Studies on the valence state of Ce and Eu in some new boron and silicon containing rare earth intermetallic compounds

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Abstract. Compounds of the formula $\text{RPd}_3\text{B}_x$ ($R = \text{rare earth with} \ 0 \leq x \leq 1$) and $\text{RPd}_3\text{Si}_x$ ($R = \text{La, Ce, Eu with} \ 0 \leq x \leq 0.3$) can be prepared by alloying boron or silicon with parent RPd$_3$ compounds. Addition of boron (silicon) does not change the structure but results in lattice expansion. The valence state of Ce in CePd$_3$ and that of Eu in EuPd$_3$ is strongly influenced by boron and silicon. Ce is known to be in a valence fluctuating state in CePd$_3$ while Eu is trivalent ($J = 0$) in EuPd$_3$. The increase in the lattice parameter as a function of boron concentration is observed to be larger in CePd$_3$B$_x$ and EuPd$_3$B$_x$ compared to that in other RPd$_3$B$_x$ alloys giving the first indication of the change in the valence state of Ce and Eu. This is confirmed from susceptibility measurements. With the addition of boron, susceptibility increases and the effective paramagnetic moments approach the values corresponding to Ce$^{3+}$ ($J = 5/2, \mu_{eff} = 2.54 \ \mu_B$) and Eu$^{2+}$ ($J = 7/2, \mu_{eff} = 7.94 \ \mu_B$) in the two alloy systems CePd$_3$B$_2$ and EuPd$_3$B$_2$, respectively. In the case of europium alloys, $^{151}$Eu Mössbauer studies point out the importance of near-neighbour environment effects. Further, in EuPd$_3$B$_2$ where all the europium ions are crystallographically equivalent, a single Mössbauer line, with an isomer shift characteristic of europium ions in valence-fluctuating state, is observed at 300 K. However, at 88 K the Mössbauer absorption splits into two lines corresponding to europium ions in two valence states, e.g. divalent- and trivalent-like. Such a behaviour indicates thermally-induced charge ordering of europium ions. Addition of silicon to CePd$_3$, like boron, results in unusual lattice expansion and changes the valency of cerium towards $3^+$. The valence change is further corroborated by susceptibility measurements. In EuPd$_3$Si$_x$ alloys, susceptibility and Mössbauer studies indicate that in the limiting single phase alloy EuPd$_3$Si$_{0.25}$ the europium ions are on the verge of valence instability. Susceptibility results on CeRh$_3$B$_2$ alloys are also presented.

Keywords. Valence state; boron; silicon; rare earth compounds; europium; Mössbauer studies; cerium.

1. Introduction

The rare earth ions from La to Lu normally exist in the trivalent state. However, Ce, Sm, Eu, Tm and Yb sometimes occur in a different integral valence state, $4^+$ for Ce and $2^+$ for the rest. A physical property that is determined by valence is the ionic radius. Figure 1 shows the ionic radii of triply-ionised rare earths. Also plotted are the values of ionic radii for the divalent state of Sm, Eu, Yb and quadrivalent Ce. It is observed that the size of the trivalent rare earth ions decreases smoothly with the increase in atomic number. This is called the lanthanide contraction and arises due to the imperfect shielding of one $4f$ electron by another $4f$ electron (Jorgensen 1955). It is also observed that for a given atomic number the ionic radius of $f^{n-1}$ configuration is smaller than $f^n$. This follows from the fact that in $f^{n-1}$ configuration the outer electrons experience an extra positive charge in the core and shrink inwards. It is a remarkable fact that rare earth ions maintain this dependence of ionic size on the atomic number and valence even in their alloys and compounds with other elements.
2. Non-integral occupation of the 4f shell-valence fluctuations

Although the integral occupation of the 4f shell is observed in most of the rare earth compounds, experimental evidence accumulated in recent years suggests that in some rare earth compounds and alloys the time average occupation of the 4f shell and hence valence is non-integral. In such cases the mixing interaction between the 4f shell and the conduction band causes the rare earth ion to fluctuate between two ionic-like configurations, differing in the occupation of the 4f shell by one, i.e. $4f^n(5d6s)^m \leftrightarrow 4f^{n-1}(5d6s)^{m+1}$. This phenomenon has been termed as valence fluctuations, mixed valence, interconfiguration fluctuations etc (Parks 1977; Falicov et al 1981) and is observed in rare earth ions Ce, Sm, Eu, Tm and Yb. Whenever the energy required to take the rare earth ion from one 4f configuration to another by transferring an electron to the conduction band at the Fermi level is approximately zero, valence fluctuations will take place. In other words, the two configurations $4f^n$ and $4f^{n-1}$ should be nearly degenerate. It may be emphasised here that valence fluctuations involve real temporal fluctuations of the rare ion between two 4f configurations.

