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CORRELATION EFFECTS ON STABILITY IN Pu METAL AND ITS ALLOYS

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INTRODUCTION

The existence of six crystallographic allotropes from room temperature up to the solid-liquid transition just above 913 K at atmospheric pressure makes solid Plutonium unique among the elements in the periodic table. Among these phases (labeled α, β, γ, δ, δ', and ε), the δ phase, stable between 593 K and 736 K, has commanded considerable interest in the metallurgical and solid state communities[1]. In contrast to the low-temperature monoclinic α phase, which is brittle, the face-centered cubic (fcc) δ phase is ductile, a property that makes it convenient for engineering applications. This phase can also be stabilized through alloying with a number of other elements such as Ga, Al, Sc, and Am.

The low-symmetry and small atomic volume of the low-temperature phases of U, Np, and Pu is attributed to the role played by the *f*–electrons in determining the bonding in these materials. The unusually large 24 % volume increase in going from the α to the δ phase of Pu[2,3] has been argued on phenomenological grounds to be the result of decreased *f* bonding. Many attempts have been made to study this transition from the point of view of first-principles electronic structure calculations[4-7].

These calculations have been carried out within the framework of density-functional theory (DFT) and its local-density approximation (LDA), as well as the generalized gradient approximation (GGA)[4] designed to account for non-local effects of the electron density. In spite of these attempts, a fundamental understanding of the electronic structure properties of Pu, and the mechanisms responsible for the δ to α volume collapse is still lacking. As a direct consequence of this lack of understanding, the phase stability properties of Pu alloys are still poorly described from a fundamental standpoint[10-12]. For example[13,14], the solubility limits of Ga in δ and ε Pu (respectively 12.5 and 20 at.%), and the definite tendency toward ordering and phase formation (with the existence of six intermediate phases stable at room temperature) still need to be explained.

This paper briefly reports on a study of the electronic structure of Pu and Pu-Ga alloys that is designed to examine directly the effect of the electron-electron interaction on the equilibrium properties and on stability of these systems. As part of this study, the electronic structure and ground-state properties of Pu and Pu-Ga alloys were calculated using the LDA, a constrained version of the LDA in which the *f*-electrons were confined to core states, and finally the so-called LDA+U method. Although essentially phenomenological, this latter treatment sheds some light on the role of the partially localized *f*-electrons on properties. It also emphasizes the need for an *ab initio* treatment that accounts not only for spectral properties, but also for equilibrium properties, phase stability, and energetics of correlated metals and alloys.

METHODOLOGY

Electronic-structure method

The electronic structure calculations are based on the full-potential linear-muffin-tin-orbital (FLMTO) method[15], which includes non-spherical terms within the muffin-tin spheres. The calculations provided a fully relativistic treatment of electrons in core states, while valence electrons were treated semi-relativistically, but with spin-orbit coupling taken into account. The form proposed by Ceperley and Alder[16] and parametrized by Perdew and Zunger[17] was used for the exchange-correlation potential.

The basis sets include the 6s, 6p, 7s, 7p, 6d, and 5f partial waves for Pu and 3d, 4s, 4p, and 4d for Ga. Three energy panels were characterized by three different κ values set to the average kinetic energy in the interstitial region. In the case of Pu-Ga alloys, two of these panels (κ_1 and κ_2) were associated with the semi-core states, 6s and 6p, and the third (κ_3) with the valence states, 7s, 7p, 6d, and 5f of Pu, whereas for Ga κ_2 and κ_3 were associated with 3d, and 4s, 4p, and 4d, respectively. The muffin-tin potential and the charge density were expanded in spherical harmonics up to an angular momentum l=8. A reciprocal-lattice vector cutoff of $6a_0^{-1}$ (where a_0 is the Bohr radius) was used, and the integrations over the Brillouin zone were carried out according to a special k-point method[18]. Specifically, in the irreducible wedge of the Brillouin zone, 56 k-points were used for fcc-based Pu and Ga, and 60 (75) k-points for the $L1_2$ ($L1_0$) ordered structures Pu_3Ga and $PuGa_3$ (PuGa). In these calculations atomic relaxations were ignored and equilibrium properties were obtained by minimizing the total energy with respect to the atomic volume. The muffin-tin radii of Pu and Ga were chosen so that in the pure elemental systems as well as in the compounds the ratio of the interstitial volume over the total volume was kept constant.

