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Electronic structure of δ-plutonium and of single Al, Ga, and Sc impurities in δ-plutonium

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Fully relativistic Korringa-Kohn-Rostoker calculations are reported for δ-Pu (fcc) at the experimentally observed δ-Pu and α-Pu densities. The calculated band structure at the δ density is compared with previous results. By using the Green's-function approach the density of states (DOS) and the partial local densities of states (PDOS) functions are presented for δ-Pu and for single impurities of Al, Ga, and Sc in δ-Pu. The effects of alloying and the stabilization of the δ phase are discussed in terms of the electronic structure of the host and the impurity PDOS functions. It is found that the impurity DOS functions below E_F are similar at the δ-Pu density indicating similar changes in the electronic structure of δ-Pu upon alloying with these three metals. The coupling between the impurity $p^{3/2}$ states and the Pu $f^{5/2}$ states, which cut through E_F, should yield diffuse f bands and no sharp Fermi surfaces for these materials. We speculate that the movement of these diffuse f bands relative to the s-d bands leads to less f bonding and the stability of the fcc phase.

I. INTRODUCTION

Plutonium metal has six different crystallographic allotropes from room temperature until it melts just above 600 °C. Its room-temperature α phase is monoclinic, which is the lowest-symmetry crystal structure of any pure element. Only its δ phase (fcc) possesses one of the traditional close-packed structures, but in plutonium this is the phase with the lowest density, including the liquid. Therefore, the δ phase most closely resembles a d-bonded transition metal because of an assumed minimum of f bonding. This multiplicity of phases has been associated with the fact that the f bonding in plutonium is on the edge of disappearing when the f electrons become localized.[1] Thus, the 17% volume decrease in going from δ-Pu to α-Pu has been argued on phenomenological grounds to result from turning on f bonding.

In spite of the differences in the properties of α- and δ-Pu, it is not difficult to retain the δ phase into the temperature range of α-Pu by alloying. The phase diagrams of *Pu*Al,[2] *Pu*Ga,[3] and *Pu*Sc,[4] show this clearly. The heuristic explanation has been that the highly directional f bonds that pull α-Pu into a dense, low-symmetry structure[5] are turned off by the presence of impurity atoms in the lattice. In fact, most lattice parameter effects due to impurities in α-Pu can be accounted for by assuming that each impurity atom causes four α-Pu size atoms to be converted to δ-Pu size atoms.[6] Then, at some concentration, the impurities finally cause the alloy to convert completely to δ-Pu. Once in the δ phase it is expected that there is a close correlation of the size of the impurity atom with lattice parameter changes in the alloy. This works in *Pu*Al and *Pu*Ga, but in *Pu*Sc the small Sc atom increases the lattice parameter. Thus, there are shortcomings in the phenomenological understanding of plutonium and its alloys. Heat-capacity measurements have been made of these materials to make available the electronic heat capacity coefficients for comparison to calculations,[7] but until the present work, there has been no attempt to compare an electronic structure calculation with the heuristic models or the heat-capacity results. To this end, the underlying assumption of this paper is that the stability of various phases of plutonium is controlled by changes in the electronic structure of the host upon alloying. Our second assumption (which seems to hold for transition-metal alloy systems) is that the local impurity density of states (DOS) is indicative of the DOS of the corresponding concentrated alloy system.[8]

Considering these facts we have determined the electronic structure of the δ phase of Pu at two lattice constants in terms of fully relativistic band calculations (Sec. III). Using these calculations we have constructed the DOS and partial local density of states (PDOS) functions for the pure metal. We have also calculated the local DOS functions for single impurities in the Pu host at the two lattice constants. The details of the calculations are outlined in Secs. II and III. The electronic changes that would occur upon compressing the pure metal (fcc) to the α-phase density are discussed in Sec. IV. The effects of the impurities are discussed (using muffin-tin impurity DOS functions, Sec. V) in terms of the host band structure and the local impurity DOS functions in the vicinity of the host Fermi energy (Sec. VI). A possible mechanism for the stabilization of the δ phase by "impurities" (alloying) is suggested.

