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THEORETICAL STUDIES OF THE CRYSTAL STRUCTURE OF RARE EARTHS AND ACTINIDES AT ZERO TEMPERATURE

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Accurate total energy electronic structure calculations have recently been carried out over a range of volumes for selected rare earth and actinide elements in crystal structures experimentally observed in these elements. Correct zero temperature crystal structures are obtained, and calculated equilibrium properties are in reasonable agreement with experiment. The results of these calculations indicate that the interactions underlying crystal structure stability are similar in itinerant *f* electron metals and transition metals. The stable crystal structure at a particular volume is determined by a balance between one electron bandwidths and band fillings and the electrostatic energy of the crystal lattice. Broad bands favor high symmetry, close packed structures while narrow bands favor low symmetry, open structures; allowing for expansion as well as contraction, both transition and actinide elements can be stabilized in both low and high symmetry crystal structures.

INTRODUCTION

The elementary equilibrium bonding properties of the light actinides Th → Pu are similar to those found in the transition metals. The volumes, cohesive energies and bulk moduli show parabolic trends characteristic of successive filling of bonding throught anti-bonding orbitals. Despite this general similarity, there are distinctive differences between the bonding properties of actinides and transition metals. One striking difference is to be found in a comparison of the stable crystal structures. With few exceptions, the transition metals exhibit an hcp → bcc → hcp → fcc crystal structure sequence as the *d*-bands are filled accross a series. In contrast, the actinides form in progressively more open, lower symmetry crystal structures as the number of *f* electrons is increased. The sequence is Th (fcc), Pa (bct), U (base centered orthorhombic), Np (orthorhombic), and Pu (monoclinic).

Ab-initio electronic structure calculations, using density functional theory in the local density approximation, have been carried out for the majority of the transition metals, Ce, and many of the actinides.[1,2,3] These calculations have shown that, with few exceptions, the equilibrium bonding properties are obtained in the local density approximation with good accuracy.

The structural phase stability of the transition metals has also been successfully treated by these calculations.[1] The mechanism determining the equilibrium crystal structures of the transition metals is well understood. Duthie and Pettifor[1] and Skriver[1] showed that the crystal structure stability of a transition series is determined by the number of electrons in canonical *d* bands; the high symmetry structure (fcc, bcc, or hcp) that minimizes the one electron eigenvalue sum for a particular number of *d* electrons is the stable crystal structure. The crystal structure stability of the light actinides, in contrast, is not well understood. It has been speculated[5] that the reason these materials prefer open, low symmetry structures, in contrast to the close packed structures of the transition metals, may be traced to the increased directionality of *f* orbitals, compared with *d* orbitals, giving rise to covalent bonds that in turn yield the open structures.

Recently, accurate electronic structure calculations have been applied to the calculation of the structural phase stability of Ce and the light actinides Th → U. In this paper we will briefly discuss the results of these calculations, and discuss the implications of the results for understanding the crystal structures of itinerant f electron materials.

RESULTS

It has been only recently that electronic structure calculations have been successfully applied to the calculation of Ce and the light actinides in their true crystal structures. These calculations include the (zero temperature) high pressure phase diagram of Ce,[6,7] the equilibrium phase diagrams of the light actinides Th → U,[8] and the high pressure phase diagram of Th.[9] In all cases, good agreement with experiment was obtained for the stable crystal structures and structural parameters, transition pressures, and equilibrium bonding properties. In all these calculations, we find similar trends. The f band occupation increases, with a corresponding decrease in sd band occupation, continuously with decreasing volume. With decreasing volume, the f band density of states (DOS) broadens although its shape remains approximately the same. And, at a fixed volume, the crystal structure sequence fcc → bct → α-U structure is characterized by successive breaking of degeneracies in the DOS, while the bandwidth remains (approximately) constant.

