Anomalous fcc Crystal Structure of Thorium Metal

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It is standard practice to consider thorium as a traditional tetravalent d transition metal, belonging to the same group of elements as Ti, Zr, and Hf. We demonstrate, however, that the observed fcc crystal structure for thorium is in complete disagreement with this picture. Instead we show that it is the itinerant $5f$ electrons which stabilize the fcc phase. Thereby we have established a close connection between thorium and the heavier actinide metals (Pa-Pu), which has previously been overlooked.

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For many years there was a controversy regarding the electronic structure of the actinide metals Pa-Pu (protactinium-plutonium). The question was whether these elements should be described as a part of a $6d$ or a $5f$ transition series of elements [1]. However, today it is agreed upon that these elements are $5f$ electron metals, with a most significant f bonding. In contrast to this, the element preceding Pa in the actinide series, thorium, was regarded as uncontroversial. This agreement has remained until today, and a chemist's view of the actinide element thorium is that it is a normal tetravalent transition metal comparable to titanium, zirconium, and hafnium [2]. Also physicists have strongly argued in favor of this picture of thorium [3–5]. Among the earlier actinide metals, thorium is the only one which shows a simple ground state atomic arrangement, namely, the face centered cubic (fcc) crystal structure, while for the subsequent metals much more complicated structures are found: protactinium has a body centered tetragonal (bct) structure and uranium an orthorhombic structure [6]. For the two following elements, Np and Pu, the observed low temperature structures [6] are even less symmetric than for Pa and U. These distorted structures for Pa-Pu have often been interrelated to the itinerant behavior of the $5f$ electrons [7], while the high symmetry fcc structure in Th has been taken as strong evidence for normal d transition metal properties. This very clear distinction in crystallographic behavior has been used to make a sharp separation between Th, on one hand, and the next four heavier actinides, on the other hand [3–5]. The melting temperature [8] and the superconductivity transition temperature [9] are other properties that have been quoted in favor of a simple tetravalent d metal picture for Th. Also the atomic ground state configuration $6d^2 7s^2$ supports this view. It has, of course, also been understood that there will be a rather broad band of unoccupied $5f$ states above the Fermi level [10], but it has been taken for granted that they will only give rise to a minor and insignificant perturbation to the occupied valence electron states, thereby leaving the tetravalent d metal assignment for Th unchanged.

Very little, if any, attention has been paid to the fact that Th, when compared to Ti, Zr, and Hf, actually should be expected to be a hexagonal close packed (hcp) metal like all other group IVA elements. Since this is not the case, the next step is to investigate whether Zr or Hf transform to the fcc structure when subject to high pressure. The reason why one should look for such a possibility is that pressure induced crystallographic transitions establishing connections between elements in the same row of the periodic table are well known for other groups of elements [5,11]. Indeed, the high pressure behavior of the elements Ti, Zr, and Hf shows that there is such a relationship between these three metals. However, neither Zr nor Hf undergo a transition to the fcc phase under pressure, but instead they are observed to transform into the body centered cubic (bcc) structure at 300 and 710 kbar, respectively [12]. Thus, among these tetravalent elements, Th is the only one showing an fcc atomic arrangement. Therefore we have to conclude that the fcc crystal structure for Th is indeed anomalous, and it becomes a challenge to investigate the fundamental reason for this.

Today electronic structure calculations have reached a high level of accuracy. This also means that by manipulating the calculations one has the possibility to clarify certain aspects of the electronic structure and its effect on the physical and chemical properties. In the present work we will use such an approach in order to achieve a new understanding of the behavior of thorium metal. This is accomplished by performing restricted calculations where, on purpose, the $5f$ states are not included in the theoretical treatment.

In order to study the anomalous behavior of thorium we have considered its electronic structure by means of the full-potential linear muffin-tin-orbital (FPLMTO) method [13]. The calculations were based on the local-density approximation, and we used the Hedin-Lundqvist [14] parametrization for the exchange and correlation potentials. Basis functions, electron densities, and potentials were calculated without any geometrical approximation [13]. The spin-orbit coupling is included explicitly. In

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the calculations reported here, we made use of pseudo-core p and valence band s, p, d, and f basis functions with two corresponding sets of energy parameters, one appropriate for the semicore p states, and the other appropriate for the valence states. The resulting basis formed a single, fully hybridizing basis set. This approach has previously proven to give a well-converged basis [13]. For sampling the irreducible wedge of the Brillouin zone (BZ) we used the special k-point method [15]. In order to speed up the convergence we have associated each calculated eigen-value with a Gaussian function of width 5 mRy. A number of different tests, such as, for example, the effect of increasing the number of **k** points used in the summations over the BZ, were made in order to ensure convergence.

