Half-magnetization plateaux in Cr spinels

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Abstract. Magnetization plateaux, visible as anomalies in magnetic susceptibility at low temperatures, are one of the hallmarks of frustrated magnetism. An extremely robust half-magnetization plateau is observed in the spinel oxides CdCr₂O₄ and HgCr₂O₄, where it is accompanied by a substantial lattice distortion. We give an overview of the present state experiment for CdCr₂O₄ and HgCr₂O₄, and show how such a half-magnetization plateau arises quite naturally in a simple model of these systems, once coupling to the lattice is taken into account.

1. Introduction

Spinels AB₂X₄, where A and B are metal ions and X= {O, S, Se...}, are among the most ubiquitous of crystal structures. While the undistorted spinel lattice has overall cubic symmetry, the network of B–ion sites forms a highly frustrated pyrochlore lattice, built of corner–sharing tetrahedra. Simple nearest–neighbour interactions on the pyrochlore lattice cannot select a unique magnetic or charge ordered ground state. It is this fact which makes the properties of magnetic spinels — and in particular their high field behaviour — so interesting.

Chromium spinel oxides ACr₂O₄ offer the opportunity to study magnetic frustration in the absence of charge and orbital effects. The Cr ion has a strong Hund’s rule coupling and lives in an octahedral crystal field. Therefore, if A={Zn, Cd, Hg...} is a divalent metal ion, the Cr will be in a [Ar]3d⁵ high–spin state for which all of its t₂g symmetry orbitals are singly occupied, and all of the e_g symmetry orbitals are empty — see Figure 1. The resulting bulk state is a Mott insulator in which all charge and orbital effects are quenched. The magnetic properties of a spinel oxide like CdCr₂O₄ therefore depend by the way in which a set of S = 3/2 spins behave on a pyrochlore lattice.

This is a far from simple problem. The minimal magnetic model suggested by the chemical structure of ACr₂O₄ is

\[ \mathcal{H}_0 = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - h \sum_i \mathbf{S}_i \]
Figure 1. Structure of spinel oxide \( \text{ACr}_2\text{O}_4 \). \( \text{O}^{2-} \) ions shown in yellow define an octahedral environment for the \( \text{Cr}^{3+} \) ions, which have a full \( t_{2g} \) shell of \( 3d \) electrons with moment \( S = 3/2 \). Detailed control of lattice parameters can be achieved by substitution of different A-site metal ions.

Figure 2. Cubic unit cell of pyrochlore lattice, showing first– and third–neighbour bonds.

where \( J_1 \) is a Heisenberg exchange interaction, \( h \) the applied magnetic field and the sum \( \langle ij \rangle_1 \) runs over the nearest–neighbour bonds of a pyrochlore lattice (Figure 2). In conventional magnetic insulators, exchange interactions select a unique ground state for which the classical energy per bond is minimized. However, because of the special corner–sharing geometry of the pyrochlore lattice, the classical energy of any state can be rewritten as

\[
E_0 = 4J_1 \sum_{\text{tetr.}} \left( \frac{M - h}{8J_1} \right)^2 - \frac{h^2}{16J_1} + \text{const.} \tag{2}
\]

where \( M = (S_1 + S_2 + S_3 + S_4)/4 \) is the magnetization per spin of a given tetrahedron and the sum runs over all tetrahedra. The three components of \( M = (M_x, M_y, M_z) \) fix only three of the four independent classical spin angles per tetrahedron. Thus nearest–neighbour interactions do not select a unique ground state, but rather an entire manifold of states for which \( M \equiv h/8J_1 \) in every tetrahedron. Cr spinels can therefore be expected to exhibit very exotic magnetic properties.

At high temperatures, Cr spinels exhibit very little anisotropy in their magnetism. Their susceptibility has the form \( \chi = C/(T + \theta_{\text{CW}}) \), where \( C \approx 1.9 \) emu/mol K is in the range expected for a \( S = 3/2 \) moment with \( g_L \approx 2.0 \). Values of \( \theta_{\text{CW}} \) vary from 370 K in MgCr\(_2\)O\(_4\) to 32 K in HgCr\(_2\)O\(_4\) (see Table 1), suggesting dominantly antiferromagnetic (AF) exchange interactions between Cr spins. However the Curie–Weiss form of the magnetic susceptibility persists down to very low temperatures, and magnetic order is achieved only for \( T < T_N \ll \theta_{\text{CW}} \), where it is accompanied by a structural transition. In CdCr\(_2\)O\(_4\), ZnCr\(_2\)O\(_4\) and MgCr\(_2\)O\(_4\), this changes the overall crystal structure from cubic to tetragonal and introduces a weak easy–plane anisotropy in the magnetism; in HgCr\(_2\)O\(_4\) the change is from cubic to orthorhombic (Table 1).
Table 1. Ordering temperatures and crystal symmetries of Cr spinels in zero applied field. Values of $T_N$ and $\theta_{CW}$ are for samples prepared by Ueda et al. [2]. The nearest neighbour exchange $J_1$ is estimated from $\theta_{CW} \approx zJ_1S(S+1)/3$.

