# Defect Structure of Nonstoichiometric Plutonium Oxide

*Nuclear fuel systems typically require decades to optimize, since the assessment of behavior of nuclear fuel is made based on empirical data and irradiation testing. As a general trend, it is tried to assess them on basic scientific understanding. In this work, an oxygen defect of plutonium oxide has been studied by the first principle calculations, which predict the electron structure of materials without experimental data.*

Plutonium, which is generated in an operating nuclear reactor due to transmutation of uranium, is one of important materials as nuclear fuel. Plutonium is mainly used in the nuclear reactor in the chemical form of oxide. Plutonium oxide has a wide range of non-stoichiometry, determined by temperature and oxygen partial pressure. Non-stoichiometric plutonium oxide is represented by $PuO_{2-x}$, where x is non-stoichiometry. The oxygen partial pressure is a key parameter, which controls chemical reactions in the fuel pin.

It is very important to develop a model, which is able to predict well the correlation between the non-stoichiometry of $PuO_{2-x}$ and the partial pressure of oxygen. In the design of nuclear fuel, the model based on defect chemistry has been used for calculation of oxygen potential. The defect chemistry model is essentially empirical one, since the parameters in the defect chemistry model are adjusted by the experimental data. In this study, the first principle calculations were used to check the validity of the defect chemistry model.

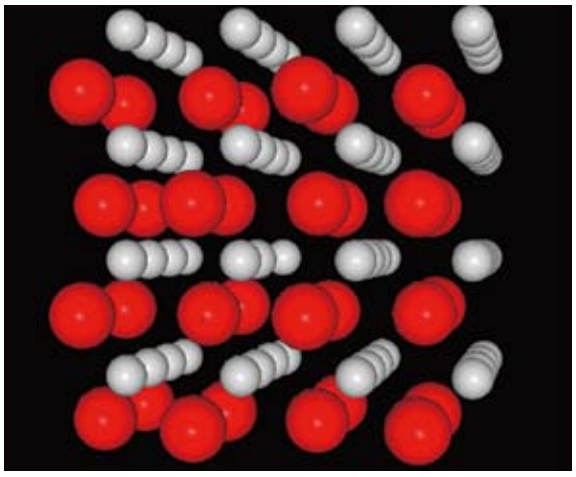

Fig.1 Supercel for plutonium oxide with oxygen defect. Red and white spheres indicate plutonium and oxygen atoms, respectively.

The total energy and the electronic structure of $PuO_{2-x}$ have been calculated by PAW method within the GGA. We also used the DFT+U methodology to check localization of f-electron. Figure 1 shows a supercell of 96 atoms containing 32 plutonium atoms, 63 oxygen atoms and one oxygen vacancy. The calculations were performed with the HITACHI/SR-8000 in Tohoku University. The calculated lattice parameter and the enthalpy of formation of plutonium dioxide are in good agreement with the experimental values. The vacancy formation energy, which was defined as the energy required for extraction of an oxygen atom from the perfect lattice, was calculated to be 4.20eV. This value is close to that calculated from the experimental data.

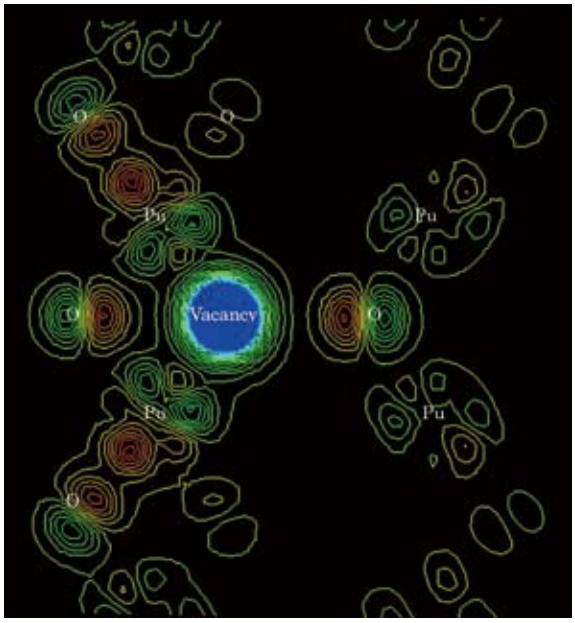


Fig. 2 Differential charge densities near oxygen vacancy

Difference in the charge density between the defect model and the perfect model has been calculated to make the effect of vacancy clear (Fig. 2). The six nearest neighbor oxygen atoms moved from original site toward the oxygen vacancy site. The two atoms of those were shown in Fig. 2. It is also shown that the charge densities around the two nearest neighbor plutonium atoms are affected by the oxygen vacancy. The calculation results show that only the nearest neighbor plutonium atoms are affected by the oxygen vacancy. This agree with the following picture used in the classical defect chemistry, that is, the oxygen has two electrons provided by plutonium, which are left behind when an oxygen atom is leaving lattice position. These two electrons are localized on two plutonium atoms, turning $Pu^{+4}$ into $Pu^{+3}$.

**References**

[1] K. Konashi H. Matsui, Y. Kawazoe, M. Kato and S. Minamoto, J. Phys. Soc. Jpn. **75** suppl., 143 (2006).

[2] K. Konashi, M. Kato, S. Minamoto, 'First Principle Plane-Wave Pseudopotential Calculation of Point Defects in $PuO_{2-x}$', ANS 2005 Winter Meeting, Nov. 15-19, 2005, Washington, D.C., USA

Contact to
Kenji Konashi (International Research Center for Nuclear Materials Science)
e-mail:konashi@imr.tohoku.ac.jp