Constrained LDA

It is generally accepted that the unique properties of Pu and its alloys derive from the behavior of the 5*f*-electrons and their hybridization to the other valence states. For example, the more these "localized" electrons contribute to the bonding, the higher the density of the material. To examine this property, we considered the extreme case in which all 5*f*-electrons were constrained to occupy core states with no *f*-symmetry allowed for the valence states.

The LDA+U method

The so-called LDA+U method is designed to correct in a phenomenological way for the treatment of the Coulomb interaction among the "localized" electrons that is accounted for rather poorly within the LDA. This methodology has been described in detail in the literature[19-21]. In its simplest form, one assumes that the LDA provides a correct treatment of the electron-electron interaction in terms of the total number (N) of electrons, here the 5*f*-electrons. Hence, one can write an expression for the total-energy functional through the addition of a Hubbard-like term with a renormalized Coulomb interaction parameter *U* (here for simplicity the Coulomb exchange term is dropped along with non-spherical terms) as follows,

$$E = E_{LDA} - \frac{U}{2} N(N-1) + \frac{U}{2} \sum_{i \neq j} n_i n_j ,$$

where E_{LDA} is the usual total electron energy of the ground state, and n_i is the number of localized electrons in state *i*. The value of *U* can be estimated from constrained LDA-type supercell calculations[22], according to

$$U = E(n_f + 1) + E(n_f - 1) - 2E(n_f) .$$

The energy $E(n_f+1)$ $[E(n_f-1)]$ associated with a configuration containing one more (one less) *f* electron is obtained within LDA by considering a supercell based here on a fcc lattice, with one of the simple-cubic sublattices occupied by n_f+1 (n_f-1) *f*-electrons (the other valence electrons being undisturbed).

RESULTS

Figure 1 shows the total densities of states (DOSs) of fcc-based (δ) paramagnetic Pu obtained in the LDA, panel (a), in the constrained LDA, panel (b), and in the LDA+U scheme, panel (c), with a value of $U \approx 3.2$ eV, at the same lattice parameter, a=8.7 a.u. The DOS of the LDA is dominated by the 5*f* contribution. The 5*f* DOS is mainly composed of two peaks associated, respectively, with the $5f_{5/2}$ and $5f_{7/2}$ states, and with a Fermi energy lying in a valley between these two peaks, as has been found in previous calculations[5]. The constrained LDA DOS, with the five 5*f*-electrons treated as core states, consists primarily of contributions of *s*, *p*, *d* character, with the Fermi level located on a peak in the DOS. Finally, the LDA+U yields a DOS in which the *f*-electrons of 5/2 symmetry are partially localized as a result of the presence of *U*. It should be pointed out that experimentally the coefficient of the linear term in the specific heat suggests a high DOS at the Fermi level that is not found in these calculations.

