Synthesis, structural characterization and magnetic properties of RCrO$_4$ oxides, R=Nd, Sm, Eu and Lu

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Abstract

This paper reports the specific conditions used in the preparation of RCrO$_4$ oxides, R=Nd, Sm, Eu and Lu, the structural determination, and the study of their magnetic behaviour. The structure of these compounds has been refined from X-ray powder diffraction by the Rietveld method, assigning the zircon type, space group I$_4$/amd. A linear decrease has been observed in the lattice parameters from NdCrO$_4$ to LuCrO$_4$, according to the lanthanide contraction. Magnetic susceptibility measurements reveal the existence of an antiferromagnetic ordering in which both Cr$^{3+}$ and R$^{3+}$ sublattices are involved. In the case of NdCrO$_4$, the estimated Néel temperature appears to be lower than 2 K; for the remaining oxides, it is 14.9 K, 15.9 K and 9.9 K for Sm, Eu and Lu, respectively. A superexchange mechanism has been proposed to explain such a magnetic behaviour. The pathways through which these interactions take place have also been analysed, taking into account the structural features that these oxides present. The Cr$^{3+}$ plays an important role as a promoter of these interactions in the R$^{3+}$ sublattice.

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

1. Introduction

The RXO$_4$ compounds, where R is a trivalent rare-earth ion and X is phosphorous, arsenic and vanadium have been intensively investigated for their attractive crystallographic, magnetic and luminescent properties [1–5]. They crystallise in two different structural types, depending on the size of both R and X. The majority of the RPO$_4$ compounds, with R=La–Tb, adopts the monazite type, space group P2$_1$/n, together with the first member of the vanadates, LaVO$_4$. The remaining members of both families of compounds crystallise with the so-called zircon-type structure, showing tetragonal symmetry, space group I$_4$/amd.

As far as we know, few studies have been carried out concerning the RCrO$_4$ oxides, probably due to the difficulty in preparing pure samples. In fact, single crystals have still not been obtained, because of the instability of the Cr$^{5+}$ at the synthesis temperatures. In this sense, it is remarkable that these phases decompose in air at 600°C.

RCrO$_4$ oxides form a family of compounds that crystallise with two structural types: LaCrO$_4$ shows monazite structure [6,7], while from Pr to Lu the RCrO$_4$ compounds crystallise with the zircon type [8]. This fact corresponds with the structural features observed in the vanadates. However, the PrCrO$_4$ is dimorphic and adopts both structures simultaneously [9]. Attempts to isolate one of the above-mentioned phases in the PrCrO$_4$ oxide have been unsuccessful up to now.

In this paper we report the specific conditions used in the preparation of RCrO$_4$ oxides, R=Nd, Sm, Eu and Lu, as pure phases, and a detailed analysis of the structure is also included. All these compounds are isostructural showing the zircon-type structure [10–12], which can be described as built up by chains of edge-sharing distorted (RO$_4$) bisdisphenoids running parallel to the a-axis connected by CrO$_4$ tetrahedra, sharing edges along the c-axis, as can be seen in Fig. 1(a). The ab plane is shown in Fig. 1(b), where the presence of rows RCrO$_4$ connected by corners, can be visualized along the b-axis.

2. Experimental

The samples were prepared by heating stoichiometric amounts of R(NO$_3$)$_3$·6H$_2$O and Cr(NO$_3$)$_3$·9H$_2$O, follow-
The products obtained are green, and the X-ray diffraction patterns show the existence of single phases in all the cases.

Powder X-ray diffraction patterns were registered at a rate of 0.1° (2θ) min⁻¹ using a Philips X’Pert MPD, Ni filtered CuKα radiation. A step scan of 0.04° (2θ) in the range 10°–120° and a counting time of 15 s for each step was employed. Rietveld full-profile refinement was done using the FULLPROF program [13].

Magnetic susceptibility measurements were performed in a Quantum Design XL-SQUID magnetometer at 100 Oe between 1.7 and 300 K. The susceptibilities were corrected for ionic diamagnetism using the values of -20×10⁻⁶ emu mol⁻¹ for R³⁺, -12×10⁻⁶ emu mol⁻¹ for O²⁻ and -5×10⁻⁶ emu mol⁻¹ for Cr⁵⁺ [14].

3. Results and discussion

3.1. Structural characterization

The structures of these oxides have been refined from X-ray powder diffraction patterns using the Rietveld method (FULLPROF program), starting from the isostructural phase YVO₄ [15]. The reflection conditions are compatible with the space group I₄/amd (Z=4). The atoms occupy the following positions: rare earth in 4a (0, 3/4, 1/8), chromium in 4b (0, 1/4, 3/8) and oxygen in 16h (0, y, z).

