Structural and magnetic characterization of novel stoichiometric LnCaCrO₄ oxides (Ln, rare earth)

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Abstract

Rietveld refinement of the powder X-ray diffraction patterns of the stoichiometric dark brown LnCaCrO₄ oxides allows us to assign orthorhombic symmetry, space group *Bmab*, for all members of this isostructural family of compounds. At about 420 °C marked exothermic effects have been observed which could be due to a phase transition of the type *Bmab → I4/mmm*. Magnetic susceptibility data reveal a clear antiferromagnetic ordering in the chromium sublattice above room temperature. Between 120 and 200 K, depending on the lanthanide cation, a marked jump in the susceptibility is observed which is probably related to the tilt of the CrO₆ octahedra as has been reported earlier in the case of the isostructural Ln₂NiO₄ oxides.

1. Introduction

A large number of oxides with the general formula A_2BO_4 showing the tetragonal or distorted K_2NiF_4 structure have been synthesized and fully characterized. The relatively short B–O–B distances making an angle of 180° in the perovskite ABO_3 layers, which are well isolated from each other by rock salt AO layers along the c axis, justify the two-dimensional (2D) character reported earlier for these materials as their main property. However, it was not until 1986, after the discovery of superconductivity in $La_{2-x}Ba_xCuO_4$ by Bednorz and Muller [1], that the study of many aspects such as non-stoichiometry, phase transitions, transport and magnetic properties led to a great interest in this type of oxide [2].

It has been reported recently that the Ln_2MO_4 oxides (Ln, rare earth; M ≡ Co, Ni and Cu) are actually non-stoichiometric phases of the type Ln_2MO_{4+x} [3]. The value of x depends on the synthesis method and/or the nature of M. In many papers the important role of this interstitial oxygen in the structural and physical properties of these oxides has also been demonstrated [4–6]. In contrast, as far as we know, only a few studies have been reported in the case of the isostructural LnCaCrO₄ oxides [7–9], where the Ln and Ca atoms are randomly distributed in the A positions. Moreover, non-stoichiometric effects, *i.e.* oxygen excess, which appear to be a general feature of these isostructural oxides have not been taken into account in the case of the LnCaCrO₄ oxides.

In the present work we report the structural characterization and study of the magnetic properties of the stoichiometric LnCaCrO₄ oxides where Ln ≡ Pr, Nd, Sm, Eu, Dy, Ho and Y.

2. Experimental details

Polycrystalline samples were prepared by mixing stoichiometric amounts of the high purity oxides Ln_2O_3 (99.99%), Cr_2O_3 and $CaCO_3$ (AR grade). The homogenized mixture was heated under an argon flow to 1000 °C for 24 h, then reground to enhance the reactivity

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and reheated in argon to 1300 °C for 24 h. When the dark brown samples obtained were annealed in oxygen at 1000 °C they became black, while subsequent annealing in argon at 1000 °C yielded in a reversible way the starting brown $LnCaCrO_4$ oxides. These results are indicative of the existence of non-stoichiometry in these oxides annealed in oxygen. Reduction of $LnCaCrO_{4+x}$ under a hydrogen flow confirms the above assumption and from the weight loss obtained in the temperature range 400–500 °C it is possible to determine the value of the oxygen excess x, which is 0.09 for $SmCaCrO_{4+x}$. In contrast, the samples obtained under an argon flow do not experience any loss when heated in hydrogen to 800 °C. This confirms our assumption about the stoichiometric character of the samples prepared under an argon atmosphere.

X-ray powder diffraction patterns were recorded using a Siemens Kristalloflex 810 diffractometer and D-500 goniometer with nickel-filtered radiation ($\lambda = 1.540\,881\,45$ Å) selected with a graphite monochromator. Diffraction data were collected by step scanning over an angular range of $10° < 2\theta < 120°$ in increments of $0.05°$ with a counting time of 15 s per step. The data were analysed by the Rietveld [10] method using the FULLPROF program [11]. A pseudo-Voigt profile function without preferred crystallite orientation was used.

