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Magnetism of $RCaCrO_4$ (R: Pr, Nd, Sm and Eu) oxides

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Abstract

$SmCaCrO_4$ and $EuCaCrO_4$ oxides have been characterized by means of X-ray powder diffraction and magnetization measurements. Both oxides present a distorted K_2NiF_4-type structure with orthorhombic symmetry, space group *Bmab*. The orthorhombic strain in the $RCaCrO_4$ (R: Pr–Eu) oxides increases with decreasing R^{3+} ion size, taking the S_o parameter values of 4.0×10^{-3} and 13.3×10^{-3} for praseodymium and europium compounds, respectively. Samarium and europium compounds show antiferromagnetic behavior on the chromium sublattice with an estimated T_N of 150 and 160 K, respectively. The observed $T_N^{Cr^{3+}}$ variation in the $RCaCrO_4$ (R: Pr–Eu) oxides has been explained taking into account the competition between intra and interlayer magnetic interactions that take place in the CrO_2 layers of the structure. Concerning the rare earth sublattice, the Sm^{3+} ions present antiferromagnetic order below 3 K while the Eu^{3+} ions remain magnetically disordered because of their non-magnetic ground state.

Keywords: $RCaCrO_4$ oxides; Orthorhombic distortion; Antiferromagnetic order

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1. Introduction

In two previous papers [1,2] we have reported the preparation of $RCaCrO_4$ oxides with R: Pr and Nd as pure phases and their characterization by means of neutron powder diffraction and magnetization measurements. Both oxides present at room temperature (RT) a distorted K_2NiF_4-type structure, with orthorhombic symmetry, space group *Bmab*.

From the magnetic point of view, both oxides show antiferromagnetic ordering in the chromium sublattices below RT. In the case of the $PrCaCrO_4$ oxide [1], a Néel temperature of 182 K has been determined from magnetic susceptibility measurements. Below this temperature, the magnetic structure of this oxide has been explained on the basis of a propagation vector $\boldsymbol{k}=\boldsymbol{0}$. The magnetic moments of the Cr^{3+} ions are ordered along either [100] or [010] direction, with a symmetry mode G_x or C_yF_z ($F_z=0$), respectively. The antiferromagnetic ordered magnetic moment determined at 1.5 K is 2.38(9) μ_B. On the other hand, magnetization versus temperature measurements reveal temperature-independent paramagnetism below 30 K, owing to the non-magnetic ground term of Pr^{3+} ion under the influence of the crystal field. This non-magnetic nature of the ground term of Pr^{3+} has been confirmed [3] by simulation of the magnetic susceptibility by means of the simple overlap model (SOM) [4] considering the non-diagonal elements of the van Vleck equation.

$NdCaCrO_4$ oxide [2] presents antiferromagnetic ordering in the chromium sublattices around 170 K from magnetic susceptibility measurements. The magnetic structure of $NdCaCrO_4$ below 170 K is the same as that one proposed for $PrCaCrO_4$ oxide. However, a spin reorientation has been characterized at 30 K, that consists of the gradual appearance of an antiferromagnetic ordered component along [001] direction. On the other hand, the use of the SOM to simulate the magnetic susceptibility of Nd^{3+} ion below 140 K has allowed us to reveal the existence of a gradual loss of the susceptibility signal that begins to take place at about 30 K. The spin reorientation mentioned earlier could be induced by the onset of local magnetic interactions of antiferromagnetic type between Nd^{3+} and Cr^{3+} ions. The ordered chromium magnetic moment determined at 1.5 K is 2.73(9) μ_B.

In this work, we present the synthesis of $SmCaCrO_4$ and $EuCaCrO_4$ oxides as pure phases and their structural and

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magnetic characterization by means of X-ray powder diffraction and magnetization measurements. A comparison is also done by taking into account the obtained results on the isostructural $RCaCrO_4$, R: Pr and Nd, phases.

