Revealing a Triangular Lattice Ising Antiferromagnet in a Single-Crystal CeCd$_3$As$_3$

Y. Q. Liu$^1$, S. J. Zhang$^1$, J. L. Lv$^2$, S. K. Su$^2$, T. Dong$^1$, Gang Chen$^{3,4}$, and N. L. Wang$^{1,5,6}$

1International Center for Quantum Materials, School of Physics, Peking University, Beijing 100871, China
2Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
3State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Shanghai 200433, China
4Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, China and
5Collaborative Innovation Center of Quantum Matter, Beijing, China

We report the single-crystal growth and the fundamental magnetic and thermodynamic properties of a rare-earth triangular lattice antiferromagnet CeCd$_3$As$_3$. In this rare-earth antiferromagnet, the Ce local moments form a perfect triangular lattice. Due to the spin-orbital-entangled nature of the Ce local moments, the compound exhibits extremely anisotropic antiferromagnetic couplings along the c direction and in the ab plane respectively. We show that CeCd$_3$As$_3$ represents a rare experimental realization of an antiferromagnetic Ising model on a two dimensional triangular lattice and thus provides a prototype example for geometrical frustration. We further discuss the quantum effect of the perturbative interactions on the top of the predominant Ising interaction.

Geometrically frustrated spin systems have been a subject of considerable theoretical and experimental interest in modern condensed matter physics because of the potential to host novel ground states and exotic phenomena [1]. The prototype example of frustration is the antiferromagnetically coupled Ising spins on a two dimensional (2D) triangular lattice that was first studied by Wannier [2]. When two of the spins are antiparallel arranged, the third spin is unable to be antiparallel to both of them, as illustrated in Fig. 1(a). Then, any spin configuration that satisfies “two spin up one spin down” or “two spin down one spin up” condition in a triangle would be a ground state. Apparently, the frustration leads to highly degenerate classical ground state, which is expected to cause strong quantum fluctuation and lead to various emergent quantum phenomena when quantum spin interactions are included. Strong quantum fluctuations, in the extreme cases, may prevent spin ordering even at zero temperature and lead to exotic ground states such as quantum spin liquids.

Experimental exploration of geometrically frustrated spin systems has been made on a number of lattices and materials, for example, on organic salts $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ [3, 4] and EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ [5, 6] with a $s = 1/2$ triangular lattice, ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite) [7, 8] and BaCu$_3$V$_2$O$_5$(OH)$_2$ (vesignieite) [9] with a $s = 1/2$ kagome lattice, Na$_4$Ir$_5$O$_8$ with a $s = 1/2$ hyperkagome lattice [10], and a number of rare-earth pyrochlore materials. Quite recently, significant progress has been made in the study of a perfect rare-earth triangular lattice antiferromagnet YbMgGaO$_4$ [11–19]. This compound was found to be disordered down to 0.048K despite a Weiss temperature $\Theta_W \approx -3$ K [16]. Specific heat [11, 12], $\mu$SR [16], neutron scattering [17, 18], and thermal transport [19] measurements provide compelling evidence for the formation of a gapless U(1) quantum spin liquid ground state in this exciting compound. In fact, YbMgGaO$_4$ is simply the first compound that has been studied carefully among the families of the rare-earth triangular lattice magnets [20] where the strong spin-orbit coupling of the rare-earth local moments comes into an interplay with the geometric frustration of the underlying lattice. In this Letter, we propose and study the magnetic properties of another rare-earth triangular lattice antiferromagnet CeCd$_3$As$_3$ on a single-crystal sample (see Fig. 1(b)). CeCd$_3$As$_3$ belongs to a series of compounds ReA$_3$Pn$_3$ (Re = Y, La-Nd, Sm, Gd-Er; A = Cd, Zn; Pn = As, P) [21–24], which crystallize in the ScAl$_3$C$_2$-type structure with the space group symmetry of P6$_3$/mmc, as displayed in Fig. 1 (c) and (d). In this compound, the lattice constants are $a = 4.4051$ Å and $c = 21.3511$ Å. The Ce$^{3+}$ ions form a perfect 2D triangular lattice, and the Ce triangular layers are well separated from each other by a distance of about 10.7 Å with Cd and As ions sitting in between. Therefore it is an ideal system for studying the geometrical frustration in a

