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Abstract. EPR and magnetic measurements were carried out on specially prepared samples of the EuBa$_{2-x}$Eu$_x$Cu$_3$O$_{7-\delta}$ compound in the tetragonal phase, in the temperature range 100–4.2 K. The EPR spectra of Eu^{2+}, Cu^{2+}, coupled pairs of divalent copper ions and the superexchange interaction between Cu ions over oxygen bridges have been observed. The EPR spectrum of europium ions indicates the existence of a crystal-field splitting of the ^{8}S$_{7/2}$ ground state of Eu^{2+} ions with a value of the spin-Hamiltonian parameter b_2^0 of about 14×10^{-2} cm^{-1}. This parameter is analysed within the framework of Newman's superposition model. Anomalies in the temperature variation of the magnetic susceptibility are attributed to the presence of divalent and trivalent europium ions. The susceptibility of Eu^{3+} ions is non-zero because the excited states are thermally populated and they contribute to the result of the ground state with $J = 0$.

1. Introduction

Of the various polycrystalline oxides REBa$_2$Cu$_3$O$_{7-\delta}$ (where RE $\equiv$ rare-earth ions), compounds containing europium atoms attract particular interest for many reasons. Firstly, there is evidence that Eu^{2+} ions substitute for Ba^{2+} ions (Alekseevski *et al* 1989, Guskos *et al* 1992). Eu^{2+} ions have a ground state ^{8}S$_{7/2}$ ($\langle L \rangle = 0$) and can easily be studied by the EPR technique. Secondly, compounds with Eu atoms usually exhibit the highest T_c of the various members of the RE 1:2:3 series (Guskos *et al* 1991b, c). Thirdly, a signal presumably arising from superexchange interaction between Eu^{2+} ions over oxygen bridges has been reported (Guskos *et al* 1992).

Causa *et al* (1988) have reported a determination of the crystal-field splitting of the ground state of Gd^{3+} ions in dilute Gd$_x$Eu$_{1-x}$Ba$_2$Cu$_3$O$_{7-\delta}$ compounds. Additionally, they analysed the microscopic origin of the measured spin-Hamiltonian parameters using Newman's superposition model (Newman and Urban 1975).

We report here magnetic and EPR results of specially thermally treated EuBa$_{2-x}$Eu$_x$Cu$_3$O$_{7-\delta}$ compounds in the tetragonal phase, in the temperature range 100–4.2 K. This thermal treatment could destroy the superexchange bonding between divalent europium ions over oxygen bridges and make it possible to analyse the crystal-field splitting. We also report the effect of the Eu^{2+} and Eu^{3+} ions on the magnetic susceptibility.

2. Experimental results

Samples with the nominal composition $EuBa_2Cu_3O_{7-\delta}$ were prepared by sintering mixed powders of Eu_2O_3, $BaCO_3$ and CuO in appropriate concentrations, as previously reported in detail (Guskos *et al* 1992). After the initial XRD and EPR measurements the samples were reannealed at 450 °C for 12 h under an O_2 gas flow and then they were slowly cooled to room temperature (RT). In order to obtain the tetragonal phase, they were submitted to further annealing at 450 °C in flowing He for 5 h following fast cooling to RT in a reducing atmosphere.

The samples were identified at RT using a powder diffractometer with Co Kα radiation (XRD). The XRD pattern could be indexed (Guskos *et al* 1992) on the basis of a tetragonal unit cell with the same values of lattice constants. Traces of $BaCuO_2$ were identified which have a negligible contribution to the magnetic susceptibility (Gamari-Seale *et al* 1992).

The measurements of the magnetization versus temperature were carried out using a PAR 155 vibrating-sample magnetometer. These measurements did not reveal any transition to the superconducting state.

