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Magnetic ordering in the pyrochlore Ho$_2$CrSbO$_7$ determined from neutron diffraction, and the magnetic properties of other RE$_2$CrSbO$_7$ phases (RE=Y, Tb, Dy, Er)

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The magnetic structure of the pyrochlore Ho$_2$CrSbO$_7$, which orders magnetically below 13 K, has been studied using neutron powder diffraction. Ho$_2$CrSbO$_7$ is found to form an "ordered spin-ice structure" where the magnetic moments are constrained along the 111 axes, but with a ferromagnetic moment in one direction. The Cr$^{3+}$ ions order ferromagnetically and this is thought to lift the degeneracy of the x, y and z directions in the cubic structure causing the ferromagnetic component from the Ho$^{3+}$ ions to align. The pyrochlores RE$_2$CrSbO$_7$ where RE=Y, Tb, Dy and Er have also been prepared and studied using SQUID magnetometry.

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1. Introduction

Mixed metal oxides with the pyrochlore structure are of considerable interest because of their susceptibility to chemical modifications which gives rise to a wide range of possible compositions and useful properties [1,2]. Their structure has been suggested as a host for magnetic monopoles [9].

The magnetic structure of the pyrochlore Ho$_2$CrSbO$_7$, which orders magnetically below 13 K, has been studied using neutron powder diffraction. Ho$_2$CrSbO$_7$ is found to form an "ordered spin-ice structure" where the magnetic moments are constrained along the 111 axes, but with a ferromagnetic moment in one direction. The Cr$^{3+}$ ions order ferromagnetically and this is thought to lift the degeneracy of the x, y and z directions in the cubic structure causing the ferromagnetic component from the Ho$^{3+}$ ions to align. The pyrochlores RE$_2$CrSbO$_7$ where RE=Y, Tb, Dy and Er have also been prepared and studied using SQUID magnetometry.

The pyrochlore structure is interesting magnetically because it contains two interlinked sublattices of A and B corner-sharing tetrahedra (Fig. 1) and if one or both of the cations are magnetic this leads to highly frustrated systems with interesting and unusual magnetic properties [5]. Often this frustration prevents long-range ordering of the magnetic moments and spin-glass behaviour is seen, where the random arrangement of the moments is frozen in at low temperatures, but there are also pyrochlores which show transitions to long-range ordered, anti-ferromagnetic and ferromagnetic, states and pyrochlores with more exotic types of magnetic behaviour such as spin-liquids and spin-ices [5,6].

The spin-ice magnetic state was first observed for the pyrochlore oxide Ho$_2$Ti$_2$O$_7$ [7]. The magnetic moments are constrained along the crystallographic directions and order only at very low temperatures so that in any given tetrahedron two of the spins are pointing in to, and two are pointing out from, the centre of the tetrahedron (Fig. 2). As the x, y and z directions in a cubic structure are equivalent there is no preferred direction for the spins to align along, unless a field is applied, giving a macroscopically degenerate ground state [6]. This is closely related to the residual entropy arising from the arrangement of protons in hexagonal water ice [8]: each oxygen atom is tetrahedrally surrounded by four hydrogen atoms and forms two short and two long O–H bonds (Fig. 2). The spin-ice pyrochlores are of interest because their structure has been suggested as a host for magnetic monopoles [9].
Despite the magnetic frustration inherent within the cation sublattices of the pyrochlore structure, a previous study of the magnetic susceptibility and magnetisation of $\text{RE}_2\text{CrSbO}_7$ found the compounds $\text{Ho}_2\text{CrSbO}_7$ and $\text{Dy}_2\text{CrSbO}_7$ to be ferromagnetic below $T_c = 10$ K and 16 K respectively [10]. Given the spin-ice magnetic behaviour of, for example, $\text{Ho}_2\text{Ti}_2\text{O}_7$, the reason for a ferromagnetic ground state in these phases with mixed $\text{Cr}^{3+}$ and $\text{Sb}^{5+}$ on the B-sites has not been established and prompted the current investigation. Here we report magnetic data for the pyrochlores $\text{RE}_2\text{CrSbO}_7$ ($\text{RE} = \text{Y, Tb, Dy, Ho, Er}$) and the magnetic structure of $\text{Ho}_2\text{CrSbO}_7$ as determined from neutron powder diffraction data. The magnetic structures of the compounds have not previously been reported.

