Structure and magnetic properties of cation-disordered perovskites SrLaCrSnO₆ and Ca₂CeCr₂TiO₉

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ABSTRACT

Polycrystalline samples of the new perovskites SrLaCrSnO₆ and Ca₂CeCr₂TiO₉ have been synthesised using the ceramic method and characterized by x-ray diffraction, neutron diffraction and magnetometry. Both crystallise in the space group Pbnm, with a disordered distribution of B-site cations, and both exhibit G-type antiferromagnetism at low temperatures. The antiferromagnetic order develops over a large temperature range. It is proposed that isolated antiferromagnetic clusters grow in size upon cooling to form a long-range antiferromagnetically-ordered backbone running through the structure. Cations with few magnetic nearest-neighbours remain decoupled from the backbone down to 2 K. More decoupled clusters are present in Ca₂CeCr₂TiO₉ than in SrLaCrSnO₆. This is attributed to the increase in frustration that accompanies the increase in strength of the next-nearest-neighbor interactions that occurs when d²Sn⁴⁺ is replaced by d²Ti⁴⁺.

1. Introduction

A simple cubic perovskite has the empirical formula ABO₃ where A is normally a relatively-large divalent or trivalent cation and B is a smaller transition-metal or p-block cation. The perovskite structure has been shown to be very amenable to cation substitution at the A site, the B site transition-metal or p-triple perovskite LaSr₂Cr₂SbO₉. In this compound two crystallographically-distinct B sites are ordered in a 1:1 checkerboard arrangement [3]; 87% of the sites on one sublattice and 46% of those on the other are occupied by Cr. Hence, even though the dominant superexchange interaction between the two sites is antiferromagnetic the magnetisations of the two sublattices do not cancel, and ferrimagnetic behaviour is observed below a Curie temperature of 150 K. Ferrimagnetism is relatively rare in insulating mixed-metal oxides. However, although the double perovskite Sr₂CrSbO₆ is, as might be expected, an antiferromagnet, Ca₂CrSbO₆ is ferromagnetic below 14 K [4,5].

We have carried out a number of syntheses in an attempt to find other compounds that behave similarly to those described above. Our attempts to prepare new ferrimagnets in which the six-coordinate sites are occupied by Cr³⁺ and a diamagnetic cation in a 2:1 ratio have led us to Ca₂CeCr₂TiO₉ and, guided by the behaviour of Sr₂CaCrSbO₆, our search for new ferrimagnets in which Cr³⁺ and a diamagnetic cation occupy the B sites in a 1:1 ratio has led to the synthesis of SrLaCrSnO₆. Neither of these compounds shows the type of behaviour we were seeking but they do have interesting magnetic properties and both are reminiscent of SrLaFeSnO₆ [6]. The similarities between them have prompted us to present the results of our two initially-independent studies in the same paper.

2. Experimental

Polycrystalline samples of Ca₂CeCr₂TiO₉ and SrLaCrSnO₆ were synthesised using the traditional ceramic method. To form SrLaCrSnO₆ stoichiometric quantities of SrCO₃, Cr₂O₃, SnO₂ and pre-dried La₂O₃ were ground and re-pelleted. Stoichiometric quantities of SrCO₃, Cr₂O₃, SnO₂ and pre-dried La₂O₃ were ground and re-pelleted. Stoichiometric quantities of SrCO₃, Cr₂O₃, SnO₂ and pre-dried CeO₂ were used as starting materials to form Ca₂CeCr₂TiO₉. The same firing sequence was used to form
SrLaCrSnO$_6$ using the instrument D2b at the ILL, Grenoble. NPD data to model the peak shapes and the background was modelled using a 20-term shifted Chebyshev function.

The progress of the syntheses was monitored using X-ray powder diffraction (XRD) data collected in our laboratory on a PANalytical Empyrean diffractometer operating with Cu K$_{\alpha 1}$ radiation over an angular range of $0 \leq 2\theta \leq 125$ at room temperature. Further powder diffraction data were collected using a Si-calibrated wavelength of $\lambda = 0.8259$ Å on the instrument I11 at the RAL Diamond Light Source [7]. In the latter case, the samples were loaded into a 0.3 mm diameter borosilicate glass capillary and data were collected at room temperature using the Mythen position-sensitive detector (PSD) over an angular range of $2 \leq 2\theta \leq 92$. The data were analysed using the Rietveld method [8], as implemented in the GSAS program suite [9], in order to determine the unit cell parameters. A cylindrical absorption correction for each sample was estimated using the Argonne X-ray absorption correction for each sample was estimated using the Argonne X-ray absorption correction calculator [10]. A pseudo-Voigt function [11] was employed to model the peak shapes and the background was modelled using a 20-term shifted Chebyshev function.

