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Theoretical Studies of Actinide Intermetallic Compounds*

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Abstract

The electronic structure of the AnRh$_3$ intermetallic compounds has been studied for the actinides (An) Ac–Cm. As a function of the actinide atomic number, a change from itinerant to localized 5f behaviour is inferred from the calculations. This gives a good account of the dramatic increase of the experimental equilibrium lattice constants for the heavier AnRh$_3$ compounds. Similarly, the series of UM$_3$(4d) (where M = Mo–Ag) intermetallic systems has been investigated theoretically. In these studies it was found that a drastic change in the 5f behaviour takes place between URh$_3$ and UPd$_3$. The reason for this is the relative lack of 5f–4d hybridization in UPd$_3$ in comparison with URh$_3$. This is because the energies of the 5f states in UPd$_3$ are situated in a hybridization gap between the M-4d and actinide-6d states. This explains the experimentally observed 5f localization in UPd$_3$.

Also the equation of state for PuTe has been investigated theoretically. The recently discovered pressure-induced crystallographic change from NaCl to CsCl structure for this system is discussed and within the one-particle description this phase transition is found to be accompanied by a sudden change of conductivity properties.

1. Introduction

The stability of intermetallic compounds is an old and well-known problem in material science and solid state chemistry [1]. Of course, since intermetallic compounds are formed, they must be the thermodynamically favoured arrangement of atoms, but so far no *a priori* quantum mechanical treatment has been able to give an in-depth elucidation of this problem. However, intuitively it seems clear that when metal A and metal B are such that the mutual nearest neighbour interaction between atom A and atom B, ϕ_{AB}, is much stronger than the interaction between the same type of atoms, ϕ_{AA} or ϕ_{BB}, then there is a strong tendency towards compound formation. Thereby a maximization of the number of AB bonds is realized. A randomization of such an intermetallic compound would inevitably create more AA and BB bonds at the expense of the number of AB bonds, and therefore lead to an energetically less favourable atomic arrangement.

When regarded as d-transition elements the lanthanides and actinides are early members of a 5d and 6d transition series, respectively. Therefore, due to their d electron behaviour, these elements tend to form strong bonds with the late elements of each of the d series (such as Ni, Pd and Pt) as we will discuss in detail in section 3. This is the fundamental reason why so many intermetallic compounds between the lanthanides (actinides) and the late d-transition series elements are formed.

The formation of a certain type of crystallographic arrangement of the constituent atoms can be related to several factors, such as atomic size differences and the type of chemical bonds [1]. The latter may in limiting cases be characterized as ionic, covalent or metallic bonds. When covalency predominates the requirements from the bond directionality produce severe constraints on the crystal structure. For intermetallic compounds, the metallic-type bond tends to produce space filling structures with the highest symmetry and as many nearest neighbours as possible. In such situations the size differences between the atoms often play an important role.

Normally there are several structures which have very similar local bondings, but differ in the long-range ordering. Therefore the energy difference between such structures can be relatively small compared to the heat of formation of the compound

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itself. Thus the local ordering or local bonding is a first-order effect and the long-range ordering is a second-order effect. Recent developments of electronic structure calculations indicate that it may soon become possible to treat such subtle second-order differences on a quantitative level, as exampliﬁed by successful calculations of the crystal structure of the elemental metals [2]. There are, however, instances of a change in crystal structure being accompanied by a first-order change in electron structure and in section 6 we suggest that this occurs in PuTe as a function of pressure.

When comparing lanthanide and actinide intermetallic compounds one notices that in general there is a remarkable similarity between the two series, both as regards the type of compound, A_NB_M, and the crystallographic structure. Since for the lanthanides the 4f electrons generally are inert as far as bonding is concerned, this would at a first glance point towards a similar inertness of the 5f electrons. However, since it is now well known that for the early actinides the 5f electrons often do contribute to the bonding, a less restrictive statement (namely that it is mainly the d electrons which determine the crystal structure) seems to be more appropriate. In the case of a compound with bonding 5f electrons their influence should therefore generally not be strong enough to induce new crystallographic structures.

