Spin–lattice instability to a fractional magnetization state in the spinel HgCr_2O_4

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Magnetic systems are fertile ground for the emergence of exotic states¹ when the magnetic interactions cannot be satisfied simultaneously owing to the topology of the lattice—a situation known as geometrical frustration^{2,3}. Spinel, AB_2O_4 , can realize the most highly frustrated network of corner-sharing tetrahedra^{1–3}. Several novel states have been discovered in spinels, such as composite spin clusters¹ and novel charge-ordered states^{4–6}. Here, we use neutron and synchrotron X-ray scattering to characterize the fractional magnetization state of HgCr_2O_4 under an external magnetic field, H . When the field is applied in its Néel ground state, a phase transition occurs at $H \sim 10$ T at which each tetrahedron changes from a canted Néel state to a fractional spin state with the total spin, S_{tet} , of $S/2$ and the lattice undergoes an orthorhombic to cubic symmetry change. Our results provide the microscopic one-to-one correspondence between the spin state and the lattice distortion.

Field-induced states in frustrated Heisenberg antiferromagnets are not easy to obtain experimentally. This situation arises mainly because the fundamental spin degrees of freedom in this class of materials are nanoscale spin clusters with zero net moment^{1,7,8} and are therefore highly insensitive to external magnetic field. The magnetic field has to be high enough so that the Zeeman energy can break the spin-zero clusters. More often than not, the required field is very high for frustrated Heisenberg antiferromagnets and is not easily accessible for experimental investigations. For instance, ZnCr_2O_4 , a highly studied and almost ideal model system for the pyrochlore lattice with isotropic $S = 3/2$ spins, has strong magnetic couplings between nearest neighbouring Cr^{3+} ions owing to the direct overlap of their half-filled t_{2g} orbitals^{9,10} and thus requires a very high critical field. The strong coupling is evinced by the large Curie–Weiss temperature, $Q_{\text{CW}} = JzS(S+1)/3k_B = -390$ K (refs 3,11), where J is the coupling constant, z is the number of bondings and k_B is the Boltzmann constant. To break such strong magnetic couplings would require an external field of $H_c = gSJ/(g \sim 2$ is the gyromagnetic ratio) that is about 100 T and is out of reach with current technology.

Recently, progress has been made in chemical synthesis to reduce J , which is a very strongly dependent function of Cr^{3+} – Cr^{3+} distance, by replacing Zn with larger Cd and Hg, and thereby increasing the distance between the magnetic Cr^{3+} ions^{12,13}. Bulk

Figure 1 Q - and T -dependence of magnetic neutron scattering from a powder sample of HgCr_2O_4 . **a**, Magnetic neutron diffraction pattern obtained with $H = 0$ and 13.5 T. The elastic intensity was measured below and above the Néel transition temperature T_N and the higher-temperature data were subtracted from the lower-temperature data to remove non-magnetic contributions. **b**, Temperature dependence of the peak intensities of the magnetic Bragg reflections at $(0, 1, 1)$ and $(3/2, 0, 1)$ measured with $H = 0$ and 13.5 T. The data indicate that T_N in the plateau phase increased to 7.5 K. Statistical errors were determined by the Poisson distribution—that is, they are the square root of the intensities.

Table 1 The measured and calculated Q -integrated intensities of magnetic Bragg peaks for the HgCr_2O_4 polycrystalline sample obtained with $H = 0$ and 13.5 T. The intensities were normalized to the integrated intensity of the nuclear (2, 2, 2) Bragg reflection. The calculated intensities were obtained with the following frozen moments: for $H = 0$ data, $\langle M_{ab} \rangle = 1.02(2) \mu_B/\text{Cr}^{3+}$ lying on the bc plane for the $\{1/2, 0, 1\}$ reflections, and for the $\{1, 0, 0\}$ reflections, $\langle M_c \rangle = 1.42(4) \mu_B/\text{Cr}^{3+}$ along the a axis for the $\{1, 0, 0\}$ reflections. Assuming that the zero-field Néel phase is a single phase, the magnitude of the frozen spin is $\langle M \rangle = 1.74(6) \mu_B/\text{Cr}^{3+}$. For $H = 13.5$ T data, $\langle M \rangle = 2.22(8) \mu_B/\text{Cr}^{3+}$ along H .

