Magnetic-Field Induced Transition to the 1/2 Magnetization Plateau State in the Geometrically Frustrated Magnet $CdCr_2O_4$

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The magnetization of the geometrically frustrated spinel $CdCr_2O_4$ was measured in pulsed fields of up to 47 T. We found a metamagnetic transition to a very wide magnetization plateau state with one half of the full moment of $S = 3/2$ Cr^{3+} at 28 T, independent of the field direction. This is the first observation of magnetization plateau state realized in Heisenberg pyrochlore magnet. The plateau state can be ascribed to a collinear spin configuration with three-up and one-down spins out of four spins of each Cr tetrahedron. A large magnetostriction is observed at the transition in spite of the negligible spin-orbit couplings. We argue that spin frustration plays a vital role in this large spin-lattice coupling.

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Antiferromagnets with geometrical frustration suffer from the presence of strongly degenerating low lying magnetic excitations, which prevents the system from finding a unique ground state. As a result, they remain paramagnetic even at temperatures far below the point where classical theory predicts long-range ordering. The entropy, however, should be zero at 0 K according to the third law of thermodynamics and, in fact, it eventually undergoes phase transitions to ordered states. The ordered states marginally achieved are often very exotic and have attracted considerable interest. The pyrochlore lattice, which consists of corner sharing tetrahedra, is one of the well-known playgrounds for strong geometrical frustration. It is realized not only in pyrochlore compounds but also in a sublattice of spinel compounds. Recent explorations of spinels and pyrochlores unveiled many exotic ground states that are almost certainly associated with frustration, including a novel spin liquid state [1], a spin Jahn-Teller state [2,3], a spin ice state [4,5], and a heavy fermion metal [6,7].

$CdCr_2O_4$ and $ZnCr_2O_4$ crystallize in a normal cubic spinel structure AB_2O_4, where chromium ions occupy the B sublattice and form a pyrochlore lattice. Because of the geometrical frustration, these spinels remain paramagnetic down to low temperatures and form a spin liquid state with well developed spin hexagons [1]. It has been reported that they experience transitions to a noncollinear antiferromagnetic state [8] at 7.8 K and 12 K [9,10], respectively, which are accompanied by a structural transition from cubic to tetragonal. Structural transitions from cubic to tetragonal are quite common in spinel oxides and are usually regarded as a textbook example of Jahn-Teller effect to reduce orbital degeneracy. However, since the Cr^{3+} ions have three electrons in their triply degenerate t_{2g} orbital, there remains no orbital degree of freedom. This makes these chromium spinels distinct from the conventional spinel oxides and the driving force of structural phase transition should be ascribed to something other than orbital degeneracy. It has been proposed that strong spin degeneracy due to geometrical frustration is responsible for the structural phase transition from cubic to tetragonal: In order to reduce the spin degeneracy, the lattice spontaneously distorts and the spin system simultaneously switches from a paramagnetic spin liquid to an antiferromagnetically ordered state. Recent x-ray diffraction measurements revealed that the structure below the magnetic ordering is much more complicated than the simple tetragonal commonly observed in spinel oxides, in accord with the complicated spin structure [11,12]. Indeed, experimental result of $ZnCr_2O_4$ [13] can be interpreted in terms of three-dimensional analog of the spin-Peierls transition. This spin driven structural phase transition can be described as a spin Jahn-Teller transition.

The application of a magnetic field will align the spins and therefore suppress the magnetic frustration. The system then will look for a new ordered state with a controlled strength of frustration. If the ground state is a kind of spin Jahn-Teller state, this spin state transition should be accompanied by a substantial change in lattice parameters. Such a cooperative transition of frustrated spins and lattice, induced by magnetic field, was explored in $CdCr_2O_4$ and $ZnCr_2O_4$. In this Letter, we report that $CdCr_2O_4$ does indeed show a metamagnetic transition to a 1/2 magnetization plateau state with three-up and one-down spins out of four spins of each chromium tetrahedron. This 3:1 ordering may be viewed as three-dimensional version of a 1/3 plateau state in a two-dimensional triangular lattice. This transition is accompanied by a large magnetostriction comparable with that observed in conventional magnets with substantial spin-orbit couplings. We argue that this is

an evidence for the presence of magnetoelastic couplings produced by spin frustration, supporting the spin Jahn-Teller picture.

Single crystals of $CdCr_2O_4$ were grown by a flux method [14]. Polycrystalline samples of $ZnCr_2O_4$ were synthesized by a solid-state reaction. High field measurements at up to 47 T were performed using an induction method with a multilayer pulse magnet at the ultrahigh magnetic-field laboratory of the Institute for Solid State Physics. The magnetostriction measurement was carried out using a capacitance method in the pulsed magnetic fields.

