

Theoretical study of the pressure-concentration diagram for the Ce-Th alloy system

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The high pressure and low temperature phase diagram of CeTh_3 , CeTh , and CeTh_3 compounds has been investigated and compared to experimental data for three $\text{Ce}_x\text{Th}_{1-x}$ alloys. At higher pressures, the theoretical calculations compare very well with experimental observations whereas at lower pressures, the agreement is less accurate. The general pressure behavior of the $\text{Ce}_x\text{Th}_{1-x}$ is, however, in agreement between theory and experiment. Analysis of the theoretical model reveals that the phase stability in these alloy systems is driven by electronic structure effects and in particular an increased f -electron character with increasing pressure. Density functional theory shows that the Ce-Th alloy systems will undergo crystallographic phase transitions from fcc to bct at elevated pressures. The transition pressures are shown, in agreement with experiment, to increase with Th content in the Ce-Th alloy in a nonlinear fashion. At very high pressures, above 200 GPa, the $\text{Ce}_x\text{Th}_{1-x}$ alloys display a unified picture with a saturated c/a axial ratio close to 1.65. Both these features are shown to be related to the increased f -band character with pressure and the preference for distorted structures which comes with increasing f -electron dominance. Specifically, our first-principle calculations show that the f -band population saturates to about 1.5 f electron at high pressures over 200 GPa explaining the saturation of the c/a axial ratio for the Ce-Th alloys. Simple model calculations, utilizing unhybridized and pure canonical f bands in conjunction with Madelung energy corrections, show that an f -electron metal with about 1.5 f electrons, stabilizes in the bct structure with an axial c/a ratio close to 1.65, in accordance with the first-principle calculations and available experimental data. [S0163-1829(99)05837-3]

I. INTRODUCTION

The lanthanide and actinide metals have been the focus of intense research, experimental and theoretical, during the past decades.^{1,2} Their electronic structure is very pressure dependent; lowering of the f -band relative to other bands favor f -electron character and as a consequence crystallographic phase transitions may occur. As the narrow f bands become populated in the Ce-Th systems their fcc structure becomes increasingly unstable compared to lower symmetry structures and eventually they undergo phase transitions. The reason has been explored in detail and can be compared to a Jahn-Teller or Peierls distortion where a symmetry breaking mechanism takes place to lower the energy of the system.³ This mechanism is intimately linked to the occurrence of narrow (f) bands in the vicinity of the Fermi level and is responsible for the complex (distorted and with low symmetry) crystal structures found in the light actinide metal series as well.⁴ On the other hand, at higher pressures all bands broaden and this will decrease the importance of the Peierls distortion. Electrostatic effects and overlap repulsion dominates at higher pressures and they favor more symmetric structures over the complex ones. This interplay between competing effects and their pressure dependence results in rich and interesting phase diagrams of f -electron systems and in this paper we have chosen to focus upon a subset of those, the Ce-Th alloys.

Before discussing the Ce-Th alloys in Sec. III we would like to pay some attention to their pure metal components. Cerium has a very interesting and somewhat controversial

phase diagram with two fcc phases, the γ and the α phase. The latter is considerably denser than the former and there is a volume collapse (16%) associated with the phase transition between these two phases which occur at ~ 1 GPa at room temperature. The nature of this transition is the subject of some controversy although there is evidence that one could describe this in terms of an f delocalization (Mott) transition.⁵ At somewhat higher pressures the controversy continues with another phase transition at about 5 GPa. Experimentally, two structures have been suggested for this phase, the orthorhombic (α') (Refs. 6,7) and the body centered monoclinic (α'') phase.⁸ Recent experimental studies⁹ of this part of the phase diagram of Ce indicates a phase mixture of α' and α'' which is consistent with previous measurements.⁷ McMahon and Nelmes¹⁰ also suggested that the confusion regarding the α' and α'' phases have arisen from sample production and preparation. Theoretical calculations show that these two structures are indeed close in energy, but generally favor the α'' phase.^{4,11} This uncertain region in the phase diagram of Ce precedes a region in which the bct (body centered tetragonal) phase is stable.^{8,12} Both theory¹³ and experiment⁸ show this although the exact transition pressure is in somewhat disagreement between the two. At higher pressures theory and experiment agree very nicely and the calculated c/a ratio for bct Ce is more or less identical to the measured one at the same pressure.¹³

