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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. $I$4/ 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$^{3+}$ sublattice below 25 K. When the temperature decreases, the superexchange Er$^{3+}$–O–Cr$^{3+}$–O–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$^{3+}$ and Er$^{3+}$ sublattices are involved. Such ordering takes place with a propagation vector $k=[0]$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Magnetically ordered materials; X-ray diffraction; Neutron diffraction; Exchange and superexchange; Magnetic measurements

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. $I$4/ amd (No. 141) [4,5]. It is worth mentioning that the PrCrO$_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 Nd$_{1-x}$Ca$_x$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 Cr$^{3+}$–Cr$^{5+}$ [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 antiferromagnets, 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 Er(NO$_3$)$_3$·6H$_2$O (Merck) and Cr(NO$_3$)$_3$·9H$_2$O (Merck), according to the overall reaction:

$$\text{Er(NO}_3\text{)}_3 \cdot 6\text{H}_2\text{O} + \text{Cr(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} = \text{ErCrO}_4 + 6\text{NO}_2 + 15\text{H}_2\text{O}$$

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...
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 $-18 \times 10^{-6}$ emu mol$^{-1}$ for Er$^{3+}$, $-12 \times 10^{-6}$ emu mol$^{-1}$ for O$^{2-}$ and $-5 \times 10^{-6}$ emu mol$^{-1}$ for Cr$^{3+}$ [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 4$_a$, chromium in 4$_b$ and oxygen in 16$_h$.

In this structure the Cr cations present a tetrahedral coordination, while the R ions are surrounded by eight oxygen atoms in the corners of a bisdisphenoid polyhedra. Edge-sharing (RO$_4$) 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

<table>
<thead>
<tr>
<th>Space group</th>
<th>$I4_1/amd$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>7.062(1)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>6.201(3)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>309.2(5)</td>
</tr>
<tr>
<td>$R_1$</td>
<td>15.0</td>
</tr>
<tr>
<td>$R_{wp}$</td>
<td>11.2</td>
</tr>
<tr>
<td>$R_b$</td>
<td>5.0</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>2.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atomic coordinates</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Er</td>
<td>4$a$ (0, 3/4, 1/8)</td>
</tr>
<tr>
<td>Cr</td>
<td>4$b$ (0, 1/4, 3/8)</td>
</tr>
<tr>
<td>O</td>
<td>16$h$ (0, y, z) $y = 0.433(5), z = 0.199(5)$</td>
</tr>
</tbody>
</table>

Experimental bond lengths (Å)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er–O</td>
<td>2.261(3)×4</td>
</tr>
<tr>
<td>Er–O</td>
<td>2.393(1)×4</td>
</tr>
<tr>
<td>Cr–O</td>
<td>1.714(5)×4</td>
</tr>
</tbody>
</table>
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 \(\chi\) 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\(_3\) 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.
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$^{3+}$ 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
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\(^{3+}\) sublattices. Below 25 K, the superexchange sequence Cr\(^{5+}\)-O-O-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 Cr\(^{5+}\)-Cr\(^{5+}\) distance (3.86 Å), with angles far from 180°. When lowering the temperature the superexchange antiferromagnetic interactions Er\(^{3+}\)-O-Cr\(^{5+}\)-O-Er\(^{3+}\) (mechanism I and II) become operative, overcoming the ferromagnetic ordering in the Cr\(^{3+}\) 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. 6. M vs. H plot up to 2500 Oe at different temperatures.](image)

![Fig. 7. Variation of the dM/dH with the applied magnetic field.](image)
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$^{3+}$ 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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References