Structural ground states of \((A,A')\)Cr\(_2\)O\(_4\)\((A=\text{Mg, Zn}; A' = \text{Co, Cu})\) spinel solid solutions: Spin-Jahn-Teller and Jahn-Teller effects

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We examine the effect of small amounts of magnetic substituents in the \(A\) sites of the frustrated spinels MgCr\(_2\)O\(_4\) and ZnCr\(_2\)O\(_4\). Specifically we look for the effects of spin and lattice disorder on structural changes accompanying magnetic ordering in these compounds. Substitution of Co\(^{2+}\) on the non-magnetic Zn\(^{2+}\) site in Zn\(_{1-x}\)Co\(_x\)Cr\(_2\)O\(_4\) where 0 < \(x\) ≤ 0.2 completely suppresses the spin-Jahn-Teller distortion of ZnCr\(_2\)O\(_4\) although these systems remain frustrated, and magnetic ordering occurs at very low temperatures of \(T < 20\) K. On the other hand, the substitution of Jahn-Teller active Cr\(^{2+}\) for Mg\(^{2+}\) and Zn\(^{2+}\) in Mg\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\) and Zn\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\) where 0 < \(x\) ≤ 0.2 induce Jahn-Teller ordering at temperatures well above the Néel temperatures of these solid solutions, and yet spin interactions remain frustrated with long-range magnetic ordering occurring below 20 K without any further lattice distortion. The Jahn-Teller distorted solid solutions Mg\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\) and Zn\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\) adopt the orthorhombic \(Fdd\alpha\) structure of ferrimagnetic CuCr\(_2\)O\(_4\). Total neutron scattering studies of Zn\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\) suggest that there are local AO distortions in these Cu\(^{2+}\)-containing solid solutions at room temperature and that these distortions become cooperative when average structure distortions occur. Magnetism evolves from compensated antiferromagnetism in MgCr\(_2\)O\(_4\) and ZnCr\(_2\)O\(_4\) to uncompensated antiferromagnetism with substitution of magnetic cations on the non-magnetic cation sites of these frustrated compounds. The sharp heat capacity anomalies associated with the first-order spin-Jahn-Teller transitions of MgCr\(_2\)O\(_4\) and ZnCr\(_2\)O\(_4\) become broad in Mg\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\), Zn\(_{1-x}\)Co\(_x\)Cr\(_2\)O\(_4\), and Zn\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\) when \(x > 0\). We present a temperature-composition phase diagram summarizing the structural ground states and magnetic properties of the studied spinel solid solutions.

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Triangular lattice topologies are at the center of complex ground states in functional oxides as has been shown in the charge ordered triangular metallic AgNiO\(_2\) where charge ordering rather than a Jahn-Teller distortion lifts orbital degeneracy\(^{11}\) and in geometrically frustrated spin systems such as ZnCr\(_2\)O\(_4\) where magnetic ordering is accompanied by a lattice distortion.\(^{12}\) The ground states of the canonical spin frustrated systems ACr\(_2\)O\(_4\) \((A = \text{Mg, Zn, Cu, Hg})\) have been extensively explored. To understand the degenerate ground states of ACr\(_2\)O\(_4\) spinels, the effect of spin disorder on the magnetic properties of these systems has been investigated; spin disorder is introduced by substituting magnetic ions on the non-magnetic \(A\) sublattice of these materials.\(^{13,14}\) Similarly, the effect of low concentrations of magnetic vacancies on the Cr sublattice of ZnCr\(_{2(1-x)}\)Ga\(_x\)O\(_4\) has been studied showing that the freezing temperature of these systems for small \(x\) is independent of the spin vacancy concentration.\(^{15}\) However, the effect of spin and lattice disorder on the structural ground states of the canonical frustrated systems MgCr\(_2\)O\(_4\) and ZnCr\(_2\)O\(_4\) has so far not been studied.

Here, we study magnetic ordering and correlated or uncorrelated structural changes in MgCr\(_2\)O\(_4\) and ZnCr\(_2\)O\(_4\) when low concentrations of magnetic cations are substituted on the non-magnetic \(A\) site. MgCr\(_2\)O\(_4\) and ZnCr\(_2\)O\(_4\) are ideal candidates for the present study as they are: (i) Strongly frustrated with expected ordering temperatures of about 400 K yet suppressed antiferromagnetic ordering occurs below 15 K;\(^{16}\) (ii) Their structural and magnetic ground states are strongly coupled with a lattice distortion occurring concomitantly with antiferromagnetic ordering;\(^{17}\) (iii) Finally, Cr\(^{3+}\) 3d\(^3\) strongly prefers the octahedral site where it has a non-degenerate electronic configuration thus enabling compositional variation only on the tetrahedral \(A\) site. The effect of spin disorder on the structural ground states of ZnCr\(_2\)O\(_4\) is investigated by substituting magnetic Co\(^{2+}\) with a tetrahedral ionic radius of 0.58 Å for Zn\(^{2+}\) which has an ionic radius of 0.6 Å in tetrahedral coordination.\(^{17}\) The similarity in ionic radii between Co\(^{2+}\) and Zn\(^{2+}\) minimizes the effects of lattice distortion while allowing us to probe the effect of dilute \(A\) site spins on the structural ground states of ZnCr\(_2\)O\(_4\). Jahn-Teller active Cu\(^{2+}\) with an ionic radius of 0.57 Å is introduced to the \(A\) sites of MgCr\(_2\)O\(_4\) and ZnCr\(_2\)O\(_4\) to study the effect of both structural and spin disorder on the structural ground states of these systems.\(^{18}\) Mg\(^{2+}\) has a Shannon-Prewitt ionic...
radius of 0.57 Å in tetrahedral coordination.22

This study is enabled by variable-temperature high-resolution synchrotron X-ray diffraction, which is a powerful tool for investigating the coupling of spin and lattice degrees of freedom in magnetic oxides. For example, it has been used to show that exchange striction drives further distortions to orthorhombic symmetry in the already Jahn-Teller distorted tetragonal spinels NiCr$_2$O$_4$ and CuCr$_2$O$_4$.26 Similarly, high-resolution synchrotron X-ray diffraction revealed phase coexistence in the spin-Jahn-Teller phases of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$.25 Barton et al. have also shown a spin-driven rhombohedral to monoclinic structural distortion in Co$_{10}$Ge$_3$O$_{16}$.27

We show that ≥10% Co$^{2+}$ ions on the Zn$^{2+}$ site of ZnCr$_2$O$_4$ suppress the structural distortion that accompanies antiferromagnetic ordering in ZnCr$_2$O$_4$. We also find that concentrations ≥10% of Jahn-Teller active Cu$^{2+}$ on the Mg$^{2+}$ site of MgCr$_2$O$_4$ and on the Zn$^{2+}$ site of ZnCr$_2$O$_4$ induce average structure distortions at temperatures above the magnetic ordering temperature. The Jahn-Teller average structure distortion in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ occurs at higher temperatures with increase in $x$. Despite the lattice distortions in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ when $x$ ≥ 0.1, magnetic interactions remain frustrated and no further average structure distortions are observed at the Néel temperature. The Jahn-Teller distorted systems Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ when $x$ ≥ 0.1, are orthorhombic in the space group $Fd\bar{3}m$. In all the studied solid solutions, magnetism evolves from frustrated antiferromagnetism to glassy uncompensated antiferromagnetism.

