博士論文（要約）

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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Abstract

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, a topological order and fractionalization into nonlocal quasiparticles arise under the strong quantum fluctuations. 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. On this long-standing problem, Alexei Kitaev has brought breakthrough in 2006 by proposing a novel model for the QSL. In the Kitaev honeycomb model, the localized spin $S = 1/2$ moments on a two-dimensional honeycomb structure interact with each other by bond-dependent Ising-type interactions. The salient feature of this model is that the ground state is exactly obtained as a QSL with fractional excitations.

The discovery of the exact QSL 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). Specifically, they proposed two important conditions. The first one is the low-spin d^5 electron configuration under the octahedral crystal field for the magnetic ions, which yields pseudospins with the effective magnetic moment of $j_{\mathrm{eff}} = 1/2$. The second one is particular quantum interference in the exchange processes by the virtual hopping of electrons. The set of the two conditions, dubbed the Jackeli-Khaliullin mechanism, has evoked a huge amount of material exploration of the Kitaev QSL. Unfortunately, most of the candidate materials do not realize the Kitaev QSL ground state, presumably due to other parasitic interactions. Also, while the study of the Kiaev QSLs has been rapidly growing, the candidate materials are still investigated mostly in d-electron systems.

In this thesis, we propose the materials design of the Kitaev-type magnets beyond the Jackeli-Khaliullin mechanism, 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 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. Adopting the Lea-Leask-Wolf parameterization scheme, we find that there are many candidates of f-electron ions with the Kramers doublet. Among these many possibilities, Pr^{4+} is particularly interesting as there are several experimentally-synthesized compounds in which these ions comprise quasi-two-dimensional honeycomb and three-dimensional hyperhoneycomb structures.

First, we consider the quasi-two-dimensional honeycomb cases. We systematically study the lattice structure and the electronic structure of 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. In addition, we find that the $4f^1$ states below the Fermi level predominantly originate from the Γ_7-like doublets for all the cases. By using the tight-binding parameters estimated by the maximally-localized Wannier functions, we construct the multiorbital Hubbard model for each compound. 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 antiferromagnetic (AFM) Kitaev interaction, in stark contrast to the ferromagnetic (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. Meanwhile, the effective Hamiltonian has the subdominant AFM Heisenberg interaction, which does not change significantly for the A-site substitution. We also find that the trigonal distortion, which increases as the A-site ionic radius increases, induces a weak symmetric off-diagonal interaction called the Γ' term. We also compute the ground-state phase diagram of the effective pseudospin model in an extended parameter space by the Lanczos exact diagonalization method to clarify the plausible ground states of A_2PrO_3. We find that the A=Li case is most proximate to the AFM Kitaev QSL.

To reveal the origin of the unprecedented AFM Kitaev interaction, 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 the Kitaev interaction in the low-spin d^5 case. In the d-electron case, however, the contribution is very small compared to the FM one, due to the large crystal field splitting between the t_{2g} and e_g manifolds. In contrast, the crystal field splitting is rather small for the f-electron compounds, and hence, the above perturbation processes give rise to the large AFM Kitaev interaction.

Next, we consider the three-dimensional hyperhoneycomb case β-Na_2PrO_3 that was experimentally synthesized. By using the experimental crystal structure with $C2/c$ symmetry, we study the electronic and magnetic properties following the above procedure. We show that the effective pseudospin Hamiltonian is similar to that

for the quasi-two-dimensional honeycomb case, well described by the Heisenberg-Kitaev model with the dominant AFM Kitaev interaction. Our result indicates that β-Na_2PrO_3 would be a good candidate proximate to the three-dimensional AFM Kitaev QSL.

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. We showed that these compounds provide unique candidates for the Kitaev-type magnets with the predominant AFM Kitaev interaction. 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.