Neutron powder diffraction (NPD) data were collected on SrLaCrSnO$_6$ using the instrument D2b at the ILL, Grenoble. NPD data were collected at 3.5 K, 60 K, 110 K, 200 K and at room temperature over an angular range of $0 \leq 2\theta \leq 150$ in steps of $\Delta 2\theta = 0.05^\circ$ using a wavelength of 1.594 Å. The sample was loaded into a 6 mm diameter vanadium can and mounted in a displex refrigerator for all measurements below room temperature. Each dataset was fully analysed using the Rietveld method. A pseudo-Voigt function was employed to model the peak shapes and the background was modelled using a 12-term shifted Chebyshev function.

Neutron powder diffraction (NPD) data were collected on Ca$_2$CeCr$_2$TiO$_9$ on the WISH time-of-flight diffractometer [12] at the ISIS spallation source at 1.6 K, 60 K, 110 K, 200 K and at room temperature in the temperature range $0 \leq 2\theta \leq 150$ in steps of $\Delta 2\theta = 0.05^\circ$ using a wavelength of 1.594 Å. The sample was loaded into a 6 mm diameter cylindrical vanadium can and mounted in an Oxford Instruments cryostat when data were to be collected below room temperature. The data collected on banks 2–9 were refined simultaneously using the Rietveld method. A pseudo-Voigt function was employed to model the peak shapes and the background was modelled using a 12-term shifted Chebyshev function for banks 2/9 and 3/8 and a 20-term shifted Chebyshev function for banks 4/7 and 5/6. The scattering angles for the different detector banks are as follows: banks 2/9, 58°; banks 3/8, 90°; banks 4/7, 122° and banks 5/6, 153°.

DC magnetometry data were collected on both compounds using a Quantum Design SQUID magnetometer. The measurements were taken on warming the samples through the temperature range $2 \leq T/K \leq 300$ in a field of 100 Oe, firstly after cooling from room temperature to 2 K in zero field (ZFC) and subsequently after cooling in the measuring field (FC). The magnetisation per formula unit (f. u.) of the samples was also measured as a function of applied field at 5, 60, 110 and 200 K for SrLaCrSnO$_6$ and at 5, 100 and 200 K for Ca$_2$CeCr$_2$TiO$_9$ over a field range of $-50 \leq H/KOe \leq 50$.

### 3. Results

Our XRD data showed that both SrLaCrSnO$_6$ and Ca$_2$CeCr$_2$TiO$_9$ crystallise in the space group $Pbnm$. The 4e site is occupied by a disordered arrangement of either 1:1 Sr/La or 2:1 Ca/Ce, and the 4f site by a disordered arrangement of either a 1:1 Cr/Sn or 2:1 Cr/Ti. Two crystallographically-distinct oxide ions occupy 4e and 8f sites. The Rietveld fits to the data collected on I11 are shown in Fig. 1; $R_{wp} = 0.0162$ for SrLaCrSnO$_6$ and $R_{wp} = 0.0365$ for Ca$_2$CeCr$_2$TiO$_9$.

SrLaCrSnO$_6$ was found to be contaminated with 0.44(2) wt% La$_2$Sn$_2$O$_7$ and Ca$_2$CeCr$_2$TiO$_9$ with 3.77(3) wt% CaTiO$_3$ and 0.1(1) wt% CeO$_2$.

