Theoretical Studies of the High Pressure Phases in Cerium

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We present full potential linear-muffin-tin-orbital calculations based on the local-density approximation, which reproduce the $T=0$ phase diagram of cerium (Ce), including the volumes and transition pressures for both the $\alpha\rightarrow\alpha'$, and the $\alpha'\rightarrow$ bct transitions. The $\alpha\rightarrow\alpha'$ transition is largely determined by a balance of two competing terms: a Madelung term and a $4f$ one-electron term. The $\alpha'\rightarrow$ bct transition is driven by both $4f$ and $5d$ partial-wave contributions. This is the first successful, *ab initio* calculation of a crystallographic ($T=0$) phase diagram of an f-electron system.

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Most of the elements in the periodic table can by now be fairly well characterized in terms of their rudimentary electronic-structure-related properties. For example, transition metals are known to have itinerant and bonding d electrons, whereas the $4f$ electrons in most of the rare-earth elements are known to be localized, polarized, and nonbonding. The present investigation of crystal structure stabilities follows the work of Duthie and Pettifor [1] and more important the self-consistent *ab initio* calculations of Skriver [2], who showed that by accurate and systematic calculations one may correctly predict the crystal structures of metals. Their calculations showed that only by assuming itinerant d electrons can the correct crystal structures of the transition and rare-earth elements (excluding Ce) be obtained, and that the d-electron contribution governs the different close-packed crystal structures [1,2]. Thus the magnetic, superconducting, transport, crystallographic, and bonding properties can be fairly well classified and understood for most transition metals and rare-earth elements. The elements with low symmetry structures (early actinides and Ce) where f-electron bonding is believed to play a role are less understood. The $4f$-electron behavior in Ce has often been seen as an analog to $5f$-electron behavior in the early actinides.

Cerium has a very interesting phase diagram [3]. At atmospheric pressure and low temperatures the α phase is stable (fcc structure); this allotrope is an enhanced Pauli paramagnet. With increasing temperature α-Ce transforms into the β phase [double hcp (dhcp)] and then to the γ phase (fcc). These two phases show magnetic ordering. At room temperature and a pressure of 7 kbar the trivalent low-density γ phase collapses into the much denser, but isostructural, α phase, with a decrease in volume of about 14%. A further increase in pressure transforms α-Ce to (orthorhombic) α'-Ce at ~ 50 kbar [3,4] with a very small volume collapse. This phase has been shown to exhibit superconductivity below 1.9 K [5] [The possibility of a related crystal structure of Ce at these pressures has been pointed out [6].] Further increase in pressure (~ 120 kbar) drives the α' phase to a body-centered-tetragonal (bct) structure, which is stable up to 500 kbar [3-6]. The $\alpha\rightarrow\alpha'$ (α-U structure) transition is consistent with delocalized f-electron behavior which yields lower symmetry structures, whereas the $\alpha'\rightarrow$ bct transition is not consistent with this pattern. This unusual pattern seen in Ce but not in the actinides under pressure is part of the study presented in this Letter, along with the theoretical results for the full phase diagram (at $T=0$) and an analysis of the $4f$-electron behavior near the $\gamma\rightarrow\alpha$ transition.

Although most theoretical and experimental efforts on Ce have attempted to explain the isostructural $\gamma\rightarrow\alpha$ transition [7-15], we will only briefly comment on this transition. The volume collapse in this transition is similar to that in the late actinides under pressure, but maintaining high symmetry (fcc) indicates that the transition is different because the actinides have a reduction in symmetry along with the volume decrease. There have been two calculations of this transition; one based upon quenching the spin moment (Kondo volume collapse model [16]) and the other based upon quenching the total moment (spin and orbital polarization [17]). Both of these models are consistent with most of the experimental data indicating no change in the f-electron count (~ 1) upon making the transition. The Kondo volume collapse model, which has its energy scale and temperature dependence set by the experimental Kondo temperature T_K of the two phases, demonstrates that the spin quenching mechanism is consistent with other temperature-dependent data. It includes no change in the orbital moment through the transition. The orbital polarization model includes orbital and spin quenching through the transition but includes no temperature dependence. Probably both orbital quenching and temperature dependence are needed for the correct model of the transition. The contribution that the present calculation can add to the understanding of the transition is an evaluation of the f-f hopping and f-spd hybridization in the α phase near the transition density and this we do.