At any given site the rare earth ion will have a certain probability of being found in any one of the two configurations and will therefore be defined by an average non-integral valence, i.e. the ensemble of rare earth ions is homogeneous. This is very different from inhomogeneous mixed valence compounds where one finds a static distribution of two different charge states at inequivalent lattice sites.

The early experiments which led to the identification of valence fluctuations in rare earth systems were the high pressure studies on Ce and SmS. Under ambient conditions Ce exists in the trivalent form. On application of pressure there is an isomorphic first order phase transition from $\gamma$-Ce to $\alpha$-Ce accompanied by $\sim 15\%$ reduction in the cell volume (Koskenamaki and Gschneidner 1978). The application of pressure would favour the quadrivalent state of Ce as the ionic radius of $\text{Ce}^{4+} < \text{Ce}^{3+}$. However, evidence based on the relationship between lattice constant and valence suggest a non-integral valence of 3-67 in $\alpha$-Ce. The susceptibility of $\alpha$-Ce does not show a local moment but only a local exchange enhancement (MacPherson et al 1971). SmS under ambient conditions is a semiconductor and Sm exists in the divalent state. On application of pressure of $\sim 6$ kbar the lattice collapses and undergoes an isomorphic first order phase transition to a metallic state (Jayaraman et al 1960). The lattice constant of SmS in the high pressure metallic state does not correspond to trivalent
state of Sm but suggests a non-integral valence of 2.75. Magnetic susceptibility of high pressure-metallic phase of SmS indicates a non-magnetic ground state (Maple and Wohleben 1971). Since the high pressure studies on Ce and SmS, numerous rare earth compounds exhibiting valence instability have been identified. While some of these undergo valence fluctuations only under the application of pressure or by being alloyed with suitable constituents, others exhibit valence instability at ambient conditions; to mention a few SmB6 (Vainshtein et al 1965; Kasuya et al 1977) CeN (Danan et al 1969; Baer et al 1978), YbAl2 (Klaasse et al 1976), TmSe (Bucher et al 1975) and EuPd2Si2 (Sampathkumaran et al 1981).

Valence fluctuating compounds exhibit anomalous physical properties when compared with normal rare earth systems. Several experimental techniques such as x-ray diffraction, Mössbauer spectroscopy, magnetic susceptibility, xps, x-ray absorption spectroscopy, neutron scattering, NMR etc have been used to elucidate the behaviour shown by these compounds (Lawrence et al 1981). These various techniques have different "probe-time" and the nature of the spectrum that one obtains depends upon whether the probe time is greater or smaller than the average time scale (∼1/ν) on which the valence fluctuations occur.

Some of the anomalous features encountered in these systems are the following.

(i) The lattice constant or cell volume as deduced from x-ray diffraction is intermediate between the values that the compound would have if the rare earth ions were in either of its two integral valence states. In fact the observation of a deviation of the lattice constant from the usual lanthanide contraction for trivalent rare earth ions in a series of isotypic compounds is the first indication that the rare earth ion may be in a valence fluctuating state.

(ii) A motionally narrowed Mössbauer line with an isomer shift between the values obtained when the rare earth ion is in either of the two possible integral valence states is observed. The observation of a single Mössbauer line suggests that the valence fluctuations occur on a time scale much faster than the Mössbauer probe time which is typically ∼10\(^{-11}\) sec.

(iii) The electronic specific heat co-efficient γ of valence fluctuating compounds is large (Lawrence et al 1981).

(iv) The xps spectra show two sets of multiplet structure corresponding to the rare earth ions in two different integral valence states (Campagna et al 1976) indicating that valence fluctuations occur on a time scale greater than 10\(^{-16}\) sec, the characteristic probe time of xps. However it may be mentioned that the xps technique does not distinguish between inhomogeneous and homogeneous mixed valent compounds. Also, the spectra obtained from the surface and the bulk of the compound may be different.

(v) Valence fluctuating rare earth ions have normally the non-magnetic ground state. With the exception of TmSe which orders antiferromagnetically at 3.2 K (Batlogg et al 1979; Moller et al 1977), all the mixed valent compounds known upto now do not undergo magnetic ordering. At high temperatures susceptibility follows a Curie Weiss behaviour with effective moment intermediate between that of two integral valence states. Often large paramagnetic Curie temperatures are observed.

Recently we described (Dhar et al 1981; Dhar 1982) the synthesis of new rare earth
alloys of the formula \( \text{RPd}_3\text{B}_x \) (0 \( \leq x \leq 1 \); \( R = \text{La to Lu} \)), \( \text{RPd}_3\text{Si}_x \) (0 \( \leq x \leq 0.3 \); \( R = \text{La, Ce and Eu} \)) and \( \text{RRh}_3\text{B} \) (R = La to Lu). The \( \text{RPd}_3 \) compounds are known to crystallize in the cubic \( \text{AuCu}_3 \) type structure. The x-ray diffraction patterns of \( \text{RPd}_3\text{B}_x \) and \( \text{RPd}_3\text{Si}_x \) compounds are identical to those of \( \text{RPd}_3 \) compounds and hence can be fitted to cubic structure type. However, the lattice parameter of the boron or silicon containing compounds is observed to be larger than that of the corresponding parent \( \text{RPd}_3 \) compounds. The relatively small boron atoms presumably occupy the vacant body centred position in the \( \text{RPd}_3 \) unit cell to give rise to an anti-perovskite arrangement. The same may be the case in \( \text{RRh}_3\text{B} \) compounds also.