The temperature dependence of the magnetic susceptibility of $CdCr_2O_4$ is shown in Fig. 1, together with that of $ZnCr_2O_4$. A discontinuous change of susceptibility is observed at 7.8 K and 12 K for $CdCr_2O_4$ and $ZnCr_2O_4$, respectively, which corresponds to the antiferromagnetic transition. We observe a small but finite hysteresis, indicating that the transition is of first order. Well above the transition temperature, the data are well described by a Curie-Weiss law. This yields Curie-Weiss temperatures $\Theta = -70$ K and -390 K for $CdCr_2O_4$ and $ZnCr_2O_4$, respectively, which are 1 order of magnitude larger than the antiferromagnetic transition temperatures. These results, indicative of the strong frustration effect, agree well with those previously reported [15,16]. The much smaller antiferromagnetic interaction in $CdCr_2O_4$ means that a lower magnetic field is required to align the spins. The magnetic anisotropy of $CdCr_2O_4$ was examined in the ordered state, by aligning the tetragonal domains below the transition temperature. A weak uniaxial pressure was applied on $CdCr_2O_4$ single crystal along the cubic [100]. The inset of Fig. 1 shows the anisotropic magnetic susceptibilities with fields along the tetragonal [001], [100], and [110] directions. While the [100] and [110] susceptibilities decrease discontinuously at the transition, [001] susceptibility does not show appreciable change at the transition. This indicates that the antiferromagnetically ordered phase below $T_N = 7.8$ K in $CdCr_2O_4$ has an easy-plane type anisotropy, as proposed for $ZnCr_2O_4$ [17].

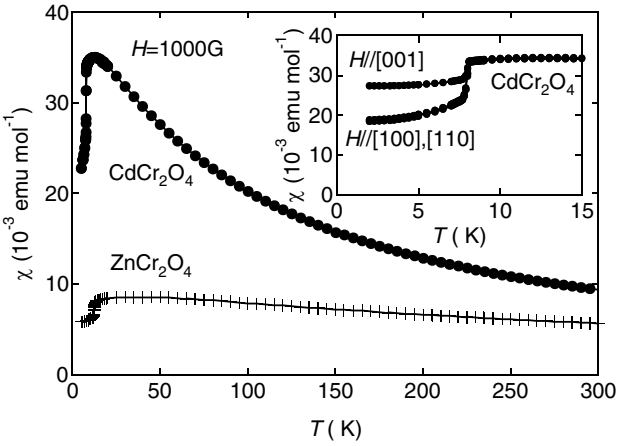

FIG. 1. Temperature dependence of magnetic susceptibility of $CdCr_2O_4$ single crystal. The data for $ZnCr_2O_4$ polycrystalline sample is also shown for comparison. The inset demonstrates the anisotropy of the magnetic susceptibility in the tetragonal phase of $CdCr_2O_4$.

We have attempted to suppress the geometrical frustration in $S = 3/2$ pyrochlore antiferromagnet $CdCr_2O_4$ by applying a magnetic field. The magnetization curves of $CdCr_2O_4$ up to 47 T at 1.8 K are shown in Fig. 2. The magnetic fields were applied parallel to [100], [110], and [111] in cubic indices, but no appreciable field orientation dependence was observed except for very low fields below a few Tesla, indicating a very small anisotropy of the spin system. Spin-orbit couplings should be negligible due to the completely filled t_{2g}^3 configuration of Cr^{3+} ions. It is clear that a discontinuous jump of magnetization occurs at 28 T, followed by a magnetization plateau. The plateau state is remarkably stable over a wide range of magnetic fields from 28 T to at least up to 47 T. We observed a hysteresis at the magnetization jump and, therefore, the transition is of first order. The presence of well defined plateau implies that the system can find a new ordered state by suppressing its geometrical frustration. For chromium ion with $S = 3/2$, a magnetic field of 1 T is equivalent to the temperature at about 2 K. Curie-Weiss temperatures Θ, which indicate the magnitude of exchange energy, correspond to 35 T and 195 T for $CdCr_2O_4$ and $ZnCr_2O_4$, respectively. The value 35 T for $CdCr_2O_4$ is quite reasonable with the transition field 28 T. The magnetization curve of $ZnCr_2O_4$ did not show any jump and is almost linear up to 47 T as shown in Fig. 2, as expected from the larger magnetic interaction than $CdCr_2O_4$.

