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EPR SPECTRA OF Mn ION WITH TWO PHASES IN THE Y-Ba-Cu-Mn-O HIGH T_C SUPERCONDUCTOR

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Abstract-In this paper, Mn^{2+} ion was doped in Y-Ba-Cu-O as an EPR probe. The following samples were prepared by conventional solid-state reaction method : $YBa_2Cu_{2.96}Mn_{0.04}O_{7-\delta}$ (MN-I), annealed $YBa_2Cu_{2.96}Mn_{0.04}O_{7-\delta}$ (AMN) and $YBa_2Cu_{2.94}Mn_{0.06}O_{7-\delta}$ (MN-II). AMN sample was obtained from MN-I by annealing for 1 hr under the Ar gas atmosphere at 600℃. X-band (~9.05 GHz) EPR spectra were measured from 103 K to room temperature by employing a JES-RE3X spectroscopy with a TE_{011} cylindrical cavity and 100 kHz modulation frequency.

In MN-I we have observed only the Cu^{2+} signal. The fact that no Mn^{2+} signal was observed, in spite of Mn^{2+} being a very sensitive EPR probe, indicates that most likely isolated Mn^{2+} ions don't exist in the MN-I sample. Most probably Mn^{2+} ions in the MN-I sample interact antiferromagnetically and hence are EPR silent. The AMN spectra of at room temperature and 103 K indicate not only the Cu^{2+} signal but also an extra signal, which increases with decreasing temperature. It is suggested that the extra signal originates from Mn ions that were antiferromagnetically coupled before the annealing process. In MN-II, from 103 K to room temperature, also, the extra signal was observed together with the Cu^{2+} signal. The extra signal in MN-II, however, decreases with decreasing temperature and nearly disappears at 103 K. The signal originates from Mn ions in impurity phases that include Mn^{2+} ions. We suppose that there exist at least two Mn^{2+} doped phases in Y-Ba-Cu-O. The Mn^{2+} signal of one phase is undectable at all temperature and that of another phase decreases with decreasing temperature and disappears around 103 K.

I. INTRODUCTION

The effect of doping on the structural and physical properties of transition metal ($3d^N$) doped Y-Ba-Cu-O were reported by several groups [1]. In Y-Ba-Cu-O the doping of $3d^N$ ions drastically reduces T_c. The $3d^N$ ions destroy the orthorhombic chain ordering in Y-Ba-Cu-O structure, which may be the reason of the reduction of T_c.

There are many observations of electron paramagnetic resonance (EPR) in Y-Ba-Cu-O in the absence of any specially introduced magnetic probe in the sample [2]. Experimental studies have shown that Cu is bivalent (Cu^{2+}, $3d^9$) in high-T_c superconductor (HTSC) materials, including the Y systems in particular . However, in the "extreme type" system $YBa_2Cu_3O_7$, the EPR spectrum is not observed at all. Some researchers reported that this effect is mostly due to the d states of Cu, which form an energy band that broadens the spectral lines and makes EPR undectable [3]. EPR can be observed, however, if the number of oxygen atoms in the immediate vicinity of the copper ion in the Y-Ba-Cu-O lattice changes,

because the energy level of the corresponding Cu^{2+} is "pushed " out of the band. This situation can occur in the case of oxygen deficiency in the lattice [4] or its excess [5], when Ba is partially replaced by La.

In this paper, Cu is partially replaced by Mn. Mn^{2+} ion was used in Y-Ba-Cu-O as an EPR probe. We prepared samples of the form Y-Ba-Cu-Mn-O because the ionic size and orbital structure of the Mn is close to those of Cu. Hence it could be expected that the Mn ions occupy the Cu sites if substituted in the Y-Ba-Cu-O. A. Moto et al. [6] and G. Kallias et al. [7] reported that Mn ions preferentially occupy the site of Cu in the CuO_2 plane. However, the neutron diffraction study [8] and the extended x-ray absortion fine-structure study [9] indicate that Mn perfers the site of Cu in the CuO chain.

II. EXPERIMENTAL

The following samples were prepared : $YBa_2Cu_3O_{7-\delta}$ (Y-Ba-Cu-O), $YBa_2Cu_{2.96}Mn_{0.04}O_{7-\delta}$ (MN-I), annealed $YBa_2Cu_{2.96}Mn_{0.04}O_{7-\delta}$ (AMN) and $YBa_2Cu_{2.94}Mn_{0.06}O_{7-\delta}$ (MN-II). The samples were prepared by conventional solid-state reaction method. Powders of Y_2O_3, $BaCO_3$, CuO and MnO were mixed and ground in jade bowl. The ground powders were calcinated at 910℃ for 10 hrs in an oxygen atmosphere. Reground samples were pressed into pellets and sintered at 930℃ in the same atmosphere, in order to optimize the oxygen content of the samples, and then slowly cooled in the furnace. AMN sample was obtained from MN-I by annealing for 1 hr under the Ar gas atmosphere at 600℃.