Differential scanning calorimetry (DSC) was carried out in the temperature range 100–900 K by means of a Perkin–Elmer DSC7, PC Series calorimeter provided with either a CCA7 liquid-nitrogen-controller cooling accessory (100–300 K) or a controlled water-circulating system (300–900 K). The temperature response of the instrument was calibrated with the melting points of high purity chemicals such as cyclohexane, n-pentadecane and gallium (low range) and tin, lead, zinc and potassium sulphate (high range). The ordinate output was calibrated with the melting enthalpy of 99.999% pure indium. Samples of around 20 mg (100 mg for the low range), weighed to ± 0.002 mg by a Perkin–Elmer AD4 electronic balance, were encapsulated in gold or graphite (low range) pans and scanned at a heating rate of 10 K min^{-1} under a 30 cm^3 min^{-1} purge of dry nitrogen or helium (low range).

Magnetic susceptibility measurements were made using a fully automatic DSM8 magnetosusceptometer based on the Faraday method in the temperature range 300–4.2 K. The magnetic field strength was 12 KG, with $HdH/dz = 18$ kg^2 cm^{-1}. The set-up was calibrated with $Hg(Co(SCN)_4)$ as a standard and the data were corrected for ionic diamagnetism using the values in 10^{-6} e.m.u. mol^{-1} of -16 for O^{2-}, -20 for Ln^{3+}, -8 for Ca^{2+} and -11 for Cr^{3+} [12].

3. Results and discussion

3.1. Structural characterization

The X-ray diffraction pattern of $SmCaCrO_4$ (Fig. 1) has been indexed on the basis of an orthorhombic unit cell, space group $Bmab$, which can be considered as a distortion of the tetragonal K_2NiF_4 structure type. In the refinement of the structure Sm and Ca are randomly distributed in the 8f sites. The final refinement is satisfactory, as can be observed in the difference plot included in Fig. 1. Small impurities peaks have not been included in the refinement, since we consider their effect to be very small, as can be observed in the fitting factors obtained. The characteristic distances in the octahedra are $2\times$ Cr–O(2) = 2.054(1) Å and $4\times$ Cr–O(1) = 1.917(2) Å, which give rise to elongated octahedra (Table 1).

The other $LnCaCrO_4$ oxides are isostructural with samarium chromate and the lattice parameters for these compounds are given in Table 2. As was expected assuming the ionic model, a decrease is observed in both the lattice parameters and the volume of the unit cell in going from $PrCaCrO_4$ to $YCaCrO_4$ according to the decreasing ionic radius of the lanthanide cation as a consequence of the lanthanide contraction.

3.2. DSC

Figures 2 and 3 show normalized DSC records for the various $LnCaCrO_4$ oxides in the high temperature range. It can be observed that all the compounds exhibited a complex thermal behaviour in the sense that they present a rather sharp endothermic transition appearing above a broad endothermic event which extends over a wide temperature interval of 200–300 K. These effects were not recorded in subsequent runs, the samples thus exhibiting a decrease in their heat capacity data, but reversibility was achieved after the encapsulated materials had been allowed to stand at room temperature for a long time. The peak onset temperature appears to be independent of the Ln ion, about 700 K, being nearly the same for all the oxides except for the Ho^{3+} and Y^{3+} samples where it was somewhat lower, about 650 K. In relation to the associated enthalpy change, however, the oxides may be classified into two groups, as can be easily seen from the ordinate scales of Figs. 2 and 3, the first being five times the second. The larger enthalpy changes (hump effects excluded) corresponded to the oxides with the bigger cations (Pr^{3+}, Nd^{3+} and Sm^{3+}), ranging from 110 to 180 J g^{-1}, while the enthalpy changes were about a fifth of these values for the smaller lanthanide cations. Initially (neutron diffraction experiments in progress) these sharp endothermic effects seem to be related to the structural phase transition of the orthorhombic $(Bmab) \rightarrow$ tetragonal $(Immm)$ type already
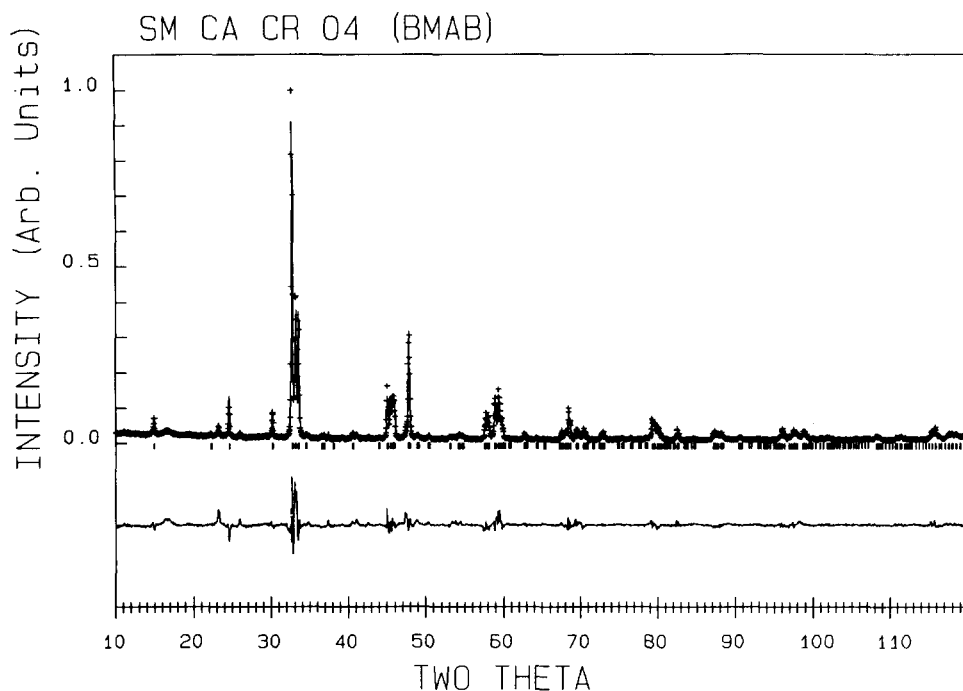
Fig. 1. Experimental X-ray diffraction data and data calculated (solid curve) by the Rietveld method for the SmCaCrO₄ oxide.

