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fcc → bct phase transition in Th at extreme compressions: Theory

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The experimentally observed fcc → bct crystallographic phase transition in Th, at ~1 Mbar, is reproduced by means of full-potential, linear-muffin-tin-orbitals calculations. Both the calculated volume and pressure for which the transition occurs, agrees with the experimental data. The calculated pressure dependence of the c/a ratio of the bct structure is also in good agreement with experimental data. Calculations for La predict the fcc phase to be stable over the bct phase up to ~7 Mbar.

Very recent experimental high-pressure studies[1] of Th showed that the body-centered-tetragonal (bct) crystal structure becomes stable at 1.02 Mbar, which corresponds to a volume compression $V/V_0=0.534$. Th crystallizes in the fcc structure at ambient pressures, and the fcc → bct transition was suggested to be electronically driven, mainly by the supposedly increasing contribution from the $5f$ electrons at elevated pressures.[1] The present work is a response to these interesting experiments. It has been demonstrated that the correct crystal structures as well as pressure-induced crystallographic phase transitions of [spd] metals can be obtained from first principles.[2] Furthermore, for f systems we have recently obtained similarly encouraging results, e.g., our previous calculations reproduce the zero-temperature phase diagram of Ce (fcc → α-U → bct),[3] as well as the zero-temperature crystal structures of Th, Pa, and U.[4] It was demonstrated that the low-symmetry structures encountered in Ce, and in the light actinides are correlated with the occupation of itinerant f orbitals. The occupation of the f orbitals increases with decreasing volume, hence one may expect an onset of low-symmetry structures at extreme compressions for Th, and this is exactly what Vohra and Akella found.[1] It is therefore of interest to perform total-energy calculations at compressed volumes to investigate if the observed phase transition in Th can be reproduced. Similar arguments can be used for La, and we have therefore studied the possibility of low-symmetry structures (bct) at extreme compressions for this material also.

The calculations were performed as described in Refs. 3 and 4. We used a full potential linear-muffin-tin-orbital technique,[5,6] and exchange and correlation were treated in the local-density approximation using the Hedin-Lundqvist exchange-correlation functional. The calculations were all electron, fully relativistic (spin-orbit coupling included at each variational step[7]), and employed no shape approximation to the charge density or potential.

The basis set, comprised of augmented linear muffin-tin orbitals,[7,8] contained $6s$, $6p$, $7s$, $7p$, $6d$, and $5f$ partial waves for Th, and $5s$, $5p$, $6s$, $6p$, $5d$, and $4f$ partial waves for La, in a single, fully hybridizing "energy panel" [since we are studying volume compressions of the order of $V/V_0\sim0.25$ we found it necessary to include the $6s$ (Th) and $5s$ (La) states as valence electrons]. Two sets of energy parameters,[7,8] one with energies appropriate to the semicore bands and one with energies corresponding to the valence bands, were used to calculate the radial functions for the expansions of the bases in the muffin-tin spheres. Similarly, three sets of tail parameters (the kinetic energy of the bases in the interstitial[7,8]), corresponding to semicore s, semicore p, and valence energies, were used. Approximate orthogonality between bases with the same l value was maintained by energy separation.

Integration over the Brillouin zone was done using "special point" sampling.[9] The results reported here used 60 points in the irreducible wedge of the fcc Brillouin zone, and 80 points in the irreducible wedge of the body-centered-tetragonal zone. In order to test the convergence of the k-space sampling we calculated the energy difference between the two structures, at a volume close to the fcc → bct transition (see below), using different numbers of k points. These tests were performed using between 10 and 60 points in the irreducible part of the fcc zone, and between 12 and 80 points in the irreducible part

of the bct zone. In agreement with our previous findings,[3,4] we found that the energy difference between bct and fcc was converged to better than ~0.1 mRy, using the 60 and 80 k-point sets for the fcc and bct structures, respectively.