We find a structural phase transition in Ce, from α (fcc) to α' (α-U structure), at a $4f$ occupation of ~ 1.1 and a pressure of ~ 70 Kbar (the α'' structure was not considered in these calculations). This transformation is clearly a result of increasing $4f$ occupation; the transition occurs at the point where the occupation of the $4f$ band lowers the one electron eigenvalue sum sufficiently to overcome the increase in electrostatic energy on transforming to the α-U structure. Th exhibits similar behavior. With decreasing volume, the $5f$ band occupation increases until, at an occupation of ~ 1 $5f$ electron and a pressure of ~ 1 Mbar, Th transforms from fcc → bct[9,10] (the bct phase, with c/a = 1.56, is a distorted fcc structure).

With decreasing volume, although the f occupation continues to increase, Ce transforms from the α-U structure to a higher symmetry structure; at a pressure of ~ 150 Kbar with an f occupation of ~ 1.2, the bct structure (distorted fcc) becomes stable. Again, Th behaves similarly. With decreasing volume, although the f occupation increases, Th transforms back to the fcc phase. The phase diagram of U, calculated for the fcc, bct, and α-U structures predicts a structural transformation from the α-U structure to a bct structure at ~ 790 Kbar. This increased symmetry transformation is similar to the second phase transition in Ce, but the c/a ratio in bct-U is ~ 0.83 (distorted bcc). Again, the f-band occupation increases continuously with decreasing volume.

DISCUSSION

The stability of low-symmetry structures in Ce and the light actinides is correlated with the filling of sufficiently narrow f bands. A metal with degenerate electronic states at the Fermi energy can lower its one electron energy by Jahn-Teller distortion;[11] *i.e.*, by lowering its symmetry to break degeneracies at the Fermi energy and thus move occupied states to a lower energy and unoccupied states to a higher energy. If the density of states at the Fermi energy is sufficiently large, the one electron energy will be lowered enough to overcome the increase in electrostatic energy accompanying the distortion.

This mechanism for lowering the energy is demonstrated in Fig. 1 for Al. Shown in this figure is the density of states (DOS) of bct Al with $c/a = 0.45$, calculated at fourfold expansion in volume. Superimposed on the bct DOS is the fcc DOS at the same volume. At this volume, the bct structure is lower in energy than the fcc structure (the structure at equilibrium) by ~ 25 mRy; the width of the Al p band at this volume is comparable to the bandwidth of U at equilibrium. The source of this difference is evident in Fig. 1: the sharp peak in the Al fcc DOS is split by tetragonal symmetry, moving occupied states to lower energies and thereby lowering the total energy. More relevant to the discussion here, but somewhat more complex, is the DOS of α-U, compared with the DOS of fcc U, near equilibrium shown in Fig. 2. The same mechanism discussed in connection with Fig. 1 for lowering the energy is evident in Fig. 2.

If the total energy is to be lowered by lowering the symmetry, the DOS at the Fermi energy must be large enough for the gain in one electron energy to overcome the increase in electrostatic energy; hence the onset of low symmetry structures as the actinide series is traversed and as the f occupation increases with pressure. With decreasing volume, despite the increase in occupation, the f bands broaden, and the Jahn-Teller mechanism becomes less effective, while the gain in electrostatic energy in higher symmetry structures increases; hence the increase in symmetry exhibited by U, and ultimately by Ce and Th,

