Spin-induced symmetry breaking in orbitally ordered \( \text{NiCr}_2\text{O}_4 \) and \( \text{CuCr}_2\text{O}_4 \)

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At room temperature, the normal oxide spinels \( \text{NiCr}_2\text{O}_4 \) and \( \text{CuCr}_2\text{O}_4 \) are tetragonally distorted and crystallize in the \( I4_1/amd \) space group due to cooperative Jahn-Teller ordering driven by the orbital degeneracy of tetrahedral \( \text{Ni}^{2+} \left( t_2^0 \right) \) and \( \text{Cu}^{2+} \left( t_2^0 \right) \). Upon cooling, these compounds undergo magnetic ordering transitions; interactions being somewhat frustrated for \( \text{NiCr}_2\text{O}_4 \) but not for \( \text{CuCr}_2\text{O}_4 \). We employ variable-temperature high-resolution synchrotron X-ray powder diffraction to establish that at the magnetic ordering temperatures there are further structural changes, which result in both compounds distorting to an orthorhombic structure consistent with the \( Fddd \) space group. \( \text{NiCr}_2\text{O}_4 \) exhibits additional distortion, likely within the same space group, at a yet-lower transition temperature of \( T = 30 \text{ K} \). The tetragonal to orthorhombic structural transition in these compounds appears to primarily involve changes in \( \text{NiO}_4 \) and \( \text{CuO}_4 \) tetrahedra.

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I. INTRODUCTION

Strong coupling between spin, lattice, and orbital degrees of freedom in functional transition metal oxide compounds results in rich behavior such as the tendency for cooperative Jahn-Teller\( ^{11} \) and spin-Peierls distortions\( ^{9} \). Such coupling between the different degrees of freedom enables multifunctionality as observed in multiferroics \( R\text{MnO}_3 (R = \text{late rare earth}) \).\( ^{34} \) In these systems, manipulation of one property can influence another, exemplified by the electric field control of magnetic polarization in \( \text{HoMnO}_3 \).\( ^{25} \) Seeking out such strong links between distinct degrees of freedom represents a powerful strategy in the search for new multifunctional systems, and affords unique opportunities for a deeper understanding of these interactions.\( ^{32} \)

One such frequently studied interaction is magnetocrystalline coupling in geometrically frustrated antiferromagnets,\( ^{39} \) where a structural distortion lifts the large ground state degeneracy allowing long range magnetic order.\( ^{10,11} \) However, frustration-driven magnetocrystalline coupling is not expected in the ferrimagnetic spinels with the formula \( A\text{Cr}_2\text{O}_4 \) where \( A \) is a magnetic cation. This is a consequence of the magnetic \( A-\text{O}-\text{Cr}^{3+} \) interaction usually being collectively stronger than the frustrated interactions between the \( \text{Cr}^{3+} \). Furthermore, Jahn-Teller activity of the \( A \) site cation can cause tetragonal distortions that should further alleviate frustration in the \( \text{Cr}^{3+} \) sublattice. Nonetheless, previous structural, thermodynamic, and magnetic studies of \( \text{NiCr}_2\text{O}_4 \)\( ^{12,13} \) report a coupled magnetic and structural transition, and infrared spectroscopy measurements suggest concurrent magnetic and structural transitions in \( \text{CuCr}_2\text{O}_4 \).\( ^{14} \)

Structural transitions at the magnetic ordering temperatures have been observed in numerous transition metal oxide antiferromagnets such as \( \text{Cr}_2\text{O}_4 \),\( ^{15} \) \( \text{MnO} \), \( ^{16,17} \) \( \text{FeO} \), \( ^{16,17} \) \( \text{CoO} \), \( ^{16,17} \) and \( \text{NiO} \).\( ^{16,17} \) Cubic to rhombohedral transformations are found in \( \text{MnO}, \text{FeO}, \) and \( \text{NiO} \), while \( \text{CoO} \) undergoes a cubic to tetragonal transition. The rhombohedral lattice constants of \( \text{Cr}_2\text{O}_4 \) change at its antiferromagnetic ordering temperature. Two mechanisms of magnetostructural coupling have been suggested in these compounds based on neutron and X-ray diffraction measurements. Li has suggested that magnetostructural coupling in \( \text{NiO}, \text{MnO}, \text{CoO}, \) and \( \text{FeO} \) is driven by magnetostriction\( ^{15} \) where anisotropy arises from the selection of a magnetic ordering axis and drives the magneto-crystalline deformation. Smart and Greenwald alternatively proposed that distortions in the above binary oxides are caused by exchange striction, which is the displacement of interacting ions to strengthen exchange coupling thus modifying the underlying lattice.\( ^{19} \)

The relations between crystal distortions and exchange interactions are challenging to identify. For example, it is difficult to find a unique solution to certain magnetic scattering patterns\( ^{17,19} \).