II. METHOD OF CALCULATION

The fully relativistic Korringa-Kohn-Rostoker (KKR) method in the "constant energy mode" is applied to calculate the site-diagonal Green's function for Pu as a host. This method was used rather successfully for single impurities in Au and Pt;[8] the present application is an extension of this approach to f-electron systems. It should be noted that due to the O_h^* symmetry of the point lattice (double point-group symmetry) the site-diagonal scattering path operator[9,10] for an fcc lattice has 17 irreducible components. Six of these components correspond to off-diagonal elements of the site-diagonal scattering path operator, namely, the $\Gamma_8^+(d^{3/2}-d^{5/2})$, $\Gamma_8^-(f^{5/2}-f^{7/2})$, $\Gamma_7^-(f^{5/2}-f^{7/2})$, $\Gamma_6^-(p^{1/2}-f^{7/2})$, $\Gamma_8^-(p^{3/2}-f^{5/2})$, and $\Gamma_8^-(p^{3/2}-f^{7/2})$ "interactions."

The obvious advantage of the applied scheme is that the obtained results (site-diagonal Green's function) can be used to calculate quite a variety of physical properties. Since the method is on the same numerical footing as the fully relativistic KKR coherent-potential approximation (KKR-CPA) method,[9] which is presently being applied to concentrated $\mathrm{Pu}_x\mathrm{Al}_{1-x}$ alloys,[11] it is part of a uniform scheme to calculate the electronic structure of the pure metals, isolated impurities, and concentrated alloys.

Energy bands shown in this paper are calculated using the fully relativistic KKR method in the "constant **k** mode,"[12,13] since within this mode it is easier to apply **k**-dependent symmetrization. Formally, of course, both applied schemes are identical. The symmetrization corresponds to a labeling of quasiparticle eigenstates according to allowed irreducible representations of the double point group of the wave vector **k**.[14]

III. COMPUTATIONAL DETAILS

The electronic structure δ-Pu (fcc) was determined for two different lattice constants, namely, $a=8.249\,82$ a.u. and $a=8.761\,52$ a.u. The smaller lattice constant corresponds to a lattice spacing near the transition to α-Pu. The second value seems to cover the case of vanishing Al or Ga concentrations in *Pu*Al (Ref. 2) and *Pu*Ga (Ref. 3) (near the δ-phase density).

The applied potentials are obtained self-consistently in terms of the paramagnetic linear muffin-tin orbital (LMTO) method[15] using the mass-velocity term and the Darwin shift as relativistic corrections to the radial Schrödinger equation. The potentials for the impurities are obtained in exactly the same manner, however, they are shifted to equal Fermi energies with the corresponding Pu cases. In all cases, the Barth-Hedin local-density functional[16] is used. Within the LMTO method the frozen core approximation is applied, including for Pu the $6p^{1/2}$ and $6p^{3/2}$ atomic levels.[17]

For the calculation of the site-diagonal scattering path operator[8] the Brillouin-zone integration is carried out using five special directions[18] in the irreducible wedge of the Brillouin zone (BZ) and allowing a smallest increment of $|\mathbf{k}|$ along a particular direction of 10^{-4} $|k_{\mathrm{BZ}}|$ (where k_{BZ} refers to the BZ vector along this direction). This setup implies up to 3000 different values of **k** per energy. The energy is varied in steps of $0.01(4\pi^2/a^2)$ Ry throughout the whole valence region and in steps of $0.005(4\pi^2/a^2)$ Ry in the vicinity of the f band. The resulting DOS functions and the corresponding local spectral functions are folded with a Lorentzian of a half width corresponding to the applied energy increment used for the calculation of the site-diagonal scattering path operator (see also, the discussion in Ref. 8).

IV. ENERGY BANDS

Figures 1 and 2 show the energy bands for δ-Pu at $a=8.249\,82$ a.u. and 8.761 52 a.u., along the symmetry axes (100), (111), and (110). As one can see from these two figures, the differences in electronic structure between the two lattice constants are well pronounced. For $a=8.761\,52$ a.u., along (100) the bottom Δ_6 band (which is an s-like state at Γ and is d like at X) is separated from the "f"-band complex, whereas at the smaller lattice constant this band (which we will call an s-d band) penetrates considerably into the regime of f-like bands. The f bands

