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Generalized phase diagram for the rare-earth elements: Calculations and correlations of bulk properties

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A "generalized" phase diagram is constructed empirically for the lanthanides. This diagram makes it possible, not only in one picture, to assemble a lot of information but also to predict phase transitions not yet experimentally accessible. Further, it clearly illustrates the close relation between the members of the lanthanide group. To account for some of its features, the pseudopotential method is applied. The trend in crystal structure through the lanthanide series can thereby be qualitatively accounted for, as can the trend in crystal structure for an individual element, when compressed. A scaling procedure makes it possible to extend our treatment to elements neighboring the lanthanides in the Periodic Table. In total 25 elements are considered. An atomic parameter f (relatable to the pseudopotential) is introduced, by means of which different phase transitions, both for an individual rare-earth element and intra-rare-earth alloys, can be correlated to certain critical values of this parameter. A nonmagnetic rare-earth series (Sc, Lu, Y, La, and Ac) is introduced and the occurrence of superconductivity is discussed with special emphasis on the pressure dependence of the transition temperature. This temperature can be correlated to the above-mentioned parameter f, both for intra-rare-earth alloys and pure elements at different pressures. The found correlation implies that actinium is a superconductor with a critical temperature which could be as high as (11–12) °K. It is also argued that the actinide series can be viewed upon as a second delayed rare-earth series. From this, several analogies between the two series are pointed out, which might throw new light upon several problems concerning the rare-earth themselves, e.g., the nature of the γ-α transition in cerium and the occurrence of the dhcp structure in the light lanthanides. Finally, valence transitions at high pressure for europium and ytterbium are discussed. Calculations give that these elements should become trivalent at a pressure of the order of 150 kbar.

I. INTRODUCTION

The series of elements called the lanthanides or the rare earths is characterized by a gradual filling of the $4f$ shell. Since in most of these elements the $4f$ shell is located deeply within the atom, the associated magnetic moments are highly localized. This means that the outer regions of the different lanthanide atoms are very similar to each other and that one may expect related similar behavior in the solid modifications.[1-3] This is to be contrasted to the other transition series of the elements characterized by a filling of a d shell, since for these elements the d shell in question is relatively more extensive. In the solid state of such transition elements the d shell is therefore more readily deformed by the influence of neighboring atoms, and one cannot *a priori* expect such similarity of behavior between the d transition elements.

One must be cautious in attempting to apply these considerations to the actinide series, where the $5f$ shell is gradually filled, because, although the $5f$ shell is fairly localized, it still forms a more extensive part of the actinide atoms than does the $4f$ shell in the lanthanide atoms. In fact, energy-band calculations for the earlier actinide metals give good evidence for an itinerant character of the $5f$ electrons.[4] In the latter part of the $5f$ series, however, the usual shell contraction has diminished the spatial extension of the $5f$ shell to the extent that it can no longer maintain its band character.[5] Instead, it becomes a localized state of the same type as in the lanthanide series. The heavier actinides will therefore form a kind of a *second rare-earth series*, in which the solids are analogous to the lanthanides.

In the same way we may expect the similarity between the different lanthanide elements to become increasingly clear-cut as we proceed to the heavier elements in which the $4f$-shell contraction is so pronounced that the $4f$ electrons nearly behave like members of a closed shell. In the lighter rare-earth elements, even though the $4f$ orbitals still have associated localized magnetic moments, they are sufficiently spatially extensive to be influenced by the surrounding crystal field. This has, in fact, been demonstrated in the magnetic studies of the lanthanides.[6]

Further evidence for the somewhat more complicated situation for the light lanthanides is provided by the behavior of cerium under pressure.

This may be interpreted as being due to a delocalization of the $4f$ state[7] (Mott transition). Among the lanthanides, cerium has the largest extension of the $4f$ shell (lanthanum is usually assigned an unoccupied $4f$ shell). The findings from the actinide series lead one to expect that, as pressure is applied to cerium, thus increasing the extent of the $4f$ state relative to the atomic volume, the $4f$ electrons will ultimately display itinerant behavior. This picture is, however, in contradiction to the at present widely spread opinion about the nature of the γ-α transition in cerium. The transition is commonly thought of as being driven by a promotion of the $4f$ electron into the $(5d6s)$ conduction band.[8,9] The $4f$ level is thereby assumed to remain localized but to be only partly occupied in the α phase. The severe deficiences of this picture have been extensively discussed elsewhere.[7]

In addition to cerium with its deviating behavior there are two other rare-earth metals which cannot be expected to behave as the other members of the lanthanide group. These elements are europium and ytterbium. Because of the tendency of the $4f$ shell to be half filled or filled, these two elements are divalent in the solid state, in contrast to the other elements which are trivalent. However, under compression both europium and ytterbium are expected to undergo a valence transition into a trivalent metallic state and will therefore under such conditions be similar to the other rare-earth metals.

During the last decade, high-pressure experiments have been performed on the pure trivalent-rare-earth metals (except promethium for obvious reasons) with special emphasis on crystal structure. From these, it has been suggested that a general trivalent-rare-earth metal under pressure undergoes a structure sequence hcp → Sm type → dhcp → fcc.[10] Also, very instructive experiments have been performed on binary alloys of trivalent-rare-earth metals. These alloys exhibit the same type of structure sequence as do the pure elements themselves, in the sense that when a light element is alloyed with a heavy one, the mentioned sequence is developed as a function of alloying.[11-13] This fact can be rather nicely correlated with an effective atomic number, Z^{eff}, defined as $Z^{\text{eff}} = (1-x)Z_A + xZ_B$, where x is the fraction of alloying, Z_A and Z_B are the atomic numbers of the alloy components. Thus in the lanthanide solids there is a close relationship between structure and atomic number. In this paper we will combine the individual (P, T) phase diagrams for each element into a *single* phase diagram containing the entire rare-earth series (Fig. 2). For reasons mentioned above only europium and ytterbium (divalent) as well as cerium (itinerant $4f$ state) cannot be fitted into this generalized phase diagram. The possibility of assembling in one diagram, without any change of scale, the structural phase diagrams of the individual rare-earth elements is a further demonstration of the close relationship between these elements. At the same time it allows one to collect a large amount of data into a single picture. From our earlier discussion, it seems also clear that such a generalized phase diagram cannot be found for any other of the transition series in the periodic system, at least not in such a simple form as for the lanthanides.

From the theoretical point of view, it has always been very difficult to correctly predict the actual atomic arrangement a specific element adopts when it forms a solid. For metals the only relatively easily accessible method that exists today is the pseudopotential method.[14,15] However, even for the simplest metals it is somewhat unreliable as a predictive tool. Furthermore, it is well known that the pseudopotential method in its simple form in principle should be applicable only to free-electron-like metals. Ten years ago the free-electron-like nature of the rare-earth metals was commonly accepted. Nowadays, when extensive band calculations have been performed for the lanthanides, it is understood that they are not that simple. In fact, from these calculations it has turned out that there are $5d$ bands present which strongly hybridize with the $(6s, 6p)$ bands near the Fermi level.[16] Therefore, because of the presence of the $5d$ band, one is very hesitant about the applicability of the conventional form of the pseudopotential method to the rare-earth metals (at least, to detailed properties such as the Fermi surface). Even so, the comparative ease with which one can calculate and compare the energy of different structures makes it an attractive tool. Furthermore, since we must here deal with about fifteen elements, it seems to be the only practicable method. We discuss the applicability of our pseudopotential in Sec. VIII.

The elements scandium, yttrium, and actinium all have an electronic structure similar to the lanthanides. If these elements are included to the rare-earth series we obtain a subseries of nonmagnetic metals. Normally, in the rare earths, the localized magnetic moments due to the $4f$ electrons prevent the formation of a superconducting phase. However, depending on the external conditions, superconductivity has been discovered in some of the nonmagnetic elements. In the present paper we present empirical correlations between an atomic parameter and the transition temperature.

The outline of the present paper is as follows. In Sec. II we present our generalized phase diagram and describe its construction. In Sec. III we present the pseudopotential and our calculations for the equilibrium density, the compressibility, and the

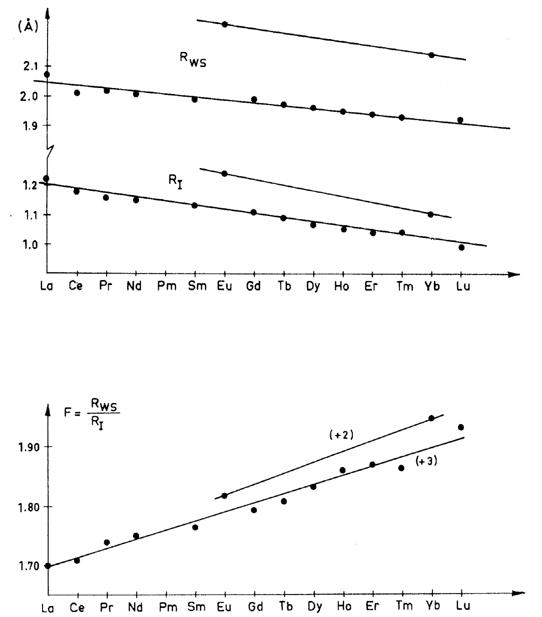

FIG. 1. (a) Experimental Wigner-Seitz radius (Ref. 20) R_{WS} and ionic radius (Ref. 21) R_I for the lanthanides. (b) Ratio F between the Wigner-Seitz radius and the ionic radius for the lanthanides.

binding energy. Section IV is devoted to a discussion of crystal structure. In Sec. V we discuss the nonmagnetic rare-earth series and give arguments for the possibility of superconductivity in actinium. In Sec. VI the actinide series is directly compared with the rare-earth series. In Sec. VII we discuss pressure-induced valence transitions in europium and ytterbium and present calculations of the transition pressure. Section VIII, finally, contains some concluding remarks.

II. GENERALIZED PHASE DIAGRAM FOR THE RARE-EARTH METALS

When one proceeds from the heavier lanthanides towards the lighter elements one can recognize a structure sequence, hcp → samarium type → dhcp → fcc. The same sequence is also exhibited by alloys between trivalent lanthanides as well as by all individual elements when supplied to high pressure. This pressure-induced series of structures was discussed by McWhan,[17] who correlated compressions with crystal structures for the rare earths. For the heavier lanthanides some earlier high-pressure experiments indicated that the hcp phase transformed directly to the dhcp structure.[18] However, more recent work seems to show that the samarium-type structure is attained for all the heavier rare-earth elements.[19] This is also the point of view we are going to take in the present paper. It has been pointed out by Gschneider and Valleta that the structure sequence cannot be explained by the size of the atoms.[12] As we proceed from the lighter to the heavier lanthanides the atomic volume decreases. However, when the atomic volume of any given element is decreased by pressure, a structural sequence is displayed corresponding to proceeding from the heavy to the light elements. At first sight, it is an astonishing fact that the more an element is compressed the more its structure will be "light-element-like." A "second-order" understanding of this fact can be obtained by considering the variation of the Wigner-Seitz radius,[20] R_{WS} and of the ionic radius[21] throughout the lanthanide series. These quantities are displayed in Fig. 1(a). Applying pressure to a particular element will decrease R_{WS}, and from Fig. 1(a) this would, for example, mean that applying pressure to dysprosium will "in first order" simulate the R_{WS} of holmium. At the same time, however, a reduction of R_{WS} means that the valence electrons themselves have got less space available. Since the ionic radius is relatively insensitive to pressure, it therefore becomes larger with respect to R_{WS} under pressure, which means that in a *relative sense* the electrons will recognize that the ionic radius of the element has increased. From this point of view a high pressure upon dysprosium will in a sense simulate the greater ionic radius of terbium, as seen in Fig. 1(a). Then it becomes a question of which of these two effects outweighs the other one. A relevant parameter to answer this question would be something like the ratio F of the Wigner-Seitz radius to the ionic radius, as a function of Z [Fig. 1(b)]. From the dependence of F on Z, the observed structure sequence is now more clearly understood. A compression of an element will decrease R_{WS} and therefore also the ratio F, and from Fig. 1(b) we thus notice that this simulates the conditions of an earlier element in the series.