Here, we determine the low temperature structures of \( \text{NiCr}_2\text{O}_4 \) and \( \text{CuCr}_2\text{O}_4 \) across the transitions associated with magnetic ordering using high resolution synchrotron powder X-ray diffraction. These compounds are fully ordered and stoichiometric normal cubic spinels with the space group \( Fd\beta m \) at temperatures above \( 320 \text{ K} \)\( ^{20,21} \) for \( \text{NiCr}_2\text{O}_4 \) and \( 853 \text{ K} \)\( ^{21,22} \) for \( \text{CuCr}_2\text{O}_4 \).\( ^{23} \) \( \text{Cr}^{3+} \) \( 3d^3 \) preferentially populates the octahedral sites because of the strong crystal field stabilization of the half occupied non-degenerate \( t_2g \) states and empty \( e_g \) states, while \( \text{Ni}^{2+} \) \( 3d^8 \) and \( \text{Cu}^{2+} \) \( 3d^9 \) are found on the tetrahedral sites.\( ^{14} \) The tetrahedral crystal field around \( \text{Ni}^{2+} \) \( 3d^8 \) and \( \text{Cu}^{2+} \) \( 3d^9 \) in the cubic phase results in fully occupied low energy \( e \) levels and triply degenerate \( t_2 \) levels rendering...
this structure potentially unstable. A cooperative lattice distortion – from cubic to tetragonal symmetry – lifts the orbital degeneracy in NiCr₂O₄ at 320 K [12,24,25].

Group Prince postulated that the noncentrosymmetric space group $I4_2d$ was a better structural fit than $I4_1/amd$. More recently, Dollase and O’Neill showed no statistically significant advantage to using the $I4_1/amd$ model over the centrosymmetric structure $I4_1/amd$. In the tetragonal structure of CuCr₂O₄, CuO₄ tetrahedra are compressed toward a square planar configuration thus lifting orbital degeneracy. The tetragonal structure of NiCr₂O₄ is known to crystallize in the space group $I4_1/amd$ with elongated NiO₄ tetrahedra. Previous work has also shown further distortion of tetragonal NiCr₂O₄ to an orthorhombic phase, which occurs at the magnetic transition temperature $T_N = 60$ K and has been observed in thermodynamic, X-ray diffraction, and magnetic studies.

Noncollinear ferrimagnetism that is not described by the Néel model is observed in both NiCr₂O₄ and CuCr₂O₄. Tomiyasu and Kagomiya describe a magnetic structure comprising of a ferrimagnetic component and an antiferromagnetic component in NiCr₂O₄. These authors used neutron scattering to show that the antiferromagnetic component orders at $T = 31$ K while the ferrimagnetic component orders at $T = 74$ K. A saturation magnetization moment of $0.3 \mu_B$ per formula unit has been reported for NiCr₂O₄. Neutron scattering studies on CuCr₂O₄ suggest a magnetic structure comprising of two canted Cr³⁺ sublattices with a net moment, and Cu²⁺ sublattice that couples antiferromagnetically to the net moment of the Cr³⁺ sublattices below $T_N = 135$ K. The magnetic moment of CuCr₂O₄ in this structure is $0.5 \mu_B$ per formula unit.

Given this prior evidence of concurrent magnetic and structural transitions in NiCr₂O₄ and CuCr₂O₄, there is a clear need for further exploration of these compounds. In this study, we employ high-resolution temperature-dependent powder X-ray diffraction, magnetic susceptibility, and heat capacity measurements to investigate magnetostructural coupling in NiCr₂O₄ and CuCr₂O₄. This is the first observation by X-ray powder diffraction of the tetragonal to orthorhombic structural distortion of CuCr₂O₄ at the ferrimagnetic ordering temperature. We also reveal for the first time X-ray diffraction evidence of further symmetry lowering in orthorhombic NiCr₂O₄ at the second magnetic transition $T = 30$ K. These results affirm strong magnetostructural coupling can also occur in spinels that are not expected to be frustrated. This new understanding of coupling between spin and lattice degrees of freedom in NiCr₂O₄ and CuCr₂O₄ suggests that these compounds are promising magnetoelectrics, and provides considerable motivation for further investigation of magnetostructural coupling in related spinel compounds.