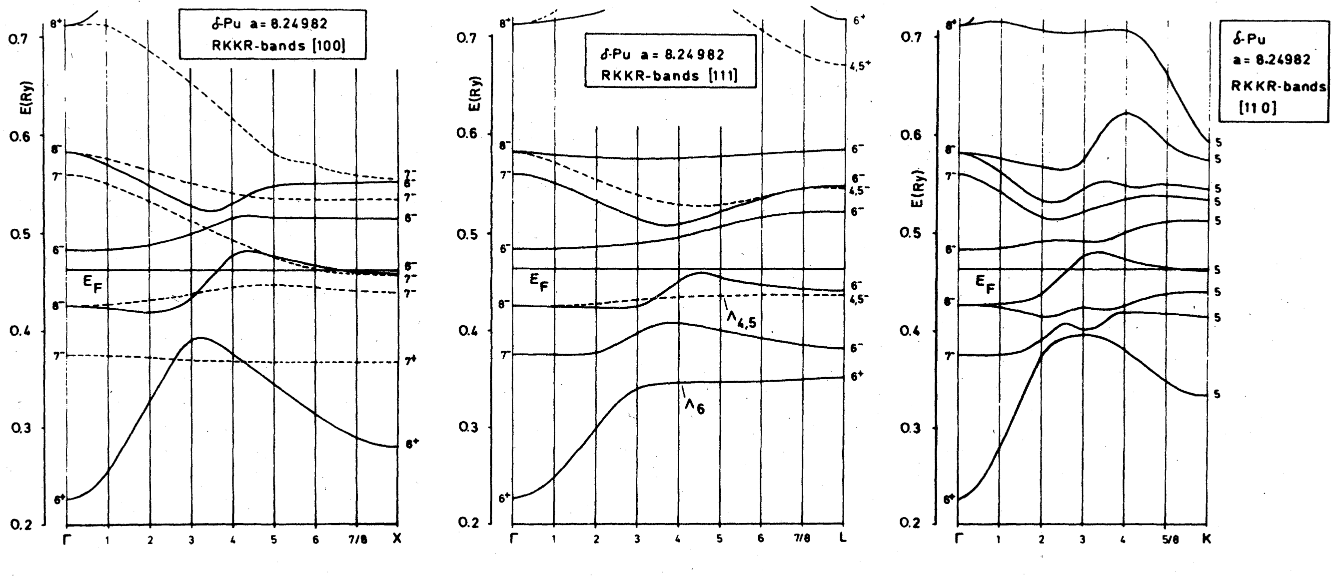

FIG. 1. Energy bands for δ-Pu at $a=8.249\,82$ a.u.: (a) (100), (b) (111), and (c) (110).

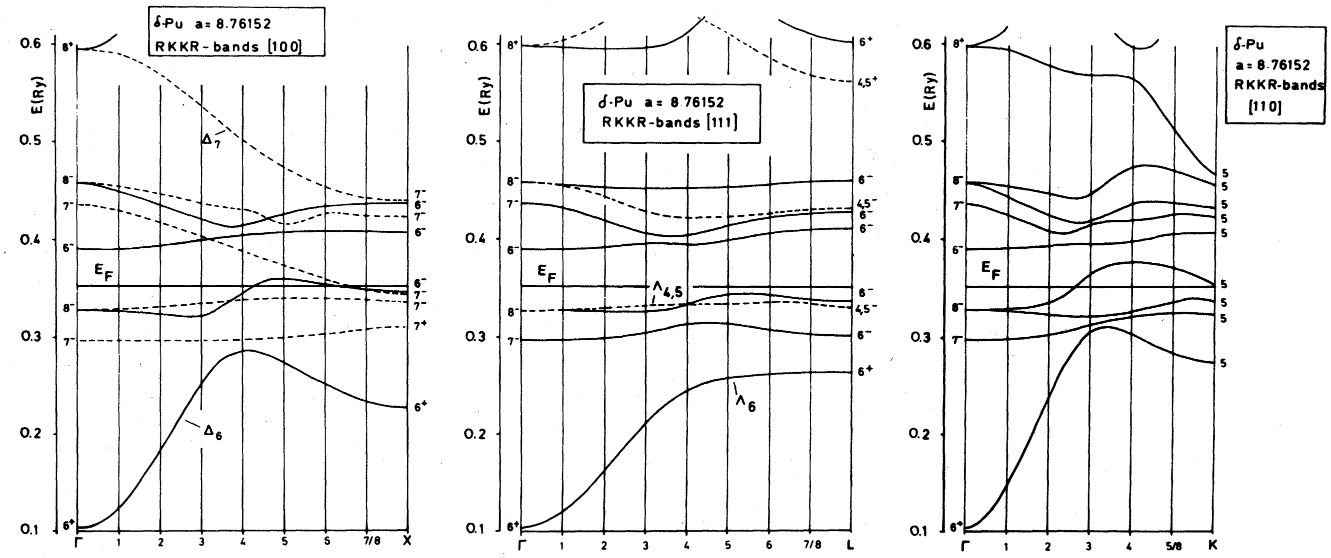

FIG. 2. Energy bands for δ-Pu at $a = 8.761\,52$ a.u.: (a) (100), (b) (111), and (c) (110).

