PHYSICAL REVIEW B, VOLUME 64, 235112

Theory of the electronic structure of the alloys of the actinides

Walter A. Harrison
Los Alamos National Laboratory, T1, MS B221, Los Alamos, New Mexico 87545
and Department of Applied Physics, LAM/McCullough Bldg., Stanford, California 94305-4045

(Received 19 March 2001; revised manuscript received 22 June 2001; published 28 November 2001)

An earlier theory of the electronic structure of the actinides is improved, generalized to alloys of actinides, and applied to plutonium and its alloys with other trivalent metals. The theory combines the s and d electrons as free electrons, treating them to second order in an empty-core pseudopotential. The f levels produce bands in this theory, which are actually broadened by electron correlations, but their role in the bonding is decreased. The effects both of the coupling between neighboring f shells and of the correlation are included in a second moment in terms of which the total energy is estimated using a Friedel model. This allows all contributions to be rewritten in terms of near-neighbor interactions and on-site terms. It is found that f-shell contribution alone favors a much smaller spacing than the free-electron contribution alone, and the competition makes the resulting structure very sensitive to the parameters of the theory. Adjustment of the parameters seems essential. An f-shell radius is adjusted, within the range of previous estimates, so that the minimum in the f-shell contributions for plutonium comes at a spacing of 2.5 Å, and the total is scaled back such that the minimum is of the same depth. The same scaling factors are applied to other actinides. Then the pseudopotential core radius is adjusted for each actinide and trivalent simple metal in the face-centered-cubic structure to yield the observed atomic volume (that for the delta structure in the case of plutonium). The resulting electronic structure is tested successfully by using it to predict the bulk modulus of all of these metals. Using the same parameters for plutonium, the energy is calculated in the α structure, found to have higher energy than the fcc structure at the atomic volume of δ plutonium, but lower energy at a reduced volume, near that of the observed low-temperature α structure. The same formulas and parameters are applicable to random alloys of any of these metals, evaluating each term in an alloy of x atomic fraction of B in A with the appropriate weighting of x, $x(1-x)$, or $(1-x)^2$. This does not predict correct variations with concentration x of the lattice spacings unless we introduce the interaction between simple-metal core d states and actinide valence d states, absent in the pure materials. A moderate scaling of previously predicted d-state radii brings the dilute-alloy spacings into accord with experiment for plutonium alloys with gallium, indium, and thallium. Aluminum, without core d states, was initially in accord and is not affected. The ordered alloys, Pu_3Ga, Pu_3In, and Pu_3Al, are found to have larger spacings than the random alloys, in accord with experiment, though Pu_3Al is not found to be the stable structure. For alloys of two actinides, or with rare earths, the effects of d-state couplings are expected to be negligible, but additional terms in the f-state energy arise from the contribution of f levels of different energy to the global f bands. With this effect included, cerium, americium, and curium are found to increase the spacing of δ plutonium, in accord with experiment, but the lighter actinides, as well as the type-B simple metals, Al, Ga, In, and Tl decrease the spacing, also in accord with experiment. Alloys with the type A metals Sc, Y, and La are found to increase the spacing. Initial studies of the displacement of plutonium neighbors to substituted gallium atoms showed α-like reconstructions, as in pure plutonium.

DOI: 10.1103/PhysRevB.64.235112 PACS number(s): 71.20.−b

I. TOTAL ENERGY OF ELEMENTAL ACTINIDES

We have given[1,2] a simple theory of the electronic structure of actinide metals. It was similar to the theory for transition metals given in both references. For transition metals it was generalized to alloys, following the approach of Pettifor[3,4] in order to estimate heats of solution. We now generalize the theory of the actinides to alloys in a way which provides a much wider range of applications. This involved including the effects of the pseudopotential to second order, rather than to first as in the theory of transition metals. We also rewrite the theory in terms of near-neighbor interactions, rather than in an atomic-sphere approximation. We retain the effects of electron correlations, which are important for actinides but could be, and were, omitted for transition metals. These correlations were included by a generalization of an exact solution of a two-level problem to the case of f-shell bands (Ref. 1, 598 ff, Ref. 2, 67ff). We describe the theory for all of the actinides and a series of other trivalent metals in order to have parameters for alloys of all of these, but we consider plutonium in detail as the most interesting material, and the metal for which the properties of the alloys have been discussed quite completely by Hecker.[5] When we discuss the alloys of actinides with gallium and indium we find it necessary to include also the effects of coupling between the core d states on these simple metals and the valence d states on actinides. No such core d states arise for aluminum.

In this theory the actinides are regarded as having three electrons per atom in free-electron-like states, and the effects of the remaining electrons, in f states, were treated separately. As pure elements the energy per atom, or ion, was given by Eq. (16-26) in Ref. 1. That equation for the total energy per ion contains two contributions $E_{\text{tot}}/\text{ion}=E_{sd}$

©2001 The American Physical Society

$+E_{ff}$, with E_{ff} being the contribution from the *f*-like bands, of bandwidth W_f, but with their effect reduced by electron correlations represented by a Coulomb interaction U_f,

$$E_{ff}=-\frac{Z_f(1-Z_f/14)}{2}\left(\sqrt{W_f{}^2+U_f{}^2}-U_f\right)+816Z_f\frac{\hbar^2 r_f{}^{10}}{m r_0{}^{12}}. \tag{1}$$

E_{sd} is the energy of a free-electron-like metal, in this case arising from *s* and *d* states on the atom. We now take them to be given by [Ref. 1, Eq. (14-12), Ref. 2, Eq. (1-15)]

$$E_{sd}=Z\left(\frac{3\hbar^2k_F{}^2}{10m}-\frac{3e^2k_F}{4\pi}+\frac{2e^2k_F{}^3}{4\pi\kappa^2}(\kappa^2r_c{}^2-1)\right)$$
$$-\frac{Z^2e^2\kappa}{2}\cosh(\kappa r_c)e^{-\kappa r_c}+\frac{1}{2}\Sigma_{j\neq i}V(\mathbf{r_i}-\mathbf{r_j}) \tag{2}$$

for a metal of valence Z, 3 in the cases we treat here, and Fermi wave number k_F, related to the atomic sphere radius r_0 by $k_F{}^3=9\pi Z/(4r_0{}^3)$. The earlier treatment of actinides in Ref. 1 used a simple-metal energy of only first order in the empty-core pseudopotential [Ref. 1, Eq. (13-18)] rather than this form which is of second order in that pseudopotential. This was suggested by the fact that in Ref. 1 predictions such as the bulk modulus of the simple metals (arising in the cases of Al, Ga, In, and Tl from *s* and *p* electrons, rather than *s* and *d* electrons) were much improved if the energy was calculated to second order.

The first line of Eq. (2) depends upon atomic arrangements only through the total volume. The first term is the electronic kinetic energy per atom; the second is the exchange energy per atom. The third term comes from the pseudopotential and is proportional to the square of the empty-core pseudopotential radius r_c. Values for this radius can be obtained from the *s*-state term value (Ref. 1, p. 481), from the third ionization potential of a trivalent metal (Ref. 6, p. 380), or from computed pseudopotential form factors (Ref. 6, p. 361), and vary between 0.45 and 0.86 Å for trivalent metals (Ref. 6, the Solid-State Table), including actinides and rare earths. Here it will be preferable to adjust them, once we have decided on approximations for other terms in the energy, so that the calculated energy is minimum at the observed spacing. Then the exact value in each calculation will depend upon which approximation is being made. It will be gratifying to find that this adjustment always leaves them in the same range.

