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The actinides—a beautiful ending of the Periodic Table

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Abstract

The 5f elements, actinides, show many properties which have direct correspondence to the 4f transition metals, the lanthanides. The remarkable similarity between the solid state properties of compressed Ce and the actinide metals is pointed out in the present paper. The α–γ transition in Ce is considered as a Mott transition, namely, from delocalized to localized 4f states. An analogous behavior is also found for the actinide series, where the sudden volume increase from Pu to Am can be viewed upon as a Mott transition within the 5f shell as a function of the atomic number Z. On the itinerant side of the Mott transition, the earlier actinides (Pa–Pu) show low symmetry structures at ambient conditions; while across the border, the heavier elements (Am–Cf) present the *dhcp* structure, an atomic arrangement typical for the trivalent lanthanide elements with localized 4f magnetic moments. The reason for an *isostructural* Mott transition of the f electron in Ce, as opposed to the much more complicated cases in the actinides, is identified. The strange appearance of the δ-phase (fcc) in the phase diagram of Pu is another consequence of the border line behavior of the 5f electrons. The path leading from δ-Pu to α-Pu is identified.

Keywords: Actinides; High-pressure behaviors; Electronic structure

The last row of elements in the Periodic Table starts with the elements francium, radium and actinium. After this follows the series of elements called the actinides. From the electronic point of view they form a series of elements of their own as a consequence of the gradual filling of the 5f shell. In this sense, they are also the direct analogue to the lanthanides, where the 4f shell is gradually filled when the nuclear charge is increased through this series. In the *free* lanthanide atom, the electrons occupying the 4f shell arrange themselves relative to each other in such a way that the so called Hund's rules are fulfilled. This means in particular that the spin moment of the $4f^n$ configuration is optimized, hereby giving a maximum lowering of the total energy for the $4f^n$ states (Hund's first rule). Similar internal electronic arrangements within the atom originate from the other two Hund's rules. This gives a very particular atomic arrangement for the ground state of the $4f^n$ configuration. This is rather straightforward for the lanthanides and actinides in their atomic state; the question we address here is how this picture is modified in the condensed phase of these atoms, i.e. in the metallic state.

In particular, there are two main questions regarding the solid phase of the atoms. First to what extent will there be an occupation of the f levels in the solid? Second, to what extent will Hund's rules be obeyed in the solid, if at all. In other words will the atomic multiplet configuration of the f^n state remain intact in the solid or will it be totally dissolved into a state with for example equally many spin up and spin down electrons, i.e. a non-magnetic state? Such a disintegration of the parallel spin configuration can not take place in the free atom since here the 4f and 5f levels are sharp. In the solid phase, however, the 4f (5f) level will interact with the surrounding f levels on the neighboring atoms as well as with the conduction band states of s, p and d type, and thereby, widening into a band of f levels. This widening is exactly the mechanism which might lead to dissolution of the f^n (multiplet) configuration.

The earlier understanding of the electronic structure of the actinides, at least up to and including plutonium, was such that the actinides were believed to form a new *d* transition series of elements, namely 6d. This picture, most commonly favored in the chemistry community, was however shown to be wrong.

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Especially the theoretical work by Hill [1], Freeman and co-workers [2] and Johansson [3,4] showed that this could not be the case. Johansson used a number of different physical properties to show the presence of 5f electrons in these metals. Also experimental photoemission work very clearly showed that there are 5f electrons present in the solid state of the early actinides metals [5]. The theoretically calculated equilibrium volumes for the early actinides conclusively demonstrated that 5f electrons are heavily involved in the cohesion of these elements [6]. A new and consistent understanding of the electron bonding behavior of the actinide series started to emerge.

For the lanthanides, on the other hand, it is well known that the $4f^n$ atomic configuration remains essentially unaltered in the solid (metal) phase. It is also very well understood why europium and ytterbium are divalent metals, in contrast to all the other lanthanides which are trivalent metals. Again this is due to the correlation energy within the f^n multiplets, a purely atomic effect. This has been well explained in details by Gschneidner [7] and Johansson [8].