Thorium, similar to Ce, is fcc at ambient conditions. The phase diagram of Th, however, is much simpler than that of cerium with no intermediate phases stable below the fcc to bct phase transition. Again, at higher pressures theory and

experiment are in great agreement concerning the c/a axial ratios.^{13,14} It was found that the c/a axial ratio increased with pressure in these studies but saturated close to $c/a = 1.65$ for both Ce and Th. This is true also for their alloys and the explanation for this is investigated below. Both for Ce and Th the fcc \rightarrow bct transition pressure is not in exact agreement between theory and experiment but the fact that it is higher for Th (theory: 45 GPa, expt: 60 GPa) than for Ce (theory: 10 GPa, expt: 12 GPa) is clear. Thorium requires higher pressure than Ce to stabilize its bct phase and this becomes important for the transition pressures of the Ce-Th alloy; a larger Th content in the alloy will push the transition to higher pressures and we will discuss this in detail in Sec. III.

The paper is organized as follows: In Sec. II we deal with details of our calculations and in Sec. III show and discuss our results for the Ce_3Th , CeTh , and CeTh_3 compounds and compare those with experimental data for $\text{Ce}_{76}\text{Th}_{24}$, $\text{Ce}_{43}\text{Th}_{57}$, and $\text{Ce}_{20}\text{Th}_{80}$ alloys. We conclude in Sec. IV, the final section.

II. COMPUTATIONAL APPROACH

Most of our computational details are the same as for our previous work for Ce and Th (Ref. 13) but we will repeat the more important details. The calculations are performed in the frame work of density functional theory with a local approximation to the electron exchange/correlation effects. In practice we are solving the Kohn–Sham equations self-consistently for a periodic system. For the exchange/correlation potential we have employed a modern approximation that introduce corrections from the gradient of the electron density, the so-called generalized gradient approximation.¹⁵ Our implementation is without geometrical approximations for the charge density and potential. We accomplish this by dividing space into nonoverlapping muffin-tin spheres (60% of the total volume) and an interstitial region (40%). Wave functions inside the spheres are expanded in so-called muffin-tin orbitals with tails reaching into the interstitial regions. They have kinetic energy specified by an energy parameter (κ^2). Depending on sign of this parameter the basis functions in the interstitial region is either Neumann or Hankel functions. Actually, two energy parameters, $\kappa^{2'}$ s, are used for each muffin-tin basis function expanding the whole basis set with a factor of 2 (double basis set). For f -electron metals it is standard to also include semicore states (s and p) to the valence states (s , p , d , and f). Spin-orbit coupling, in addition to the scalar relativistic terms, was included in the calculations as a variational term in the Hamiltonian.

The alloys were approximated by ordered compounds, for Ce_3Th and CeTh_3 we used the Cu_3Au structure (4 atoms/cell) and for the CeTh we used the CsCl (2 atoms/cell). The symmetry was lowered to allow the c/a ratio to be optimized as a function of volume. The Brillouin zone sampling was accomplished by the special k -point method¹⁶ and each eigenvalue was convoluted with a Gaussian broadening with a 10 mRy width. The number of k points in the irreducible Brillouin zone was 189 and 75 for the CsCl and Cu_3Au structure, respectively.

The total energy was calculated for 13 volumes for each compound. The c/a axial ratio was optimized on this volume

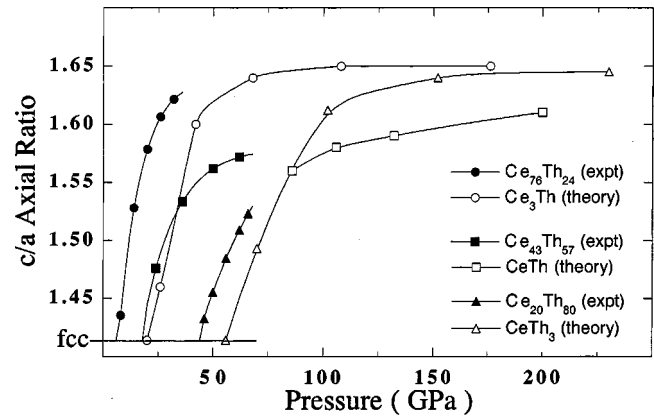


FIG. 1. Pressure dependence of the c/a axial ratio in the bct structure for Ce-Th alloys (experiment) and ordered Ce-Th compounds (theory). Filled symbols denote experimental data and open symbols theoretical data.