The final results of this refinement are presented in Table 1 (for the crystallographic parameters and the R factors), and Table 2 (for the bond length distances). Figs. 2 and 3 show, as examples, the observed, calculated and difference X-ray profiles of powder diffraction for Nd and Eu oxides.

As can be observed in Table 1, the lattice parameters of these phases decrease linearly with the reduction of the ionic radius of the rare earth from Nd to Lu, according to the lanthanide contraction. The R ions are centred in their respective distorted bisdisphenoids with an octa-coordination, while the coordination of Cr is tetrahedral (Table 2).

3.2. Magnetic measurements

Amongst the members of this family of compounds, LuCrO₄ presents the simplest magnetic behaviour, since only the Cr⁵⁺ contribution must be considered. The temperature dependence of magnetic susceptibility for LuCrO₄ is shown in Fig. 4. The susceptibility obeys a Curie-Weiss behaviour in the temperature range 40–300 K and the effective magnetic moment calculated from the slope of the straight line is 1.61μₜₕ. Such a value is lower than the calculated one considering the spin only contribution for Cr⁵⁺ with S = 1/2, which is 1.73μₜₕ. This difference can be explained by taking into account the fact that the crystal field ground state of Cr⁵⁺ in tetrahedral
Table 1
Rietveld refinement data for RCrO₄, R = Nd, Sm, Eu and Lu⁴

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit cell parameters</th>
<th>Oxygen position</th>
<th>Reliability factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R₀ (Å)</td>
<td>c (Å)</td>
<td>y</td>
</tr>
<tr>
<td>Nd</td>
<td>7.305(2)</td>
<td>6.394(7)</td>
<td>0.426(1)</td>
</tr>
<tr>
<td>Sm</td>
<td>7.244(4)</td>
<td>6.347(7)</td>
<td>0.429(3)</td>
</tr>
<tr>
<td>Eu</td>
<td>7.218(2)</td>
<td>6.327(3)</td>
<td>0.428(2)</td>
</tr>
<tr>
<td>Lu</td>
<td>7.020(4)</td>
<td>6.193(1)</td>
<td>0.431(5)</td>
</tr>
</tbody>
</table>

⁴ Rᵣ = 100 Σ (yᵢ - yᵢ) / Σ (yᵢ); Rₑₚ = [100 Σ (yᵢ - yᵢ) / Σ (yᵢ)]¹/²; Rₑ = 100 Σ (Iᵢ - Iᵢ) / Σ (Iᵢ).

Table 2
Interatomic distances (Å) for RCrO₄, R = Nd, Sm, Eu and Lu

<table>
<thead>
<tr>
<th>R</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>R–O</td>
<td>2.422(5)×4</td>
<td>2.382(5)×4</td>
<td>2.385(1)×4</td>
<td>2.310(2)×4</td>
</tr>
<tr>
<td>R–O</td>
<td>2.503(4)×4</td>
<td>2.485(1)×4</td>
<td>2.484(1)×4</td>
<td>2.486 (5)×4</td>
</tr>
<tr>
<td>Cr–O</td>
<td>1.667(1)×4</td>
<td>1.673(5)×4</td>
<td>1.653 (3)×4</td>
<td>1.597 (5)×4</td>
</tr>
</tbody>
</table>

coordination is ⁴E. This term is mixed with the higher-lying ⁴T excited state via spin-orbit coupling, giving rise to a magnetic moment that depends on both the orbit coupling constant A and the 10 Dq value [16]. Since Cr⁵⁺ has just one unpaired electron and the A constant is positive, the experimental value of 1.61μ₀ can be fully justified. Moreover, the net maximum observed at 9.9 K and the negative value of the Weiss constant θ = −7.84 K (Table 3) is indicative of the existence of antiferromagnetic interactions in the Cr⁵⁺ sublattice.

A detailed analysis of the structure is important to establish the possible pathways through which these interactions take place. The superexchange interactions are quite complex, since the CrO₄ tetrahedra are isolated from each other by the diamagnetic LuO₈ bisdisphenoids. The pathways include the sequences Cr⁵⁺→O→O→Cr⁵⁺ or Cr⁵⁺→O→Lu→O→Cr⁵⁺, being diamagnetic atoms involved in both cases (Fig. 5). The bond angles are very different to 180° and the Cr–Cr distance presents a value of 6.4 Å, yielding a poor overlap of the d-orbitals. This fact could justify the low Néel temperature estimated for LuCrO₄ (9.9 K).

The variation of the magnetic susceptibility with the temperature for SmCrO₄ and EuCrO₄ is shown in Figs. 6 and 7, respectively. The presence of a net maximum at 14.9 K and 15.9 K can be attributed to the existence of antiferromagnetic interactions in which both R⁵⁺ and Cr⁵⁺ sublattices are involved. The influence of the temperature on the magnetic susceptibility for these RCrO₄ oxides (R = Sm and Eu) above 40 K can be explained considering the Cr⁵⁺ paramagnetic contribution and the characteristic magnetic behaviour of Sm⁳⁺ and Eu⁳⁺. It is well known that the spacing of the multiplet levels are not large compared to kT, which implies that not all the ions are in their ground state, so the excited states should be taken into consideration in the calculations of the magnetic interactions.