Experimentally, it has also been established that most of the trivalent rare earths will pass through a body-centered cubic phase, bcc, before melting. The exceptions to this behavior appear to be the heaviest elements, erbium, thulium, and lutetium. This high-temperature bcc phase is also influenced by pressure. The temperature interval of its existence increases with pressure for the heavy rare earths, while the opposite is true for the light elements. This means, in particular, that for neodymium, praseodymium, and lanthanum the bcc region ceases to exist beyond a certain critical pressure.

Starting from these experimentally determined trends, we tried to empirically construct one single-phase diagram for the trivalent elements, a generalized phase diagram (Fig. 2). We started by drawing the phase diagrams of the individual elements on different transparancies; the purpose

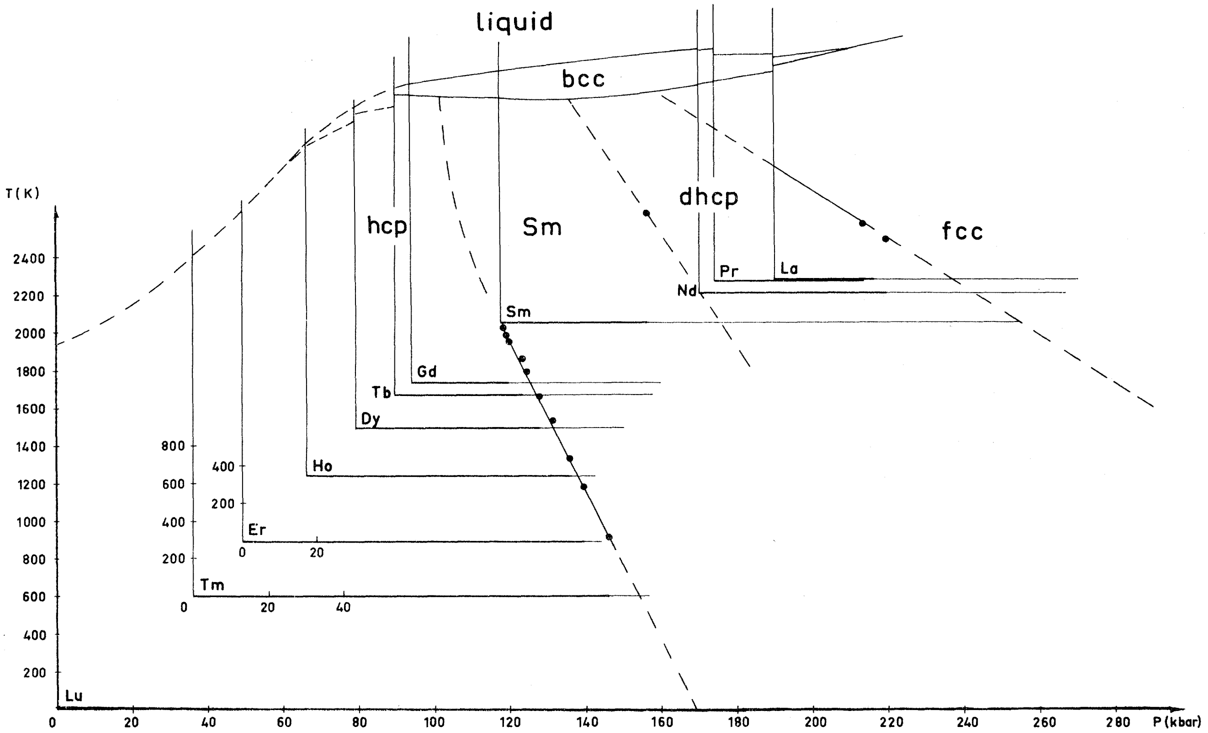

FIG. 2. Generalized phase diagram for the lanthanides. Its construction is explained in the text and based on data given in Refs. 10 and 22–25. The points denote the measured transitions. The thick filling on the pressure axis for an element denotes the highest pressure for which a known phase transition of the element has been utilized for the construction of the diagram. For example, the thick filling on the axis of neodymium denotes that the thick point farthest to the right in the diagram, which point represents a dhcp–fcc transition, belongs to this particular element.

of this was to "puzzle" them together in as simple a way as possible. We chose to start with the phase diagram of thulium. Upon this we then superposed the phase diagrams for erbium and holmium. We adjusted the origins of these diagrams relative to that of thulium such that, first, the fusion curve was continuous and, second, the transitions from the hcp structure to the samarium-type structure fell upon a straight line.

Upon these three diagrams, the positions of which were now fixed, we then superimposed in turn the diagrams of dysprosium, terbium, and gadolinium. They were adjusted to the three fixed diagrams in exactly the same way as erbium and holmium were fitted to thulium. It is significant that we could get all known transitions from hcp structure to samarium-type structure to fall upon *one straight line, simultaneously fitting their respective melting curves*.

After this promising start, we added the phase diagram for samarium. Its position relative to the above-mentioned elements could not be established as "accurately" as for the heavier elements because the phase diagram of samarium exhibits no hcp structure. Instead, we determined the position of samarium in our diagram by simultaneously fitting its melting curve and its phase line for the bcc-samarium structure transition to corresponding phase lines for gadolinium. The "true" position of samarium might therefore turn out to be a little more to the right in our generalized diagram, but this would not lead to any drastic changes.

After this, we added the diagram of neodymium. Once more we had to apply the same procedure as for samarium, because neodymium has no samarium structure in its diagram. We had to be satisfied with fitting of the bcc phase lines of neodymium with corresponding lines of samarium, with the restriction that no samarium structure overlapped the neodymium diagram.

Next, we simultaneously added the diagrams of praseodymium and lanthanum. For neodymium and praseodymium we knew of a transition from dhcp structure to fcc structure. These transitions were fitted to the known phase line of the corresponding transition in lanthanum. We were, however, not able to simultaneously accurately adapt the two phase lines of the bcc phase when proceeding from neodymium to praseodymium in the diagram. Instead we chose to join smoothly the lower phase line of the bcc region in these two elements. Nor was it possible to obtain a continuous transition between praseodymium and lanthanum for the bcc phase.

Finally, we included the phase diagram of lutetium. For this element the transition pressure for the hcp to samarium-type structure transformation is not yet accurately determined. However, in this paper we later estimate this pressure to be about 170 kbar. From this value and an adjustment of its melting curve to that of thulium, lutetium was incorporated to the diagram.

We note that in the generalized phase diagram the construction is such that the lines for the bcc phase of an element are valid only in the region between the temperature axes of the element and its lighter neighbor. Originally we had intended simply to smooth out the discontinuities between the different elements and thus to produce a qualitative phase diagram. However, this turned out to be unnecessary.

After we had drawn the generalized phase diagram, we learned of another transition from dhcp structure to fcc structure in praseodymium. Below its bcc region along the temperature axis, there was found a fcc phase which transformed into the dhcp phase at 560 °C.[24] This transition was incorporated into the diagram and thereby fell "exactly" upon the earlier constructed straight phase line of this transition. Further, it has also been established that neodymium has a fcc structure before it transforms into a bcc phase.[24] However, it has not yet been possible to determine the temperature of the transition, since this is very sluggish. From our phase diagram we would expect it to occur at about 960 °K. The existence of the high-temperature fcc phase in neodymium is also supported by the lanthanum-neodymium phase diagram as given by Daane and Spedding.[26] The validity of this diagram has been questioned by Gschneider,[1] since the bcc region of solid solution transformed to another region of complete solubility. However, in view of the fcc phase in both these elements below the bcc region this is just what can be expected. Therefore, since lanthanum is nonmagnetic, it could be employed as an excellent tool for diluting the fcc praseodymium and neodymium phases, both of which exhibit unusual magnetic properties.

The above-mentioned structure sequence hcp → samarium type → dhcp → fcc is clearly seen in the generalized phase diagram. We further notice that there are certain irregular gaps in the spacing of the origins between the different elements. These gaps reflect the missing rare earths in the diagram (ytterbium, europium, promethium, and cerium). We can speculate a little about these remaining rare earths. Regarding the two divalent elements, europium and ytterbium, one can imagine that at high pressure these will, by a promotion of one of the localized $4f$ electrons into the conduction band, adopt a trivalent state. They will thereby, so to speak, be "pressed into" the diagram. For cerium the situation is just the opposite. A high pressure will delocalize the $4f$ electrons, and cerium is "pressed out" of the diagram. Since at low temperature this character change of the $4f$ state has already taken place, not even the atmospheric part of its phase diagram[27] can be placed into our generalized phase diagram. Interestingly enough, it still shows a trace of its original membership among the trivalent rare earths in the following way. At low pressure and above 120 °K it has a dhcp crystal structure. At higher temperatures it eventually goes over into a fcc structure (γ phase), as well as exhibits a bcc phase before melting. In these structures it has been demonstrated that the cerium ions possess a localized magnetic moment, due to one electron in the $4f$ shell. Therefore, when trivalent, cerium nicely resembles its neighbors praseodymium and lanthanum. Furthermore, the slope of the dhcp → γ-fcc phase in the (T, P) plane is negative as in lanthanum, although it is somewhat steeper.

Too little is known about the phase diagram of the unstable element promethium to enable us to decide "exactly" where it should be placed between neodymium and samarium. At room temperature it has been reported to have a dhcp structure.[28] From this information we can use our phase diagram to estimate its melting point to be about 1350 ± 50 °K. From the same experiments it was claimed that promethium remains in the dhcp structure down to 7.5 °K. However, the experience from high-pressure work is that the transformation from a dhcp structure back to a samarium-type structure is very slow, and the dhcp phase is in fact easily retained at atmospheric pressure and room temperature. Therefore the experiments on promethium do not exclude the possibility of a samarium structure at low temperatures. From our diagram this low-temperature phase seems, instead, very likely.