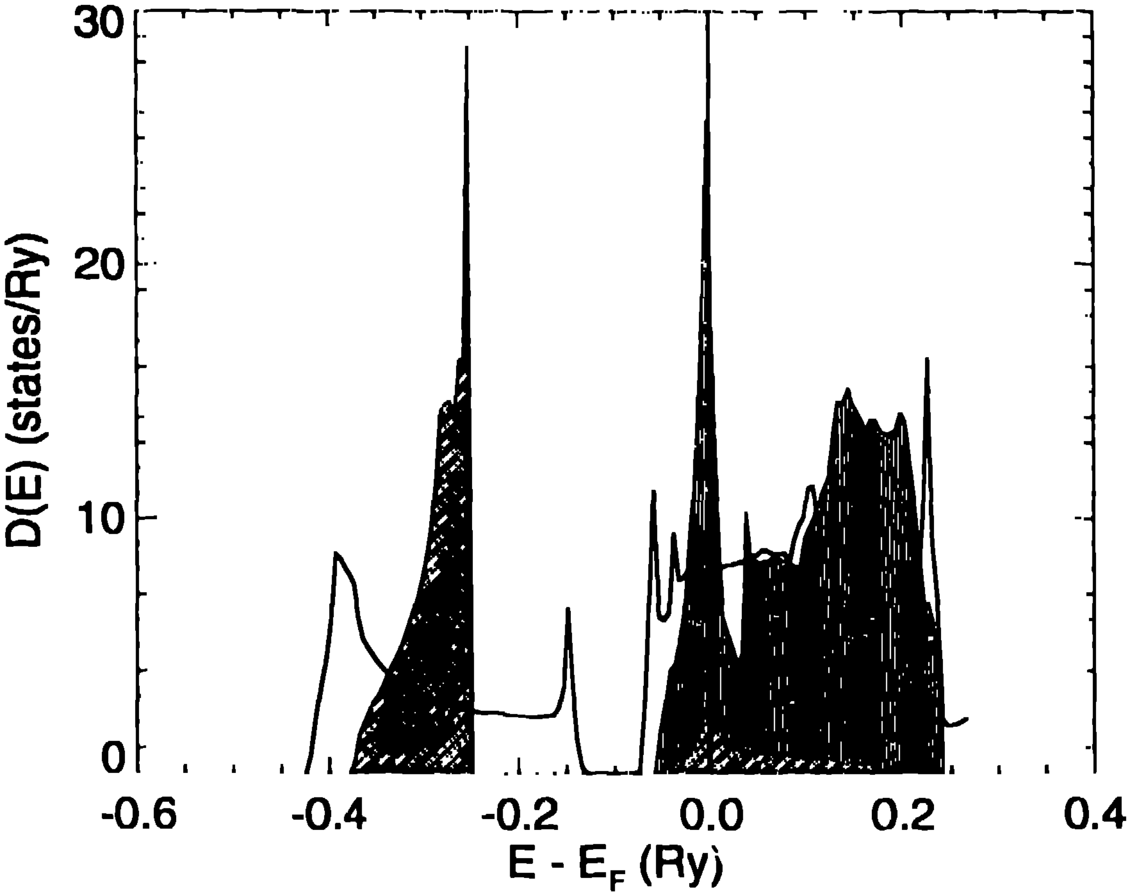

Figure 1. The density of states (DOS) of bct Al (solid line, unshaded), $c/a = 0.45$, at a volume $V = 4V_0$, where V_0 is the equilibrium volume. Superimposed on the bct DOS is the DOS of fcc Al (shaded curve) at the same volume.

