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Prediction of a bcc structure in compressed yttrium

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Crystallographic phase transitions between close-packed structures in Y have been studied theoretically, using a full-potential, linear muffin-tin orbitals method. At the equilibrium volume the hcp structure is correctly found to have the lowest energy, and at a calculated pressure of 60 kbar the fcc phase becomes stable. It is found that the so-called ω phase is only marginally lower than the hcp and the fcc structures over a large volume range. At even higher pressures another crystal phase in yttrium is found, namely the bcc phase, which is predicted to become stable at a pressure of 2.8 Mbar.

Yttrium is the first element in the row of the 4*d* transition metals and also qualifies as a member of the rare-earth series. A lot of attention has been paid to the crystal structures of the lanthanides, like, for example, the construction of a generalized phase diagram encompassing all the trivalent 4*f* metals.[1] Furthermore, using canonical energy-band theory,[2,3] as well as fully self-consistent energy-band calculations,[3] it has been shown that the *d*-occupation number acts as an important parameter for determining the crystallographic properties of the rare-earth metals. Yttrium displays many physical and chemical properties that are very close to those of the lanthanides. This can be understood from the fact that yttrium as well as the lanthanides (except α-Ce, Eu, and Yb) are trivalent $(spd)^3$ metals. Although the bonding properties of yttrium are determined by the 5*s*, 5*p*, and 4*d* bands, whereas in the lanthanides the bonding properties are determined by the 6*s*, 6*p*, and 5*d* bands, the resulting chemical and physical properties are very similar. In Ref. 1 it was predicted that yttrium under pressure will show the same structure sequence as the lanthanides. This was nicely confirmed experimentally by Vohra *et al.*[4] The understanding of this crystal structure sequence is based upon the gradual increase of the *d* occupation of the valence band when the volume decreases[5] or similarly on the increase of the ratio $R_I/R_{\rm WS}$ (R_I=ionic radius, $R_{\rm WS}$=Wigner-Seitz radius).[1] Although previous studies have accounted for many of the crystallographic transitions at lower pressures the present work is, to our knowledge, the first investigation of the crystal structures of yttrium at extreme compressions. As a function of volume we have compared the total energies for the two close-packed hcp and fcc structures as well as for the somewhat more open bcc structure and for the very open ω structure (found experimentally in Ti, Zr, and Hf, see below) down to a compression of $(V_0-V)/V_0 \sim 86\%$ (V_0=equilibrium volume). This work is part of an ongoing research project where the electronic structure of highly compressed materials is investigated. The motivation for the present study is to investigate the conditions and nature of a transition to the bcc phase in yttrium at high pressures. Conventional ideas of the electronic structure of transition metals predict that under compression the *d* occupation increases. It is thus expected that given a sufficiently high pressure the *d* occupation in Y should reach the values of Zr. Since Zr displays a crystallographic sequence hcp $\rightarrow\omega\rightarrow$bcc under pressure we have in addition to the bcc structure also considered the stability of the ω structure in compressed yttrium.

The calculations were performed by means of a full-potential linear muffin-tin orbital scheme[6] and the local density approximation (LDA), using the Hedin-Lundqvist density parametrization for the exchange-correlation potential. In the construction of the potential the muffin-tin radius was taken to be 0.822 times the Wigner-Seitz radius. The wave functions forming the basis sets for the valence electrons comprised 4*s*, 4*p*, 4*d*, 5*s*, and 5*p* partial waves. Since we investigated compressions down to 14% of the equilibrium volume the 4*s* and 4*p* levels have been included and treated as pseudocore levels in an energy panel common with the standard valence states. Approximate orthogonality between two states was ensured by using two sets of energy parameters. The tails of our basis functions are linear combinations of Hankel and Neumann functions with nonzero kinetic energy. Integration over the Brillouin zone was done using "special-point" sampling.[7] The results reported here used 60 points in the irreducible wedge of the fcc Brillouin zone, 70 in bcc, 76 in hcp, and 16 in the ω structure. Tests using more as well as less *k*-points showed that the convergence in the structural energy differences is better than 1 mRy at the most compressed volumes and better than 0.1 mRy at the equilibrium volume.