One is tempted to view those cases where the lanthanides and actinides do show different crystallographic behaviour as an indication of 5f bonding. There are other factors, however, which might invalidate such inferences. For example, the number of d electrons available for the bonding in the earlier actinide elements is generally larger than in the lanthanide elements, a circumstance which might cause the difference between the two f series. Also size differences between the lanthanides and actinides might be of importance. Thus the possible interplay between metallic 5f electrons and the crystal structure of a particular intermetallic compound has not yet been clearly demonstrated for any system. Therefore, at the present stage of development, it is more appropriate to first focus attention on the properties of the 5f electrons in a particular compound (bonding or inert) and only later try to identify the possible influence of the 5f bonding on the crystal structure.

In order to have itinerancy, it is important that the width of the 5f band be substantial [3–5]. There are essentially two factors that determine this width. One is the spatial extension of the 5f orbital on a given atom, and the other is the electronic structure and position of the atoms surrounding the 5f atoms (ligand effects). In the second case it is the hybridization between the 5f wave-function and the ligand orbitals that determines the energy distribution of the 5f states. Since this hybridization is also dependent on the extension of the 5f orbital, the above-mentioned two factors are not independent.

In this paper we will illustrate how these two factors induce a transformation from itinerant to localized behaviour for some actinide intermetallic compounds. For the $AnRh_3$ systems it is the contraction of the 5f orbital, as a function of the actinide atomic number, that determines the change in the 5f electron behaviour. In the case of UM_3, where M is a heavy 4d transition element, Mo–Ag, it is the change in the ligand character that influences the properties of the 5f electrons. Thus, in the first case, the ligand is kept fixed, and the importance of the 5f orbital extension studied. In the second case, the actinide element is kept fixed and the effect of the change of ligand atoms is distinguished.

2. Details of the Theoretical Calculations

In the calculations of the electronic structure for the UM_3(4d) compounds, scalar relativistic linear muffin tin orbital (LMTO) energy bands in the atomic sphere approximation (ASA), including the combined correction terms, were performed [6]. The frozen core approximation was used and the self-consistent valence charge density was converged to 10^{-3}. The local spin density approximation, with the Barth–Hedin exchange and correlation potential [7–9], was used. The energy eigenvalues were computed at 120 K points in the irreducible part of the Brillouin zone. Lattice parameters and ground state properties were obtained from the zero temperature equation of state calculations.

3. A General Remark on Early–Late Transition Metal Compounds

The unusually strong stability of intermetallic compounds between an early and a late d transition metal can be understood in simple terms, as follows. To illustrate the prominent features of the electronic structure change upon compound formation we simplify by considering only the d density of states, which is the important factor for the bonding. For an early element the d energy levels are much higher than for a late element.

In Fig. 1A we show a schematized form of the density of states for the two separated metals. For the early transition metal we have a low filling of the d density of states (e.g. by one electron) and for the heavy element an almost filled d density of states (e.g. by nine electrons). When the elements are brought together to form a compound, the d orbitals of the two elements start to hybridize with each other. Then the total density of states of the combined

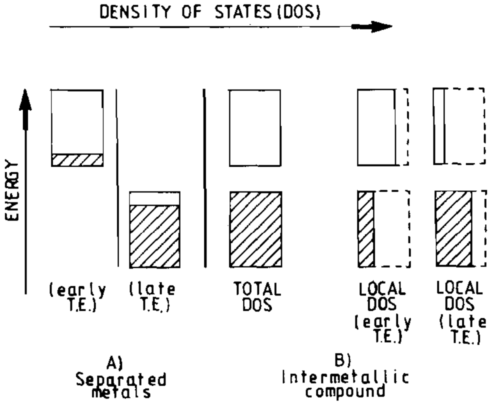

Fig. 1. Illustration of the d electron structure change upon compound formation between an early and late d transition element (T.E.). In Fig. 1A the d densities of states for the two separated metals are plotted. To the left in Fig. 1B the d density of states for the compound is shown. The local d density of states for the two transition metals in the compound is also drawn to the right in Fig. 1B.

system takes the simplified form shown to the left in Fig. 1B, which could be classified as composed of a bonding and antibonding part. For a 1:1 compound and with the assumed number of d electrons the bonding part would be completely filled. Compared to the two separated metals in Fig. 1A, considerable energy has been gained in the formation of the intermetallic system. This explains the strong tendency to compound formation between an early and a late transition metal and there is a similarity to ionic bonds, which of course are well known for stability.

