Antiferromagnetic Kitaev Interaction in $f$-Electron Based Honeycomb Magnets

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We theoretically propose a family of $f$-electron based magnets that realize Kitaev-type bond-dependent anisotropic interactions. Based on ab initio calculations, we show that $A_2$PrO$_3$ ($A$: alkali metals) crystalize in a triclinic structure with honeycomb layers of edge-sharing PrO$_6$ octahedra. Each Pr$^{4+}$ cation has a $4f$ electron in the $\Gamma_7$ doublet, which comprises a spin-orbital entangled Kramers pair with the effective moment $J_{\text{eff}} = 1/2$. By using the Wannier orbitals from the ab initio calculations, we find that the effective interactions between the $J_{\text{eff}} = 1/2$ moments are predominantly of antiferromagnetic Kitaev type for light alkali metals $A$=Li and Na, in stark contrast to the ferromagnetic ones in 4$d$- and 5$d$-electron based materials. Our finding would provide a playground for the Kitaev spin liquids that is hard to be accessed by the candidates ever discovered.

Quantum spin liquid (QSL) is an exotic magnetic phase in a system with interacting localized spins [1–4]. In the QSL, spins remain disordered even at zero temperature because of competing interactions and strong quantum fluctuations, while they are strongly correlated and quantum entangled. The quantum entanglement gives rise to a topological order [5, 6] and fractionalization of spins into emergent quasiparticles [7, 8]. The peculiar nature of the QSLs has attracted growing interest, since it is potentially utilized in quantum computation [9].

The QSL has been long sought for antiferromagnets with triangular-based lattice structures, where the antiferromagnetic interactions compete with each other due to geometrical frustration [10, 11]. Several candidates have been intensively studied, e.g., in triangular [12, 13], kagome [14, 15], hyperkagome [16], and pyrochlore compounds [18, 19]. Another route to the QSLs has also been pursued for magnets with directionally dependent interactions [20, 21]. Such directional dependence originates from the coupling between the spin and orbital degrees of freedom, which may lead to severe competition even for nonfrustrated lattice structures [22, 24].

Recently, a model in the latter category, called the Kitaev model, has attracted upsurge interest, as it provides an exact QSL ground state [25]. The model has antiferromagnetic Kitaev candidates but also provide the possibility of ferromagnetic ones presumed for the 4$d$ candidates. We substantiate these ideas by ab initio calculations for the rare-earth oxides $A_2$PrO$_3$ ($A$: alkali metals). By deriving the low-energy effective model, we find that the magnetic property is dominated by the Kitaev-type interactions for light alkali metals $A$=Li and Na, and remarkably, the interactions are antiferromagnetic, in stark contrast to the ferromagnetic ones presumed for the 4$d$ and 5$d$ candidates [20, 25, 30]. The qualitative difference originates from the peculiar spatial anisotropy of the $f$ orbitals as well as the weak crystal field. Our results not only add the Kitaev candidates but also provide the possibility of antiferromagnetic Kitaev QSLs, which have recently attracted much attention owing to the intriguing properties in an applied magnetic field [37, 41].

Let us first discuss the electronic state of an $f$ electron subject to the spin-orbit coupling and the octahedral crystal field. The 14 energy levels of the $f$ orbitals with the angular momentum $l = 3$ are split into the low-energy $2F_{5/2}$ sextet and the high-energy $2F_{7/2}$ octet by the spin-orbit coupling [see the left and middle panels of Fig. 1(a)]. The $2F_{5/2}$ sextet is further split into the low-energy $\Gamma_7$ doublet and the high-energy $\Gamma_5$ quartet under the octahedral crystal field [see the right panel of...
The electronic states realize the $\Gamma_7$ doublet; see Eq. (1).

