Statics and dynamics of an incommensurate spin order in a geometrically frustrated antiferromagnet CdCr$_2$O$_4$

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Using elastic and inelastic neutron scattering we show that a cubic spinel, CdCr$_2$O$_4$, undergoes an elongation along the c-axis ($c > a = b$) at its spin-Peierls-like phase transition at $T_N = 7.8$ K. The Néel phase ($T < T_N$) has an incommensurate spin structure with a characteristic wave vector $Q_M = (0, \delta, 1)$ with $\delta \sim 0.09$ and with spins lying on the ac-plane. This is in stark contrast to another well-known Cr-based spinel, ZnCr$_2$O$_4$, that undergoes a c-axis contraction and a commensurate spin order. The magnetic excitations of the incommensurate Néel state has a weak anisotropy gap of 0.6 meV and it consists of at least three bands extending up to 5 meV.

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When a transition metal oxide has degeneracy, orbital or magnetic, a novel phase transition can occur through the coupling of the relevant degrees of freedom to the lattice to lift the degeneracy. A well-known example is the Jahn-Teller lattice distortion that involves either doubly degenerate $e_g$ orbitals or triply degenerate $t_{2g}$ orbitals. Geometrically frustrated magnets provide a fertile ground for similar novel phase transitions because the degeneracy can be macroscopic both for quantum and for classical spins. Until now the most frustrating system known is the one that consists of a network of corner-sharing tetrahedra, the pyrochlore lattice, with the simplest spin hamiltonian, $H_1 = J \sum_{NN} S_i \cdot S_j$ with isotropic antiferromagnetic nearest neighbor interactions only. Theoretically, it has been shown that in the ideal case, the spins alone cannot order even at zero temperature. Experimentally the magnetic lattice can be realized in several materials such as in the pyrochlores $A_2B_2O_7$, spinels $AB_2O_4$ and C15 Lave phases $AB_2$. Among them, Cr-based spinels $ACr_2O_4$ ($A$=Zn, Cd) realize the most frustrating lattice with the dominant antiferromagnetic nearest neighbor interactions due to the direct overlap of the $t_{2g}$ orbitals of the neighboring $Cr^{3+}$ ($3d^3$) ions. Consequently, $ACr_2O_4$ remains paramagnetic to temperatures far below the characteristic strength of the interactions between the spins, the Curie-Weiss temperature $|\Theta_{CW}| = 390$ K and 88 K for $A$ = Zn and Cd, respectively. Upon further cooling, however, the system undergoes a first-order spin-Peierls-like phase transition from a cubic paramagnet to a tetragonal Néel state at $T_N = 12.5$ K and 7.8 K for $A$ = Zn and Cd, respectively.

Recently, ZnCr$_2$O$_4$ has been studied extensively using neutron scattering techniques. Its tetragonal distortion involves a contraction along the c axis ($c < a$). Its Néel state has a rather complex commensurate spin structure. The spin structure has four different characteristic wave vectors, $Q_M = (\frac{1}{2}, \frac{1}{2}, 0), (1.0, \frac{1}{2}, \frac{3}{2}), (\frac{1}{2}, \frac{1}{2}, 0)$ and $(0, 0, 1)$. Furthermore, the relative ratios of the neutron scattering intensities of these wave vectors vary depending on the subtle chemical conditions during sample preparation. This suggests that even in the tetragonal phase, ZnCr$_2$O$_4$ is critically located close to several spin structures, that makes it difficult to understand the true nature of its ground state. The CdCr$_2$O$_4$ compound in this class has not received much attention partly because it was commonly believed that the same physics hold true as in ZnCr$_2$O$_4$, which we found is not the case. As the pyrochlore lattice possesses many ground states and multiple ways for lifting the ground state degeneracy, CdCr$_2$O$_4$ provides a venue for understanding phase transitions in this seemingly complex class of materials.