TABLE 1. Structural parameters and bond lengths M–O (Å) of the SmCaCrO₄ oxide obtained from X-ray powder diffraction data

Atom	Site	x/a	y/b	z/c
Cr	$4a$	0	0	0
Sm/Ca	$8f$	0	−0.115(7)	0.3771(1)
O(1)	$8e$	0.25	0.25	−0.19(1)

$R_p = 9.57$, $R_{wp} = 12.9$, $R_{exp} = 4.69$, $\chi^2 = 2.24$, $R_b = 9.26$
Number of reflections, 291

Cr–O(1)×4	1.917(1)
Cr–O(2)×2	2.054(2)
Ca/Sm–O(2)	2.21(1)
Ca/Sm–O(1)×2	2.433(8)
Ca/Sm–O(2)	2.44(2)
Ca/Sm–O(1)×2	2.68(1)
Ca/Sm–O(2)×2	2.703(2)
Ca/Sm–O(2)	3.01(1)

reported for these oxides [8]. In this respect it is interesting to note that the transition temperatures given in ref. 8 from dilatometric data are strongly dependent on the lanthanide cation. These marked differences between the members of the series in ref. 8 could be due to the different amounts of oxygen in the LnCaCrO₄₊ₓ oxides. In contrast, as was mentioned earlier, the samples we have studied in the present work are actually stoichiometric LnCaCrO₄ and isostructural compounds. Hence it could be expected that the possible phase transition they show would occur

TABLE 2. Lattice parameters a, b and c and unit cell volume V for the LnCaCrO₄ oxides

Compound	a (Å)	b (Å)	c (Å)	V (Å³)
PrCaCrO₄	5.386(1)	5.419(1)	11.983(3)	349.8
NdCaCrO₄	5.369(1)	5.410(1)	11.944(2)	346.3
SmCaCrO₄	5.364(1)	5.410(1)	11.902(2)	345.4
EuCaCrO₄	5.3494(9)	5.4075(8)	11.862(2)	343.1
DyCaCrO₄	5.332(1)	5.380(1)	11.795(3)	338.3
HoCaCrO₄	5.307(1)	5.366(1)	11.736(3)	336.0
YCaCrO₄	5.295(2)	5.342(2)	11.701(3)	326.6