There are two ways in which this can happen. (a) Hybridization between the two types of atomic orbitals is weak; in this case the bonding band is filled by electron transfer and the compound is essentially ionic. (b) Hybridization between the two types of atomic orbitals is strong; in this case the density of states is made up of the local density of states evenly distributed between the two types of metal atoms, as illustrated to the right in Fig. 1B. There is little or no charge transfer. The filled bonding band is built up from a dominating late transition element d density of states, but also includes a significant contribution from the d density of states of the early transition element. In the actual calculations, charge transfer turns out to be small.

For an early actinide element the 5f states should also be included in the discussion. A similar picture should apply and the f–d hybridization between the actinide and late d transition element should also contribute to the bonding. Accordingly, there should be an increased tendency towards compound formation, relative to early 3d and 4d transition elements and the lanthanides; to what extent this extra bonding could give rise to different crystal structures than those due to simple d–d hybridization has not yet been investigated. It is, however, also conceivable that such an f–d hybridization bonding would favour the same type of structures as the d–d hybridization. Furthermore, this also indicates that there might be classes of compounds whose existence derives exclusively from the f–d hybridization bonding. In further studies of the actinide intermetallic systems such possibilities will be given more attention.

4. $AnRh_3$ Intermetallic Systems

The $AnRh_3$ intermetallic systems form an ideal set of compounds to study theoretically, since all of them have the same $AuCu_3$ cubic crystal structure [10]. In Fig. 2 we have plotted the lattice constant for the known $AnRh_3$ systems. We notice that the molar volume trend is similar to that of the pure elements. Between $PuRh_3$ and $AmRh_3$ there is a distinctive jump in the lattice constant. This corresponds to a change of the molar volume of about 4.4 $Å^3$. This is, however, considerably smaller than the atomic volume change between elemental Pu and Am, which is about 8 $Å^3$. Since it is most likely that americium in $AmRh_3$ remains in its normal localized trivalent f^6 configuration, this reduction (from 8 to 4.4 $Å^3$) in actinide volume difference between $PuRh_3$ and $AmRh_3$ indicates a rather different property of the Pu atom in $PuRh_3$ from that in the pure metal.

Experimentally it has been found that $ThRh_3$ and URh_3 show essentially temperature-independent paramagnetism [10]. $NpRh_3$ behaves like a spin fluctuating material, while $PuRh_3$ is an antiferromagnet. The electronic specific heat γ for $ThRh_3$, URh_3 and $NpRh_3$ is 10, 10 and 95 mJ/mol K^2, respectively. Thus $NpRh_3$ can be classified as a relatively heavy fermion system. The magnetic entropy for $PuRh_3$ is Rln2, strongly indicating a local moment for Pu. The resistivity exponent n in $\rho \sim T^n$ is 4 for $ThRh_3$, 3 for URh_3 and 2 for $NpRh_3$. Thus there is a gradual change when proceeding from $ThRh_3$, namely that

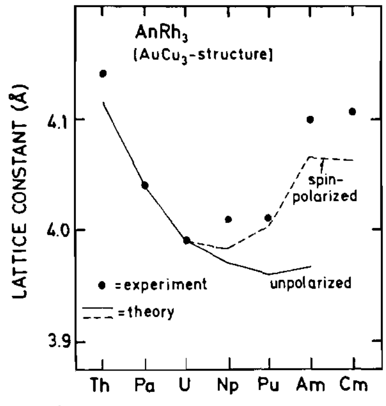

Fig. 2. Experimental and theoretical lattice constants for the $AnRh_3$ systems.

$ThRh_3$ has a low density of states at the Fermi level, $N(E_F)$, URh_3 a somewhat higher $N(E_F)$, $NpRh_3$ is a spin fluctuation metal (on the border-line to be classified as a heavy fermion system) and $PuRh_3$ is a localized moment antiferromagnet. Finally in $AmRh_3$ and $CmRh_3$, one encounters localized trivalent behaviour. Unfortunately no magnetic measurements have been reported for these two latter systems as yet. In Fig. 2 we see how this trivalence is reflected in the behaviour of the lattice constants. Provided that the measured magnetic entropy of $PuRh_3$ only can be interpreted in terms of localized 5f behaviour, then it is obvious from the lattice constants that $PuRh_3$ must have a tetravalent Pu configuration, *i.e.*, $5f^4$ or possibly a mixed valence state (presumably between 3^+ and 4^+). From this it is clear that the $AnRh_3$ series of compounds contains most of the aspects of a transition from itinerant to localized behaviour, and therefore this class of systems should be investigated by more microscopic types of experiment than have been the case up to now. It is especially important to study $NpRh_3$, $PuRh_3$ and $AmRh_3$.

