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Document Version

Final published version

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Citation for published version (APA):

Jimenez-Melero, E., Isasi, J., & Saez-Puche, R. (2000). Synthesis, structural characterization and magnetic properties of RCrO_4 oxides, $\text{R}=\text{Nd}$, Sm , Eu and Lu . *Journal of Alloys and Compounds*, 312(1-2), 53–59.

Published in:

Journal of Alloys and Compounds

Citing this paper

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Synthesis, structural characterization and magnetic properties of RCrO_4 oxides, $\text{R}=\text{Nd}, \text{Sm}, \text{Eu}$ and Lu

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Received 30 May 2000; accepted 21 June 2000

Abstract

This paper reports the specific conditions used in the preparation of RCrO_4 oxides, $\text{R}=\text{Nd}, \text{Sm}, \text{Eu}$ 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 $I4_1/amd$. 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^{5+} 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^{5+} plays an important role as a promoter of these interactions in the R^{3+} sublattice. © 2000 Elsevier Science B.V. All rights reserved.

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 $\text{R}=\text{La}-\text{Tb}$, 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 $I4_1/amd$.

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 crys-

tallise 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, $\text{R}=\text{Nd}, \text{Sm}, \text{Eu}$ 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_8) 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 RO_8/CrO_4 connected by corners, can be visualized along the b -axis.

2. Experimental

The samples were prepared by heating stoichiometric amounts of $\text{R}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, follow-

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Fig. 1. (a) Perspective view of the zircon-type structure showing the chains of edge-sharing (RO_8) bisdisphenoids polyhedra along the a -axis connected by CrO_4 tetrahedra. (b) Projection of the structure considering two chains, constituted by RO_8 groups.

ing the thermal scheme: 30 min at 433 K, 30 min at 473 K and 60 min at 853 K. An oxygen flow is used in order to stabilise the 5+-oxidation state in the chromium. The reaction takes place according to:

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 $0.1^\circ (2\theta) \text{ min}^{-1}$ using a Philips X'Pert MPD, Ni filtered $CuK\alpha$ radiation. A step scan of $0.04^\circ (2\theta)$ 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 $-20 \times 10^{-6} \text{ emu mol}^{-1}$ for R^{3+} , $-12 \times 10^{-6} \text{ emu mol}^{-1}$ for O^{2-} and $-5 \times 10^{-6} \text{ emu mol}^{-1}$ for Cr^{5+} [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 YVO_4 [15]. The reflection conditions are compatible with the space group $I4_1/amd$ ($Z=4$). 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, $LuCrO_4$ presents the simplest magnetic behaviour, since only the Cr^{5+} contribution must be considered. The temperature dependence of magnetic susceptibility for $LuCrO_4$ 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 $1.61 \mu_B$. Such a value is lower than the calculated one considering the spin only contribution for Cr^{5+} with $S = 1/2$, which is $1.73 \mu_B$. This difference can be explained by taking into account the fact that the crystal field ground state of Cr^{5+} in tetrahedral

Table 1
Rietveld refinement data for RCrO_4 , R=Nd, Sm, Eu and Lu^a

Compound R	Unit cell parameters		Oxygen position		Reliability factors			
	<i>a</i> (Å)	<i>c</i> (Å)	<i>y</i>	<i>z</i>	<i>R_p</i>	<i>R_{wp}</i>	<i>R_b</i>	<i>R_{exp}</i>
Nd	7.305(2)	6.394(7)	0.426(1)	0.210(2)	12.6	16.4	5.4	4.7
Sm	7.244(4)	6.347(7)	0.429(3)	0.208(1)	12.3	15.9	4.8	5.5
Eu	7.218(2)	6.327(3)	0.428(2)	0.210(5)	11.5	15.0	5.4	5.7
Lu	7.020(4)	6.193(1)	0.431(5)	0.219(5)	13.8	18.4	6.3	5.4