I. METHODS

Powder samples of Zn$_{1-x}$Co$_x$Cr$_2$O$_4$, Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$, and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ were prepared using solid state preparation methods. The samples Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ were prepared from stoichiometric solution mixtures of the nitrates Mg(NO$_3$)$_2$.6H$_2$O, Cu(NO$_3$)$_2$.6H$_2$O, and Cr(NO$_3$)$_3$.9H$_2$O. The nitrate precursor was calcined at temperatures between 700 °C and 1000 °C for 10 hours as reported in Shoemaker and Seshadri.25 Powders of Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ were prepared from stoichiometric amounts of ZnO, CuO, and Cr$_2$O$_3$ that were ground, pressed into pellets, and calcined at 800 °C for 12 hours. These samples were reground, pressed into pellets, and annealed at 1000 °C for 48 hours followed by further annealing at 800 °C for 12 hours. Stoichiometric powders of Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ were prepared from Co$_2$O$_4$.2H$_2$O, ZnO, and Cr$_2$O$_3$. These powders were mixed, pressed into pellets, and calcined at 800 °C for 12 hours. The samples were then reground, pressed into pellets, and annealed at 1150 °C for 12 hours followed by further annealing at 800 °C for 24 hours. Samples were structurally characterized by high-resolution ($\delta$Q/Q ≤ 2 × 10$^{-4}$) variable-temperature (6 K ≤ T ≤ 300 K) synchrotron X-ray powder diffraction at beamline 11BM at the Advanced Photon Source, Argonne National Laboratory. Diffraction patterns were fit to structural models using the Rietveld method as implemented in the EXPGUI/GSAS software program.21,22 Crystal structures are visualized using the program VESTA.23 Magnetic properties were measured using the Quantum Design MPMS 5XL superconducting quantum interference device (SQUID). Heat capacity measurements were performed using a Quantum Design Physical Properties Measurement System. Time-of-flight neutron scattering data was collected on the NPDF instrument at Los Alamos National Laboratory. The neutron pair distribution function (NPDF) with a maximum Q of 35 Å was processed using the PDFGETN program.23 Least squares refinement of the NPDFs was performed using PDFGUI.25

II. RESULTS AND DISCUSSION

A. Zn$_{1-x}$Co$_x$Cr$_2$O$_4$

ZnCr$_2$O$_4$ and CoCr$_2$O$_4$ are normal cubic spinels in the space group $Fd\bar{3}m$ at room temperature. These systems vary significantly in their magnetic properties, primarily due to the differences in properties of the A site cations. Zn$^{2+}$ has the closed electron configuration [Ar]3d$^{10}$ which renders it magnetically inert. Direct antiferromagnetic Cr$^{3+}$-Cr$^{3+}$ interactions in the pyrochlore Cr sublattice of ZnCr$_2$O$_4$ give rise to geometric frustration. A spin-Jahn-Teller distortion partially lifts spin frustration in ZnCr$_2$O$_4$ enabling the onset of antiferromagnetic order at the Néel temperature.23,26,27 The nuclear structure of the spin-Jahn-Teller phase of ZnCr$_2$O$_4$ has been extensively studied.20,28,29,30 Recently, our group has proposed a structural model of coexisting tetragonal $I4_1/amd$ and orthorhombic $Fd\bar{3}d$ phases for ZnCr$_2$O$_4$.20 On the other hand, Co$^{2+}$ has the electronic configuration [Ar]3d$^7$ with three unpaired spins that interact ferrimagnetically with Cr$^{3+}$ through Co$^{2+}$-O-Cr$^{3+}$ superexchange interactions. CoCr$_2$O$_4$ shows complex magnetic behavior; it undergoes a magnetic phase transition from a paramagnetic state to a ferrimagnetic long-range ordered state near 94 K.28,29 A recent report by Chang et al. shows long range spiral order in CoCr$_2$O$_4$ below 25 K with an incumensurate propagation vector and a transition at 14 K to commensurate spiral order.21 While no studies report a lowering of structural symmetry in CoCr$_2$O$_4$, ultrasound propagation measurements performed on single crystals of CoCr$_2$O$_4$ by Tsurkan et al. show a field-induced structural distortion to cubic symmetry at high magnetic fields.32 CoCr$_2$O$_4$ exhibits spin charge coupling; the onset of incumensurate spiral order in CoCr$_2$O$_4$ is accompanied by a change in the dielectric constant.30,31 In addition, the dielectric constant shows magnetic field dependence below 95 K.33 We examine the changes in structural ground states of ZnCr$_2$O$_4$ when 10% and 20%
Co\textsuperscript{2+} cations are substituted on the non-magnetic Zn\textsuperscript{2+} site.

At room temperature, the prepared compounds Zn\textsubscript{1−x}Co\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4} where x < 0.2 are cubic spinels in the space group Fd\textit{3}m (Fig. 2 and Table IV of the appendix). The similarity in the tetrahedral ionic radii of Co\textsuperscript{2+} and Zn\textsuperscript{2+} allows the entire solid solution Zn\textsubscript{1−x}Co\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4} to retain cubic Fd\textit{3}m symmetry at room temperature.\textsuperscript{12} Despite the smaller ionic radius of Co\textsuperscript{2+}, a unit cell expansion occurs with substitution of Co\textsuperscript{2+} for Zn\textsuperscript{2+} in Zn\textsubscript{1−x}Co\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4}. The observed unit cell expansion has been previously reported and is attributed to higher cation-cation repulsion with increasing substitution of the more ionic Co\textsuperscript{2+} for Zn\textsuperscript{2+} in Zn\textsubscript{1−x}Co\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4}.\textsuperscript{12}

Antiferromagnetic interactions of the geometrically frustrated spinel ZnCr\textsubscript{2}O\textsubscript{4} [Fig. 2 (a)] evolve to uncompensated antiferromagnetic interactions in Zn\textsubscript{0.8}Co\textsubscript{0.2}Cr\textsubscript{2}O\textsubscript{4} [Fig. 2 (c)]. Compensated interactions of ZnCr\textsubscript{2}O\textsubscript{4} are illustrated by the upward turn of the inverse susceptibility below the magnetic ordering temperature and this contrasts with uncompensated antiferromagnetic interactions in Zn\textsubscript{0.8}Co\textsubscript{0.2}Cr\textsubscript{2}O\textsubscript{4} where magnetic ordering yields a downward turn of the inverse susceptibility. An increase in the number of magnetic interactions is expected in Zn\textsubscript{1−x}Co\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4} with increase in x. Accordingly, Curie-Weiss fitting in the paramagnetic regime (300 ≤ T ≤ 390 K) of Zn\textsubscript{1−x}Co\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4} yields an increasing Θ\textsubscript{CW} with x (Table I). Similarly, the expected increase in effective moment with Co\textsuperscript{2+} substitution is also observed (Table I). When spins are substituted on the non-magnetic A sites of ABC\textsubscript{2}O\textsubscript{4} spinels at concentrations greater than 20%, spin frustration is lifted.\textsuperscript{12,13} However, at dilute A site spin concentrations, disorder in the spin interactions has been shown to further suppress magnetic ordering.\textsuperscript{12,13} Due to the disorder in spin interactions, magnetic ordering in Zn\textsubscript{0.9}Co\textsubscript{0.1}Cr\textsubscript{2}O\textsubscript{4} and Zn\textsubscript{0.8}Co\textsubscript{0.2}Cr\textsubscript{2}O\textsubscript{4} occurs at lower temperatures compared to ZnCr\textsubscript{2}O\textsubscript{4} (Table I).