2. Experimental

$\text{Ho}_2\text{CrSbO}_7$ was prepared by heating stoichiometric amounts of $\text{Ho}_2\text{O}_3$ (≥ 99.9%), $\text{Cr}_2\text{O}_3$ (99%) and $\text{Sb}_2\text{O}_3$ powders in air for 3 days at 950 °C and then regrinding and reheating at 1200 °C for 4.5 days with several intermediate regrindings. $\text{Sb}_2\text{O}_3$ was prepared by heating $\text{Sb}_2\text{O}_3$ (99%) in air at 640 °C.

$\text{Y}_2\text{CrSbO}_7$, $\text{Tb}_2\text{CrSbO}_7$, $\text{Dy}_2\text{CrSbO}_7$ and $\text{Er}_2\text{CrSbO}_7$ were prepared by heating stoichiometric amounts of $\text{CrSbO}_4$ and $\text{RE}_2\text{O}_3$ (99.9% – 99.99+) powders in air for 5.5 days at 1200 °C with one intermediate regrind. $\text{CrSbO}_4$ was prepared by heating $\text{Cr}_2\text{O}_3$ (99%) and $\text{Sb}_2\text{O}_3$ (99%) in air for 7 days at 1200 °C; several intermediate regrindings with addition of excess $\text{Sb}_2\text{O}_3$ were necessary to compensate for a loss of $\text{Sb}_2\text{O}_3$ due to volatilisation.

X-ray powder diffraction data were collected at room temperature using a Bruker D8 diffractometer (Cu $K\alpha_1$ radiation, wavelength 1.5406 Å; Ge crystal monochromator) operating in transmission mode, using a moveable $3\theta$ position sensitive detector and a step size of approximately 0.02°.

Constant wavelength neutron powder diffraction (NPD) data were collected using the high-resolution powder diffractometer for thermal neutrons (HRPT) at the neutron source SINQ at the Paul Scherrer Institute in Switzerland. Diffraction patterns were recorded at 300 and 1.5 K at a wavelength of 1.8857 Å.

Rietveld refinements were performed on both the X-ray and neutron diffraction data using the General Structure Analysis System (GSAS) [11] and the graphical user interface EXPGUI [12].

Magnetisation measurements were performed using a Quantum Design MPMS SQUID magnetometer. Zero-field cooled (ZFC) and field cooled (FC) data were collected between 5 and 300 K using an applied fields between 100 and 5000 Oe. Hysteresis measurements for $\text{Ho}_2\text{CrSbO}_7$ and $\text{Dy}_2\text{CrSbO}_7$ were taken between −500 and 500 Oe at 5 K. A small sample size (approximately 6 mg) had to be used as the lanthanide and moments were too large to give good quality hysteresis data when using a sample size of around 60–80 mg. Hysteresis measurements for $\text{Y}_2\text{CrSbO}_7$ were taken between −48,000 Oe and 48,000 Oe at 5 K.
3. Results and discussion

3.1. Structural characterisation

All the compounds were confirmed to be single phase using X-ray powder diffraction. Rietveld refinements were performed on the X-ray diffraction data using the general structure for a pyrochlore which has cubic space group \(Fd\overline{3}m\), the \(01\) \(x\) value being the only variable in the atomic positions. The unit cell sizes, \(01\) \(x\) values and thermal parameters are shown in Table 1. A Rietveld refinement performed on room temperature neutron diffraction data for the compound \(Ho_2CrSbO_7\) (Fig. 3) gave values of \(a=10.1739(3)\) Å and \(01\) \(x=0.3318\) \((\chi^2=1.924; R_{wp}=0.040; R_B=0.039)\). The data fit to the model very well and the Cr:Sb ratio was found to be approximately 1:1 as expected.