In Fig. 2 we also compare our calculated equilibrium volumes with those found by experiment. For the unpolarized calculations we notice a very good agreement for $ThRh_3$, $PaRh_3$ and URh_3. For $NpRh_3$ some deviations can be distinguished, something which is even more pronounced for $PuRh_3$ and becomes most serious for $AmRh_3$. For the $ThRh_3$–URh_3 systems the Stoner criterion for magnetism is not fulfilled, while the product $IN(E_F)$ is larger than the critical value of one for the heavier $AnRh_3$ systems. In Fig. 2 we have also included the results from our ferromagnetic spin polarization calculations. As is normally the case, magnetism gives rise to a considerable volume expansion, whereby improved agreement with experiment is obtained for $NpRh_3$. For $PuRh_3$ the agreement becomes very good. However, it should be remembered that our calculations correspond to itinerant ferromagnetism, while the specific heat data mentioned above for $PuRh_3$ suggest localized behaviour. In $NpRh_3$ we calculate a small spin moment, while experimentally $NpRh_3$ is an exchange-enhanced material. This relatively small discrepancy between theory and experiment might disappear when the spin–orbit interaction is included. In such a calculation the volume would also become somewhat expanded as compared with the present paramagnetic results [11].

The spin-polarized calculations for $AmRh_3$ and $CmRh_3$ also give quite good agreement with experiment. Due to the fact that the spin up f-band is not completely filled for $AmRh_3$ (when filled it should be equivalent to a non-bonding state which would mimic a localized f-state), there is still some f-bonding present in the calculations. By removing this contribution artificially, *i.e.*, by putting the contribution to the pressure from the f-states equal to zero, the equilibrium volumes so obtained agree well with the experimental data.

In comparison with the pure elements, the change from itinerant towards localized behaviour seems to be more gradual for the $AnRh_3$ systems. As for the pure elements [4] the electronic structure calculations reproduce quite well the dramatic change in the lattice parameter. However, it should be stressed once more that the calculations are performed for an itinerant 5f state, while there is experimental evidence that $PuRh_3$ is more appropriately described by a localized picture. Extensions of the calculations to include orbital correlation would be highly desirable.

5. The 5f Localization in UPd_3

Assuming that the experimental evidence [12, 13] for localized 5f electrons in UPd_3 is correct, we will here investigate to what extent electronic structure calculations support this picture. For URh_3 we have found good evidence for itinerant 5f electrons. The early band calculations by Koelling and coworkers [14] on this system are in good agreement with the de Haas–van Alphen data, a circumstance which strongly supports this view. For the next element after rhodium (palladium) and the compound UPd_3, the 5f electrons have apparently undergone a sudden localization. The molar volume difference between UPd_3 and URh_3 is about 6 Å^3. For comparable systems (at least as far as positions in the Periodic Table are concerned) like UNi_2 and UCo_2, the formula unit volume difference is only 1 Å^3. In the latter case the 5f electrons are itinerant in both UCo_2 and UNi_2. The present large difference of 6 Å^3 indicates a rather drastic change in properties between URh_3 and UPd_3. For the pure elements the atomic volume increase of Pd relative to Rh is 1 Å^3, so that only half of the volume expansion can be explained by the difference in atomic constitution.

