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Thorium: A 5f-band metal at ultrahigh pressures

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The electronic structure of thorium is computed to study the recently reported [Phys. Rev. Lett. 67, 3563 (1991)] high-pressure fcc-bct structural transition. We find that elemental thorium is unique in that unoccupied f levels become populated at ultrahigh pressures, with the Fermi level intercepting the f band at a volume fraction of 0.6. The total energies show that the resulting occupation of f bands by about 1 electron drives the fcc-to-bct transition near 80-GPa pressure, and thorium then resembles the f-band metal cerium. The 6p electrons must be treated as band states in estimating the transition pressure and 0-K isotherm.

The present range of the diamond anvil cell has reached static pressures exceeding 400 GPa.[1] This has added new dimensions to material studies because at these pressures the changes in bonding character due to increased overlap of electronic orbitals, band broadenings, and band crossings, etc., usually lead to new phase transitions. This has also opened up new testing grounds for theoretical electronic-structure methods. An exciting example of such an ultrahigh pressure study is the recent experiments on thorium [$z=90$, face centered cubic (fcc) at ambient conditions] by Vohra and Akella,[2] where x-ray diffraction measurements up to 300 GPa have been carried out. These have revealed a structural transformation in thorium from the fcc to the body-centered-tetragonal (bct) phase between 75- and 100-GPa pressure (volume fraction, V/V_0 of about 0.6). This phase transition is remarkably similar to that observed in cerium ($Z=58$) at 12 GPa. The similarity suggests that at high pressures the electronic structures of the two elements might be similar, especially with respect to occupation and delocalization of the f band, though their normal-volume electronic structures are quite different, with cerium having a localized 4f electron, whereas the 5f levels of thorium are unoccupied.

We present here a first-principles electronic-structure computation on thorium to explore the relevant changes in its electronic properties under pressure. Previous electronic structure computations on thorium indicate that the bottom of the 5f-band remains above the Fermi level (E_F) and moves only a little closer to E_F up to the pressures studied (40 GPa corresponding to a volume fraction of about 0.7).[3] Dynamic shock[4] and static high-pressure[5] data did not indicate any structural transition. Hence, all the electronic structure computations,[3] and the shock Hugoniot equation of state studies[6] were carried out for the fcc phase, and possible structural transformations were not investigated. Though Skriver[7] had studied total energies of thorium in the bct structure at normal volume V_0, the emphasis was to show that the fcc phase is stable under ambient conditions. In fact, in a closely related study on cerium under compression in the bct structure, Skriver speculates that 4f states are not responsible for the pressure-induced structural transition to the bct phase in cerium.[7] However, a very recent study by Wills, Eriksson, and Boring[8] has shown that this transition is driven by 4f and 5d partial-wave contributions. Hence, the present theoretical studies focus on the f-band population in thorium at multiple GPa pressures (up to a volume fraction of 0.4), and examine the stability of the fcc phase against transformation to the bct structure by total-energy calculations.

We have employed the linear-muffin-tin-orbital (LMTO) method[9] for self-consistent electronic structure studies. A frozen core with $6p^6 6d^2 7s^2$ valence configuration is assumed, with Barth-Hedin exchange.[10] Though the results presented below are based on scalar relativistic computations, they have been checked for consistency by including spin-orbit coupling through perturbation. The calculations include the combined corrections to the atomic sphere approximation (ASA). The total energy is computed under the frozen-core approximation,[11] and the electrostatic muffin-tin correction is applied.[12] Separate energy panels were used for 6p and 6d7s electron. The irreducible wedge of the bct Brillouin zone was sampled at 462 **k** points.

The total energies for thorium have been computed in the bct structure for various axial ratios c/a (fcc corresponding to $c/a=1.414$). Figure 1 shows these total-energy curves at different volume fractions. It may be noted that these total-energy curves are qualitatively similar to those of cerium.[7] The normal-volume total-energy curve gives the lowest energy for the fcc structure. It is interesting to see that the fcc structure in thorium continues to be stable up to a volume fraction of about 0.6, at which the bct structure becomes more stable. For higher compressions the bct structure with $c/a>1.414$ is the most stable configuration. As seen from Fig. 2, the c/a ratio increases rapidly to the value of 1.64 at the volume fraction of 0.45, and changes little for higher compressions. Figure 2 also depicts some data from Ref. 2. Our results are in quantitative agreement with the data of Vohra and Akella.[2] It may be noted that the inclusion of 6p electrons in the calculations was essential for this agreement. Otherwise, i.e., when 6p electrons were treated as the frozen core, the fcc-to-bct transition occurred near $V/V_0=0.7$ and the c/a ratio was 1.72 at a