Figure 1 presents the plot of the reciprocal static susceptibility χ^{-1} as a function of temperature for the $EuBa_{2-x}Eu_x Cu_3O_{7-\delta}$ compound in the tetragonal phase. The trivalent europium ions are in the $^7F_0$ ground state with a magnetic moment $\mu = gJ(J+1) = 0$. However, an experimental value of $3.4\mu_B$ is generally accepted (Kittel 1966) which is in good agreement with calculations according to the Van Vleck model giving a value of $3.5\mu_B$. For $EuBa_2Cu_3O_{7-\delta}$ a paramagnetic susceptibility was reported (Hioba *et al* 1987) above 100 K ascribed to the thermal population of the low-lying states of the ^7F_J manifold of the Eu^{3+} ion. The magnetic susceptibility measurements indicate a Curie–Weiss law (figure 1) above 200 K. From this high-temperature region the derived paramagnetic Curie temperature T_p and the effective magnetic moment μ_{eff} obtained by least-squares fitting are 5 K and $4.10\mu_B$ per formula unit, respectively. This value is different from that expected for Eu^{3+} ions including contributions from the thermally excited state. The discrepancy could be explained if one assumes that a small fraction of Ba^{2+} ions are substituted by Eu^{2+} ions which have $\mu_{eff} = 7.94\mu_B$. This assumption is supported by EPR observations of divalent europium ions, as reported below. Our compound should be of the type $EuBa_{2-x}Eu_xCu_3O_{7-\delta}$. From the contribution of Eu^{2+} ions to the magnetic susceptibility their concentration is estimated to be approximately $x \simeq 0.07$.

Below 200 K the graph deviates from the Curie–Weiss law and below 50 K there exists a strong decrease in χ^{-1} with decreasing temperature. The measurements were performed under applied fields of 0.2, 2 and 10 kOe only at around 100 K. Above this temperature the measurements were carried out only for an applied field of 2 kOe. For the field of 0.2 kOe the susceptibility remains constant above 35 K but measurements above this temperature were not possible as the signal obtained was within the limits of the resolution of the apparatus. The behaviour below 50 K might be explained by the crystal-field effect, as has been pointed out in a study using similar measurements by Ghamaty *et al* (1991).

The EPR measurements were performed with a Bruker X-band ($\nu = 9.47$ GHz) spectrometer type 200D using 100 kHz field modulation. The modulation amplitude was chosen to be 1.2×10^{-3} T while the level of the microwave power on the sample was kept at 31 mW. Temperature dependence measurements were performed using an Oxford flow cryostat system operating between 4.2 and 100 K. The magnetic induction
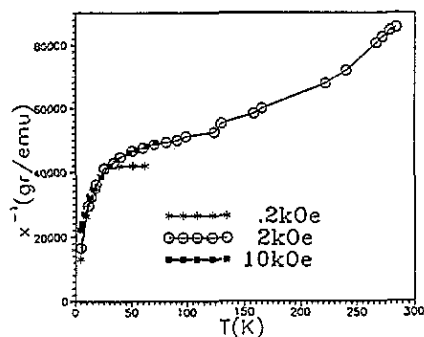
Figure 1. Reciprocal static magnetic susceptibility of EuBa$_{1.93}$Eu$_{0.07}$Cu$_3$O$_{7-\delta}$ in the tetragonal phase as a function of temperature.

B and the EPR linewidths were measured using a digital NMR magnetometer, whereas the microwave frequency was controlled with a high-Q wavemeter. The measurements were performed on powder (30 mg) samples of cylindrical shape.

Figure 2 shows the temperature dependence of the EPR spectra of the EuBa$_{1.93}$Eu$_{0.07}$Cu$_3$O$_{7-\delta}$ compound in the tetragonal phase. Below 10 K the superposition of two EPR spectra was observed. The first arises from the exchange interaction between pairs of copper ions (Guskos *et al* 1990, 1991e). The spin-Hamiltonian parameter g and linewidths ΔH are summarized in table 1. The second comes from Eu^{2+} ions. The Eu^{2+} spectrum is satisfactorily described by the separate spin-Hamiltonian

$$\hat{H} = g\mu_B B S + \tfrac{1}{3}\sum_m b_2^m O_2^m(S) + \tfrac{1}{60}\sum_m b_4^m O_4^m(S) + \tfrac{1}{1260}\sum_m b_6^m O_6^m(S) \qquad (1)$$