Antiferromagnetic order in ZnCr\textsubscript{2}O\textsubscript{4} occurs concurrently with a structural distortion (middle panel of Fig. 2). The structural ground state of ZnCr\textsubscript{2}O\textsubscript{4} has been extensively investigated and a recent report from our group shows that the spin-Jahn-Teller phase of ZnCr\textsubscript{2}O\textsubscript{4} is best described by the combination of tetragonal I\textit{4}1/amd and orthorhombic F\textit{dd}d space groups.\textsuperscript{21,22} While ZnCr\textsubscript{2}O\textsubscript{4} exhibits a clear lattice distortion at the Néel temperature, the cubic Fd\textit{3}m (800) reflection for samples x = 0.1 and x = 0.2 shows no divergence illustrating the complete suppression of long-range structural distortion in these materials. As a result, the average nuclear structures of Zn\textsubscript{0.9}Co\textsubscript{0.1}Cr\textsubscript{2}O\textsubscript{4} and Zn\textsubscript{0.8}Co\textsubscript{0.2}Cr\textsubscript{2}O\textsubscript{4} near 5 K are well modeled by the cubic space group Fd\textit{3}m as illustrated in Fig. 2. However, a clear peak broadening of the (800) reflection occurs near 5 K in Zn\textsubscript{0.9}Co\textsubscript{0.1}Cr\textsubscript{2}O\textsubscript{4} and Zn\textsubscript{0.8}Co\textsubscript{0.2}Cr\textsubscript{2}O\textsubscript{4} as shown in Fig. 2 (c) and (f) respectively. This broadening is indicative of higher strain at low temperatures that can result from local distortions in these materials. The structural parameters of Zn\textsubscript{0.9}Co\textsubscript{0.1}Cr\textsubscript{2}O\textsubscript{4} and Zn\textsubscript{0.8}Co\textsubscript{0.2}Cr\textsubscript{2}O\textsubscript{4} are tabulated in Table IV of the appendix.

The spin-Jahn-Teller distortion of ZnCr\textsubscript{2}O\textsubscript{4} yields a sharp heat capacity anomaly at T\textsubscript{N} [Fig. 2 (d)]. This heat capacity anomaly is slightly suppressed in Zn\textsubscript{0.9}Co\textsubscript{0.1}Cr\textsubscript{2}O\textsubscript{4} and it becomes very broad in Zn\textsubscript{0.8}Co\textsubscript{0.2}Cr\textsubscript{2}O\textsubscript{4} [Fig. 2 (e) and (f)]. The suppression of the heat capacity anomalies in Zn\textsubscript{0.9}Co\textsubscript{0.1}Cr\textsubscript{2}O\textsubscript{4} and Zn\textsubscript{0.8}Co\textsubscript{0.2}Cr\textsubscript{2}O\textsubscript{4} shows that these systems host residual spin and structural disorder.

We have shown the differences in structural ground state when ≥ 10% of Co\textsuperscript{2+} are substituted on the non-magnetic A site of ZnCr\textsubscript{2}O\textsubscript{4}. The structural distortion that accompanies magnetic ordering in ZnCr\textsubscript{2}O\textsubscript{4} is completely suppressed even for only 10% Co\textsuperscript{2+} substitution in Zn\textsubscript{0.9}Co\textsubscript{0.1}Cr\textsubscript{2}O\textsubscript{4}. This suggests that random Co-O-Cr superexchange interactions in Zn\textsubscript{1−x}Co\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4}, partially break the spin ground state degeneracy of these systems, allowing the onset of a magnetic ground state without the

\begin{table}[h]
\centering
\caption{Magnetic parameters of Zn\textsubscript{1−x}Co\textsubscript{x}Cr\textsubscript{2}O\textsubscript{4}.}
\begin{tabular}{|c|c|c|c|c|}
\hline
Material & T\textsubscript{N} (K) & \(\mu_{\text{eff}}(\mu_{B})\) & \(\mu_{\text{calc}}(\mu_{B})\) & \(\Theta\textsubscript{CW} (K)\) \\
\hline
ZnCr\textsubscript{2}O\textsubscript{4} & 12.3 & 5.2 & 5.48 & -288 \\
Zn\textsubscript{0.9}Co\textsubscript{0.1}Cr\textsubscript{2}O\textsubscript{4} & 9 & 5.4 & 5.61 & -350 \\
Zn\textsubscript{0.8}Co\textsubscript{0.2}Cr\textsubscript{2}O\textsubscript{4} & 11 & 5.6 & 5.74 & -369 \\
\hline
\end{tabular}
\end{table}
FIG. 2: (Color online) Suppression of the spin-Jahn-Teller distortion in Zn_{1-x}Co_{x}Cr_{2}O_{4} with increase in x. (a) Inverse scaled magnetic susceptibility as a function of temperature for (a) ZnCr_{2}O_{4}, (b) Zn_{0.9}Co_{0.1}Cr_{2}O_{4}, and (c) Zn_{0.8}Co_{0.2}Cr_{2}O_{4} measured in a 1000 Oe field. Compensated antiferromagnetic interactions of ZnCr_{2}O_{4} shown by the upward turn of the inverse susceptibility below the magnetic ordering temperature become uncompensated with the introduction of Co^{2+} in place of Zn^{2+} as illustrated by downward turn of the susceptibility of Zn_{0.8}Co_{0.2}Cr_{2}O_{4} below the Néel temperature. The middle panel shows variable-temperature high-resolution X-ray powder diffraction of the cubic (800) reflection. Geometric frustration in ZnCr_{2}O_{4} drives the lattice distortion shown by the splitting of the (800) reflection at the Néel temperature (12.3 K) of ZnCr_{2}O_{4}. The spin-Jahn-Teller distortion of ZnCr_{2}O_{4} is suppressed even when only 10% Co^{2+} cations are substituted for Zn^{2+} as discussed in the following sections. (d) The sharp heat capacity anomaly observed at the spin-Jahn-Teller distortion temperature of ZnCr_{2}O_{4} is suppressed in Zn_{0.9}Co_{0.1}Cr_{2}O_{4} (e) and strongly suppressed in Zn_{0.8}Co_{0.2}Cr_{2}O_{4} (f).

need for a long range structural distortion. It is also plausible that random Co-O-Cr superexchange interactions could be disrupting the coherency of Cr-Cr exchange coupling paths thus inhibiting spin-Jahn-Teller distortions in Zn_{0.9}Co_{0.1}Cr_{2}O_{4} and Zn_{0.8}Co_{0.2}Cr_{2}O_{4}. Small substitutions of Co^{2+} for Mg^{2+} will likely suppress the Spin-Jahn-Teller distortion of MgCr_{2}O_{4}; this is supported by the similar structural effects of Cu^{2+} substitutions for Mg^{2+} and Zn^{2+} in MgCr_{2}O_{4} and ZnCr_{2}O_{4} as discussed in the following sections.

