Nature of the 5f electrons in the actinide series

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The nature of the 5f electrons in the actinide metals is discussed within the framework of the Hubbard model. Thereby, good evidence for itinerant 5f states is found for the lighter actinides (plutonium or lighter). This supports the picture that has recently emerged from energy-band calculations.

I. INTRODUCTION

On the experimental side, quite a substantial amount of new information has in recent times become available on the actinide elements. This is especially true for the elements protactinium, americium, curium, and berkelium, about which there was practically nothing known ten years ago. This development has partly been due to the technological possibilities these new elements seem to provide and partly due to a desire to compare their properties to the other and more well-known elements of the actinide series (thorium, uranium, and plutonium). In this way it also becomes possible to relate the actinide series to the other transition series of the Periodic Table.

On the theoretical side, there has been a corresponding increase of understanding of the actinide metals, mostly empirical however. A commonly employed concept was introduced in a paper by Zachariasen,[1] where he correlated the metallic radii in various structures with a scheme of metallic valency. However, it depended on the assumption that the 5f electrons did not contribute to bonding. In view of more recent theoretical work, this assumption is not generally valid, especially not for the pure metals. This critical view has emerged mainly from energy-band calculations. Hill and Kmetko,[2] using a nonrelativistic augmented-plane-wave (APW) method, reached the conclusion that the 5f electrons are *band electrons* and not localized as had been widely accepted earlier. Moreover, they concluded that protactinium is the first element in the series for which the 5f state is populated, and therefore this metal should be the first proper 5f transition element. In the later part of the series, beginning with americium, they found that the 5f electrons ought to be considered as localized. Therefore, it is only in the heavier part of the series that the actinides start to resemble the rare-earth metals.

An extensive study of the energy bands for the actinide elements has also been performed by Freeman and co-workers[3] employing a relativistic APW method. They show the importance of relativistic

effects, and their calculated bands differ markedly from those obtained by Kmetko and Hill. However, concerning the delocalized versus localized nature of the 5f electrons, they reach the same conclusion as Kmetko and Hill, as well as suggest the appearance of a second rare-earth series starting with americium. Freeman and Koelling[3] stress the problem of the reliability of energy-band calculations in the case of narrow bands. The point is that energy-band calculations neglect the intra-atomic Coulomb correlation. For a sufficiently wide band (say > 5 eV), however, this is probably not so serious. Therefore, the Coulomb correlation should not drastically change their results for the earlier actinides, but should be of the utmost importance for the latter part of the series. For these heavier elements the band picture of the 5f electrons actually breaks down and instead these electrons are more appropriately described within a localized picture. This implies localized magnetic moments, and therefore similar magnetic orderings as for the rare earths are expected.

The picture of localized 5f electrons in the whole of the actinide series has also met with difficulties from the thermodynamic point of view. Brewer[4] pointed out this serious problem for the case of plutonium. A more extensive study of this has been made by Johansson and Rosengren,[5] who conclude that for none of the earlier actinides do the measured cohesive energies fit into a localized picture of the 5f electrons. Instead one is led to allow for a substantial bonding contribution from these electrons. This contribution is most readily understood in terms of a metallic band, and therefore a band picture of the 5f state was concluded.

Magnetic-susceptibility experiments do not indicate any localized magnetic moments in the lighter actinide metals,[6] but rather point to a Pauli-paramagnet type of behavior. In the case of curium[7,8] and berkelium,[9] however, the experiments definitely imply a localized magnetic moment, whose magnitude is of the order expected for the free ionic state. These experimental results are most easily understood in a delocalized as opposed to localized picture of the 5f state.

A somewhat different point of view of the $5f$ state has been put forward by Jullien *et al.*[10] They consider the $5f$ electrons as localized throughout the whole actinide series but being strongly hybridized with the $6d$ state. As a result of this hybridization, the magnetic property of the $5f$ electrons is lost for the strongly hybridized metals—uranium, neptunium, and plutonium—but not for the less so—curium and berkelium. However, owing to the hybridization, the magnetic moments for the two latter metals were found to be considerably smaller than the experimental values. This model was rejected by Freeman and Koelling[3] who claim that primary focus must be on the question of localization versus itineracy of the $5f$ electrons. Hybridization becomes only important in a secondary fashion, namely between delocalized $5f$ states and $6d$ and $7s$ states.

