Néel to Spin-Glass-like Phase Transition versus Dilution in Geometrically Frustrated \( \text{ZnCr}_{2-2x}\text{Ga}_{2x}\text{O}_4 \).

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\( \text{ZnCr}_{2}\text{O}_4 \) undergoes a first order spin-Peierls-like phase transition at 12.5 K from a cubic spin liquid phase to a tetragonal Néel state.\(^5\) Using powder diffraction and single crystal polarized neutron scattering, we determined the complex spin structure of the Néel phase. This phase consisted of several magnetic domains with different characteristic wave vectors. This indicates that the tetragonal phase of \( \text{ZnCr}_{2-2x}\text{Ga}_{2x}\text{O}_4 \) is very close to a critical point surrounded by many different Néel states. We have also studied, using elastic and inelastic neutron scattering techniques, the effect of nonmagnetic dilution on magnetic correlations in \( \text{ZnCr}_{2-2x}\text{Ga}_{2x}\text{O}_4 \) (\( x = 0.05 \) and 0.3). For \( x = 0.05 \), the magnetic correlations do not change qualitatively from those in the pure material, except that the phase transition becomes second order. For \( x = 0.3 \), the spin-spin correlations become short range. Interestingly, the spatial correlations of the frozen spins in the \( x = 0.3 \) material are the same as those of the fluctuating moments in the pure and the weakly diluted materials.

I. INTRODUCTION

There has been a long standing fascination in the physics community with placing antiferromagnetically coupled spins on lattices with triangular motifs.\(^2\)\(^,\)\(^3\)\ In two dimensions, one can consider the simple triangular lattice. When classical XY spins are placed on this lattice, it orders at zero temperature. For many years, the excitations above this ground state provided a playground for studying topological excitations. These chiral excitations destroy the ground state at finite temperatures and experimental investigations of these systems are still underway. One can increase the complexity of this problem by considering the case of the even less constrained system of corner sharing triangles, the kagome lattice.\(^4\)\(^,\)\(^8\)\(^,\)\(^9\)\(^,\)\(^10\)\(^,\)\(^11\) There have been many theoretical questions about the nature of the ground state\(^12\)\(^,\)\(^13\)\(^,\)\(^14\)\(^,\)\(^15\) even for classical spins on this lattice.\(^5\)\(^,\)\(^6\)\(^,\)\(^7\) Experimentally, good experimental realizations of this system have been hard to obtain. Recently, however, single crystals of Fe-jarosite that realize the kagome lattice with classical (\( S = 5/2 \)) spins were grown and detailed neutron scattering studies have been performed.\(^16\) More recently, \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) was found as a good model system for the quantum kagome antiferromagnet.\(^17\)\(^,\)\(^18\)\(^,\)\(^19\)\(^,\)\(^20\)\(^,\)\(^21\) Unfortunately, it turned out that there is 5-10% site switching of \( \text{Zn}^{2+} \) and \( \text{Cu}^{2+} \) ions,\(^21\) which obscures the quantum physics of the kagome antiferromagnet.

In three dimensions, when spins form a network of corner sharing tetrahedra, it leads to a macroscopically degenerate ground state for classical as well as quantum spins.\(^22\)\(^,\)\(^23\) Theoretically novel low temperature properties are expected to appear. For example, quantum spin liquid phases, fractional excitations, or non-Ginzburg-Landau phase transitions. Experimentally, spinels \( \text{AB}_2\text{O}_4 \) have attracted lots of attention because the B sublattice forms a network of corner-sharing tetrahedra. In the spinel, the B site cations are octahedrally coordinated by six oxygens and neighboring \( \text{BO}_6 \) octahedra share an edge. Thus, when the B site is occupied by a transition metal ion with \( t_{2g} \) electrons, the system can realize the simple and most frustrating Heisenberg spin Hamiltonian, \( H = J \sum \text{S}_i \cdot \text{S}_j \) with uniform nearest neighbor interactions.

\( \text{ACr}_2\text{O}_4 \) (\( A = \text{Zn}[1], \text{Cd}[25], \text{Hg}[26] \)) realizes the most frustrating Hamiltonian because the \( t_{2g} \) orbital of the \( \text{Cr}^{3+} (3d^3) \) is half filled and the nearest neighbor interactions due to the direct overlap of the neighboring \( t_{2g} \) orbitals are dominant and spatially uniform.\(^27\) In comparison, in the case of \( \text{AV}_2\text{O}_4 \) where the \( \text{V}^{2+} (3d^2) \) ion has an orbital degeneracy, a Jahn-Teller distortion can occur at low temperatures, which makes the vanadates effectively one-dimensional spin chain systems.\(^28\)\(^,\)\(^29\)\(^,\)\(^30\)\(^,\)\(^31\) Several novel discoveries have been made in \( \text{ACr}_2\text{O}_4 \). For instance, collective excitations of local antiferromagnetic hexagonal spins were found in the spin liquid phase of \( \text{ZnCr}_2\text{O}_4 \) that embody the zero-energy excitations amongst the degenerate ground states.\(^24\)\(^,\)\(^32\) Unfortunately, the lattice of \( \text{ACr}_2\text{O}_4 \) is not infinitely firm and it distorts at low temperatures to lift the magnetic frustration. The novel three-dimensional spin-Peierls phase transition, i.e., the lattice instability driven by magnetic interactions, occurs and drives the system into a Néel state. The lattice distortion can occur in different forms, depending on details of the crystal environment: tetragonal \( I4/m \) symmetry for \( \text{ZnCr}_2\text{O}_4 \),\(^33\) tetragonal \( I4_1/amd \) for \( \text{CdCr}_2\text{O}_4 \),\(^34\) and orthorhombic \( Fddd \) for \( \text{HgCr}_2\text{O}_4 \).\(^26\)\(^,\)\(^34\) When an external magnetic field is applied to the Néel state, the half-magnetization plateau states appear in \( \text{CdCr}_2\text{O}_4 \)\(^35\) and \( \text{HgCr}_2\text{O}_4 \)\(^26\)\(^,\)\(^34\) due to the field-induced lattice instability.\(^36\)\(^,\)\(^37\)

In this paper, we investigated the nature of the 3D spin-Peierls transition in the chromite by performing elastic and inelastic neutron scattering measure-
ments on ZnCr$_2$-$_{2x}$Ga$_{2x}$O$_4$ for $x=0$, 0.05, and 0.3. Our principal results are the following. For $x=0$, the Néel state has four characteristic wave vectors, $\mathbf{k} = (1, 0, 0)$, $(1, 1, 1)$, $(1, 0, 1)$ and $(1, 1, 0)$. The large size of the magnetic unit cell (64 Cr$^{3+}$ ions) has made it difficult to uniquely determine the spin structure of this system. We have determined the spin structure, employing powder diffraction, single crystal polarized neutron diffraction data and a systematic group theoretical approach. We find that the system is composed of three types of domains whose relative fractions vary from sample to sample. The dominant domain is a multik structure with $\mathbf{k} = (1, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$. This spin structure is coplanar and noncollinear with spins pointing along either the $a$ or $b$ axis with each tetrahedron having two pairs of antiparallel spins to have zero net moment. The $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ domain has a rather simple spin structure. The spinel lattice can be decomposed into alternating kagome and triangular layers when viewed along the $<111>$ direction. In this spin structure, the spins in the kagome layer order in the “$q=0$” configuration. The spins in the triangular layer point along the $<111>$ direction and are parallel within a layer. Spins in alternating layers are antiparallel. The $\mathbf{k} = (1, 0, 0)$ domain has a collinear spin structure with spins parallel to the $z$-axis, as in ZnV$_2$O$_4$. In each tetrahedron the net spin is zero.