Q	$H = 0$ T		$H = 13.5$ T	
	$I^{\text{obs}}(Q)$	$I^{\text{cal}}(Q)$	$I^{\text{obs}}(Q)$	$I^{\text{cal}}(Q)$
(1/2, 1, 0)	0.028(3)	0.029	0	0
(0, 1, 1)	0.049(3)	0.050	0.16(2)	0.15
(1, 1, 1)	0	0	0.07(1)	0.06
(3/2, 0, 1)	0.090(1)	0.086	0	0
(1, 0, 2)	0.058(6)	0.057	0.17(2)	0.19
(-1/2, 2, 1)	0.061(6)	0.061	0	0
(2, 1, 1)	0	0.01	0.07(2)	0.08
(5/2, 0, -1)	0.035(6)	0.038	0	0
(0, 3, 1)	0	0.016	0.03(2)	0.04
(2, 2, 2)	0	0	0.04(2)	0.04
(3, 0, 2)	0	0.008	0.04(1)	0.05

magnetization measurements on ACr_2O_4 ($A = \text{Cd}, \text{Hg}$) under pulsed fields up to 47 T have revealed field-induced transitions to half-magnetization plateau phases in the low-temperature Néel phase. For CdCr_2O_4 with $Q_{\text{CW}} = -88$ K, the half-magnetization plateau phase occurs for $H > 28$ T (ref. 12). For HgCr_2O_4 with $Q_{\text{CW}} = -32$ K, on the other hand, the half-magnetization plateau

phase occurs for $10 \text{ T} < H < 28 \text{ T}$ and the full magnetization plateau phase for $H > 40 \text{ T}$ (ref. 13). The hysteretic nature of the field-induced transitions is observed on ramping down the field, indicating that the transitions are first order¹³. The synthesis of HgCr_2O_4 is significant, even though it is in a polycrystalline form, because its critical field, ~ 10 T, can be achieved at neutron and X-ray scattering facilities and thereby it enables us to study in detail the nature of the half-magnetization state of the frustrated Heisenberg antiferromagnets. The key finding of our neutron and X-ray diffraction measurements on a polycrystalline sample of HgCr_2O_4 is that the stability of the half-magnetization state over $10.5 \text{ T} < H < 28 \text{ T}$ is due to a spin–lattice coupling that drives the spins and lattice to a field-induced state with cubic $P4_332$ symmetry. We explain the field-induced phase transition in terms of a simple modulation of the nearest-neighbour (NN) spin interactions due to lattice distortion.

