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Abstract
The low temperature structural and magnetic transition in the normal spinel MgCr₂O₄ has been
studied using high resolution neutron powder diffraction. The transition from a cubic,
paramagnetic phase (space group $Fd\bar{3}m$, $a = 8.3329(1)$ Å at 19 K) to a tetragonal,
antiferromagnetically ordered structure ($I4_1/amd$, $a = 5.8961(1)$ and $c = 8.3211(1)$ Å at
10 K) occurs via a sharp first order transition at 12.4 K. A small hysteresis of 0.15 K between
cooling and warming experiments is observed. The structural and magnetic transitions are
coincident and their order parameters (the tetragonal strain and Cr moment) scale with each
other. The structural transition partially relieves magnetic frustration in the Cr network,
although remaining frustration is evident from the low value (1.63 μ_B) of the saturated
Cr^{3+} moment.

1. Introduction

Chromium rich spinels MCr_2O_4 are constituents of many igneous and metamorphic rocks of the earth's crust and upper mantle [1] and so have attracted geological interest in trying to establish the thermodynamics that govern mineral formation [2]. From the physics viewpoint they are part of a group of exciting and challenging materials that have attracted much research interest in recent years due to complex magnetic ground states resulting from high geometrical frustration [3].

MCr_2O_4 are normal spinels, with M^{2+} and Cr^{3+} fully ordered at tetrahedral and octahedral sites, respectively. This arrangement results in a 'pyrochlore lattice' of chromium ions consisting of a three-dimensional network of corner-sharing Cr_4 tetrahedra in which Cr atoms have a six-fold coordination by oxygen. The dominant magnetic exchange interactions are antiferromagnetic due to the direct overlap of the t_{2g} orbitals of the nearest neighbouring Cr^{3+} ($3d^3$) ions. The six equivalent antiferromagnetic interactions for each Cr cation result in a highly frustrated lattice. This type of geometrically frustrated magnet can remain in a strongly-correlated paramagnetic state far below the absolute value of the Weiss temperature,

θ ($\theta = -390, -400$ and -330 K for M = Zn^{2+}, Mg^{2+} and Cd^{2+}, respectively) [4, 5]. Theory has shown that in the ideal case, the spins alone cannot order even at zero temperature [6]. In reality, however, three-dimensional magnetically ordered states are achieved at low temperatures in these spinels. The observed transition temperatures are $T_N = \sim 12.5, \sim 12.5$ and ~ 7.8 K, for Zn^{2+}, Mg^{2+} and Cd^{2+}, respectively, yielding very high frustration parameters, defined as $|\theta|/T_N$ [7], ranging from 30 to 40. The transition to an ordered state takes place through a spin–lattice coupling that partially lifts the magnetic degeneracy [8]. In consequence, these systems undergo a first order structural transition from the ideal cubic spinel structure (space group $Fd\bar{3}m$) to a tetragonally distorted phase (with either $I4_1/amd$ or $I\bar{4}m2$ space groups) in which magnetic interactions between Cr^{3+} ions are no longer equivalent.

Theoretical and experimental studies have focused on this type of transition. It is generally agreed that this is a spin-Peierls-like transition from a paramagnetic high temperature state to an antiferromagnetic low temperature state. It has been proposed that the transition could occur in two steps, first, a high temperature spin-Peierls transition, which partially

relieves frustration of spins; and then, at a lower temperature, a transition into a magnetically ordered state [9]. Inelastic neutron experiments carried out on $ZnCr_2O_4$ showed that as the temperature is lowered below $|\theta|$, the system gradually enters a paramagnetic state with strong correlations between spins [10]. Nevertheless, magnetic order is only developed when the structural transition takes place with no apparent intermediate state, although this might not be the case under high pressure [11].

Recently Lee *et al* [8] have found subtle differences between the structural transitions that accompany the magnetic order in $ZnCr_2O_4$ and $CdCr_2O_4$. Superstructure peaks not observed in the Cd sample were observed in the synchrotron x-ray diffraction pattern of $ZnCr_2O_4$ below T_N, indicating that the transition involves more local distortions than in the Cd phase. There are, however, several other differences between these phases: $CdCr_2O_4$ appears to show a complex incommensurate spiral antiferromagnetic structure along the *c*-axis apparently as a result of elongation in this direction at the structural transition [12, 13]. $ZnCr_2O_4$, on the other hand, develops a commensurate antiferromagnetic structure after a decrease of the *c*-axis below the transition.