B. Mg_{1-x}Cu_{x}Cr_{2}O_{4}

We examine the effect of both spin and lattice disorder on the spin-Jahn-Teller ground state of MgCr_{2}O_{4} by substituting ≥ 10% of Jahn-Teller active Cu^{2+} for Mg^{2+}. At room temperature the normal spinels MgCr_{2}O_{4} and CuCr_{2}O_{4} have different structural ground states; MgCr_{2}O_{4} is cubic while CuCr_{2}O_{4} is tetragonal. The tetragonal structure of CuCr_{2}O_{4} results from cooperative Jahn-Teller ordering of CuO_{4} tetrahedra at \( T = 853 \text{ K} \). MgCr_{2}O_{4} is a frustrated antiferromagnet, and its transition to an ordered magnetic state at \( T_N = 12.9 \text{ K} \) is accompanied by a structural distortion. The spin-Jahn-Teller distorted phase of MgCr_{2}O_{4} had been previously described by the tetragonal \( I_{41}/amd \) structure but we have recently shown that this system consists of coexisting tetragonal \( I_{41}/amd \) and orthorhombic \( Fddd \) phases. CuCr_{2}O_{4} is ferrimagnetic, with magnetic Cu^{2+} and Cr^{3+} sublattices contributing to a non-collinear magnetic structure where two canted Cr^{3+} sublattices yield a magnetic moment that is partially compensated by the Cu^{2+} sublattice at \( T_N = 135 \text{ K} \). In addition to the high temperature Jahn-Teller driven cubic-tetragonal phase transition, CuCr_{2}O_{4} undergoes yet another structural distortion from tetragonal \( I_{41}/amd \) to orthorhombic \( Fddd \) symmetry near 130 K.
FIG. 3: (Color online) Low temperature synchrotron X-ray powder diffraction of (a) Zn$_{0.9}$Co$_{0.1}$Cr$_{2}$O$_4$, and (d) Zn$_{0.8}$Co$_{0.2}$Cr$_{2}$O$_4$ modeled to the cubic space group $Fdar{3}m$. The (800) reflections of Zn$_{0.9}$Co$_{0.1}$Cr$_{2}$O$_4$ and Zn$_{0.8}$Co$_{0.2}$Cr$_{2}$O$_4$ at room temperature are shown here in (b) and (e) respectively and near 5 K in (c) and (f) respectively. A broadening of the (800) reflection is observed at low temperature in Zn$_{0.9}$Co$_{0.1}$Cr$_{2}$O$_4$ and Zn$_{0.8}$Co$_{0.2}$Cr$_{2}$O$_4$.

![Image](image.png)

FIG. 4: (Color online) Rietveld refinement of room temperature high resolution synchrotron X-ray powder diffraction of (a) MgCr$_2$O$_4$ (b) Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and (c) Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$. All samples show a very small Cr$_2$O$_3$ impurity with concentrations <1% in all samples. (d) The cubic lattice constant in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ decreases linearly with increase in Cu$^{2+}$ concentration. Error bars are smaller than data symbols.

![Image](image.png)

TABLE II: Magnetic parameters of Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$.

| $T_N$ (K) | $\mu_{exp}(\mu_B)$ | $\mu_{calc}(\mu_B)$ | $\Theta_{CW}$ (K) |
|-----------|---------------------|----------------------|-------------------|
| MgCr$_2$O$_4$ | 12.9 | 5.2 | 5.47 | -368 |
| Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ | 11 | 5.3 | 5.50 | -361 |
| Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ | 15 | 5.2 | 5.53 | -329 |

due to magnetostructural coupling.$^{[13]}$

The prepared spinel solid solutions Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ where $x \leq 0.2$ are cubic with the space group $Fd\bar{3}m$ at room temperature [Fig. 4(a), (b), and (c)]. While tetrahedral Mg$^{2+}$ and Cu$^{2+}$ have identical Shannon-Prewitt ionic radii, we observe a lattice contraction with increase in Cu$^{2+}$, following Vegard’s law [Figure 3(d)]. This decrease in lattice constant with Cu$^{2+}$ substitution is consistent with the earlier work by Shoemaker and Seshadri.$^{[20]}$ and with the smaller pseudocubic cell volume of CuCr$_2$O$_4$ (566.38 Å$^3$)$^{[13]}$ compared with that of MgCr$_2$O$_4$ (579.017 Å) at room temperature.$^{[9]}$ The structural parameters of Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ for $x = 0.1$ and 0.2 at 300 K are tabulated in Table [V] of the appendix.

The evolution of magnetism in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ where $x \leq 0.2$, is similar to that observed in Zn$_{1-x}$Co$_x$Cr$_2$O$_4$; frustrated antiferromagnetism in MgCr$_2$O$_4$ evolves to uncompensated antiferromagnetism in Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$[Fig. 5 (a), (b), and (c)]. Antiferromagnetic ordering in Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ occurs at a lower temperature than in MgCr$_2$O$_4$ due to dilute J$_{\text{Cu-O-Cr}}$ couplings interfering with J$_{\text{Cr-Cr}}$ couplings (Table II). However, the increase in Cu$^{2+}$ concentration in Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ yields a higher magnetic ordering temperature and this is consistent with the findings that sufficient magnetic A site spins lift frustration in geometrically frustrated ACr$_2$O$_4$ spinels.$^{[12,13]}$ Curie-Weiss fitting in the paramagnetic regime 300 K $\leq T \leq 390$ K, of Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ yields a slight increase in the effective moment of Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and a weakening of the overall strength of magnetic interactions shown by the decrease in the magnitude of $\Theta_{CW}$ (Table IV). Weaker antiferromagnetic interactions with Cu$^{2+}$ substitution are attributed to the effects of spin disorder due to dilute A site spins. The decrease in $\Theta_{CW}$ in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ with increase in $x$ contrasts with the increase in $\Theta_{CW}$ in Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ with increase in $x$; this difference is attributed to the higher spin of Co$^{3+}$ 3$d^7$ $s = \frac{3}{2}$ compared to Cu$^{2+}$ 3$d^9$ $s = \frac{1}{2}$. The higher spin of Co$^{3+}$ contributes to stronger magnetic interactions in Zn$_{1-x}$Co$_x$Cr$_2$O$_4$.

Structural distortions are observed in all compounds Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ when $x \leq 0.2$. The spin-Jahn-Teller distortion of MgCr$_2$O$_4$ is illustrated by the splitting of the (800) reflection to several low temperature peaks (Leftmost middle panel of Fig. 5).
FIG. 5: (Color online) Spin-Jahn-Teller and Jahn-Teller ordering in MgCr$_2$O$_4$. The top panel shows the scaled inverse susceptibility of MgCr$_2$O$_4$ (a), Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ (b) and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ (c) measured in a 1000 Oe field. Compensated antiferromagnetic interactions in MgCr$_2$O$_4$ (a) and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ (b) evolve to uncompensated antiferromagnetic interactions in Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ (c). Geometric frustration of spins in MgCr$_2$O$_4$ drives a structural distortion at $T_N \approx 12.9$ K that is indicated by the splitting of the high symmetry (800) reflection. Cooperative Jahn-Teller ordering spurs average structure distortions in Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ at $T \sim 35$ K and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ at $T \sim 110$ K. The structural distortions in Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ are decoupled from the magnetism and no further structural distortions occur near the Néel temperature of these compounds although they exhibit spin frustration. (d) There is a sharp heat capacity anomaly at the Néel temperature of MgCr$_2$O$_4$ with a shoulder feature plausibly indicating a slight separation in temperature of the magnetic and structural transitions. (e) Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ shows a broad heat capacity anomaly with a kink at $T_N$. (f) Similarly, Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ shows a broad heat capacity peak in the temperature range $6\,\text{K} \leq T \leq 80\,\text{K}$.

acy in spin ground states drives the structural distortion in MgCr$_2$O$_4$, degeneracy in the orbital configurations of tetrahedral Cu$^{2+}$ drive Jahn-Teller distortions in Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ at 35 K and 110 K respectively. The middle panel of figure 5(d) shows the splitting of the coincident (731) and (553) reflections in Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$. The Jahn-Teller distortion increases with Cu$^{2+}$ concentration as shown by the larger separation between the low-temperature reflections of Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ and the onset of this distortion at higher temperature in this compound. We note that magnetic transitions do not accompany the structural distortions of Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$. The Jahn-Teller phases of Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ are well modeled by the orthorhombic Fddd structure (Fig. 6) that is ascribed to CuCr$_2$O$_4$ following its magnetostructural distortion. An important difference between CuCr$_2$O$_4$ and these systems studied here is that the orthorhombic structure of CuCr$_2$O$_4$ occurs due to magnetostructural coupling while the orthorhombic structure of Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ occurs in the paramagnetic regime driven primarily by cooperative Jahn-Teller ordering.