![FIG. 1. (a) A triangle of antiferromagnetically interacting Ising spins leads to the geometrical frustration. (b) CeCd$_3$As$_3$ single crystal grown by a vapor transport method. (c) The crystal structure of CeCd$_3$As$_3$. (d) The crystal structure in the ab-plane. (e) The spin-orbit coupling (SOC) splits the Ce$^{3+}$ J=5/2 and J=7/2 states. The 6 fold degenerate $J=5/2$ state is further splitted into three Kramers doublets by the crystal electric field (CEF).](image-url)
2D triangular lattice of the Ce moments.

In CeCd$_3$As$_3$, Ce$^{3+}$ has a $4f^5$ electron configuration and carries a local moment. For the earth earth element, the spin-orbit coupling is the dominant energy scale. The atomic spin-orbit coupling entangles the orbital angular momentum $L$ with the spin $s = 1/2$, leading to the total angular momentum $J = L - s = 5/2$, which has $2J + 1 = 6$ fold degeneracy on each lattice site. Under the crystal electric field with the space group symmetry of P6$_3$/mmc, the six fold degeneracy is further split into three Kramers doublets (see Fig. 1 (e)). Each doublet is two fold degenerate and is protected by time reversal symmetry. Like the Yb$^{3+}$ ion in YbMgGaO$_4$, the Ce$^{3+}$ moment in CeCd$_3$As$_3$ is also described by an effective spin $S = 1/2$ Kramers doublet [15] if the crystal field field gap is much larger than the exchange energy scale of the local moments. The effective spin $S$ for the Ce$^{3+}$ ion involves a significant spin-orbit entanglement. As we show below, CeCd$_3$As$_3$ represents an experimental realization of an antiferromagnetic Ising model on a 2D triangular lattice.

The CeCd$_3$As$_3$ single crystals were grown by a vapor transport method using Iodine as transport agent, similar to the earlier report by Stoyko and Mar [22]. Mixtures of Ce, Cd and As powders with a ratio of 1:3:3 were sealed in an evacuated quartz tube and heated at 760 °C for a week. The mixtures were reground and sealed together with Iodine (4 mg/liter) in a quartz tube, which was placed into a two stage horizontal furnace. The hot end with the mixture was heated at 800 °C and the cold end at 700 °C for two week. Single crystals of CeCd$_3$As$_3$ (ScAl$_3$C$_3$-type) were obtained in the form of hexagonal plate-shape (see the picture in Fig. 1 (b)). Energy-dispersive X-ray (EDX) analysis with a scanning electron microscope (SEM) on the crystals revealed chemical compositions of Ce:Ce:As=1:3:3.

Magnetization measurements were performed using a Quantum Design physical property measurement system (PPMS) in the temperature range of 1.8 - 400 K under 0 - 16 T. Figure 2 shows the temperature dependent magnetic susceptibilities measured at a field of 1T with H parallel and perpendicular to the triangular plane, respectively. For H || ab-plane, the magnetic susceptibility displays a Curie-Weiss like behavior. There is no indication of magnetic order down to the lowest measured temperature of 1.8 K. As we shall see below from the specific heat measurement in the He3 temperature range, no sign of magnetic order was seen down to 0.6 K. The inverse of the susceptibility below 20 K shown in the inset of Fig. 2 (a) could be well fitted by the Curie-Weiss law with an antiferromagnetic Weiss temperature $\theta_W = -4.4$ K. According to the generic Hamiltonian proposed for the rare-earth triangular systems in earlier studies on YbMgGaO$_4$ [11, 12] (also see Eq. 1 below), the Weiss temperature is related to the antiferromagnetic interaction by $\theta_W = -3J_z$ [12, 15], then we obtain in-plane antiferromagnetic coupling $J_z \approx 1.5$ K. As a comparison, $J_z \approx 0.9$ K for YbMgGaO$_4$ [12].