$MgCr_2O_4$ has been less studied than the above phases. Early magnetic studies by neutron diffraction were centred on solving the complex magnetic structure and briefly indicated that the phase might develop a structural transition at low temperatures [14]. Shaked and co-workers [15] studied several samples of this material, finding that some showed two different magnetic transitions (at 13.5 and 16 K) and spin structures, although no structural distortion was considered. Subsequent studies have focused on the short range antiferromagnetic interactions and spin dynamics that exist in the critical region of the transition [5, 16, 17]. Synchrotron powder x-ray diffraction patterns collected at 10 and 16 K [18] showed that $MgCr_2O_4$ undergoes a first order structural transition to a tetragonally distorted phase. Specific heat studies [2] reveal a sharp transition peak at 12.5 K, with a small shoulder at ∼12.7 K. In order to clarify whether the structural and magnetic changes are coincident in $MgCr_2O_4$, or are accompanied by any intermediate phases or other magnetic structures, we have carried out a detailed structural study of the critical region using high resolution neutron powder diffraction.

2. Experimental details

10 g of $MgCr_2O_4$ were synthesized by a ceramic method under a constant flow of CO_2. Starting materials were MgO (99.99%) and Cr_2O_3 (99.999%) weighted in stoichiometric amounts. The mixture of oxides was pelletized and then heated at 1400 °C for 24 h, then slowly (5 °C h^{-1}) cooled to 900 °C and held for another 24 h. Phase purity was confirmed by powder x-ray diffraction.

Neutron powder diffraction data were collected using the Super D2B diffractometer at the Institut Laue Langevin (ILL, Grenoble, France). Neutrons of wavelength 1.5943 Å were incident on a 8 mm vanadium can contained in a liquid helium cryostat. Initially, temperature dependent patterns were
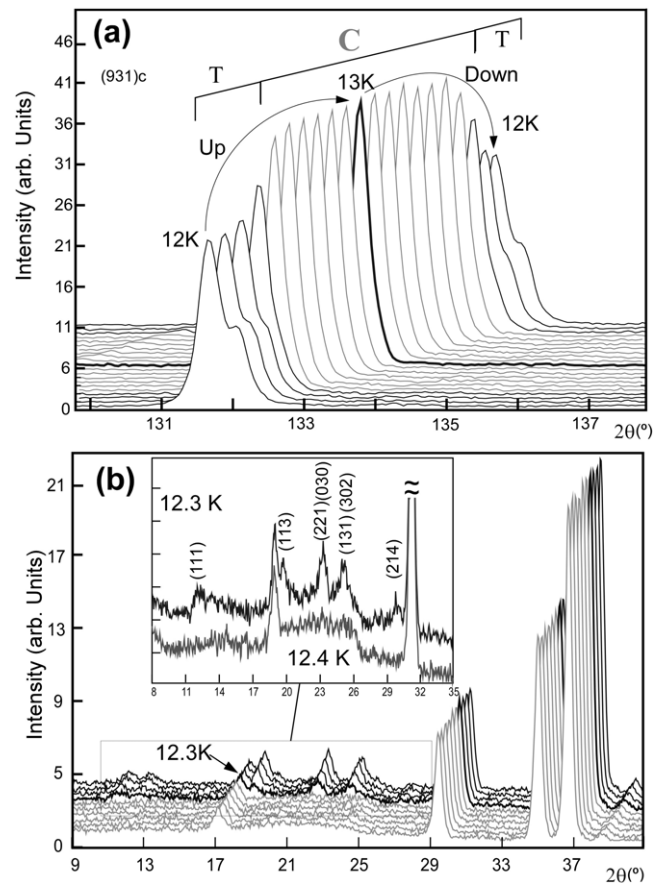

Figure 1. Temperature resolved neutron powder diffraction data for $MgCr_2O_4$ collected in 0.1 K steps on cooling and warming between 12 to 13 K. (a) The splitting of the $(931)_C$ reflection due to the tetragonal (T) to cubic (C) structural transition. (b) The evolution of the low angle scattering on cooling from 13 to 12 K. The inset shows the magnetic peaks appearing between 12.3 and 12.4 K, which are indexed on the tetragonal cell.

collected every 1 K from 10 to 19 K on warming, with no collimation used for the beam. Data were recorded in the angular range $5° < 2\theta < 160°$ in steps of 0.05° with an integration time of 300 000 monitor counts per step giving an overall collection time of 2 h. Additional data were collected every 0.1 K from 12 to 13 K on warming and cooling. 10′ beam collimation was used in this case in order to gain peak resolution. Data were collected in the angular range $5° < 2\theta < 160°$ in steps of 0.05° with an integration time of 150 000 monitor counts (2 h per pattern).