The $\Gamma_7$ doublet can be treated as pseudospins with the effective moment of 1/2, similar to the $J_{\text{eff}} = 1/2$ states in the $d^5$ low-spin case. The time-reversal pair is represented by

$$|+\rangle = \frac{1}{\sqrt{21}} \left( 2i c^\dagger_{\xi \uparrow} - 2c^\dagger_{\eta \downarrow} + 2i c^\dagger_{\zeta \uparrow} + 3c^\dagger_{A \uparrow} \right) |0\rangle,$$

$$|\rangle = \frac{1}{\sqrt{21}} \left( 2i c^\dagger_{\xi \uparrow} + 2c^\dagger_{\eta \downarrow} - 2i c^\dagger_{\zeta \uparrow} + 3c^\dagger_{A \uparrow} \right) |0\rangle,$$

where ($\xi$, $\eta$, $\zeta$) and $A$ denote the $f$ orbitals with the irreducible representations $T_{2u}$ and $A_{2u}$, respectively \cite{82}, and $c^\dagger_{\nu \sigma}$ is a creation operator of an electron with orbital $\nu$ and spin $\sigma$. Figure 1(b) displays the pseudospin state $|+\rangle$, which has a similar profile to the $d^5$ $J_{\text{eff}} = 1/2$ state \cite{75} but different directional spin dependence. Then, the pseudospin operator $S = (S^x, S^y, S^z)^T$ can be defined by

$$S^\mu = -\frac{3}{5} \left[ \langle +|J^\mu|+\rangle - \langle +|J^\mu|-\rangle - \langle -|J^\mu|+\rangle + \langle -|J^\mu|-\rangle \right] = \frac{1}{2} \sigma^\mu,$$

where $J$ and $\sigma$ are the total angular momentum operator and the Pauli matrix, respectively.

The above observation leads us to consider analogous Kitaev systems to the $4d$ and $5d$ materials by using the $f^1$ $\Gamma_7$ Kramers doublet. As an isostructural candidate with the iridium oxides $A_2\text{IrO}_3$, we consider Pr-based oxides $A_2\text{PrO}_3$ ($A$: alkali metals) with the $4f^1$ electron configuration in the $\text{Pr}^{4+}$ cations. We investigate the stability of the Pr oxides by \textit{ab initio} calculations, and check if the electronic states realize the $\Gamma_7$ doublet. The \textit{ab initio} calculations with the structure optimization are performed by using \textsc{Quantum ESPRESSO} \cite{74}, and the maximally-localized Wannier functions (MLWFs) are extracted with \textsc{WANNIER90} \cite{75}. See Supplemental Material for further details \cite{82}. We calculated the compounds with $A=$ Li, Na, K, Rb, and Cs, and found that all the results converge onto a triclinic structure with P1 symmetry. In the following, we focus on two materials with $A=$ Li and Na since they are most interesting from the viewpoint of the effective magnetic couplings as discussed later. The comprehensive analyses including other compounds will be reported elsewhere.

The optimized lattice structures of $A_2\text{PrO}_3$ ($A=$ Li, Na) are composed of honeycomb layers of edge-sharing $\text{PrO}_6$ octahedra, as exemplified in Fig. 2. The structural parameters are summarized in Table I. Each Pr layer is close to a perfect honeycomb structure with $C_3$ symmetry. We note that there are small trigonal distortions, indicated by the deviations of $a/n$ and $\theta_{\text{Pr-O-Pr}}$ from their ideal values $3/\sqrt{2}$ and $90^{\circ}$, respectively.

The electronic band structures obtained by the \textit{ab initio} calculations are shown in Fig. 3. In both $A=$ Li and Na cases, the Pr 4$f$ bands are well isolated from the lower-energy O 2$p$ bands and the higher-energy Pr 6$s$, A 2$p$, and A 2$s$ bands \cite{82}. The bandwidth is slightly wider in the Li case, reflecting the smaller lattice constants in Table I. As expected in Fig. 1(a), the energy bands originating from the $2F_{5/2}$ sextet and the $2F_{7/2}$
octet are split by the strong spin-orbit coupling; see the projected density of states in the right panels of Fig. 3. In comparison with the results by nonrelativistic calculations, the spin-orbit coupling coefficient is estimated as \( \sim 120 \) meV, close to the empirical values \([16, 17]\). In the \( 4f^1 \) state, the lowest-energy shallow bands (doubly degenerate) separated from the others lie below the Fermi level in both Li and Na cases. Thus, the results indicate that the systems are band insulators with two \( f \) electrons per unit cell on average. We confirm that the MLWFs for the occupied states have the \( \Gamma_7 \)-like profile.

