論 文 の 内 容 の 要 旨

論文題目　Materials design of *f*-electron based Kitaev-type magnets
（*f*電子系キタエフ型磁性体の物質設計）

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Quantum spin liquid (QSL) is an exotic state of matter which is achieved when interacting localized magnetic moments do not show any conventional symmetry breaking down to zero temperature. In the QSL, the magnetic moments are strongly entangled under quantum fluctuations, resulting in a topological order and fractionalization of the magnetic excitations into nonlocal quasiparticles. The unique quantum nature of the QSL has attracted much attention as a feasible playground of decoherence-free quantum computation. Since Philip Anderson's proposal in 1973, the QSL has been hunted for decades mostly in antiferromagnets on triangular-based lattices with geometrical frustration. In this long-standing problem, Alexei Kitaev has brought breakthrough in 2006 by proposing a model for the QSL, which is now called the Kitaev model. In this model, the localized spin S=1/2 moments on a two-dimensional honeycomb structure interact with each other by bond-dependent Ising-type interactions, and their competition hampers the formation of long-range order down to zero temperature. The salient feature of this model is that the ground state is exactly obtained as a QSL with fractional excitations. Furthermore, the model is straightforwardly extended to any tricoordinate lattices, which provides a variety of QSLs, such as chiral spin liquids with broken time-reversal symmetry and three-dimensional realizations of QSLs.

The discovery of the exact QSLs in the Kitaev model has motivated theoretical and experimental challenges for its realization in materials science. It was George Jackeli and Giniyat Khaliullin in 2009 who theoretically showed that the Kitaev-type bond-dependent interaction can be realized in a certain class of correlated electron systems with strong spin-orbit coupling (SOC), called the spin-orbit coupled Mott insulators. Specifically, they proposed two important conditions. The first one is the low-spin d^5 electron configuration under the octahedral crystal field (OCF) for the magnetic ions. This electron configuration potentially leads to the spin-orbit Mott insulating state, whose low-energy physics is described by pseudospins with effective j_{eff}=1/2 magnetic moments arising from the ground state of Γ_7 Kramers doublet. The second one is particular quantum interference in the exchange processes by the virtual hopping of electrons. It was pointed out that the edge-sharing octahedral network can realize the

quantum interference for the indirect hopping processes via the ligands, resulting in a ferromagnetic (FM) Kitaev-type interaction. The set of the two conditions, dubbed the Jackeli-Khaliullin mechanism, has evoked a huge amount of materials exploration of the Kitaev QSL. Thus far, several candidates have been nominated, for instance, iridium oxides A_2IrO_3 (A: alkali metals) and a ruthenium halide α-$RuCl_3$. Unfortunately, these materials do not realize the Kitaev QSL ground state despite the dominant FM Kitaev interaction; instead, they exhibit some magnetic orders at low temperature, presumably due to other parasitic interactions such as the Heisenberg interaction. While some signatures of the proximate Kitaev QSL were identified by raising temperature or applying an external magnetic field to suppress the magnetic order, it is desired to expand the candidates for better identification of the Kitaev QSL. In addition, it would be interesting to find a new class of materials that achieve antiferromagnetic (AFM) Kitaev interactions, since the AFM Kitaev model has recently attracted great attention for the possibility of another QSL in a magnetic field. For further exploration of the candidates for the Kitaev QSLs including the AFM case, it is worth exploring another mechanism for the Kitaev-type interactions beyond the Jackeli-Khaliullin mechanism.

In this thesis, we propose the materials design of the Kitaev-type magnets, focusing on *f*-electron compounds that have least studied as the candidates for the Kitaev QSL. While the *f*-electron systems have strong SOC as required in the Jackeli-Khaliullin mechanism, they have different energy scheme among the electron correlation, the SOC, and the crystalline electric field. Furthermore, *f*-electron orbitals have different spatial anisotropy compared to the *d*-electron ones, which gives rise to different exchange processes beyond the Jackeli-Khaliullin mechanism. We here systematically investigate all *f*-electron configurations in the OCF to find out the possible realization of the spin-orbit coupled Mott insulating state with pseudospin degree of freedom from the Kramers doublet. Among many possibilities, we focus on a series of compounds with f^1-electron configuration, A_2PrO_3 (A: alkali metals), possessing lattice structures with edge-sharing octahedra similar to the existing *d*-electron candidates. Based on combined studies of *ab initio* calculations and model calculations, we study the electronic band structure, construct the multiorbital models, and derive effective magnetic interactions between the pseudospins, to explore new candidates for the Kitaev-type magnets.

