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LATTICE RELAXATION AND THE STABILITY OF PLUTONIUM-BASED ALLOYS AND INTERMETALLICS

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Abstract

The topic of this study is the electronic structure of the compounds Pu_3X [X = In, Ga, Aℓ, or Tℓ], reported to have room temperature $L1_2$ structures. The measured Pu-Pu bond length in δ-phase Pu is 3.28 Å. The Pu-Pu bond lengths in Pu_3Ga and $Pu_3Aℓ$ are 3.18 Å. The similarity in bonding in Pu_3Ga and $Pu_3Aℓ$ is especially notable as the equilibrium atomic volume in Ga is 18% higher than that of Aℓ. Likewise, in Pu_3In and $Pu_3Tℓ$ the bond lengths are 3.33 Å and 3.32 Å, respectively, although the atomic volumes of In and Tℓ differ by 10%. The electronic mechanism by which the δ stabilizers Aℓ and Ga contract the Pu-Pu bonds and whereby In and Tℓ stretch them may relate the stability of pure Pu to that of the Pu_3X compounds. For example, does the addition of Ga or Aℓ shorten the bond length enough to make the close-packed $L1_2$ structure more stable than does the addition of In or Tℓ? *The incipient localization of the f electrons and the stabilization of open structures may be indicated through LDA total energies and densities of states.*

Overview

The δ (*fcc*) phase of pure Pu is stable from 320°C to 463°C. Small additions of group IIIB metals (X=Aℓ, Ga, In, or Tℓ) can stabilize the δ phase to room temperature. The X-saturated δ-phase alloys form a two phase equilibrium with a Pu_3X compound. The low-temperature limit of the impurity-stabilized δ alloys in Pu-Ga and Pu-Aℓ is disputed. The Pu-Ga phase diagram by Chebotarev *et al* [1] indicates a eutectoid decomposition of the high-temperature δ phase with composition 9 at.% Ga into the α-Pu (monoclinic) at 0.1 at.% and Pu_3Ga at 25 at.% phases at 100°C. By contrast Ellinger *et al* [2] report no such decomposition, and show a nearly vertical Ga-rich solvus line to 0°C. Adler [3] estimates a eutectoid equilibrium of the Aℓ-stabilized δ phase at 9 at.% Aℓ with the α and $Pu_3Aℓ$ phases at 62°C and a eutectoid temperature of 81°C for the Ga-stabilized δ alloy. Clearly, the stability of the δ phase depends upon the stability of the Pu_3X compound, and a first-principles study of the compounds is a necessary precedent to a finite-temperature simulation of the partially ordered δ phase.

In general, alloy structural stability is determined by a balance between bandwidths (and filling) and the Madelung energy. For sufficiently narrow bands (large volumes) the splitting of the degenerate bands near the Fermi energy may be comparable to the bandwidth – hence a lowering of symmetry may lower the energy. At small volumes the breaking of degeneracies is less pronounced (compared with the bandwidth) and the Madelung energy dominates – favoring close-packed structures. To elucitate this physics, we have calculated total energies of the *fcc* structures [Pu, X = In, Ga, Aℓ, or Tℓ] and $L1_2$ [Pu_3X] structures with the full-potential LMTO method. [4] Both the Generalized Gradient Approximation (GGA) [5] and the Local Density Approximation are used. This enables us to calculate formation energies as well as other properties of the Pu_3X compounds.

As expected, each compound displays covalent bonding between the Pu-*d*, *f* and X-*p*. Two regimes of behavior are seen: $Pu_3A\ell$ and Pu_3Ga exhibit very similar properties (e.g. atomic volume, bulk modulus, formation energy, and density of states) as do Pu_3In and $Pu_3T\ell$. The formation energies of Pu_3In and $Pu_3T\ell$ are 30 mRy/atom higher (less stable) than those of $Pu_3A\ell$ and Pu_3Ga. The apparent instability in the latter compounds is linked to the more pronounced *pdf* hybridization near the Fermi energy in Pu_3In and $Pu_3T\ell$ and the consequent opportunity for Jahn-Teller/Peierls distortion.

Results and Discussion

The LDA Pu-Pu bond length in δ Pu is 2.85 Å. The bond lengths for Pu_3Ga and $Pu_3A\ell$ are 2.83 Å and 2.84 Å, respectively, and 2.96 Å and 2.99 Å for Pu_3In and $Pu_3T\ell$. In the GGA approximation the δ-phase Pu-Pu bond length is 2.94 Å. In Pu_3Ga and $Pu_3A\ell$ the bond lengths are, 2.92 Å, and for Pu_3In and $Pu_3T\ell$, 3.09Å and 3.11 Å, respectively. As with the experimentally determined values, the computed bond lengths in δ Pu are bracketed by those of Pu_3Ga and $Pu_3A\ell$ on the low side and by Pu_3In and $Pu_3T\ell$ on the high side.