grid by calculating the so-called Bain transformation path (total energy versus c/a axial ratio of a bct system).¹⁷ For some volumes up to 15 different c/a ratios were considered but for most volumes 7–8 c/a values were enough to accurately determine the optimized (lowest energy) axial ratio.

III. RESULTS AND DISCUSSION

Our main results are summarized in Fig. 1. Here we compare the calculated c/a ratio for three tetragonal Ce-Th alloy-systems with experimental data.^{18,19} Full line with filled circles denote measured c/a ratios and the open circles denote theoretical data for the ordered compounds. Let us first consider the experimental data. The Ce-rich alloy, $\text{Ce}_{76}\text{Th}_{24}$, shows the lowest fcc \rightarrow bct transition pressure, 7.4 GPa. This is rather close to the published data⁸ for the fcc \rightarrow bct transition in metallic Ce (12 GPa). At 16.9 GPa the alloy with almost equal amount of Ce and Th ($\text{Ce}_{0.43}\text{Th}_{0.57}$) undergoes the same transition and at considerably higher 42.9 GPa the $\text{Ce}_{0.20}\text{Th}_{0.80}$ transforms from fcc to bct.¹⁹ It is evident that alloys with higher Th content are more stable in the fcc structure. However, at the highest experimental pressure,¹⁹ 70 GPa, all alloys are bct. The same behavior is found theoretically for two of the ordered compounds; the transition pressures are 20 GPa and 56 GPa for Ce_3Th and CeTh_3 , respectively. Both these pressures compare fairly well with their corresponding experimental pressures for the alloys and the discrepancy is similar to what was found for metallic Ce and Th.¹³ The third ordered compound, CeTh , shows a different behavior with a $c/a = 1.55$ at about 80 GPa. Before studying this interesting fact in more detail, let us observe another general behavior in Fig. 1. At sufficiently high pressure, the theoretical (and extrapolated experimental) data suggests that all compounds (and alloys) will become bct with a c/a ratio close to about 1.65. This behavior was also discovered in theoretical calculations for elemental Ce and Th.¹³ The fact that the c/a ratio is increasing with pressure but saturates to about 1.65 at Mbar pressures is related to the driving force behind the stabilization of the bct structure, namely, the occurrence of f -electron character in the electronic structure. It was shown by Eriksson *et al.*²⁰ that increasing f -band occupation in Th drove the fcc \rightarrow bct transi-

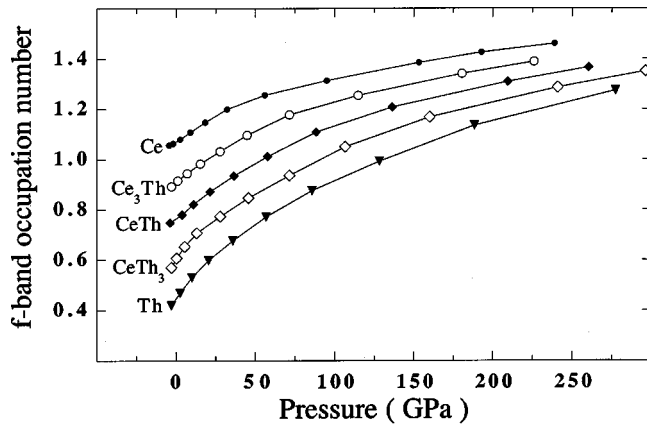


FIG. 2. Calculated (FP-LMTO) f -band occupation number of Ce, Th, and Ce-Th compounds as a function of pressure.