In this paper we present detailed results of lattice constant, susceptibility and \( ^{151}\text{Eu} \) Mössbauer studies on \( \text{CePd}_3\text{B}_x(\text{Si}_x) \) and \( \text{EuPd}_3\text{B}_x(\text{Si}_x) \) alloys. These studies reveal that the addition of smaller non-metallic elements B and Si to \( \text{CePd}_3 \) and \( \text{EuPd}_3 \) change the valence state of the rare earth ion in these two compounds. Susceptibility studies on \( \text{CeRh}_3\text{B}_x \) alloys are also presented here.

As has been remarked earlier, an anomaly in the unit cell volume of the rare earth containing compound, in relation to the value expected from the usual lanthanide contraction for the trivalent ions is the first obvious indication that the rare earth exists in an abnormal valence state. In the quadrivalent state there is a decrease in the 4\( f \) ionic radius which results in a decrease in the unit cell volume. Likewise when the rare earth ion is in a divalent state, there is an increase in the 4\( f \) ionic radius and the cell volume increases. It is possible to change the volume and hence the valence state of the rare earth ions by application of pressure. The two archetypal examples of pressure-induced valence change are \( \gamma \)-Ce and SmS. The externally applied pressure brings about a contraction in the cell volume which may cause a change towards the higher valence state. In some cases the pressure can be generated internally by replacing one or more constituents with others having different ionic radii. In this case the valence change is in the direction determined by whether the cell volume increases or decreases. Many examples of valence change due to "lattice pressure" have been observed, for instance, \( \text{Sm}_{1-x}\text{R}_x\text{S} \) and \( \text{SmS}_{1-x}\text{M}_x \) (\( M \) represents a pnictide) (Jayaraman 1975; Holtzberg et al 1977; Beeken et al 1968), \( \text{Ce}_{1-x}\text{Th}_x \) (Lawrence et al 1977) and \( (\text{Ce}_{1-x}\text{R}_x)^{0.9}\text{Th}_{0.1} \) (Manheimer and Parks 1979). From this viewpoint, the lattice expansion due to inclusion of boron and silicon at body centred position of \( \text{CePd}_3 \) and \( \text{EuPd}_3 \) may be thought to simulate the effects of negative pressure. This way of generating lattice pressure is quite novel and is somewhat different from the way it is achieved in systems derived from SmS and \( \text{Ce}_{1-x}\text{Th}_x \) where one of the constituents is simply substituted partially by another chemically similar element.

3. Boron induced valence change of cerium in \( \text{CePd}_3 \)

3.1 Lattice parameter of \( \text{CePd}_3\text{B}_x \) alloys

Figure 2a compares the lattice parameter of \( \text{RPd}_3 \) and \( \text{RPd}_3\text{B} \) compounds for \( R = \text{La to Lu} \). To start with, the lattice parameter of \( \text{CePd}_3 \) in \( \text{RPd}_3 \) series is anomalous. It has been well established from lattice parameter (Harris and Raynor 1965) and other studies such as susceptibility (Gardner et al 1972), xps (Gupta et al 1980), neutron diffraction (Holland-Moritz et al 1977) etc, that Ce in \( \text{CePd}_3 \) is in a valence fluctuating state. The average 4\( f \) occupation has been estimated to be 4\( f \) 0.55 (Gardner et al 1972).
Valence state of Ce and Eu

Figure 2a. Lattice parameter of RPD₃ and RPD₃B (R = rare earth) compounds.

Figure 2b. Variation of lattice parameter as a function of boron concentration x in RPD₃Bₓ (R = La, Ce and Gd) alloys.

The addition of boron to CePD₃ increases the lattice parameter to such an extent that the volume of CePD₃B fits nicely with the value determined by lanthanide contraction.

The variation of lattice parameter in LaPD₃Bₓ, CePD₃Bₓ and GdPD₃Bₓ as a function of boron concentration x is plotted in figure 2b. It is seen that as the boron concentration is increased, the lattice parameter increases (except in LaPD₃Bₓ where almost no change in the lattice parameter is observed) up to the boron concentration corresponding to x = 0.5 beyond which no further expansion is observed. As remarked earlier, it is noted that the lattice expansion in CePD₃Bₓ is larger than that found in GdPD₃Bₓ. The increase in the cell volume would favour the lower trivalent state, 4f₁, of cerium. The ionic radius of Ce³⁺ being larger, any valence change of cerium ions thus enhances the lattice expansion. Thus we take the results in figures 2a and 2b to imply that cerium has changed from mixed valent in CePD₃ to nearly trivalent state in CePD₃Bₓ alloys. This is corroborated by the susceptibility measurements discussed below.

