구두발표 I-1

First-principles study on the electronic structure of CeO_2 crystal

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1. Introduction

In the lanthanide especially cerium and its compounds, the most important and long-standing issue has been the nature of the Ce 4f electrons and their role in various physical phenomena such as in structural phase transitions, magnetism and conductivity, and chemical bonding. However, the Ce 4f occupation is still a controversial issue even in the ground state of the nonmagnetic insulating CeO_2 crystal. There are two models that differ in the 4f occupation: the fully ionized model (Ce^{4+}, $4f^0$) and the partially ionized model ($Ce^{(4-n)+}$, $4f^n$ where n=0.5). However, in these models usually much less attention has been payed to the role of the Ce 5d states. The aim of the present talk is to analyze the role of the Ce 4f and 5d electrons in the CeO_2 crystal using first-principles electronic structure calculations.

2. Experimental Methods

The calculations are carried out using the density functional theory in the generalized gradient approximation, norm-conserving, non-local, scalar-relativistic pseudopotentials, and numerical double zeta plus polarization basis functions for 5s, 5p, 5d, 4f, 6s, and 6p of Ce as well as for 2s, 2p, and 3d of O. The spacing of the regular real space grid is determined by the maximum kinetic energy of the plane waves that can be still represented in the grid. We use here the cutoff value of 280 Ry. The first Brillouin zone is sampled using a uniform Monkhorst-Pack grid of 51x51x51.

3. Results and Conclusions

We find that the Ce 4f and 5d electrons remain localized around the Ce nuclei and form with the O 2p electrons covalent Ce-O bonds in the CeO_2 crystal. The Ce 6s electrons are found to be transferred from the Ce to O atoms. The Ce-O bonds are consequently of mixed covalent/ionic type and the Ce atoms in the CeO_2 crystal are actually in the (about) 2+ charge state, not in the 3+ or 4+ state. The calculated electronic band structure is insulating and nonmagnetic and can explain the main features of the experimental core level and optical spectra in a satisfactory way.