Crystal and magnetic structures of the brownmillerite \( \text{Ca}_2\text{Cr}_2\text{O}_5 \)

Angel M. Arevalo-Lopez and J. Paul Attfield*

Powder neutron diffraction and magnetic susceptibility measurements at 10–300 K have been used to determine the crystal and magnetic structures of brownmillerite type \( \text{Ca}_2\text{Cr}_2\text{O}_5 \), which was obtained by reduction of the high pressure phase \( \text{CaCrO}_3 \) through hard–soft chemistry. The ambient temperature crystal structure of \( \text{Ca}_2\text{Cr}_2\text{O}_5 \) is refined in space group \( \text{i2} \text{m} \) and the unusual tetrahedral coordination of \( \text{Cr}^{3+} \) results in local structural distortions. \( \text{Cr}^{3+} \) spins order antiferromagnetically below 220 K and a substantial observed canting of moments shows that Heisenberg exchange is weak or frustrated and competes with antisymmetric Dzialoshinskii–Moriya interactions.

Introduction

Metastable, perovskite-related oxides of transition metals in unusual oxidation states or coordination geometries offer new materials that may have useful magnetic or electronic properties.\(^1\) We have recently used ‘hard–soft’ chemistry, in which the instability of a dense precursor prepared under ‘hard’ high pressure-temperature conditions is partially relieved through ‘soft’ post-synthesis modification, to synthesise new vacancy-ordered perovskite oxides.

Low-temperature hydrogen reductions of the cubic perovskite \( \text{SrCrO}_3 \), which requires synthesis pressures in excess of 4 GPa,\(^2,3\) gave two new \( \text{SrCrO}_{3-\delta} \) phases with oxygen deficiencies \( \delta = 0.2 \) and 0.25.\(^4\) These have complex superstructures due to oxide loss and reconstruction of widely-spaced cubic-(111) anion planes, which relaxes \( \text{Cr}^{4+} \) coordination from the octahedral geometry imposed at high pressure to tetrahedral. The \( \text{SrCrO}_{3-\delta} \) superstructure has subsequently been stabilised at ambient pressure by substitution of \( \text{Fe} \) for \( \text{Cr} \).\(^5\) The perovskite \( \text{SrCrO}_3 \) and the reduced \( \text{SrCrO}_{2.8} \) structure were also stabilised epitaxially as thin films, with rapid oxygen uptake or loss on cycling between the two phases.\(^6\)

The hard–soft route was also used to discover three reduced \( \text{CaCrO}_3 \) phases.\(^7\) The high pressure precursor \( \text{CaCrO}_3 \) has an orthorhombically-distorted perovskite structure.\(^8,9\) Reductions using a 90% Ar /10% H\(_2\) gas mixture at 400–450 °C revealed that three oxygen-deficient superstructure phases were formed, as shown in Fig. 1. The \( \text{CaCrO}_{3-\delta} \) perovskite superstructures are based on stacking of tetrahedral (T) and octahedral (O) layers, with increasing \( \text{T}/(\text{T} + \text{O}) \) ratio \( \delta = 0.33 \to 0.4 \to 0.5 \) as reduction proceeds. This structural mechanism had not previously been reported for reduced ternary \( \text{ABO}_{3-\delta} \) perovskites but is found in \( \text{CaTi}_{1-x}\text{Fe}_{x}\text{O}_{3-x} \) where \( \text{Fe} \)-content determines the \( \text{T}/(\text{T} + \text{O}) \) layer ratio.\(^10\) Magnetic ordering transitions were observed for the three reduced \( \text{CaCrO}_{3-\delta} \) phases at 150–200 K.\(^7\)

The most reduced \( \text{CaCrO}_{3-\delta} \) phase, \( \text{Ca}_2\text{Cr}_2\text{O}_5 \), has a brownmillerite \( (\text{Ca}_2\text{Fe}_2\text{O}_5) \)\(^11\) type structure where tetrahedral layers are stacked out-of-phase with their neighbours resulting in the \( \text{OTOT}^* \) stacking sequence shown in Fig. 1. There is one prior report of a \( \text{Ca}_2\text{Cr}_2\text{O}_5 \) brownmillerite prepared at ambient pressure,\(^12\) but the structure was not characterized. \( \text{Ca}_2\text{Cr}_2\text{O}_5 \) is notable as the brownmillerite structure contains \( \text{Cr}^{3+} \) in both octahedral and tetrahedral environments. The latter coordination is rare as crystal field effects provide strong stabilisation of \( \text{Cr}^{3+} \) in octahedral environments. The structure of \( \text{Ca}_4\text{Cr}_2\text{O}_9 \) was refined in the aristotype \( \text{Imma} \) brownmillerite structure, in which the chains of tetrahedra in the T layers are disordered, as the X-ray data in the previous study were not

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sensitive to possible ordered superstructures. Here we report a neutron diffraction study of Ca$_2$Cr$_2$O$_5$ which has provided structural characterisation of the chain order, and has also enabled us to solve the low temperature magnetic order of Cr$^{3+}$ spins.

