論 文 の 内 容 の 要 旨

論文題目　Theoretical study of spin-orbit coupled systems with honeycomb-layered structures
（ハニカム層状構造をもつスピン軌道結合系の理論的研究）

氏　　名　杉田　悠介

Since the discovery of a monolayer graphene, the study of atomically-thin layered materials has grown as one of the leading issues in condensed matter physics. Electrons confined in a two-dimensional atomic layer show distinct behavior from those in three-dimensional bulk crystals. The archetypal example is the Dirac electrons in graphene, whose energy spectrum exhibits a point node at the Fermi level and linear momentum dependence near the node. The peculiar nodal structure leads to interesting transport phenomena, such as the anomalous integer quantum Hall effect and the Klein tunneling. In the past decade, however, tremendous efforts have been devoted to the quest for layered materials beyond graphene. One direction is to investigate the effect of strong spin-orbit coupling (SOC). For instance, stimulated by a theoretical proposal that the SOC gaps out the Dirac node and potentially changes the system into a Z_2 topological insulator, similar honeycomb-monolayer forms of heavier elements with larger SOC, such as Si, Ge, and Sn, have been studied. Another direction is to explore the effect of electron correlations. Recent findings of ferromagnetism in a few-layer form of transition metal (TM) compounds with 3*d* electrons, e.g., TM trichalcogenides and TM trihalides, opened up a new field, materials science of atomically-thin magnets, where strong electron correlations of TMs play a crucial role. These advances on the SOC and electron correlations have been gained almost independently, and their cross section has not been discussed intensively thus far. Synergy between the SOC and electron correlations has recently attracted much attention as a clue for realizing potentially new topological states of matter. It will be very intriguing to investigate the synergetic effects in two-dimensional electronic states in layered materials.

The purpose of this thesis is to theoretically investigate layered TM compounds with 4*d* and 5*d* electrons, where the synergy between the SOC and electron correlations can be expected in their two-dimensional electronic states. In particular, we focus on honeycomb-layered TM compounds, where TM cations comprise a honeycomb network by sharing the edges of ligand octahedra. The honeycomb structure is commonly seen in a variety of layered TM compounds, such as TM trichalcogenides, TM trihalides, and the corundum structures. In these systems, the cubic crystalline electric field from the ligands splits the *d* levels into energetically higher e_g and lower t_{2g} manifolds. In this thesis, we study both cases where the Fermi level is in the e_g or t_{2g} manifold. In the e_g case, the relevant *d* orbitals are largely extended toward the surrounding ligands, and hence, the transfer integrals are sensitive to distortions of the octahedra. We therefore expect flexible "engineering" of the e_g band structures. On the other hand, the *d* orbitals are rather localized in the t_{2g} case, and the cooperation between the SOC and electron correlations may lead to exotic magnetism like quantum spin liquids. Hence, we are interested in "material design" of unusual magnetic interactions in the t_{2g} manifold. Bearing these points in mind, we theoretically investigate a wide range of 4*d* and 5*d* TM compounds, mainly by employing *ab initio* calculations. We also try to construct microscopic models based on the *ab initio* results for elucidating the essential physics behind and enabling theoretical predictions.

First, we discuss the electronic band structure and possible magnetic properties in a family of layered materials, TM trichalcogenides, MBX_3, where *M* is transition metals, *B* = P, Si, or Ge, and *X* is chalcogens. We find by using *ab initio* calculations that the electronic band structures of monolayer TM trichalcogenides with group 10 TM elements exhibit multiple Dirac nodes near the half-filled level in the e_g manifold: two independent Dirac nodes at the *K* and *K*' points in the Brillouin zone like graphene, and additional six Dirac nodes on the Γ-*K* and Γ-*K*' lines. We elucidate that the multiple Dirac nodes originate from the peculiar electron transfers in the e_g manifold. In the honeycomb network of ideal octahedra, the indirect *d*-*p*-*d* transfers for neighboring TM cations vanish from the symmetry, while the *d*-*p*-*p*-*d* transfers for third neighbors have considerable amplitudes. The network of the dominant third-neighbor transfers forms honeycomb superstructures with the lattice spacing twice longer than the original honeycomb network. This brings about the six Dirac nodes around the midpoints of the Γ-*K* lines corresponding to the folding of the *K* and *K*' points. We also find that although the orbital angular momenta in the e_g orbitals are quenched, the Dirac nodes are gapped out by an effective SOC arising from hybridization between the e_g and t_{2g} orbitals in the presence of trigonal lattice distortions. This means that, in these e_g-orbital systems, the magnitude of the Dirac gaps, the positions of nodes in energy and momentum space, and the Fermi velocities can be tuned by applying tensile strain as well as chemical substitutions via the trigonal distortions. We demonstrate such flexible tunability by *ab initio* calculations. Furthermore, we also show that electron correlations and carrier doping can turn the multiple Dirac semimetal into the quantum anomalous Hall insulator with a high Chern number. We clarify that the peculiar topological property can

