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## Itinerant f-electron Elements

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### Abstract

To obtain a proper understanding of the  $5f$  elements, the actinides, it is very useful to compare their behavior with the  $4f$  transition elements, the lanthanides. It is especially rewarding to capitalize on the remarkable similarity between the solid state properties of compressed Ce and the actinide metals. The intensively studied  $\alpha$ - $\gamma$  transition in Ce is considered to be a Mott transition, namely, the  $4f$  electron changes its behavior from being localized to become delocalized (itinerant / metallic). This change also means that the  $4f$  electron transforms from a non-bonding to a bonding configuration which in its turn gives rise to a volume collapse. This collapse happens to be isostructural in character, a circumstance that strongly contributes to the immense interest in this phase transition. An analogous and most remarkable change in bonding (cohesive) properties is also found *within* the actinide series, where the sudden volume increase from Pu to Am

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3 (50%) can be viewed upon as a Mott transition within the  $5f$  shell as a function of atomic  
4 number  $Z$ . The elements on the metallic side of the  $5f$  Mott transition, i.e. the earlier  
5 actinides (Pa-Pu), show low symmetry structures at ambient conditions; while the  
6 heavier elements (from Am and beyond) adopt structures typical for the lighter trivalent  
7 lanthanide elements with localized  $4f$  electrons. A most important consequence of the  
8 localized and trivalent behavior in Am is a non-magnetic  $5f^6$  ( $J = L + S = 0$ )  
9 configuration for the  $f$  electrons. This led to the prediction of superconductivity in  
10 americium and later on to its experimental verification.  
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24 In this paper we will give some examples of the present understanding of the pure  
25 actinide metals. In ref. 1, an excellent and extensive review of actinide research in  
26 general can be found. However for a comprehensive account of the understanding of the  
27 Elements we recommend ref. 2. A short review related to the present one can be found in  
28 ref. 3.  
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36 The actinides are the elements following Fr, Ra and Ac in the last row of the  
37 Elements in the Periodic Chart. Electronically they arise as a consequence of the gradual  
38 filling of electrons in the  $5f$  shell. Consequently this series of elements is therefore a  
39 direct analogue to the lanthanides, where the  $4f$  shell is gradually being filled with  
40 electrons when the nuclear charge is increased through this series. In the atomic state,  
41 these  $4f$  electrons are correlated so that the so called Hund's rules are fulfilled.  
42 Accordingly, this means in particular that the spin moment of the  $4f^n$  configuration is  
43 maximised, and consequently thereby giving an optimal energy for the  $4f$  electrons  
44 (Hund's first rule). Similar internal correlations among the  $4f$  electrons within the atom  
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3 give rise to the other two Hund's rules. The combination of this gives rise to a well-  
4 defined ground state of the  $4f^n$  configuration. In the present context of solid state physics  
5 the question we want to address is how this picture is modified in the condensed phase of  
6 these atoms. In this respect exactly the same problem is also present for the actinide  
7 elements, the only difference being that we here deal with  $5f$  electrons instead of  $4f$   
8 electrons.  
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10 Obviously there are two main effects that need to be clarified for the solid phase  
11 of the atoms;  
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13 A) How many  $f$  electrons per atom will there be in the solid?  
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15 B) Will Hund's rules remain relevant for the solid?  
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17 In other words will the atomic multiplet configuration of the  $f^n$  state remain intact in the  
18 solid? If not - has it then become dissipated into a state with for example equally many  
19 spin up and spin down electrons, i. e. a non-magnetic state where obviously Hund's first  
20 rule is totally irrelevant? Such a disintegration of a maximum parallel spin configuration  
21 can not take place in the free atom since here the  $4f$  and  $5f$  levels are sharp. In the solid  
22 phase, however, the  $4f$  ( $5f$ ) level will couple to the surrounding  $f$  levels on the  
23 neighboring atoms (as well as with the conduction band states of  $s$ ,  $p$  and  $d$  type), and  
24 thereby, widening into a set of  $f$  levels (band, energy band). This broadening of the  $f$  level  
25 is exactly the mechanism which might lead to dissolution of the  $f^n$ -multiplet  
26 configuration. A sufficiently wide broadening gives rise to an energy gain (of kinetic  
27 type) which overwins the energy gains originating from Hund's rules.  
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The previous understanding of the actinide metals was such that they were believed to form another *d* transition series, namely the *6d* metals. This in principle attractive picture was however shown to be wrong. For example the work by Hill<sup>4</sup>, Freeman and coworkers<sup>5</sup>, Johansson<sup>6</sup> and Johansson and coworkers<sup>7</sup> showed that this could not be the case. One of the present authors (BJ) used a number of different physical and chemical properties to show the prominent role of *5f* electrons in these metals. Also careful experimental electron spectroscopy work very clearly showed the presence of *5f* electrons in the metallic state of the early actinides metals.<sup>8</sup> The early calculations of the equilibrium volumes<sup>9</sup> for the early actinide metals very clearly demonstrated that *5f* electrons are strongly engaged in the bonding properties of these systems.

