A rare-earth Kitaev material candidate YbCl$_3$

Jie Xing, Huibo Cao, Eve Emmanouilidou, Chaowei Hu, Jinyu Liu, David Graf, Arthur P. Ramirez, Gang Chen, and Ni Ni

1Department of Physics and Astronomy and California NanoSystems Institute, University of California, Los Angeles, CA 90095, USA
2Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
3National High Magnetic Field Laboratory, 1800 E. Paul Dirac Drive, Tallahassee, FL 32310, USA
4Department of Physics, University of California, Santa Cruz, CA 95064, USA
5Department of Physics and Center of Theoretical and Computational Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, China
6State Key Laboratory of Surface Physics and Department of Physics, Fudan University, Shanghai 200433, China

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Most of the searches for Kitaev materials deal with 4$d$/5$d$ magnets with spin-orbit-coupled $J = 1/2$ local moments such as iridates and $\alpha$-RuCl$_3$. Here we propose a new Kitaev material candidate YbCl$_3$. We perform thermodynamic, ac susceptibility and angle-dependent magnetic torque measurements on YbCl$_3$ single crystal. We find that the Yb$^{3+}$ ion exhibits a Kramers doublet ground state that gives rise to an effective spin $J_{\text{eff}} = 1/2$ local moment with likely strong anisotropic exchange interactions. The compound exhibits short-range magnetic ordering at around 1.20 K followed by long-range ordering at 0.60 K. These orderings can be suppressed by in-plane and out-of-plane magnetic fields, resulting in a quantum critical point at around 6 and 10 T, respectively. Furthermore, the non-monotonic decrease of Neel temperature under out-of-plane magnetic fields and the 99.8% of ground state entropy release across the short range ordering, strongly suggest that YbCl$_3$ is more two-dimensional than $\alpha$-RuCl$_3$ and thus a closer realization of a Kitaev system.

Introduction.—In recent years, there has been a tremendous effort aimed at finding a material that supports a Kitaev spin liquid. The Kitaev spin liquid is a $Z_2$ state with gapless and nodal Majorana fermion excitations and gapped bosonic visons. It was solved exactly by A. Kitaev for a pairwise anisotropic spin model on a honeycomb lattice [1]. A material realization of the Kitaev model was suggested to be present in honeycomb iridates A$_2$IrO$_3$ (A = Na, Li, H$_2$Li, Cu) and $\alpha$-RuCl$_3$ [2-19]. The spin-orbit coupling of the iridium or ruthenium moments has been proposed to create highly anisotropic spin interactions including the nearest-neighbor Kitaev interaction [20]. Due to the extended nature of 4$d$/5$d$ orbits, in A$_2$IrO$_3$ and $\alpha$-RuCl$_3$, in addition to a nearest-neighbor Kitaev interaction, further neighbor interactions often exist, leading to greater complexity. It has been suggested theoretically, however, that rare-earth magnets, especially Yb-based ones may provide a more faithful realization of the Kitaev model [21-23]. The rare-earth 4$f$ electrons experience much stronger spin-orbit coupling than the 4$d$/5$d$ electrons [21]. The crystal electric field (CEF) enters as a subleading energy scale after the spin-orbit coupling, which often creates an effective spin-1/2 local moment ground state. Due to the strong localization of the 4$f$ electrons, the spin exchange interaction is usually limited to the nearest neighbors. Although the large magnetic moments of rare earth ions can result in strong long range dipole-dipole interaction coupling that exceeds the exchange energy, for Yb$^{3+}$ with $J_{\text{eff}} = 1/2$, the dipole-dipole interaction was calculated to be small [22]. These properties suggest that Yb-based compounds may be good host systems to realize the Kitaev model. In this paper, we carry out the first experimental study of a rare-earth based Kitaev material candidate, YbCl$_3$. The ground state of YbCl$_3$ is a $J_{\text{eff}} = 1/2$ magnet with short range magnetic ordering (SRO) at 1.20 K, long range magnetic ordering (LRO) at 0.60 K and strong in-plane magnetic anisotropy. The balance of entropy between SRO and LRO demonstrates that YbCl$_3$ is indeed a quasi-two dimensional (2D) magnet that may provide a platform for Kitaev physics.

Millimeter-sized transparent YbCl$_3$ single crystals with shiny as-grown flat ab surfaces were grown by the modified Bridgeman method. Commercial YbCl$_3$ powder (Alfa Aesar 99.99%) was sealed in a quartz tube under the vacuum and quickly heated up to 800°C. The ampoule was kept at 800°C for 10 hours and then cooled to 500°C at a rate 10°C/h. The crystals are soft and can be cleaved easily due to its quasi-2D crystal structure. The crystals decompose into white powder in air (producing YbCl$_3$·6H$_2$O) within a few minutes. Covering the sample with a thin layer of N grease can prevent it from decomposing for hours. During our measurements, we have ensured that samples were not exposed to air either by sealing it with N-grease or encapsulating it inside a non-magnetic NMR tube.

