

α - δ transition in plutonium as a Mott transition in an f subsystem

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The transition of plutonium from its α phase to its δ phase is accompanied by the localization of $5f$ states. An antiferromagnetism of δ -Pu is predicted.

It is generally acknowledged that the $5f$ electrons in light actinides are collectivized, while those in heavy actinides are localized.¹ On the other hand, the particular metal in which the nature of the $5f$ states changes and just how this change occurs are not yet understood. This is a matter of general physical interest, for (for example) comparing the properties of actinides and lanthanides. This comparison is important both for applications (radiochemistry) and for solving several fundamental problems (the nature of mixed valence and other anomalous properties of f -element compounds). In the present letter we work from relativistic spin-polarized band-theory calculations to show that, as we move through the actinide series, the localization of the $5f$ electrons occurs first in plutonium. We study the features of this localization process.

Several unique features distinguish plutonium from all other pure metals: an

abundance of stable phases at standard pressure (the α , β , γ , δ , δ' , and ϵ phases, in order of increasing temperature), many of which have a complex crystal structure; sharp anomalies in the thermal expansion in the δ and δ' phases; and, finally, an 18% increase in volume upon the transition from the "compressed" α , β , and γ phases to the "inflated" δ phase.² This volume increase is totally uncharacteristic of systems with metallic binding. Its only analog is in the abrupt change in volume upon a pressure-induced isostructural transition in cerium from a trivalent state (the γ phase) to the α phase with a mixed valence. According to Ref. 3, what occurs in the latter case is not an f - d transition, as was proposed in the early studies, but a delocalization of $4f$ electrons as the result of an increase in the direct overlap of wave functions: a Mott transition in an f subsystem. As was shown in Ref. 4, the microscopic reason for this

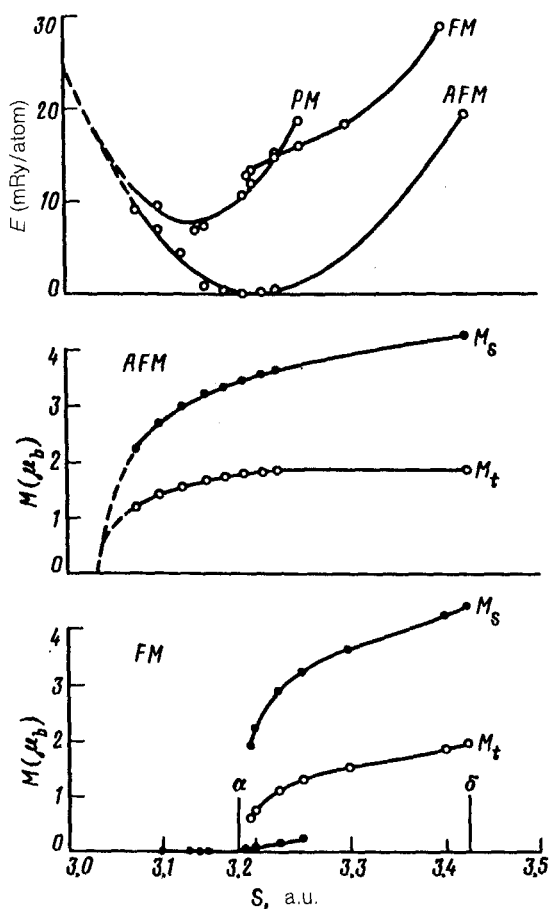


FIG. 1. The total energy E , the spin magnetic moment M_s , and the total magnetic moment $M_t = M_s + M_L$ (M_L is the orbital moment) versus the radius of the Wigner-Seitz sphere, S , in the paramagnetic (PM), ferromagnetic (FM), and antiferromagnetic (AFM) phases of Pu.

behavior is the collapse of the wave function as we go from the $4f^2$ configuration to the $4f^1$ configuration of the Ce atom. A corresponding effect occurs in the U, Np, and Pu atoms. One gets the impression that the α - δ transition in Pu is similar in nature to the α - γ transition in Ce, but the only way to resolve this question is to calculate the electronic structure of metallic Pu and analyze the results.

The δ phase of Pu has an fcc structure. The more complex α modification crystallizes in a monoclinic structure with 16 atoms per unit cell. Since the interatomic distance is the most important factor in a study of the direct overlap of f states of different centers of a crystal, the α phase was modeled by an fcc structure in the calculations (the experimental radii of the Wigner-Seitz spheres were $S_\alpha = 3.181$ and $S_\delta = 3.424$ a.u.). The calculations were carried out by a completely relativistic, spin-polarized approach (the calculation method is described in Ref. 5) for the paramagnetic phase, for the ferromagnetic phase, and for the antiferromagnetic phase with a wave vector $\mathbf{Q} = (\pi/a)(0,0,1)$. From the results calculated for the total energy and the magnetic moment (Fig. 1) we see that (a) the antiferromagnetic phase has the lowest energy and (2) the magnetic moments in the ferromagnetic and antiferromagnetic phases are similar in magnitude for the parameter values corresponding to the δ modification, while with the value of S_α the solution corresponding to the ferromagnetic phase is missing.

