

The Crystal and Magnetic Structures of $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ at 2.1 K

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The crystal and magnetic structures of the brownmillerite $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ have been refined from neutron powder diffraction data collected at 2.1 K, space group $Pnma$, $a = 5.4083(1) \text{ \AA}$, $b = 14.6561(3) \text{ \AA}$, $c = 5.5923(1) \text{ \AA}$. The 4-coordinate cation sites are occupied only by iron; the 6-coordinate sites are occupied by a random 1:1 distribution of iron and chromium. The compound shows G-type antiferromagnetism at 2.1 K with average ordered magnetic moments of 3.23(4) and 3.95(5) μ_B , aligned along \hat{x} , at the 6- and 4-coordinate sites respectively. © 1991 Academic Press, Inc.

Introduction

Since the discovery of "high-temperature" superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_7$, there has been a resurgence of interest in the structural and electronic properties of anion-deficient perovskites. This has encompassed the well-established brownmillerite structure (1) known to be adopted by some compounds having the general formula $A_2B_2O_5$ ($A = \text{Ca}, \text{Sr}; B = \text{Fe}, \text{Co}$), and the related Grenier phases (2) $A_2\text{LaFe}_3\text{O}_8$. Our own work has included a study of $\text{Sr}_2\text{CoFeO}_5$ (3), a brownmillerite containing two

different transition metals, and in this paper we describe the structural characterization of another such compound, $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$, using neutron powder diffraction techniques.

The brownmillerite structure can be thought of as a perovskite with 16% of the anion sites vacant. The vacancies are not randomly distributed through the crystal structure; they order in chains along the [110] direction of the primitive cubic perovskite unit cell in such a way as to give alternate layers of 4-coordinate and 6-coordinate transition metal ions. The resulting orthorhombic unit cell, of size $\sqrt{2}a_p \times 4a_p \times \sqrt{2}a_p$, is drawn in Fig. 1. The strength of the magnetic superexchange interactions between the transition metal cations in this structure is sufficiently great

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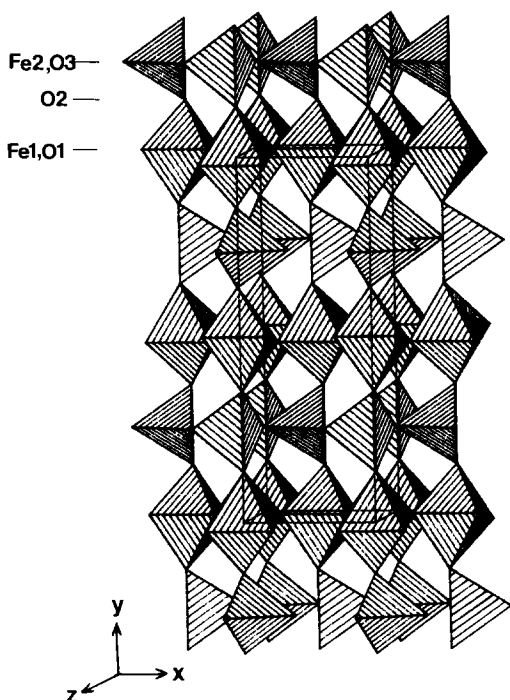


FIG. 1. The transition metal polyhedra in the brownmillerite structure. The distribution of atoms in $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ is indicated.

to ensure that $\text{Sr}_2\text{Fe}_2\text{O}_5$, $\text{Sr}_2\text{Co}_2\text{O}_5$, and $\text{Ca}_2\text{Fe}_2\text{O}_5$ are all antiferromagnetic at room temperature. The introduction of a second magnetic species having a different number of electrons in the outer $3d$ shell may perturb this magnetic ordering and modify the Néel temperature but, more interestingly, it may also introduce a ferromagnetic component into the superexchange. It has been predicted (4) that the superexchange between a d^3 ion and a d^5 ion will be ferromagnetic if the bond angle at the intervening anion is sufficiently close to 180° . We have recently observed such coupling between Fe^{3+} and Fe^{5+} in $\text{BaLaFe}_2\text{O}_{5.91}$ (5), and one aim of the present work was to establish whether or not the same effect could be detected between $\text{Cr}^{3+} : 3d^3$ and $\text{Fe}^{3+} : 3d^5$ in $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$. Previous studies (6, 7) of this compound by ^{57}Fe Mössbauer spectroscopy