For the hcp phase we used the experimental c/a ratio of 1.571 and for the ω structure we used a c/a ratio of

TABLE I. Comparison of the present results (FP-LMTO) with experimental values (Ref. 10). V_{eq} is the equilibrium volume, c/a the axial ratio, and B is the bulk modulus. $p_{A\rightarrow B}$ is the calculated transition pressure for the crystallographic change from A to B. $V_{A\rightarrow B}$ is the calculated transition volume at which phase A transforms into phase B.

	Expt.	FP-LMTO
V_{eq} (Å^3)	33.01	29.66
c/a	1.57	1.56
B (GPa)	41	45
$p_{\mathrm{hcp}\rightarrow\mathrm{fcc}}$ (kbar)		60
$V_{\mathrm{hcp}\rightarrow\mathrm{fcc}}$ (Å^3)		26.6
$p_{\mathrm{fcc}\rightarrow\mathrm{bcc}}$ (Mbar)		2.83
$V_{\mathrm{fcc}\rightarrow\mathrm{bcc}}$ (Å^3)		10.15

0.61, which is close to the experimental value reported in Zr. The hcp structure was found to be stable at our calculated equilibrium volume and the equilibrium volume was found to be 29.8 Å^3, which is ~10% smaller than the experimental volume of 33.03 Å^3. At the calculated equilibrium volume, we also optimized the c/a ratio. It was found to be 1.56, which is in good agreement with the experimental value. The bulk modulus, B, was computed to be 45 GPa at the calculated equilibrium volume [the experimental bulk modulus is 41 GPa (Ref. 2)]. The ~10% deviation of the equilibrium volume and the bulk modulus is consistent with other full-potential results for equilibrium volumes and bulk moduli in transition metals.[9] In general, calculations based upon the LDA are known to give an underestimation of the equilibrium volume. With this in mind, we consider our results acceptable. In Table I we list our results together with experimental data.

In Fig. 1, we compare our calculated equation of state with recent experimental data.[10] Notice that the theoretical equation of state is in fair agreement with experiment, but that our calculations systematically underestimate the electronic pressure by ~75 kbar over a wide volume range. Next, the calculated energies of the hcp, ω, and bcc phase are plotted relative to the fcc energy as a function of volume in Fig. 2. Notice that although the ω structure never becomes stable it has for certain volumes only marginally higher energies than the stable structures (fcc or hcp). As a matter of fact the ω structure is calculated to have energies very close to the hcp structure over a large volume range, ~25–12 Å^3, and it is possible that this structure could be stabilized in this volume range at elevated temperatures. The computed crystallographic hcp→fcc transition is in agreement with previous theoretical work.[3,11] The calculated transition pressure for the hcp→fcc phase transition is 60 kbar, and the corresponding volume for the hcp phase is 26.6 Å^3. Furthermore, the transition is accompanied by a small volume collapse of 1.2%. This transition cannot be directly compared to experimental work since yttrium transforms first to a Sm-type structure, then to the double hexagonal close packed (dhcp) structure and finally to the fcc structure. Since the main purpose of the present report is to predict a particular crystal structure in yttrium at ultrahigh pressures, from fcc to bcc, we refrained from an investigation of the Sm-type and dhcp structures. Still, one would expect the calculated transition pressure and volume from hcp to fcc to lie somewhere between the experimental transition pressures and volumes from hcp to Sm type (100 kbar and 27.3 Å^3) and from dhcp to fcc (390 kbar and 19.9 Å^3). For the transition volume this is the case, since our computed value (26.6 Å^3) lies between 19.9 and 27.3 Å^3. However, the calculated pressure is lower than the lower bound (the transition pressure from hcp to Sm type). This is due to the fact that the calculated equation of state (Fig. 1) systematically underestimates the pressure by ~75 kbar.