The spin-Jahn-Teller distortion of MgCr$_2$O$_4$ results in a sharp heat capacity anomaly with a slight shoulder feature [Fig. 5(d)]. The shoulder feature is likely due to a slight separation in temperature of the magnetic and structural changes. The onset of heat capacity changes in Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ occur at high temperatures where structural changes begin and they persist to low temperatures where magnetic ordering occurs [Fig. 5(e) and (f)].

While the substitution of Co$^{2+}$ for Zn$^{2+}$ suppresses spin-Jahn-Teller distortion in ZnCr$_2$O$_4$, ≥10% substitution of Jahn-Teller active Cu$^{2+}$ for Mg$^{2+}$ induces structural distortions in Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ at temperatures above the mag-
magnetic ordering temperatures of these compounds. The structural distortions in Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ affect the pyrochlore Cr sublattice; while there is only one Cr-Cr bond length at room temperature in the cubic phases of these systems, there are three Cr-Cr bond lengths in the orthorhombic phases of these materials. Surprisingly, spin interactions remain frustrated in Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ with magnetic ordering occurring below 18 K despite the presence of distortions in the pyrochlore Cr sublattice of these materials at temperatures above their Néel temperatures. No further structural distortions are observed in Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ near the Néel temperature.

C. Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$

We examine the effect of Cu$^{2+}$ substitutions for Zn$^{2+}$ on the spin-Jahn-Teller distortion of ZnCr$_2$O$_4$. All prepared samples Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ where $x \leq 0.2$ are cubic spinels in the space group $Fd\bar{3}m$ at room temperature as shown in Fig. 7. Like in the solid solutions Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$, the substitution of Cu$^{2+}$ for Zn$^{2+}$ results in a steady decrease of the lattice constant [Fig 7 (d)]. This lattice decrease is in good agreement with the smaller cell volume of CuCr$_2$O$_4$ (566.38 Å$^3$) at room temperature compared to ZnCr$_2$O$_4$ (577.520 Å$^3$). The structural parameters of Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ are tabulated in Table VII of the appendix.

Compensated antiferromagnetic interactions in ZnCr$_2$O$_4$ and Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ evolve to uncompensated antiferromagnetic interactions in Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ [Figure 8(a), (b), and (c)]. The onset of magnetic ordering in Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ occurs at lower temperatures than in ZnCr$_2$O$_4$ due to disorder arising from dilute A site spins while Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ shows the highest ordering temperature of the studied Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ compounds (Table III). A slight decrease in the effective moment is observed with Cu$^{2+}$ substitution in ZnCr$_2$O$_4$ and this is attributed to the presence of short range spin interactions in the paramagnetic regime contributing to the underestimation of the effective moment (Table III). As observed in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$, a decrease in the magnitude of ΘCW occurs in Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ with increase in $x$ suggesting that dilute Cu$^{2+}$ substitutions weaken the overall strength of magnetic interactions in MgCr$_2$O$_4$ and ZnCr$_2$O$_4$. Geometric spin frustration drives a lattice distortion at the antiferromagnetic ordering temperature of ZnCr$_2$O$_4$ while Jahn-Teller distortion of tetrahedral Cu$^{2+}$ in Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ drive structural distortions.
in Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ at 45 K and 110 K respectively (middle panel of Fig. 8). The lattice distortions of Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ are shown by the divergence of the coincident (511) and (333) reflections at the respective distortion temperatures of these materials (Fig. 8). The structural changes of Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ are decoupled from antiferromagnetic ordering (Table III), nonetheless there is a change in slope of the inverse susceptibility of these systems at the structural distortion temperatures. Jahn-Teller distortion is enhanced in Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ with increase in Cu$^{2+}$ content, occurring at higher temperatures and involving larger lattice distortions (Fig. 8). Like in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$, the Jahn-Teller phases of Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ [Fig. 8(a)] and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ [Fig. 8(d)] are well modeled by the orthorhombic Fddd space group. The complete structural descriptions of these compounds at room temperature and near 6 K are tabulated in Table VI of the appendix.

The large heat capacity anomaly of ZnCr$_2$O$_4$ at the spin-Jahn-Teller distortion temperature [Fig. 8(d)] evolves into a broad transition in Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ [Fig. 8(e)] and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ [Fig. 8(f)] over the temperature range were structural and magnetic changes take place.

We further explore the structural distortions of Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ by performing sequential Rietveld refinements from the high temperature cubic phase to the low temperature orthorhombic phase. The cubic lattice constant diverges into three independent orthorhombic

| TABLE III: Magnetic parameters of Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$. | $T_N$ (K) | $\mu_{exp}(\mu_B)$ | $\mu_{calc}(\mu_B)$ | $\Theta_{CW}$(K) |
|---|---|---|---|---|
| ZnCr$_2$O$_4$ | 12.3 | 5.2 | 5.47 | -288 |
| Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ | 11 | 4.9 | 5.50 | -239 |
| Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ | 16 | 5.0 | 5.53 | -270 |

FIG. 8: (Color online) Spin-Jahn Teller and Jahn-Teller distortions in Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$. The top panel shows inverse scaled susceptibility measurements of Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ measured under a 1000 Oe field. Compensated antiferromagnetism is observed in ZnCr$_2$O$_4$ (a) and Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ (b) below the Néel temperature while Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ (c) shows uncompensated antiferromagnetism. A lattice distortion accompanies magnetic ordering in ZnCr$_2$O$_4$ as shown by the splitting of the high symmetry (800) reflection at the Néel temperature. Jahn-Teller active Cu$^{2+}$ on the A sites of Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ drive lattice distortions at approximately 45 K and 110 K respectively, where the coincident (511) and (333) reflections split into several low temperature reflections. There is a large heat capacity anomaly at the spin-Jahn-Teller distortion temperature of ZnCr$_2$O$_4$ (d). Broad heat capacity anomalies are observed in Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ (e) and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ (f) over the temperature range where structural and magnetic changes occur. The line features in the variable temperature data of sample Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ are due to slight temperature fluctuations during the measurement.
bypassing the tetragonal Fd\(_3d\) bic distortion in CuCr