X-band (~9.05 GHz) EPR spectra were measured from 103 K to room temperature by employing a JES-RE3X spectroscopy with a TE_{011} cylindrical cavity and 100 kHz modulation frequency. The powdered samples used for EPR measurments were put through a sieve (47×47 μm^2).

III. RESULTS AND DISCUSSION

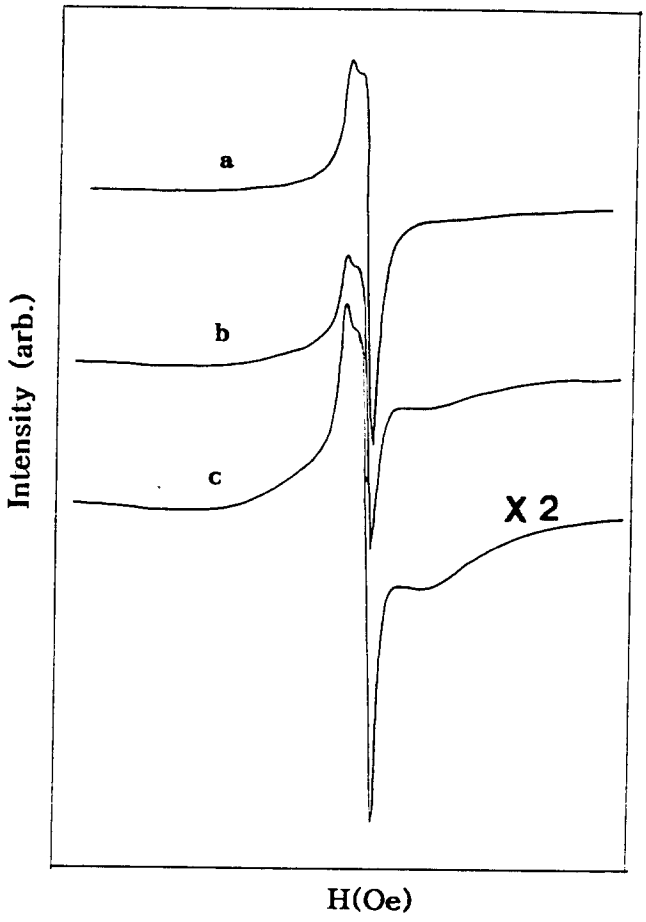

Fig. 1 The EPR spectra of the MN-II sample at a) 103 K, b) 203 K and c) room temperature.

In Y-Ba-Cu-O we have obtained the Cu^{2+} EPR signal, which exhibits tetragonal symmetry. The electronic Zeeman parameters are $g_{\parallel}$=2.231, $g_{\perp}$=2.051, whereas the linewidth is $\Delta H \approx 250$ Oe. No resolved hyperfine structure due to Cu^{2+}(I=2/3) could be observed in all spectra. The

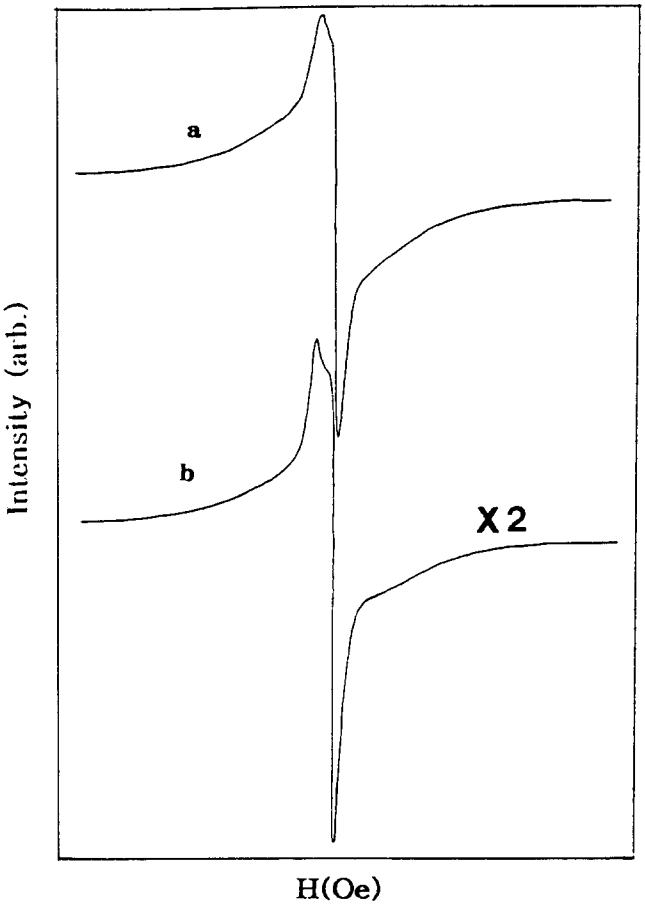

Fig. 2 The EPR spectra of the AMN sample at a) 103 K and b) room temperature.

