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INCONSISTENCIES

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ABSTRACT SHEET

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ABSTRACT

Light actinide elements alone, and in some of their alloys, may exist as a static or dynamic mixture of two configurations. Such a state can explain both a resistivity maximum and lack of magnetic order observed in so many actinide materials, and still be compatible with the existence of f-electrons in narrow bands. Impurity elements may stabilize slightly different intermediate valence states in U, Np and Pu, thus contributing to inconsistencies in published results. The physical property behavior of mixed-valence, rare-earth compounds is very much like that observed in development of antiphase (martensitic) structures. Martensitic transformations in U, Np, and Pu, from high-temperature b. c. c. to alpha phase, may be a way of ordering an alloy-like metal of mixed or intermediate valence. The relative stability of each phase structure may depend upon its electron-valence ratio. A Hubbard model for electron correlations in a narrow energy band has been invoked in most recent theories for explaining light actinide behavior. Such a model may also be applicable to crystal symmetry changes in martensitic transformations in actinides.

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INTRODUCTION

The results of low-temperature physical property measurements made on the early actinide elements (U, Np and Pu) show a variability or inconsistency between test specimens. Anomalies appear especially in α -Pu, in transport phenomena such as electrical resistivity, thermoelectric power and Hall effect. Results have a surprisingly great dependence on impurity content and this may be a clue to the source of inconsistencies. The variability in physical property results for α -Pu, shown through publications of different experimentalists, has been previously surveyed by this author.^{1,2}

The ground state of the early actinides is a combination of electron energy configurations, and the structures of the alpha phases of Np and Pu and the gamma phase of Pu have been classified as metallic alloys. These bits of information have suggested to this writer that at least the above-mentioned phases of Np and Pu must exist in a type of mixed-valence state. They certainly exist as mixed configurations. A comparison has been made of the low-temperature physical properties of α -U and α -Pu and those of rare-earth metallic compounds shown to have a fluctuating valence.³ This comparison favors a fluctuation temperature in these two actinide phases. Support for the possibility of valence fluctuations in the light actinides and their compounds or alloys also comes from other sources.^{4,5}

There is another complicating factor in the early actinides. The $\beta \rightarrow \alpha$ phase transformations in U, Np and Pu may be martensitic, and the β phases are often retained to low temperatures. The

case for a martensitic transformation in α -U at ~ 42 K has been summarized by this author.⁶ The $\gamma \rightarrow \alpha$ transformation in cerium metal is possibly martensitic.⁷ A theory based on configurational crossover has been presented by Hirst⁸ to explain this cerium transformation (although it is controversial - see ref. 5). This leads to the speculation that there is some connection between valence fluctuations and the tendency for a martensite-like behavior in the rare earth and actinide systems. Antiphase and martensitic structures are compatible. It is remarkable that, with the exception of heat capacity, the physical property behavior of so many mixed-valence R.-E. compounds is like that observed in the development of antiphase structures. The inference being developed by this author is that antiphase ordering, martensitic transformations, and an intermediate valence state may not be mutually exclusive and may be explainable by a variation of the Hubbard theory⁹ for electron correlations in narrow energy bands.

APPLICABILITY OF AN INTERCONFIGURATION FLUCTUATION (ICF) THEORY TO ACTINIDE SYSTEMS

There are similarities between the physical property behavior of certain actinide materials and the ICF compounds. These similarities are as follows: a maximum in the electrical resistivity curves, an absence of magnetism, an unusually high electronic specific heat, a discontinuity in the derivative of lattice constant upon cooling or upon application of pressure, a humping in thermoelectric power versus temperature curves, a minimum in Young's modulus curves, and an extreme sensitivity to impurities. These similarities have been briefly discussed before by this author³ and only a few will be discussed in greater detail.