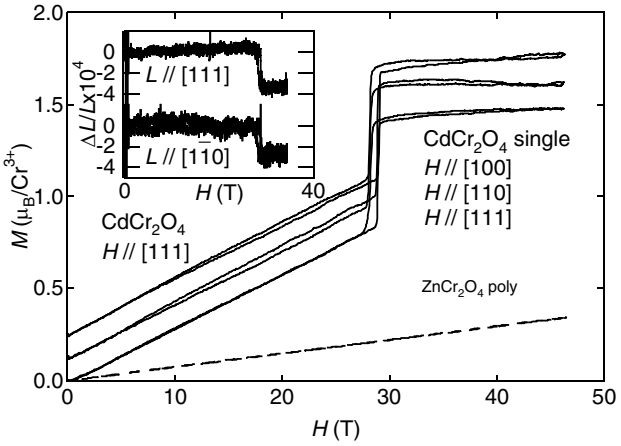

FIG. 2. Magnetization curves of $CdCr_2O_4$ single crystal in fields of up to 47 T, taken at a temperature of 1.8 K. Magnetic fields are applied along [100], [110], and [111] in cubic indices. The curves are shifted to avoid overlapping. The inset shows longitudinal (along [111]) and transversal (along $[1\bar{1}0]$) magnetostriction measured at 4.2 K, when a magnetic field is applied along the [111] direction of the crystal. Magnetization curve for $ZnCr_2O_4$ polycrystalline sample is shown for comparison in the main panel.

The magnetic moment in the plateau phase is $1.5\mu_B/Cr^{3+}$, which corresponds to one half of the full moment of $S = 3/2$ Cr^{3+}. This unique moment can be naturally understood as a ferrimagnetic state, with a collinear three spin-up and one spin-down (3:1) configuration of each Cr^{3+} tetrahedron. The $1/2$ magnetization plateau state observed in this $CdCr_2O_4$ is viewed as a three-dimensional analogue of $1/3$ plateau state in two-dimensional triangular antiferromagnets. It is well established that in the triangular antiferromagnet a ferrimagnetic state is stabilized under magnetic fields with two spin-up and one spin-down (2:1) configuration of each spin triangle [18–21]. This ferrimagnetic state manifest itself as a $1/3$ magnetization plateau in the magnetization curve.

Another way to take a look at the 3:1 ordering in $CdCr_2O_4$, may be a spin analog of 3:1 charge ordering in AlV_2O_4 spinel [22]. In AlV_2O_4, B-site V ions are mixed valent nominally with 1:1 ratio of V^{2+} and V^{3+}, which is a typical Verway problem and should give rise to a strong degeneracy of charge excitations. To suppress the degeneracy, a valence skipping configuration of V^{2+} and V^{4+} with 3:1 ratio, instead of strongly frustrated 1:1 V^{2+} and V^{3+}, is realized and, by coupling with a rhombohedral distortion along [111], forms a very stable charge ordering below 700 K. In analogy with the suppression of charge frustration in AlV_2O_4, 3:1 ratio of up spins and down spins substantially reduces the degeneracy associated with frustration in the antiferromagnetic spinel oxides. Such 3:1 spin ordering is likely stabilized by applying magnetic fields in $CdCr_2O_4$. 3:1 ordering may be quite a universal route to overcoming frustration in the pyrochlore lattice.

At first glance, field stabilized 3:1 spin ordering is analogous to those observed in Ising spin ice pyrochlores when field is applied along [111] direction [23–26]. While Ising magnetic anisotropy have an essential role in these spin ice compounds, $CdCr_2O_4$ is a typical Heisenberg antiferromagnet. Indeed, the behavior of the present Heisenberg spin system shows no field direction dependence. We should note that the present plateau behavior is distinct from those observed in spin ice compounds.

Because of strong spin-lattice interaction effects, as expected from a spin Jahn-Teller picture, a field induced magnetic structure makes the lattice structure different from those of low temperature tetragonal phases and high temperature cubic phases. Structural change by applying a field can be clearly detected by the magnetostriction measurements. In the inset of Fig. 2, the magnetostriction along [111] and $[1\bar{1}0]$ with applied field parallel to [111] are shown. A magnetostriction of 4×10^{-4} is clearly observed at the transition to the 3:1 ordered state. Since these materials have no orbital degree of freedom and so no spin-orbit coupling, the magnetostriction in this system is essentially due to exchangestriction, which is normally very small. Nevertheless, the observed magnetostriction is comparable with those observed for magnets with a substantial spin-orbit couplings. It is natural to ascribe this enhanced spin-lattice couplings to an interplay between the strongly frustrated spin system and the lattice. Theories of triangular lattice revealed that for an Ising system, 2:1 state is stabilized at $T = 0$ by applying a magnetic field, however, a Heisenberg system requires additional anisotropic interaction to obtain finite region of 2:1 ground state [18]. By analogy, our observation of a wide plateau state in Heisenberg pyrochlore magnet suggests that there is a certain interaction to stabilize 3:1 ordering in chromium spinel. It is very likely that spin-lattice couplings play a vital role.