Fig. 2. X-ray diffraction pattern for NdCrO₄.
Fig. 3. X-ray diffraction pattern for EuCrO$_4$.

Fig. 4. Temperature dependence of the molar magnetic susceptibility for LuCrO$_4$. The inset is the $\chi^{-1}$ vs. $T$ plot.

Table 3

<table>
<thead>
<tr>
<th>R</th>
<th>$\mu_0$ ((\mu_B))</th>
<th>$\mu_\text{m}$ ((\mu_B))</th>
<th>$T_\text{N}$ (K)</th>
<th>$\theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>4.06</td>
<td>4.02</td>
<td>–</td>
<td>–54.5</td>
</tr>
<tr>
<td>Sm</td>
<td>2.38*</td>
<td>2.36*</td>
<td>14.9</td>
<td>–</td>
</tr>
<tr>
<td>Eu</td>
<td>3.75*</td>
<td>3.89*</td>
<td>15.9</td>
<td>–</td>
</tr>
<tr>
<td>Lu</td>
<td>1.61</td>
<td>1.59</td>
<td>9.9</td>
<td>–7.84</td>
</tr>
</tbody>
</table>

* At room temperature.

The magnetic moments obtained at room temperature agree with those calculated for these oxides, after discounting the Cr$^{3+}$ contribution obtained from the LuCrO$_4$ (Table 3).

The antiferromagnetic interactions assigned to the Sm, Eu and Lu phases contrast with the ferromagnetic behaviour reported for the remaining isostructual zircon-type RCrO$_4$ compounds, where R=Gd–Yb [18]. Moreover, in the case of the isostructural RXO$_4$, where X is a diamagnetic cation, cooperative interactions have not been de-
detected in the rare earth sublattice down to 4.2 K [10,19,20]. This fact indicates the important role that the Cr$^{5+}$ plays as a promoter of the ferro- or antiferromagnetic interactions in the rare earth sublattice.

The temperature dependence of the reciprocal molar magnetic susceptibility between 2 and 300 K for NdCrO$_4$ is shown in Fig. 8. The variation of the susceptibility in this oxide obeys the Curie–Weiss law from 300 to 50 K approximately. The downwards deviation in the $\chi^{-1}$ vs. $T$ observed below 20 K and the negative value of the Weiss constant (Table 3) can be ascribed to the crystal field effects. Similar results have been reported earlier for different neodymium oxides for which non-cooperative interactions are operative [19,20]. However, the small value of $\chi T$ obtained at 2 K (Fig. 8, inset), which is only 0.11 emu K mol$^{-1}$, indicates that antiferromagnetic interactions could be operating at these low temperatures.

Taking into account the obtained results and structural description of these compounds, it is very important to establish the mechanism through which the antiferromagnetic interactions take place. Direct $R^{3+}$-$R^{3+}$ and/or superexchange of the type $R$–O–R between the RO$_4$ units, which share edges forming chains along the $a$-axis, must be considered. However, this type of interaction should be
neglected, since, as was mentioned earlier in the case of the isostructural RXO₄, where X=P, V and As, they are not operative down to 4.2 K [21]. The reason for such behaviour is mainly due to the 4f orbitals being well-shielded by the outer 5s and 5p. A more realistic mechanism should involve the CrO₄ tetrahedra that connect the RO₈ rows, originating two superexchange pathways of the type R¹⁺−O−Cr⁵⁺−O−R¹⁺, as can be observed in Fig. 5.

The so-called mechanism I implies an intrachain coupling along the a-axis, while mechanism II considers interchain interactions between the RO₈ bidisphenoids connected via CrO₄ tetrahedra, producing a R¹⁺−R¹⁺ distance of 6.354(1) Å in the case of the samarium compound. Since both mechanisms are operative, a three-dimensional character must be proposed for these interactions. Both the relatively large R¹⁺−R¹⁺ distances obtained in these

Fig. 7. Variation of the molar magnetic susceptibility with temperature for EuCrO₄.

![EuCrO₄](image1)

Fig. 8. Temperature dependence of the reciprocal molar susceptibility of NdCrO₄. The inset is the $\chi T$ vs. $T$ plot.
compounds and the superexchange angle, which is very different to $180^\circ$, justify the low values of the estimated Néel temperatures, see Table 3.

Neutron diffraction experiments are now in progress, in the case of LuCrO$_4$ and NdCrO$_4$, in order to get a deeper knowledge of the low-temperature magnetic behaviour and to solve the magnetic structure of these oxides.

Acknowledgements

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References