The constructed generalized phase diagram for the rare-earth elements exhibits a rich variety of behavior, and it is partly our aim of this paper to try to account for some of its features. We will especially be concerned with the structure variation through the rare-earth series as well as the structure variation as a function of pressure.

III. PSEUDOPOTENTIAL CALCULATION OF SOME BULK PROPERTIES

For the rare-earth elements it is probably sufficient to consider the total energy of the metals as the sum[3]

$$E_{\mathrm{el}} + E_{\mathrm{ion}} + E_{\mathrm{ion\text{-}el}} + \epsilon_{4f} + \epsilon_{\mathrm{d\text{-}d}} + \epsilon_{\mathrm{Q\text{-}Q}} + \epsilon_{\mathrm{exch}} \quad . \tag{3.1}$$

Here these terms represent, respectively, the energies of the conduction electrons, the ion-ion interaction energy, the interaction energy of the ions with the electrons, the contribution to the bonding arising from $4f$ wave-function overlap, the magnetic dipole-dipole and quadrupole-quadrupole interactions, and the exchange between magnetic moments arising from polarization of the conduction electrons. The first three terms are definitely dominant. On the other hand, since the energy differences between the close-packed structures observed in the rare-earth elements probably are very small, this does not rule out the possibility that some of the other terms, though small on an absolute scale, can be decisive for determining structure. Several attempts to relate the structure sequence to some of the ϵ's in Eq. (3.1) have been made.[2,3,12,29,30] Gschneider has especially emphasized the role of the ϵ_{4f} term. However, in this paper, we will assume that only the E terms are the structure-determining ones and thus ignore the contribution of the others. For simple metals these E terms are easily obtained from a pseudopotential theory. To second order in the potential, the energy can then be expressed[15]

$$E = E_{\text{kin}} + E_{\text{HF}} + E_{\text{corr}} + E_{\text{pseud}} + U_{\text{bs}} + U_{\text{EW}} . \qquad (3.2)$$

Here, E_{kin} is the energy of a noninteracting electron gas. The electron-electron interaction is taken account of by the terms E_{HF} and E_{corr}, the electron-gas Hartree-Fock energy and correlation energy, respectively. For the latter we employ the analytic expression given by Vashishta and Singwi.[31] The first- and second-order pseudopotential contributions are given by E_{pseud} and U_{bs}, respectively. For evaluating the term U_{bs} we have used the Lindhard dielectric function.[32] Finally the ion-ion interaction energy is given by the Ewald electrostatic energy of point ions in a uniform gas of electrons, U_{EW}.

In the case of rare-earth metals our assumption that the localized $4f$ electrons do not contribute to the binding properties allows us to simplify the problem by simply ignoring their presence (as has in fact been done in many band-structure calculations in the past). Then we are left with a xenon core and a valence part of form $(5d6s6p)^3$. From the pseudopotential point of view, there are no serious problems with the s and p electrons since they are orthogonal to the $5s$ and $5p$ core states which form the outer region of the ion. Further, since these latter two orbitals have nearly the same spatial extension, a common ionic radius could be assigned to them. The difficulty with the d electrons, penetrating to the inner region of the ion, is somewhat ameliorated by the fact that band-structure calculations show that only the lowest part of the $5d$ band is occupied. This part of the d band is of a rather delocalized nature. This could explain why a pseudopotential approach still may be applicable. It would imply that we should associate one ionic radius with the $6s$, $6p$ electrons and a smaller one with the $5d$ electrons. However, since we are going to employ a *local* pseudopotential, i.e., in a sense treat all the electrons alike, we have just one radius available. Thus the effect of the $5d$ valence electron would be to imply the use of an averaged radius, somewhat smaller than that expected from the extent of the $5s$ and $5p$ orbitals themselves. Admittedly, this is a very drastic reduction of the real ionic potential and we should not, *a priori*, expect a true representation of all features of the energy bands of the rare-earth metals by such a procedure. On the other hand, we are here only interested in *bulk properties*, and it could be that the more detailed influence of the presence of the d band is not especially important for integrated, or averaged, quantities.

As a representation of the potential we employed the mathematical expression

$$v_{\text{KG}}^{\text{ion}}(r) = Z\left(\frac{e^{-r/r_c} - 1}{r} + \frac{a}{r_c}\, e^{-r/r_c}\right) , \qquad (3.3)$$

where a and r_c are the model parameters. This potential was used by Krasko and Gurskii (KG) for simple metals.[33,34] An attractive feature of this potential is its analyticity. Its Fourier transform,

$$v_{\text{KG}}^{\text{ion}}(q) = \frac{4\pi Z}{q^2}\, \frac{(2a-1)(qr_c)^2 - 1}{[(qr_c)^2 + 1]^2} , \qquad (3.4)$$

therefore falls off more rapidly with large q than is the case for the empty-core model.[35] Krasko and Gurskii determined their potential partly from ionic data. At the time the present work was initiated, there was, however, a scarcity of information on ionization energies for the rare earths. Therefore we had to turn to a less satisfactory method, namely, to choose some element and adjust our parameters so as to fit some of its bulk properties. The procedure we actually employed was the following one. At an early stage of the calculations we somewhat arbitrarily put $a = 3.0$ for all elements, in order to reduce the otherwise rather formidable number of possible variations. Second for gadolinium we chose $r_c = 0.37$ a.u. By this choice the spatial extension of the potential nearly coincided with the extension of the $5s$ and $5p$ core orbitals[36] (taken as the position of the maximum of $r^2|\varphi_{\text{orb}}|^2$). Finally, we introduced a second radius, r_c', in the diagonal part of the pseudopotential (just as in the case of the empty-core model as employed by Ashcroft and Langreth[37]), in order to account for the equilibrium density of gadolinium. Thereby we found $r_c' = r_c + 0.05$ (a.u.), a relation which then was kept for all the elements. The

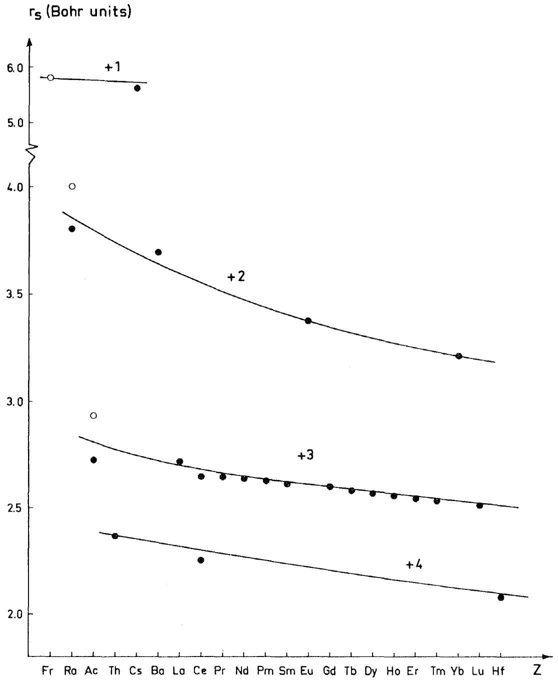

FIG. 3. Radius r_s of the sphere containing one electron for the elements considered in this paper. The "effective" atomic numbers for Fr–Th are 51–54, as derived in Ref. 38 (see also Sec. V). The filled and open circles denote experimental (Refs. 20, 39–42) and estimated (Refs. 20, 38, 43, 44), values, respectively, and the curves our calculated values.

model parameters for the other trivalent elements were then determined from ionic properties as calculated by Waber and Cromer.[36] This was done by simply scaling the parameter r_c against the calculated spatial extension of the orthogonalizing orbitals with the same scaling factor as found for gadolinium. For the divalent and tetravalent elements, europium and thorium were chosen as the tie-point elements, from which the scaling factors between the orthogonalizing core and the parameter r_c were derived. For a detailed account of the derivation of the pseudopotential parameters, see Ref. 38.

By minimization of the energy, as given in Eq. (3.2), we obtain the equilibrium atomic volume. These minimizations were all performed for the experimentally established equilibrium crystal structure. In the case of the lighter lanthanides this means that our calculations actually were performed with an "effective" hcp structure. As mentioned, the parametrization is such that, at the outset, we are bound to be right for the elements gadolinium, europium, and thorium. The results are shown in Fig. 3, where we have chosen the electron-gas parameter r_s (a.u.) as a representation of the equilibrium volume. The largest deviation from calculated atomic volume is found in actinium[39] ($r_s^{\exp} = 2.72$). However, for this element the experimental result has been criticized. Zachariasen[43] and Matthias *et al.*[45] have estimated that its atomic volume should rather correspond to a value of $r_s \approx 2.91$. This value is also included in Fig. 3, and we note that our calculation gives an intermediate value, $r_s = 2.81$. In view of the scepticism expressed regarding actinium, we have also given Zachariasen's[43,44] estimated value for radium. For francium, where no experimental data are available, we include an estimated value.[38]

For the lanthanides our calculated densities resemble a smooth interpolation of the experimental data, even though there is a somewhat systematic deviation for the lighter elements. The reason for the deviation may be that their more extended $4f$ orbitals do give some contribution to the binding.[12] This effect should be related to the more complex magnetic orderings found in these elements. The particularly low experimental atomic volume of γ-cerium is, under all circumstances, associated with its proximity to the transition to the dense α phase. If we attribute this fact to a $4f$ wave-function overlap, this would mean that $4f$ bonding is much more pronounced in cerium than in the immediately following rare earths. This is in accord with the most extensive $4f$ orbital's being found in cerium. Therefore, if the particularly large depletion in cerium is due to this effect, the wave-function overlap must be interpreted as a precursor of the transition. Since for all phase transitions the nature of its precursor is directly related to the nature of the condensed state, this would then imply that in α-cerium the full advantage is taken of the increased $4f$ overlap. This means that the $4f$ electrons in α-cerium should become $4f$-band electrons and as such give a substantial contribution to the binding.

For the tetravalent metals, our scaling procedure gives a surprisingly good agreement in the case of hafnium ($r_s^{\text{calc}} = 2.10$, $r_s^{\exp} = 2.08$[20]). For the metal cerium with the *assumed* $6s^2 5d^2$ configuration, however, we obtain a somewhat too low value for the density. Some authors claim that α-cerium is a mixture of trivalent and tetravalent cerium atoms.[46] With such a picture of the α phase, its density should be somewhere between that of pure trivalent and pure tetravalent cerium. With the present parameters for cerium, this picture cannot apply, since already our tetravalent state gives too low a density.

