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Electronic structure of f-shell metals

Walter A. Harrison
Center for Materials Science, Los Alamos National Laboratory, Los Alamos, New Mexico 87545
*and Department of Applied Physics, Stanford University, Stanford, California 94305**

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Free-electron theory to first order in an empty-core pseudopotential, with radius determined spectroscopically, is found to predict successfully equilibrium spacings and bulk moduli for the rare-earth metals. This provides also a simple two-body interaction, second order in the same pseudopotential, for calculating other elastic and vibrational properties. For the light actinides a tight-binding f-band theory is formulated, leading to interatomic matrix elements of the form $V_{ffm}=\eta_{ffm}\hbar^2 r_f^{\,5}/md^7$. Coefficients η_{ffm} are derived and r_f values fit for the light actinides. Spin-orbit coupling is included and a bandwidth obtained from a second-moment analysis to be used with the Friedel model for the density of states in the calculation of energetics. It is found necessary to include also the next-order correction to the interatomic interactions, a repulsion proportional to $\hbar^2 r_f^{10}/md^{12}$ which, though small, is significant for the bulk modulus. With the use of pseudopotential core radii fit to the equilibrium spacing, the bulk moduli and thermal-expansion coefficients are predicted. All contributions can be written as two-body interactions, but adjustment is needed before using them to calculate properties. Inclusion of intra-atomic exchange fails to predict localization for americium.

I. INTRODUCTION

A few years ago Moruzzi, Williams, and Janak[1] carried out a first-principles, self-consistent calculation of the energy bands for a major segment of the simple and transition metals in the Periodic Table. These were carried out as a function of volume and the total energy summed to obtain predictions for the equilibrium density, the cohesion, and the bulk modulus, all in reasonable accord with experiment. These results showed that the density-functional theory of the electron-electron interactions and the corresponding one-electron description, the principal approximation required to make these calculations possible, was adequate for understanding at least the ground-state properties of these systems.

During the same period Andersen[2] developed the atomic-sphere approximation and muffin-tin orbital theory, also based upon density-functional theory, which predicted the same quantities much more directly and much more simply. The interpretation of the electronic structure in terms of the atomic-sphere approximation was explored extensively by Pettifor.[3] It is found that many of the details of the band structure are quite inessential to the prediction of these cohesive, or bonding, properties.

More recently Harrison and Froyen[4,5] combined one of the features of Andersen's muffin-tin orbital theory with the older transition-metal pseudopotential theory[5,6] to obtain a very much simpler, and perhaps more physical, formulation of the d-band structure of transition metals. In this formulation the electronic states are separated into local, nonoverlapping d states and free-electron states with coupling between them. The muffin-tin orbital theory, in contrast, treated all states on a similar footing in terms of s, p, or d symmetry. Still more recently Harrison and Wills[7] and Chelikowsky[8] found that the bonding properties of simple metals could be very well described in the context of Fermi-Thomas theory. This was a sufficiently great simplification to bring the calculation of elastic and vibrational properties of simple metals down to the level where they could even be carried out by hand.

The present study has a twofold purpose. The first is to extend the Harrison-Froyen theory to the light actinides, systems where f bands play the role which the d bands play in transition metals. This is achieved by including the effects of spin-orbit coupling and the effects of nonorthogonality in shifting the band center, neither of which were included in the earlier theory. The second purpose is to combine the simple theory of the f bands with the simple Fermi-Thomas theory of the free-electron component to obtain an elementary systematic theory of the f-shell metals.

We have reason to be optimistic about this separation of contributions for the light actinides since a similar effort by Johansson and Skriver[9] has indicated that a model for the actinides based upon the Friedel Model[10] for the f-band density of states and Murnaghan's phenomenological equation of state for the electron gas was quite consistent with the results of the full calculations by Skriver, Andersen, and Johansson.[11] Johansson and Skriver took Th, Pa, and U to be tetravalent, but we treat them all the same, as trivalent.

We begin in Sec. II with a direct application of simple-metal theory[12] to the rare-earth metals and heavy actinides, where any effect of the f states on the bonding is suppressed by the localization of the electrons. We find that the theory applies as well as it does for the simple metals, though states in the rare-earth metals unquestionably contain considerably more d character. Pseudopotential parameters obtained from the first ionization potential of the atom are close to those we obtain by requiring that the theory lead to the correct equilibrium spacing of the metal. We list the pseudopotential core radii so derived and test the model by prediction of the bulk modulus for these systems. Finally, we see that we may describe other properties of the metals using the simple Fermi-Thomas form,

$$V_0(d)=Z^2e^2\cosh^2\kappa r_c e^{-\kappa d}/d\ ,$$

for the two-body interaction.

We then turn to the analysis of the f bands for the light actinides. In Sec. III we derive formulas for the interatomic matrix elements between f states and give the parameters needed to evaluate them; this follows closely the earlier theory for d states. In Sec. IV we derive the matrix elements associated with spin-orbit coupling and the needed parameters. These together are enough to allow an elementary band calculation for the f-like states. However, we only use them in Sec. V to evaluate the second moment of the f bands, and we then use that second moment to define the f-band width in the Friedel model for the density of f states. In Sec. VI we proceed to higher order in the coupling to obtain the shift in the center of gravity of the f band, and we collect all contributions to the energy in Sec. VII. In Sec. VIII we construct the state of each actinide, both with and without f-band localization, and calculate the bulk modulus and thermal-expansion coefficient for each observed state. In Sec. IX we see how these terms in the energy can be represented as two-body interactions. In Sec. X we introduce intra-atomic exchange and consider criteria for a ferromagnetic state and for f-state localization.

II. APPLICATION OF SIMPLE-METAL THEORY

We begin with a direct extension of the simple-metal theory, given in Ref. 5, to the f-shell metals, leaving out any role of the f states. This is treating the sd-electron gas the same as an sp gas for a simple metal. It is not obvious that this is appropriate but the present study strongly supports it. The energy of the electron gas of Z electrons per atom, to first order in the empty-core pseudopotential of radius r_c, is[12]

$$E_{fe}=\frac{3Z\hbar^2k_F^2}{10m}-\frac{Z^2e^2\alpha k_F}{(18\pi Z)^{1/3}}-\frac{3Ze^2k_F}{4\pi}+\frac{2Ze^2r_c^2k_F^3}{3\pi} \tag{1}$$

per ion. The first term is the electronic kinetic energy. The second is the Madelung energy; we take $\alpha=1.8$, suitable for all metallic structures. The third term is the exchange of a free-electron gas, and the fourth is the shift due to the empty-core pseudopotential. For our purposes it is preferable to write this result in terms of the number of free electrons per ions Z_s and the atomic volume Ω. This is done by noting $k_F=(3\pi^2Z_s/\Omega)^{1/3}$. Then Eq. (1) becomes

$$E_{fe}=\frac{21.88Z_s^{5/3}}{\Omega^{2/3}}-\frac{20.89Z_s^2}{\Omega^{1/3}}-\frac{10.64Z_s^{4/3}}{\Omega^{1/3}}+\frac{90.48Z_s^2r_c^2}{\Omega} \tag{2}$$

in electron volts per ion, with r_c in Å and Ω in Å^3.

