5f-electron Delocalization in Americium

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The pressure-volume relation for americium has been obtained without adjustable parameters from self-consistent, spin-polarized band calculations. Around 100 kbar we find a first-order transition to a state with low volume and no spin. This is consistent with preliminary high-pressure measurements.

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Americium is the first element in the actinide series which behaves like a rare earth: Its cohesive,[1] structural,[1,2] magneitc,[3] and superconducting[4] properties indicate that the 5f electrons are *localized* and occupy a nonmagnetic ($J=0$) 5f^6 configuration. The preceding element, plutonium, has properties which can only be understood on the basis of *itinerant* 5f electrons.[5] This change of behavior between plutonium and americium is usually said to originate from the 5f-orbital contraction through the actinide series, and it has been expected that americium under compression will undergo a transition to a dense phase where the 5f electrons are itinerant.[6]

We recently[7] calculated the equilibrium atomic volumes and bulk moduli at zero temperature for the metals radium through americium using the effective one-electron theory for the ground state developed by Hohenberg, Kohn, and Sham[8]; that is, for each metal we performed self-consistent band-structure calculations[9] as a function of atomic volume. The 5f electrons were treated on the same footing as the 6d, 7s, and 7p conduction electrons and, by allowance for spin polarization, the (first) Hund's-rule coupling was included. For convenience, the spin order was taken to be ferromagnetic. The only input to these calculations was thus the atomic numbers and the fcc crystal structure. Our results agreed well with the experimental values (better than 5% for the Wigner-Seitz radii and better than 20% for the bulk moduli) and hence we could account quantitatively for the fundamental change in the cohesive properties between plutonium and americium.

In this Letter we publish for americium our pressure-volume relation which exhibits a first-order transition from localized to itinerant f-electron behavior at a pressure around 100 kbar (Fig. 1). Furthermore, we propose to identify this behavior with the phase transition recently observed by Akella, Schock, and Johnson[11] at 110 kbar.

It is surprising that the cohesive aspect of the delocalization transition is described quantitatively by spin-polarized band theory and, in the following, we shall explain how our pressure-volume relation arises from the energy bands so that it may be understood which of their features are essential.

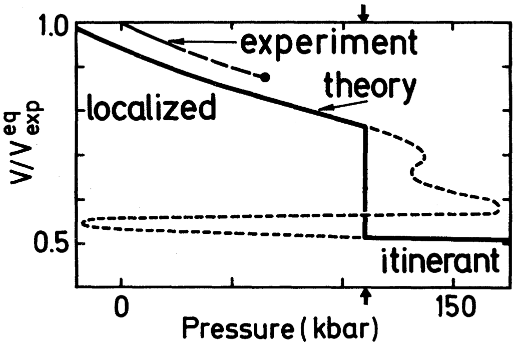

FIG. 1. Theoretical and experimental pressure-volume relations. The experimental curve is that of Stephens, Stromberg, and Lilley (Ref. 1) and the point that of Akella *et al*. (Ref. 10). The arrows point to the pressure for the phase transition observed by Akella, Schock, and Johnson (Ref. 11).

It has been shown[12, 13] that the pressure, $P \equiv -dU/dV$, may be expressed as the volume derivative of the sum of the one-electron energies, without any correction for double counting, provided that the one-electron potential in each Wigner-Seitz cell is kept rigid upon the infinitesimal change of volume. If, further, the band states are expanded in partial-wave components in each cell, and the atomic-sphere approximation[9] is used, the pressure may be decomposed into angular momentum components.

In Fig. 2 the curve labeled "*spd*" is the sum of the s, p, and d partial pressures. We have here chosen to plot $3PV$ $(=-dU/d\ln s)$ vs $\ln s$, with s being the Wigner-Seitz radius, i.e., $4\pi s^3/3 = V$. The *spd* pressure curve is the appropriate one when the f electrons do not contribute to the binding, i.e., when they are completely localized.[14] When the f pressure is included, but spin polarization is not allowed for, the pressure curve labeled "Non" is obtained; this is the curve appropriate for itinerant f electrons. The f pressure is seen to be negative, that is attractive, and it is approximately given by[12]

$$(3PV)_f{}^{\text{Non}} \approx -n\left(\frac{\delta C}{\delta \ln s} + (\bar{E} - C)\frac{\delta \ln W}{\delta \ln s}\right) \qquad (1)$$