The remaining terms include the Madelung energy and effects of the screened pseudopotential. Screening was based upon the Fermi-Thomas theory, with the Fermi-Thomas screening parameter given by

$$\kappa^2=\frac{4e^2k_Fm}{\pi\hbar^2}. \tag{3}$$

The final sum in Eq. (2) is over the screened interatomic interaction given by

$$V(r)=\frac{Z^2e^2\cosh^2\kappa r_c e^{-\kappa r}}{r}. \tag{4}$$

Except for this sum, the simple-metal energy E_{sd} of Eq. (2) depends upon the total volume, through k_F, but is otherwise independent of the atomic positions.

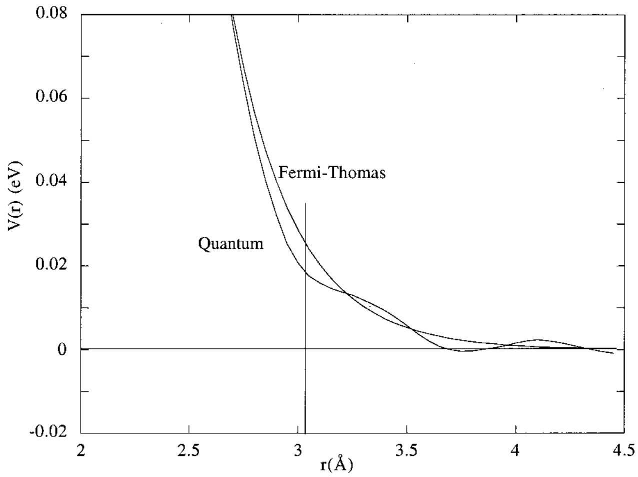

FIG. 1. The screened interatomic interaction for gallium, calculated with Fermi-Thomas screening, and given in Eq. (4), and with a full quantum calculation based upon the same empty-core pseudopotential. The nearest-neighbor distance is indicated by the vertical line, and will fall in the same point relative to the oscillations in all trivalent metals.

It is not difficult to use a full quantum calculation to second order in the pseudopotential which has the effect of adding Friedel oscillations to Eq. (4), as shown in Fig. 1. We explored the consequences of doing this in detail by returning to the second-order perturbation theory from which Eq. (4) was derived. This came in the form of a sum in wave-number space of an energy wave-number characteristic $F(q)$ (Ref. 1, p. 484), which could be written in full quantum form (as in the Lindhard dielectric function) or the Fermi-Thomas form. The sum of the difference over the wave-number lattice was then the quantum correction to Fermi-Thomas theory. It gave a significant contribution to the energy, varying in volume in a way comparable to the sum over the interactions of Eq. (4), and depended weakly on distortions of a face-centered-cubic lattice, but seemed not essential to the problems we address here and we dropped it in the end. We in fact will in the end reduce all sums over neighbors to very few, usually just nearest neighbors, in order to simplify the calculations, allow more accurate inclusion of distortions, and to assist in interpreting the results. The nearest-neighbor distance is indicated in Fig. 1 and suggests that a small shift in core radius might give quite similar results to use of full quantum screening.

The sum of the quantum form over distant neighbors was somewhat slowly converging, particularly in comparison to the Fermi-Thomas form, requiring more than 300 terms in the sum over lattice wave numbers, so considerable simplification is provided by this approximation. The simple form, Eq. (4), gives a stable fcc structure, without the tetragonal distortion appropriate for indium, or an instability that would suggest a gallium structure (whether using all neighbors, or only nearest neighbors). The quantum corrections to the

TABLE I. Preliminary parameters for the actinides and other trivalent metals. $Z_f = Z-3$ is the number of f electrons per atom. r_f values were obtained from two different sources, to be discussed. U_f was based upon experimental values from Brewer (Ref. 10).

	Z_f	r_0 (Å)	r_f (Å)		U_f (eV)
			Straub[a]	Skriver[b]	
Sc	0	1.80	0		
Y	0	1.98	0		
La	0	2.08	0		
Ce	1	2.02	0.46		7.2
Ac	0	2.10		1.11	3.00
Th	1	1.99		0.87	3.20
Pa	2	1.80	0.877	0.70	3.35
U	3	1.69	0.836	0.64	4.09
Np	4	1.66	0.814	0.60	3.90
Pu	5	1.81[c]	0.791	0.58	4.61
Am	6	1.91	0.787	0.58	4.96
Cm	7	2.03	0.773	0.61	5.10
Al	0	1.58	0		
Ga	0	1.67	0		
In	0	1.84	0		
Tl	0	1.89	0		

[a] Calculated with the atomic surface method by Straub (Ref. 8).

[b] Based upon LMTO band widths from Skriver (Ref. 9).

[c] $r_0 = 1.68$ Å for α-Pu.

screened empty-core pseudopotential do not rectify this for parameters appropriate to these metals, so nonlocal terms in the pseudopotential, and/or terms beyond second-order perturbation theory are necessary to obtain these structures for the simple metals. This point and these features have been thoroughly discussed by Hafner,[7] who also pointed out that the effects of the quantum screening are not nearly so small in the monovalent and divalent metals as they are in the trivalent metals illustrated in Fig. 1. For learning the essential features of the actinides it seems preferabe to use the much simpler Fermi-Thomas theory. Probably the most important missing ingredients from Eq. (2) are the effects of core d states in the simple sp metals. They must ultimately be responsible for the complex structures of the simple metals which have core d states[7] and we shall in fact need to include their coupling with the actinide valence d states when we treat alloys in Sec. III.

Equation (1) gives the contribution to the energy of the Z_f f electrons, which are treated separately. The first term comes from the partially filled f bands, with a band width (Ref. 1, p. 603)

$$W_f = 181 \frac{\hbar^2 r_f^{\,5}}{m r_0^{\,7}} \tag{5}$$

obtained from a second moment of the bands. Values for the f-state radii r_f based upon Straub's atomic-surface-method calculations[8] and upon Skriver's linear muffin-tin orbital (LMTO) calculations[9] will be listed in Table I. A number Z_f of f electrons (less than or equal to 14 per atom), placed in the lowest levels for a constant density of states, $14/W_f$ over the energy range $\pm W_f/2$, has an energy per atom $-Z_f(1-Z_f/14)W_f/2$. The form given in Eq. (1) incorporates the effects of the Coulomb repulsion U_f, also in Table I, which is the extra repulsion within the f shells, relative to that between an f and an s electron on the same atom. The final term in Eq. (1) is from repulsion between nearest-neighbor shells, arising from nonorthogonality of neighboring f states and evaluated for 12 nearest neighbors as in a face-centered-cubic structure. It is written in terms of r_0, the atomic sphere radius, related to the nearest-neighbor spacing d in the face-centered-cubic structure assumed by $4\pi r_0^{\,3}/3 = (\sqrt{2}d)^3/4$ (with $d\sqrt{2}$ being the edge of the face-centered cube of four atoms) or

$$d = \left(\frac{4\sqrt{2}\pi}{3}\right)^{1/3} r_0 \approx 1.809 \;\; r_0 \tag{6}$$

for face-centered-cubic, or hexagonal close-packed, structures.