The temperature dependence of the molar magnetic susceptibility, $\chi(T)$, of SrLaCrSnO$_6$ is shown in Fig. 2. There is a slight divergence of the ZFC and FC curves below 200 K, which is most noticeable in the plot of the inverse molar susceptibility against temperature shown in the inset. This divergence becomes more marked below 150 K. The ZFC susceptibility levels out at 80 K and there is a clear change in the gradient of both the ZFC and FC curves below 150 K. Below 35 K there appears to be a paramagnetic-like upturn that becomes more prominent below 12 K. From a Curie-Weiss fit to the inverse susceptibility in the temperature range $200 \leq T/K \leq 300$, the effective magnetic moment per Cr$^{3+}$ cation was found to be 4.25(13) $\mu_B$ and the Weiss temperature was found to be $-360(3)$ K. The field dependence of the magnetisation per formula unit at 5, 60, 110 and 200 K is shown in Fig. 3. $M(H)$ is linear at 200 K and at 110 K but at 60 K there is a small amount of magnetic hysteresis and a slight non-linearity to the curve, which is more pronounced at 5 K. The magnetisation does not saturate and is only 0.14 $\mu_B$ per formula unit at 5 K and 50 kOe.

The temperature dependence of the molar magnetic susceptibility of Ca$_2$CeCr$_2$TiO$_9$ shown in Fig. 4, shows similar behaviour to that of SrLaCrSnO$_6$ except that the transitions are sharper and larger in magnitude. The ZFC and FC susceptibilities differ below 175 K; this is again more obvious in $\chi'$ (T). A Curie-Weiss fit to the region $200 \leq T/K \leq 300$ gave an effective magnetic moment per Cr$^{3+}$ cation of 4.53(13) $\mu_B$ and a Weiss temperature of $-466(2)$ K. At 80 K there is a sharp change in gradient in both the ZFC and FC susceptibilities, with both increasing in magnitude on cooling. At 2 K this increase is tending towards a plateau of 1.44 cm$^3$ mol$^{-1}$ for the FC curve and 0.36 cm$^3$ mol$^{-1}$ for the ZFC curve. Fig. 5 shows that $M(H)$ is linear at 200 K but a small amount of hysteresis is present at 100 K and an increased level is...
clearly present at 2 K. At 2 K the magnetisation does not saturate but has a coercive field of 2.45 kOe and a remanent magnetisation of ~0.034 µB per formula unit.

Rietveld analysis of the NPD patterns collected at room temperature confirmed that both compounds crystallise in the space group Pbnm. In view of the relatively high level of CaTiO3 detected at the synchrotron X-ray source, the occupancies of the cation sites in Ca2CeCr2TiO9 were allowed to vary during our analysis of the NPD data collected at room temperature. Constraints were applied to ensure that both the A and B sites remained fully occupied and that Ca2+ and Ti4+ cations left the structure in equal numbers, whilst rescaling the composition to leave no vacancies on the oxygen sites. This strategy gave a refined composition of Ca1.969Ce1.031Cr2.062Ti0.938O9, corresponding to an impurity concentration of 2.64 wt%, which was used subsequently during the analysis of the diffraction data collected at lower temperatures. Note that for simplicity we shall continue to use the ideal formula in our text. The fits to the diffraction patterns recorded from both compounds at room temperature are shown in Fig. 6. The corresponding structural parameters and selected bond lengths and angles are listed in Table 1–6. No cation ordering was detected in either compound when test refinements were carried out in the monoclinic space group P21/n.

The NPD pattern collected from SrLaCrSnO6 at 200 K could be accounted for using the same structural model that was used in the analysis of the data collected at room temperature. On cooling to 110 K a small amount of diffuse scattering at the position of the (101)/(011) reflection is visible, see Fig. 7, but it was not included in our quantitative analysis of the pattern. By 60 K it had developed into a Bragg reflection which grew in intensity on cooling to 3.5 K. This reflection can be accounted for by the inclusion in the model of a Gz magnetic structure [13] involving the Cr3+ cations on the B site, see Fig. 8. The ordered magnetic moment per Cr3+ cation, MO, refined to be 1.63(4) µB and 2.24(3) µB at 60 K and 3.5 K, respectively. The atomic coordinates, bond lengths and bond angles determined in these analyses are included in Tables 1–3.

