PHYSICAL REVIEW B VOLUME 11, NUMBER 4 15 FEBRUARY 1975

Interpolation scheme for the cohesive energies for the lanthanides and actinides

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(Received 24 September 1974)

An interpolation scheme for the binding energies is shown to give a good account for the cohesive energies of the rare-earth metals. From this the divalent nature of europium and ytterbium can be concluded. The same method is applied to the actinide elements. The observed deviations from experiment are interpreted in terms of itinerant $5f$ states. Further, a divalent metallic character of the heavier actinide elements, starting with einsteinium, is predicted.

I. INTRODUCTION

The rare-earth metals form a series of elements with almost identical chemical properties.[1] When electrons are added to these atoms, as the nuclear charge is increased, they go into the $4f$ shell, and since this shell lies in the interior of the xenon core region the bulk properties of the metals are thereby essentially unchanged. However, some macroscopic properties as, for example, the cohesive energy[2] vary quasi irregularly in the series and seem at first sight to be in contradiction to the expected smooth behavior. This is, however, due to the occurrence of different types of *atomic* configurations for the rare earths. Thus La, Ce, Gd, and Lu hold a $4f^n 5d^1 6s^2$ (trivalent) atomic configuration, while the rest of the lanthanides has a $4f^{n+1} 6s^2$ (divalent) configuration.[3] In the solid phase, however, most of the elements are found in the trivalent configuration, and therefore in the condensation of the atoms one of the $4f$ electrons has been promoted into the $5d$ state. Apparently the gain of binding energy in this process overcomes the energy cost of the promotion involved. Only in the case of europium and ytterbium do the elements remain in a divalent state when a solid. For these two metals, however, high pressure is expected to transform them into a trivalent metallic form.

An important aspect of the understanding of the rare-earth metals is that such a knowledge also provides information about the actinide elements. The low abundance of especially the heavier actinides make this even more important, since for these elements a knowledge of their bulk crystalline properties will not be experimentally available in a foreseeable future. However, from the known behavior of the rare earths some of their metallic properties can be predicted with good confidence.

Recent work in atomic spectroscopy has made available data on the energy separation between different atomic configurations in the rare earths.[3] These data have been successfully correlated to some thermodynamic properties by Brewer[3] and by Nugent *et al.*[4] Their results show that in case the cohesive energy is measured relative to the same atomic configuration, $4f^n 5d^1 6s^2$, it becomes a fairly smoothly varying function with atomic number. One of the key assumptions in their work is the nonbonding property of the $4f$ shell, which in view of the present knowledge of the rare earths is a most reasonable assumption.

In the present paper we will complement the work by Nugent *et al.* by an independent approach and reinforce their results and conclusions. Instead of considering the cohesive energy as a smoothly varying function with atomic number, we turn to the binding energy. This is defined as the energy gained when free ions and free electrons are brought together to form a solid. This means that this quantity is obtained by adding to the cohesive energy the ionization energies required to form the trivalent ions. The binding energy is then required to vary smoothly with atomic number. This proposed interpolation procedure thus requires a knowledge of the ionization energy to the trivalent ionic configuration.[5-9] In the case of the actinides there are no such data available presently and for these elements we have to turn to a somewhat less reliable procedure in order to be able to apply our method.

In Sec. II we derive the cohesive energies of the rare earths. In Sec. III we apply a scheme for obtaining the ionization energies for the actinides and after this we derive their cohesive energies. Due to the more complex behavior of the lighter actinides an additional quantity is required before we can estimate their experimental cohesive energies. This is described in Sec. IV. In Sec. V, finally, we discuss the question of the valence state attained by the actinide metals, a question which is also partly discussed in Sec. III.

II. RARE-EARTH METALS

The assumptions in our interpolation scheme are as follows: First, the smoothness of the binding energy as a function of atomic number and second the nonbinding property of the $4f$ shell. From the binding energies of the elements Ce, Gd, and Lu a second-order polynomial in Z is constructed. The reason why we exclude lanthanum in this scheme is that between La and Ce there is a kind of a small discontinuity in the atomic-energy levels of the valence electrons. This is due to the somewhat abrupt screening difference between a nonoccupied and an occupied f orbital, respectively. From the interpolated binding-energy values the cohesive energy for the rest of the elements is then derived by a subtraction of their experimental ionization energies. The resulting predicted cohesive energies are given in Table I together with experiments.[4] Also the results derived by Nugent *et al.*[4] are included for comparison. From this table we notice that the present scheme, especially in the case of the heavier elements, produce accurate estimates. From the deviations between experiments and the present interpolated values we may estimate the cohesive energy of promethium to be about 75 kcal/mole.