3.2. Magnetic properties of \(Ho_2CrSbO_7\).

3.2.1. Fully ordered region (below 13 K).

The presence of a magnetically ordered state was evidenced by a transition in the magnetic susceptibility data at ca. 13 K (Fig. 4) and by the appearance of additional magnetic Bragg peaks in NPD recorded at 298 K (above) and 1.5 K (below).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(a) (Å)</th>
<th>(01) (x)</th>
<th>(U_{av}) (Å(^2))</th>
<th>(\chi^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Y_2CrSbO_7)</td>
<td>10.1621(1)</td>
<td>0.3466(6)</td>
<td>0.0057(3)</td>
<td>1.921</td>
</tr>
<tr>
<td>(Tb_2CrSbO_7)</td>
<td>10.2199(1)</td>
<td>0.3315(6)</td>
<td>0.0114(4)</td>
<td>1.847</td>
</tr>
<tr>
<td>(Dy_2CrSbO_7)</td>
<td>10.1954(1)</td>
<td>0.3319(6)</td>
<td>0.0104(3)</td>
<td>1.364</td>
</tr>
<tr>
<td>(Ho_2CrSbO_7)</td>
<td>10.17503(9)</td>
<td>0.3365(5)</td>
<td>0.0070(3)</td>
<td>1.804</td>
</tr>
<tr>
<td>(Er_2CrSbO_7)</td>
<td>10.1464(1)</td>
<td>0.3329(6)</td>
<td>0.0112(3)</td>
<td>2.838</td>
</tr>
</tbody>
</table>

In the magnetic susceptibility data (see Fig. 4), an increase in the susceptibility is seen at low temperatures with divergence of the FC and ZFC data indicative of a ferromagnetic component. The inset of Fig. 4 reveals a weak magnetic transition at 146 K. This was shown to be caused by a very small impurity of HoCrO\(_3\), which orders to give a canted antiferromagnetic structure below this temperature [13]. Some very small HoCrO\(_3\) impurity peaks were also seen in the NPD data (Fig. 3). Ho\(_2\)CrSbO\(_7\) contains two different magnetic ions: Ho\(^3+\) on the A-sites and Cr\(^3+\) occupying half the B-sites.

The neutron diffraction pattern taken at 1.5 K (Fig. 3) revealed that Ho\(_2\)CrSbO\(_7\) is not a simple ferromagnet. The nuclear structure was refined with space group \(Fd\overline{3}m\) and the magnetic structure was refined as a separate phase with \(P1\) symmetry such that the directions of the moments were unrestricted. Moments were initially input for the Ho\(^3+\) ions on the A-sites with a component aligned along one axis only, similar to the magnetic model for the antiferromagnetic pyrochlore Er\(_2\)Ru\(_2\)O\(_7\) [14] which also has magnetic A- and B-sites. Neither a simple ferromagnetic nor an antiferromagnetic structure would allow all the magnetic peaks to be modelled. Looking at the low temperature neutron diffraction pattern of Ho\(_2\)CrSbO\(_7\), it appeared similar to that of the pyrochlore Tb\(_2\)Sn\(_2\)O\(_7\) taken at 0.1 K [15]. Tb\(_2\)Sn\(_2\)O\(_7\) is a spin-liquid which undergoes a transition at 0.87 K to an ordered spin-ice state with both ferromagnetic and antiferromagnetic orders [15]. Therefore a model with antiferromagnetic ordering along two axes, \(x\) and \(y\), and a ferromagnetic component along the third axis, \(z\), was tested which modelled all the peaks. The moments were constrained to be along the \(\langle111\rangle\) axes to give an ordered spin ice model.