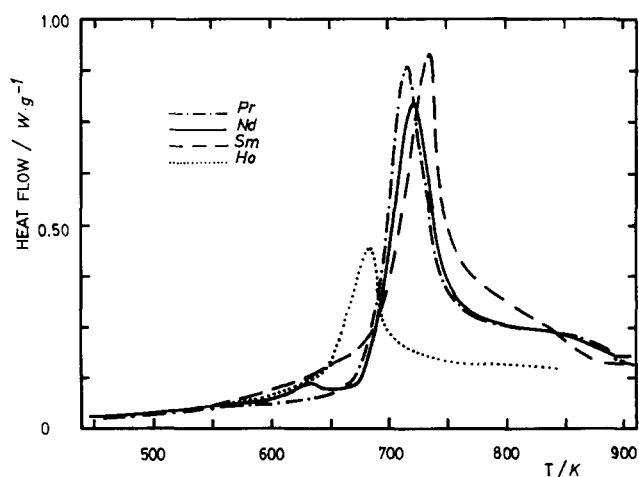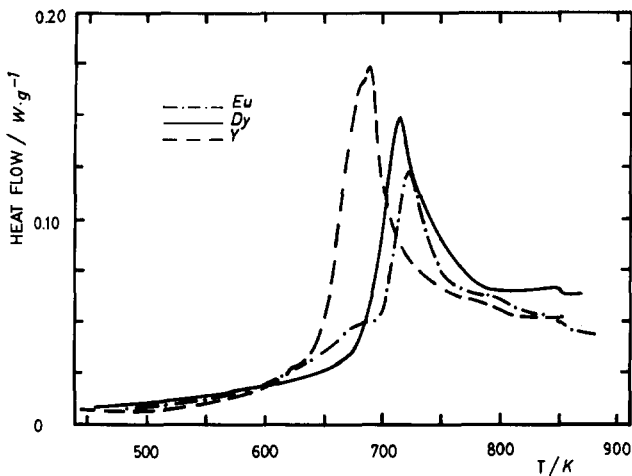Fig. 2. DSC curves obtained for various LnCaCrO₄ oxides.

Fig. 3. DSC curves obtained for various LnCaCrO₄ oxides.
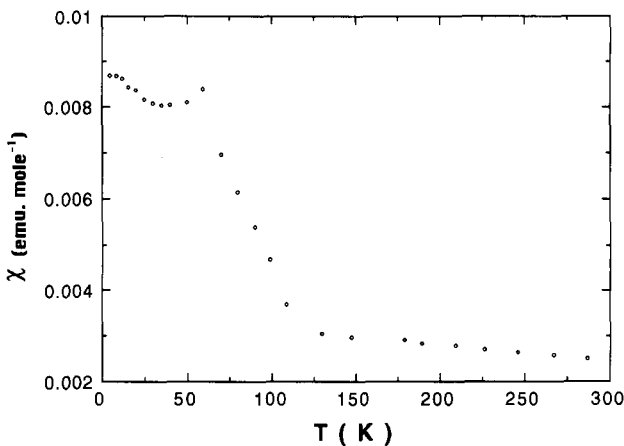

Fig. 4. Temperature dependence of the molar magnetic susceptibility for YCaCrO₄.

at about the same temperature. Similar results have already been obtained in the case of the stoichiometric and isostructural Ln_2NiO_4 oxides, for which a phase transition of the type $Bmab \rightarrow Immm$ takes place at about 1400 K for both lanthanum and praseodymium oxides [13, 14].

3.3. Magnetic properties

Figure 4 shows the variation in the molar magnetic susceptibility with temperature for YCaCrO₄. It can be observed that the susceptibility remains almost constant in the temperature range 300–120 K, taking a value as small as 4×10^{-3} e.m.u. mol⁻¹, which yields a magnetic moment of only 1.90 BM at room temperature, somewhat smaller than expected for Cr^{3+} with $S = \frac{3}{2}$. This behaviour can be attributed to the superexchange interactions due to the strong $O-t_{2g}-O$ overlapping at 180° of the oxygen p orbitals and the Cr^{3+} half-filled t_{2g} orbital, which according to Goodenough's rules [15] give rise to strong antiferromagnetic interactions in the Y/CaCrO₃ perovskite layers of the

structure of YCaCrO₄. Below 120 K the susceptibility shows an upward jump and stays nearly constant down to 4.2 K. The presence of this ferromagnetic component at 120 K could be due to spin canting of the antiferromagnetically ordered chromium ions above room temperature. Similar results have been found previously in the case of the isostructural R_2NiO_4 oxides and it has been reported from low temperature neutron diffraction data that this canting is closely related to phase transitions of the type orthorhombic (Bmab) → tetragonal (I4/mmm), which involves tilting of the NiO₆ octahedra at the transition temperature [16, 17]. However, preliminary results obtained from neutron diffraction data in these LnCaCrO₄ oxides indicate a somewhat different behaviour and this ferromagnetic component appears to be due to magnetic transitions rather than structural changes [18]. Moreover, low temperature DSC measurements do not reveal the existence of any thermal effect down to 100 K, which indicates that the enthalpy associated with this spin canting must be very small.

