



Magnetic properties of new oxides of the type $R_2Ba_2CuPtO_8$ ($R=Er$ and Lu)

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Abstract

The magnetic properties of these oxides have been studied by means of the magnetic susceptibility and magnetization measurements. Luthetium oxide behaves as an antiferromagnetic compound and the estimated Néel temperature is 5.2 K. However, the isostructural $Er_2Ba_2CuPtO_8$ is a ferromagnetic compound with a Curie temperature close to 25 K. The saturation magnetic moment obtained is 9.71 BM, lower than that expected for this oxide. The net maximum observed in the magnetic susceptibility at 3 K and the metamagnetic transition detected at 2 K in the M vs. H measurement are indicative of the magnetic phase transition from ferromagnetic to antiferromagnetic state. © 1998 Elsevier Science S.A.

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1. Introduction

During the synthesis of superconductor $RBa_2Cu_3O_{7-x}$ oxides as single crystals using the CuO flux method, different impurities were detected and identified as a new series of oxides containing rare earth, barium, copper and platinum [1]. Two new families of compounds with the stoichiometries $R_2Ba_2CuPtO_8$ and $R_2Ba_2Cu_2PtO_{10}$ have been reported and fully characterised by different authors [2–5]. More recently, it has also been found that attempts to prepare single crystals of R_2BaCuO_5 oxide in platinum crucibles lead to $R_2BaCu_{1-x}Pt_xO_5$ oxides, showing the so-called Nd_2BaPtO_5 structure type, where the Pt^{2+} and Cu^{2+} are randomly distributed in the $4j$ crystallographic sites of the $P4/mbm$ space group of this structure [6] and where the amount of x depends on the synthesis temperature [7].

The $R_2Ba_2CuPtO_8$ oxides crystallise with so-called $Y_2Ba_2CuPtO_8$ prototype, showing orthorhombic symmetry, space group $Pnma$ [2]. This structure is rather complex, it is formed by square pyramids (CuO_5) and distorted octahedra (PtO_6) which are connected to each other by

sharing corners, giving rise to double zigzag $O-Pt-O-Cu$ chains running parallel to the b -axis, as it is shown in Fig. 1. The rare earth atoms are located in two different crystallographic positions, but showing seven coordination.

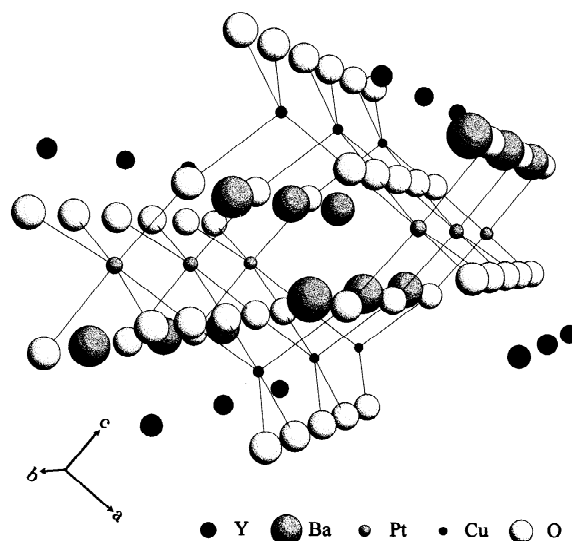


Fig. 1. Perspective view along b -axis of the $Y_2Ba_2CuPtO_8$ structural type.

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The main purpose of our work is the synthesis and study of the magnetic properties of two representative members of this series of compounds. In the case of the $\text{Lu}_2\text{Ba}_2\text{CuPtO}_8$ oxide the magnetic behaviour will be only due to Cu^{2+} , while in the case of the isostructural $\text{Er}_2\text{Ba}_2\text{CuPtO}_8$ the presence of paramagnetic Cu^{2+} will promote the magnetic interactions in the Er^{3+} sublattice and even the possibility of the Er^{3+} – Cu^{2+} interactions will also be analysed taking into account the different pathways through these interactions which could take place.

2. Experimental

The materials have been obtained as powdered samples from the stoichiometric amounts of BaCO_3 , CuO , R_2O_3 and Pt as fine powder. This mixture was heated in air at 1050°C for 10 days, with several intermediate grindings to homogenise the reaction products. The minor amounts of impurities detected from the X-ray diffraction data can be neglected regarding the magnetic properties, since the impurity $\text{Lu}_2\text{Ba}_4\text{O}_7$ identified in the case of the $\text{Lu}_2\text{Ba}_2\text{CuPtO}_8$ is diamagnetic, while in the case of the homologous compound, erbium, the small traces of Er_2BaO_4 identified do not show cooperative interactions [8].