tion in Th. This is true also for Ce and the present Ce-Th systems. In Fig. 2 we plot the f -band occupation number for Ce, Ce_3Th , CeTh, CeTh_3 , and Th as a function of pressure. Notice that the plots begin to converge at a pressure of about 200 GPa (2 Mbar). The f -band population is close to the same for all these compounds at higher pressures and consequently their structural behavior becomes very similar. Notice also that the occupation of the f band decreases with Th content at all pressures. This explains why a higher pressure (resulting in a higher f -band population) is needed for the Th-rich compounds to reach the bct transition. It should be noted here that these occupation numbers are obtained from projections of electronic states inside the muffin-tins spheres and not from the interstitial regions in our calculations. Therefore these numbers are approximations but are nevertheless accurate for studying the trends, especially when comparing calculations done with the same volume of the muffin-tin spheres.

As mentioned in the previous section, our calculations for the ordered CeTh compound (CsCl structure) are in disagreement with measurements for the $\text{Ce}_{0.43}\text{Th}_{0.57}$ alloy, although at higher pressures, close to 1 Mbar (100 GPa), extrapolated experimental data seem to lie close to the theoretical results, see Fig. 1. In calculating the full Bain path (total energy versus c/a axial ratio for a bct system) it was discovered that there were two minima in this transformation path. One was for a c/a above fcc ($c/a = \sqrt{2}$) and one below. At about 85 GPa these two minima are rather close in energy, see Fig. 3. This behavior with two, almost degenerate, local minima in the Bain transformation path was not found in the other ordered compounds in this study and was not found in the study of metallic Ce and Th either.¹³ As a consequence, the pressure dependence of the c/a axial ratio for CeTh is very interesting and plotted in Fig. 4. At a rather low pressure of about 10 GPa this compound undergoes a phase transition from fcc to bct with a c/a ratio below 1.414 ($\sqrt{2}$). The c/a ratio is slowly decreasing with pressure down to about 1.32 at about 85 GPa. Then at higher pressures the c/a ratio jumps up to about 1.55 and continues to slowly increase with pressure. At pressures above 1 Mbar (100 GPa) the CeTh compound behaves similar to the other ordered compounds in this study. Below about 85 GPa this CeTh compound is not in agreement with experimental data for $\text{Ce}_{0.43}\text{Th}_{0.57}$ al-

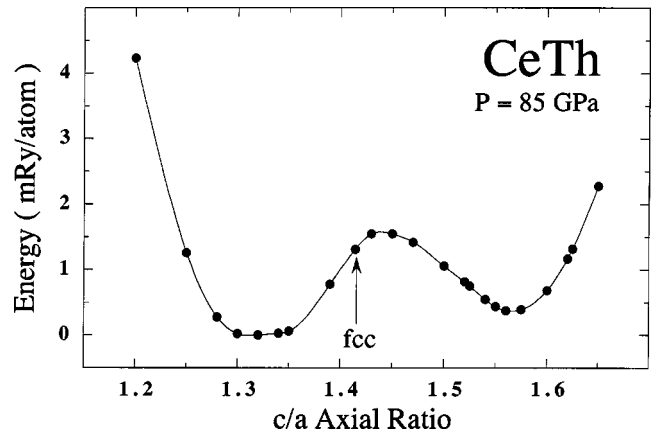


FIG. 3. The Bain transformation path for CeTh compound at about 85 GPa. At $c/a = \sqrt{2}$ the structure corresponds to the fcc structure.

loy. This may not be surprising considering that the approximation to model the alloy with an ordered compound is worst in this particular case. It may be necessary to use more sophisticated alloy approximations such as CPA (coherent potential approximation) to accurately describe the low pressure phase diagram of $\text{Ce}_{0.43}\text{Th}_{0.57}$. Sometimes a much simpler approach has been successfully applied for alloys, namely, the VCA (virtual crystal approximation), in which the atoms in the true alloy are replaced by “average” atoms, whose atomic number is the concentration weighted atomic number for the alloy. In the spirit of the VCA, calculations were also performed for a hypothetical ThPa alloy at 85 GPa. This alloy was mixed such that the f -band occupation was the same ($\sim 1.1 f$) as for the ordered CeTh compound at this pressure. The appropriate concentration was 65% Th and 35% Pa to accomplish this. Then, for this hypothetical system, we calculated the Bain path and the results are compared to the CeTh ordered system in Fig. 5. Notice that the two paths show similarities in that they both have two minima, one below $c/a = 1.414$ (fcc) and one above. However, the hypothetical ThPa alloy is stable at the larger c/a value and the CeTh at the lower c/a value. In this regard, the ThPa VCA alloy is similar to the other Ce-Th systems. The difference between our VCA ThPa and our ordered CeTh calculations can not be explained by the f -band population

