

Structural and magnetic investigations of some new boron containing rare earth intermetallic compounds

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Abstract. By alloying boron with RPd_3 (R = rare earth) compounds, new ternary alloys of the formula RPd_3B_x ($0 \leq x \leq 1$) have been prepared. The parent RPd_3 compounds crystallise in the cubic $AuCu_3$ type structure. The addition of boron does not change the structure but results in an expansion of the lattice. Therefore, it is likely that the small boron atoms occupy the vacant body centred position in $AuCu_3$ type structure. It is also observed that compounds of the composition RRh_3B can be formed in the cubic structure for all rare earths R though the parent RRh_3 compounds exist only for $R = Ce$ ($AuCu_3$ type) and La, Sm, Nd and Gd (all hexagonal $CeNi_3$ type). This points out the role of boron in stabilising new crystallographic phases. The results of susceptibility measurements on some of the RPd_3B and RRh_3B compounds are presented. In particular, it is noted that while $GdPd_3$ orders antiferromagnetically with $T_N = 6$ K, $GdPd_3B$ does not order magnetically down to 4.2 K.

Keywords. Boron: rare earths; magnetic susceptibility; structural investigations.

1. Introduction

During the last few years a new class of rare earth compounds known as rare earth ternary borides have attracted a great deal of attention. The interest in these compounds is due to their fascinating magnetic and superconducting properties. For example, in the series of ternary borides represented by the formula RRh_4B_4 (R = rare earth), first synthesized by Matthias *et al* (1977a, b), the compounds with Th, Y, Nd, Sm, Er, Tm and Lu are superconducting whereas those with Gd, Tb, Dy and Ho undergo ferromagnetic ordering. Following the RRh_4B_4 series of compounds, many other ternary borides forming at different stoichiometries have been synthesised and investigated for magnetic and possible superconducting behaviour. In this paper we report the formation of new boron containing rare earth compounds represented by the formula RPd_3B_x ($0 \leq x \leq 1$) and RRh_3B where $R = La$ to Lu . Magnetic studies on some of these alloys are also presented.

An indication that alloys of the formula RRh_3B_x and RPd_3B_x may well exist came first during the course of our investigations on RRh_3B_2 compounds described elsewhere (Malik *et al* 1983). In the initial stages of our work on these, we observed, in the x-ray diffraction pattern of $CeRh_3B_2$, the existence of some extra lines which could not be ascribed to hexagonal $CeRh_3B_2$ compound. A careful analysis showed that these extra lines could be indexed on the basis of a cubic structure. The lattice constant of this cubic phase turned out to be slightly larger than that of $CeRh_3$ which crystallises in the cubic $AuCu_3$ structure type (Harris and Norman 1967). Because of the structural considerations of the $AuCu_3$ type crystal lattice, to be discussed below, the formula of this new cubic phase was presumed to be $CeRh_3B_x$ ($0 < x \leq 1$). Subsequently we found that starting with appropriate amounts of Ce, Rh and B , cubic compounds having the formula $CeRh_3B_x$ ($0 < x \leq 1$) could indeed be formed. The formation of alloys of the

above composition immediately suggested the likely existence of RPd_3B_x compounds. The RPd_3 compounds also crystallise in the $AuCu_3$ structure type (Harris and Raynor 1965) with lattice constants comparable to that of $CeRh_3$. Later investigations (Dhar *et al* 1981a) verified the formation of RPd_3B_x ($0 < x \leq 1$) alloys for all the rare earths R. Further extension of the work showed that RPd_3Si_x alloys could also be formed, though silicon content is much smaller.

