

TEMPERATURE DEPENDENCE OF THE EPR SPECTRA OF $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ IN ORTHORHOMBIC AND TETRAGONAL PHASES

N. GUSKOS, M. CALAMIOTOU, C. A. LONDOS and V. LIKODIMOS

Solid State Section, Department of Physics, University of Athens, Solonos Str. 104, G-10680 Athens, Greece

and

A. KOUFOUDAKIS, C. MITROS, H. GAMARI-SEALE and D. NIARCHOS

Institute of Material Science, N.C.S.R. "Democritos", Aghia Paraskevi, G-15310 Athens, Greece

(Received 12 December 1990; accepted 27 March 1991)

Abstract—EPR spectra between 9.7 K and room temperature (RT) were taken for $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in tetragonal and orthorhombic phases. Our results indicate significant differences between the EPR spectra of Cu^{2+} ions in the tetragonal and orthorhombic phase. It is concluded that in the tetragonal phase, the Cu^{2+} complex has axial symmetry. Furthermore, at low temperatures the observed EPR signal is associated with superexchange interaction between Eu^{2+} ions across oxygen bridges.

Keywords: Superconductors, EPR, XRD, magnetic measurements, $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$, exchange interactions.

1. INTRODUCTION

Recently, the high- T_c superconductors $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been extensively investigated using different experimental methods [1–6]. It has been shown that the europium ions could be placed in two different positions in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ type compounds (displacing substitutionally Y or Ba ions), a fact which may influence the physical properties of these materials.

In this paper we report the results of XRD, magnetic and EPR measurements of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the temperature range from 4.2 K up to RT, both for the tetragonal (non-HTC, with large oxygen deficiency) and the orthorhombic (HTC) phases. In the tetragonal phase we observed an EPR spectrum arising from Cu^{2+} ions in axial local symmetry. Some features in the EPR spectrum at low temperature have been interpreted as a manifestation of a superexchange interaction between Eu^{2+} ions across oxygen bridges.

2. EXPERIMENTAL RESULTS AND DISCUSSION

The polycrystalline sample was prepared by the solid state reaction method by mixing appropriate compositions of Eu_2O_3 , BaO_2 and CuO at 900–950°C. The calcined powder was then pressed into pellets and repeatedly heated between 850 and 920°C for 12–100 h. The samples were then slowly cooled down to RT at a rate of 100°C h⁻¹. After this process the reaction between the above materials was complete.

The structure characterization of the samples was done using a Philips X-ray powder diffractometer with Co-K α radiation. The so-obtained orthorhombic structure of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ had the following lattice parameters: $a = 3.8431(3)$ Å, $b = 3.8948(3)$ Å and $c = 11.6943(9)$ Å. These prepared samples were annealed at 900°C for 24 h in an oxygen atmosphere at a pressure of about 5 mm Hg and then quenched to RT. The final product of this procedure was samples of tetragonal structure (lattice constants: $a = b = 3.8826(3)$ Å and $c = 11.8048(9)$ Å).

Magnetic susceptibility measurements in the temperature range from 4.2 K to RT were performed with a PARI55 vibrating sample magnetometer in an applied field of 2×10^{-2} T. For the HTC sample the Meissner signal obtained corresponds to an almost perfect diamagnetic situation and the transition temperature to the superconducting state was found to be $T_c = [93 \mp 1]$ K. For the non-HTC sample our measurements showed that the magnetic susceptibility follows the Curie–Weiss law.

X-band ($\nu = 9.41$ GHz) EPR spectra were recorded from 9.7 K up to RT using an Oxford temperature system and a Bruker spectrometer type ER-200D. Its reflection cavity operated with a magnetic field modulation of 100 kHz. The magnetic induction and the linewidths were measured by using a digital NMR magnetometer, whereas the microwave frequency was measured with a high-Q wavemeter. DPPH was used as a standard ($g = 2.0037$). The measurements were performed on a powdered (30 mg) sample of cylindrical shape.