In this paper, we report the results from elastic and inelastic neutron scattering measurements on $^{114}$CdCr$_2$O$_4$ (space group $Fd\bar{3}m$, $a = 8.58882$ Å for $T = 10$ K). Surprisingly, we find that it undergoes a phase transition that is qualitatively different in nature from the one observed in ZnCr$_2$O$_4$. CdCr$_2$O$_4$ elongates along the c-axis ($c > a$) and undergoes an incommensurate (IC) Néel order. The high Q-resolution data indicate that the incommensurate magnetic structure has a single characteristic wave vector of $Q_M = (0, \delta, 1)$ with $\delta \sim 0.09$ perpendicular to the unique c-axis. We present two possible high symmetry spin structures that are consistent with the particular $Q_M$. The interplay between the lattice distortion and the IC spin structure is discussed along with dispersion of the spin wave excitations.

Preliminary measurements were initially performed on the TAS2 thermal triple-axis spectrometer of Japan...
A single crystal weighing ~ 100 mg was used for the elastic measurements, while three of these crystals were co-mounted within 1° mosaic for the inelastic measurements. The crystals were mounted in the (h0k0) scattering plane, that allowed the investigations of three equivalent planes, (h0k0), (0kl), and (h0l) planes due to the crystallographic domains.

Fig. 1 shows the Q-dependence of the spin fluctuations in the spin liquid phase of CdCr$_2$O$_4$ measured above $T_N$. The ring-shaped intensity around (2,2,0) is essential characteristic incommensurate wave vectors are also due to the collective low energy excitations of antiferromagnetic hexagonal spin clusters in the pyrochlore lattice. This suggests that the cubic phase of CdCr$_2$O$_4$ can be well represented by the Hamiltonian $H_1$ as in ZnCr$_2$O$_4$. $J$ is estimated from the Curie-Weiss temperature $|\Theta_{CW}| = 88.97$ K (see Fig. 2(a)), to be $J = -1.02$ meV. Although CdCr$_2$O$_4$ appears to have the same fundamental spin degrees of freedom in the cubic phase as in ZnCr$_2$O$_4$, it exhibits strikingly different behaviors in the tetragonal phase below $T_N = 7.8$ K. It undergoes an elongation along the $c$ axis (Fig. 2(b) and (d)) and the magnetic long range order has an incommensurate characteristic wave vector (see Fig. 2(c)).

The positions of the magnetic Bragg reflections found in the scattering plane are shown in Fig. 3(a). The possible characteristic incommensurate wave vectors are $Q_M = (0, \delta, 1)$ or $(0,1,\delta)$ or $(1, \delta, 0)$ with $\delta = 0.0894(3)$. ($h$ and $k$ are interchangeable.) However, since $c > a$, the three possible $Q_M$’s would produce the magnetic Bragg reflections at slightly different positions in the scattering plane. We performed elastic scans with a high Q-resolution over a set of three IC positions to distinguish between the different scenarios. Fig. 3(b) shows the results. The black solid, blue dotted and red dashed arrows correspond to the expected peak positions for $Q_M = (0, \delta, 1), (1, \delta, 0)$, and $(0, 1, \delta)$, respectively. All three of the experimental peak positions are consistent with $Q_M = (0, \delta, 1)$, which indicates that the incommensurability occurs either along the $a$- or the $b$-axis, perpendicular to the elongated $c$-axis. Furthermore, we have performed polarized neutron diffraction at TAS1 of JAERI (the details and results of the experiment will be reported elsewhere), and found that the spins are lying on the plane that is perpendicular to the incommensurability direction. For convenience, we chose $Q_M = (0, \delta, 1)$ with the spins lying in the ac-plane. The resulting breakouts of the magnetic Bragg reflections into three crystallographic and two magnetic domains are shown as different symbols in Fig. 3(a).