2. RPd_3B_x ($0 < x \leq 1$; R = Rare earth) alloys

2.1 Synthesis and structure

Master RPd_3 alloys were first prepared by melting together stoichiometric amounts of the rare earth and the Pd metal in an arc furnace. The alloy ingots were turned and melted several times to ensure homogeneity. Approximately half the amount of each RPd_3 alloy was remelted with an appropriate amount of boron in a water cooled copper boat in an induction furnace to form RPd_3B alloys. This preliminary mixing of boron with RPd_3 achieved by induction heating was necessary as otherwise boron chunks were found to shatter and fly away on coming under the arc in the arc furnace. In order to ensure complete mixing the fused charge of RPd_3 and boron was remelted in the arc furnace. Alloy formation at the stoichiometry RPd_3B_x ($0 < x \leq 1$) was tried for few rare earths only, *e.g.* La, Ce, Pr, Eu, Gd and Dy and these were obtained by remelting appropriate proportions of RPd_3 and RPd_3B . In the case of europium and ytterbium compounds, excess amount of the rare earth was taken to compensate for the loss due to evaporation during melting. Powder x-ray diffraction patterns were recorded using CuK_α radiation.

The RPd_3 compounds are known to crystallise in the cubic $AuCu_3$ type structure, space group $Pm\bar{3}m$ (figure 1a). The rare earth atoms occupy the cube corners and Pd atoms are on the face centred positions. The various atomic positions in the unit cell are given by (Pearson 1967).

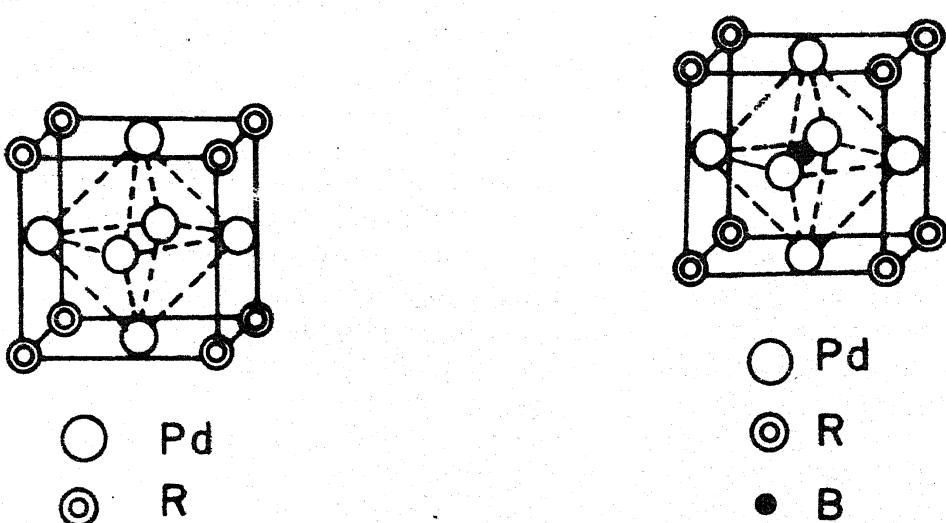


Figure 1a. The unit cell of RPd_3 (R = rare earth) compounds crystallising in $AuCu_3$ type structure. b. The proposed crystal structure of RPd_3B compounds.

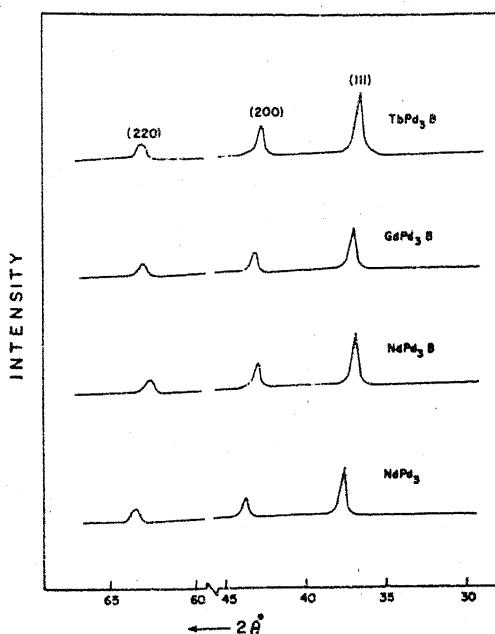


Figure 2. The x-ray diffraction patterns of NdPd_3 and some RPd_3B ($\text{R} = \text{Nd}, \text{Gd}$ and Tb) compounds.