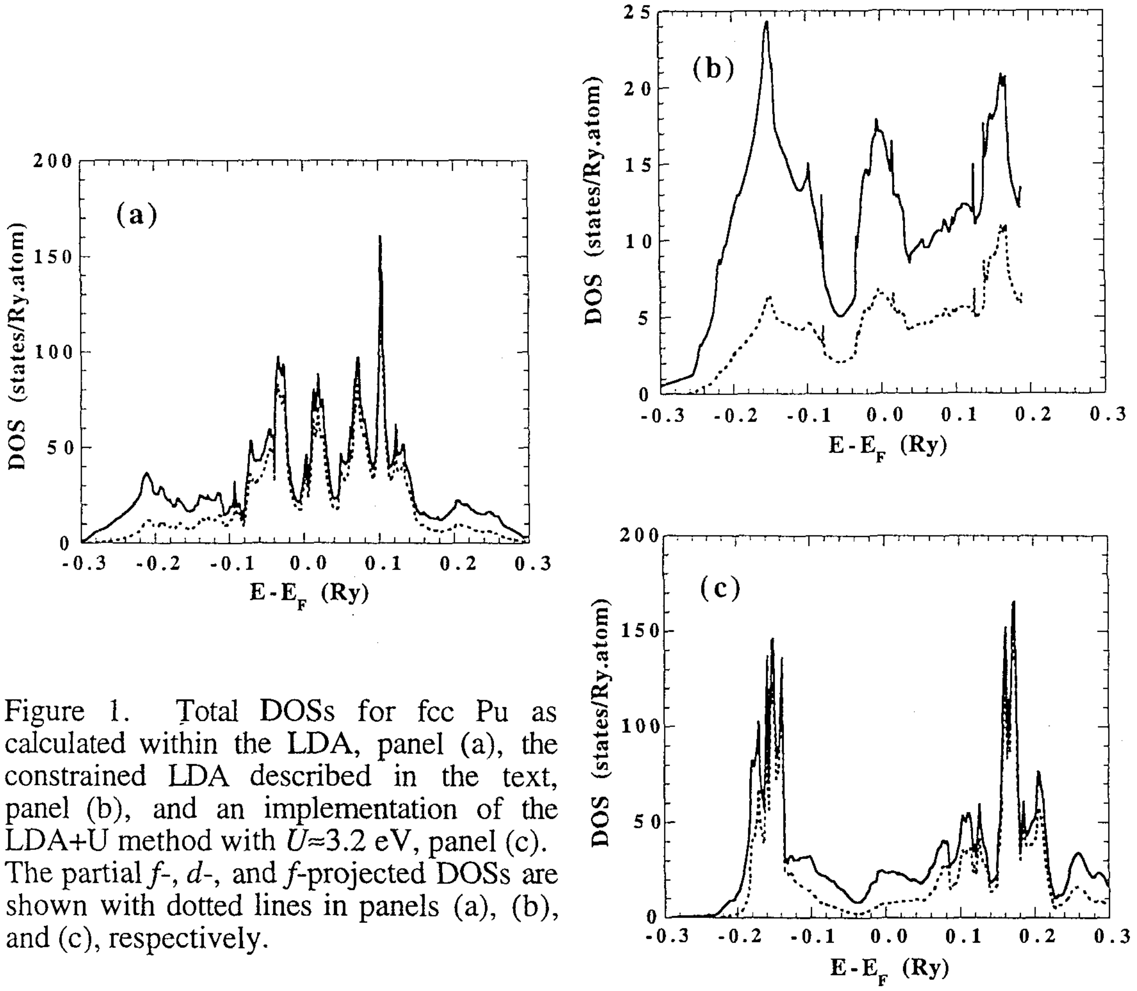

Figure 1. Total DOSs for fcc Pu as calculated within the LDA, panel (a), the constrained LDA described in the text, panel (b), and an implementation of the LDA+U method with $U \approx 3.2$ eV, panel (c). The partial *f*-, *d*-, and *f*-projected DOSs are shown with dotted lines in panels (a), (b), and (c), respectively.

The variation of *U* with the fcc lattice constant is presented in Fig. 2(a). This behavior is compatible with the fact that at small lattice constant the system is expected to behave as a Fermi gas, where the LDA provides an accurate description of the electronic behavior, whereas with increased expansion the *U* approaches a "screened atomic" value. Figure 2(b) shows the behavior of the equilibrium lattice constant as a function of *U*. This is consistent with the expectation that a large *U* results in the localization of the *f*-electrons and hence a larger atomic volume.