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For the rare earth metals - the lanthanides - it has been well known for a long time that the  $4f^n$  atomic configuration remains essentially intact when introduced into a solid (metal) phase. It has also been very well established why europium and ytterbium are divalent metals, in contrast to the rest of the lanthanides which are trivalent metals. Again this is due to the correlation energy within the localized  $f^n$  multiplets, which is a purely atomic effect. This has been well understood even at a quantitative level from the work by Gschneidner<sup>10</sup> and Johansson<sup>11</sup>.

Among the lanthanides, the spatially most extended *4f* orbital is found for Ce, the first element with an occupied *4f* level. The extension of the *5f* orbital for the actinides is larger than for the *4f* orbital in the corresponding lanthanide element. Due to the orbital contraction with increasing atomic number the extension of the *5f* orbital in plutonium/ameridium is in a relative sense similar to the extension of the *4f* orbital in cerium. Analysis based on thermodynamic data as well as conclusions based on

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electronic structure calculations both predicts that there will be a cross-over in properties of the  $5f$  electrons between plutonium and americium. This means that for the early actinides the extension of the  $5f$  orbital is sufficient to permit a substantial broadening of the  $5f$  level, such that the magnetic moment correlations present for the atoms can no longer prevent a delocalization of the  $5f$  electrons into an itinerant (delocalized or band) state. In sharp contrast to this for americium (and the elements beyond americium), the energy gained in maintaining a localized magnetic moment is sufficient to retain its localized behavior also in the metallic state<sup>9</sup>.

Experimentally it has been observed that under pressure cerium undergoes an isostructural volume collapse of about 15% at 7 kbar<sup>12</sup>. This clearly illustrate that cerium is behaving very anomalously relative to the other lanthanide elements. For higher pressures the  $\alpha$ -uranium structure as well as the bct structure have been observed<sup>12</sup>. This suggested that the  $4f$  electron in cerium changes its character at the volume collapse from a localized non-bonding behavior to an itinerant state with metallic bonding, i.e. essentially a Mott transition. In the region for the  $\alpha$ -uranium phase Nelmes and coworkers<sup>13</sup> have later observed even more complex structural phases. Actually such a possibility was suggested already long ago<sup>14</sup>, in fact even before the discovery of the  $\alpha$ -uranium structure in cerium. In this early work<sup>14</sup> also a generalized phase diagram was put forward for the actinides based on a comparison with the phase diagram of cerium. The reason behind this idea was that in cerium as well as in the early actinides the  $f$  electrons are itinerant. In Fig. 1 we have plotted the phase diagram for cerium next to a generalized phase diagram for the actinides. This comparison shows the similarity between cerium under pressure and the individual actinide elements. This is very well

