The Crystal Structure of the Close-Packed Polymorphs of Ytterbium: A Quantum Chemical Study

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Comparative first-principles calculations for the crystal structures of two polymorphs of ytterbium, α-Yb (hcp) and β-Yb (fcc), using local density (LDA) or generalized gradient approximation (GGA), provide insight into the contribution of different atomic shells to the binding in the bulk metal. The contributions of the 6s, 6p and 5d shells, but not of the 4f shell, significantly differ between the two polymorphs, independent of the density functional actually applied.

1.   Introduction

The recent years have seen a renewed and increased interest in detailed *ab initio* electronic structure calculations for bulk metals based on application of the method of increments (MOI) [1] to the correlation part of the (total bulk or cohesive) energy. This new approach to the electronic structure of bulk metals combines a mean-field (Hartree-Fock) calculation for the periodic system with size-consistent coupled-cluster calculations for a sequence of suitably embedded metal atom clusters. One-body, two-body, etc. contributions to the correlation energy are extracted from the coupled-cluster calculations. The contributions of electron correlation from different atomic shells can be resolved. Successful applications of this method include studies of crystal structure, cohesive energy and bulk modulus for metals from group 2 (Be, Mg [2]) and from group 12 (Zn, Cd and Hg [3]). Complementary to the MOI approach, these studies always included first-principles calculations based on Kohn-Sham density functional theory (KS-DFT), both to identify strengths and weaknesses of the various approaches and to provide data for future density functional improvement.

We present here results from a first-principles study of the crystal structure of the two close-packed polymorphs of ytterbium, α-Yb (hcp) and β-Yb (fcc). This work is complementary to a Hartree-Fock/MOI study currently in progress in our group. In contrast to previous studies [4] our approach includes all shells with principal quantum number $n = 4$ or higher in the calculation, i.e., 42 electrons per atom.

Like the metals mentioned above, Yb is also formally composed of atoms with a closed-shell atomic ground state ([Xe] $4f^{14}$ $6s^2$ ^1S). It can thus be seen as a natural intermediate case between Ba ([Xe] $6s^2$ ^1S, also under study in our group) and Hg ([Xe] $4f^{14}$ $5d^{10}$ $6s^2$ ^1S). Low-lying excitations of the free Yb atom lead to states with occupied 6p shell (2.14 eV: 6s $\rightarrow$ 6p) or 5d shell (2.88 eV: 4f $\rightarrow$ 5d), the first ionization potential is 6.25 eV ($6s^2 \rightarrow 6s^1$) [5]. Atomic structure calculations, both non-relativistic [6] and scalar-relativistic (excluding spin-orbit coupling) [7], show the 6s shell to be highest in energy and radially far extending, whereas the 4f shell, although next in energy, has a radial extension comparable to the other outer-core shells (4s, 4p and 4d). This "local" character of the 4f shell allows one to expect to find a comparatively narrow 4f band in the electronic band structure, but the location of this band on the energy scale, its width and dispersion, and its position relative to the Fermi energy cannot be predicted from atomic data. The bulk metal is known to exist in three polymorphs at ambient pressure [8]: hexagonal close packed (hcp) α-Yb is reported as being the most stable

polymorph below 260 K, face centred cubic (fcc) β-Yb is the most stable form at room temperature, and body centred cubic (bcc) γ-Yb is the preferred form in a small temperature range below the melting point (1097 K). Its low melting point and large molar volume, compared to the neighbouring lanthanoids, are frequently interpreted as indications for the divalency of ytterbium in the bulk metal, i.e., only two (instead of three) electrons are thought to be released by each atom for binding in the metallic state. In the bulk, the 4f levels show the lowest electronic binding energy (relative to the Fermi level [9]): 2.5 eV (N $_{VI}$, $4f_{5/2}$) and 1.3 eV (N$_{VII}$, $4f_{7/2}$), respectively.