In Fig. 1 we show the total energies for Th both in the bct and fcc structure, and in the inset in Fig. 1 we show the energy difference between the bct and fcc structures. Notice that in the inset the fcc structure is the reference level, and has its energy set to zero. For the results in Fig. 1, we used the high pressure, experimental c/a ratio (1.65). We also calculated this ratio; the result is described below. This choice of the c/a ratio is different than in our previous studies of Th at ambient pressures where we used $c/a=0.814$ (since this is the c/a ratio found in Pa).[4] When comparing the total energy of the bct structure for these two choices of c/a ratio we find that $c/a=1.65$ is favored at all volumes. Notice in Fig. 1 that the fcc structure is (correctly) obtained to be stable at zero pressure, with the bct phase having ~6 mRy higher energy. Moreover, the energy difference between the fcc and bct structures is initially insensitive to volume, but at ~25 Å^3 it decreases with decreasing volume, and at a volume of 16.9 Å^3 the bct structure becomes stable. The calculated pressure for the transition is 1.1 Mbar, and there is essentially no volume change. This agrees well with the experimental data,[1] $V_{\text{trans}}=17.6$ Å^3 and $P_{\text{trans}}=1.02$ Mbar.

In order to investigate the contribution of the f orbitals to the cohesion we show in Fig. 2 the f (and d) occupation as a function of volume, both for the fcc and bct structures. Notice that the f occupation is increasing at the expense of the d orbital, as well as the s and p orbitals (the latter two are not shown).[10] At volumes where the fcc→bct transition takes place the f occupation is close to 1 and Th has become an f electron material (at zero pressure Th is essentially a normal s,p,d material, see Fig. 2). The onset of the low-symmetry bct structure is therefore in agreement with previous studies of the light actinides at ambient pressure, i.e., the onset of low-symmetry structures is correlated with an increasing occupation of the itinerant f orbitals.[4,11] Notice also in Fig. 2 that there is only a small difference in d and f occupation for the two structures.

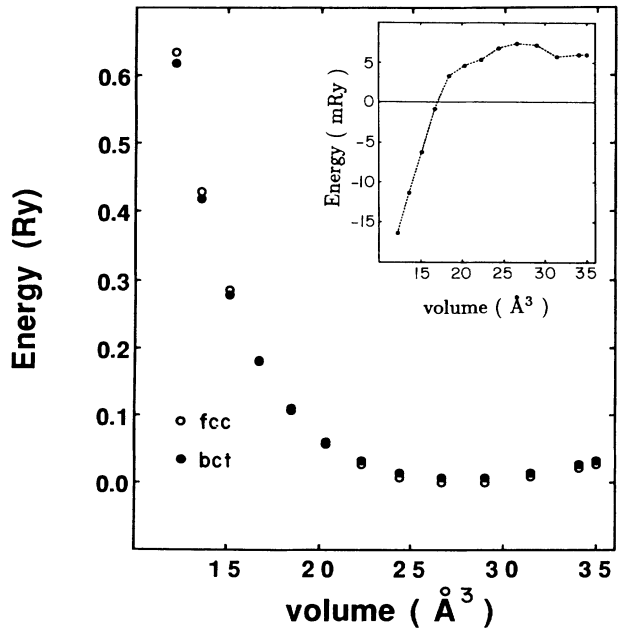

FIG. 1. Calculated total energy for Th in the fcc (open circles) and bct (solid circles) structures. The inset shows the bct-fcc energy difference. The energy of the fcc phase is here the reference level, and is set to zero.

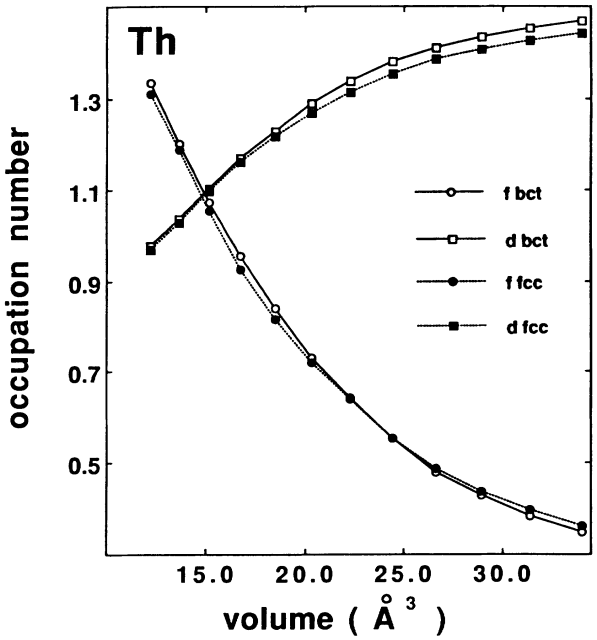

FIG. 2. Calculated occupation numbers for Th in the bct (open symbols, solid lines) and fcc (solid symbols, dotted lines) structures. The d occupation is represented by squares and the f occupation by circles.