To illustrate this volume anomaly for UPd_3 more quantitatively we consider the quantity ΔV for the intermetallic system UM_3 defined as:

$$\Delta V = V_{mol}(UM_3) - V_{mol}(U) - 3V_{mol}(M) \tag{1}$$

Thus ΔV is the molar volume change upon compound formation. In Fig. 3 we plot the experimental value of ΔV as a function of the 4d transition elements. From this Figure it is clear that UPd_3 exhibits anomalous behaviour. For comparison, we also include in this Figure ΔV for ThM_3, ZrM_3 and HfM_3, and its behaviour accentuates the UPd_3 anomaly. However, it is also clear that URu_3 and URh_3 present an anomaly when compared with normal d-transition elements, namely that the molar volume change upon compound formation is positive. The reason for this is that the f-bonding in the compound

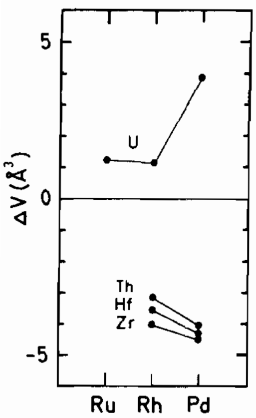

Fig. 3. Molar volume change ΔV upon compound formation for various AB_3 systems ($A = U$, Th, Hf and Zr; $B = Ru$, Rh and Pd).

is not as pronounced as it is in the pure uranium metal, although it is still quite substantial. Thus even though the 5f electrons are bonding, the bond strength is sensitive to the effect of the ligand. This also illustrates the fact that although uranium is an itinerant 5f transition metal, the itinerancy is not as well developed as it is for the 4d and 5d valence electrons in the d-transition elements, since the properties of the 5f states are clearly very sensitive to the character of the surrounding atoms.

If in eqn. (1) the experimental atomic volume for uranium is replaced by an estimated value for tetravalent uranium (*i.e.* with a non-bonding $5f^2$ configuration) then the corresponding ΔV value for UPd_3 becomes comparable to the ΔV values for the tetravalent metals thorium, zirconium and hafnium. Therefore the 5f localization picture is strongly supported by the experimental equilibrium volume data. This $5f^2$ configuration is in fact the same as derived from the neutron scattering data for UPd_3 [12].

To study this change in 5f character theoretically we have calculated the electronic structure for the series of compounds UMo_3–UAg_3. Of these systems only URu_3 to UPd_3 have been reported in the literature. In Fig. 4 we display the density of states for the paramagnetic state of UMo_3–UAg_3, all calculated for the $AuCu_3$ structure with a lattice constant of 4.0 Å. The 4d and 6d orbitals hybridize and form two rather well separated contributions to the density of states, which we will refer to as bonding and antibonding parts. For example, for URh_3 the bonding part of the density of states is to the left and the antibonding part to the right in Fig. 4, and in the intermediate range the 5f density of states can be seen. The bonding part is dominated by the 4d contribution and the antibonding part by uranium 6d orbitals. For UMo_3 the uranium 5f states hybridize strongly with the 4d and give rise to a broad 5f band. Proceeding to UTc_3 and URu_3, the energy of the 5f orbitals moves upwards relative to the bonding part of the d-bands. When we reach URh_3, the 5f states lie at the topmost edge of the bonding part, but still hybridize quite strongly. For UPd_3, on the other hand, a predominant part of the 5f orbitals lie in the energy window between bonding and antibonding d-orbitals. Thereby the hybridization between the 5f and 4d states is substantially reduced, and accordingly the 5f band narrows considerably. Since the Fermi energy lies within the 5f manifold,

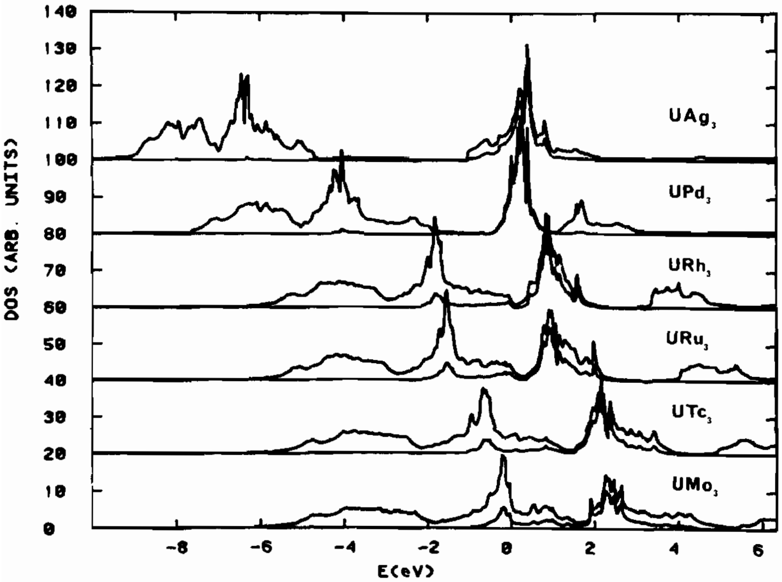

Fig. 4. Density of states for the UM_3 systems calculated for a lattice constant $a = 4.00$ Å. The lower curve in the figure is the 5f-partial wave component of the density of states.