The spatial extension of the 4f orbital shrinks when the atomic number increases. Thus, among the lanthanides, the spatially most extended 4f orbital is found for Ce, the first element to have an occupation of the 4f level. The same shrinking of the extension of the 5f orbital is found for the actinides, with the largest orbital for the earlier elements. In comparison, element by element, the 5f orbital for the actinides is larger than for the corresponding 4f orbital in the lanthanide. Due to the orbital contraction the extension of the 5f orbital in plutonium/americium is in a relative sense similar to the extension of the 4f orbital in cerium.

Both estimations based on thermodynamic data as well as theoretical electronic structure calculations predict that there will be a cross-over in behaviors between plutonium and americium. For the early actinides the extension of the 5f orbital is sufficient to permit a substantial broadening of the 5f level, such that the magnetic moment correlations present for the atoms are not sufficient to prevent a delocalization of the 5f electrons into an itinerant (delocalized or band) state. On the contrary, for americium and the elements beyond americium, the energy gained in the formation of the localized magnetic moment is sufficient to keep its localized character also in the metallic state [9].

It is now most interesting to realize that in fact the cerium metal is just on the border between a localized and itinerant state. The experimental observation in cerium of an isostructural transition at around 7 kbar involving a volume collapse of about 15%, gives clear evidence for a most anomalous behavior relative to the other lanthanide elements [10]. At even higher pressures one has observed the α-uranium structure as well as the bct structure. Even more complicated structures were later observed by Nelmes and co-workers [11] in the pressure region for the α-uranium phase. This clearly suggests a correspondence between cerium under pressure and the actinide elements. Actually such a relationship was put forward long ago [12], in fact even before the discovery of the α-uranium structure in cerium. In this work, also a generalized phase diagram was put forward for the actinides. The idea behind a comparison between cerium and the early actinides is the common itinerant behavior of the f electrons, i.e. the 4f and 5f electrons respectively. More and more pressure on cerium gives rise to a wider and wider 4f energy band. For the actinides, on the other hand, the 5f band is wider for thorium/protactinium than for neptunium/plutonium. Therefore, as regards the width of the 5f bands at the equilibrium volumes, one can notice that going from plutonium to thorium is like increasing the pressure. In Fig. 1, we have placed the pressure/temperature phase diagram for cerium next to a generalized phase diagram for the actinides. To get the direction of the pressure axis equal for the two cases, we start for the actinides with Cm and Am to the left and protactinium and thorium to the right. From this figure the similarity between the behavior of cerium under pressure and the individual actinide element can now be clearly recognized. This is especially obvious as regards the crys-