The effect of site disorder on the magnetic correlations and phase transition in ZnCr$_2$O$_4$ by doping nonmagnetic Ga ions into Cr sites has been previously studied by Fiorani et al. using bulk property measurements and neutron powder diffractions in the ZnCr$_2$-$_{2x}$Ga$_{2x}$O$_4$ series. Fig. 2 shows the phase diagram that they have constructed from the measurement. Néel phase survives up to $x \sim 0.2$. For $0.2 < x < x_c$ with $1 - x_c = 0.390(3)$ being the percolation threshold for the corner-sharing tetrahedra, the system exhibits spin-glass-like properties in bulk susceptibility measurements. However, the nonlinear susceptibility of ZnCr$_2$-$_{2x}$Ga$_{2x}$O$_4$ ($x=0.2$) does not display the divergence expected of an ordinary spin glass. This suggests that the low temperature phase is not an ordinary spin glass.

Our data show that in the weakly diluted ZnCr$_2$-$_{2x}$Ga$_{2x}$O$_4$ ($x=0.05$) Néel ordering occurs with the same spin structure as the parent compound. However, the ordering now develops gradually and the phase transition becomes second order. The appearance of the Néel ordering and the cubic-to-tetragonal structural phase now also proceed in a second order manner. This consanguinity of the order of the structural phase transition and the appearance of long-range magnetic ordering supports our interpretation that the phase transition is magnetically driven.

For ZnCr$_2$-$_{2x}$Ga$_{2x}$O$_4$ ($x=0.3$), the magnetic long range order is replaced by static short range order even though the Cr concentration, $1 - x = 0.7$, is well above the percolation threshold, 0.390. Interestingly, the spatial correlations of the frozen spins in the spin-glass sample are the same as those of the fluctuating moments present in the pure and weakly diluted materials. Magnetic neutron scattering intensity, $I(Q)$, vanishes as $Q \to 0$ and has a broad peak at $Q_c \approx 1.5$ Å$^{-1}$ with full-width-of-half-maximum (FWHM) of $\kappa = 0.48(5)$ Å$^{-1}$. This indicates that fundamental spin degree of freedom in the corner-sharing tetrahedra involves an antiferromagnetic
hexagonal spin loop with zero net moment, which distinguish the geometrically frustrated magnet from an ordinary spin glass.

The structure of this paper is the following: In section II, we describe the experimental details of material synthesis and the neutron scattering techniques that were used. In Section III, we explain the determination of the spin structure of $\text{ZnCr}_2\text{O}_4$. In Section IV, we discuss inelastic neutron scattering data on the material and how the spin freezing and short range spin correlations in the diluted compound resemble those in other frustrated magnets. This paper concludes with a discussion and summary in section V.

II. EXPERIMENTAL DETAILS

Three 20 g powder samples of $\text{ZnCr}_2\text{O}_4$, one $\text{ZnCr}_{1.9}\text{Ga}_{0.1}\text{O}_4$ sample and $\text{ZnCr}_{1.4}\text{Ga}_{0.6}\text{O}_4$ sample were prepared by the standard solid state reaction method with stoichiometric amounts of $\text{Cr}_2\text{O}_3$, $\text{Ga}_2\text{O}_3$ and $\text{ZnO}$ in air. Neutron powder diffraction measurements performed on the samples at the National Institute of Standards and Technology (NIST) BTI diffractometer show that the samples were stoichiometric single phase spinels with the exception of one $\text{ZnCr}_2\text{O}_4$ sample (sample 2) which had a minority phase of 1% f.u. unreacted $\text{Cr}_2\text{O}_3$. The results of the structural refinement are summarized in Table I. The $\text{ZnCr}_2\text{O}_4$ samples will be denoted by sample 1, sample 2, and sample 3 in this paper.

A 0.1 g single crystal of $\text{ZnCr}_2\text{O}_4$ was grown by the chemical transport method and used for polarized neutron diffraction measurements at the NIST cold neutron triple-axis spectrometer, SPINS. Spectrometer configuration was guide-PG(002)-Be-Pol.-40'-Samp.-Flip.-Pol.-40'-PG(002)-Det. The sample was mounted such that the scattering plane were the (hk0) and (h0l) zones due to twinning. A vertical guide field was applied. The polarization efficiency was determined by measuring the scattering intensities of a nuclear (2,2,0) Bragg peak with the flipper on and off. Correction for the finite polarizing efficiency, 0.85(1), was made.

For inelastic neutron scattering measurements on powder samples, we utilized a multiplexing detection system of SPINS consisting of a flat analyzer and a position-sensitive detector. The details of the experimental setup are reported elsewhere. High angle backgrounds were measured by defocusing the analyzer while low angle backgrounds from air scattering were measured by extracting the sample from the cryostat. The absolute efficiency of the detection system was measured using incoherent elastic scattering from vanadium and nuclear Bragg peaks from the samples. The corresponding correction factor was applied to the background subtracted data to obtain normalized measurements of the magnetic scattering cross section.

III. ANTFERROMAGNETIC LONG-RANGE ORDER IN $\text{ZnCr}_2\text{O}_4$

A. Powder diffraction data

![FIG. 3: Powder diffraction data from $\text{ZnCr}_2\text{O}_4$ at 25 K and 2 K taken on the powder diffractometer BT 1 at NIST. The line through the data in (a) shows the Rietveld fit to the crystal structure of which parameters are shown in Table I. The line in (b) is the fit to the crystal structure and the magnetic structure that are explained in the text for sample 1. The upward pointing arrows with plain line are magnetic reflections which belong to $k = (\frac{2}{5}, \frac{1}{5}, 0)$. From the left, they are $(\frac{2}{5}, \frac{1}{5}, 0), (\frac{2}{5}, \frac{1}{5}, 1), (\frac{2}{5}, \frac{1}{5}, 0), (\frac{2}{5}, \frac{1}{5}, 1), (\frac{2}{5}, \frac{1}{5}, 0)$. The downward pointing plain arrows are from the $k = (1,0,0)$ family of magnetic reflections. From the left, they are $(\frac{1}{5}, \frac{1}{5}, 0), (\frac{1}{5}, \frac{3}{5}, 0), (\frac{3}{5}, \frac{1}{5}, 0)$, and $(\frac{3}{5}, \frac{1}{5}, 0)$. Figures (c) and (d) show the data and fits for samples (2) and (3) respectively, also discussed in the text.](image-url)
from the incomplete instrumental polarization efficiency of 0.85(1). For magnetic Bragg reflections that belong to the \( k = (\frac{1}{2}, \frac{1}{2}, 0) \) family, Eq. (1) becomes
\[
\begin{align*}
\sigma_{NSF} &= \sigma_M^c \\
\sigma_{SF} &= \sigma_{M\perp}^a + \sigma_{M\perp}^b.
\end{align*}
\] (2)

As shown in Fig. 4 (b), the magnetic \( (\frac{1}{2}, \frac{1}{2}, 0) \) Bragg reflection has dominantly SF intensity and a weak signal in the NSF channel. The weak NSF intensity is due to contamination from incomplete polarization. We investigated five magnetic Bragg reflections: \( (\frac{1}{2}, \frac{1}{2}, 0), (\frac{3}{2}, \frac{3}{2}, 0), (\frac{1}{2}, \frac{1}{2}, 0), (\frac{5}{2}, \frac{5}{2}, 0), \) and \( (\frac{9}{2}, \frac{9}{2}, 0) \). After the correction for the incomplete polarization, at these reflections only SF scattering is present. This means that the spins are in the ab-plane, \( \sigma_M^c = 0 \).