The trend of increasing binding energies with atomic number among the trivalent lanthanides is well reproduced in our calculations (Fig. 4). A general trend can be observed in the discrepancy between experimental and calculated values. A closer inspection shows that the largest disagree-

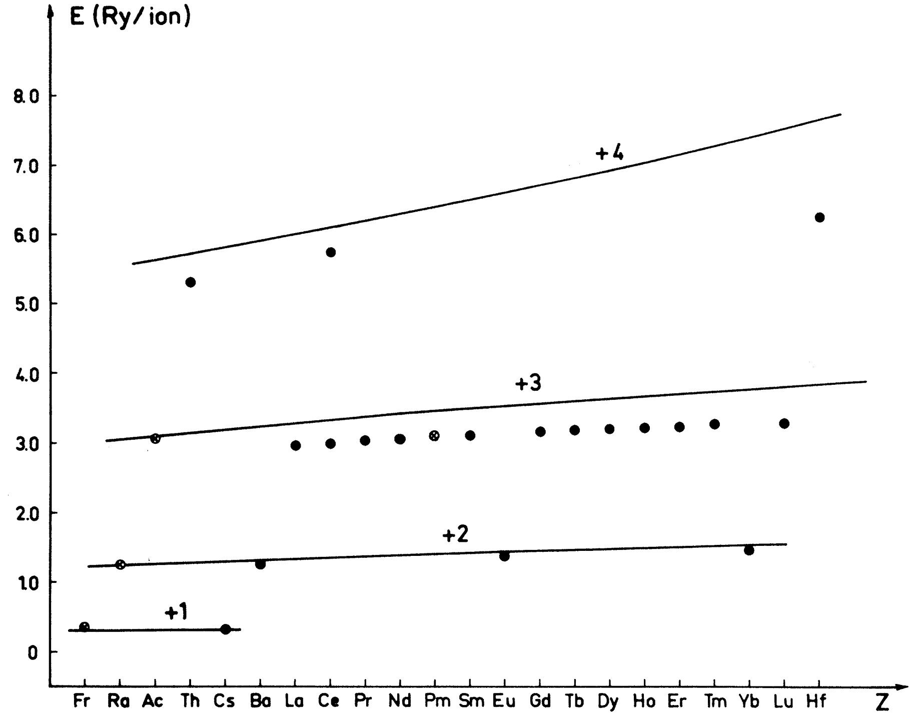

FIG. 4. Binding energy. The filled circles denote experimental data and the curves calculations. The ionization data are from Refs. 47–54 and cohesive energies from Ref. 55. Crossed open circles are used for elements for which the cohesive energy is estimated in Refs. 20 and 56.

ment is found in elements where the d-band widths are somewhat more narrow than in the other elements of the same valency. Further, we find the best agreement for the monovalent and divalent elements, where the influence of a d band should be least important. The worst disagreement is found for the tetravalent elements, where the presence of d bands is most important. Therefore we can discern two different effects of the d band: first, its width and second, its degree of occupation.

A most difficult quantity to account for theoretically is the compressibility. This is defined as

$$K^{-1} = \Omega \frac{d^2E}{d\Omega^2} \quad , \tag{3.5}$$

and thus involves the second volume derivative of the internal energy. This, and the fact that it involves a detailed balance between large numbers,[14] account for the above-mentioned difficulty, which becomes increasingly crucial as we move to higher valence. In Fig. 5, we have plotted the results for the different elements together with the experimental data. In view of the theoretical difficulties we find the overall agreement satisfactory. The most noticeable disagreement is found for γ-cerium and lanthanum. For the former this should be expected because of its vicinity to a large volume discontinuity (14%) taking place around 7 kbar at room temperature. Its particularly high value of the compressibility must be a precursor of this transition, undoubtedly due to the same mechanism causing its low atomic volume. The high compressibility of lanthanum is more difficult to understand, but probably it must somehow be coupled to the known rapid rise in superconductivity transition temperature with pressure. As an explanation of this rise, some authors have introduced a $4f$ state close to the Fermi level.[57] As a function of pressure it is claimed that the position of this state might change appreciably, and possibly in a way preferable also to a high compressibility.

If we disregard lanthanum and cerium, we note that our calculated compressibility curve for the trivalent lanthanides gives a sort of mean description of the actual behavior. It should be remarked that these calculations were all performed for an hcp phase. This simplification may explain some of the discrepancies. We note especially a "discontinuous" drop in the *experimental* points when proceeding from samarium to gadolinium. Also when samarium is compared to its preceding elements its compressibility appears to be somewhat enhanced. The existence of a "true" discontinuous jump between samarium and gadolinium is supported by experimental work on hardness of alloys between light and heavy lanthanides.[11] Although this quantity is not equivalent to the inverse compressibility, these concepts are still closely related. As a function of concentration there appears an almost instantaneous drop in hardness when passing from an hcp alloy to one of samarium type. Therefore it looks as if the enhanced compressibil-

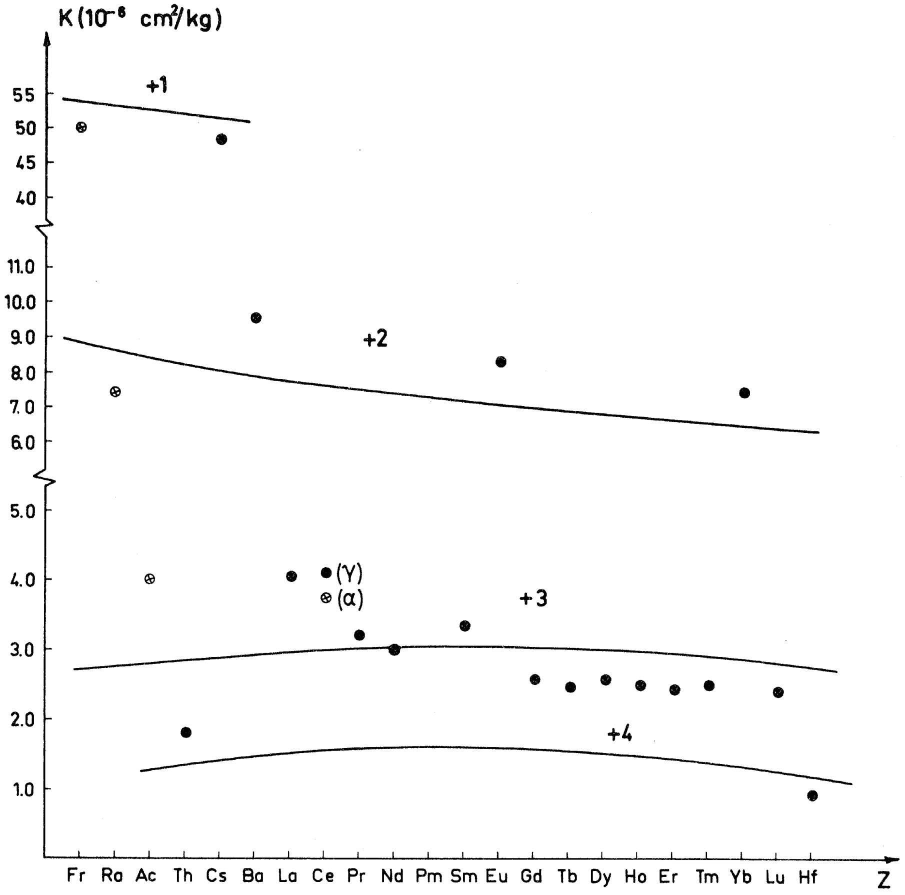

FIG. 5. Plot of the compressibility. Dots denote experimental values (Refs. 20, 54), crossed open circles estimated values (Ref. 20), and curves present calculation.

ity of samarium should be due to its vicinity to the hcp phase, in that enhanced fluctuations make the material softer. The same situation of enhanced fluctuations, although to a less degree, might be expected for promethium. Therefore we would estimate its compressibility to be about 3.15×10^{-6} cm^2/kg.

For α-cerium, the experimental point[20] given in Fig. 5 is almost certainly an overestimate. The value is derived from a pressure-volume relation extracted too close to the α-γ transition and thus cannot be considered as representative of "normal" α-cerium. Our own crude estimates from lattice-constant measurements certainly imply a much lower value, although it could not be as low as normally found in tetravalent metals. For hafnium and thorium the comparatively small deviation of our calculations from experiment is remarkable in view of their high valency and transition-metal character.

IV. CRYSTAL STRUCTURE

As discussed earlier in this paper, the rare-earth metals exhibit a remarkably consistent structure sequence as a function of atomic number. In fact, this property was the very basis for the construction of the generalized phase diagram. In Sec. II we introduced a quantity F, the ratio of the Wigner-Seitz radius to the experimental ionic radius, and indicated how the structure sequence of the rare earths could qualitatively be understood in terms of this parameter. A similar characterization was undertaken by Gschneider, who empirically correlated the structure sequence to the ratio between the metallic radius and the $4f$ orbital radius.[12] However, within the present approach we can more quantitatively account for the following choice of a characterizing parameter f:

$$f=r_s/r_c \; . \qquad (4.1)$$

Here r_s is the value which minimizes the energy for a given value of the pseudopotential core radius r_c. (Note that r_c is an atomic parameter, proportional to the radius of the outer orbital of the ion.) In the upper part of Fig. 6 this quantity f is plotted for the trivalent lanthanides and is found to increase with atomic number.

In this discussion of crystal structure we will not explicitly consider the samarium structure but employ a somewhat indirect method to correlate the

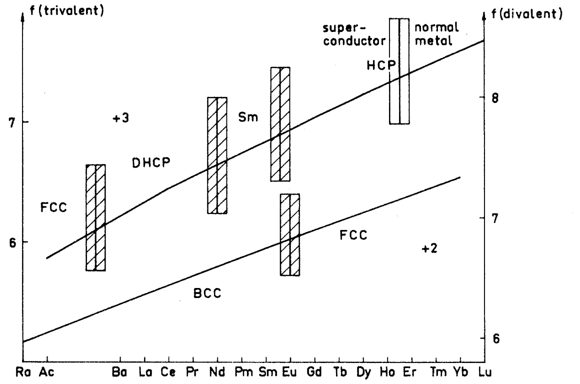

FIG. 6. Values of the ratio f [Eq. (4.1)] for the divalent and trivalent elements. The empirical critical values of f for different phase transitions are indicated by vertical bars. Note the different f axes for different valencies. The critical value of f for superconductivity is derived from Fig. 7.

critical pressures for the hcp→ samarium transition among the heavier elements. At the same time, this procedure will constitute a link between intra-rare-earth alloys and compressed metals. First, we consider the experimentally determined critical concentration in alloys of gadolinium and praseodymium for the onset of the samarium structure. This occurs at about 30% praseodymium.[11] The effective r_c value for the alloy is taken as $r_c^{\text{eff}} = (1-x)r_c^{\text{Gd}} + x r_c^{\text{Pr}}$, where x is the percentage of praseodymium in the alloy. From the critical concentration we can thus determine the value of r_c for which the samarium structure is favored. This gives $r_c = 0.381$, a value corresponding to a fictitious "element" between samarium and gadolinium. Second, for this fictitious element we calculate the corresponding equilibrium density and thus determine a critical value for f $(=6.88)$, below which a samarium structure is favored. For this "critical element" we also calculate the energy as function of the axial ratio c/a. The same calculation for gadolinium at equilibrium conditions gives a c/a dependence of the energy shaped differently from that of the critical element. However, calculations for compressed gadolinium show that, for a certain volume, this shape can be brought into the same form as for the critical element. The compression required is interpreted as being the same as for the onset of the samarium structure. Although our calculations are hampered by convergency difficulties, the relative differences found from one element to another should remain essentially unchanged in a convergent calculation; so the described procedure should be reasonable.