Europium and ytterbium are the only elements for which we find a substantial deviation between our interpolation and experiment. This is due to their retainment of a divalent configuration in the crystal state. We notice that in europium the energy difference between the di and trivalent states is about 18 kcal/mole and in ytterbium 12 kcal/mole. Due to the more rapid rise of the enthalpy of divalent metals as compared to the trivalent modifications when compressed, one expects a valence transition to take place for these two elements when sustained to high pressure. For europium this has been calculated to occur at about 150 kbar and in case of ytterbium at around 120 kbar.[10]

For the rest of the lanthanides the predicted values are close to experiment and their trivalent character is thus confirmed. From similar considerations as the present one it has also been concluded that all the rare earths are stable against formation of a tetravalent metallic state.[11] Therefore, the assumption of a nonbinding contribution of the $4f$ electrons combined with the knowledge of the atomic spectroscopic levels make it possible to assign the proper valence states of the rare-earth metals.

TABLE I. The cohesive energies (or rather the room-temperature enthalpies of sublimation) of the lanthanides in units of kcal/mole. The first column gives the experimental values, the second column the results from the present interpolation, and the third column, finally, contains the results from the interpolation scheme employed by Nugent *et al.* (Ref. 4). The values within frames are utilized in the construction of the interpolation scheme.

	Expt.	Present work	Nugent *et al.*
La	103.0	···	$\boxed{103}$
Ce	101.0	$\boxed{101.0}$	101
Pr	85.0	85.2	88
Nd	78.3	76.0	80
Pm	···	74.7	81
Sm	49.4	51.1	53
Eu	42.4	24.0	24
Gd	95.0	$\boxed{95.0}$	$\boxed{95}$
Tb	92.9	92.1	95
Dy	69.4	72.9	75
Ho	71.9	72.8	77
Er	75.8	75.9	78
Tm	55.0	55.0	62
Yb	36.4	24.3	35
Lu	102.2	$\boxed{102.2}$	$\boxed{102}$

III. ACTINIDE METALS

Due to the absence of ionization data on the actinides, the procedure outlined in Sec. II cannot be immediately applied to these elements. However, when such data become available, just as reliable predictions as for the rare earths should be possible. In the meantime we have to content ourselves with somewhat less accurate methods.

Generally, the actinide metals are not directly comparable to the rare earths. For example, the thorium metal is tetravalent with essentially no occupation of the $5f$ state. This fact is, however, already obvious from its atomic configuration being of $6d^27s^2$ type.[3] Therefore the promotion of the $5f$ electron to the $(6d7s)$ configuration has already "taken place" in the atomic limit. The possibility of similar transitions in protactinium and uranium will be discussed in a following section. A second and perhaps even more fundamental difference between the lanthanides and the actinides concerns the character of the f states. From band calculations[12] and other physical properties (some of which will be derived in the present work) the itineracy of the $5f$ electrons in the earlier actinide elements can be concluded. Therefore these electrons will contribute to the cohesive energy by metallic binding and the assumption of a nonbonding contribution of the f electrons is then no longer valid. However, from the present interpolation scheme we can only obtain the cohesive energy in case the 5f electrons are nonbonding. By utilizing the independent measurements of the standard enthalpy of formation $\Delta H_f^0(M(\text{III}), \text{aq.})$ of the metal aqueous ion in aqueous solution at room temperature, we can circumvent this difficulty and still derive the measured cohesive energy. At the same time we can thereby estimate how much of the cohesive energy is due to the 5f electrons. For the heavier elements, beginning with americium, the similarity to the rare-earth metals is, however, fully established[10] since for these elements the 5f electrons do form localized states.