fact indicates that the Cu^{2+} derived paramagnetic species do not exist as isolated states in the sample, and an unpaired electron is delocalized around the vicinity of the defects. The signal shape is same Fig.1a) and independent of temperature. All the samples used in this paper exhibit a single phase when using the x-ray diffractometer. Although within the accuracy of the x-ray experements no impurity phases are detected, the small amount of impurity phases is enough to be seen in the EPR spectra. Therefore, we suppose that the Cu^{2+} signal comes from the impurity phase. Actually, many other researchers have made similar suggestions.

In MN-I we have only observed the Cu^{2+} signal. The signal shape is the same as in Fig.1a) and independent of temperature. The fact that no Mn^{2+} signal was observed, in spite of Mn^{2+} being a very sensitive EPR probe, indicates that most likely isolated Mn^{2+} ions don't exist in the MN-I sample. Most probably Mn^{2+} ions in the MN-I sample interact antiferromagnetically and hence are EPR silent.

Figure 1 shows the EPR signals of MN-II from 103 K, 203 K and room temperature. In this sample, also, an extra signal was observed together with the Cu^{2+} signal. The extra signal in MN-II, however, decreases with decreasing temperature and nearly disappears at 103 K. The signal originates from Mn ions in impurity phases that includes Mn^{2+} ions. This agrees with the result of Y. Yamada et al. [10].

Figure 2 shows the EPR spectra of the AMN at room temperature and at 103 K. The spectrum of AMN indicates not only the Cu^{2+} signal but also an extra signal (i.e. a broad line with Lorentzian shape), which increases with decreasing temperature. It is suggested that the extra signal originates from Mn ions that were antiferromagnetically coupled before the annealing process.

IV. CONCLUSION

The observed EPR spectra indicate that Mn^{2+} ions in the MN-I sample interact antiferromagnetically and hence are EPR silent. After annealing, however, Mn^{2+} signal with Lorentzian shape, which increases with decreasing temperature is observed in the AMN sample. Unfortunately, it is difficult to decide whether Mn^{2+} ions are doped in the superconducting phase or some impurity phases in MN-I.

Mn^{2+} signal with Lorentzian shape, which

is decreases with decreasing temperature is observed in the MN-II sample. It originates from Mn ions in some impurity phases that include Mn^{2+} ions.

The results suggest that Mn^{2+} ions can be doped into two phases in Y-Ba-Cu-O : one phase which includes Mn^{2+} ions interacting antiferromagnetically and the other phase which includes paramagnetic, Mn^{2+} ions.

REFERENCES

[1] E. V. Vladimirskaya and V. E. Gasumyants, Phys. Solid State **36**, 54 (1994).
[2] N. Guskos, V. Likodimos, J. Kuriata, H. Metz, W. Windsch, M. Wabia, C. Mitros and D. Niarchos, Phys. Stat. Sol. (b) **181**, K69 (1994).
[3] V. F. Masterov, V. V. Isaev-Ivanov and I. B. Patrina, Supercond. Sci. Technol. **7**, 17 (1994)
[4] S. K. Misra and L. E. Misiak, Solid State Commun. **72**, 351 (1988).
[5] N. P. Baranskaya, V. S. Grunin, I. B. Patrina and M. V. Razumeenko, Sverkhprovodn., Fiz. Khim. Tekh. **13**, 2815 (1990).
[6] A. Moto, A. Morimoto, M. Kumeda and T. Shimizu, Supercond. Sci. Technol. **3**, 579 (1990) ; in Russian.
[7] G. Kallias and D. Niarchos, Supercond. Sci. Technol. **5**, 56 (1992)
[8] N. L. Saini, K. B. Garg, H. Rajagopal and A. Sequeira, Solid State Commun. **82(11)**, 895 (1992)
[9] B. D. Padalia, S. J. Gurman, P. K. Mehta and Om Prakash, J. Phys. Condens. Matter **4**, 6865 (1992)
[10] Y. Yamada, K. Sugawara and Y. Shiohara, Adv. in Superconductivity II, 547 (1990).

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