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Applicability of a valence fluctuation model to the observed physical property response of actinide materials

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Résumé. — On montre que le comportement des propriétés physiques des éléments légers des actinides, U, Np, et Pu et certains de leurs alliages, est similaire à celui des composés intermétalliques de terres rares de valence mixte. On déduit que la théorie d'interconfiguration pourrait être aussi applicable aux matériaux d'actinides.

Abstract. — It is shown that the physical property behaviour of the light actinide elements, U, Np, and Pu, and certain of their alloys, is like that of known mixed-valence, R.E. metallic compounds. It is inferred that interconfiguration fluctuation (ICF) theory could also be applicable to actinide materials.

1. Introduction. — Many theories have been advanced for explaining the low-temperature physical property behaviour of the early actinides. The greatest number of these have been directed at explaining the maximum in the ρ vs. T curve of α -phase plutonium at ~ 100 K. Most of the theories have proven to be unsatisfactory because they could not simultaneously explain the absence of magnetism.

Theories or models that can explain the appearance of a resistivity maximum along with absence of magnetism are based on mixed-valence and associated valence instabilities. They have been developed to explain the anomalous behaviour of rare earth metals or alloys. Valence instabilities (fluctuations) are also designated as interconfiguration fluctuations (ICF).

There is considered to be hybridization of f and d states in the rare earth elements or compounds which show properties of the mixed-valence state [1]. Jullien and Coqblin [2] have proposed that the absence of localized magnetism in U, Np, and Pu metals could be accounted for by a large d-f hybridization in these elements.

The theories for the behaviour of interconfiguration fluctuation (ICF) compounds will be presented briefly. Comparisons of the physical property behaviour of certain actinide materials and R.E. mixed-valence compounds will be made. The concept of valence instabilities in light actinides has been considered by Brodsky [3].

An objection that can be raised to the mixed-valence state in light actinides, is the absence of an appreciable lattice contraction indicative of a valence transition at a critical point [4]. However the following considerations are advanced, to stimulate thought as to whether a mixed valence concept might be of some usefulness, in advancing an understanding of the early actinides.

2. Interconfiguration fluctuation (ICF) theory. — Interconfiguration fluctuations (valence fluctuations) have been observed mainly in metallic rare earth compounds under application of pressure or upon low-temperature cooling. These compounds are also referred to as mixed valence compounds because the atom-like f levels and the wide s-d band coexist at the Fermi level [5].

A model for explaining the different integral occupations of the 4f shell was first developed by Hirst [6]. Interconfiguration fluctuations are understood by Hirst as arising when the energy levels are arranged in such a way that two configurations compete for stability. He considers that valence fluctuations arise in a system at configurational crossover. The absence of magnetism is considered to arise because of fluctuations between two ionic configurations of different valences.

3. Existing evidence for the mixed-valence state in actinide phases and compounds. — The crystal structures of certain U, Np, and Pu phases suggest that these elements exist in the mixed valence state, i.e., they are effectively *metallic alloys*.

3.1 β -PHASE URANIUM. — There are 30 atoms in the unit cell of the tetragonal structure of β -phase U and six sets of inequivalent sites. Thewlis and Steeple [7] pointed out that atoms appear to be present in the structure in four different electronic states with valencies 3, 4, 5, and 6 respectively, and that bonding suggests a tendency towards U_2 molecules.

3.2 α -PHASE NEPTUNIUM. — There are two inequivalent atom sites in the α -Np crystal structure. These correspond to different configurations. The existence of different states for different atoms of α -Np seems to be suggested by the experimental

evidence of Dunlap *et al.* [8]. A tendency towards Np_2 molecules was also noted by Thewlis and Steeple [7].

3.3 α - AND β -PHASE OF PLUTONIUM. — There are eight inequivalent atom sites in the primitive monoclinic unit cell of α -Pu and seven different atomic sites exist in the b.c. monoclinic unit cell of β -Pu. The atoms in the different configurations of each of these phases of plutonium have about the same stability. There must be a different electronic correlation on each type of site.

3.4 $\text{UNi}_{5-x}\text{Cu}_x$ COMPOUNDS. — The possibility of mixed valency of uranium in $\text{UNi}_{5-x}\text{Cu}_x$ compounds was investigated by van Daal *et al.* [9]. They suggested that in UCu_5 the uranium ions were neither tetravalent nor trivalent but mixed tetravalent and trivalent.

3.5 HYBRIDIZATION AND THE MIXED-VALENCE STATE. — Freeman and Koelling [10] have noted that the 5f electrons in the actinides are not well localized in the first part of the series. Their itinerant nature makes them hybridize strongly with the 6d and 7s bands. The hybridization in a mixed-valence, rare earth compound, such as SmB_6 , is considered to be among ionic states. A crystal can minimize its free energy by a compromise in which the ions have a mixture of configurations [11].

4. Similarities in physical property response of ICF rare earth compounds and actinide materials. — The important aspects of physical property behaviour of known ICF compounds are : a maximum in ρ vs. T curves [12], an almost temperature-independent susceptibility (lack of magnetism) [12], a change in lattice constant in the mixed-valence state [9], an

unusually high electronic specific heat [9, 12], a humping in thermoelectric power vs. T curves [12], a minimum in Young's modulus vs. T curves [13], and an extreme sensitivity to impurities [14]. This general behaviour is shown by the light actinide elements and some of their alloys or compounds.

Polycrystalline α -Pu, α -Pu₍₁₀₀₎, Pu₆Fe, PuZn₂, PuAl₂ and β -Pu have widely differing crystal structures, yet a maximum is observed in ρ vs. T curves for all of these materials. A relatively large, but temperature-independent magnetic susceptibility and lack of magnetic order has been observed in many actinide materials [3].

Large values have been reported for the electronic contribution to specific heat of α -Pu and other actinide materials [3]. Values also vary considerably. Humping has been observed in the low-temperature thermoelectric power curves of the alpha phases of U, Np, and Pu. Sales and Viswanathan [12] note that there is a large thermoelectric power in ICF compounds, one which exhibits a peak at about the fluctuation temperature.

The lattice appears to expand below ~ 50 K in both α -U and α -Pu. Minima have been seen in the Young's modulus vs. T curves of α -U at 36 K and α -Pu at ~ 50 K. The thermoelectric power maximum, along with a lattice expansion and a minimum in Young's modulus, all taking place at ~ 36 -50 K, suggest that this is the temperature range for configurational crossover in α -U and α -Pu.

Small amounts of certain impurities were shown by Joel *et al.* [15] to have a large effect on ρ vs. T curves of α -Pu. The residual resistivity was high in specimens containing elements known to stabilize β phase (Ti) and α phase (Al, Ga, Ce). A possibility is that these particular elements stabilize regions of an intermediate (different) valence state even in the presence of the valence of the bulk phase (α -Pu).

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