

EPR Spectrum of the High-Temperature Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Doped with Ytterbium

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EPR spectra of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ doped with ytterbium have been measured at 77-300K. The superconducting, orthorhombic phase shows a spectrum at $g = 2.08$ (Spectrum O). As the temperature is lowered, another line ascribable to Yb^{3+} grows gradually at $g = 3.31$. The intensity of Spectrum O was determined using Yb as the internal reference. The semiconducting, tetragonal phase shows a spectrum at $g = 2.06$ (Spectrum T), different from Spectrum O. The origins of these spectra are discussed.

Introduction

Various experimental techniques have been used to study the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) first prepared by Chu *et al.*¹ One of them is electron paramagnetic resonance (EPR). Since EPR can give information on the unpaired electrons in the system, it might be useful in clarifying the nature of the superconducting mechanism.

Several EPR spectra attributed to the Cu^{2+} ions of YBCO have been reported.²⁻⁵ But these spectra are generally very weak, and it has been suggested that they may be due to spurious phases present in the samples.⁶⁻⁹ BaCuO_2 and $\text{Y}_2\text{-BaCuO}_5$ (the green phase) may be the impurities responsible for the spectrum.⁸

$\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$, another high-temperature superconductor, contains a second EPR-active ion $\text{Gd}^{3+}(4f^7)$, and the EPR spectra of $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ and Gd-doped YBCO have been studied.^{6,9,10} But the three-line, polycrystalline spectrum of Gd-doped YBCO is difficult to interpret, for the fine-structure energy levels of the $S = 7/2$ system are very complicated.

We have been studying EPR spectra of YBCO, Gd-doped YBCO, and Yb-doped YBCO, and also the spectra of the semiconducting, tetragonal phases of these compounds. The dopant Gd^{3+} or $\text{Yb}^{3+}(4f^{13})$ may serve as an electron spin probe for the superconducting electrons, if there is any interaction between them. Yb^{3+} seems more useful than Gd^{3+} , for the former gives a simpler spectrum, which overlaps less with the spectrum at $g = 2.0$. Since the orthorhombic phase of YBCO is prepared from the tetragonal phase by annealing under oxygen, the tetragonal phase can exist as an impurity in the YBCO sample. So we have also studied the EPR spectrum of the tetragonal phase. This paper reports the EPR spectra of the orthorhombic and tetragonal phases of Yb-doped YBCO.

Experimental

Preparation of Compounds. The compounds were prepared using the standard solid state reaction. Fine powders of Y_2O_3 , Yb_2O_3 , BaCO_3 , and CuO were mixed according to the formula $(\text{Y}_{0.99}\text{Yb}_{0.01})\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$. The mixture was calcined at 930 °C for 12 hours, and then was pressed into pellets of 10 mm in diameter. Three different samples were prepared from these pellets.

Some pellets were sintered under flowing oxygen at

930 °C for 12 hours. Then the pellets were annealed under flowing oxygen at 500 °C for 5 hours, and cooled slowly to room temperature. The product (Sample O) showed superconductivity with onset T_c at 90K and zero resistance at 84K. The powder X-ray diffraction pattern agreed with that of the orthorhombic YBCO.^{12,13}

Some pellets were sintered in the air at 930 °C for 12 hours, and then quenched by dropping into liquid nitrogen. The electrical resistance of the product (Sample T) showed temperature dependence characteristic of a semiconductor. The powder X-ray diffraction pattern agreed with that of the tetragonal YBCO.¹³

Some pellets were sintered in the air at 930 °C for 12 hours, cooled to 500 °C, and then quenched by dropping into liquid nitrogen. The product (Sample M) showed superconductivity with onset T_c at 89K and zero resistance at 63K. The powder X-ray diffraction pattern was close to that of the orthorhombic YBCO.^{12,13}

Measurements. DC electrical resistance was measured using the standard four-probe method. The measurements were made by reading the voltage drop across the inner leads of the sample while maintaining a constant sample current of less than 1.0mA. Samples were attached to the cold finger of a closed cycle refrigerator (Palm Beach Cryophysics Model 4075) and the electrical resistance was measured as a function of temperature.

