Crystal structures of spin-Jahn–Teller-ordered MgCr$_2$O$_4$ and ZnCr$_2$O$_4$

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Abstract
Magnetic ordering in the geometrically frustrated magnetic oxide spinels MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ is accompanied by a structural change that helps to relieve the frustration. Analysis of high-resolution synchrotron x-ray scattering reveals that the low-temperature structures are well described by a two-phase model of tetragonal $I4_1/amd$ and orthorhombic $Fddd$ symmetries. The Cr$_4$ tetrahedra of the pyrochlore lattice are distorted at these low-temperatures, with the $Fddd$ phase displaying larger distortions than the $I4_1/amd$ phase. The spin-Jahn–Teller distortion is approximately one order of magnitude smaller than is observed in first-order Jahn–Teller spinels such as NiCr$_2$O$_4$ and CuCr$_2$O$_4$. In analogy with NiCr$_2$O$_4$ and CuCr$_2$O$_4$, we further suggest that the precise nature of magnetic ordering can itself provide a second driving force for structural change.

1. Introduction
Degenerate ground states, commonly known to occur in amorphous, glassy and spin frustrated compounds, are fertile grounds for the realization of novel phenomena such as zero energy excitations [1]. The properties of liquid ground states, for example the precise nature of excitations and the explicit ground state configurations, are not well known. Spin frustrated systems are ideal models for investigating such behaviour. Antiferromagnetically coupled spins on the pyrochlore Cr sublattice of ACr$_2$O$_4$ spinels, where A is non-magnetic cation, are geometrically frustrated and they show spin liquid states over a wide temperature range facilitating studies of these highly degenerate ground states.

The highly degenerate spin liquid states of ACr$_2$O$_4$ spinels can order at low temperature in conjunction with a lattice distortion, in a manner sometimes referred to as spin-Jahn–Teller ordering [2, 3]. Despite extensive studies of the spin-Jahn–Teller phases of ACr$_2$O$_4$ spinels, there is little agreement on the full description of the low-temperature structures of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ [4, 5]. At room temperature, ACr$_2$O$_4$ are cubic spinels in the space group $Fd\bar{3}m$, provided the A ions are non-magnetic. A cations occupy tetrahedral sites while Cr$^{3+}$ with spin $S = \frac{3}{2}$ populate octahedral sites. These are normal spinels: Cr$^{3+}$ shows a strong preference for the octahedral site [6]. Magnetic frustration in ACr$_2$O$_4$ spinels is known to decrease from $A = \text{Zn to Mg to Cd to Hg}$ with the respective spinels showing Weiss intercepts of $\Theta_{CW}$ of $\approx -390$ K [7], $\approx -346$ K [7, 8], $\approx -71$ K [7], and $\approx -32$ K [7, 9] and spin-Jahn–Teller ordering temperatures ($T_N$) of $\approx 12.7$ K [10], $\approx 12.5$ K [2], $\approx 7.8$ K [11–13], and $\approx 5.8$ K [9].

Several low-temperature nuclear structures have been proposed for ACr$_2$O$_4$ spinels. x-ray diffraction studies
reveal $Fdd\bar{d}$ symmetry in the spin-Jahn–Teller phase of HgCr$_2$O$_4$ [9]. A tetragonal $I4_1/amd$ structure of MgCr$_2$O$_4$ was identified in low-temperature synchrotron x-ray [14] and neutron powder diffraction studies [10]. A tetragonal distortion has also been observed in the antiferromagnetic phase of CdCr$_2$O$_4$, identified by Aguilar et al using infrared spectroscopy [13], and by Chung et al from elastic and inelastic neutron scattering studies [12].