Similarly, no magnetic Bragg scattering is apparent in the diffraction pattern collected at 200 K from Ca2CeCr2TiO9 but Bragg peaks corresponding to the (101)/(011) reflection of a Gz magnetic structure appear at d ~4.4 Å on cooling, see Fig. 9 and Figs. S1–S5. The peak is first visible in the data collected at 110 K and grows in intensity on cooling to 60 K and 1.6 K. The increase in intensity is reflected in the refined ordered moments of the Cr(III) cation; at 110 K MO = 0.89(1) µB, at 60 K MO = 1.490(5) µB and at 1.6 K MO = 1.974(5) µB. The atomic coordinates, bond lengths and bond angles determined in these analyses are included in Tables 4–6.
Table 1

Structural parameters of SrLaCrSnO₆ at 300 K, 200 K, 110 K, 60 K and 3.5 K.

|          | 300 K          | 200 K          | 110 K          | 60 K           | 3.5 K          |
|----------|----------------|----------------|----------------|----------------|----------------|
| Sr/La−O1 | 2.459(3)       | 2.454(3)       | 2.449(3)       | 2.447(3)       | 2.445(3)       |
| Sr/La−O1 | 2.686(3)       | 2.675(2)       | 2.665(2)       | 2.659(2)       | 2.660(2)       |
| Sr/La−O1 | 2.966(3)       | 2.972(2)       | 2.982(2)       | 2.988(2)       | 2.986(2)       |
| Sr/La−O1 | 3.166(3)       | 3.167(3)       | 3.168(3)       | 3.170(3)       | 3.172(3)       |
| Sr/La−O2 | 2.526(2)       | 2.520(2)       | 2.5175(18)     | 2.5172(2)      | 2.515(2)       |
| Sr/La−O2 | 2.526(2)       | 2.520(2)       | 2.5175(18)     | 2.5172(2)      | 2.515(2)       |
| Sr/La−O2 | 2.718(2)       | 2.7142(19)     | 2.7079(17)     | 2.7092(2)      | 2.710(2)       |
| Sr/La−O2 | 2.718(2)       | 2.7142(19)     | 2.7079(17)     | 2.7092(2)      | 2.710(2)       |
| Sr/La−O2 | 2.8252(18)     | 2.8199(17)     | 2.8180(16)     | 2.8138(17)     | 2.8138(17)     |
| Sr/La−O2 | 2.8252(18)     | 2.8199(17)     | 2.8180(16)     | 2.8138(17)     | 2.8138(17)     |
| Sr/La−O2 | 3.1833(17)     | 3.1917(16)     | 3.1993(15)     | 3.2028(17)     | 3.2025(17)     |
| Sr/La−O2 | 3.1833(17)     | 3.1917(16)     | 3.1993(15)     | 3.2028(17)     | 3.2025(17)     |
| < Sr/La−O1 > | 2.815 | 2.813 | 2.812 | 2.812 | 2.812 |
| Cr/Sn−O1 | 2.0141(4)      | 2.0126(4)      | 2.0127(3)      | 2.0127(4)      | 2.0130(4)      |
| Cr/Sn−O2 | 2.0109(14)     | 2.0125(14)     | 2.0136(13)     | 2.0133(15)     | 2.0124(15)     |
| < Cr/Sn−O2 > | 2.011 | 2.011 | 2.010 | 2.011 | 2.011 |

Table 2

Bond lengths (Å) in SrLaCrSnO₆ at 300 K, 200 K, 110 K, 60 K and 3.5 K.

|          | 300 K          | 200 K          | 110 K          | 60 K           | 3.5 K          |
|----------|----------------|----------------|----------------|----------------|----------------|
| O1−Cr/Sn−O2 | 90.01(8)       | 90.01(8)       | 90.04(7)       | 90.12(8)       | 90.14(8)       |
| O1−Cr/Sn−O2 | 90.14(8)       | 90.14(8)       | 90.16(7)       | 90.17(8)       | 90.14(8)       |
| O2−Cr/Sn−O2 | 91.108(12)     | 91.132(12)     | 91.138(11)     | 91.134(12)     | 91.139(12)     |
| < O−Cr/Sn−O > | 90.42 | 90.43 | 90.45 | 90.47 | 90.47 |
| Cr/Sn−O1−Cr/Sn | 158.99(11)   | 158.89(11)     | 158.58(10)     | 158.50(11)     | 158.42(11)     |
| Cr/Sn−O2−Cr/Sn | 161.29(6)   | 160.79(6)      | 160.54(6)      | 160.43(6)      | 160.40(6)      |
| < Cr/Sn−O−Cr/Sn > | 160.14 | 159.84 | 159.56 | 159.47 | 159.41 |

Table 3

Bond angles (deg) in SrLaCrSnO₆ at 300 K, 200 K, 110 K, 60 K and 3.5 K.