Several different mechanisms to reduce frustration in the absence of an external magnetic field have been studied^{11,13–22}—for instance, the Jahn–Teller distortion in orbitally degenerate AV_2O_4 ($A = \text{Zn}$ (refs 18–20), Cd (ref. 21)) and the spin-Peierls-like transition in ACr_2O_4 ($A = \text{Zn}$ (ref. 11), Cd (ref. 22)). These are demonstrated by sudden drops in their bulk susceptibility measurements without field, which involve cubic-to-tetragonal distortions. HgCr_2O_4 also shows similar behaviour at low temperatures to the other chromium spinels. On cooling without field, HgCr_2O_4 undergoes an orthorhombic distortion with $Fddd$ symmetry at the Néel ordering temperature $T_N = 6$ K (ref. 13). Elastic magnetic neutron scattering data obtained in zero field (blue circles in Fig. 1a) show that in the low-temperature phase the spins order long range with two characteristic magnetic wavevectors $\mathbf{Q}_M = (1/2, 0, 1)$ and $(1, 0, 0)$. As listed in Table 1, the relative intensities of different magnetic reflections tell us that the $\{1, 0, 0\}$ peaks are due to a collinear spin structure where spins are parallel to the characteristic wavevector (the a axis when we choose $\mathbf{Q}_M = (1, 0, 0)$) (Fig. 2b). On the other hand, the $\{1/2, 0, 1\}$ reflections are due to either a collinear or a non-collinear spin structure where spins are lying on the plane perpendicular to the doubling axis (the a axis for $\mathbf{Q}_M = (1/2, 0, 1)$) (Fig. 2a). Note that in both spin structures, each tetrahedron is made of two up-spins and two down-spins, and has total zero spin. Having two different characteristic wavevectors suggests that the system may have two separate magnetic phases with $\mathbf{Q}_M = (1, 0, 0)$ and $(1/2, 0, 1)$, respectively. It is also possible that the Néel state of HgCr_2O_4 has a single magnetic phase where the a component of the spin orders with the $\mathbf{Q}_M = (1, 0, 0)$, whereas their bc components order with $(1/2, 0, 1)$. A frozen moment, $\langle M \rangle$, was estimated from the comparison of the model and data to be $1.74(6) \mu_B/\text{Cr}^{3+}$, which is less than the value of $gS\mu_B/\text{Cr}^{3+}$ with $S = 3/2$. This discrepancy indicates that strong frustrations exist even in the zero-field Néel phase.

Now let us turn to the half-magnetization plateau phase of HgCr_2O_4 . With $H = 13.5$ T that puts the system well in the half-magnetization state, we measured the Q -dependence of the elastic neutron scattering intensity at $T = 3.2$ and 10 K, below and above the transition. The 10.5 K data were subtracted from the 3.2 K data to obtain the magnetic contribution alone, which is shown as red circles in Fig. 1a. Strikingly, the $\{1/2, 0, 1\}$ magnetic peaks that were present at $H = 0$ have completely disappeared, whereas the $\{1, 0, 0\}$ magnetic peaks became stronger. Furthermore, new magnetic peaks appeared at several nuclear Bragg reflection points such as $(1, 1, 1)$, $(1, 3, 1)$ and $(2, 2, 2)$ but not at other nuclear Bragg reflection points such as $(2, 2, 0)$. Note that the field-induced transition is rather sharp even though the sample is polycrystalline (Fig. 3a,b). This suggests that the magnetic interactions are nearly isotropic even in the low-temperature Néel phase, and regardless

Figure 2 Possible spin structures of the Cr^{3+} ($3d^3$) ($S = 3/2$) moments in HgCr_2O_4 . **a,b**, At ambient field for $\mathbf{Q}_M = (1/2, 0, 1)$ (**a**) and $\mathbf{Q}_M = (1, 0, 0)$ (**b**). **c,d**, For the magnetization plateau state corresponding to the structures for $\mathbf{Q}_M = (1, 0, 0)$ with $R\bar{3}m$ (**c**) and $P4_332$ (**d**) symmetry. Blue and red spheres represent up and down spin directions, respectively. In **d**, the distortion of each tetrahedron is exaggerated for display. The spins along the (110) chain directions in the bc planes in those models are $++--++--$ for the models in **a**, **b** and **d**, respectively.

Figure 3 External magnetic field (H) effects on magnetic and nuclear Bragg scattering from a powder sample of HgCr_2O_4 . **a, b**, H dependence of the neutron scattering intensities at various reflections measured at 3.2 K, at (2, 2, 0) and (1, 1, 1) (**a**) and at (3/2, 0, 1), (0, 1, 1) and (2, 1, 1) (**b**). As H increases up to 9 T, the neutron diffraction pattern does not change (Fig. 1a). However, the (111) Bragg intensity increases by $\sim 90 \pm 40$ counts per 5 min. This increase is due to canting of spins along H , and we estimate the canting angle at 9 T to be $17(4)^\circ$. The field-induced transition to the half-magnetization plateau phase occurs abruptly at $H \sim 10$ T. **c, d**, Synchrotron X-ray diffraction data measured at several different temperatures with different H values: the nuclear (10, 4, 2) Bragg reflection (**c**); the nuclear (4, 4, 1) and (5, 2, 2) reflections (**d**). Statistical errors were determined by the Poisson distribution.