3.2 Susceptibility of CePD₃Bₓ alloys

The susceptibility behaviour of cerium compounds depends, besides other factors, on the valence state of cerium. While quadrivalent cerium compounds show Pauli paramagnetism only, compounds of trivalent cerium exhibit Curie Weiss behaviour (deviations from Curie Weiss behaviour at low temperature may arise due to various factors, such as crystalline electric field splitting of the ground multiplet) and undergo, in most cases, magnetic ordering at low temperatures. The susceptibility of valence fluctuating cerium compounds shows a Curie Weiss behaviour at high temperatures, the effective paramagnetic moment being determined by the value of average 4f occupation. At low temperatures, the susceptibility of these compounds shows temperature-independent enhanced Pauli paramagnetism.

Figure 3 shows the temperature dependence of the susceptibility of CePD₃Bₓ alloys in the temperature range 77 to 400 K. In the case of CePD₃, the susceptibility flattens out below 120 K. This behaviour is characteristic of valence fluctuation compounds as remarked above. However, on adding boron to CePD₃, a striking change in the
temperature dependence of the susceptibility is observed. Even for small addition of boron, e.g. \( x = 0.12 \), the susceptibility starts following Curie Weiss behaviour with effective magnetic moment \( \mu_{\text{eff}} = 2.24 \mu_B \) and paramagnetic Curie temperature \( \theta_p \sim -64 \text{ K} \). With further increase of boron \( (x = 0.25, 0.35 \text{ and } 1.0) \) the Curie Weiss behaviour persists with \( \mu_{\text{eff}} \) becoming closer and closer to the free ion value for \( \text{Ce}^{3+} \) ion. Thus, the susceptibility measurements clearly demonstrate that boron has caused a valence change of cerium from a mixed valent to largely trivalent state (Dhar et al 1981). To our knowledge this is the first observation of boron-induced valence change in a rare earth alloy. The results of the lattice parameter and susceptibility measurements are summarised in table 1.

It is possible that environment effects are important in CePd\(_3\)B\(_x\) alloys in the sense that the change from fractional occupation of the 4f shell to integral occupation may require a minimum number of near-neighbour boron atoms. Evidence for this comes from Mössbauer measurements in EuPd\(_3\)B\(_x\) system to be discussed below. Therefore, for small \( x \) values, some cerium ions may continue to be in a valence fluctuating state, while some others may have fully become trivalent.

**Table 1.** The lattice constant, \( \mu_{\text{eff}} \) per formula unit and paramagnetic Curie temperature \( \theta_p \) of CePd\(_3\)B\(_x\) alloys \( (x = 0.12, 0.25, 0.35 \text{ and } 1.0) \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice constant</th>
<th>( \mu_{\text{eff}} (\mu_B) )</th>
<th>( \theta_p (\text{K}) )</th>
</tr>
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<tr>
<td>CePd(_3)</td>
<td>4.124</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CePd(<em>3)B(</em>{0.12})</td>
<td>4.156</td>
<td>2.24</td>
<td>-64.6</td>
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<td>CePd(<em>3)B(</em>{0.25})</td>
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<td>2.30</td>
<td>-2.2</td>
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<tr>
<td>CePd(<em>3)B(</em>{0.5})</td>
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<td>2.36</td>
<td>-3.6</td>
</tr>
<tr>
<td>CePd(_3)B</td>
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<td>2.69</td>
<td>-43.0</td>
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</table>
4. Valence change of cerium in CePd$_3$Si$_x$ alloys

4.1 Lattice parameter and susceptibility measurements

After having observed the considerable change in the magnetic properties of cerium ions in CePd$_3$ brought about by alloying with boron, it seemed natural to investigate the effect of incorporating other interstitial atoms in CePd$_3$ lattice. In this direction we synthesised CePd$_3$Si$_x$ alloys. It was found that the introduction of silicon gives rise to similar effects as seen in boron-doped alloys (Malik et al 1983).

Figure 4 gives the lattice parameter of CePd$_3$Si$_x$ alloys. These alloys were found to be single phase only up to $x \sim 0.3$. For the sake of comparison, the lattice parameter of LaPd$_3$Si$_x$ alloys is also plotted. It may be noted that while addition of boron to LaPd$_3$ does not lead to lattice expansion, the addition of Si increases the cell volume after an initial decrease. The lattice expansion in the cerium alloys is far more substantial than that in corresponding La alloys. It is worth noting that the lattice parameter of CePd$_3$Si$_{0.3}$ even exceeds that of CePd$_3$B thereby implying a valence change of Ce ions. Susceptibility measurements have been carried out to confirm this.