|       | MgCr$_2$O$_4$ [3] | ZnCr$_2$O$_4$ [4] | CdCr$_2$O$_4$ [3] | HgCr$_2$O$_4$ [2] |
|-------|------------------|--------------------|-------------------|-------------------|
| $T_N$ [K] | 12.5             | 12                 | 8                 | 5.8               |
| $\theta_{CW}$ [K] | 370              | 390                | 70                | 32                |
| $T_N/\theta_{CW}$ | 0.03             | 0.03               | 0.11              | 0.18              |
| $J_1$ [K] | 49               | 53                 | 9                 | 4                 |

Unit cell ($T < T_N$) tetragonal, $c < a$  tetragonal, $c < a$ tetragonal, $c > a$ orthorhombic

The thermodynamic properties of ACr$_2$O$_4$ at high temperature and in zero field are typical of a wide range of frustrated magnets, and entirely compatible with the minimal model Equation 1. The special feature of these systems is the structural transition accompanying magnetic order at low temperature. This enables the system to lift the infinite classical ground state degeneracy exhibited by Equation (2) — a mechanism dubbed order by distortion [5].

The question addressed in this paper is what happens to the magnetic properties of Cr spinels in applied magnetic field. The scale of exchange interactions in the Cd and Hg compounds implies the bulk of their magnetization process occurs over a range of fields now routinely accessible in large pulsed magnets. As we shall see, the order by distortion mechanism remains active in applied magnetic field, and has some very dramatic consequences.

2. Magnetization process and half–magnetization plateau

The magnetization process $M(h)$ of a classical Heisenberg AF on the pyrochlore lattice at zero temperature is linear up to a saturation field of $8J_1$ — c.f. Equation (2). Under the assumption that longer range interactions are weak, values of $J_1 \approx 9$ K and $J_1 \approx 4$ K can be inferred from $\theta_{CW} \approx zJ_1S(S+1)/3$ for CdCr$_2$O$_4$ and HgCr$_2$O$_4$, respectively (Table 1). These suggest that the saturation field is experimentally accessible for both compounds.

Measurements of $M(h)$ for CdCr$_2$O$_4$ and ZnCr$_2$O$_4$ were initially made in pulsed magnetic fields of up to 48 T at the ultrahigh magnetic field facility of the Institute for Solid State Physics (ISSP) in Tokyo [3]. More recently these measurements have been repeated for a range of Cr spinels, including HgCr$_2$O$_4$ [2]. Measurements on CdCr$_2$O$_4$ have been made at fields of up to 70 T at the High Magnetic Field Laboratory in Osaka [7], and preliminary measurements on the same system at fields of up to 100 T made at ISSP [8].

Results for a variety of Cr spinels taken at ISSP are shown in Figure 8. The magnetization of all compounds is indeed linear over a wide range of (low) magnetic fields. However both CdCr$_2$O$_4$ and HgCr$_2$O$_4$ exhibit a broad magnetization plateau for intermediate values of magnetic field. The plateau in CdCr$_2$O$_4$ has its onset at 28 T [6], and extends up to approximately 60 T [5]. It has a magnetization of 1.5$\mu_B$ per Cr — exactly half the full moment of an $S = 3/2$ Cr$^{3+}$ ion. The plateau in HgCr$_2$O$_4$ extends from 10 T to 27 T, with a saturation field approaching 50 T. Once again the plateau occurs for exactly half the saturation magnetization. It is somewhat more rounded than in CdCr$_2$O$_4$; this can be attributed to disorder in the polycrystalline sample used [2].

The transition into the plateau state is strongly first–order in both cases, displaying a marked hysteresis, and is accompanied by a large change in the unit cell volume of $|\Delta V|/V \approx 0.33 \times 10^{-3}$ in CdCr$_2$O$_4$ and $|\Delta V|/V \approx 1.6 \times 10^{-3}$ in HgCr$_2$O$_4$ [2]. In CdCr$_2$O$_4$, where good single crystals are available, a colossal negative magnetostriction $\Delta L/L = -4 \times 10^{-4}$
can be resolved parallel to field in the [111] direction, accompanied by a magnetostriction of similar order in the [110] direction (i.e. perpendicular to the field) — see Figure 4. This scale of magnetostriction would not be unusual in a system with Jahn–Teller active $e_g$ orbitals, but is exceptional for an oxide in which orbital degrees of freedom are quenched. Taken together these, results suggest that the magnetization plateau has its origin in a very strong exchange striction. Coupling to the lattice appears to be somewhat stronger in HgCr$_2$O$_4$ than in CdCr$_2$O$_4$. This is also reflected in a higher ratio of $T_N/\theta_{CW}$ for the magnetically ordered phase in zero field (Table 1).

