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EMISSION AND ESR STUDY ON HIGH T_c SUPERCONDUCTORS

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After discussing the emission spectra of the YBaCuO and YBaCuMnO samples, we give a tentative explanation of the luminescence of Cu^+ and Cu^{2+} centers on different sites, i.e. the sites on the Cu–O planes and the sites on the Cu–O chains. The luminescence of Mn^{2+} and Mn^{4+} in the YBaCuMnO samples has also been observed for the first time; and the intensity of the 618.8 nm band from Mn^{2+} centers on the Cu–O planes decreases sharply when the sample become superconducting around 90 K, which can be interpreted by the difference in the structure between the superconducting state and the normal state. An ESR study shows a contrary behaviour in one of our YBaCuMnO samples to the generally obtained results, which may have something to do with the superconductivity.

1. Introduction

Emission studies of high T_c superconductors have been carried out since they were discovered in 1986, although experiments are difficult because of their strong self-absorption. As a means of studying the structural characteristics of the superconductors, the emission has proved to be effective by many authors [1,2]. In this paper, we concentrate on emissions of Cu ions of $YBa_2Cu_3O_{7-x}$ and Mn ions which partly substitute Cu ions.

In the distorted perovskite-type superconductor $YBa_2Cu_3O_{7-x}$ there exist two kinds of Cu ions, that is the Cu ions on the Cu–O chains and the Cu ions on the Cu–O planes. It is well known that the order–disorder transition on the Cu–O chains at high temperature coincides with the transition of $YBa_2Cu_3O_{7-x}$ from superconducting to non-superconducting. So the chains may be significant in the superconducting mechanism. But in other high T_c superconductors such as Bi-SrCaCuO and TlBaCaCuO,we can find only Cu–O planes and no Cu–O chains, which implies that the Cu–O planes might play a more important role for superconductivity. Up to now, nothing can be made clear for want of the experimental evidence, and for the first time we have studied Cu and Mn emissions on both the chains and the planes above and below T_c (90 K).

The ESR study on high T_c superconductors has also evoked the interest of many authors [3]. They obtained the ESR signal of Cu^{2+} and calculated the g values. The results are almost identical. But one of our samples ($YBa_2(Cu_{0.95}Mn_{0.05})_3O_{7-x}$) shows a sharply different characteristic in its ESR signal. We believe it must be related to its superconducting nature.

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2. Experimental

The $YBa_2Cu_3O_{7-x}$ and the $YBa_2(Cu_{0.95}Mn_{0.05})_3O_{7-x}$ superconducting samples were prepared by the solid state reaction of Y_2O_3, $BaCO_3$, CuO, and $MnCO_3$ powders. They were mixed in the nominal proportion, ground and initially calcined at 920 °C for 8 h. Then after cooling they were reground and cold-pressed into cylindrical pellets. The pellets were sintered again at 960 °C for 10 h and the sintering was followed by slow furnace cooling to room temperature. The X-ray diffraction shows that $YBa_2Cu_3O_{7-x}$ is of a distorted, oxygen-deficient perovskite structure and its T_c is about 90 K and it retains its high temperature superconductivity when Cu is replaced by Mn by a small amount.

When taking the emission measurements, we used the 488 nm laser line of an Ar laser or the 308 nm line of an excimer laser as the excitation source, respectively. The pellets were mounted on the cold finger of a closed cycle He refrigerator capable of maintaining the temperature of approximately 10 K. The emission spectra measured at 10 K through 300 K were recorded with a T-800 spectrometer for the 488 nm excitation and with GDM-1000 spectrometer for the 308 nm excitation.

3. Results and discussions

Fig. 1 shows the emission spectrum of a $YBa_2Cu_3O_{7-x}$ sample with 308 nm excitation. We can see 4 bands peaking at about 408 nm, 445 nm, 525 nm and 565 nm after deconvolution with a micro-processor. The emission spectrum of the same sample under 488 nm excitation is shown in fig. 2. It consists of 3 bands peaking at 523 nm, 528.8 nm and 568.4 nm approxi-

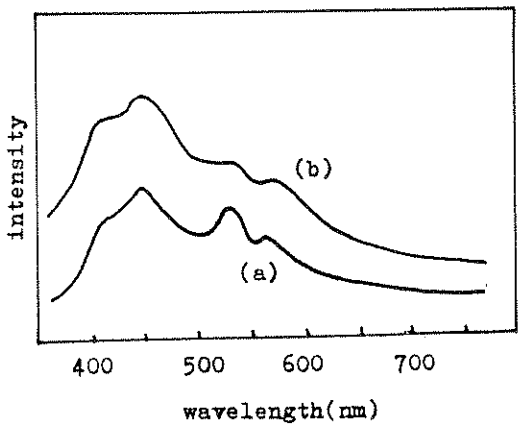

Fig. 1. Emission spectra of $YBa_2Cu_3O_{7-x}$ at (a) 10 K and at (b) 295 K. Excitation 308 nm.