Our main difficulty for the actinides is to obtain good estimates of their ionization energies. There are many possible ways to proceed and the chosen method is certainly open to criticism, but is probably just as reliable as any other procedure. In this we are going to partly employ atomic calculations. It is well known that such calculations badly fail in reproducing the energy levels of the f electrons. However, from the work by Brewer[3] and Nugent *et al.*[4] we obtain reliable values of the excitation energy of the reaction $f^{n+1}s^2 \to f^n d^1 s^2$ both for the rare earths and the actinides. To minimize the uncertainties inherent in the theoretical values we only employ calculated ionization energies from the trivalent atomic configuration (d^1s^2) to the trivalent ionic state. From the calculations by Carlson *et al.*[13] on the rare earths we obtain the theoretical values in the case of Ce, Gd, and Lu. Between these elements we interpolate smoothly and compare the results to the corresponding experimental values of the reaction $R(5d^1 6s^2) \to R^{3+}$, where R is a rare earth. The so obtained theoretical values are all too low and has to be corrected by a factor ranging between 1.06 and 1.08 in order to fit the experimental data. The small variation in this factor is noticeable. After this we turn to the actinides. Again we employ the calculations by Carlson *et al.*[13] to obtain the ionization energies from the trivalent atomic configuration in the case of Th, Cm, and Lw. From these elements we perform a smooth interpolation in order to conform to our treatment of the lanthanides. After this we multiply with the same correcting factor as previously found for the corresponding rare earth analog element. The same procedure is then also applied to lanthanum as a special case and we derive the corresponding ionization energy in the case of actinium. After this we add the excitation energy of the process $5f^{n+1}7s^2 \to 5f^n 6d^1 7s^2$ (when positive). These values are taken from Nugent *et al.*[4] The so derived results for the ionization energies to the trivalent ionic state is given in the first column in Table II. It may be that the absolute values so obtained are fairly erroneous, but the variation from one element to another should be much more reliable. In fact, the way our interpolation scheme for the cohesive energies is chosen, this is also the only thing that matters. It should be mentioned that the value of thorium in Table II corresponds to a $5f^1 6d^1 7s^2$ atomic configuration instead of the true $6d^2 7s^2$ one.

In order to obtain the binding energies we also need the cohesive energies of Th, Cm, and Lw. This energy should be taken relative to the trivalent atomic configuration. Only in the case of Cm is this quantity known experimentally, 89 ± 4 kcal/mole.[14] From the dip in the cohesive energies of the rare-earth elements La, Ce, Gd, and Lu, Nugent *et al.*[4] conclude a corresponding dip among the actinides. From this they obtain a cohesive energy of 98 kcal/mole of trivalent Th (i.e., assuming a $5f^1 6d^1 7s^2$ configuration and a nonbonding 5f electron) and 99 kcal/mole for Lw. The value for thorium can be given additional support from the general pattern of the cohesive energy of the elements. The increase in cohesive energy, when proceeding from a trivalent to a tetravalent element in the beginning of the transition series, is consistently about 45 kcal/mole. The experimental

TABLE II. Interpolated ionization energies and cohesive energies (or rather the room-temperature enthalpies of sublimation) for the antinides (A). The first column contains the interpolated ionization energies, the second the experimental values of the cohesive energy, the third our interpolated values of the same quantity. (The values within parentheses are derived in Sec. IV.) The fourth column gives the result of the interpolation scheme employed by Nugent *et al*. (Ref. 4). The values within frames are utilized in the construction of the interpolation scheme.

	Cohesive energy (kcal/mole)		
$A \to A^{3+}$ (eV)	Expt.	Present interpolation	Nugent *et al*.
Ac 35.50	···		$\boxed{100}$
Th 36.36	142.8	$\boxed{98.0}$	98
Pa 37.07	···	93.4	97
U 37.68	128 ± 2	90.8(124)	95
Np 38.54	110[a]	86.6(111)	94
Pu 39.45	84.1	71.9(81)	74
Am 40.98	66[b]	47.3	48
Cm 39.61	89 ± 4	$\boxed{89.0}$	$\boxed{89}$
Bk 41.04	···	65.9	69
Cf 42.57	···	40.2	44
Es 43.29	···	32.8	38
Fm 43.68	···	32.7	37
Md 45.11	···	8.5	18
No 46.74	···	−20.7	−9
Lw 41.89	···	$\boxed{99.0}$	$\boxed{99}$

[a] R. J. Ackerman (private communication).

