論 文 の 内 容 の 要 旨

論文題目　　*Ab initio* studies on superconductivity in alkali-doped fullerides
（アルカリ金属をドープしたフラーレン化合物における超伝導の第一原理的研究）

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The superconductivity in the A_3C_{60} systems with A = K, Rb, Cs (alkali-doped fullerides) has been intensively studied since its discovery in 1991. The maximum superconducting transition temperature T_c of ~ 40 K is the highest among the molecular superconductors. The superconductivity was seemingly well understood by the conventional phonon mechanism, in which the intramolecular H_g modes played a main role: Experimentally, the conventional *s*-wave pairing symmetry and the positive correlation between the superconducting transition temperature and the lattice constant strongly supported this scenario. Theoretically, it has been claimed in the literature that the total electron phonon coupling $\lambda \sim 0.5$-1 and the high phonon frequencies on the order of ~ 0.1 eV produce a high transition temperature comparable to the experimental ones.

However, the recent success in synthesizing the fcc/A15 Cs_3C_{60} raised a severe contradiction with the conventional scenario. They are both Mott insulators at ambient pressure, and the superconductivities are realized only when the lattice constant is shrunken by applying the pressure. T_c as a function of the lattice constant shows dome-like shape for both the A15 and fcc systems. These features cannot be explained by the conventional Migdal-Eliashberg theory. In fact, the existence of the superconducting phase in the vicinity of the Mott insulating phase indicates that the electron correlation might be essential. Furthermore, the observed low-spin state and the dynamical Jahn-Teller effect in the insulating phase revealed a substantial role of the electron-phonon interactions. Therefore, in order to understand the pairing mechanism, the Mott transition, and the low-spin state in Mott-insulating phase in a comprehensive manner, it is necessary to elucidate the non-trivial interplay between the electron correlations and the electron-phonon interactions.

In this thesis, we aim to obtain a unified description of the phase diagram. Especially, we try to answer why the *s*-wave superconductivity is stabilized in the vicinity of the Mott insulating phase in contrast to a naïve expectation that the strong electron correlations are incompatible with the *s*-wave pairing. While it was proposed that a new type of the phonon-mediated superconductivity distinct from the BCS superconductivity emerges near the Mott transition by the cooperation of the Jahn-Teller phonons and the strong correlations, to obtain conclusive statements, we need as unbiased arguments as possible.

Another goal of the thesis is the non-empirical calculation of the transition temperatures of the alkali-doped fullerides. Historically, the T_c calculation crucially relies on empirical parameters, such as the Coulomb pseudopotential. While the recent progress has enabled the fully *ab initio* T_c calculations in high accuracy for the conventional superconductors, there is still no reliable way to predict T_c for the unconventional superconductors.

To achieve the goals, we derive, from first principles calculations, the effective low-energy models for the fcc A_3C_{60} systems. The derived models consist of the electron transfer term, the Coulomb interaction term, the electron-phonon interaction term, and the phonon-one-body term. By analyzing them accurately with a model calculation technique, we study the low-energy phenomena. This scheme requires only the chemical composition and the crystal structure, which enables the quantitative studies without employing any empirical parameters.

Since there exists a previous study in which the electron transfer and the Coulomb interaction parameters were evaluated, in this thesis, we focus on the derivation of the phonon-related terms. To this end, we formulate a novel *ab initio* scheme, a constrained density functional perturbation theory (cDFPT). In the cDFPT, the partially renormalized phonon frequencies and electron-phonon couplings are calculated with excluding the low-energy-subspace renormalization effects, which are used as the parameters in the low-energy models. The partial renormalization allows us to take into account the effects of high-energy bands and to avoid the double counting of the low-energy-subspace renormalization effects, which are to be considered when the models are analyzed.

We apply the cDFPT to the alkali-doped fullerides. Then, the static part of the phonon-mediated negative exchange interactions $J_{\mathrm{ph}}(\omega=0)$ is estimated to be $J_{\mathrm{ph}}(\omega=0) \sim -0.05$ eV. We find that the magnitude of the negative $J_{\mathrm{ph}}(\omega=0)$ is larger than that of the positive Hund's coupling $J_{\mathrm{H}} \sim 0.035$ eV. It means that, effectively, negative exchange and pair-hopping interactions are

realized in the A_3C_{60} systems, while the amounts of the interactions (~ −0.015 eV) are very tiny compared to the Hubbard repulsion U ~ 1 eV. Furthermore, we see that, due to the phonon-mediated attractions, the effective interorbital repulsion U'_{eff} becomes slightly larger (~ 5 %) than the effective intraorbital repulsion U_{eff}.

To analyze the models, we adopt the extended dynamical mean-field theory (extended DMFT) with employing the continuous-time quantum Monte Carlo method based on the strong coupling expansion as the impurity-model solver. The extended DMFT is one of the most powerful methods to study the strongly correlated materials in three dimensions, which can accurately treat the local phonon dynamics and the dynamical screening effects originating from the long-range Coulomb interactions, on top of the local electron correlations.

We perform the extended DMFT analysis of the derived *ab initio* models and draw the theoretical phase diagram as a function of the lattice constant and temperature. We obtain the paramagnetic metal, the superconducting phase, and the paramagnetic Mott insulator, which well reproduce the experimentally observed phases. As a consequence of the effective negative exchange interaction, the low-spin state is realized in the insulating phase. Remarkably, the agreement is not only in a qualitative level but also in a quantitative level. In particular, the calculations reproduce the maximum T_c of ~ 28 K, in good agreement with the experimental result (~ 35 K).

As for the pairing mechanism, we identify two crucial factors. One is the singlet pair generation by $U'_{\mathrm{eff}} > U_{\mathrm{eff}}$, and the other is the tunneling of the pairs by the negative pair-hopping interactions (Suhl-Kondo mechanism). The inequality $U'_{\mathrm{eff}} > U_{\mathrm{eff}}$ and the negative pair-hopping term originate from the phonon-mediated attractions, thus the superconductivity essentially relies on the phonons. However, this superconductivity differs from the conventional ones in that the strong electron correlations also play an important role: The pair formation is originally inefficient since the difference between U'_{eff} and U_{eff} is very small (~ 0.03-0.04 eV) compared to the typical kinetic energy ~ 0.5 eV, and becomes efficient only when the electronic kinetic energy is suppressed by the correlations. As a result, we see the increase of T_c with the increase of the correlation strength. These considerations lead to the conclusion that the alkali-doped fullerides are the phonon-mediated superconductors assisted by the strong electron correlations.