where the first term accounts for the Zeeman energy and O_n^m are the Stevens (1952) operators describing the crystal-field interaction. Eu^{2+} ions have axial symmetry owing to the tetragonal unit cell (figure 3) and their spectra could be described by the spin-Hamiltonian parameters b_2^0, b_4^m and b_6^m. In the analysis below, only O_2^0 terms have been taken into account since, for powder samples, terms of higher order are of negligible importance. According to the powder spectrum analysis for paramagnetic centres with spin $\tfrac{7}{2}$ in axial symmetry, resonance transitions (besides the $-\tfrac{1}{2} \longleftrightarrow +\tfrac{1}{2}$) arise from divergence of the probability distribution $P(H)$ at $\theta = 90°$. For $\theta = 0°$, each transition is also expected to give rise to a shoulder in the spectrum of weak intensity and thus is not observable. The position of the resonance lines determined in this way are given by second-order perturbation theory (Odermaat 1981):

$$H_m = H_0 + b_2^0(M_S - \tfrac{1}{2}) - (b_2^0)^2/8H_0[2S(S+1) - 6M_S(M_S - 1) - 3] \qquad (2)$$

where H_0 ($= h\nu/g\mu_B$) is the central field and M_S is the component of the spin. Using equation (2), a value of $b_2^0 \simeq 14 \times 10^{-2}$ cm^{-1} was estimated.

Inclusion of second-order terms in equation (2) turns out to be necessary, allowing for the large value of b_2^0 which is not so small compared with the Zeeman energy at that frequency. This explains why the resonance transition lines are not equally separated as expected, if only first-order perturbation theory is taken into account. In our case an anisotropic $-\tfrac{1}{2} \longleftrightarrow +\tfrac{1}{2}$ transition should also be observed owing to two divergences of $P(H)$ at different values of θ, but this was impossible as the transition was completely masked by a very intense line arising from exchange-coupled pairs of copper ions (figure 2).
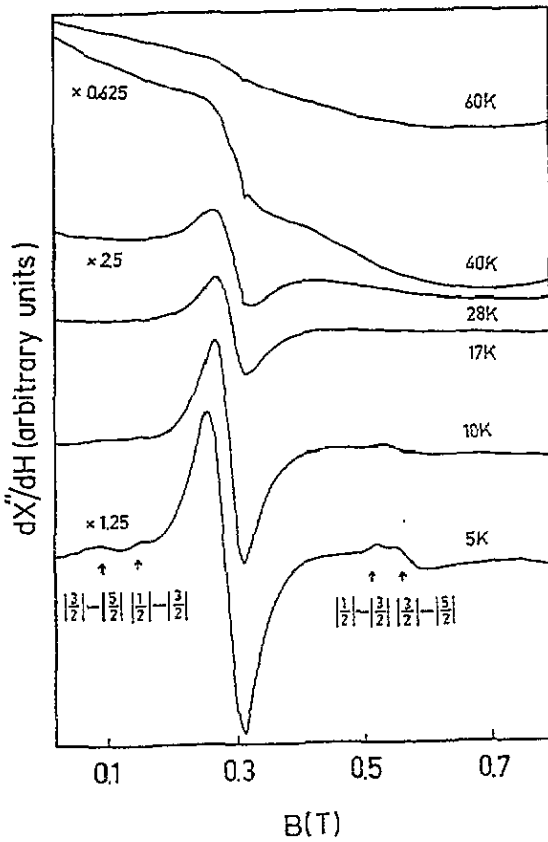
Figure 2. Temperature dependence of the EPR spectra of $EuBa_{1.93}Eu_{0.07}Cu_3O_{7-\delta}$ in the tetragonal phase.
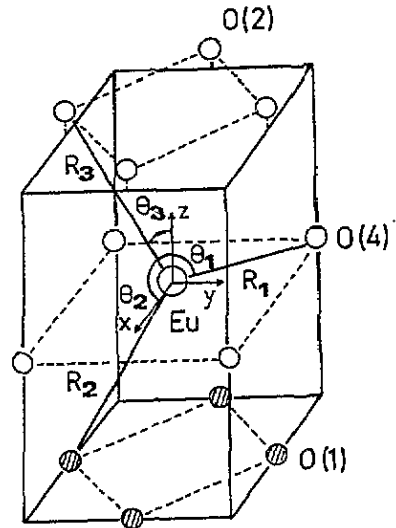
Figure 3. The local structure of Eu^{2+} ions occupying barium atom positions.