|          | 300 K          | 200 K          | 110 K          | 60 K           | 3.5 K          |
|----------|----------------|----------------|----------------|----------------|----------------|
| Sr/La−O1 | 90.01(8)       | 90.01(8)       | 90.04(7)       | 90.12(8)       | 90.14(8)       |
| Sr/La−O1 | 90.14(8)       | 90.14(8)       | 90.16(7)       | 90.17(8)       | 90.14(8)       |
| Sr/La−O1 | 91.108(12)     | 91.132(12)     | 91.138(11)     | 91.134(12)     | 91.139(12)     |
| < Sr/La−O > | 90.42 | 90.43 | 90.45 | 90.47 | 90.47 |
| Cr/Sn−O1−Cr/Sn | 158.99(11)   | 158.89(11)     | 158.58(10)     | 158.50(11)     | 158.42(11)     |
| Cr/Sn−O2−Cr/Sn | 161.29(6)   | 160.79(6)      | 160.54(6)      | 160.43(6)      | 160.40(6)      |
| < Cr/Sn−O−Cr/Sn > | 160.14 | 159.84 | 159.56 | 159.47 | 159.41 |

Fig. 6. Observed (red crosses) and calculated (green line) neutron powder diffraction profiles of a) SrLaCrSnO₆ and b) Ca₂Ce₂Cr₂TiO₉ at room temperature. Reflection markers are shown top to bottom for a) La₂Sn₂O₇ (red) and SrLaCrSnO₆ (black) and b) Ca₂Ce₂Cr₂TiO₉ (blue), and Ca₂TiO₃ (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article)
Table 4
Structural parameters of Ca$_2$CeCr$_2$TiO$_9$ at 300 K, 200 K, 110 K, 60 K and 1.6 K.

|          | 300 K         | 200 K         | 110 K         | 60 K          | 1.6 K         |
|----------|---------------|---------------|---------------|---------------|---------------|
| a/Å      | 5.3534(16)    | 5.3482(15)    | 5.3448(15)    | 5.3430(14)    | 5.3438(14)    |
| b/Å      | 5.4570(15)    | 5.4569(16)    | 5.4563(16)    | 5.4561(15)    | 5.4558(14)    |
| c/Å      | 7.6292(23)    | 7.6235(22)    | 7.6194(22)    | 7.6187(22)    | 7.6182(21)    |
| V/Å$^3$  | 222.88(11)    | 222.49(11)    | 222.20(11)    | 222.15(11)    | 222.10(10)    |
| R$_{wp}$ | 0.0396        | 0.0377        | 0.0380        | 0.0386        | 0.0388        |
| Ca/Ce   | x 0.01058(17) | -0.01068(16)  | -0.01052(16)  | -0.01052(16)  | -0.01044(17)  |
|         | y 0.04265(12) | 0.04416(12)   | 0.04492(12)   | 0.04522(12)   | 0.04521(12)   |
|         | z 0.0871(13)  | 0.08707(13)   | 0.08782(13)   | 0.08729(13)   | 0.08705(13)   |
| U$_{iso}$/Å$^2$ | 0.01058(17) | -0.01054(16)  | -0.01051(16)  | -0.01051(16)  | -0.01044(17)  |

Table 5
Bond lengths (Å) in Ca$_2$CeCr$_2$TiO$_9$ at 300 K, 200 K, 110 K, 60 K and 1.6 K.

|          | 300 K         | 200 K         | 110 K         | 60 K          | 1.6 K         |
|----------|---------------|---------------|---------------|---------------|---------------|
| Ca/Ce-O  | 2.2963(12)    | 2.2965(11)    | 2.2942(12)    | 2.2942(12)    | 2.2948(12)    |
|          | 2.4200(7)     | 2.4099(7)     | 2.4042(7)     | 2.4022(7)     | 2.4015(7)     |
| Ca/Ce-O  | 3.1080(12)    | 3.1055(12)    | 3.1061(12)    | 3.1062(12)    | 3.1051(12)    |
|          | 3.1381(8)     | 3.1481(7)     | 3.1533(7)     | 3.1525(7)     | 3.1548(8)     |
| Cr/Ti    | 0.0871(13)    | 0.08707(13)   | 0.08782(13)   | 0.08729(13)   | 0.08705(13)   |
| O1       | x 0.01058(17) | -0.01068(16)  | -0.01052(16)  | -0.01052(16)  | -0.01044(17)  |
|          | y 0.04265(12) | 0.04416(12)   | 0.04492(12)   | 0.04522(12)   | 0.04521(12)   |
|          | z 0.0871(13)  | 0.08707(13)   | 0.08782(13)   | 0.08729(13)   | 0.08705(13)   |
| U$_{iso}$/Å$^2$ | 0.01058(17) | -0.01054(16)  | -0.01051(16)  | -0.01051(16)  | -0.01044(17)  |