We could substitute pseudopotential core radii for the systems for which they were obtained from known pseudopotentials or atomic spectra from Ref. 5 and make a direct prediction of the equilibrium volume by minimizing Eq. (2). An equivalent test can be made by reversing the process. We then determine from Eq. (2) what core radii would lead to the observed equilibrium spacing and compare these with the radii obtained earlier. This gives a consistent set of r_c values to be used in other applications and still allows comparison with whatever pseudopotential core radii are available from other sources.

The values of r_c so deduced are listed in Table I and

TABLE I. Parameters for the rare-earth metals and light actinides.

				B (10^{12} dyn/cm^2)		
	Z_s	r_0 (Å)	r_c (Å)	Theory	Experiment[a]	κ (Å^{-1})
Cs	1	3.00	1.39	0.018	0.020	1.24
Ba	2	2.47	1.05	0.13	0.10	1.53
La	3	2.08	0.84	0.55	0.24	1.79
Ce	3	2.02	0.81	0.61	0.26	1.82
Pr	3	2.02	0.81	0.61	0.30	1.82
Nd	3	2.01	0.80	0.62	0.24	1.82
Pm						
Sm	3	1.99	0.79	0.64	0.29	1.83
Eu	2	2.27	0.95	0.18	0.15	1.60
Gd	3	1.99	0.79	0.64	0.39	1.83
Tb	3	1.95	0.77	0.69	0.40	1.85
Dy	3	1.96	0.78	0.68	0.39	1.84
Ho	3	1.95	0.77	0.69	0.40	1.85
Er	3	1.94	0.77	0.71	0.41	1.85
Tm	3	1.93	0.76	0.72	0.40	1.86
Yb	2	1.99	0.80	0.30	0.13	1.71
Lu	3	1.92	0.76	0.74	0.41	1.86
Fr	1	3.07	1.43	0.016	0.02	1.23
Ra	2	2.49	1.06	0.13	0.13	1.53
Ac	3	2.10	0.84	0.52	0.25	1.78

[a] K. A. Gschneidner, Jr., in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 275.

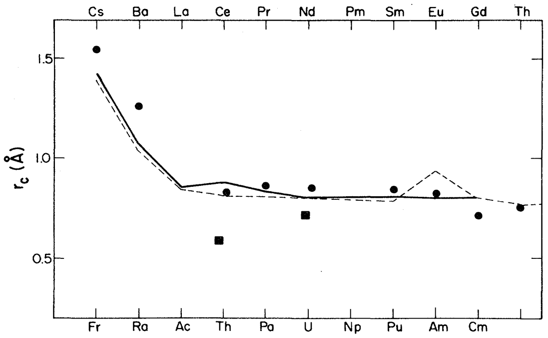

FIG. 1. Dashed line gives the pseudopotential core radius for the rare-earth metals (and elements preceding them) chosen to lead to the observed atomic volume if they are treated as simple metals of valence 1 for Cs, 2 for Ba, Eu, and Yb, and 3 for the rest. The solid circles, from Ref. 5, are taken more directly from pseudopotential theory. The solid line, and solid squares, are the corresponding results for the actinides.

plotted as the dashed line in Fig. 1 and compared with values obtained[13] from Ref. 5 (except for the value for Ba which was recalculated from the node in the pseudopotential form factor). We include the alkali metal and alkaline earth metal which preceded each f-metal series. The values are remarkably close, particularly for the rare-earth metals themselves, for which r_c was obtained from the atomic spectra. This justifies the extension to the rare-earth metals and gives us revised values of r_c, listed in Table I.

The fluctuation at europium is associated with its divalency, while its neighbors are trivalent. The same term values were used in the spectra, so there is no fluctuation in the spectroscopic values, but the significant difference in volume means that the empty-core fit is made under a different condition. This could be interpreted as a suggestion that in one material a different r_c should be used if the volume is altered very significantly. If we were to treat any property of europium or ytterbium at a reduced volume it could be preferable to use an r_c close to its neighbor values.

We plot also in Fig. 1 values of r_c for the actinides deduced in the same way, except for Th, Pa, U, Np, and Pu, which are strongly influenced by f bands. The r_c values for those, included in the figure, will be deduced after we have treated the f bands. The value for americium was taken as 0.80 Å rather than the 0.75 Å which fit the observed lattice parameter. This makes it nearly equal to the value for its neighbors. We have more confidence in the smooth variation of these atomic parameters than in the direct relation with atomic volume. The values lie remarkably close to the lanthanide values and not too far from the earlier estimates for Th and U. The discrepancies there may well be due to relativistic effects which have significant effects on the spectra but, as we shall see, have little effect on the total energy. There is certainly no evidence for new difficulties arising in the actinides (except for the f banding), so that this supports our use of the free-electron theory there also.

As a second test of the extension to actinides we may directly predict the bulk modulus $B=\Omega\partial^2E/\partial\Omega^2$ from Eq. (2) using the parameters in Table I. The resulting values are listed also in Table I and compared with experiment. The errors are larger in the actinides than in the alkali metals and alkaline earth metals but this is presumably from greater sensitivity due to greater cancellation. Similar discrepancies arise[5] in aluminum and indium, in comparison to their divalent and monovalent neighbors. We take these results as confirmation of the validity of the extension, though the numerical accuracy is not high.