[b] J. Ward (private communication).

value for thorium is 143 kcal/mole[15] and refers of course to the tetravalent state. Hence, also from this one may conclude a value of 98 kcal/mole for trivalent thorium. From the ionization energies and the cohesive energies we are now in a position to apply our interpolation scheme. The results for the cohesive energy is given in the third column of Table II. All the values given there thus refers to an *assumed* trivalent ionic configuration in the metals with nonbonding $5f$ electrons. In the same table we also include the values derived by Nugent *et al.*[4] From the experience from the rare earths we expect our values to be more accurate.

From the so obtained cohesive energies we may also discuss divalency contratrivalency among the actinides. Consider first the rare earths for which it is known that europium and ytterbium are divalent. By including barium, being the divalent element preceding the lanthanides, we may construct an interpolation curve, from which we can obtain the cohesive energy of the rest of the rare earths, in case they had remained divalent in their metallic modification. This energy is then compared with the cohesive energy of their trivalent metallic state and from this their most profitable valence state can be concluded. In Fig. 1 the full drawn curves corresponds to the rare earths. From this figure it is clear that most of the rare earths prefer a trivalent state. The reason for this is that the gain of binding in a trivalent state as compared to a divalent one exceeds the loss of

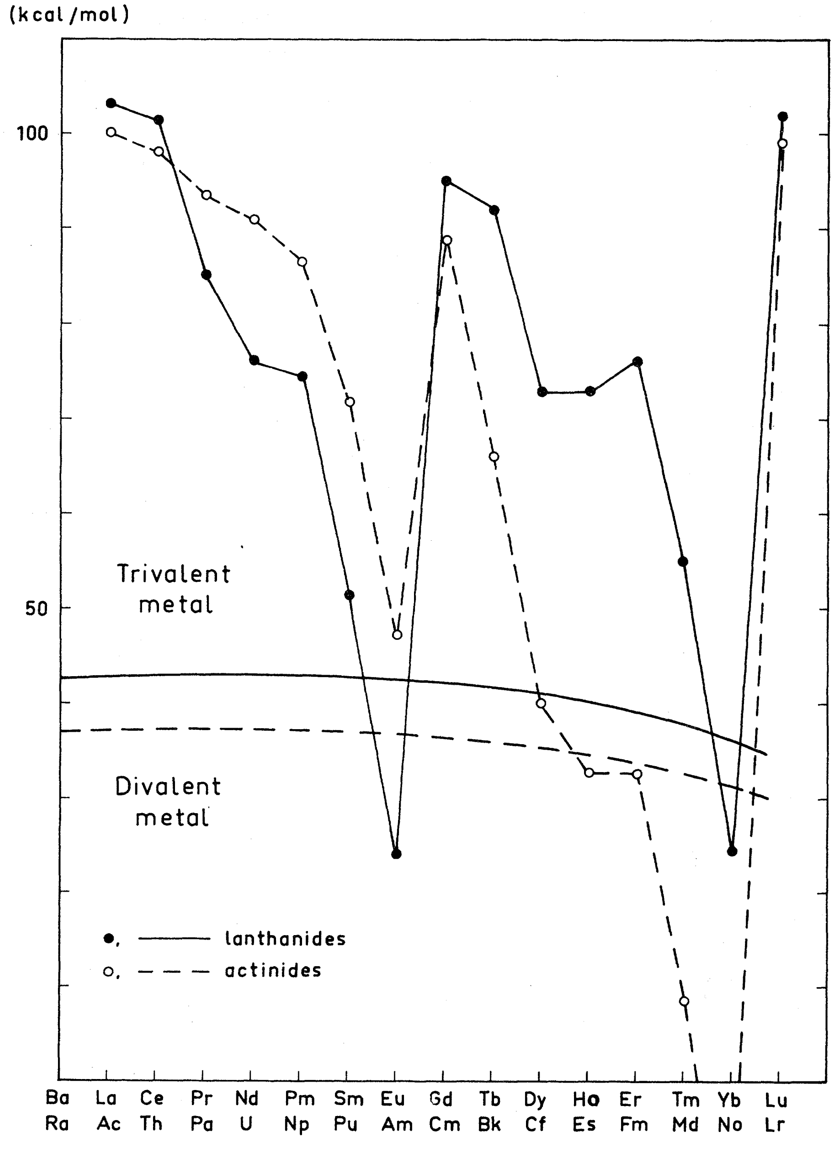

FIG. 1. Cohesive energy for the rare earths (full curves) and actinides (dashed curves). The smooth curves denote the cohesive energy in case these elements had remained divalent in their metallic modification, the jagged curves the cohesive energy of their trivalent metallic state.