of the crystalline orientations, on application of the external magnetic field, the spins reorient along the field. Such a weak anisotropy is due to the absence of orbital degeneracy in the system and the subsequent negligible spin–orbit couplings. The fact that the magnetization plateau phase over $10 \text{ T} < H < 28 \text{ T}$ has $\langle M \rangle \sim (gS/2)\mu_B/\text{Cr}^{3+}$ suggests that each tetrahedron has three up-spins and one down-spin. With such tetrahedra, we can construct numerous spin structures for the lattice of corner-sharing tetrahedra with several different characteristic wavevectors. Among them, there are two non-equivalent spin configurations that would produce magnetic scattering at the $\{1, 0, 0\}$ reflection points: one with rhombohedral $R\bar{3}m$ symmetry (Fig. 2c) and the other with cubic $P4_332$ symmetry (Fig. 2d). In the magnetic structure with $R\bar{3}m$ symmetry, spins on the Kagomé planes (blue spheres in Fig. 2c) along the $\langle 111 \rangle$ direction are up-spins (parallel to H), whereas spins on the triangular planes (red spheres in Fig. 2c) are down-spins (antiparallel to H). On the other hand, in the structure with $P4_332$ symmetry, the nearest neighbouring down-spins are separated by distances of $d_{\downarrow\downarrow}^{\text{NN}} = \{-1/4, 1/4, 1/2\}$, and the second-nearest neighbouring down-spins are separated by $d_{\downarrow\downarrow}^{\text{second}} = \{-1/2, 3/4, 1/4\}$. The $R\bar{3}m$ symmetry can be ruled out because it does not allow scattering at the observed (1, 1, 1) reflection, whereas it should produce magnetic scattering at the (2, 2, 0) reflection where no field-induced magnetic signal has been observed (see Figs 1a and 3a). On the other hand, all of the observed field-induced magnetic reflections shown in Figs 1 and 3 are allowed for $P4_332$ symmetry. A quantitative comparison between

the experimental data and the model calculation is summarized in Table 1, which shows the excellent agreement between the data and the $P4_332$ spin structure with the frozen moment of $\langle M \rangle = 2.22(8)\mu_B/\text{Cr}^{3+}$.

Why is the half-magnetization phase stable over such a wide range of H ? To address this issue, we carried out synchrotron X-ray diffraction measurements with different fields and temperatures. Figure 3c shows that at 3.2 K ($T < T_N$), for $H < 10$ T the (10, 4, 2) reflections split into three peaks because, as discussed earlier, the lattice in the low-field Néel phase is orthorhombic. However, for $H > 10.5$ T the peaks become one peak, which indicates that the external magnetic field changes the crystal structure from orthorhombic to cubic simultaneously as the system enters the half-magnetization plateau phase. Furthermore, as shown in Fig. 3d, new nuclear peaks appeared at (4, 4, 1) and (5, 2, 2) reflections. This indicates that the crystal structure of the field-induced half-magnetization state has the same $P4_332$ symmetry as the magnetic structure. In the $Fddd$ symmetry, Cr^{3+} ions sit on crystallographically equivalent $16d$ symmetry sites that have inversion symmetry. On the other hand, in the $P4_332$ symmetry, Cr ions occupy two distinct symmetry sites, $4b$ and $12d$. The $4b$ site is the common vertex of two neighbouring tetrahedra each of which is composed of three $12d$ sites and one $4b$ site. The tetrahedra are twisted and contracted along the local $\langle 111 \rangle$ direction that connects the $4b$ site and the centre of the $12d$ triangles: the inversion symmetry is lost. Instead, the $4b$ site has a three-fold symmetry about a $\langle 111 \rangle$ axis and the $12d$ site has a two-fold symmetry along

