Journal of Magnetism and Magnetic Materials 104–107 (1992) 563–564
North-Holland

journal of magnetism and magnetic materials

EPR spectrum of Tm^{2+} ions in the tetragonal phase of (La, Tm)–Ba–Cu–O compound

W. Likodimos [a], N. Guskos [a], C.A. Londos [a], S.M. Paraskevas [b], A. Koufoudakis [c], C. Mitros [c], H. Gamari-Seale [c], and D. Niarchos [c]

[a] *Solid State Section, Department of Physics, University of Athens, Panepistimiopolis, 157 71 Athens, Greece*
[b] *Organic Chemistry, Chemistry Department, University of Athens, Greece*
[c] *Institute of Materials Science, NCSR "Democritos", 153 10 Aghia Paraskevi, Attiki, Athens, Greece*

EPR measurements at room temperature (RT) on the oxygen deficient (La, Tm)–Ba–Cu–O compound (tetragonal phase) revealed a line centered at $g = 2.895(5)$ with linewidth $\Delta H = 0.015(1)$ T. The line is ascribed to Tm^{2+} ions ($4f^{13}$, $^2F_{7/2}$) assuming that the $\Gamma(7)$ doublet is the ground state. A characteristic EPR spectrum of divalent copper ions was also observed.

Recently we have presented the EPR spectrum of the polycrystalline compound Tm–Ba–Cu–O [1]. For the samples in tetragonal phase (due to large oxygen deficiency) at liquid nitrogen temperature (LN) an EPR line centered at $g = 3.33(1)$ has been observed in addition to the signal arising from divalent copper ions. This line was ascribed to the ground state of Tm^{2+} ions ($4f^{13}$, $^2F_{7/2}$) under the condition that it results from a $\Gamma(7)$ doublet provided that the reduction of the orbital angular momenta was quite large, a phenomenon that arises from covalent effects and dynamic coupling to the lattice [1].

In the present work, the (La, Tm)–Ba–Cu–O compound in the tetragonal phase, characterised by large oxygen deficiency, has been investigated using the EPR method.

We first prepared oxygenated samples of (La, Tm)–Ba–Cu–O compound by using the solid-state reaction technique previously reported in detail [2]. Afterwards, in order to obtain samples in the tetragonal phase, part of the oxygenated powder was annealed at 650 °C in flowing He for 6 h and cooled fast to RT in reducing atmosphere. XRD measurements showed that the sample could be indexed on the basis of a tetragonal unit cell with lattice constants $a = b = 3.8711(3)$ Å, $c = 11.7549(9)$ Å, whereas the initial oxygenated sample was indexed on a basis of an orthorhombic unit cell with lattice constants $a = 3.8317(3)$ Å, $b = 3.8944(3)$ Å and $c = 11.6958(9)$ Å.

Magnetic measurements have shown that the sample in tetragonal phase exhibits a characteristic paramagnetic behaviour. For the orthorhombic sample the Meissner signal obtained corresponds to an almost perfect diamagnetic material and the transition temperature was 78 K.

The EPR spectra have been recorded on an X-band spectrometer Varian E-4 type having a reflection cavity operating with magnetic field modulation of 100 kHz. The EPR spectrum of the tetragonal sample at RT revealed an anisotropic line, resulting from divalent copper ions in orthorhombic local symmetry with g values $g(x)$, $g(y)$, $g(z)$ identical to those reported in ref. [3]. Apart from this characteristic signal another EPR line was recorded at lower magnetic fields with $g = 2.895(5)$ and linewidth $\Delta H = 0.015(1)$ T (fig. 1). At both sides of this line some other weak lines reminding hyperfine structure also observed. We assume that this line is originated from Tm^{2+} ions. The ground state of Tm^{2+} is $^2F_{7/2}$ and under the influence of a crystalline field of eightfold cubic symmetry, the $J = \frac{7}{2}$ level splits into two doublets $\Gamma(6)$, $\Gamma(7)$ and a quartet $\Gamma(8)$. The $\Gamma(7)$ level has the lowest energy and transitions between the components of this doublet are expected theoretically to give rise to an isotropic spectrum with $g = 3.429$ [4]. The deviation of the observed g value from the theoretical one of a pure $\Gamma(7)$ doublet could be attributed to a large orbital reduction (with an estimated k factor $k = 0.846$) which implies the exis-

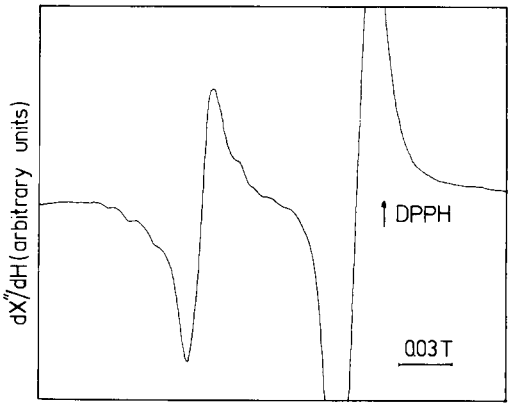

Fig. 1. The EPR spectrum of $La_{0.5}Tm_{0.5}Ba_2Cu_3O_{7-\delta}$ compound in tetragonal phase at RT.

tence of strong covalent effects and dynamic coupling to the lattice. The same phenomena were found [1] to play an essential role in the EPR spectrum of Tm^{2+} ions in the Tm–Ba–Cu–O compound in tetragonal phase but to a lesser extent. The separation between the two closest to the central line and more intense lines is about 0.042 T which is almost twice the hyperfine constant of divalent thulium ions.

The EPR spectrum of divalent thulium ions is usually observable up to LN. It is of major importance that in this work it was detected at RT, which may mean that the spin–lattice relaxation time is adequately long in our compounds.

For the orthorhombic sample only the signal from copper ions was detected. This is plausible if allowance is made for the oxidizing conditions that prevail in this sample which favour the trivalent state for the thulium ions. The ground state of Tm^{3+} ions ($4f^{12}$, $^3H_6$) is nonmagnetic over a wide range of crystal field parameters in a cubic field. Therefore it is not expected to be detected by EPR. The question which remains to be answered concerns the role of oxygen deficiency in the valence state of the rare-earth ions in the 123 compounds.

References

[1] N. Guskos et al., Proc. Congr. AMPERE-25, Stutgart, Sept. 9–13, 1990, FRG, eds. M. Mehring, J.V. von Schutz and H.C. Wolf (Springer, Berlin, 1990) p. 263.

[2] N. Guskos, G.P. Triberis, Ch. Trikcalinos, M. Calamiotou, A. Koufoudakis, C. Mitros, H. Gamari-Seale and D. Niarchos, Phys. Stat. Sol. (b) 162 (1990) 243.

[3] N. Guskos, Th. Leventouri, Ch. Trikalinos and M. Calamiotou, Phys. Stat. Sol. (b) 149 (1988) K157.

[4] E.S. Sabisky and C.H. Anderson, Phys. Rev. 159 (1967) 234.