$$\approx -3.5n(1 - \tfrac{1}{14})W \approx -12W. \qquad (2)$$

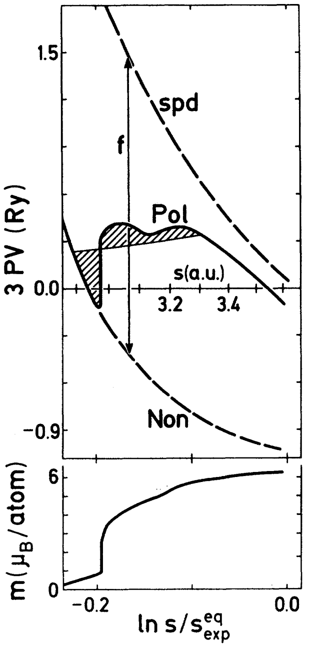

FIG. 2. Theoretical partial pressure, $3PV$, and spin-polarization, m, as functions of the Wigner-Seitz radius, s, on logarithmic scale.

Here δ denotes the change with a rigid atomic-sphere potential and we have separated the volume dependence of the f-band center, C, from those of the f-band energies, E, measured relative to the center. W is the f bandwidth, $\bar{E}$ is the center of gravity of the occupied part of the f band, and n is the number of f electrons. In deriving the estimate (2) from (1) we have approximated $\bar{E} - C$ by $-\frac{1}{2}(1 - \frac{1}{14})W$, which holds exactly for a rectangular shape of the f-projected density of states. Furthermore, we have used expressions given in Ref. 12 ro estimate that $\delta C/\delta \ln s \approx 0$ and $\delta \ln W/\delta \ln s \approx -(2l+1) = -7$. The self-consistent band calculations show that, through the volume range of interest, the number n of f electrons per atom remains constant and equal to 6.4. We thus realize that the volume dependence of the f pressure is that of the f bandwidth. From the self-consistent calculations[15] $W = (95\ \text{mRy})[s/(3.6\ \text{a.u.})]^{-5.9}$ and this describes the difference between the localized (*spd*) and itinerant (Non) curves in Fig. 2 rather well.

In Fig. 3 we show the total and the *spd*-projected densities of states per atom and per spin, their difference being the f-projected density of states. The volume dependence of the latter is seen to be essentially that of W, such that $WN_f(E)$,

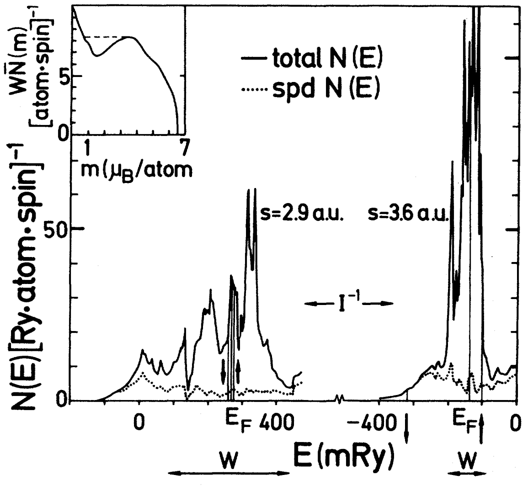

FIG. 3. Total (full curves) and *spd*-projected (dotted curves) densities of states per spin for two different Wigner-Seitz radii, s. The zero of energy is the electrostatic potential at the Wigner-Seitz radius. The Fermi levels corresponding to the occupancies $\frac{1}{2}n$ (nonpolarized) and $\frac{1}{2}(n \pm m)$ (spin polarized) are indicated by E_F and $\downarrow\uparrow$, respectively. The inset shows the average density-of-states function, $W\bar{N}(m)$, constructed from the f-projected density of states as described in the text.

considered as a function of E/W, is approximately independent of volume.

