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Electronic Structure and Phase Stability of Pu-Ga Alloys

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INTRODUCTION

Plutonium metal has six different crystallographic allotropes from room temperature until it melts just above 600 ^{0}C. The room-temperature α phase is monoclinic with 32 atoms per unit cell, (an α phase with 16 atoms per cell also exists), which is the lowest-symmetry crystal structure known of any pure element. In fact, only the high-temperature δ (fcc) phase of Pu possesses one of the traditional close-packed structures. The low-symmetry and small lattice constants of the lowest-temperature phase of the light actinides can be used as an argument for f-bonding in these materials. The large volume increase in Pu in going from the α to the δ phase has been argued on phenomenological grounds to be the result of decreased f-bonding.

In addition, XPS data have been obtained for both the α and the δ phases. Both sets of data show the presence of a peak below the Fermi level (E_F). This peak is 2.0 eV wide in the α phase and 3.0 eV wide in the δ phase. The XPS intensity calculations (for the two phases) which treat the f-electrons as bonding states agree with the measurements of the α phase spectra, but not with those of the δ phase. The calculated spectrum shows a narrow f-peak pinned at E_F instead of the wide f-peak below E_F seen in the XPS spectra. It can be argued that the wide spectra seen experimentally are due to the multiplet structure of localized f-states that do not participate very actively in the bonding.

In spite of the difference in the properties of the α and δ phases of Pu (for example α-Pu is brittle while δ-Pu is ductile), it is not difficult to retain either phase by alloying. Indeed, it is often desirable to retain the ductile δ phase for engineering purposes, by alloying, for example, Pu with Al, Ga, or Si.

DESCRIPTION OF WORK

We report on results of first-principles electronic structure calculations based on the full-potential LMTO (FP-LMTO) method for pure Pu as well as for Pu-Ga alloys. The aim of these calculations is to determine the energetics of Pu-Ga alloys, the bonding between impurity and host atoms, the relevant atomic interactions between atoms of different species and, ultimately, the phase-stability tendencies of Pu-Ga alloys. We use the Connolly-Williams method for determining these interactions through the study of ordered configurations of the alloy at stoichiometric concentrations, with the aim of eventually using methods based on the coherent-potential approximation (CPA) which can be carried out at arbitrary concentrations.

RESULTS

Figure 1 shows the energy of mixing as a function of atomic volume for Pu-Ga alloys at three Ga-concentrations. The main result that can be read from this figure is the tendency of the alloy to form at any composition (mixing energy negative). The density of states (DOS), shown in Fig. 2, of the alloy Pu_3Ga in the LI_2 (of Cu_3Au-type) structure together with the bonding charge density (not represented here) indicate that the presence of Ga modifies the electronic properties of pure Pu. In particular, we find that in the (100) plane the nature of the bonding tends to be ionic in character, with charge being transferred from Pu to Ga cells. The effect of these modifications on the stability of Pu-Ga alloys will be discussed.