The total energy versus volume for fcc-based Pu, calculated in the three different schemes outlined above, is displayed in Fig. 3. The volume shown is normalized to the LDA result. The usual LDA calculation yields an atomic volume in accordance with previous results[4] that is much smaller than what is observed experimentally. It also leads to a value of the bulk modulus of about 240 GPa, which is almost five times larger than the experimental value. On the other hand, the constrained LDA calculations provides a rather accurate value for the equilibrium volume and improves substantially the calculated bulk modulus, which now equals 96 GPa.

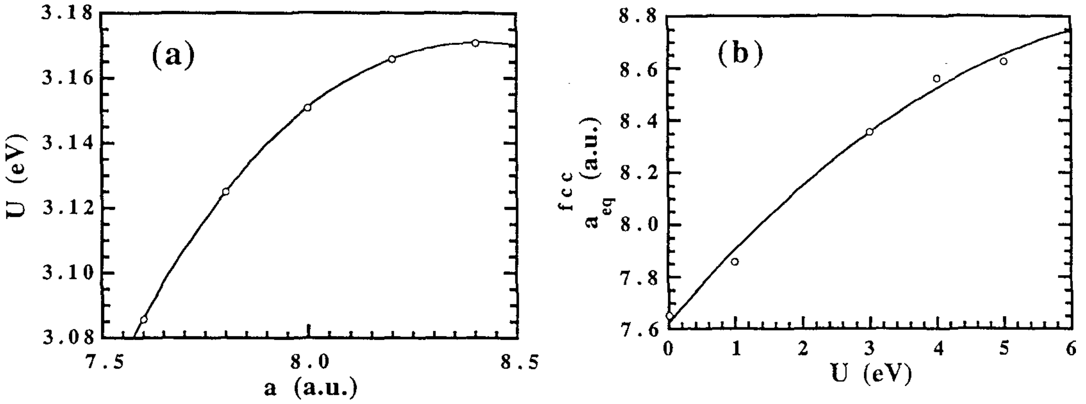

Figure 2. Variation of *U* with lattice parameter, panel (a), and equilibrium lattice constant as a function of *U* for fcc-based Pu.

Regarding the LDA+U results, the calculations give values for the equilibrium volume and the bulk modulus which are close to those of the constrained LDA. These calculations were performed by varying *U* for each lattice parameter according to the behavior exhibited in Fig. 2(a). Although the constrained LDA and the LDA+U results display an evident similarity the former correspond to a higher ground-state energy. Moreover, we note that the LDA+U results derive from a self-consistent treatment of the on-site Coulomb interaction between the *f*-electrons and are not a simple translation downward by *U* of the constrained LDA results.

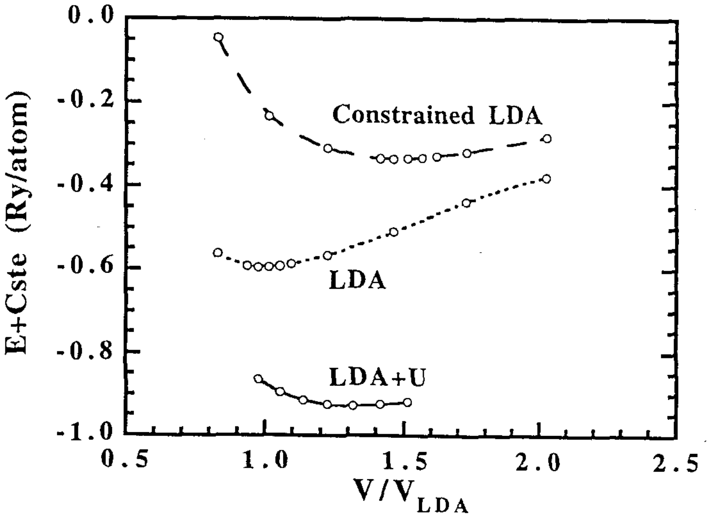

Figure 3. Total energy vs. normalized volume for fcc-based Pu calculated within the LDA (dotted line), the constrained LDA described in the text (dashed line), and the LDA+U scheme with varying *U* as explained in the text (solid line).

