beginning of the discovery of high temperature superconductivity.[1] For several reason this search has been unsuccessful. First, it appears, from angle resolved photo emission, that the gap, at least in $Bi_2Sr_2CaCu_2O_8$, is highly anisotropic in k-space. The corresponding optical spectrum would not exhibit a sharp onset of conductivity.

Secondly, it is known that the materials are in the clean limit, and from momentum selection rules, an onset of absorption at the gap frequency is not possible. In this limit, absorption starts at twice the gap frequency, plus the frequency of the relevant excitations responsible for transport scattering. Thus given the combination of a d-wave density of states and a smoothly rising excitation spectrum any sharp feature corresponding to the gap will be washed out. Recent interest has focussed on breaking down the momentum selection rules using defects, introduced either by doping,[2] or radiation damage.[3,4] Surprisingly, the effect of defects on the optical absorption spectrum in the gap region does not produce dirty-limit behaviour as seen in conventional superconductors – an onset of absorption at 2Δ . Instead, a new low frequency, Drude-like, absorption appears in the superconducting state, taking spectral weight away from the superconducting condensate. The total low frequency spectral weight remains constant[3,4] and equal to the Drude spectral weight in the normal state.

In this review we will cover some recent work on the ab-plane conductivity in the cuprates. There have been substantial improvements in the technology of crystal growth [5,6] as well as optical spectroscopy of smaller and smaller crystals. [7]

2. RESULTS

2.1 a-axis Conductivity of $YBa_2Cu_3O_{7-\delta}$

YBa₂Cu₃O_{7- δ} is the most studied of the cuprates but it is important to study detwinned crystals since the optical properties are quite anisotropic.[8] Much of the variability in the properties of YBa₂Cu₃O_{7- δ} seems to stem from the quality of the chains which tend to incorporate aluminum and gold from the crucibles used for growth.[9] The a-direction properties do not depend as much on currents carried in the chains and material variability is much reduced. This is illustrated in Fig. 1.

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Fig 1. The a-axis optical conductivity of $YBa_2Cu_3O_{6.95}$ from three groups. There is overall agreement to the value of the conductivity for crystals from different sources. Note the absence of a true gap and a fairly constant conductivity of $350 \ (\Omega \text{ cm})^{-1}$ at the minimum.

Fig. 1 shows the a-axis optical conductivity with light polarized normal to the chains. Curves from three laboratories are shown. The heavy line is a spectrum from Pham et al.[10] measured by direct absorption and therefore having perhaps the highest absolute accuracy. The dashed curve is a recent measurement by Basov et al. on crystals grown in zirconia crucibles with highly conducting chains. In contrast, the light solid curve, measured by Scützmann et al.[11] is on crystals with fragmented chains that show effects of localization. Two things are clear from these data: there is good overall agreement between the measurements over a large range of frequency on crystals from a wide range of sources. A fourth data set, by the Florida group, using crystals from the Illinois group, not shown here, is in excellent agreement with these.[9]

The spectra are characterized by a broad minimum centered at 400 cm⁻¹ where the conductivity reaches a value of 400 Ω^{-1} cm⁻¹. At lower frequencies the conductivity rises again and if extrapolated to zero frequency reaches a value of about 2000 Ω^{-1} cm⁻¹. This is approximately half of the residual conductivity seen in samples from the same source by microwave techniques, 4500 Ω^{-1} cm⁻¹.[12]

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2.2 Conductivity of $Tl_2Ba_2CuO_{6+\delta}$.

The Tl₂Ba₂CuO_{6+ δ} material has a single copper-oxygen plane and a T_c close to 90 K at optimal doping. Its T_c can be reduced to zero by oxygen annealing. At optimal doping, it shows a linear resistivity variation with temperature, typical of most high T_c materials, changing towards a T^2 in the over doped region. We report here preliminary results of the optical conductivity of this material.[13]



Fig 2. The the optical conductivity of $Tl_2Ba_2CuO_{6+\delta}$ The thick line is the 90 K curve just above the superconducting transition of 88 K and the thin line the low temperature spectrum. The spectrum is dominated by a large peak. a pseudogap develops at 70 cm⁻¹ already in the normal state.

Figure 2. shows the ab plane conductivity of a crystal of optimally doped $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+\delta}$ with $T_c = 88$ K. Two temperatures are shown, 90 K just above the superconducting transition, and 15 K in the superconducting state. The conductivity is unusual for a metal since, instead of a Drude absorption the spectrum consists of a peak at approximately 100 cm⁻¹. In the superconducting state this peak sharpens and moves to lower frequency.