2. Experimental details

The polycrystalline brown $SmCaCrO_4$ and $EuCaCrO_4$ oxides were prepared by solid state reaction of the stoichiometric amounts of the high purity oxides R_2O_3 and Cr_2O_3, and an amount of 25–30 wt% excess of $CaCO_3$ (AR grade) to avoid the presence of $RCrO_3$ as impurity [5]. The homogenized mixtures were heated under argon flow at 1360°C for 40 h, then the samples were ground and reheated in argon at 1370°C for 10 h. The X-ray diffraction patterns show the existence of $RCaCrO_4$, CaO (~4%) and R_2O_3 (~2%) phases, the later owing to the Cr_2O_3 volatility. In order to check the presence of interstitial oxygen, giving rise to the non-stoichiometric $RCaCrO_{4+\delta}$ samples, we carried out TGA measurements in a Cahn D-2000 electrobalance under reducing atmosphere He–(5%)H_2. The obtained result shows that the samples can be formulated as $RCaCrO_4$ ($\delta \approx 0$).

X-Ray powder diffraction patterns at RT were recorded using a Philips X' Pert MPD diffractometer that works with λ_{Cu}: 1.5418Å. The powder diffraction data were analyzed with the Rietveld method [6], using the FULLPROF program [7]. A pseudo-Voigt profile function without preferred crystallite orientation was used.

Magnetization measurements were performed in a Quantum Design XL-SQUID magnetometer, between 2 and 300 K. The magnetization data versus temperature were obtained in a zero field cooling way with an applied magnetic field of 500 Oe.

3. Results and discussion

3.1. Structural characterization

$SmCaCrO_4$ and $EuCaCrO_4$ oxides show orthorhombic symmetry, space group *Bmab*, at RT. Table 1 shows the lattice parameters obtained from Rietveld refinement of X-ray diffraction data and the orthorhombic strain parameter S_o, defined as $2(b-a)/(a+b)$. It has been observed that the orthorhombic distortion of the ideal K_2NiF_4 structure in the $RCaCrO_4$ oxides increases with the decreasing of the rare earth ion size, taking values of 4.0×10^{-3} and 7.0×10^{-3} in the case of praseodymium and neodymium compounds, respectively [3]. The value obtained for $EuCaCrO_4$ is three times higher than the observed in the case of the $PrCaCrO_4$. This orthorhombic distortion can be explained regarding the two-dimensional misfit between the $RCaO_2$ and CrO_2 layers that are intergrown along the *c*-axis. The former is smaller than the latter and with the aim of reducing this mismatch a coupled tilt of the CrO_6 octahedra has been observed [1–3]. As the size of the trivalent rare earth ion decreases the misfit increases, the tilt is bigger and so the orthorhombic distortion increases.

Several attempts to prepare $RCaCrO_4$ oxides with a R^{3+} ion smaller than Eu^{3+} have been unsuccessful. It is always obtained as a black phase, that shows the distorted K_2NiF_4 structure, together with a large amount of R_2O_3 oxide ($>15\%$). This amount increases thus decreasing the size of the rare earth ion. This has been understood considering the possible formation of $R_{1-x}Ca_{1+x}CrO_4$ phases instead of $RCaCrO_4$ ones, where the partial substitution of Ca^{2+} for R^{3+} produces the stabilization of the structure. For rare earth ions smaller than Eu^{3+} the difference of size between $RCaO_2$ and CrO_2 layers is too big to make stable the structure only through the tilting of the CrO_6 octahedra and the system can reduce that difference replacing R^{3+} (for example, $r^{IX}_{Y^{3+}} = 1.10$ Å) by Ca^{2+} ($r^{IX}_{Ca^{2+}} = 1.18$ Å) [8,9]. Furthermore, it is worth noting that this later produces an increase of the formal oxidation state of the chromium ions, with the consequent diminishing of the lattice constant of CrO_2 layers.

All this goes to show that the $EuCaCrO_4$ compound is probably the last member of the $RCaCrO_4$ family and, in this regard, to point out that the S_o parameter of europium phase is three times the praseodymium one, as has been indicated above.