The low-temperature structure of CdCr$_2$O$_4$ was assigned to the $I4_1/amd$ space group as reported by Lee et al from synchrotron x-ray and neutron scattering studies of single crystals [4]. In the same report, single crystals of ZnCr$_2$O$_4$ were reported to adopt the tetragonal $I4_1/amd$ phase below the Néel temperature [4]. However, x-ray powder diffraction by Kagomiya et al suggested, without describing the complete structure, that at low-temperatures ZnCr$_2$O$_4$ is modelled by the orthorhombic space group $Fddd$ [5]. Recent electron-spin resonance studies of single crystal ZnCr$_2$O$_4$ by Glazkov et al showed that tetragonal and orthorhombic distortions coexist in the Néel phase of ZnCr$_2$O$_4$ [15].

We report coexisting tetragonal $I4_1/amd$ and orthorhombic $Fdd\bar{d}$ symmetries in the spin-Jahn–Teller phases of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$, observed using high-resolution synchrotron x-ray powder diffraction. Phase coexistence is suggested for the first time in these materials from diffraction studies. This is the first complete description of the spin-Jahn–Teller structures of the important frustrated compounds MgCr$_2$O$_4$ and ZnCr$_2$O$_4$. We provide all structural details including the atom positions in both the tetragonal and orthorhombic phases of these systems. This new understanding of the structural ground states of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ is pivotal for theoretical studies and interpretation of excitations in the spin-Jahn–Teller phases of these compounds.

2. Experimental details

MgCr$_2$O$_4$ was prepared by calcination of appropriate solution mixtures of the nitrates Mg(NO$_3$)$_2$·6H$_2$O and Cr(NO$_3$)$_3$·9H$_2$O at 1000°C for 10 h. ZnCr$_2$O$_4$ and CdCr$_2$O$_4$ were prepared by solid-state methods from ZnO, CdO, and Cr$_2$O$_3$ powders. Samples were annealed in the temperature range 800–1100°C. A separate ZnCr$_2$O$_4$ sample was prepared in a Pt crucible by heating ZnO in an excess K$_2$Cr$_2$O$_7$ flux at 800°C for 24 h, followed by cooling at 15°C h$^{-1}$ to room temperature. Samples were structurally characterized by high-resolution ($\Delta Q/Q \leq 2 \times 10^{-4}$) synchrotron x-ray powder diffraction at temperatures between 6 and 295 K. These measurements were performed at beamline 11-BM of the Advanced Photon Source, Argonne National Laboratory. Structural models were refined against diffraction data using the Rietveld method as implemented in the EXPGUI/GSAS software program [16, 17]. Atom positions for the low-symmetry structures were obtained using the internet-server tool ISODISPLACE [18]. Crystal distortions were analysed using the program VESTA [19]. Magnetic properties were characterized using a Quantum Design MPMS 5XL superconducting quantum interference device (SQUID). Heat capacity measurements were performed using a Quantum Design Physical Properties Measurement System.

3. Results and discussion

At room temperature, the prepared ACr$_2$O$_4$ spinels are homogeneous compounds in the space group $Fd\bar{3}m$ as shown in figure 1. MgCr$_2$O$_4$ has a cubic lattice constant of 8.33448(8) Å and it contains a 3.0 wt% Cr$_2$O$_3$ impurity. We study two samples of ZnCr$_2$O$_4$: one sample, labelled ZnCr$_2$O$_4$ c, is prepared by solid-state routes (figure 1(b)) while the other, labelled ZnCr$_2$O$_4$ x, is prepared through a self-limiting flux approach (figure 1(c)). In the later, the K$_2$Cr$_2$O$_7$ flux decomposes to yield Cr$_2$O$_3$ which reacts with available Zn$^{2+}$ species to form ZnCr$_2$O$_4$. The solid-state ZnCr$_2$O$_4$ sample is phase pure and has a lattice constant of 8.32765(8) Å while the flux-prepared ZnCr$_2$O$_4$ sample has a lattice parameter of 8.331945(19) Å and contains very small impurities that are almost undetectable in figure 1(c). The lattice parameters of all the compounds studied here are $\approx 0.1\%$ larger than those of stoichiometric compounds [20]. We discuss the effects of stoichiometry on the properties of these materials later in the paper.