2.   Computational details

The results presented here were obtained with the Crystal06 program [10] using a scalar-relativistic effective core potential for ytterbium, simulating the [Ar] 3d ^{10} atomic core, with associated valence triple-zeta quality Gauss-type basis set [7,11]. The basis set was modified with respect to number and parameters of diffuse functions to meet the requirements for calculations on periodic structures. Density functionals used in this study include the local density approximation (LDA: SVWN [12]) and two functionals based on the generalized gradient approximation (GGA: PBE [13], PW91 [14]). The number of k-space points taken into account in the irreducible Brillouin zone was 370 (195) for the hcp (fcc) polymorph, the total energy of the primitive cell was converged to 10^{-7} Hartree. The minimum-energy structure was determined for both polymorphs and with all three functionals. In the case of α-Yb (hcp), the energy $E(a,c)$ was automatically minimized [10] with the aid of numerical gradients. For β-Yb (fcc), on the other hand, a sequence of energies $E(a)$ with $0.8 \leq a / a_{exp} \leq 1.1$ was calculated and fitted to a fourth-degree polynomial.

3.   Results

In the following we discuss some results as obtained from the crystal structure optimization for the two close-packed polymorphs of Yb. The three density functionals mentioned above were used. We discuss first the crystal structure itself and switch then to its electronic structure.

3.1   Crystal structure

All three density functionals used in this study lead to optimized crystal structures that are more compact than the experimental structures. The cell parameters are calculated as too small and correspondingly the densities are obtained too high (see Table 1). This behaviour is very well known for the local density approximation (LDA). Remarkably, the density of β-Yb is obtained higher than the one for α-Yb, as in experiment, only with the LDA functional.

The two GGA type functionals show very similar results for the cell parameters, and these results are closer to experiment than those from LDA for both polymorphs. But the calculated values are still too small, by 0.1 Å to 0.3 Å, so that the resulting densities are larger than the experimental ones by ≈ 13 %. For any given polymorph, the cell parameter values closest to experiment are not obtained with just one single GGA functional.

The difference between calculated and experimental values for the cell parameters can be attributed, to some extent, to the fact that the experimental values are taken from room temperature measurements. Other, more recently developed density functionals, in particular those including exact exchange (EXX, see, e.g. [15]) could also possibly reduce the difference between experiment and theory.

The difference of total energy per atom between the two polymorphs, $\Delta E = E_\beta - E_\alpha$, is calculated as -44 meV (LDA), +12 meV (PBE) and -34 meV (PW91), i.e., only the PBE functional finds α-Yb as the more stable polymorph (in accord with experiment).

3.2. Electronic structure

The occupation numbers, as obtained from the Mulliken population analysis [16], provide first insight into details of the electronic structure in the metal. Data in Table 1 show how the 16 electrons from the valence part $4f^{14} 6s^2$ of the free atom electron configuration have been redistributed (the numbers subtracted, as indicated in the table head, account for the 26 electrons in the filled outer core shells 4s, 4p, 4d, 5s, and 5p). For both polymorphs, about 0.2 electrons per atom have been released from the 4f shell, and about 1.5 electrons from the 6s shell. The released electrons occupy bands formed from 5d and 6p shells. Interestingly, differences between the two polymorphs are seen only in the occupation numbers for 6s, 6p and 5d, but not for 4f. Independent from the applied density functional, the change from α-Yb (hcp) to β-Yb (fcc) slightly decreases the occupation numbers for the 6s and 6p shells and clearly increases the one for the 5d shell, whereas the occupation number for the 4f shell remains practically constant. The occupation number increase found for the 5d shell possibly just reflects perfect suitability of the d orbitals for binding in the cubic symmetry.

Table 1. Crystal structure parameters and occupation numbers for the two close-packed polymorphs of Yb (results from KS-DFT calculations *vs.* exptl. data [8], see text for more details).

Method	a / Å	c / Å	d_{nn} / Å	ρ / g cm^{-3}	n_s-4	n_p-12	n_d-10	n_f
α-**Yb** (hcp, $Z = 2$):								
LDA/SVWN	3.600	5.798	3.567, 3.600	8.876	0.48	0.59	1.17	13.76
GGA/PBE	3.734	6.161	3.734, 3.760	7.763	0.49	0.68	1.04	13.80
GGA/PW91	3.786	6.076	3.743, 3.786	7.660	0.51	0.67	1.02	13.81
Expt. (296 K)	3.880	6.386	3.880, 3.900	6.903	--	--	--	--
β-**Yb** (fcc, $Z = 4$):								
LDA/SVWN	5.041	--	3.565	8.971	0.47	0.57	1.20	13.76
GGA/PBE	5.295	--	3.744	7.744	0.48	0.66	1.07	13.80
GGA/PW91	5.281	--	3.735	7.802	0.49	0.64	1.07	13.80
Expt. (297 K)	5.485	--	3.878	6.966	--	--	--	--

