

FIRST-PRINCIPLES CALCULATION OF CRYSTAL FIELD IN DIOXIDES<sup>1</sup>

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Electronic structure of  $\text{UO}_2$  and  $\text{PrO}_2$  insulators was calculated using the general potential LAPW method in the local density approximation (LDA). The crystal field splitting of  $\text{Pr}^{4+}$  and  $\text{U}^{4+}$  ionic ground states was determined by an integration of the product of the aspherical component of the crystal potential and radial density of the 4f (5f) electrons. The f-electron density was taken from LDA or the LDA+self interaction corrected atomic calculations. We have found that  $B_{40}$  crystal field parameter has its sign in accordance to experiment in both compounds studied. However, the absolute values are 4 times (31 times) smaller than experimental values for  $\text{PrO}_2$  ( $\text{UO}_2$ ). Validity of the computational scheme used for calculation of crystal field is discussed for 4f and 5f systems.

## 1. Introduction.

Uranium dioxide is frequently studied for the long time due to both technological applications and scientific interest [1]. Its magnetic properties are significantly influenced by crystal field effects, and according to recent results of inelastic neutron scattering experiments (see e.g. [2]), the standard crystal field (CF) model [3] works well in contrast to numerous uranium compounds where the 5f states are fairly delocalized. According to CF model, the ground state multiplet  $^3H_4$  of the  $\text{U}^{4+}$  ion is split by cubic crystal field acting on 5f-states, as described by the effective crystal field hamiltonian

$$H_{CF} = B_{40}(O_{40} + 5O_{44}) + B_{60}(O_{60} - 21O_{64}), \quad (1)$$

where  $B_{LM}$  are so called crystal field parameters and  $O_{LM}$  Stevens operators [3].

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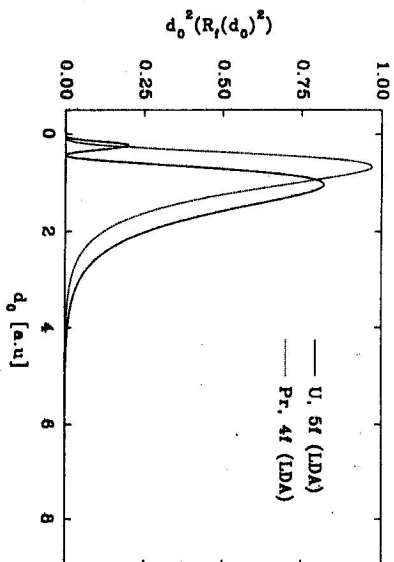


Fig. 1: The radial dependence of 4f (Pr) and 5f (U) charge density calculated using LDA method.

Goodman [4] estimated CF parameters using 'molecular-orbital' calculations in good agreement with experiment. On the other hand, he used cluster-type approach with adjustable Slater parameter  $\alpha$  whereas from our previous *ab initio* studies of 4f CF-systems [5, 6] it follows that the local density approximation (LDA) gives better results. Moreover we have shown that the contributions from the charge density located outside the nearest neighbours should be taken into account. This requirement should be even more critical for actinides because 5f wave function is more spread in space than 4f one (see Fig. 1.). Therefore we have used the *ab initio* based method [5, 6] which allows us to derive the CF parameters from aspherical components of electronic potential.

## 2. Method of calculation.

The  $\text{UO}_2$  compound crystallizes in the cubic fluorite structure (space group  $Fm\bar{3}m$ ;  $a = 0.547$  nm) [2]. Electronic structure of  $\text{UO}_2$  was calculated using the full-potential LAPW (FLAPW) method [7]. Uranium 7s, 6p, 6d states and oxygen 2s, 2p states were treated as valence states. Uranium 5f states were considered as special semi-core states and the effective one electron equation was solved at the  $\Gamma$  point only [6]. Aspherical components of 5f states density were removed to avoid self-interaction. Scalar relativistic corrections were included for valence and semi-core states calculation. Core electrons were treated fully relativistically. We obtained the valence band width to be 5.5 eV, which agrees with value of 5.6 eV found in [8] using LMTO-ASA method. Our band gap of 3.7 eV is slightly lower than 5.35 eV given also in [8].

