Crystal and electronic structure connections between the 4f and 5f transition metals

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Abstract

The present understanding of the connection between the electronic structure and the crystallographic behaviour of the lanthanide and actinide elements is reviewed. The heavier, rare earth-like, actinide metals have crystal structures in direct correspondence to the lighter lanthanide metals such as La and Pr. On the other hand, the earlier actinide metals Th–Pu, have properties which are comparable to those for α-Ce and other high-pressure phases of Ce. Two generalized phase diagrams are used to illustrate these relationships. From the good agreement between theory and experiment as regards the crystal structure behaviour under compression, it is concluded that the 4f electrons in α-cerium contribute most significantly to the metal bonding. In this way the dramatic influence on the density, necessary to explain the volume collapse associated with the γ–α transition, is explained as being due to a Mott transition from localized to itinerant 4f electrons. It is stressed that the valence assignments for the earlier actinide metals often made in the literature have no meaning. However, for the heavier elements, Am–Cf, a valence assignment is appropriate, namely a valence of three. For the even heavier actinides, Es–No, the most likely valence assignment for the metal state is two.

*Keywords:* Crystal structure; Electronic structure; Transition metals

1. Introduction

The crystal structures of the elements give important information about their basic electronic structure. This should be obvious since it is the electronic state that determines the ground-state atomic arrangement at zero temperature. Thus the experimental observation of a particular crystal structure at equilibrium and also under compression [1] gives most valuable data that have to be matched by theory. In this way, high-pressure experiments can be used as an important guide for the theoretical understanding of the electronic structure. As it turns out, this relationship between crystal and electronic structures is extremely useful and enlightening for the case of the 4f and 5f transition series and there are a number of close connections between the two series [2]. Many of these were predicted in Ref. [2], and have now become experimentally verified.

Today the theory of the electronic structure of the lanthanide and actinide metals is almost as well developed as for the rest of the metallic elements in the Periodic Table [3]. Most interestingly, among these f elements some of the most dramatic electronic structure transformations discovered so far for solids take place as a function of compression [4–10] or as a function of atomic number [11]. Therefore, this part of the Periodic Table offers a number of research areas, involving fundamental questions regarding our understanding of electronic structure. The common feature uniting the actinides and lanthanides is, of course, the f shell and its gradual filling as one proceeds through the 4f and 5f series of elements [2].

First we notice that at zero pressure there is a profound difference between the early and late actinide metals, in the sense that the 5f electrons are itinerant (metallic) for the elements up to and including Pu, whereas they are localized and non-bonding (atomic-like) for the elements beyond Pu [11,12]. Thus, in this respect the later (heavier) actinides and their 5f electrons behave like most of the lanthanides with their localized 4f^n atomic-like configurations. On the other hand, among the lanthanides the first element with a substantial occupation of the 4f shell, i.e. cerium, shows at fairly low pressures or at low temperatures a behaviour very reminiscent of the early actinides [13]. Thus for the actinides there are five elements (Th–Pu) showing

itinerant 5f behaviour before localization sets in when the atomic number is increased from Pu to Am, whereas for the lanthanides only one element exhibits 4f itinerant properties, i.e. cerium, and thereafter localization is energetically favoured for all the heavier 4f elements. We illustrate this by arranging the actinides relative to the lanthanides introducing a displacement in atomic number [2]:

	Ce	Pr	Nd	Pm	Sm	Eu	Gd
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm
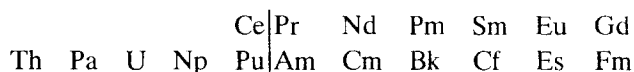
(The physical reason for this displacement is the larger spatial extent of the 5f orbital as compared with the 4f orbital.) This is indeed a close connection between the 4f and 5f series, but one that has not yet been fully explored.

Further evidence for the validity of this picture comes from the fact that the element following cerium, i.e. praseodymium, shows a volume collapse [10] of about 10% at 200 kbar and the dense phase shows similarities with the early actinides. Thus application of a moderate pressure moves the division line between itinerant and localized 4f behaviour one atomic unit so that now, under these new external conditions, two lanthanide elements show correspondence to the early actinides. The important conclusion is that depending on the external pressure, more than one element of the lanthanides can be brought into a state with close similarities to the early actinides. This relationship between the two f series was first pointed out in 1974 and a generalized phase diagram for the actinides was constructed [13] and compared with the individual pressure–temperature phase diagram for cerium metal (Fig. 1). This diagram for the actinides was later developed further by Smith and Kmetko [14], who constructed a generalized phase diagram for actinide alloy systems, i.e. for alloys between actinide metals.