be traced back to the multiple Dirac nodes in the paramagnetic state. We also extend our analysis to the bilayer and bulk systems. In the bilayer case, we find that the Dirac nodes on the Γ-*K* and Γ-*K*' lines are split in momentum space according to the symmetry of the stacking manner, while Dirac nodes at the *K* and *K'* points behave like those of the bilayer graphene. Meanwhile, the bulk system becomes a simple metal but it possesses remnant features of the multiple Dirac nodes in the quasi-two-dimensional band structure.

Next, motivated by the finding of multiple Dirac nodes, we perform a systematic analysis of the topology of e_g band structures in the monolayer honeycomb systems. From the tight-binding analysis, we show that the ratio between first- and third-neighbor transfers strongly depends on the trigonal distortion of the ligand octahedra. Analyzing a tight-binding model with the first- and third-neighbor transfers, we find that a variety of band crossings appear at the half-filled level of the e_g orbitals while changing the ratio. The results not only reproduce the previous *ab initio* works for the related e_g-orbital systems, including our results for the TM trichalcogenides, but also uncover new types of band crossings in the e_g systems, such as semi-Dirac point nodes, quadratic band crossings, and a line node. The band crossings are gapped out by the effective SOC, and the system realizes a variety of topological phases distinguished by the spin Chern numbers. We show that some of the topological phases have unconventionally high spin Chern numbers and that some others are Z_2 topological insulators with odd spin Chern numbers. We also perform *ab initio* calculations for candidate materials by changing strain and chemical pressure, and confirm the flexible band engineering found in the tight-binding results.

Finally, we theoretically investigate the systems in the t_{2g} manifold. Cooperation between the SOC and electron correlations can lead to highly anisotropic magnetic interactions. Of particular interest is the so-called Kitaev interaction, a bond-directional Ising interaction, as it can stabilize an exotic magnetic state, quantum spin liquid. It was pointed out that ferromagnetic Kitaev interactions are realized for the d^5-electron configuration in the t_{2g} manifold in the presence of quantum interference between indirect *d-p-d* transfers through different ligands of the edge-sharing octahedra in the honeycomb structure. We here pursue an alternative scenario by introducing a polar crystalline structure that unbalances the quantum interference. By using the second-order perturbation theory for a multiorbital Hubbard model, we find that the imbalance gives rise to antiferromagnetic Kitaev interactions. In order to confirm our scenario, we perform *ab initio* calculations for polar monolayer systems with multiple anions. We show that Ru trihalides with multiple anions potentially exhibit antiferromagnetic Kitaev interactions following our mechanism.

To summarize, in this thesis, we theoretically revealed peculiar electronic properties originating in both the honeycomb-layered crystal structure and *d*-orbital degrees of freedom under strong SOC and electron

correlations. The results indicate several new directions in the study of 4*d* and 5*d* honeycomb-layered TM compounds. Our findings for the e_g-orbital systems suggest that the e_g-orbital manifold provides an interesting playground for the band topology as the e_g-orbital transfers can be flexibly tuned by lattice distortions as well as chemical substitutions. It is of great interest to investigate the effect of electron correlations on various types of band crossings as a future issue. Moreover, the edge modes associated with a variety of topological phases might be useful for applications to electronic devices. On the other hand, our results for the t_{2g}-orbital systems provide a new strategy to design peculiar magnetism in layered TM compounds. Our results could contribute to materials science of the Kitaev model, which has recently attracted much attention for realizing quantum spin liquids and quantum computation, via proposing a scenario to realize unconventional antiferromagnetic Kitaev interactions. Thus, we believe that our results enlighten the promising routes for further progress of the study on the layered TM compounds.