Finally, we report on calculations of the energetics of stoichiometric Pu-Ga alloys. To estimate the alloy mixing energies, we consider a hypothetical fcc-based Ga solid. Here, LDA calculations lead to an equilibrium lattice constant of 7.831 a.u. that is consistent with the equivalent lattice constants of 8.086 and 7. 805 a.u. one derives, respectively, from the two observed complex structures oC8 and tI2 (in Pearson notation) of Ga. In addition, the calculated bulk modulus of 58.2 GPa is consistent with the experimental fact that Ga is extremely soft with a melting point close to room temperature.

Calculated energies of mixing of Pu-Ga alloys for the three ordered structures, namely $L1_2$ of Cu_3Au type for Pu_3Ga and $PuGa_3$ and $L1_0$ of CuAu-I type for PuGa, are shown in Fig. 4. Here, the dotted curve corresponds to an LDA calculation, the dashed curve to the constrained LDA, and the solid curve to LDA+U. We note that the LDA results fail to explain the definite tendency toward phase formation and chemical order exhibited by this alloy system. On the contrary this tendency is clearly reflected in both the constrained LDA and the LDA+U results. These results will be used as a basis for further analysis of the stability and chemical ordering trends in Pu-Ga alloys.

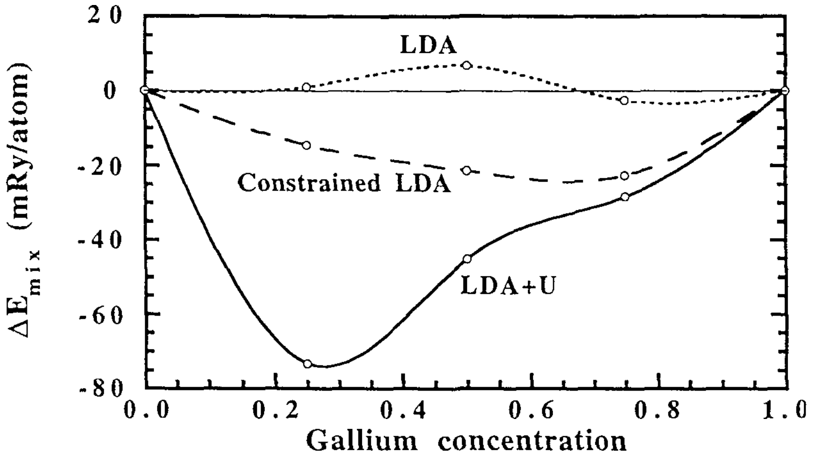

Figure 4. Energies of mixing of Pu-Ga alloys vs. Ga concentration at zero temperature within the LDA (dotted line), the constrained LDA described in the text (dashed line), and the LDA+U scheme with varying *U* as explained in the text (solid line).

CONCLUSIONS

The work briefly reported here represents an attempt to understand at the fundamental level the electronic origins of the equilibrium and phase stability properties of Pu and Pu-Ga alloys. As expected, the results clearly indicate that for systems in which electron-electron correlations are known to be important, the LDA fails to provide an accurate description of the electronic structure and related properties. Some improvement can derive from constrained LDA calculations and from the application of the LDA+U method. However, the former of these leads to an unacceptably large ground-state energy, while the phenomenological nature of the second precludes a fundamental understanding at the *ab initio* level. In addition, the LDA+U also leads to values of the linear coefficient of the electronic specific heat that are far from experimental values (although the calculations neglect such physical effects as electron-phonon coupling which may be playing an important role in these systems). Also, effects associated with possible magnetic behavior are neglected[23]. At the same time, the LDA+U calculations lend support to the long-held view that the properties of Pu and its alloys are closely tied to the behavior of its *f*-electrons. As already alluded to above, they further increase the motivation to search for a predictive theory of correlated-electron systems that properly describes not only spectroscopic properties but also energetics at equilibrium and phase stability properties.

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