3. Results and discussion

The prominent splitting of many cubic reflections between 12 and 13 K observed in the initial data confirmed the presence of the tetragonal to cubic structural transition reported previously [18]. Detailed measurements collected every 0.1 K between 12 and 13 K indicated that the transition occurred at $T_{st} \approx 12.4$ K on warming with a small hysteresis of 0.1 K between warming and cooling (see figure 1). Magnetic diffuse scattering is observed above the transition (figure 1(b)) evidencing spin correlations in the paramagnetic region.
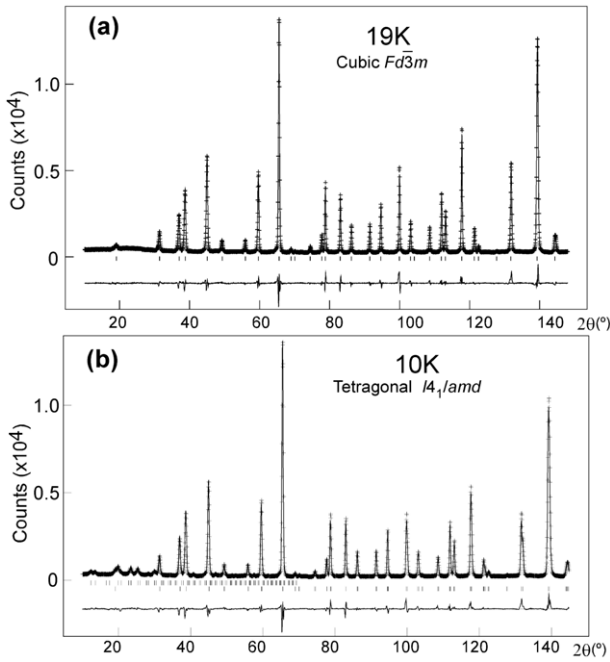
Figure 2. Rietveld fits to (a) 19 K and (b) 10 K neutron powder diffraction data for MgCr$_2$O$_4$, respectively. The upper tick marks in (b) indicate the magnetic peaks.

All data were Rietveld analysed using the GSAS software package [19] starting with the models proposed by Ehrenberg *et al* [18]: at 12.4 K and above MgCr$_2$O$_4$ spinel can be described by the cubic space group $Fd\bar{3}m$ whereas at lower temperatures the $a/\sqrt{2} \times a/\sqrt{2} \times 2a$ tetragonal model with space group $I4_1/amd$ was used. Weak magnetic peaks (see figures 1(b) and 2(b)) appearing below the structural transition are indexed by the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ propagation vector with respect to the tetragonal lattice. A satisfactory fit to the magnetic peaks was obtained using the antiferromagnetic model proposed by Plumier [14]. This may not be an optimal description of the magnetic structure but the weakness of the powder magnetic intensities, reflected by the high magnetic residual in table 1, precluded attempts to fit more complex models. Figure 2 shows the fits to the 10 and 19 K data as examples. Final refined parameters, residuals and selected bond distances at these temperatures are given in table 1. The temperature dependences of the lattice parameters and unit cell volume are shown in figure 3.

The result of the structural transition is a compression along the c axis and an expansion in the ab plane, with an overall reduction of the unit cell volume, consistent with a loss of magnetic frustration. The observed hysteresis between cooling and warming processes in the lattice parameters and the marked discontinuity in the volume confirm that the transition is first order.

