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Crystal distortions in geometrically frustrated ACr_2O_4 ($\text{A} = \text{Zn}, \text{Cd}$)

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Abstract

In this paper, we discuss neutron and synchrotron x-ray diffraction data obtained from single crystals of ACr_2O_4 ($\text{A} = \text{Zn}, \text{Cd}$). The Cr spinels undergo three-dimensional spin-Peierls transitions at low temperatures that involve cubic-to-tetragonal lattice distortions and magnetic long-range ordering. Our results show that the magnetic structures selected by these systems are closely related to the lattice distortions that are undertaken.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Spin–lattice coupling has recently been found to be an effective mechanism for lifting frustration in geometrically frustrated Heisenberg antiferromagnets [1–3]. One of the best examples is ACr_2O_4 (Zn, Cd) [1, 4] where the magnetic Cr^{3+} ions form a network of corner-sharing tetrahedra [5, 6] (see figure 1(a)). A Cr^{3+} ion has three unpaired electrons in the triply degenerate t_{2g} levels, and thus does not have orbital degeneracy [1, 7]. Due to the electronic

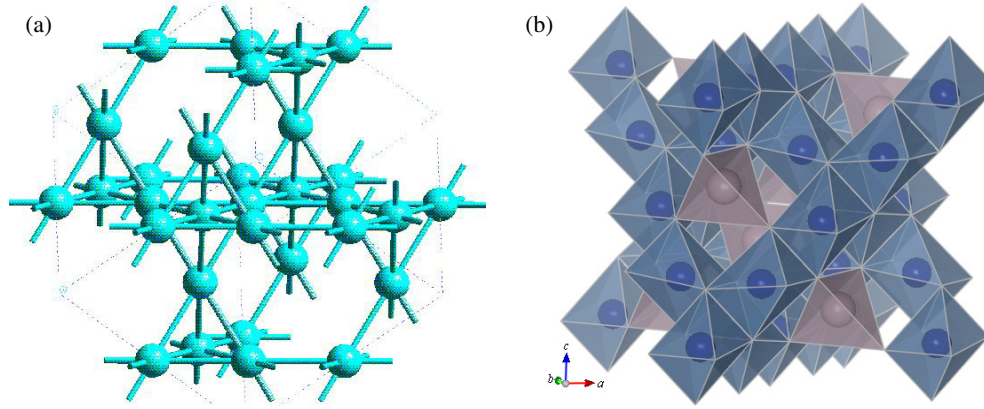


Figure 1. (a) The network of corner-sharing tetrahedra that is formed by Cr³⁺ ions in ACr₂O₄ spinels. (b) Crystal structure of ACr₂O₄. Octahedral (blue) polygons represent oxygen octahedra that surround Cr ions. Neighbouring oxygen octahedra share an edge. Grey polygons represent AO₄ tetrahedra.

configuration and the edge-sharing network of oxygen octahedra, which each surround a Cr ion (figure 1(b)), the dominant antiferromagnetic nearest neighbour interaction between the Cr³⁺ magnetic moments is through the direct overlap of their t_{2g} orbitals [8, 9]. Interactions between further neighbours require overlapping of Cr³⁺ and oxygen orbitals and are negligible because of the empty e_g state of Cr³⁺ ions. This leads the ACr₂O₄ to being the most ideal system to date for realizing the most frustrated lattice with the simplest Heisenberg Hamiltonian:

$$H = J \sum_{NN} S_i \cdot S_j.$$

Theoretically, it has been shown that in this ideal case the spins alone cannot order even at zero temperature [10, 11]. In real systems, the spins exist with other degrees of freedom, such as orbital and lattice, and many such systems order at low temperatures. For instance, upon cooling ACr₂O₄ (A = Zn²⁺, Cd²⁺) undergoes a three-dimensional spin-Peierls 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. However, the nature of the ordered phase is yet to be fully understood.

2. Magnetic structure of the Néel states of ACr₂O₄ (A = Zn, Cd)

It is not trivial to determine the spin structures of ACr₂O₄. The difficulty mainly comes from the fact that there are several crystal domains that cannot be easily distinguished even in the tetragonal phase because the crystal distortion is weak. In the case of ZnCr₂O₄ the problem becomes more difficult because its Néel state has four different characteristic wave vectors, \mathbf{Q}_M (two of the \mathbf{Q}_M , $(1/2, 0, 1)$ and $(1/2, 1/2, 0)$, are plotted in figure 2(a)) [1]. Furthermore, the relative ratios of the neutron scattering intensities of these wavevectors vary depending on the subtle chemical conditions used during sample preparation. This suggests that even in the tetragonal phase, ZnCr₂O₄ is critically located close to several spin structures, which makes it difficult to understand the true nature of its ground state. On the other hand, CdCr₂O₄ has an incommensurate spin structure [4]. And due to the reasonably strong tetragonal distortion in CdCr₂O₄, as discussed later, our high Q -resolution experiment could determine the characteristic wavevector of the incommensurate magnetic structure to be $\mathbf{Q}_M = (0, d, 1)$ with $d \sim 0.09$ (see figure 2(b)).

