COHESIVE PROPERTIES OF URANIUM DIOXIDE

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We report the results of self-consistent linear muffin-tin orbital calculations for uranium dioxide as a function of lattice parameter. The change of total energy with volume is zero for a lattice parameter within 0.5% of the experimental equilibrium. The gap between valence and conduction bands is determined to be 5.35 eV and the valence bandwidth to be 5.6 eV.

1. Introduction

Recent advances in band structure techniques for metals [1] and compounds [2] have made it possible to perform self-consistent calculations for even quite complex crystal structures. We describe here self-consistent calculations for UO_2. The Hedin–Lundqvist [3] parameterization of the local density approximation to exchange and correlation [4] was used. Within this scheme we expect, apart from inaccuracies introduced by the spherical averaging of the atomic sphere approximation (ASA), a sound description of ground state properties. Although the theory is less rigorous for the purpose, we shall also discuss the optical properties briefly. The computations were semi-relativistic, spin-orbit coupling being included only for the f-orbitals.

2. Numerical results

The band structure was converged to 1 mRyd for the eigenvalues at 20 K points in the irreducible Brillouin zone, which is better than other errors inherent in band structure calculations, in particular the minimum 15 mRyd of the linear muffin orbital (LMTO) method in the atomic sphere approximation (ASA) [5]. The symmetry of the fluorite structure has been described previously [6, 7]. There are two oxygens per unit cell giving rise to bonding ($\Gamma_{25'}$) and antibonding (Γ_{15})

valence bands which merge into a common oxygen valence band. In earlier non-self-consistent calculations we have found that this valence band is rather broader (4–5 eV) than the valence bands of fluorites reported by other authors (1–2 eV) [8]. This conclusion is verified by the self-consistent calculations. In fig. 1 we show the total density of states of UO_2. The valence bandwidth is 5.6 eV and an examination of the wavefunctions shows that the bonding ($\Gamma_{25'}$) states lie lowest. The band gap is 5.35 eV at the theoretical equilibrium lattice parameter which is determined, using the pressure formula [9], to be just 0.5% less than the experimental value of 5.45 Å. The bottom of the conduction band complex at Γ is the d-like Γ_{12} band followed by the Γ_1 s-like band. The charge is transferred from oxygen to uranium by hybridization between oxygen and uranium states.

The degree of this charge transfer is a reasonable measure of the deviation from a fully ionic picture towards covalency and is closely related to the valence bandwidth and the valence–conduction band gap. In first order perturbation theory the charge transfer from oxygen p-states to uranium d-states is proportional to the unhybridized valence bandwidth and inversely proportional to the band gap [2]. For UO_2 we find that the valence band contains not 12 oxygen electrons but 10.85, and 1.15 electrons are transfered to uranium by hybridization. This is double the charge transfer that we have obtained for CaF_2 in another study and reflects

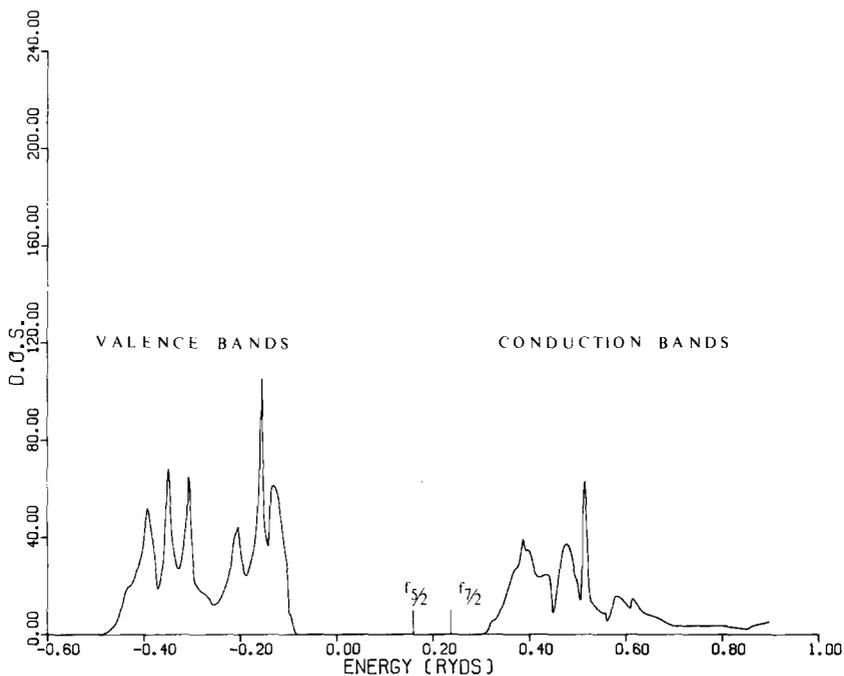* Present address: Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Federal Republic of Germany.