In Fig. 3 we also show the tight-binding band structures with transfer integrals between neighboring Pr cations estimated from the MLWFs in Fig. 3 [45]. The \( ab \) initio results are well reproduced, especially for the low-energy bands, indicating that further-neighbor hoppings are less important because of the localized nature of \( 4f \) orbitals.

The above analysis suggests that the \( 4f^1 \) compounds may become the spin-orbit coupled Mott insulators under strong electron correlations. We here consider an effective model for the \( \Gamma_7 \) pseudospins in Eqs. (1) and (2) by the second-order perturbation in terms of the nearest-neighbor transfer integrals between Pr cations in the same honeycomb layer [45]. The calculations are performed by taking into account all the 91 intermediate \( 4f^2 \) states of \( \text{Pr}^{3+} \) whose multiplet levels are treated by the Russel-Saunders scheme following the literature [48]. In the perturbation calculation, we take into account both the direct \( 4f-4f \) and the indirect \( 4f-2p-4f \) paths; we symmetrize the transfer integrals for three different directions by taking their average so as to recover the \( C_3 \) symmetry that is weakly broken in our optimized structures.

The effective pseudospin Hamiltonian for one of three types of bonds on the honeycomb structure (\( z \) bond) is given in the matrix form

\[
\mathcal{H}_{i,j}^{(z)} = S_i^T \begin{bmatrix} J & \Gamma & \Gamma' \\ \Gamma & J & \Gamma' \\ \Gamma' & \Gamma' & J + K \end{bmatrix} S_j,
\]

where \( S_i \) is the pseudospin defined in Eq. (3) at site \( i \). The total Hamiltonian is given by the sum over the neighboring \( \mu = x, y, z \) bonds, \( \mathcal{H}_{\text{eff}} = \sum_{\mu} \sum_{(i,j)} \mathcal{H}_{i,j}^{(\mu)} \), where \( \mathcal{H}_{i,j}^{(x)} \) and \( \mathcal{H}_{i,j}^{(y)} \) are given by cyclic permutations of \( \{xyz\} \) in \( \mathcal{H}_{i,j}^{(z)} \). In Eq. (4), the diagonal terms \( J \) and \( K \) represent the isotropic Heisenberg coupling and the bond-dependent anisotropic Kitaev coupling, respectively, and \( \Gamma \) and \( \Gamma' \) are the symmetric off-diagonal couplings [35]. The coupling constants are plotted in Fig. 4 as functions of the ratio of the Hund’s-rule coupling \( J_H \) to the intraorbital Coulomb repulsion \( U \). We find that, as increasing \( J_H/U \), the Kitaev coupling \( K \) is largely enhanced, while

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**TABLE I. Structural parameters of the optimized structures for \( \text{Li}_2\text{PrO}_3 \) (\( \text{Li} = \text{Li}, \text{Na} \)). See Fig. 2(b) for the definitions of \( a, b, c, \alpha, \beta, \gamma, \) and \( n \). The ratio \( a/n \) becomes \( 3/\sqrt{2} \approx 2.12 \) in an ideal edge-sharing octahedra under the \( O_h \) symmetry. \( d_{\text{Pr-Pr}} \) and \( \theta_{\text{Pr-O-Pr}} \) denote the averages of the Pr-Pr bond length and the Pr-O-Pr bond angle, respectively, for the neighboring Pr pair within the same honeycomb layer.**