X-ray diffraction patterns were taken with a powder diffractometer using Cu-K radiation.

EPR spectra at 95-300 K were recorded on a Bruker EPR spectrometer (Model ER 200E) equipped with a variable temperature accessory. The spectrum at 77K was recorded using a liquid nitrogen dewar.

Results and Discussion

Orthorhombic Phase. The EPR spectra of the orthorhombic, Yb-doped YBCO at several temperatures are shown in Figure 1. The spectrum consists of two distinct components, one at $g = 2.08$ and the other at $g = 3.31$. At room temperature only the component at $g = 2.08$ (Spectrum O) is observed. As the temperature is lowered, the component at $g = 3.31$ (Spectrum Y) grows gradually.

Spectrum Y can be ascribed to Yb^{3+} in the near cubic environment. The EPR spectrum of Yb^{3+} doped into CaF_2 or CdF_2 ^{14,15} could be interpreted according to the cubic spin Hamiltonian:

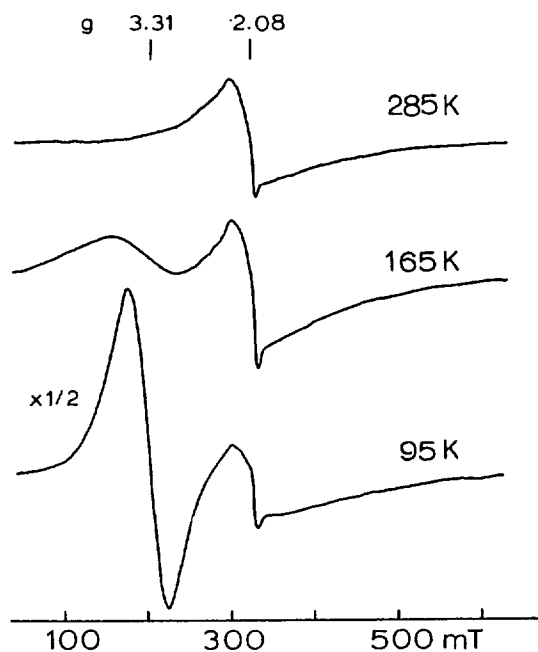


Figure 1. EPR spectra of orthorhombic $(\text{Yb}_{0.01}\text{Y}_{0.99})\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$. The base line has been corrected.

$$H = g\beta \mathbf{B} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S} \text{ with } S = 1/2.$$

There are two isotopes of ytterbium with nonzero nuclear spin, namely ^{171}Yb (14.3%, $I = 1/2$) and ^{173}Yb (16.1%, $I = 5/2$). The parameters determined for two different host crystals are essentially the same; the data for the Yb/CdF_2 are $g = 3.436$, $A_{171} = 0.0883 \text{ cm}^{-1}$, $A_{173} = 0.0242 \text{ cm}^{-1}$. Since the g value of Spectrum Y is close to that of Yb/CdF_2 , this spectrum should be interpreted not as the perpendicular component of an anisotropic spectrum, but as an isotropic one.

Since $\text{YbBa}_2\text{Cu}_3\text{O}_{7-x}$ and YBCO are isomorphous, it is certain that Yb^{3+} replaces Y^{3+} in YBCO. Although the structure of YBCO is orthorhombic, the environment of Y^{3+} is close to cubic,¹² and an isotropic EPR spectrum is not unreasonable for such a site.

It is seen that Spectrum Y and Spectrum O overlap in the 95K spectrum. If the two components can be separated, the doped ytterbium may be used as an internal standard for measuring the absolute intensity of Spectrum O. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ has been used as an external reference to measure the EPR intensity of YBCO. But an external reference cannot be used when the grain size of the sample is larger than the skin depth, which is $\sim 10 \mu\text{m}$ for YBCO above T_c .¹⁷ This problem can be avoided by using an internal reference such as Yb^{3+} .