The contribution from Cr\(^3+\) ions to the magnetic reflections was expected to be small due to the much larger Ho\(^3+\) moment and the Ho:Cr ratio of 2:1. The Cr\(^3+\) ions occupy half the B-sites and the magnetic interactions between them are diluted by non-magnetic Sb\(^5+\) ions. Various Cr ordering models were tested and a model with ferromagnetic ordering of the Cr\(^3+\) ions was seen to give a significantly better fit. The arrangement of magnetic moments on the Ho and Cr tetrahedra is shown in Fig. 5. The final magnetic model gave Ho\(^3+\) moments along the \(x\), \(y\) and \(z\) axes of 5.78(3) \(\mu_B\), resulting in a total Ho\(^3+\) moment of 10.02(5) \(\mu_B\), and a Cr\(^3+\) moment of 2.72(5) \(\mu_B\) \((\chi^2=2.978; R_{wp}=0.042; R_B=0.020)\). The Ho\(^3+\) moment is in excellent agreement with the expected moment of 10.0 \(\mu_B\); the reduction in the Cr\(^3+\) moment the ideal value of 3.0 \(\mu_B\) primarily relates to covalence effects. The unit cell contracts at low temperature as expected giving an \(a\)-parameter at 1.5 K of 10.1648(1) Å.
Hysteresis data were collected below the magnetic ordering transition, at 5 K (Fig. 6). The saturated moment obtained from the plot was 11.2 $\mu_B$ per formula unit, much lower than the value of 23 $\mu_B$ expected for complete alignment of the moments on all the magnetic ions. However, reduced moments for the lanthanide ions in these types of pyrochlore have been seen previously due to a local 111 Ising anisotropy\[7,15–17\]. The full moment cannot be seen because the magnetic moments are constrained along the 111 axes and the field applied is too weak to turn them away from this direction. Assuming the moments lie along the 111 axes with the ferromagnetic component in the z-direction, the reduced moment observed in the z-direction is calculated to be 5.8 $\mu_B$. This gives a total calculated saturated moment of 14.6 $\mu_B$ which is much closer to the observed value of 11.2 $\mu_B$. The calculated value is still too high but would be expected to be reduced further due to the average arrangement of the crystallites in a powder sample.

The presence of magnetic Ho$^{3+}$ ordering in this highly frustrated magnetic system and the breaking of cubic magnetic symmetry is interesting and suggests that there must be an influence from the magnetic B-site ions. The related compound Ho$_2$FeSbO$_7$ was also prepared and shown to be paramagnetic at all temperatures. This suggests that the Cr$^{3+}$ ions are crucial in inducing magnetic order in the systems. Mixed compounds Ho$_2$Cr$_{1-x}$Fe$_x$SbO$_7$ (x=0.25, 0.5, and 0.75) were also prepared and magnetic ordering at low temperatures was indicated from preliminary SQUID magnetometry data showing that even small amounts of Cr (x=0.25) can induce a ferromagnetic transition. The B-sites are 50% occupied by Cr$^{3+}$ ions and 50% occupied by Sb$^{5+}$ ions; therefore a given B$_4$ tetrahedron is likely to contain two Cr$^{3+}$ ions and two Sb$^{5+}$ ions. The B$_4$ tetrahedra are corner linked and the Cr$^{3+}$ ions can interact magnetically through 130° Cr–O–Cr links. Each Cr$^{3+}$ would therefore have two Cr$^{3+}$ neighbours it could interact with forming magnetically linked Cr$^{3+}$ chains throughout the structure (Fig. 7). It is likely that such chains are responsible for the ferromagnetic ordering of the Cr$^{3+}$ ions, which induces the ferromagnetic moments on the Ho$^{3+}$ ions to be along a single axis, here assumed to be z (Fig. 5).

3.2. Paramagnetic region.

The inverse susceptibility data above $T=150$ K can be fitted to the Curie–Weiss law giving a total moment, $\mu_{\text{total}}=15.4 \mu_B$ and a Weiss constant, $\theta=-3.4$ K. The moment is almost exactly as expected for two Ho$^{3+}$ ions ($\mu_{\text{spin}}=10.60 \mu_B$) and one Cr$^{3+}$ ion ($\mu_{\text{spin}}=3.87 \mu_B$). The negative Weiss constant is suggestive of dominant antiferromagnetic exchange interactions in this region but the small value provides an element of uncertainty.

