

Optical Excitations in the CuO_2 Planes of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$: The Effect of Doping with Zn and Fe

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The optical absorption spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the range 2000 to 10,000 cm^{-1} shows a broad absorption band near 5500 cm^{-1} (0.7 eV). The integrated intensity of this band decreases at T_c , demonstrating that the excitation is coupled with the superconducting order parameter. We show that the intensity and energy of the absorption are both raised when Cu atoms in the CuO_2 planes are substituted by Zn, but that the absorption is unaffected by the substitution of CuO chain Cu atoms with Fe. This indicates that the absorption is associated with an excitation in the CuO_2 planes, where the main superconducting action takes place, and not an excitation in the CuO chains. We suggest that the absorption is caused by excitations of (bi)polaronic states, which become localized by Zn defects. © 1992 Academic Press, Inc.

Introduction

The infrared spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) high-temperature superconductor has been intensively studied as a tool for probing the spectrum of low-energy excitations (1–18) of this material. Low-energy excitations are central to various of the theoretical models which have been proposed to explain the superconductivity, such as those involving excitons (19, 20), plasmons (21), negative-U Hubbard interactions (22), resonating valence bonds (23), or bipolarons (24–27).

One such excitation has been observed in the form of a broad asymmetric absorption band at 0.7 eV in YBCO (6–18) and at 0.8 eV in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) (28–31).

The integrated intensity of the peak observed in LSCO ceramics has been found

(28, 29) to show the same dependence on Sr doping as the superconducting transition temperature and the dc Meissner effect, which implies that this excitation is directly relevant to the superconductivity. Experiments on single crystal and thin film samples (30, 31) have shown that the peak, which is absent in semiconducting La_2CuO_4 , grows and shifts to higher energies with increasing Sr content up to the maximum T_c at $x = 0.2$. Upon further doping with Sr, the peak sharpens and shifts back toward lower energies, but does not disappear, even when the compound is no longer a superconductor.

The peak near 5500 cm^{-1} (0.7 eV) in YBCO, which we consider in this paper, besides being observed directly in absorption experiments (6–8), has been deduced from Kramers–Kronig analysis of the reflection spectra of ceramic (9–11), thin film

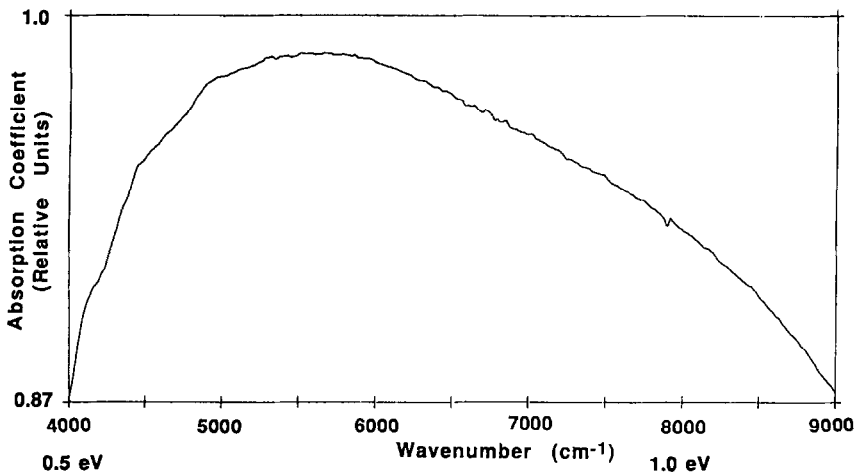


FIG. 1. The infrared absorption spectrum of a (001) epitaxial thin film of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ between 4000 and 9000 cm^{-1} (7).

(12, 13), and single crystal samples (13–18). We have also (7) calculated the (001) plane absorption coefficient directly from transmission and reflection data collected from oriented thin film samples. The result of this calculation (Fig. 1), which does not require extrapolation of the data sets to zero and infinite energy for a Kramers–Kronig analysis, is in excellent agreement with the spectrum obtained from a powder sample (Fig. 2). The similarity between the two results

demonstrates that this region of the powder spectrum is not unduly influenced by the anisotropy of the material, which is an important factor to be taken into account in the analysis of spectra measured on powder samples (32).