We stress here that calculations of crystal structure stabilities are very delicate and that no successful *ab initio* calculations of crystallographic phase diagrams of an f-electron system have been published. Skriver [2] very accurately accounted for the crystal structures of the transition metals, but his spherically averaged frozen potential approach did not quite reproduce the experimental data for Ce [2]. In particular, for the open α' structure the energy was 4.5 mRy too high and, consequently, the stability of the bct phase was overestimated. Skriver did indicate the importance of the contribution of the $4f$ electrons. However, with great physical insight, as we shall see below, Skriver did argue on the basis of his results that α-Ce is a $4f$ metal [2]. The present work relies on a much more accurate computational technique and, therefore, we obtain the correct results for the high-pressure phases.

For the computational accuracy required we used a new full potential linear-muffin-tin-orbital (LMTO) technique in the calculations reported here. The details of the method will be presented in a longer paper. In brief, the calculations were all electron, fully relativistic, and employed no shape approximation to the charge density or potential [18]. The base geometry was a muffin-tin geometry with a true interstitial; the basis functions, charge density, and potential were expanded in spherical harmonic series within the muffin tins and in Fourier series in the interstitial. The volume in the muffin-tin spheres was kept the same in all structures and was a fixed fraction (approximately 0.50) of the total volume. The optimized basis set was comprised of augmented linear-muffin-tin orbitals [19] with accurate kinetic energy in the interstitial; three tail functions were used for each basis. These calculations contained $5s$, $5p$, $6s$, $6p$, $5d$, and $4f$ orbitals in a single energy panel. The difference in energy between the different structures was converged to approximately 0.1 mRy. The method has previously been used to investigate the electronic structures of cerium, actinide, and transition-metal systems [20,21].

α'-Ce may be described as a one-face-centered orthorhombic (α-U) lattice with two atoms per unit cell at positions (0,0,0) and $(0,0.5,1-2y)$ in units of the a, b, and c lattice translations. The lattice constants are known, but experimentally the value of $2y$ is not known. We performed a set of calculations to find the minimum in the total energy as a function of $2y$, using experimental values for the lattice constants, at a volume close to the experimental transition volume (22.3 Å^3 per atom). The minimum energy was found at $2y=0.225$ (Skrivers calculated value was ~ 0.21 [2]); this value, together with the experimental ratios of the lattice constants, was then used at all volumes in calculating the equation of state of the α' phase. In the calculations of the bct phase we used the experimental c/a ratio.

The main result of this work—the total energy as a function of volume for the α, α', and bct phases of Ce—is displayed in Fig. 1. The important features of Fig. 1 have been collected in Table I. At zero pressure, the structure of Ce is (correctly) found to be fcc with an equilibrium volume of 28.1 Å^3 (experimental value $\sim$28–29 Å^3 [3–6]). The calculated bulk modulus at the experimental volume is 370 kbar, compared to the experimental room-temperature value of $\sim$240–290 kbar [3–6]. We find a transition to the α' phase at a volume of 24.2 Å^3 (experimental value $\sim$24 Å^3). The calculated volume collapse is, in agreement with experiment, quite small, $\sim$1 Å^3, and the calculated transition pressure (slope of the common tangent) is 70 kbar (experimental value at $T=0$, $\sim$65 kbar [3–6]). From Fig. 1 it is seen that at even smaller volumes ($\sim$20 Å^3) the α' phase transforms to the bct phase. The calculated pressure for this transition is 150 kbar and is also in good agreement with experimental data, 120 kbar at room temperature [3–6].

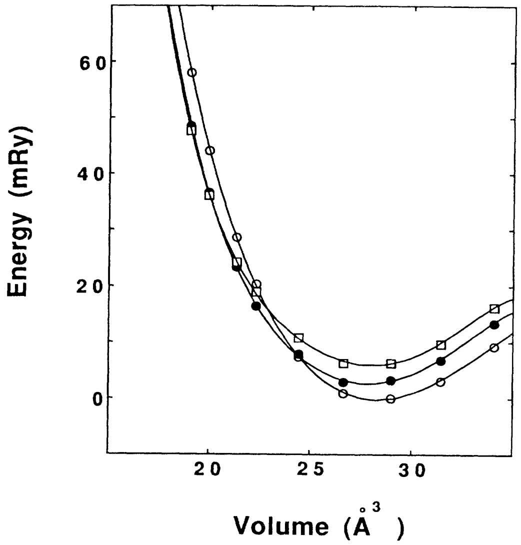

FIG. 1. Calculated total energy of α (fcc, open circles), α' (orthorhombic, solid circles), and bct (open squares) Ce. The energies refer to the minimum energy of the fcc phase. The calculated pressure for the phase transitions is obtained from the slope of the common tangent of the energy curves.