Table 1. The values of the spin-Hamiltonian parameters g and the linewidths ΔH.

T (K)	g	ΔH (T)
5	2.267(5)	0.051(1)
10	2.230(5)	0.045(1)
17	2.185(5)	0.045(1)
28	2.185(5)	0.054(1)

According to the superposition approximation of Newman's model, b_2^m is expressed as

$$b_2^m = \sum_i K(\vartheta_i, \varphi_i) \bar{b}_2(R_i) \tag{3}$$

where R_i, ϑ_i, φ_i are the spherical coordinates of the ith ligand (Newman and Urban 1975). The second-order spin Hamiltonian b_2^0 could be written as

$$b_2^0 = \sum_i \tfrac{1}{2}(3\cos^2 \vartheta_i - 1)\bar{b}_2(R_i) \tag{3a}$$

where

$$\overline{b}(R_i) = \overline{b}_2(R_0)(R_i/R_0)^{12}. \tag{3b}$$

$\overline{b}_2$ is the 'intrinsic' spin-Hamiltonian parameter and R_i is the metal–ligand distance. In figure 3 the local structure of Eu^{2+} ions occupying barium atom positions is indicated. The metal–ligand distances and angles have been calculated using the experimental data of Jorgensen *et al* (1987). The following values were obtained: $R_1' = 2.787$ Å, $R_2'' = 2.98$ Å, $R_3''' = 2.94$ Å; $\vartheta_1' = 100°$, $\vartheta_2'' = 139.35°$ and $\vartheta_3''' = 41.3°$. Substituting these values into (3a) the following expression for b_2^0 is deduced:

$$b_2^0 = -1.8\overline{b}_2' + 1.44\overline{b}_2'' + 1.4\overline{b}_2'''. \tag{4}$$

The values of the $\overline{b}_2$ parameters were estimated using their radial dependence corresponding to equilibrium spacing in the zircon systems where the ordinate scale is appropriate to O^{2-} ligands (Stedman and Newman 1974). In our case we find that $\overline{b}' \simeq -0.13$ cm^{-1}, $\overline{b}'' \simeq -0.08$ cm^{-1} and $\overline{b}''' \simeq -0.12$ cm^{-1}, resulting in a value of $b_2^0 \simeq -5 \times 10^{-2}$ cm^{-1}, which is in good agreement with the experimental value that we found above. However, since O(1) sites are only partially occupied, a smaller value of the respective b_2^0 parameter is expected which furthermore slightly reduces the crystal-field splitting. The same model was used to make an estimate of the $\overline{b}_4$ parameter. Taking into account contributions from the three oxygen sites and their symmetry around europium atoms we obtained an approximate value of $b_4^0 \simeq 0.3\overline{b}_4$. The order of $\overline{b}_4$ at these distances is at least 10^{-4} cm^{-1} or smaller (Stedman and Newman 1974) yielding a value of $b_4^0 \simeq 10^{-5}$ cm^{-1} which justifies our initial assumption to neglect this term in comparison with b_2^0.

At 17 K a new, very broad and intensive line appears centred at $g = 2.14(1)$ with increasing linewidth ΔH when the temperature increases. This broad line might originate from an exchange interaction over oxygen bridges between copper ions (Guskos *et al* 1991a). At 40 K, at the centre of this broad line the EPR spectrum of Cu^{2+} ions in the axial local symmetry appears (figure 2).