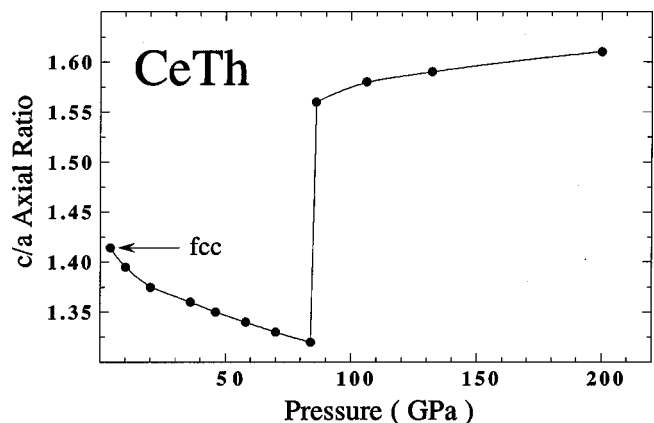


FIG. 4. Pressure dependence of the c/a axial ratio for the CeTh compound.

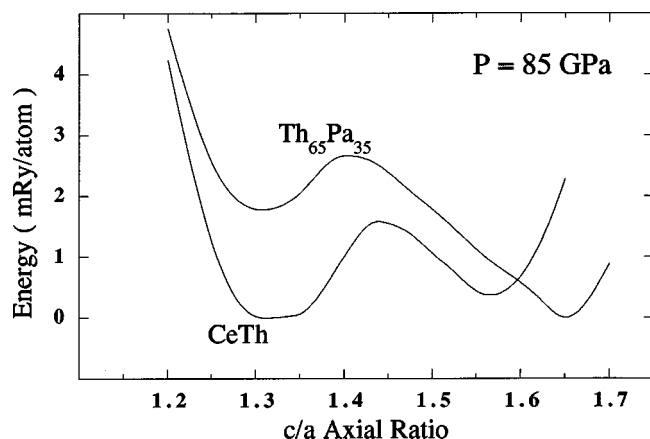


FIG. 5. Bain transformation paths for CeTh order compound and ThPa alloy (VCA see text) at about 85 GPa.

alone because it was the same for both calculations. Instead one has to conclude that other effects, related to the composition of the alloy, make the difference. It seems reasonable that also the difference between our ordered CeTh compound and the $\text{Ce}_{0.43}\text{Th}_{0.57}$ alloy is related to our approximation of the alloy with an ordered compound.

IV. CONCLUSION

We have performed first-principles calculations for ordered Ce-Th compounds in order to explain the low temperature phase diagram of Ce-Th alloys. There is good agreement between theory and experiment at elevated pressure whereas at lower pressures there are some discrepancies, especially when comparing ordered CeTh (theory) with the $\text{Ce}_{0.43}\text{Th}_{0.57}$ alloy (experiment). Two trends are identified when studying the high pressure behavior of Ce, Th, and their alloys. First, the amount of Th in the alloy is very important for the transition pressure (fcc \rightarrow bct), and a higher Th content pushes the transition to higher pressures. Secondly, all alloys and their components behave similarly at high pressures, and they attain the bct structure with a c/a close to 1.65. These two general features can be understood from filling of the f band in the Ce-Th alloy systems. First, the f band is responsible for the tetragonal distortion of the crystal structure in these alloys. The f -electron character is shown to increase with pressure and eventually this will drive the fcc \rightarrow bct transition. Ce and the Ce-rich alloys have more f states occupied at lower pressures than Th and consequently the transition will occur earlier (lower pressures). We also show that the f occupation increases faster for Th and Th-rich compounds as a function of pressure than for Ce and the Ce rich compounds. At Mbar pressures the f -band population saturates close to 1.5 f electrons for all systems and at these pressures all alloys are stabilized in the bct structure with nearly the same c/a ratio (close to 1.65). This demonstrates an intimate connection between f -band occupation and crystal structure. This connection is quite often found, both for f -bonded and d -bonded materials, and the explanation for this is that the shape of the f -band is quite similar for 4 f and 5 f states, apart from the fact that the 4 f bands are narrower. Hence, if the occupation of the f band is the same for a 4 f