II. METHODS

NiCr₂O₄ was prepared by dissolving stoichiometric amounts of Ni(NO₃)₂·6H₂O and Cr(NO₃)₃·9H₂O in deionized water. The nitrate solution was heated to evaporate the solvent, leaving a precipitate that was ground and calcined at 1000°C for 24 hours. A dark green powder of NiCr₂O₄ was obtained. Black shiny single crystals of CuCr₂O₄ were prepared following the flux method described by Ye et al. K₂Cr₂O₇ was used as a reactive flux that partly decomposes to Cr₂O₃ at ~ 700 K. Ye et al. propose that the reduction of Cr⁶⁺ into Cr³⁺ plays an important role in stabilizing the oxidation state of Cr³⁺ during the synthesis of CuCr₂O₄. K₂Cr₂O₇ acts both as a flux and a source of Cr₂O₃. A 20 g mixture of 17.8% mass CuO (Sigma Aldrich 98%) and 82.2% mass K₂Cr₂O₇ (Fisher 99%) with 0.2 g Bi₂O₃ as a second flux was prepared. The mixture was ground using an agate mortar and pestle, placed in a covered platinum crucible, heated to 800°C with a ramp of 100°C/h, held for 24 h, and slowly cooled to ambient temperature at 15°C/h.

After the reaction, black crystals of CuCr₂O₄ were collected and washed in boiling water. It should be noted that more conventional solid state preparation yielded samples with significantly broader linewidths in the synchrotron X-ray diffraction profile, potentially obscuring the ability to fully characterize the low-temperature structure.

High-resolution ($\Delta d/d \approx 10^{-4}$) synchrotron X-ray powder diffraction data were recorded on beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory. Scans were collected using a 2Θ step size of 0.001° with $\lambda = 0.413441$ Å for NiCr₂O₄ and $\lambda = 0.41326$ Å for CuCr₂O₄ in a closed-flow helium cryostat over the temperature range 7 K to 300 K. The sample was in direct contact with the helium exchange gas during data collection, and was spun at 5 Hz to improve powder averaging. Structural models of NiCr₂O₄ and CuCr₂O₄ were fit to the diffraction data using the Rietveld refinement method as implemented in the EXPGUI/GSAS software program. Crystal structures were visualized using the program VESTA. Both samples prepared here had a small, second impurity phase that was also quantitatively fit using the Rietveld method. The NiCr₂O₄ sample was determined to have a 0.5 wt.-% of Cr₂O₃, and the CuCr₂O₄ sample a 1.1 wt.-% CuO impurity.

Magnetic susceptibility measurements on powder samples were performed using a Quantum Design MPMS 5XL superconducting quantum interference device (SQUID) magnetometer. Heat capacity measurements were collected on pellets of 50% mass silver and 50% mass sample using a Quantum Design Physical Properties Measurement System. The pellets were prepared by grinding equal amounts of silver and sample in an agate mortar and pestle followed by pressing at ∼ 330 MPa. Apiezon N grease was used to enhance thermal coupling between the sample and the stage. The heat capacity of the Apiezon N grease and silver were...
FIG. 1: (Color online) Magnetic measurements of the spinel NiCr$_2$O$_4$. (a) Zero field cooled and field cooled temperature dependent magnetic susceptibility measured under a 1000 Oe DC field show three anomalies at 310 K, 65 K and 30 K. NiCr$_2$O$_4$ displays little change in the magnetism at 310 K, and is seen to order ferrimagnetically at 65 K, with an additional change in the magnetic structure at 30 K. (b) The isothermal field dependent magnetization measured above the magnetic ordering temperature shows paramagnetic behavior. At 2 K, the coercive field and saturation magnetization are significantly larger than what is observed at 45 K.

