Frustrated magnetism in the Heisenberg pyrochlore antiferromagnets \( A Yb_2X_4 \) (\( A = \text{Cd, Mg, } X = \text{S, Se} \))

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Our polycrystalline sample study on the chalcogenide spinels \( A Yb_2X_4 \) (\( A = \text{Cd, Mg, } X = \text{S, Se} \)) has revealed frustrated magnetism due to the antiferromagnetically coupled Heisenberg spin on the pyrochlore lattice. Our crystal electric field analysis indicates the Yb ground state has nearly Heisenberg spins characterized by a large weight of \( J_z = 1/2 \) wave function. All the materials exhibit an antiferromagnetic order at 1.4–1.8 K, much lower temperature than the antiferromagnetic exchange coupling scale of \( \sim 10 \) K. Significantly reduced size of the ordered moment in comparison with the bare moment size around 1.3\( \mu_B \)/Yb inferred from the \( \mu \)SR measurements indicates strong quantum fluctuations in the commensurate and incommensurate ordered states in \( \text{CdYb}_2\text{S}_4 \) and \( \text{MgYb}_2\text{S}_4 \). In particular, the nearly gapless character found in the specific heat suggests that \( \text{CdYb}_2\text{S}_4 \) stabilizes the Palmer-Chalker state or \( \psi_2 \) order on the pyrochlore lattice.

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Quantum magnetism in geometrically frustrated magnets have attracted great interest in recent years. Various candidate materials of spin liquid states have been discovered in quasi two-dimensional systems based on triangular, Kagome, and honeycomb based lattices with quantum spin \( S = 1/2 \) systems. Examples include BEDT-TTF, EtMe₃Sb[Pd(dmit)₂]₂, Herbersmithite, Volborthite, and Ba₃CuSb₂O₉. In three-dimensional systems, the frustrated magnetism on the pyrochlore lattice has been intensively studied. One of the most prominent examples is the spin ice⁷–¹¹, which is based on an Ising spin with a ferromagnetic coupling. Recent theoretical and experimental studies have found that quantum melting of spin ice may lead to a formation of a quantum spin liquid state with emergent topological excitations. Spin ice states have been mainly studied using rare-earth based pyrochlore oxides having Ising type of 4\( f \) moments such as Dy₂Ti₂O₇ and Ho₂Ti₂O₇.¹₂–¹⁴ On the other hand, various quantum magnetism has been discovered in the pyrochlore oxides having non-Ising type of ground Kramers doublet. Significant quantum effects have been discussed for the low temperature magnetism found in \( \text{Yb}_2\text{Ti}_2\text{O}_7 \) and \( \text{Er}_2\text{Ti}_2\text{O}_7 \).¹⁷–²⁰,²³–²⁸ The combination of strong easy-plane anisotropy for low-energy magnetic doublets selected by the local crystalline electric field (CEF) and anisotropic bilinear exchange coupling enhances quantum fluctuations that play important role in determining the ground state.¹⁹,²⁹

An antiferromagnetic (AF) pyrochlore magnet with isotropic bilinear exchange coupling between nearest neighbor Heisenberg spins has been predicted to host spin disordered ground states in both classical and quantum cases.³⁰–³¹ As one of the archetypes of a Heisenberg pyrochlore oxide, \( \text{Gd}_2\text{Ti}_2\text{O}_7 \) has attracted much attention and extensive studies have been made and revealed frustrated magnetism with unconventional AF ordering. Rare-earth ions of pyrochlore oxides are known to have a strong trigonal CEF that stabilizes either Ising or XY planar local symmetry. While the anisotropy in the exchange coupling terms are unavoidable for the rare-earth based pyrochlore magnets, geometrical frustration may be enhanced if the local site symmetry becomes close to cubic.