For the magnetic Bragg reflections that belong to \( k = (1, 0, \frac{1}{2}) \), there are NSF as well as SF scattering. The ratio of SF to NSF scattering intensity, \( \sigma_{SF}/\sigma_{NSF} \), is different at different Q, as shown in Fig. 5. Table I lists the ratios for three different reflections. The ratio, \( \sigma_{SF}/\sigma_{NSF} \), increases as \( l \) increases. This information places a strict restriction on any possible spin configuration for ZnCr₂O₄. For these reflections, Eq. (1) becomes
\[
\begin{align*}
\sigma_{NSF} &= \sigma_M^c \\
\sigma_{SF} &= \sigma_{M\perp}^a + \sigma_{M\perp}^b.
\end{align*}
\] (3)

Therefore, using \( \sigma_M^c = 0 \),
\[
\frac{\sigma_{SF}}{\sigma_{NSF}} = \left( 1 - \frac{h^2}{h^2 + l^2} \right) \frac{|F_M|^2}{|F_M|^2}.
\] (4)

The fact that the measured \( \sigma_{SF}/\sigma_{NSF} \) follows \( 1 - \frac{h^2}{h^2 + l^2} \) within the experimental accuracy indicates \( |F_M^a| = |F_M^b| \) for the \( k = (1, 0, \frac{1}{2}) \) reflections.
C. Group theoretical approach to determination of spin structure

We have employed a group theoretical approach developed by Izyumov et al.\textsuperscript{[50]} to determine the spin structure. The basic idea of the method is that any magnetic structure with a characteristic wave vector \( \mathbf{k} \) can be expanded in terms of basis functions, \( \psi^{k_L}_\lambda \), of irreducible representations of the spin space of the crystal \( G_k \) which is a subgroup of the crystal space group \( G \).

The star of a wave vector \( \mathbf{k} \), \{\( \mathbf{k} \)\}, is the set of nonequivalent vectors that can be obtained by acting on \( \mathbf{k} \) with an element of the crystal space group \( g \in G \). For instance, the star \( \{\mathbf{k}\} = \{(1,0,\frac{1}{2})\} \) has six arms: \( \mathbf{k}_L = (1,0,\frac{1}{2}), (1,0,\frac{1}{2}), (0,1,0), (\frac{1}{2},0,1), (\frac{1}{2},0,1) \), and \( (\frac{1}{2},0,1) \). Once \( S_{0j}^{(\mathbf{k})} \) is determined, all spins at other primitive cells, \( S_{nj} \), can be derived by\textsuperscript{[50]}

\[
S_{nj} = \sum_L \exp(i\mathbf{k} \cdot \mathbf{t}_n) S_{0j}^{k_L}.
\]

Here \( 0j \) represents a magnetic ion at site \( j \) in zeroth primitive cell. \( L \) runs over the arms of the star \( k_L \) and \( \lambda \) over irreducible representations of the star arm \( k_L \). The star of a wave vector \( \mathbf{k} \), \{\( \mathbf{k} \)\}, is the set of nonequivalent vectors that can be obtained by acting on \( \mathbf{k} \) with an element of the crystal space group \( g \in G \). For instance, the star \( \{\mathbf{k}\} = \{(1,0,\frac{1}{2})\} \) has six arms: \( \mathbf{k}_L = (1,0,\frac{1}{2}), (1,0,\frac{1}{2}), (0,1,0), (\frac{1}{2},0,1), (\frac{1}{2},0,1) \), and \( (\frac{1}{2},0,1) \). Once \( S_{0j}^{(\mathbf{k})} \) is determined, all spins at other primitive cells, \( S_{nj} \), can be derived by\textsuperscript{[50]}

\[
S_{nj} = \sum_L \exp(i\mathbf{k} \cdot \mathbf{t}_n) S_{0j}^{k_L}.
\]

where \( \mathbf{t}_n \) is the translation vector for the \( n \) cell from the zeroth primitive cell. How to obtain the basis functions of the irreducible representations, \( \psi^{k_L}_\lambda \) for a given \( G_k \) has been explained in a great detail in a book by Izyumov et al.\textsuperscript{[50]} and will not be repeated here. The basis functions \( \psi^{k_L}_\lambda \) for \( \mathbf{k} = (\frac{1}{2},\frac{1}{2},0) \) and \( \mathbf{k} = (1,0,\frac{1}{2}) \), are listed in Table II and III respectively. Note that \( \psi^{k_L}_\lambda \) are complex but their simple superposition at the two arms \( C_1 \psi^{k_1\tau}_\lambda + C_2 \psi^{k_2\tau}_\lambda \) with \( k_2 = -k_1 \) can generate a real function, provided that the coefficients \( C_1 \) and \( C_2 \) are appropriately selected. Table IV and V list such superpositions for \( \mathbf{k} = (\frac{1}{2},\frac{1}{2},0) \) and \( \mathbf{k} = (1,0,\frac{1}{2}) \), respectively. The superpositions of two irreducible representations \( C_1 \psi^{k_1\tau}_\lambda + C_2 \psi^{k_2\tau}_\lambda \) do not yield nonzero spins for all 16 magnetic ions in a chemical unit cell. Instead the superposition yields four nonzero spins for \( \mathbf{k} = (\frac{1}{2},\frac{1}{2},0) \)

\[
\text{and eight nonzero spins for } \mathbf{k} = (1,0,\frac{1}{2}) \text{ in a chemical unit cell. This means that to put all } 16 \text{ nonzero spins into a chemical unit cell we have to consider at least four of the } C_1 \psi^{k_1\tau}_\lambda + C_2 \psi^{k_2\tau}_\lambda \text{ listed in Table III for } \mathbf{k} = (\frac{1}{2},\frac{1}{2},0) \text{ and at least two of } C_1 \psi^{k_1\tau}_\lambda + C_2 \psi^{k_2\tau}_\lambda \text{ listed in Table IV for } \mathbf{k} = (1,0,\frac{1}{2}) \text{. Obviously the number of such combinations is very large. To narrow down the possible spin structure, we used the constraints that were obtained from polarized neutron diffraction data: (1) spins are in the ab-plane, } S_c = 0, \text{ and (2) } |F_M^0| = |F_M^1| \text{ for the } (1,0,\frac{1}{2}) \text{ family reflections. We also assumed that (3) all spins have the same magnitude and that (4) all tetrahedra have zero net spin.}

Since for this domain, there are two characteristic wave vectors involved in the Néel state of ZnCr\(_2\)O\(_4\), we rewrite Eq. (5) to separate \( S_{0j}^{(\mathbf{k})} \) into two components;

\[
S_{0j}^{(\mathbf{k})} = \sum_L S_{0j}^{k_L} = \sum_L \sum_\lambda C^{k_L}_\lambda \psi^{k_L}_\lambda.
\]

Note that \( S_{0j}^{(1,0,\frac{1}{2})} \) contribute only to the \( \mathbf{k} = (1,0,\frac{1}{2}) \) family reflections and \( S_{0j}^{(\frac{1}{2},\frac{1}{2},0)} \) only to the \( \mathbf{k} = (\frac{1}{2},\frac{1}{2},0) \) reflections. Therefore we can obtain the two components separately.