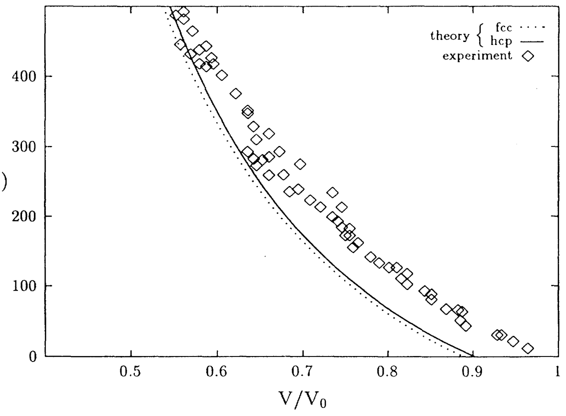

FIG. 1. Calculated equation of state (solid and dotted lines) compared to experimental data (diamonds) from Ref. 10.

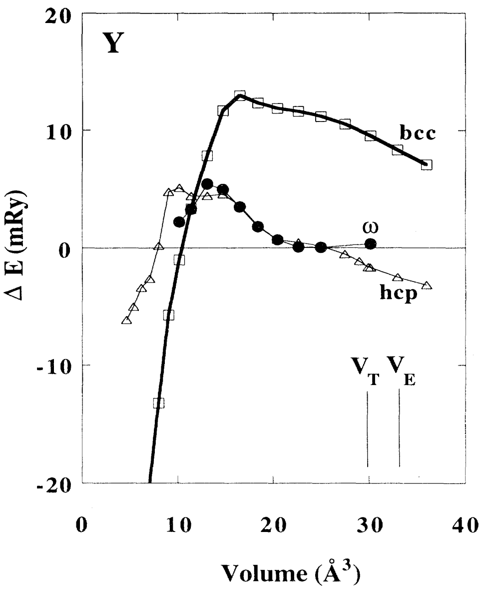

FIG. 2. Calculated structural energy differences (hcp-fcc, bcc-fcc, and ω-fcc) for Y as a function of volume. The reference level is the energy of the fcc phase, which is set equal to zero. The bcc structure is denoted by open squares, the hcp structure by open triangles, and the ω phase by filled circles. The theoretical and experimental equilibrium volumes are denoted by V_T and V_E, respectively.

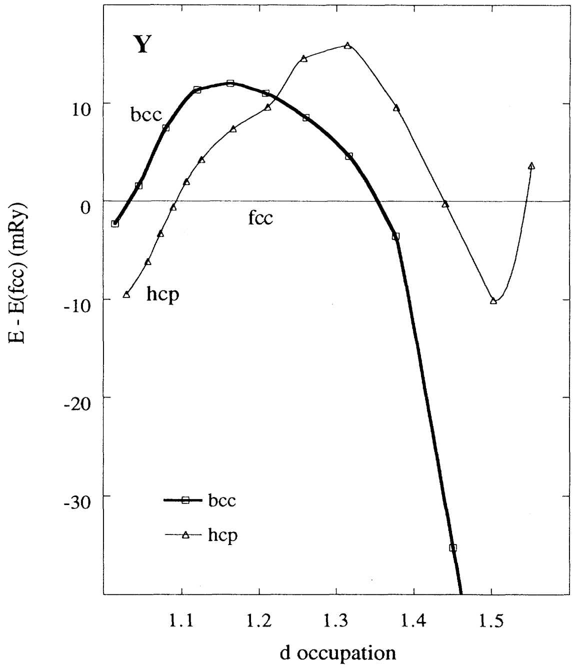

FIG. 3. Calculated structural energy differences for Y as a function of the *d* occupation number within the muffin-tin sphere. The reference level is the energy of the fcc phase, which is set equal to zero.