have indicated that it is magnetically ordered below 455 K, but they did not give any definitive information about the relative orientation of Cr^{3+} and Fe^{3+} spins. This information can, however, be gleaned from a neutron diffraction experiment. The extent to which local ferromagnetic superexchange is reflected in the long-range magnetic ordering will, of course, depend on the degree of positional ordering of the two cation species over the 6- and 4-coordinate sites. The first Mössbauer study of $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ (6) led to the rather surprising conclusion that 25% of the Cr^{3+} ions occupied 4-coordinate sites whereas our own Mössbauer data (7) suggest that Cr occupies only 6-coordinate sites. The difference between the neutron scattering lengths of iron and chromium is sufficiently large to ensure that the experiments described below are very sensitive to this particular structural parameter.

Experimental

The preparation and X-ray characterization of $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ have been described previously (7). Powder neutron diffraction data were collected at 2.1 K on the diffractometer D1a at ILL Grenoble using a mean neutron wavelength of 1.9118 \AA and a 2θ step size of 0.05° in the angular range $0 < 2\theta < 156^\circ$. The sample was contained in a thin-walled vanadium can during data collection, which took approximately 11 hr to complete.

Results

The neutron diffraction data were analyzed using the Brookhaven version (8) of the Rietveld profile analysis method (9). The following coherent scattering lengths were used: $b_{\text{Ca}} = 0.490$, $b_{\text{Cr}} = 0.352$, $b_{\text{Fe}} = 0.945$, $b_{\text{O}} = 0.58 \times 10^{-12} \text{ cm}$. Although $\text{Sr}_2\text{Fe}_2\text{O}_5$, $\text{Ca}_2\text{Fe}_2\text{O}_5$, and $\text{Sr}_2\text{Co}_2\text{O}_5$ are all regarded as isostructural, there are subtle differences in their space group symmetry (3). We were

able to refine the crystal structure of $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ in space group $Pnma$, as used previously for $\text{Ca}_2\text{Fe}_2\text{O}_5$ (10). The observed diffraction pattern contained additional maxima due to magnetic scattering, and the relative positions of these peaks suggested that $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ is a G-type antiferromagnet at low temperatures. This type of magnetic ordering, very common among perovskites, leaves each magnetic cation antiferromagnetically aligned with respect to the six nearest-neighbor cations, irrespective of whether they are in 6- or 4-coordination. Refinement of the crystal and magnetic structures (assuming a brownmillerite structure with G-type ordering) involved 33 variable parameters and 325 reflections in the angular range $13^\circ < 2\theta < 153^\circ$. The parameters included 21 structural parameters and 12 profile parameters. The background was fitted using a three-parameter function and the peak shape, a Gaussian, was described by three parameters. The free-ion form factor for Fe^{3+} (11) was used to describe the angular variation of the magnetic scattering from both the 6- and the 4-coordinate sites. Preliminary refinements showed no evidence for the presence of Cr^{3+} on the latter, and the cation distribution was held fixed during our final refinements, which converged at agreement factors of $R_{\text{wpr}} = 5.4\%$, $R_{\text{Nuc}} = 2.7\%$. The resultant structural parameters are listed in Table I and the corresponding bond lengths and bond angles are presented in Table II. The final observed, calculated, and difference diffraction profiles are drawn in Fig. 2.