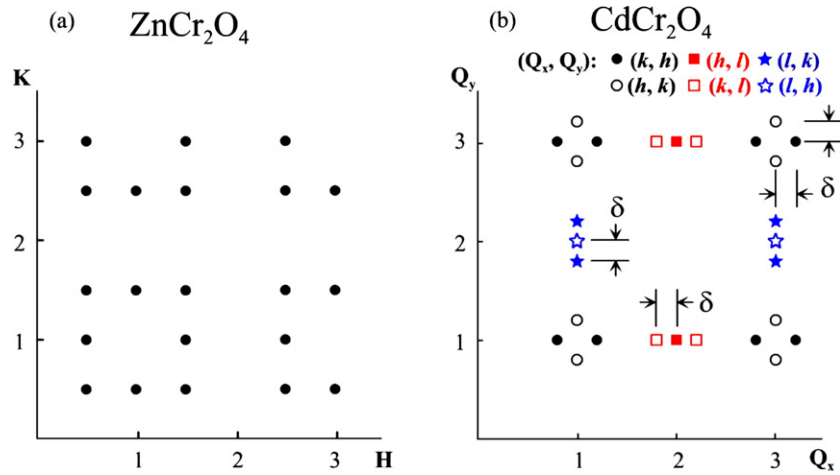


Figure 2. (a) Two commensurate characteristic wavevectors of the Néel state of ZnCr₂O₄ and (b) an incommensurate wavevector for the Néel state of CdCr₂O₄.

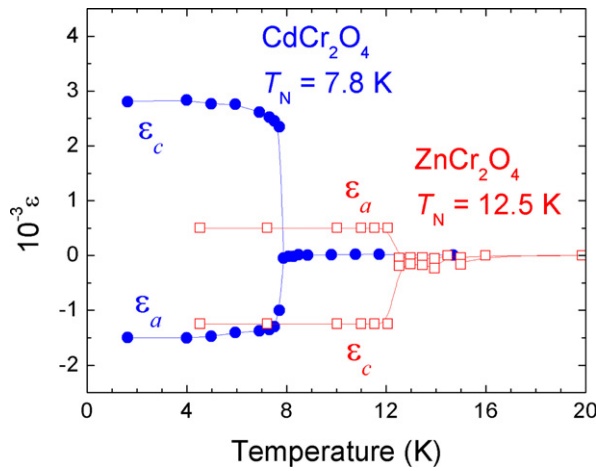


Figure 3. Lattice strains $\epsilon_{a,c} = \frac{(a,c)_{\text{tetra}} - (a,c)_{\text{cubic}}}{(a,c)_{\text{cubic}}}$ versus temperature in ZnCr₂O₄ and CdCr₂O₄.

3. Crystal structure of the Néel states of ACr₂O₄ (A = Zn, Cd)

The magnetic ordering in ACr₂O₄ (A = Zn, Cd) is due to a spin–lattice coupling that partially lifts the magnetic degeneracy. Thus, the magnetic structure that is selected by the system is closely correlated with the lattice distortion that is undertaken. For instance, the commensurate spin structure observed in ZnCr₂O₄ is stabilized by a tetragonal distortion with the contracted *c*-axis [1], while the incommensurate spin structure observed in CdCr₂O₄ is accompanied by a tetragonal distortion with an elongated *c*-axis (see figure 3) [4].

In order to understand the nature of the tetragonal distortion, we have performed synchrotron x-ray measurements on single crystals of ACr₂O₄ (A = Zn, Cd). In the case of ZnCr₂O₄, we have observed the appearance of new superlattice peaks with a $(1/2, 1/2, 1/2)$ characteristic wavevector below T_N , as shown in figure 4. On the other hand, we did not observe any superlattice peaks in CdCr₂O₄ at low temperatures. This tells us that the symmetry of the tetragonal crystal structure is $I4m2$ for ZnCr₂O₄ while it is $I4_1/amd$ for CdCr₂O₄. Thus,

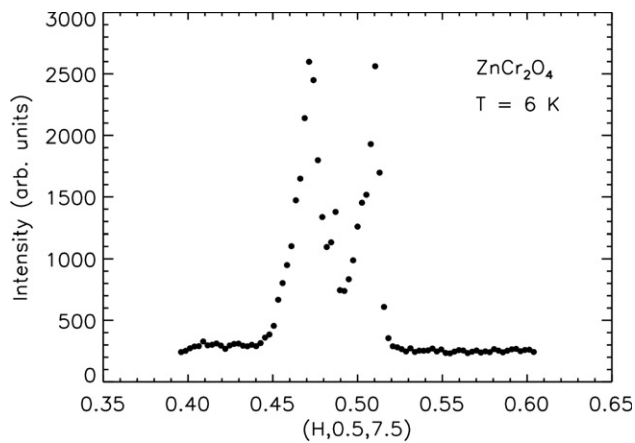


Figure 4. A superlattice peak at (0.5, 0.5, 7.5) observed from a single crystal of ZnCr_2O_4 at 6 K by synchrotron x-ray scattering measurements. The two peaks are due to the crystal domains in the tetragonal ($c < a$) phase.

in ZnCr_2O_4 with its commensurate spin structure, the tetragonal lattice distortion involves more local distortions than a simple overall contraction along the c -axis. In CdCr_2O_4 with its incommensurate spin structure, it seems that a simple elongation along the c -axis occurs at the transition.

4. Discussion

The pyrochlore lattice possesses many ground states and multiple ways of lifting the ground state degeneracy. Here we have shown, by neutron and synchrotron x-ray diffraction, that selection of a particular spin structure is strongly correlated with the particular lattice distortion that the system undertakes. In the tetragonal phase, the crystal structure of ZnCr_2O_4 has $I\bar{4}m2$ symmetry while CdCr_2O_4 has $I4_1/amd$. Thus, in ZnCr_2O_4 the complicated commensurate spin structure is associated with a tetragonal lattice distortion which involves more local distortions than the simple overall contraction along the c -axis. This is in contrast to CdCr_2O_4 , where the incommensurate spin structure is associated with what seems to be a simple elongation along the c -axis which occurs at the transition. Further experimental and theoretical studies are needed to fully understand the mechanism of how the spin and lattice are coupled in this highly frustrated pyrochlore antiferromagnet.

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