The regular symmetries of the CrO$_6$ octahedra and the Cr$_4$ tetrahedra are broken as a consequence of the structural transition. The interatomic distances at 10 K (table 1) show that the Cr–O bond lengths remain equal within error, but the Cr–Cr distances split into two distinctive groups differing by 0.1%. This demonstrates that the structural distortion
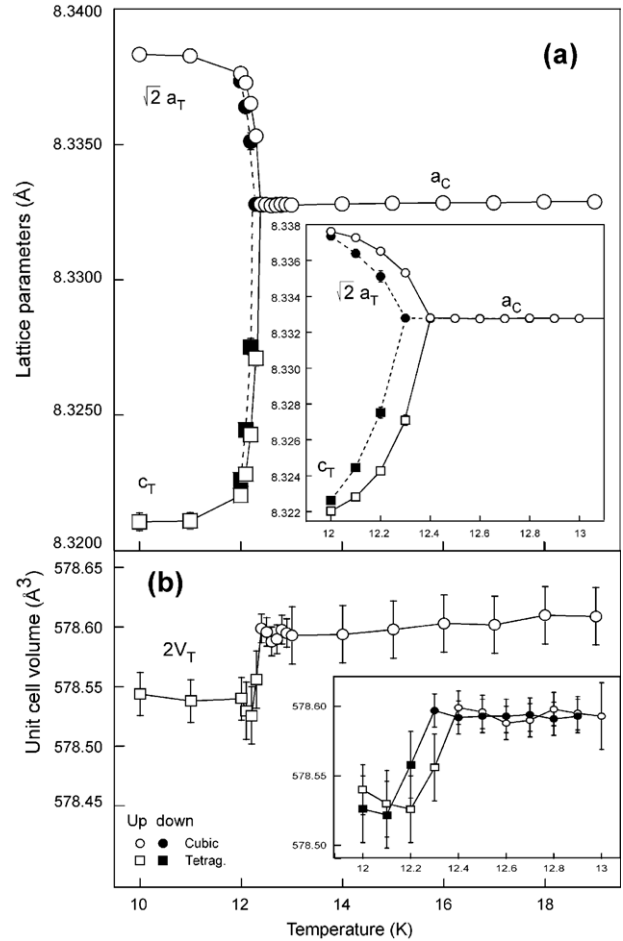
Figure 3. Temperature variations of (a) lattice parameters and (b) cell volume for MgCr$_2$O$_4$ through the structural transition. The insets show the 12–13 K regions.

is driven by the relief of magnetic frustration, rather than single-ion effects (which are not expected to be significant for non-degenerate, t$_{2g}^3$ Cr^{3+}). Axial contraction of the unit cell results in shorter Cr–Cr distances along the c-axis (light-coloured bonds in figure 4(a)) than in the ab plane (darker bonds) and their thermal evolution is shown in figure 4(b). The elongation of the Cr–Cr distances in the ab plane suggests that these interactions are more frustrated than the other Cr–Cr connections in the spin ordered structure.

The magnetic peaks from the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ superstructure are observed to appear at the same temperature as the cubic to tetragonal structural distortion. No other peaks appear below 12.4 K, contradicting the previous claim [15] of a secondary magnetic transition in MgCr$_2$O$_4$. The magnetic peaks and the structural distortion features appear at the same temperature, to a resolution of 0.1 K, with no intermediate phases evident. The coupling between lattice distortion and magnetic order is further illustrated by the scaling between the values of the tetragonal strain, $e_T = 3(\sqrt{2}a_T - c_T)/(2\sqrt{2}a_T + c_T)$, and the ordered Cr moment, shown in figure 5. Both quantities behave as an order parameter for the transition. The saturation moment of 1.63(2) μ_B is substantially reduced from the ideal value of 3 μ_B for Cr^{3+}, showing that large thermal fluctuations remain due to magnetic frustration in the tetragonal phase.
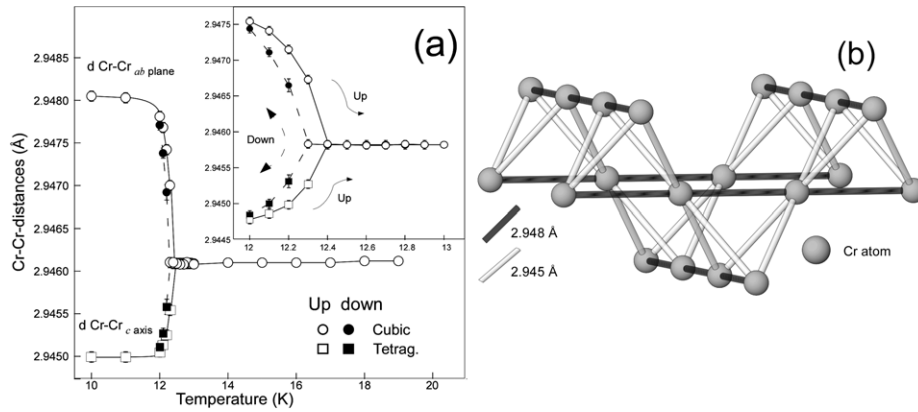
Figure 4. (a) Temperature dependence of the Cr–Cr distances in the tetrahedral network of $MgCr_2O_4$. The inset shows the behaviour between 12 and 13 K. (b) The chromium tetrahedral framework (oxygen and magnesium atoms are not shown) showing the long and short Cr–Cr distances in the low temperature structure.