This description of the electronic structure has given us only the dependence of energy upon volume. It would seem likely that Chelikowsky's method[8] would allow simple estimates, based on properties of the free atom, of the cohesion also, as they did for the other simple metals. It would appear also that the simple analysis of two-body forces, based upon Fermi-Thomas theory, given by Harrison and Wills[7] should be directly applicable. This allows predictions of elastic properties, vibrational spectra, etc., in terms of the parameters of Table I. This two-body interaction is given by

$$V_0(d)=Z_s^2e^2\cosh^2\kappa r_c e^{-\kappa d}/d \ . \tag{3}$$

The Fermi-Thomas screening parameter,

$$\kappa=(4e^2k_Fm/\pi\hbar^2)^{1/2} \ ,$$

has been added to Table I for that purpose. Note in particular that this allows an independent calculation of the bulk modulus in terms of the velocity of sound waves. (The equality of the two is not guaranteed because of the explicit volume-dependent terms.) It gives values similar to those in Table I: for example, 0.015, 0.098, and 0.393×10^{12} erg/cm^3 for Cs, Ba, and La.

Direct predictions, such as those given by Harrison and Wills for the simple metals,[7] may be of interest. One may also adjust parameters (such as the screening parameter and r_c) in order to model the real systems with a form close to a theoretically derived one.

III. DETERMINATION OF THE f-f MATRIX ELEMENTS

The elementary theory of transition metals[4,5] was based upon transition-metal pseudopotentials[6] and an assumption due to Andersen[14] about the zero of the muffin-tin potential. This theory leads to a free-electron band of energy $\langle\vec{k}\,|\,W\,|\,\vec{k}\rangle+\hbar^2k^2/2m$ with states $|\,\vec{k}\rangle$ coupled to the atomic d states by

$$\langle\vec{k}\,|\,\Delta\,|\,d\rangle=\frac{\hbar^2k^2}{m}\left[\frac{4\pi r_d^3}{3\Omega}\right]^{1/2}Y_2^m(\theta_k,\varphi_k)e^{-i\vec{k}\cdot\vec{r}_j} \ , \tag{4}$$

where r_d is a radius characteristic of the element (with a value of order 1 Å), Ω is the volume of the system, Y_2^m is the spherical harmonic associated with the state $|\,d\rangle$ at $\vec{r}_j$, and its argument gives the orientation of $\vec{k}$ with respect to the axes for the d states. The d states in turn are found to be coupled to each other by

$$V_{ddm}=\eta_{ddm}\hbar^2r_d^3/(md^5) \ , \tag{5}$$

where m is the angular momentum about the axis (of length d) between the two atoms in units of $\hbar$. The Koster-Slater notation for the coupling is $(ddm)=V_{ddm}$. The coefficients η_{ddm} are $\eta_{dd\sigma}=-45/\pi$, $\eta_{dd\pi}=30/\pi$, and $\eta_{dd\delta}=-15/2\pi$ for $m=0$, 1, and 2, respectively.

The inclusion of f-like states is closely parallel to the earlier treatment of the d states. We follow the procedure as described in Ref. 5 (see p. 512). The state $|\vec{k}\rangle$ is written as an orthogonalized plane wave (OPW) and expanded in spherical harmonics and spherical bessel functions around one atomic nucleus. The perturbation Δ which couples this OPW to the atomic f state arises from the difference in potential δV between the metal and what it would be in the free atom, since if the f state were an eigenstate of the Hamiltonian it would have no matrix element with any function orthogonal to it. At this stage we make Andersen's approximation to the potential in the metal.[14] We take it to be the atomic potential within a muffin-tin sphere and to be the f-state atomic energy outside; we may choose the sphere radius such that this potential is continuous, but this is not necessary. The δV is zero within the muffin-tin sphere and equal to $\epsilon_f - V_{\text{atomic}}(r)$ outside. It is equivalent to use a plane wave rather than an OPW if we take $\Delta=\delta V-\langle f|\delta V|f\rangle$. After the angular integration the matrix element becomes

$$\langle\vec{k}|\Delta|f,m\rangle=\frac{4\pi}{\sqrt{\Omega}}Y_3^m(\theta_k,\varphi_k)\int j_3(kr)\Delta R_{n3}(r)r^2dr\ , \tag{6}$$

where R_{n3} is the radial f-state wave function. Since the f state is strongly localized the spherical bessel function may be expanded for small r, keeping only the leading $(kr)^3$ term. The integral is actually most conveniently performed by using the Schrödinger equation to write Δ in terms of the kinetic energy operator, so only the function R_{n3} is needed and not the potential. Then we see from Eq. (6) that if the k^3 in the leading term for j_3 is taken out of the integral, the remaining integral depends only on the f-state radial function and the result may be written

$$\langle\vec{k}|\Delta|f,m\rangle=\left[\frac{4\pi r_f^3}{3\Omega}\right]^{1/2}\frac{\hbar^2k^2}{m}kr_fY_3^m(\theta_k,\varphi_k)\ , \tag{7}$$

where r_f depends only upon the atomic f state. This provides a particularly clear way to write the scale factor arising from the integration. This is analagous to Eq. (4) above for the d state. An additional factor $e^{-i\vec{k}\cdot\vec{r}_j}$ should be inserted so that the origin of coordinates need not be taken at the atom in question.

We then obtain the coupling between f states on different atoms as a second-order coupling through the conduction electrons,

$$\langle f'|H|f\rangle=\sum_k\frac{\langle f'|\Delta|\vec{k}\rangle\langle\vec{k}|\Delta|f\rangle}{\epsilon_f-E_k}\ . \tag{8}$$

If we again take the form Andersen assumed for the potential, the denominator may be written simply as $\hbar^2k^2/(2m)$. Then using the form of Eq. (7) for the matrix elements the integrals may be performed analytically. It is not difficult to see that the result will be a numerical constant times $\hbar^2r_f^5/md^7$. The integration follows closely the one given for d states in Refs. (4) and (5), leading to

$$V_{ffm}=\eta_{ffm}\hbar^2r_f^5/md^7\ , \tag{9}$$

with

$$\begin{aligned}&\eta_{ff\sigma}=20(525/2\pi),\quad \eta_{ff\delta}=6(525/2\pi)\ ,\\&\eta_{ff\pi}=-15(525/2\pi),\quad \eta_{ff\varphi}=-(525/2\pi)\ .\end{aligned} \tag{10}$$

It would be possible to calculate the r_f for each element from the known atomic orbitals, as Froyen did for the d states.[4] However, Froyen found that the small-k approximation used was of limited accuracy and depended upon the choice of muffin-tin radius; his values were in error by a factor of approximately $\frac{3}{2}$ in comparison to values obtained by fitting more accurate band calculations. Here we shall therefore also obtain our parameters r_f from calculated bandwidths. In Table II we present values fit to bandwidths obtained by Skriver[15] as discussed in Sec. V.