The same type of calculations can be accomplished also for the remaining heavy lanthanides. At the obtained critical compressions, we then calculated the corresponding pressures which, according to our interpretation, are the critical pressures for the hcp→ samarium transition. These transition pressures are given in Table I, together with the corresponding value of f at the critical volume. From this table it is clear that the calculated pressures are in satisfactory agreement with experiment. Further, it is nice to note that the stable value of f^{crit} is close to that of the critical element representing the onset of the samarium structure $(f=6.88)$. This is certainly good evidence for the appropriateness of f as a characterizing parameter for the rare earths. This choice of f can in fact be given *theoretical* support from the pseudopotential theory. The dominant contribution to the structure-dependent term in the energy expression comes from the first few sets of reciprocal lattice vectors. It is important to consider the magnitude of these vectors relative to q_0, where q_0 is the value of q for which the pseudopotential $v(q)$ equals zero. The lengths of the reciprocal-lattice vectors $\vec{G}_i$ and the vector length q_0 are inversely proportional to r_s and r_c, respectively. The ratio of r_s/r_c will therefore be a quantity which specifies the relative magnitudes of q_0 and $|\vec{G}_i|$. According to our interpretation it becomes then quite natural that the structural phase transitions should occur for almost the same f, independently of element.

If we now proceed to treat the samarium→ dhcp transition, we can rather confidently base our calculations on the parameter f. Thus as a critical value of f for which the dhcp structure is favorable to the samarium phase we simply choose $f=6.64$ derived from neodymium at equilibrium, the first element with a dhcp structure. We then find 35 kbar as the critical pressure for the transition in samarium. This should be compared with the observed transition at 40 kbar near 300 °C.[10] For gadolinium we calculate a critical pressure of about 80 kbar.

Similar considerations can also be applied to the

TABLE I. Calculated and experimental values for the hcp→ samarium-type structure transition.

Element	Critical pressure (kbar) Calculated	Critical pressure (kbar) Experimental[a]	Critical value of f
Gd	23	32	6.89
Tb	36	38	6.90
Dy	54	52	6.91
Ho	73	72	6.92
Er	92	99	6.93
Tm	117	119	6.94
Lu	167	not known	6.96

[a] Extrapolated to 0 °K from our generalized phase diagram (Fig. 2).

dhcp → fcc transition. In Fig. 6 we have indicated the different regions for the particular crystal structures as a function of the parameter f. Here we have been mainly concerned with properties under pressure, but it should be remarked that the behavior of intra-rare-earth alloys can be fitted into the same picture.

A structure sequence can also be distinguished for the divalent metals. Ytterbium has at room temperature and zero pressure a fcc structure which goes over into a bcc structure with pressure. In the next element, europium, only a bcc phase has been observed. Also barium has at STP conditions a bcc crystal structure. For the last element in the sequence, radium, very little is known, but a bcc structure has been observed at equilibrium conditions.[41] Therefore there seems to be a fcc → bcc structure sequence for these divalent metals. Also here the parameter f can favorably be introduced. Because of lack of data for europium-ytterbium alloys we could not introduce a critical f value for the fcc → bcc transition by means of any critical concentrations. Instead, we simply chose the f value for europium as the critical one. From this we calculate the critical pressure for the fcc → bcc transition for ytterbium to be 49 kbar at 0 °K, which should be compared to the experimental value of about 40 kbar at room temperature.[58] In Fig. 6 we have plotted the parameter f also for the divalent metals and indicated the critical value for the fcc → bcc transition.

Having discussed trends in crystal structure by means of a parametrization, a natural question to ask is: What would an orthodox comparison of binding energies for different structures give? To start with the trivalent elements, we found that the bcc structure was not favored for any of them. However, for lanthanum a comparison between the hcp and fcc structures gave that the fcc structure was favored, in disagreement with the experimentally established low-temperature hexagonal phase. In fact this disagreement was found for most of the rare earths, and we had to proceed to the element thulium before we found that the hcp phase was lower in energy than the fcc phase. Therefore it was only for the elements lutetium and thulium that we obtained the correct structure.

In order to see what an application of pressure to an individual element would give, we investigated lutetium. Thereby we found that the fcc phase becomes more favorable than the hcp phase for a rather small volume reduction.

In conclusion we may thus say that even though we obtained the wrong structure for most of the rare-earth elements, we could at least account for the tendency towards the fcc structure both with pressure and with lowering of the atomic number. It should also be mentioned that in our calculations for the hcp structure there was found a consistent *tendency* in the band-structure energy, such that lower values of c/a are more favored for the heavier than for the lighter elements. This is in line with the experimental findings that elements with an hcp structure have axial ratios of about 1.57–1.59, while those of samarium and dhcp structure are associated with values 1.60 and 1.61–1.62, respectively.[1,59]

For the rest of the treated elements the results concerning structure are summarized in Table II.

V. NONMAGNETIC RARE-EARTH SERIES
(Sc, Lu, Y, La, Ac)

Among the trivalent lanthanide elements only lanthanum and lutetium are nonmagnetic metals. All the other metals in the series have localized magnetic moments (except α-cerium), this being the main reason why none of them is a superconductor. In view of this, it would be interesting to look for superconductivity in europium under high pressure, since under such conditions this element is believed to become trivalent and attain a nonmagnetic configuration ($4f^6$).

In column IIIb of the periodic table there are, besides lanthanum, three other nonmagnetic metals, actinium, yttrium, and scandium. Following our scaling procedure (Sec. III), we assigned a core parameter r_c to each of them. Thereby an effective atomic number could be derived and their place in the periodic table in relation to the rare earths was found to be in positions 53, 69, and 85

TABLE II. Calculated and observed crystal structures for some elements.

Element[a]	Calculated	Observed
Rb	bcc[b]	bcc
Cs	bcc	bcc
Fr	bcc	• • •
Sr	fcc[c]	fcc
Yb	fcc	fcc
Eu	fcc	bcc
Ba	fcc[d]	bcc
Ra	bcc	bcc
Hf	fcc	hcp
Th	hcp	fcc

[a] For the divalent elements the calculation was restricted to bcc and fcc structures (Refs. 38 and 60).

[b] Only after including nuclear zero-point energy (Ref. 61).

[c] With compression our calculations favor the bcc phase, the critical pressure being similar to that obtained by Animalu (Ref. 60).

[d] Since our pseudopotential for barium is very similar to that employed by Animalu (Ref. 60), a closer investigation of Ba was undertaken. Thereby we found that a slight increase of r_c would in fact give the correct bcc phase.

for actinium, yttrium, and scandium, respectively. Since as yet no structure change with pressure has been reported for scandium and yttrium we could not directly place these metals into our generalized phase diagram. However, we can discuss whether their equilibrium properties fit into our diagram or not with respect to the mentioned effective atomic number assignments. (A more detailed discussion of this is given in Ref. 38).

To start with yttrium, this metal is known to have nearly the same atomic volume as gadolinium.[54] Alloyed with light lanthanides it exhibits the hcp → samarium-type → dhcp structure sequence with critical concentrations similar to those found for holmium and erbium.[62] Thus, when the more detailed atomic structure is determinant for its behavior, yttrium is most similar to the heavier lanthanides. This conclusion is also supported by electron band calculations. For the heavier lanthanides a trend can be discerned from the webbing features of the Fermi surface, and yttrium in this respect is found to be most similar to lutetium.[63,64] Therefore, in an averaged sense, our present assignment of an effective atomic number of 69 is most reasonable.

From a Darken-Gurry plot, it is clear that scandium will have only a limited solubility in the rare-earth metals.[1] This is certainly consistent with the above-mentioned assignment of an effective atomic number being rather remote from those of the lanthanides. In our generalized phase diagram, scandium thus should appear far to the left, this being in accordance with its hcp crystal structure. The axial ratio[54] of 1.59 also supports this point of view. From the trend of a decreasing compressibility with atomic number for the lanthanides (Fig. 5), also the low compressibility of scandium[65] (1.75×10^{-6} cm^2/kg) fits in.

The experimentally established properties of actinium are naturally very sparse, and as we have already pointed out even the determination of its atomic volume is not commonly accepted. It has, however, been reported to have a fcc structure.[39] The effective "rare-earth atomic number" was extrapolated to be 53. Therefore its (T, P) phase diagram should be placed to the right of our generalized phase diagram (Fig. 2). In view of this, its fcc crystal structure fits well into the diagram.

Together with lanthanum and lutetium the elements just discussed form an interesting nonmagnetic rare earth series with the following ordering: Sc, Lu, Y, La, Ac. Within this series it is only lanthanum which has been found superconducting at atmospheric pressure. We hasten to say, however, that actinium has not yet been investigated in this respect.

A very interesting investigation of the influence of pressure on the superconducting properties of most of these elements has been performed by Wittig.[66] Here it is our purpose to discuss his results in relation to our generalized phase diagram. The experimental findings by Wittig were the following. In the case of scandium he did not find any superconductivity (at attainable temperatures) up to a pressure of about 150 kbar. However, for the elements lutetium and yttrium he discovered that, if sufficiently compressed, they will become superconductors. Extrapolation of his data indicates that lutetium does so for a pressure of about 40 kbar and yttrium around 50 kbar.[67] From the strong pressure dependence of the transition temperature of lanthanum, one may also conclude that this metal should remain a superconductor for rather appreciable negative pressures. From these results a pressure sequence may be discerned which is in qualitative agreement with our present assignment of effective rare-earth atomic numbers to the elements scandium and yttrium. Therefore it is nice to conclude that superconductivity also shows the same type of interdependence between pressure and atomic number as does the crystal structure.

Further, Wittig was able to demonstrate that the transition temperature increased sharply with pressure for all these elements. The largest rise is shown by lanthanum. This difference may, however, be due to the much lower compressibility of yttrium and lutetium at the pressures involved than for lanthanum at zero pressure (our calculations give a factor of about 2.5). Therefore the rise in the transition temperature as a function of volume may be of the same order of magnitude for all these metals.

As we have seen concerning crystal structure, the effects of pressure and intra-rare-earth alloying are essentially equivalent. Therefore it is of interest to consider the influence of alloying also on superconductivity. If lanthanum is alloyed with yttrium or lutetium the superconductivity temperature is known to decrease.[1] In experiments on lanthanum-yttrium alloys, Satoh and Ohtsuka[68] discovered, for the first time, superconductivity in a samarium crystal structure. Noticeable in their data is the continuous behavior of the transition temperature as a function of concentration despite the different crystal structures involved.