Table 1. Structure refinement results for $MgCr_2O_4$ from the Rietveld fit to the 19 and 10 K neutron powder diffraction data.

	Temperature = 19 K				
Space group: $Fd\bar{3}m$, $a = 8.3329(1)$ Å, volume = $578.61(1)$ Å^3, $Z = 8$; Residuals: $R_{wp} = 8.2\%$, $R_p = 6.0\%$, $\chi^2 = 3.8$, $R_F^2(\text{nuc}) = 1.9\%$					
Atom	Wyckoff position	x	y	z	Uiso (Å^2)
Mg	8a	0.125	0.125	0.125	0.002
Cr	16d	0.5	0.5	0.5	0.002
O	32e	0.2612(1)	0.2612(1)	0.2612(1)	0.002

	Temperature = 10 K				
Space group: $I4_1/amd$, $a = 5.8961(1)$, $c = 8.3211(1)$ Å, volume = $289.27(1)$ Å^3, $Z = 4$; Residuals: $R_{wp} = 8.1\%$, $R_p = 6.2\%$, $\chi^2 = 3.8$, $R_F^2(\text{nuc}) = 2.9\%$, $R_F^2(\text{mag}) = 16.7\%$					
Atom	Wyckoff position	x	y	z	Uiso (Å^2)
Mg	4a	0	0.75	0.125	0.002
Cr	8d	0	0	0.5	0.002
O	16h	0	0.5224(3)	0.7393(3)	0.002

Selected distances (Å)

| $T = 19$ K		$T = 10$ K	
Mg–O (×4)	1.966(1)	Mg–O (×4)	1.964(1)
Cr–O (×6)	1.9940(3)	Cr–O (×2)	1.996(1)
Cr–Cr (×6)	2.9461(1)	Cr–O (×4)	1.995(1)
		Cr–Cr (×2)	2.9481(1)
		Cr–Cr (×4)	2.9450(1)

The lattice distortion in $MgCr_2O_4$ is similar to that observed in the analogue $ZnCr_2O_4$, in which a compression along the c-axis is also observed. However, no superstructure peaks that would indicate a reduction in the tetragonal symmetry from $I4_1/amd$ to $I\bar{4}m2$, as recently proposed for $ZnCr_2O_4$ [8], are observed in the neutron patterns. This further superstructure was also not observed in the previous 10 K synchrotron x-ray study [18].

4. Conclusions

Detailed analysis of the low temperature structural and magnetic transition in $MgCr_2O_4$ has been obtained by analysis of highly-resolved powder neutron diffraction data. Both magnetic and structural transitions occur at the same temperature (12.4 K) to within a resolution of 0.1 K. The magnetostrictive transition is first order and shows a small hysteresis of 0.15 K between cooling and warming experiments. The antiferromagnetic structure has a $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ propagation vector with respect to the tetragonal lattice and no other magnetic phases were observed. The tetragonal lattice strain scales with the magnitude of the ordered Cr moment. Magnetic frustration in the tetrahedral Cr network is partially relieved by the structural transition to a tetragonally compressed structure, although remaining frustration is evident from the low value of the saturation moment.
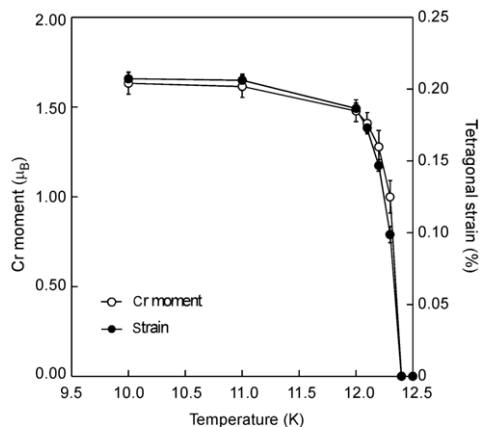
Figure 5. Thermal variations of the ordered Cr moment and the tetragonal lattice strain e_T on warming through the 12.4 K transition in $MgCr_2O_4$.

Acknowledgments

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