Figure 1 shows the EPR spectrum of Cu^{2+} ions from powdered $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound in the orthorhombic phase at RT. This spectrum is characteristic for all good quality high- T_c superconductors 123. Its spin-Hamiltonian parameters have the same values as previously reported [7]. In the range from RT to T_c the observed changes in the intensity of the EPR lines of Cu^{2+} ions were practically unimportant within the context of the present work. Below T_c the above spectrum was also observed, but the analysis was very difficult because the spectrometer could not be tuned properly [8].

For samples in the tetragonal phase, the observed EPR spectra and their temperature dependence showed quite different behaviour to those of the orthorhombic phase (Fig. 2). At RT we observed two different EPR spectra; one that comes from Cu^{2+} ions with $g_{\text{eff}} = 2.19(1)$ and another one of unknown origin with $g = 1.93(1)$ and linewidth $120(10) \times 10^{-4} T$ (Fig. 2e). Below 150 K, the observed EPR signal arises from the superposition of two spectra. The first comes from Cu^{2+} ions in axial local symmetry with spin-Hamiltonian $g_{\parallel} = 2.48(1)$ and $g_{\perp} = 2.01(1)$ [9]. The intensity of the EPR spectrum of the Cu^{2+} ions increases with decreasing temperature; a phenomenon which might be attributed to the skin effect [10]. Using the relation $g_{\text{eff}} = (g_{\parallel} + 2g_{\perp})/3$ we obtained a value for the spin-Hamiltonian parameter equal to 2.181(1) which is almost similar for g_{eff} of Cu^{2+} ions at RT. The second spectrum ($g = 2.20(1)$) consists of a broad single line. Its linewidth was found to depend strongly and monotonically on the temperature. Its origin will be discussed later.

The observed EPR line at 32 K (Fig. 2b) has $g = 2.20(1)$ and linewidth $\Delta H = 125(5) \times 10^{-3} T$ and exhibits hyperfine structure with distance between lines $\Delta_{\text{I}} = 22 \times 10^{-3} T$ and $\Delta_{\text{II}} = 19 \times 10^{-3} T$. The intensity of the second spectrum increases strongly with decreasing temperature overlapping completely the signal from Cu^{2+} ions at low temperatures. Finally, at 9.7 K, a very intense single symmetrical EPR line was observed with $g = 2.12(1)$ and linewidth $\Delta H = 75(3) \times 10^{-3} T$ (Fig. 2a). In a pre-

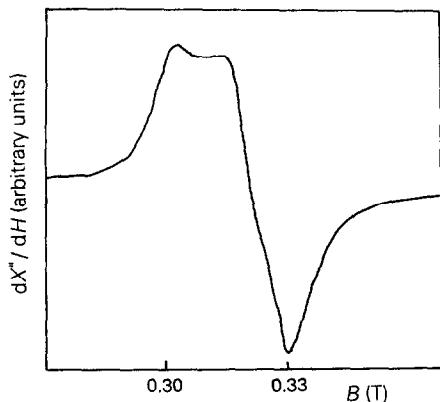


Fig. 1. The EPR spectrum of Cu^{2+} ions in $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the orthorhombic phase at RT.

