論文の内容の要旨

論文題目

Theoretical study on anion-doping induced metal-insulator transition of metal oxides
(アニオンドープによる金属酸化物の金属絶縁体転移に関する理論的研究)

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1. Introduction

Synthesis and characterization of anion-doped transition metal oxides are an active research topic in recent years. Among changes in physical properties caused by doping, metal-insulator transition (MIT) has been attracted the interest of researchers seeking promising materials for next-generation electronic devices. However, not much progress has been made in the researches of MIT by anion doping because fabrication procedure of high-quality crystalline samples needed for transport-property measurements has not been established so far. Until now, indeed, MIT was observed only in a few anion-doped compounds which can be prepared as thin films. Moreover, some compounds lack structural information, hindering detailed discussion about the mechanisms.

In such a situation, theoretical calculation is a powerful tool to complement experimental observations. Recent calculation techniques based on the density functional theory enable us to predict crystal structures of solid-state materials with good accuracy. In addition, subsequent electronic-state calculations provide us valuable information to discuss the mechanisms of MIT. In this thesis work, I theoretically investigated the crystal structures and the mechanisms of MIT of three anion-doped metal oxides: H-doped $SrFeO_2$, $NdNiO_2F$, and $Sr_2RuO_3F_2$.

2. Insulator-to-metal transition of $SrFeO_2$ by hydrogen doping

The composition and crystal structure of H-doped $SrFeO_2$ were theoretically determined by structural sampling and total energy calculations combined with thermodynamic analysis. It was suggested that the doped hydrogen atoms exist in hydride form (H^-) replacing lattice oxide ions. This hydride incorporation resulted in electron doping and changed the occupation state of d_{zx} and d_{z^2} bands of the adjacent Fe. A certain structure with a specific hydride arrangement acquired a metallic electronic state. However, thermodynamic analysis showed that such a metallic phase is meta-stable and the other structure in which the doped electrons are localized is most stable. This result suggested that H-doped $SrFeO_2$ is a mixture of an insulating matrix and percolating metallic domains, accounting for the experimental observation that the carrier density of H-doped $SrFeO_2$ was much lower than the amount of doped hydrogen.

3. Metal-to-insulator transition of $NdNiO_3$ by fluorine doping

The crystal structure of the F-doped $NdNiO_3$ ($NdNiO_2F$) was determined by exhaustive structure sampling. It was found that the fluorine atoms favor a two-dimensional *cis*-type configuration. The structure optimization including epitaxial strain and subsequent electronic state calculation reproduced both the experimental out-of-plane lattice constant and the insulating state of $NdNiO_2F$. The detailed analysis using density of states (DOS) for $3d$ electrons showed that the Ni^{2+} ion in $NdNiO_2F$ has $e_g^{\uparrow\uparrow}$ d-electron configuration. This configuration has a strong tendency to form insulating band structures because strong Coulomb repulsion precludes electron hopping through the $e_g^{\uparrow\uparrow}$ array. In contrast, Ni^{3+} in $NdNiO_3$ has $e_g^{\uparrow}$ configuration which allows electronic conduction. Therefore, I concluded that the change in occupation state of the e_g orbitals by fluorine doping is the trigger of MIT.

4. Metal-to-insulator transition of Sr_2RuO_4 by fluorine doping.

The experimental lattice constants and the insulating state of $Sr_2RuO_3F_2$ were theoretically reproduced by assuming the same structure as $Sr_2TiO_3F_2$. The DOS calculation for Sr_2RuO_4 and $Sr_2RuO_3F_2$ revealed that the d electron configuration of Ru^{4+} (d^4) changed from $(xy, yz, zx)^4$ to $(xy)^{\uparrow}(yz, zx)^{\uparrow\uparrow}(3z^2{-}r^2)^{\uparrow}$ by fluorination. Accordingly, occupation number per band also changed from non-integer 4/3 to integer 1, resulting in the metal-insulator transition. The occupation of the $3z^2{-}r^2$ orbital in $Sr_2RuO_3F_2$ was attributed to the change in crystal field around Ru. Sr_2RuO_4 has almost regular RuO_6 octahedra and well separated t_{2g} and e_g orbitals. As a result, all the four d electrons occupy the lower t_{2g} band. On the other hand, $Sr_2RuO_3F_2$ has RuO_5F octahedra with long Ru−F bonds and the resulting square pyramidal crystal field stabilizes the $3z^2{-}r^2$ orbital.

5. Conclusion

In my thesis work, I studied metal-insulator transitions induced by anion doping by theoretical calculations. The calculation of H-doped $SrFeO_2$ revealed that the doped hydrogen exists as hydride, and the experimental carrier density could be explained by a two-component model with different electron trapping characters. In case of $NdNiO_2F$, I found the change in occupation state of e_g orbitals triggers MIT. The last investigation of the redox-neutral transition between $Sr_2Ru^{4+}O_4$ and $Sr_2Ru^{4+}O_3F_2$ demonstrated that the transitions is caused by modification of crystal field associated with anion substitution. These new knowledges of metal-insulator transitions would provide a new perspective to design functional anion-doped compounds in further researches.