X-ray diffraction data were obtained using a Philips Diffractometer PW1800. The data were analysed by the Rietveld method using the Fullprof program [9]. The lattice parameters obtained agree with those reported for these stoichiometric phases [8].

Magnetic susceptibility measurements have been done in the 1.9–300 K temperature range using a Quantum Design SQUID MPMS magnetometer. Magnetization measurements were made up to 90 KOe in a Quantum Design PPMS equipment at different temperatures.

3. Results and discussion

In Fig. 2 the variation of magnetic susceptibility for $\text{Lu}_2\text{Ba}_2\text{CuPtO}_8$ against temperature is shown. It can be observed that the susceptibility follows a Curie-Weiss law in a very wide temperature range from 250–10 K. The calculated magnetic moment, 2.06 BM, agrees with the expected value for Cu^{2+} with one unpaired electron located in the $d_{x^2-y^2}$ orbital, taking into account the square pyramidal coordination of Cu^{2+} . The negative value of the Weiss constant, -6.5 K, and the net maximum observed in the χ vs. T plot are indicative of the existence of antiferromagnetic interactions in the copper sublattice, with an estimated Néel temperature of 5.2 K. The analysis in detail of the structure, Fig. 1, shows that there are two main different pathways to explain these superexchange interactions. In both cases the sequence of atoms involved

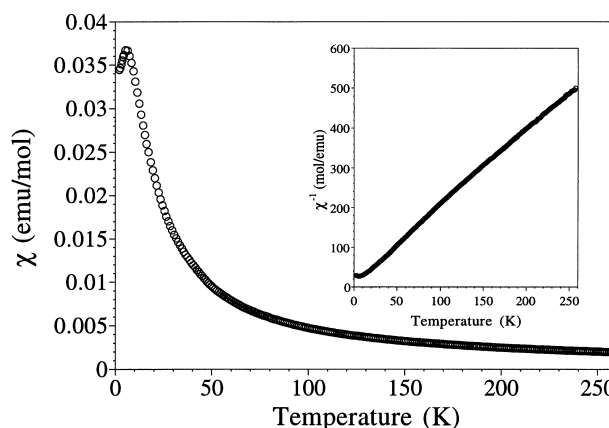


Fig. 2. Temperature dependence of the molar magnetic susceptibility for $\text{Lu}_2\text{Ba}_2\text{CuPtO}_8$, the inset is the χ^{-1} vs. T plot.

in the pathway is Cu-O-Pt-O-Cu along the b -axis, i.e., two (CuO_5) square pyramids are linked by a (PtO_6) octahedron. In one case, the two oxygen atoms involved in the superexchange are one axial and one equatorial of the (PtO_6) octahedron, giving rise to a zigzag pathway, and in the second case the oxygen atoms are two equatorial oxygens of the (PtO_6) octahedron. In both cases the angles are very far from 180° and the distances are similar, around 8 Å, which justifies the small value close to 5 K found for Néel temperature.

The substitution of the diamagnetic Lu^{3+} by the paramagnetic Er^{3+} strongly modifies the magnetic behaviour. In Fig. 3 the variation of the magnetic susceptibility for $\text{Er}_2\text{Ba}_2\text{CuPtO}_8$ is shown. It can be observed that the susceptibility obeys a Curie-Weiss behaviour in the 390–30 K temperature range and the obtained magnetic moment is 13.81 BM, which agrees well with the theoretical value expected for this compound taking into account the paramagnetic contribution of two Er^{3+} and the Cu^{2+} ions. Below 20 K the observed jump is due to the presence of ferromagnetic interactions. However, as it can be seen in

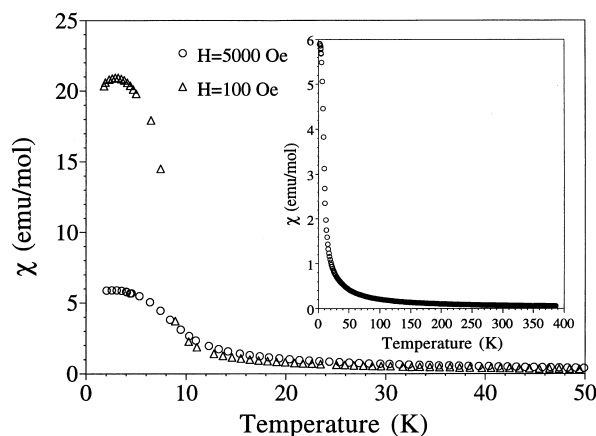


Fig. 3. Temperature dependence of the molar magnetic susceptibility for $\text{Er}_2\text{Ba}_2\text{CuPtO}_8$. The χ vs. T curve in the 1.9–390 K range is shown in the inset.

