# Geometric Spin Frustration in $Zn_{1-x}Ni_xCr_2O_4$ System

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Abstract

At room temperature, the cubic spinel $ZnCr_2O_4$ is known as the typical geometrically frustrated spin system. Upon cooling this compound undergoes a crystal structure change driven by removing the frustrated degenerated states, accompanying with the magnetic ordering. In the tetragonal phase the c-axis is larger than the a-axis. Another spinel compound $NiCr_2O_4$ takes the cubic structure above 310 K. Below 310 K $NiCr_2O_4$ is tetragonally distorted (c/a < 1) due to cooperative Jahn-Teller ordering. In the previous reports, the geometrical frustrated spin fluctuations still exist in $NiCr_2O_4$. In this report we investigated how the geometrical frustration changes and how the ratio of the crystal axis, c/a changes in $Zn_{1-x}Ni_xCr_2O_4$ system by the low temperature x-ray diffraction measurement and the SQUID magnetometer.

## 1. Introduction

Geometric frustration is one of the most interesting topics in the study of condensed matter systems. Frustrated interactions often cause extensive degeneracy in the ground state of the system and prevent any ordering down to low temperatures. The ground state of a frustrated system is quite intriguing and can be modified into a novel and interesting state, such as a spin liquid, associated with quantum fluctuations. The degenerated states, however, is removed its degeneracy in general by a broken symmetry, such as a crystal distortion at low temperatures.

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S.-H. Lee et al [1] have found the resonance-like excitation mode in the inelastic neutron scattering spectrum in spinel ferrimagnet $ZnCr_2O_4$. The similar resonance like spectrum modes were also observed in the magnetic and crystal structure ordered phase in $NiCr_2O_4$ and $FeCr_2O_4$ [2]. These modes have been identified to be the spin hexamer and heptamer, defined as antiferromagnetic spin correlation in the molecule units. So even the degenerated states of the geometric frustrated states remove its degeneracy in the broken symmetry, the dynamical fluctuations still remain in the large scale molecular unit. The study of the geometric frustration enters into the new fascinating stage. The spinel compound $ZnCr_2O_4$ is considered as a typical geometric fluctuating spin system with $Cr^{3+}$ ions. On the other hand in $NiCr_2O_4$, Jahn-Teller (*J.T.*) ion $Ni^{2+}$ distorts the crystal structure, resulting in the broken symmetry of the geometrical frustration. Moreover the magnetic moment of $Ni^{2+}$ ion also disturbs the geometric frustration, since the magnetic $Ni^{2+}$-O-$Cr^{3+}$ interaction usually being stronger than the frustrated interaction between the $Cr^{3+}$ ions. We have already reported the study of frustration induced the crystal structure change and the magnetic order on $ZnCr_2O_4$ and $Zn_{0.5}Ni_{0.5}Cr_2O_4$ [3] and also on $Zn_{1-x}Ni_xCr_2O_4$ for x = 1, 0.8 and 0.6 [4]. With the magnetic measurements by SQUID for $Zn_{1-x}Ni_xCr_2O_4$ for x = 1, 0.8 and 0.6, we will discuss the geometric frustration system of $Zn_{1-x}Ni_xCr_2O_4$ from the new point of view based on dynamical spin fluctuation in the hexamer and heptomer.

## 2. Experiment

### a) Sample preparation

The single crystals of $ZnCr_2O_4$ and $Zn_{0.5}Ni_{0.5}Cr_2O_4$ were grown with a $Bi_2O_3$-flux in Platinum crucibles of 1.5 liters volume. The cooling rate was 0.5°C/hr. For the powder specimens for the powder x-ray diffraction, the single crystals were grinded. The powder samples $Ni_xZn_{1-x}Cr_2O_4$ with x = 0.6, 0.8 and 1 were prepared from the raw material powders of ZnO, NiO, and $Cr_2O_3$. The powders were mixed in appropriate proportions in an agate mortar under acetone for 3 hrs. The mixtures were then pre-sintered at $800^0$ C for 5 hrs. Resultant mixtures were reground and hand milled for 3 hrs under acetone. Pressing the mixture into pellet and sintering at $1200^0$C for 5 hrs. Powder x-ray diffraction (XRD) pattern at room temperature confirmed that the final product has a cubic-type spinel single phase for 0.6 and 0.8 and tetragonal spinel single phase for x = 1. Also XRD indicated no impurities for the samples x = 0.6 and 0.8. But the XRD for the sample $NiCr_2O_4$ indicated impurity phases, this is due to $NiO_2$ or $Cr_2O_3$ and Cu.