The normal state dc conductivity is metallic (linear with a positive temperature coefficient) whereas the optical conductivity shows a low-lying peak rising from the dc value (shown as a black point at zero frequency). A positive *frequency* coefficient of conductivity is usually associated with localization and is then accompanied by a *negative* temperature coefficient of resistivity. The superconducting state conductivity is also anomalous. First, there is no sign of an energy gap, but the pseudogap visible in the normal state deepens in the superconducting state. The onset frequency of this gap is 70 cm⁻¹.



Fig 3. The the optical conductivity of $Pb_2Sr_2(Y/Ca)Cu_3O_{8+\delta}$. The 85 K curve is in the normal state. As superconductivity develops a pseudogap develops around 70 cm⁻¹. There is no sign of a superconducting gap only a pseudogap which is already present in the normal state.

A careful analysis of the spectral weight, using the conductivity sum rule, shows that the region from 0 to 600 cm⁻¹ supplies all the spectral weight for the superconducting condensate. The London penetration depth, calculated from this missing spectral weight, is 2400 ± 200 Å. The condensate density, per copper plane, is similar to the a-axis value of YBa₂Cu₃O_{7- δ} which is 1600 Å[9] ($2400/\sqrt{2} = 1700$ Å).

2.3 Conductivity of $Pb_2Sr_2(Y/Ca)Cu_3O_{8+\delta}$

The third material we want to discuss here is $Pb_2Sr_2(Y/Ca)Cu_3O_{8+\delta}$. Structurally it shares elements with $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_8$. There is a copper oxide bi-layer, and like the former, it has a third single copper layer midway between the bilayers. By varying the Ca/Y ratio, a T_c close to 90 K can be obtained.[14,15,16]

Fig. 3 shows the optical conductivity of $Pb_2Sr_2(Y/Ca)Cu_3O_{8+\delta}$ with $T_c = 80$ K at a series

of temperatures. A broad peak can be seen, centered around 200 cm⁻¹ in the normal state, moving to 80 cm⁻¹ in the superconducting state. The peak is similar in appearance to the peak in Tl₂Ba₂CuO_{6+ δ}but has much less spectral weight associated with it. Again, there is no sign of a superconducting gap and the spectral weight for the condensate appears to originate from a wide frequency range to account for the relatively large condensate density, measured by dc techniques such as magnetization[17] where a penetration depth of 2575 Å is obtained, and μ SR where a similar value is found.[18]

1. DISCUSSION

In what follows we would like to focus on a common element in in the spectra of these three materials – finite conductivity in the region of the spectrum where a conventional superconductor is expected to be gapped. Before discussing possible sources for this conductivity we address the question of the reality of this conductivity, since it is claimed by one group at least, that the a-axis conductivity in $YBa_2Cu_3O_{7-\delta}$ is gapped.[8,19] The current consensus is however that there is a non-zero minimum conductivity and that the conductivity rises towards lower frequencies. There is general agreement on the value of the minimum conductivity (400 \pm 50 Ω^{-1} cm⁻¹) and since the bolometric experiment of the Maryland group is intrinsically an order of magnitude more sensitive than any reflectance data, we must accept this value as being a fundamental characteristic of the fully doped material.

More important than a non-zero minimum value is the general rise of conductivity toward lower frequencies. Very strong minima in conductivity are caused by coupling to LO phonons[20] and for example in YBa₂Cu₄O₈ there is a minimum in the conductivity at 400 cm⁻¹ where the conductivity value is only 200 Ω^{-1} cm⁻¹.[9] Similar strong minima have been seen in Tl₂Ba₂CaCu₂O₈.[21] Nevertheless, all materials investigated have a background conductivity away from the minima that ranges from 250 to 1000 Ω^{-1} cm⁻¹, ref. 1, fig. 56, summarizes some of the early data.

One explanation that has been used to account for this residual conductivity has been in terms of defects or disorder. The difficulty with this explanation is the fact that the background absorption shows relatively little sample-to-sample variation. For example the ab plane dc resistivity of single crystals of $YBa_2Cu_3O_{7-\delta}$ varies by more than a factor of two from laboratory to laboratory whereas, as we see in Fig. 1, the variation in the background conductivity is quite small.

A potential solution to the problem is provided by a recent suggestion of Lee[22] in terms of the limiting conductivity for a d-wave superconductor in the presence of resonance scattering defects, predicted to be $\sigma_{00} = \omega_p^2 / \pi \Delta_0$. Taking the a-axis value $\omega_p = 10000 \text{ cm}^{-1}$ [9] we find the limiting conductivity to be $\approx 2300 \ \Omega^{-1} \text{ cm}^{-1}$, which is in rough agreement with the low frequency limit of the optical conductivity. Furthermore the conductivity is predicted to be *independent* of defect concentration. This process would account for the magnitude of the observed conductivity as well as the lack of sample-to-sample variation.