We begin with the systematic investigation of the ground-state multiplet to clarify which *f*-electron configurations can accommodate the Kramers doublet described by the pseudospin degree of freedom. For the multiplet classification, we use the Lea-Leask-Wolf scheme under the OCF and the Duan-Tanner spectroscopic data. We find that the plausible ground-state multiplets for the $4f^1$ $^2F_{5/2}$, $4f^3$ $^4I_{9/2}$, $4f^5$ $^6H_{5/2}$, $4f^9$ $^6H_{15/2}$, $4f^{11}$ $^4I_{15/2}$, and $4f^{13}$ $^2F_{7/2}$ states are given by Γ_7 doublet, Γ_8 quartet, Γ_7 doublet, Γ_6 doublet, Γ_8 quartet, and Γ_6 doublet, respectively. Thus, there are many candidates of *f*-electron ions with the Kramers doublet, for instance, Ce^{3+} and Pr^{4+} for $4f^1$, Pm^{2+} and Sm^{3+} for $4f^5$, Gd^{+}, Tb^{2+}, and Dy^{3+} for $4f^9$, and Er^{+}, Tm^{2+}, and Yb^{3+} for $4f^{13}$. Among these many possibilities, Pr^{4+} and Yb^{3+} are particularly interesting as there are some experimentally-synthesized compounds in which these ions comprise quasi-two-dimensional honeycomb and three-dimensional hyperhoneycomb structures. For the Yb^{3+}-based compounds, however, a previous study showed that the interaction between the pseudospins

from the Γ_6 doublet is predominantly not Kitaev-type but the conventional Heisenberg one. We therefore focus on the Pr^{4+}-based compounds for our materials design. Amongst others, we study A_2PrO_3 (A: alkali metals) since the compounds are polymorphic and host various edge-sharing PrO_6 networks.

First, we consider the quasi-two-dimensional honeycomb cases. Bearing the experimentally-synthesized Na_2PrO_3 in mind, we systematically study the lattice structure and the electronic structure for A_2PrO_3 for A=Li, Na, K, Rb, and Cs by the relativistic *ab initio* calculations. We find that for all the cases the crystal structures are optimized with space group $C2/m$, indicating that the quasi-two-dimensional honeycomb structures are at least locally stable. We clarify the systematic evolution of the lattice structure with the increase of the A-site ionic radii. The optimized unit cell is gradually expanded along all the crystal axes, and at the same time, the Pr-O-Pr bond angle is increased. The results indicate that the trigonal distortion grows with the A-site ionic radii; while the A=Li case is closest to the ideal octahedral symmetry, the PrO_6 octahedra are flattened in the perpendicular direction to the honeycomb plane from A=Li to A=Cs.

In all the cases, we find that the electronic band structure has relatively narrow Pr 4f bands near the Fermi level, which are well isolated from the other bands. From the analyses of the density of states projected onto each $4f^1$ multiplet as well as the maximally-localized Wannier functions (MLWFs), we conclude that the $4f^1$ states below the Fermi level predominantly originate from the Γ_7-like doublets for all the cases. The lowest-energy doubly-degenerate shallow bands are fully occupied to form a two-sublattice band insulator, which is expected to naturally evolve into the spin-orbit coupled Mott insulator by electron correlations. We show that the tight-binding band structures with nearest-neighbor transfers estimated by the MLWFs are in good agreement with the original *ab initio* results, particularly in the low-energy regime.