Magnetostructural coupling drives further structural dis-

tortion in CuCr

\[ 2 \]

\[ \text{I} \]

\[ \text{b} \]

\[ \text{Mg} \]

\[ \text{Fddd} \]

\[ 2 \]

\[ t \]

tortion in CuCr

The difference is in blue. The high temperature coincident cubic Fd\(_{3m}\) reflections (511) and (333) shown in (b) for Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\) and in (e) for Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\) are split at lower temperatures following the cubic to orthorhombic lattice distortion. These low temperature reflections as indexed to the orthorhombic Fddd structure are shown in (c) and (f) for Zn\(_{0.9}\)Cu\(_{0.1}\)Cr\(_2\)O\(_4\) and Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\) respectively.

lattice parameters at 110 K [Fig. 10(a)]. The \( a \) lattice constant decreases steeply with temperature while the \( b \) and \( c \) lattice constants increase. The orthorhombic distortion increases with decrease in temperature. Although the structural distortions of Mg\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\) and Zn\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\) occur primarily due to the Jahn-Teller activity of tetrahedral Cu\(^{2+}\), there is a distinct difference in the distortions observed in the spinel solid solutions compared to the spinel CuCr\(_2\)O\(_4\). Jahn-Teller distortion in CuCr\(_2\)O\(_4\) occurs near 853 K and involve a cubic Fd\(_{3m}\) to tetragonal \( I4_1/amd \) lattice distortion\(^{[23]} \). Magnetostructural coupling drives further structural distortion in CuCr\(_2\)O\(_4\) from tetragonal \( I4_1/amd \) to orthorhombic Fddd symmetry\(^{[23]} \). In the solid solutions Mg\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\) and Zn\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\), we observe a cubic Fd\(_{3m}\) to orthorhombic Fddd distortion, completely bypassing the tetragonal \( I4_1/amd \) structure observed in CuCr\(_2\)O\(_4\) and the lattice distortions occur without the onset of magnetic ordering. The different character of distortion in Mg\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\) and Zn\(_{1-x}\)Cu\(_x\)Cr\(_2\)O\(_4\) compared to CuCr\(_2\)O\(_4\) is attributed to poor connectivity

FIG. 9: (Color online) Synchrotron powder diffraction patterns of Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\) (a) and Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\) (d) collected near 6 K and indexed to the orthorhombic space group Fddd. Data is shown in black, the model is in orange while the difference is in blue. The high temperature coincident cubic Fd\(_{3m}\) reflections (511) and (333) shown in (b) for Zn\(_{0.9}\)Cu\(_{0.1}\)Cr\(_2\)O\(_4\) and in (e) for Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\) are split at lower temperatures following the cubic to orthorhombic lattice distortion. These low temperature reflections as indexed to the orthorhombic Fddd structure are shown in (c) and (f) for Zn\(_{0.9}\)Cu\(_{0.1}\)Cr\(_2\)O\(_4\) and Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\) respectively.

FIG. 10: (Color online) (a) The evolution of lattice parameters of Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\) as a function of temperature revealing a structural distortion at 110 K where three orthorhombic Fddd lattice constants emerge from the cubic Fd\(_{3m}\) lattice constant. (b) There is a slight change in slope in the temperature dependent cell volume of Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\) at the structural distortion temperature. Error bars are smaller than data symbols.

FIG. 11: (Color online) The spinel structure of Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\) in the cubic Fd\(_{3m}\) phase near 300 K and in the orthorhombic Fddd phase near 6 K are shown in (a) and (b) respectively. Edge sharing CrO\(_6\) (blue) octahedra are corner connected to (Zn/Cu)O\(_4\) (grey) tetrahedra. The shared (Zn/Cu) atomic site is shown in grey (Zn atomic fraction) and dark red (Cu atomic fraction). The ideal tetrahedral angle of 109.54° observed in the cubic phase(a) of Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\) is distorted to two angles of 111.898° and 105.99° in the orthorhombic phase(b); the (Zn/Cu)O\(_4\) (grey) tetrahedra appear more flattened in the orthorhombic phase(b) filling the tetrahedral voids between the CrO\(_6\) octaheda while small gaps can be seen between the (Zn/Cu)O\(_4\) (grey) tetrahedra and the CrO\(_6\) (blue) octahedra in the cubic phase(a) of Zn\(_{0.8}\)Cu\(_{0.2}\)Cr\(_2\)O\(_4\).
between CuO$_4$ tetrahedra. Dilute randomly distributed CuO$_4$ tetrahedra in the solid solutions results in average distortions in all axes of the unit cell and hence these systems adopt orthorhombic symmetry in the Jahn-Teller phases. Group-subgroup relations show that structural distortion from cubic Fd$ar{3}$m to orthorhombic Fddd symmetry goes through an intermediate tetragonal $I4_1/amd$ space group. It is plausible that the Jahn-Teller ordering systems Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ quickly go through the tetragonal $I4_1/amd$ structure before adopting the orthorhombic structure. A similar cubic Fd$ar{3}$m to orthorhombic Fddd lattice distortion driven by charge ordering has been observed in the cathode spinel material LiMn$_2$O$_4$ near room temperature.

The Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ unit cell contracts with decrease in temperature as reflected in Fig. 10 (b). There is a slight change in slope of the unit cell volume at the structural distortion temperature. This small change in slope of the cell volume at 110 K and the broad heat capacity anomaly of Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ suggest it undergoes a second-order structural distortion.

The AO$_4$ tetrahedra of the cubic phase of Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ are distorted in the orthorhombic phase. Specifically, a single A-O distance is preserved while two distinct O-A-O bond angles of 111.898° and 105.99° emerge from the ideal tetrahedral angle 109.47° of the cubic phase. The overall effect of these angle distortions in Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ is a compression of the tetrahedra. This is illustrated in Fig. 11 (a) where the ideal AO$_4$ tetrahedra of the cubic phase leave small voids in the surrounding CrO$_6$ network while the flattened AO$_4$ tetrahedra of the orthorhombic phase completely fill the tetrahedral voids [Fig. 11 (b)]. The compression of AO$_4$ tetrahedra is similar to the flattening of CuO$_4$ tetrahedra in the orthorhombic phase of CuCr$_2$O$_4$.

The AO$_4$ distortions of Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ do not lift spin degeneracy and magnetic ordering in these materials still takes place below 20 K (Table II and III).

Real space structural descriptions of Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ for $x > 0$ give insights as to the nature of the Jahn-Teller distortions in these compounds. There are differences in the pair distribution functions of Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ collected at room temperature and at
15 K as shown in Fig. 12 (a) and (b). The differences are mainly in the intensity of atom pair correlations; at low temperature, the distribution functions have slightly higher intensity than at room temperature where atomic vibrations broaden the pair distribution function [Fig. 12 (a) and (b)]. The low temperature average structural model, orthorhombic Fddd, describes the local structure of Zn₀.₉Cu₀.₁Cr₂O₄ and Zn₀.₈Cu₀.₂Cr₂O₄ at 15 K [Fig. 12 (c) and (d)].