The discovery of superconductivity in $(sd)^3$ elements other than lanthanum was employed by Wittig[69] to discuss the old idea of the possibility of a $4f$ band superconductor in lanthanum. Since in both lutetium and yttrium there is no $4f$ level close to the Fermi surface and yet they become superconductors, an $(sd)^3$ band configuration is in itself capable of giving superconductivity. Therefore the implication for lanthanum would be that it is just an ordinary $(sd)^3$ superconductor, without

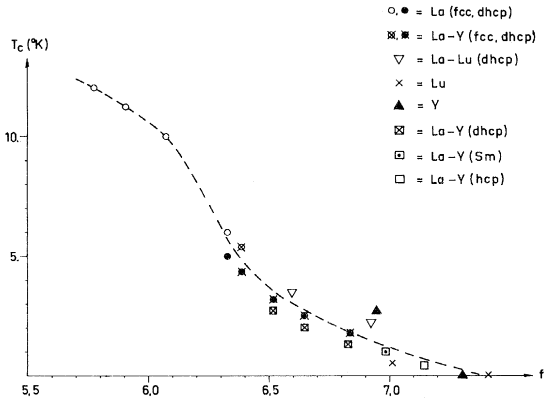

FIG. 7. Superconductivity transition temperature as a function of f [Eq. (4.1)] for various intra-rare-earth alloys and for pure elements at different atomic volumes (for further discussion, see text). The dashed curve is a smooth fit to the points. Data for La-Lu and La-Y in Ref. 1 and for La-Y in Ref. 68.

having to invoke the $4f$ level in the discussion. However, Wittig went one step further in the argument and stated that the *high* value of the transition temperature in lanthanum was an enhancement effect superposed on the "ordinary" $(sd)^3$ value, this enhancement being due to the presence of a $4f$ band. Lanthanum has a transition temperature of about 6 °K in the fcc phase at zero pressure and reaches a value of about 12 °K at 150 kbar. This latter value was compared to those of yttrium and lutetium at 150 kbar of 2.7 °K and 0.5 °K, respectively. The large difference between these temperatures and those of lanthanum was interpreted by Wittig as being due to a $4f$ band enhancement. This may turn out to be partly true, but here we just indicate that this argument in its present form cannot really be considered as conclusive. From our generalized phase diagram we note that a fair comparison between the different elements can only be said to have been made if at the same time it is demonstrated that lutetium and yttrium have reached at least the dhcp structure. When this has happened we can argue that the reduced atomic volume in lutetium and yttrium starts to resemble the conditions present in lanthanum. If this can be demonstrated to have happened at 150 kbar the argument concerning the $4f$ band enhancement would have been conclusive. However, as our earlier calculations indicate, in the case of lutetium not even the samarium phase has been reached at these pressures and considerable further compression seems necessary before the dhcp phase is induced.

In order to investigate these questions a bit more quantitatively we have employed all the data mentioned above to construct an empirical relation between the transition temperature and the parameter f. Since for most of the present elements we have calculated a pressure versus volume relation, we could translate pressure to volume and in this way obtain the quantity f as a function of pressure. For the alloys we averaged between our calculated equilibrium properties for the elements involved to establish f as a function of alloying. By this method we obtained the result shown in Fig. 7. The obtained interdependence is strikingly similar in form to an empirical curve derived by Shaw.[70] His curve was obtained in the context of the variation of the superconductivity transition temperature versus certain pseudopotential parameters. In fact our curve could have been put on the same basis, but here we preferred to limit ourselves to the parameter f. In view of Shaw's work, our curve has quite a plausible shape, and it seems a bit difficult to *definitely* infer any $4f$ band enhancement in lanthanum from its appearance.

Up to now we have not explicitly included actinium in our discussion of superconductivity. Unfortunately, there are no experiments performed on this element in this respect, but if they ever will be done they will certainly be very enlightening regarding the theoretical problems outlined above. It has been speculated that its atomic volume, assumed greater than that of lanthanum, should disfavor superconductivity.[71] However, such an argument must be an oversimplification. Instead, actinium should rather be expected to be simulated by compressed lanthanum. Since in actinium the $5f$ level is far away from the Fermi level, its atmospheric pressure properties should be of a normal $(sd)^3$ type. Therefore its superconducting transition temperature will be revealing as regards the actual situation in lanthanum. If there is nothing special about lanthanum, the curve in Fig. 7 should be "universal" for the nonmagnetic rare-earth metals. In this case, assuming that our parameters for actinium are not too unrealistic, it looks as if the transition temperature in actinium could be as high as (11–12) °K. Thus it may turn out that actinium has the highest transition temperature among the elements. In case it turns out to be low, this result would instead be a strong confirmation of a $4f$ band enhancement in lanthanum.

From the critical f for superconductivity given in Fig. 6, it is clear that if metallic europium could be obtained in a trivalent state it would be a superconductor (assuming that a nonmagnetic $4f^6$ configuration does not influence on superconductivity). In this connection it is interesting to discuss the actinide analogue of europium, namely americium. All available experimental evidences indicate that metallic americium is trivalent and has no localized magnetic moments[72,73] ($5f^6$ configuration). In the Sec. III, we will see that there are good reasons to place americium somewhere around praseodymium in its position relative to the rare earths. From the plot in Fig. 7 this would imply a superconductivity transition temperature of about (2–4) °K.

VI. ACTINIDES–A SECOND DELAYED RARE-EARTH SERIES

Our scaling procedure made it possible to relate actinium to the rare-earth series. Starting from this element, it is then rather natural to go further and examine how the rest of the actinide elements fit into the present scheme. A bit regrettable is the lack of well established data concerning the earlier elements in the seventh row of the periodic table, but our calculations are in consistent agreement with existing experimental information. From this we infer that the effective-atomic-number labeling for francium → thorium as 51 → 54 in relation to the rare earths should be quite appropriate. From this assignment we can then proceed and make a direct comparison between the lanthanide and actinide series.

Concerning the properties of the early actinide elements, it seems now well established that the 5*f* electrons form a narrow conduction band.[4,5] The observed absence of localized magnetic moment for these metals is thereby given a natural interpretation as being due to the itineracy of the 5*f* electrons. Further, Brewer has from spectroscopic data concluded that the plutonium metal cannot be using more than three non-*f* electrons in bonding.[74,75] However, from the data on heat of sublimation and interatomic distances one must then allow for a quite significant contribution of 5*f* electrons to the bonding. Again, such a substantial contribution is most easily understood in terms of a metallic 5*f* bonding. A more extensive study of this type has been made for all the earlier actinides,[56] and the same conclusion regarding the 5*f* state was reached.

In the early part of the actinide series the atomic volume shows, as a function of Z, a type of decrease similar to that found in the normal transition series (3*d*, 4*d*, and 5*d*). The trend is, however, broken around plutonium.[76] An attractive explanation of this behavior is that there starts to be a tendency towards localization of the 5*f* band electrons. In fact, when we proceed to the element americium this tendency seems to have been fully developed. This conclusion is supported by, for example, the atomic volume and compressibility of this element, which both are close to values typical for the lanthanides. In the 3*d* transition series the localization is never fully realized, even though the rival theories concerning itinerant or localized magnetic moments certainly are a reflexion of the proximity to it. A negative pressure (by some form of dilution) would rather easily turn the 3*d* electrons into localized states. The marked difference in rapidness of localization in the actinides compared to the 3*d* series can be understood qualitatively in the following way. The 3*d* orbitals are to a large extent found outside the argon core, while in the actinides a large fraction of the 5*f* wave function is within the radon core. As we proceed in the 3*d* transition series, the extension of the 3*d* wave function decreases more rapidly than the argon core, this being the main reason for the localization tendency. In case of the actinides, we have the same type of behavior in that the size of the 5*f* wave functions decreases faster than the radon core. In this case, however, the relative decrease is more pronounced. Therefore the localization process is, via the intermediate case plutonium, completed already in americium. A suggestive picture of this occurrence is to consider it as a Mott transition of the 5*f* state, viewed as a function of atomic number.[5]

How does this fit to our assignment of actinium as an effective-rare-earth element with atomic number 53? By arranging the actinides in an effective-atomic-number row to be compared to the lanthanides, we obtain the following:

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	
53	54	55	56	57	58	59	60	61	62	63	···
				La	Ce	Pr	Nd	Pm	Eu	Sm	

To begin with we notice that the first localized 5*f* metals americium, curium, and berkelium are placed above praseodymium, neodymium, and promethium, respectively. Interestingly enough all these three actinides have a dhcp phase,[76] which otherwise for the elements at equilibrium conditions is found only for the light lanthanides.[77] Moreover, experimental data show that these actinides have an axial ratio of about 1.62,[78] just as in the light lanthanides. In addition, all these elements have been observed in a fcc phase at elevated temperatures, as is also true for the light lanthanides. The crystal properties of americium have been comparatively well investigated, and rather clear evidence has also been found for a high-temperature bcc phase.[73] In fact, the known part of the phase diagram of americium could very properly replace that of praseodymium in our generalized phase diagram (only letting its pressure axis be displaced about 250 °K). Also, its compressibility is close to that of the light lanthanides.

Next we remark on that lanthanum is placed below neptunium. This seems to imply that in case lanthanum has a 4*f* occupation this ought to be in an itinerant state. Whether this could be the explanation of its high superconducting temperature or not is still not fully understood, as already commented on in Sec. V.

The present arrangment of the actinides places plutonium above cerium. This is most interesting in view of the itineracy of the $5f$ electrons in plutonium. This evidently gives support to the idea expressed by one of the authors[7] of the γ-α transition in cerium as a Mott transition, i.e., the $4f$ electrons in the α phase form a narrow conduction band. Here we want to point out some further similarities between these two metals. First of all, both of them have unusually low melting temperatures. If they were considered as tetravalent (s^2d^2) metals they ought to melt around 2000 °K, but the actual melting temperatures are only about 1000 °K. Second, the pressure dependences of their melting temperatures are strikingly similar.[79,80] Both show, with compression, a melting temperature initially decreasing towards a minimum and then gradually increasing with pressure. In cerium it was early recognized that this minimum "happens" to lie on the extension of γ-α transition line. Further, the γ-α transition is accompanied by a large volume discontinuity (~14%).[81] In plutonium, it has been verified[76] that its higher-temperature phases have considerably higher atomic volumes than the zero-temperature phase [~(15–20)%]. Moreover, there is some evidence of localized magnetic moments in these higher-temperature phases, although their magnitude is much smaller than the free ionic magnetic moment.[82] Therefore we suggest that in plutonium the true correspondence to the γ-α transition is to be found for *negative* pressures. This means that at zero pressure, as a function of temperature, we do not pass the true localization-delocalization transition line, but only its extension. This extension could by analogy with cerium be suspected to intersect the minimum of the melting curve. Therefore, as a function of temperature, at zero pressure there should be not a real but only a gradual transition accompanied by an extensive volume expansion. However, much of this behavior is partly disguised by the wide occurrence of distorted structures in plutonium. Recently, it has been discovered[83] that cerium in its high-pressure ($\gtrsim$55 kbar) phase α' has the same crystal structure as α-uranium and at still higher pressures ($\gtrsim$62 kbar) transforms to a monoclinic body-centered structure. Unusual metal structures are also present in the phase diagram of plutonium. This strongly supports the present idea about the close similarity between cerium and plutonium. Therefore the distorted structures in plutonium may also be found in cerium.

