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Calculated lattice relaxation in Pu-Ga alloys

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Abstract

Hellman-Feynman forces on atoms in Pu_{32} and $Pu_{31}Ga$ supercells are calculated with the full-potential LMTO method in the local density approximation. These forces are minimized by adjusting atomic positions using an iterative Broyden scheme. A Pu_{32} supercell shows no tendency to relax from a perfect fcc lattice. In $Pu_{31}Ga$ the nearest-neighbor shell of plutonium atoms relaxes inward by 1.04% of the initial theoretical bond length (2.86 Å) compared with a measured (EXAFS) value of 3.7% for an alloy with similar composition. Possible sources of the discrepancy between theory and experiment are discussed. © 1998 Elsevier Science S.A.

Keywords: LMTO; Plutonium; Hellman-Feynman; Gallium; EXAFS

1. Introduction

The δ (nominally fcc) phase of plutonium is stable from 320°C to 463°C. Addition of small amounts (the solvus lines are not precisely known) of gallium stabilizes the δ phase to room temperature — at least the phase is kinetically stable. No fundamental description of the δ phase yet exists. Söderlind et al. [1] demonstrate the suitability of the application of the local density approximation (LDA) and the related general gradient approximation (GGA) to the ground state of Pu. Due to the high density of states at the Fermi energy of the itinerant f states the ground state of Pu is determined by the band filling and the tendency to split the band via a Peierls-Jahn-Teller distortion. They obtain excellent agreement for the density of the low-temperature, monoclinic α phase by treating the f states as itinerant. However, this approach leads to large errors in the density calculation (~30%) for δ-Pu [2–9] as well as in the Pu_3X compounds for the δ-stabilizers X=Al, Ga, In, or Tl [9]. Additionally, the LDA predicts that the Pu_3X compounds are metastable in calculations treating f states as itinerant [9].

X-ray absorption fine-structure spectroscopy (EXAFS) determines the local environment around specific sites whereas x-ray diffraction yields only average properties. Cox et al. [10] performed EXAFS measurements on 3.3 at.% Ga alloy. They report that the plutonium atoms in the nearest-neighbor shells surrounding gallium atoms relax inward by 3.7% of the ideal bond length, 4.61 Å. Faure et al. [11] performed EXAFS analyses on alloys ranging from 3.43 at.% Ga to 10.43 at.%. For the 3.43 at.% alloy they find an inward relaxation of 3.5%. They also show a minimum in the relaxation (with respect to concentration of gallium) of 1.6% of the average bond length at a concentration of 7.0 at.%.

In this study the question as to whether the LDA can reflect the modification of the transition temperature of δ Pu from 320°C to near room temperature by small additions of Ga is explored by first-principles calculation of the electronic structure and atomic forces in an ordered 3.125 at.% Ga alloy. The structural disorder around the Ga sites modifies the electronic structure, and this change is examined for implications on the structural stability of the alloy.

2. Computational method

The minimum energy volume of an fcc-based 32 atom supercell ($Pu_{31}Ga$ with the Ga atom in the center) is determined with the full-potential LMTO method [12–14] in the local density approximation (LDA) with the von Barth-Hedin [15–17] density functional. The calculations are all-electron and scalar relativistic. To keep the force calculation to a reasonable size spin-orbit interaction is excluded.

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The basis sets include the 6s, 6p, 7s, 7p, 6d and 5f partial waves for Pu, the 3d, 4s, and 4p for Ga. Two sets of energy parameters are used for the calculation of the basis within the muffin tin, the lower energy being appropriate for semi-core states and the higher for valence levels. The orbitals are defined within a single energy panel to allow hybridization, i.e. matrix elements connecting basis functions associated with different sets of energy parameters are included in the Hamiltonian and overlap matrix elements. The sampling over the irreducible wedge of the Brillouin zone is performed with the special *k*-point method [18]. Ten points per atom in the irreducible wedge of the zone — corresponding to 216 points per atom, or 6912 points in the full Brillouin zone — are used. The convergence is accelerated by associating each eigenvalue with a small Gaussian function of width 10 mRy.