We have also optimized the c/a ratio of bct Th at $V/V_0=0.405$ and at the transition volume, $V/V_0=0.534$. The computed results are 1.63 and 1.58, which should be compared to the experimental data of 1.65 and 1.56, respectively. Hence this crystallographic parameter also can be reproduced by our calculations. The energy difference between $c/a=1.65$ and $c/a=1.58$, at $V/V_0=0.534$, is rather small, and the transition volume and pressure obtained from Fig. 1 is not changed much by using the high pressure c/a ratio in the calculations. Furthermore, notice that both experiment and theory predict a more open structure (increasing c/a ratio) with increasing pressure. This behavior is similar to bct Ce, where the c/a ratio also is increasing with increasing pressure.[12]

Turning to La, we show in Fig. 3 the total energy for La in the fcc and bct structures; the inset shows the calculated total energy around the experimental volume. The c/a ratio was chosen to be 1.65 also in these calculations. As can be seen from Fig. 3 there is no fcc→bct phase transition. Optimizing the c/a ratio does not change this picture, the total energy as a function of the c/a ratio has a minimum at $c/a=\sqrt{2}$, i.e., for the fcc structure. These

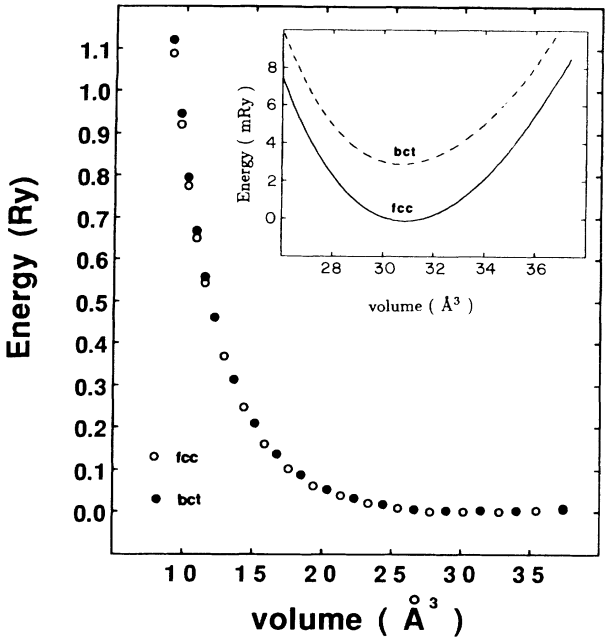

FIG. 3. Calculated total energy for La in the fcc (open circles) and bct (solid circles) structures. The inset shows the total energy data for the fcc structure (solid line) and the bct structure (dashed line), for volumes between 26 and 38 Å^3.

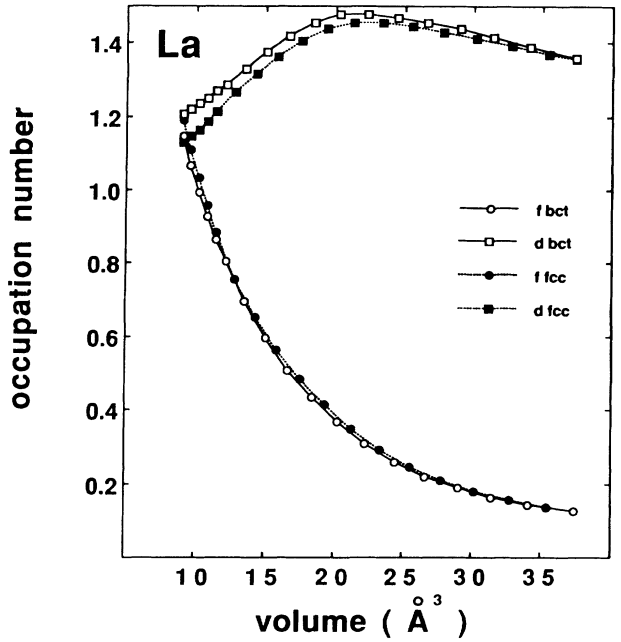

FIG. 4. Calculated occupation numbers for La in the bct (open symbols, solid lines) and fcc (solid symbols, dotted lines) structures. The d occupation is represented by squares and the f occupation by circles.