Fig. 1. Total density of states of UO₂. The f-levels are shown in the band gap and are split by 1 eV.

the greater covalency of the oxide, although it is not an unambiguous measure of it.

Under compression the electron density increases, thereby increasing the electronic kinetic energy. The conduction levels are most affected by this increase and they rise in energy and broaden. The valence band also rises and broadens under compression, but more slowly. The net effect is therefore a broadening of the band gap. The mean occupied centre of the valence band rises more rapidly under compression than the unhybridized valence band centre due to the rapid increase in hybridization with the uranium p-state. This results in a rapid increase in the total energy and, in our analysis, the electronic pressure which we interpret to be the result of core–core repulsion via the orthogonality constraint. It is the balance of this pressure (plus the positive uranium sp pressure) by the negative Madelung and uranium d-band pressure that determines the lattice parameter.

The f-states were not included in the band structure in these calculations, but treated as resonant orbitals. They were allowed to contribute to the self-consistent charge density but all hybridization was suppressed, leaving a level that is allowed to relax – but not a band. If they had been included in a band structure calculation they would have contributed an enormous negative f-bond pressure and would have provided the compound with a Fermi surface. By treating the f-levels self-consistently we were able to determine their energy which is shown as a line in fig. 1 at 4 eV above the valence band. They are spin–orbit split by 1 eV.

3. Comparison with experiment and discussion

Normally, in ASA, an accuracy for the lattice parameter of the order of 3% is to be expected (or 5–6% in difficult cases). The density of states shown in fig. 1 compares very well with photoemission experiments. The overall valence bandwidth has been observed in high resolution XPS [10] and UPS [11, 12] experiments to be between 5 and 6 eV. The agreement between theory and experiment is therefore at least better than 1 eV. The band gap obtained in the self-

consistent calculations is 5.35 eV at the equilibrium lattice parameter and is about 3 eV less than that reported previously from non-self-consistent calculations [7]. The band gap has recently been determined by Bremsstrahlung Isochromat Spectroscopy (BIS) to be (5.0 ± 0.4) eV [10], therefore the agreement between theory and experiments is excellent.

Doubts about the interpretation of reflectivity experiments [13, 14] remain, since this depends critically upon the positioning of the f-levels which, since they are localized, we do not obtain accurately. The mean of the f-state energies are 4 eV above the top of the valence band in the calculation and the f 5/2 and f 7/2 energies are split by 1 eV. The 5f 5/2 level is then quite close to 2.8 eV which appears to be the centre of the f-distribution in XPS experiments [10, 15] but higher than the centre of the f-distribution in UPS experiments [11, 12]. The fact that XPS and UPS experiments are not in agreement with regard to the position of the f-levels complicates the discussion of the optical properties. However, both indicate that the f-distribution lies less than 3 eV above the top of the valence band, which is the Γ_{15} (anti-bonding) part according to our calculations. The optical model that describes most closely this situation has been proposed by Schoenes [14] after a comparison of reflectivity and XPS [15] data.

The foregoing discussion suggests that uranium dioxide is not the simplest of materials to analyse – either theoretically or experimentally. The self-consistent band structure calculations are in excellent agreement with experiment for the quantities that a band structure calculation should describe well, e.g. the valence band width and, to a lesser extent, the valence to conduction band gap. The valence band width, in particular, is a considerable improvement upon earlier cluster studies [16] where it was found to be less than 3 eV. We have not, on the other hand, been able to understand the problems concerned with the position of the f-levels and we find the experimental evidence to be conflicting.

Acknowledgements

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