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The Quantum Chemical Cluster Model Calculations on the Perovskite-Type Titanium Oxides

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Previously, we have performed the quantum chemical cluster model calculations for the strongly correlated perovskite-type transition metal solids, in order to clarify magnetism, superconductivity, ferroelectricity, ionic conductivity and so on. It was concluded that the hybrid-density functional theory (DFT) is one of the proper calculation methods for the species. It is because the delocalized and localized effects in the strongly correlated system are taken into account by the use of DFT and Hartree-Fock (HF) terms, respectively. For example, BHHLYP and B2LYP, which are one of hybrid-DFT methods and contain the fifty percent HF term, can reproduce the antiferromagnetic interaction between transition metals via bridge anion in the perovskite-type transition metal solids. [1-3] In the magnetic interaction on the large biological molecules, they also showed the reasonably good agreement with the experimental results. [4-5]

In this study, we have estimated the bandgap in the perovskite-type titanium oxide of $SrTiO_3$. The cluster model of $SrTiO_3$, where counter cation is located in the center of the cube, has been constructed, as shown in FIG. 1. In order to investigate the relationship between bandgap, and delocalized and localized effects, HF and hybrid-DFT methods have been employed. All-electron calculations have been performed by GAMESS program package. [6] $SrTiO_3$ shows the luminescent process by the Ar^+ irradiation. [7] At low temperature, the green and ultraviolet emissions appear. On the other hand, at room temperature, blue emission is observed. It is considered that the oxygen deficiency and tetragonal distortion are related to the luminescent process. Here, we have also considered the oxygen deficient and tetragonal distorted cluster models. FIG. 2 shows HOMO and LUMO orbitals in $SrTi_8O_{12}$ and oxygen deficient $SrTi_8O_{11}$ cluster models.

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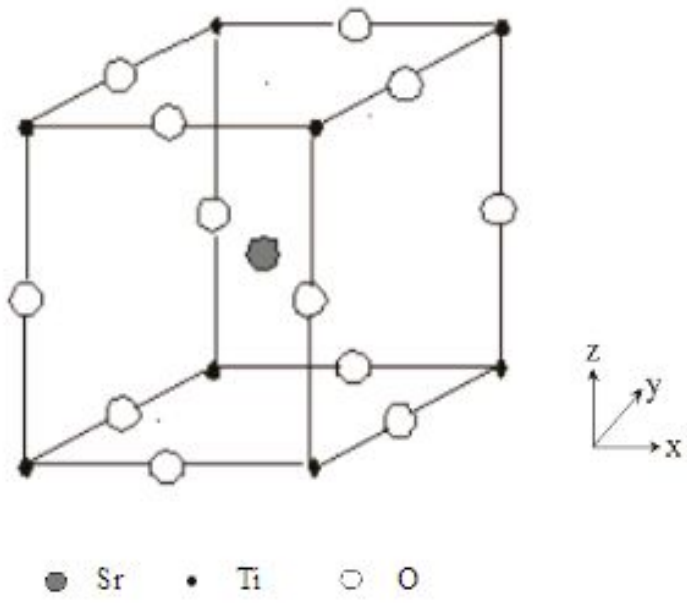

FIG. 1. The cluster model of $SrTiO_3$.

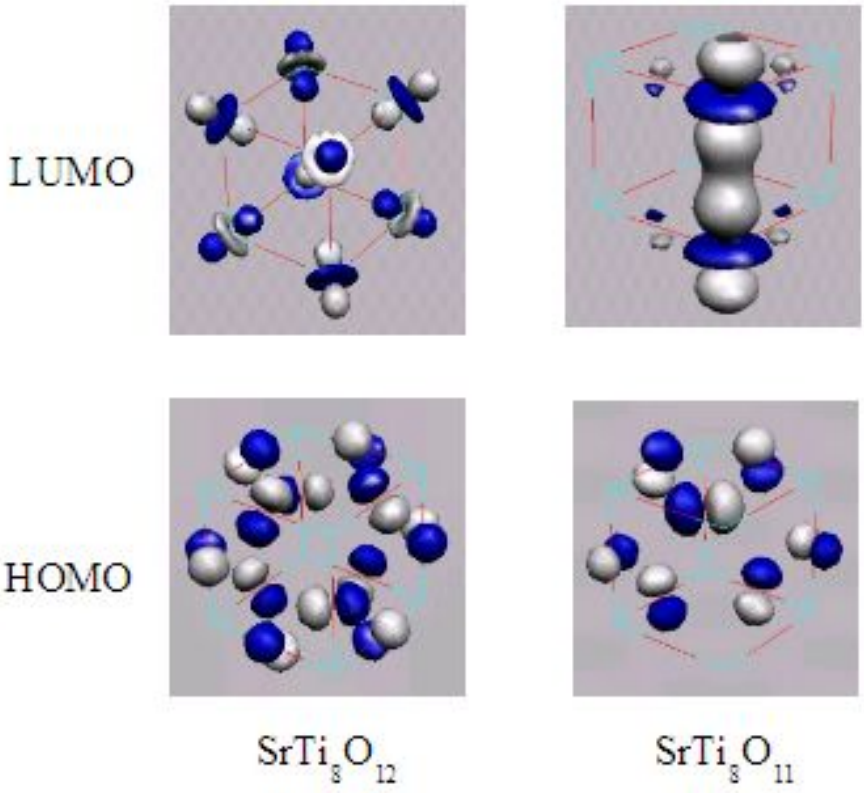

FIG. 2. HOMO and LUMO orbitals in $SrTi_8O_{12}$ and oxygen deficient $SrTi_8O_{11}$ cluster models (by BHHLYP).