To realize the cubic local symmetry, here, we focus on spinel type compounds \( AR_2X_4 \), because the rare-earth element \( R \) in \( AR_2X_4 \) forms the pyrochlore lattice with the different coordination of \( R \) from the oxides and possesses a nearly cubic site symmetry that may lead to nearly Heisenberg spins. While \( \text{CdR}_2\text{X}_4 \) (\( X = \text{S, Se} \)) systems have been already investigated in the context of geometrical frustration, detailed low temperature measurements have been limited to the \( R = \text{Er} \) case, where unique magnetic behaviors reflecting the effect of the magnetic anisotropy of rare-earth ions have been found. On the other hand, nearly cubic site symmetry has been also found in the related \( \text{Yb} \)-based compound \( \text{Ba}_3\text{Yb}_2\text{Zn}_2\text{O}_{11} \) with the breathing pyrochlore lattice (an alternating array of small and large tetrahedra). In this compound, the strong quantum effects are manifest in the formation of the spin singlet ground state.

Here, we show that the \( \text{Yb} \)-based chalcogenide spinels \( A Yb_2X_4 \) (\( A = \text{Cd, Mg, } X = \text{S, Se} \)) are good candidate systems of a quantum Heisenberg antiferromagnet on the pyrochlore lattice. To date, only the study at
A spinels to geometrical frustration.

relaxation measurements have revealed that the ordered higher temperatures than \(\sim 1.3\) K. Experiments have found that the systems exhibit a Néel order at 1.4-1.8 K, lower temperature than the AF in-

dependent of (b) the inverse magnetic susceptibility \(1/\chi\) measured under 0.1 T and (c) the total specific heat \(C_p\) at 0 T in CdYb\(_2\)S\(_4\) (red circles), MgYb\(_2\)S\(_4\) (blue squares), CdYb\(_2\)Se\(_4\) (green triangles), and MgYb\(_2\)Se\(_4\) (orange diamonds).

TABLE I. Effective moment \(P_{\text{eff}}\) estimated from the Curie-Weiss fit for the high-temperature region between 200 K and 350 K, Weiss temperature \(\theta_W\) estimated from the Curie-Weiss fit for the low-temperature region between 5 K and 20 K, antiferromagnetic transition temperature \(T_N\) estimated from the specific heat, and spin wave velocity \(v_{\text{sw}}\) in the chalcogenide spinels \(AYb_2X_4\) (\(A = \text{Cd, Mg, } X = \text{S, Se}\)).

| Sample    | \(P_{\text{eff}}\) (\(\mu_B/\text{Yb}\)) | \(\theta_W\) (K) | \(T_N\) (K) | \(v_{\text{sw}}\) (m/s) |
|-----------|---------------------------------|-----------------|------------|------------------|
| CdYb\(_2\)S\(_4\) | 4.67                       | -10.0(4)       | 1.8        | 144(2)           |
| MgYb\(_2\)S\(_4\) | 4.70                       | -10.4(3)       | 1.4        | 100(2)           |
| CdYb\(_2\)Se\(_4\) | 4.78                       | -9.3(3)        | 1.7        | 131(1)           |
| MgYb\(_2\)Se\(_4\) | 4.77                       | -9.2(3)        | 1.4        | 107(1)           |

higher temperatures than \(\sim 2\) K has been made on these compounds\(^{39,44–47}\). Our low temperature comprehensive experiments have found that the systems exhibit a Néel order at 1.4-1.8 K, lower temperature than the AF interaction scale of \(\sim 10\) K. Furthermore, our muon spin relaxation measurements have revealed that the ordered moment size is much smaller than the bare moment size around \(1.3\mu_B/\text{Yb}\), indicating strong quantum effects due to geometrical frustration.