Scaled inverse field-cooled susceptibilities of ACr$_2$O$_4$ as described by the recast Curie–Weiss equation are shown in the top panel of figure 2. Antiferromagnetic ordering occurs when $T/\Theta_{CW} \ll 1$, indicating geometrically frustrated
Figure 2. Spin-Jahn–Teller distortions in \( \text{A} \text{Cr}_2\text{O}_4 \) spinels. The top panel shows the scaled inverse field-cooled susceptibility. The dashed black line models ideal paramagnetism. \( \text{MgCr}_2\text{O}_4 \) and \( \text{ZnCr}_2\text{O}_4 \) were measured under a 1000 Oe field while \( \text{CdCr}_2\text{O}_4 \) was measured in 6000 Oe. Antiferromagnetic order is suppressed to low temperatures in \( \text{MgCr}_2\text{O}_4 \) \( (T_N = 12.9 \text{ K}) \), \( \text{ZnCr}_2\text{O}_4 \) \( (T_N = 12.3 \text{ K}) \), and \( \text{CdCr}_2\text{O}_4 \) \( (T_N = 7.86 \text{ K}) \). The splitting of high-symmetry cubic diffraction peaks into several low-symmetry peaks shows the onset of spin-driven structural distortions (middle panel). \( \text{CdCr}_2\text{O}_4 \) shows a subtle structural distortion that is indicated by a slight decrease in intensity and increase in width of the high-symmetry peak. The bottom panel shows the change in entropy at the Neel temperature.

Table 1. Magnetic parameters of \( \text{A} \text{Cr}_2\text{O}_4 \) spinels.

|          | \( T_N (\text{K}) \) | \( \Theta_{\text{CW}} (\text{K}) \) | \( f = |\Theta_{\text{CW}}|/T_N \) | \( \mu_{\text{exp}} (\mu_B) \) | \( \mu_{\text{calc}} (\mu_B) \) |
|----------|---------------------|-----------------|-----------------|-----------------|-----------------|
| \( \text{MgCr}_2\text{O}_4 \) | 12.9                | −368            | 29              | 5.4             | 5.47            |
| \( \text{ZnCr}_2\text{O}_4 \) | 12.3                | −288            | 23              | 5.2             | 5.47            |
| \( \text{CdCr}_2\text{O}_4 \) | 7.86                | −69.7           | 8.9             | 5.3             | 5.47            |

spin interactions (top axis scale of figure 2). Slight antiferromagnetic spin correlations are observed above \( T_N \) in \( \text{ZnCr}_2\text{O}_4 \) and \( \text{CdCr}_2\text{O}_4 \). We define \( T_N \) as the temperature at which \( d\chi_{\text{ZFC}}/dT \) is maximized. The magnetic properties of the samples presented here are tabulated in table 1. Experimental magnetic moments of these compounds are within error of the calculated effective moment of 5.47 \( \mu_B \) (table 1). There is a \( \approx 0.3 \text{ K} \) thermal hysteresis between the zero-field-cooled and field-cooled temperature dependent susceptibilities of the \( \text{A} \text{Cr}_2\text{O}_4 \) spinels. We observe a \( \Theta_{\text{CW}} \) of −288 K for \( \text{ZnCr}_2\text{O}_4 \) which is consistent with the earlier work by Melot \textit{et al} [21] but is lower than other \( |\Theta_{\text{CW}}| \) values reported in the literature [10, 8]. The lower \( |\Theta_{\text{CW}}| \) value could be due to slight off-stoichiometry in \( \text{ZnCr}_2\text{O}_4 \). The magnetic ordering transitions of \( \text{A} \text{Cr}_2\text{O}_4 \) spinels are associated with changes in entropy (figure 2) and this agrees well with the earlier work of Klemme \textit{et al} [22, 23]. \( \text{ZnCr}_2\text{O}_4 \) and \( \text{CdCr}_2\text{O}_4 \) have smooth heat capacity anomalies while \( \text{MgCr}_2\text{O}_4 \) has a sharp anomaly with a shoulder feature that could indicate that its structural and magnetic transitions occur at slightly different temperatures.