2. Lanthanides

For the lanthanides with localized 4f^i configurations, it was demonstrated [2] that the individual pressure–temperature $(P-T)$ phase diagrams could be brought together into one single generalized phase diagram (Fig. 2). (For more recent work, see Refs. [9] and [15]. Here the crystal data are correlated with the ratio $r_f = R_{ws}/R_{5p}$, i.e. the ratio between the Wigner–Seitz radius and the radius of the 5p core orbital. The latter radius can be related to the size of the ionic core. This quantity r_f is directly related to the parameter F used in Ref. [2] to describe various properties of the lanthanide metals.) This clearly demonstrates the close relationship between the lanthanide metals. The observed high-pressure behaviour of yttrium [16], i.e. a trivalent rare earth element but not a lanthanide, clearly
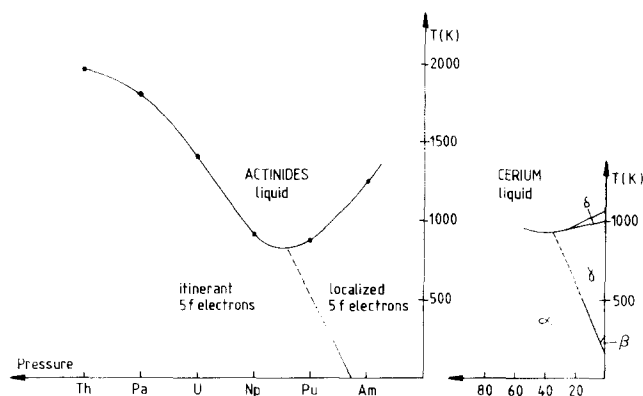

Fig. 1. Melting temperatures for the actinide elements (left) and the P–T phase diagram for cerium (right) [13]. The effect of pressure on an individual element is to make it behave more similarly to its predecessor in the series. This is schematically indicated by a tentative pressure axis on the left. The indicated transition line for the transition between localized and itinerant 5f behaviour (Mott transition) as a function of atomic number Z (or pressure for an individual element) has been included schematically. Its extension to the minimum point of the melting curve has been drawn as a suggestive analogy to the behaviour in cerium metal. Also, in the P–T phase diagram for cerium an extension of the γ–α transition line to the minimum of the melting temperature is indicated by a dashed line.
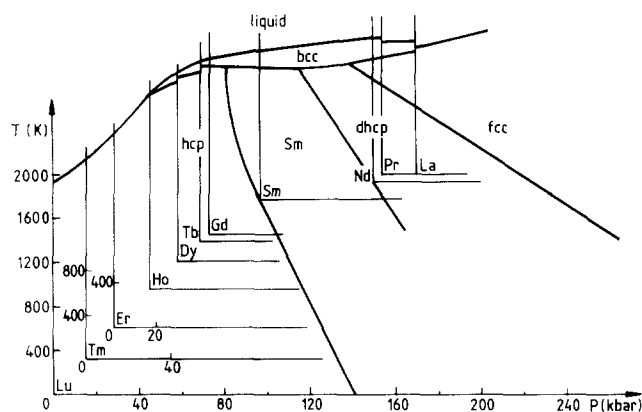

Fig. 2. A generalized phase diagram [2] for the trivalent lanthanide metals. The experimental P–T phase diagrams for the trivalent lanthanides are put together as consistently as possible. Note the obvious appearance of empty space where missing elements (due to divalent behaviour, to itinerant 4f states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

shows that the f electrons for the heavier lanthanides play no part in the structural properties, since yttrium behaves exactly like gadolinium under pressure, showing the same crystal structure changes. The exceptions to this standard trivalent structural behaviour are the two divalent ($4f^{n+1}$) elements europium and ytterbium and the compressed cerium metal. It is interesting that the low-pressure, high-temperature part of the cerium phase diagram can still be fitted into the generalized phase diagram in Fig. 2, i.e. this part of the Ce phase diagram agrees well with the other lanthanides. However, with increasing pressure cerium attains properties that are

not at all compatible with the rest of the lanthanides, i.e. cerium is brought out of the generalized phase diagram when subject to high compressions. It is important to note that these high-pressure data for cerium are strongly supported by state-of-the-art calculations [17] regarding the crystal structure behaviour under pressure, where the experimental observation of the fcc→α-uranium [18]→bct [19] structure changes in Ce is fully confirmed. In this theoretical study the 4f electrons are included as part of the conduction band, i.e. they are treated as itinerant electrons.