Polycrystalline samples of the Yb based chalcogenide spinels \(AYb_2X_4\) (\(A = \text{Cd, Mg, } X = \text{S, Se}\)) are obtained by solid state synthesis\(^{39}\). Mixtures of raw elements, Cd(4N) or Mg(3N), Yb(3N), S(5N) or Se(5N) with a ratio 1 : 2 : 4.04, were sintered for a week or two at 900 °C twice after sealing them in an evacuated quartz ampule. Our powder X-ray measurements confirmed single phase of the spinel structure for each compound. The lattice constants are obtained as \(a = 11.075(1)\) \(\text{Å}\) (CdYb\(_2\)S\(_4\)), \(a = 10.972(1)\) \(\text{Å}\) (MgYb\(_2\)S\(_4\)), \(a = 11.539(1)\) \(\text{Å}\) (CdYb\(_2\)Se\(_4\)), \(a = 11.464(1)\) \(\text{Å}\) (MgYb\(_2\)Se\(_4\)), which are consistent with the previous report\(^{39}\). The susceptibility was measured using a commercial SQUID magnetometer (MPMS, Quantum Design) between 2 and 300 K under a field of 0.1 T. For the measurements below 2 K down to 30 mK, a home-made SQUID magnetometer in conjunction with a dilution refrigerator was used to measure the DC component under a field of 1 mT, and the AC component with a frequency of 23, 337, 3337 Hz under an AC field of 2.2 \(\mu\)T. A commercial system (PPMS, Quantum Design) was used to obtain the temperature dependence of the specific heat between 0.4 and 20 K using a relaxation method. Muon spin rotation/relaxation (\(\mu\)SR) experiments were carried out at J-PARC Muon facility, Tokai, Japan. We have implanted spin-polarized positive muons into polycrystalline specimens of CdYb\(_2\)S\(_4\) and MgYb\(_2\)S\(_4\), which should have a similar grain size distribution. The samples were glued on the silver backing holder of the dilution refrigerator by using Apiezon-N grease.

Let us first discuss the exchange pathways in the chalcogenide spinels. As shown in Fig. 1(a), the \(AYb_2X_4\) families have the spinel structure with the space group \(Fd3m\). The Yb\(^{3+}\) (4\(^1\)\(^3\)) forms the pyrochlore lattice with the sixfold chalcogen \(X^2^-\) coordination and the point symmetry is \(D_{3d}\). The nearest neighbor coupling should be based on the superexchange coupling through...
the Yb-X-Yb pathway, as the direct hybridization between Yb 4f states is impossible for the nearest neighbor distance (e.g. ~ 3.9 Å for CdYb2S4). The second and third neighbor coupling should be significantly reduced in comparison with the nearest neighbor one, as they require a higher order exchange coupling through Yb-X-Yb pathway with a longer distance. Thus, the spinel chalcogenides can be viewed as model systems to study frustrated magnetism based on the pyrochlore lattice only with an anisotropic nearest neighbor coupling, similarly to the rare-earth pyrochlore oxides.

The chalcogenide spinels AYb2X4 exhibit almost the same magnetic behavior. Figure 1(b) shows the temperature dependence of the inverse susceptibility 1/χ(T) = B/M(T). The effective moments \( P_{\text{eff}} \) obtained from the Curie-Weiss fit for the high-temperature region between 200 K and 350 K using the equation, \( \chi(T) = C/(T - \theta_W) \), are closed to the hypothetical value (4.54μB/Yb) known for an Yb3+ ion having a \( ^2F_{7/2} \) multiplet with \( g = 8/7 \). Fittings in the low-temperature region between 5 K and 20 K give the negative values of the Weiss temperature \( \theta_W \sim -10 \) K for all compounds. As we will discuss below, the estimated Weiss temperature is consistent with the exchange coupling \( \theta_W \) obtained from the molecular field constant \( \lambda \), which indicates the antiferromagnetic coupling between 4f magnetic moments. These fitting results are summarized in Table I.

To reveal the magnetic ground state, we have measured the specific heat \( C_P \) as a function of temperature under zero field. As shown in Fig. 1(c), \( C_P \) for all samples clearly exhibits peaks at \( T_N \) as summarized in Table I. The transition temperature of each compound is then determined to be the point where the sign changes in the first derivative of the heat capacity curve with respect to temperature. As we will discuss, these are associated with an antiferromagnetic order.