Fig. 3, below this temperature the susceptibility becomes field dependent and higher values are obtained at lower magnetic field, i.e., 100 Oe. At this field, a net maximum is also present at 3 K, while in the case of 5000 Oe the susceptibility remains constant below 4 K. This ferromagnetic behaviour is confirmed from the magnetization vs. field measurements, shown in Fig. 4. These data permit the determination of the Curie temperature which has a value of 25 K. Below this temperature the magnetization increase with the temperature and the saturation moment at 10 K and 90 KOe has a value of 9.72 BM. This value is smaller than the theoretical value of 12.77 BM expected for this oxide. Since the Er^{3+} ions are located in two crystallographic positions, the contribution to the magnetic moment appears to be a function of the erbium site and the obtained magnetic moment could be due mainly to one Er^{3+} ion. Similar results have been recently obtained in the case of the $\text{Yb}_2\text{BaNiO}_5$ oxide, where the saturation magnetic moment was explained taking into account mainly the magnetic contribution of the Yb(2), while the Yb(1) contribution is almost zero [10]. Neutron diffraction studies are now in progress in order to confirm this magnetic behaviour.

On the other hand, as can be observed in Fig. 4, the magnetization isotherms obtained at 2 K and 5 K are very close and above 40 KOe are almost coincident, which is indicative of the saturation. However, the analysis is illustrative of the data obtained at these temperatures below 5000 Oe. A crossover around 2500 Oe can be observed in Fig. 5 and the data obtained at 2 K become higher than those obtained at 5 K above this field as is expected for a ferromagnetic material. However, the data obtained below 2500 Oe for both temperatures are rather unusual for a ferromagnetic compound. A break is observed at about 150 Oe in the M vs. H plot obtained at 2 K and then the magnetization suddenly increases which is characteristic of a metamagnetic (field induced) transition. This could take place from an antiferromagnetic state, detected at 3 K in the susceptibility measurement taken at

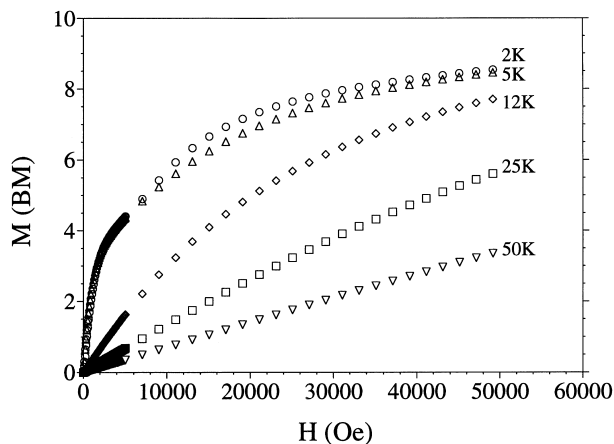


Fig. 4. Magnetization isotherms for $\text{Er}_2\text{Ba}_2\text{CuPtO}_8$.

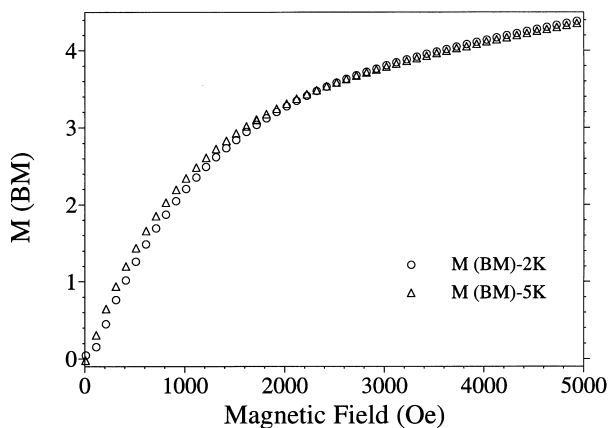


Fig. 5. Magnetization vs. magnetic field plots at 2 K and 5 K.

100 Oe, to a ferromagnetic state. The estimated critical field is as small as 170 Oe and at higher values the moments become aligned and above 2500 Oe both magnetization curves are almost identical.

This interpretation is the most coherent with our present data. We will continue the study with different isomorphous compounds of this series with different paramagnetic rare earth ions, as well as by means of neutron powder diffraction studies in order to observe the different magnetic structures at different temperatures and applied magnetic fields.

Acknowledgements

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