In a recent theoretical paper [16] it was found that under high pressure all the tetravalent $3d$, $4d$, and $5d$ transition elements should exhibit the crystal structure sequence hcp $\rightarrow$ ω $\rightarrow$ bcc, where ω stands for the hexagonal AlB_2 crystal structure. In this work it was also demonstrated that this structure sequence is driven by an increasing d occupation. For Zr and Hf the above mentioned structure sequence has also been observed experimentally [12]. Therefore we have chosen to study and compare these three structures for Th together with the fcc phase, first by using only s, p, and d orbitals in the basis set and second by including f orbitals as well. With the restricted s,p,d basis we treat Th on the same footing as the $3d$-$5d$ IVA elements, and thereby we can actually simulate the situation where Th would be equivalent to a normal d transition metal. The results, as a function of volume, are summarized in Fig. 1. As can be seen, already at the observed equilibrium volume ($V/V_{eq} = 1$) the bcc structure is considerably lower in energy than the other structures.

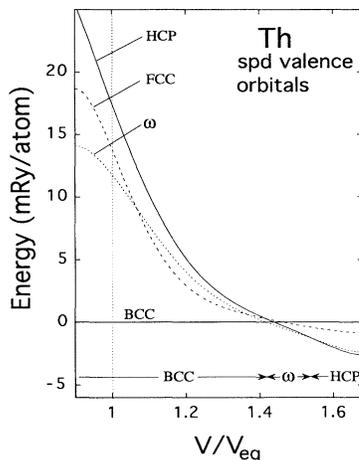FIG. 1. Energy difference between the bcc, fcc, hcp, and ω crystal structures for Th as a function of volume (V/V_{eq}, with V_{eq} the equilibrium volume) for the case when Th is treated as a tetravalent d transition metal (see text). The bcc structure is used as the zero energy reference level, and the dotted vertical line denotes the equilibrium volume.

Since the present calculations use no shape approximation for the potential, they give accurate energy differences between the different structures, and the results in Fig. 1 can be looked upon as a faithful representation of the properties of Th in the case it would be a genuine d metal. Thus we conclude that if Th had been a normal tetravalent d transition metal, its crystal structure would have been bcc and remained so even for compressed volumes (compare Fig. 1). Interestingly, however, upon expansion we find that for a volume 40% larger than the equilibrium volume the ω phase is the favored structure and at slightly larger volumes the hcp phase is more stable than the ω phase. This is very similar to the behavior obtained for Ti, Zr, and Hf, with the same type of volume dependence as regards the energy of the ω and hcp phases relative to the bcc crystal structure. Thus when thorium is considered as a tetravalent d transition metal it displays, as a function of volume, the same crystal structure sequence behavior as Ti, Zr, and Hf, demonstrating that it is clearly a group IVA element [17]. However, the most spectacular circumstance is the fact that the fcc structure is not found to be stable anywhere over the whole volume range shown in Fig. 1. *Therefore we have to conclude that Th with its observed fcc structure is not a standard tetravalent d transition metal. It does not belong to the group IVA elements in a simple manner.*

In order to investigate in more detail this surprising conclusion it is useful to consider the occupation of the $6d$ orbital. Within the full potential method the d occupation number is, however, less well defined. Therefore, in order to facilitate an analysis of the results, we made parallel calculations within the atomic sphere approximation (ASA) [18] to obtain a consistent set of d occupation numbers as a function of volume. Thereby we found that at the observed equilibrium volume Th has the highest and Ti the lowest d occupation. This explains the stability of the bcc phase in Th around the equilibrium volume where the d occupation is high, while, for example, for Ti a rather substantial compression is needed before the d occupation becomes sufficiently increased to support the bcc structure. This $s \rightarrow d$ transfer under compression is typical for transition metals, and therefore an expansion of Th metal is actually needed before the standard group IVA hcp structure is obtained. This structural behavior is in accordance with what one would expect from canonical band theory [19] for crystal structure stabilities, a circumstance which again underlines the anomaly of the observed fcc structure in Th.

In Fig. 2 we show the results from a full calculation of the energy difference between the hcp, fcc, ω, and the bcc phases for thorium as a function of volume. In these calculations, we have used s, p, d, and f orbitals in the basis set, which is indeed the appropriate choice for Th. Clearly, we now find that the fcc structure is lowest in energy, in full agreement with experiment. As shown in Fig. 2, this holds for a very large range of
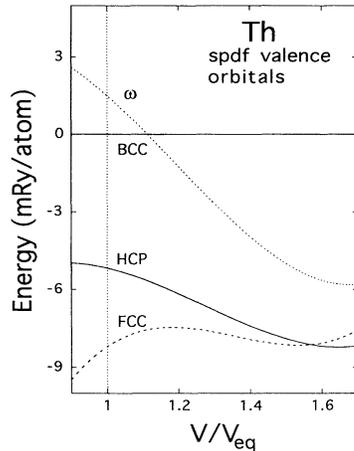
FIG. 2. Energy difference between the bcc, fcc, hcp, and ω crystal structures for Th as a function of volume (V/V_{eq}, with V_{eq} the equilibrium volume) for the case when Th is treated as an actinide metal, i.e., when the $5f$ states are included in the basis set. The bcc structure is used as the zero energy reference level, and the dotted vertical line denotes the equilibrium volume.