(with Γ_7^- at the bottom and Γ_8^- at the top) are relatively flat, but show more dispersion at the smaller separation ($a = 8.249\,82$). From the semirelativistic LMTO and fully relativistic KKR calculations we determined that the nonrelativistic level ordering at Γ (bottom to top) is $\Gamma_2(\Gamma_7^-)$, $\Gamma_{15}(\Gamma_8^- + \Gamma_6^-)$, and $\Gamma_{25}(\Gamma_7^- + \Gamma_8^-)$. This means that the Γ_2 subband is the most occupied band at both lattice constants. (These states which have *xyz* symmetry are nonbonding in the fcc lattice.) The Γ_{15} states, which point toward second nearest neighbors in the fcc structure and are only weakly bonding, are cut by E_F and so change occupancy as the lattice constant is reduced. The Γ_{25} states, which are the most bonding of the *f* states in the fcc symmetry, only drop below E_F along the (100) direction. (Away from the Γ point these *f* states hybridize with *s*, *p*, and *d* states which leads to a more complicated bonding picture.) The highest band shown is the triply degenerate $\Gamma_{25}(\Gamma_8^+)$ *d* band. Therefore, along symmetry lines the most visible changes occur along the (100) direction where the *s*-*d* band (Δ_6) below the *f* bands interacts more strongly with the Γ_{15} states as the lattice spacing decreases. Interestingly, the interactions between the *d*-band (Δ_7) states above E_F and the *f* states is such that it pushes the Δ_7 component of the Γ_{25} state further below E_F (at the *X* point) at the expanded lattice spacing. At $a = 8.761\,52$ a.u. the width of the *f* band is 0.160 Ry (top Γ_8^- minus bottom Γ_7^- state), and at $a = 8.249\,82$ a.u., the "*f*"-band width is about 20% larger, namely, 0.207 Ry. The bands along (110) show all the complexity of bands along a general direction, because along Γ-*K* there is only one allowed irreducible representation (Σ_5) of the double point group of the wave vector **k**. In particular, for $a = 8.249\,82$ a.u., one can see how the penetration of the *s*-*d* band into the *f*-band complex is "damped" by the double group compatibility relations. From Figs. 1 and 2 it is evident that the density of states will have sharp features since some of the bands show very little dispersion. The only previous work to which we can compare our results are the non-self-consistent results of Freeman and Koelling.[19] While there is some resemblance of our results to their $\alpha = 1$ case, we find that the *f* bands have much less dispersion in our self-consistent field calculations.

V. DENSITY OF STATES AND IMPURITY DENSITIES OF STATES

In Fig. 3 the *d*- and *f*-like partial local densities of states are shown for δ-Pu at both lattice spacings. First, although the *d*-like phase shifts in the energy range shown in Figs. 1 and 2 are very broad indicating almost free-electron-like behavior, it is seen that due to the strong hybridization with the *f* bands the *d* PDOS have the same sharp features exhibited by the *f* bands. Of course, as expected, the PDOS functions at the larger lattice constant show the sharper features of flat bands. It is also seen that the $d^{3/2}$- and $d^{5/2}$-like PDOS are of comparable strength below E_F, whereas for the *f* bands the $f^{5/2}$-like PDOS are mainly below E_F, while $f^{7/2}$-like states are mainly above E_F. At the larger lattice constant there is very little *d* or *f* character in the lower part of the *s*-*d* band (starting at Γ_6^+), whereas there is *f* and *d* character in this part of the *s*-*d* band at the smaller lattice spacing.