The plot of susceptibility as a function of temperature in the range 4·2 to 300 K for CePd$_3$Si$_x$ ($x = 0, 0.05, 0.1, 0.2$ and $0.3$) is depicted in figure 5. A Curie Weiss behaviour is

![Graph of susceptibility vs. temperature for CePd$_3$Si$_x$.](image)

**Figure 5.** Susceptibility vs. temperature of CePd$_3$Si$_x$ ($x = 0, 0.05, 0.1, 0.2$ and $0.3$) alloys.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice constant $a$ (Å)</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$)</th>
<th>$\theta_s$ (K)</th>
</tr>
</thead>
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<tr>
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<td>2.24</td>
<td>-50</td>
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<td>CePd$<em>3$Si$</em>{0.05}$</td>
<td>4.158</td>
<td>2.40</td>
<td>-21</td>
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<tr>
<td>CePd$<em>3$Si$</em>{0.1}$</td>
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<td>2.44</td>
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<tr>
<td>CePd$<em>3$Si$</em>{0.2}$</td>
<td>4.219</td>
<td>2.66</td>
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</tr>
<tr>
<td>CePd$<em>3$Si$</em>{0.3}$</td>
<td>4.244</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.** The lattice constant, $\mu_{\text{eff}}$ per formula unit and paramagnetic Curie temperature $\theta_s$ of CePd$_3$Si$_x$ alloys ($x = 0.05, 0.1, 0.2$ and $0.3$).
observed in silicon-doped alloys. The $\chi^{-1}$ vs $T$ plots are linear (inset of figure 5). The $\mu_{\text{eff}}$ increases with increasing silicon concentration and in the limiting single phase CePd$_3$Si$_{0.3}$ alloy Ce ions are largely trivalent. The crystallographic and magnetic data are summarised in table 2. The small increase in the susceptibility in CePd$_3$ at low temperatures may be due to the presence of magnetic Ce$^{3+}$ impurity. The presence of isolated magnetic impurities, which may arise either due to imperfect sample preparation or induced by lattice defects and other factors, often gives rise to a Curie Weiss like tail in the susceptibility of valence fluctuating compounds at low temperatures (Lawrence 1979).

It is obvious that even in the limiting single phase alloy CePd$_3$Si$_{0.3}$ there will be a predominant number of unit cells which have the body-centred position lying vacant as in CePd$_3$. At first this may suggest that an appreciable number of Ce ions would still be in a mixed valent state in CePd$_3$Si$_{0.3}$ alloy. However, $\mu_{\text{eff}}$ as already remarked above is close to the free ion value of Ce$^{3+}$. This perhaps suggests that the effect of overall band structure may be significant in the silicon alloy system.

5. Valence state of europium ions in EuPd$_3$B$_x$ alloys

5.1 Lattice expansion

The lattice parameter as a function of rare earth ions from La to Lu in RPd$_3$ and RPd$_3$B compounds is plotted in figure 2a. Unlike the case of CePd$_3$, the lattice parameter of EuPd$_3$ falls on the curve determined by lanthanide contraction for trivalent rare earth ions indicating Eu to be trivalent in EuPd$_3$. This is also confirmed by susceptibility (Gardner et al 1972) and Mössbauer measurements (Wickman et al 1968). The lattice constant of EuPd$_3$B, however, shows an appreciable deviation from the value that would correspond to trivalent state of Eu in this compound. Therefore, Eu in EuPd$_3$B seems to be either in a mixed valent or in a divalent state. The differential change in the lattice constant as a function of boron concentration $x$ in EuPd$_3$B$_x$ is plotted in figure 6. The lattice parameter increases till $x \sim 0.75$ and then becomes constant. Susceptibility and $^{151}$Eu Mössbauer studies were carried out on EuPd$_3$B$_x$ alloys in the temperature

![Figure 6. Variation of lattice parameter as a function of boron concentration $x$ in RPd$_3$B$_x$ (R = La, Eu, Cd and Dy) alloys.](image)

![Figure 7. The temperature dependence of susceptibility of EuPd$_3$B$_x$ ($x = 0, 0.25, 0.5$ and $1.0$) alloys.](image)
range 77 to 300 K to study the valence change of Eu ions and are discussed below. An interesting temperature behaviour of Mössbauer spectra, indicating charge ordering of europium ions, is observed in EuPd₃B.

5.2 Susceptibility

The Eu³⁺ ion has a singlet ground state ⁷F₀ (J = 0) and does not possess a magnetic moment. Compounds of trivalent Eu, therefore, show Van Vleck paramagnetism. On the other hand, divalent Eu has a half filled ⁴f shell (S = 7/2) and possesses a local moment. Compounds of divalent europium undergo magnetic ordering and in the paramagnetic region their susceptibility follows a Curie Weiss behaviour. With reference to figure 7, the susceptibility of EuPd₃ shows very little variation with temperature and tends to become constant at low temperatures. Such a behaviour is expected as Eu is trivalent in EuPd₃.