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3 illustrated by the crystal structures of Th-U and compressed cerium. An extension of this  
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5 generalized actinide phase diagram was later developed by Kmetko and Smith<sup>15</sup>.  
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8 It is very interesting to point out that the experimentally observed fcc structure for  
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10 Th is in fact highly anomalous.<sup>16</sup> Normally one would expect that a simple fcc  
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12 arrangement is a sign of a standard d-transition element behaviour. However if thorium  
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14 behaved as a d-transition element it should be expected to be an hcp crystal structure  
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16 metal as is the case for Ti, Zr and Hf. Instead it has been shown that the fcc structure in  
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18 thorium is due to the presence of occupied itinerant  $5f$  states.<sup>16</sup> In Fig. 2 we show the  
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20 results from two different types of calculations. One where the energies are compared as  
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22 a function of volume when only  $s$ ,  $p$  and  $d$  valence states are included in the theoretical  
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24 treatment and another one where in addition also  $5f$  valence states are included. As can  
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26 be seen it is only when the  $5f$  states are included that one obtains the correct fcc structure  
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28 as the ground state. Thus already thorium is a genuine  $5f$  metal, since without the  
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30 presence of  $5f$  electrons thorium would otherwise be a normal tetravalent hcp metal.  
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32 Under pressure thorium enters the same structure as protactinium (the element next to  
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34 thorium in the series) due to the increased occupation of the  $5f$ -band upon compression.  
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36 In the same way, under pressure Pa enters into the  $\alpha$ -uranium structure due to the  
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38 increasing number of  $5f$  electrons under compression.<sup>17</sup>  
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46 From Fig. 1 we also notice that zero pressure (or rather a negative pressure) in  
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48 cerium corresponds to the actinide element americium. Both americium and cerium have  
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50 localized  $f$  electrons and both adapt a dhcp structure at low temperature, an fcc phase at  
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52 higher temperature and a bcc phase before melting. Accordingly one expects that  
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54 americium at high pressure must enter phases with itinerant  $5f$  electrons. To illustrate the  
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3 conventional lanthanide behavior ( *i. e.* for example as above for cerium at negative  
4 pressure) we show in Fig. 3 a generalized phase diagram for the lanthanide metals<sup>11</sup> It is  
5 very interesting that such a diagram can be constructed, based on the individual P-T  
6 phase diagrams of the lanthanide metals, since this demonstrates a very close similarity  
7 between all the trivalent lanthanide metals. In addition this generalized lanthanide phase  
8 diagram proves clearly the inertness of the 4*f* electrons with respect to their participation  
9 in bonding. In Fig. 4 we now plot the value of a parameter *f* defined as

$$f = r_s / R_c$$

10  
11 ( where  $R_c$  is the ionic radius and  $r_s$  is the standard length parameter for the electron gas  
12 formed by the valence electrons) as a function of the atomic number of the lanthanide  
13 element.<sup>11</sup> In this manner one can correlate the observed crystal structure to the value of  
14 the parameter *f*. By a simple extension the trivalent 4*d* transition element yttrium can be  
15 directly compared to the lanthanides and is found to have the same value of *f* as the  
16 lanthanide element number 69.  
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36 In Fig 5 we plot the observed superconductivity temperature  $T_C$  as a function of  
37 the parameter *f* for a number of trivalent lanthanide alloys.<sup>11</sup> In this plot we also include  
38 results for  $T_C$  from high pressure data. Since americium is a non-magnetic trivalent  
39 lanthanide like element (  $J=0$  ) one can also assign a value of *f* for this element. From the  
40 plot in Fig. 5 one can then immediately predict that americium must become a  
41 superconductor at around 2-3 K. This prediction was very soon verified experimentally  
42 by Smith and Haire<sup>18</sup>.  
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53 After cerium in the lanthanide series comes praseodymium metal, which also  
54 show a delocalization of the 4*f* electrons under pressure.<sup>19,20</sup> However, in contrast to  
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3 cerium the transition is *not* isostructural in praseodymium. The reason for this is that here  
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5 we meet a situation where there are two itinerant *f* electrons in the volume collapsed  
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7 phase. Two itinerant *f* electrons favor the  $\alpha$ -uranium phase as they do in the uranium  
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9 metal and this is in fact the crystal structure observed for praseodymium.  
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Fig. 1. Phase diagram for cerium<sup>12,14</sup> (left) and melting temperatures for the actinide elements (right). The extension of the  $\gamma$ - $\alpha$  transition line in cerium to the minimum of the melting temperature is shown as a dashed line. Similarly, for the actinides a schematic transition line for the transition between localized and itinerant 5f behavior (Mott transition) has been drawn. Its extension to the minimum of the melting curve has been made as a suggestive analogy to cerium metal.