As stated above, the main result of this report is the transition from fcc to bcc, which was calculated to occur at 2.8 Mbar and $V = 10.4$ Å^3 (corresponding to 31% of the experimental volume). This pressure is within the capabilities of present experimental techniques and it is our hope that our work will stimulate experimental work in this pressure region. Due to the similarity between yttrium and the trivalent lanthanides we also suggest that the bcc structure should be found at ultrahigh pressures in trivalent lanthanide metals as well. Our values for the above mentioned crystallographic transitions are collected in Table I.

In Fig. 3 we present structural energy differences for the hcp and bcc phases relative to the fcc phase as a function of the *d* occupation number within the muffin-tin sphere. The *d* occupation number in the muffin-tin sphere increases monotonically with decreasing volume down to a volume equal to ~35% of the equilibrium volume. However, since the relation between *d* occupation and volume is slightly different from structure to structure, the presented energy differences in Fig. 3 are not a projection of the energy differences as a function of volume. For example, the *d* occupation at small volumes is largest in the bcc phase. Therefore, to obtain a certain high *d* occupation number, a smaller compression is needed in the bcc structure than in the fcc or hcp structures. A result that we would like to stress is that the shape of the structural energy difference curves in Fig. 3 shows a surprising similarity to the results of canonical band theory by Skriver.[3] A difference between our results and those of Skriver is that our *d* occupation number is smaller, since it is defined only within the muffin-tin sphere rather than within the Wigner-Seitz sphere. Nevertheless, from the similarity with canonical results it is tempting to conclude that arguments from canonical band theory applied to structural transitions are valid here also. However, such comparisons should be made with some care since already the hcp→fcc transition in yttrium is somewhat in contrast to the canonical picture. Namely, from the canonical picture one concludes that both Y and Zr, as well as systems with a *d* occupation larger than in Y and smaller than in Zr, crystallize in the hcp structure. Applying a pressure on Y increases the *d* occupation to an amount smaller than the *d* occupation found in Zr and the canonical picture thus suggests that the hcp structure should be stable. The onset of the fcc structure is therefore somewhat surprising. Moreover, the monotonic increase of the *d* occupation within the muffin-tin sphere takes on a different curvature at a compression of $(V_0 - V)/V_0 = 65\%$, i.e., at a volume higher than the bcc transition volume. We thus conclude that the onset of the bcc structure is therefore not correlated to a single parameter.

We now make some observations of the electronic structure, which contributes to the stabilization of the bcc structure. With decreasing volume there is a broadening of the bands and as stated above this causes the 4*s* and 4*p* pseudocore states to overlap in energy with the valence states. The resulting occupied part of the density of states (DOS; not shown) is ~60 eV broad (at ~5 Å^3) and has strong hybridization between all orbitals. Due to the broadening of the bands the typical structural features in the DOS are smoothened out. However, the DOS for the *d* states in the bcc phase, which at ambient volume shows two distinct peaks with a valley between, partly retains these characteristic variations even at large compressions. Since at low volumes the Fermi energy (E_F) lies in the valley between the two peaks, the stabilization of the bcc structure can be understood.[2,3] We have quantified this observation by computing the one-electron contribution to the total energy for the three phases. This analysis shows that the onset of the bcc structure with decreasing volume is mainly driven by the one-electron term. The Madelung contribution, which favors the bcc structure, is not of any substantial importance; it favors the bcc phase over the fcc phase by less than 0.5 mRy at 5 Å^3.

To summarize, we have reproduced the ground-state properties of yttrium at ambient pressure, and more importantly predicted a bcc structure, at extreme compressions. The stabilization of the bcc structure at high pressures can, to a large extent, be explained from band-filling arguments. The calculated pressure for the onset of the bcc structure is 2.8 Mbar and is thus within the capabilities of present experimental techniques. Due to the similarity between yttrium and the trivalent lanthanides it should be possible to stabilize the bcc structure in these latter systems as well, for instance in Gd, at high pressures. We encourage experimentalists to try and confirm or disprove our predictions.

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