0.7 eV excitation in $YBa_2Cu_3O_{7-\delta}$: evidence from epitaxial thin film and powder samples

LETTER TO THE EDITOR

0.7 eV excitation in $YBa_2Cu_3O_{7-\delta}$: evidence from epitaxial thin film and powder samples

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Abstract. We have measured the optical absorption spectrum of $YBa_2Cu_3O_{7-\delta}$ crystalline thin films and powders in the range 2000 to 10 000 cm^{-1}. A broad absorption band near 5500 cm^{-1} (0.7 eV) is observed, which has the same absorption profile in both cases. Our work on thin-film samples shows that the excitation causing this absorption is polarized in the *ab* plane. Further work on doped powder samples provides evidence that the excitation is localized in the CuO_2 planes of the structure, which are known to be the principal carriers of the superconductivity. Studies of the temperature dependence of the absorption have revealed that the peak intensity undergoes a transition at the superconducting transition temperature, providing firm evidence that the excitation is coupled to the superconducting order parameter.

The mechanism by which superconductivity occurs in the high-T_c cuprate superconductors is still a matter of debate. Evidence of the important role of the lattice in the mechanism is, however, increasing [1], giving added weight to those theories involving the lattice, for example in the formation of bipolaronic [2–4] or spin-bipolaronic [5] states.
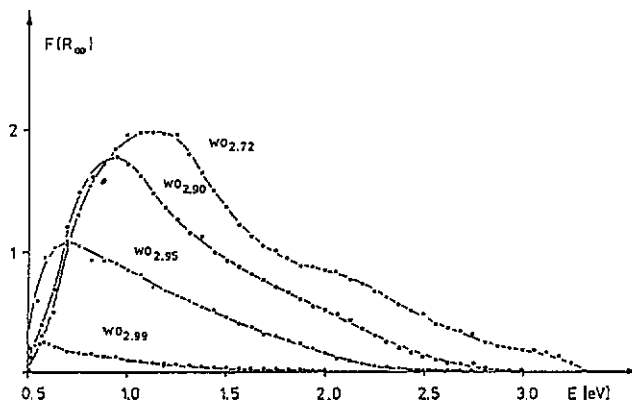

Figure 1. Absorption spectra of WO_{3-x}, with various levels of oxygen substoichiometry.

An important experimental test for a bipolaronic theory of high-T_c superconductivity, is in the study of the near-infrared spectra of these materials, which would be expected to show similar behaviour to that observed in other oxides in which bipolarons are known to exist, such as TiO_{2-x} [6,7], $NbO_{2.5-x}$ [7], WO_{3-x} [8,9] and MoO_3 [10]. These materials all show a broad assymetric absorption band at around 1 eV, as shown in figure 1 for WO_{3-x} [9]. Such an absorption band has indeed been observed in powder samples of $YBa_2Cu_3O_{7-\delta}$ [11]. In this letter, we will show that this excitation is observed in the near-infrared spectra of both crystalline thin films and powder samples of $YBa_2Cu_3O_{7-\delta}$ (YBCO). We also confirm [11] that this excitation is coupled to the superconducting order parameter.

The existence of this peak at 0.7 eV has previously been inferred from the Kramers–Kronig analysis of reflection spectra obtained from thin film and single crystal samples by many groups [12–16]. High-energy excitations in YBCO, however, introduce errors into the Kramers–Kronig analysis [17,18], which make it difficult to study small changes in this region of the excitation spectrum using reflectivity data alone. Here, we have overcome this problem by combining data from reflection and transmission experiments on thin films to give α, the absorption coefficient, as a function of frequency without the need to extrapolate our data sets to zero and infinite frequency.

Thin film samples were prepared by laser ablation onto MgO and $SrTiO_3$ substrates and characterized by x-ray diffraction and resistance measurements. At room temperature, the samples used for the optical measurements gave excellent single-crystal diffraction without any finite size broadening. No misfits between grains were found, although the misfit with the substrate was the usual 1%. The transition point was at 88 K with a transition width of 2 K. In transmission experiments, an MgO substrate was used as a reference. In reflection experiments, a silver mirror was used as a reference.

Powder samples of YBCO, were prepared by powder sintering and characterized by resistance measurements [19] and hard-mode phonon spectroscopy [20]. The samples were ground in a spex electrical mill then mixed with dry KBr powder in the ratio 1:200 by weight and pressed at 10 tons cm^{-2} and room temperature for 10 min into 200 mg pellets of 13 mm diameter. Pure KBr reference pellets were made by the same procedure. The pellets were stored in a dessicator and measurements were taken within 12 h of the sample preparation.

