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ZERO-FIELD SPLITTING OF THE GROUND STATE OF Eu<sup>2+</sup> IONS  
IN EuBa<sub>2</sub>CuO<sub>7-δ</sub> COMPOUND WITH LARGE OXYGEN DEFICIENCY  
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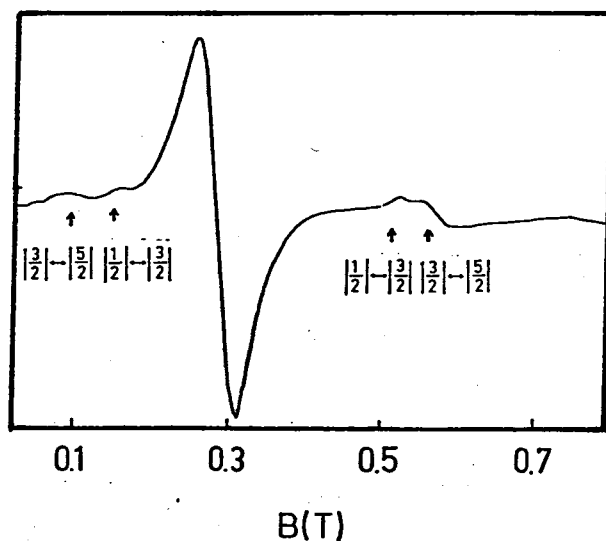
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**ABSTRACT.** This paper shows the existence of divalent europium ions in the oxygen deficient Eu-Ba-Cu-O compound. The zero-field splitting of the S ground state of the divalent europium ions is studied by means of EPR. An approximate value of 0.04 1/cm for the second-order spin Hamiltonian parameter is deduced.

**INTRODUCTION.** In a previous paper [1] on Eu-Ba-Cu-O in tetragonal phase an EPR signal was tentatively ascribed to a superexchange interaction between divalent europium ions over oxygen bridges. This communication extends the analysis to the case of an oxygen deficient Eu-Ba-Cu-O sample obtained after additional thermal treatment which revealed the EPR spectrum of divalent europium ions.

**RESULTS AND DISCUSSION.** The measured sample Eu-Ba-Cu-O in [1] was re-annealed at 450 C for 12 h under O<sub>2</sub> gas flow and then it was slowly cooled to room temperature (RT). In order to receive the oxygen deficient phase, the sam-



ple were submitted to further annealing at 450 C in flowing He for 5 h following fast cooling to RT in reducing atmosphere. XRD characterization showed that it could be indexed on the base of a tetragonal unit cell with the same value of lattice constant as in [1]. EPR measurements were carried out on powders using a standard Bruker 200D spectrometer ( $\nu = 9.41$  GHz). Fig.1 presents the EPR spectra taken at 5 K. It contains signals from two different paramagnetic centers. The first signal is very intense and arises from coupled pairs of copper ions [2]. It is centered at  $g = 2.267(5)$  with linewidth  $\Delta H = 0.051(1)$  T. The second signal comes from divalent europium ions. Its spectrum is satisfactorily described by the following spin Hamiltonian:

$$H = g \mu_B B S + \frac{1}{60} b_2 O_2 \quad (1)$$

where the first term accounts for the Zeeman energy and the second describes the crystal-field interaction. In the second order perturbation theory the position of the resonance lines (besides the  $|1/2\rangle \rightarrow -1/2$  transition) for a powder sample are given by the following relation [3]:

$$H = H_0 + b_2 \left( \frac{M - 1/2}{S} \right) - \frac{b_2}{8H} [2S(S+1) - 6M(M-1) - 3] \quad (2)$$

where  $H_0 = h\nu/g\mu_B$  is the central field and  $M(S)$  is the component of the spin. Using this relation, a value of the second-order spin Hamiltonian about  $b_2 = 10.04$  1/cm is obtained.

In summary, our results indicate that special thermal treatment could destroy the superexchange bonding between divalent europium ions over oxygen bridges and help to reveal the existence of isolated Eu(2+) ions.

#### References

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