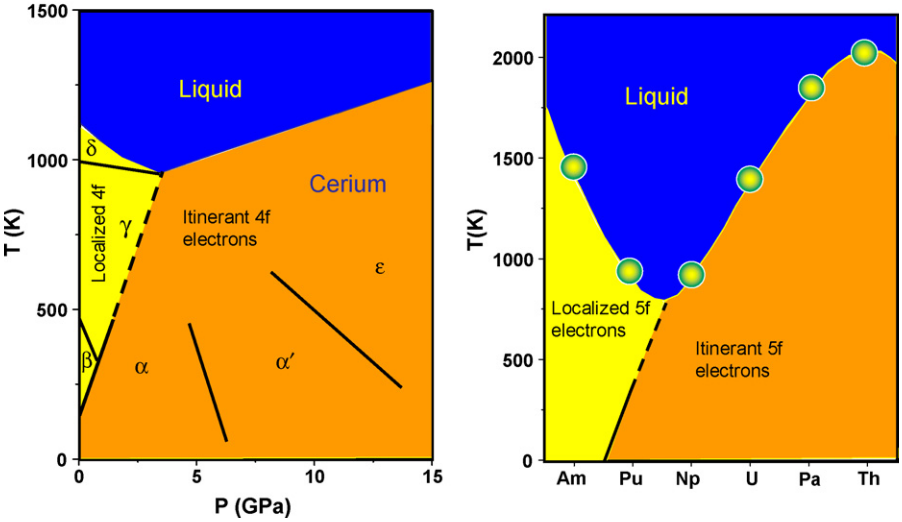

Fig. 1. The *P*–*T* phase diagram for cerium [10,12] (left) and melting temperatures for the actinide elements (right). In the *P*–*T* phase diagram for cerium an extension of the γ–α transition line to the minimum of the melting temperature is indicated by a dashed line. The effect of pressure on an individual element is to make it behave more similar to its predecessor in the series. The indicated transition line for the transition between localized and itinerant 5f behavior (Mott transition) as a function of atomic number Z (or pressure for an individual element) has been included schematically. Its extension to the minimum point of the melting curve has been drawn as a suggestive analogy to the behavior in cerium metal.

tal structures of Th–U and compressed cerium. For Np–Pu the number of 5f electrons is considerably higher than for cerium which gives rise to very unique crystal structures for Np and Pu. We would also like to point out that the fcc structure for Th is highly anomalous [13]. It is of course tempting to argue that the simple fcc arrangement is due to that Th should be regarded as a standard d-transition elements like the 3d, 4d and 5d elements. However this is wrong. If thorium behaved as a d-transition element it should attain the hcp crystal structure as found for Ti, Zr and Hf. Instead it has been shown that the fcc structure in thorium is due to the presence of occupied itinerant 5f states [13]. For low f-occupations of the 5f conduction band the fcc structure is favored relative to other crystal structures. In fact, under pressure thorium adapts the same structure as protactinium due to the increased occupation of the 5f-band upon compression (in the same way, under pressure Pa enters into the α-uranium structure due to the increasing number of 5f electrons under compression). If we compare Fig. 1(b) with Fig. 1(a), we notice the fact that the zero pressure (or rather negative pressure) in cerium corresponds to americium. Both have localized f electrons. Furthermore, Am adapts a dhcp structure at low temperature, a fcc phase at higher temperature and a bcc phase before melting, all this is in accord with cerium. At a pressure of 2.5 GPa, Ce resembles Pu; both have delocalized f electrons and show enhanced exchange properties. Beside that, Pu and Ce show an initial decrease of the melting temperature with pressure and a subsequent minimum. Finally, at a pressure of 5 GPa, cerium simulates uranium, both show an increasing melting temperature with pressure as well as superconductivity under pressure. A more detailed description of the relationship between the lanthanide and actinide elements can be found elsewhere [14,15].

Let us return to the case of Ce in its α-phase. The great interest in Ce-metal originates from the isostructural transition between the α-phase and the γ-phase. First, the fact that Ce in its γ-phase, with no f bonding, has the fcc structure is due to its metallic 5d electrons, which is just in accordance with the rest of the lanthanide metals. To illustrate this conventional lanthanide behavior we show in Fig. 2 a generalized phase diagram for the lanthanide metals [8]. The very fact that such a diagram can be constructed, based on the individual *P–T* phase diagrams of the lanthanide metals, gives very strong evidence for the close similarity between the lanthanide metals. In fact this generalized phase diagram clearly demonstrates the inertness of the 4f electrons as regards their participation in the bonding. One can clearly also notice the absence of Eu and Yb in this diagram, the reason being their divalent metallic behavior in contrast to the common trivalent lanthanide property. Also the absence of cerium can be identified, now the reason is that high pressure destroys the inertness of the 4f electrons in cerium and therefore it is no longer an adequate trivalent metal. (Also the absence of Pm can be noticed in Fig. 2, here the reason is the strong radioactivity preventing high pressure experimental work.) It is most interesting to notice that when the f electrons in Ce become itinerant their number is slightly larger than 1. This number means (compare with thorium) that the now bonding f electrons prefer the fcc structure. Since already the number of d-electrons is such that they also favor an fcc atomic arrangement, the combined effect of the d- and f-electrons definitely will give rise to an fcc structure. *This most favorable circumstance is the fundamental reason why the f delocalization in Ce is accompanied with an isostructural phase transition*. On the localized side the d electrons give an fcc structure, and on the itinerant side the metallic f electron adds further bonding where again the fcc structure is the preferred structure. Further pressure on Ce increases the number of f electrons and therefore structures like bct and α-uranium become favored [16] just as they do in the actinide elements thorium and protactinium under pressure.