The unusual behavior of the melting curve can also be qualitatively understood from the picture given above. Since the delocalization $\leftrightarrow$ delocalization transition line has a positive slope in the (P, T) plane, this means that for a given pressure, starting within the delocalized phase, an increase of temperature will eventually lead to a state where the localization has taken place to a large degree (say in the liquid phase). The difference of entropy of the liquid and solid states is important in the melting process. Since the ions in the liquid are free to move translationally, the main gain in the liquid is due to the translational entropy absent in the solid. However, in the present case this is counteracted by a totally reverse process regarding the f electrons so the melting temperature will be increased by this process. For pressures above the minimum melting point there is no essential difference between the solid and liquid state as regards the f electrons; so the melting curve shows the normal behavior of an increase with pressure. For pressures below this minimum point, however, the melting process is opposed by the localization of the f electrons and therefore requires higher temperatures to be induced. In principle, this should result in a kink on the melting curve exactly at the place where the extension of the localization $\leftrightarrow$ delocalization phase line intersects the melting curve. For cerium and plutonium, this effect apparently is enough pronounced to even develop a minimum in the melting curve.

VII. VALENCE TRANSITIONS IN THE RARE-EARTH METALS

In the atomic state most of the rare-earth atoms are found to be essentially divalent in character, i.e., they hold a $6s^24f^{n+1}$ configuration. The only trivalent cases are lanthanum, cerium, gadolinium, and lutetium. When the atoms form a solid, however, most of the lanthanides act in a trivalent state. Therefore, if the formation of a solid is looked upon as a process where separated atoms are gently brought together, most of the lanthanides must somewhere have undergone a valence transition from the divalent to the trivalent state. The interesting cases are then europium and ytterbium, neither of which undergoes this transition all the way down to equilibrium crystal conditions. In a laboratory, however, this ideal way to form a solid can never be realized but is imitated by the condensation of metallic vapor to metallic liquid, which upon further cooling is brought to the crystalline state. From the heat of vaporization data for the rare earths,[1] it is evident that the valence transition in this case is connected to the vapor-liquid transition. The latter transition always ends in a critical point in the (P, T) plane, but it is not obvious that the valence transition has to be locked to the condensation process right up to its critical point. In case a pronounced kink is found for the condensation line, this must be interpreted as being caused by a separation of the two transitions. Such a behavior is in fact likely to occur at a rather low pressure for samarium and thulium, and their actual critical points should accordingly be close to those of the divalent metals europium and

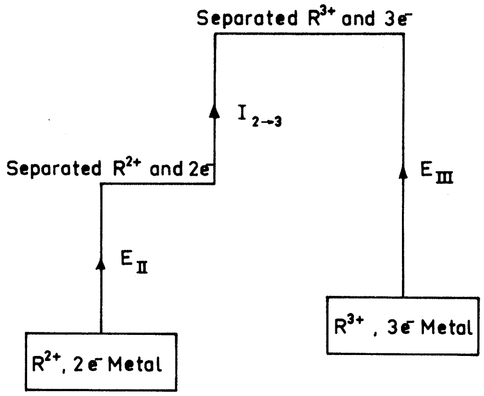

FIG. 8. Schematic diagram for the relation between the divalent and trivalent binding energies for a rare-earth metal R (see text for further discussion).

ytterbium. Despite the severe experimental difficulties, we call for more experimental attention to the lanthanides close to their vaporization, since in the general study of liquid metals and vapors under pressure as well as in the study of valence transitions one could greatly benefit from the close similarity of these elements. Interesting behaviors are also to be found in the two divalent metals ytterbium and europium. For example, at high pressures and moderate temperatures the metallic liquid should be expected to be in a trivalent state. This may very well turn out to be the reason for the observed maximum[58] in the melting temperature of europium as a function of pressure and a similar behavior in ytterbium as well.

From the atomic point of view, the transition involved is of type-$6s^2 4f^{n+1} \to 6s^2 5d^1 4f^n$. From spectroscopic data one finds that the excitation energy of this transition is greatest for europium and ytterbium.[74] Apparently this energy is big enough to maintain the divalent character even in the crystal state for these two elements. It is also found that samarium and thulium barely escape the divalent crystal state in favor of the trivalent one. This is, in fact, the reason why both of them frequently appear in a divalent state in compounds with chalcogenic atoms. However, since their "natural" form at crystalline densities still is the trivalent state, the energy required to promote a localized electron from the $4f$ level to an extended $5d$ band state must be very small in these compounds. As a matter of fact, such valence transitions have been induced by pressure[84] and constitute at present a very active area of research. In connection with such experiments the idea of so-called intermediate valencies has been introduced.[85] Here we are going to treat valence transitions in a more conservative way, in that we consider the transition from the totally divalent state to the totally trivalent state. By this we by no means imply any repudiation of the concept of intermediate valencies. Whether a system passes through a stable intermediate state or not when it changes valence is expected to be dependent on the strength of the matrix elements between the localized and extended states. An evaluation of this effect is certainly beyond the scope of the present paper.

In the transition of the localized electron to a delocalized state, the bonding properties of the solid must change significantly. Therefore the transition must be expected to be accompanied by a large decrease of volume. In case the $f \to d$ promotion is self-sustaining, the volume must change discontinuously. If the promotion on the other hand takes place only gradually, which may happen at higher temperatures, the volume will also change in a continuous way, although its variation will still be dramatic.

In order to study the relative stability between a divalent and a trivalent metallic state we must refer their binding energies to a common energy level. This can be accomplished in the following way (Fig. 8). Imagine we start from the divalent metal. First, we separate all the valence electrons and divalent ions from each other. By this process we loose the divalent binding energy E_{II} (per ion). In this separated limit we then ionize the divalent ions to the trivalent state, this requiring the ionization energy $I_{2\to3}$. After this we bring together the electrons and the *trivalent* ions to form a trivalent solid. In the last process we gain the trivalent binding energy E_{III}. From Fig. 8 it is clear that the position of this final state relative to the original state will determine whether the solid is divalent or trivalent. Therefore the stability condition for the divalent crystal may be written simply

$$|E_{II}| + I_{2\to3} > |E_{III}| \quad . \tag{7.1}$$

In exactly the same way one may formulate the stability condition for a trivalent crystal against formation of a tetravalent one.[86]

Within the given pseudopotential formulation we find for europium and ytterbium that the difference in the binding energies between the trivalent and divalent states is 28.4 and 30.4 eV, respectively. Experimentally, the ionization energy of the divalent ion has been found to be 24.70 eV for europium and 25.03 eV for ytterbium.[53] Thus our calculations give preference for the trivalent metallic state, which of course is in disagreement with known facts. Therefore we have to employ an empirical method to derive the energy margin maintaining europium and ytterbium in the divalent state.

Because of the similarity between the lanthanide elements one can with good confidence perform interpolations and thereby obtain accurate results. Among the trivalent metals, it is easy to construct

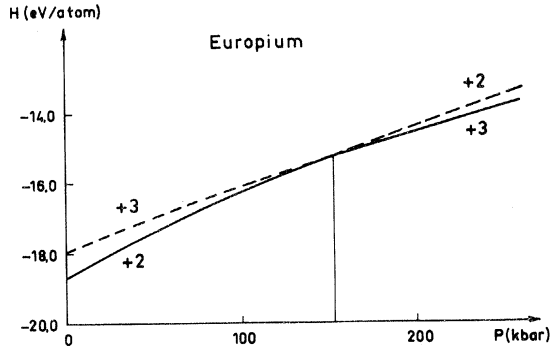

FIG. 9. Calculated enthalpies for di- and trivalent europium as a function of pressure. The solid curve denotes the stable state, and a transition is seen to occur at about 150 kbar.

an interpolation curve of the binding energy. Actually, we drew this curve through the binding-energy values for three elements which are trivalent both in the crystal and atomic state (La, Gd and Lu). Thereby it turned out that the remaining trivalent metallic lanthanides did not miss the interpolation curve with more than maximum 0.25 eV.[87] From this we can deduce the binding energies of *hypothetical* trivalent europium and ytterbium. Thereby we obtain the differences in binding energy between the di- and trivalent states as 23.95 and 24.53 eV (± 0.05). From the third ionization potential we thus find that europium and ytterbium are divalent with a margin of 0.75 and 0.50 eV (± 0.05), respectively. By adjusting our energy difference between the di- and trivalent states, as calculated by the pseudopotential method, in such a way that it agrees with this "experimental" difference, we now compare these two states as a function of pressure. Since our calculated compressibilities for the lanthanides are in fair agreement with experiment, this method should not be too unrealistic for the present purpose. At zero temperature the transition may be determined from a comparison of the enthalpy

$$H = U + PV \ . \qquad (7.2)$$

In Fig. 9 this is illustrated for europium. From this figure we note that the trivalent state becomes stable for pressures exceeding 153 ± 15 kbar. In Stager and Drickamer's high-pressure experiments on europium[88] a drastic change in resistivity was seen taking place around 150 kbar, which in view of our calculations very well may turn out to be associated with a valence change. The calculated volume discontinuity is a 17% volume decrease. In Fig. 10 we have plotted the calculated pressure-volume relation for europium together with experiments. In the low-pressure region our calculations agree with the experimental data of Stephens.[89] However, these experiments have been criticized by Monfort and Swenson,[90] and further work by McWhan *et al.*[91] supports this criticism. A recalculation with parameters fitting the compressibility found in these latter works would give a somewhat higher transition pressure and lower volume decrease. The shock-wave data [92,93] seem to support our conclusion that europium is trivalent at high pressures.[94]

For ytterbium we calculated the critical pressure for the valence transition to be 136 ± 15 kbar. In Fig. 11 we have plotted the pressure-volume relation and compared with experiments. It has been suggested[95] that the fcc → bcc transition is accompanied by a valence change. However, in our view this seems very unlikely, since ytterbium in its trivalent state undoubtedly should appear in a hexagonal crystal structure. Our calculated volume

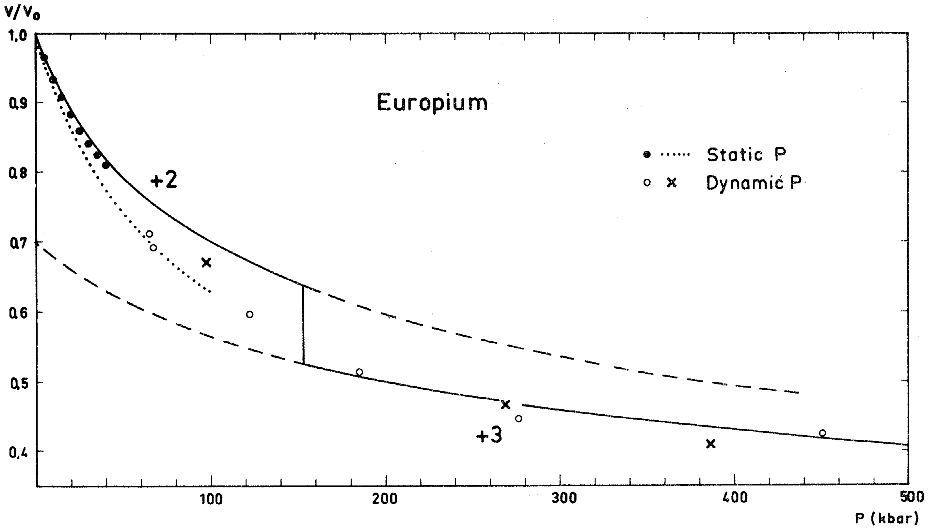

FIG. 10. Reduced volume against pressure for europium. Full curve: this calculation; Dots: data from Ref. 89; Dotted curve: experimental data from Ref. 91; Crosses and open circles: shock-wave data from Refs. 92 and 93, respectively.

