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Magnetic behavior of ErCrO_4 oxide

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Abstract

ErCrO_4 has been synthesized as a single phase by the nitrate precursor method under an oxygen flow at 753 K. The structure of this compound has been refined from X-ray and neutron powder diffraction data, showing the zircon-type structure, S.G. $I4_1/amd$ and lattice parameters $a=7.062(1)$ Å, $c=6.201(3)$ Å. Magnetic susceptibility and magnetization measurements reveal the existence of incipient ferromagnetic interactions in the Cr^{5+} sublattice below 25 K. When the temperature decreases, the superexchange $\text{Er}^{3+}-\text{O}-\text{Cr}^{5+}-\text{O}-\text{Er}^{3+}$ antiferromagnetic interactions become predominant. The estimated Néel temperature is 15 K. A metamagnetic transition has been detected at the critical field of 375 Oe. Neutron diffraction data show a three-dimensional antiferromagnetic ordering in which both Cr^{5+} and Er^{3+} sublattices are involved. Such ordering takes place with a propagation vector $\mathbf{k}=[0]$.

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1. Introduction

RCrO_4 oxides form a family of compounds where the chromium is stabilised in its rather unusual 5+-oxidation state. They crystallise in two structural types, depending on the size of the rare earth ion. The LaCrO_4 presents the monazite structure [1–3], while the remaining members of this series crystallise with the zircon-type structure, showing tetragonal symmetry, S.G. $I4_1/amd$ (No. 141) [4,5]. It is worth mentioning that the PrCrO_4 is dimorphic, and the zircon phase has just been successfully isolated [6].

Recently, it has been reported that both LaCrO_4 and NdCrO_4 behave as n-type semiconductors. The doping with Ca^{2+} to give the solid solutions $\text{Nd}_{1-x}\text{Ca}_x\text{CrO}_4$ ($x=0.2$) decreases the activation energy from 20 to 15 kJ mol⁻¹, due to operation of a hole hopping mechanism arising from the mixed valence state $\text{Cr}^{5+}-\text{Cr}^{6+}$ [7,8].

Although these RCrO_4 (R=Nd–Yb) oxides have been described as ferromagnets [9], our research work reveals that the magnetic properties of the RCrO_4 are strongly influenced by the external magnetic field [6]. By contrast, the RCrO_4 oxides (R=Sm, Eu and Lu) are antiferro-

magnets, while the NdCrO_4 remains paramagnetic down to 2 K [10].

These previous studies provide the RCrO_4 oxides with the proper scenario to delve into the influence of the magnetic field on their properties, which will throw light on the mechanism of the magnetic interactions between transition metal and lanthanide ions. As a representative example, the study of the magnetic properties of ErCrO_4 oxide is undertaken in this paper from susceptibility, magnetization and neutron diffraction data.

2. Experimental

ErCrO_4 oxide has been synthesized by the nitrate precursor method from the stoichiometric amounts of $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Merck) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck), according to the overall reaction:

The starting mixture was transferred to a porcelain boat and then placed in a tubular furnace. An oxygen flow is required to stabilize the unusual +5-oxidation state of the chromium ion. The heating sequence was: 30 min at 393 K, 30 min at 473 K and 24 h at 753 K. As the precursors

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Fig. 1. Perspective view of the zircon-type structure, showing the chains of edge-sharing RO_8 bisdisphenoids polyhedra, being connected by CrO_4 tetrahedra units.

melt below 373 K, the synthesis process is enhanced, taking place at a temperature as low as 753 K.

The product obtained is green-coloured, and the X-ray diffraction pattern shows the existence of the zircon-type as single phase.

Powder X-ray diffraction pattern was registered at a rate of $0.1^\circ (2\theta) \text{ min}^{-1}$ using a Philips X'Pert MPD, Ni filtered $\text{Cu K}\alpha$ radiation. A step scan of $0.04^\circ (2\theta)$ between 10° and 120° and a counting time of 15 s for each step was employed. Neutron diffraction powder diffraction data were collected using the D1B ($\lambda = 2.52 \text{ \AA}$) diffractometer at the Institut Laue Langevin (Grenoble, France) at different temperatures from 100 to 2 K over an angular range $15 < 2\theta < 95^\circ$ with a step of 0.2° . Diffraction data were

analysed with the Rietveld full-profile method using the FULLPROF program [11].