Spectra were measured in vacuum in the wavenumber range from 2000 to 10000 cm^{-1} using a Bruker 113V FTIR spectrometer equipped with a liquid-nitrogen cooled InSb detector. The temperature of the sample was varied between 30 and 300 K using a Leybold He cryostat with KRS5 windows. An aspect 3000 computer was used for data collection and processing.

The calculation to obtain the absorption coefficient from the thin-film transmission and reflection data uses the expression for the absorption coefficient, α:

$$\alpha = -1/x\left[\log_e(I_t/I_i) - \log_e(1 - I_r/I_i)\right]$$

where x is the sample thickness, I_t is the transmitted intensity, I_i is the incident intensity and I_r is the reflected intensity.

The spectrum of α for a (001) film is shown in figure 2, which reveals a broad absorpton peak near 5500 cm^{-1} (0.7 eV). The fact that the excitation is visible in the excitation spectrum of an (001)-orientated film implies that it is polarized in the a–b plane of the crystal.
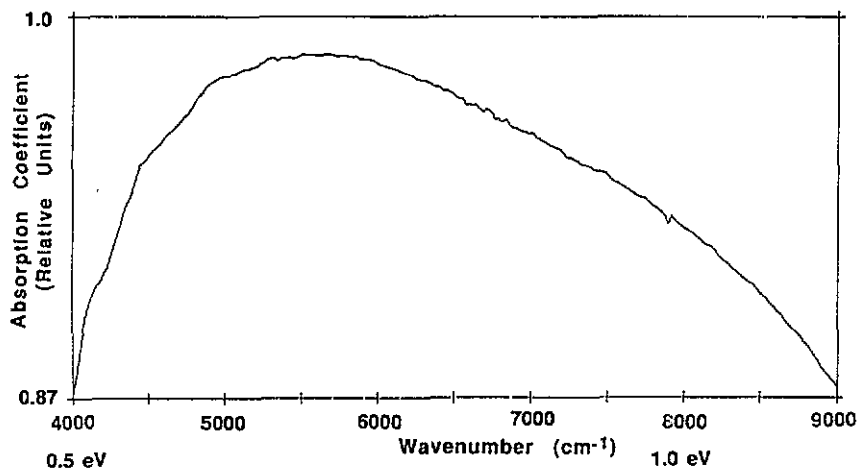
Figure 2. The absorption coefficient of an (001) oriented single-crystal thin-film sample of $YBa_2Cu_3O_{7-\delta}$ between 4000 and 9000 cm^{-1}.

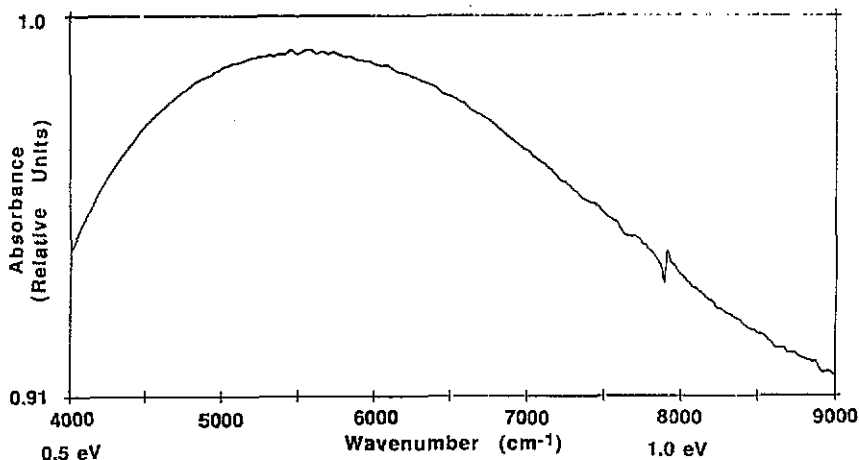**Figure 3.** The infrared powder absorption spectrum of $YBa_2Cu_3O_{7-\delta}$ between 4000 and 9000 cm^{-1}.

The absorbance spectra of the powder samples of YBCO were obtained by sub-traction of the spectrum of the KBr reference pellet from that of the sample. This gives a result like that in figure 3, which again shows the broad absorption peak observed at 5500 cm^{-1}. Here, the effect of reflection may be ignored because the grain size of the powder is sub-micron, and therefore comparable to or shorter than the wavelength of the light involved. The validity of this assumption is justified by the excellent agreement between these results and those obtained from thin film sam-ples (figure 2). This similarity between the two spectra demonstrates that the peak observed in the powder absorption spectrum is an intrinsic property of the material, and is not a result of anisotropy or an artifact of the experimental technique.