For our studies here it will be convenient to rewrite a number of these contributions in terms of sums over neighbors. The final term in Eq. (1) was initially derived in Ref. 1 in terms of neighbor distances as $83\,780\, Z_f \Sigma_j \hbar^2 r_f^{\,10}/(m d_{ij}^{\,12})$ [Eq. (16-15) of Ref. 1. Then replacing the sum over nearest neighbors j by a factor of 12 for close-packed structures, using the exact form in Eq. (6) to convert d to r_0, and rounding 816.4 to 816 gave the final form which we quoted as the last term in Eq. (1) here.] The final sum in Eq. (2) is already in terms if distances, with neighbor distances $|\mathbf{r}_i - \mathbf{r}_j|$ written d_{ij}. The terms preceding this sum in Eq. (2) depend only upon total volume and can be evaluated directly in terms of the free-electron Fermi wave number, given above as

$$k_F = 3(\pi/4)^{1/3}/r_0 = 2.768/r_0 \tag{7}$$

for our systems with $Z=3$ free electrons per atom.

Similarly we may write the bandwidth W_f in terms of a sum over neighbors since Eq. (5) was obtained by equating the second moment of a square distribution of width W_f, which is $W_f^{\,2}/12$, to the second moment obtained as a sum over the squared couplings of the seven f orbitals (numbered by i) on one atom to the f orbitals on its 12 nearest neighbors, $(1/7)\Sigma_{i,j} V_{ij}^{\,2}(d_{ij})$. Thus we may square both sides of Eq. (5), and rewrite the result in terms of the nearest-neighbor distance using Eq. (6). We then replace $1/d^{14}$ by a sum over neighbors $(1/12)\Sigma_j\, 1/d_{ij}^{\,14}$ and take the square root to obtain

$$\begin{aligned} W_f &= 181(1.809^7)\frac{\hbar^2 r_f^{\,5}}{m}\sqrt{\frac{1}{12}\sum_j \frac{1}{d_{ij}^{\,14}}} \\ &= 3318\frac{\hbar^2 r_f^{\,5}}{m}\sqrt{\sum_j \frac{1}{d_{ij}^{\,14}}}. \end{aligned} \tag{8}$$

With these rewritings, Eqs. (1) and (2) can be combined to become

$$\frac{E_{\rm tot}}{\rm ion}=3\left(\frac{3\hbar^2{k_F}^2}{10m}-\frac{3e^2k_F}{4\pi}+\frac{2e^2{k_F}^3}{3\pi\kappa^2}(\kappa^2{r_c}^2-1)\right)$$
$$-\frac{Z^2e^2\kappa}{2}\cosh(\kappa r_c)e^{-\kappa r_c}+\frac{1}{2}\Sigma_{j\neq i}V(d_{ij})$$
$$-S_f\frac{Z_f(1-Z_f/14)}{2}(\sqrt{{W_f}^2+{U_f}^2}-U_f)$$
$$+S_f 83\,780 Z_f\Sigma_{j\neq i}\frac{\hbar^2{r_f}^{10}}{m{d_{ij}}^{12}}. \qquad (9)$$

The first line depends only upon volume. The remaining lines contain sums over neighbors, in the expression for ${W_f}^2$ obtained from Eq. (8) as well as in the first and last explicit sums. S_f is a scale factor which will be discussed and taken equal to 0.15 in the following section. With Eqs. (3), (4), (6), (7), and (8), this is essentially a computer program for computation of the structural-dependent energy of the actinide, or simple metal.

By specifying the atomic positions determining the d_{ij} we might think that it is a zero-temperature theory but of course we can use it to calculate the vibration spectrum, and therefore the corresponding entropy at any temperature, and it could even be used to obtain the forces for molecular dynamics.

This will be a good starting point for the generalization of the theory to alloys and to various structures. For close-packed structures and nearest neighbors only the sums over j become a factor of 12 with the d_{ij} replaced by the nearest-neighbor distance. Before proceeding to alloys we should make an application to the pure actinides, which will make it clear that some adjustment of parameters is needed.

II. STRUCTURAL STABILITY OF PLUTONIUM

For any given atomic-sphere radius r we may obtain k_F from Eq. (7), and κ from Eq. (3) as well as d for a close-packed structure from Eq. (6) and evaluate the energy from Eq. (9). We have given two sets of values for r_f and one for U_f for each actinide in Table I, and we now consider plutonium. The difference in the two r_f values is really quite large, since it enters the bandwidth of Eq. (8) as the fifth power. Thus the two predicted W_f values differ by a factor of nearly 5. If we select the smaller of the two values, $r_f = 0.58$ Å, and adjust r_c such that the minimum in that energy occurs at the observed atomic volume, which we do for the fcc structure for which the observed atomic-sphere radius is $r_0 = 1.81$ Å, we obtain $r_c = 0.518$ Å. The resulting energy as a function of nearest-neighbor distance, $d = 1.809r$, is shown in Fig. 2 as the curve labeled $r_f = 0.58$ Å.

The essential feature was noted already in Ref. 1, that though we have indeed fit a minimum at $d = 1.809 \times 1.81 = 3.275$ Å, a second minimum occurs at smaller spacing. This is because the E_{sd} by itself has a minimum near the larger spacing, but E_{ff} has a minimum near the smaller spacing and the sum has two minima. Further, the two energies very nearly cancel each other over this entire region leaving the quite flat $E(d)$ seen there. We believe that *this cancellation is responsible for the complex structural properties of plutonium, and the other light actinides*, and that is the essence of the understanding of them which we present here. At the same time, the cancellation of these two large energies for which we have only approximate descriptions means that we cannot reliably predict the properties. Our description and parameters have in fact indicated an equilibrium spacing at approximately $d = 2.2$ Å, much smaller even than spacings in alpha plutonium.

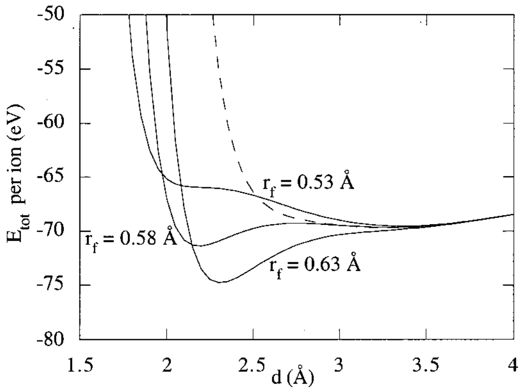

FIG. 2. The energy as a function of spacing for plutonium in the fcc structure from Eq. (9), using the smaller of the predicted r_f values (0.58 Å), as well as with smaller and larger values. $r_c = 0.518$ Å yields a minimum near the observed 3.27 Å in all cases. The dashed curve is our adjusted total energy, with $r_f = 0.74$, but with the entire E_{ff} energy scaled down by a factor $S_f = 0.15$, and $r_c = 0.522$ Å.