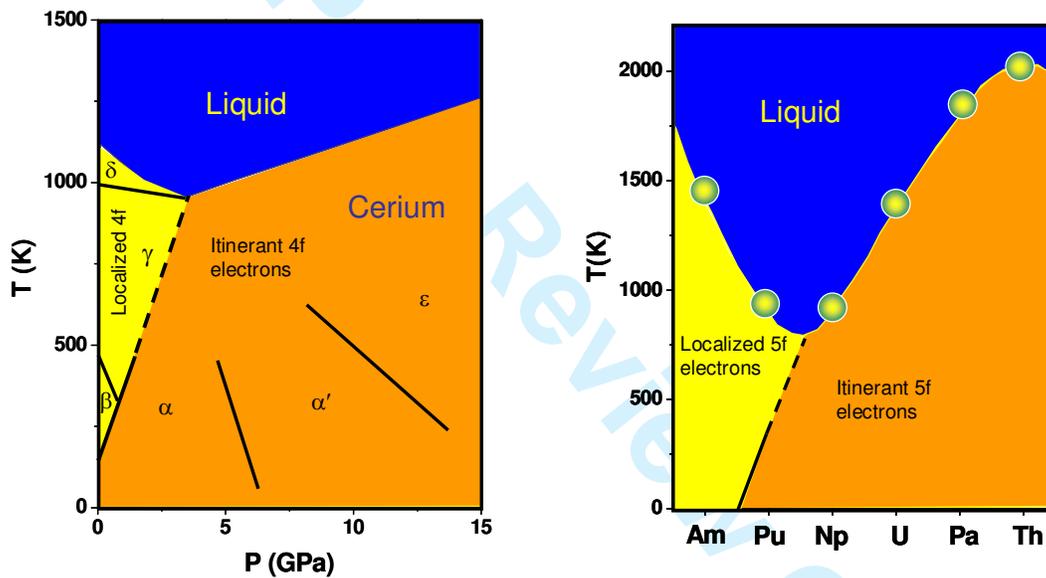


Fig. 2. Energy difference between the bcc, fcc, hcp, and  $\omega$  crystal structures for Th as a function of volume ( $V/V_{eq}$ ,  $V_{eq}$  = equilibrium volume)<sup>16</sup> where the bcc structure is used as the zero energy reference level. . (Bottom figure): Here Th is treated as a standard tetravalent  $d$  transition metal. (Top figure); Here Th is treated as an actinide metal, *i.e.* the  $5f$  states are included in the basis set.