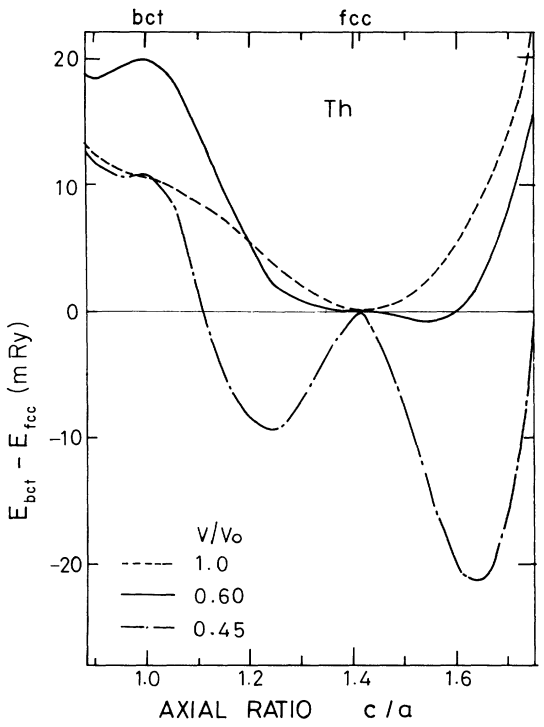

FIG. 1. Total energy E_{bct} of thorium in the bct structure (relative to that in the fcc phase), calculated as a function of axial ratio c/a. The curves at various compressions are as indicated in the legend.

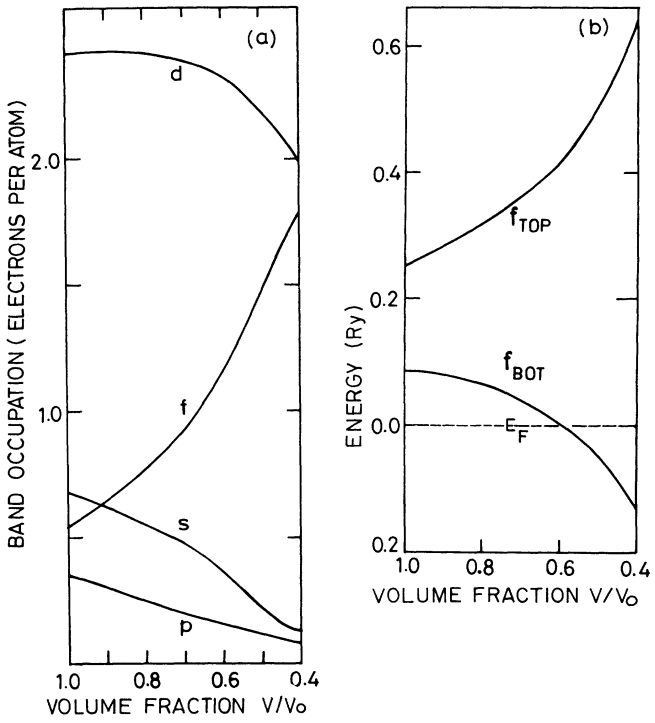

FIG. 3. (a) l-band decomposition of electrons at various volume fractions in thorium; (b) position of the $5f$ band relative to Fermi energy E_F in thorium at various compressions.

volume fraction of 0.45.

To study the $5f$-band characteristic through the fcc-to-bct transition, we analyzed the l decomposition of occupied electron states, and the position of the $5f$ band with respect to the Fermi level E_F. Figure 3(a) shows these l decompositions of electrons. Note that the $5f$-band population increases with pressure,[13] with the band containing more than one electron per atom at the volume fraction of 0.6. Figure 3(b) clarifies that the bottom of the $5f$ band descends through the Fermi level around this compression. Due to the proximity of this crossing to the fcc-to-bct transition, it is reasonable to assume that the f-band occupation is central to this structural transition. We verified this interpretation in