Layered honeycomb lattice with $J_{\text{eff}} = 1/2$ ground state—We performed single crystal neutron diffraction for YbCl$_3$ at room temperature on the Four-Circle Diffractometer (HB-3A) at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) [24]. A good fit to the experimental data suggests the sample is of high quality. The refined crystallographic...
data are summarized in Table I. The compound crystallizes in the monoclinic C2/m space group, the same as α-RuCl3. The slightly distorted edge-sharing YbCl6 octahedra form layered honeycomb ab planes, as shown in Fig. (a). The out-of-plane nearest neighbor distance of Yb3+ is 6.3326 Å and the in-plane nearest neighbor distance is 3.90(1) Å with the ratio of them being 1.62, slightly less than 1.75 found in α-RuCl3. As a Kramers ion, under the crystal electric field (CEF) with C2 point group symmetry, the eight-fold degenerate J = 7/2 states of the Yb3+ ion are split with the CEF ground state being at least two-fold degenerated due to time reversal symmetry.

Magnetic specific heat is a powerful tool to identify the ground state since it provides the entropy release across phase transitions. Upon warming, S_m(T) exhibits a two-plateau feature, suggesting a substantial CEF energy gap between the ground state and the first excited state. S_m(T) at the first plateau reaches 5.3(4) J/mol at 8 K, which is very close to R ln 2 expected from a doublet, indicating the J_{eff} = 1/2 ground state. Around 180 K, S_m(T) almost saturates at 11.4(8) J/mol, consistent with the full magnetic entropy release R ln (8/2) expected from the Yb3+ ion with ground state degeneracy as two. This sets the upper limit of the CEF energy of the excited states to be smaller than ~ 15 meV.

Whereas an obvious interpretation of the 1.20 K hump is the development of SRO related to the behavior of a continuous order parameter in a 2D geometry and the 0.60 K kink is associated with LRO, given the importance of honeycomb systems, other scenarios should be entertained. These include in particular a crossover to quantum spin liquid and possible signatures of the thermal fractionalization of S = 1/2 into the itinerant and localized Majorana fermions. While we do not observe such fractionalization, the SRO hump releases...
99.8% of the ground state entropy, leaving only 0.2% for the LRO, which is almost 100 orders of magnitude smaller than the entropy release of LRO in α-RuCl₃ [27]. This observation strongly suggests that YbCl₃ is more 2D-like than α-RuCl₃, being a closer realization of a 2D magnet. Furthermore, since the site order of the $J_{\text{eff}} = 1/2$ spins can be observed via the LRO peaks, which are very sharp, implying that correlation lengths, at least for classical order, are very large (likely at least 100 Å).

The inset of Fig. 2(b) shows the $C/T$ vs. $T^2$ plot of LuCl₃. By fitting the data from 1.8 K to 6 K with the low temperature limit of 3D Debye model $C = \beta T^3$, we obtain the Debye temperature as 260(5) K, a little higher than $\sim 210$ K of α-RuCl₃ [12, 14]. Although $C^{\text{LuCl₃}}$ follows the 3D Debye model at low temperatures, large deviations from the model can be seen in Fig. 2(b) at higher temperatures, suggesting the failure of using this 3D model to describe the phonons here. This may not be surprising considering that phonons in α-RuCl₃ above 15 K can be fitted by 2D Debye model [14].

The effect of external magnetic field.—To further investigate the nature of the anomalies presented in Fig. 1(c), the magnetic susceptibility and specific heat measurements were performed in a magnetic field. In Fig. 2(a) we show the magnetic susceptibility of YbCl₃ measured at 1 T. No LRO is observed above 1.8 K. The magnetic susceptibility of YbCl₃ is clearly less anisotropic than α-RuCl₃ with $\chi_{ab}$ being slightly larger than $\chi_{c}$ at 1.8 K [17]. A Curie-Weiss (CW) fit is made using $1/\chi = C/(T + \Theta_{w})$, where $\Theta_{w}$ is the Weiss temperature and $C$ is the Curie constant, being related to the effective moment $\mu_{\text{eff}}$ by $\mu_{\text{eff}} \approx \sqrt{SC}$. The fit of the inverse susceptibility from 3 K to 15 K is presented in the inset of Fig. 2(a). The fitted $\Theta_{w} = 6(1)$ K, $\Theta_{c} = -9(1)$ K, $\mu_{\text{eff}} = 3.1(1)\mu_{B}/\text{Yb}^{3+}$ and $\mu_{\text{eff}} = 3.0(1)\mu_{B}/\text{Yb}^{3+}$. The negative $\Theta_{w}$ is consistent with the antiferromagnetic in-plane and out-of-plane exchange interactions. The inferred $\mu_{\text{eff}}$ is much smaller than 4.54$\mu_{B}$ of a free $J = 7/2 \text{Yb}^{3+}$ spin, because $\text{Yb}^{3+}$ ions should enter into a Kramers doublet state below 15 K. $g$-factors of $g^\parallel = 3.6(1)$ and $g^\perp = 3.5(1)$ are extracted using $\mu_{\text{eff}} = g[J(J + 1)]^{1/2}$ and $J_{\text{eff}} = 1/2$.