energy connected with the promotion of one $4f$ electron to the $5d$ state. Only in the case of europium and ytterbium do we find a substantially lower value of cohesive energy in the trivalent state as compared to the divalent one.

A similar discussion can be applied to the actinides. Radium being the analog element to barium has a cohesive energy of 37 ± 1 kcal/mole.[16] By assuming the same relative change of the divalent cohesive energies among the actinides as for the lanthanides, we arrive at the dashed smooth curve in Fig. 2 for their divalent cohesive energies. In the same figure the open circles are the derived cohesive energies for the trivalent configuration. From the figure we conclude that Es, Fm, Md and No all prefer a divalent state. The small energy barrier for Es and Fm is noticeable and implies that a very modest compression will turn them into the trivalent metallic state. The trivalent character of americium can also be established from that figure. The neighborhood of Cf to the divalent state implies that this element in many compounds will be found in a divalent configuration. This conclusion is based on the behavior of the rare-earth elements thulium and samarium. A further discussion of the valence state of the earlier actinides is deferred to Sec. IV.

IV. COHESIVE ENERGY OF EARLIER ACTINIDES

From Table II we notice a wide disagreement between the derived cohesive energies and the experimental ones for the lighter actinide elements. There may be two reasons for this discrepancy. First, a depopulation of the $5f$ level into the $6d7s$ conduction-band state can take place, thus converting these metals to a higher valence state than three. Second, the nonbonding assumption about the $5f$ electrons may be invalid. Whatever the true reason for the found discrepancy is, we can make use of an independent type of measurement to derive the cohesive energies. The quantity we will consider is the standard enthalpy of formation $\Delta H_f^0(M(\text{III}), \text{aq.})$ of the metal aqueous ion in aqueous solution at room temperature. The behavior of this quantity among the rare earths is remarkably constant[4] and the same should be expected to hold true for the actinides. However, this is of course based on the assumption of a trivalent actinide metallic state. Therefore, any deviation between the expected value and the experimental one is due to a different metallic state than the simple trivalent one. In Fig. 2 we represent the energy levels of the different states. From this figure it is apparent that a knowledge of the difference between the experimental and derived values of $\Delta H_f^0(M(\text{III}), \text{aq.})$, together with the earlier derived cohesive energy with the trivalent assumption, can be used to derive the experimental cohesive energy. In Table III we give the experimental values of $\Delta H_f^0(M(\text{III}), \text{aq.})$ for the rare earths.[4] In the case of europium and ytterbium we have added the energy margin between the di and trivalent states in order to make their values equivalent to the other rare earths. The remarkable constancy in these values should be noticed. The only exception to this is ytterbium. We are not in a position to judge the reliability of the measured value of 161.2 kcal/mole for $\Delta H_f^0(\text{Yb(III)}, \text{aq.})$, only mention that the general consistency rather seems to require a value of about 155 kcal/mole.

In the case of the truly trivalent actinide metals there is only data available for[4] Am and[17] Cm, and their measured values of $\Delta H_f^0(M(\text{III}), \text{aq.})$ are 147.4 and 145.9 kcal/mole, respectively. Since $\Delta H_f^0(M(\text{III}), \text{aq.})$ for the rare earths is a slowly varying function of atomic number, the same behavior should be expected for the assumed trivalent metallic actinides. By transferring the relatively small variations found in the rare-earth series to the actinides we arrive at the values given in Table III. In case experimental data are available for ΔH_f^0 we can, as illustrated in Fig. 2, derive the experimentally measured cohesive energy. The results obtained in this way for U, Np, and Pu are given in parentheses in Table II and compare favorably to the experimental values.