b) Magnetic measurement

Magnetic susceptibility was measured between 1.8 and 300 K by a SQUID magnetometer MPMS system (Quantum Design Co. Ltd.). Magnetization vs magnetic field was also measured up to 7 Tesla at several temperatures.

c) Low temperature x-ray diffraction

Two different types of cooling systems were used in our low temperature x-ray diffraction experiments. Above about 10 K, a $^4$He circulating cryocooler was used and below about 10 K, a $^3$He-$^4$He dilution refrigerator (D.R.) was used. X-ray diffraction measurements for powder specimens were performed using the RINT 2500 system, Rigaku Co. From the observed diffraction profile the lattice constant d, the integrated intensity (I.I.) and the full width at half maximum (FWHM) were obtained.

d) Debye-Waller Factor

The temperature dependence of the I.I. can be obtained by the Debye-Waller factor. (see; for example, C. Kittel; Introduction to Solid State Physics, John Wiley & Sons, Inc. Sixth edition, Appendix A.)

When a x-ray beam is scattered by a crystal: let the position of atom nominally at $r_j$ contain a term $u(t) = r_j + u(t)$. We suppose each atom fluctuates independently about its own equilibrium position. Then the scattered intensity of the x-ray beam is

$$I = I_0 \exp(-1/3 <u^2>G^2), \qquad (1)$$

where $I_0$ is the scattered intensity from the rigid lattice and G is the reciprocal lattice vector. When we assume a classical harmonic oscillator for a crystal atom, then,

$$M\omega^2 <u^2> = 3k_B T, \qquad (2)$$

where M is the mass of the atom and $\omega$ is the frequency of the harmonic oscillator, then

$$I (hkl) = I_0 \exp(-k_B T G^2/M\omega^2). \qquad (3)$$

For quantum oscillators $<u^2>$ does not vanish even at T = 0; there is zero point motion. The zero point energy is $3/2\hbar\omega$, so that in the ground state

$$<u^2> = 3 \hbar/2M\omega , \qquad (4)$$

by (1),

$$I (hkl) = I_0 \exp(-\hbar G^2/2M\omega) \qquad (5)$$

at absolute zero. The exponential factor is the Debye-Waller factor. At higher temperatures, the intensity of the x-ray scattering spectrum depends on the temperature following eq. (3). When the temperature is low enough, the intensity gives the constant value due to the eq. (5). But when the frequency of the lattice fluctuation changes, such as the softening of the lattice,

that is, ω becomes low, the intensity is going to decrease following eq. (5).

## 3. Experimental results and Discussion

Experimental results for $ZnCr_2O_4$ and $Zn_{1-x}Ni_xCr_2O_4$ have been reported by some of the present authors [3]. Magnetic properties for $NiCr_2O_4$ have been also reported by some groups [5,6]. The temperature dependences of the magnetic susceptibility were shown in Fig. 1a for $Zn_{0.2}Ni_{0.8}Cr_2O_4$ and in Fig. 1b for $Zn_{0.4}Ni_{0.6}Cr_2O_4$. The Neel temperature $T_N$ can be obtained as the maximum of the magnetic susceptibility. Though the shape of the maximum is different between these two compounds, but the temperature is nearly same as 30 K. All the values of $T_N$ were shown in Table 1 for each compound. From these figures the inverse of the magnetic susceptibility is plotted against temperature for $Zn_{0.2}Ni_{0.8}Cr_2O_4$ and $Zn_{0.4}Ni_{0.6}Cr_2O_4$. From these figures the asymptotic Curie temperature $\theta_{CW}$ are obtained. The $\theta_{CW}$ in whole $Zn_{1-x}Ni_xCr_2O_4$ system is listed together with the data for other previously reported compounds. The $\theta_{CW}$ gives the strength of the antiferromagnetic interaction. Though the antiferromagnetic interaction is rather strong, that is, $|\theta_{CW}|$ is rather high such as from 388 to 870, the magnetic ordering is low due to the geomagnetic frustration.
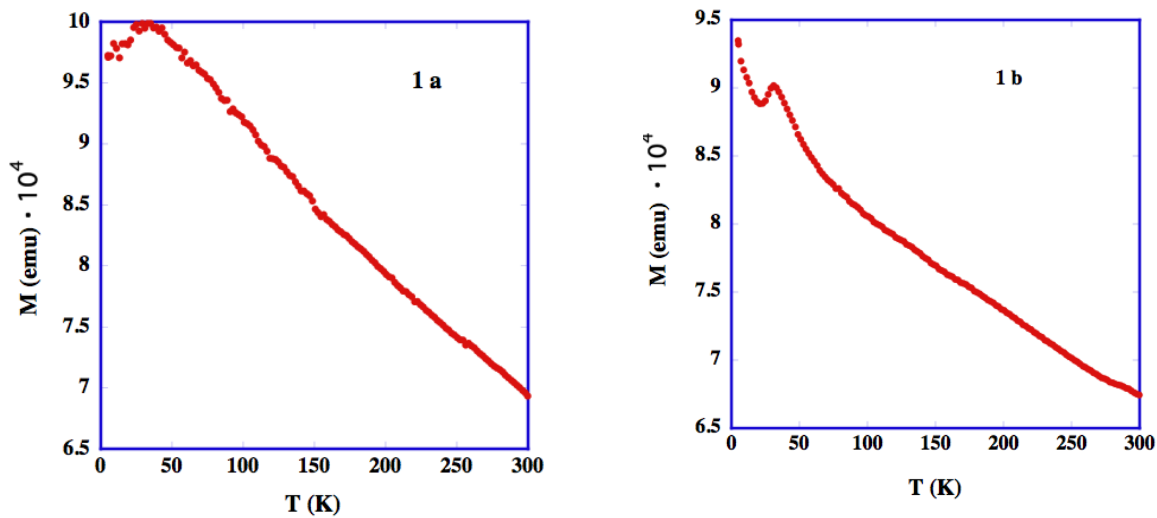