We construct the multiorbital Hubbard model for each case composed of the one-body part estimated by the MLWF analysis and two-body Coulomb interactions. Then, we derive the effective exchange interactions between the pseudospins by the second-order perturbation in terms of the f-electron transfers in the strong correlation limit. We find that the resultant effective pseudospin Hamiltonian has a predominant AFM Kitaev interaction, in stark contrast to the FM one predicted by the Jackeli-Khaliullin mechanism for the low-spin d^5 electron configuration. The AFM Kitaev interaction is reduced systematically with the increase of the A-site ionic radii, and eventually turns into a weak FM one for A=Cs. In addition, the effective Hamiltonian has the subdominant AFM Heisenberg interaction, which does not change significantly for the A-site substitution. Thus, the system is well described by the so-called Kitaev-Heisenberg model with the dominant AFM Kitaev (K) and subdominant Heisenberg interactions (J) especially for A=Li and Na, while the trigonal distortion induces a weak symmetric off-diagonal interaction called the Γ' term for A=K, Rb, and Cs. We note that this Γ' term is different from the one called the Γ term relevant to some low-spin d^5 Kitaev-type magnets. Thus, we conclude that the effective pseudospin models for the Pr-based $4f^1$ compounds have distinguished features compared to the previous ones derived from the Jackeli-Khaliullin mechanism: the predominant AFM Kitaev interaction and the weak Γ' instead of Γ.

To reveal the origin of the unprecedented AFM K, we analyze the perturbation processes in detail. We

find that it comes mainly from the indirect hopping processes between f_ξ and f_α orbitals via the ligand p_x orbital (and the symmetrically equivalent ones). These are similar to the d_{xy}-p_x-$d_{3x^2-r^2}$ hopping, which was discussed as an AFM contribution to K in the low-spin d^5 case, in the sense that they both involve the σ-bond overlap. In the d-electron case, however, the contribution is very small compared to the FM one, due to the large OCF splitting between the t_{2g} and e_g manifolds. In contrast, the OCF splitting is rather small for the f-electron compounds, which gives rise to the large AFM K. While the trigonal distortion increases with the A-site ionic radii, the f_ξ-p_x-f_α type hopping is reduced, and instead, the f_ζ-p_z-f_α type is induced and contributes to a FM K. This is the reason why the AFM K is systematically reduced from A=Li to Cs. Likewise, we also clarify the origin of the systematic evolution of J and Γ' for the A-site substitution by similar analysis.

We also compute the phase diagram of the J-K-Γ' model by the Lanczos exact diagonalization method to clarify the plausible ground states of A_2PrO_3. We find that although all the cases are in the Neel ordered region, the system gets close to the AFM Kitaev QSL region with the decrease of the A-site ionic radii and the value of Coulomb interactions. We conclude that the A=Li case is most proximate to the AFM Kitaev QSL.

Next, we consider the three-dimensional hyperhoneycomb case that was experimentally-synthesized for β-Na_2PrO_3. By using the experimental crystal structure with $C2/c$ symmetry, we study the electronic and magnetic properties following the above procedure. We find that the electronic structure is qualitatively similar to the quasi-two-dimensional honeycomb case α-Na_2PrO_3. We show that the effective pseudospin Hamiltonian derived from the multiorbital Hubbard model constructed from the MLWFs is also similar to that for α-Na_2PrO_3, well described by the Heisenberg-Kitaev model with the dominant AFM K. This is the first report of the three-dimensional AFM Kitaev-type candidates.

In summary, we have theoretically proposed the candidates for the Kiteav-type magnets in the f-electron compounds. By screening possible formation of the Kramers doublet out of all the f-electron configurations, we have studied A_2PrO_3 (A: alkali metals) in quasi-two-dimensional honeycomb and three-dimensional hyperhoneycomb crystal structures. Based on *ab initio* calculations and model calculations for systematic substitution of the A-site ion, we showed that these compounds provide unique candidates for the Kitaev-type magnets with the predominant AFM Kitaev interaction which was not obtained in the existing d-electron candidates. We also clarified that the AFM Kitaev interaction originates from the small crystal field and the peculiar spatial anisotropy of the f orbitals beyond the Jackeli-Khaliullin mechanism. Our results will stimulate the experimental material exploration of the AFM Kitaev QSL in f-electron compounds, which has attracted great interest for the possibility of another QSL in the magnetic field. While our analyses have been limited to the $4f^1$ case, other f-electron configurations are also worthy to study for further exploration of the Kitaev magnets beyond the Jackeli-Khaliullin mechanism, such as $4f^5$ Γ_7, $4f^9$ Γ_6, and $5f^1$ Γ_7.