The magnetic behaviour of the other LnCaCrO₄ oxides will be more complex because of the coexistence of two (Ln^{3+} and Cr^{3+}) paramagnetic cations. In the case of LnCaCrO₄ where Ln ≡ Pr, Nd and Ho the susceptibility obeys a Curie–Weiss behaviour over a very wide temperature range (Figs. 5–7 respectively). The magnetic moments obtained from the slope of the linear part of the χ^{-1} vs. T plot agree fairly well with those expected for these Ln^{3+} ions without taking into account Cr^{3+} with $S = \frac{3}{2}$. As in the case of the above-mentioned YCaCrO₄ oxide, the antiferromagnetic ordering in the chromium sublattice justifies the non-contribution of Cr^{3+} with three unpaired electrons to the magnetic moment below room temperature. Below 200 K in all cases it is still possible to see a jump in the magnetic susceptibility, although this ferromagnetic contribution is strongly masked by the paramagnetic signal of the
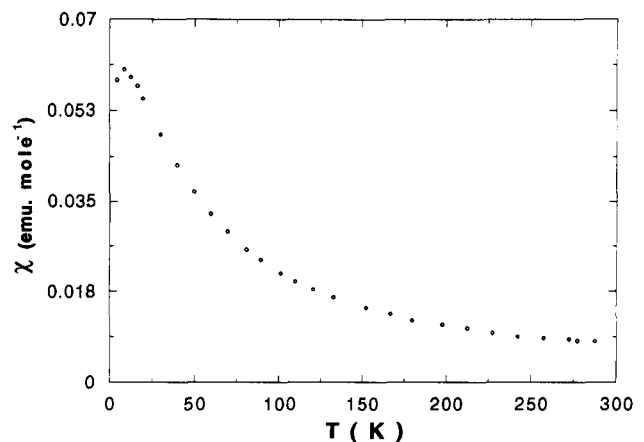

Fig. 5. Temperature dependence of the molar magnetic susceptibility for PrCaCrO₄.
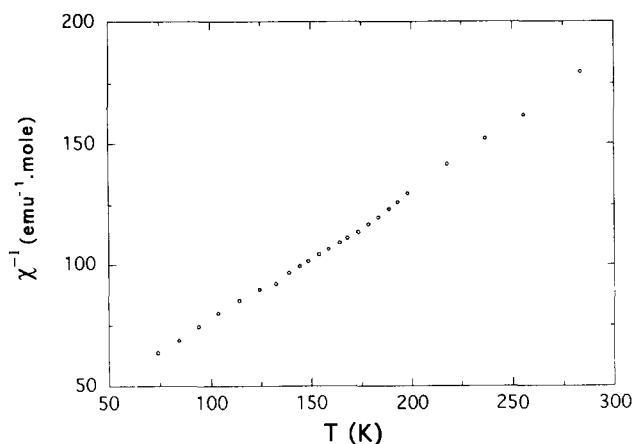
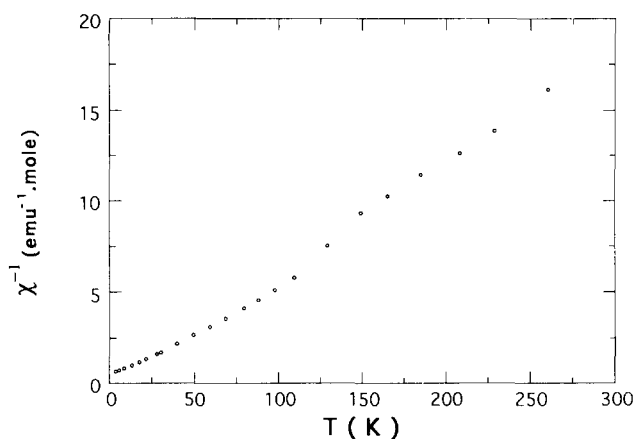Fig. 6. Variation in the reciprocal magnetic susceptibility with temperature for NdCaCrO₄.

Fig. 7. Variation in the reciprocal magnetic susceptibility with temperature for HoCaCrO₄.