Figure 1. Temperature dependence of the magnetization , a) for $Zn_{0.2}Ni_{0.8}Cr_2O_4$ and b) for $Zn_{0.4}Ni_{0.6}Cr_2O_4$.

The frustration index (F.I.) defined as $|\theta_{CW}/T_N|$ is also listed in Table 1. Though the strongest antiferromagnetic interaction can be observed at around $Zn_{0.4}Ni_{0.6}Cr_2O_4$, the F.I. changes rather smoothly against Ni concentration x as shown in Fig. 2 .

|  | $\theta_{CW}$(K) | $T_N$(K) | F.I. ($|\theta_{CW}/T_N|$) |
|---|---|---|---|
| $NiCr_2O_4$ | - 470 | 65 | 7.2 |
| $Zn_{0.2}Ni_{0.8}Cr_2O_4$ | - 510 | 30 | 17 |
| $Zn_{0.4}Ni_{0.6}Cr_2O_4$ | - 870 | 30 | 29 |
| $Zn_{0.5}Ni_{0.5}Cr_2O_4$ | -520 | 16.5 | 31.5 |
| $ZnCr_2O_4$ | -388 | 12 | 32.33 |

Table. 1. List of asymptotic Curie temperature $\theta_{CW}$ and Neel temperature $T_N$. Frustration Index (F.I.) is also calculated and listed.

In $ZnCr_2O_4$, to remove the geometric frustrated degenerated state, the spin-Piels-like crystal distortion occurs at about $T_S$ = 12K accompanying with an antiferromagnetic ordering. In the quantum critical spin-1/2 antiferromagnetic chain, small symmetry breaking perturbations lead to the spin-Peiels transition, that is, a lattice distortion that lowers the energy of the spin system by introducing a gap in the magnetic excitation spectrum. In the case of ZnCr2O4, the spin lattice is not a linear chain but a triangle lattice. But the situation is the same. In the tetragonal phase below Ts, the ratio of the lattice constants c/a – 1 > 0.



Figure 2. Frustration index against Ni concentration.