In the 32 atom supercell (see Fig. 1) only the nearest- and third-nearest neighbors are allowed to move under the constraint of cubic symmetry. The nearest neighbors move along the diagonals $\langle 0\ 1\ 1\rangle$ of the $\{2\ 0\ 0\}$ planes, and the third nearest neighbors move along the cell-face diagonals ($\langle 1\ 1\ 0\rangle$ of the $\{1\ 0\ 0\}$ planes). The Pu atoms in the 2nd shell surrounding Ga are halfway between Ga atoms in adjacent supercells and are therefore fixed by symmetry.

The forces on the Pu atoms in the nearest-neighbor and third nearest-neighbor shells surrounding the Ga atom are calculated for a self-consistent potential. These forces, constrained to reflect the crystal symmetry, are parallel to the aforementioned degrees of freedom. The positions of those atoms are then adjusted to lower the forces by a modified Broyden technique. The force calculation is repeated with subsequent corrections to the lattice configuration until the projected corrections are less than 0.001% of the initial bond length. This corresponded to magnitudes of the forces of less than 1×10^{-13} N. For this study six iterations were required to find the 'relaxed' configuration.

3. Results and discussion

A Pu_{32} supercell with the same lattice as Fig. 1 is examined for local distortions. The space group is lowered to orthorhombic to allow more complicated distortion modes. The calculated forces on all of the atoms are less than 1×10^{-8} Ry/a.u. (1 Ry/a.u.$=4.119\times10^{-8}$ N) and is judged, therefore, to be at equilibrium.

The $Pu_{31}Ga$ supercell minimum energy lattice parameter is 8.096 Å. For the initial — perfect fcc — lattice, the forces on the atoms in the nearest and third nearest neighbor shells are -0.0055 Ry/a.u. and 0.004 Ry/a.u. respectively. The negative sign on the nearest-neighbor force indicates a force with a sense acting toward the gallium atom at the center, and the positive sign on the third nearest neighbor force means a force pushing the atom away from the face center — and further from the gallium atom.

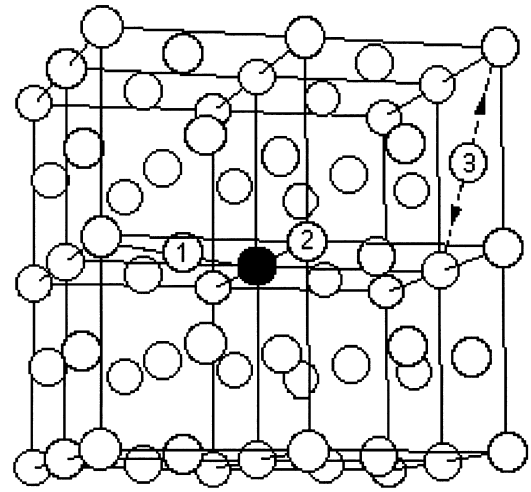

Fig. 1. $Pu_{31}Ga$ supercell. Gallium atom is denoted by filled circle. A typical nearest-neighbor plutonium site is labeled 1, second-nearest 2, and third-nearest 3. Arrows show relaxation modes.

In the final configuration the Pu atoms in the nearest-neighbor shell have contracted inward by 1.0414% of the initial Pu–Ga bond length, 2.86251 Å. The third-nearest neighbor shell has relaxed away from the gallium site by 0.474% of the original distance of 4.958 Å. The nearest-neighbor shell surrounding each of gallium's 5th neighbors (sites at supercell corners) contracts isotropically by 1.416% of the original bond length 2.86251 Å to 2.82198 Å. This contraction leads to a δ-Pu-like environment for these sites.

The decrease in total energy from the initial to final configuration is 0.0283 mRy/atom. The formation energy of the alloy is +0.295 Ry/atom with respect to the elemental constituents in the fcc structure. As in the case of the Pu_3X compounds the positive formation energies of the LDA calculations indicate the 'Ga-stabilized' alloys are actually metastable at low temperature. As noted by Adler [19] consideration of thermodynamic measurements in the Pu-rich alloys implies a low-temperature decomposition of the d phase into $\alpha+Pu_3X$.