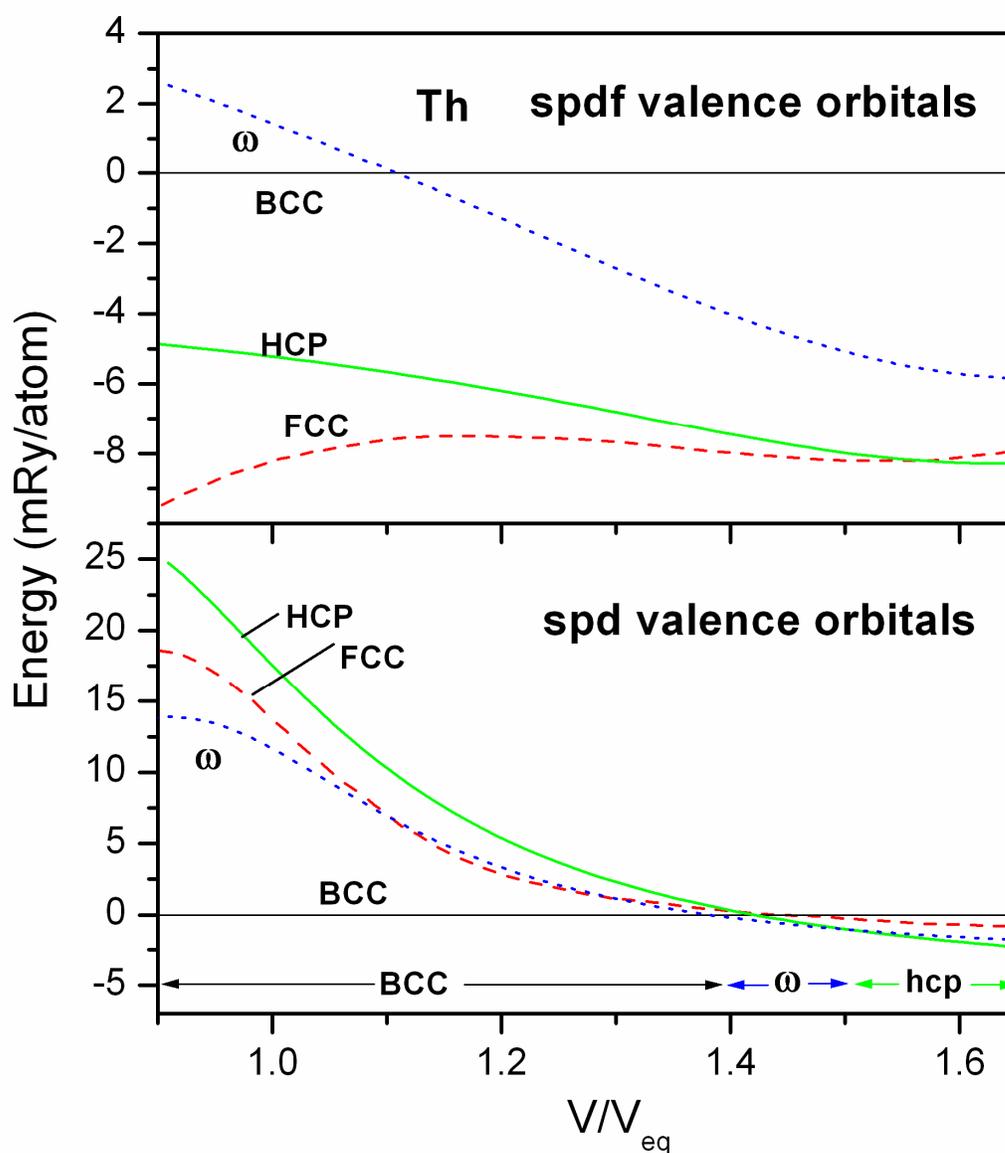


Fig. 3. A generalized phase diagram<sup>11</sup> for the trivalent lanthanide metals. The experimental phase diagrams for the trivalent lanthanides are put together as concisely as possible.

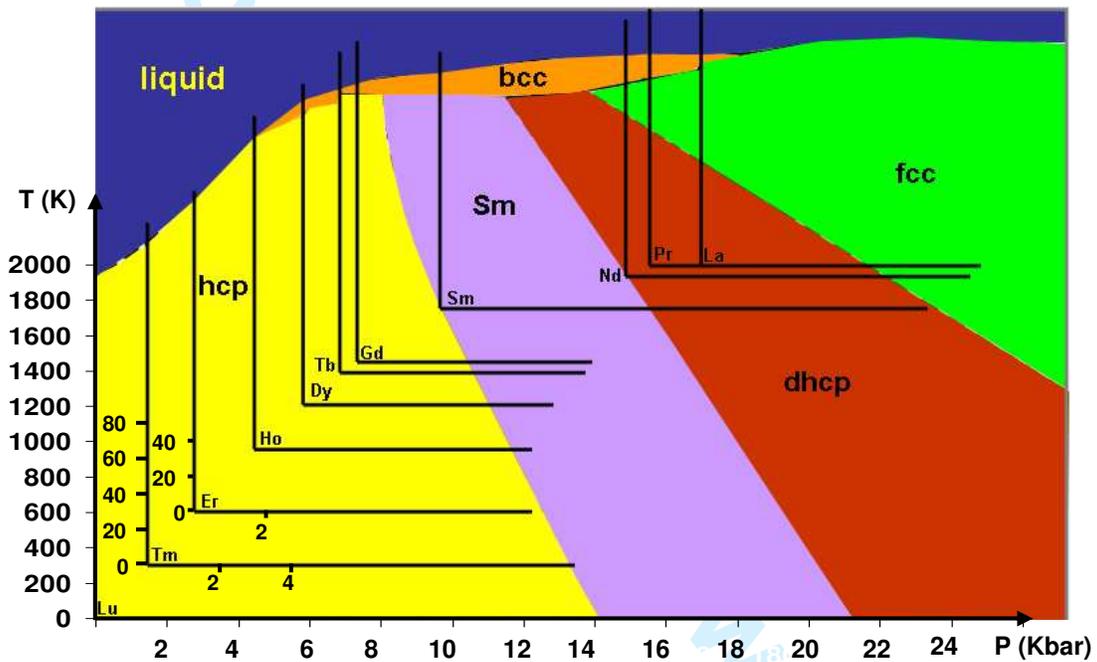


Fig. 4. Values of the ratio  $f$  for the divalent and trivalent elements<sup>11</sup>. The empirical critical values of  $f$  for the different phase transitions are indicated by vertical bars. Note the different  $f$  axes for divalent and trivalent elements. The critical value of  $f$  for superconductivity is derived from Fig. 5 (see later).