optimizations were found to give the same results (energy minimized for $c/a=\sqrt{2}$) for several pressures, up to ~ 1 Mbar. However, it is interesting that these optimizations yield a local minimum for the bct phase with a c/a ratio of ~ 0.8. The energy of this local minimum is from 5 mRy (at zero pressure) to 20 mRy (at the highest pressure) higher than the fcc phase. Our findings for La are in contrast to the calculations of Skriver[2] who found the bct phase to be stabilized at a volume of ~ 29 Å^3. The fact that Skriver's calculations relied on the atomic sphere approximation, and were scalar relativistic, as opposed to our fully relativistic full-potential treatment, may explain this difference.

Our results for La are different than for Th despite the fact that at the highest calculated pressures the $4f$ occupation is appreciable (Fig. 4). Notice also that for La, the (d,f) occupation numbers are very close for the two structures, and that, in agreement with the findings of McMahan, Skriver, and Johansson,[10] initially both the d and f occupation numbers are increasing, but for the lowest volumes the f orbital occupation is increasing at the expense of all other orbitals.

To conclude, we have, by means of full-potential, fully relativistic linear-muffin-tin-orbital calculations, reproduced the observed fcc→ bct phase transition in Th. Both the calculated transition volume and pressure agree with the experimental data, as well as the variation of the c/a ratio with pressure, in the bct phase. The calculations support the suggestion[1] that this transition is electronically driven, and influenced by the increasing occupation of the f orbitals. At the highest pressures studied we calculate an f orbital occupation of ~ 1.5, which is close to the occupation found in Pa at zero pressure (also bct). Therefore it is interesting to compare these results with our previous results for Pa (Ref. 4) and Ce.[3] An f occupation of approximately 1.5 seems to favor bct structures. However, the value of the c/a ratio can vary widely depending on the system; Th~ 1.65, Pa~ 0.82, and Ce ~ 1.66. As a matter of fact, it seems that these systems can exhibit several minima as a function of the c/a ratio, Skriver[2] showed that Ce and Pa have three local energy minima at $c/a\sim 0.8$, $c/a=\sqrt{2}$ (fcc), and $c/a\sim 1.7$. Our present results show that Th (at compression) minimizes its total energy for $c/a\sim 1.7$, and that La has a local minimum at $c/a\sim 0.8$. Depending on the system and external parameters, one of the three various c/a ratios minimizes the total energy.

Furthermore, within the actinide series, increasing the f occupation from 1.5 (Pa) to 2.5 (u) favors even less symmetric structures; α-uranium is orthorhombic. One can argue that these low-symmetry structures can be stabilized since degeneracies in the partially occupied f bands may be lifted by lowering the crystal symmetry. Occupied, degenerate states, in the fcc phase, which are close to E_F can therefore lower the total energy by lowering the crystal symmetry, since by doing this one band is pushed up above E_F (and therefore not affecting the total energy) and one band is pushed down, lowering the total energy. The scenario outlined above can minimize the one-electron contribution to the total energy. However, other terms also play a role, and, in particular, the Madelung term favors high-symmetry structures.[2] Crystallographic phase transitions are therefore determined by a change in the balance between the various terms that minimizes the total energy. Our calculations of the phase diagram of Ce show that the structural transitions are driven by a change

in the balance between the one-electron and Madelung terms.[3] Our results for Th can also be understood using these arguments, and the phase transition is a balance between d- (high-symmetry structures) and f-electron (low-symmetry structures) behavior. The variation of the c/a ratio can also be understood from this; the Madelung term is minimized at $c/a=1.0$ (bcc) whereas the one-electron term favors distortions, and with increasing pressure the one-electron term becomes more important[3] pushing the c/a ratio to higher values.

The arguments outlined above rely on a rather narrow band at E_F, and if the f band is too broad, high-symmetry structures should be favored. This is apparently what happens in La. Our results for La show no fcc→bct phase transition despite a rather high f occupation, since at volumes where we find an appreciable f occupation La has very broad bands. At these pressures the $5p$ states are also very broad and the occupied bandwidth (including the $5p$ states) is $\sim$28 eV. The fact that La is trivalent may also be connected to why the fcc phase is stabilized, despite a high f occupation.

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