The conductivity of the other two materials, $Tl_2Ba_2CuO_{6+\delta}$ and $Pb_2Sr_2(Y/Ca)Cu_3O_{8+\delta}$ cannot be explained by this process since the observed peak is already present in the normal state and only grows in sharpness as superconductivity is established. Nevertheless localization may be responsible for these structures as well. Both materials have wide transitions and the doping process involves oxygen vacancies.[23] Anther process that is capable of producing a low temperature peak is the development of spin density wave correlations.[24]

REFERENCES

- A review of the background to this paper is found in D.B. Tanner and T. Timusk, *Physical Properties of High-Temperature Superconductors, vol III* D.M. Ginsberg, editor, (World Scientific, Singapore, 1992) p. 363.
- M.J. Sumner, J-T. Kim, and T.R. Lemberger, *Phys. Rev. B* 47 12248 (1993).
- 3. T. Strach, thesis, McMaster University, 1992
- D.N. Basov, A.V. Puchkov, R.A. Hughes, T. Starch, J. Preston, T. Timusk, D.A. Bonn, R. Liang and W.N. Hardy, *Phys. Rev. B* 49 12165 (1994).
- T.A. Friedmann, M.W. Rabin, J. Giapintzakis, J.P. Rice, and D.M. Ginsberg, Phys. Rev. B 42 6217 (1990).
- R. Liang, P. Dosanjh, D.A. Bonn, D.J. Baar, J.F. Carolan, and W.N. Hardy, Physica C 195

51 (1992).

- C.C. Homes, M.A. Reedyk, D.A. Crandles, and T. Timusk, Applied Optics 32, 2976, (1993).
- Z. Schlesinger, R.T. Collins, F. Holtzberg, C. Feild, S.H. Blanton, U. Welp, G.W. Crabtree, Y. Fang, and J.Z. Liu, *Phys. Rev. Lett.* 65 801 (1990).
- D.N. Basov, R. Liang, D.A. Bonn, W.N. Hardy, B. Dabrowski, M. Quijada, D.B. Tanner, J.P. Rice, D.M. Ginsberg, and T. Timusk (unpublished).
- T. Pham, H.D. Drew, S.H. Mosley, and J.Z. Liu, *Phys. Rev. B* 44 5377 (1991).
- J. Schützmann, B. Gorshunov, K.F. Renk, J. Münzel, A. Zibold, H.P. Geserich, A. Erb, and G. Müller-Vogt *Phys. Rev. B* 46 512 (1992).
- K. Zhang, D.A. Bonn, S. Kamal, R. Liang, D.J. Baar, W.N. Hardy, D. Basov, and T. Timusk, *Phys. Rev. Lett.* **73** 2484 (1994).
- 13. A.V. Puchkov, T. Timusk, S. Doyle, and A.M. Hermann, (unpublished).
- 14. R.J. Cava et al. Nature 336 211 (1988).
- 15. M. Reedyk, Thesis, McMaster University (1992).
- 16. J.S. Xue, Thesis, McMaster University (1992).
- M.A. Reedyk, C.V. Stager, T. Timusk, J.S. Xue, and J.E. Greedan, *Phys. Rev. B* 44 4539 (1994).
- 18. J.H. Brewer (private communication)
- L.D. Rotter, Z. Schlesinger, R.T. Collins, F. Holtzberg, C. Feild, U. Welp, G.W. Crabtree, J.Z. Liu, Y. Fang, K.G. Vabdervoort, and S. Flesher, *Phys. Rev. Lett.* 67 2741 (1991).
- M. Reedyk and T. Timusk, Phys. Rev. Lett. 69 2705 (1992).
- C.M. Foster, K.F. Voss, T.W. Hagler, D. Mihailović, A.J. Heeger, M.M. Eddy, W.L. Olsen, and E.J. Smith, *Solid State Comm.* 76 651 (1990).
- 22. P.A. Lee Phys. Rev. Lett. 71 1887 (1993).
- J.S. Xue, M. Reedyk, J.E. Greedan, T. Timusk, and N. Tanaka, J. of Solid State Chemistry, 102 492 (1993)
- D.A. Bonn, J.D. Garrett, and T. Timusk, *Phys. Rev. Lett.* 61 1305 (1988).