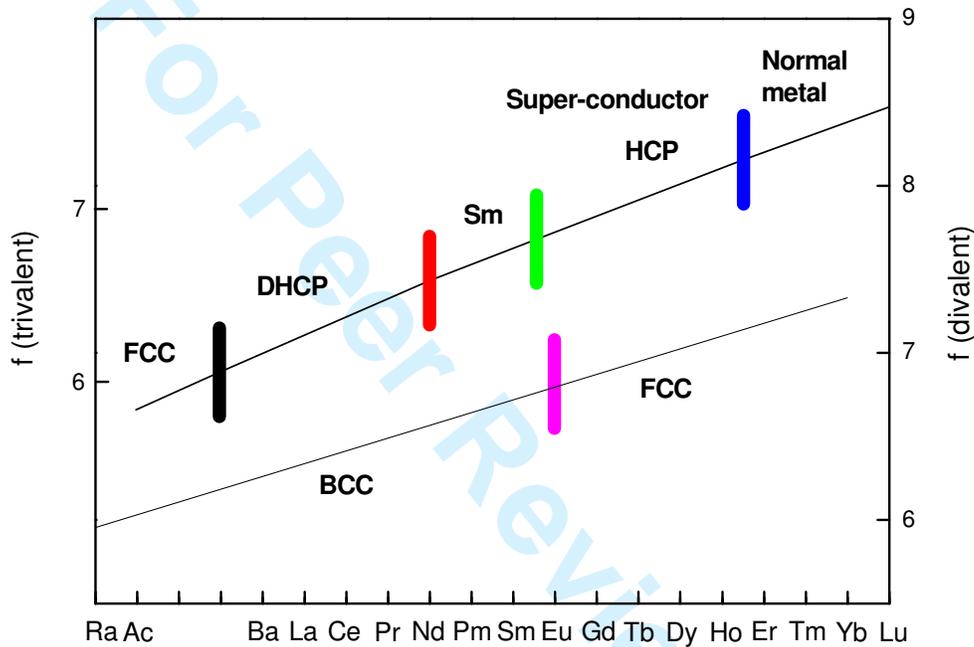
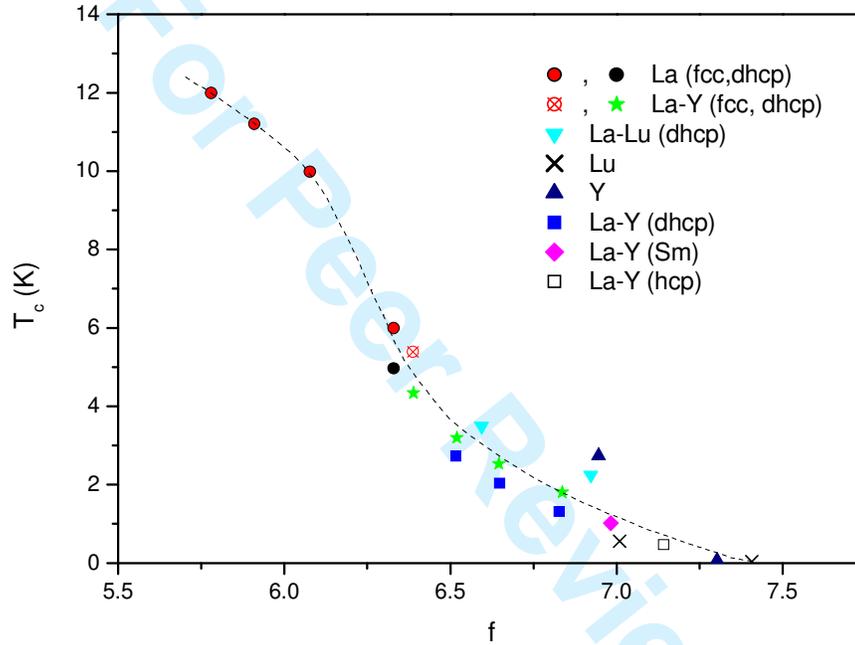


Fig. 5. Superconductivity transition temperature as a function of  $f$  for intra-rare-earth alloys<sup>11</sup> and for pure elements at different atomic volumes. The dashed curve is a smooth fit to the data.

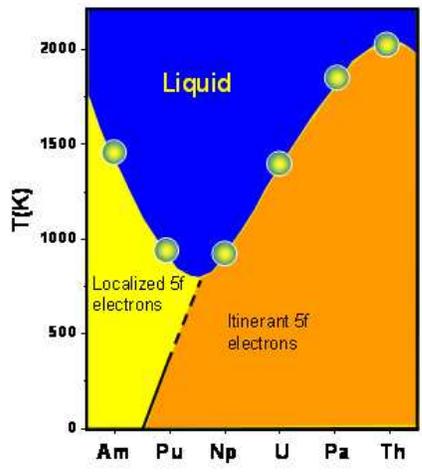
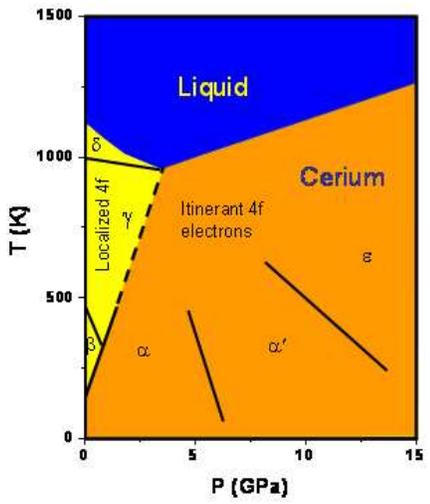