The transition out of the plateau state at high field is of second order in both compounds. Above this second critical field, the magnetization process is again approximately linear, suggesting that the new phase arises simply through a canting of the ordered moments of the plateau phase. For HgCr$_2$O$_4$, it is possible to map out the entire magnetization process up to saturation at $h \approx 45$ T — see Figure 3. A further, first-order magnetic phase transition is observed at $h \approx 37$ T. While no direct structural data measurements presently exist, this is presumably also accompanied by a change in crystal structure or bond length.

As the temperature of the sample is raised, the magnetization plateau acquires a finite slope. Above a characteristic transition temperature $T_c \approx 10$ K (CdCr$_2$O$_4$), $T_c \approx 7$ K (HgCr$_2$O$_4$) the plateau washes out entirely and the magnetization process $M(h)$ remains linear up to fields approaching saturation. Thermal fluctuations clearly contribute to the stability of the plateau state; its width in $h$ increases with increasing temperature $T$, and its transition temperature is somewhat higher than that for the (canted) Néel order at low fields. Quantum and thermal fluctuations are known to favour collinear spin configurations [9], and in the light of these results it seems natural to attribute the half–magnetization plateau to a collinear “$uuud$” spin configuration with three up and one down spins per tetrahedron. It is also interesting to note that the critical field for the transition from the canted Néel state into the half–magnetization plateau is almost independent of temperature.

In summary — the magnetic phase diagram for HgCr$_2$O$_4$ deduced from pulsed field measurements is shown in Figure 5. It exhibits four phases, which we can identify as:

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**Figure 3.** Magnetization processes of a variety of single crystal and polycrystalline samples of Cr spinels taken at 1.8K, showing dramatic half–magnetization plateaux in CdCr$_2$O$_4$ and HgCr$_2$O$_4$. Data taken from [2].

**Figure 4.** Colossal negative magnetostriction accompanying first–order transition into half–magnetization plateau state in CdCr$_2$O$_4$. Data taken from [6].
Magnetic phase diagram of HgCr$_2$O$_4$ as a function of temperature, taken from [2]. Solid lines denote first order phase transitions; dashed lines second order.

Phase diagram of effective spin model Equation (4) taken from [14], as a function of magnetic field $h$ and dimensionless coupling constant $b$. Solid lines denote first order phase transitions; dashed lines second order. All order parameters can be classified in terms of the irreps of the tetrahedral symmetry group $T_d$.

- a canted Néel state at low field
- a collinear half–magnetization plateau state for intermediate field
- a second canted state approaching saturation
- a saturated paramagnetic state for large magnetic field

Recent elastic neutron scattering data suggest that the half–magnetization plateau state in HgCr$_2$O$_4$ has cubic symmetry and a 16–sublattice magnetic order [10]. The saturated paramagnetic state at high field is, presumably, also cubic. We return to these points below.

3. Theory of half–magnetization plateau
Magnetization plateaux are very common in frustrated magnets. They are known to occur, for example, in both the Ising [11] and Heisenberg [12, 13] models on the triangular lattice. The conventional explanation for magnetization plateaux is that quantum and/or thermal fluctuations act to favour a collinear state in which all spins point either parallel or antiparallel to the applied magnetic field. This state may (or may not) exhibit long range magnetic order, but since the number of spins in the system is an integer, it must exhibit a magnetization which is a rational fraction of the full moment — $M = 1/3$ in the case of the triangular lattice. This leads to plateaux which are weak (being a fluctuation effect), and uncorrelated with lattice distortion.

The essential features of the half–magnetization plateau seen in Cr spinels are its extreme robustness and the large accompanying lattice distortion. Any model which seeks to explain it should therefore include the coupling between spins and the lattice, as well as the interactions...
between spins. We therefore consider the extended Heisenberg model

\[ \mathcal{H} = \sum_{\langle ij \rangle} \left[ J_1 (1 - \alpha \rho_{ij}) S_i S_j + \frac{K}{2} \rho_{ij}^2 \right] - h \sum_i S_i , \]  

(3)

where \( K \) is an elastic constant, and the bond variable \( \rho_{ij} \) measures the change in separation of two Cr ions relative to the state with the lowest elastic energy [14].