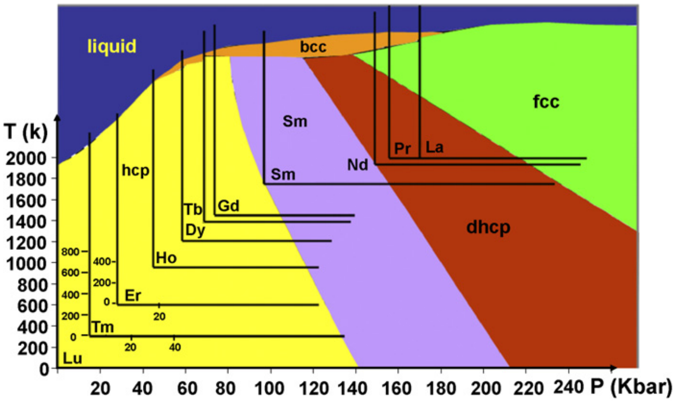

Fig. 2. A generalized phase diagram [8] for the trivalent lanthanide metals. The experimental *P–T* phase diagrams for the trivalent lanthanides are put together as concisely as possible. Note the obvious appearance of empty space where missing elements (due to divalent behavior, to itinerant 4f states and radioactivity; Yb and Eu, Ce and Pm) should have entered.

The next element after cerium in the lanthanide series, praseodymium, also show a delocalization of the 4f electrons under pressure [17,18]. However, here the transition is *not* isostructural. The reason for this is now obvious. We are here facing a situation where there are two itinerant f electrons and this is not in favor of the fcc structure thereby preventing an isostrucural transition. Thus, it seems that among the elements it is only in Ce that the electron bonding conditions are such that the delocalization process can take place without a structural change.

The early successful electronic structure calculations for the actinide elements [6] had to be limited to a treatment where all the elements were assigned the fcc structure. This is of course only correct for Th. Still such a treatment very convincingly demonstrated the dominant importance of the f electron bonding for the early members of the actinide series. However one aspect was not emphasized in that work, namely that in fact there is in Pu a high temperature phase, called the δ-phase, which actually adopts the fcc phase. This phase in Pu is a famous anomaly of a unique kind showing several peculiar properties. One is its atomic volume which is intermediate between the dense low temperature α-phase in Pu and the atomic volume for Am. Thus, the fcc structure used in the calculations by Skriver, Andersen, and Johansson was actually the correct one. It is therefore interesting to note that in addition to the paramagnetic solution—associated to the α-phase in Pu—there was an additional solution with a minimum close to the volume of δ-Pu. In the calculations this was a ferromagnetic state and in fact had a lower energy than the paramagnetic (non spin-polarized) solution. However in the paper by Skriver, Andersen and Johansson the emphasize was to demonstrate the itinerant properties of the 5f electrons for the actinides in general and little attention was given to this fcc δ-phase in Pu. In addition it is of course a well-known fact that δ-Pu is not a ferromagnet.