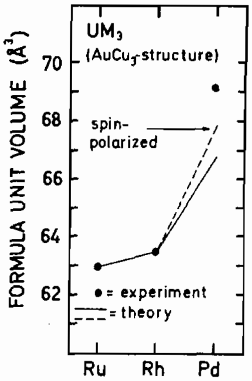

Fig. 5. Experimental and theoretical equilibrium volumes for URu_3, URh_3 and UPd_3; the calculations were performed for the $AuCu_3$ structure. Notice that experimentally UPd_3 has the hexagonal $TiNi_3$ structure.

the Stoner criterion now becomes fulfilled and magnetic spin behaviour should appear in UPd_3. Finally for UAg_3 the 5f states now enter the antibonding part of the d-band and start to hybridize rather strongly again. However, the hybridization is mainly with the Ag4d band and since that contribution to the antibonding part of the d complex is comparatively small, the 5f broadening is not as pronounced as it is for URu_3 or URh_3. Therefore the Stoner criterion for magnetism is also fulfilled for UAg_3.

For UPd_3 we have performed a spin-polarized calculation. Thereby an almost complete 5f spin polarization is found, which of course influences the equation of state. The calculated change in the equilibrium volume due to the spin polarization is shown in Fig. 5, where the calculated equilibrium volumes for URu_3 and URh_3have also been included. The polarized calculations for UPd_3 are for an itinerant ferromagnetic state, but the fact that we find an almost complete 5f spin polarization indicates that a local description is a more appropriate approach for this system, as is indeed suggested by experiments. It should also be realized that the crystal structure for UPd_3 is not $CuAu_3$, as assumed in our calculations, but $NiTi_3$. However, this difference is not expected to make any dramatic effect on the question about 5f localization. Thus the tendency towards localization of the 5f electrons in compounds with Pd (and presumably Pt) derives from the fact that the 5f states predominantly lie in the hybridization gap between 4d and 6d states.

6. Equation of State for PuTe

Although PuTe is not a proper intermetallic compound, we here take the opportunity to present some of our recent equation of state calculations for this system. Based on fully relativistic band calculations, it has recently been suggested that PuTe might be a 'relativistic semiconductor' and the calculations give a good account for the observed temperature-independent magnetism [15]. However, some new experiments indicate that PuTe at low temperatures has a high linear contribution to the specific heat [16], which would not follow from the one-particle description as calculated in ref. 15. Thus the situation is presently unclear as regards the extent to which PuTe can be classified as a relativistic semiconductor. Despite this problem we will here use the one-particle approach and calculate the bulk equation of state property of PuTe. This is of interest since, very recently, high pressure experiments [17] have been performed on this compound. In these experiments it was also found that PuTe transforms from NaCl to CsCl structure at about 150 kbar.

In Fig. 6 we compare our fully relativistic calculations for PuTe with the experimentally [17] determined pressure–volume relation. As can be seen the theory gives a good account of the experimental data for the NaCl structure. Also of interest is the fact that the calculated CsCl equation of state fairly well reproduces the crystallographic data for this phase. Thus theory accounts quite nicely for the volume difference between the NaCl and CsCl structures, and the observed large volume collapse (8%) at the crystallographic transition is in accordance with theory. Unfortunately we cannot in our calculations compare the total energies of the two phases since this requires a very high calculational precision for both phases and also that the same type of

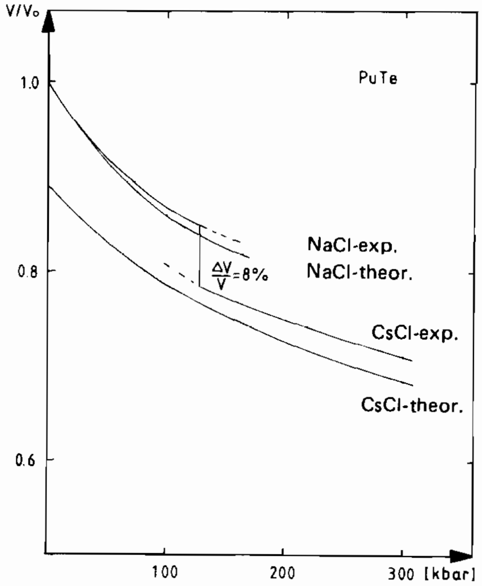

Fig. 6. The experimental and theoretical equation of state for PuTe in the NaCl and the CsCl structure. The volume V is normalized by the equilibrium volume V_0^{exp} and V_0^{theory}, respectively.