The formation energy of a Pu_3X compound is:

$$\Sigma_{Pu_3X}^{formation} = \Sigma_{Pu_3X}^{min} - \frac{3E_{Pu}^{min} + \Sigma_X^{min}}{4}$$

where E^{min} is the minimum total energy of a phase. The LDA formation energies of Pu_3Ga and $Pu_3A\ell$ are –10 mRy/atom and –5 mRy/atom respectively. The negative sign indicates the stability of the compound with respect to the constituent phases (in this case artificially assumed to be the pure elements in the fcc structure). The calculated formation energies of Pu_3In and $Pu_3T\ell$ are +20 mRy/atom and +25 mRy/atom respectively. The formation energies calculated with the GGA vary only slightly from the LDA. The large stability difference between the $Pu_3Ga/Pu_3A\ell$ compounds and those of $Pu_3In/Pu_3T\ell$, approximately 30 mRy/atom indicates the strong possibility of an instability of the $L1_2$ structure in the latter compounds. The compound instability has no definitive implications upon the high-temperature equilibrium structure because the δ-phase of pure Pu exists only at high temperatures and volumes. Using the LDA energy

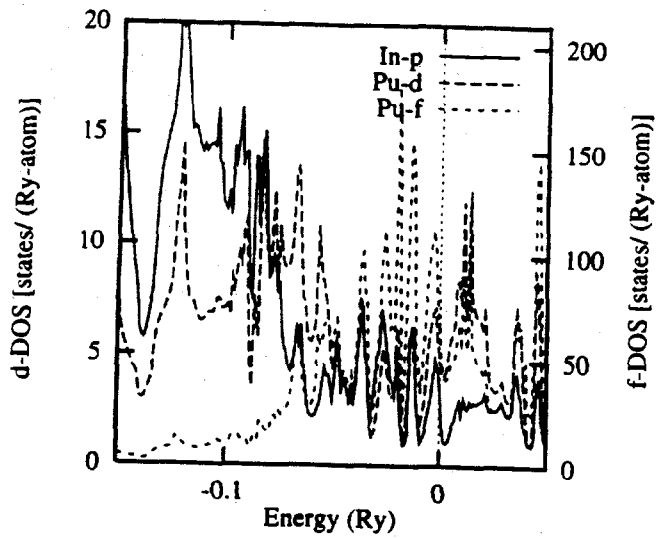

FIG 1. *l*-projected density of states for Pu_3In at the theoretical volume 18.4 $Å^3$. The Fermi energy is at 0.

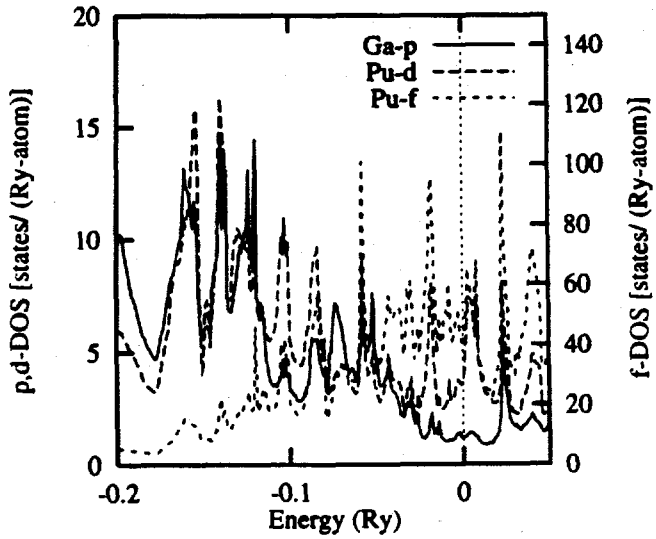

FIG. 2. l-projected density of states for Pu_3Ga at the theoretical volume 16.3 Å. The Fermi energy is at 0.

at the experimental volume of δ-Pu as a reference lowers the relevant formation energies of each of the compounds by 56.4 mRy per atom.

The *l*-projected DOS for Pu_3In at the measured equilibrium volume is shown in Fig. 1. In the *l*-projected DOS for the Pu and In sites there is a high correlation between the Pu-6*d*, –5*f* and In-5*p* states just below the Fermi energy characteristic of covalent bonding. Similarly, in $Pu_3T\ell$ the *l*-projected DOS shows strong *pdf* hybridization just below the Fermi energy.

Next we consider the differences in hybridization among the compounds in anticipation of discussing possible structural instabilities. The *l*-projected DOS for Pu_3Ga are shown in Fig. 2, and we consider the differences from the *l*-projected DOS for Pu_3In shown in Fig. 1. In each of the Pu_3X compounds there is strong Pu-6*d* 5*f*/X-*p* hybridization at energies between –0.2 Ry and the Fermi level. There is hybridization across the spectrum of valence states, but the appreciable differences between materials are seen near the Fermi energy. In the lighter compounds (Pu_3Ga and $Pu_3A\ell$) the hybridization is strongest at about 0.1 Ry below the Fermi energy; and in the heavier (Pu_3In and $Pu_3T\ell$), the hybridization is strongest in the vicinity of the Fermi energy.

This pairing is part of an overall pattern of pairing among the four compounds. Examination of the calculated and measured properties of these compounds suggests two regimes of electronic and thermodynamic behavior. $Pu_3A\ell$ and Pu_3Ga have very similar measured and calculated atomic volumes, bulk moduli, formation energies, and electronic structure, and in the same manner so have Pu_3In and $Pu_3T\ell$.

The preceding discussion suggests the hypothesis that the crucial difference between the lighter and heavier compounds is that of rather subtle changes of the Pu 5*f*-6*d*/X-*p* hybridization. The more pronounced hybridization near the Fermi energy in Pu_3In and $Pu_3T\ell$ may signal a possible structural transition triggered by the degenerate *pdf* states at the Fermi energy. The electronic "mechanism" behind the stabilization of the δ phase has been suggested by van Ek, Sterne, and Gonis [6] as follows. The addition of the impurity element shifts the Fermi level so that the *f* bonding decreases. This is accompanied by an increase in the *d* bonding – characteristic of the δ phase. Using LMTO-ASA results, van Ek *et al* [6] theorized that bonding in close-packed structures of Pu is governed primarily by *s* and *d* electrons, but in the α phase there is a significant component of 5*f* bonding. This is accomplished by formation of a small number of short bonds, reducing the itinerancy of the *d* electrons. Conceivably, the ground state of the Pu_3X compounds are similarly governed, and a complex open structure is stable at 0 K.

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