The spin structure realized in 3:1 ordered state is as yet unclear. Assuming an Ising model with an antiferromagnetic nearest-neighbor and next-nearest-neighbor interactions and 3:1 ratio of up spins to down spins, we found that two spin structures, one with rhombohedral $R\bar{3}m$ symmetry and one with cubic $P4_332$ (and its mirror image with $P4_132$), have the lowest energy among all the possible configurations within the unit cell containing 16 Cr. The former is the spin version of charge ordering in AlV_2O_4, where the ferromagnetic kagomé and triangular layers stack antiferromagnetically along [111] direction. The latter consists of a complicated arrangement with many next-nearest ferromagnetic bonds. The lattice distortion very likely plays a vital role in stabilizing the 3:1 ordered state over a wide range of magnetic fields and should be intimately related with the spin structure. The lattice contraction both along [111] and $[1\bar{1}0]$ associated with the metamagnetic transition at first glance appears incompatible with the AlV_2O_4-type ordering [22] with antiferromagnetic couplings along [111] and ferromagnetic couplings along $[1\bar{1}0]$. However, because of the possible presence of domain structure, AlV_2O_4-type ordering cannot be ruled out.

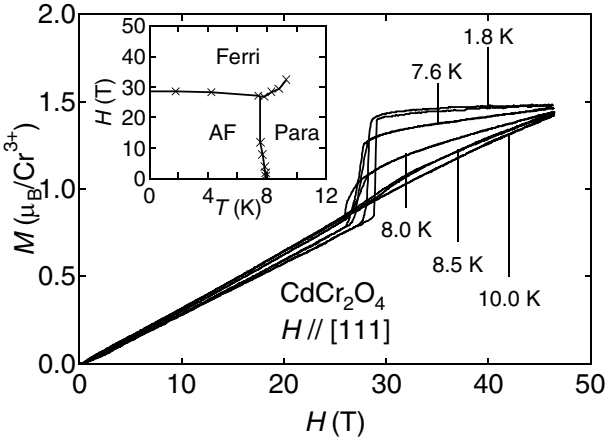

FIG. 3. Magnetization curves $M(H)$ of $CdCr_2O_4$ for $H \parallel [111]$ taken at various temperatures. The inset shows the H-T phase diagram in fields of up to 47 T, as found by $M(H)$ measurements using pulsed fields, and $M(T)$ measurement below 12 T.

To further uncover the nature of field induced transition to 1/2 magnetization plateau state, the phase diagram on the H-T plane was explored by measuring the magnetization curve (H parallel to [111]) at various temperatures. The main panel of Fig. 3 demonstrates the raw data. With increasing temperature, the critical field for the transition is almost independent of temperature with a minute decrease. The transition becomes broader and, eventually above 10 K, can hardly be identified. This may imply the presence of a critical end point. The discontinuous change of the slope below 28 T is clearly observed at $T = 7.8$ K, which represents the susceptibility jump at T_N (and very likely T_s). This means T_N is almost field independent up to 28 T. These results are visually summarized as a H-T phase diagram in the inset of the Fig. 3. At low fields and low temperatures, we have a phase extended from the spin Jahn-Teller phase. Above 28 T, the 3:1 ordered phase appears, which extends to higher temperatures than the spin Jahn-Teller phase.

A close analogy with the triangular lattice antiferromagnet can be recognized in the phase diagram of Fig. 3. In case of the triangular lattice Heisenberg antiferromagnet in applied field, it was shown that, at low temperatures, three sublattice Néel phases show up first and then the 1/3 plateau phase extending to higher temperatures follows [18], which likely make a one to one correspondence with the spin Jahn-Teller phase and 1/2 magnetization plateau state in the present system. In triangular antiferromagnet, with further increasing field, there appears a tilted ferrimagnetic phase and finally a ferromagnetic phase. Analogously, a ferromagnetic phase should show up in the present system at higher fields. A naive extrapolation of the low field magnetization slope suggests that the magnetization will saturate at about 100 T. In view of the frustration driven spin-lattice couplings, it is natural to expect the ferromagnetic phase to be cubic, as the frustration is completely suppressed. Experimental examination of this scenario under higher fields is now in progress.

In conclusion, we have explored the magnetic and temperature phase diagram of $CdCr_2O_4$ spinel which is an ideal Heisenberg $S = 3/2$ pyrochlore antiferromagnet. We have established a magnetic-field induced transition to a magnetization plateau state, which corresponds to three-up and one-down spin configuration of each Cr tetrahedron. The transition is of first order and is accompanied by large lattice distortions, indicative of the enhanced magnetostriction due to the geometrical frustration. This 3:1 ordering is a three-dimensional analogue of 1/3-magnetization plateau state in triangular antiferromagnet, giving rise to another well defined playground for physics of magnetic excitation in frustrated magnets.

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