The susceptibility of EuPd₃B₀.₂₅ is about the same as that of EuPd₃. This indicates that Eu ions are still in the trivalent state in this compound. The expansion in the lattice brought about by x = 0.25 boron concentration is still not enough to change the valence state of Eu ions. In fact, for x = 0.25 the increase in the lattice parameter is observed to be the same both in EuPd₃Bₓ and GdPd₃Bₓ (see figure 6). While a boron concentration of x = 0.12 was observed to change the valence state of Ce ions in CePd₃, such is not the case in EuPd₃. A very plausible reason for this is that Ce ions are already in a valence fluctuating state in CePd₃ and, therefore, it would be easier to trigger a valence change by slight variation of physical parameters.

As boron concentration is increased beyond x = 0.25, there is a further expansion in the lattice and the susceptibility increases appreciably. A Curie Weiss behaviour is observed in EuPd₃B₀.₅ and EuPd₃B with μₑff = 5.66 μₜ, θₑ = −58 K in the former and μₑff = 6.77 μₜ, θₑ = −24 K in the latter (μₑff for Eu²⁺ = 7.94 μₜ). The susceptibility results in these alloys clearly show that europium ions have undergone a change of valence (Dhar et al 1982).

5.3 ¹⁵¹Eu Mössbauer studies in EuPd₃Bₓ alloys

The susceptibility results discussed above give us the bulk magnetic response. Since the isomer shift (is) of divalent and trivalent europium ions is quite different, ~ −8 mm/sec to ~ −14 mm/sec for the former and ~ −1 mm/sec to ~ 4.5 mm/sec for the latter (with reference to EuF₃) (Bauminger et al 1978), the Mössbauer measurement is an excellent probe to get information about the valence state of europium ions at a microscopic level. The Mössbauer spectra obtained in EuPd₃Bₓ alloys at 300 K are shown in figure 8 (Dhar et al 1982). In EuPd₃ a single Mössbauer line with a temperature-independent is of 4.5±0.1 mm/sec (with reference to EuF₃ source) is observed, which is in good agreement with the value reported earlier in literature (Wickman et al 1968).

The Mössbauer absorption in EuPd₃B₀.₂₅ is observed to occur at the same position as in EuPd₃ and is likewise temperature-independent. This confirms the susceptibility results that Eu ions are trivalent in this alloy.

With further addition of boron, Mössbauer spectra clearly reveal the change in valence of europium ions. In EuPd₃B₀.₅ two peaks are observed; one with an is of −4.2 ±0.1 mm/sec (corresponding to europium ions in 'divalent like' state), the other peak is
broad, centred around 3·5 mm/sec and arises from europium ions in ‘trivalent-like’ state. On lowering the temperature to 107 K these peaks shift further apart to -5·6 ± 0·1 mm/sec and 4·5 ± 0·1 mm/sec respectively (figure 9). A similar behaviour has been observed in EuLa₁₋ₓRh₂ system (Bauminger et al 1974) where the Mössbauer absorption consists of lines with strongly temperature-dependent isomer shifts. This has been interpreted on the basis of near-neighbour environment-dependent excitation energies for 4f-5d conduction band transition. In a certain temperature interval the excitation energies are found to be temperature-dependent. The Mössbauer lines observed in EuPd₃B₀.₅ correspond to europium ions in ‘divalent and trivalent like’ states. These states are not pure configuration (integral occupation) states as the Mössbauer lines exhibit temperature-dependent isomer shifts. Since all the body-centred positions are not occupied in EuPd₃B₀.₅, various europium ions will have a probability distribution of boron atoms in their neighbourhood. This perhaps stabilises them in different valence states. The near-neighbour environment effects may also partially be responsible for the broadening of line occurring at 3·5 mm/sec.

In EuPd₃B, where according to stoichiometry each unit cell of the lattice has a boron atom at the centre, all the europium ions are crystallographically equivalent and one might, therefore, expect them to exhibit the same valence. This is, indeed, found in the Mössbauer spectrum at 300 K (figure 8), where a single absorption line is observed with an is of -2·7 ± 0·1 mm/sec. The value of is indicates that europium ions are in a valence fluctuating state.
5.4 Charge ordering in EuPd$_3$B

As remarked above, a single Mössbauer absorption, with an is characteristic of europium ions in a valence fluctuating state, is observed in EuPd$_3$B at 300 K. Valence fluctuating europium compounds generally show a motionally narrowed single Mössbauer line with temperature-dependent isomer shift, which tracks the change in valence as the temperature is varied. Keeping this in view, the temperature behaviour of Mössbauer absorption in EuPd$_3$B turns out to be quite different. Down to 115 K (Figure 10) the is remains unchanged from its value at 300 K but the line width increases from $3.1 \pm 0.1$ mm/sec at 300 K to $5.1 \pm 0.1$ mm/sec at 115 K. At 88 K the spectrum splits into two lines with is of $-5.4 \pm 0.1$ mm/sec and $1.4 \pm 0.1$ mm/sec respectively.