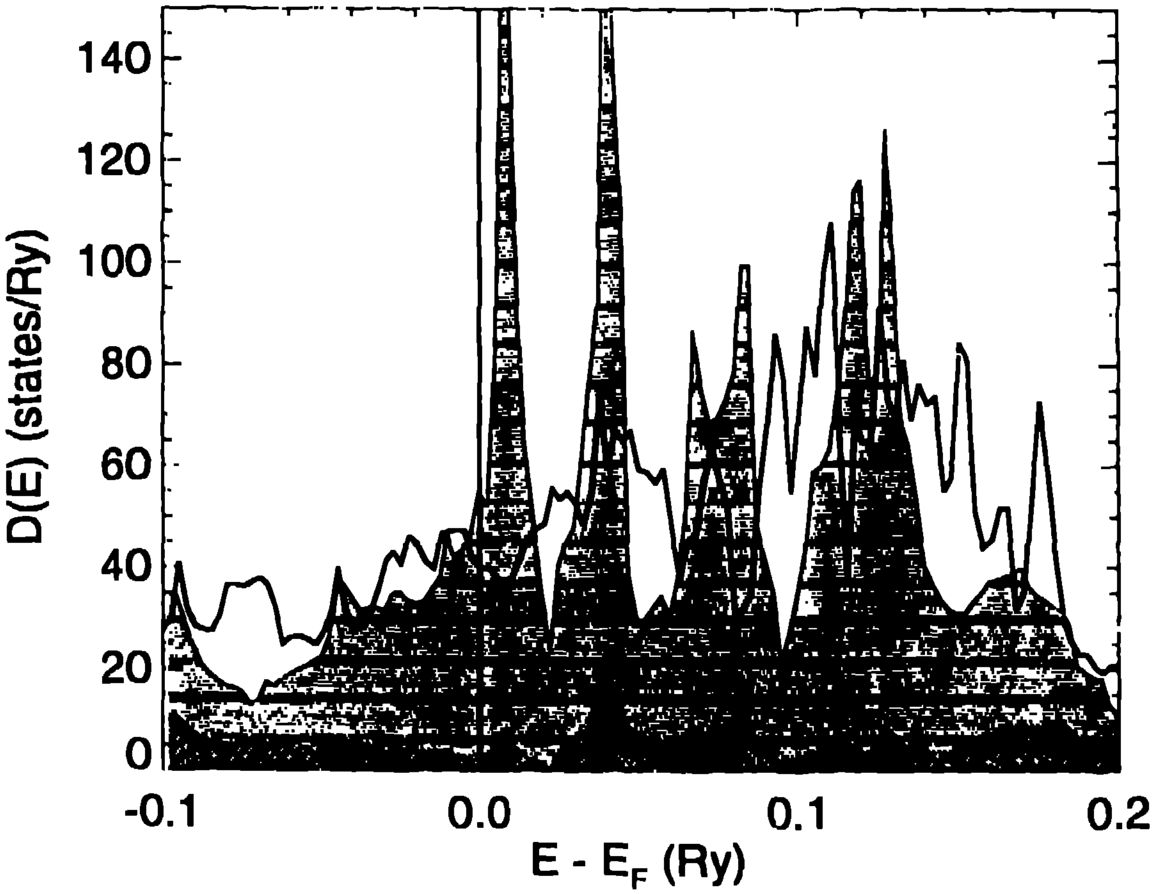

Figure 2. The density of states per atom (DOS) of α U (solid line, unshaded) at the experimental equilibrium volume. Superimposed on the α U DOS is the DOS of fcc U (shaded curve) at the same volume.

as the volume decreases. We expect, on this basis, that, at a sufficiently small volumes, all *f* electron systems will stabilize in one of the close-packed fcc, bcc, or hcp structures, the particular structure being determined by band filling, as in the transition metals.

It was shown, in Fig. 1, that Al, a simple metal, would be stabilized in a low symmetry structure (bct) at bandwidths comparable to those found at equilibrium in the actinides. In Fig. 3, we show the calculated total energy of Nb in the bct ($c/a = 0.825$) and α-U structures, relative to the bcc structure, at expanded volumes. Nb, a normal transition metal, at contracted volumes, would stabilize first in the bct structure and finally, at a *d* bandwidth comparable to the *f* bandwidth of U, in the α-U structure. In combination with the Ce and light actinide results, this suggests that when *d*- and *f*-bandwidths are comparable, transition metals, rare earths, and actinides stabilize in similar crystal structures, driven by the same mechanisms. The difference between *d*- and *f*-band widths at equilibrium accounts for the difference in stable equilibrium structures; with respect to crystal structure stability, the transition metals and the actinides represent different regimes of consistent itinerant-electron behavior.