Magnetic susceptibility and magnetization measurements were performed in a Quantum Design XL-SQUID magnetometer, at different magnetic fields in the temperature range of 1.9–300 K. The susceptibilities were corrected for ionic diamagnetism using the values of $-18 \times 10^{-6} \text{ emu mol}^{-1}$ for Er^{3+} , $-12 \times 10^{-6} \text{ emu mol}^{-1}$ for O^{2-} and $-5 \times 10^{-6} \text{ emu mol}^{-1}$ for Cr^{5+} [12].

3. Results and discussion

3.1. Structural characterization

The ErCrO_4 oxide was characterized using both X-ray and neutron powder diffraction data. Fig. 1 shows the observed, calculated and difference profiles of neutron diffraction at 100 K for this compound. The ErCrO_4 crystallizes with the zircon-type structure, tetragonal symmetry, S.G. $I4_1/amd$ (No. 141). The final results of the FULLPROF refinement, including crystallographic parameters, the R -factors and main bond length distances, are presented in Table 1. As can be observed, the atoms occupy the following crystallographic sites: praseodymium in $4a$, chromium in $4b$ and oxygen in $16h$.

In this structure the Cr^{5+} cations present a tetrahedral coordination, while the R^{3+} ions are surrounded by eight oxygen atoms in the corners of a bisdisphenoid polyhedra. Edge-sharing (RO_8) bisdisphenoids form zig-zag chains along the a - and b -axes, being connected by (CrO_4) tetrahedra along the c -axis, see Fig. 2.

3.2. Magnetic measurements

The temperature dependence of the molar magnetic susceptibility for ErCrO_4 at 50 Oe is shown in Fig. 3. The experimental data follow a Curie–Weiss behaviour, $\chi = C/(T - \theta)$, in a wide range of temperature, 300–50 K. The

Table 1
Structural parameters obtained from the Rietveld refinement for ErCrO_4

Space group	$I4_1/amd$	Experimental bond lengths ($\text{\AA}$)	
a ($\text{\AA}$)	7.062(1)	Er–O	$2.261(3) \times 4$
c ($\text{\AA}$)	6.201(3)	Er–O	$2.393(1) \times 4$
Z	4	Cr–O	$1.714(5) \times 4$
V ($\text{\AA}^3$)	309.2(5)		
R_p	15.0		
R_{wp}	11.2		
R_b	5.0		
χ^2	2.3		
Atomic coordinates			
Er	$4a$ (0, 3/4, 1/8)		
Cr	$4b$ (0, 1/4, 3/8)		
O	$16h$ (0, y , z) $y = 0.433(5)$, $z = 0.199(5)$		

$$R_p = 100 \sum_i (Y_i - Y_{ci}) / \sum_i (Y_i); R_{wp} = [100 \sum_i (Y_i - Y_{ci})^2 / \sum_i (Y_i)^2]^{1/2}; R_B = 100 \sum_i (I_i - I_{ci}) / \sum_i (I_i); \chi^2 = (R_{wp} / R_{exp})^2.$$

Fig. 2. Neutron diffraction pattern of ErCrO_4 at 100 K.

obtained value of the effective magnetic moment of Er^{3+} after discounting the Cr^{5+} contribution is $9.6 \mu_B$, which agrees well with the theoretical one [13]. At 25 K the susceptibility shows a sudden increase, originating at net maximum at around 15 K, and then the χ decreases. This sharp increase can be ascribed to the presence of a ferromagnetic component. Moreover, an antiferromagnetic ordering in which both Er^{3+} and Cr^{5+} sublattices are involved takes place below 15 K.

Fig. 4 shows the variation of the magnetic susceptibility with the temperature at different magnetic fields for the ErCrO_4 oxide. As can be observed, the susceptibility data

are field-dependent below 20 K. The Néel temperature diminishes from 15 to 14 K when increasing the applied magnetic field up to 200 Oe. Furthermore, this maximum disappears at 1000 Oe, although the ferromagnetic component persists. However, at 10,000 Oe this component has decreased and the antiferromagnetic ordering has been removed [6].