First, let us consider the \( \mathbf{k} = (1,0,\frac{1}{2}) \) reflections. We examined all possible combinations of the superpositions listed in Table V and found 24 different spin configurations which can be divided into three categories shown in Fig. 5. Fig. 6 (a) shows a non-collinear spin configuration in which spins are along either a-axis or b-axis, Fig. 6 (b) shows a non-collinear spin configuration with spins along \((1,1,0)\) or \((1,1,0)\), and Fig. 6 (c) shows a collinear spin configuration along \((1,1,0)\). A collinear spin configuration along a-axis or b-axis is ruled out by the constraint \(|F_M^0| = |F_M^1|\).

Fig. 8 shows four prototypes of \( \mathbf{k} = (\frac{1}{2},\frac{1}{2},0) \) spin configurations in which all tetrahedra satisfy the antiferromagnetic constraint to have zero net moment: (100) type collinear and noncollinear spin configurations and (110) type collinear and noncollinear spin configurations.

Now, it is possible that ZnCr\(_2\)O\(_4\) has two magnetic domains: one with \( \mathbf{k} = (1,0,\frac{1}{2}) \) and the other with \( \mathbf{k} = (\frac{1}{2},\frac{1}{2},0) \). However, to explain the neutron powder diffraction data, the population of the two domains as well as the ordered moment have to be exactly the
same for both domains. Furthermore, another spinel 
ZnFe$_2$O$_4$ also magnetically orders at low temperatures 
and the Néel state has only a single characteristic wave 
vector $\mathbf{k} = (1,0,\frac{1}{2})$. We believe it is more likely 
that the two characteristic wavevectors participate in the 
ordering of all the spins in ZnCr$_2$O$_4$. Then, the resulting 
spin structure would be a summation of $S'(1,0,\frac{1}{2})$ and 
$S'(\frac{1}{2},\frac{1}{2},0)$. All Cr$^{3+}$ ions are equivalent in this 
spinel crystal structure and are expected to have the same 
magnitude, indicating that $S'(1,0,\frac{1}{2})$ and $S'(\frac{1}{2},\frac{1}{2},0)$ have 
to be collinear and orthogonal to each other. Among 
the spin structures shown in Fig. 6 and 7, the only possibility 
would be the combination of $S'(1,0,\frac{1}{2})$ shown in Fig. 
6 (c) and $S'(\frac{1}{2},\frac{1}{2},0)$ shown in Fig. 7 (a). Fig. 8 shows 
the resulting coplanar and noncollinear spin structure, in 
which each tetrahedron has two pairs of antiparallel spins 
and have zero net moment.

For the $\mathbf{k} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ domain, there are many possible spin 
structures. From Figure 3 (b)-(d), we see that the intensities of the $\mathbf{k} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ reflections relative to other 
propagation vectors varies from sample to sample. These 
reflections are strongest for sample 1 shown in Figure 
3(b) and it is only for this sample that it is possible to 
distinguish between various models for the spin structure 
through goodness of fit. Thus, our discussion will be 
limited to sample 1.

The basis vectors are given table VI. As the transition 
is first order, multiple propagation vectors can contribute 
to the ordering. Many can be ruled out on physical grounds, 
however, a large number of possibilities remain. If one visualizes the B sublattice of the spinel 
structure along the $<111>$ direction, one can decompose it 
into alternating triangular and kagome layers. The $\gamma_1$ 
configuration, has no spins in the triangular layer and the 
"q=0" spin configuration in the kagome layer. The $\gamma_2$ 
configuration has spins only in the triangular layer 
coupled antiferromagnetically. The $\tau_3$ configuration 
is ferromagnetic in the kagome plane. The $\tau_6$ configuration 
allows for spins in the triangular layer to lie within that
plane at an arbitrary angle. We also considered linear combinations of these configurations.

In Table VII, we show the relative goodness of fits for the various spin models. Overall, we found that the model most consistent with our data was one with the "\(q=0\)" configuration in the kagome layer and an antiferromagnetic configuration within the triangular layer (see Fig. 9). Though the difference in the values of \(\chi^2\) is slight, if we examine a nuclear and a magnetic peak for goodness of fit for two different configurations, \(\tau_1 + \tau_2\) and \(\tau_1 + \tau_2 + \tau_3\) models, we can see that there is a real improvement in the fit for the \(\tau_1 + \tau_2\) spin model shown in Fig. 9 (see Fig. 10 and Table VII).

D. Summary

We have solved the magnetic structure of ZnCr\(_2\)O\(_4\). We have examined single crystals and three polycrystalline samples. From this, we have found that the system has different domains formed from different k-vectors. The relative phase fractions vary from sample to sample (see Table IX). The \(k = (1,0,0)\) is the same collinear structure as that of ZnV\(_2\)O\(_4\). The \(k = (1,0,\frac{1}{2})\) and \(bfk = (0,\frac{1}{2},0)\) domain has the in plane structure found in Fig. 8. The structure of the \(k = (\frac{1}{2},\frac{1}{2},\frac{1}{2})\) domain is found in Fig. 9. Since the antiferromagnetic transition is first order, multiple characteristic wave-vectors are allowed unlike in the usual case of second order magnetic transitions. This multiplicity of domains with different characteristic wave vectors suggests that even the ordered state of this frustrated magnet is degenerate.

IV. MAGNETIC CORRELATIONS IN

\(ZnCr_{2-2x}Ga_{2x}O_4\)

In this section, we study how magnetic correlations change with nonmagnetic doping.
A. First order transition to Néel state in ZnCr$_2$O$_4$

For completeness, we start with the phase transition in pure ZnCr$_2$O$_4$. Fig. 10 shows that in the pure ZnCr$_2$O$_4$ long range antiferromagnetic order (squares in frame (b)) and the local spin resonance (frame (a)) appear simultaneously in a spectacular first order phase transition. It also shows that the magnetic order is accompanied by a cubic to tetragonal lattice distortion (circles in frame (b)). The tetragonal distortion lifts some of the degeneracy due to geometrical frustration and allows the system to order magnetically. Furthermore the ordered state pushes spectral weight in the energy spectrum up to the local spin resonance at $\hbar \omega \approx 4.5$ meV. It is unusual that a long range ordered phase can support a local spin resonance.

The weak nonmagnetic doping in ZnCr$_{1.9}$Ga$_{0.1}$O$_4$ does not change the nature of the low $T$ phase. As shown in Fig. 11, below $T_N \approx 12.5$ K magnetic long range order (squares in Fig. 11 (b)), tetragonal distortion (circles in Fig. 11 (b)) occur along with the appearance of the local spin resonance at $\hbar \omega \approx 4.5$ meV (Fig. 11 (a)). Magnetic peaks in the doped material are the same as those in ZnCr$_2$O$_4$, which indicates that 5% doping of nonmagnetic Ga$^{3+}$ ions into Cr sites does not change the spin structure in the ordered phase. However, the three features appear gradually in a second order fashion, which is in contrast with the first order phase transition in the pure ZnCr$_2$O$_4$ shown in Fig. 10. Fig. 11 (c) shows that as soon as the static moment develops FWHM of magnetic peaks becomes $Q$-resolution limited. This indicates the static correlations are long range no matter how small the static moment is. We conclude that the magnetic ordering in the weakly doped material immediately develops in the entire material rather than in small magnetic clusters, growing in size grows as $T$ decreases.