Discussion

The crystal structure of $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ is very similar to that of $\text{Ca}_2\text{Fe}_2\text{O}_5$. The Cr^{3+} ions apparently substitute for Fe^{3+} on the octahedral sites only. This result was expected in the light of our own Mössbauer data (7), but contradicts the results of Grenier *et al.* (6). The oxygen arrangement

TABLE I
STRUCTURAL PARAMETERS FOR $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ AT 2.1 K (SPACE GROUP $Pnma$)

Atom	Site	x	y	z	B_{iso} \AA^2	$\langle \mu_x \rangle$ μ_B
Ca	8d	0.4815(3)	0.10695(8)	0.0236(3)	0.55(3)	—
Cr/Fe1	4a	0	0	0	0.03(3)	3.23(4)
Fe2	4c	0.9466(2)	1/4	0.9340(2)	0.25(3)	3.95(5)
O1	8d	0.2617(4)	0.98415(9)	0.2388(3)	0.29(3)	—
O2	8d	0.0238(3)	0.13925(8)	0.0713(2)	0.33(3)	—
O3	4c	0.5960(3)	1/4	0.8759(4)	0.47(4)	—

Note. $a = 5.4083(1)\text{\AA}$, $b = 14.6561(3)\text{\AA}$, $c = 5.5923(1)\text{\AA}$.

around the 6-coordinate site is irregular; the metal–oxygen bonds (Cr/Fe1–O1) which lie within the octahedral layers are significantly shorter than those (Cr/Fe1–O2) which are perpendicular to the layers. This geometry is common to all brownmillerites (3, 10, 12) and the distortion of the 6-coordinate site may be one reason that only 28% of the iron can be replaced by chromium, which is significantly smaller and is known to prefer a regular, octahedral environment. There was no evidence for any ordering of Fe^{3+} and Cr^{3+} over the 6-coordinate sites.

The magnetic structure of $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ is also very similar to that of $\text{Ca}_2\text{Fe}_2\text{O}_5$ (13),

TABLE II
BOND LENGTHS (IN \AA) AND BOND ANGLES (IN DEGREES) FOR $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ AT 2.1 K

Ca—O1	2.470(4)	Ca—O2	2.534(3)
Ca—O1'	2.422(4)	Ca—O2'	2.983(3)
Ca—O1''	2.459(4)	Ca—O2''	2.326(3)
Ca—O1'''	2.702(4)	Ca—O3	2.337(4)
Cr/Fe1—O1	1.960(3) $\times 2$	Fe2—O2	1.844(3) $\times 2$
Cr/Fe1—O1'	1.962(3) $\times 2$	Fe2—O3	1.924(3)
Cr/Fe1—O2	2.083(2) $\times 2$	Fe2—O3'	1.912(3)
Shortest oxygen–oxygen contacts:			
O1—O1	2.707(4)		
O1—O2	2.775(4)		
Bond angles			
O1—Cr/ Fe1—O1'	92.7	O2—Fe2—O2	123.4
O1—Cr/ Fe1—O2	93.4	O2—Fe2—O3	107.1
		O2—Fe2—O3'	106.4
Cr/Fe1—O1—Cr/Fe1	165.4		
Fe—O2—Cr/Fe1	140.2		
Fe2—O3—Fe2	124.7		

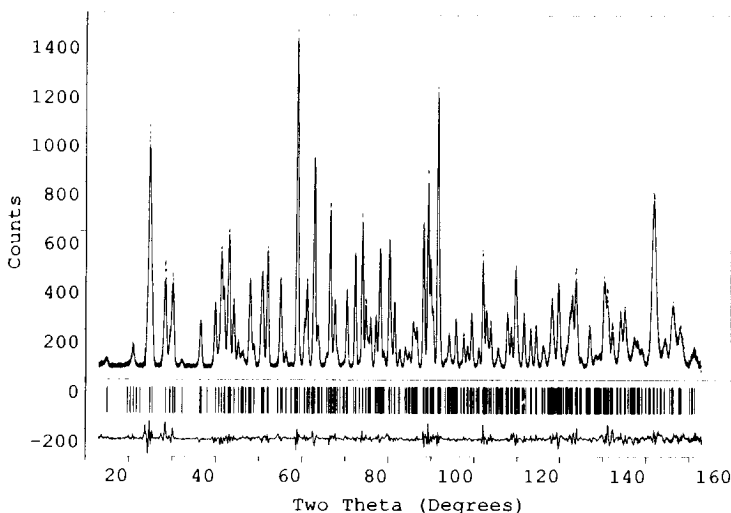


FIG. 2. Observed (---), calculated (—) and difference neutron powder diffraction profiles for $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ at 2.1 K. Reflection positions are marked.