**Experimental**

CaCrO$_3$ precursors were synthesized from a stoichiometric mixture of Ca$_3$Cr$_2$O$_6$ and Cr$_2$O$_3$ in a multi-anvil Walker-type press at 9 GPa and 1100°C. A 90% Ar/10% H$_2$ gas mixture was used to reduce CaCrO$_3$ samples to Ca$_2$Cr$_2$O$_5$.

Magnetization data were measured on a Quantum Design MPMS SQUID magnetometer. Susceptibilities in zero field cooled (ZFC) and field cooled (FC) conditions were recorded in the 2–300 K temperature range with a 0.5 T applied field.

Time-of-flight neutron diffraction data were collected using the GEM diffractometer at the ISIS neutron facility. Several samples were combined in order to obtain a suitable amount for the experiment (∼140 mg). Profiles were recorded at 10, 100, 200 and 300 K. Structural and magnetic models were fitted to data from banks 3, 4 and 5, centred respectively at 2θ = 35, 64 and 91°.

**Results and discussion**

**Crystal structure**

No structural phase changes were observed between 10 and 300 K, and the crystal structure of Ca$_2$Cr$_2$O$_5$ was refined using the 300 K neutron data. This structure was previously refined against X-ray data in the aristotype Imma brownmillerite structure, in which the tetrahedral are disordered. Ordered tilts of the tetrahedra can give rise to low symmetry superstructures, although the value for the Cr2 site is high, as often occurs for strained coordinations. The Cr1O$_6$ octahedron is tetragonally distorted due to the structural connectivity, but

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<table>
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<tr>
<th>Atom</th>
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<td>0.1074(4)</td>
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<td>0.5</td>
<td>0.5</td>
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<td>0.25</td>
<td>0.936(2)</td>
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<td>4b</td>
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Table 1 Refined parameters for Ca$_2$Cr$_2$O$_5$ in space group I2mb from the fit to 300 K neutron powder diffraction patterns.

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Fig. 2 Rietveld fits to 300 K and 10 K GEM neutron diffraction patterns for Ca$_2$Cr$_2$O$_5$. Lower tickmarks in the 10 K pattern correspond to the magnetic phase with k = (111). Data are from GEM bank 3, centred at 2θ = 35°. The inset shows the region containing magnetic peaks in the 200 K profile.

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<table>
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<tr>
<th>Bond distance (Å)</th>
<th>Bond angle (°)</th>
<th>BVS</th>
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<td>Cr1–Cr1</td>
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<td>3.65</td>
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<tr>
<td>Cr1–O1</td>
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<tr>
<td>Cr1–O2</td>
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<td>Cr2–O1</td>
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</tr>
<tr>
<td>Cr2–O2</td>
<td>1.88(1)</td>
<td>3.65</td>
</tr>
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Table 2 Bond distances (Å), bond angles (°), and bond valence sums (BVS) for the Cr sites in Ca$_2$Cr$_2$O$_5$ from refinement against 300 Kdiffraction data.

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O–Cr1–O angles are close to 90 or 180°. However, the Cr2O$_4$ tetrahedron is highly distorted with Cr2–O distances of 1.73–1.90 Å and opening of the O2–Cr2–O2 angle to 141° while other bond angles lie in the range 99–107°. The corresponding

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Fig. 2 shows the region containing magnetic peaks in the 200 K profile.
GaO₄ tetrahedron in isostructural Ca₇Ga₂O₅ is far less distorted, with Ga–O distances of 1.82–1.89 Å and O–Ga–O angles of 106–122°. As Cr³⁺ and Ga³⁺ have almost identical ionic radii (0.615 and 0.62 Å for octahedral coordination) this comparison suggests that the excess distortion of Ca₇Cr₂O₅ reflects the instability of tetrahedrally-coordinated Cr³⁺, as this cation generally has a strong preference for octahedral coordination which maximises crystal field stabilisation energy of the 3d³ electronic configuration. The Ca²⁺ site coordination is comparable to that in other brownmillerites, with seven short Ca–O bonds in the range 2.43–2.62 Å while other Ca–O distances are >2.85 Å. A previously reported study of multiple La₁₋ₓMnxO₃₋₀.₅ (A = Ca, Sr, Ba) brownmillerite compositions showed that the different structural phases fall into distinct regions on a plot of the tetrahedral layer separation (b/2), which has value 7.385 Å for Ca₇Cr₂O₅, against the deviation of the tetrahedral distances are >2.85 Å.