At low temperatures below 10 K an EPR line arising from the exchange interaction between coupled pairs of divalent copper ions appears. Its intensity I may be described by the following formula (Abraham and Bleaney 1970):

$$I = 1/T[3 + \exp(J/kT)] \tag{5}$$

where J is the exchange interaction constant and estimated to be about 29 cm^{-1}, a value which is in good agreement with those for the other RE 1:2:3 compounds in the tetragonal phase (Guskos *et al* 1991e). The g parameter initially decreases with increasing temperature and then becomes constant at about 17 K (table 1). Also, as the temperature increases, an anomalous variation in the linewidth ΔH is observed (table 1), indicating some kind of magnetic ordering (Guskos *et al* 1991d).

In summary, our results indicate that divalent europium ions could substitute for Ba^{2+} ions. This justifies the high effective moment observed by susceptibility measurements. Another explanation for this might be the effect of the crystalline field on the positions of the ^{7}F$_{7/2}$ levels of Eu^{3+} ions. This effect is not expected to increase the effective moment considerably. The crystal-field splitting of the

ground state of Eu^{2+} ions could be described by Newman's superposition model. It seems that the special thermal treatment could destroy the superexchange bonding between divalent europium ions over oxygen bridges. The anomalous behaviour of the magnetic susceptibility versus temperature is ascribed to the existence of both divalent and trivalent europium ions.

Acknowledgments

References

Abraham A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon)
Alekseevski N E, Nitin A V, Nizhanovskii V I, Garifullin I A, Garifyanov N N, Khallin G G, Khylbov E P, Kochelaev B I and Tagirov L R 1989 *J. Low-Temp. Phys.* **77** 87
Causa M T, Painstein C, Niera G, Sanchez R, Steren L B, Tovar M, Zysler R, Vier D C, Schultz S, Oseroff S D, Fisk Z and Smith J L 1988 *Phys. Rev.* B **38** 257
Gamari-Seale H, Guskos N, Koufoudakis A, Kruk I, Mitros C, Likodimos V, Niarchos D and Psycharis V 1992 *Phil. Mag.* B **65** 1381
Ghamaty S, Lee B W, Neumeier J J, Nieawa G and Maple M B 1991 *Phys. Rev.* B **43** 5430
Guskos M, Calamiotou M, Londos C A, Likodimos V, Koufoudakis A, Mitros C, Gamari-Seale H and Niarchos D 1992 *J. Phys. Chem. Solids* **53** 211
Guskos N, Likodimos V, Kontos A, Koufoudakis A, Mitros C, Gamari-Seale H and Niarchos D 1991a *Phys. Status Solidi* b **166** K19
Guskos N, Likodimos V, Londos C A, Trikalinos Ch, Koufoudakis A, Mitros C, Gamari-Seale H and Niarchos D 1991b *Mod. Phys. Lett.* B **5** 967
Guskos N, Londos C A, Trikalinos Ch, Paraskevas S M, Koufoudakis A, Mitros C, Gamari-Seale H and Niarchos D 1991c *Phys. Status Solidi* b **165** 249
Guskos N, Kuriata J, Sadiowski L, Paraskevas S M, Koufoudakis A, Mitros C, Gamari-Seale H and Niarchos D 1991d *Phys. Status Solidi* b **167** K113
Guskos N, Triberis G P, Calamiotou M, Trikalinos Ch, Koufoudakis A, Mitros C, Gamari-Seale H and Niarchos D 1990 *Phys. Status Solidi* b **162** 243
—— 1991e *Phys. Status Solidi* b **163** K89
Hioba G, Streitz F H, Gavrin A and Chien C L 1987 *Solid State Commun.* **63** 817
Jorgensen J D, Beno M A, Hinks D G, Doderholm L, Volin K J, Hitterman R L, Grace J D, Schuller I K, Segre S K, Zhang H and Kleefisch M S 1987 *Phys. Rev.* B **36** 3608
Kittel C 1966 *Introduction to Solid State Physics* 3rd edn (New York: Wiley)
Newman D J and Urban W 1975 *Adv. Phys.* **24** 793
Odermatt R 1981 *Helv. Phys. Acta* **54** 1
Stedman E G and Newman D J 1974 *J. Phys. C: Solid State Phys.* **7** 2347
Stevens K W H 1952 *Proc. Phys. Soc.* A **65** 209