For both lattice constants, the value of the total DOS at the Fermi energy is high, namely, 122.04 and 123.26 states/Ry for $a = 8.249\,82$ a.u. and 8.761 52 a.u., respectively. From Fig. 3 one can see that for $a = 8.761\,52$ a.u. the peak at the Fermi energy is much sharper than for $a = 8.249\,82$ a.u., which implies that the value of the DOS at the Fermi energy is numerically less reliable than in the other case. Experimentally it is found[7] that the linear coefficient of the specific heat, γ, is 25.0 ± 1.0 mJ/g atom K^2 for α-Pu, whereas for δ-Pu a γ value extrapolated from alloys would be 53 ± 10 mJ/g atom K^2. The theoretically calculated γ values (about 21 mJ/mole K^2)

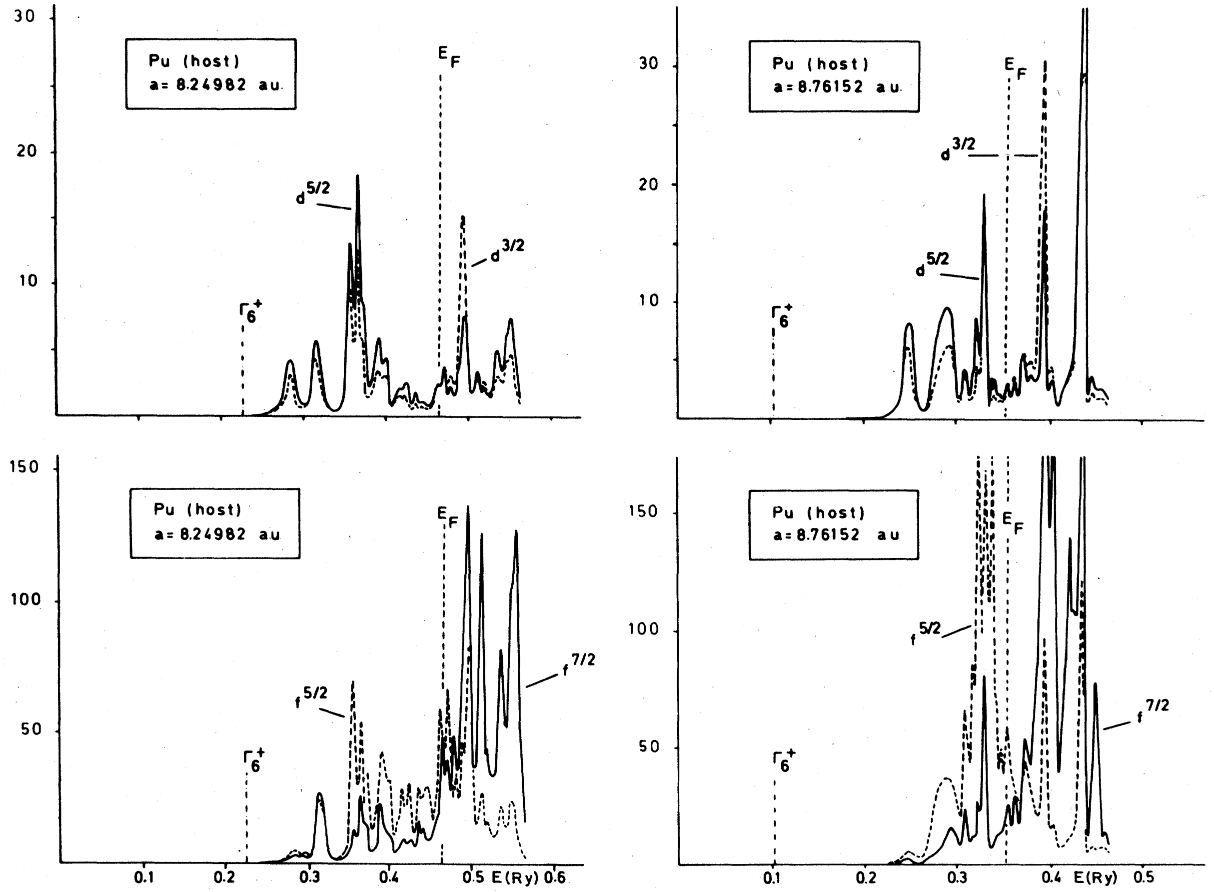

FIG. 3. $d^{3/2}$-, $d^{5/2}$-, $f^{5/2}$-, and $f^{7/2}$-like partial local densities of states for the host metals: (a) δ-Pu at $a=8.249\,82$ a.u. and (b) δ-Pu at $a=8.761\,52$ a.u.

seem more consistent with the value for α-Pu. Of course, these calculations do not allow for many-body effects that are expected to raise γ from a bare DOS value.