We may note that a similar calculation can be carried out to obtain matrix elements

$$V_{dfm}=\eta_{dfm}\hbar^2(r_d^3r_f^5)^{1/2}/md^6 \tag{11}$$

with coefficients obtained by Wills.[17] Further, the procedure used in Ref. 5 could be used to obtain V_{lfm} for coupling with s and p states of the form

$$\eta_{lfm}\hbar^2r_f^{5/2}/md^{9/2}\ .$$

IV. SPIN-ORBIT COUPLING

A calculation of the electronic states based upon the simple muffin-tin potential described above, using Schrödinger's equation, neglects relativistic effects which can become significant in the heavier elements, and the actinides in particular. Most relativistic effects simply modify the potential and therefore can be incorporated in the parameters, such as r_f, which enter the calculation. However, the spin-orbit coupling is of different form and shall be considered here. We find in the end that it has little effect on the total energy.

Spin-orbit coupling arises ultimately from the magnetic interactions between the electron spin and the field arising from its orbit. We treat it as a one-electron effect as we did the effects described in the preceding section. The form of the spin-orbit (so) term in the Hamiltonian is[18]

$$H_{\text{so}}=\frac{1}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{1}\cdot\vec{\sigma}\ , \tag{12}$$

where $V(r)$ is the spherically symmetric potential seen by the electron, and $\vec{1}$ and $\vec{\sigma}$ are the orbital and spin angular momentum operators. The form is readily derived as the magnetic interaction of a moment $e\vec{\sigma}/m$ interacting with the magnetic field $-\vec{v}\times\vec{E}/c^2$ seen by an electron moving with velocity $\vec{v}$ through an electric field $\vec{E}$ proportional to dV/dr; the factor of $\frac{1}{2}$ comes from a relativistic correction. In our treatment of f bands spin-orbit coupling will enter always through the intra-atomic matrix element,

$$V_{\text{so}}=\frac{\hbar^2}{2m^2c^2}\int\varphi_f^*\frac{1}{r}\frac{\partial V}{\partial r}\varphi_fd^3r\ . \tag{13}$$

TABLE II. Atomic parameters for the actinides. f-electron number Z_f, atomic-sphere radius r_0, empty-core pseudopotential radius r_c, f-state radius r_f [adjusted to band values from Skriver (Ref. 15)], spin-orbit coupling V_{so} [fit to values from Herbst *et al.* (Ref. 19)], intra-atomic Coulomb repulsion U and exchange interaction U_x [both from Nugent *et al.* (Ref. 16)], d-band width W_f at the observed density [values from Skriver (Ref. 15) used to obtain r_f, except where $W_f=0$ due to localization].

	Ac	Th	Pa	U	Np	Pu	Am	Cm
Z_f	0	1	2	3	4	5	6	7
r_0 (Å)	2.10	1.99	1.81	1.70	1.66	1.68	1.91	2.03
r_c (Å)	0.85	0.87	0.83	0.81	0.80	0.80	0.80	0.81
r_f (Å)	0.98	0.79	0.70	0.66	0.63	0.61	0.61	
V_{so} (eV)			0.17	0.20	0.24	0.26	0.33	0.39
U (eV)		2.3	1.7	1.9	2.0	4.4	3.9	7.0
U_x (eV)			0.111	0.134	0.146	0.160	0.178	0.198
W_f^0 (eV)	7.08	3.58	3.71	4.24	3.93	3.10	0	0
κ (Å^{-1})	1.82	1.83	1.92	1.98	2.00	1.99	1.87	1.81

We shall see that V_{so} is of order 0.3 eV in the actinides.

In evaluating matrix elements of Eq. (12) for a band calculation one requires also the matrix elements of $\vec{l}\cdot\vec{\sigma}$, which would be most conveniently written in terms of raising and lowering operators for the angular momentum and spin. For our purposes it will be simpler to write in terms of the total angular momentum operator $\vec{j}=\vec{l}+\vec{\sigma}$ for the individual electrons, as one might do for the free atom. Then

$$\vec{\sigma}\cdot\vec{l}=(\vec{j}^{\,2}-\vec{l}^{\,2}-\vec{\sigma}^{2})/2 \ .$$

For the free atom we may construct one-electron eigenstates of $\vec{j}^{\,2}$ with eigenvalues equal to $\hbar^2 j(j+1)$, where the j are integers. For f states, $l=3$ and $\sigma=\frac{1}{2}$, and the seven f levels with two spins become six eigenstates of $j=\frac{5}{2}$ and eight eigenstates of $j=\frac{7}{2}$. These are eigenstates of $\vec{\sigma}\cdot\vec{l}$ with eigenvalues

$$\hbar^2[j(j+1)-3(3+1)-\tfrac{1}{2}(\tfrac{1}{2}+1)] \ ,$$

leading to diagonal matrix elements of H_{so}, $-2V_{so}$, and $3V_{so}/2$, respectively. The value of V_{so} could be obtained for the free atom or we can conveniently take it from the calculations by Herbst *et al.*[19]; we list in Table II the value of V_{so} obtained as $\frac{2}{7}$ of the average of the difference between the tops and bottoms of the $\frac{5}{2}$ and $\frac{7}{2}$ bands which they obtained in an atomic-sphere approximation, analogous to a free-atom calculation. Similar values can be obtained spectroscopically from actinide solutions.[20] This same form for $\vec{\sigma}\cdot\vec{l}$ will suffice for our calculations also.

V. THE f-BAND WIDTH

In our total energy calculation the density of f-band states will be approximated by a constant $14/W_f$ over the width of the f band W_f, so the calculation of total energies is trivial once W_f is given. The most convenient way to obtain W_f is to evaluate the second moment of the f band in terms of the interatomic and spin-orbit matrix elements and to choose a W_f to give the same moment. This is the method of moments, similar to that used by Lannoo and Decarpigny.[21]

To obtain the second moment we imagine writing down the Hamiltonian matrix for the complete set of f orbitals for the N_a atoms in the crystal. If this were diagonalized, subject to periodic boundary conditions, it would yield each of the $14N_a$ (a factor of 2 for spin) band states for the crystal, unhybridized with the s, p, and d bands since those are not incorporated in the Hamiltonian. It is convenient to imagine the orbitals taken as real (combining states $e^{im\phi}$ and $e^{-im\phi}$ as $\cos m\phi$ and $\sin m\phi$) and the spins as $\pm\frac{1}{2}$. Then every diagonal element is the f-state energy ϵ_f and we may take it equal to zero by measuring all energies from that origin. There are interatomic matrix elements coupling states on neighboring atoms which may be obtained in terms of Eq. (9). There are also matrix elements of the spin-orbit interaction between orbitals on the same atom. The square of the Hamiltonian matrix $(H^2)_{ij}=\sum_k H_{ik}H_{kj}$ has eigenvalues which are the square of the energy, measured from ϵ_f. Thus the second moment of the energy band is simply the trace of this squared matrix $(H^2)_{ij}$ (which does not change in the diagonalization) divided by $14N_a$:

$$\langle (E_k-\epsilon_f)^2\rangle=\frac{1}{14N_a}\sum_{i,k}H_{ik}H_{ki} \ . \qquad (14)$$