The physics of the system is most easily demonstrated if we make two further simplifying assumptions — i) we treat the spins as classical variables \( S_i = (\sin \theta_i \cos \varphi_i, \sin \theta_i \sin \varphi_i, \cos \theta_i) \) and ii) we assume that the spins couple to phonons with crystal momentum \( \mathbf{q} = 0 \), i.e. that there is an overall 4-sublattice order. Under these assumptions, we can eliminate the lattice variables \( \rho_{ij} \) from the problem entirely and work with the pure spin model

\[ \mathcal{H} = J_1 \sum_{\langle ij \rangle} \left[ S_i S_j - b (S_i S_j)^2 \right] - h \sum_i S_i . \]  

(4)

where \( b = J_1 \alpha^2 / 2K \) is a dimensionless measure of spin–lattice coupling. The biquadratic term in Equation (4) is of a form which favours coplanar or collinear spin configurations, and as such is known to mimic quantum and thermal fluctuations [2]. A more general choice of spin–lattice Hamiltonian can lead to more complex interactions in the effective spin model. However these do not change the essential physics of the problem, and for our purposes it will generally be sufficient to enforce four–sublattice order by adding a ferromagnetic (FM) third–neighbour interaction \( J_3 < 0 \)

\[ \Delta \mathcal{H}_3 = J_3 \sum_{\langle ij \rangle} S_i S_j \]  

(5)

to the effective spin model Equation (4) (see Figure 2). The consequences of relaxing the assumptions (i) and (ii) will be discussed below.

The phase diagram and magnetization process of the effective spin model Equation (4) at \( T = 0 \) are shown in Figure 3 and Figure 7. The model exhibits four dominant phases:

- a 2:2 coplanar canted state with tetragonal symmetry for low field
- a 3:1 collinear \((uuud)\) half–magnetization plateau state with trigonal symmetry for intermediate field
- a 3:1 coplanar canted state with trigonal symmetry for fields approaching saturation
- a saturated \((uuuu)\) state with cubic symmetry for large magnetic field

These can be classified in terms of the two–dimensional \( E \), three–dimensional \( T_2 \) and trivial \( A_1 \) irreducible representations (irreps) of the tetrahedral symmetry group \( T_d \) [14]. The predicted magnetization \( M(h) \) for \( b \approx 0.2 \) is in striking correspondence with experiments on Cr spinels.

Furthermore, we can calculate the changes in bond lengths which occur in each of these phases, and do indeed find a giant magnetostriction on entering the half–magnetization plateau, as seen in experiment. Interestingly, the (negative) sign of the magnetostriction seen in CdCr2O4 implies that the strength of AF exchange interactions \( J_1 \) increases rather than decreases with bond length, i.e. \( \alpha < 0 \) in Equation (3). This is by no means impossible in a complex magnetic oxide with competing exchange paths, and appears to be compatible with the sign of the distortion seen in the tetragonal ground state [15].

The effective spin model Equation (4) is also amenable to low temperature expansion and Monte Carlo simulation techniques [16, 17]. Thermal fluctuations do not significantly alter the phase diagram for parameters relevant to experiment, but impose a finite transition temperature on
Figure 7. Magnetization process of effective spin model Equation (4) taken from [14], for a range of values of the dimensionless spin–lattice coupling \( b \).

Figure 8. Magnetic phase diagram of effective spin model Equation (4) for \( J_3 = -0.05 \) and \( b = 0.1 \) at finite temperature, taken from [17]. Both \( T \) and \( h \) are measured in units of \( J_1 \).

each of the phases described above. The predicted magnetic phase diagram is shown in Figure 8. Once again the agreement with experiment (Figure 5) is, for such a simple theory, striking.

The four–sublattice theory presented above is almost certainly too simple, in the sense that the conditions in real Cr spinels need not favour four–sublattice states. Indeed, where known, the Néel and half–magnetization phases of Cr spinels invariably have a more complex structure. However the present theory is none the less very successful in explaining their magnetization process \( M(h) \). This apparent piece of serendipity is in fact a profound consequence of the extreme frustration of the pyrochlore lattice. The theory presented above accurately describes the behaviour of individual tetrahedra in applied magnetic field. These tetrahedra may be assembled into arbitrarily complex magnetically ordered states without qualitative change in their thermodynamic properties (e.g. magnetization). In fact it is even possible to relax the condition of long range magnetic order entirely, and obtain a spin liquid state which exhibits much the same magnetization process [16].

4. Concluding comments
The magnetization plateau in Cr spinels is a very recent discovery, and there is every reason to believe that much more can be learnt about Cr spinels and other related systems. The mechanism proposed to explain the plateau — a coupling to lattice degrees of freedom — is very general and can be expected to function in many other frustrated magnets and magnetic molecules.

Many theoretical avenues also remain open, including the examination of quantum effects [18], the ab initio calculation of spin and lattice interactions [19], and the extension of symmetry analysis and Monte Carlo simulation to more realistic models [20].

Half–magnetization plateaux are only one of the many interesting new consequences of frustration seen in spinel oxides. However the possibility of conducting further experiments
and making a quantitative comparison with theory means that they remain one of the most rewarding problems to study.

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