We must now understand the factors determining the transition from the itinerant to the localized pressure curve. In Fig. 2 the curve labeled "Pol" is obtained by allowing for ferromagnetic spin polarization in the self-consistent calculations, and the f part of the spin polarization, $m \equiv n_\uparrow - n_\downarrow$, is shown as a function of atomic volume in the bottom panel. (The *spd* polarization is more than one order of magnitude smaller than the f polarization.) The difference between the Pol curve and the *spd* curve is described rather well with (2):

$$\begin{aligned}(3PV)_f{}^{\text{Pol}} &\approx -3.5[n_\uparrow(1-\tfrac{1}{7}n_\uparrow)+n_\downarrow(1-\tfrac{1}{7}n_\downarrow)]W\\ &=-3.5[n(1-\tfrac{1}{14}n)-\tfrac{1}{14}m^2]W\\ &\approx -12[1-(\tfrac{1}{7}m)^2]W. \qquad (3)\end{aligned}$$

The Pol curve thus follows the Non curve when m is small and it falls below the *spd* curve by approximately $2W$ when the polarization is complete. Because the f band is nearly half full the spin polarization removes the f pressure almost entirely.

The volume dependence of m may be explained by noting that a self-consistent, ferromagnetically spin-polarized band calculation essentially leads to a Stoner picture.[12,16] In Fig. 3 we have thus indicated the spin-polarized situation merely by placing the spin-up and spin-down Fermi levels on the nonpolarized state-density curve. The distance between the levels is mI and self-consistency requires that the area between them be m. This condition is conveniently formulated as $I\bar{N}(m)=1$, where $\bar{N}(m)$ is an average density-of-states function, constructed from the f-band density of states per spin in the following way: As a function of the polarization, m, we can find the energy separation, $\Delta(m)$, between the levels corresponding to the occupancies $\frac{1}{2}(n \pm m)$, and hence $\bar{N}(m) \equiv m/\Delta(m)$. The Stoner parameter obtained from the band calculations is $I = 36$ mRy, through the volume range of interest. The volume dependence of m is therefore determined by the equation

$$W\bar{N}(m) = (95/36)[s/(3.6\ \text{a.u.})]^{-5.9}, \qquad (4)$$

where, as previously remarked, $W\bar{N}$ is independent of volume.

The left-hand side of (4) is shown in the inset of Fig. 3 and, when it is turned counterclockwise by 90°, the resemblance with the m curve in Fig. 2 becomes obvious. The central peak in $N_f(E)$ (see the curve for $s = 2.9$ a.u.) gives rise to the early onset, but slow increase, of m for small volumes. Because of the m^2 dependence in (3) this has practically no consequence for the pressure curve. The two peaks at 200 and 320 mRy cause a maximum in $\bar{N}(m)$ and give rise to a discontinuity in the m curve and in the pressure curve at $s = 2.98$ a.u. The critical pressure for the first-order transition is obtained by means of the familiar Maxwell equal-area construction.

We now summarize by pointing out which features of the band model seem essential for explaining the experiment. For our determination of the volume and bulk modulus of normal Am it is important that the f band is nearly half full ($n = 6.4$) and that the spin polarization is complete ($nI \geq W$). Furthermore, 6.4 is sufficiently close to 6 so that, in the high-volume, high-spin state, the $5f$ electrons may be considered as being essentially in the local $5f^6$ configuration, for which Hund's rules give $S = 3$, $L = 3$, and $J = 0$. This agrees with the observed lack of magnetic moments in normal Am. Our determination of the critical pressure seems to indicate that the value of the Stoner parameter ($I = 36$ mRy) and the assumption of ferromagnetic spin order together with the gross features of the state density are reasonable.

Previously we found[7] that plutonium was that element among the actinides for which the calculated (zero-temperature) and experimental (room-temperature) equilibrium volumes differed most, the former being 15% smaller than the latter. This points to a failure in our description of the itinerant f state close to the phase transition and it is conceivable that long-range spin fluctuations would reduce the magnitude of the f pressure such that, for the Non curve in Fig. 2, one should, instead of (2), effectively use (3) with a small value of m. This, in addition to the strong temperature dependence of the atomic volume observed in plutonium, suggests that an experiment on americium at room temperature may give a volume change considerably smaller than the 40% predicted in Fig. 1.

It is often believed that the delocalization transition makes the f orbital expand considerably. In our model this is not the case; essentially, the orbital just renormalizes to the smaller atomic volume. This is in accord with most recent Compton-scattering results[17] for the, in our view similar,[18] γ-α transition in Ce.

It would be interesting if the high-pressure experiments for americium could be carried further. Beyond the transition one would expect to find some of the crystal structures typical for the lighter actinides and a suppression of the superconductivity by spin fluctuations.

We wish to thank Dr. J. Akella and co-workers for permission to quote their high-pressure results prior to publication.