|          | \( \text{Li}_2\text{PrO}_3 \) | \( \text{Na}_2\text{PrO}_3 \) |
|----------|-----------------|-----------------|
| \( a \) (Å) | 5.6228          | 5.9950          |
| \( b \) (Å) | 5.6270          | 5.9967          |
| \( c \) (Å) | 5.1487          | 5.9923          |
| \( \alpha \) (°) | 79.701          | 80.199          |
| \( \beta \) (°) | 100.29          | 99.802          |
| \( \gamma \) (°) | 59.981          | 60.015          |
| \( n \) (Å) | 2.3656          | 2.3328          |
| \( a/n \) | 2.3769          | 2.5698          |
| \( d_{\text{Pr-Pr}} \) (Å) | 3.2473          | 3.4628          |
| \( \theta_{\text{Pr-O-Pr}} \) (°) | 95.175          | 102.15          |
find that two types of indirect hopping paths predominantly contribute to the antiferromagnetic Kitaev coupling: for a $z$ bond, one is $f_{\xi}p_{z}-f_{\alpha}$ (equivalent to $f_{\eta}p_{y}-f_{\beta}$) [Fig. 5(a)] and the other is $f_{\xi}p_{z}-f_{\zeta}$ [Fig. 5(b)] [42]. The former $f_{\xi}p_{z}-f_{\alpha}$ looks similar to the indirect $t_{2g}$-$e_{g}$ hopping processes ($d_{xy}$-$p_{z}$-$d_{z^2}$-$e_{g}$) in the $d^{5}$ low-spin case [32, 39]. The $t_{2g}$-$e_{g}$ processes contribute to the antiferromagnetic $K$, but the contribution is usually small because of the large crystal field splitting between the $t_{2g}$ and $e_{g}$ manifolds, typically larger than 1 eV. In contrast, $f_{\xi}p_{z}-f_{\alpha}$ in the present case can largely contribute to the antiferromagnetic $K$, as the crystal field splitting between $f_{\xi}$ and $f_{\alpha}$ is small $\sim 0.1$ eV, as shown in Fig. 5(b) [42]. Meanwhile, the latter $f_{\xi}p_{z}-f_{\zeta}$ apparently resembles $d_{yz}$-$p_{z}$-$d_{z^2}$ in the $d^{5}$ case which brings about the ferromagnetic $K$ [26]. However, the distinct spatial anisotropy of the $f_{\zeta}$ orbital allows the indirect hopping between the same orbitals, and contribute differently from the $d^{5}$ case. Thus, the level scheme and the spatial anisotropy of the $f$ orbitals play a crucial role in the peculiar antiferromagnetic Kitaev coupling.

Our finding of the dominant antiferromagnetic $K$ would be important, since the known candidates for the Kitaev QSL are presumed to be ferromagnetic. Although other interactions may stabilize a parasitic long-range order, the pristine effect of the antiferromagnetic $K$ could be revealed, e.g., by thermal fluctuations [50] and an applied magnetic field. The latter has recently attracted much attention owing to the possibility of a field-induced state, which does not appear for the ferromagnetic $K$ [37–41].

Finally, let us comment on the material trend in $A_{2}$-$\text{PrO}_3$. As inferred by the comparison between Li and Na, the Kitaev coupling $K$ becomes smaller for $A$ with the larger ionic radius. This is mainly because the Pr-Pr distance $d_{\text{Pr-Pr}}$ becomes longer. At the same time, the trigonal distortion becomes larger ($a/n$ and $\theta_{\text{Pr-Pr}}$ become larger), which leads to relatively large other couplings $J$, $\Gamma$, and $\Gamma'$. Hence, the $A=$Li case is optimal for the dominant antiferromagnetic Kitaev coupling within this series of compounds. The comprehensive analyses will be reported elsewhere.

To summarize, we have proposed a class of the $f$-electron based Kitaev-type honeycomb magnets on the basis of the ab initio calculations and the effective model analysis. We found that $A_{2}$-$\text{PrO}_3$ ($A$: alkali metal) is well described by the Kitaev-Heisenberg model in the low-energy sector of the $F_{7}$ Kramers doublet for the $4f^1$ configuration of Pr$^{4+}$ cations. We showed that the peculiar spatial anisotropy of the $f$ orbitals and the weak crystal field make the Kitaev coupling antiferromagnetic, in sharp contrast to the ferromagnetic ones in the $4d$ and $5d$ Kitaev candidates ever discussed. Our results provides a platform for the Kitaev QSL, which enables to access the parameter space beyond the existing candidates.