III. RESULTS AND DISCUSSION

A. Magnetism

Three magnetic transitions are observed in the temperature dependent magnetic susceptibility of NiCr$_2$O$_4$ (Fig. 1). A high temperature transition occurs at 310 K where cooperative Jahn-Teller distortions lift the orbital degeneracy in NiCr$_2$O$_4$ and lower the structural symmetry from cubic ($Fd\overline{3}m$) to tetragonal ($I4_{1}/amd$) [Fig. 1(a)]. Weak, compensated magnetic interactions occur at 310 K, as illustrated by the scaled inverse susceptibility of NiCr$_2$O$_4$ (Fig. 2). The scaling is carried out by recasting the Curie-Weiss equation using:

$$\frac{C}{\chi} + \text{sgn}(\Theta_{CW}) = \frac{T}{|\Theta_{CW}|}$$

(1)

The linear dependence of the magnetization on the applied field at 200 K [Fig. 1(b)] suggests that NiCr$_2$O$_4$ is mainly paramagnetic down to 65 K where there is a transition to a ferrimagnetic state [Fig. 1(a)]. The normalized inverse magnetic susceptibility trace shows the development of strong uncompensated magnetic correlations at 65 K (Fig. 2). A small coercive field and saturation magnetization is observed in the field dependent magnetization of NiCr$_2$O$_4$ at 45 K [Fig. 1(b)] in agreement with the onset of ferrimagnetic order. Tomiyasu and Kagomiya attribute the magnetic transition at 65 K in NiCr$_2$O$_4$ to the ordering of the longitudinal ferrimagnetic component of NiCr$_2$O$_4$ [30]. At 30 K, another anomaly is observed in both zero field cooled (ZFC) and field cooled (FC) measurements of the temperature dependent magnetic susceptibility [Fig. 1(a)] as well as in the scaled inverse susceptibility (Fig. 2) of NiCr$_2$O$_4$. Below 30 K, an increase in the coercive field and the saturation magnetization of NiCr$_2$O$_4$ is observed [Fig. 1(b)]. Previous neutron diffraction measurements of NiCr$_2$O$_4$ attribute this anomaly to the ordering of the antiferromagnetic component of NiCr$_2$O$_4$ [30].

The temperature dependent magnetic susceptibility of CuCr$_2$O$_4$ shows a rapid increase at 130 K where there is a paramagnetic to ferrimagnetic transition [Fig. 3(a)]. The ZFC susceptibility exhibits a reduced low temperature saturation value when compared to the FC susceptibility data illustrating domain behavior. A linear dependence of magnetization with applied field occurs before the onset of magnetic order while a magnetization trace with a coercive field of 380 Oe and a saturation magnetiza-
FIG. 3: (Color online) Magnetic measurements of the spinel CuCr$_2$O$_4$. (a) Magnetic susceptibility as a function of temperature under a 1000 Oe DC field shows an increase in susceptibility at the magnetic ordering temperature $\approx 130$ K in both zero field cooled and field cooled measurements. This is a paramagnetic to ferrimagnetic transition. (b) Isothermal field dependent magnetization measured above (200 K) and below (2 K) the magnetic ordering temperature.

The Curie-Weiss (CW) equation $\chi = C/(T - \Theta_{CW})$ is applied to paramagnetic regimes of NiCr$_2$O$_4$ and CuCr$_2$O$_4$ yielding an effective moment ($\mu_{eff}$) of 6.53 $\mu_B$ per formula unit for NiCr$_2$O$_4$ and 4.27 $\mu_B$ per formula unit for CuCr$_2$O$_4$. The expected $\mu_{eff}$ of NiCr$_2$O$_4$ is 6.16 $\mu_B$ per formula unit of NiCr$_2$O$_4$. This value is slightly smaller that the experimentally determined value of 6.53 $\mu_B$ per formula unit obtained from fitting the paramagnetic regime to the Curie-Weiss model, implying a small orbital contribution to the measured moment. The expected $\mu_{eff}$ of 5.74 $\mu_B$ per formula unit of CuCr$_2$O$_4$ is much larger than the experimental value suggesting the likely presence of magnetic correlations in the paramagnetic regime. The Weiss temperature ($\Theta_{CW}$) of NiCr$_2$O$_4$ is $-487$ K while that of CuCr$_2$O$_4$ is $-147$ K. The frustration index (|$\Theta_{CW}/N$) of NiCr$_2$O$_4$ is about 7.8 and that of CuCr$_2$O$_4$ is 1.1 indicating that NiCr$_2$O$_4$ is the more frustrated compound. The negative sign of $\Theta_{CW}$ coupled with the low saturation magnetization observed in isothermal field dependent measurements is consistent with noncollinear ferrimagnetic ordering in NiCr$_2$O$_4$ and CuCr$_2$O$_4$.