Quite recently, the present author has considered the $\gamma\text{-}\alpha$ transition in cerium as being caused by a delocalization of the $4f$ electron into a $4f$ band state.[11] Further, the remarkable similarity between compressed cerium and the individual actinide metals was pointed out. This similarity has now obtained strong additional support from the experimental finding that cerium at high pressures attains the same crystal structure as found in uranium.[12] This can hardly be reconciled in a picture where the f states are considered to be localized.

In this paper we are going to treat the actinides in the same way as cerium was considered in Ref. 11. In so doing we are going to stress the importance of the intra-atomic Coulomb repulsion between the $5f$ electrons. By this, we are then able to give quantitative support to the itinerant picture of the $5f$ states in the actinides, a picture which has emerged from the recent band calculations.

In Sec. II we shortly discuss the metal-insulator transition. Section III is devoted to the effective intra-atomic interaction and its comparison to the calculated bandwidth. Finally, in Sec. IV, a short discussion is given about valency in the actinide series.

II. THE METAL-NONMETAL TRANSITION

The general question of whether a band picture or a localized picture is the appropriate one is of special importance for an unfilled shell. Intuitively one expects that when the open shells are brought closer together, thereby increasing their mutual overlap, itinerant movements will be facilitated. However, presently there is certainly no exact treatment available which locates the point where one should turn from the localized picture to the delocalized one. On the other hand, the physical meaning seems more clear. The localized picture describes an insulator, and the band picture a metal. Therefore, at the point (assuming there is a

sharp one) where we have to switch our description there will take place a transition from an insulating state to a metallic one. This aspect has been especially emphasized by Mott,[13] and the transition is now commonly referred to as a Mott transition. A mathematical expression for the critical density has been derived by Mott, but its exactness is questionable. Hubbard[14] has reformulated the problem in terms of the bandwidth W and the polar state formation energy U. For a nondegenerate case he found

$$U \approx W \tag{1}$$

as a critical expression for the transition point. On the low-density side of the transition, W is small and the polar state formation energy large enough to prevent itinerant movements of the electrons. Hubbard's formulation of the Mott transition is the more suitable one in the present case of the actinide metals. The f state is degenerated, however, but still the critical region should be fairly well represented by the condition in Eq. (1). A further complication in the actinides is the presence of a conduction band of type $(6d7s)$. Its effect on the interaction parameter U is however of extreme importance for the actual occurrence of a $5f$ band state.

III. THE EFFECTIVE INTRA-ATOMIC INTERACTION

In Ref. 11 a detailed discussion was presented for the effective intra-atomic interaction in the case of cerium. Essentially the same picture as given therein can be applied to the actinides. For simplicity we assume for the moment that in the actinide metallic state there are three electrons in the $(6d7s)$ conduction band. Of primary interest is the energy required to form a polar state, i.e. the interaction parameter U, for the metallic situation. To get an idea of its magnitude we turn to the same quantity in the atomic limit, i.e. when the atoms are well separated from each other. The energy of the reaction

$$2(5f^n 6d^1 7s^2) \rightarrow 5f^{n-1} 6d^2 7s^2 + 5f^{n+1} 7s^2$$
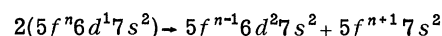
gives the required quantity. This may be obtained numerically from the tabulations on spectroscopic levels given by Brewer.[4] The results for the effective interaction parameter for the $5f$ electrons are given in Table I for the lighter actinides.

The case of real interest, however, is the metallic situation. For the d transition elements, Herring[15] argues convincingly that the screening produced by the valence electrons is even more effective in the solid than in the atom. The reason is the more compact nature of screening in a metal. For the actinides, the same arguments apply. Therefore, one expects a reduction of the effective intra-atomic interaction parameter as compared

TABLE I. Polar-state formation energy U (in eV) in the atomic limit for the lighter actinide elements. In the case of plutonium and americium the atomic ground-state configuration is of $5f^{n+1}7s^2$ type. In the metallic state, however, the divalent and trivalent configurations will become rather close in energy. In these two metals we have therefore neglected the energy difference between the divalent and trivalent configurations in our assignment of U.