On the other hand, when the field is applied parallel to the c axis, the susceptibility shows significantly different behavior. As shown in Fig. 2 (b), a broad peak is observed near 150 K. Such broad peak is commonly seen in 1D or 2D systems with strong antiferromagnetic interactions [25]. The upturn below 40 K in the susceptibility could be ascribed to the magnetic defects or impurities in the sample. The result provides clear evidence for the presence of strong antiferromagnetic coupling along the c-axis. In general, one expects that antiferromagnetic correlation of any sort would depress susceptibility, because the correlations resist the alignment of spins with the applied field. As temperature increases, the antiferromagnetic correlations are expected to decrease, leading to an increase of magnetic susceptibility. At high temperature when the antiferromagnetic correlation is weak enough and the moments are effectively decoupled, then a Curie-Weiss behavior is expected to occur. As a result, a peak would develop in the magnetic susceptibility. The location of the peak roughly reflects the energy scale of the antiferromagnetic coupling $J_z$ along c-axis. For instance, for an s=1/2 2D square lattice antiferromagnet, $J = k_BT_{max}/0.9$ [25, 26]. Another possibility for the broad peak in the susceptibility is the thermal excitations of the excited Kramers’ doublets. This effect has been observed, for instance, in Sm$_2$Ti$_2$O$_7$ [27, 28]. Whether similar effect is relevant for CeCd$_3$As$_3$ is not quite obvious, it is likely both the activation of excited doublets and strong $J_z$ interaction may be present. The following magnetization measurement with increasing fields further supports a large anisotropy for the antiferromagnetic spin interaction in the ab plane and along the c axis.

In Fig. 3, we show the field dependent magnetizations up
to 16 T at several selected temperatures with $H$ parallel and perpendicular to the triangular plane, respectively. For $H \parallel ab$ plane (Fig. 3 (a)), the magnetization increases linearly with field below 5 T, then tends to saturate at higher magnetic field. When the field is higher than 12 T, the magnetization at low temperature (e.g. at 1.9 K) becomes linearly dependent on the field with a very small slope, which is understood as the Van Vleck susceptibility. The result is similar to that seen in YbMgGaO$_4$ [11, 12], except for the slightly higher magnetic field for the magnetization saturation. The observation also suggests a bit higher in-plane antiferromagnetic coupling strength for CeCd$_3$As$_3$ than YbMgGaO$_4$. By contrast, for $H \parallel c$-axis (Fig. 3 (b)), the magnetization shows roughly a linear increase with field up to the highest measurement field (16 T) without showing any tendency towards a saturation. This is because the antiferromagnetic interaction is rather strong for $c$-axis direction, a magnetic field of 16 T is still too small as compared to the $c$-direction coupling strength $J_{zz}$. We thus conclude from the susceptibility and magnetization measurements that the antiferromagnetic coupling along the $c$-axis $J_{zz}$ may be one or two orders larger than the in-plane $J_s$.

To demonstrate whether the spins of CeCd$_3$As$_3$ become ordered at further lower temperature, we performed specific heat measurement with a He3 cryostat in PPMS system. Fig. 4 shows the specific heat data down to 0.6 K. The specific heat at zero field decreases with decreasing temperature and reaches a minimum near 3.5 K, then shows an upturn at lower temperature. The data are very similar to that seen for YbMgGaO$_4$ [11], except that the minimum appears at lower temperature for CeCd$_3$As$_3$. In YbMgGaO$_4$ the minimum locates near 10 K at zero field, below which the specific heat increases and forms a broad hump at 2.4 K. The broad hump is an indication for the crossover into a quantum spin liquid state [3, 11]. Below the hump the magnetic specific heat would follow a power-law temperature dependence. In our current measurement, we could not access to the temperature below 0.6 K, so the downward turn below 0.6 K is not yet observed for CeCd$_3$As$_3$. Nevertheless, the compound does not show any magnetic order down to our lowest measured temperature.