The cubic \( Fd\bar{3}m \) (800) diffraction peak of \( \text{MgCr}_2\text{O}_4 \) and \( \text{ZnCr}_2\text{O}_4 \) splits into several low-symmetry peaks (figure 2). \( \text{CdCr}_2\text{O}_4 \) on the other hand, while displaying some peak broadening, remains well modelled by the high-temperature \( Fd\bar{3}m \) space group even at 6.9 K (figure 2). Rietveld fits to the low-temperature synchrotron x-ray powder diffraction data of \( \text{MgCr}_2\text{O}_4 \) and \( \text{ZnCr}_2\text{O}_4 \) using structural models
reported in the literature [14, 10, 4, 5] resulted in regions of poorly fit intensity. Similarly, the low-symmetry structures F222, C2/c, and I2/a could not model the data well. Group-subgroup relations of the space group Fd$\bar{3}$m yield the lower-symmetry groups $I4_1/amd$ and Fddd. Individually, neither of these structural models can reproduce the intensities and peak splittings observed in our low-temperature diffraction patterns of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$. However, we find that the diffraction data can be well described by a two-phase model combining both tetragonal $I4_1/amd$ and orthorhombic Fddd structures (figure 3(a)). This refinement yields chemically reasonable and stable isotropic thermal displacement parameters for both phases (table 2). In figure 3(b), the low-temperature peak splitting of the cubic Fd$\bar{3}$m (800) reflection is deconvoluted into contributions from the $I4_1/amd$ and Fddd phases. Nearly equal fractions of the two phases coexist in the low-temperature nuclear structures of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ (figure 3(c)). Employing the Thompson–Cox–Hastings pseudo-voigt profile function, we observe a slight increase of the Fddd phase fraction with a decrease in temperature below $T_N$ for both MgCr$_2$O$_4$ and ZnCr$_2$O$_4$. While the estimated standard deviations suggest rather accurate phase fractions (table 2), separate refinements employing different profile functions show variations of up to 10%. Scherrer analysis of deconvoluted $I4_1/amd$ and Fddd peaks shown in figure 3(b) yield larger coherence lengths in the tetragonal phases (≈70 nm) of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ compared with the orthorhombic phases (≈40 nm). Williamson–Hall analysis yields larger room temperature crystallite sizes of 118 nm in MgCr$_2$O$_4$ and 200 nm in ZnCr$_2$O$_4$. This suggests that the larger Fd$\bar{3}$m domains split at low temperature into smaller domains of coexisting $I4_1/amd$ and Fddd phases which coexist down to the lowest temperatures studied (table 2).

We have also examined a ZnCr$_2$O$_4$ sample prepared using a K$_2$Cr$_2$O$_7$ flux to explore the effect of sample preparation conditions. High-resolution synchrotron x-ray diffraction measurements carried out at 7 K reveal that it is also described by a combination of both $I4_1/amd$ and Fddd. There are subtle differences in the low-temperature phase composition of the flux-prepared sample. The flux-prepared sample has a slightly higher Fddd phase fraction compared with the solid-state ZnCr$_2$O$_4$ sample (table 2). Coexistence of $I4_1/amd$ and Fddd phases in the spin–Jahn–Teller phases of both flux prepared and solid state ZnCr$_2$O$_4$ demonstrates that phase coexistence is independent of sample preparation methods.

The Fd$\bar{3}$m lattice parameter of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ splits abruptly into two $I4_1/amd$ and three Fddd lattice constants at $T_N$, as shown in figures 4(a) and (c), respectively. The evolution of lattice parameters of the flux-prepared