B. Second order transition to Néel state in ZnCr$_{1.9}$Ga$_{0.1}$O$_4$

The weak nonmagnetic doping in ZnCr$_{1.9}$Ga$_{0.1}$O$_4$ does not change the nature of the low $T$ phase. As shown in Fig. 11, below $T_N \approx 12.5$ K magnetic long range order (squares in Fig. 11 (b)), tetragonal distortion (circles in Fig. 11 (b)) occur along with the appearance of the local spin resonance at $\hbar \omega \approx 4.5$ meV (Fig. 11 (a)). Magnetic peaks in the doped material are the same as those in ZnCr$_2$O$_4$, which indicates that 5% doping of nonmagnetic Ga$^{3+}$ ions into Cr sites does not change the spin structure in the ordered phase. However, the three features appear gradually in a second order fashion, which is in contrast with the first order phase transition in the pure ZnCr$_2$O$_4$ shown in Fig. 10. Fig. 11 (c) shows that as soon as the static moment develops FWHM of magnetic peaks becomes $Q$-resolution limited. This indicates the static correlations are long range no matter how small the static moment is. We conclude that the magnetic ordering in the weakly doped material immediately develops in the entire material rather than in small magnetic clusters, growing in size grows as $T$ decreases.

Fig. 11 (a) shows that the local spin resonance and the low energy cooperative paramagnetic spin fluctuations coexist over the temperature range, $10$ K $\leq T \leq T_N \approx 12.5$ K (also see Fig. 12 (b)). For comparison, in the pure ZnCr$_2$O$_4$ the Néel phase has only the linear spin waves below the local spin resonance (see Fig. 10 (a)). To quantitatively study how the dynamic spin fluctuations in the weakly doped system evolve with $T$, we have fit the of $\tilde{I}(Q=1.5$ Å$^{-1}, \hbar \omega)$ in Fig. 11 (a) to two

FIG. 11: Contour map of inelastic neutron scattering for $Q = 1.5$ Å$^{-1}$. (b) $T$-dependence of magnetic Bragg scattering from a powder (squares), $\sigma_m = \left(\frac{v_m}{2\pi}\right)^3 \int \tilde{I}(Q,\omega)4\pi Q^2 dQd\omega$ where $v_m$ is the volume per Cr$^{3+}$ ion, and of lattice strain along a and c (circles) measured by single crystal neutron diffraction. The figure is reproduced from Ref. [1].

FIG. 10: The peak to the left is the $k = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ magnetic reflection. The peak to the right is the nuclear $(1, 1, 1)$ peak for comparison. (a) the fit to the spin configuration formed from a linear combination of $\tau_1$ and $\tau_2$. (b) fit to the configuration formed formed from a linear combination of $\tau_1, \tau_2$, and $\tau_3$. A. First order transition to Néel state in ZnCr$_2$O$_4$
FIG. 12: Contour maps of inelastic neutron scattering measured at $Q = 1.5 \AA^{-1}$ as a function of energy transfer $\hbar \omega$ and $T$. (a) $T$-dependence of the ordered moment (filled squares) and of crystal strains (open and filled circles) obtained by Rietveld analysis neutron powder diffraction data taken at BT1, NIST at various $T$s using GSAS. (c) $T$-dependence of full-width-of-Half-Maximum (FWHM) of the magnetic $(1/2,1/2,2)$ Bragg peak (squares). The line is instrumental angular resolution.

simple non-resonant response functions, each with single relaxation rate: one centered at $\hbar \omega = 0$ with a relaxation rate $\Gamma_1$ and the other centered at $\hbar \omega_0 \approx 4.5$ meV with a relaxation rate $\Gamma$.  

$$\tilde{I}(\hbar \omega) = \frac{\tilde{I}_1 \cdot (\frac{1}{\hbar \omega})^2}{(\hbar \omega)^2 + (\frac{1}{\hbar \omega})^2} + \frac{\tilde{I}_0 \cdot (\frac{1}{\hbar \omega})^2}{(\hbar \omega - \hbar \omega_0)^2 + (\frac{1}{\hbar \omega})^2}. \quad (8)$$

The first term is to account for the quasi-elastic scattering that exists at $T > 10$ K. Since we did not have data above 30 K, it is difficult to extract meaningful information on the low energy excitations due to cooperative paramagnetism. Here we focus on the local spin resonance. Fig. 12 (d) - (f) show the results of the fits. The peak position, $\hbar \omega \approx 12.5$ meV, (Fig. 12 (e)) is $T$-independent below $T_N$ within experimental accuracy. The relaxation rate of the local resonance decreases as $T$ decease to $\Gamma = 1.4(1)$ meV at 1.4 K. For comparison, in pure ZnCr$_2$O$_4$ $\Gamma = 1.5(1)$ meV for all $T < T_N$. The strength of the local resonance, $\tilde{I}_0$ (Fig. 12 (d)), develops as proportional to the staggered magnetization, $< M >$, shown is Fig. 11 (b). This suggests that the static spin component is necessary to support the local spin resonance.

Fig. 13 shows the spatial correlations of the fluctuating moments with different energies. The low energy lying excitations at 12 K (squares) and the local resonance at 1.7 K (filled circles) and 12 K (open circles) have almost identical $Q$-dependence with a Half Width at Half Maximum $\kappa = 0.50(5) \AA^{-1} = 0.67(6) \AA^*$. Even though their characteristic energies are different, the structure factor associated with the spin fluctuations have the same wave vector dependence. The excitations for $\hbar \omega < 3$ meV at 1.7 K (triangles) also have a broad peak centered at $Q = 1.5 \AA^{-1}$.  

FIG. 13: (a)-(c) $h\omega$-dependence of the inelastic magnetic neutron scattering intensity measured at $Q = 1.5\AA^{-1}$ at three different $T$s spanning the phase transition. Solid lines are the fits described in the text. (d) $T$-dependence of integrated intensity in the unit of $(1/\text{meV/}Cr)$, (e) of peak position, and (f) of full-width-at-half-maximum of the $h\omega \approx 4.5$ meV excitations.

FIG. 14: $Q$-dependence of the inelastic magnetic neutron scattering intensity at 1.7 K and 12 K which is integrated over different energies.
C. Spin freezing in ZnCr$_{1.4}$Ga$_{0.6}$O$_4$

In this section, we study spin correlations in ZnCr$_{1.4}$Ga$_{0.6}$O$_4$ which exhibits spin-glass-like behaviors in bulk susceptibility measurements$^{[40]}$. Fig. 14 shows elastic magnetic scattering intensities measured at 1.4 K. High temperature background was measured at 20 K and subtracted. Unlike in the pure ZnCr$_2$O$_4$ and the weakly doped ZnCr$_{1.9}$Ga$_{0.1}$O$_4$, this system does not have magnetic Bragg peaks but a broad peak centered at a finite wave vector $Q = 1.5$ Å$^{-1}$ with $\kappa = 0.48(5)$ Å$^{-1}$. This indicates that the 30% nonmagnetic doping destroys the magnetic long range order and reduces the correlation length down to distance between nearest neighboring Cr ions. $\bar{I}(Q)$ going to zero as Q approaches zero indicates that the antiferromagnetic constraints are still satisfied in the heavily doped sample. The solid line is the fit to the powder-averaged magnetic neutron scattering intensity for an isolated spin dimer$^{[53]}$.

$$\bar{I}(Q) \propto |F(Q)|^2 \frac{1 - \sin Q r_0}{Q r_0}$$

where the distance between nearest neighboring Cr$^{3+}$ ions $r_0 = 2.939$ Å. The spin pair model produces a broader peak than the experimental data. Instead, the $Q$-dependence is almost identical to that of the fluctuating spins in pure ZnCr$_2$O$_4$ and weakly diluted ZnCr$_{1.9}$Ga$_{0.1}$O$_4$ (see Fig. 13). This suggests that the same local spin objects involving more than isolated dimers are responsible for the broad $Q$-dependence in those materials even though the energy for the correlations changes with doping of the nonmagnetic ions. We can estimate the average frozen moment from the elastic neutron scattering data

$$|<M>|^2 \approx \frac{3 g^2}{2^{2.1 A^{-1}}} \frac{\bar{I}(Q)/|F(Q)|^2 Q^2 dQ}{\int_0^{2.1 A^{-1}} Q^2 dQ}.$$  

Integrating the difference data over $Q$ yields $|<M>|^2 = 0.24(4) \mu_B$/Cr, in other words, $|<M>| = g <S > \mu_B = 0.49(4) \mu_B$/Cr. This quantity is substantially less than the Néel value $|<M>| = g S \mu_B = 3 \mu_B$/Cr and also much less than those values of ZnCr$_2$O$_4$ and ZnCr$_{1.9}$Ga$_{0.1}$O$_4$.