with the atomic magnetic moments aligning in a G-type array along the shortest crystallographic axis (x). $\text{Sr}_2\text{Fe}_2\text{O}_5$ (12) and $\text{Sr}_2\text{FeCoO}_5$ (3) both adopt space group $Icmm$ rather than $Pnma$ and they therefore have disordered 4-coordinate sites. We have previously suggested that this disorder may be partly responsible for the low values of the ordered magnetic moments observed in $\text{Sr}_2\text{FeCoO}_5$ and $\text{Sr}_2\text{Fe}_2\text{O}_5$ ($<4\mu_B$ per Fe^{3+}) compared to the value of $4.5 \pm 0.2\mu_B$ found (13) in ordered ($Pnma$) $\text{Ca}_2\text{Fe}_2\text{O}_5$. The magnetic moments of $3.95(5)$ and $3.23(7)\mu_B$ found for the tetrahedral and octahedral sites respectively in $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ are slightly lower than might have been expected; for example tetrahedrally coordinated Fe^{3+} shows a magnetic moment of $4.35\mu_B$ in FePO_4 (14), a value of $4.40\mu_B$ has been reported (15) for 6-coordinate Fe^{3+} in LaFeO_3 , and $2.55\mu_B$ for Cr^{3+} in CrPO_4 (16); the latter two values would lead to an average magnetic moment of $3.47\mu_B$ per cation in a G-type antiferromagnet consisting of a 1 : 1 disordered array of Cr^{3+} and Fe^{3+} . In the case of $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ the existence of crystallo-

graphic disorder cannot be invoked as an explanation for the small discrepancy. However, the presence of atomic disorder on the 6-coordinate sites, Cr^{3+} and Fe^{3+} having different magnetic anisotropies, might lead to a slight misalignment of spin directions in the antiferromagnetic phase, and hence to a small reduction in the average ordered component of the magnetic moment, as measured in the neutron diffraction experiment. We have recently reported (5) ferromagnetic coupling between d^3 and d^5 ions randomly distributed in a 1 : 3 ratio over the transition metal sites of the perovskite $\text{BaLaFe}_2\text{O}_{5.91}$. This behavior results in an anomalously low value (ca. $1.9\mu_B$) for the average magnetic moment per cation although the overall diffraction pattern is still that of a G-type antiferromagnet. If this type of coupling occurred in $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ we would expect to see an average moment of only $\sim 0.9\mu_B$, i.e., $(\mu_{\text{Fe}^{3+}} - \mu_{\text{Cr}^{3+}})/2$, at the octahedral site. Thus, whatever the subtleties of the spin structure in $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$, it is clear from the values of the atomic magnetic moments that ferromagnetic coupling does not occur

to a significant extent in this compound, and that all the spins are essentially coupled antiparallel to those of their six nearest neighbors, giving a true G-type antiferromagnet. The lack of ferromagnetic coupling between the aliovalent ions in $\text{Ca}_2\text{Cr}_{0.5}\text{Fe}_{1.5}\text{O}_5$ can be ascribed to the deviation from linearity of the Cr–O–Fe superexchange pathway (Table II). $\text{BaLaFe}_2\text{O}_{5.91}$ is a cubic material having linear superexchange pathways between Fe^{3+} and Fe^{5+} ions. The results of this diffraction study thus confirm the conclusions drawn in a detailed Mössbauer study of perovskite solid solutions (17, 18). In order to make new magnetic materials, the properties of which depend on ferromagnetic superexchange between aliovalent cations, we must turn to high symmetry crystal structures with essentially linear superexchange pathways.

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