To further characterize the frustrated magnetism, here we focus on the magnetic properties of the sulfides AYb2S4 with \( A = \text{Cd} \) and Mg. First, to determine the local anisotropy of the 4f moments, we analyzed the crystalline electric field (CEF) scheme by fitting the temperature dependence of the susceptibility, as shown by solid lines in Fig. 2. The following CEF Hamiltonian,

\[
\mathcal{H}_{\text{CEF}} = B_2 Q_2^0 - \frac{2}{3} B_4 (O_6^0 - 20\sqrt{2}O_4^0) + \frac{16}{9} B_6 (O_6^0 + \frac{35\sqrt{2}}{4} O_4^0 + \frac{77}{8} O_6^0),
\]

was used, where \( B_n \) are the CEF parameters, \( O_n^m \) are Stevens operator equivalents and the \( \langle 111 \rangle \) direction is taken as the quantized axis (Fig. 2(b)). The exchange coupling effects were taken into account by introducing the molecular field approximation using the molecular field constant \( \lambda \) as a fitting parameter. The fitting yields the parameters, \( B_2 = 0.3 \text{ K} \), \( B_4 = -0.32 \text{ K} \), \( B_6 = 0.0015 \text{ K} \), and \( \lambda = -10.5 \text{ mol-Yb/emu for CdYb2S4} \), and \( B_2 = 0.5 \text{ K} \), \( B_4 = -0.33 \text{ K} \), \( B_6 = 0.0012 \text{ K} \), and \( \lambda = -15.0 \text{ mol-Yb/emu for MgYb2S4} \), consistent with previous reports\(^{4}\). As the exchange parameter is sensitive to sample quality, a small difference in \( \lambda \) between our and previous results may arise from e.g. the Mg deficiency in the sample. The larger \( \lambda \) in our results suggests the higher quality of our sample. The small absolute value of \( B_2 \) indicates the nearly cubic local symmetry of the Yb site, as expected from the local cubic coordination of the chalcogenide anion around an Yb ion (Fig. 2(b)). The scheme consists of four Kramers doublets, with the excitation energies, 297, 300, 630 K (CdYb2S4) and 289, 296, 646 K (MgYb2S4). Thus, the low-temperature magnetism based on the ground doublet should appear at much lower temperatures than room temperature. The wave function for the ground doublet is obtained as the following form,

\[
\psi = \mp D | \pm \frac{5}{2} > - E | \mp \frac{1}{2} > \pm F | \mp \frac{7}{2} >,
\]

\( D = 0.804 (0.803) \) and \( E = 0.513 (0.515) \), \( F = 0.301 (0.299) \) for CdYb2S4 (MgYb2S4), revealing a strongly quantum character due to a significant contribution.
of \(J_z = 1/2\) component. The ground state wave function has an isotropic Heisenberg spin with longitudinal and transverse components of \(\sim 1.33 \mu_B/\text{Yb}\). This local isotropy is in sharp contrast with the local anisotropy seen in the other rare-earth spinel \(\text{CdEr}_2\text{Se}_4\)\(^{38}\). Given that the CEF ground doublet is made of a pseudo-spin-1/2 moment with an effective g-factor \(g_{\text{eff}} = 16/7(J_z) = 2.67\), where \(\langle J_z \rangle\) is the expectation value of the \(z\) component of the angular momentum obtained from the wave function for the ground doublet, one can estimate the exchange coupling \(\theta_{\text{ff}}^J\) is \(-7.0\) K and \(-10.0\) K by using the relation \(\theta_{\text{ff}}^J = N g_{\text{eff}}^2 \mu_B^2 (1/2)(3/2)\lambda/3k_B\)\(^{48}\) (\(\lambda = -10.5\) mol-Yb/emu and \(-15.0\) mol-Yb/emu) for \(\text{CdYb}_2\text{S}_4\) and \(\text{MgYb}_2\text{S}_4\), respectively. Here, \(N\) is Avogadro’s constant. This exchange coupling is consistent with the estimate using the Curie-Weiss fit for the low-temperature region 5-20 K. The AF coupling \(J = 0.57\) K for \(\text{CdYb}_2\text{S}_4\) and 0.82 K for \(\text{MgYb}_2\text{S}_4\) can be estimated using the relation \(A = 2zJ/(N g_{\text{eff}}^2 \mu_B^2)\). Here, \(z = 6\) is the coordination number.