The present results show that the $4f$ electrons actively contribute to determining the high pressure phases of Ce, as do the d electrons in the transition metals [1,2]. To further test the importance of the $4f$ electrons, we recalculated the total energy of Ce in the α, α', and bct structures at volumes of 21.3 and 22.3 Å^3 (for these volumes it is known experimentally that the α' phase is stable), but

TABLE I. Calculated equilibrium volume and bulk modulus for α-Ce, as well as volumes, volume changes, and pressures for the $\alpha \to \alpha'$ and $\alpha' \to$ bct transitions.

V_{eq} (Å^3)	28.1
B_{eq} (kbar)	370
$V(\alpha \to \alpha')$ (Å^3)	24.2
$\Delta V(\alpha \to \alpha')$ (Å^3)	1
$P(\alpha \to \alpha')$ (kbar)	70
$V(\alpha' \to \text{bct})$ (Å^3)	20.0
$\Delta V(\alpha' \to \text{bct})$ (Å^3)	0
$P(\alpha' \to \text{bct})$ (kbar)	150

with the 4*f* band being forced to be empty (using *s*, *p*, and *d* partial waves only, but still having four valence electrons). For both volumes we find the bct phase to be stable, with the fcc phase ~10 mRy higher in energy and the α' phase ~20 mRy higher in energy. This shows that, at volumes where it is known from experiment that the orthorhombic structure is stable, *treating Ce as a normal tetravalent element is incorrect, and that the 4f electrons participate in the bonding and the formation of the crystal structure.* This is consistent with the fact that some unique features in the Ce phase diagram, e.g., the $\alpha \rightarrow \alpha'$ transition, are not seen in other systems which do not have itinerant *f* electrons, e.g., Y or Zr.

The above results show the importance of the 4*f* electrons for describing the ground-state properties of Ce in the α phase as well as in the high pressure phases. For completeness we have also calculated the equilibrium volume as well as the crystal structure stability of the γ phase. Since all experimental and theoretical data indicate that the γ phase is trivalent with a localized 4*f* electron [3-17], we have used this configuration in the calculations. In agreement with experiment we find the fcc structure stable (the bct phase is 6.8 mRy higher in energy and the α' phase is 7.1 mRy higher), and the calculated equilibrium volume, 36.1 Å^3, agrees well with experimental data, ~34.4 Å^3 [3-6].

To understand the change from high symmetry to low symmetry and back to high symmetry with increasing pressure we analyzed the various contributions to the energy in each phase. From this it was evident that the $\alpha \rightarrow \alpha'$ transition is correlated with a balance of two competing terms in the total energy: a Madelung term (we used the approximate expression of Esposito *et al.* [22]), and a 4*f* one-electron eigenvalue term. The latter was calculated from the first moment of the 4*f* partial density of states. The Madelung term favors the close-packed α structure, while the 4*f* term favors the open α' structure, since degeneracies in the partially occupied 4*f* bands may be broken by lowering the crystal symmetry. In Fig. 2, we show the calculated difference ($\alpha' - \alpha$) of the 4*f* eigenvalue term as well as the difference ($\alpha' - \alpha$) of the Madelung contribution to the energy, as well as their sum (the curve labeled "total") [23]. It is seen from Fig. 2 that the $\alpha \rightarrow \alpha'$ transition is driven by the increasing importance of the 4*f* eigenvalue term. We also did a similar energy analysis of the bct phase. However, as seen in Fig. 2 the interactions driving this transition are more complicated than the ones driving the $\alpha \rightarrow \alpha'$ transition. By isolating only the Madelung and 4*f* one-electron contribution to the total energy, we find both the α and α' phases to have lower energy than the bct phase, at all volumes. For the bct phase we find that the 5*d* contribution to the eigenvalue sum (not shown) drives the transition to that phase. This is consistent with our calculations using *s*, *p*, and *d* partial waves only, as well as calculations of La (which has no 4*f* electrons) that predict the bct phase to be stable at contracted volumes [2]. For cerium this effect is quite surprising and in a sense counterintuitive. We have argued above that the 4*f* electrons favor distorted crystal structures. With increasing pressure one expects the 4*f* contribution to become more important, favoring low symmetry structures (just as in the $\alpha \rightarrow \alpha'$ transition). However, the $\alpha' \rightarrow$ bct transition is associated with an *increase* in the symmetry of the crystal. This comes about since the 5*d* contribution also becomes more important with increasing pressure, and the latter transition is a very delicate balance between 4*f*, 5*d*, and Madelung contributions to the total energy.