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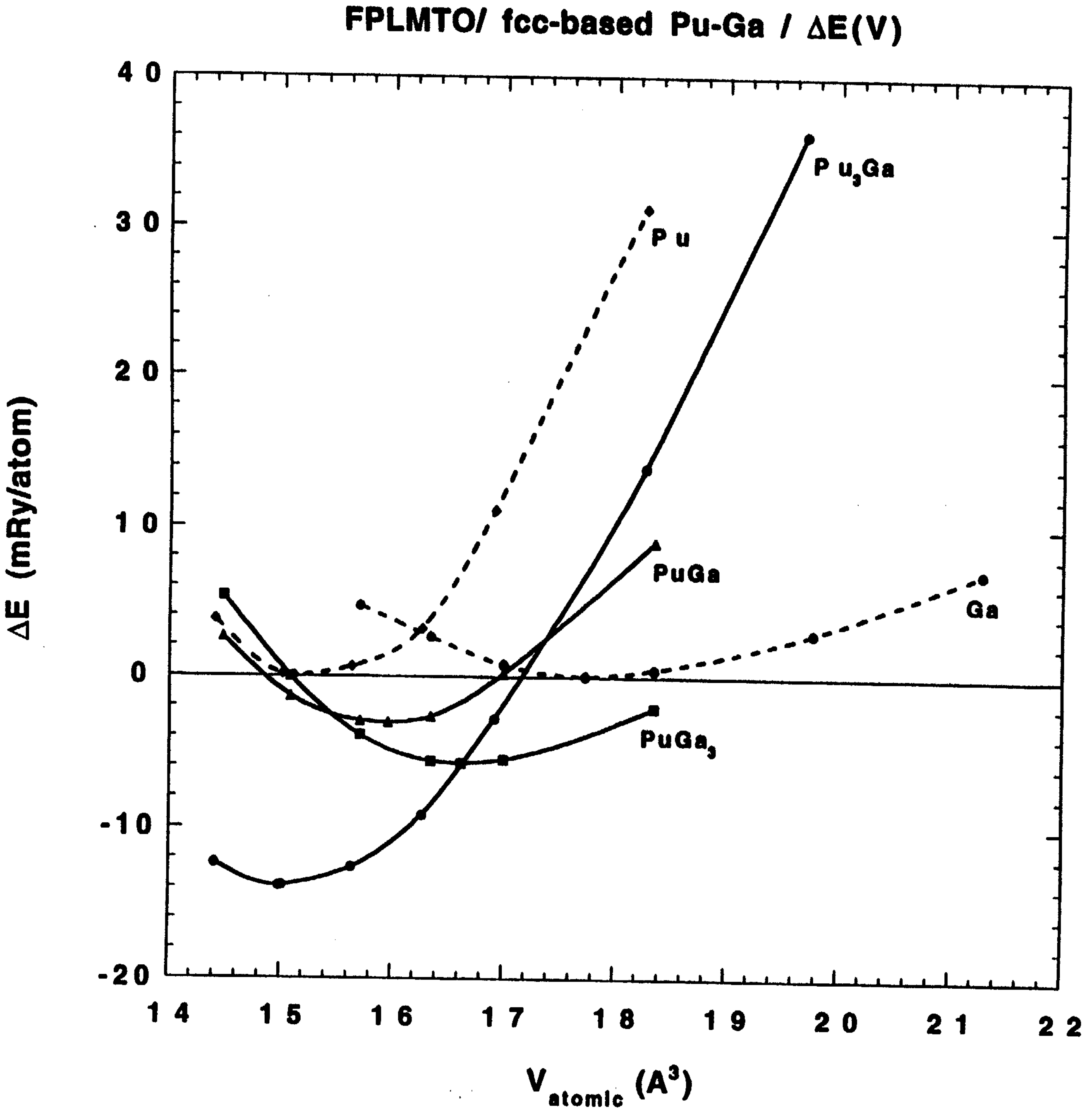
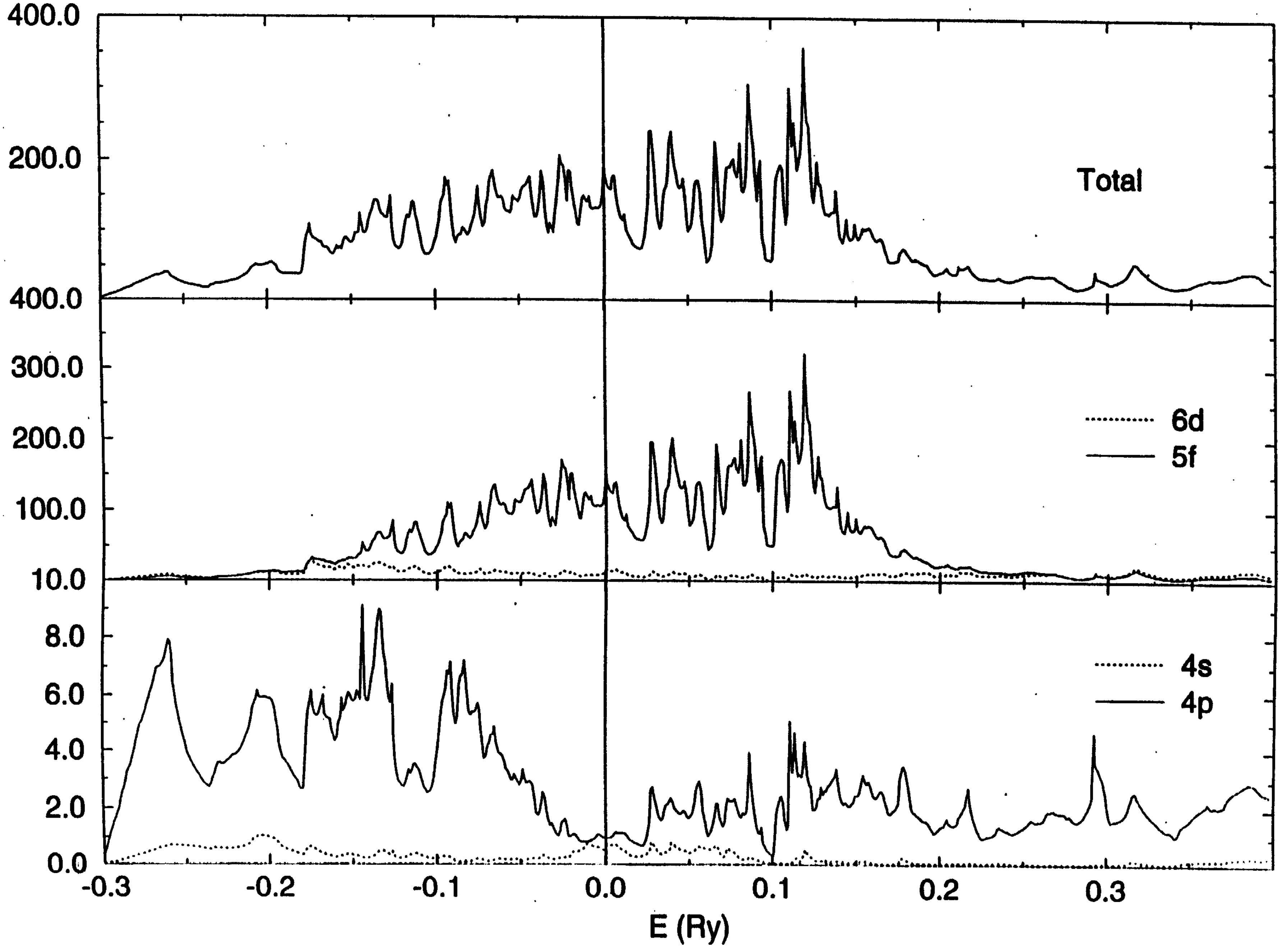

FPLMTO/ fcc-based Pu-Ga / ΔE(V)
ΔE (mRy/atom)
40
30
20
10
0
-10
-20
14
15
16
17
18
19
20
21
22
V atomic (A³)
Pu₃Ga
Pu
PuGa
Ga
PuGa₃

1

Density of States (Pu3Ga)



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