3.2. Magnetic behavior

Fig. 1 shows the temperature dependence of the magnetic susceptibility obtained between 2 and 300 K for $SmCaCrO_4$ oxide. At about 240 K is observed the characteristic broad maximum of the magnetic behavior of Sm^{3+} ions. At 150 K a maximum appears that, in the same case as the $PrCaCrO_4$ compound, can be associated with the onset of 3D antiferromagnetic interactions in the chromium sublattice. The paramagnetic behavior observed below 150

Table 1
Lattice parameters of $RCaCrO_4$ (R: Sm and Eu) oxides obtained at RT from Rietveld refinement of X-ray powder diffraction data[a]

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	$S_o\times10^3$
$SmCaCrO_4$	5.3457 (3)	5.4057 (3)	11.8610 (8)	342.75 (2)	11.2
$EuCaCrO_4$	5.3462 (5)	5.4180 (5)	11.806 (1)	341.96 (3)	13.3

[a] Numbers in parentheses are estimated standard deviations. Reliability factors: (a) $SmCaCrO_4$: $R_{wp}=24.3\%$, $R_B=7.93\%$ and $\chi^2=3.13$; (b) $EuCaCrO_4$: $R_{wp}=23.6\%$, $R_B=11.6\%$ and $\chi^2=2.25$.