Magnetic structure

Magnetization measurements for the Ca₇Cr₂O₅ sample revealed a Curie tail at low temperatures and a trace of ferromagnetic material, as found in our previous study of CaCrO₃ with two structural phases. These impurity contributions were subtracted to yield the susceptibility shown in Fig. 3. A transition is apparent near 200 K with no divergence between ZFC and FC data, suggesting that the spin order is antiferromagnetic. The inverse susceptibility shows linear variation with temperature at 240–300 K, and a Curie–Weiss fit in this range gives a paramagnetic moment of 3.0 μB and a Weiss temperature of −460 K. These values are in keeping with antiferromagnetically coupled Cr³⁺ S = 3/2 spins (ideal paramagnetic moment 3.9 μB), given the limited fitting range for the parameters. Magnetic diffraction peaks were observed in neutron profiles collected at 10 to 200 K. These peaks are indexed by magnetic propagation vector k = (111) and the possible irreducible representations (irreps) and basis vectors for spin order with this vector applied to the I2/mb space group are shown in Table 3.

Fits using a single basis vector for the spin order did not account well for the magnetic intensities. However, a good fit (as shown for the 10 K data in Fig. 2) is obtained using a combination of the basis vectors Ψ₆(Γ₃) and Ψ₇(Γ₄). These describe a C₄ᵥG₄ anti-ferromagnetic order of spins, following standard convention for magnetic order in perovskites. Although the Cr₁ and Cr₂ site moments are not symmetry-related, refining their spin components independently did not give a significantly improved fit over a model where their components were constrained to be the same, so the latter description was used as the final model. The m₁ and m₂ moment components at 10 K have values of 1.08(5) and 1.33(7) μB, and the resultant moment is m = 1.71(1) μB. Neutron diffraction shows that the Néel temperature for Ca₇Cr₂O₅ is >200 K (see inset to Fig. 2), and hence somewhat higher than the susceptibility features observed in Fig. 3. An estimate of Tₙₑ ≈ 220 K is obtained by fitting the temperature variation of the moment in Fig. 4a with a critical law m(T) = m(0)[1 − (T/Tₙₑ)]β for an exponent β ≈ 0.3, in keeping with theoretical models such as the three-dimensional XY magnet for which β = 0.34.

The magnetic structure of Ca₇Cr₂O₅ consists of antiferromagnetic planes of Cr₁ and Cr₂ moments as shown in Fig. 4b. Spins lie in the bc-plane and are tilted by 51(4)° from the b-axis. Neighbouring Cr₁ and Cr₂ spins connected through Cr₁–O–Cr₂ bridges are canted by ~100° suggesting that anti-symmetric Dzialoshinskii–Moriya exchange is significant, given the absence of a centre of symmetry or other symmetry relations between Cr₁ and Cr₂, and that Cr₁–O–Cr₂ Heisenberg exchange interactions are weak or frustrated. This reduction in the low temperature ordered moment of 1.7 μB from the ideal value of 3 μB for 3d³ Cr³⁺ is also consistent with some frustration in the spin order. Such spin canting is unusual in brownmillerites, as most have simple collinear antiferromagnetic structures with moments parallel to a or b.

Table 3 Irreducible representations and basis vectors of magnetic moments m for propagation vector (111) applied to the Cr cation positions in space group I2/mb

<table>
<thead>
<tr>
<th>Irreps</th>
<th>Basis vectors</th>
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<tr>
<td>m₁, m₂</td>
<td>(0, 1/2, 0)</td>
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<td>m₃</td>
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<tr>
<td>m₆</td>
<td>(1, 0, 0)</td>
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<tr>
<td>m₇</td>
<td>(0, 0, 1)</td>
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This study confirms that Ca$_2$Cr$_2$O$_5$ synthesised by reduction of the high pressure perovskite phase CaCrO$_3$ is a brownmillerite and adopts the ordered $I2mb$ superstructure at ambient temperature. The unusual tetrahedral coordination of Cr$^{3+}$ results in local structural distortions. The observation of Cr$^{3+}$ in this unconventional environment illustrates the use of hard–soft chemistry to stabilise unusual coordination geometries. This brownmillerite material containing a high concentration of oxygen vacancies in cubic-perovskite (100) planes may offer high mobility for oxide ion transport, as was found in the soft product SrCrO$_{2.8}$.$^9,6$ These stoichiometric reduced phases may also be useful model compounds to help understand oxide ion migration in chromium perovskite mixed conductors used in fuel cell anodes such as (La$_{1-x}$Sr)$_x$(Cr$_{1-y}$M)$_{y}$O$_{3-δ}$ (M = Mn, Fe, Co, Ni).$^{21}$

Ca$_2$Cr$_2$O$_5$ displays an antiferromagnetic spin ordering transition near 220 K, which is comparable to the 280 K Néel temperature for the perovskite LaCrO$_3$. Substantial canting of moments in successive layers is observed, suggesting that symmetric Heisenberg exchange interactions are weak or frustrated so that competing antisymmetric Dzialoshinskii–Moriya interactions determine spin directions.

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Notes and references