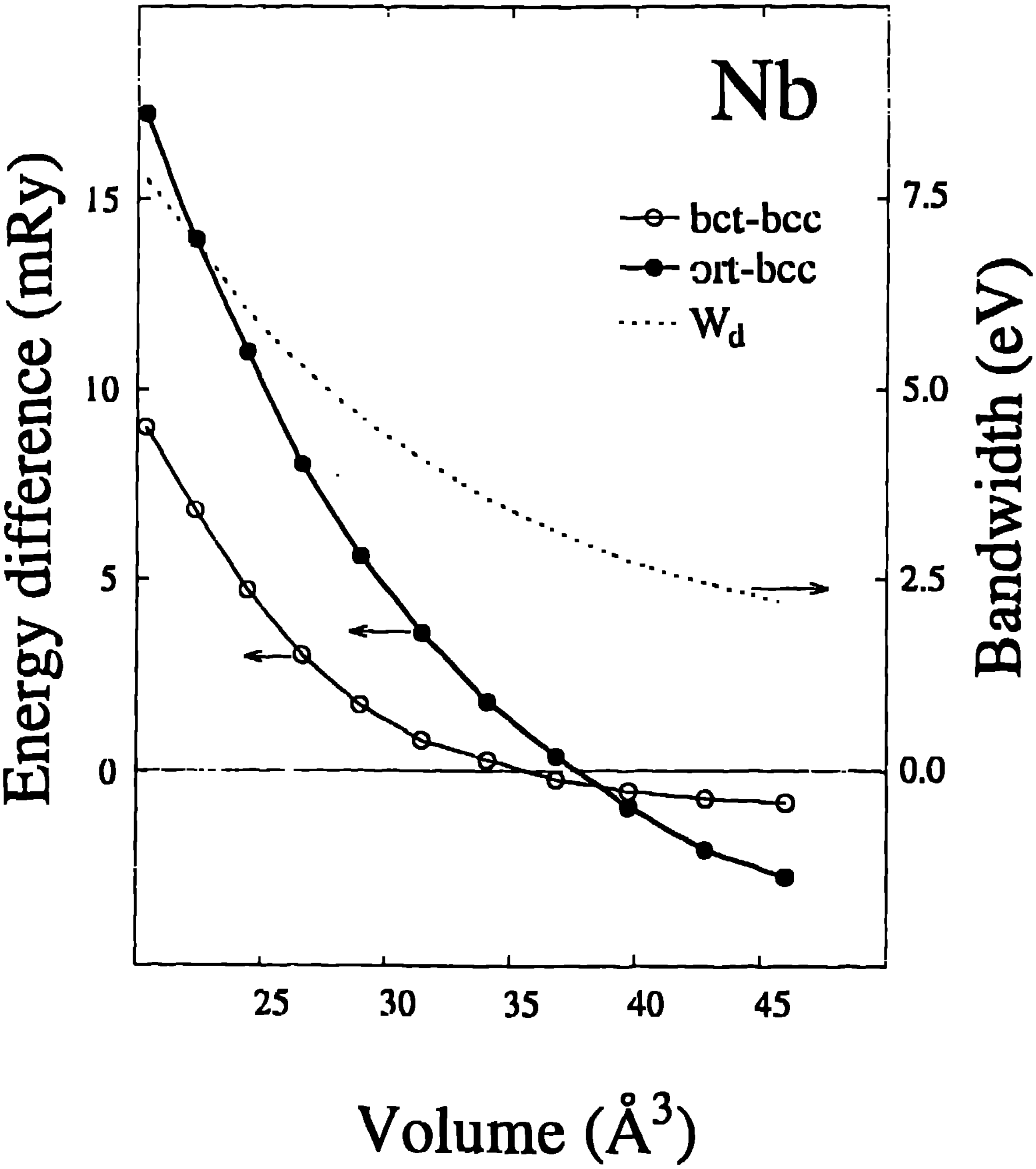

Figure 3. Calculated bct (c/a = 0.825) (open circles) and a C′ structure (filled circles) energies, relative to the bcc structure for Nb at expanded volumes.

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