The temperature dependence of the Mössbauer spectrum in EuPd$_3$B is quite interesting and suggests a thermally-activated valence fluctuation mechanism. To our knowledge, such a behaviour has so far been reported only in one other europium compound namely, Eu$_3$S$_4$ (Berkooz et al 1968) which is a semiconductor. This compound crystallises in bcc Th$_3$P$_4$ structure (Domange et al 1959; Picon et al 1960), and europium exists in two valence states though crystallographically all the europium sites are equivalent. Below 210 K the Mössbauer absorption of Eu$_3$S$_4$ shows two peaks corresponding to europium ions in two different integral valence states, i.e. divalent and trivalent. As the temperature is increased the two lines become broader and come closer to each other collapsing into one broad line, corresponding to a mean valence of 2.6, at $\sim$ 273 K. Above this temperature, the line position remains unchanged but the line width decreases reaching a constant value at $\sim$ 300 K. Conductivity of Eu$_3$S$_4$ between 77 and 300 K shows an exponential behaviour with temperature (Berkooz et al 1968) and x-ray diffraction studies show that the compound undergoes a structural phase transformation from bcc to tetragonal around 168 K (Davis et al 1970). The Mössbauer and conductivity behaviour of Eu$_3$S$_4$ has been explained (Berkooz et al 1968; Bransky et al 1970) on the basis of a hopping model (Smit and Wijn 1959; Miller et al 1961). The extra electron of Eu$^{2+}$ is assumed to jump between Eu$^{2+}$ and Eu$^{3+}$ ion. In order to do this, it has to overcome an activation energy barrier. As the temperature is increased the

![Figure 10](attachment:image.png)

Figure 10. $^{151}$Eu Mössbauer of EuPd$_3$B at various temperatures.
jump probability increases thereby decreasing the relaxation time, i.e. the time-hopping electron is bound to each ion. At sufficiently high temperatures, the relaxation time may become smaller than the Mössbauer probe time resulting in a motionally narrowed single Mössbauer line.

From the Mössbauer spectra it appears that EuPd$_3$B is another new system where the europium ions undergo charge ordering. It is likely that the relaxation time in EuPd$_3$B at 88 K is larger than the Mössbauer probe time giving rise to two well-resolved peaks corresponding to “Eu$^{2+}$ and Eu$^{3+}$ like” states. The relatively smaller difference in the is of Eu$^{2+}$ and Eu$^{3+}$, than what is generally observed, may be due to some electron hopping still taking place at 88 K. Preliminary low temperature Mössbauer measurements are in full accord with the conclusions drawn above (Micklitz 1982). At 4·2 K two peaks at $-6·7 \pm 0·1$ mm/sec and $3·5 \pm 0·1$ mm/sec are observed corresponding to Eu$^{2+}$ and Eu$^{3+}$ ions. Below 4·2 K the compound EuPd$_3$B orders magnetically and at 1·4 K the Mössbauer absorption corresponding to Eu$^{2+}$ ions shows hyperfine splitting with a hyperfine field value of 330 kOe. It should be noted that while Eu$_2$S$_4$ is a semiconductor EuPd$_3$B is metallic. Our observation is, therefore, first instance of charge ordering in a metallic system. It is likely that the crystal structure of EuPd$_3$B undergoes a lattice distortion at some temperature-stabilising europium ions in two different valence states.

6. Effect of silicon addition to EuPd$_3$

The addition of silicon to EuPd$_3$, like that of boron, leads to an increase in cell volume. The stoichiometry of the limiting single phase alloy is found to be EuPd$_3$Si$_{0.25}$. Relative to LaPd$_3$Si$_x$ alloys, the expansion in europium containing alloys, again, is larger (figure 11). The lattice expansion in going from EuPd$_3$ to EuPd$_3$Si$_{0.25}$ is less compared to that in going from EuPd$_3$ to EuPd$_3$B. From this observation one anticipates that the change in the valence of Eu ions in EuPd$_3$Si$_x$ alloys may be less substantial than that observed in EuPd$_3$B$_x$ alloys. This is confirmed by susceptibility (figure 12) and Mössbauer studies (Dhar et al 1983).