The natural approach would be to scale the uncertain r_f up or down, as illustrated in Fig. 2. This has two effects, as may be seen in the figure. Reducing r_f rapidly reduces the entire energy E_{ff}, eliminating the inner minimum in the total energy (without a very large shift in the outer minimum), but also moves the position of the inner minimum in E_{ff} to still smaller d. What seemed to be necessary to give stability to the α-plutonium structure was to shift the minimum in E_{ff} outward without deepening it. Thus for plutonium we raised r_f to 0.74 Å (still below Straub's estimate in Table I) which, however, made the minimum deeper by a factor of nearly 7. We therefore scaled the entire E_{ff} down by a factor of $S_f = 0.15$ [where indicated in Eq. (9)]. This would seem to be a very large and arbitrary scaling of E_{ff}, but in some sense our scaling is much smaller than either the r_f or E_{ff} scaling alone. We have effectively shifted the position of the minimum out from 2.0 to 2.53 Å, and reduced its depth slightly, from -25 to -20 eV. This indeed eliminates the inner minimum seen in the $r_f = 0.58$ Å curve in Fig. 2. We then reevaluated r_c as 0.522 Å, needed to place the minimum in the energy in the fcc structure of δ plutonium at 3.275 Å. We preferred this to fitting to the α spacing since the interesting alloys of plutonium are in the delta structure. The resulting total energy per ion is shown as the dashed line in Fig. 2.

These scalings do indicate the inherent uncertainty in parameters, illustrated by the fact that the *f*-band width differs by a factor of 5 depending on whether one uses Skriver's or

TABLE II. Parameters used in the theory. Values for r_f scaled from Straub's values of Table I by a factor 0.936 as for Pu. r_c was adjusted to give the atomic sphere radius, shown in column 2, in the fcc structure. U_f is as in Table I. r_d is the d-state radius and ε_d is the d-state energy, valence states for all but Ga, In, and Tl where they are core states.

	Z_f	r_0 (Å)	r_c (Å)	r_f (Å)	U_f	r_d	ε_d (eV)[a]
Sc	0	1.80	0.485	0			−9.35
Y	0	1.98	0.567	0			−6.80
La	0	2.08	0.613	0			−7.31
Ce	1	2.02	0.586	0.46	7.2		−7.36
Ac	0	2.10	0.624	1.20	3.00	2.39[b]	−6.84
Th	1	1.99	0.596	0.97	3.20	2.17[b]	−8.05
Pa	2	1.80	0.524	0.820	3.35	2.03[b]	−7.15
U	3	1.69	0.486	0.782	4.09	1.93[b]	−7.25
Np	4	1.66	0.478	0.762	3.90	1.91[b]	−7.32
Pu	5	1.81[c]	0.522	0.740	4.61	1.91[b]	−7.35
Am	6	1.91	0.554	0.736	4.96	2.06[b]	−7.35
Cm	7	2.03	0.597	0.723	5.10	2.26[b]	−7.42
Al	0	1.58	0.388	0			
Ga	0	1.67	0.427	0		0.409[d]	−32.47
In	0	1.84	0.503	0		0.574[d]	−28.92
Tl	0	1.89	0.526	0		0.705[d]	−26.34

[a] Hartree-Fock values from Mann (Ref. 12).

[b] From Straub (Ref. 8).

[c] For δ-Pu. $r_0 = 1.68$ Å for α-Pu.

[d] From Straub (Ref. 11).

TABLE III. Predicted and experimental[a] bulk moduli (in units of 10^{12} ergs/cm^3, or dyn/cm^2) based upon the parameters of Table II.

	Theory	Expt.[a]		Theory	Expt.
Ac	0.38	0.25	Al	1.07	0.72
Th	0.46	0.60	Ga	0.87	0.57
Pa	0.61		In	0.62	0.41
U	0.75	1.21	Tl	0.57	0.36
Np	0.82	0.77	Sc	0.68	
Pu	0.50	0.55	Y	0.48	
Am	0.46	0.36	La	0.40	0.24
Cm	0.41		Ce	0.59	0.26

[a] Kittel (Ref. 13).

Straub's values. Such uncertainties are not resolved by optical spectra in such strongly correlated systems; we expect the corrections for electron correlations to be comparable to the differences.

There is an interesting check on the resulting model in that we can predict the bulk modulus from the second derivative of the energy per atom with respect to atomic sphere radius. It is[1]

$$B = \frac{{r_0}^2}{9\Omega_0}\frac{\partial^2 E_{\mathrm{tot}}/\mathrm{ion}}{\partial {r_0}^2} = \frac{1}{12\pi r_0}\frac{\partial^2 E_{\mathrm{tot}}/\mathrm{ion}}{\partial {r_0}^2}, \tag{10}$$

with Ω_0 the volume per atom. This gives 0.50×10^{12} ergs/cm^3, near the observed bulk modulus[13] of 0.55 ergs/cm^3. Had we instead adjusted r_c to 0.501 Å to obtain the observed volume in the α-plutonium structure, we would have obtained a bulk modulus of 0.82×10^{12} ergs/cm^3 which may be a better comparison since the measured value is presumably for α plutonium, but we proceed with the δ-plutonium value. Bulk moduli provide a relevant test because the E_{ff} is giving a negative contribution and E_{sd} a positive contribution to the prediction, providing a sensitive test to the scale of E_{ff}.

For the other actinides we chose an r_f which is the same factor 0.936 smaller than Straub's estimates from Table I, and the same $S_f = 0.15$ for scaling E_{ff}, leading to the values shown in Table II. For actinium and thorium, for which Straub gave no values, we extrapolated the same scaling using values based on Skriver's calculations, which appeared in Table I. We scaled r_c to obtain the minimum energy at the observed pure-metal spacing in the fcc structure, though the lighter actinides have complex structures, giving the values listed in Table II. For the elements such as gallium which have no E_{ff} there is only the single parameter r_c which is adjusted to give the observed spacing, again in the fcc structure. Such values are also given in Table II. The resulting bulk moduli are reasonably well predicted, as seen in Table III. The actinides are about as close as the simple metals. For the latter, the only input parameter was the atomic sphere radius, in terms of which r_c was determined, and therefore the bulk modulus at the observed radius.

Though we have eliminated the inner minimum in the total energy as a function of volume, we have not eliminated it from the interatomic interaction at constant volume. Of all the terms in E_{sd} from Eq. (2), only the final term contributes to the two-body interaction which determines structures at fixed volume. The total two-body interaction in plutonium has a minimum at a spacing, near 2.53 Å, very different from the δ-plutonium nearest-neighbor distance and in fact this net interaction has a negative curvature at the nearest-neighbor distance. This favors distortion of the fcc structure. We may, for example, recalculate the total energy as a function of a uniaxial shear, expanding the crystal in the x and y directions by a factor $1 + e_1$, and shrinking the crystal along the z axis by a factor $1/(1+e_1)^2$, all at constant volume. We may redo the calculation at different volumes to find a stable structure. We find in fact that the original fcc structure is unstable (the energy dropping for small negative e_1) and the lowest energy is obtained with $e_1 = 0.44$ at a reduced spacing of 3.24 Å, below the spacing 3.275 Å of the lowest-energy fcc structure. This is very reminiscent of real pure plutonium which is unstable in the fcc structure and goes to the α structure with a volume corresponding to an fcc spacing of 3.04 Å. We find two other metastable states, one at $e_1 = -0.22$ at a reduced spacing near 3.16, and one at still higher energy at $e_1 = 0.12$ and a spacing nearer the original 3.275 Å.

