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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（理学）　氏名　馮　海

学 位 論 文 題 名

High-Pressure Synthesis of Osmium Oxides with Double-Perovskite Structure and Their Magnetic Properties

（２重ペロブスカイト型オスミウム酸化物の高圧合成と磁気的性質）

Double perovskite oxides $A_2BB'O_6$, in which B and B' are 3d (or nonmagnetic) ion and 5d (or 4d) ion, respectively, have attracted great attention because of the half-metallic (HM) nature found in such as Sr_2FeMoO_6 and Sr_2FeReO_6. In addition, a series of exotic magnetic states of such as spin singlet and spin freezing has been discovered in $A_2BB'O_6$. In the HM state, 3d-t_{2g} and 5d(4d)-t_{2g} electrons in the B and B' sites play a pivotal role in the highly spin-polarized conduction, which results from a generalized double exchange interaction. However, the double exchange mechanism was unable to account for the remarkably high critical temperature (T_C) of ferrimagnetic (FIM) transition at 725 K in Sr_2CrOsO_6 because of the multi-orbital Mott state. The FIM state was therefore distinguishable from the HM state: the high-T_C FIM transition was argued to be novel. To further elucidate nature of the high-T_C FIM state as well as to explore a significant magnetic state, additional 5d double perovskite oxides are highly desired to be synthesized and studied.

In this study, novel compositional 5d-3d hybrid double perovskite oxides Ca_2FeOsO_6 and Ba_2CuOsO_6 were synthesized and the fundamental properties were investigated. Ca_2FeOsO_6 crystallized into an ordered double-perovskite structure with a space group of $P2_1/n$ and showed a long-range FIM transition at a temperature of ~320 K. Although Ca_2FeOsO_6 was not a band insulator, it was electrically insulating like Sr_2CrOsO_6 (T_C ~725 K): the electronic state of Ca_2FeOsO_6 was adjacent to a HM state as well as that of Sr_2CrOsO_6. Besides, the FIM state was driven by a lattice distortion, being observed for the first time among double-perovskite oxides. Ca_2FeOsO_6 as well as Sr_2CrOsO_6 apparently established a new class of 5d-3d hybrid FIM insulators with high-T_C.

T_C of the novel solid solution $Ca_{2-x}Sr_xFeOsO_6$ increased to 320 K (Ca_2FeOsO_6) with decreasing the unit cell volume; T_C was therefore expected to further increase to some extent by additional contraction of the unit cell. In this study, partial substitution of a smaller atom of Cd for Ca was achieved for the first time, resulting in enhancement of T_C to 360 K ($Ca_{1.9}Cd_{0.1}FeOsO_6$); the result confirmed the expectation.

Ba_2CuOsO_6 crystallized into a double perovskite structure with a space group of *I*4/*m* under a certain high-pressure condition. In the strcture, Os (VI) and Cu (II) were found to alternatively order in the perovskite *B*-site. Ba_2CuOsO_6 was electrically insulating and showed antiferromagnetic characteristics on cooling at temperatures of ~55 K and ~70 K. The Jahn-Teller distortion of CuO_6 octahedra was argued to influence the magnetic transition via possible two-dimensional magnetic correlations. The first-principles study suggested that the spin-orbit interaction of Os (VI) plays a substantial role in the insulating state.

The double perovskite oxides with non-magnetic *B* atoms Ca_2InOsO_6 (Os^{5+}, $S = 3/2$), Ca_3OsO_6 (Os^{6+}, $S = 1$), and Sr_2LiOsO_6 (Os^{7+}, $S = 1/2$) were synthesized to study common magnetism of the double perovskite oxides. Ca_2InOsO_6 and Ca_3OsO_6 crystallized in a monoclinic double perovskite structure ($P2_1/n$), whereas Sr_2LiOsO_6 crystallized in a tetragonal double perovskite structure ($I4/m$). The magnetic susceptibility and heat capacity measurements revealed that the compounds show manifest antiferromagnetic characteristics on cooling at temperatures of 14 K for Ca_2InOsO_6, 50 K for Ca_3OsO_6, and 12 K for Sr_2LiOsO_6.

In the last chapter, general conclusions and future prospects are discussed.