In band magnetic materials (nickel and iron) the magnetic moments of different magnetic structures are quite different, and the magnetic moment usually "collapses" upon rotation through a sufficiently large angle.⁶ In localized (Heisenberg) magnetic

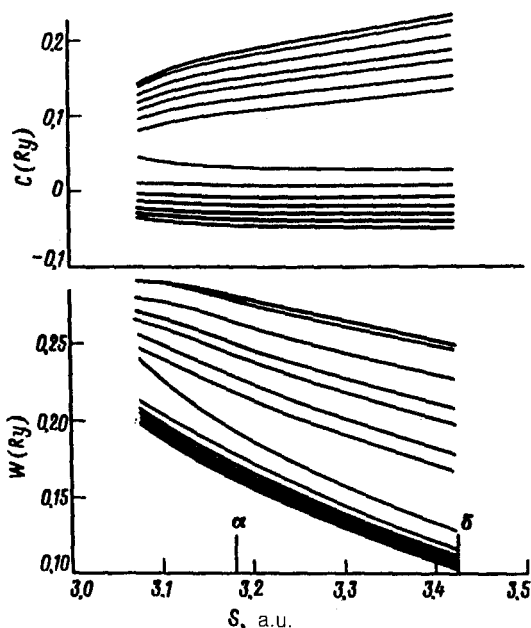


FIG. 2. Centers (C) of the canonical $5f$ bands (reckoned from the Fermi level) and their widths (W) versus S for the antiferromagnetic phase of Pu.

materials, the magnitude of the moment is of course independent of the type of magnetic order. It can thus be suggested that under the conditions $S_\alpha \ll S < S_\delta$ there is a transition from a localized magnetism (in the δ phase) to a collectivized magnetism.

Figure 2 shows the parameters of the 14 canonical f bands (these bands were calculated without a hybridization of the different orbital states, so they characterize the direct overlap of the f functions at different sites⁷). For most values of the radius S , the states can be classified in two groups, with spin projections up and down. Each of these groups is in turn split into seven sublevels by the spin-orbit coupling. A compression of the lattice reduces the spin splitting (Fig. 1) and thereby causes a regrouping of the states and a collapse of these states in the nonmagnetic limit, into sixfold-degenerate and eightfold-degenerate levels corresponding to total moments $j = 5/2$ and $7/2$ (in general, neither the total moment nor the spin projection is a good quantum number). The width of the band increases sharply as we move to higher energies for each value of S . The transition from α -Pu to δ -Pu has its greatest effect on the low-energy bands and is accompanied by a decrease in their width (by a factor of nearly 2) and a lowering of the centers by 0.12 Ry. The $5f$ wave functions are thus "pressed down" more, and the corresponding energies are "submerged" more. According to Ref. 4, the microscopic reason for this behavior may be a collapse: a pronounced sensitivity of the parameters of the atomic states to small variations in the effective potential at the threshold for the appearance of a bound state in the inner well. The parameters of the vacant $5f$ states in the high-energy region, in contrast, vary considerably more smoothly with S .

Consequently, the behavior of both the magnetic moments and the parameters of the canonical bands indicates that a "Mott" transition from a collectivized behavior to a localized behavior of the $5f$ states occurs upon the transition from α -Pu to δ -Pu. As in the case of Ce, the redistribution of electrons between f and d states is considerably less extensive (Table I).

In general, the method of a spin-density functional may prove inadequate for a detailed description of a "localized" phase.⁸ However, two facts—the existence of a magnetic order and the occurrence of a sharp change in the extent of localization of the f states—should be described correctly. On the other hand, it may be necessary to take intraatomic correlations into account (by the method of Ref. 8, for example) in order to calculate the equation of state and to describe the abrupt change in the volume of Pu upon the transition from the α phase to the δ phase.

The parameter which basically governs the degree of overlap of the $5f$ wave functions is the interatomic distance. In the series of pure actinides, Pu occupies a

TABLE I. Occupation numbers of the $5f$ and $6d$ states in the antiferromagnetic phase of Pu.

S	3,075	3,170	3,225	3,424
N_f	5.24	5.18	5.16	5.10
N_d	2.04	2.02	1.99	1.88

“critical” position. Other elements may play this role in series of isostructural chemical compounds. At the same time, we know of at least one compound of Pu which has a mixed valence: PuTe (Ref. 9). By analogy with pure Pu, one might suggest that what is important in this case is not so much $f-d$ hybridization (as in SmS) as the direct $f-f$ overlap of the wave functions (as in α - Ce).

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