We can proceed to the true α structure, which has been given by Zachariasen and Ellinger.[14] There are 16 atoms per primitive cell, with a 180° rotary reflection taking a set of eight lying in one plane to another set in a parallel plane separated by 2.411 Å. That is, if the position of one atom in the first plane is given in terms of fractions of the distance along the three edges of the monoclinic primitive cell by a, b, and c, then there is an atom in the second plane at $(1-a)$, $(1-b)$, and $(1-c)$. We begin with the atom numbered I in the first set of eight, with positions given in Table 8 of Ref. 14, calculating the distances to all atoms in either plane within 3.78 Å of the first atom. This distance was selected to include, on average, 12 neighbors to each atom. We then proceed to atom II, including all neighbors except atoms numbered I, and continue through atom VIII, excluding again all pairs previously counted. This gives a total of 48 distances, six per atom since each bond is shared between two atoms. These were approximately in accord with the values given in Table 9 of Ref. 14, except for an apparent typographical error in the spacing between III in one plane and IV in the other, for which we found 3.365 Å. For neighbors in the second plane, we counted the pair as if associated entirely with the first plane, but did not count the corresponding pair with an atom in the plane on the opposite side. The same result is obtained if we treat neighbors to atoms in the second plane.

To evaluate the total energy we again use Eq. (9), but the sums over j in the second line are now over the 48 distances rather than 12, and the sum is to be divided by 4 to give the energy per atom. This can be compared with the corresponding fcc evaluation which included a sum over 12 nearest neighbors. Evaluating this α-plutonium energy at the atomic-sphere radius 1.81 Å appropriate to δ plutonium gives an energy per atom slightly higher than the energy for the δ structure. However, if we allow the atomic-sphere radius to vary from this value, which gave minimum energy for the δ structure, we find that the energy is minimum for the α structure at the smaller radius of 1.74 Å, not so far from the observed 1.68 Å. This is just what we hoped would be the case, giving strong support to our approximation to the energy. It would also be possible to vary the individual positions of the eight atoms to see to what extent the correct structure is predicted, but that has not yet been done.

III. ALLOYS WITH SIMPLE METALS AND THE *dd* INTERACTION

We turn next to dilute alloys of an actinide with a simple metal, such as plutonium with gallium. We could proceed directly with the expression for the energy given in Eq. (9), with k_F and κ determined for the global volume and total number of *sd* electrons in the first line. Also the $\cosh \kappa r_c e^{-\kappa r_c}$ is replaced by $(1-x)\cosh \kappa r_{cA} e^{-\kappa r_{cA}} + x \cosh \kappa r_{cB} e^{-\kappa r_{cB}}$, with x the concentration of the simple metal B in the actinide A. For the sums over neighbors in the second line, and in Eq. (8), we weight each combination by the fraction of pairs of each kind, Pu-Pu, Pu-Ga, etc., and use the spacing d_{ij} appropriate to that pair, assuming a random distribution of atom species on each site. We may do this first on an undistorted fcc lattice. We find that at small concentrations x the lowest energy occurs at a spacing d which can be written in terms of the equilibrium spacings d_A and d_B of the pure components (in the fcc structure) in the form

$$d = d_A + \nu x (d_B - d_A). \tag{11}$$

If this were valid for all x, it would mean that $\nu = 1$, called Vegard's law, but that is ordinarily not a good approximation. This Vegard law may be approximately correct for alloys of simple metals,[7] where the pseudopotentials are weak, but for an alloy between an actinide and a simple metal each simple metal atom in a dilute fcc alloy eliminates 12 *ff* contributions. This disproportionately expands the lattice tending to lead to positive deviations from Vegard's law. For gallium in plutonium, $d_B - d_A$ is negative so such effects tend to decrease the magnitude of ν while the lattice parameters obtained from x rays drop *more* rapidly than Vegard's law, corresponding to (Ref. 5, Fig. 21) $\nu = 2.08$.

It is difficult to imagine how this could be true without an additional term in the energy. Our first guess was the coupling between gallium core d states and the unoccupied f states in the plutonium. The theory of this is analogous to that for the *ff* coupling described above (and Ref. 1) and Straub had previously (Ref. 11) calculated the d-state radius for gallium which could be used with the f-state radius for plutonium of Table I to estimate this contribution. It turned out to be much too small, by a factor of more than 100, so we next tried the coupling between gallium core d states and the unoccupied d states in the plutonium. We again had values for all needed parameters and found this effect much larger. These terms produce an attraction between neighboring gallium and plutonium atoms, not present in either pure material, and deviations from Vegard's law of the kind observed. Reasonable scaling of the d-state radii, as we shall see, increased the effect by the factor of 9 needed to accord with experiment.

The inclusion of *dd* coupling between states of very different energy (or d and f states of very different energy) required a rederivation of the energy given in Eq. (1). It was based upon a two level system (Ref. 6, p. 536), with the levels $|a\rangle$ and $|b\rangle$ at energy $\pm M_3$, coupled by $\langle a|H|b\rangle = M_2$, and having nonorthogonality $\langle a|b\rangle = S$. Minimizing the energy $\langle \psi|H|\psi\rangle / \langle \psi|\psi\rangle$ with respect to u and ν for $|\psi\rangle = u|a\rangle + v|b\rangle$ gave

$$\varepsilon = \frac{-M_2 S - [M_2{}^2 S^2 + (1-S^2)(M_2{}^2 + M_3{}^2)]^{1/2}}{1-S^2}$$

$$(\text{with } M_2 < 0). \tag{12}$$

A new coupling $-V_2 = M_2/(1-S^2)$ and new starting levels $\pm M_3/(1-S^2)^{1/2}$ led to the formula $\varepsilon = -\sqrt{V_2{}^2 + V_3{}^2} + SV_2$ which was generalized to obtain Eq. (1) here. We should now make an expansion of Eq. (12) for large M_3, or more specifically to second order in both S and M_2, leading to

$$\varepsilon = -M_3 - \frac{1}{2M_3}(M_2 + SM_3)^2. \tag{13}$$

The second term is of the form of a second-order shift in the level at $-M_3$ by a coupling $M_2 + SM_3$ to the level at M_3. We generalize this to the coupling of two neighboring d levels, with angular momentum $m\hbar$ around the internuclear distance as $-(V_{ddm} + M_3 S_{ddm})^2/(2M_3)$ with $M_3 = (\varepsilon_d{}^A - \varepsilon_d{}^B)/2$ and with A for plutonium and B for gallium for the case of Ga in Pu. We sum it over $-2 \leqslant m \leqslant 2$ and over neighbors to obtain the interaction in analogy with Eq. (1). We multiply by 2 for the two spins for each core level shifted, and neglect any effect of occupation of the *d*-like states in the conduction band. We are thinking of these shifts arising from the atomic levels, and then afterward recognize that the upper *d* levels become so broad that they are included with the *s* levels of the conduction band. We have given general formulas from which the V_{ddm} and S_{ddm} may be obtained in Ref. 1, pp. 606 and 607 in terms of the r_d so the evaluation is direct, leading to

$$E_{dd} = -\frac{(r_d{}^A r_d{}^B)^3}{\pi^2 M_3} \Sigma_j \left[\left(\frac{-45\hbar^2}{m d_j{}^5} + \frac{5M_3}{d_j{}^3} \right)^2 + 2\left(\frac{30\hbar^2}{m d_j{}^5} - \frac{5M_3}{d_j{}^3} \right)^2 + 2\left(\frac{-15\hbar^2}{2m d_j{}^5} + \frac{5M_3}{2d_j{}^3} \right)^2 \right]. \tag{14}$$

At large spacings the M_3 term dominates each contribution. The energy becomes deeper at smaller distances, then rises to zero between 1.4 and 2.4 Å and then drops again at smaller spacing. The results from each contribution are hardly distinguishable from values obtained from the full Eq. (12), above this zero in the energy, but we obtained spurious low total energies if we allowed deformations of the lattice beyond these unrealistically small values, so we simply added all terms only beyond the node for that term.