Th	Pa	U	Np	Pu	Am
1.5	1.6	2.3	2.6	3.5(± 1)	5(± 1)

with the values given in Table I. For further discussion on this matter we refer to Ref. 11.

From band calculations, the bandwidths of the $5f$ states are available.[2,16] For thorium[16] the width is about 5 eV, and by comparing this number with its effective U parameter in Table I, the itinerant picture of the $5f$ state must be inferred. The calculated bandwidths decrease monotonically with atomic number and in plutonium it is of the order of 2 eV. Again, a comparison with the effective U gives good evidence for a $5f$ band. Therefore, these numbers definitely support the view that the $5f$ states are itinerant for the lighter actinides (plutonium or lighter). For americium the bandwidth is of the order of a tenth of an electron volt and apparently the $5f$ states become localized. As a function of atomic number this may be looked upon as a Mott transition, taking place between plutonium and americium.

In this connection it is of interest to compare the case of metallic cerium.[11] For this element the number corresponding to those in Table I is about 5 ± 1 eV. Thus cerium seems to be intermediate between plutonium and americium. Therefore, the γ-α transition in cerium, which takes place under compression, should be viewed upon as a Mott transition as regards the $4f$ state. The large volume change accompanying this phase transition should be compared with the corresponding large atomic volume difference between plutonium and americium. Further, the close resemblance between cerium exposed to different pressures and the individual actinide elements should be recognized.[11]

IV. VALENCIES

Since the $5f$ electrons form band states, a clear-cut valence assignment to the individual elements is no longer possible. Especially the empirical relation between atomic volume and valency, as developed by Zachariasen,[1,17] is no longer a valid procedure for valence assignments. This has been further discussed elsewhere.[5]

Having a metallic $5f$ band, the highest occupied level of this band must coincide with the global Fermi energy of the system. Therefore, electron transfers between the $5f$ band and the ($6d7s$) conduction band should take place. However, in case where the $5f$ band is *narrow*, one would expect atomic-like correlations to be maintained to a high degree even in the band picture. Therefore, the deviations from an integral occupation of the $5f$ band may still be fairly small.

In Ref. 5, with the assumption of a nonbonding $5f$ state, the energetically most favorable valence state was derived empirically. Thereby it was found that Th and Pa are tetravalent [i.e., four electrons in the ($6d7s$) band]; U is with equal probability tetravalent or pentavalent; and Np and Pu, finally, are most stable in a trivalent configuration. Assuming that the broad ($6d7s$) band has a higher binding capability than a narrow $5f$ band, and that a close-to-integral occupation of the $5f$ band state is preserved, the following division of electrons between the ($6d7s$) conduction band and the $5f$ band is obtained: Th $(6d7s)^4$, Pa $(6d7s)^4 5f^1$, U $(6d7s)^4 5f^2$ or $(6d7s)^5 5f^1$, Np $(6d7s)^3 5f^4$, and Pu $(6d7s)^3 5f^5$. From these assignments, the extra contribution to the cohesive energy due to the $5f$ electrons can be obtained for some elements[5]: U, 25 kcal/mol; Np, 20 kcal/mol; and Pu, 10 kcal/mol. These numbers seem to be consistent with the decreasing bandwidth with atomic number.

Also the appearance of superconductivity among the actinides[18] can be correlated to the f bandwidth. Experimentally, it seems likely that Pa is a superconductor at zero pressure, while U has to be compressed before bulk superconductivity is established.[19] Neither Np nor Pu is found to be a superconductor. The strong correlations in a narrow band give enhanced magnetic properties which prevent superconductivity. This is apparently the case in Np and Pu with their narrow $5f$ band. In U, however, compression widens the f band sufficiently to permit superconductivity; and in Pa, finally, the $5f$ band is probably that broad that already at equilibrium superconductivity will occur.

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