TABLE 3. Observed (μ_o) and theoretical (μ_t) magnetic moments, Weiss constant (Θ) and temperature of canting (T_c) for the LnCaCrO₄ oxides

Compound	μ_o (BM)	μ_t (BM)	Θ (K)	T_c (K)
PrCaCrO₄	3.62	3.58	26.1	190
NdCaCrO₄	3.70	3.62	49.8	140
SmCaCrO₄	2.30	1.16[a]	–	180
EuCaCrO₄	3.91	3.50[a]	–	160
DyCaCrO₄	10.53	10.61	3.1	120
YCaCrO₄	2.21	1.73	70.5	90

[a]Calculated at room temperature from Van Vleck's equation [19].

trivalent lanthanide cation Ln^{3+}. The values of the temperature at which this spin canting occurs, T_c, are given in Table 3. The negative values of the Weiss constant confirm our assumption about the antiferromagnetic order in the chromium sublattice above room temperature.

The variation in the magnetic susceptibility with temperature for SmCaCrO₄ and EuCaCrO₄ is shown

in Figs. 8 and 9 respectively. Their magnetic behaviour can be understood on the basis of the Sm^{3+} or Eu^{3+} contribution only, without invoking exchange interactions either between lanthanide ions or between lanthanide and Cr^{3+} ions. The absence of a Cr^{3+} contribution to the susceptibility below 300 K, as in the case of the other oxides of this family of compounds, provides definitive evidence that these ions are antiferromagnetically ordered in the Cr–O planes of these compounds.

As can be observed in Fig. 8, the susceptibility of SmCaCrO₄ in the temperature range 300–180 K is nearly independent of temperature, as was expected because the separation of the energy levels is not too large compared with the thermal energy kT. A jump in the susceptibility at 180 K is clearly noticeable because of the weak signal of Sm^{3+}. The presence of this ferromagnetic component at about the same temperature can also be seen in the case of EuCaCrO₄ (Fig. 9). The magnetic moments obtained for the samarium
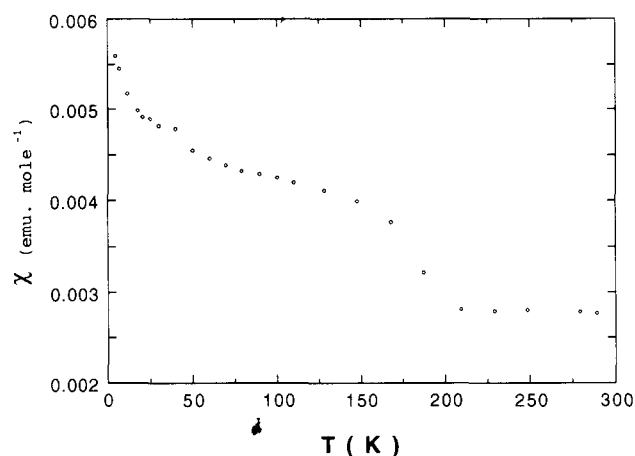

Fig. 8. Temperature dependence of the molar magnetic susceptibility for SmCaCrO₄.
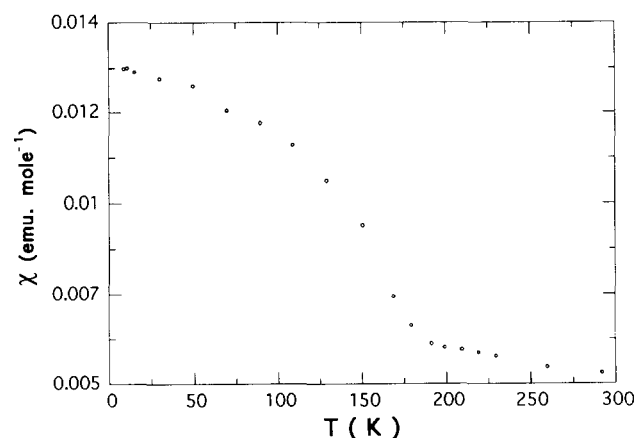

Fig. 9. Temperature dependence of the molar magnetic susceptibility for EuCaCrO₄.

and europium compounds at room temperature agree with those calculated using Van Vleck's equation [19].

In summary, we have found that this family of LnCaCrO$_4$ oxides behave as planar antiferromagnets regarding the Cr–O planes in the compounds and that the exchange interactions involving Ln^{3+} ions are relatively weak, so the magnetic susceptibility below room temperature agrees well with the expected behaviour for isolated Ln^{3+} ions under the influence of a crystal field. To further elucidate the nature of the Cr^{3+} magnetic ordering in these oxides, we are now undertaking neutron diffraction experiments to explore their magnetic structures as well as high temperature magnetic susceptibility measurements to determine their Néel temperatures.

Acknowledgment

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