In the evaluation we needed M_3, half the energy difference between the simple metal core state and the actinide *d* state. There would not seem to be difficulties associated with shifting either due to charging, as in the transition-metal *d* states (Ref. 1, p. 561). It may be adequate to simply subtract the free-atom term values, which contains the principal variations from one system to the other, and the Hartree-Fock values were listed in Table II and used here. We tried an alternative view, that in the alloy we have a single spacing and three free electrons per atom to suggest that the *s*-state energy in both atoms will have the same relation to the common Fermi energy, so we could use $\varepsilon_d - \varepsilon_s$, directly subtract and divide by 2 to obtain the corresponding M_3. This required considerably larger scaling of the E_{dd} contribution and we abandoned that approach.

For the dilute alloy, in the fcc lattice, the sum in Eq. (14) gives a factor of $12x(1-x)$ for the average number of Pu-Ga couplings per atom if we include only nearest neighbors. If we use the r_d values given by Straub and appearing in Table II, this contribution is not sufficient to give the observed deviation from Vegard's law. However, scaling it by a factor of 9, corresponding to scaling each r_d by $9^{1/6} = 1.44$ is, leading to a value of $\nu = 2.1$ for gallium in plutonium, equal to the experimental value obtained from Fig. 21 in Ref. 5. Such a scaling is not unreasonable but it should be considered as tentative because we have not included any effects of relaxation around impurities, to be discussed in the following section.

We may also treat alloys of aluminum in plutonium. Aluminum has no core *d* states so the E_{dd} vanishes, but the same program can be run with $r_d = 0$ for aluminum. For $x = 0.1$ we obtain a spacing of 3.233 Å, in this case identical to the Vegard's law prediction of 3.233 Å, and in accord with experiment.

TABLE IV. Predicted interatomic distances (in Å) based upon the parameters of Table II.

	Theory	Dilute extrapolation	Vegard's law
Pu_3Al	3.20	3.17	3.17
Pu_3Ga	3.18	3.16	3.21
Pu_3In	3.23	3.21	3.29

Similarly we may treat indium in plutonium, using parameters from Table I and the same scaling of E_{dd} by a factor of 9. Indium has slightly larger volume per atom than δ plutonium, as seen in Table I, but our calculation for small concentrations indicates a reduced spacing due to indium added to plutonium, to 3.24 Å at 10%, which would correspond to a negative ν if we use Eq. (11). Indeed this reversal is observed in dilute alloys (Ref. 5, p. 274); indium reduces the lattice parameter. A calculation of the spacing at minimum energy for the entire range of concentrations is approximately parabolic with a minimum of 3.20 Å at $x = 0.4$, and of course the pure-metal spacings at *x* equal to zero and 1. This decreasing spacing with added indium arose entirely from the *dd* coupling. If that is omitted, the spacing is found to increase with added indium, reaching a peak of 3.35 Å near $x = 0.7$. The application to thallium in plutonium is similar to that for indium. Again Vegard's law predicts an expansion but a contraction is predicted here. It would of course be possible to adjust the r_d for indium and thallium to make the initial slope correct, but we have not done that, but used the same scaling as for added gallium. In some other calculations with other parameters we found discontinuous jumps to larger spacing with increasing *x*, as would happen if we followed the minimum energy as we decreased r_f in Fig. 2, but that did not occur in this final calculation.

It is interesting to consider also the addition of trivalent metals of type *A* to plutonium, the elements Sc, Y, and La with parameters at the top of Table II. In all three cases the dilute alloys increased the spacing from that of plutonium, in all cases slightly more that suggested by Vegard's law. Scandium experimentally causes a small decrease, but we are not certain about Y and La.

One other interesting comparison is for the intermetallic compounds Pu_3M. These occur in the Cu_3Au structure, which is face-centered cubic with Pu atoms on every cube face and $M = $ Al, Ga, or In at the cube corner positions. Then half the nearest-neighbor bonds are between Pu and *M*, and half are between Pu and Pu. The energy may be evaluated directly from Eqs. (9) and (13), and the minimum as a function of *d* obtained. The values of *d* found, in Å, are listed as "Theory" in Table IV and compared to linear extrapolations of our dilute alloy results to $x = 0.25$, and to a linear interpolation between experimental pure-metal spacings, "Vegard's law." The only experimental lattice parameter we have, for Pu_3Ga (Fig. 21, Ref. 5), is 3.19 Å. This is close to our prediction and to the Vegard law value and somewhat higher than the extrapolated dilute-random-alloy result at $x=0.25$, seen in Table IV to be 3.16.

We can also compare the total energy we obtain for the Pu_3M intermetallic compound with that for the random alloy at the same concentration of 0.25. We find a lower energy for $\mathrm{Pu}_3\mathrm{Ga}$ and $\mathrm{Pu}_3\mathrm{In}$ (by 0.015 and 0.072 eV per atom, respectively) in the ordered structure than for the random alloy, but a higher value for $\mathrm{Pu}_3\mathrm{Al}$ (by 0.063 eV). Certainly all three of the 25% alloys order so the $\mathrm{Pu}_3\mathrm{Al}$ prediction is not correct. Allowing relaxation of the neighbors, to be discussed next, would presumably lower the energy of the disordered structure further, but not the ordered structure, so that neglect did not cause the difficulty for aluminum.

IV. RELAXATION OF NEIGHBORS

Of course we do not expect the lattice to remain in the undistorted fcc structure. As found by Mikkelsen and Boyce[15] for semiconductor alloys, the neighboring atoms tend to relax much of the way to their natural bond length rather than retain the average spacing. In the present case of dilute alloys we may expect that the replacement of a plutonium atom by a gallium will cause each of the 12 nearest neighbors to that gallium to relax radially. Experimental x-ray-absorption fine-structure studies of gallium in plutonium by Villella *et al.*[16] have indicated inward displacements of the nearest-neighbor plutonium atoms by 0.1 Å in delta plutonium. Such shifts are expected to result from the elimination of the *ff* interaction which was there for the plutonium replaced, but not for the gallium, and favors an outward motion of nearest-neighbor plutonium atoms. The *dd* coupling between the added gallium and its plutonium neighbors favors an inward movement of the neighbors. Further, the pseudopotential core radius is smaller for gallium than for the plutonium it replaced, also favoring an inward displacement. It is straightforward to introduce such relaxations, equal for all 12 plutonium neighbors, into our total-energy program, particularly for dilute enough alloys that each gallium is treated by itself. We did this, also neglecting relaxation of more distant neighbors except for allowing an overall scaling of the lattice as in the preceding section. The results of minimizing the energy with respect to such relaxations were not what we had hoped, but were informative.

