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Electron paramagnetic resonance studies of the oxygenated and non-oxygenated $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds

N Guskos†, C A Londos†, V Lykodimos†, M Calamiotou†, A Koufoudakis‡, C Mitros†, H Gamari-Seale‡ and D Niarchos‡

† Solid State Physics, Department of Physics, University of Athens, Panepistimiopolis, GR 15 771 Zografos, Athens, Greece

‡ Institute of Material Science, National Center for Scientific Research 'Democritos', GR 15 310 Aghia Paraskevi, Attikis, Athens, Greece

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Abstract. The EPR spectra of polycrystalline oxygenated and non-oxygenated (large oxygen deficiency) $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds, obtained at various temperatures, were studied and analysed. The oxygenated samples showed a transition temperature T_c at about 50 K. The EPR spectrum of the Cu^{2+} ions in the orthorhombic local symmetry was observed. It was found that these spectra are essentially influenced by an oxygen deficiency and thermal treatment. In the non-oxygenated samples, at a certain stage of the annealing process an EPR spectrum was detected at low temperatures. After the final anneal, this EPR spectrum showed significant changes. Changes were also observed in the corresponding XRD spectra, indicating reductions in the concentrations of the CuO and BaCuO_2 impurity phases. Additionally, the EPR spectrum of divalent copper ions in the axial local symmetry in the $d_{x^2-y^2}$ ground state was observed.

1. Introduction

Usually, for the 1:2:3 materials with La ions the phase transition to the superconducting state has been reported to be much lower than 70 K (Song *et al* 1988). Recently, it has been shown that the La substitution for Y and Ba ions in the high- T_c superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ tends to stabilize the phase transition temperature for these materials above 70 K even for a wide variety of heat treatment conditions (Wada *et al* 1989). Wada *et al* have suggested that, in order to obtain $\text{La}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$ samples with good superconducting properties, it is necessary to prepare them in the triperovskite structure where La and Ba ions have an ordered arrangement along the c axis and the occupancy factors of oxygen at $(\frac{1}{2}, 0, 0)$, i.e. O(5), and $(0, \frac{1}{2}, 0)$, i.e. O(1), are close to 0 and 1, respectively. An important question that arises for these materials concerns the role of the La ions which, participating in various kinds of interactions, presumably destroy the arrangement mentioned above. As a consequence the creation of charge carriers, e.g. bipolarons (Remova and Shapiro 1989, Mott 1990), responsible for the superconducting state is affected.

In the present work, $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds with and without a large oxygen deficiency have been investigated in the temperature range from 5.0 K up to room temperature (RT), using the EPR method.

2. Experimental results

The $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples (oxygenated and non-oxygenated) were prepared by the solid state reaction technique previously reported in detail (Guskos *et al* 1990a, b) (samples I). After the initial XRD, EPR and magnetic measurements the samples were reannealed at 450°C for 12 h under an O_2 gas flow and then were slowly cooled to RT (samples II). In order to obtain the tetragonal phase, parts of samples II were submitted to a further anneal at 650°C in flowing He for 6 h following fast cooling to RT in a reducing atmosphere.

The samples were identified at RT using a powder diffractometer with $\text{Co K}\alpha$ radiation (XRD). The XRD pattern of the oxygen-deficient samples could be indexed on a basis of a tetragonal unit cell with $a = b = 3.9163(3)$ Å and $c = 11.7641(9)$ Å. For the oxygenated samples, we could not identify, within the resolution of our diffractometer, whether the unit cell is tetragonal or orthorhombic. In all the samples, XRD measurements show the existence of some CuO and BaCuO_2 compounds. The concentrations of these impurities were drastically reduced after the annealed stage at 450°C.

Magnetic measurements performed on the oxygenated samples (I and II) in a field of 200 Oe revealed a T_c onset of about 50 K (figure 1). These results suggest that, although we have started to prepare our samples with the exact 1:2:3 stoichiometry, the obtained samples are of the form $\text{La}(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{7-\delta}$, with $x \approx 0.25$, the solid state solution limit (Segre *et al* 1977, Zhang *et al* 1992). Up to now, the origin of this low T_c -value has not been explained clearly. It is presumably the result of an as yet unknown intrinsic property of the $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound.

The EPR measurements were made in the temperature range from 5.0 K to RT using a standard X-band ($\nu = 9.41$ GHz) Bruker-type 200 D spectrometer with a magnetic field modulation of 100 kHz. The magnetic induction B and the EPR linewidths were measured with a digital NMR magnetometer whereas the microwave frequency was controlled by a high- Q wavemeter. The EPR measurements were performed on powdered (30 mg) samples of cylindrical shape.