In order to separate the two components, we have transformed the first-derivative spectrum into an absorption spectrum; see Figure 2. On the basis of the absorption spectrum at 285K, Spectrum O was assumed to be symmetric, and it was subtracted from the total spectrum. The resulting Spectrum Y is quite isotropic as shown in Figure 2. This analysis gives an intensity ratio of 2:1 for Spectrum O and Spectrum Y.

As was mentioned before, several isotopes of ytterbium contribute to Spectrum Y. A more accurate analysis would be possible, if the EPR spectrum of YBCO doped with one pure isotope of Yb is measured.

Spectrum O consists of a broad line and a weak, sharp

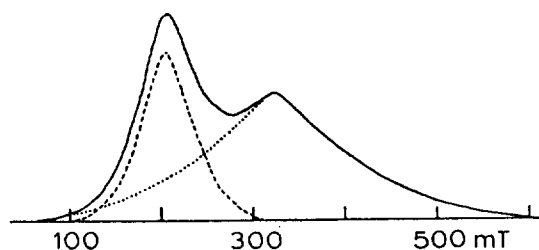


Figure 2. Analysis of the absorption EPR spectrum of orthorhombic $(\text{Yb}_{0.01}\text{Y}_{0.99})\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ at 95K into two components.

line. The sharp line, being very weak, appears only in the first derivative spectrum, whereas it is buried in the broad line in the absorption spectrum. Spectrum O is similar to that observed for undoped YBCO by Shaltiel *et al.*⁷ A broad line was also observed by Aguilar *et al.* as the background of an EPR spectrum for their YBCO sample.¹⁸ However, several authors reported EPR spectra of the orthorhombic YBCO, quite different from Spectrum O. It is noted that some of these spectra are rather similar to that of the green phase (see below).

Spectrum O is very weak; it is only twice as strong as Spectrum Y coming from the dopant, Yb^{3+} . Since the mole ratio of Yb and Cu in the sample is 1:300, the intensity of Spectrum O corresponds to 0.007 spins per copper atom in the sample.

Spectrum O can arise either from localized electrons in the vicinity of defects or from the conduction electrons. The temperature dependence of the spectral intensity can be used to distinguish between these two sources. The spectrum coming from localized electrons would be described by the Curie-Weiss law,¹⁹ whereas the intensity of the spectrum originating in conduction electrons should be temperature-independent.²

The spectra at several temperatures were analyzed as described above, and the integrated intensity of Spectrum O was measured for each spectrum. The result shows that the temperature dependence of the intensity is certainly closer to the Curie-Weiss behavior. Thus Spectrum O must originate in electrons localized at such ions as Cu^{2+} and O^- .

The question arises whether Spectrum O is intrinsic to the orthorhombic phase or due to an impurity. Recently it has been reported that samples of orthorhombic YBCO prepared from a citrate precursor do not exhibit an EPR signal.²⁰ If this report is confirmed, then Spectrum O must be ascribed to an impurity. It is certain that the source is not the green phase, a common impurity found in YBCO, for its spectrum is quite different.²¹ Aguilar *et al.*, noting that a broad line in the background of their spectrum could be observed only for samples with sufficient oxygen treatment, suggested that this broad line may be related with holes in the oxygen sites.¹⁸ This matter needs further investigation.