The magnetization versus the applied magnetic field plot at different temperatures is shown in Fig. 5. A ferromagnetic component is present at 2 K and at 17 K. However, a linear variation is obtained at 30 K, in agreement with the paramagnetic behaviour of this oxide at that temperature.

Fig. 3. Temperature dependence of the molar magnetic susceptibility at 50 Oe for ErCrO_4 . The inset is the χ^{-1} vs. T plot.

Fig. 4. Variation of the molar magnetic susceptibility with the temperature at different magnetic fields for ErCrO_4 .

The M vs. H plot up to 2000 Oe at 2 K and 15 K is very illustrative (Fig. 6), and a clear cross-over around 300 Oe is observed. The magnetization at 2 K corresponds with an S-shape curve characteristic of metamagnetic transitions [13]. The data fit a straight line up to 250 Oe. This result is an intrinsic feature of an antiferromagnetic behaviour. However, at a field higher than 375 Oe, the magnetization suddenly increases as a consequence of the spin reorientation in the metamagnetic transition. The saturation moment estimated by extrapolation to zero-magnetic field is $5.2 \mu_B$, which indicates that the Er^{3+} sublattice is also involved in the mentioned reorientation.

The magnetization vs. H plot at 15 K shows the presence of a ferromagnetic component of $0.3 \mu_B$ originated in the Cr^{5+} sublattice, which is reoriented by the anisotropy of the Er^{3+} at lower temperatures, where the compound behaves as antiferromagnetic. This result justifies the cross-over of both 2 K and 15 K curves at around 350 Oe.

The critical field (H_c) can be better visualized when the dM/dH is represented versus H as in Fig. 7. This H_c is slightly temperature-dependent and takes the values of 375 and 325 Oe at 2 K and 6 K, respectively.

The detailed analysis of the structure allows us to

Fig. 5. M vs. H plot at different temperatures.

Fig. 6. M vs. H plot up to 2500 Oe at different temperatures.

establish the possible pathways through which the mentioned antiferromagnetic interactions take place. As can be observed in Fig. 8, several pathways are possible to explain the superexchange interactions between both the Er^{3+} and the Cr^{5+} sublattices. Below 25 K, the super-superexchange sequence $\text{Cr}^{5+}-\text{O}-\text{O}-\text{Cr}^{5+}$ is responsible for the incipient ferromagnetic interactions. Such interactions are rather weak due to the poor orbital overlap, because two oxygens are involved in the magnetic exchange, originating a very large $\text{Cr}^{5+}-\text{Cr}^{5+}$ distance (3.86 Å), with angles far from 180° . When lowering the tempera-

ture the superexchange antiferromagnetic interactions $\text{Er}^{3+}-\text{O}-\text{Cr}^{5+}-\text{O}-\text{Er}^{3+}$ (mechanism I and II) become operative, overcoming the ferromagnetic ordering in the Cr^{5+} sublattice at the Néel temperature, which justifies the magnetic trend found in the susceptibility and magnetization measurements.

Neutron diffraction experiments at different temperatures between 100 and 2 K reveal the progressive increase in intensity of certain nuclear reflections when the temperature decreases. However, no extra reflections are observed in the low temperature pattern (Fig. 9). The

Fig. 7. Variation of the dM/dH with the applied magnetic field.

Fig. 8. Scheme of the two proposed superexchange mechanisms for the ErCrO_4 oxide.

determined Néel temperature of 15 K agrees well with the one estimated from the magnetic susceptibility data. The magnetic contribution can be clearly visualized in Fig. 9 as the difference between the refined pattern taking into account the nuclear contribution and the overall experimental neutron diffraction pattern. The magnetic contribution to these reflections comes from Er^{3+} and Cr^{5+} sublattices, which present magnetic moments of $9 \mu_B$ and $1 \mu_B$, respectively. This antiferromagnetic transition yields a magnetic structure which can be described by a propagation vector $\mathbf{k}=[0]$.

We are currently determining the magnetic structure by using the analysis of the irreducible representation method [14].

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Fig. 9. Intensity differences between the nuclear and magnetic reflections at 100 and 2 K. Magnetic contribution is marked by an asterisk.