Table 6
Bond angles (deg) in Ca$_2$CeCr$_2$TiO$_9$ at 300 K, 200 K, 110 K, 60 K and 1.6 K.

|          | 300 K         | 200 K         | 110 K         | 60 K          | 1.6 K         |
|----------|---------------|---------------|---------------|---------------|---------------|
| O1−Cr/Ti | 91.308(24)    | 91.211(24)    | 91.208(24)    | 91.231(24)    | 91.22(25)     |
| O1−Cr/Ti | 90.654(27)    | 90.815(26)    | 90.848(26)    | 90.851(27)    | 90.872(28)    |
| O2−Cr/Ti | 90.589(6)     | 90.583(6)     | 90.564(6)     | 90.559(6)     | 90.554(6)     |
| O−Cr/Ti  | 90.85        | 90.87        | 90.87        | 90.88        | 90.88        |
| Cr/Ti−Cr  | 151.47(4)    | 151.45(4)    | 151.38(4)    | 151.36(4)    | 151.43(4)    |
| Cr/Ti−Cr  | 151.738(23)  | 151.464(23)  | 151.374(23)  | 151.377(24)  | 151.364(24)  |
| O−Cr/Ti−Cr/Ti | 151.60 | 151.46 | 151.38 | 151.37 | 151.40 |

4. Discussion

The structural chemistry of SrLaCrSnO$_6$ is very similar to that of Ca$_2$CeCr$_2$TiO$_9$. Both crystallise in the orthorhombic space group Pbmn and hence show no cation ordering over the six-coordinate sites. The average bond lengths are as expected; <Ca/Ce-O> is significantly shorter than <Sr/La-O>, which is consistent with Ce's $^{4+}$ and Ca's $^{2+}$ both being smaller than La$^{3+}$ and Sr$^{2+}$, and <Cr/Ti-O> is significantly shorter than <Cr/Sn-O>, again consistent with the degree of tilting in the tetrahedral cations [14]. The degree of octahedral tilting in Ca$_2$CeCr$_2$TiO$_9$ is sizable; the average tilt angle is ~14°, which is comparable to the degree of tilting in Ca$_2$CeSnO$_6$ [5]. However, SrLaCrSnO$_6$ has an average tilt angle of only ~10°. There is a slight reduction in the unit cell volume upon cooling both samples but there is remarkably little change in the average bond lengths and angles. No change in space group symmetry was observed.

Fitting χ$^2$(T) to the Curie-Weiss law resulted in a large negative Weiss temperature and an effective moment per Cr$^{3+}$ ion that is much greater than the theoretical value of 3.87 µB for both SrLaCrSnO$_6$ and Ca$_2$CeCr$_2$TiO$_9$. Given that LaCrO$_3$ orders antiferromagnetically at 290 K [15], it is likely that significant short-range magnetic ordering is present in the temperature range 200 < T/K < 300, thus rendering the parameters derived from the Curie-Weiss law in that temperature range physically meaningless. The observation of a difference between the ZFC and FC χ(T) curves at temperatures as high as 200 and 175 K in SrLaCrSnO$_6$ and Ca$_2$CeCr$_2$TiO$_9$, respectively, is consistent with this explanation. The behaviour of both curves below 200 K is unusual and will be discussed below.