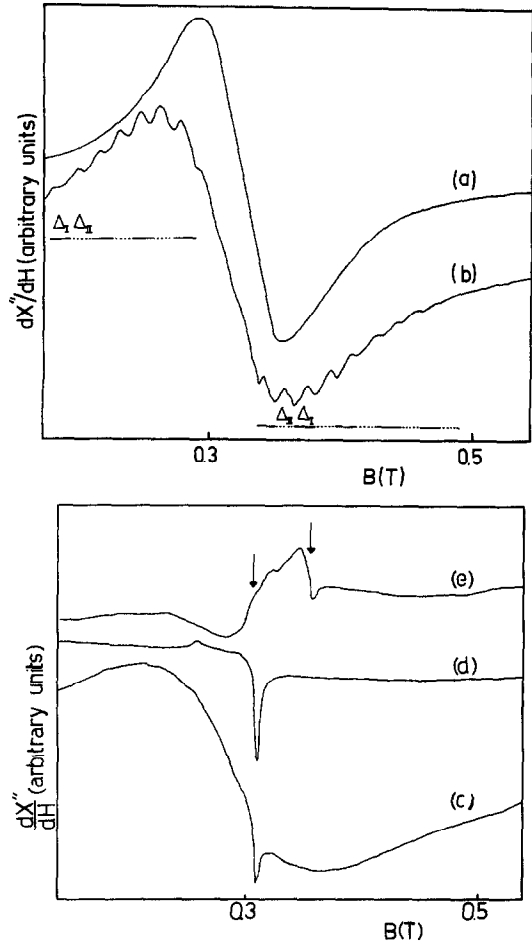


Fig. 2. Temperature dependence of the EPR spectra for $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the tetragonal phase at (a) 9.7 K, (b) 32 K (c) 58 K, (d) 120 K and (e) 300 K across.

vious paper [10] EPR measurements for $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the tetragonal phase were reported. An observed line below 30 K was suggested that arises from the isotropic part of the exchange interaction of Cu-Cu ions. A change of the g parameter between 20 and 30 K was also reported there. We believe that a kind of phase transition might be behind the above observations. However, the observed low temperature EPR spectrum in $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is different from that in $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the tetragonal phase since the spin-Hamiltonian parameters and linewidths are different for these two materials.

Typical hyperfine coupling constants for the divalent europium isotopes $^{151}\text{Eu}^{2+}$ (47.82% abundance, $I = 5/2$) and $^{153}\text{Eu}^{2+}$ (52.18% abundance, $I = 5/2$) in a cubic environment are $^{151}A = 3.28 \times 10^{-3} T$ and $^{153}A = 1.46 \times 10^{-3} T$ [11]. Our values are clearly about one order of magnitude larger than these. At first we notice that in our case Eu ions are not free and probably an interaction between them might occur. There are presumably other reasons for these differences which we do not wish to comment on at the present stage. We suggest that the EPR spectrum

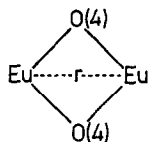


Fig. 3. Europium ions across the oxygen bridges (O(4)) with $r = 3.8826 \text{ \AA}$ for $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the tetragonal phase.

at 32 K originates from superexchange interaction between europium ions across oxygen bridges. The EPR spectra of the superexchange interaction between 59-cobalt (^{59}Co) ions [12] and Mn ions [13] across oxygen bridges have been previously reported and are quite similar to those observed here by us. Two coupled europium ions must give $2(I_1 + I_2) + 1 = 11$ lines and their relative intensities are expected to be as 1:2:3:4:5:6:5:4:3:2:1. In our EPR spectrum we observed about 10 lines on the left and 10 lines on the right side of the main EPR line. The obtained intensities ratios of the left side are 1:1:2:3:3:4:5:6:11:16 and of the right side are 1:1:2:2:3:4:6:7:13:16. As shown in Fig. 2b some of the lines of the hyperfine structure are masked in the central region of the main line. As discussed previously Eu ions in $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ substitute either rare earth ions or Ba ions [6]. We think that the above hyperfine lines come from the Eu ions located at Ba sites. We assume that some europium ions occupying adjacent Ba sites are coupled together through oxygen (O)(4) ions [14] (Fig. 3). Their distance along the x -axis is $r = 3.8826 \text{ \AA}$, which is reasonable for this kind of interaction [13]. The fact that similar phenomena have not been observed in $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds in the tetragonal phase is now easily explained since Gd ions do not substitute for Ba ions in these structures. It is worth noticing that superexchange interaction, over oxygen bridges, has been postulated [6] previously but in the orthorhombic phase. We tend to believe that these kinds of interaction play an important role in samples with large oxygen deficiency.

The variations of the linewidth of this line with temperature may be fitted to the general formula $\Delta H = a - bT$ with $a = 52(3) \times 10^{-3} \text{ T}$ and $b = 22(4) \times 10^{-4} \text{ T K}$. Presumably, the conduction electrons lead to a thermal broadening of the EPR line. The temperature dependence of the intensity of this line has been given by the following relation [15]:

$$I \sim 1/T[3 + \exp(J/kT)], \quad (1)$$

where J is the usual exchange interaction parameter which has been estimated to be about 20 cm^{-1} . This value is in good agreement with the value of the exchange interaction parameter between Mn ions [13].