There are two nonvanishing sets of terms in this sum. First are those for which i and k represent orbitals on neighboring atoms. We select out of those terms the set corresponding to i designating an orbital on a particular atom, and k designating an orbital of the same spin (since the interatomic matrix elements between states of different spin vanish) on a particular neighboring atom. The sum of these terms is the trace of a 7×7 matrix (for the seven orbitals on the first atom) with matrix elements $\sum_k H_{ik}H_{kj}$ based upon this particular set of interatomic matrix elements. This sum over k is unchanged if we make a unitary transformation to orbitals k with angular momentum quantized around the internuclear axis, and the trace is unchanged if we transform to orbitals i and j with this quantization. For that particular choice the 7×7 matrix is diagonal and the trace is obtained trivally as

$$V_{ff\sigma}^2+2V_{ff\pi}^2+2V_{ff\delta}^2+2V_{ff\phi}^2 \ .$$

There is such a contribution for each of the n nearest neighbors to the first atom and N_a such atoms. (We shall take $n=12$ in our evaluations.) We may multiply by 2 for spin to obtain a contribution to Eq. (14) of

$$\langle (E_k-\epsilon_f)^2\rangle_{\text{inter}}=\frac{n}{7}(V_{ff\sigma}^2+2V_{ff\pi}^2+2V_{ff\delta}^2+2V_{ff\phi})^2 \ . \tag{15}$$

The second set of nonvanishing terms comes from matrix elements of the spin-orbit coupling interaction in which i and j designate orbitals on the same atom. The trace of each of these 14×14 matrices is unchanged by transforming to eigenstates of $\vec{\sigma}\cdot\vec{1}$. We have seen that for these H_{so} is diagonal with six diagonal elements $-2V_{\text{so}}$ and eight diagonal elements $3V_{\text{so}}/2$. The corresponding trace of the squared matrix is $42V_{\text{so}}^2$, and adding the contribution for each of the N_a atoms we obtain a contribution to Eq. (14) of $3V_{\text{so}}^2$.

We may equate the resulting second moment to the second moment of a constant density of states of $14/W_f$ for energies

$$\epsilon_f-\tfrac{1}{2}W_f<E<\epsilon_f+\tfrac{1}{2}W_f \ .$$

That moment is

$$\langle (E_k-\epsilon_f)^2\rangle = W_f^2/12 \ ,$$

leading to

$$W_f^2=(W_f^0)^2+36V_{\text{so}}^2 \ , \tag{16}$$

where W_f^0 is the bandwidth without spin-orbit coupling,

$$\begin{aligned} W_f^0&=\left[\frac{12n}{7}(V_{ff\sigma}^2+2V_{ff\pi}^2+2V_{ff\delta}^2+2V_{ff\phi}^2)\right]^{1/2} \\ &=\sqrt{11n}\,\frac{3150}{\pi}\,\frac{\hbar r_f^5}{md^7}=\sqrt{n}\,\frac{\hbar^2}{m\Omega_0^{7/3}}(4.31r_f)^5 \ , \end{aligned} \tag{17}$$

with Ω_0 the atomic volume. This result will be central to our treatment of the bonding properties of the actinides. It is interesting that the spin-orbit term and the band terms add as the sum of squares. Spin-orbit coupling is already small but because it adds to the total energy this way its effect on the bonding is further suppressed, and may reasonably be neglected as we shall see in Sec. VII.

We may now also see how the values for r_f were obtained from the bandwidths obtained by Skriver[15] using the atomic-sphere approximation. He specifically obtained f-band masses μ_f in terms of which the f-band width may be obtained as $W_f^0=22.5\hbar^2/(\mu_f m r_0^2)$ with the atomic-sphere radius r_0 related to the atomic volume by $\Omega_0=4\pi r_0^3/3$. These were obtained without the spin-orbit term, so Eq. (17) was used to obtain r_f. The values obtained for W_f^0, r_f, and the r_0 used are listed in Table II. One estimate of the degree of significance of these values can be obtained from Skriver's calculations of the f-band masses for americium also at a volume 31% smaller than observed. This indicated a bandwidth varying as $d^{-5.9}$ rather than d^{-7} and an r_f value of 0.60 Å at the smaller spacing, rather than 0.61 Å.

VI. THE SHIFT IN THE f-BAND CENTER

In the preceding section we obtained the second moment for the bands arising from the coupling between levels on neighboring atoms. If these orbitals were orthogonal to each other, the corresponding Hamiltonian matrix would be Hermitian and the diagonalization would not shift the average energy of the bands. In fact our starting f states were taken as nonoverlapping and therefore orthogonal, but the coupling between states arose through the free-electron states. A way of stating the method of calculation, equivalent to what we did, is to say that we computed the coupling of first-order f states,

$$(\,|f\rangle-\sum_k|\vec{k}\rangle\langle\vec{k}\,|\,\Delta\,|f\rangle)/(\hbar^2k^2/2m) \ ,$$

leading directly to Eq. (8). A calculation similar to the evaluation of Eq. (8), but without the Hamiltonian, shows that the first-order states (which we might regard as approximations to Andersen's muffin-tin orbitals[14]) are not orthogonal. They have an overlap given by

$$S_{f'f}=\sum_k\langle f'\,|\,\Delta\,|\,\vec{k}\rangle\langle\vec{k}\,|\,\Delta\,|f\rangle/(\hbar^2k^2/2m)^2 \ . \tag{18}$$