In Fig. 4 the DOS function for δ-Pu is displayed together with the impurity DOS functions for Al, Ga, and Sc in the corresponding hosts. In this figure the host DOS is calculated by integrating the configurational space representative of the site-diagonal Green's function over the Wigner-Seitz cell, whereas the impurity DOS is confined to an integration over the "muffin-tin" sphere, i.e., a muffin-tin density of states.[8,9] Because the impurity DOS cannot be used for a quantitative description of the electronic structure of dilute alloys[8] and because the Friedel sum rule is never fulfilled for single impurities in the Fermi sea of the host, a muffin-tin DOS is sufficient for the present purposes.

First, looking at the impurity DOS functions at the larger lattice spacing it is seen that in the energy region of the host f bands (above about 0.3 Ry) the impurity DOS reflect the sharp features of the host DOS. It is also seen that all three impurity DOS functions are similar below E_F and have considerable intensity below the hybridiza-

TABLE I. Partial local impurity densities of states at the Fermi energy.

Host		$s^{1/2}$	$p^{1/2}$	$n(E_F)$ $p^{3/2}$	$d^{3/2}$	$d^{5/2}$
Pu, $a=8.249\,82$ a.u.	Al	0.4120	0.8314	1.6005	1.5960	3.8304
	Ga	0.3047	0.5712	1.6139	0.8378	2.3060
	Sc	0.3094	0.1884	0.2428	6.6752	7.1859
Pu, $a=8.761\,52$ a.u.	Al	0.4254	0.3122	1.8671	0.9419	2.1095
	Ga	0.2431	0.2751	1.8583	0.9479	1.8365
	Sc	0.1309	0.1355	0.2912	1.7582	3.1508