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[1] L. B. Asprey, B. B. Cunningham, F. H. Ellinger, D. B. McWhan, J. C. Wallman, and W. H. Zachariasen, J. Inorg. Nucl. Chem. 15, 185 (1960); Dr. R. Stephens, H. D. Stromberg, and E. M. Lilley, J. Phys. Chem. Solids 29, 815 (1968).

[2] B. Johansson, in *Rare Earths and Actinides—1977*, edited by W. D. Corner and B. K. Tanner, The Institute of Physics Conference Series No. 37 (The Institute of Physics, Bristol and London, 1978), p. 39.

[3] W. Nellis and M. B. Brodsky, in *The Actinides; Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby (Academic, New York, 1974), Vol. 2, p. 265.

[4] J. L. Smith and R. G. Haire, Science 200, 535 (1978).

[5] A. J. Freeman and D. D. Koelling, in *The Actinides; Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby (Academic, New York, 1974), Vol. 1, p. 51; E. A. Kmetko and H. H. Hill, in *Plutonium 70*, edited by W. N. Miner (AIME, New York, 1970), p. 233; B. Johansson, Phys. Rev. B 11, 2740 (1975); B. Johansson and A. Rosengren, Phys. Rev. B 11, 1367 (1975).

[6] B. Johansson, J. Phys. Chem. Solids 39, 467 (1978).

[7] H. L. Skriver, O. K. Andersen, and B. Johansson, Phys. Rev. Lett. 41, 42 (1978).

[8] W. Kohn and L. J. Sham, Phys. Rev. 140, A1135 (1965); U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).

[9] The one-electron calculations employed the local-spin-density approximation (Ref. 8) and the linear combination of muffin-tin orbitals method in the atomic-sphere approximation [see O. K. Andersen, Phys. Rev. B 12, 3060 (1975)]. The electron density of the Rn cores was frozen. The zero-point motion was neglected when calculating the pressure. The relativistic shifts were included but *not* the spin-orbit coupling. For the $5f$ electrons this is reasonable because, within a localized $5f$ shell, the LS coupling is known to yield a far better description than the jj coupling and, when the $5f$ electrons are delocalized, the f bandwidth exceeds the maximum spin-orbit splitting. [For Am ($\frac{7}{2}$), $\xi_{5f} \approx 85$ mRy and $W_{5f} \approx 300$ mRy.] For the conduction electrons, however, the spin-orbit coupling should have been included in the band calculations [see B. R. Judd, Phys. Rev. 125, 613 (1962)], but its effect on the cohesive properties considered in the present work is negligible.

[10] J. Akella, Q. Johnson, W. Thayer, and R. N. Schock, to be published.

[11] J. Akella, R. N. Schock, and Q. Johnson, private communication. These authors find a phase transition in americium at 110 kbar. Because of experimental difficulties the crystal structure of this high-pressure phase has not yet been determined, and therefore the volume change which accompanies the transition cannot be evaluated.

[12] U. K. Poulsen, J. Kollar, and O. K. Andersen, J. Phys. F 6, L241 (1976); A. R. Mackintosh and O. K. Andersen, in *Electrons at the Fermi Surface*, edited by M. Springford (Cambridge Univ. Press, Cambridge, England, 1979).

[13] D. G. Pettifor, Commun. Phys. 1, 141 (1976).

[14] This is not quite true because the partial pressures refer to partial-wave components rather than to orbitals. s, p, and d orbitals will therefore contribute to the f pressure too.

[15] The f width is defined in terms of the f partial wave, normalized to unity in the Wigner-Seitz sphere and evaluated at the energy C and at the Wigner-Seitz radius s as $W = 22.5\, s\varphi_f{}^2(C,s)$. This would be the f bandwidth in the fcc structure if hybridization were neglected. See Ref. 9.

[16] S. H. Vosko and J. P. Perdew, Can. J. Phys. 53, 1385 (1976); O. Gunnarsson, J. Phys. F 6, 587 (1976).

[17] U. Kornstädt, R. Lässer, and B. Lengeler, in Proceedings of the International Conference on Magnetism, Munich, 1979 (unpublished); J. Felsteiner, M. Heilper, and K.-F. Berggren, Solid State Commun. 32, 343 (1979).

[18] D. Glötzel, J. Phys. F 8, L163 (1978).