Figure 3. Low-temperature diffraction and Rietveld refinement of MgCr$_2$O$_4$ (left panel) and ZnCr$_2$O$_4$ c (right panel). (a) High-resolution synchrotron x-ray powder patterns collected at ~6 K and indexed to a two-phase model of tetragonal $I4_1/amd$ and orthorhombic Fddd symmetries (data (black), combined $I4_1/amd$ and Fddd fit (orange), difference (blue)). (b) The high-symmetry (800) peak splits into several $I4_1/amd$ and Fddd reflections. The $I4_1/amd$ and Fddd fits have been offset from the data for clarity. ($I4_1/amd$ (blue), Fddd (red), and Cr$_2$O$_3$ impurity (grey)) (c) Nearly equal amounts of $I4_1/amd$ (blue) and Fddd (red) phases coexist below $T_N$; the Fddd phase fraction increases slightly with decreasing $T$. 

\[ \text{ZnCr} \text{ decrease in temperature below } T \]

\[ \text{observe a slight increase of the Thompson–Cox–Hastings pseudo-voigt profile function, we } \]

\[ \text{two phases coexist in the low-temperature nuclear structures } \]

\[ \text{of MgCr}_2\text{O}_4 \text{ and ZnCr}_2\text{O}_4. \]
ZnCr$_2$O$_4$ sample follows a similar trend. The Fddd $a$ and $c$ parameters of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ show the greatest distortion from cubic symmetry. The smaller cell volume of the Fddd phase of each compound compared to its I4$_1$/amd counterpart, suggests that Fddd is the lower energy structure. MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ undergo a first-order structural transition at $T_N$ indicated by the change in slope of the cell volume (figures 4(b) and (d)), the onset of a two-phase regime (figure 3(b)), and the release of entropy (figure 2).

Cr$_4$ tetrahedra of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ are distorted below $T_N$. We compute a tetrahedral distortion index of Cr$_4$ tetrahedra, $D = 1/n \sum_{i=1}^{n} |l_i - \bar{l}|/\bar{l}$, where $l_i$ is the $i$th Cr–Cr bond distance and $\bar{l}$ is the average Cr–Cr bond distance. [24] A larger $D$ is seen for the Fddd phases of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ in comparison to the I4$_1$/amd phases (figures 5(a)–(c)). Similarly, we compute an angle variance of Cr$_4$ tetrahedra, $\sigma^2 = 1/(m-1) \sum_{i=1}^{m} (\phi_i - \phi_0)^2$, where $\phi_0$ is the ideal tetrahedron angle of 109.47°, $\phi_i$ is the measured angle, and $m$ is (the number of faces of a tetrahedron) × 3/2 [25, 19]. A greater angle variance occurs in the orthorhombic phases of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ rather than in the tetragonal phases (figures 5(d)–(f)). The ZnCr$_2$O$_4$ sample prepared from a K$_2$Cr$_2$O$_7$ flux has less distortion of its Cr$_4$ tetrahedra compared with the solid-state ZnCr$_2$O$_4$ compound (figure 5). The differences in distortion of the two ZnCr$_2$O$_4$ samples is likely due to higher strain effects in the K$_2$Cr$_2$O$_7$ flux-prepared sample. Of the two compounds studied, Cr$_4$ tetrahedra are more distorted in MgCr$_2$O$_4$ than in ZnCr$_2$O$_4$.

The lattice parameters and magnetic properties of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ are sensitive to stoichiometry [20]. Lattice constants of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ reported in the literature show a large distribution with the most stoichiometric compounds showing the smallest lattice parameters [$20, 21, 26, 10, 14, 5, 27, 7$]. Our samples are slightly non-stoichiometric with lattice parameters ≈0.1% larger than those of stoichiometric compounds [20]. There appears to be a correlation between stoichiometry and the extracted $\Theta_{CW}$ values. Stoichiometric compounds of ZnCr$_2$O$_4$ yield $\Theta_{CW}$ values of $\approx-400$ K [20, 7] while slightly off-stoichiometric compounds have $\Theta_{CW}$ values of $\approx-288$ K as reported here. The effect of stoichiometry on the low-temperature nuclear structures of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ should be examined. We anticipate that stoichiometric samples will show one or both of the low-symmetry structures reported here.