Our neutron diffraction data indicate that, in contrast to Ca$_2$CeSnO$_6$ and LaSr$_2$Cr$_2$SnO$_6$, respectively, SrLaCrSnO$_6$ and Ca$_2$CeCr$_2$TiO$_9$ both adopt a G-type antiferromagnetic ground state with no net magnetisation in the absence of an applied field. In the case of Ca$_2$CeCr$_2$TiO$_9$ this is clearly attributable to the absence of the B-site cation ordering that is directly responsible for the ferrimagnetism of LaSr$_2$Cr$_2$SnO$_6$. The ferrimagnetism of Ca$_2$CeSnO$_6$ has been attributed to the high tilt angle of the CrO$_6$ octahedra therein. A similar level of tilting is present in SrLaCrSnO$_6$ but the absence of cation ordering leads to the presence of strong nearest-neighbour antiferromagnetic Cr-O-Cr superexchange interactions that are absent from the cation-ordered antimonate and so, once again, the change in magnetic behaviour can be traced to the absence of cation ordering. The loss of cation ordering is a consequence...
of the small charge difference between Cr$^{3+}$ and either Sn$^{4+}$ or Ti$^{4+}$. However, the temperature dependence of the magnetic susceptibilities of these compounds is not characteristic of simple antiferromagnets. Furthermore, the ordered magnetic moment per Cr$^{3+}$ cation is unusually low in both SrLaCrSnO$_6$ and Ca$_2$CeCr$_2$TiO$_9$, and particularly so in the latter. In order to understand these results it is useful to compare the magnetic behaviour of SrLaCrSnO$_6$ below 200 K with that of the iron analogue, SrLaFeSnO$_6$, which also crystallises in the space group $Pbnm$ [6]. The ZFC and FC susceptibilities of SrLaFeSnO$_6$ do not overlie below 250 K; the ZFC curve reaches a maximum at 38 K, suggesting the onset of antiferromagnetic ordering, while the FC curve reaches a constant value at around the same temperature. Neutron diffraction data collected at 1.7 K revealed a G$_z$ antiferromagnetic spin arrangement at that temperature. Mössbauer spectroscopy showed that magnetic hyperfine interactions were present in SrLaFeSnO$_6$ below 215 K, leading Attfield et al. to postulate that short-range magnetic interactions start to develop below 250 K and that long-range antiferromagnetic ordering occurs at 38 K. Gibb expanded on this model by envisaging clusters of antiferromagnetically coupled spins gradually increasing in size and linking together as the temperature is lowered until long-range order occurs along a magnetic ‘backbone’ [16]. Simulations showed that while 87% of Fe atoms in a fully disordered structure are expected to be biconnected to the magnetic backbone of the lattice, only 63% are connected by more than two nearest-neighbour pathways. Clusters with few connections to the backbone are more susceptible to competing superexchange interactions and will be the first to decouple from the magnetic backbone as the temperature is raised. They are likely to carry a small net moment due to the incomplete cancellation of spins and they will therefore enhance the susceptibility and be strongly influenced by an external magnetic field, hence the observed hysteresis in the magnetic susceptibility. The
ordered magnetic moment per Fe\(^{3+}\) cation at 1.5 K, 2.94 \(\mu_B\) \[6\], is very low, suggesting that even at this temperature not all of the spins and clusters are linked to the magnetic backbone.

Attfield et al. only collected neutron diffraction data on SrLaFeSnO\(_6\) at room temperature and 1.7 K but we have been able to collect data on SrLaCrSnO\(_6\) over a greater range of temperatures and hence to follow the temperature evolution of the long-range magnetic ordering. At 110 K, well below the temperature at which the ZFC and FC curves cease to overlie, no sharp magnetic Bragg peaks have developed but we do observe a broad, weak, diffuse magnetic peak showing that significant short-range antiferromagnetic interactions are present. We suggest that the decrease in gradient of \(\chi(T)\) at 80 K marks the onset of truly long-range antiferromagnetic ordering and the formation of a backbone of ordered spins. This type of ordering is certainly present at 60 K, as is shown by the presence of a sharp magnetic Bragg peak in the diffraction pattern, see Fig. 7(c). As the temperature decreases further the intensity of the magnetic Bragg scattering, representing the magnitude of the ordered moment, increases as more spin clusters join the magnetic backbone of the lattice and partake in the long-range magnetic order. The refined ordered moment per Cr ion at 3.5 K of 2.24(3) \(\mu_B\) is only slightly smaller than expected given that the ordered moment per Cr\(^{3+}\) ion in LaCrO\(_3\) is 2.63(3) \(\mu_B\) \[17\] and 2.56(3) \(\mu_B\) in Ca\(_2\)CrSbO\(_6\) \[5\]. If we assume that only Cr\(^{3+}\) ions that are at least biconnected to the magnetic backbone (~87%) contribute to the long-range magnetic order at this temperature then the moment per Cr\(^{3+}\) ion becomes a more reasonable 2.57 \(\mu_B\). The rise in the susceptibility at the lowest temperatures measured can be attributed to the presence of the disconnected spins.