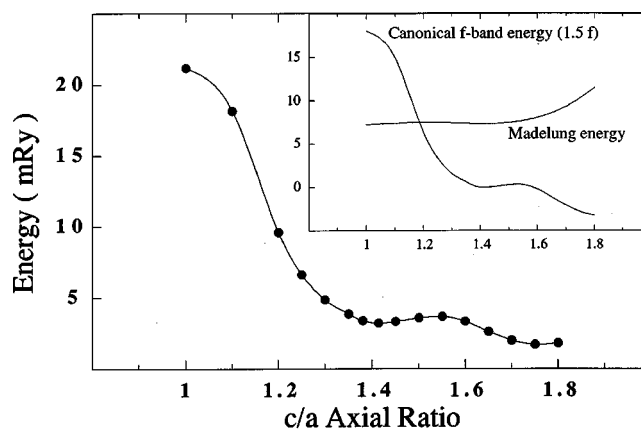


FIG. 6. Bain transformation path estimated from a simple canonical band model using 1.5 f electron band-filling. The inset shows contributions from the canonical f -band energy including the Born-Mayer overlap repulsion together with an estimate of the electrostatic Madelung contribution.

and 5 f bonded material, it is likely that their structural stability is very similar as well.

At lower pressures some differences were found in comparing the theoretical with experimental data, most notably for the CeTh compound. Some discrepancy at lower pressures was certainly expected since this was the case also for the pure Ce and Th metals,¹³ but for the equal amount CeTh alloy the discrepancy was surprisingly large. We argue that for this alloy our model with the ordered CeTh compound is not a good approximation at lower pressures and as a result the calculated c/a ratio is much lower than for the corresponding alloy. Calculations using VCA and a hypothetical ThPa alloy supports this suggestion.

Our main conclusion is that the structural behavior of the studied Ce-Th alloys is determined by the occurrence of a partially filled f band in these systems. To illuminate this conclusion further we can isolate the f -band contribution to the bct stability in a simple model. Using canonical band theory combined with Pettifor's structure theorem and an analytical Madelung correction we can estimate the energy of the Bains transformation path for a hypothetical metal with arbitrary f -band occupation. This simple model was described in detail in a paper by Söderlind *et al.*²¹ It suffices to say that the model includes bonding energy from occupying unhybridized (element independent) canonical f bands, Born-Mayer overlap repulsion, and electrostatic Madelung contribution. In Fig. 6 we show the results from these model calculations. The results depend upon the chosen f -band occupation and in this example we used 1.5 f electrons which corresponds rather closely to the high pressure state of the studied Ce-Th alloy systems. Note that the path has two minima with the global minimum being located at about $c/a = 1.75$. The overall shape of the Bain path is rather similar to that of the ThPa alloy in Fig. 5, although here the minimum in energy occurs at a somewhat lower (1.65) c/a ratio. Even in absolute numbers they compare well; the energy difference between the minima in the Bain path and the bcc structure ($c/a = 1$) is about 20 mRy for the simple canonical band model which is in close comparison to the 18 mRy for the same difference for ThPa alloy. The success of

this simple model, whose electronic structure consists of pure and unhybridized f bands, suggests that the structural properties of the Ce-Th alloy systems are dominated by this contribution.

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- ¹See, for instance, articles in J.J. Katz, G.T. Seaborg, and L.R. Morss, *The Chemistry of the Actinide Elements* (Chapman and Hall, New York, 1986), Vol 1-2.
- ²See articles, in *Handbook on the Physics and Chemistry of the Actinides*, edited by A.J. Freeman and G.H. Lander (North-Holland, Amsterdam, 1984).
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