The magnetic transitions of CuCr$_2$O$_4$ and NiCr$_2$O$_4$ are strongly coupled to the lattice. All magnetic changes in NiCr$_2$O$_4$ are accompanied by structural transitions. The known Jahn-Teller cubic to tetragonal structural distortion in NiCr$_2$O$_4$ at 310 K causes a small change in the temperature dependent magnetization [Fig. 1(a)]. Ishibashi and Yasumi reported further distortion from tetragonal to orthorhombic symmetry at the onset of ferrimagnetic order ($T_N = 65$ K). We observe this tetragonal to orthorhombic distortion occurring concurrently with the onset of ferrimagnetic order in NiCr$_2$O$_4$ in Fig. 4. A low temperature anomaly at $T = 30$ K, has been observed in magnetic susceptibility and heat capacity measurements of NiCr$_2$O$_4$, however, there is no prior report of a concurrent structural distortion. In the current study, using high-resolution X-ray powder diffraction, we find evidence for a structural distortion at $T = 30$ K, as described in detail in a later section. Similarly, an orthorhombic distortion of the already Jahn-Teller distorted tetragonal CuCr$_2$O$_4$ occurs concurrently with ferrimagnetic ordering at 130 K (Fig. 5). This transition in CuCr$_2$O$_4$, not previously noted in structural or diffraction studies, is observed here using variable-
temperature high-resolution synchrotron X-ray powder diffraction performed on a sample of crushed single-crystals.

B. Crystal structure

The ambient temperature structure of both compounds can be indexed in the tetragonal centrosymmetric space group $I4/\text{amd}$. At 298 K, NiCr$_2$O$_4$ is still undergoing the Jahn-Teller driven cubic-tetragonal transition and better structural parameters of the tetragonal phase are obtained at 100 K. Structural parameters obtained from Rietveld refinement of 100 K diffraction data for NiCr$_2$O$_4$ and 298 K diffraction data for CuCr$_2$O$_4$ to the space group $I4/\text{amd}$ are shown in Table I and are in good agreement with previous reports.

Magnetic ordering drives further structural distortions in NiCr$_2$O$_4$ and CuCr$_2$O$_4$. The low symmetry structures of NiCr$_2$O$_4$ and CuCr$_2$O$_4$ are described by the orthorhombic space group $Fddd$. $Fddd$ is a maximal non-isomorphic subgroup of $I4/\text{amd}$ and is derived from the parent $Fd\bar{3}m$ by loss of all threefold rotation axes and part of the twofold screw axes. Rietveld refinement fits of 10 K diffraction data to the orthorhombic space group $Fddd$ for both NiCr$_2$O$_4$ and CuCr$_2$O$_4$ are shown in Fig. 6. Symmetry lowering in NiCr$_2$O$_4$ and CuCr$_2$O$_4$ is demonstrated by the splitting of certain high symmetry diffraction peaks as illustrated in Fig. 6(c) and (f). The current work is the first description of the orthorhombic $Fddd$ structure for CuCr$_2$O$_4$. In NiCr$_2$O$_4$, variable-temperature synchrotron X-ray diffraction measurements show additional structural changes below 30 K, in concurrence with anomalies in specific heat and susceptibility measurements of NiCr$_2$O$_4$ reported both here and previously in the literature. This low temperature structural change of NiCr$_2$O$_4$ is discussed in detail in a later subsection.