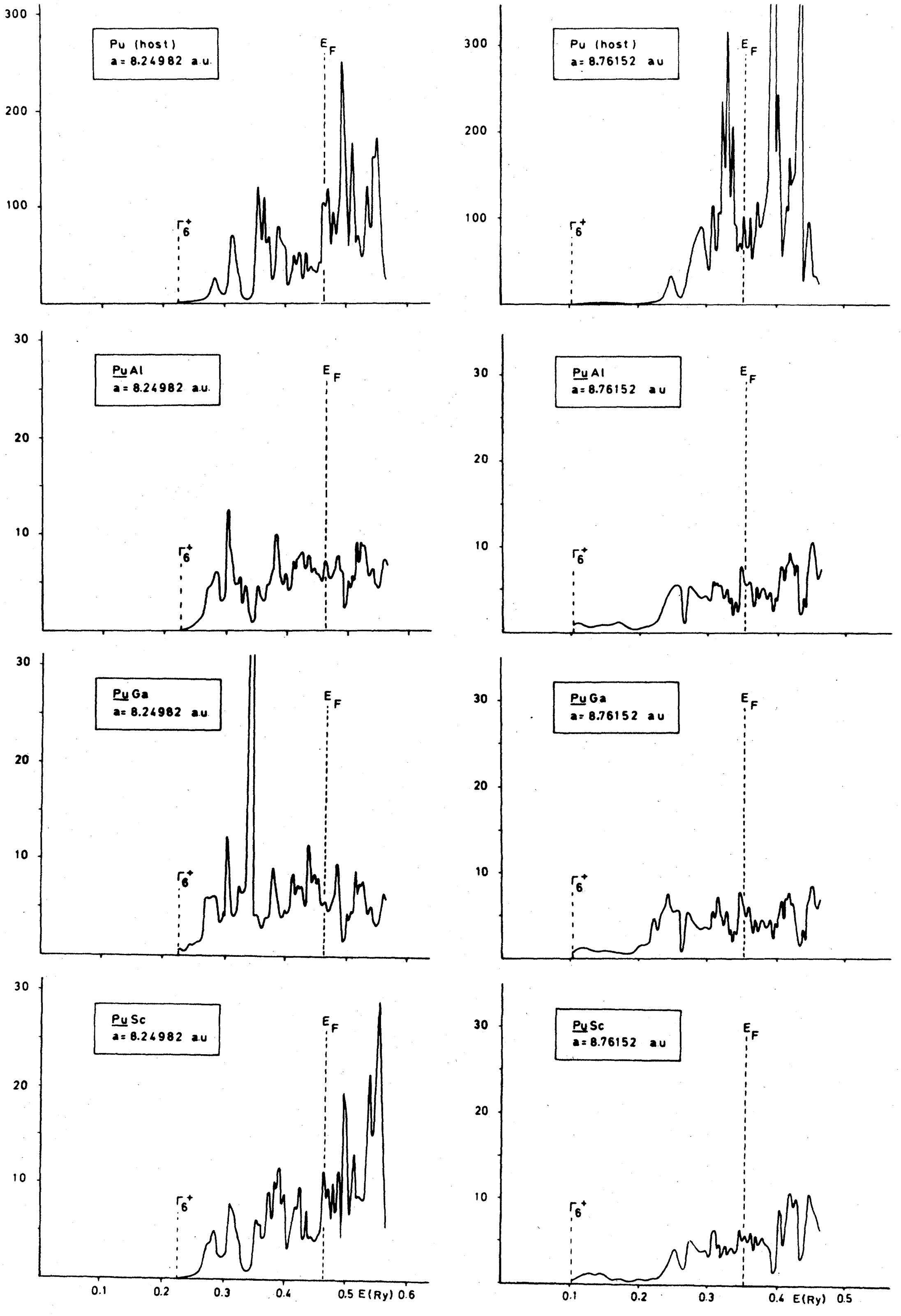

FIG. 4. Density of states for δ-Pu and impurity density of states in (a) δ-Pu at $a = 8.249\,82$ a.u. and (b) δ-Pu at $a = 8.761\,52$ a.u.

tion or backscattering region (below 0.3 Ry). The intensity in this region is mostly of *s* and *p* character. At the smaller lattice spacing, the impurity DOS are quite a bit different and show a lot of structure below the backscattering region (below 0.30 Ry).

To analyze the muffin-tin DOS at the Fermi energy for the impurities in more detail the corresponding partial local densities of states are given in Table I. From this table one can see that for Al and Ga the impurity density of states at the Fermi energy has considerable $p^{1/2}$ and $p^{3/2}$ character. For Sc the contributions from these two channels are rather small. In all three impurity cases the *d*-like character is predominant. The *d*-like character for Al and Ga may be just the reexpansion of Pu orbitals about the impurity, while for Sc, part of this *d*-like character is due to *d* states in Sc.

VI. DISCUSSION

From band-structure calculations on transition metals in which the partial pressures (for each *l* value) have been obtained, it is known that the *s*- and *p*-band states contribute a repulsive pressure near equilibrium density, whereas the *d* contribution is attractive in this region.[20] The band calculations on the actinide metals indicate a more complicated picture. In Fig. 5 the partial pressure curves for δ-Pu as a function of volume (Wigner-Seitz radius) are shown.[21] As can be seen there is a delicate balance between the attractive *f* partial pressure and the negative *s* and *p* pressure near equilibrium. These results indicate that any increase of the *s*, *p*, and *d* occupancy would lead to an expanded lattice. From Fig. 4 it is seen that all of the impurities add states (mostly of *s* and *p* character) below E_F. From Table I it is also seen that Sc has some *d* states near E_F. If, as more impurity atoms are added to the system there is an increase in the number of *s*, *p*, and *d* electrons in the system, then from Fig. 5 this would yield repulsive terms to the bonding. This suppression of *f* bonding, which leads to noncubic structures, would allow the crystal to maintain its cubic structure.

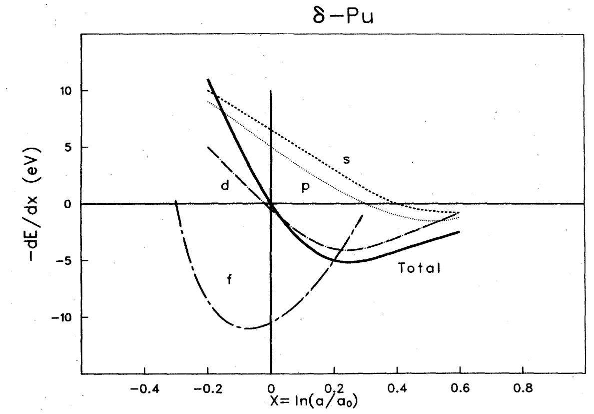

FIG. 5. Partial pressure curves for fcc Pu. The a_0 is the calculated equilibrium lattice constant. At $x=0.25$ the *f* band becomes so narrow that it is treated as localized states beyond that point with no contribution to the total pressure. Also the calculated values at less than $x=-0.2$ are not very accurate because the frozen core approximation was used. The values between -0.2 and 0.25, however, represent the one-electron bonding picture of this material.