Below T_c a strong signal appears with a maximum near 0 mT and a long tail. This peak has been attributed to an intergrain Josephson junction effect.^{4,8} The high intensity of this signal has prevented us from measuring a good spectrum for the weak signals at 77K. But a spectrum showing weak signals could be observed at 77K for a sample containing both orthorhombic and tetragonal phases of YBCO (see below). It has been reported that both the spectrum at $g = 2.0$ for the undoped YBCO and the spectrum of Gd^{3+} for the Gd-doped

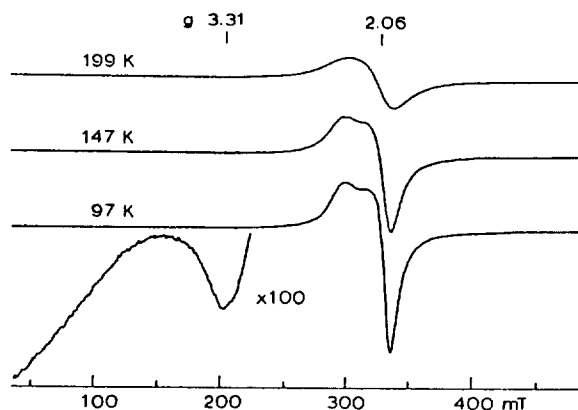


Figure 3. EPR spectra of tetragonal $(Yb_{0.01}Y_{0.99})Ba_2Cu_3O_{7-x}$.

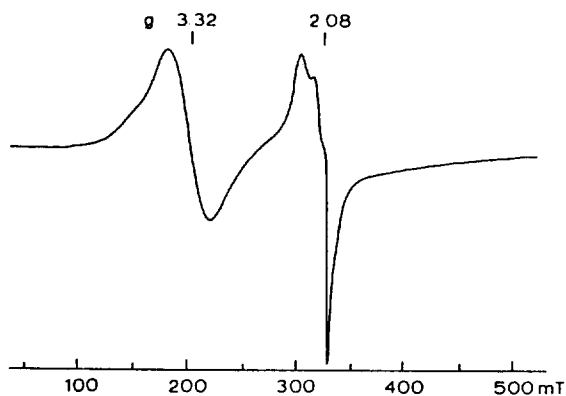


Figure 4. EPR spectrum of Sample M at 96 K.

YBCO weaken below T_c and disappear around 60 K.⁷

Tetragonal Phase. The EPR spectra of the tetragonal, Yb-doped YBCO at several temperatures are shown in Figure 3. Here the spectrum at $g = 2.06$ (Spectrum T)¹⁶ dominates over the spectrum of Yb^{3+} , as can be seen from the 97 K spectrum at two different signal levels. Spectrum T is a two-line spectrum at low temperatures, but it becomes rounded as the temperature increases. The absolute intensity of Spectrum T, measured using $CuSO_4 \cdot 5H_2O$ as the external reference, accounts for 2% of the total copper atoms in the sample. And the temperature dependence of the spectral intensity showed the Curie-Weiss behavior.

It has been reported that the tetragonal $YBa_2Cu_3O_6$ is EPR-inactive, while the tetragonal $YBa_2Cu_3O_{6.15}$ is EPR-active.²⁰ The EPR spectrum of the latter has been measured at 300-500 K. Its spectral shape is quite similar to the low-temperature form of Spectrum T, but the temperature dependence of its intensity shows a maximum at 460 K, indicating an antiferromagnetic transition. Therefore, this spectrum, the intensity of which decreases as the temperature is lowered below 460 K, cannot be identified with Spectrum T showing the Curie-Weiss behavior.

The low-temperature form of Spectrum T is also similar to that²¹ of Y_2BaCuO_5 (the green phase). But the green phase shows a two-line spectrum even at room temperature, indicating that Spectrum T does not originate in green phase impurity. Moreover, the intensity of Spectrum T was found to depend upon the amount of the tetragonal phase present in the sample. Sample M was prepared by cooling the sintered pellets to 500 °C in the furnace before quenching so that the