A maximum in the resistivity vs temperature curves of two plutonium phases and of plutonium alloys with widely differing crystal structures has been noted by Brodsky et al.¹⁰ It seemed improbable to these authors that the listed plutonium phases and alloys all had similar f bands and appropriate values of $N'(E)$ and $N''(E)$. According to Sales and Viswanathan,¹¹ the resistivities of ICF compounds fall phenomenologically into two broad categories. In one of these the conductivity appears to be dominated by the very electrons which fluctuate in and out of the f shell. The effect is large, and the resistivities of these compounds increase with decreasing temperature, as is the case with α -Pu. In ICF compounds falling into the second category, both an "s-like" and an "f-like" band take part in the conduction to yield an S-shaped resistivity curve.¹¹ Other actinide materials appear to show a resistivity behavior which falls into this second category.¹⁰

There appears to be a density maximum in both α -U¹² and α -Pu¹³ at about 50 K. The lattice change is not great in these two actinide

elements, but it could indicate a critical point. Müller-Hartman¹⁴ predicts that there will be a low-temperature anomaly in thermal expansion in all R.-E. compounds of intermediate valence. His theory should also be applicable to actinides, and as with R.-E. compounds, a temperature dependent self-energy may also lead to change in occupation of f levels with falling temperature. The smaller volume discontinuity in actinides may result from the much more extended nature of the 5f wave functions as compared to 4f electrons, and so there may be no clear correlation between the actinide valence and lattice constant.⁵

The magnetic susceptibility of many actinide elements and compounds is temperature independent at high temperatures. The absence of magnetism can imply an itinerant 5f behavior or be due to rapid spontaneous fluctuations in a mixed-valence system. The low-temperature magnetic susceptibility curve for α -Pu presented by Fournier¹⁵ suggests that this phase exists in an intermediate valence state at 80 K. His curve is remarkably like that shown for CeNi₅ by Buschow et al.,¹⁶ if the latter data are plotted as χ vs T. They¹⁶ interpret the maximum in the χ vs T curve of CeNi₅ at 90 K as suggesting that Ce is present in an intermediate valence state. The χ vs T curve for α -Pu does not show a maximum at 80 K because the susceptibility is temperature independent above this temperature, but the susceptibility decreases below 80 K to show a minimum at 40 K. The minimum was also observed with CeNi₅. Spin fluctuation theory¹⁷ should be applicable in α -Pu particularly below $\sim$ 80 K because the susceptibility results have been interpreted by Fournier as an electronic transition with 5f electrons condensing to give local moments. One could also interpret Fournier's susceptibility curve for α -U¹⁸ with its maximum at $\sim$ 80 K and a minimum at $\sim$ 40 K as indicating an intermediate valence state in that actinide element.

INTERMEDIATE VALENCE STATE IN ACTINIDES

Herbst et al.⁴ predicted valence changes and fluctuations in actinides of the type observed in many R.-E. compounds. This was possible because their calculations indicated the presence of unoccupied f levels rather near ϵ_F for uranium onward into the series. Robinson's⁵ expectation was that one would find more examples of valence instabilities and intermediate valence states among actinide materials than among R.-E. materials.

The intermediate valence state and valence-fluctuation models have been recently reviewed by Jefferson and Stevens,¹⁹ Robinson,⁵ and Brandow.²⁰ The case for valence instabilities in actinides has been principally presented by Robinson. He questions whether the 5f electrons are completely localized or itinerant. His view is that probably the correct model has properties intermediate to those of the localized and band approaches. He notes that there

are two sharply distinct theoretical approaches to explaining the origin of valence transitions. These are: an electronic model and the lattice-change model. He believes both effects are important. Robinson begins with the localized or configuration-based model of the f-electron states and then adds the interactions (hybridization) leading to some degree of itinerant motion. His model is formulated in terms of Hubbard's⁹ atomic representation.