For the oxygenated $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples I and II the EPR spectra at RT and liquid-nitrogen temperature are similar, as is shown in figure 2. At both temperatures the spectra consist of the superposition of two lines: an anisotropic line arising from divalent copper ions with $g_y = 2.041(3)$, $g_x = 2.099(3)$, $g_z = 2.233(4)$, and another very broad line of weak intensity.

Figure 3 presents the temperature dependence of the EPR spectrum of the $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound in the very-oxygen-deficient phase, in the temperature range 9.7–125 K (sample I). At RT the spectrum is not very well resolved. At a low temperature (9.7 K) an almost symmetrical EPR line appeared (figure 3, curve(a)) with the spin-Hamiltonian parameter $g = 2.394(4)$ and linewidth $\Delta B = 0.123(5)$ T. It is worth noting that, in the $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound of tetragonal phase, in this temperature range a symmetrical line was observed with a similar g -parameter, tentatively ascribed to an exchange interaction of coupled pairs of divalent copper ions (Guskos *et al* 1990b, 1991c). Interestingly, the linewidth of that line was about three times smaller than that observed here. Additionally, the EPR spectrum of the $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compound exhibits (Guskos *et al* 1991b) a single broad line with a strong temperature dependence which is centred at $g = 2.098(5)$. This broad line was tentatively attributed to an exchange interaction over oxygen bridges between copper ions. In the present studies, above 30 K our line has $g = 2.265(5)$ and linewidth

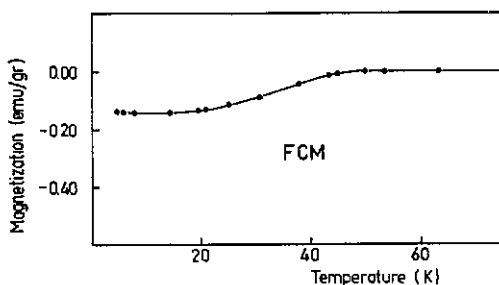


Figure 1. Magnetization versus temperature of an oxygenated $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample.

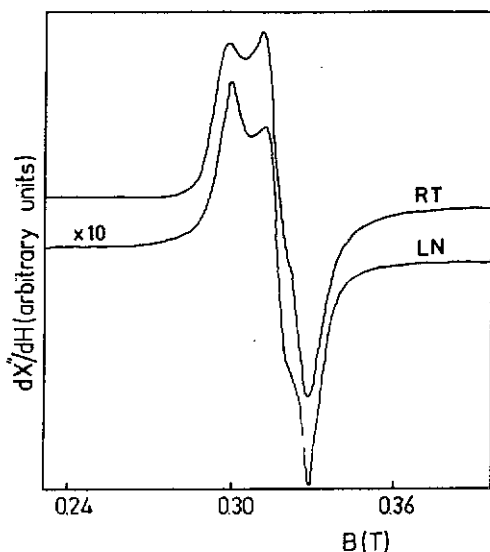


Figure 2. The EPR spectrum for oxygenated $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample at RT and liquid-nitrogen (LN) temperature.

following the formula $\Delta B = a + bT$ where $a = 0.081(5)$ T and $b = 0.0041(5)$ T K^{-1} . For $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the tetragonal phase (Guskos *et al* 1991a), similar observations were made. It was suggested there that the line arises from an exchange interaction over oxygen bridges between divalent europium ions. It is well known from the literature that lanthanum is incorporated in various compounds as a trivalent ion. Nevertheless, one could speculate that some of the lanthanum ions occupying adjacent Ba sites may be coupled together through four oxygen (O(4)) ions. The exchange interaction constant J could be estimated from the relation (Abragam and Bleaney 1970)

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

where I is the intensity of the EPR line and k is the Boltzmann constant. The estimated value of $J \simeq 19 \text{ cm}^{-1}$ is in good agreement with the value of exchange interaction constants for Eu and Mn ions (Guskos *et al* 1991a, Owen 1961).