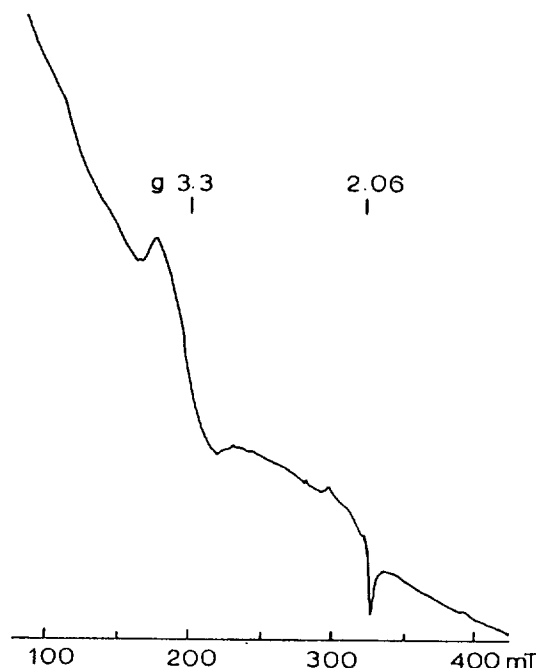


Figure 5. EPR spectrum of Sample M at 77 K.

tetragonal-to-orthorhombic phase transformation could occur partially. The broad range of its transition temperature, $\Delta T_c = 26$ K, indicates that the phase transformation is not complete. But the powder X-ray diffraction pattern shows that the orthorhombic phase is prevalent in this sample. Certainly some tetragonal phase remains unchanged in Sample M, and this phase is expected to contribute to the line at $g = 2.08$; see Figure 4. It is seen that this line is much weaker than Spectrum T, when compared using the same internal reference. This is exactly what is expected if Spectrum T is intrinsic to the tetragonal phase and thus its intensity is proportional to the amount of the tetragonal phase present in the sample. If the green phase or any other impurity, which cannot change into an EPR-inactive form during the cooling process, were responsible for Spectrum T, its intensity should be the same for Sample T and Sample M. These results lead us to believe that Spectrum T arises from the Cu^{2+} ions in the tetragonal phase, which are in an environment similar to that in the green phase. But the relation of Spectrum T with the spectrum²⁰ reported for $YBa_2Cu_3O_{6.15}$ needs clarification.

It is noted that some spectra^{2,8} reported for the orthorhombic phase of YBCO are similar to the low-temperature form of Spectrum T (or that of the green phase). Since Spectrum T accounts for only 2% of the total copper atoms in the tetragonal sample of YBCO, an impurity amount of this phase would not give an observable EPR signal. On the other hand, the green phase present as an impurity in the sample can give rise to such a spectrum, for all copper atoms in the green phase contribute to the EPR spectrum.^{21,22}

Three-line spectra^{3,5} have also been reported for the orthorhombic phase of YBCO. Sample M containing both orthorhombic and tetragonal phases show such a spectrum; see Figure 4. Here the three-line spectrum arises from overlapping of Spectrum T and Spectrum O. But a similar spectrum is expected when Spectrum O and the spectrum of green phase impurity overlap; this is the most likely explanation for the three-line spectra reported for the orthorhombic samples of

YBCO.

Sample M at 77K also exhibits a signal near 0 mT characteristic of the superconducting state; see Figure 5. Since the intensity of this signal starts to increase at onset T_c and reaches a plateau at offset T_c^8 , its intensity for Sample M is much weaker than that of Sample O at 77K. The low intensity of this line allowed us to observe weak signals at $g = 3.3$ and $g = 2.06$ at 77K.

In summary, we have observed three different spectra in the orthorhombic and tetragonal phases of Yb-doped YBCO. Spectrum Y can be ascribed to Yb^{3+} . The sources of Spectrum O and Spectrum T are less clear. Most spectra reported for the orthorhombic YBCO can be explained in terms of Spectrum O and the spectrum of green phase impurity.

Acknowledgement. The support of this research by the Korea Science Foundation is gratefully acknowledged. We are indebted to Prof. Gwangseo Park and Mr. Kiejn Lee of Physics Department for measurements of electrical resistivity, and to Mr. Dohyung Seung of Samsung Research Center for measurements of X-ray powder diffraction patterns.

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