The spin-Jahn–Teller distortion of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ resembles martensitic phase transitions, which are displacive solid–solid transitions. Much like martensitic phase transformations, the spin-Jahn–Teller distortions of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ are induced by varying temperature, involve changes in crystal symmetry without a change in chemical composition, and show hysteresis. Volume changes between the parent and product phases of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$, that occur at the spin-Jahn–Teller distortion

\[ \text{Figure 4. Temperature evolution of lattice parameters in MgCr}_2\text{O}_4 \text{ and ZnCr}_2\text{O}_4 \text{ through their magnetostructural distortions. The cubic lattice constants of MgCr}_2\text{O}_4 \text{ (a) and ZnCr}_2\text{O}_4 \text{ (c) separate into I}4_1/\text{amd and Fddd lattice constants at } T_N = 12.9 \text{ K and } T_N = 12.3 \text{ K respectively. The lattice parameters of MgCr}_2\text{O}_4 \text{ are normalized by the lattice constant at } 57.1 \text{ K (a}_0 = 8.32871 \text{ Å) while the lattice parameters of ZnCr}_2\text{O}_4 \text{ are normalized by the lattice constant at } 59.3 \text{ K (a}_0 = 8.3216 \text{ Å). The I}4_1/\text{amd lattice constants have been multiplied by } \sqrt{2}. \text{ The Fddd phases of MgCr}_2\text{O}_4 \text{ (b) and ZnCr}_2\text{O}_4 \text{ (d) have smaller volumes compared to the I}4_1/\text{amd phases. In some cases, error bars are smaller than the data symbols.} \]
temperature, could induce strains that result in the coexistence of multiple phases.

It is important to consider whether a single low-symmetry space group could model the data. Our refinements using $F\bar{2}22$, $C2/c$, or $I2/\alpha$ were unable to generate the observed peak separations. Analysis of the Cr$_4$ tetrahedra distortions shows that the $Fd\bar{3}m$ phase is more distorted than the $I4_1/amd$ phase. Additionally, the $Fd\bar{3}m$ phase fraction increases slightly with a decrease in temperature below $T_N$. The combination of these two effects would be challenging to describe using a single low-symmetry structural model. Further, the two-phase $I4_1/amd$ and $Fd\bar{3}m$ model is robust against changes in sample preparation conditions.

Phase coexistence following a phase transition is not unusual. Compositional inhomogeneity contributes to multiple low-temperature phases in Nd$_{0.33}$Sr$_{0.67}$MnO$_3$ [28]. Similarly, complex phase behaviour featuring three coexisting phases occurs in the relaxor-ferroelectric systems Pb(Mg, Nb, Ti)O$_3$ due to internal strain, and are proposed to be intrinsic to the system [29]. Distortion from $Fd\bar{3}m$ to $I4_1/amd$ symmetry, driven by orbital ordering, occurs in the related spinel compounds NiCr$_2$O$_4$ and CuCr$_2$O$_4$. This is followed by further distortion to $Fd\bar{3}m$ symmetry due to magnetostructural coupling [30]. The magnetostructural distortions of NiCr$_2$O$_4$ and CuCr$_2$O$_4$ are of the same order of magnitude as the structural distortions we observe in MgCr$_2$O$_4$ and ZnCr$_2$O$_4$. We make the suggestion that while tetragonal distortion alone may be sufficient to lift spin degeneracy in MgCr$_2$O$_4$ and ZnCr$_2$O$_4$, magnetostructural coupling could drive further distortion from tetragonal to orthorhombic symmetry.

4. Conclusion

In summary, we report coexisting $I4_1/amd$ and $Fd\bar{3}m$ phases in the spin-Jahn–Teller structures of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$. Nearly equal phase fractions of the $I4_1/amd$ and the $Fd\bar{3}m$ phase coexist below $T_N$. The tetragonal phases have larger coherence lengths than the orthorhombic phases. We make comparisons between the spin-Jahn–Teller phase transitions of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ and martensitic phase transitions. We propose that two mechanisms, spin frustration and magnetostructural coupling, could potentially give rise to the observed structural phase coexistence in MgCr$_2$O$_4$ and ZnCr$_2$O$_4$. We note that temperature-dependent heat capacity measurements of MgCr$_2$O$_4$ show two features that likely correspond to a slight separation in temperature of the structural and magnetic phase transitions.