To reveal the ground state magnetism of \(\text{AYb}_2\text{S}_4\) with \(A = \text{Cd} \text{ and Mg}, \text{ the DC and AC susceptibility measurements were performed using a dilution refrigerator}. \) The results near the transition temperatures are shown in Figs. 3(a) and 3(b). Both of them show anomalies at \(\sim 2\) K. No frequency dependence was found in the temperature dependence of the AC susceptibility, indicating that the anomalies come from an antiferromagnetic order, not from a spin freezing (Fig. 3). On the other hand, for \(\text{CdYb}_2\text{S}_4\), the DC susceptibility shows a tiny bifurcation below the Néel point, \(T_N = 1.8\) K, which may come from a domain formation, as will be discussed below.

The \(4f\) moment contribution to the specific heat \(C_P\) is obtained by subtracting the lattice part estimated by using \(C_P\) of the isostructural analogue \(\text{CdIn}_2\text{S}_4\)\(^{49}\). To account for the volume and mass difference, we followed the same conversion procedure using the Debye equation as described in Ref.\(^{50}\). Figure 3(c) indicates the temperature dependence of the magnetic part of the specific heat \(C_M\) under zero field. The specific heat \(C_M\) clearly exhibits a sharp increase below \(\sim 2\) K, and a peak at 1.8 K (1.4 K) for \(\text{CdYb}_2\text{S}_4\) (\(\text{MgYb}_2\text{S}_4\)), indicating a bulk character of the antiferromagnetic transition. The separation between \(T_N\) and \(\theta_{\text{ff}}^J\), quantified by \(f = |\theta_{\text{ff}}^J|/T_N\sim 4\) for \(\text{CdYb}_2\text{S}_4\) and 7 for \(\text{MgYb}_2\text{S}_4\), clearly shows the effects of magnetic frustration. A broad peak at 5 K and a tail extending up to \(\sim 10\) K seen in the magnetic part \(C_M\) may well come from a formation of a magnetic short-range order formed below \(T \sim |\theta_{\text{ff}}^J|\).

Interestingly, in the AF phase below \(T_N\), the magnetic part of the specific heat \(C_M\) exhibits the temperature power law behavior, \(C_M = AT^3\) (Fig. 4(a)). This gapless feature is expected for a linearly dispersive Nambu-Goldstone mode in three dimension and consistent with the results seen in the electron spin resonance (ESR) measurements for \(\text{CdYb}_2\text{S}_4\)\(^{51}\). A similar \(T^3\) power law dependence of \(C_M\) was observed in the antiferromagnetic \(XY\) pyrochlore oxide \(\text{Er}_2\text{Ti}_2\text{O}_7\)\(^{23,25,52}\). It should be noted that recent heat capacity and neutron scattering measurements have revealed the presence of a small gap of 0.05 meV (\(<0.5\) K) induced by quantum fluctuations in \(\text{Er}_2\text{Ti}_2\text{O}_7\)\(^{25,28}\), while the \(T^3\) behavior is observed above the gap energy scale. Further measurements are required to confirm the presence of the gapless state in the chalcogenide spinels \(\text{AYb}_2\text{X}_4\) (\(A = \text{Cd, Mg}, X = \text{S, Se})\) compared to \(\text{Er}_2\text{Ti}_2\text{O}_7\)\(^{23}\).