We found very large *outward* relaxations, of the order of an angstrom. In hindsight this is not surprising. Shifting reach gallium-plutonium distance by a factor $1+\varepsilon$ shifts the plutonium-plutonium distance to the atom on the opposite side by a factor $1-\varepsilon$, so 12 Ga-Pu shifts of $1+\varepsilon$ are accompanied by 12 Pu-Pu shifts of $1-\varepsilon$. Furthermore the 24 Pu-Pu distances between the nearest-neighbor plutonium atoms are shifted by a factor $1+\varepsilon$ and the 48 distances between these nearest-neighbor atoms to third-nearest-neighbor (to Ga) atoms are increased by $\sqrt{1-\varepsilon+\varepsilon^2}\approx 1-\varepsilon/2$ and 24 distances between nearest neighbors and second neighbors are increased by $\sqrt{1+\varepsilon^2}$. The nearest-neighbor distances to 78 different atoms are modified by the introduction of this one gallium atom. It seems clear that the plutonium is expressing its instability toward formation of α plutonium, and the instability under axial shears e_1 which we discussed near the end of Sec. II. Such distortions would likely reduce the energy of *pure* plutonium in the fcc structure, without the presence of gallium, leading finally to the α structure. The result of our calculation may be approximately correct, but it does not address the question of relaxation in the real alloy which we had in mind.

These considerations suggest that in fact the stabilization of the δ structure by gallium requires the effects of neighboring gallium atoms, rather than the simple sum of the effects of individual gallium atoms. The finding above that even with only nearest-neighbor relaxation 78 neighboring atoms are affected by each gallium makes it plausible that one or two percent of gallium can show such cooperative effects. This is also consistent with the need for rapid quenching of dilute gallium alloys to retain the δ structure (Ref. 5, p. 273); presumably slower cooling allows the gallium to diffuse to favorable sites for the formation of the lower-energy α structure. It is also consistent with the finding by Villella *et al.*,[16] of significant shifts in the positions of more distant neighbors to the added gallium atoms. It may be very interesting to consider the distortions in the context of neighboring gallium atoms. It should not be too difficult with our nearest-neighbor interactions, but it has not yet been done.

These relaxations presumably do not occur in the Pu_3M structure, since each Pu is at the center of a square of four Ga neighbors, and has no tendency to move in any direction. Only if the structure breaks symmetry can this occur and this would correspond to the formation of a new structure, not the $\mathrm{Cu}_3\mathrm{Au}$ structure. We are not aware of evidence that this happens.

V. ALLOYS BETWEEN ACTINIDES

The application of Eqs. (8) and (9) to alloys involving two actinides is rather direct. The simple metal terms, including the sum over $V(d_{ij})$, is the same as for actinide alloys with simple metals, but with different r_c. There are again three free electrons per atom and a Fermi wave number determined by the total volume. The terms from coupling between core *d* states and valence *d* states, Eq. (14), do not arise since the actinide core *d* states are so deep as to be irrelevant.

For the evaluation of the *f*-band width, Eq. (9), we again need the second moment and if all nearest-neighbor distances are taken the same, ${r_f}^5$ is simply replaced by $(1-x)^2{r_{fA}}^5+2x(1-x){r_{fA}}^{5/2}{r_{fB}}^{5/2}+x^2{r_{fB}}^5$. If different neighbors have different spacings r_f is taken under the square root in Eq. (8) and the appropriate ${r_f}^{10}$ used for each spacing. A similar generalization applies to the *ff* repulsion, the final term in Eq. (9), with the Z_f *f* electrons on each atom shifted by coupling with a neighbor in proportion to the ${r_F}^5$ of both atoms, leading to a $(1-x)^2Z_{fA}{r_{fA}}^{10}+x(1-x)(Z_{fA}+Z_{fB}){r_{fA}}^5{r_{fB}}^5+x^2Z_{fB}{r_{fB}}^{10}$ replacing the $Z_f{r_f}^{10}$ appearing in Eq. (9). For the term in Eq. (9) based upon ${W_f}^2$, the square of the global band width, it is appropriate to replace Z_f by the global number of electrons per atom, and we replace the Coulomb U_f by its weighted average,

$$\langle Z_f\rangle=(1-x)Z_{fA}+xZ_{fB},$$

$$\langle U_f \rangle = (1-x) U_{fA} + x U_{fB} . \tag{15}$$

There are additional terms in the second moment which did not occur in the elemental materials, from the diagonal terms in $M_2 = (1/7N)\Sigma_{ij} H_{ij} H_{ji}$. The $H_{ii}{}^2 = \varepsilon_f{}^2$ (with ε_f measured from the average ε_f for the crystal, since the moment is evaluated relative to the average energy) are now different for different atoms. These were included for transition-metal alloys[1,2] and we include them here. We note first the fact that in the pure metal the f-state energy ε_{fi} lies at the middle of the f band for atom i, $W_{fi}/2$ [evaluated for the pure metal from Eq. (8) with $d = 1.809 r_0$ for fcc structures] above the f-band minimum, while the Fermi energy, common to the alloy, lies at $(Z_{fi}/14) W_{fi}$ above the minimum. Thus the diagonal energy H_{ii} is given by

$$\varepsilon_{fi} = \left(\frac{1}{2} - \frac{Z_{fi}}{14} \right) W_{fi} \tag{16}$$

relative to the Fermi energy in the pure metal, and we take that to be true for elements of each atom in the alloy with W_{fi} obtained from Eq. (8) using an fcc lattice with the same atomic sphere radius as for the alloy. When the element B had no f states, e.g., gallium, then all f states which entered had the same value and there was no diagonal contribution to the second moment. For an alloy of two actinides the average value is $\langle \varepsilon_f \rangle = (1-x)\varepsilon_{fA} + x \varepsilon_{fB}$ and the contribution of the diagonal terms to the second moment is

$$\begin{aligned} M_{2\ \mathrm{diag}} &= (1-x)(\varepsilon_{fA} - \langle \varepsilon_f \rangle)^2 + x(\varepsilon_{fB} - \langle \varepsilon_f \rangle)^2 \\ &= x(1-x)(\varepsilon_{fB} - \varepsilon_{fA})^2, \end{aligned} \tag{17}$$

with the ε_{fA} and ε_{fB} obtained from Eq. (16), an additional contribution to the second moment of the band, $W_f{}^2/12$, so that the band width from Eq. (8) becomes

$$\begin{aligned} W_f{}^2 = 11.06 \times 10^6 \left(\frac{\hbar^2}{m} \right)^2 & \\ \times [(1-x)^2 r_{fA}{}^{10} &+ 2(1-x) x r_{fA}{}^5 r_{fB}{}^5 + x^2 r_{fB}{}^{10}] \\ \times \sum_n \frac{1}{d_n{}^{14}} &+ 12x(1-x)(\varepsilon_{fB} - \varepsilon_{fA})^2, \end{aligned} \tag{18}$$

which can be directly generalized to d_n values differing for different terms in $\langle r_f{}^{10} \rangle$. For nearest-neighbor coupling in an fcc lattice, $\Sigma_n 1/d^{14}$ becomes simply $12/d^{14}$.

We may note that there is an unphysical feature in the square-root term in Eq. (18) in that there can be contributions to $W_{fi}{}^2$ [Eq. (18)] from changes in spacing between nearest-neighbor pairs which are themselves far apart, and that there are contributions to $\sqrt{W_f{}^2 + [(1-x)U_{fA} + xU_{fB}]^2}$ from the cross term between these two distant distortions. Such long-range interactions are unphysical but may not be important here. The form is appropriate for a perfect lattice, for a uniformly deformed lattice and for a lattice with alternate atoms displaced in opposite directions. The latter two of these correspond to lattice vibrations of maximum and minimum wavelength and the theory makes a reasonable interpolation between them, this spanning the entire spectrum of distortions.