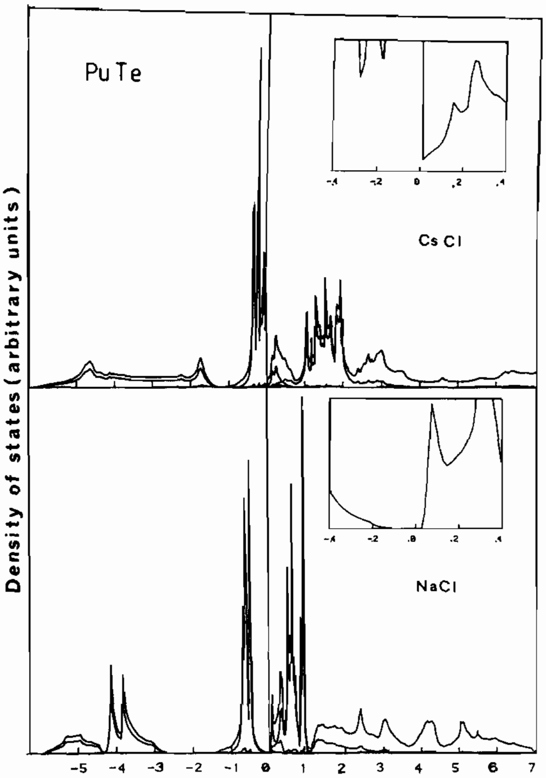

Fig. 7. Calculated density of states for PuTe in the NaCl (lower figure) and CsCl (upper figure) crystal structures. Energies are in electron volts and zero is the Fermi level. The inserts show enlarged density of states close to the Fermi level.

systematic errors are made in the computations for the two crystallographic structures. Since for the open NaCl structure we have introduced so-called empty spheres in the calculations, but not in the case of the more densely packed CsCl structure, a comparison between the total energies for the two phases becomes somewhat inaccurate.

In Fig. 7 we show the calculated total density of states for the two phases NaCl and CsCl. For NaCl we notice that there is an energy gap between the filled and unfilled energy states, something which was discussed in more detail in ref. 18. It is most interesting, however, that for the CsCl structure there is no longer such a gap in the density of states. This means that within the present one-particle description the NaCl–CsCl crystallographic change is accompanied by a semiconductor–metal transition, where in the metallic CsCl structure there is a rather substantial 5f contribution to the density of states at the Fermi level. Thus, provided the present approach to the electronic structure of PuTe is appropriate, there should be a most interesting dramatic change in the conductivity properties between the two phases. A severe test of the present theoretical results would be high pressure resistivity measurements.

7. Conclusions

In the present work we have shown that theoretical electronic structure calculations can give a quite good account of the equilibrium conditions for actinide intermetallic systems. The 5f localization as a function of atomic number for the $AnRh_3$ compounds has also been investigated and results quite consistent with experiments were obtained. Also the 5f localization for the UM_3(4d) compounds as a function of the 4d transition element was rather well described by theory. It remains true, however, that a complete description of the 5f localization is still lacking. Finally the equation of state for PuTe was calculated and compared with experiment and again a quite good agreement was obtained.

In the near future it seems likely that one will be able to treat theoretically questions like chemical and crystal structure stability of actinide intermetallic systems. Thereby it will be of particular significance to map out the influence of 5f electron bonding on these questions. For the pure actinide elements there is a very strong correlation between the appearance of distorted crystallographic structures and the presence of metallic 5f bonding. However, presently there are no calculations available which support this quantitatively. Again it is likely that relatively soon such treatments will become available. Thereby a better understanding of the long-range effects of the 5f bonding would be obtained.

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