This agreement between theory and experiment is a very strong confirmation of the delocalized nature of the 4f electrons in the α-phase of cerium. Even the observed details of the pressure dependence of the c/a axial ratio [20] in the bct phase of cerium have now been reproduced by theory [21]. The agreement with experiment in fact is of the same high quality as for the bct phase in thorium. This, of course, constitutes another close link between actinide and lanthanide behaviour, namely that at pressures of the order of 0.1–1.0 Mbar both cerium [20] and thorium [22] show the same crystal structure and a similar c/a variation. In a relatively recent paper by Eriksson et al. [23], even the delocalization process of the atomic-like 4f configuration in Ce could be described, and a comparatively good account of the observed data was obtained, such as the volume collapse associated with the $\gamma \to \alpha$ phase transformation. Similar results were recently also obtained by Svane [24] and Szotek et al. [25] applying the self-interaction correction (SIC) method to the cerium metal, strengthening the evidence for the correctness of the theory that explains the $\gamma \to \alpha$ transition as a Mott transition within the 4f shell.

3. Heavy actinides

The heavier actinides, i.e. those with localized 5f electrons, can also be directly compared with the lanthanides. Such a comparison led to the prediction of superconductivity in actinium and americium [2]. The latter prediction was verified experimentally [26], but the extreme difficulties associated with handling actinium have prevented any measurements of its physical properties. Recently, high-pressure experiments have shown a pressure dependence of the superconductivity transition temperature for americium [27], which has a direct correspondence among the lanthanides, again confirming the relationship between americium and the early lanthanides. Thus not only its crystal structure, which is dhcp, finds a correspondence among the light lanthanides. For Cm, Bk and Cf, a similar electronic structure relation to the early lanthanides is also expected, as is nicely confirmed by their dhcp crystal structure. Under a moderate compression all the ele-

ments Am–Cf show a phase transition to the fcc structure [5,28], which again is a crystallographic phase change also found for the early lanthanides, and this gives an excellent verification [29] of the 4f–5f correspondence. Hence all the elements Am–Cf are clearly trivalent metals, i.e. with a localized $5f^n$ atomic-like configuration, a fact that settles all the earlier speculations concerning the valence configurations for these actinides. In view of what we previously said about the earlier actinides, the kind of valence assignment that is being made for the lanthanides and the heavier actinides loses its meaning for these elements, where the f electrons actively take part in the bonding. For the elements beyond Cf, i.e. Es–No, one expects a divalent behaviour [3,30] just as with europium and ytterbium. The reasons for the different valence behaviour in the lanthanides and actinides as regards the occurrence of metallic divalency have also been fully explained [30]. In short, it follows from the much steeper variation of the $f^{n+1} \to f^n d$ promotion energy through the series for the actinides than for the lanthanides. This, for example, makes the element corresponding to europium, i.e. americium, trivalent instead of divalent, and gives rise to the expectation that for the heaviest actinides a series of three elements (Es–No) will be divalent as metals.

4. Volume collapse under pressure

The volume collapses under pressure observed for Cm, Bk and Cf fit very well into the picture of a delocalization of the 5f shell. This was in fact predicted by theory ahead of the experiment [11,31]. However, one problem has remained, namely that in the case of americium metal, one has not observed the theoretically expected volume collapse under high pressure, but only some crystallographic transformations involving relatively minor volume changes. This has remained mysterious and we can only hope that future experiments will soon resolve this dilemma. Except for this questionable case, the rest of the data for the volume collapses in the other elements fit very well with what is expected theoretically [32]. For example, the transition pressure for Cm is higher than that for Bk, despite the fact that the 5f orbital for Cm has a larger spatial extension than the 5f orbital for Bk. However, the spin pairing energy of the 5f shell electrons within the localized phase has a maximum for Cm with its seven 5f electrons, corresponding to a half-filled fully spin-polarized shell. Thus the localized configuration is particularly stable energetically for Cm, making it harder to delocalize the $5f^7$ configuration than the $5f^8$ configuration in Bk.