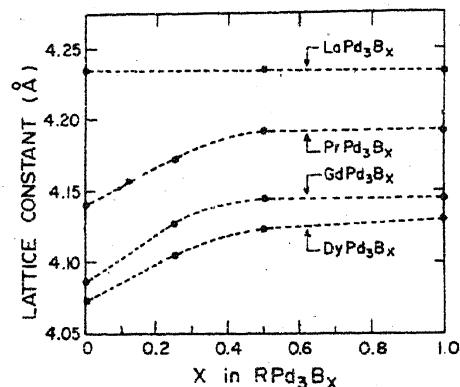


Figure 3. Lattice parameter of RPd_3B_x ($\text{R} = \text{La}, \text{Pr}, \text{Gd}$ and Dy) alloys as a function of boron concentration x .

R	$(1a)$	$m3m$: 0, 0, 0
Pd	$(3c)$	$4/mmm$: 0, 1/2, 1/2; 1/2, 0, 1/2; 1/2, 1/2, 0.

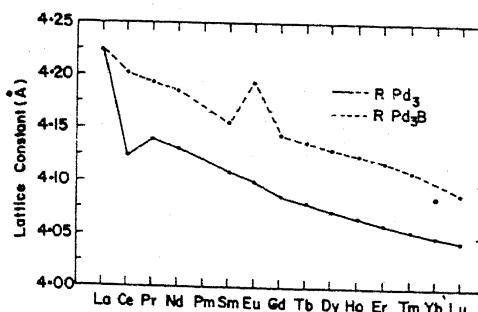
The x-ray diffraction patterns of RPd_3B_x (for all x) compounds are identical to that of the RPd_3 compounds (figure 2) and hence can be fitted to cubic structure type. However, the lattice parameter of the former is observed to be slightly larger than that of the parent RPd_3 compound and depends on the boron concentration x . Figure 3 shows the dependence of lattice parameter on boron concentration in some of these alloys. The relatively small boron atoms presumably occupy the vacant body-centred position in the RPd_3 unit cell to give rise to an E_{21} anti-perovskite arrangement, space group $Pm3m$ (figure 1b). Thus RPd_3B_x alloys may be considered to result from "addition" of boron to parent RPd_3 compound. Many compounds which have the AuCu_3 type structure are known to accommodate smaller non-metallic elements like B, C, N, Si etc. at the body-centred position resulting in anti-perovskite compound formation (Gschneidner *et al* 1978). The various atomic positions in the RPd_3B unit cell are given by (Pearson 1967)

R	$(1a)$	$m3m$: 0, 0, 0
Pd	$(3c)$	$4/mmm$: 0, 1/2, 1/2; 1/2, 0, 1/2; 1/2, 1/2, 0.
B	$(1b)$	$m3m$: 1/2, 1/2, 1/2.

Table 1 lists the lattice constants of RPd_3 and RPd_3B compounds and the same information is plotted graphically in figure 4. It should be noted that the expansion in the cell volume of Ce and Eu compounds is relatively larger. Because of the highly volatile nature of Yb, efforts to make single phase YbPd_3B did not succeed. However, the extra phase in the alloy is estimated to be less than 10%.

Table 1. Lattice constants of RPd_3 and RPd_3B (R = rare earth) compounds

Compound	Lattice constant a (\AA)	Compound	Lattice constant a (\AA)
$LaPd_3$	4.229	$LaPd_3B$	4.229
$CePd_3$	4.124	$CePd_3B$	4.203
$PrPd_3$	4.141	$PrPd_3B$	4.194
$NdPd_3$	4.132	$NdPd_3B$	4.187
$SmPd_3$	4.110	$SmPd_3B$	4.156
$EuPd_3$	4.102	$EuPd_3B$	4.196
$GdPd_3$	4.087	$GdPd_3B$	4.146
$TbPd_3$	4.080	$TbPd_3B$	4.138
$DyPd_3$	4.073	$DyPd_3B$	4.132
$HoPd_3$	4.067	$HoPd_3B$	4.126
$ErPd_3$	4.061	$ErPd_3B$	4.121
$TmPd_3$	4.055	$TmPd_3B$	4.111
$YbPd_3$	4.050	$YbPd_3B$	4.088
$LuPd_3$	4.045	$LuPd_3B$	4.090

Figure 4. Lattice parameter of RPd_3 and RPd_3B (R = rare earth) compounds.