Reversely, if only the cohesive energy is known we may derive ΔH_f^0. This is the case for thorium. Since thorium has a tetravalent $6d^2 7s^2$ atomic configuration we must in addition also take into account the excitation energy to the $5f^1 6d^1 7s^2$ configuration which is 22.29 kcal/mole.[4] This gives,

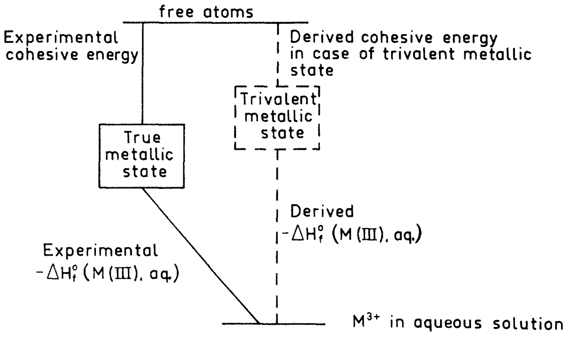

FIG. 2. Energy-level diagram used to derive experimental cohesive energy from, first, interpolated values of the cohesive energy (in the case of a trivalent metallic state) and the standard enthalpy of formation $\Delta H_f^0(M(\text{III}), \text{aq.})$, of the metal aqueous ion in aqueous solution at room temperature and, second, the measured value of this last-mentioned quantity.

TABLE III. Experimental values of $\Delta H_f^0(M(\mathrm{III}), \mathrm{aq})$ for the lanthanides and actinides, as well as interpolated values of the same quantity for the actinides. The values within brackets are constructed by smooth interpolation, and those within parentheses, except for Pa, are derived by taking into account the true metallic state, not the assumed trivalent metallic state. The value of 95 for Pa is derived in Sec. V.

	Expt.		Expt.		Interpol.	Expt.		Interpol.	Expt.
La	168.8			Ac	153				...
Ce	166.1	Tb	164.4	Th	150(83)	...	Bk	147	...
Pr	167.7	Dy	[166.7]	Pa	152(95)	...	Cf	150	...
Nd	166.4	Ho	169.4	U	150	117.2	Es	152(150)	...
Pm	[166]	Er	169.5	Np	150	125.9	Fm	152(151)	...
Sm	164.1	Tm	167.6	Pu	148	139.0	Md	150(130)	...
Eu	163.0	Yb	173.3(?)	Am	147	147.4	No	150(125)	...
Gd	163.0	Lu	166.7	Cm	146	145.9	Lu	150	...

after simple algebra, 83 kcal/mole for the ΔH_f^0(Th(III)aq.). A similar procedure must be used for the divalent heavier actinides, where the energy margin between the divalent and trivalent metallic states has to be subtracted. The resulting values are given within parentheses in Table III.

The over-all agreement between the experimental and interpolated values for the cohesive energies can be said to be quite satisfactory. The only exception in this respect is americium, for which element even the most recent experiments give a value of 66 kcal/mole,[18] this being in sharp disagreement with our derived value of 47 kcal/mole. Still, all other experimental data on americium definitely point to a truly trivalent rare-earth-like behavior of this element and we have no explanation to offer for the found marked deviation.

V. VALENCE STATE OF EARLIER ACTINIDES

From well-known plots, originally introduced by Zachariasen,[19,20] between atomic number and atomic volume, combined with a comparison to the other transition series, different valence states have been proposed for the actinide elements. The reason for the diverging results is mainly due to the particular element which was selected as the tiepoint element for the valence assignment. The basic assumption in this approach is the nonbonding property of the $5f$ electrons. In view of recent band calculations, however, this simple picture must be abandoned. Also experimentally it is quite clear that the $5f$ electrons do not form localized states in the earlier elements.