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

Table 2
Interatomic distances (Å) for RCrO_4 , R=Nd, Sm, Eu and Lu

R	Nd	Sm	Eu	Lu
R–O	2.422(5)×4	2.382(5)×4	2.385(1)×4	2.310(2)×4
R–O	2.503(4)×4	2.485(1)×4	2.484(1)×4	2.486 (5)×4
Cr–O	1.667(1)×4	1.673(5)×4	1.653 (3)×4	1.597 (5)×4

coordination is 2E . This term is mixed with the higher-lying 2T excited state via spin-orbit coupling, giving rise to a magnetic moment that depends on both the orbit coupling constant λ and the 10 Dq value [16]. Since Cr^{5+} has just one unpaired electron and the λ constant is positive, the experimental value of $1.61\mu_B$ can be fully justified. Moreover, the net maximum observed at 9.9 K and the negative value of the Weiss constant $\theta = -7.84$ K (Table 3) is indicative of the existence of antiferromagnetic interactions in the Cr^{5+} 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 CrO_4 tetrahedra are isolated from

each other by the diamagnetic LuO_8 bisdisphenoids. The pathways include the sequences $\text{Cr}^{5+}-\text{O}-\text{O}-\text{Cr}^{5+}$ or $\text{Cr}^{5+}-\text{O}-\text{Lu}-\text{O}-\text{Cr}^{5+}$, 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 LuCrO_4 (9.9 K).

The variation of the magnetic susceptibility with the temperature for SmCrO_4 and EuCrO_4 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 R^{3+} and Cr^{5+} sublattices are involved. The influence of the temperature on the magnetic susceptibility for these RCrO_4 oxides (R=Sm and Eu) above 40 K can be explained considering the Cr^{5+} paramagnetic contribution and the characteristic magnetic behaviour of Sm^{3+} and Eu^{3+} . 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

Fig. 2. X-ray diffraction pattern for NdCrO_4 .

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 χ^{-1} vs. T plot.

Table 3

Observed (μ_0) and theoretical (μ_t) magnetic moments, Weiss constant (θ) and Néel temperature (T_N) for RCrO_4 oxides, R=Nd, Sm, Eu and Lu

R	$\mu_0(\mu_B)$	$\mu_t(\mu_B)$	T_N (K)	θ (K)
Nd	4.06	4.02	—	−45.5
Sm	2.38 ^a	2.36 ^a	14.9	—
Eu	3.75 ^a	3.89 ^a	15.9	—
Lu	1.61	1.59	9.9	−7.84

^a At room temperature.

susceptibility [17]. The magnetic moments obtained at room temperature agree with those calculated for these oxides, after discounting the Cr^{5+} 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 isostructural 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-

Fig. 5. Scheme of the two proposed superexchange pathways of the type R–O–Cr–O–R for the RCrO_4 oxides.

tected 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 χ^{-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 χT obtained at 2 K (Fig. 8, inset), which is only $0.11 \text{ emu K mol}^{-1}$, 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 $\text{R}^{3+}\text{--R}^{3+}$ and/or superexchange of the type R–O–R between the RO_8 units, which share edges forming chains along the a -axis, must be considered. However, this type of interaction should be

Fig. 6. Variation of the molar magnetic susceptibility with temperature for SmCrO_4 .

Fig. 7. Variation of the molar magnetic susceptibility with temperature for EuCrO_4 .

neglected, since, as was mentioned earlier in the case of the isostructural RXO_4 , where $X = \text{P}, \text{V}$ 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 CrO_4 tetrahedra that connect the RO_8 rows, originating two superexchange pathways of the type $\text{R}^{3+}-\text{O}-\text{Cr}^{5+}-\text{O}-\text{R}^{3+}$, 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 RO_8 bidisphenoids connected via CrO_4 tetrahedra, producing a $\text{R}^{3+}-\text{R}^{3+}$ 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 $\text{R}^{3+}-\text{R}^{3+}$ distances obtained in these

Fig. 8. Temperature dependence of the reciprocal molar susceptibility of NdCrO_4 . The inset is the χT vs. T plot.

compounds and the superexchange angle, which is very different to 180° , 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

We thank CICYT for financial support, under Project No. MAT-97-0697-C02-01.

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