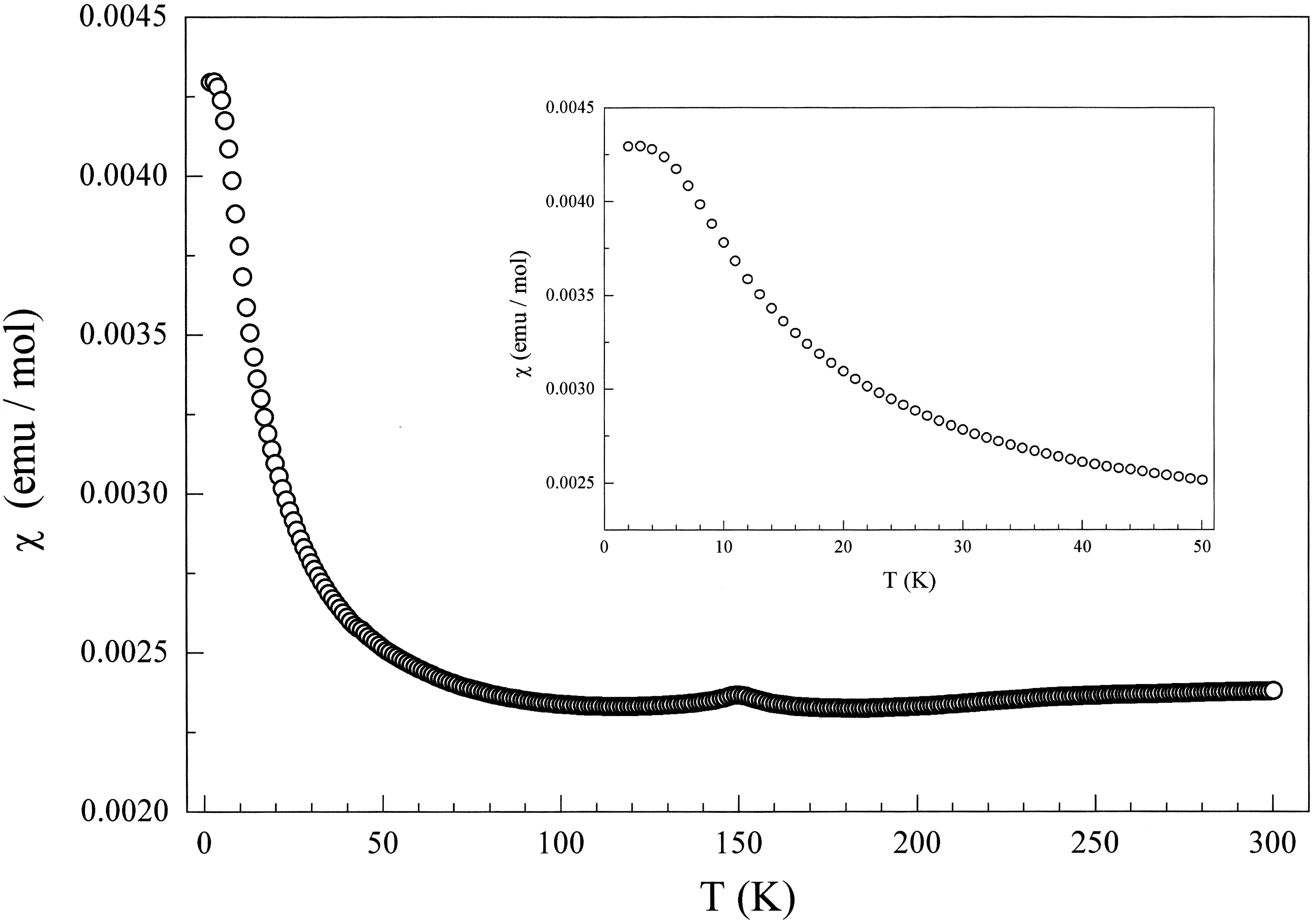

Fig. 1. Temperature dependence of the magnetic susceptibility for $SmCaCrO_4$ oxide. The inset shows the magnetic susceptibility below 50 K.

K is explained only considering the contribution of the Sm^{3+} ions. However, as can be clearly observed, the change of the magnetic susceptibility below 10 K reveals the onset of antiferromagnetic interactions in the samarium sublattice with an estimated Néel temperature of 3 K, see inset of Fig. 1.

Taking into account that the Sm^{3+} ions are magnetically diluted by the presence of diamagnetic Ca^{2+} ions in the same Wyckoff position, this could explain the low value of the Néel temperature obtained for this compound. Therefore, this observed antiferromagnetism could probably be induced by local magnetic interactions between the samarium ions and the ordered magnetic moments of the chromium ions, which are the promoter of the interactions in the Sm^{3+} sublattice. In this respect, as has been reported earlier, similar incipient short-range magnetic interactions have been proposed in $NdCaCrO_4$ to explain the loss of the paramagnetic susceptibility signal of the Nd^{3+} ions at low temperature, although the Nd^{3+} ions show no long-range magnetic order down to 1.5 K as has been observed from neutron diffraction data [2].

Fig. 2 shows the temperature dependence of the magnetic susceptibility obtained in the 2–300 K range for $EuCaCrO_4$ oxide. As it can be observed, the magnetic susceptibility progressively increases, decreasing the temperature down to 100 K. Below this temperature, the magnetic susceptibility remains almost constant. This behavior corresponds to the temperature-independent paramagnetism associated with the non-magnetic ground term $^7F_0$ of Eu^{3+} ions. The small increase observed below 15 K is due to paramagnetic impurities. At about 180 and 160 K two anomalies can be observed. The first one can be attributed to the presence of a small amount of $EuCrO_3$, non-detected by X-ray diffraction, that orders antiferromagnetically at 181 K [10]. The second one, at 160 K, can indicate the onset of 3D antiferromagnetic interactions in the chromium sublattice.

The magnetic properties of oxides showing the K_2NiF_4 structure are influenced by the two-dimensional character of the magnetic interactions that take place in the MO_2 layers (M: transition metal) of the structure. Such two-dimensional interactions will be promoted by the diminution of the magnetic interactions between MO_2 planes. The presence of diamagnetic cations in the double rock salt-type layer that separates the nearest-neighbor MO_2 layers will favor such intralayer magnetic interactions.