Measurements [10,11,20] in alloys with concentrations of Ga between 3.3% and 25% reveal that there is little change in the Pu–Ga bond length (from 3.154 Å to 3.22 Å) as a function of Ga content. This suggests that the main modification of the electronic structure due to a Ga impurity is realized with the addition of, at most, 3.3 at.% Ga. This is supported by analysis of the bands and densities of states of the compounds and elements. Fig. 2 shows the densities of states projected onto Pu and Ga sites for Pu_3Ga, δ Pu, fcc Ga, and $Pu_{31}Ga$. The hybridization of Ga 4p states with Pu 6d is apparent in $Pu_{31}Ga$ even in the 5th neighbor shells surrounding the Ga atoms. The effect upon the 5f states is less pronounced in the 5th neighbors where the f-projected DOS is much more like that of pure δ Pu, than in those of the nearest neighbor Pu sites where the impurity-induced spectra resemble those of the Pu_3Ga

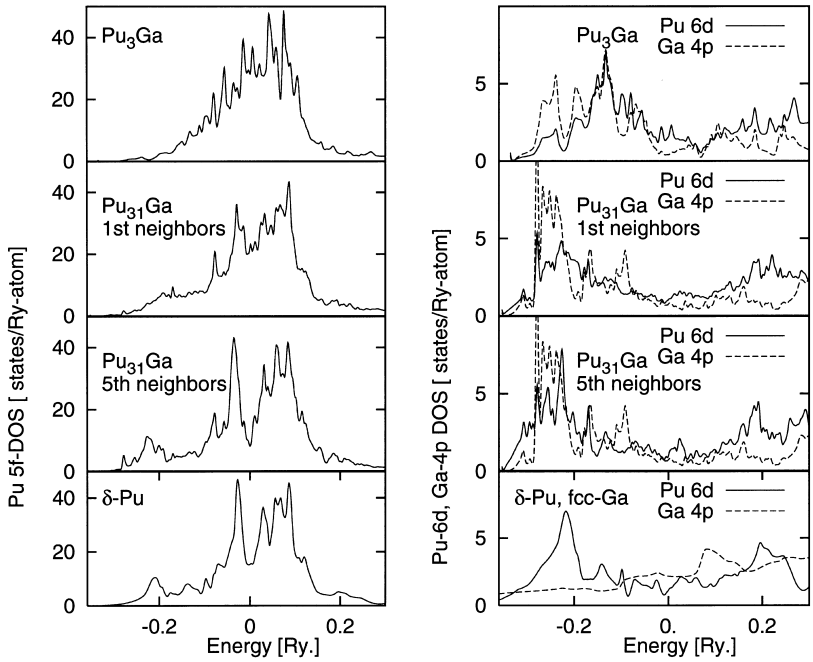

Fig. 2. Projected densities of states in δ-Pu, fcc Ga, and in the $Pu_{31}Ga$ supercell. The graphs on the left show the 5f-projected DOS, and the 6d, 4p-projected DOS are on the left. All spectra are smoothed by convolution with a Gaussian of width 10 mRy.

compound. The projected spectra associated with the other three crystallographic sites in the supercell show less pronounced trends.

The discrepancy between the measured and calculated relaxed bond lengths may originate in the treatment of the Pu 5f electrons. Perhaps the magnitude of the relaxation is limited primarily by the much lower unit cell volume in the LDA model, or perhaps the over bonding inherent in the LDA restricts the relaxation as well. The very question of the 'volume problem' in δ-Pu has been explored with ad hoc studies. For example, Eriksson et al. (unpublished results) and Pénicaud [21] use constrained Hamiltonians to localize some f states resulting in volumes that are very close to the measured values. Méot-Reymond and Fournier [22] hypothesize a Kondo compensated ground state for δ-Pu. They note that the similar magnetic susceptibilities for α- and δ-Pu and significantly different values of the *c* coefficient of electronic specific heat are consistent with the presence of a Mott-like transition between α- and δ-Pu. These calculations all support the long-held notion that a rigorous, predictive theory for the partial localization of f-states is required in order to capture fully the enigmatic properties of Pu.

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