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— Supplemental Material —

Details of \textit{ab initio} calculations

In the \textit{ab initio} calculations, we adopt the pseudopotentials of scalar-relativistic norm-conserving von Barth-Car type \cite{53}, non-relativistic norm-conserving Hartwigesen-Goedecker-Hutter type \cite{54}, and full-relativistic ultrasoft projector-augmented-wave-method Perdew-Zunger type \cite{55,56} for $A$(=Li, Na), O, and Pr, respectively. We set the kinetic energy cutoff at 250 Ry. The lattice structures are optimized starting from the structural parameters for Rb$_2$CeO$_3$ listed in Materials Project \cite{57}. In the structure optimization, the criteria for the maximum crystal stress is set at 0.1 GPa. The remnant maximum atomic forces are less than 0.009 Ry/Bohr in the \textit{ab}-plane and less than 0.0003 Ry/Bohr along the axis perpendicular to the plane. In the self-consistent field calculations for the structure optimization and the non-self-consistent field calculations for the electronic band structures, the (projected) density of states, and the construction of MLWFs, we use the Monkhorst-Pack grids \cite{58} of $4 \times 4 \times 4$ and $8 \times 8 \times 8$ \textit{k}-points, respectively. The convergence threshold in the self-consistent field calculations is set at $1.0 \times 10^{-10}$ Ry.

Electronic band structures

We show the electronic band structures and the projected density of states for Li$_2$PrO$_3$ and Na$_2$PrO$_3$ in Figs. S1 and S2, respectively. In each case, (a) displays the results in a wide energy range from $-25$ eV to 20 eV, and (b) is for the middle energy range from $-6$ eV to 2 eV, including the Pr 4$f$ bands and the O 2$p$ bands. Figure 3 in the main text shows the narrow energy range from $-0.1$ eV to 1.3 eV, focusing on the Pr 4$f$ bands hybridized with the O 2$p$ bands. In both compounds, the 4$f$-2$p$ bands are isolated from other bands, which facilitates the MLWF construction and the effective model analysis in the main text.

In Li$_2$PrO$_3$ in Fig. S1, the hybridized bands of Pr 6$s$, Li 2$s$, and Li 2$p$ orbitals are located above 3.0 eV, and the bands in the range of 3.1 $\sim$ 4.0 eV are mostly ascribed to Li 2$p$ orbitals. The Pr 4$f$ bands hybridized with the O 2$p$ bands lie in the range of $-0.1$ $\sim$ 1.3 eV, where the localized nature of the $f$ orbitals is manifested in the narrow bandwidth and the relatively high projected density of states. The main O 2$p$ bands are located in the range of $-5.7$ $\sim$ $-2.0$ eV with weak hybridization with the Pr 4$f$ bands. The bands in the deep energy levels of $-21.1$ $\sim$ $-13.9$ eV are, mainly from the hybridization of Pr 5$p$ and O 2$s$.

The overall feature of the band structure is shared with Na$_2$PrO$_3$, as shown in Fig. S2. In Na$_2$PrO$_3$, the hybridized bands of Pr 6$s$ and Na 3$s$ orbitals are located above 3.6 eV, and the bands lie in the range of 1.7 $\sim$ 3.6 eV are mostly ascribed to Na 3$s$ orbitals. The Pr 4$f$ bands hybridized with the O 2$p$ bands in the range of $-0.1$ $\sim$ 1.2 eV are well separated from the main O 2$p$ bands in the lower range of $-5.2$ $\sim$ $-2.2$ eV. The bands in the deep energy levels of $-21.1$ $\sim$ $-14.0$ eV are mainly from the hybridization of Pr 5$p$ and O 2$s$.