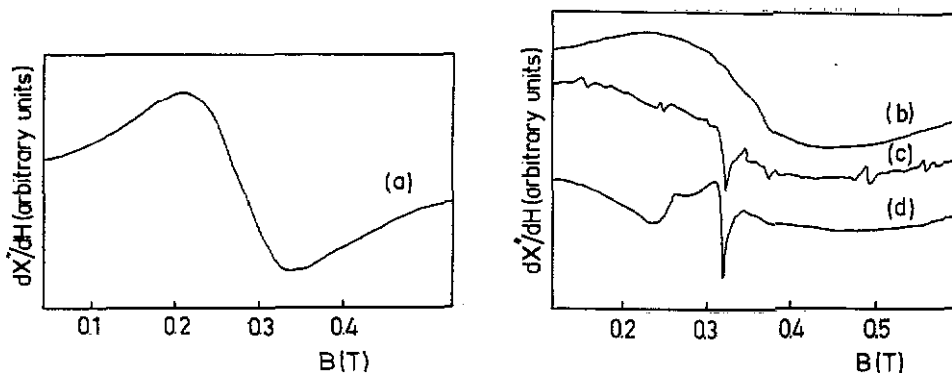


Figure 3. Temperature dependence of the EPR spectra for $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample I (tetragonal phase) at various temperatures; curve (a) 9.7 K; curve (b) 33 K; curve (c) 58 K; curve (d) 125 K.

At 58 K some additional weak EPR lines appeared (see figure 3, curve (c)). These lines occurred at about the same positions of the external magnetic field as those resulting from the EPR spectrum of the four copper ion complex with spin $S = 2$, reported in TGFB single crystals doped with Cu^{2+} ions (Stankowski and Mackowiak 1972). The fine structure of the EPR spectrum for this quartet with $S = 2$ in orthorhombic crystal-field symmetry is described by the following spin-Hamiltonian (Mackowiak and Kurzynski 1972):

$$\hat{H} = -\frac{2}{3}DP_0^2(S) - E[P_2^2(S) + P_{-2}^2(S)] + a\left\{\frac{14}{45}P_0^4(S) + \frac{1}{3}[P_4^4(S) + P_{-4}^4(S)]\right\} \\ + b\left\{-5\frac{14}{45}P_0^4(S) + \frac{7}{3}[P_4^4(S) + P_{-4}^4(S)]\right\} + \frac{7}{3}c[P_2^4(S) + P_{-2}^4(S)] \quad (2)$$

where P_m^l are irreducible spherical tensor operators, a is the spin-Hamiltonian parameter describing the cubic crystal field, D and b are the parameters for the tetragonal component of the crystal field, and E and c are the parameters describing the orthorhombic crystal field. Furthermore, their intensity was reported (Stankowski and Mackowiak 1972) to increase strongly with decreasing temperature from RT down to liquid-helium temperature. In our measurements, these weak lines were not observed at low temperatures because they were masked by the broad line whose intensity increases more rapidly with decreasing temperature. We tentatively ascribe these lines to the exchange interaction of four copper ions.

In the centre of the broad EPR line, at temperatures above 33 K, two separate signals with $g_1 = 2.402(5)$ and $g_2 = 2.037(5)$ begin to appear (figure 3, curves (b)–(d)). These signals correspond closely to previously reported lines (Guskos *et al* 1991a, Hoffman *et al* 1980) arising from Cu^{2+} ions in axial crystal-field symmetry, with a $d_{x^2-y^2}$ or d_{xy} ground-state wavefunction.

Figure 4 presents the temperature dependence of the EPR spectra of the non-oxygenated material (sample II). The spectra consist of the superposition of two lines: an isotropic line arising from the exchange interaction of Cu–Cu ion pairs (Guskos *et al* 1990b, 1991c) with $g = 2.212(5)$, $\Delta B = 0.040(1)$ T at 5 K and another line arising from Cu^{2+} ions in the axial local symmetry with $g_1 = 2.303(5)$, $g_2 = 2.076(5)$.