The hallmark of a frustrated system is a highly degenerate ground state configuration. The manifold of degenerate ground states is susceptible to slight perturbations that...
often give rise to emergent behaviour. Examples of novel properties include the observation of zero energy excitations in the degenerate ground state of ZnCr$_2$O$_4$ [1]. This work presents new insights into the ground state nuclear structures of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$. This new understanding of the crystal structure of the canonically frustrated systems MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ has important consequences for theoretical studies of these systems and the interpretation of excitations in the spin-Jahn–Teller-ordered phases of these compounds.

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Table 2. The low-temperature structures of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ as determined from Rietveld refinement of high-resolution synchrotron x-ray powder diffraction data. All atomic parameters were allowed to vary during the structural refinement except for isotropic thermal parameters that are constrained to be the same for both low-temperature phases. Tabulated coherence lengths are determined from Scherrer analysis of well resolved peaks. This is the lower limit of crystallite size and assumes that all peak broadening is due to crystallite size.

| MgCr$_2$O$_4$ | ZnCr$_2$O$_4$ | Coherence length (nm) | Mg/Zn | Space group | Space group | Coherence length (nm) | Mg/Zn | Space group |
|---------------|---------------|-----------------------|-------|-------------|-------------|-----------------------|-------|-------------|
| $T$ (K)       | $\lambda$ (Å) | $a$ (Å)               | $b$ (Å) | $c$ (Å) | $Z$          | $\alpha$ (Å)$^3$     | $\omega$ (Å)$^3$ | $\phi$ | $R_p$ |
| 5.7           | 0.413393      | 5.89351(2)            | 3.28228(2) | 8.31503(7) | 4           | 288.809(2)           | 0.0231(2)  | 0.0331 | 0.0582 | 0.0823 |
| 5.4           | 0.413399      | 5.88753(1)            | 3.28141(4) | 8.30895(4) | 4           | 288.013(2)           | 0.0231(2)  | 0.0331 | 0.0582 | 0.0823 |
| 6.9           | 0.413331      | 5.88919(2)            | 3.27427(8) | 8.3103(5)  | 4           | 288.456(2)           | 0.0231(2)  | 0.0331 | 0.0582 | 0.0823 |

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Table 2. The low-temperature structures of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ as determined from Rietveld refinement of high-resolution synchrotron x-ray powder diffraction data. All atomic parameters were allowed to vary during the structural refinement except for isotropic thermal parameters that are constrained to be the same for both low-temperature phases. Tabulated coherence lengths are determined from Scherrer analysis of well resolved peaks. This is the lower limit of crystallite size and assumes that all peak broadening is due to crystallite size.

| MgCr$_2$O$_4$ | ZnCr$_2$O$_4$ | Coherence length (nm) | Mg/Zn | Space group | Space group | Coherence length (nm) | Mg/Zn | Space group |
|---------------|---------------|-----------------------|-------|-------------|-------------|-----------------------|-------|-------------|
| $T$ (K)       | $\lambda$ (Å) | $a$ (Å)               | $b$ (Å) | $c$ (Å) | $Z$          | $\alpha$ (Å)$^3$     | $\omega$ (Å)$^3$ | $\phi$ | $R_p$ |
| 5.7           | 0.413393      | 5.89351(2)            | 3.28228(2) | 8.31503(7) | 4           | 288.809(2)           | 0.0231(2)  | 0.0331 | 0.0582 | 0.0823 |
| 5.4           | 0.413399      | 5.88753(1)            | 3.28141(4) | 8.30895(4) | 4           | 288.013(2)           | 0.0231(2)  | 0.0331 | 0.0582 | 0.0823 |
| 6.9           | 0.413331      | 5.88919(2)            | 3.27427(8) | 8.3103(5)  | 4           | 288.456(2)           | 0.0231(2)  | 0.0331 | 0.0582 | 0.0823 |

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