The Mössbauer spectra at 300 K in EuPd$_3$Si$_x$ alloys for $x = 0, 0·1, 0·2$ and $0·25$ are

![Figure 11. Lattice constant of LaPd$_3$Si$_x$ and EuPd$_3$Si$_x$ as a function of silicon concentration $x$.](image1.png)

![Figure 12. Temperature dependence of susceptibility of EuPd$_3$Si$_x$ ($x = 0, 0·2$ and $0·25$) alloys.](image2.png)
shown in figure 13. As remarked earlier, a temperature-independent Mössbauer line with is of $4.5 \pm 0.1$ mm/sec is observed in EuPd₃. As silicon is added the is becomes successively less positive, e.g. $4.4 \pm 0.1$ mm/sec in EuPd₃Si₀.₁ and $4.0 \pm 0.1$ mm/sec in EuPd₃Si₀.₂. In the latter the is shows a weak temperature dependence with a value of $4.1 \pm 0.1$ mm/sec at 88 K. These results show that up to $x = 0.2$ europium ions are essentially trivalent. In EuPd₃Si₀.₂₅ a stronger temperature dependence of the is is observed (figure 14). It varies from $2.8 \pm 0.1$ mm/sec at 85 K to $3.8 \pm 0.1$ mm/sec at 300 K. Though these values fall in the range for Eu³⁺ ions in metallic systems, the temperature dependence of is suggests that the europium ions are not in a pure trivalent configuration. We attribute the variation of is with temperature in EuPd₃Si₀.₂₅ to europium ions which are in a valence-fluctuating state with an average valence close to ³⁺. In addition, in EuPd₃Si₀.₂₅ a small absorption is observed with an is of $-7.0 \pm 0.2$ mm/sec at 300 K and it shows a weak temperature dependence. This peak presumably arises from europium ions which have been stabilised in ‘divalent like’ or mixed valent state due to near neighbour environment effects.

Magnetic susceptibility results (77 to 400 K) on EuPd₃Siₓ alloys (figure 12) are in consonance with those obtained from Mössbauer measurements. The susceptibility of EuPd₃Si₀.₁ and EuPd₃Si₀.₂ is more or less the same as that of EuPd₃. An increase in the susceptibility of EuPd₃Si₀.₂₅ over that of EuPd₃ is observed.

7. CeRh₃Bₓ alloys: lattice constant and susceptibility

It is interesting to note that the alloys CeRh₃Bₓ form for all $x(0 < x < 1)$ though for other R only RRh₃B (x = 1) compounds can be stabilised. The addition of boron to CeRh₃ also results in the expansion of the lattice.

Figure 15 depicts the lattice parameter of CeRh₃Bₓ alloys as a function of boron.
concentration $x$. A very interesting feature is observed in CeRh$_3$B$_{0.12}$ and CeRh$_3$B$_{0.25}$; the x-ray diffraction patterns of these compounds show split lines, i.e. each line corresponding to various ($hkl$) values of AuCu$_3$ type structure is split in two lines. While one set of lines in both CeRh$_3$B$_{0.12}$ and CeRh$_3$B$_{0.25}$ can be fitted to a value of lattice parameter observed in CeRh$_3$, the other set corresponds to an expanded lattice. For alloys with boron concentration $x > 0.5$ only a single set of lines is observed.

To our knowledge, the only other instance where a splitting of x-ray lines in a cerium compound has been observed is that in Ce$_{1-x}$Sc$_x$Pd$_3$ (Gambke et al 1980). As already remarked, CePd$_3$ is a valence fluctuating system. The replacement of Ce by Sc contracts the lattice and in the range $0.3 < x < 1$, Ce ions go to a quadrivalent state. The onset of the change from quadrivalent (starting from ScPd$_3$ rich end) to mixed valent state is marked with the occurrence of split x-ray lines. A similar situation may occur in CeRh$_3$B$_x$ alloys also. It may, however, be remarked that the occurrence of two sets of x-ray lines is not a characteristic feature of systems where two different valence states co-exist.

The magnetic susceptibility of CeRh$_3$B$_x$ for $x = 0$, 0.25, 0.5, 0.75 and 1 is shown in figure 16. Susceptibility of CeRh$_3$ is almost temperature-independent consistent with the quadrivalent and hence non-magnetic nature of Ce ions in this compound (Harris and Norman 1967). The boron-doped alloys show a small enhancement of susceptibility over that of CeRh$_3$. Surprisingly, CeRh$_3$B shows a susceptibility even less than that of CeRh$_3$. We feel that because of the limited temperature range of investigation it is not possible to distinguish the susceptibility of CeRh$_3$B$_x$ ($x > 0$) alloys from that of CeRh$_3$. Extension of susceptibility to low temperatures would be useful in elucidating the effect of boron addition on the valence of Ce ions in CeRh$_3$B$_x$ alloys.

8. Conclusion

The ‘addition’ of boron and silicon to CePd$_3$ and EuPd$_3$ results in unusual lattice expansion. It has been shown from lattice parameter, susceptibility and $^{151}$Eu Mössbauer measurements that boron and silicon when alloyed with CePd$_3$ and EuPd$_3$, cause a change in the valence state of cerium and europium ions. Besides lattice
expansion, changes in the band structure may also be responsible for the valence change. Mössbauer studies on EuPd$_2$B reveal that europium ions undergo charge ordering at low temperatures. This is the first europium containing rare earth metallic system where such an effect has been observed.

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