Transfer integrals estimated from MLWFs

We construct the MLWFs for the Pr 4$f$ and O 2$p$ bands in Figs. S1(b) and S2(b). From the MLWFs, we estimate the transfer integrals for constructing the tight-binding model. We here present the values for the Pr 4$f$ orbitals at the nearest-neighbor sites on a $z$ bond for Li$_2$PrO$_3$ and Na$_2$PrO$_3$ in Tables S1 and SII, respectively. The transfer
integrals are calculated as $t_{\mu\nu} = \langle i, \mu | H_0 | j, \nu \rangle$, where $H_0$ is the ab initio Hamiltonian, $|i, \nu\rangle$ is the MLWF at site $i$ with orbital $\nu(=\xi, \eta, \zeta, A, \alpha, \beta, \text{and } \gamma)$; $i$ and $j$ denote the neighboring sites on a $z$ bond. The values include both direct and indirect (via O 2p) paths, and averaged over three types of bonds to recover the C$_3$ symmetry. For simplicity, we focus on the spin diagonal components; the off-diagonal ones mixing different spins are small (the absolute values are all less than 1 meV), and neglected in the perturbation in the main text. These values as well as the transfer integrals between the neighboring Pr 4f and O 2p orbitals are used for the tight-binding band structures in Fig. 3 in the main text. As shown in Tables SI and SII the most dominant transfer integrals are $t_{\xi\alpha}(=-t_{\eta\beta}^*)$ and $t_{\zeta\zeta}$, both of which are discussed in the main text to give dominant contributions to the antiferromagnetic Kitaev coupling $K$; see Fig. 5 in the main text. Note that the diagonal components for $\alpha$ and $\beta$ are large but do not contribute to the perturbation.
FIG. S1. Electronic band structures and the projected density of states for Li$_2$PrO$_3$ in the energy range from (a) $-25$ eV to $20$ eV and (b) $-6$ eV to $2$ eV. The Fermi level is set to zero.
FIG. S2. Electronic band structures and the projected density of states for Na$_2$PrO$_3$ in the energy range from (a) $-25$ eV to $20$ eV and (b) $-6$ eV to $2$ eV. The Fermi level is set to zero.
TABLE SI. The nearest-neighbor transfer integrals $t_{\mu\nu}$ on a z bond for Li$_2$PrO$_3$; $\mu$ is in the row and $\nu$ is in the column. The unit is in meV. The upper-right half of the table is omitted as the matrix is Hermite conjugate. See the text for details.

| $\xi$ | $\eta$ | $\zeta$ | $A$ | $\alpha$ | $\beta$ | $\gamma$ |
|-------|-------|--------|-----|---------|--------|--------|
| 32.4  | 29.8 + 0.4i | 3.51 + 0.04i | -2.14 - 0.17i | -87.9 + 0.8i | -1.13 + 0.51i | -6.17 + 0.33i |
| $\eta$ | 32.4  | 3.51 - 0.04i | 2.14 - 0.17i | 1.13 + 0.51i | 87.9 + 0.8i | 6.17 + 0.33i |
| $\zeta$ | 29.8 + 0.4i | 3.51 - 0.04i | 0.01 - 0.55i | -9.22 + 0.12i | 4.07 + 0.55i | -0.03 - 0.40i |
| $A$ | 2.14 - 0.17i | 0.01 - 0.55i | -57.1 | -23.2 - 1.7i | -23.2 - 1.7i | -35.1 |
| $\alpha$ | -87.9 + 0.8i | -9.22 + 0.12i | 153 | -0.28 + 0.42i | -0.28 + 0.42i | 153 |
| $\beta$ | -1.13 + 0.51i | 4.07 + 0.55i | 132 | 4.33 + 0.41i | 4.33 + 0.41i | 132 |
| $\gamma$ | -6.17 + 0.33i | -0.03 - 0.40i | -35.1 | 4.33 + 0.41i | 4.33 + 0.41i | 45.0 |

TABLE SII. The nearest-neighbor transfer integrals $t_{\mu\nu}$ on a z bond for Na$_2$PrO$_3$; $\mu$ is in the row and $\nu$ is in the column. The unit is in meV. The upper-right half of the table is omitted as the matrix is Hermite conjugate. See the text for details.

| $\xi$ | $\eta$ | $\zeta$ | $A$ | $\alpha$ | $\beta$ | $\gamma$ |
|-------|-------|--------|-----|---------|--------|--------|
| 14.6  | 14.6  | 14.6  | 14.6 | 14.6    | 14.6    | 14.6    |
| $\eta$ | 14.6  | 14.6  | 14.6 | 14.6    | 14.6    | 14.6    |
| $\zeta$ | 14.6  | 14.6  | 14.6 | 14.6    | 14.6    | 14.6    |
| $A$ | 14.6  | 14.6  | 14.6 | 14.6    | 14.6    | 14.6    |
| $\alpha$ | 14.6  | 14.6  | 14.6 | 14.6    | 14.6    | 14.6    |
| $\beta$ | 14.6  | 14.6  | 14.6 | 14.6    | 14.6    | 14.6    |
| $\gamma$ | 14.6  | 14.6  | 14.6 | 14.6    | 14.6    | 14.6    |