Figure 2(b) shows the isothermal magnetization up to 7 T. No spontaneous magnetism is observed, again consistent with dominant antiferromagnetic interactions. $M(H)^\parallel$ starts to saturate around 6 T, but no sign of saturation is seen for $M(H)^\perp$ up to 7 T, indicating that the spins prefer to lie in the $ab$ plane, similar to that seen in α-RuCl₃ [14]. At 7 T, the value of magnetic moment is $1.7\ \mu_{B}$ with $H \parallel ab$ and $1.1\ \mu_{B}$ with $H \perp ab$, resulting in $M_0/M_{\perp} \sim 1.5$ at 7 T. This value is almost 4 times smaller than that of α-RuCl₃, suggesting the spins are more Heisenberg-like and thus stronger quantum fluctuation can be expected.

Field-dependent $ac$ susceptibility with $H \parallel ab$ and $H \perp ab$ were measured and shown in Fig. 2(c) and (d). In both directions, a cusp feature is seen at moderate fields, suggesting sharp slope change in $M(H)$. For $H \parallel ab$, the feature occurs at around 5.7 T for temperatures below 0.6 K while for $H \perp ab$, it appears at around 9.5 T for temperatures below 0.6 K. Combined with the specific heat data under fields (Fig. 3(a)), we will see that the cusp feature is associated with the suppression of LRO and these two fields are near to the critical fields where quantum critical point emerges.

In Fig. 3(a) we plot the temperature dependent $C/T$ at various magnetic fields. With increasing fields, the $T_2$ transition becomes more dominant while the hump at $T_1$ gets slowly suppressed. Figure 3(a) provides a quantitative visualization of how the entropy transfers from SRO to LRO under fields. Furthermore, an unusual response of $T_2$ to the applied field is observed. Instead of being monotonically suppressed by field, $T_2$ first increases from 0.60 K at 0 T to 0.85 K at 3 T and then gets smoothly suppressed down to 0.50 K at 9 T. This behavior contradicts the mean-field theory which suggests negative $\partial T_N/\partial H$ with field, but rather can be understood when theoretical treatment beyond the mean-field theory is employed which has shown that the reduction of spin dimensionality can induce a positive $\partial T_N/\partial H$ [28]. The reduction of spin dimensionality is small effect leading to a 0.1% increase of Néel temperature in 3D magnet, but is larger with decreasing dimensionality. Recently, based...
has a honeycomb lattice of $J_{\text{eff}} = 1/2$ Yb$^{3+}$ spins. Since the Kitaev model describes a spin $1/2$ honeycomb lattice with highly anisotropic couplings between nearest neighbors, to obtain some information of the nearest neighbor coupling, we investigated the in-plane magnetic anisotropy by measuring the angular dependence of the magnetic torque on the YbCl$_3$ single crystal with $H \parallel ab$ using a cantilever. The data taken at 2.1 K and 5 T are depicted in the inset of Fig. 3(c). $\theta$ is the angle between $H$ and the arbitrarily chosen crystal axis $l$ in the $ab$ plane. The magnetic torque corresponds to the magnetization according the formula $\tau = \vec{M} \times \vec{H} = \mu_0 V (M_{ll} H_{ll} - M_{lL} H_{ll})$ where $\mu_0$ is the permeability, $V$ is the sample volume, $M_{ll}$, $M_{lL}$, $H_{ll}$, and $H_{lL}$ are the projections of $\vec{M}$ and $\vec{H}$ along and perpendicular to the $l$ axis in the $ab$ plane. Therefore, $\tau$ is very sensitive to the anisotropy of the in-plane magnetization. For the Yb$^{3+}$ ion, a large portion of the local moment comes from the orbital degrees of freedom. Because the orbitals have orientation, the spin-orbit-coupled local moment would inherit the orbital orientation, and thus the interaction between the local moment would have a strong orientation dependence (or equivalently, bond orientation dependence) $^{33}$. Therefore, the lattice symmetry, that determines the bond dependent interaction, would be the key guiding factor of the magnetic anisotropy. As shown in Fig. 3(c), this bond dependent anisotropy is readily manifested in the magnetic torque measurement. In the low magnetic field, the magnetic torque indeed shows four-fold symmetry which agrees with the monoclinic structure in YbCl$_3$.

In conclusion, we propose YbCl$_3$ as a 2D Kitaev material candidate with $J_{\text{eff}} = 1/2$ local moments and strong bond-dependent in-plane anisotropy. This compound exhibits SRO at 1.20 K and LRO at 0.60 K with spins likely in the $ab$ plane. The application of external magnetic fields can suppress these orders at around 6 T (in-plane field) and 10 T (out-of-plane field), resulting in a QCP. Further investigation in the quantum critical region where quantum fluctuation dominates may lead to the discovery of a Kitaev QSL state.

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