Experiments on oxygen deficient ceramic (8, 10) and single crystal (17) samples of YBCO have shown that the 0.7-eV excitation, which is absent in $\text{YBa}_2\text{Cu}_3\text{O}_6$, grows in intensity and moves toward lower energy

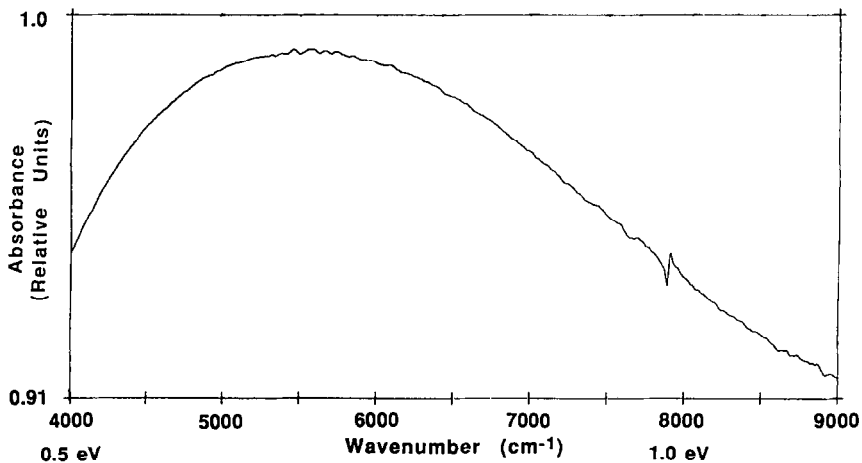


FIG. 2. The infrared powder absorption spectrum of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ between 4000 and 9000 cm^{-1} .

with increasing oxygen content and T_c . This again suggests that there may be a relation between the disposition towards superconductivity and the existence of this excitation. It is, however, noteworthy that the peak in LSCO moves toward higher energy with increasing T_c , while the peak in YBCO moves toward lower energy with increasing T_c .

More recently (6, 7), we have shown that the intensity of the peak increases approximately linearly with decreasing temperature down to the superconducting transition, below which the peak intensity decreases and ultimately becomes independent of temperature. The transition observed at T_c clearly demonstrates that the excitation is coupled to the superconducting order parameter. Furthermore, the change below T_c is of the order of 12%, which is equivalent to the fraction of the charge carriers which we believe (33) take part in the condensation.

In order to investigate the excitation further and determine its localization in terms of the crystal structure, we have measured the absorption spectra of samples of YBCO, which were doped with Zn and Fe. Zn replaces Cu in the CuO_2 planes (34–36), whereas Fe replaces Cu in the CuO chains (37). We find that Zn has a profound effect on the peak position and intensity, which is not observed in the Fe-doped samples. Our conclusion is that the absorption is primarily due to excitations in the CuO_2 planes and not the CuO chains. We analyze the effects of oxygen substochiometry and doping with Fe and Zn on this region of the absorption spectrum in terms of a polaronic model for the excitation.

Experimental

Samples of $\text{YBa}_2(\text{Zn}_x\text{Cu}_{3-x})\text{O}_{7-\delta}$ and $\text{YBa}_2(\text{Fe}_x\text{Cu}_{3-x})\text{O}_{7-\delta}$ were prepared by powder sintering and characterized by resistance measurements (38) and hard mode phonon spectroscopy (39).

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/cm² 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 desiccator and measurements were taken within 12 hr.

Spectra between 2000 and 10,000 cm^{-1} were taken under vacuum at room temperature using a Bruker 113V FTIR spectrometer equipped with a liquid-nitrogen-cooled InSb detector. An Aspect 3000 computer was used for data collection and processing.

The absorbance of the YBCO was obtained by subtraction of the spectrum of the reference pellet from that of the sample, to give a result like that in Fig. 2, which shows the broad peak around 5500 cm^{-1} . The spectra were then baseline corrected between 4000 and 900 cm^{-1} , and scaled by a factor of 1/(maximum height of the uncorrected spectrum). The result (see Figs. 3 and 6) is a peak whose height is given as a fraction of the total absorption at the maximum point. This scaling is necessary to make comparisons possible between the different sample pellets, whose absolute absorbance depends on experimental rather than intrinsic factors.