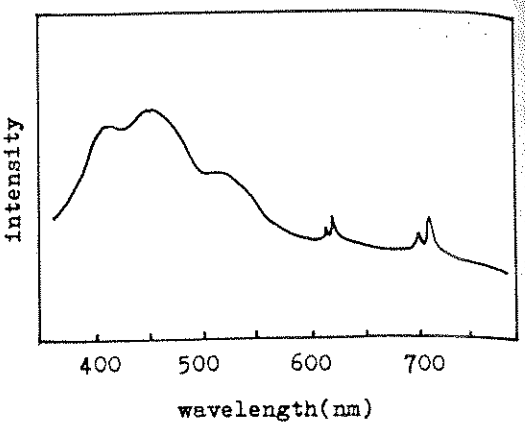

Fig. 3. Emission spectrum of $YBa_2(Cu_{0.95}Mn_{0.05})_3O_{7-x}$ at 295 K. Excitation 308 nm.

mately. The 565 nm band under 308 nm excitation obviously corresponds to the 568.4 nm band under 488 nm excitation. And the 525 nm band in fig. 1 is likely to be the superimposition of the 523 nm and the 528.8 nm bands in fig. 2. This has been proved by the time-resolved spectra in which, when the delay time is up to 1 ms, the 525 nm band excited by the 308 nm laser line can be apparently deconvoluted into 2 bands, i.e. the 523 nm and the 528.8 nm bands. Therefore we have 5 bands totally belonging to the emissions of Cu^+ and Cu^{2+} ions. Having considered the energy levels of Cu ions in the crystal field and compared the emissions with the emissions of Cu_2O and CuO [4], we conclude tentatively that the 408 nm, 445 nm and 568.4 nm bands come from the transitions from the excited states ^3E, $^2B_2$, ^1E and $^1B_2$ to the ground state $^1A_1$ of Cu^+ ions, while the 523 nm and 528.8 nm bands come from the ^2E, ^2B states to the $^2A_1$ state transitions of Cu^{2+} ions.

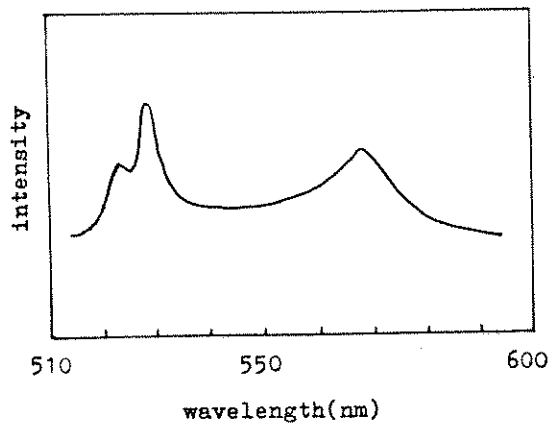

Fig. 2. Emission spectrum of $YBa_2Cu_3O_{7-x}$ at 295 K. Excitation 488 nm.

The 568.4 nm band was also found in BiSrCaCuO superconductors which only have Cu–O planes and no Cu–O chains [5]. Therefore we can make sure that the 568.4 nm band results from the Cu^+ ions on the Cu–O planes.

Measurements of emission spectra at 10 K through 300 K have been undertaken. The 408 nm, 445 nm and 568.4 nm bands of Cu^+ become intense compared to the 523 nm and 528.8 nm bands of Cu^{2+} when the temperature rises, and no characteristic change can be seen around 90 K.

Fig. 3 gives the emission spectrum of the $YBa_2(Cu_{0.95}Mn_{0.05})_3O_{7-x}$ sample at room temperature under 308 nm excitation. Besides the Cu bands, 4 Mn emission bands appear. Among the 5 Cu bands, the 568.4 nm band is greatly reduced compared with that of pure $YBa_2Cu_3O_{7-x}$ shown in fig. 1. This fact is clearer at lower temperature. As we pointed out previously, the 568.4 nm band is due to the transition of Cu^+ ions on the Cu–O planes. We can conclude that it is Mn ions that cause the reduction of the Cu emission on the Cu–O planes, hence the Mn ions mainly replace the Cu ions on the Cu–O planes.

