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論 文 要 約

THESIS OUTLINE

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Thesis Outline

In Chapter 1, the following introductions and discussions are mentioned: the major and distinguished discoveries, observations, and suggestions about perovskites as well as the correlation between their structural distortions and physical properties. My studies about perovskites are based on the philosophy of structural distortions, which leads to exploring novel physical properties and unreported materials.

In Chapter 2, the theoretical background of quantum chemistry and density functional theory is described, along with ground-state-structure exploration methods and the computational details of the first-principles calculations.

In Chapter 3, I mainly focus on exploring "polar metals" by applying biaxial strain. In 1965, P. W. Anderson indicated the existence of metals with polar symmetry, so to speak, "ferroelectric-like metals" or "polar metals". After more than 50 years, a strained thin film of $NdNiO_3$ has recently been reported as a polar metal. Assuming that inexpensive Ni is an important element for polar metals, strained $La_3Ni_2O_7$ was considered as a metal with a polar distortion driven by the hybrid-improper ferroelectric (HIF) mechanism. As a result, unexpectedly, in-plane compressive strain was found to induce breathing distortion X_2^-, resulting in the metal-to-insulator transition. It was elucidated that Fermi-surface nesting, which is triggered by the coupling of strong electron correlation in Ni 3*d* and breathing distortion X_2^-, gives rise to the metal-insulator transition with the Peierls mechanism. Alternatively, to design a polar metal, a representative Ni-based antiperovskite $MgCNi_3$ was focused on because its *p*-*d* orbital overlap is increased more than that of $La_3Ni_2O_7$. My calculations predicted that $MgCNi_3$ is a polar metal under compressive strain of -4.5% to -2.8%, which is generated by the softmode Γ_3^-. These results are startling because of the following reason: metals are thought to have difficulty in exhibiting polarity since conduction electrons screen the long-range electrostatic interactions, which are key to breaking the inversion symmetry. For instance, from the experiments and calculations, it has been shown that the conversion of the ferroelectric materials such as $BaTiO_3$, $PbTiO_3$, and $Sr_{1-x}Ca_xTiO_3$ into polar metals by electron doping is challenging. The COHP analyses have elucidated that the strain-induced nonpolar-to-polar phase transition is accompanied by enhanced hybridization between C and Ni, and the creation of bonding states a few eV below the Fermi level.

In Chapter 4, layered perovskite $Li_2SrNb_2O_7$ (LSNO) is mainly studied and discussed, which has a weak ferroelectricity and an antiferroelectricity triggered by the rotational distortions X_3^- and X_2^+. My first-principles studies of $Li_2SrNb_2O_7$ and $Li_2SrTa_2O_7$ have clarified that (i) the weak-ferroelectric phase transition of LSNO originates from the zone-boundary Y_2^- softmode, (ii) Ta substitution in LSNO stabilizes the paraelectric *Amam* phase, and (iii) the Y_2^- mode enhances the π-bonding states of Nb 4*d* and O 2*p*, indicating that the origin of the phase transition is a second-order Jahn-Teller (SOJT) effect. These theoretical results led to the discovery of a quantum paraelectric $Li_2Sr(Nb_{0.6}Ta_{0.4})_2O_7$. On the other hand, my first-principles calculations of $Li_2SrNb_2O_7$ and $Li_2CaNb_2O_7$ have shown that (i) Ca substitution in LSNO destabilizes the paraelectric *Amam* phase, leading to enlarging the total energy difference between antiferroelectric *Pnam* and paraelectric *Amam* phases, and (ii) Ca substitution enlarges both of

the rotational distortion and Nb^{5+} displacement. These theoretical predictions indicate that (i) Ca substitution heightens the paraelectric-to-ferroelectric phase-transition temperature and (ii) enlarges the polarization, which are confirmed from the experiments performed by Takayuki Nagai *et al.* of Nagoya university. Further, in $Li_2CaNb_2O_7$, I found that the Y_2^- soft phonon mode stabilizes the system by enhancing the σ-bonding states of Nb 4*d* and O 2*p*. From all these results, the unique ferroelectric phase transition in LSNO originates from the two coexisting mechanisms: the second-order Jahn-Teller effect and the rotational-distortion driven hybrid improper ferroelectricity.

In Chapter 5, minxed-anion antiperovskite semiconductors are focused. Antiperovskites normally exhibit metallic behavior and distortion-free structures. However, some of the antiperovskites M_3AN (M = Mg, Ca, Sr, Ba; A = P, As, Sb, Bi) possess narrow bandgaps and distorted structures. To uncover their fundamental physical properties, theoretical exploration was performed. My study elucidated the followings: (i) the octahedral rotational distortions in M_3AN reduce their Madelung energy and stabilizes the system, the phenomenon of which is not common in conventional perovskites; (ii) the degrees of phase stability and octahedral-rotational-distortions amplitude can be described by the tolerance factor; (iii) their bandgaps are 0.54 to 2.35 eV; (iv) the effective masses for electrons and holes are 0.16 to 1.17 and 0.09 to 1.39, respectively; (v) the electronic structures around the bandgaps of Mg_3AN and $M_3'AN$ (M' = Ca, Sr, Ba) are respectively created mainly by *p*-*p* and *d*-*p* interactions; (vi) the unreported Mg_3PN and Sr_3PN have direct bandgaps of 2.35 and 1.74 eV; and (vii) their absorption coefficients are comparable to those of GaAs and CdTe.

In Chapter 6, the general conclusions are described. By integrating all the results, we can understand that (i) a polar distortion can be created not only from long-range electrostatic interaction but also from bonding-state enhancement, (ii) a perovskite with a small tolerance factor tends to have a large octahedral rotational distortions regardless of electronic structures (orbital interaction type), (iii) second-order Jahn-Teller effect emerges also in layered perovskites, (iv) metallic antiperovskites do not have rotational distortions because their Madelung potentials are screened by free electrons, and (v) the rotational distortions do not always increase the bandgaps.