![FIG. 15: Q-dependence of elastic magnetic neutron scattering intensity measured with energy window of $|\hbar\omega| < 0.05$ meV.](image)

![FIG. 16: T-dependence of elastic magnetic neutron scattering intensity integrated over $|\hbar\omega| < 0.05$ meV and inelastic magnetic neutron scattering intensity integrated over 0.3 meV $< h\omega < 0.6$ meV. Both data were measured at $Q = 1.5$ Å$^{-1}$.](image)
V. DISCUSSIONS AND SUMMARY

ZnCr$_2$O$_4$ is so far the best realization of an antiferromagnet on the magnetic lattice of corner-sharing tetrahedra with uniform nearest neighbor interactions and without any site-disorder. Upon cooling, this system undergoes a cubic-to-tetragonal distortion to settle into a Néel phase with a local spin resonance\[1\]. The three features, tetragonal distortion, long range order, and the local spin resonance, occurs abruptly in a first order fashion. The spins in the Néel phase have reduced staggered magnetization, $<S^z> < 1$ (see the inset of Fig. 2) due to geometrical frustration. Weak 5% nonmagnetic doping into the magnetic lattice further suppresses the staggered magnetization but does not destroy the Néel phase at low temperatures. The phase transition from cooperative paramagnetic phase to Néel phase, however, occurs gradually upon cooling in a second order fashion. The cubic to tetragonal lattice distortion also follows the development of the magnetic phase transition. This supports that the phase transition is magnetically driven. It is understandable that the nature of the low temperature phase does not change with 5% doping because for 5% dilution in the magnetic lattice, the majority of tetrahedra have all 4 spins (81% of tetrahedra have all 4 spins and 17% have 3 spins\[11\]). For 30% dilution ($x=0.7$), 24% of tetrahedra have 4 spins, 41% have 3 spins and 27% have 2 spins. Even though it is still above the percolation threshold ($1 - x_c = 0.39$), the long range correlations are destroyed and replaced with short range correlations. Despite these differences, all three materials contain spin correlations with a common broad $Q$ dependence even though the energetics of the local correlations change with the occupancy of the magnetic lattice and the existence of long range order. This indicates that the local spin object responsible for the common $Q$ dependence is robust against strong disorder. This finding may explain why bulk properties in geometrically frustrated magnets are robust against dilution. In SCGO(x), where the magnetic entity relevant to geometrical frustration can be viewed as quasi-two dimensional (111)-slabs of corner-sharing tetrahedra, the bulk susceptibility shows field hysteresis and the nonlinear susceptibility diverges, typical of spin glasses, the specific heat $C(T)$ is proportional to $T^2$ as in an ordinary two-dimensional antiferromagnet.\[14\] These bulk behaviors are very robust against magnetic dilution.\[15\] Our finding indicates that the fundamental spin degree of freedom is the hexagonal loop of antiferromagnetic spins observed in the pure ZnCr$_2$O$_4$.\[24\] The low energy physics is governed by the excitations of the local spin degree of freedom and therefore is robust to dilution.

In summary, we have determined the spin structure of the Néel phase in ZnCr$_{2−x}$Ga$_x$O$_4$ which would provide a starting point for a theory for this system. We have studied, using neutron scattering, how nonmagnetic doping changes the first order magnetoelastic phase transition in pure ZnCr$_2$O$_4$ into the second order spin-glass-like phase transition. We have found that a broad $Q$ dependence is robust against dilution, suggesting that such local spin correlations both in Néel phase and in short range ordered phase is intrinsic to the geometrically frustrated magnets and distinguishes these systems from the ordinary spin glasses.

Acknowledgments

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TABLE I: Measured ratios of SF to NSF scattering intensities for three magnetic reflections that belong to \( k = (1, 0, \frac{1}{2}) \) and the plane of the \( k = (1/2, 1/2, 0) \) is parallel with or perpendicular to the contracted \( c \)-axis. Recently, however, neutron diffraction measurements with uniaxial pressure along a few different directions proved \( 39 \) that the half integer of \( k = (1, 0, \frac{1}{2}) \) is along the \( c \)-axis and the \( k = (1/2, 1/2, 0) \) is perpendicular to the \( c \)-axis.

\[
\begin{array}{|c|c|c|}
\hline
(h,l,k) & (\sigma_{SF}/\sigma_{NSF})_{obs} & 1 - \frac{k^2}{\text{const}} \\
\hline
(1,0.5,0) & 0.4(1) & 0.2 \\
(1,1.5,0) & 0.7(1) & 0.6923 \\
(1,2.5,0) & 0.83(5) & 0.862 \\
\hline
\end{array}
\]
TABLE II: The basis functions of the irreducible representation of group $O_h^a$ for the two-arm star of the wave vector $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$. Here $\mathbf{k}$ is in terms of the cubic notation and $\mathbf{k} = \frac{1}{2}(2, 1, 1)$ in Kovalev’s notation. Here $\mathbf{k}_1 = \mathbf{k}$ and $\mathbf{k}_2 = -\mathbf{k}$. The notation of representations, such as $\tau_1$, $\tau_1'$ and so on, followed the Kovalev’s notation. $\psi^\mathbf{k}_i (i = 1, 2, 3, 4)$ represent the basis functions for the spins located at $(0.5,0.5,0.5)$, $(0.5,0.75,0.75)$, $(0.75,0.5,0.75)$, and $(0.75,0.75,0.5)$ in the cubic notation, respectively. This table was taken from Table 22 in page 131 of Ref. [50].