Using the slope \(A\), the relation\(^{25}\)

\[
A = \frac{\pi^2}{120} N_A \frac{k_B^4 a^3}{h^2 v_{sw}^3},
\]

allows us to estimate the spin wave velocity \(v_{sw}\). The obtained velocities of the chalcogenide spinels \(\text{AYb}_2\text{X}_4\) are between 100 and 140 m/s (Table I). These values are larger compared to \(\text{Er}_2\text{Ti}_2\text{O}_7\) (66(1) m s\(^{-1}\)) and lead to the estimate of the AF exchange coupling \(J \approx 0.6-0.7\) K using the equation \(v_{sw} = \sqrt{8\pi d g_{\text{eff}}^2 (1/2) (7/8) f^3/h}\), where \(d\) is the distance between two Yb atoms, roughly consistent with another estimate using \(\theta_{\text{ff}}^J\). The existence of the linearly dispersive mode in the AF phase put a strong constraint in the determination of the ground state.

Figure 3(d) indicates the temperature dependence of the entropy \(\Delta S_M = S_M(T) - S_M(0.4\) K) obtained by integrating \(C_M/T\) vs. \(T\) above 0.4 K. The entropy gradually decreases from \(R \ln 2\) on cooling, consistent with the ground state doublet obtained by the above CEF
that the local field at the muon site is quite small. For example, it was reported $\sim \pi f/\gamma K$. Compared CdYb$_2$S$_4$ to, for example, Er$_2$Ti$_2$O$_7$ where about 80% of $R \ln 2$ is released below Néel temperature. This entropy suppression is significant when compared to the entropy change of the chalcogenide spinels $\Delta \ln 2$ below Néel temperature.

From the muon spin precession frequency $\lambda$ of the entropy $\Delta S_M = S_M(T) - S_M(0.4 \text{ K})$. Here we plot the entropy change of the chalcogenide spinels $\lambda$ (Fig. 4(b)). All $\lambda$ compounds show nearly $T^3$ dependence and the entropy change is suppressed to $\sim 30\%$ of $R \ln 2$ below Néel temperature.

In order to further characterize the magnetic ordered state, we performed muon spin relaxation measurements. Strikingly, the size of the magnetic ordered moment was estimated to be much smaller than that of the bare moment $\sim 1.3 \mu_B$/Yb as discussed below. Figure 5(a) shows the $\mu$SR spectra under zero magnetic field in CdYb$_2$S$_4$. Spontaneous muon spin precession was seen below 2 K, indicating the static antiferromagnetic ordering state. From the muon spin precession frequency $f \sim 2.2$ MHz, the local field ($= 2\pi f/\gamma \mu_0$, gyromagnetic ratio of muon) at the muon site is estimated as $\sim 15$ mT at 0.025 K. Compared CdYb$_2$S$_4$ with the other $B$-site spinel, the local field is quite small. For example, it was reported that the local field at the muon site is $\sim 450$ mT in $B$-site spinel antiferromagnet CdCr$_2$S$_4$. Assuming the same relation between the local field and magnetic moment in CdCr$_2$S$_4$, the ordered magnetic moment is estimated to be much smaller than $1 \mu_B$/Yb in CdYb$_2$S$_4$.

Static magnetic ordering was also observed in MgYb$_2$S$_4$ below 1.5 K, as shown in Fig. 5(b). However, a spontaneous spin precession was not seen in MgYb$_2$S$_4$, indicating distribution of the local field. This fact suggests that the magnetic structures in CdYb$_2$S$_4$ and MgYb$_2$S$_4$ are different, and MgYb$_2$S$_4$ has an incommensurate spin order. The $\mu$SR spectra was fitted by using a function

$$P(t) = A_1\exp(-\Delta^2 t^2) + A_2\exp(-\lambda t),$$

Here $\Delta$ and $\lambda$ indicate the dipolar width at muon site and dynamic relaxation rate ($= 1/T_1$), respectively. The average local field at the muon site in MgYb$_2$S$_4$ is obtained as $\Delta/\gamma \mu_0 \sim 7$ mT at 0.04 K. This value is close to that in CdYb$_2$S$_4$ and the ordered moment is estimated to be much smaller than $1 \mu_B$/Yb. $\lambda$ shows the critical divergence behavior above $T_N$, indicating a second order phase transition.