Changes in structural symmetry are reflected in the temperature dependence of lattice parameters. At 310 K there is a cubic to tetragonal transition in NiCr$_2$O$_4$ that splits the cubic $a$ lattice constant into tetragonal $a$ and $c$ lattice parameters [Fig. 7(a) and (b)]. Below 310 K, the tetragonal NiCr$_2$O$_4$ distortion grows, with an increasing $c$ and a decreasing $a$ lattice constant (plotted as $\sqrt{2}a$). Below 65 K, magnetic ordering occurs concurrently with
a transition to orthorhombic symmetry. The tetragonal
a lattice parameter of NiCr₂O₄ diverges into distinct or-
thorhombic a and b lattice constants [Fig. 7(b)]. At 30 K,
a slope change clearly visible in the a and c lattice param-
eters [Fig. 7] matches anomalies in other property mea-
surements as will be discussed later. CuCr₂O₄ is already
tetragonal at ambient temperature due to cooperative
Jahn-Teller ordering at 853 K. The tetragonal lattice con-
stants of CuCr₂O₄ 4
are observed in the cubic NiCr₂O₄ structure above 310 K
[Fig. 8(a) and (b)]. Orbital ordering results in a dis-
torted tetrahedron with a single Ni-O bond distance, but
two O-Ni-O angles [Fig. 8(a) and (b)] in the tetrago-
nal phase. Below 65 K, the orthorhombic structure pre-
serves a single Ni-O bond length, but splits the O-Ni-
O angles into three distinct O-Ni-O angles in the NiO₄
tetrahedra [Fig. 8(a) and (b)]. These distortions in Ni-
O bond lengths and O-Ni-O bond angles result in an
elongation of NiO₄ tetrahedra. At ambient temperature,
CuO₄ tetrahedra are already significantly distorted with
two different O-Cu-O angles and a single Cu-O bond dis-
tance. With decrease in temperature and the onset of the
orthorhombic structural transition, we note a decrease in
Cu-O bond lengths [Fig. 9(a)], an increase in the larger
O-Cu-O angle [Fig. 9(b)] and a decrease in the smaller
O-Cu-O angle [Fig. 9(c)]. The two smaller O-Cu-O angles
divide into two. The overall effect of these structural
changes is a flattening of the CuO₄ polyhedra toward a
square planar configuration. The differences in the dis-
tortion of the CuO₄ and NiO₄ tetrahedra are apparent in
the average low temperature structures of NiCr₂O₄ and
CuCr₂O₄ shown in Fig. 11.

Structural changes in NiCr₂O₄ and CuCr₂O₄ originate
from deformations of NiO₄ and CuO₄ polyhedra. In a
perfect tetrahedron, all bond lengths are equal and all
O-Cation-O angles are 109.5°. Ideal NiO₄ tetrahedra

| NiCr₂O₄       | CuCr₂O₄       |
|---------------|---------------|
| **Orthorhombic** | **Tetragonal** | **Orthorhombic** | **Tetragonal** |
| **T**          | 10 K          | 100 K            | 10 K          | 298 K          |
| **Space group**| Fddd          | I₄₁/amd          | Fddd          | I₄₁/amd          |
| **Setting**    | origin 2      | origin 2         | origin 2      | origin 2         |
| **Z**          | 8             | 4                | 8             | 4               |
| **a (Å)**      | 8.18139(5)    | 5.79029(2)       | 7.1271(2)     | 6.03277(1)       |
| **b (Å)**      | 8.16699(4)    | 5.79029(2)       | 8.53611(2)    | 6.03277(1)       |
| **c (Å)**      | 8.56786(4)    | 8.54639(4)       | 8.54357(2)    | 7.78128(1)       |
| **Vol/Z (Å³)** | 71.5601(6)    | 71.6346(4)       | 70.3098(3)    | 70.7986(2)       |
| **Ni/Cu**      | 8a (1/8,1/8,1/8) | 4a (0,1/4,3/8)  | 8a (1/8,1/8,1/8) | 4a (0,1/4,3/8) |
| **U_iso (10² Å²)** | 0.01(1)       | 0.019(1)         | 0.07(1)       | 0.29(1)         |
| **Cr**         | 16d (1/2,1/2,1/2) | 8d (0,0,0)      | 16d (1/2,1/2,1/2) | 8d (0,0,0)      |
| **U_iso (10² Å²)** | 0.01(1)       | 0.019(1)         | 0.07(1)       | 0.29(1)         |
| **O**          | 32h (x,y,z)   | 16h (0 ,y,z)    | 32h (x,y,z)   | 16h (0 ,y,z)    |
| **x**          | 0.2561(2)     | 0                | 0.2446(1)     | 0               |
| **y**          | 0.2589(2)     | 0.5152(2)       | 0.2675(2)     | 0.5364(1)       |
| **z**          | 0.2683(1)     | 0.2322(2)       | 0.2675(2)     | 0.2526(1)       |
| **U_iso (10² Å²)** | 0.03(2)       | 0.16(2)          | 0.06(2)       | 0.55(1)         |
| **χ²**         | 3.85          | 4.15             | 2.31          | 3.84            |
| **R_p (%)**    | 6.25          | 7.06             | 7.50          | 8.96            |
| **R_wpp (%)**  | 8.39          | 9.41             | 8.39          | 6.65            |