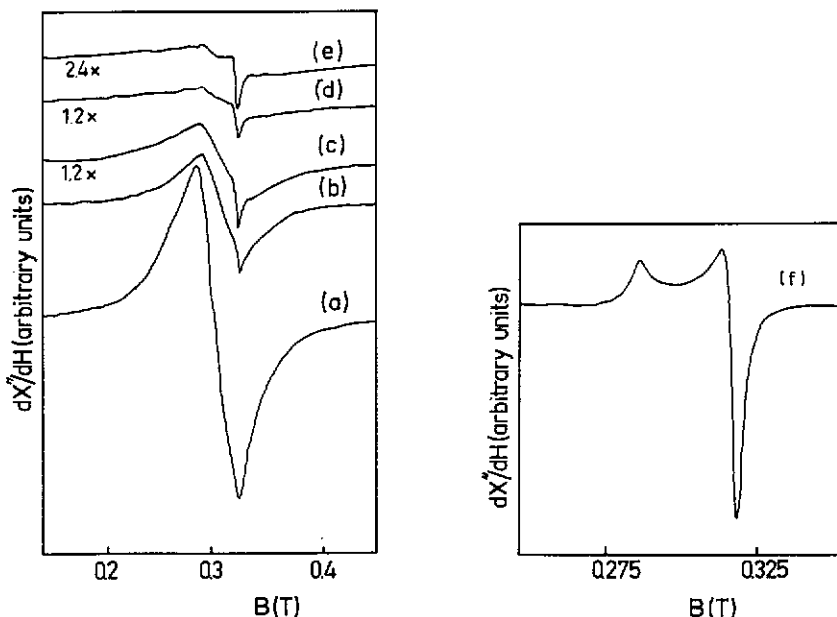


Figure 4. Temperature dependence of the EPR spectra for $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample II (tetragonal phase) at various temperatures: curve (a) 5 K; curve (b) 17 K; curve (c) 27 K; curve (d) 37 K; curve (e) 63 K; curve (f) RT.

Using relation (1) and related intensities from figure 4 for the line of the exchange interaction between pairs of Cu–Cu ions, we estimated that $J/k \approx 10$ K.

Recent measurements have shown (Hoffman *et al* 1990) that the existence of CuO in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramics does not affect the EPR spectra. The EPR spectrum of powdered BaCuO_2 at RT consists of a very weak signal of Cu^{2+} ions with spin-Hamiltonian parameters $g_z = 2.23$, $g_y = 2.12$, $g_x = 2.05$. At liquid-nitrogen temperature the BaCuO_2 spectrum is superimposed on a very broad line with $\Delta B_{pp} \approx 80$ mT centred at about $g_{\text{eff}} = 2.13$. This line narrows continuously on cooling to 5 K (Hoffman *et al* 1990). Our spectrum of Cu^{2+} ions in $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at RT is quite different (figure 4). Thus it could not be attributed to these spurious phases. The observed change in local symmetry of Cu^{2+} ions from orthorhombic (figure 2) to axial (figures 3 and 4) could only be the result of oxygen ordering.

If the ground state is $|x^2 - y^2\rangle$, then we have $g_{\parallel} > g_{\perp}$ and in the first approach the following relation is obtained:

$$(g_{\parallel} - 2)/(g_{\perp} - 2) \approx 4 \quad (3)$$

Our results, for the non-oxygenated sample (II) are in good agreement with this value. EPR measurements cannot identify whether the ground state is $|x^2 - y^2\rangle$ or $|xy\rangle$. The spin-Hamiltonian parameters g_{\parallel} and g_{\perp} (up to first order) may be given by the relations (Roy *et al* 1970)

$$g_{\parallel} = 2 - 8\lambda/\Delta_0 \quad (4a)$$

$$g_{\perp} = 2 - 2\lambda/\Delta_1 \quad (4b)$$

where the spin-orbit constant $\lambda = -829$ cm^{-1} for free Cu(II) ions. Δ_0 is the crystal-field-splitting energy between the ground state $|x^2 - y^2\rangle$ and the excited state $|xy\rangle$

and Δ_1 is the corresponding difference between degenerate $|x^2 - y^2\rangle$, and $|zy\rangle$, $|zx\rangle$ states for the d^9 configuration. Using (4) and the experimental values of g -parameters, the following values of Δ are obtained; $\Delta_0 = 21\,888\text{ cm}^{-1}$ and $\Delta_1 = 21\,816\text{ cm}^{-1}$. These values are larger than usual. However, the 3d and 4d ions are strongly coupled to the crystal environment. This coupling arises from the relative large extent of the 3d and 4d orbitals and the lack of shielding electrons in the high shells. The unpaired electron density a^2 of the Cu^{2+} ion (this parameter reflects the spin density) usually has the value 0.8 which leads to a spin-orbit constant $\lambda = a^2\lambda = -663\text{ cm}^{-1}$. The obtained values of Δ are $\Delta_0 = 17\,510\text{ cm}^{-1}$, $\Delta_1 = 17\,450\text{ cm}^{-1}$ and are consistent with previous reports (Abragam and Bleaney 1970).

In conclusion, the EPR spectrum of Cu^{2+} ions in the oxygenated samples shows orthorhombic symmetry and in the non-oxygenated sample local axial symmetry. In the latter material the results are consistent with an $|x^2 - y^2\rangle$ ground state. Evidently, the oxygen content and its ordering affects the valence of copper ions (Cava et al 1990) and their local symmetry. Additionally, our results indicate that heat treatments have a strong influence on the various interactions occurring in $\text{LaBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

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