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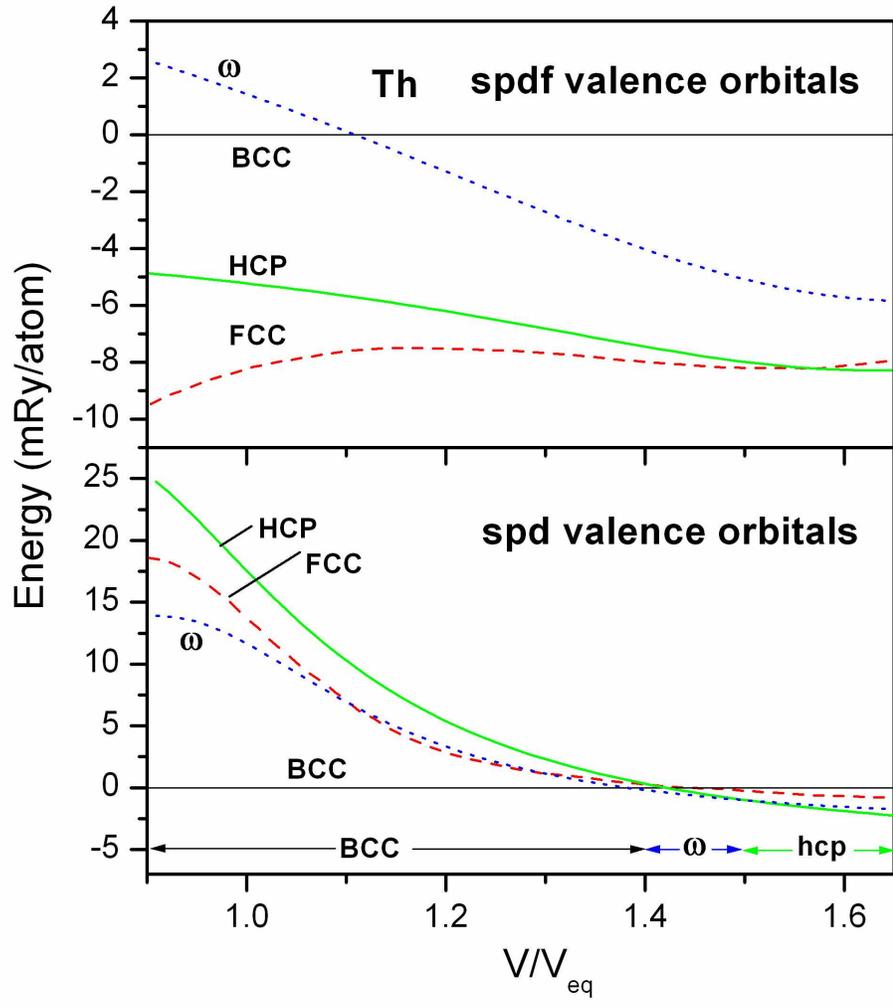
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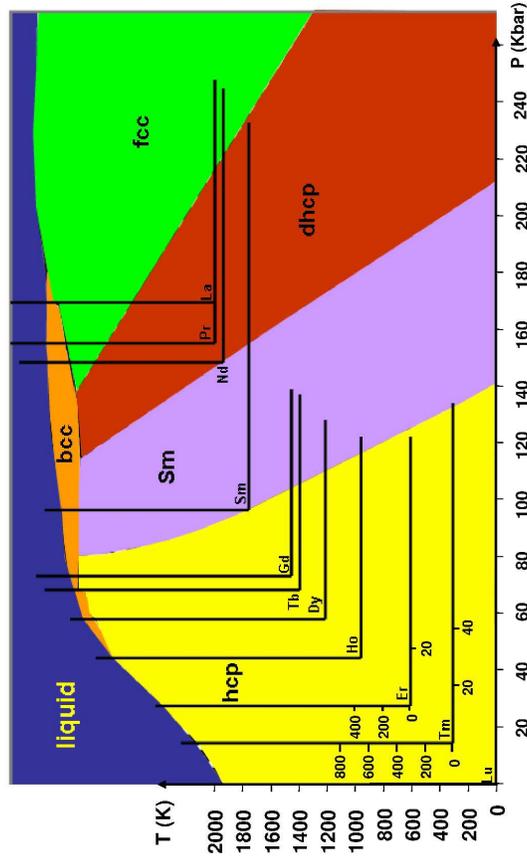
254x190mm (72 x 72 DPI)