3.3. Magnetic properties of RE$_2$CrSbO$_7$ (RE=Y, Tb, Dy, Er).

To investigate the interactions between Cr$^{3+}$ B-site ions without the presence of magnetic A-site cations, the compound Y$_2$CrSbO$_7$ was prepared and studied using SQUID magnetometry (Fig. 8). Y$_2$CrSbO$_7$ is reported in the literature to have ferromagnetic Cr–Cr interactions [10]. As for Ho$_2$CrSbO$_7$ inverse susceptibility plots revealed a transition at 143 K which was assigned to a very small YCrO$_3$ impurity [18,19]. The presence of a ferromagnetic
transition was not obvious from the susceptibility plot but hysteresis behaviour was observed at 5 K.

The presence of ferromagnetic Cr$^{3+}$ ordering in Y$_2$CrSbO$_7$ at low temperatures indicates that the Cr$^{3+}$ ion order is inherent in these systems and not due to the presence of magnetic lanthanide ions on the A-site. In fact, it is thought that the field provided by the ferromagnetic Cr$^{3+}$ ions at low temperature is enough to lift the degeneracy of the x, y and z axes and induce ordering of the Ho$^{3+}$ moments.

These results indicate that related materials containing B-site Cr$^{3+}$ ions would show magnetic lanthanide ion ordering at low temperatures and the samples Tb$_2$CrSbO$_7$, Dy$_2$CrSbO$_7$ and Er$_2$CrSbO$_7$ were prepared.

The compound Dy$_2$CrSbO$_7$ has been reported to order magnetically below 16 K [10]. Transitions were seen in the susceptibility data for Dy$_2$CrSbO$_7$ at approximately 18 K and 150 K corresponding to ordering of the Dy$^{3+}$ moments and DyCrO$_3$ impurity [19], respectively. Fitting the data to the Curie–Weiss law gave a total moment, $\mu_{\text{total}} = 15.7 \mu_B$ and a Weiss constant, $\theta = -6.0$ K. The moment is as expected for two Dy$^{3+}$ ions ($\mu_{\text{exp}} = 10.63 \mu_B$) and one Cr$^{3+}$ ion, and the Weiss constant is, again, indicative of antiferromagnetic behaviour. Hysteresis data collected at 5 K gave a saturated moment of 11.96 $\mu_B$, showing that the Dy$^{3+}$ moment is also reduced by the 111 anisotropy.

The high temperature transition attributed to RECrO$_3$ impurity was also observed in the susceptibility data for Tb$_2$CrSbO$_7$ (at 161 K) and Er$_2$CrSbO$_7$ (at 139 K) [18,20].

4. Conclusions

The magnetic ordering in the pyrochlor e Ho$_2$CrSbO$_7$ has been studied using neutron powder diffraction. Often magnetic ordering cannot occur in the frustrated magnetic sublattice of the pyrochlor structure but Ho$_2$CrSbO$_7$ forms an "ordered spin-ice structure" below 13 K where the Ho$^{3+}$ moments are constrained along the (111) axes. Ferromagnetic ordering of the Cr$^{3+}$ ions lifts the degeneracy of the x, y and z directions in the cubic structure and causes the ferromagnetic Ho$^{3+}$ moment to align in one direction, unlike the spin-ice pyrochlores Ho$_2$Ti$_2$O$_7$ and Dy$_2$Ti$_2$O$_7$. The Cr$^{3+}$ ions are therefore thought to be crucial for inducing magnetic Ho$^{3+}$ ordering at low temperatures. At present, the precise nature of the Cr$^{3+}$ interactions has not been established, and the effect the transition metal ion has on rare earth magnetic ordering provides interesting possibilities for further research.

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