On the other hand, in $NiCr_2O_4$ we also observed the ratio c/a - 1 < 0 below Ts = 310 K.  So at which composition of $Zn_{1-x}Ni_xCr_2O_4$ the ratio c/a – 1 changes its sign is interesting.  In Fig. 3 it is shown that c/a is larger than 1 in $Zn_{0.2}Ni_{0.8}Cr_2O_4$. The crystal structure changes below Ts = 160 K.  In $Zn_{0.4}Ni_{0.6}Cr_2O_4$ compound, the temperature  dependence of the d value for (440) reflection is shown in Fig.4. Due to the inhomogeneity of the Zn and Ni atoms, the clear split of the reflection spectrum in x-ray diffraction cannot be observed. Only a broad spectrum can be observed. The (440) spectrum in cubic phase should be split into two peaks, (440) and (404), (044). When we assume the equivalent domain structure below tetragonal distortion, the peak of (404), (044) should have twice intensity than the (440) peak. So the temperature dependence of the (440) spectrum in cubic phase can be mostly determined in tetragonal
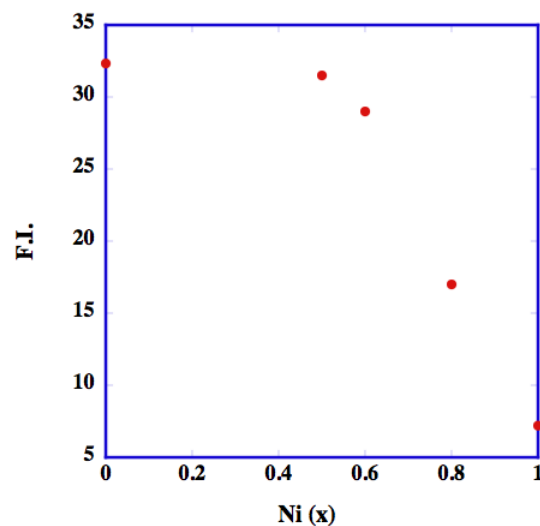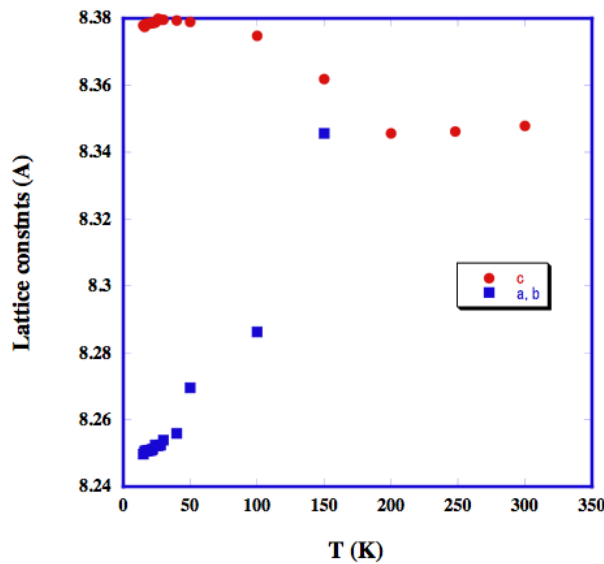
Figure 3. Temperature variation of the lattice constants of $Zn_{0.2}Ni_{0.8}Cr_2O_4$.
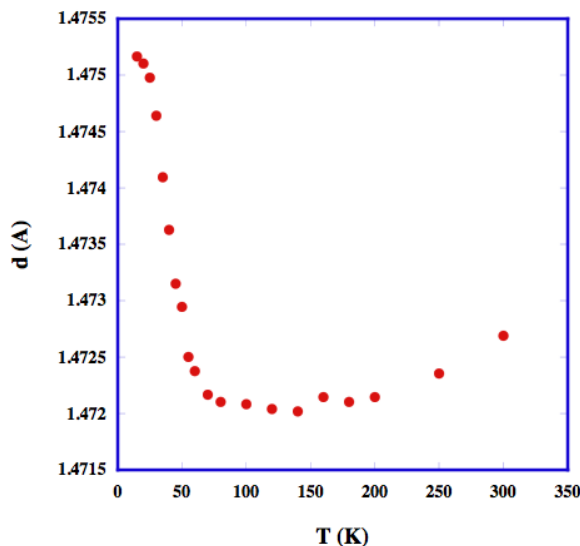


Figure 4. Lattice spacing against temperature for $Zn_{0.4}Ni_{0.6}Cr_2O_4$.

phase by the (404), (044) peak. Fig. 4 tells us lattice constant c is larger than a, b axis. In $Zn_{0.5}Ni_{0.5}Cr_2O_4$, the split of the spectrum below Ts cannot be also observed. But since the temperature dependence of the d value is rather small at around the transition temperature, it seems that c/a > 1 and c/a < 1 competed to each other. So the value of (c/a -1) changes its sign at around Ni concentration 0.5.

Now we would like to discuss the fluctuation of the lattice from the experimental results of the I.I. of x-ray spectrum. As for the typical result the I.I. in $Zn_{0.2}Ni_{0.8}Cr_2O_4$ compound is shown in Fig. 5. $Zn_{0.2}Ni_{0.8}Cr_2O_4$ shows the crystal distortion at 160 K and the magnetic order around 30 K. The temperature, 160 K is rather high, so the softening due to the crystal structure change should be rather small. In the figure the hump around 150 K can be seen. In $Zn_{0.2}Ni_{0.8}Cr_2O_4$, the structure change is due to the Jahn-Teller effect of $Ni^{2+}$.

With decreasing temperature magnetic transition accompanying with the crystal distortion occurs at 30K. So the I.I. for decreases rather clearly don to about 30 K.