F BONDING, CRYSTAL STRUCTURES AND MARTENSITIC BEHAVIOR IN ACTINIDES

The phase transitions that occur with decreasing temperature in the early actinides are transitions to structures of decreasing symmetry. It has been suggested that the unusual crystal structures found in U, Np and Pu are due to f-electron bonding. Kmetko and Hill²¹ have also suggested that f bonding is minimal in the δ (fcc) and ϵ (bcc) phases of Pu. They imply that the asymmetric nature of f bonding is not compatible with an undistorted cubic structure.

The crystal structures observed on cooling plutonium metal from the bcc(ϵ) phase to room-temperature monoclinic (α) phase are those observed in non-ferrous martensites on cooling from the bcc phase. In the latter, the structures formed at temperatures below the bcc phase may consist of an array of close-packed planes of complicated stacking. Although the Pu phases which occur between ϵ (bcc) and α (monoclinic) have structures like those seen in non-ferrous martensites, only those transitions between δ (fcc) and the lower temperature phases have been observed to be martensitic.²²

Structures which consist of an array of close-packed planes of complicated stacking have been given special designations. The fcc structure with an ABC stacking sequence is designated as 3R, and the orthorhombic structure with an ABCBCACAB stacking sequence as 9R. If the close-packed 9R structure becomes distorted monoclinic because of atom-size effects, then such a structure has been designated as a modified (non-ideal) 9R structure by Kajiwara.²³ The high density of α -Pu suggests that its structure is that of a modified 9R type. Orthorhombic and monoclinic structures, when observed as 9R martensites, are regarded as fcc structures with shuffles in the stacking period.

Although low-temperature physical properties suggest an antiphase structure in α -Pu, this is not the case with α -U. Instead, the martensitically formed structure observed in α -U is twinning with several different types of twins being observed.²⁴

POSSIBILITY OF AN ANTIPHASE STRUCTURE IN α -PHASE PLUTONIUM

Martensitic transformations can lead to antiphase as well as long-period stacking shift structures. Evidence for the possibility

of these structures in alpha and δ -stabilized phases of Pu has been previously presented.¹ Long²⁵ describes α -Pu as being composed of blocks that are quite large and which are weakly coupled to each other. This could be a description of an antiphase or stacking modulated structure. Development of an antiphase structure in α -Pu appears possible because of the results given in a recent publication, which show effects of heat treatment on ρ vs T curves and on ρ_0 values of a material (Cu_3Au) known to develop an antiphase structure.²⁶ The corresponding curves and ρ_0 values for α -Pu show a similar variability, as reported by Joel et al.²⁷ The ρ vs T curves for α -Pu show a dependence upon impurity elements present, but low-temperature processing also affects the level of ρ vs T curves.

The original concept of an antiphase structure was an out-of-step boundary between ordered domains. Resistivity increases because of scattering from antiphase boundaries and internal strain caused by nucleation and growth of ordered domains. The resistivity decreases again as domains become large and the boundary area decreases. Domain formation and growth in an antiphase structure also causes heat evolution effects on heat capacity measurements. These heat effects have been observed in α -Pu.^{1,2} Many Pu specimens show no evidence of low-temperature heat evolution, so a consistent appearance of an antiphase structure is unlikely.

Stacking fault boundaries are also a form of low energy boundary which can result from a martensitic transformation. They can modulate a crystal lattice and would tend to increase the resistivity because of creation of barriers for electron scattering. This appears to be the more likely case and such a modulation may augment electrons which fluctuate in and out of the f shell¹¹ in causing resistivity maxima in certain plutonium phases and alloys.

SUMMARY

An effort has been made to show a possible connection between f-electron bonding, asymmetric structures, consequences of martensitic transformations and valence fluctuations in actinide systems.

A Hubbard model⁹ has been used by Long²⁵ to develop a theory to explain the behavior of α -Pu (optical phonons with strong electron-phonon interactions and electron hopping) and by Johansson²⁸ in a theory for the properties of a Mott insulator as they apply to the actinide system. It is suggested that such a model may also be applicable to the crystal symmetry changes in martensitic transformations in the actinides.

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