To calculate crystal field parameters we used following formulae [5, 6]:

$$B_{LM}/\alpha_L = \eta_{LM} \int_0^\infty V_{LM}(r) R_{5f}^2(r) r^2 dr \quad (2)$$

where  $\alpha_L$  are Stevens factors [3],  $\eta_{LM}$  numerical conversion coefficients and  $V_{LM}$  aspherical components of Coulomb potential.  $R_{5f}$  denotes the radial wave function of 5f

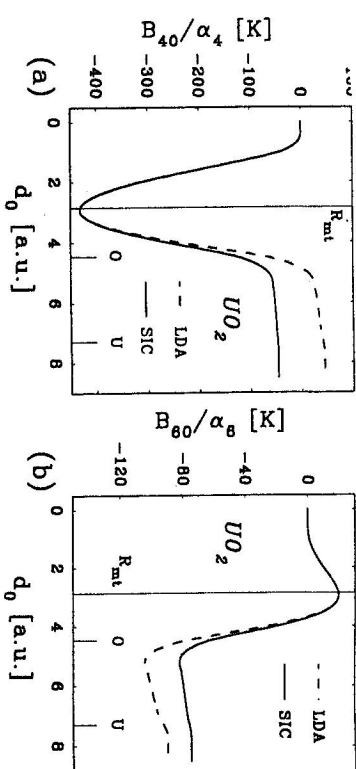


Fig. 2: The spatial dependence of (a)  $B_{40}/\alpha_4$ , (b)  $B_{60}/\alpha_6$  calculated with LDA and LDA + SIC 5f wave function for  $\text{UO}_2$ . The position of nearest neighbours oxygen and uranium atoms are also indicated.

states. We encountered two problems when we evaluated the value of the integral in the formulae (2).

First, FLAPW code used provides aspherical components of the potential only inside muffin-tin (MT) spheres, so that one should construct expansion to spherical harmonics also outside these spheres to some reasonable distance from the center of uranium. This distance is given by the condition that the value of  $B_{LM}/\alpha_L$  changes negligibly with a change of this distance. In practice, we can replace upper integration limit  $\infty$  in the above integral by some finite value  $d_0$ .

Second, the convergence of the integral depends also on the decay of 5f radial wave function. To inspect this effect we used two radial wave functions: (i) LDA atomic wave function and (ii) LDA self-interaction corrected (SIC) wave function [9, 6].

## 3. Results and discussion.

In Fig. 2., we present results of our calculations for  $\text{UO}_2$ . Figure (a) shows the dependence of  $B_{40}$  value on the upper integration limit in the equation (2). The solid line represents results obtained using LDA + SIC 5f wave function. LDA results are plotted using dashed curve. Analogically, figure (b) shows results for the sixth order parameter  $B_{60}$ . The position of muffin-tin radius is marked by vertical line.

We can see that the SIC-based curves are almost saturated for large values of  $d_0$  in contrast to LDA curves. There is also further noticeable result: we cannot restrict upper integration limit  $d_0$  to muffin-tin radius because the contribution from the outside of muffin-tin sphere is significant (even can change the sign of the result). On the other hand, the agreement with experiment ( $B_{40}/\alpha_4 = -1430$  K,  $B_{60}/\alpha_6 = 310$  K [2]) is rather poor. For the fourth order parameter our value is approximately by one order smaller (in magnitude). In the case of the  $B_{60}$  parameter we even obtained wrong sign.