At about 16 K, there is another small anomaly which can correspond to another magnetic transition. In $NiCr_2O_4$, the J.T. distortion occurs at 310 K and the ferrimagnetic transition accompanying with the crystal distortion at 65 K and another magnetic transition around 30 K. Then as shown in Fig. 6 the I.I. first starts from the bottom, then increases following to the

temperature dependence of the Debye-Waller factor, eq. (3). Then the I.I. decreases down to
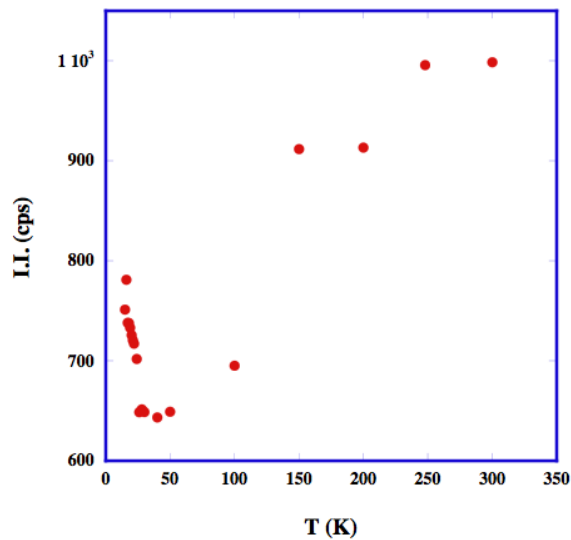


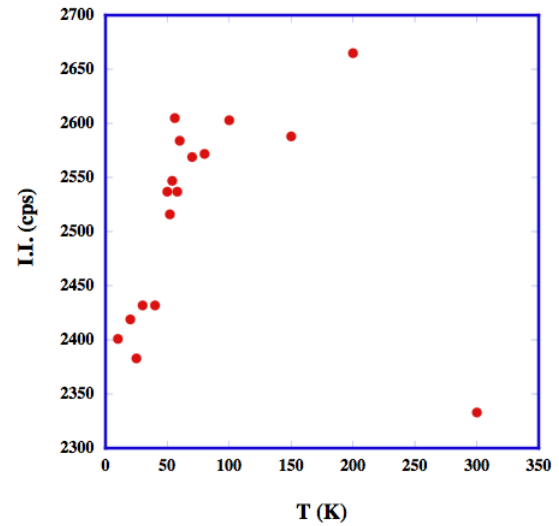Figure 5.  I.I. against T for $Zn_{0.2}Ni_{0.8}Cr_2O_4$.

Figure 6. I.I. against T for $NiCr_2O_4$.

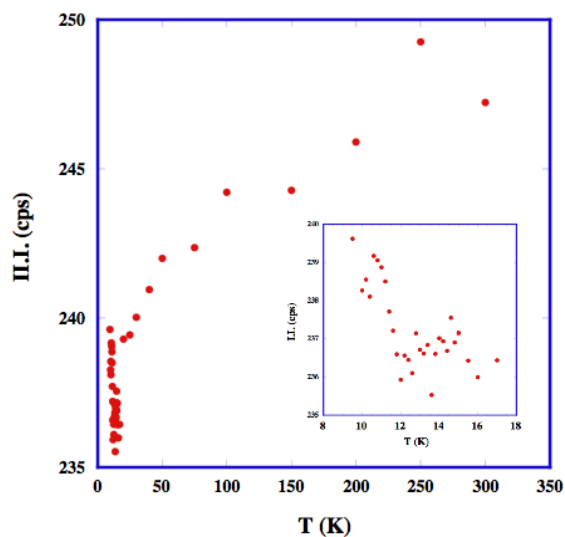about 60 K. In the vicinity of that temperature the I.I. shows the steep peak and then decreases



Figure 7.  I.I. against T for $ZnCr_2O_4$.
The intersect shows low temperature
part in the expanded scale.

down to about 30 K. In $ZnCr_2O_4$ the geometric frustration induces the crystal structure change accompanying with the magnetic order at about 12 K. The temperature dependence of the I.I. of $ZnCr_2O_4$ compound clearly shows this phase transition as shown in Fig. 7. From these results it can be said that in $Zn_{1-x}Ni_xCr_2O_4$ system the magneto- structure coupling is rather strong. Each magnetic transition corresponds to the anomaly of the I.I. of the x-ray diffraction spectrum.

Neutron inelastic scattering experiments reported the dynamical spin fluctuation modes exist in the paramagnetic and also in the magnetic ordered and  the  distorted structure phases in the spin molecule hexamer and heptamer. At present experiments we cannot distinguish these mode in our x-ray experiment.

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