| Rep. Arms | $\psi^\mathbf{k}_1 \tau_1$ | $\psi^\mathbf{k}_2 \tau_1$ | $\psi^\mathbf{k}_3 \tau_1$ | $\psi^\mathbf{k}_4 \tau_1$ |
|-----------|-----------------|-----------------|-----------------|-----------------|
| $\tau_1$  | $k_1$ (1, 1, 0) (0,0,0) (0,0,0) $i(1, 1, 0)$ |
|           | $k_2$ (1, 1, 0) (0,0,0) (0,0,0) $-i(1, 1, 0)$ |
| $\tau_1'$ | $k_1$ (0,0,0) (1,1,0) (1, 1, 0) (0,0,0) |
|           | $k_2$ (0,0,0) $-i(1, 1, 0)$ $-i(1, 1, 0)$ (0,0,0) |
| $\tau_2$  | $k_1$ (1,1,0) (0,0,0) (0,0,0) $i(1, 1, 0)$ |
|           | $k_2$ (1,1,0) (0,0,0) (0,0,0) $-i(1, 1, 0)$ |
| $\tau_2'$ | $k_1$ (0,0,0) (1,1,0) (1, 1, 0) (0,0,0) |
|           | $k_2$ (0,0,0) $-i(1, 1, 0)$ $-i(1, 1, 0)$ (0,0,0) |
| $\tau_3$  | $k_1$ (1,1,0) (0,0,0) (0,0,0) $i(1, 1, 0)$ |
|           | $k_2$ (1,1,0) (0,0,0) (0,0,0) $-i(1, 1, 0)$ |
| $\tau_3'$ | $k_1$ (0,0,0) (1,1,0) (1, 1, 0) (0,0,0) |
|           | $k_2$ (0,0,0) $-i(1, 1, 0)$ $-i(1, 1, 0)$ (0,0,0) |
| $\tau_3''$ | $k_1$ (0,0,0) (0,0,1) (0,0,0) (0,0,1) |
|           | $k_2$ (0,0,0) $-i(0, 0, 1)$ $-i(0, 0, 1)$ (0,0,1) |
| $\tau_3'''$ | $k_1$ (0,0,0) (0,0,1) (0,0,0) (0,0,1) |
|           | $k_2$ (0,0,0) $-i(0, 0, 1)$ $-i(0, 0, 1)$ (0,0,1) |
| $\tau_4$  | $k_1$ (1, 1, 0) (0,0,0) (0,0,0) $i(1, 1, 0)$ |
|           | $k_2$ (1, 1, 0) (0,0,0) (0,0,0) $-i(1, 1, 0)$ |
| $\tau_4'$ | $k_1$ (0,0,0) (1, 1, 0) (1, 1, 0) (0,0,0) |
|           | $k_2$ (0,0,0) $-i(1, 1, 0)$ $-i(1, 1, 0)$ (0,0,0) |
| $\tau_4''$ | $k_1$ (0,0,0) (0,0,1) (0,0,1) (0,0,1) |
|           | $k_2$ (0,0,0) $-i(0, 0, 1)$ $-i(0, 0, 1)$ (0,0,1) |
TABLE III: The basis functions of the irreducible representation of group $Fd\bar{3}m(O_h^3)$ for the two-arm star of the wave vector $\mathbf{k} = (1, 0, \frac{1}{4})$. Here $\mathbf{k}$ is in terms of the cubic notation and $\mathbf{k} = \frac{1}{4}(1, 1, 0) + \frac{1}{4}(0, 1, 1)$ in Kovalev’s notation using primitive reciprocal unit vectors. Here $\mathbf{k}_1 = \mathbf{k}$ and $\mathbf{k}_2 = -\mathbf{k}$. The notation of representations, such as $\tau_1$, $\tau_1'$ and so on, followed the Kovalev’s notation. $\psi_i^{k\tau'}(i = 1, 2, 3, 4)$ represent the basis functions for four spins in the primitive cell located at $(0.5, 0.5, 0.5)$, $(0.5, 0.75, 0.75)$, $(0.75, 0.5, 0.75)$, and $(0.75, 0.75, 0.5)$ in the cubic notation, respectively.

| Rep. Arms | $\psi_1^{k\tau}$ | $\psi_2^{k\tau}$ | $\psi_3^{k\tau}$ | $\psi_4^{k\tau}$ |
|-----------|------------------|------------------|------------------|------------------|
| $\tau_{11}$ | $k_1$ (1, 0, 0) | $i(0, 1, 0)$ | $-i(0, 1, 0)$ | (1, 0, 0) |
|           | $k_2$ (1, 0, 0) | (0, 1, 0) | (0, 1, 0) | (1, 0, 0) |
| $\tau_{12}$ | $k_1$ (1, 0, 0) | (0, 1, 0) | (0, 1, 0) | (1, 0, 0) |
|           | $k_2$ (1, 0, 0) | $i(0, 1, 0)$ | $i(0, 1, 0)$ | (1, 0, 0) |
| $\tau_{11}'$ | $k_1$ (0, 1, 0) | $i(1, 0, 0)$ | $i(1, 0, 0)$ | (0, 1, 0) |
|           | $k_2$ (0, 1, 0) | (1, 0, 0) | (1, 0, 0) | (0, 1, 0) |
| $\tau_{12}'$ | $k_1$ (0, 1, 0) | (1, 0, 0) | (1, 0, 0) | (0, 1, 0) |
|           | $k_2$ (0, 1, 0) | $-i(1, 0, 0)$ | $-i(1, 0, 0)$ | (0, 1, 0) |
| $\tau_{11}''$ | $k_1$ (0, 0, 1) | $-i(0, 0, 1)$ | $i(0, 0, 1)$ | (0, 0, 1) |
|           | $k_2$ (0, 0, 1) | (0, 0, 1) | (0, 0, 1) | (0, 0, 1) |
| $\tau_{12}''$ | $k_1$ (0, 0, 1) | (0, 0, 1) | (0, 0, 1) | (0, 0, 1) |
|           | $k_2$ (0, 0, 1) | $i(0, 0, 1)$ | $i(0, 0, 1)$ | (0, 0, 1) |
| $\tau_{21}$ | $k_1$ (1, 0, 0) | $i(0, 1, 0)$ | $i(0, 1, 0)$ | (1, 0, 0) |
|           | $k_2$ (1, 0, 0) | (0, 1, 0) | (0, 1, 0) | (1, 0, 0) |
| $\tau_{22}$ | $k_1$ (1, 0, 0) | (0, 1, 0) | (0, 1, 0) | (1, 0, 0) |
|           | $k_2$ (1, 0, 0) | $i(0, 1, 0)$ | $i(0, 1, 0)$ | (1, 0, 0) |
| $\tau_{21}'$ | $k_1$ (1, 0, 0) | (1, 0, 0) | (1, 0, 0) | (0, 1, 0) |
|           | $k_2$ (1, 0, 0) | $-i(1, 0, 0)$ | $-i(1, 0, 0)$ | (0, 1, 0) |
| $\tau_{22}'$ | $k_1$ (0, 0, 1) | $i(0, 0, 1)$ | $i(0, 0, 1)$ | (0, 0, 1) |
|           | $k_2$ (0, 0, 1) | (0, 0, 1) | (0, 0, 1) | (0, 0, 1) |
| $\tau_{22}''$ | $k_1$ (0, 0, 1) | (0, 0, 1) | (0, 0, 1) | (0, 0, 1) |
|           | $k_2$ (0, 0, 1) | $i(0, 0, 1)$ | $i(0, 0, 1)$ | (0, 0, 1) |
TABLE IV: Superpositions of two irreducible representations, $C_1\psi^{k_1r} + C_2\psi^{k_2r}$, which give real spins to the atoms for $k_1 = (1, \frac{1}{2}, 0)$ and $k_2 = -k_1$. 1(1, I, 0) represents the spin at site 1 is along (1, I, 0). Positions of the 1 to 16 sites are shown in Fig. 6 (a).