The magnetic properties observed in $RCaCrO_4$ oxides, with R: Pr, Nd, Sm and Eu, reveal the existence of a strong

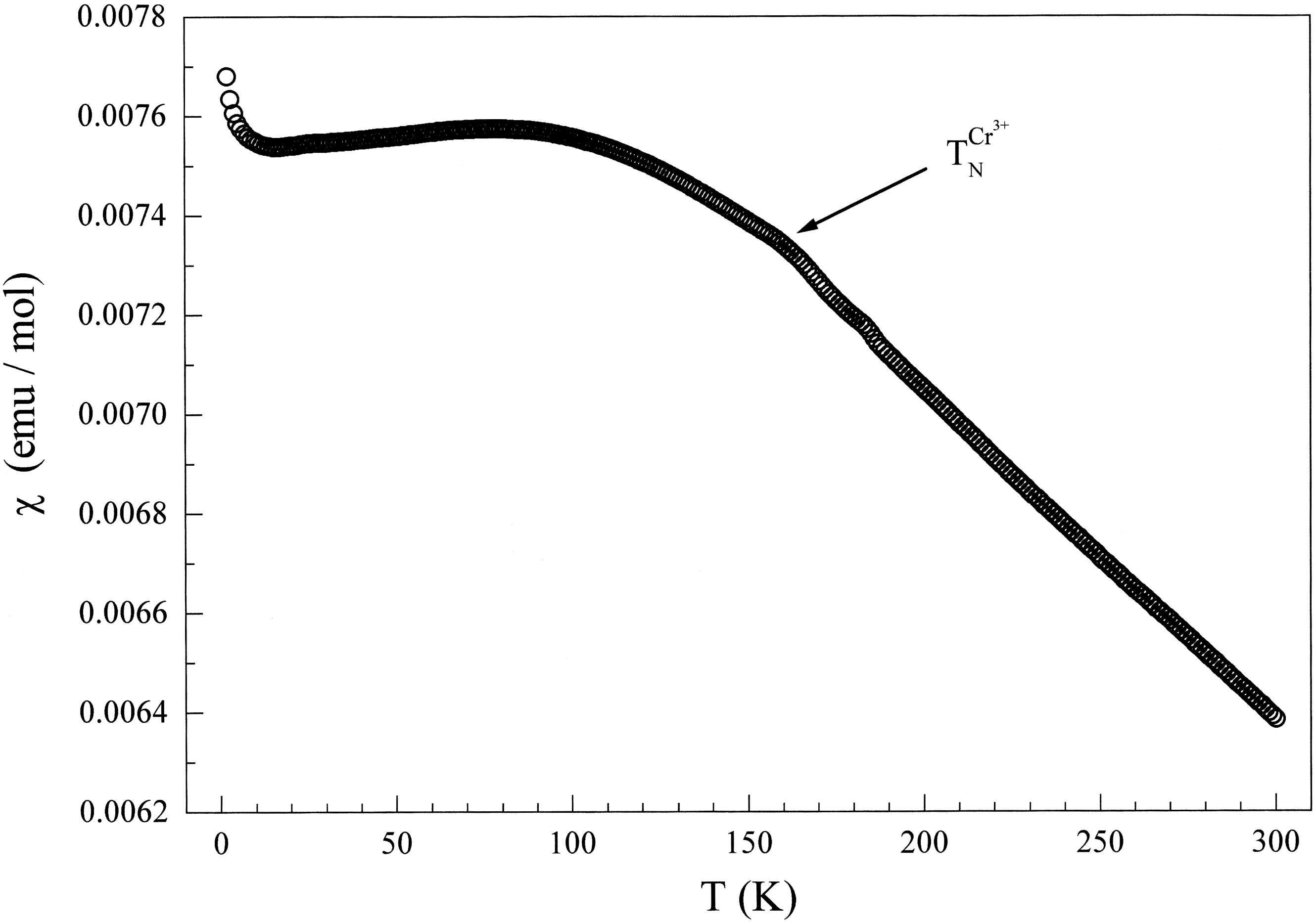

Fig. 2. Temperature dependence of the magnetic susceptibility for $EuCaCrO_4$ oxide.