We emphasize that the spectra obtained by this technique are equivalent to those obtained from thin films and single crystals (7, 12–18), with the advantage that small relative changes can be studied more easily in powder spectra.

Results and Discussion

The baseline corrected and scaled spectra of the Zn doped samples are shown in Fig. 3. The position of the scaled peak's maximum is plotted against T_c in Fig. 4, and its maximum height is plotted against T_c in Fig. 5. Both these properties show a linear correlation with T_c : as T_c decreases, the peak

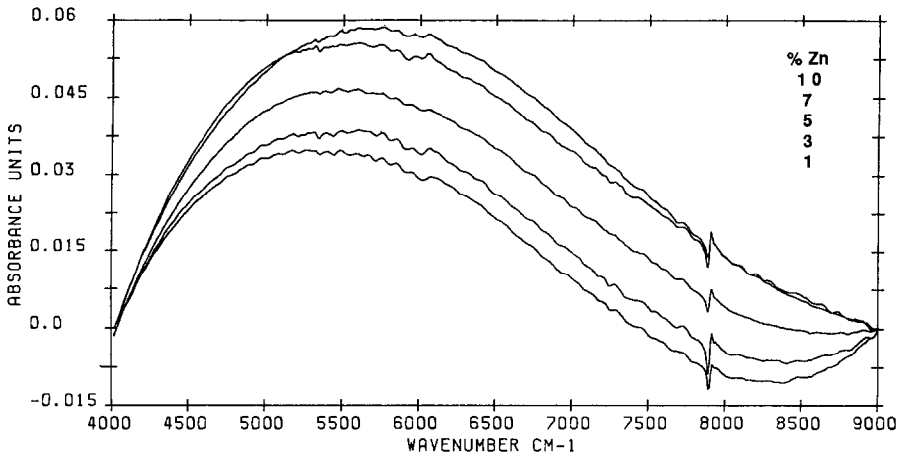


FIG. 3. The absorption spectra of samples of $\text{YBa}_2(\text{Zn}_x\text{Cu}_{3-x})\text{O}_{7-\delta}$. As the level of Zn doping is increased, the peak intensity increases and the peak position shifts to higher energy.

shifts to higher energies and its intensity, which is proportional to its height, increases. The linewidth of the peak was found to remain approximately constant at $2750 \pm 150 \text{ cm}^{-1}$, and the lineshape was asymmetric for all samples, as shown in Fig. 3.

The baseline corrected and scaled spectra of the Fe-doped samples are shown in Fig. 6, and the peak position is plotted against the percentage of Fe in Fig. 7. These clearly show that the peak does not shift with increasing Fe concentration.

The experimental observation that Zn doping increases the peak energy and absorption cross section, whereas Fe has little effect on the absorption spectrum, provides firm evidence that the excitation is localized in the CuO_2 planes of the structure, where the Zn atoms substitute for Cu, and not in the CuO chains where the Fe atoms substitute for Cu. This conclusion is in agreement with the results of polarized reflectivity measurements on untwinned single crystals (16), which can distinguish the contribution

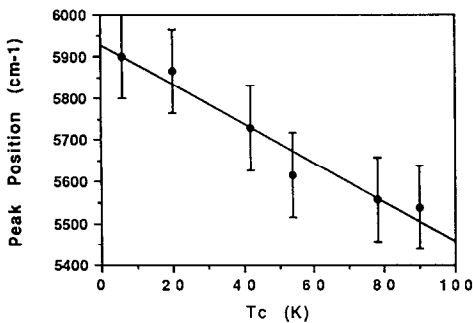


FIG. 4. A plot showing the linear increase in peak position with decreasing T_c for samples of $\text{YBa}_2(\text{Zn}_x\text{Cu}_{3-x})\text{O}_{7-\delta}$ (T_c decreases linearly with increasing Zn doping).

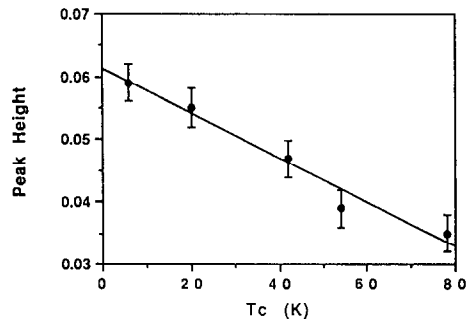


FIG. 5. A plot showing the linear increase in peak height with decreasing T_c for samples of $\text{YBa}_2(\text{Zn}_x\text{Cu}_{3-x})\text{O}_{7-\delta}$ (T_c decreases linearly with increasing Zn doping).