volumes. The immediate conclusion is naturally that it is the inclusion of the $5f$ states that gives the correct crystal structure results. From this we are then led to conclude that the fcc structure in Th originates from the itinerant nature of the $5f$ electrons and that without the f electrons erroneous results are obtained. Thus not only are the distorted crystal structures of the elements Pa-Pu caused by the $5f$ electrons, but also the crystal structure of Th can only be explained by occupied itinerant $5f$ states. Therefore the innocent-looking high symmetry fcc crystal structure is in reality a beautiful demonstration that Th is the first element in the unique $5f$ transition series of elements, where the occupation of $5f$ band states significantly influences the ground state properties. In this respect there is, therefore, no basic difference between Th and the neighboring actinide elements with higher atomic number and the distinction that has previously been made between Th and the somewhat heavier actinides is unjustified. Thus the common use of Th as an actinide reference material for tetravalent metallic behavior has to be abandoned.

By restricting the crystal structure comparison to the bcc, fcc, and hcp structures, which all have similar electrostatic (Madelung) energies, one can apply the canonical band theory for the d states and thereby obtain a simple picture for the understanding of the crystallographic behavior throughout the $4d$ and $5d$ series [19]. Here we apply this scheme to an analysis of the thorium results from the restricted s,p,d-basis calculations at the observed equilibrium volume (Fig. 1). From calculations using the ASA we obtain a d occupation of about $n_d = 2.9$. Since it is known that the d states dominate the structural energy differences, we notice that this d occupation number

corresponds to a region where the bcc structure is lower in energy than the hcp and fcc structures. Inserting the calculated band mass into the canonical energy difference we find that the bcc structure is favored by about 8 and 14 mRy relative to the fcc and hcp structures, respectively. The full calculations give 14 mRy (fcc) and 17 mRy (hcp) for the same energy differences showing that the canonical picture is rather adequate. Turning to the results of the s,p,d,f-basis calculations we again consider the canonical picture and assume that the d and f electron contributions to the structural energy difference can be treated separately. The calculated ASA occupation numbers are $n_{5f} = 0.4$ and $n_{6d} = 2.5$. In comparison with the spd calculation, the $6d$ occupation has been lowered by 0.4 electron, which all have been transferred into the $5f$ band. In the canonical picture a d occupation of 2.5 gives almost no energy difference between the hcp, fcc, and bcc structures [19]. Therefore we are left with the f contribution. From canonical f bands [20] one finds that an occupation of 0.4 electron favors the fcc structure. Inserting the calculated f band mass one finds that the fcc and hcp structures are favored by 12 and 8 mRy, respectively, relative to the bcc structure. This agrees relatively well with the results of the full calculation, which are 8 and 5 mRy, respectively. Thus already the canonical picture clearly shows that it is the presence of the $5f$ electrons which determines that Th is an fcc metal. Therefore the occupation of f states is not just a minor detail concerning the electronic states of Th, but instead it is of crucial importance for the crystal structure of thorium.

The derived understanding of the thorium metal also gives rise to new questions. At high temperatures just before melting thorium transforms to the bcc structure. The same behavior is also observed for Ti, Zr, and Hf, and one could argue that this is evidence that Th at high temperature is becoming a group IVA element. However, a high temperature bcc phase is also observed for all the elements Pa-Pu [6], again just before melting. Therefore the appearance of a high temperature bcc phase in thorium cannot be used as an unambiguous argument against f electron bonding. One could also argue that because the melting temperature of thorium metal is comparable to that of Ti, Zr, and Hf thorium appears to behave just like a normal tetravalent d transition metal. For the heavier actinides next to thorium the melting temperature is strongly reduced relative to the expected values for a transition series, a fact that can be related to the increasing complexity of the crystal structures when proceeding from Th to Pu. Since in thorium the f participation in the bonding gives rise to a high symmetry structure, this suggests that in this case f bonding should not act as a suppression of the melting temperature. This would explain that the melting temperature for thorium appears normal relative to the group IVA elements.

To conclude, we have shown that in addition to the low symmetry structures of the actinide elements Pa-Pu

also the fcc crystal structure in Th is anomalous. In fact, thorium is the first element in the actinide series showing properties which crucially depend on the presence of itinerant 5f electrons.

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