In obtaining this we noted that $\langle f'\,|\,\vec{k}\rangle$ and $\langle\vec{k}\,|f\rangle$ are zero and that $\langle\vec{k}\,'\,|\,\vec{k}\rangle=\delta_{k'k}$. This expression is of the form of the matrix element in Eq. (8), except for an additional factor of $\hbar^2k^2/2m$ in the denominator. It has been evaluated by the same method to give

$$S_{ffm}=\sigma_{ffm}(r_f/d)^5 \ , \tag{19}$$

with

$$\begin{aligned} &\sigma_{ff\sigma}=-8\left[\frac{105}{2\pi}\right], \quad \sigma_{ff\delta}=-4\left[\frac{105}{2\pi}\right], \\ &\sigma_{ff\pi}=7\left[\frac{105}{2\pi}\right], \quad \sigma_{ff\phi}=\left[\frac{105}{2\pi}\right] . \end{aligned} \tag{20}$$

The eigenvalues for two coupled degenerate levels with overlap S are easily written down, the eigenstates being the normalized even and odd combinations. The result is[22]

$$E_{\pm}=\epsilon\pm\frac{\langle 1\,|\,H\,|\,2\rangle}{1-S^2}-\frac{\langle 1\,|\,H\,|\,2\rangle}{1-S^2}S \ . \tag{21}$$

We have obtained our matrix elements from the band splitting and so $\langle 1\,|\,H\,|\,2\rangle/(1-S^2)$ is to be identified with the appropriate V_{ffm} and the shift in the center of gravity from Eq. (21) becomes simply $-S_{ffm}V_{ffm}$. For weak coupling we may sum the shifts from different interactions and the evaluation of the total shift in energy becomes very much the same as the evaluation of the second moment. The average shift in energy of the seven levels on one atom due to nonorthogonality with levels on a particular neighbor is

$$\begin{aligned} \delta\bar{\epsilon}_f&=-(\tfrac{1}{7})\sum_{m=-3,+3}S_{ffm}V_{ffm} \\ &=\hbar^2(3.11r_f)^{10}/md^{12} \\ &=\hbar^2(2.71r_f)^{10}/m\Omega_0^4 \ . \end{aligned} \tag{22}$$

This should be multiplied by the number of neighbors n to obtain the shift in the center of the band, and then by Z_f to obtain the contribution to the total energy per ion due to this nonorthogonality.

We see that this is the next term in the expansion of the energy in Δ or in $r_f^{3/2}$. It is comforting that it is small, 0.5 eV per ion in uranium, suggesting that we are safe in truncating the expansion. However, because of its rapid variation with distance and because of cancellation among other terms, we shall see that it is not negligible in the actinides.

VII. THE CONTRIBUTION OF THE f-BAND TO THE ENERGY

In obtaining the total energy from simple-metal theory in Sec. II we neglected all coupling between f-like states in the rare-earth metals and heavy actinides, and therefore neglected their contribution to the energy. We shall see more clearly in Sec. X why that is appropriate. Now we need to directly add the contributions to the energy from that coupling. Because of the nonorthogonality we first add $Z_d n\,\delta\bar{\epsilon}_f$ for each ion. The f levels then broaden into a band of width W_f, and by filling only the lower states we gain an energy

$$\delta E_{\text{band}}=Z_f(1-Z_f/14)W_f/2\ , \tag{23}$$

with W_f given by Eq. (16). There might finally be a change in energy due to redistribution of electrons between the f band and the free-electron band but we shall continue to treat the metals as trivalent and neglect such redistribution. Thus we are simply to add the nonorthogonality term and the band term, Eq. (23), to the free-electron energy of Eq. (2), and proceed with the volume-dependent properties as in the rare-earth metals.

We first consider the specific effect of spin-orbit coupling. From Eq. (23) we see that the shift in energy with volume is proportional to the shift in W_f and from Eq. (16), since only W_f^0 varies with volume, we see that

$$\frac{\partial W_f}{\partial \Omega_0}=\frac{W_f^0}{[(W_f^0)^2+36V_{\text{so}}^2]^{1/2}}\frac{\partial W_f^0}{\partial \Omega_0}\ . \tag{24}$$

The only effect of the spin-orbit coupling is to reduce the effect of the bandwidth by the leading factor, which may be evaluated using Table II. It is 0.96, 0.96, 0.94, and 0.89 for Pa, U, Np, and Pu, respectively. These corrections are so small that we shall proceed with the rest of the analysis without spin-orbit coupling but will note the magnitude of the effect when we discuss Fig. 2.

We may combine Eqs. (17), (22), and (23) to obtain the contribution of the f bands,

$$E_{ff}=nZ_f\frac{\hbar^2(2.71r_f)^{10}}{m\Omega_0^4}-\frac{\sqrt{n}Z_f(1-Z_f/14)}{2}\frac{\hbar^2(4.31r_f^5)}{m\Omega_0^{7/3}}\ . \tag{25}$$

This is to be added directly to Eq. (2) for the free-electron contribution to the energy. [Actually the first term should, in principle, be added to Eq. (2) even when the f electrons are localized, but we shall see that it is small even in the light actinidies and becomes quite negligible at the larger atomic volumes associated with the localized electrons.]

VIII. THE VOLUME-DEPENDENT PROPERTIES

We could first minimize the energy to obtain the equilibrium spacing, but as for the rare-earth metals we have turned that around and used that calculation to obtain the r_c of Table II, which are consistent with the observed spacing. The calculation is done by setting the pressure,

$$P=\partial(E_{fe}+E_{ff})/\partial\Omega_0\ ,$$

equal to zero at the observed volume. The resulting r_c are only good to a percent or so since r_f is given only to two decimal places.

We plot in Fig. 2 the observed atomic-sphere radii, which are fit by our free-electron calculations for Fr, Ra, and Ac. For the next elements we have calculated the atomic-sphere radii which would occur if there were no f-band formation; using our parameters, but setting $r_f=0$, we minimize the energy. This gives a curve much like that for the lanthanides. The difference between this curve and the observed radii is our calculated effect of the f bonding. We have chosen the pseudopotential core radius to vary continously through americium, rather than using the observed radius to determine r_c; thus the americium point does not lie on the line though we regard the electrons as localized. In this context the observed americium radius is smaller than expected. We also used our parameters to calculate the radius which would be expected for americium if f bands did form. It appears as the open circle. This figure nicely demonstrates the picture of two alternative states for the actinides with the cross over occurring at americium in accord with Skriver, Andersen, and Johansson.[11]

We may discuss the role of spin-orbit coupling in the context of this figure. Since we have fit the pseudopoten-

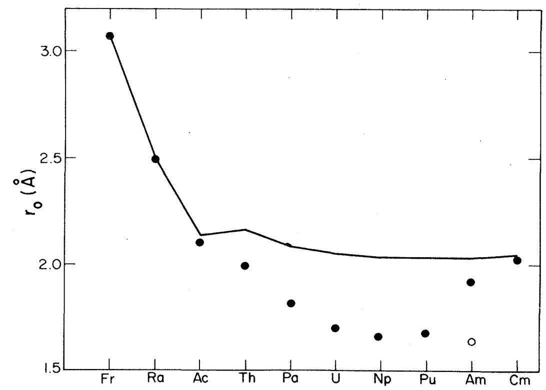

FIG. 2. Points are the experimental atomic-sphere radii for the actinides. The line indicates values obtained if the effect of the f bands is subtracted off. For americium r_c was chosen for consistency with its neighbors so the line does not contain the experimental radius. The open circle is the expected radius if there were f bands.