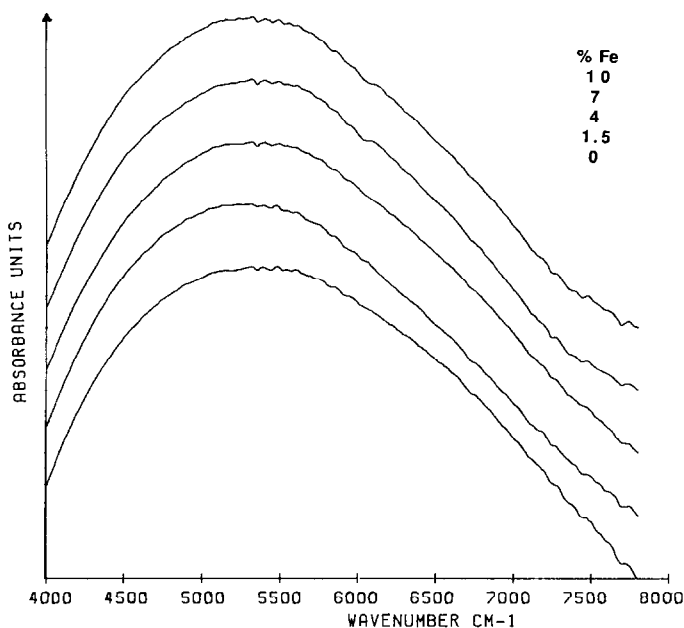


FIG. 6. A stack plot showing spectra of samples of $\text{YBa}_2(\text{Fe}_x\text{Cu}_{3-x})\text{O}_{7-\delta}$. The peak is unaffected by changes in the level of Fe doping.

of the CuO_2 planes from that of the CuO chains.

Bearing in mind the evidence that the charge carriers in YBCO may be of polaronic character (for a review see (40)), we now analyze the results in terms of a bipolaronic theory of superconductivity. In this theory,

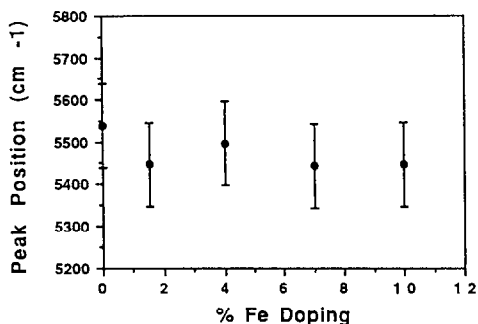


FIG. 7. A plot showing the insensitivity of the peak position to Fe doping for samples of $\text{YBa}_2(\text{Fe}_x\text{Cu}_{3-x})\text{O}_{7-\delta}$.

the internal excitations of the bipolaronic state are expected to show similar infrared activity to that observed in the transition metal oxides TiO_{2-x} (41, 42), $\text{NbO}_{2.5-x}$ (42), MoO_3 (43), and WO_{3-x} (44–46), in which bipolaronic states are known to exist. These compounds all show a broad asymmetric absorption band at around 1 eV, which is attributed to Frank–Condon transitions between neighboring polaron sites (44–47).

Other models, such as the fine structure of the lower Hubbard band (22, 23), could also explain our observations and it is not fully clear to what extent these models are mutually exclusive. We note, however, the striking similarity between the bipolaron absorption profiles observed in the transition metal oxides (41–46) and that observed at 0.7 eV in YBCO (6–18) and at 0.8 eV in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) (28–31).

In the bipolaron model, the intensity of the absorption is proportional to the number density of polaronic states in the material.