In Fig. 1 we show the total density of states (DOS) for both polymorphs as obtained with the PBE functional. Qualitatively similar DOS are obtained with the other two functionals and are not further discussed, for the sake of brevity. A feature of interest in the DOS is that the 4f band is found closely below the Fermi energy (ε_F = -0.221 Hartree for α-Yb, ε_F = -0.222 Hartree for β-Yb, respectively), in acceptably good agreement with experiment.
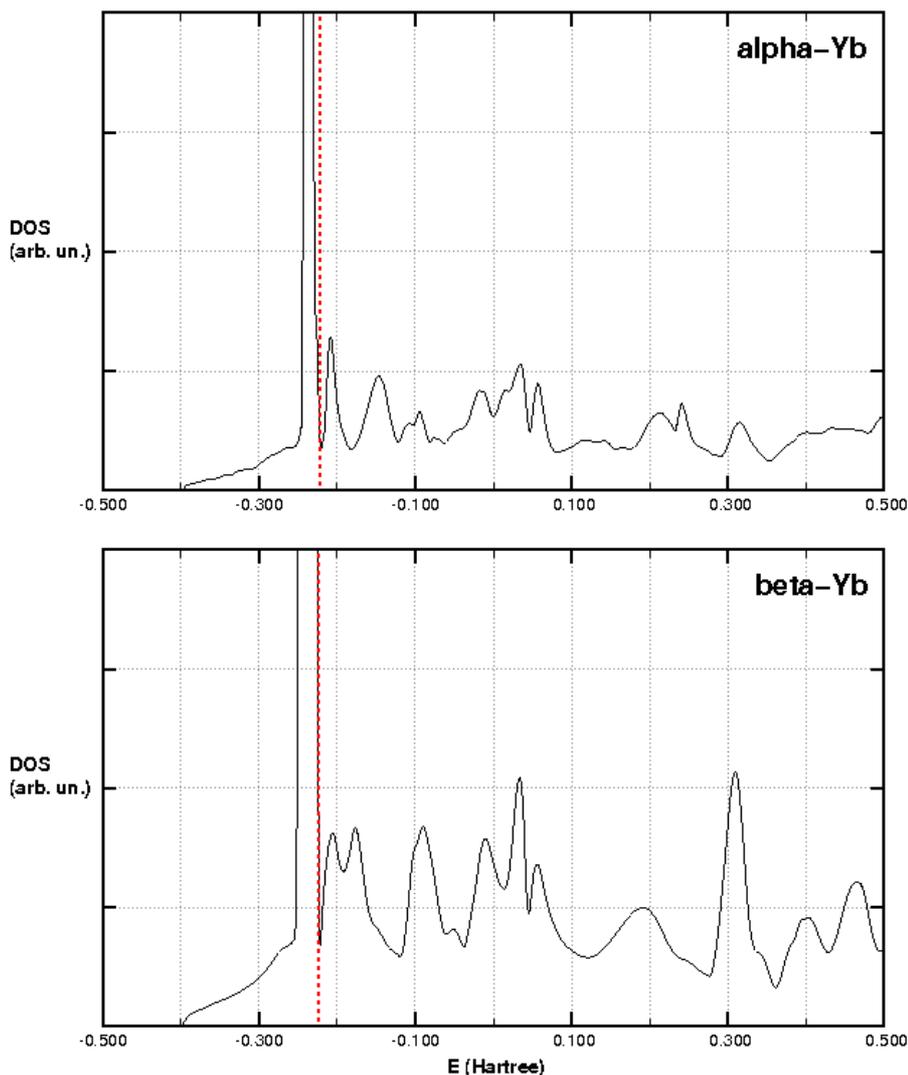
Fig. 1. Total density of states for α-Yb (hcp, top) and β-Yb (fcc, bottom) as obtained from KS-DFT calculations with the PBE density functional. The Fermi energy is indicated by a vertical dotted red line in each case.

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