TABLE I: Structural parameters of NiCr₂O₄ and CuCr₂O₄ obtained from Rietveld refinement of high-resolution synchrotron X-ray diffraction data collected at temperatures above and below the orthorhombic distortion of both compounds.
FIG. 7: (Color online) Changes in lattice parameters as a function of temperature in NiCr$_2$O$_4$. (a) A cubic to tetragonal structural transition occurs at 310 K where the $a$ lattice constant of the cubic phase diverges into $a$ and $c$ lattice parameters of the tetragonal phase. The $a$ lattice constant of the tetragonal cell is multiplied by $\sqrt{2}$ to clearly follow trends in the lattice parameters of NiCr$_2$O$_4$. In the tetragonal phase, the $a$ parameter decreases (b) while $c$ increases (a) with decreasing temperature. At 65 K, a tetragonal to orthorhombic structural distortion occurs resulting in three distinct lattice constants as shown in (a) and (b). (c) Variation of the cell volume normalized by the number of formula units ($Z$) in each cell. A further structural distortion of orthorhombic NiCr$_2$O$_4$ occurs at 30 K where there is a slight discontinuity of the lattice parameters (a) and (b) and cell volume (c); this is highlighted by the dashed line at $T = 30$ K. In (a), (b) and (c) the error bars are smaller than the data symbols.

C. Heat capacity

There are several interesting features in the heat capacity of NiCr$_2$O$_4$ and CuCr$_2$O$_4$ that occur concurrently with magnetic and structural transformations in these compounds. Klemme and Miltenburg report three anomalies in the heat capacity of NiCr$_2$O$_4$ occurring at 310 K, 75 K, and 30 K. Our heat capacity measurements over the temperature range 3 K $\leq$ $T$ $\leq$ 200 K for NiCr$_2$O$_4$ show two anomalies at 65 K and 30 K [Fig. 12(a)]. The Jahn-Teller cubic-tetragonal structural distortion of NiCr$_2$O$_4$ causes the anomaly in heat capacity at 310 K reported by Klemme and Miltenburg. The transition into a ferrimagnetic ordered state [Fig. 12(a)] that occurs concurrently with a structural change [Fig. 12(b)] results in the change in entropy that we observe at 65 K and was reported by Klemme and Miltenburg to occur at $T = 75$ K. Klemme and Miltenburg also reported an additional anomaly in specific heat at 30 K; Ishibashi and Yasumi noted a change in

FIG. 8: (Color online) (a) The thermal evolution of lattice parameters of CuCr$_2$O$_4$ reveals a tetragonal $I4_1/amd$ to orthorhombic $Fddd$ structural transition at $\sim 130$ K. The tetragonal $a$ lattice parameter has been multiplied by $\sqrt{2}$ to match the low temperature $b$ and $c$ lattice values of the orthorhombic $Fddd$ cell. (b) Temperature dependence of the cell volume normalized by the number of formula units ($Z$) in each cell shows a steady decrease with temperature. In both (a) and (b), the error bars are smaller than the data symbols.

FIG. 9: (Color online) The variation in NiO$_4$ polyhedra as a function of temperature. (a) The Ni-O bond length remains relatively constant in all the structural phases (b) The single O-Ni-O angle of the cubic phase separates into a larger angle and a smaller angle in the tetragonal phase. Below the orthorhombic transition, there are three distinct O-Ni-O angles.
FIG. 10: (color online) Changes in the CuO$_4$ polyhedra as a function of temperature. (a) There is an overall decrease in the Cu-O bond distance, (b) an increase in the larger O-Cu-O angle, and (c) a decrease in the smaller O-Cu-O angle coupled with a splitting of this angle. These trends are obtained from Rietveld refinement of synchrotron X-ray diffraction data.

magnetic susceptibility at this temperature. We observe this anomaly in the heat capacity of NiCr$_2$O$_4$ at 30 K and attribute it to an additional change in the magnetic [Fig. 12(b)] and crystal structure [Fig. 4(b)] as will be discussed in section D of this paper.