| Superposition | Nonzero spins in a chemical unit cell |
|---------------|-------------------------------------|
| $k_1\tau_1 + k_2\tau_1$ | 1(1, I, 0) 8(I, 1, 0) 9(1, 1, 0) 16(1, 1, 0) |
| $-ik_1\tau_1 + ik_2\tau_1$ | 4(I, 1, 0) 5(1, I, 0) 12(1, I, 0) 13(1, 1, 0) |
| $k_1\tau_1 + ik_2\tau_1$ | 2(1, 1, 0) 3(I, 1, 0) 10(I, 1, 0) 11(1, 1, 0) |
| $ik_1\tau_1 + k_2\tau_1$ | 6(I, 1, 0) 7(I, 1, 0) 14(1, 1, 0) 15(1, 1, 0) |
| $k_1\tau_2 + k_2\tau_2$ | 1(1, 1, 0) 8(1, 1, 0) 9(I, 1, 0) 16(1, 1, 0) |
| $-ik_1\tau_2 + ik_2\tau_2$ | 4(1, 1, 0) 5(I, I, 0) 12(1, I, 0) 13(1, 1, 0) |
| $k_1\tau_2 + ik_2\tau_2$ | 2(1, 1, 0) 3(1, 1, 0) 10(I, I, 0) 11(I, 1, 0) |
| $ik_1\tau_2 + k_2\tau_2$ | 6(1, 1, 0) 7(1, 1, 0) 14(1, 1, 0) 15(1, 1, 0) |
| $k_1\tau_3 + k_2\tau_3$ | 1(0, 0, 1) 8(0, 0, 1) 9(0, 0, 1) 16(0, 0, 1) |
| $-ik_1\tau_3 + ik_2\tau_3$ | 4(0, 0, 1) 5(0, 0, 1) 12(0, 0, 1) 13(0, 0, 1) |
| $k_1\tau_3 + ik_2\tau_3$ | 4(I, 1, 0) 5(I, I, 0) 12(1, I, 0) 13(1, 1, 0) |
| $ik_1\tau_3 + k_2\tau_3$ | 2(I, 1, 0) 3(I, 1, 0) 10(I, 1, 0) 11(I, 1, 0) |
| $ik_1\tau_3 + k_2\tau_3$ | 6(I, 1, 0) 7(I, 1, 0) 14(1, 1, 0) 15(1, 1, 0) |
| $k_1\tau_3' + k_2\tau_3'$ | 1(0, 0, 1) 8(0, 0, 1) 9(0, 0, 1) 16(0, 0, 1) |
| $-ik_1\tau_3' + ik_2\tau_3'$ | 4(0, 0, 1) 5(0, 0, I) 12(0, 0, 1) 13(0, 0, 1) |
| $k_1\tau_3'' + ik_2\tau_3''$ | 2(0, 0, 1) 3(0, 0, 1) 10(0, 0, I) 11(0, 0, I) |
| $ik_1\tau_3'' + k_2\tau_3''$ | 6(0, 0, 1) 7(0, 0, 1) 14(0, 0, 1) 15(0, 0, 1) |
| $k_1\tau_3'' + k_2\tau_3''$ | 2(1, 1, 0) 3(1, 1, 0) 10(1, 1, 0) 11(1, 1, 0) |
| $ik_1\tau_3'' + k_2\tau_3''$ | 6(1, 1, 0) 7(1, 1, 0) 14(1, 1, 0) 15(1, 1, 0) |
| $ik_1\tau_3'' + k_2\tau_3''$ | 6(0, 0, 1) 7(0, 0, I) 14(0, 0, 1) 15(0, 0, 1) |
TABLE V: Superpositions of two irreducible representations, $C_1 \psi^{k_1 \tau} + C_2 \psi^{k_2 \tau}$, which give real spins to the atoms for $k_1 = (1, 0, 4)$ and $k_2 = -k_1$.

| Superposition | Nonzero spins in a chemical unit |
|---------------|----------------------------------|
| $k_1 \tau_{1a} + k_2 \tau_{1b}$ | 1(1, 0, 0) 6(0, 1, 0) 7(0, 1, 0) 9(0, 0, 0) 12(1, 0, 0) 14(0, 1, 0) 15(0, 0, 0) |
| $-ik_1 \tau_{1a} + ik_2 \tau_{1b}$ | 2(0, 1, 0) 3(0, 1, 0) 5(1, 0, 0) 8(1, 0, 0) 10(0, 1, 0) 11(0, 1, 0) 13(1, 0, 0) 16(1, 0, 0) |
| $k_1 \tau_{2a} + k_2 \tau_{2b}$ | 1(1, 0, 0) 2(0, 1, 0) 3(0, 1, 0) 4(1, 0, 0) 9(1, 0, 0) 10(0, 1, 0) 11(0, 1, 0) 12(1, 0, 0) |
| $-ik_1 \tau_{2a} + ik_2 \tau_{2b}$ | 5(1, 0, 0) 6(0, 1, 0) 7(0, 1, 0) 8(1, 0, 0) 10(1, 0, 0) 11(1, 0, 0) 13(0, 1, 0) 15(0, 1, 0) |
| $k_1 \tau_{3a} + k_2 \tau_{3b}$ | 1(0, 1, 0) 4(0, 0, 1) 6(0, 1, 0) 7(0, 0, 1) 9(0, 1, 0) 12(0, 1, 0) 14(0, 0, 1) 15(0, 1, 0) |
| $-ik_1 \tau_{3a} + ik_2 \tau_{3b}$ | 2(0, 1, 0) 3(0, 1, 0) 4(1, 0, 0) 9(0, 0, 1) 10(1, 0, 0) 11(0, 0, 1) 12(1, 0, 0) |

TABLE VI: The basis functions of the irreducible representation of group $Fd\bar{3}m(O_4^k)$ for the two-arm star of the wave vector $k = \left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right)$.

| Rep. | $\psi^{k_1 \tau}$ | $\psi^{k_2 \tau}$ | $\psi^{k_3 \bar{\tau}}$ | $\psi^{k_4 \bar{\tau}}$ |
|------|------------------|------------------|------------------|------------------|
| $\tau_1$ | (0, 0, 0) | (0, 1, 1) | (1, 0, 1) | (1, 1, 0) |
| $\tau_2$ | (1, 1, 1) | (0, 0, 0) | (0, 0, 0) | (0, 0, 0) |
| $\tau_3$ | (0, 0, 0) | (0, 1, 0) | (0, 1, 0) | (0, 1, 0) |
|       | (0, 1, 1) | (1, 0, 1) | (1, 1, 0) |
| $\tau_6$ | (0, 0, 0) | (0, 2, 0) | (0, 0, 1) | (0, 0, 0) |
|       | (0, 0, 0) | (0, 1, 0) | (0, 1, 0) | (0, 2, 0) |
|       | (0, 0, 0) | (0, 0, 2) | (1, 0, 0) | (0, 0, 0) |
|       | (0, 0, 0) | (0, 0, 1) | (2, 0, 0) | (0, 0, 1) |
|       | (0, 0, 0) | (0, 0, 0) | (0, 0, 0) | (0, 0, 0) |
| $\tau_6$ | (0, 1, 0) | (0, 0, 0) | (0, 0, 0) | (0, 0, 0) |
|       | (0, 0, 0) | (0, 0, 0) | (0, 0, 0) | (0, 0, 0) |
TABLE VII: Goodness of the fit of the different spin models with \( k = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \) to the \( \{\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\} \) reflections obtained from different ZnCr₂O₄ polycrystalline samples. The best fit was obtained with the \( \tau_1 + \tau_2 \) model (see Fig. 10 (a)).

| Sample | Rep. T (K) | \( \chi^2 \) | \( R_{wp} \) |
|--------|------------|---------|-----------|
| 1      | \( \tau_1 \) | 1.5     | 4.915 .0664 |
|        | \( \tau_1, \tau_2 \) |          | 4.888 .0662 |
|        | \( \tau_1, \tau_2, \tau_3 \) |          | 4.911 .0664 |
|        | \( \tau_1, \tau_6 \) |          | 4.998 .067 |
|        | \( \tau_2, \tau_3 \) |          | 4.995 .067 |
| 2      | \( \tau_1, \tau_2 \) | 7.3     | 1.368 .0618 |
| 3      | \( \tau_1, \tau_2 \) | 2       | 4.003 .0592 |