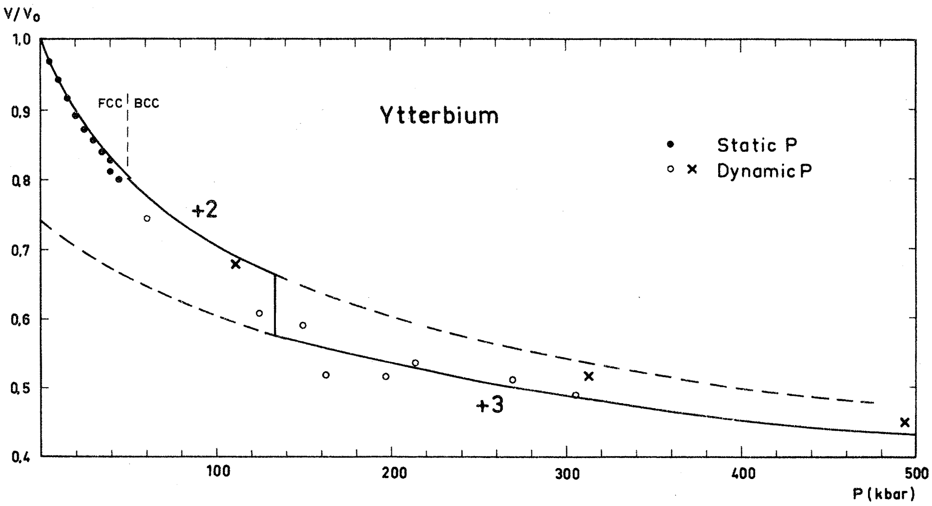

FIG. 11. Reduced volume against pressure for ytterbium. Notation same as in Fig. 10. The calculated fcc-bcc transition was determined from the critical value of the parameter f (Fig. 6).

discontinuity for the valence transition in ytterbium is about 14% and thus of the order of magnitude one should expect. The measured volume discontinuity at the fcc → bcc transition, on the other hand, is just a few percent, and again this low value is strong evidence against an accompanying valence transition. Also for ytterbium the shock-wave data at high pressures[92,93] agree quite well with our PV relation for the trivalent state. Again, our present calculations for divalent ytterbium probably underestimate the compressibility, and therefore also for ytterbium the calculated transition pressure is somewhat too low.

An enlightening diagram concerning the valence states in the lanthanides in general can be derived as follows. From the consistency among the divalent elements (barium, europium, and ytterbium) the construction of an equivalent interpolation scheme as for the trivalent metals should be quite reliable also for the divalent binding energies. In this manner it is thus possible to derive the difference in binding energy $E_{\mathrm{III}} - E_{\mathrm{II}}$ between the two valence states involved for each separate element. This difference is plotted in Fig. 12 together with the experimental ionization energies of the doubly ionized lanthanides.[53] The diagram shows in a clear way the balanced situation prevailing in the lanthanides which cause their characteristic valences. This diagram constructed from the clear trivalent (lanthanum, gadolinium, and lutetium) and divalent (barium, europium, and ytterbium) elements can be looked upon as an *empirical proof* of the trivalency of the remaining lanthanides.

For the actinides an equivalent discussion of valency can be made, even though restricted by a substantial lack of data. Of special interest is americium. In its rare-earth atomic analog, europium, the $4f^7 6s^2$ to $4f^6 5d 6s^2$ transition energy is 3.1 eV while the corresponding value of the $5f^7 7s^2$ to $5f^6 6d 7s^2$ transition in americium is about 2.1 eV.[74] Therefore we would expect americium to lie about 1 eV below europium in Fig. 12, which, in accordance with experiment, implies that americium is a trivalent metal. A similar investigation of the heavy actinides shows that both mendelevium and nobelium should be divalent metals. We thus notice that for the actinides there is a strong tendency among the heavier elements to behave as divalent metals. In fact this is so pronounced that even fermium and einsteinium may turn out to be divalent metals.[75,96]

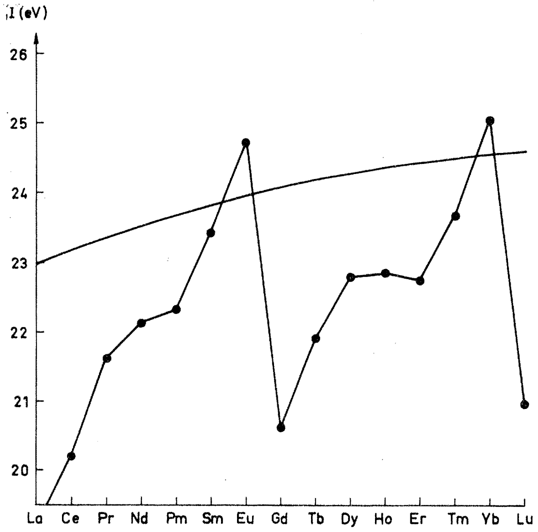

FIG. 12. Ionization energy I for divalent rare-earth ions (Ref. 53). The smooth curve is the interpolated binding-energy difference between divalent and trivalent metallic states.

VIII. DISCUSSION AND SUMMARY

As mentioned in the Introduction one is very hesitant about the applicability of the conventional form of the pseudopotential method to the rare-earth metals. In the literature the difficulty is sometimes said to be caused by the open $4f$ shell. In our opinion, however, the dominant problem is not so much the $4f$ electrons but rather the presence of the $5d$ band. In most of the rare earths the $4f$ electrons are found in highly localized states with a minor direct influence on the valence electrons (practically no hybridization), and therefore they do not constitute a real objection to the use of a pseudopotential. Even in metals like copper and zinc, where the filled d shell does have a profound influence on the valence electrons, the pseudopotential method has been applied. Therefore the main cause of *our* hesitance is the presence of the $5d$ band. From band calculations[16] it has been found that the d bands are rather wide (6–8 eV). Further, it is known that the lowest part of a d band is of a rather delocalized nature. Therefore these two features of the d band may interplay to make a pseudopotential approach feasible, at least for ground-state properties. From the calculations presented in this paper it appears that a fair account of macroscopic properties of the lanthanides in fact can be given. However, it remains to be seen how far down to more detailed microscopic properties such an approach can be useful. For the tetravalent element thorium, however, the d band is much wider and our pseudopotential approach should be more appropriate. This is supported by the fact that calculations of the phonon spectrum[97] reproduce experiment within 10%.

In the course of our calculations we have kept the number of variable parameters as low as possible. In fact, we fitted parameters only for gadolinium (trivalent), europium (divalent), and thorium (tetravalent). From these we obtained the characteristic parameters for the rest of the elements by a simple scaling procedure using theoretically calculated ionic properties. In terms of the pseudopotential theory this means that we have taken the concept of an orthogonalizing inner-core region as our guiding principle. The extension of this region should be directly related to the spatial distribution of the core orbitals themselves. Therefore we let our parameter r_c, which specifies the extension of the core, be proportional to the radius of the orthogonalizing core orbital. From the fitted values of r_c for gadolinium and europium we thus derive model parameters for all the lanthanides and several neighboring elements. By this procedure we are also able to assign model parameters to the elements scandium, yttrium, and actinium. Together with lanthanum and lutetium these elements constitute an interesting series of elements which could be characterized as a nonmagnetic rare-earth series. Because of the absence of magnetic moments in these elements they can become superconductors, and a general trend was demonstrated in their transition temperatures. It turned out that actinium must be expected to be a superconductor and in fact may have the highest transition temperature among the Elements.

From a more model-independent point of view, we have shown that many of the bulk properties can be linearly parametrized by the quantity f $(=r_s/r_c)$. By means of this parameter, not only the structures attained by a particular element, but also alloying properties, pressure-induced structural phase changes, and superconductivity among the nonmagnetic elements could be parametrized. It should be remarked that within the pseudopotential formulation the reason why the parameter f is useful can be clearly understood.

From our comparison between the actinides and lanthanides it also appeared that the heavier actinides (heavier than plutonium) can be considered as a kind of a second rare-earth series. From our scaling procedure it turned out that the actinide elements americium, curium, and berkelium are placed in positions equivalent to those of praseodymium, neodymium, and promethium, respectively. This is certainly quite satisfying since all these elements have a dhcp crystal structure. Further, the bordering element, plutonium, was discussed in relation to cerium and their similarities were interpreted as being due to the presence of a narrow itinerant f state.

The rather good agreement between calculation and experiment for the binding energies and compressibilities of the divalent and trivalent elements made it possible to theoretically discuss the valency of the different lanthanide elements. This is of special interest in the case of the elements europium and ytterbium, both of which are expected to become trivalent at high pressure. Our calculations give critical pressures of the order of 150 kbar, and we call for more detailed experiments to secure the actual occurrence of these transitions.

ACKNOWLEDGMENTS

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Note added in proof. (a) High pressure work by Lin-Gun Liu, J. Phys. Chem. Solids 36, 31 (1975), has explicitly demonstrated that lutetium transforms to the samarium-type of structure at 230 ± 5 kbar. Thus all the heavier rare-earth elements have been shown to undergo the hcp → samarium-type crystal transformation, confirming the validity of the present generalized phase diagram (Fig. 2) in this respect. (b) The melting temperature of promethium has recently been measured [P. Angelini and H. L. Adair, Proceedings of the 11th Rare-Earth Conference, Traverse City, Michigan, 1974 (unpublished), p. 662], and was found to be 1315 ± 5 °K. These authors also found a phase transformation taking place at 1163 ± 5 °K. In view of our phase diagram (Fig. 2) this latter temperature must refer to the lower bound of the bcc region. (c) A revised value of the ionization energy for the divalent free ion of europium has recently been published by J. Sugar and N. Spector, J. Opt. Soc. Am. 64, 1484 (1974). The new value is 24.92 eV instead of 24.70 eV. Further, a more recent compilation of cohesive energies [K. A. Gschneider, Jr. (private communication)] gives for divalent europium a value of 42.4 kcal/mol. These matters together lead to an energy difference between divalent and trivalent metallic europium of 1.02 eV instead of the value 0.75 eV which was derived in this paper. With this new value we obtain 245 ± 20 kbar as the critical pressure for the valence transition in europium.

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