The collapsed volume phases in Cm, Bk and Cf all show distorted crystal structures, where the α-uranium

structure seems to be a common structural base for the observations. This is closely related to the observed high-pressure crystallographic structures in cerium and praseodymium. The correspondence with the uranium metal is, of course, obvious. Several theoretical calculations have been done for the earlier actinides, where the total energies for the hcp, bct and fcc and a number of structures met among the actinides are compared as a function of volume [33,34]. Thereby the observed low-temperature structures are confirmed by the calculations for all the elements Th–Np, i.e. the experimentally determined structures are found to have the lowest energies (the investigations for Pu are not yet completed). This shows that the present calculational methods are sufficiently accurate to account for the delicate differences between the different crystal structures for the actinide elements. Therefore, we have now reached a level of accuracy and understanding from which we can start to treat other physical and chemical properties, such as the elastic behaviour of the actinides. The same also applies to α-cerium and the other compressed phases of cerium. In our preliminary calculations for praseodymium metal [35], it is interesting that at high pressure the α-uranium structure is lowest in energy and that it is paramagnetic and accordingly has a collapsed volume. At less compressed volumes the paramagnetic fcc phase is lower in energy than the α-uranium structure, just like in cerium! When further theoretical investigations have been completed, it seems highly likely that for Pr one will find a situation where the localized f^2 configuration directly transforms to a delocalized α-uranium phase. Therefore, we do not meet an isostructural phase change in Pr as we do in Ce, since the pressure needed to delocalize the f^2 configuration is so high that we have entered a volume range where the α-uranium structure has become the energetically favoured atomic arrangement. If, in the case of cerium, the pressure needed for delocalization of the 4f electron in fcc cerium had been higher, the same situation as for Pr would also have occurred for Ce metal, that is, a crystallographic structural transition driven by an electronic phase change between localized and itinerant 4f behaviour. Hence the observed crystal structure in the high-pressure region is a direct consequence of the itinerant properties of 4f states at these volumes. Therefore, the itinerant property of the 4f states in the collapsed phase gives an immediate explanation of the observation that the volume collapse is not of an isostructural type for praseodymium.

5. Conclusion

We have given a short review of some of the close similarities between the crystal structure behaviour of the 4f and 5f transition elements. It should be clear that not only do the later, rare earth-like, actinides have direct similarities with the lanthanides, but also the earlier elements with bonding 5f states have connections to the early lanthanides when the latter are compressed. At zero pressure it is only at low temperatures that cerium shows a behaviour, originating from bonding 4f electrons, that can be compared with that of the itinerant 5f metals Th–Pu.