One can consider the *f*-band dispersion as due to both direct *f*-*f* overlap between sites and the mixing of *f* states with states of different angular momentum character (hybridization). In general, one cannot separate these two effects. However, one can say that the positions of the other bands relative to the *f* bands do reflect the degree of hybridization, i.e., the nearer the other bands, the larger the hybridization. As Al or Ga impurities are added, there is a contraction of the lattice and an increase in the *f*-*f* overlap and an increase in the *f*-band dispersion. For Sc the lattice expands as impurities are added leading to less *f*-band dispersion. Since the Sc atoms are smaller than the Pu atoms this expansion must be due to the breaking of *f* bonds. For Al and Ga, the contraction does not lead to a breaking of the cubic symmetry again due to suppression of *f* bonding. Therefore, we conclude that the size of the impurities (which effects the *f*-*f* overlap) is not as important as the electronic structure of the impurities (which effects the hybridization of the *f* bands).

The details of the "alloying" (impurities) effects on the host electronic structure should be as follows. From the impurity DOS functions (Fig. 4) and Table I it is seen that there are impurity states (of *s* and *p* character) in the energy region of the *s*-*d* band and impurity states of *p*- and *d*-like character near the Fermi energy (E_F). From similar calculations in transition-metal alloys we would expect low-lying states to keep the *s*-*d* band at low energies (relative to E_F) and increase the number of *s*, *p*, and *d* states below E_F. Unlike *d*-band alloys, such as $\mathrm{Au}_x\mathrm{Ni}_{1-x}$ (Ref. 22) or $\mathrm{Au}_x\mathrm{Pt}_{1-x}$ (Ref. 23), in which the bands far from E_F remain sharp, here there is coupling between the impurity states and all of the host bands. Because of the strong host *d*-*f* hybridization (Fig. 3) and the fact that the impurity *p* states couple to the host *f* bands indicates that most of host bands should become diffuse and these materials will not have sharp Fermi surfaces. Normally in transition-metal alloys the sharp bands maintain their position relative to E_F while the diffuse bands show movement relative to the E_F of the host structure. Here, all of the bands should move relative to E_F of the host. However, *s*-*d* bands should not become as diffuse as the *f* bands or the *d* bands that hybridize with them because they can only couple weakly to the impurity *p* states. Therefore, the movement of the diffuse bands above the *s*-*d* band should be such as to move the *f* bands up relative to E_F and decrease the number of *f* electrons in the system. From the arguments given above these changes in the electronic structure should stabilize the fcc phase.

A quantitative comparison of these effects can only be given by actually performing KKR-CPA[9] calculations with varying concentrations of the alloy component and calculating the electronic structure and Fermi surface. For the present, it seems sufficient to indicate the nature of the changes in electronic structure by which the δ phase of Pu may be stabilized when alloyed and to stress that, in general, it is not simply the value of the DOS at the Fermi energy which must be increased in order to stabilize the δ phase. This paper must be considered as a first step towards a theory of the electronic structure of Pu alloys, in particular, and actinide alloys, in general. Calculations for the concentrated alloys are in progress.[11] Much data can already be extracted from the calculated results, including, for example, spin-lattice relaxation times for NMR or x-ray emission intensities.[9,24] Some of these quantities will be discussed in the context of the concentrated alloys.[11]

Future theoretical goals will be an improvement of the Brillouin-zone integrations by using more special directions and by attempting to avoid using the LMTO method for generating potentials to implement a self-consistent scheme based on the properties of the site-diagonal Green's function. By means of such a scheme, the solution of the Dirac equation in the presence of an internal or external field can be envisaged. However, just as this paper is only a first theoretical step, experiments are needed. Fermi surface properties have to be measured and angle-resolved photoemission and isochromat spectroscopy have to follow. Studies as in this paper can only point out problems, such as the effects of impurities on the electronic structure of δ-Pu. In the end, all comparisons to experiment have to be done in their proper theoretical framework.

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