The 697.8 nm and 703 nm bands are the double red lines of Mn^{4+} similar to those of the ^2E to $^4A_2$ transitions of Cr^{3+} in ruby. The 615.7 nm and 618.8 nm bands result from the transitions of $^4T_1$ to $^6A_1$ of Mn^{2+} ions on 2 different sites, i.e. on the Cu–O planes and on the Cu–O chains. The weak 615.7 nm band comes from the transitions of the small amount of Mn ions on the Cu–O chains while the strong 618.8 nm band arises from the transitions of Mn ions on the Cu–O planes.

Fig. 4 gives the integrated intensities of the 615.7 nm and the 618.8 nm bands as a function of the temperature. The intensity of the 615.7 nm band is approxtmately linearly dependent on the temperature. But it is interesting to see that for the 618.8 nm band, the

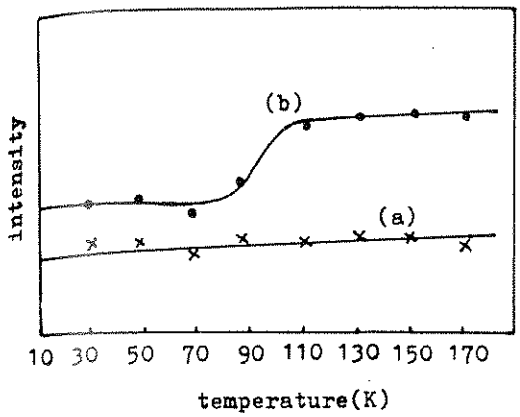

Fig. 4. Temperature dependence of Mn^{2+} bands. (a) 615.7 nm; (b) 618.8 nm.

emission band of Mn^{2+} ions on the Cu–O planes greatly weakens when the sample becomes superconducting at 90 K.

The transition from the ^4G state to the $^6A_1$ state of Mn^{2+} ions is forbidden. It is partly relaxed when in a crystal field with no symmetrical centre. The degree of its relaxation is mainly determined by the interaction of the Mn ions with the crystal field. The reduction of the 618.8 nm band accompanied by the superconducting transition gives us an idea that when the temperature drops to 90 K and lower, some changes of the crystal field around the Mn^{2+} ions on the Cu–O planes take place and the sample becomes superconducting, and at the same time the Mn^{2+} emission undergoes a significant change. Therefore we can imagine that it is likely that the Cu–O planes play a more important part in the superconducting mechanism than the Cu–O chains.

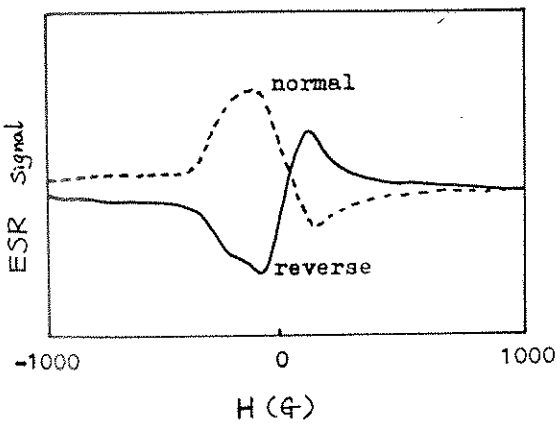

Fig. 5. The normal and the reverse ESR spectra of $YBa_2(Cu_{0.95}Mn_{0.05})_3O_{7-x}$ samples. Field set 3200 G; scan range 2000 G.

Another interesting result we obtained in ESR study of high T_c superconductors is that the ESR signal of one of our $YBa_2(Cu_{0.95}Mn_{0.05})_3O_{7-x}$ samples is entirely the reverse of that of other samples and that of other authors' work, as shown in fig. 5. This experiment was repeated several times and the results were all the same. The X-ray diffraction of this sample shows no difference from those of other samples. So far we have no idea about why and how the result arises but we believe it must be related to the superconductivity and further studies should be pursued.

4. Conclusion

We have studied the laser induced Cu and Mn luminescence of $YBa_2Cu_3O_{7-x}$ and $YBa_2(Cu_{0.95}Mn_{0.05})_3O_{7-x}$ and confirmed the emission bands of transitions from different levels of Cu^+, Cu^{2+}, Mn^{2+} and Mn^{4+} on the Cu–O chains or on the Cu–O planes. The temperature dependence of the emission intensity of Mn^{2+} bands shows the different activities between the Mn^{2+} ions on the Cu–O chains and those on the Cu–O planes. The 618.8 nm band, the emission band of Mn^{2+} ions on the Cu–O planes reduces sharply when temperature is dropped to 90 K, which may be the evidence that Cu–O planes play a significant role in the superconducting mechanism.

The ESR study shows a reverse result to the normal signal in one of our superconducting samples. The relations between this result and the superconductivity are under further consideration.

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