Diagonalizing the hamiltonian (1) with above CF parameters calculated up to the  $d_0 = 2.86$  a.u. (muffin-tin radius) we have found the following CF energies: 0 ( $T_5$  triplet),

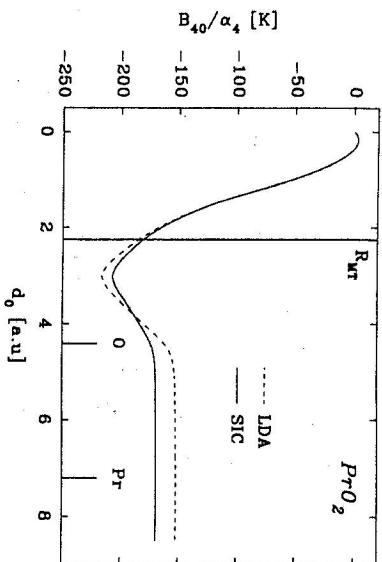


Fig. 3: The spatial dependence of  $B_{40}/\alpha_4$  calculated with LDA and LDA + SIC  $4f$  wave function for  $\text{Pr-O}_2$ . The position of nearest neighbours oxygen and Pr atoms are also indicated.

275 ( $\Gamma_3$  doublet), 655 ( $\Gamma_4$  triplet), 1186 K ( $\Gamma_1$  singlet) which can be compared with experimental energies: 0 ( $\Gamma_5$ ), 1742 ( $\Gamma_3$ ), 1935 ( $\Gamma_4$ ), 2029 K ( $\Gamma_1$ ), which were obtained from the analysis of inelastic neutron spectroscopy on the ground state multiplet  ${}^3H_4$  [2]. We emphasize that this theoretical splitting qualitatively agrees with the experimental analysis which provides  $\Gamma_5$  triplet as the CF ground state. However, the saturated values ( $d_0 \rightarrow \infty$ ) of CF parameters provides the following sequence of levels: 0 ( $\Gamma_3$ ), 194 ( $\Gamma_5$ ), 277 ( $\Gamma_4$ ), 666 K ( $\Gamma_1$ ), so the total CF splitting is substantially reduced and a position of first two levels is interchanged.

For the sake of comparison we have performed similar calculation for the isostructural  $4f$  system  $\text{Pr-O}_2$  ( $a = 0.537$  nm [10]). The CF splits the ionic ground state of the Pr ( $4f^1$ ) ion ( ${}^2F_{5/2}$ ) into a  $\Gamma_7$  doublet and a  $\Gamma_8$  quartet. As it follows from inelastic neutron scattering spectra these CF energy levels are separated by a 1570 K and the ground state is  $\Gamma_8$  quartet [10]. We note that the CF hamiltonian (1) contains only fourth-order terms in this case. Results of our preliminary calculations of CF parameter  $B_{40}/\alpha_4$  using Pr LDA+SIC wave function and exact continuation of Coulomb crystal potential outside the MT spheres are summarized in Fig. 3. It is seen that the major contribution to the value of  $B_{40}/\alpha_4$  comes from the potential and  $4f$  charge density from the region inside the Pr-MT sphere. This is consistent with results which we have obtained in a similar study of RE intermetallics recently [5]. The calculated value  $B_{40}/\alpha_4$  for  $d_0 \rightarrow \infty$  is -169 K which after the diagonalization of the CF hamiltonian yields the total splitting 383 K between the quartet and the doublet. The theoretical value of  $B_{40}/\alpha_4$  has the correct sign and corresponds better with experimental value -661 K [10] than it is in the case of  $\text{UO}_2$ . To pursue our study of the microscopic origin of the CF splitting in more detail we have solved the one dimensional radial Poisson equation considering the  $(L, M)$ -decomposed valence charge density inside the sphere. We have found that the 80% of the calculated value of  $B_{40}/\alpha_4$  ( $d_0 \rightarrow \infty$ ) comes from the asphericity of the valence charge density (mainly of  $5d$ -type) which is restricted to Pr-MT sphere.

#### 4. Conclusions.

We can conclude that the *ab initio* based method for calculation of CF parameters, which we tested, is less reliable for  $5f$  systems in comparison with systems containing  $4f$  electrons. We speculate on limitations of the LDA scheme for the description of the wave function of  $5f$  localized electrons ( $R_5f$ ). Moreover, this standard concept of calculation of crystal field seems to be doubtful for  $5f$  systems due to significant contribution from the outside of the localization region of  $5f$  wave function. It follows from this viewpoint that the crystal field splitting is not well defined as a one ion property, in contrast to  $4f$  systems. Further investigations in this region are in progress.

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