Recently, there has been a renewed interest in the literature regarding the understanding of δ-Pu. For example the work by Kotliar and co-workers [19] presents a promising approach. Here we would like to discuss the particular stability of the δ-phase and its stabilization by addition of impurities like Al and Ga. The correlation driving the stability of the δ-phase is certainly to a large extent accounted for in the mentioned ferromagnetic solution [20]. The correlations among the electron spins confined to a particular atom are included in such a magnetic configuration. Recent calculations (L. Vitos and B. Johansson (unpublished)) have been performed for a disordered magnetic state (disordered local moment calculations). Again the crystal structure was restricted to fcc. Here one finds two minima as a function of volume (as shown qualitatively in Fig. 3). The one close to the volume for α-Pu is non-magnetic and the other one has local moments of the order of 5 μ_B with an energy minimum for a volume close to the value for δ-Pu. The most interesting finding in the present context is the energy gain in the disordered local moment state relative to the paramagnetic solution. This energy is about 60 mRy, i.e. a quite large stabilization energy for the δ-phase. From this we conclude that there is a very large energy barrier between the disordered local moment fcc state (representing the δ-phase) and the non-magnetic fcc phase. It now becomes most interesting to go back to the results from non-magnetic calculations for a large number of crystal structures by Söderlind and co-workers [21,22]. In these calculations one could very well account for the experimentally observed structures for all the elements Th–Pu. One large surprise from these calculations was the really large energy difference between the low symmetry structures and the fcc structure of the actinides. This difference was namely found to be of the order of 50 mRy, which is most unusual when comparing different crystal structures, especially since we are dealing with a close-packed fcc structure for a metal. The reason for this is the large energy gain which can be achieved from induced energy band splittings originating from Jahn–Teller distortions [23]. This energy gain of about 50 mRy in the α-phase has now a most interesting consequence, namely that our description above for the δ-phase (fcc) in Pu and the itinerant 5f description of the paramagnetic α-phase for Pu results in a close energy balance between the two states. Thus, the large energy preference for the α-phase relative to the paramagnetic fcc structure compensates for the energy barrier within the fcc structure. This is of course necessary since experimentally both the α- and δ-phases appear in the same phase diagram. However, we have now achieved a theoretical description of this energy balance. We can now understand the mechanism behind the important stabilization of the δ-phase found upon adding impurities to δ-Pu. In the δ-phase there are still contributions from the 5f electrons to the bonding. This is already obvious from its atomic volume being intermediate between α-Pu and that of Am. Addition of for example Al will break part of this bonding. However, simultaneous with this there will be a gain in the local internal spin polarization energy. Therefore the addition of Al is actually not affecting the energy of the δ-phase too much. On the other hand, addition of Al to the α-structure has a much more serious effect on the stabilization energy of the α-structure (and other distorted structures) relative to the fcc phase. Thus, the well-known stabilization of the δ-phase in Pu is not an impurity induced stabilization of the fcc phase, but rather an impurity induced destabilization of the α-phase. Our finding of a large energy barrier between the α-phase and the δ-phase also explains the long time stability of the δ-phase, a property of uttermost importance in the use of plutonium.

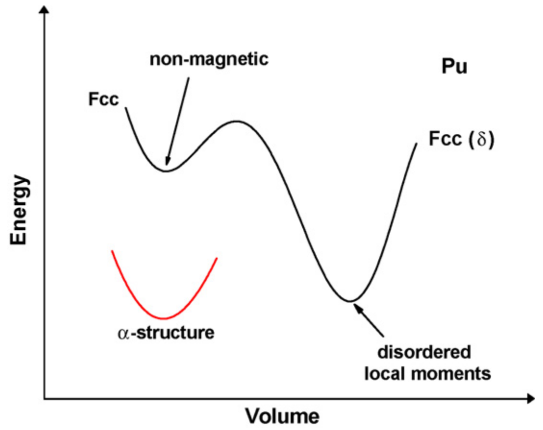

Fig. 3. A schematic representation of the energy balance between α-Pu and δ-Pu. The upper curve shows, as a function of volume, the energy of the disordered local moment state relative to the paramagnetic (non-magnetic) state within the fcc structure. The volume for the minimum of the non-magnetic δ-phase (fcc) is close to the equilibrium volume for the α-phase.

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