While it is hard to identify the spin structure for the incommensurate order suggested for MgYb$_2$S$_4$, there is only a few candidate states that may host a gapless commensurate magnetic order as found for CdYb$_2$S$_4$ based on the combination of the specific heat and $\mu$SR measurements. In these Yb systems, as we discussed above, the superexchange coupling is the dominant intersite magnetic interaction. Given the localized character of the 4$f$ moments, the interaction should be dominated by the nearest neighbor coupling. For a pyrochlore magnet that can be described by anisotropic nearest-neighbor exchange Hamiltonian, the commensurate order is most likely $q = 0$ type order, which includes the four types of states 1) two-in/two-out, 2) all-in/all-out, 3) Palmer-Chalker, and 4) $\psi_2$ order. Among them, Palmer-Chalker and $\psi_2$ order can have a gapless character. As the nearest neighbor coupling $J_1$ should be dominant for the spinel chalcogenides, the above argument should be applicable for the case of CdYb$_2$S$_4$ as well, indicating the magnetic order would be most likely Palmer-Chalker type or $\psi_2$ type. The $\psi_2$ type order is found in Er$_2$Ti$_2$O$_7$, which is considered to be stabilized by order by quantum disorder mechanism. Palmer-Chalker and $\psi_2$ phases have non-collinear types of magnetic order with the zero total moments on each tetrahedron. Thus, when the domains are formed below $T_N$, the domain wall most likely carries a ferromagnetic component. This may induces a weak ferromagnetic hysteresis between the FC and ZFC susceptibility measurements as observed in CdYb$_2$S$_4$ (Figs. 3(a)). Similar hysteretic behavior was reported in non-collinear antiferromagnets which have the pyrochlore and fcc lattices.

The significantly reduced size of the moment $\ll 1 \mu_B$/Yb is striking for a magnetic order in three dimension. This is consistent with the fact that only 1/3 of $R \ln 2$ is released below $T_N$, and in sharp contrast to the Er$_2$Ti$_2$O$_7$ case where 0.8$R \ln 2$ is released below $T_N = 1.25$ K (Fig. 4(b)). This indicates that the relatively strong Heisenberg character and the reduced size of

![FIG. 5. (Color online) $\mu$SR spectra in (a) CdYb$_2$S$_4$, and (b) MgYb$_2$S$_4$ measured at various temperature under 0 T.](image)
the bare moment in comparison with the $XY$ character and the moment size of $3.01 \mu_B$ of Er$_2$Ti$_2$O$_7$ enhances the quantum fluctuation effects and further decrease the ordered moment size while the $XY$ anisotropy in the exchange coupling terms exists in the chalcogenide spinels $A\text{Yb}_2X_4$.

In summary, the rare-earth chalcogenide spinels $A\text{Yb}_2X_4$ ($A = \text{Cd}, \text{Mg}, X = \text{S}, \text{Se}$) in which Yb forms the pyrochlore lattice with the different coordination from the pyrochlore oxides, has revealed frustrated magnetism due to the antiferromagnetically coupled Heisenberg spin on the pyrochlore lattice. Our CEF analysis indicates the Yb ground state has nearly Heisenberg spins characterized by a significant contribution of $J_z = 1/2$ wave function. All the materials exhibit antiferromagnetic order at 1.4-1.8 K, much lower temperature than the antiferromagnetic exchange coupling scale of $\sim 10$ K. Significantly reduced size of the ordered moment in comparison with the bare moment of $\sim 1.3 \mu_B$/Yb inferred from the $\mu$SR measurements indicates strong quantum fluctuations in the commensurate and incommensurate ordered states in CdYb$_2$S$_4$ and MgYb$_2$S$_4$, respectively. Further measurements such as neutron scattering and electron spin resonance are required to identify the exotic magnetic ground state of the candidate systems of quantum Heisenberg antiferromagnets on the pyrochlore lattice.

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