The similarity of the magnetic susceptibility and NPD data collected on Ca\(_2\)CeCr\(_2\)TiO\(_9\) to those from SrLaFeSnO\(_6\) suggests that the magnetic cluster model can also be applied to this system. The ZFC and FC \(\chi(T)\) curves differ below 175 K, see Fig. 4, and a magnetic Bragg peak is apparent in the NPD data collected at 110 K. The refined value of the ordered moment, 0.89(1) \(\mu_B\), is, however, very small. Below the increase in gradient of \(\chi(T)\) at 80 K the intensity of the magnetic scattering increases but the ordered moment per Cr\(^{3+}\) cation at 1.6 K, 1.974(5) \(\mu_B\), is smaller than that found in SrLaCrSnO\(_6\). This suggests that at base temperature cluster formation is extensive but that fewer spins are connected to the magnetic backbone in Ca\(_2\)CeCr\(_2\)TiO\(_9\) than in SrLaCrSnO\(_6\). This is consistent with the larger molar susceptibility at 2 K, the larger hysteresis in \(M(H)\) and the greater difference between the ZFC and FC \(\chi(T)\) of Ca\(_2\)CeCr\(_2\)TiO\(_9\) compared to SrLaCrSnO\(_6\). However, the B sites in Ca\(_2\)CeCr\(_2\)TiO\(_9\) contain a greater proportion of paramagnetic ions than in SrLaCrSnO\(_6\) so more ions will be at least biconnected to the magnetic backbone of the lattice. This would be expected to result in fewer clusters being decoupled from the magnetic backbone at low temperature.

The origin of this apparent contradiction may lie in the differences between the electronic structures of \(d^{10}\):Sn\(^{4+}\) and \(d^{10}\):Ti\(^{4+}\); the filled \(d\) orbitals of a \(p\)-block cation lie too low in energy to be involved in superexchange whereas the empty orbitals of the \(d\) cation are able to hybridise with the \(p\) orbitals of the \(O^2\) cation and hence can play a role in the magnetic coupling \[18\]. Like SrLaCrSnO\(_6\) and SrLaFeSnO\(_6\), Sr\(_2\)FeNbO\(_6\) and Sr\(_2\)FeTaO\(_6\) are orthorhombic perovskites with a disordered distribution of cations over the six-coordinate sites \[19,20\]. At ~23 K both they undergo a transition to a spin-glass state; no long-range magnetic order was seen in a neutron diffraction experiment despite the fact that, when only nearest-neighbour interactions are considered, magnetic frustration is absent from the perovskite structure. This behaviour was explained by assuming that antiferromagnetic next-nearest-neighbour (NNN) interactions between Fe\(^{3+}\) cations, ~5.5 Å apart, were in competition with the nearest-neighbour interactions, thus introducing frustration. The NNN interactions take place along a 90° pathway of the form Fe–O–M–O–Fe and they will thus be stronger when \(M\) is a \(d^0\) cation, for example Nb\(^{5+}\) or Ta\(^{5+}\), rather than a \(d^{10}\) cation, for example Sn\(^{4+}\). This argument can be
extended to include Ca$_2$CeCr$_2$TiO$_9$ wherein we propose that NNN interactions, mediated by Ti$^{4+}$, compete with NN Cr–O–Cr interactions. However, the relatively high concentration of Cr$^{3+}$ cations ensures that in this case a G-type magnetic structure is established, although the competition from the NNN interactions ensures that, compared to SrLaCrSnO$_6$, a relatively small fraction, ~76%, of the sites join the magnetic backbone.

5. Conclusion

The novel perovskites SrLaCrSnO$_6$ and Ca$_2$CeCr$_2$TiO$_9$ crystallise in the orthorhombic space group Pbnm. The magnetic properties of both can be explained by the formation of G$_x$-type antiferromagnetic clusters that grow in size upon cooling until they form a long-range-ordered magnetic backbone throughout the structure. Magnetic frustration, caused by competing superexchange interactions, can prevent all of the magnetic backbone at low temperature in Ca$_2$CeCr$_2$TiO$_9$ than in SrLaCrSnO$_6$.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2018.10.037.

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