論文の内容の要旨

論文題目

Modulation of physical properties of 4*d*-5*d* transition metal oxide thin films by anion doping

（アニオンドープによる4*d*-5*d*遷移金属酸化物薄膜の物性変調）

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1. Introduction

4*d*-5*d* based transition metal oxides (TMOs) show distinctive electronic properties due to large overlap of electron orbitals and large spin-orbit interaction (SOI). Some 4*d*-5*d* based TMOs, such as $SrMoO_3$ and ReO_3, are good conductors, of which resistivity is comparable to those of conventional metals, due to the spatially spread *d* orbitals, and Sr_2RuO_4 is known to be an unconventional spin-triplet superconductor. Iridium oxides exhibit unique physical properties, including Weyl semimetal phases, owing to the large SOI of Ir ions.

Recently, doping of anion, such as H^-, N^{3-} and F^-, into 4*d*-5*d* TMOs has attracted much attention as a powerful method to modulate their physical properties through carrier doping, control of local anion arrangement, and so on. A typical example is $RbLaNb_2O_6F$, which possesses high electronic conductivity with ion exchange ability. $SrNbO_2N$ shows large positive magnetoresistance, which originates from the random distribution of oxygen and nitrogen in the crystal.

In this thesis study, I have focused on two 4*d*-5*d* TMOs, $EuNbO_3$ and Sr_2IrO_4, and attempted to modify their electronic properties by nitrogen and fluorine doping, respectively. Nb in $EuNbO_3$ has electrons in 4*d* orbitals, which interact with large spins at Eu, resulting in rich physical properties. For modulation of the interaction, I introduced anion randomness by nitrogen doping. Ir in Sr_2IrO_4 is a typical element with large SOI. I examined how the electronic properties are affected by anion randomness and change in dimensionality associated with fluorine doping. For these purposes, I synthesized nitrogen doped $EuNbO_3$ and fluorine doped Sr_2IrO_4 thin films and discussed the modulation of physical properties.

2. Magnetotransport properties of perovskite $EuNbO_3$ thin films

Before studying nitrogen-doped $EuNbO_3$, I investigated the magnetic and transport properties of perovskite $EuNbO_3$ single-crystalline thin films deposited by pulsed laser deposition. The obtained $EuNbO_3$ thin films showed metallic transport properties and ferromagnetism with a Curie temperature (T_C) of ~6 K. The carrier concentration and mobility of the $EuNbO_3$ thin films were nearly independent of temperature, suggesting that the excess oxygen in the films behaves as a scattering center. The sign of magnetoresistance changed around T_C, possibly due to competition between the weak anti-localization effect and magnetic coupling between Eu^{2+} 4*f* localized spins and Nb^{4+} 4*d* itinerant electrons.

3. Nitrogen content dependence of negative magnetoresistance in $EuNbO_{3-x}N_x$ thin films

Perovskite-type europium niobium oxynitride $EuNbO_2N$ is known to exhibit colossal negative magnetoresistance (MR > −99%) at low temperature. In order to investigate the role of nitrogen in the negative MR, I fabricated $EuNbO_{3-x}N_x$ (ENON) single-crystalline thin films with different nitrogen contents (N/Eu = 0.6, 0.7, 1.0) and measured their magnetotransport properties. All the oxynitride thin films showed saturation magnetization of ~3.0 μ_B/f.u., indicating that nearly half of the Eu ions exist in trivalent oxidation states independent of the nitrogen content. The transport properties of the $EuNbO_{3-x}N_x$ thin films gradually changed from metallic behavior to semiconducting behavior as the nitrogen content x increased. The semiconducting conduction was described by three-dimensional variable-range hopping, suggesting that carrier localization occurs due to the random distribution of nitrogen in the anion sites. With increasing x, the negative MR ratio at 2 K increased from 20 % to 98 %, accompanied by an increase of Nb^{5+} amount in the films. Based on results of magneto-transport measurements, I proposed that the exchange interaction between Eu^{2+} and Nb $4d^1$ localized spins and Nb $4d^1$ spins in the random potential was a key to the colossal negative MR of ENON.

4. Influence of fluorination on electronic states and electron transport properties of Sr_2IrO_4 thin films

I fabricated layered-perovskite $Sr_2IrO_{4-x}F_{2x}$ thin films by combining pulsed-laser deposition with topotactic fluorination and investigated their structures, electronic states, and electron transport properties. In the fluorination process, the insertion of fluorine into SrO rocksalt layers and the partial removal of oxygen occurred simultaneously while keeping Ir^{4+}. The fluorine amount was evaluated to be $2x \approx 3$, which was much larger than the bulk value. Optical and photoemission measurements revealed that the effective total angular momentum $J_{eff} = 3/2$ is stabilized upon fluorination owing to the large electronegativity of fluorine. The conduction mechanism was observed in both Sr_2IrO_4 and $Sr_2IrO_{4-x}F_{2x}$ thin films, where $\rho(T)$s of Sr_2IrO_4 and $Sr_2IrO_{4-x}F_{2x}$ were proportional to $T^{-1/4}$ and $T^{-1/2}$, respectively. The change of the temperature dependence upon fluorine doping indicates that the conduction mechanism was modulated from the Mott variable-range hopping mechanism to the Efros–Shklovskii variable-range hopping mechanism. The change of conduction mechanism could result from the increase of Coulomb interaction among electrons, which may be induced by confinement of electrons in the $Ir(O, F)_6$ layer and by suppression of electron screening effect due to the random potential in $Ir(O, F)_6$. Our research provides valuable insight into how electronic states can be modified by anion doping to explore unprecedented physical properties in RP-type iridates.

5. Conclusion

I successfully modulated the physical properties of $4d$-$5d$ TMO thin films by anion doping and provided valuable insights into the intrinsic role of the anion. In the study of $EuNbO_{3-x}N_x$, it was revealed that randomly distributed nitrogen ions locally modulate the exchange interaction between Eu^{2+} localized spins and Nb $4d^1$ spin. In the study of $Sr_2IrO_{4-x}F_{2x}$, it was proposed that fluorine doping could increase the Coulomb interaction among electrons by strengthening two-dimensionality and by introducing random distribution of oxygen and nitrogen. Deep understanding of the role of the anions would lead to the finding of unprecedented physical properties of in $4d$-$5d$ transition metal-based mixed anion compounds.