TABLE III. Prediction of the bulk modulus $\Omega^2\partial^2E/\partial\Omega^2$ (eV/ion) for the light actinides.

	Ac	Th	Pa	U	Np	Pu	Am
Free electron	12.59	19.66	27.34	34.17	36.71	34.76	17.93
f band	0	−12.48	−24.44	−38.83	−44.07	−38.80	0
f overlap	0	3.11	5.80	10.24	11.41	8.95	0
Total	12.59	10.29	8.70	5.58	4.05	4.91	17.93
Expt.	6.05	12.48		15.32	9.16	6.65	6.65

tial core radii to obtain the observed radii the inclusion of spin-orbit coupling would simply have lowered the curve in Fig. 2 by 4%, 4%, 6%, and 11% of the distance between it and the points for Pa, U, Np, and Pu, respectively. These are slightly smaller corrections than the estimates by Brooks,[23] but they do not greatly alter the picture in any case and it appears justified to neglect them.

We could also estimate the extra cohesive energy due to the presence of the f bands. This was in fact done by Johansson and Skriver[9] and our treatment of the f states is sufficiently close to theirs that we could also expect rough accord with experiment.

Of more interest here are direct predictions of the bulk modulus $B=\Omega\partial^2E/\partial\Omega^2$, with E the energy of the system of volume Ω. There are contributions from the free-electron energy of Eq. (2), and from the repulsive overlap and band-broadening terms given in Eq. (25). It is of interest to list these separately, and this has been done in Table III. B has units of energy per unit volume but we prefer to give contributions in electron volts per ion. To obtain the usual form one may multiply our results by 1.6×10^{-12} ergs/eV and divide by the atomic volume in cm^3.

These results are quite interesting. As quantitative predictions they may not be impressive, but the errors are small compared to the very large individual and cancelling contributions; the errors in the total prediction correspond to quite small errors in individual contributions. The f-overlap term, which we have indicated is small, was in fact essential to obtaining a positive bulk modulus and therefore a stable system, for U, Np, and Pu. If one wished to use this theory for predictions of other properties, it would be desirable to adjust one of the parameters to obtain the correct bulk modulus rather than proceed with direct prediction as we have done here.

A final interesting volume-dependent property is the thermal-expansion coefficient. We first compute the Grüneisen constant from Eqs. (2) and (25):

$$\gamma=-\frac{\Omega}{2B}\frac{dB}{d\Omega}=-\frac{1}{2}\left[1+\frac{\Omega^3\partial^3E/\partial\Omega^3}{\Omega^2\partial^2E/\partial\Omega^2}\right]. \tag{26}$$

The results for the actinides with f bands are given in Table IV. For these third derivatives, the overlap repulsion is even more important than in the bulk modulus. The coefficient of thermal expansion is related to the Grüneisen constant by[24]

$$\alpha=\gamma C_V/3B\ , \tag{27}$$

where C_V is the heat capacity at constant volume, approximately $3k_B$ per ion. In this evaluation, $k_B=86.20\times10^{-6}$ eV/K and we use theoretical values for both γ and B. The accord with experiment is remarkable for Th, Pa, and Am, but clearly there is an additional source of thermal expansion for U, Np, and Pu which is not included in the theory. There is very considerable cancellation between the two terms in the Grüneisen constant and it would not have taken large changes in parameters to obtain a negative γ and therefore a negative α as observed in δ plutonium.

IX. REPRESENTATION AS A TWO-BODY INTERACTION

All of the properties discussed in Sec. VIII were obtained from the energy as a function of volume alone. As indicated at the close of Sec. II, we would also like to discuss the change in energy as the atoms are rearranged at constant volume and this can be accomplished if the total energy can be written as a sum of two-body interactions.

The contribution to the energy from the free-electron component is of just the same form in the light actinides as it was in the simple metals and rare-earth metals, so we can again write this energy in terms of the simple interaction potential given in Eq. (3). To that purpose we have included values for the Fermi-Thomas screening parameter in Table II. The energy associated with the f bands, Eq. (25), contains two terms. The first was the repulsion due to nonorthogonality of muffin-tin orbitals on adjacent atoms and was explicitly derived as a two-body term in the energy, Eq. (22). The shift $\delta\bar{\epsilon}_f$ there applies to the Z_f electrons in both atoms in the pair so the corresponding repulsion can be written

$$V_r(d)=2Z_f\hbar^2(3.11r_f)^{10}/md^{12}\ . \tag{28}$$

The second term is less direct.

This term depended upon the ionic positions through

TABLE IV. Prediction of thermal-expansion coefficient.

	Th	Pa	U	Np	Pu	Am
γ	1.46	1.15	0.78	0.30	0.37	1.48
α (10^{-6}/K)	12.2	11.4	12.1	6.4	6.5	7.1
α_{expt}[a]	~12	~11	~19	~28	53.8	7.1

[a] R. O. Elliott (private communication).

the bandwidth W_d given in Eq. (17); we drop the superscript zero but do not include spin-orbit effects. This may be rewritten for an arbitrary arrangement of ions (the derivation is the same) as

$$W_f = \left[\frac{12}{N_a} \sum_{j,i}{}' V_f(d_{ij})^2 \right]^{1/2} \tag{29}$$

for N_a ions, with the prime indicating that $i=j$ is omitted, and where

$$V_f(d)^2 = \tfrac{1}{7}(V_{ff\sigma}^2 + 2V_{ff\pi}^2 + 2V_{ff\delta}^2 + 2V_{ff\phi}^2) \tag{30}$$

is a simple function of separation. If we vary a single $d_{ij}=d_{ji}$ we obtain a δW_f given by

$$\delta W_f = \frac{2(12/N_a)V_f(d_{ij})\delta V_f(d_{ij})}{\left[(12/N_a) \sum_{i,j}{}' V_f(d_{ij})^2 \right]^{1/2}} \ . \tag{31}$$

For the case of small deviations from a perfect crystal, every $V_f(d_{ij})$ is identical and for coupling with n nearest neighbors this becomes

$$2\sqrt{12n}\, \delta V_f(d_{ij})/N_a n \ .$$

The total change in energy for the N_a ions (with only one $d_{ij}=d_{ji}$ change) is obtained by multiplying by $N_a Z_f(1-Z_f/14)/2$ as indicated in Eq. (23). If we add such energy changes for a large number of displacements, the result could be written as arising from an interaction potential:

$$V_{f\,\mathrm{band}}(d) = \sqrt{12n}\, Z_f(1-Z_f/14) V_f(d)/n \ . \tag{32}$$

We obtain the total energy summing the δd for each pair only once.