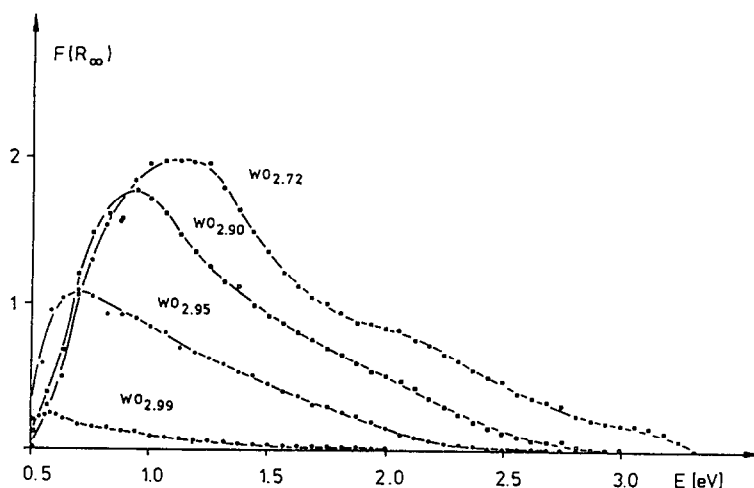


FIG. 8. Absorption spectra of WO_{3-x} . As the oxygen substoichiometry is increased, the peak grows and shifts to higher energy (46).

We also expect that the maximum point of the absorption will shift to higher energy when neighboring sites have different ground states, which may be caused by the introduction of structural disorder or doping, for example.

Both of these effects are clearly demonstrated in the optical spectra (Fig. 8) of WO_{3-x} (45), which is known to contain bipolaronic charge carriers (44–47). Upon depletion of oxygen, two effects occur: the carrier density is increased and disorder is introduced into the crystal structure. The former increases the absorption cross section, while the latter causes the spectral weight of the absorption to shift towards higher energies.

The behavior of the peak in YBCO and LSCO is consistent with these predictions. Increased doping of LSCO with Sr raises the carrier density, but increases localization of the carriers by the formation of defect states, causing the peak to grow and move to higher energies. Decreasing the oxygen content of YBCO below stoichiometry introduces defects into the structure and decreases the carrier concentration, causing

the peak to shrink and shift to higher energies. Doping YBCO with Zn raises the carrier concentration slightly, as has been observed in Hall measurements (48, 49), which causes the absorption cross section to increase. At the same time, however, Zn raises the peak energy because it introduces defects into the structure, which strongly localize the carriers, as illustrated (48, 49) by the rapid decrease in T_c and the change in the normal state resistivity from a metallic to semiconducting character. Doping YBCO with small amounts of Fe, on the other hand, has little effect on the charge carriers or the superconductivity, and hence no observable effect on the excitation at 0.7 eV.

Finally, in bipolaronic theories of high- T_c it is suggested that the polaronic charge carriers form pairs, which Bose condense into the superconducting state at T_c , in a way analogous to the superfluidity of ^4He . For bipolaronic superconductivity to occur, therefore, there are two constraints of paramount importance: that there be a sufficient number density of bipolaronic charge carriers in the material for Bose condensation

to occur, and that these charge carriers be mobile. These two requirements may conflict with one another if, for example, increasing the level of doping in the material raises the number density of polaronic charge carriers, but at the same time decreases their mobility by introducing defects into the structure with which the polarons form bound states. This would appear to be the case in LSCO, where increasing the level of Sr doping increases the carrier density at the expense of decreased mobility, but not in YBCO, where decreasing the oxygen substochiometry increases both the charge carriers' number density and their mobility. It is suggested that this combination of positive factors in YBCO as compared to the conflict observed in LSCO might go some way toward explaining the much higher T_c observed in YBCO (90 K) than that in LSCO (40 K).

Conclusions

The effect of substituting Zn and Fe for Cu on the infrared absorption near 5500 cm^{-1} of YBCO has been studied. It was found that both the energy and intensity of the peak increased linearly with increasing Zn doping, but that doping with Fe had no effect on the infrared absorption in this spectral region.

This dependence on Zn doping and insensitivity to Fe doping implies that the excitation which causes this absorption is associated with the CuO_2 planes, which are known to be the primary carriers of the superconductivity, and not the CuO chains. This fact provides further evidence that this absorption band is of significance for the superconductivity.

We propose that the absorption is due to the excitations of polaronic states, pairs of which Bose condense at T_c , giving rise to the superconductivity. The effect of the Zn dopant is to localize the (bi)polarons, raising their excitation energy and destroying the

superconductivity by demobilizing the carriers.

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