3. CONCLUSIONS

We observed differences in the EPR spectra of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ between a superconducting sample

and a sample with suppressed superconductivity after removal of oxygen. At first, from the EPR spectrum of divalent copper ions, the local symmetry of the centers is concluded to be radically different between the two samples. For the HTC sample the Cu^{2+} complexes show orthorhombic local symmetry. On the other hand our results for non-HTC sample indicate that the crystal field symmetry is axial for Cu^{2+} complexes with the ground state wavefunction being $d(x^2 - y^2)$ or $d(xy)$. Secondly, in the non-HTC sample an EPR spectrum arising from the superexchange interaction of Eu^{2+} ions across the oxygen bridges was observed. This spectrum has not been detected in the HTC sample. Finally, we think that investigation of the exchange interaction in high- T_c 123 compounds as the function of oxygen deficiency may throw new light on the properties exhibited by $\text{ReBa}_2\text{Cu}_3\text{O}_{7-\delta}$ materials.

Acknowledgements—We wish to acknowledge with thanks Dr Petruleas from the "Democritos" Research Center, Greece, for the EPR spectrometer and helpful discussions

REFERENCES

- Oseroff S. B., Vier D. C., Smyth J. F., Salling C. T., Schultz S., Dalichaugh Y., Lee B. W., Maple M. B., Fisk Z., Thompson J. D., Smith J. L. and Zirngiel E., *Solid State Comm.* **64**, 241 (1987).
- Lue J. T., *Phys. Rev. B* **38**, 4592 (1988).
- Mukhopadhyay P., Multani M. S., Palkar V. R., Narwanker P. and Guptasarma P., *Ferroelectr. Lett. (U.K.)* **10**, 57 (1989).
- Atsarkin V. A., Vasneva G. A., Demidov V. V. and Sobolev A. T., *Sov. Phys.-Solid State* **31**, 508 (1981).
- Golovenchits E. I., Sanina V. A., Sapozhnikova L. M. and Syrnikov P. P., *Sov. Phys.-Solid State* **31**, 513 (1989).
- Alekseevski N. E., Mitin A. V., Nizhankovskii V. I., Garifullin I. A., Garifyanov N. N., Khaliullin G. G., Khylyboy E. P., Kochelaev B. I. and Taginov L. R., *J. Low Temp. Phys.* **77**, 87 (1989).
- Guskos N., Londos C. A., Trikalinos Ch., Paraskevas S. M., Koufoudakis A., Mitros Ch., Gamari-Seale H. and Niarchos D., *Phys. Stat. Sol. (b)* **165**, (1991).
- Guskos N., Leventouri Th., Trikalinos Ch. and Calamiotou M., *Phys. Stat. Sol. (b)* **149**, K15 (1988).
- Hoffman S. K., Goslar J. and Osman M., *Acta Physica Pol.* **A70**, 43 (1986).
- Guskos N., Triberis G. P., Calamiotou M., Trikalinos Ch., Koufoudakis A., Mitros Ch., Gamari-Seale H. and Niarchol D., *Phys. Stat. Sol. (b)* **162**, 243 (1990); **163** K89 (1991).
- Cheema S. U. and Smith M. J. A., *J. Phys C: Solid State Phys.* **4**, 1231 (1971).
- Jezowska-Trzebiatowska B., *Radiospectroscopy of Solid State*, p. 115. Polish Academy of Science, Warsaw (1975).
- Owen J., *J. appl. Phys.* **32**, 2135 (1961).
- Jorgensen J. O., Veal B. W., Paulikas A. P., Nowicki L. J., Crabtree G. W., Claus H. and Kwok W. K., *Phys. Rev. B* **41**, 1863 (1990).
- Abragam A. and Bleaney B., *Electron Paramagnetic Resonance of Transition Ions*, p. 534. Clarendon Press, Oxford (1970).