a $\langle 110 \rangle$ axis. Thus, there are two different Cr–Cr bond lengths in each Cr tetrahedron: one between the $12d$ site ions and the other between the $4b$ and $12d$ site ions. By comparing an X-ray scattering peak corresponding to the $\{6, 2, 0\}$ reflections with another peak corresponding to the $\{5, 4, 0\}$, $\{4, 4, 3\}$ and $\{6, 2, 1\}$ reflections, we estimate the difference between the two bond lengths to be about 2%. Analysis of a series of chromium oxides indicates that J decreases when the distance between the Cr ions increases²³. This implies that the distortion yields stronger antiferromagnetic NN couplings, J_1 , between the $12d$ and $4b$ sites, and weaker antiferromagnetic NN couplings, J'_1 , between the $12d$ and $12d$ sites. This NN spatial exchange anisotropy will lift the degeneracy of the pyrochlore lattice composed of the excited tetrahedra and favour the spin structure that has the same cubic $P4_332$ symmetry as the lattice, that is, the down-spin and the up-spin occupy the $4b$ and the $12d$ site, respectively (see Fig. 2d). Therefore, we conclude that the half-magnetization state in HgCr_2O_4 is achieved and stabilized by the field-induced spin–lattice coupling that changes the system from the orthorhombic ($Fddd$) Néel state with total zero-spin ($S_{\text{tet}} = 0$) tetrahedra to the cubic ($P4_332$) Néel state with $S_{\text{tet}} = S/2$ tetrahedra.

Previous studies have shown that spin–lattice coupling can lift the ground-state degeneracy in frustrated magnets^{11–17}. However, the detailed microscopic mechanism, that is, the one-to-one correspondence between the selected Néel state and the local lattice distortion, has not yet been fully understood owing to the complexity of the ensuing spin and lattice structures. Our neutron and synchrotron X-ray studies demonstrate for the first time how the spin–lattice instability leads to a particular lattice distortion and how the distortion favours the particular spin structure. These results enable us to test the validity of several theoretical models proposed towards understanding the spin–lattice coupling in frustrated magnets. For instance, two spin structures with $R\bar{3}m$ and $P4_332$ symmetries have been theoretically proposed for the field-induced half-magnetization state of ACr_2O_4 (refs 24–26). The $R\bar{3}m$ spin structure proposed in ref. 24 is preferred if the lattice undergoes a simple contraction along the $\langle 111 \rangle$ direction because such distortion will yield stronger antiferromagnetic NN interactions between the Kagomé (occupied by up-spins) and triangular (down-spins) planes, and weaker antiferromagnetic NN interactions in the Kagomé planes. On the other hand, the $P4_332$ spin structure proposed in ref. 25 based on a purely magnetic mechanism is preferred if the local $\langle 111 \rangle$ lattice contraction is not uniform but propagates over the lattice with $P4_332$ symmetry, as has been observed in HgCr_2O_4 . However, the fact that a lattice distortion occurs simultaneously with the magnetic symmetry breaking strongly indicates the necessity of a lattice distortion for the transition²⁶.

METHODS

A polycrystalline sample of HgCr_2O_4 weighing about 2 g was pressed into a pellet and used for neutron and synchrotron X-ray scattering measurements. The neutron scattering measurements under magnetic field were carried out on the thermal neutron triple-axis spectrometer TAS2 at the JRR-3 reactor at the Japan Atomic Energy Agency, whereas measurements with no field were

carried out at the cold-neutron triple-axis spectrometer SPINS at the National Institute of Standards and Technology. The particular magnet used at TAS2 was a split-pair superconducting magnet cooled by cryocoolers and can reach fields of up to 13.5 T. The fixed initial neutron energies were 14.7 and 5 meV on TAS2 and SPINS, respectively. Contamination from higher-order beams was effectively eliminated using the polycrystalline graphite and cooled Be filters at TAS2 and at SPINS, respectively. Synchrotron X-ray scattering was carried out on BL19LXU at Spring-8 using an energy of 30 keV.

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Competing financial interests

The authors declare no competing financial interests.

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