Further information about the localization of the excitation within the struc-ture was obtained from experiments on Zn- and Fe-doped YBCO powders,
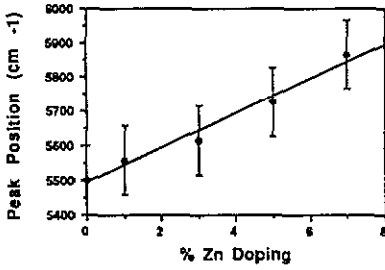
Figure 4. A plot showing the linear increase in peak position with increasing Zn concentration for samples of $YBa_2(Zn_xCu_{1-x})_3O_{7-\delta}$.

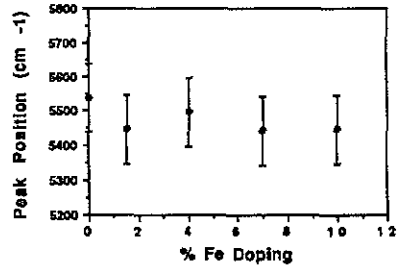**Figure 5.** A plot showing the insensitivity of the peak position to Fe doping for samples of $YBa_2(Fe_xCu_{1-x})_3O_{7-\delta}$.

$YBa_2(M_xCu_{1-x})_3O_{7-\delta}$ (M = Zn, Fe). Zn predominantly replaces Cu in the CuO_2 planes [21], while Fe replaces Cu in the CuO chains [22] of the structure. It was found that Zn-doping causes a shift in the peak position (figure 4), while Fe-doping has no such effect (figure 5). Because we see a shift in the peak position for doping in the CuO_2 planes but no shift for doping in the CuO chains, we conclude that the absorption is primarily due to excitations in the CuO_2 planes and not the CuO chains. This increases the likelihood that this absorption is relevant to the superconductivity, because it is known that the superconducting charge carriers have their greatest amplitude in the CuO_2 planes.
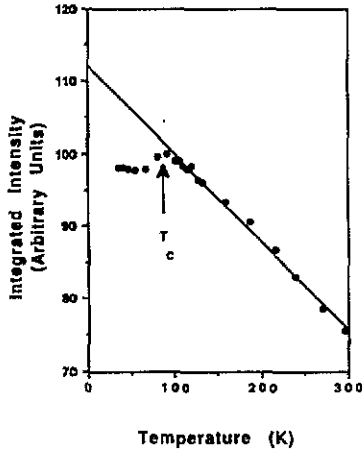

Figure 6. The integrated intensity of the absorption peak observed in a powder sample of $YBa_2Cu_3O_{7-\delta}$ plotted as a function of temperature, showing the superconducting phase transition at T_c.

Indeed, we find that studies of the temperature dependence of the absorption [11] provide firm evidence of the relevance of the excitation to the superconductivity. Plotting the integrated intensity of the peak in the powder absorption spectrum against temperature gave the result shown in figure 6. The peak intensity increases linearly with decreasing temperature down to T_c, where there is a transition. Below T_c, the peak intensity decreases to a constant value, becoming independent of temperature at temperatures well below T_c. This transition at T_c clearly demonstrates that the excitation is coupled to the superconducting order parameter.

The linear increase in the absorption cross section with decreasing temperature which is observed in the normal state reflects the linear behaviour of the electrical

resistivity [23] and Hall coefficient [24] in this region. This correlation may be explained by the hypothesis that this is a polaronic excitation of the normal-state charge carriers, in which case the reduction in intensity below T_c would correspond to the fraction of the normal-state charge carriers which have condensed into the superconducting state. Extrapolating to absolute zero temperature, we estimate there to be a reduction of around 12%. This value is of the same order of magnitude as the estimated 10% of the total carrier concentration which is believed to take part in the condensation [25].

A broad assymetric absorption band has been observed in the near-infrared spectra of crystalline thin film and powder samples of YBCO. Experiments on high-quality films and doped samples show that this absorption is due to an excitation with a–b polarization in the CuO_2 planes of the structure. Furthermore, we found that the intensity of the peak, which shows a linear temperature dependence in the normal state, undergoes a transition at T_c indicating that the excitation is coupled to the superconducting transition.

We believe that this absorption may be due to excitations of polaronic normal-state charge carriers similar to those observed in other compounds such as WO_{3-x}. These polarons, in the form of bipolaron pairs, would then condense at T_c into the superconducting state, causing a reduction in the absorption cross section such as that observed.

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