Combined average and local structure studies can distinguish whether Jahn-Teller distortions occur spontaneously at the average structure distortion temperatures of Zn₀.₉Cu₀.₁Cr₂O₄ and Zn₀.₈Cu₀.₂Cr₂O₄ or whether local distortions of CuO₄ tetrahedra persist in the cubic phases of these materials with these distortions becoming cooperative at the Jahn-Teller distortion temperature. In Figure 13 we model the room temperature pair distribution functions of Zn₀.₉Cu₀.₁Cr₂O₄ (a) and Zn₀.₈Cu₀.₂Cr₂O₄ (b) to the cubic average structure model Fd3m and to the Jahn-Teller distorted orthorhombic Fddd structure. At room temperature, the cubic Fd3m fit yields slightly larger goodness-of-fit parameters compared to the lower symmetry Fddd fits [Fig. 13 (c) and (d)]. The better description of the local structure of these compounds at room temperature by the lower symmetry structural model suggests that local CuO₄ distortions are present in the cubic phases of Zn₀.₉Cu₀.₁Cr₂O₄ and Zn₀.₈Cu₀.₂Cr₂O₄ and that these distortions become cooperative at the respective Jahn-Teller distortion temperatures of these systems. The presence of local distortions in Zn₀.₉Cu₀.₁Cr₂O₄ and Zn₀.₈Cu₀.₂Cr₂O₄ is further distinguished by the different pair distribution functions around Cu and Zn at low temperature.

FIG. 14: (Color online) Least squares refinement of the pair distribution function of Zn₀.₉Cu₀.₁Cr₂O₄ (a) and Zn₀.₈Cu₀.₂Cr₂O₄ (b) to a two phase model of ZnCr₂O₄ and CuCr₂O₄ shows that the environment around Cu⁺ at low r as shown by the different Zn-O and Cu-O bond lengths of the ZnO₄ and CuO₄ tetrahedra. The phase fractions of the ZnCr₂O₄ model are 90% for Zn₀.₉Cu₀.₁Cr₂O₄ and 80% for Zn₀.₈Cu₀.₂Cr₂O₄. The differences in Zn-O and Cu-O bond lengths of the AO₄ tetrahedra are smaller at high r.

FIG. 15: (Color online) Temperature-composition phase diagrams of the spinel solid solutions Zn₁₋ₓCuₓCr₂O₄ (a), Mg₁₋ₓCuₓCr₂O₄ (b), and Zn₁₋ₓCuₓCr₂O₄ (c). At high temperatures all systems are paramagnetic (PM) and cubic in the space group Fd3m. Magnetism evolves from frustrated compensated antiferromagnetism (AFMc) in ZnCr₂O₄ and MgCr₂O₄ to glassy uncompensated antiferromagnetism (gAFMc) when x = 0.2. A transition from cubic Fd3m to orthorhombic Fddd symmetry occurs in Mg₁₋ₓCuₓCr₂O₄ and Zn₁₋ₓCuₓCr₂O₄ when x ≥ 0.1 due to Jahn-Teller distortions of tetrahedral CuO₄. We have recently reported that tetragonal I₄/amd and orthorhombic Fddd structures coexist in the spin-Jahn-Teller phases of MgCr₂O₄ and ZnCr₂O₄.
ther corroborated by least squares refinements of the pair distribution functions to a structural model of two cubic phases assigned to either ZnCr$_2$O$_4$ or CuCr$_2$O$_4$ [Fig. 14(a) and (b)]. Structural models consisting of stoichiometrically weighted end-member structures have been previously successfully employed to describe the pair distribution function of the frustrated spinel CoAl$_2$O$_4$ at low $r_{\text{cutoff}}$. In the two phase refinement, the ZnCr$_2$O$_4$ and CuCr$_2$O$_4$ structural models are scaled to correlate with the mole fractions of Zn$^{2+}$ and Cu$^{2+}$ and only the lattice parameters and Zn$^{2+}$/Cu$^{2+}$ thermal parameters are allowed to vary. There is a large difference in the Zn-O and Cu-O bond lengths in the two phases at low $r_{\text{cutoff}}$ for both Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ and this difference decreases at high $r_{\text{cutoff}}$ (Fig. 14). This suggests that there are local distortions in Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ that are best modeled by differentiating the environment around Zn$^{2+}$ and Cu$^{2+}$. As one examines the pair distribution functions to higher $r_{\text{cutoff}}$, these local distortions are averaged out becoming less apparent as observed by the smaller difference in $A$-O bond lengths of ZnCr$_2$O$_4$ and CuCr$_2$O$_4$. The presence of local distortions in Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ is in good agreement with total scattering studies of the spinels Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ by Shoemaker and Seshadri that show more distortions of the local CuO$_4$ environments compared to MgO$_4$ environments in this spinel solid solution.

$\text{Cu}^{2+}$ substitution on the non-magnetic $A$ sites of MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ has very similar effects on the structure and magnetic properties of the resulting solid solutions. Average structure distortions due to Jahn-Teller ordering of CuO$_4$ tetrahedra occur in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ without accompanying long-range magnetic ordering. The distortions of CuO$_4$ tetrahedra are present in the cubic phases of Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ when $x \geq 0.1$ and become cooperative at the Jahn-Teller distortion temperature where average structure distortions are observed. The Jahn-Teller distorted phases are described by the orthorhombic $Fdd2$ space group. The degeneracy of Cr-Cr bond distances is broken when average structure distortions occur in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$, however, antiferromagnetic interactions remain largely frustrated with magnetic ordering occurring below 20 K. We contrast the propensity for Jahn-Teller distortions compared with spin-Jahn-Teller distortion in the systems Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ where only few Cu$^{2+}$ cations drive Jahn-Teller distortions while these small concentrations of magnetic ions on the non-magnetic $A$ sites of these materials completely suppress spin-Jahn-Teller distortion. The evolution of structure and magnetism in the solid solutions Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$, Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$, and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ are summarized in the phase diagrams presented in Fig. 15.

D. Conclusions

We report the effect of magnetic $A$ site substitutions on spin and structural ordering in MgCr$_2$O$_4$ and ZnCr$_2$O$_4$. We contrast the effect of Co$^{2+}$ 3$d^7$ substitutions in Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ with Cu$^{2+}$ 3$d^9$ substitutions in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$. Spin disorder induced by Co$^{2+}$ 3$d^7$ substitutions in Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ suppress the spin-Jahn-Teller distortion of ZnCr$_2$O$_4$. On the other hand, spin and lattice disorder due to Cu$^{2+}$ 3$d^9$ substitutions in Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$ and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ induce Jahn-Teller distortions in the paramagnetic phases of these compounds yet antiferromagnetic interactions in these systems remain frustrated with long-range magnetic ordering occurring below 20 K with no accompanying structural transformations. In other words, the Jahn-Teller active Cu$^{2+}$ ions decouple structural and magnetic ordering, even when only substituted in small amounts. The low-temperature nuclear structure of Cu$^{2+}$ substituted MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ is orthorhombic $Fdd2$. Analysis of distortions in Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ indicate a flattening of AO$_4$ tetrahedra in the orthorhombic phase. Total neutron scattering studies of Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$ suggest that AO$_4$ are likely distorted locally at room temperature with these distortions becoming cooperative where average structure distortions are observed. Addition of magnetic Co$^{2+}$ and Cu$^{2+}$ induce uncompensated antiferromagnetic interactions in Zn$_{1-x}$Co$_x$Cr$_2$O$_4$, Mg$_{1-x}$Cu$_x$Cr$_2$O$_4$, and Zn$_{1-x}$Cu$_x$Cr$_2$O$_4$. Compounds with dilute A site spins have broad heat capacity features suggesting remanent disorder in these materials. We find that spin-Jahn-Teller ordering is extremely sensitive to spin disorder while Jahn-Teller ordering is robust, and occurs even when only few Jahn-Teller active cations are substituted into the spinel structure.