This is the form we propose but before discussing it further we should note that there are difficulties with the derivation. We will in fact always be interested in changes in energy which are at least quadratic in δd since the system is in equilibrium before the δd was made. Terms can be obtained from the second variation which are exactly consistent with Eq. (32), but there are also cross terms from different δd. These are small, by a factor of order $1/N_a$, but they are of arbitrarily long range so it is not clear mathematically that they can be neglected. (Physically, they would seem quite inappropriate.) However, for the specific case of a uniform compression we can calculate the dependence of Eq. (29) on d exactly and it is correctly given by Eq. (32); all of the long-range interbond interactions have cancelled out. We assume that that is true for other distortions and proceed writing the energy variations for rearrangement at constant volume as a sum of two-body central force interactions, each given by $V_0 + V_r + V_{f\,\mathrm{band}}$, and the calculation of properties for simple metals[7] generalizes directly.

It may be interesting to think of this contribution to the energy, Eq. (32), as a resonating bond. In an ordinary homopolar two-center bond the energy gain is given by a matrix element times the number of electrons, two, which occupy the bond. In a resonating bond, such as in benzene, the contribution to each bond site is divided by the number of sites each pair shares, two for benzene, but the strength of the bond is enhanced also by the square root of the number of sites shared.[25] (Such square roots generally appear in methods based upon second moments.[21]) This would suggest a bonding energy of $2\sqrt{n}\, Z_f V_f/n$, to be compared with Eq. (32). In Eq. (32) the Z_f is replaced by $Z_f(1-Z_f/14)$, corresponding to the continuous filling of levels even including antibonding levels. The same $\sqrt{n}\,/n$ factor appears and the numerical constant $\sqrt{12}$ came from the particular assumption as to the form of the density of states. It is also convenient for calculation to write the coupling explicitly as

$$\begin{aligned} V_{f\,\mathrm{band}}(d) &= Z_f(1-Z_f/14) W_f(d)/n \\ &= \sqrt{n}\, Z_f(1-Z_f/14) \\ &\quad \times \hbar^2 (5.06 r_f)^5/(m d^7 n) \ , \end{aligned} \tag{33}$$

where we have used Eq. (17) in the evaluation.

There is very considerable cancellation between terms, as there was in Table III, and it appears that a calculation of the bulk modulus in terms of the method of long waves would lead to a negative bulk modulus, and instability, in the center of the series. This reflects rather small errors in individual terms but if it is to be useful in calculations it will be necessary to make some adjustments. The essential form of the theory appears to be correct and the estimates of the individual terms are rather well given.

X. ELECTRON LOCALIZATION

We turn finally to the electronic localization which distinguishes the rare-earth metals and the heavy actinides from the light actinides. Skriver, Andersen, and Johansson[11] addressed this question by allowing the electrons to spontaneously spin polarize, as in a ferromagnet, and minimized the energy as a function both of volume and spin polarization. They found that americium, but not the preceding elements, spin polarized and expanded to a large volume. This is in some sense a modeling of the effect since with six f electrons in americium the individual f-band energies, proportional to $Z_f(1-Z_f/7)$, go very nearly to zero in the spin-polarized state, having very nearly the effect that a true decoupling of the f states would, though the calculated bands remain broad. Also, in that model the transition is driven by the exchange energy U_x which favors aligned spins; this would seem to be the kind of energy and the magnitude of energy which drives true localization.

This ferromagnetic criterion is very easily applied to the Friedel model of the density of states. When applied to d states[26] it gives the criterion for a transition at constant volume: Ferromagnetism is indicated if $U_x > W_d/5$. The same analysis for f states indicates ferromagnetism if

$$U_x > W_f/7 \ . \tag{34}$$

Experimental values for U_x have been extracted from spectroscopic studies of acqueous actinide ions by Nugent[16] and these may be used also in the metal. These values are listed in Table II. (Also listed there are values of the intra-atomic Coulomb repulsion U which can be used in determining f-state energies in actinide compounds using the method of Froyen.[27] They are not used here.) The energy difference which must become negative

TABLE V. Localization parameters for the actinides.

	Pa	U	Np	Pu	Am
$W_f - 7U_x$ (eV)	2.93	3.30	2.91	1.98	2.59
ΔE_{local} (eV)	1.88	2.44	2.32	1.64	1.64

for ferromagnetism is given in the first line in Table V and is not close to indicating a transition at constant volume. It is probably correct that holding americium at the low volume (the radius indicated by an open circle in Fig. 2 was used) would prevent the transition. The volume should be allowed to change in the comparison, a calculation which can readily be done using the parameters given here.

We choose instead to carry out a calculation more closely related to true localization. We compare the energy of the banded state, which corresponds to the points in Fig. 2, with the energy of the localized state (as with $r_f = 0$) indicated by the line, including the exchange energy for the two configurations. The exchange energy in the expanded (localized) state is $-U_x Z_f(Z_f - 1)/2$, lower than that of the state with equal numbers up and down by $U_x Z_f^2/4$. The band energy is lower in the contracted (band) state by $Z_f(1 - Z_f/14)W_f/2$ and the free-electron energy is lower in the expanded state by an amount which can be computed from Eq. (2). The increase in computed energy in going to the expanded state is the ΔE_{local} listed in Table V. We see that the tendency increases at Pu and Am but we do not predict the transition at americium. The ferromagnetic transition would appear to be close to occcurring at relaxed volume because some band energy is retained, but the localization criterion would seem to be the correct one and our model and parameters appear inadequate to predict the transition.

An isostructural transition in cerium presumably comes from a similar localization[28] but we do not discuss it here. Neither did we discuss the energy bands themselves, which have been extensively considered by Koelling, Freeman, and Arbman.[29] These were sidestepped by the use of the model density of states.

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