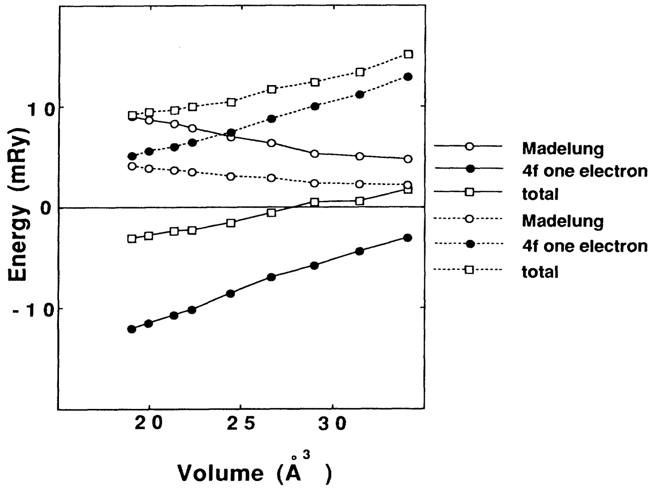

FIG. 2. Calculated difference, $\alpha' - \alpha$ (solid lines) and bct $- \alpha$ (dotted lines), of the Madelung and 4*f* one-electron contributions to the total energy, as well as their sum.

By studying the charge-density contour plots (not shown) we find that the fcc phase has a very symmetric nondirectional charge density, whereas the bct and orthorhombic phases show more pronounced covalent character in the bonds. This further supports the importance of the 4*f* contribution to the chemical bond, since the 4*f* spherical harmonics would, from simple geometrical grounds, favor distorted structures with directional bonding.

All of our calculated results indicate that the 4*f* electrons play a crucial role for determining the equation of state as well as the crystal structures of the high pressure phases of Ce. The 4*f* contribution to the cohesion in α-Ce is in principle accounted for both in the Kondo model [16] (through hybridization only) as well as in the present and previous [14-17] calculations. The latter calculations include both hybridization terms as well as direct 4*f*-4*f* hopping. In order to get an estimate of the relative importance of the direct hopping versus hybridization effects for the 4*f* band formation, we performed LMTO-atomic-sphere-approximation calculations [19] with the various contributions forced to be zero. In agreement with previous results [24], we find that the calculation without 4f hopping has a bandwidth that is ~70% of the full calculation. The corresponding equation of state underestimates the 4f bonding, and the equilibrium volume of α-Ce is ~32 Å^3, i.e., close to the γ volume. The bandwidth obtained from the calculation without hybridization is ~85% of the full bandwidth (this can also be estimated by scaling the canonical 4f bands with the appropriate potential parameters [19]). This shows that the two contributions are not additive and are about equally important.

In conclusion, we have, within an itinerant 4f picture, given a good account of the high pressure phases in Ce. This is the first time a phase diagram has been successfully calculated for an f-electron system. We have shown that the phase diagram cannot be reproduced when neglecting the 4f contribution to the cohesion, except in the trivalent γ phase where we find the ground state well described with a localized 4f electron. Our results indicate that f-f hopping is not small in the α phase near the $\alpha \rightarrow \gamma$ transition, implying that a future calculation of the transition should have this contribution included for the α phase. Therefore, excluding the γ phase, we have shown that the contribution of the 4f electrons to the bonding is essential in describing stable phases; *thus, the 4f electrons need to be treated as itinerant in the high pressure phases, including the α phase.* Furthermore, we have shown that the $\alpha \rightarrow \alpha'$ transition is driven by the counterplay between the *Madelung term and the 4f one-electron term,* whereas the counterintuitive $\alpha' \rightarrow$ bct transition is driven by *5d bonding, balanced with the 4f and Madelung contribution.*

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