We also performed the specific heat measurement under the external magnetic field parallel to the ab-plane. The data are also shown in Fig. 4. If there exists an antiferromagnetic order, i.e. presence of a sharp $\lambda$-shape peak, below our lowest measured temperature of 0.6 K, we expect that the magnetic field would suppress the values of specific heat above the ordering temperature and shifts the $\lambda$-shape peak to lower temperature. However, applying the magnetic field actually increases the value of specific heat at high temperature above 1.5 K. A broad hump is clearly visible for a magnetic field of 6 T. The result is again very similar to the case of YbMgGaO$_4$ for which the applied magnetic field induces a shift of the broad hump to a higher temperature. The field dependent measurement may indicate an absence of magnetic order even below our lowest measured temperature.

Now let us discuss the implication of the experimental data. Due to the spin-orbit-entangled nature of the Kramers doublets, the interaction between the effective spin-1/2 moments is highly anisotropic. Based on earlier works, the most generic spin Hamiltonian allowed by the space group symmetry of the
rare-earth triangular system is given by [12–15]
\[
\mathcal{H} = \sum_{\langle ij \rangle} J_{x} S_{i}^{x} S_{j}^{x} + J_{z} (S_{i}^{z} S_{j}^{z} + S_{i}^{z} S_{j}^{z}) \\
+ J_{zz} (\gamma_{ij} S_{i}^{z} S_{j}^{z} + \gamma_{ij} S_{i}^{z} S_{j}^{z}) \\
- \frac{J_{zz}}{2} [(\gamma_{ij} S_{i}^{z} - \gamma_{ij} S_{j}^{z}) S_{j}^{z} + S_{i}^{z} (\gamma_{ij} S_{j}^{z} - \gamma_{ij} S_{i}^{z})],
\]
where \( S_{i}^{\pm} = S_{i}^{x} \pm i S_{i}^{y} \), and \( \gamma_{ij} = \gamma_{ji} = 1, e^{i2\pi/3}, e^{-i2\pi/3} \) are the phase factors for the bond \( ij \) along three 120° directions, respectively. The first line of Eq. (1) is the standard XXZ model. The \( J_{x} \) and \( J_{z} \) are the antiferromagnetic interactions within and perpendicular to the triangular layer. The \( J_{zz} \) and \( J_{zz} \) terms of Eq. (1) define the anisotropic interactions that arise from the strong spin-orbit coupling. According to the experiments presented above, both \( J_{x} \) and \( J_{z} \) are very small for \( \text{YbMgGaO}_4 \) and relatively close antiferromagnetic coupling strengths along c-axis and ab-plane, leading to a gapless U(1) quantum spin liquid ground state, whereas \( \text{CeCd}_3\text{As}_3 \) shows extremely anisotropic antiferromagnetic coupling strengths, realizing a 2D Ising antiferromagnet on a triangular lattice. Another difference is that the antiferromagnetic coupling \( J \) is very small for \( \text{YbMgGaO}_4 \) (both \( J_{z} \) and \( J_{x} \sim 1 \text{ K} \)), while for \( \text{CeCd}_3\text{As}_3 \), the antiferromagnetic coupling along c-direction \( J_{z} \) is considerably larger. Since the spins are not ordered down to at least 0.6 K, the compound represents an extremely frustrated system. In fact, rare earth geometrical frustration structures can be realized in many different compounds, for example, in the \( \text{CaAl}_2\text{Si}_2 \)-type trigonal structure with a \( \text{P}3_{1}^{\text{m}1} \) space group [48], besides a few structures mentioned in the introduction. Exploration of quantum magnetism in those different systems would be of much interest.

FIG. 5. (a) The three-sublattice ordered structures in the ground state for the antiferromagnetic Ising model on the triangular lattice with presence of a transverse field [31]. (b) A spin configuration with two of the sublattices showing up-spins and the remaining down. It corresponds to a 1/3-plateau of the saturation value in magnetization.

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* gangchen.physics@gmail.com
† nlwang@pku.edu.cn
[1] L. Balents, Nature 464, 199 (2010).
[2] G. H. Wannier, Phys. Rev. 79, 357 (1950).
[3] S. Yamashita, Y. Nakazawa, M. Oguni, Y. Oshima, H. Nojiri, Y. Shimizu, K. Miyagawa, and K. Kanoda, Nature Physics 4, 459 (2008).