Acknowledgements

References

[1] D.A. Young, Phase Diagrams of the Elements, University of California Press, Berkeley, CA, 1991.
[2] B. Johansson and A. Rosengren, Phys. Rev. B, 11 (1975) 2836.
[3] B. Johansson and M.S.S. Brooks, in K.A. Gschneidner, Jr., L. Eyring, G.H. Lander and G.R. Choppin (eds), Handbook on the Physics and Chemistry of Rare Earths, Vol. 17, Elsevier, Amsterdam, 1993, p. 149.
[4] A.W. Lawson and T.Y. Tang, Phys. Rev., 76 (1949) 301.
[5] U. Benedict, J.R. Peterson, R.G. Haire and C. Dufour, J. Phys. F, 14 (1984) L43.
[6] U. Benedict, J.P. Itié, C. Dufour, S. Dabos and J.C. Spirlet, in N.M. Edelstein, J.D. Navratil and W.W. Schulz (eds.), Americium and Curium Chemistry and Technology, Eeidl, Dordrecht, 1985, p. 213.
[7] R.B. Roof, R.G. Haire, D. Schiferl, L.A. Schwalbe, E.A. Kmetko and J.L. Smith, Science, 207 (1980) 1353.
[8] U. Benedict, in A.J. Freeman and G.H. Lander (eds.), Handbook on the Physics and Chemistry of the Actinides, Vol. 4, North-Holland, Amsterdam, 1987, p. 227.
[9] U. Benedict and W.B. Holzapfel, in K.A. Gschneidner, Jr., L. Eyring, G.H. Lander and G.R. Choppin (eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 17, Elsevier, Amsterdam, 1993, p. 245.
[10] G.S. Smith and J. Akella, J. Appl. Phys., 53 (1982) 9212; W.A. Grosshans, Y.K. Vohra and W.B. Holzapfel, J. Phys. F, 13 (1983) L147.
[11] B. Johansson, Phys. Rev. B, 11 (1975) 2740.
[12] H.L. Skriver, O.K. Andersen and B. Johansson, Phys. Rev. Lett., 41 (1978) 42.
[13] B. Johansson, Philos. Mag., 30 (1974) 469.
[14] J.L. Smith and E.A. Kmetko, J. Less-Common Met., 90 (1983) 83.
[15] T. Krüger, B. Markau, W.A. Grosshans and W.B. Holzapfel, High-Press. Res., 2 (1990) 193.
[16] Y. Vohra, H. Olijnik, W. Grosshans and W.B. Holzapfel, Phys. Rev. Lett., 47 (1981) 1065.
[17] J.M. Wills, O. Eriksson and A.M. Boring, Phys. Rev. Lett., 67 (1991) 2215; O. Eriksson, J.M. Wills and A.M. Boring, Phys. Rev. B, 46 (1992) 12981.
[18] F.H. Ellinger and W.H. Zachariasen, Phys. Rev. Lett., 32 (1974) 773.

[19] S. Endo, H. Sasaki and T. Mitsui, *J. Phys. Soc. Jpn.,* **42** (1977) 882.

[20] S.J. Olsen, L. Gerward, U. Benedict and J.P. Itié, *Physica B,* **133** (1985) 129.

[21] P. Söderlind, O. Eriksson, J.M. Wills and B. Johansson, *Phys. Rev. B,* to be published.

[22] Y.K. Vohra and J. Akella, *Phys. Rev. Lett.,* **67** (1991) 3563; O. Eriksson, P. Söderlind and J.M. Wills, *Phys. Rev. B,* **45** (1992) 12588.

[23] O. Eriksson, M.S.S. Brooks and B. Johansson, *Phys. Rev. B,* **41** (1990) 7311.

[24] A. Svane, *Phys. Rev. Lett.,* **72** (1994) 1248.

[25] Z. Szotek, W.M. Temmerman and H. Winter, *Phys. Rev. Lett.,* **72** (1994) 1244.

[26] J.L. Smith and R.G. Haire, *Science,* **200** (1978) 535; J.L. Smith, *Physica B,* **102** (1980) 22.

[27] P. Link, D. Braithwaite, U. Benedict, J. Wittig and R.G. Haire, *J. Alloys Comp.,* in press.

[28] J. Akella, Q. Johnson, W. Thayer and R.N. Shock, *J. Less-Common Met.,* **68** (1979) 95; R.G. Haire, J.R. Peterson, U. Benedict and C. Dufour, *J. Less-Common Met.,* **102** (1984) 119.

[29] O. Eriksson, M.S.S. Brooks and B. Johansson, *J. Less-Common Met.,* **158** (1990) 207.

[30] B. Johansson and A. Rosengren, *Phys. Rev. B,* **11** (1975) 1367; L.J. Nugent, J.L. Burnett and L.R. Morss, *J. Chem. Thermodyn.,* **5** (1973) 665.

[31] H.L. Skriver, O.K. Andersen and B. Johansson, *Phys. Rev. Lett.,* **44** (1980) 1230.

[32] B. Johansson, L. Fast, P. Söderlind and O. Eriksson, *Physica B,* **190** (1993) 12.

[33] J.M. Wills and O. Eriksson, *Phys. Rev. B,* **45** (1992) 13879.

[34] P. Söderlind, J.M. Wills, A.M. Boring, B. Johansson and O. Eriksson, *J. Phys. Condens. Matter,* **6** (1994) 6573.

[35] J. Trygg et al., to be published.