Following group theory arguments, the magnetic lattice with the characteristic wave vector of $Q_M$ consists of four independent sublattices as represented by spheres with different colors in Fig. 3(c) and (d). Each sublattice connects every third nearest neighboring Cr$^{3+}$ ions that are separated by the symmetrically equivalent distance of $(\frac{1}{2}, \frac{1}{2}, 0)$. These are the second nearest neighbors along the chains represented by lines in Fig. 3(c) and...
two different sublattices would favor a phase difference of
with stronger AFM interactions among all other spin pairs
stacking of the sublattices, the magnetic interactions in the tetragonal
plane, respectively, where $2 \alpha = \delta = 16.2^\circ$. In order to
construct the relative orientation between the different sublattices, the magnetic interactions in the tetragonal
phase of CdCr$_2$O$_4$ are considered. Analysis of a series of
crystallographic domains. (b) Elastic Q-scans centered at the three peaks under a grey shadow in
(a). (c),(d) two possible spin structures deduced from $Q_M
(0, \delta, 1)$. Spins are rotating on the ac plane. The double
and single lines represent the nearest neighbor bonds in the
basal ab plane with $J_{ab}$ and in the out-of-plane with $J_c,
respectively. In (c) the NN spin orientations along $J_c$ are close to
perpendicular while in (d) they are close to collinear.

(d). Within the sublattice, spins are aligned according to $S_j = S_0 e^{2 \pi n_i Q_M (r_j - r_v)}$ and therefore the neighbour
spins rotate by $2 \alpha$, $\pi$, and $2 \alpha + \pi$ in the $ab$, ac- and bc-plane, respectively, where $2 \alpha = \delta - \pi = 16.2^\circ$. In order to
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chains are stacked almost orthogonally along the c axis
(Fig. 3(c)) and the other, the chains are stacked almost
collinearly (Fig. 3(d)).

To understand the elementary excitations of the IC
Néel state, constant-$\hbar \omega$ and constant-$Q$ scans were performed (Fig. 4). The constant-$Q$ scan at an IC zone
center (Fig. 4(d)) shows that there is a gap, $\Delta$, of 0.65
meV along with at least two additional excitation peaks
around 2.3 and 4.7 meV. At $Q$ values away from the zone
center, the lowest energy peak shifts considerably in energy
while the two higher energy peaks shift only slightly
(Fig. 4(e)-(f)). Fig. 4(a)-(c) show the dispersiveness at low energies. Additional scans were performed to map out the dispersion relation of the magnetic fluctuations
along the $(1, k, 0)$ direction (the arrow from $Q_y = 0.5$ to
2.5 in Fig. 3(a)), summarized in Fig. 3(e).

What kind of spin Hamiltonian would select the ob-
served IC Néel state as the ground state of CdCr$_2$O$_4$
in the tetragonal phase? The exchange anisotropy of
the nearest neighboring (NN) couplings, $J_c \neq J_{ab}$, alone
would favor a commensurate spin structure rather than
the IC one, which means that additional perturbations to $\mathcal{H}_1$ are present. However, $\Delta \simeq 0.6$ meV is small compared to the entire energy band width of the dispersion, $\sim 5$ meV, that suggests that the additional perturbations must be small. Let us first discuss the effect of the exchange anisotropy of the NN couplings, $J_c \neq J_{ab}$, on the dispersion of the two model spin structures shown in Fig. 3(c) and (d). In the ideal isotropic case, $J_c = J_{ab}$, there is a four-fold (six-fold) degenerate
flat zero energy mode and another four-fold (two-fold) degenerate dispersive mode that extends to higher energies in the orthogonal (collinear) model (Fig. 3(a)).
The actual incommensurability seems to be caused by other perturbative terms, such as further nearest interactions and/or DM interactions. We also considered the exchange interactions between third nearest neighbor interactions, and extensively examined the phase space as a function of $J$. We found a region where an incommensurate spin structure can be selected as a ground state but the incommensurability was along the $<110>$ direction, as recently observed in LiCuVO$_4$ [21], rather than the observed $<010>$ direction. This suggests that the tetragonal distortion involves distortions of the oxygen octahedra that lowers the crystal symmetry.

In summary, we identified a spin-lattice coupling mechanism that lifts the magnetic frustration in CdCr$_2$O$_4$ and that is distinctly different from the one observed in ZnCr$_2$O$_4$. The tetragonal distortion involves an elongation along the $c$-axis and the Néel state has a helical spin structure with the single characteristic wave vector of $Q_M = (0,\delta,1)$. Our identification of the spin structure and dynamics of the low temperature phase of CdCr$_2$O$_4$ should provide a unique test to theoretical attempts to explain the spin-Peierls-like phase transitions in the Heisenberg pyrochlore antiferromagnets.

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