View Only



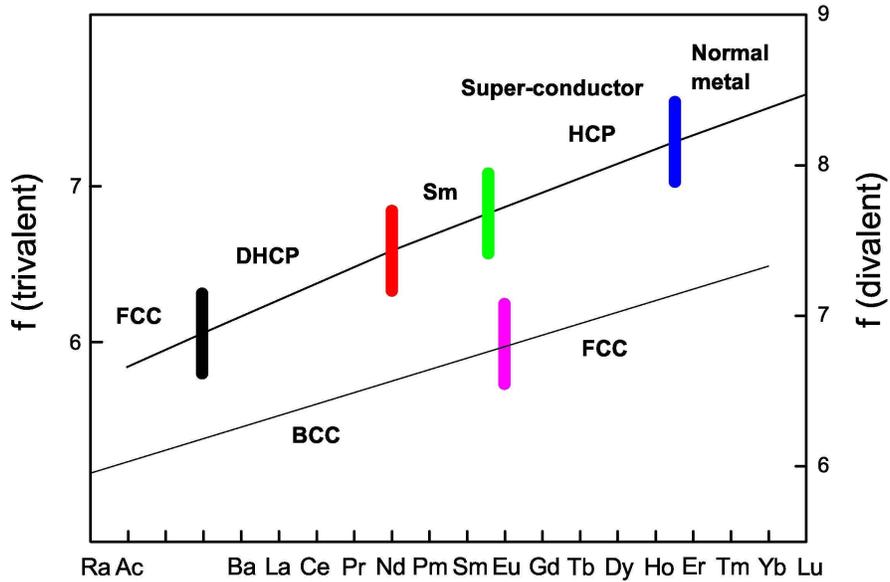
355x406mm (150 x 150 DPI)

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209x297mm (600 x 600 DPI)

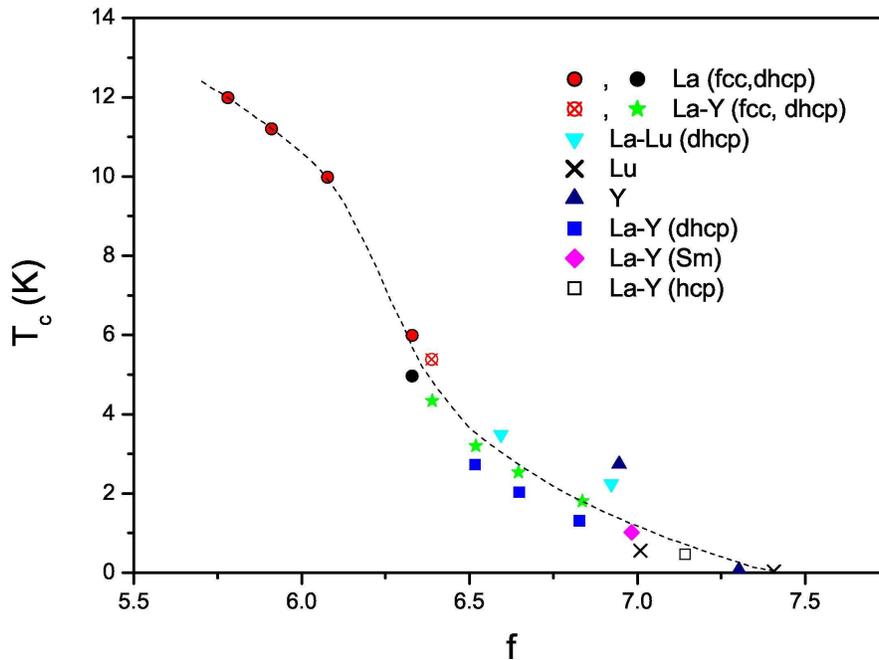
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109x75mm (600 x 600 DPI)

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103x81mm (600 x 600 DPI)