The cohesive energies can also be used to conclude the inappropriateness of the assumption of a nonbonding $5f$ state. Just as the atomic volume has a regular variation in the transition series there is a similar regularity in the earlier elements of the transition periods as regards their cohesive energies. From this regularity it can be deduced that a general increase of about 45 kcal/mole in cohesive energy takes place when the metal transforms from a trivalent to a tetravalent state. Similarly, from the behavior of the transition elements, an increase of about 30 kcal/mole in cohesive energy can be expected when a tetravalent metal transforms to a pentavalent one. All this is based on the assumption of a nonbonding $5f$ state. The gain of cohesive energy is, however, counteracted upon by the energy cost of promoting $5f$ electrons into the $6d7s$ state. These excitation energies are available from the tabulations by Brewer.[3] Applying these considerations to the earlier actinides we obtain Table IV, where the cohesive energies for the different valence states are given.

From this table we may thus deduce the most stable valence state in the case the $5f$ electrons do not contribute to the binding. Therefore, Np and Pu are trivalent, Pa and Th tetravalent, and finally U is tetra or pentavalent. The numbers so deduced for the cohesive energy are, however, still far from the experimental ones. Therefore *we have to allow for a significant contribution of the 5f electrons to the binding*. Such large con-

TABLE IV. Experimental cohesive energy and interpolated values of this quantity for different valence states. The underlined values are those energetically most favorable.

Element	Expt.	Trival.	Tetraval.	Pentaval.
Th	143	98	$\underline{143}$	
Pa		93	$\underline{132}$	105
U	128 ± 2	91	$\underline{103}$	$\underline{103}$
Np	110	$\underline{87}$	76	62
Pu	84.1	$\underline{72}$	14	

tributions are, however, only understandable if the $5f$ state is metallic, i.e., of an itinerant type. Therefore, already the cohesive energies and the spectroscopic atomic levels provide enough information for concluding the itineracy of the $5f$ electrons.

In case the $5f$ state is metallic it has a Fermi level which must coincide with that of the $6d7s$ conduction band. Therefore one must expect transfers of electrons between these bands and a clear statement of the valence state is no longer possible. On the other hand, if the $5f$ band is narrow, intraband correlation should be important, and a transfer of electrons into this band will rapidly increase its energy. Because of this the actual occupancy of the $5f$ level may still be fairly close to an integral value. From Table IV one should conclude an occupancy of about one $5f$ electron in Pa, one or two in U, four in Np, and five electrons in the $5f$ state in Pu. From the same table we also conclude that the effective contribution of the $5f$ electrons to the cohesive energy is about 25 kcal/mole in U, somewhat less in Np, and about 10 kcal/mole for the Pu metal. From this we may crudely estimate the cohesive energy of Pa to be about $130+20=150$ kcal/mole, and $\Delta H_f^0(M(\text{III}), \text{aq.})$ of the order of 95 kcal/mole.

VI. CONCLUSIONS

From the good agreement between the interpolations and experiments we may conclude that the properties of the rare-earth metals vary smoothly with atomic number. As could be seen from Table I our assumption of a smooth binding energy produces more accurate estimates than the scheme applied by Nugent *et al.*[4] In their approach the cohesive energy relative to the trivalent atomic configuration was the basis for the interpolation. This must mean that the electronic configuration in the rare-earth solids are more "similar" to the separated ion-electron system than to the separated trivalent atomic system ($4f^n5d^16s^2$). This seems to express that the rare earths are fairly free-electron-like and there should only be a weak occupation of the $5d$ band state in the solid. The same would be expected to hold true for the trivalent actinides.

Although the ionization energies of the actinides are hampered with uncertainties, the derived cohesive energies should be fairly accurate. Due to the very small energy difference between the di and trivalent states found among the heavier actinides, their valence state cannot be safely predicted. Still it can definitely be stated that there is a much stronger tendency towards divalency among the heavier actinides than among the rare earths. In compounds many of these elements will therefore appear in a divalent configuration.

Of great interest is also that the present interpolation scheme may be used to infer the metallic property of the $5f$ state for the lighter actinides. The valence states derived from this principle differ markedly from those predicted by Zachariasen.[20] It should be mentioned that Zachariasen has raised objections against the present type of method.[20] However, these objections have been shown to be invalid.[21] In a forthcoming paper the question about itineracy contra localization of the $5f$ electrons will be more fully discussed.

ACKNOWLEDGMENTS

The authors are indebted to Professor L. J. Nugent, Oak Ridge National Laboratory, and Professor L. Brewer, University of California, Berkeley, for a most valuable help concerning the availability as well as reliability of experimental data.

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