There are two anomalies in the specific heat of CuCr$_2$O$_4$ at 130 K and 155 K [Fig. 12(c)]. The anomaly at 130 K is coincident with ferrimagnetic [Fig. 12(d)] and tetragonal-orthorhombic [Fig. 5(b)] phase transitions in the compound. The transition into the orthorhombic ferrimagnetic state in CuCr$_2$O$_4$ occurs through an intermediate step with signatures in Fisher heat capacity measurements at 155 K [Fig. 12(c)] and (d). Slight structural effects accompany this second transition as shown in Fig. 8(b) where there is a subtle inflection point of the evolution of cell volume with temperature. Further characterization of this intermediate change in the magnetism of CuCr$_2$O$_4$ at about 155 K requires careful investigation in future study.

D. 30 K magnetostructural transition of NiCr$_2$O$_4$

During the ferrimagnetic transition of NiCr$_2$O$_4$, a simultaneous cooperative crystal distortion from tetragonal to orthorhombic symmetry occurs as reported by Ishibashi and Yasumi. We observe this magnetostructural transition in NiCr$_2$O$_4$ at $T = 65$ K [Fig. 12(c)]. Magnetic susceptibility measurements by Ishibashi and Yasumi show yet another low temperature magnetic transition in NiCr$_2$O$_4$ at $T = 31$ K that was reported by Tomitasu and Kagomiya as corresponding to the ordering of the antiferromagnetic component of the magnetic structure of NiCr$_2$O$_4$. Klemme and Miltenburg also observed a change in entropy at this temperature, however, no changes of the average structure of NiCr$_2$O$_4$ have been observed at $T = 31$ K. Our measurements reveal similar anomalies in the magnetism and specific heat measurements of NiCr$_2$O$_4$ [Fig. 13(a)] at $T = 30$ K. Furthermore, we observe a slight change in average structure at

FIG. 11: (Color online) Low temperature (10 K) orthorhombic crystal structures of (a)NiCr$_2$O$_4$ and (b) CuCr$_2$O$_4$ projected down the [101] direction. Ni(grey) and Cu(red) are tetrahedrally coordinated by oxygen (orange). Chromium is shown in blue. The elongation of NiO$_4$ tetrahedra along with the compression of CuO$_4$ polyhedra is clearly seen in the low temperature average structures.

FIG. 12: (color online) (a) Entropy changes in NiCr$_2$O$_4$ and CuCr$_2$O$_4$ resulting from structural and magnetic transformations. (a) The heat capacity of NiCr$_2$O$_4$ shows two anomalies at 65 K and 30 K. (b) Fisher heat capacity of NiCr$_2$O$_4$ indicating release of magnetic entropy occurring at the same temperatures where changes in specific heat are observed. (c) CuCr$_2$O$_4$ also shows two transitions in the heat capacity at 155 K and 130 K. Concurrent with these changes in heat capacity of CuCr$_2$O$_4$ are variations in magnetic structure as illustrated by Fisher heat capacity shown in (d).
FIG. 13: (color online) Changes in magnetic order and heat capacity of NiCr$_2$O$_4$ at $T = 30$ K are accompanied by a structural change. (a) Zero field cooled and field cooled temperature dependent magnetic susceptibility measurements of NiCr$_2$O$_4$ show a change in magnetic order at $T = 30$ K. Concurrent with this transition in magnetism is a change in entropy indicated by the anomaly in heat capacity. The central panel tracks changes in intensity of the orthorhombic $080$ and $800$ reflections at $T = 30$ K illustrating that a structural change takes place at $T = 30$ K. (c) This structural change is also reflected in the temperature dependent lattice constants of NiCr$_2$O$_4$ which vary at this temperature.

IV. CONCLUSIONS

Structural changes occur concurrently with magnetic phase transitions in NiCr$_2$O$_4$ and CuCr$_2$O$_4$. We have resolved details of the crystal structure of the low temperature phase of NiCr$_2$O$_4$ and CuCr$_2$O$_4$ in the orthorhombic space group $Fddd$ and present the first structural description of orthorhombic CuCr$_2$O$_4$. We find that the magnetic transition at 30 K in NiCr$_2$O$_4$ is also accompanied by further, subtle structural anomaly. Pronounced elongation of NiO$_4$ tetrahedra, and compression of CuO$_4$ tetrahedra toward a square planar configuration drive the distortions into the orthorhombic phase in these compounds. As postulated by Smart and Greenwald, we suggest that multiple exchange coupling pathways in the distorted orthorhombic structure are likely to be the reason behind the strong magnetostructural coupling observed in these compounds. We anticipate that this study will inspire further investigation of such coupling in ferrimagnetic spinels.

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