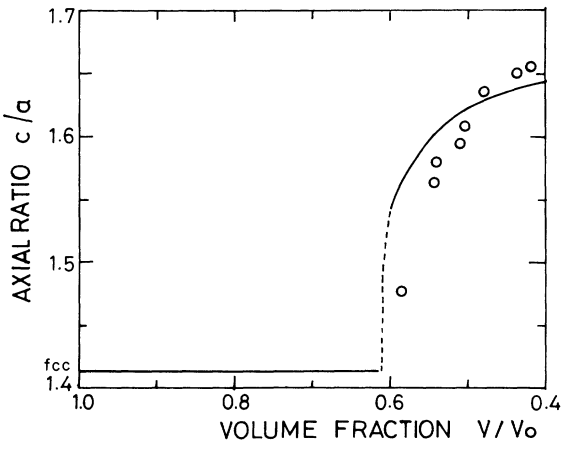

FIG. 2. Axial ratio c/a vs V/V_0. The c/a values correspond to the minimum of the total-energy curves (see Fig. 1) at various volume fractions. Circles represent a few experimental data read from Fig. 2 of Ref. 2.

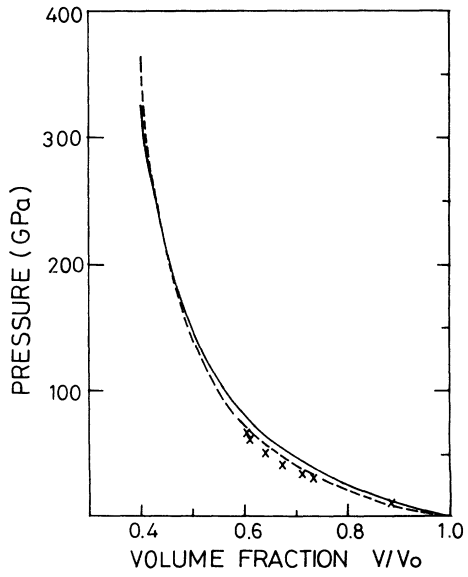

FIG. 4. 0-K isotherm of thorium compared to the experimental data (— — — Vohra and Akella, Ref. 2; × Benjamin *et al.*, Ref. 5).

greater detail by carrying out a few total-energy calculations with $5f$ electrons not contributing to metallic bonding (i.e., by restricting the muffin-tin-orbital expansion of the electron wave function up to only $l=2$). Then the minimum of the total energy in the bct structure corresponds to the axial ratio $c/a=1$, i.e., the body-centered-cubic (bcc) phase gets stabilized, under ambient conditions and continues to be stable through to the smallest volume fraction ($V/V_0=0.4$) studied. This result is consistent with the bcc structure prevailing in tetravalent group IV B elements, Ti ($Z=22$), Zr ($Z=40$), and Hf ($Z=72$), at high pressures where the d-band population increases to about 3 electrons/atom or more.[14]

Finally we discuss the equation of state (EOS). Figure 4 shows the 0-K isotherm of thorium. The pressure has been evaluated as the sum of two terms (see Ref. 15 for details).

(i) P_{LMTO}, the electronic pressure due to conduction electrons, is evaluated in the ASA. Below the volume fraction of 0.60, the $6p$ (core) states are found to contribute significantly to the electronic pressure[16] (i.e., about 100 GPa at $V/V_0=0.4$).

(ii) P_{MT}, which is due to muffin-tin correction, i.e., intercellular Coulomb interaction beyond ASA. Figure 4 also depicts the room-temperature isotherm data from Refs. 2 and 5 showing agreement with our computations. Again, our calculated results of EOS indicate that the $5f$ electrons play a crucial role for this agreement. For example in our s,p,d calculations, as described above, the calculated pressures were 18.5 GPa at $V/V_0=1$ and 168 GPa at $V/V_0=0.6$.

In summary, our total energy calculations show that the bct structure with axial ratio c/a greater than 1.414 is preferred to the fcc structure at pressures above 80 GPa (i.e., volume fraction of 0.6). The nature of the fcc-to-bct transition, the variation of the axial ratio (c/a) with pressure, and the isotherm show excellent agreement with the recent experimental data.[2] This is remarkable for a spherically averaged local-density-approximation calculation. We have also shown that $5f$ partial-wave contributions play an important role in this high-pressure structural transformation, and interestingly, thorium behaves as a $5f$-band metal under megabar pressures similar to cerium.

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[13]It may be noted that near the normal volume the $5f$ electron occupation in the partial-wave analysis is due to the tails of s, p, and d waves, and hence this does not mean that $5f$ orbitals in thorium are significantly occupied. At higher compressions it is essentially hybridization effect and only at $V/V_0=0.6$ is the f electron occupation caused by $5f$ orbitals. However, it is not possible to separate these different effects.

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