We have then the energy per ion, or atom, for a random alloy of B in A of

$$\begin{aligned} \frac{E_{\mathrm{tot}}}{\mathrm{ion}} = E_{sd} - S_f \left(\frac{\langle Z_f \rangle (1 - \langle Z_f \rangle /14)}{2} \left(\sqrt{W_f{}^2 + \langle U_f \rangle^2} - \langle U_f \rangle \right) \right) & \\ + S_f 83780 \Sigma_{j \neq i} \frac{\hbar^2 [(1-x)^2 Z_{fA} r_{fA}{}^{10} + x(1-x)(Z_{fA} + Z_{fB}) r_{fA}{}^5 r_{fB}{}^5 + x^2 Z_{fB} r_{fB}{}^{10}]}{m d_{ij}{}^{12}} &. \end{aligned} \tag{19}$$

with

$$\begin{aligned} E_{sd} = 3 \Bigg(& \frac{3\hbar^2 k_F{}^2}{10m} - \frac{3e^2 k_F}{4\pi} + \frac{2e^2 k_F{}^3}{3\pi\kappa^2} \\ & \times \{ \kappa^2 [(1-x) r_{cA}{}^2 + x r_{cB}{}^2] - 1 \} \Bigg) - \frac{Z^2 e^2 \kappa}{2} \\ & \times \Big[(1-x) \cosh(\kappa r_{cA}) e^{-\kappa r_{cA}} + x \cosh(\kappa r_{cB}) e^{-\kappa r_{cB}} \Big] \\ & + \frac{1}{2} \sum_{j \neq i} V(\mathbf{r_i} - \mathbf{r_j}) \end{aligned} \tag{20}$$

and $W_f{}^2$ obtained from Eq. (18). An interesting feature of these forms is that they are not equivalent to the formulas used for alloys with simple metals, even if we set the simple metal r_f equal to zero. The form in which x enters $\langle Z_f \rangle$ and $W_f{}^2$ is different, and $\langle U_f \rangle$ is different from the plutonium U_f, while it was the same before. We regard these differences as appropriate to the different systems.

We ran a program incorporating these changes for an alloy of plutonium and americium, using the parameters of Table II, and found that the minimum-energy spacing was very close to Vegard's law, the spacing increasing with americium concentration as observed. The same program could be run also for cerium, a rare earth but having an f shell and no important core d states. Cerium is also found to increase the spacing, in agreement with experiment, showing in this case a considerably steeper slope than Vegard's law at small concentrations corresponding to $\nu = 1.8$ in Eq. (11), while experimentally ν is closer to 0.5. We do not know if local relaxation helps with these quantitative inconsistencies.

In both cases, the increase was also suggested by Vegard's law. It was interesting to try the light actinides such as thorium, for which Vegard's law would also suggest increasing spacing, but in this case we found the spacing to drop sharply with added thorium, dropping to an fcc spacing of 3.15 Å at about 25%, before rising to 3.60 for pure thorium. The same was true of all of the other light actinides listed in Table II. On the other hand, curium was found to increase the spacing, as did americium. As far as we know, all of these results are in qualitative accord with experiment.

VI. SUMMARY

We did not succeed in our initial effort to predict the properties of actinide alloys using existing theory and existing parameters. It was necessary to adjust the *f*-state radius for plutonium, within the range of earlier predictions, in order to accommodate to the known properties of that element, and we used the same adjustment factor for the other actinides. It was also necessary to scale the entire *f*-state energy, and as planned we adjusted the pseudopotential core radius for all elements to fit the observed atomic volume of that pure element. In addition, when we discussed alloys it was necessary to introduce the effects of coupling between simple metal core *d* states and the *d* states on the actinides, and to scale the predicted *d*-state radii by a factor of 1.44.

The resulting representation of the electronic structure yielded reasonably good predictions of the bulk modulus for all elements considered. It indicated that δ plutonium, for which the parameters were fit, was unstable against shear distortions and against the formation of the α structure at smaller volume. It also yielded shifts in the lattice parameter of δ plutonium with dilute alloying with simple metals and with other actinides which were in rather good accord with experiment. This included the prediction that of the *f*-shell metals checked only americium, curium, and cerium increased the lattice spacing, while contrary to Vegard's law indium and thorium decreased it, all in accord with experiment. The same theory indicated that the ordered alloys Pu_3Ga and Pu_3In were more stable than the disordered alloy at the same concentration and that the spacing was larger for the ordered alloy, in agreement with experiment. It incorrectly predicted that the ordered alloy Pu_3Al is not stable, but again predicted a larger spacing.

A comparison of the energies of the δ and α phases for the random alloy failed to show the stabilization of the δ phase in the very dilute random alloy with gallium. Also allowing radial relaxations of the plutonium neighbors to isolated gallium atoms indicated an instability analogous to the α structure. This suggests that the real stabilization may not be a simple additive effect of the individual gallium atoms, but may be a cooperative effect from neighboring gallium atoms. This has not yet been explored but we expect the extensive information available from extended x-ray-absorption fine-structure studies by Villella *et al.*[16] to provide a guide to doing this.

ACKNOWLEDGMENTS

The author is indebted to Dr. Siegfried Hecker for motivating this study and for useful discussions. The author also appreciates help from Dr. Angus Lawson in understanding the α structure, and to Dr. Galen Straub for providing the many parameters essential to the study.

---

[1] W. A. Harrison, *Elementary Electronic Structure* (World Scientific, Singapore, 1999).

[2] W. A. Harrison and Galen K. Straub, Los Alamos Report 1266, 1999.

[3] D. G. Pettifor, Phys. Rev. Lett. **42**, 846 (1979).

[4] D. G. Pettifor, *Bonding and Structure of Molecules and Solids* (Clarendon, Oxford, 1995).

[5] S. S. Hecker, Los Alamos Sci. **26**, 244 (2000).

[6] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980) [reprinted by Dover (New York, 1989)].

[7] J. Hafner, *From Hamiltonians to Phase Diagrams*, Solid State Sciences, Vol. 70 (Springer-Verlag, Heidelberg, 1987).

[8] K. Galen Straub (private communication), reported in Ref. 1, p. 604.

[9] H. L. Skriver, *The LMTO Method, Muffin-Tin Orbitals and Electronic Structure* (Springer-Verlag, Berlin, 1984).

[10] Leo Brewer, J. Opt. Soc. Am. **61**, 1101 (1971).

[11] W. A. Harrison and Galen K. Straub, *Proceedings of the 24th International Conference on the Physics of Semiconductors*, Jerusalem, 1998, edited by David Gershoni (World Scientific, Singapore, 1998), paper II A7.

[12] J. B. Mann, 1967, *Atomic Structure Calculations, 1. Hartree-Fock Energy Results for Elements Hydrogen to Lawrencium*, distributed by Clearinghouse for Technical Information, Springfield, Virginia 22151.

[13] C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976).

[14] W. H. Zachariasen and F. H. Ellinger, Acta Crystallogr. **16**, 777 (1963).

[15] J. C. Mikkelsen and J. B. Boyce, Phys. Rev. B **28**, 7130 (1983), discussed also in Ref. 1, pp. 298 and 299.

[16] P. Villella, J. F. Espinosa, L. E. Cox, B. Martinez, R. Martinez, R. Pereyra, J. Terry, J. C. Lashley, L. Morales, and S. D. Conradson (unpublished).