3D magnetic behavior. The superexchange antiferromagnetic interactions in the CrO_2 layers involve a Cr^{3+}–O^{2-}–Cr^{3+} pathway, where the best overlapping of the $t_{2g}(Cr^{3+})$–$p_\pi(O^{2-})$–$t_{2g}(Cr^{3+})$ orbitals corresponds to a bond angle of 180°. On the other hand, the interlayer magnetic interactions between the CrO_2 planes, that gives rise to the 3D character, take place along the *c*-axis through the $RCaO_2$ layers.

Table 2 shows the Néel temperature of the $RCaCrO_4$ oxides obtained from magnetization measurements. As can be observed, the $T_N^{Cr^{3+}}$ decreases going from the praseodymium to the samarium compound, and it slightly increases in the case of the europium oxide. This Néel temperature dependence on the rare earth ion size can be explained taking into account both intra and interlayer magnetic interactions. As can be observed in Table 2, the Cr^{3+}–O^{2-}–Cr^{3+} bond angle obtained at RT is smaller than 180° due to the tilting of the CrO_6 octahedra. It decreases going from the praseodymium to the europium compound with the corresponding decrease of the magnetic interactions in the CrO_2 layers. On the other hand, the observed variation of the *c* parameter, see Table 2, indicates a progressive approach of the CrO_2 layers and so an increase in the 3D magnetic interactions. Therefore, the observed fall in the $T_N^{Cr^{3+}}$ going from praseodymium to samarium compounds indicates that the intralayer magnetic

Table 2

Néel temperature (T_N) of the chromium and rare earth sublattices determined from magnetization versus temperature measurements, Cr^{3+}–O^{2-}–Cr^{3+} bond angle in the CrO_2 layer and *c* parameter of $RCaCrO_4$ oxides

Compound	$T_N^{Cr^{3+}}$ (K)	α (Cr^{3+}–O^{2-}–Cr^{3+})	*c* (Å)	$T_N^{R^{3+}}$ (K)
$PrCaCrO_4$	182 [1]	174.3 (2)[a]	12.0055 (9) [3]	–
$NdCaCrO_4$	~170 [2]	173.3 (2)[a]	11.9488 (8) [3]	See text
$SmCaCrO_4$	150	168 (1)	11.8610 (8)	3
$EuCaCrO_4$	160	166 (1)	11.806 (1)	–

[a] Neutron diffraction data from Refs. [2] and [3].

interactions, with the decrease in the overlapping of the $t_{2g}(Cr^{3+})$–$p_{\pi}(O^{2-})$–$t_{2g}(Cr^{3+})$ orbitals, are the dominant factor. A similar behavior has been characterized in the $RCrO_3$ (R: La–Lu) perovskites [10]. In these oxides the T_N of the chromium sublattice ranges from 282 ($LaCrO_3$) to 112.4 K ($LuCrO_3$) due to the progressive smaller overlapping of the $t_{2g}(Cr^{3+})$ and $p_{\pi}(O^{2-})$ orbitals involved in the magnetic interactions, that takes place decreasing the rare earth ion size. However, the observed $T_N^{Cr^{3+}}$ in the $EuCaCrO_4$ oxide points out that the effect of the interlayer CrO_2 interactions becomes dominant.

Concerning the rare earth sublattice, as has been commented earlier, the R^{3+} ions are magnetically diluted by the presence of Ca^{2+} ions in the same Wyckoff position. This situation causes the onset of short-range magnetic interactions between chromium and rare earth ions that only in the case of the samarium compound give rise to antiferromagnetic order, although the Nd^{3+} ions in the neodymium compound represent incipient antiferromagnetic ordering below 10 K. In the case of the $PrCaCrO_4$ and $EuCaCrO_4$ oxides, the Pr^{3+} ions do not order down to 1.5 K and the Eu^{3+} ones remain magnetically disordered because of their non-magnetic ground state, respectively.

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