

ELECTRONIC STRUCTURE OF CRYSTALLINE

URANIUM NITRIDE:

LCAO DFT CALCULATIONS

R. A. Évarestov, A. I. Panin, and M. V. Losev

UDC 539.19+539.21

The results of electronic structure calculations performed for the first time for crystalline uranium nitride and using a LCAO basis are discussed. For calculations we used the density functional method with the PW91 exchange correlation potential and a variety of relativistic core potentials for the uranium atom. The calculated atomization energy of the crystal agrees well with the experimental data and with the results of calculations with the plane wave basis. It is shown that a chemical bond in crystalline uranium nitride is a metal covalent bond. The metal component of the bond is due to the $5f$ electrons localized on the uranium atom and having energies near the Fermi level and the bottom of the conduction band. The covalent component of the chemical bond results from an overlap between the uranium $6d$ and $7s$ valence orbitals and the nitrogen $2p$ atomic orbitals. Inclusion of the $5f$ electrons in the core of the uranium atom introduces relatively minor changes in the calculated binding energy and electron density distribution.

Keywords: crystal structures, density functional method, LCAO calculations, relativistic pseudopotentials, uranium nitride.

In contrast to heavy actinides, the uranium atom forms crystalline compounds over a wide range of the degrees of oxidation from two, three, and four in UO , UN , and UO_2 crystals, respectively, to five or six in U_2O_5 , UO_3 , and UN_2 crystals [1].

Crystalline uranium compounds are now being widely investigated experimentally because of their practical utility as fuel for nuclear reactors. Uranium dioxide is now widely employed in nuclear energetics. However, nuclear fuel based on uranium nitride is more promising; it has higher thermal conductivity, which is favorable for the active reactor zone. Uranium dioxide is well studied experimentally, while uranium nitride is still to be investigated.

Theoretical investigation of the electronic structure of uranium-containing crystals is hindered by the necessity to take into account the relativistic effects, electron correlation, and magnetic ordering of electrons from the open shells of the U atom, whose ground state corresponds to the $5f^3 6d^1 7s^2$ configuration of valence electrons [2].

Uranium dioxide UO_2 (cubic crystal with a fluorite structure) is best studied theoretically; the ab initio electronic structure calculations for this crystal were performed in the plane wave (PW) [3-5], *muffin tin* (MT) orbitals [6], and localized atomic type functions (LCAO) bases [7, 8]. The relativistic effects for the core electrons were included in calculations by introducing the relativistic effective core potentials (RECP), and electron correlation effects were included by the density functional (DFT) method or using the Hartree–Fock (HF)–DFT hybrid functional. The calculations gave the fundamental properties of crystalline uranium dioxide (structural, one-electron, and magnetic properties), which were in good agreement with the experimental data. Also, point defects in UO_2 crystals (oxygen vacancies, interstitial atoms, Frenkel and Schottky