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TABLE IV: Structural parameters of Zn$_{0.9}$Co$_{0.1}$Cr$_2$O$_4$ and Zn$_{0.8}$Co$_{0.2}$Cr$_2$O$_4$ obtained from Rietveld refinement of high-resolution synchrotron powder X-ray diffraction collected at 295 K and near 6 K and modeled to the cubic space group Fd$ar{3}$m.

| Temperature (K) | 5.5  | 295  | 5.6  | 295  |
|----------------|------|------|------|------|
| Setting        | origin 2 | origin 2 | origin 2 | origin 2 |
| Z              | 8    | 8    | 8    | 8    |
| a(Å)           | 8.32037(2) | 8.327641(1) | 8.32038(1) | 8.327686(5) |
| Vol/ (Å$^3$)   | 576.008(4) | 577.519(3) | 576.009(2) | 577.566(1) |
| Zn/Co          | 8a (1/8, 1/8, 1/8) | 8a (1/8, 1/8, 1/8) | 8a (1/8, 1/8, 1/8) | 8a (1/8, 1/8, 1/8) |
| $U_{iso}$ (10$^2$ Å$^2$) | 0.24(1) | 0.389(5) | 0.128(7) | 0.398(5) |
| Cr             | 16d (1/2, 1/2, 1/2) | 16d (1/2, 1/2, 1/2) | 16d (1/2, 1/2, 1/2) | 16d (1/2, 1/2, 1/2) |
| $U_{iso}$ (10$^2$ Å$^2$) | 0.196(9) | 0.213(4) | 0.145(6) | 0.230(4) |
| O              | 32e (x, y, z) | 32e (x, x, x) | 32e (x, y, z) | 32e (x, x, x) |
| $U_{iso}$ (10$^2$ Å$^2$) | 0.54(3) | 0.32(1) | 0.35(2) | 0.360(1) |
| $\chi^2$       | 15.73 | 5.263 | 6.976 | 7.434 |
| $R_p$(%)        | 8.10 | 9.12 | 7.54 | 9.33 |
| $R_{wp}$(%)     | 10.12 | 11.54 | 9.43 | 12.56 |

TABLE V: Structural parameters of Mg$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Mg$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ obtained from Rietveld refinement of high-resolution synchrotron powder X-ray diffraction collected at 295 K and near 6 K.

| Orthorhombic | Cubic | Orthorhombic | Cubic |
|---------------|-------|---------------|-------|
| Temperature (K) | 6.5  | 295  | 5.7  | 295  |
| Space group    | Fddd | Fd$ar{3}$m | Fddd | Fd$ar{3}$m |
| Setting        | origin 2 | origin 2 | origin 2 | origin 2 |
| Z              | 8    | 8    | 8    | 8    |
| a(Å)           | 8.293741(1) | 8.332613(3) | 8.231110(8) | 8.330362(3) |
| b(Å)           | 8.35834(1) | 8.332613(3) | 8.360256(9) | 8.330362(3) |
| c(Å)           | 8.3488(5) | 8.332613(3) | 8.373391(5) | 8.330362(3) |
| Vol/ (Å$^3$)   | 577.196(4) | 578.554(1) | 576.208(4) | 578.085(1) |
| Mg/Cu          | 8a (1/8, 1/8, 1/8) | 8a (1/8, 1/8, 1/8) | 8a (1/8, 1/8, 1/8) | 8a (1/8, 1/8, 1/8) |
| $U_{iso}$ (10$^2$ Å$^2$) | 0.384(2) | 0.651(7) | 0.371(2) | 0.696(7) |
| Cr             | 16d (1/2, 1/2, 1/2) | 16d (1/2, 1/2, 1/2) | 16d (1/2, 1/2, 1/2) | 16d (1/2, 1/2, 1/2) |
| $U_{iso}$ (10$^2$ Å$^2$) | 0.179(9) | 0.321(3) | 0.102(1) | 0.344(3) |
| O              | 32e (x, y, z) | 32e (x, x, x) | 32e (x, y, z) | 32e (x, x, x) |
| $U_{iso}$ (10$^2$ Å$^2$) | 0.144(2) | 0.651(7) | 0.25(0) | 0.59(1) |
| Cr$_2$O$_3$ wt% | 0.89(8) | 0.89(8) | 0.87(7) | 0.87(7) |
| $\chi^2$       | 4.37 | 2.550 | 6.81 | 2.571 |
| $R_p$(%)        | 6.7  | 5.98 | 6.29 | 6.23 |
| $R_{wp}$(%)     | 9.16 | 8.12 | 8.14 | 8.15 |
TABLE VI: Structural parameters of Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ and Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ obtained from Rietveld refinement of high-resolution synchrotron powder X-ray diffraction collected at 295 K and near 6 K.

|                          | Zn$_{0.9}$Cu$_{0.1}$Cr$_2$O$_4$ | Zn$_{0.8}$Cu$_{0.2}$Cr$_2$O$_4$ |
|--------------------------|---------------------------------|---------------------------------|
|                          | Orthorhombic | Cubic | Orthorhombic | Cubic |
| Temperature (K)          | 5.6           | 295   | 5.9           | 295   |
| Space group              | Fddd           | Fd3m   | Fddd           | Fd3m   |
| Setting                  | origin 2      | origin 2 | origin 2     | origin 2 |
| Z                        | 8              | 8      | 8              | 8      |
| a(Å)                     | 8.328150(7)    | 8.326101(6) | 8.244895(8) | 8.324244(7) |
| b(Å)                     | 8.335862(5)    | 8.326101(6) | 8.358441(5) | 8.324244(7) |
| c(Å)                     | 8.289697(5)    | 8.326101(6) | 8.3409(1)   | 8.324244(7) |
| Vol/ (Å$^3$)             | 575.490(3)     | 577.198(1) | 574.809(5)  | 576.812(2) |
| Zn/Cu                    | 8a (1/8, 1/8, 1/8) | 8a (1/8, 1/8, 1/8) | 8a (1/8, 1/8, 1/8) | 8a (1/8, 1/8, 1/8) |
| $U_{iso}$ (10$^2$ Å$^2$) | 0.309(8)       | 0.455(5) | 0.281(13)    | 0.470(5) |
| Cr                       | 16d (1/2, 1/2, 1/2) | 16d (1/2, 1/2, 1/2) | 16d (1/2, 1/2, 1/2) | 16d (1/2, 1/2, 1/2) |
| $U_{iso}$ (10$^2$ Å$^2$) | 0.297(8)       | 0.259(4) | 0.254(13)    | 0.305(5) |
| O                        | 32h (x, y, z)  | 32e (x, x, x) | 32h (x, y, z) | 32e (x, y, z) |
|                          | x 0.2577(3)    | x 0.26205(47) | 0.260315(184) | 0.261641(53) |
|                          | y 0.2642(3)    | y 0.26205(47) | 0.266652(262) | 0.261641(53) |
|                          | z 0.2628(2)    | z 0.26205(47) | 0.257599(340) | 0.261641(53) |
| $U_{iso}$ (10$^2$ Å$^2$) | 0.329(21)      | 0.411(14) | 0.304(33)    | 0.527(16) |
| Cr$_2$O$_3$ wt%          | 0.97(2)        | 0.97(2) | 1.05(15)     | 1.05(15) |
| $\chi^2$                | 4.494          | 6.582  | 7.808         | 7.805  |
| $R_p$ (%)                | 2.52           | 8.53   | 3.81          | 7.20   |
| $R_{wp}$ (%)             | 3.49           | 11.97  | 5.85          | 11.30  |
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