2.2 Magnetic susceptibility measurements

From figure 4 it is seen that with the exception of $EuPd_3B$, the lattice constant of other RPd_3B compounds follows the usual lanthanide contraction for trivalent rare earth ions. Susceptibility measurements carried out on some of these compounds, *i.e.* for $R = Pr, Nd, Sm, Gd, Tb, Dy, Er$ and Tm , in the temperature range 77 to 300 K, confirm the trivalence of rare earth ions. For $GdPd_3$ and $GdPd_3B$ susceptibility behaviour down to 4.2 K was recorded for reasons given below. (The addition of boron to $CePd_3$ and $EuPd_3$ results in unusual lattice expansion and changes the magnetic properties of Ce and Eu ions drastically; results are discussed elsewhere (Dhar *et al* 1981b; 1982).

With the exception of $SmPd_3B$ all other RPd_3B compounds, investigated for magnetic behaviour, show a linear $\chi^{-1} vs T$ behaviour (figures 5 and 6). The effective paramagnetic moments were determined by using the formula $\chi(T) = N\mu_{\text{eff}}^2/[3k_B(T - \theta_p)]$. The values of μ_{eff} thus obtained are seen to be almost equal to the free ion value for the trivalent state and are listed in table 2. Small θ_p values suggest that magnetic ordering in RPd_3B compounds may occur only at very low temperatures. The nonlinear behaviour of $\chi^{-1} vs T$ observed in $SmPd_3B$ (figure 6) is a

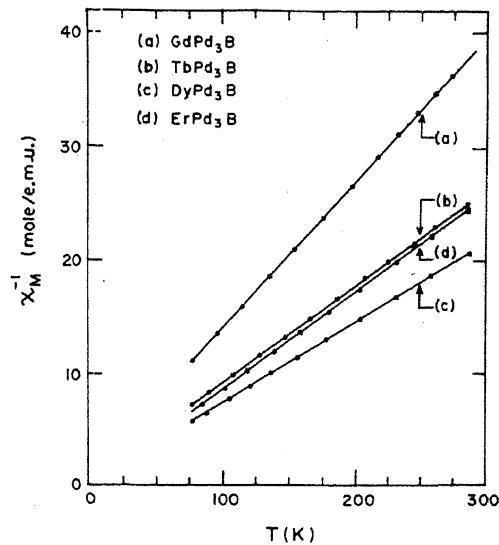


Figure 5. The plot of inverse susceptibility ν vs temperature of RPd_3B ($R = Gd, Tb, Dy$ and Er) compounds.

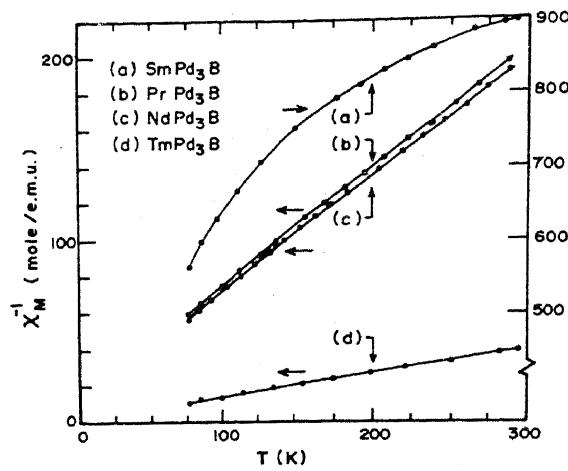


Figure 6. The temperature dependence of inverse susceptibility of RPd_3B ($R = Sm, Pr, Nd$ and Tm) compounds.

Table 2. The effective paramagnetic moment μ_{eff} and paramagnetic Curie temperature θ_p in some RPd_3B and RRh_3B (R = rare earth) compounds.

Compound	$\mu_{eff} (\mu_B)$	$\theta_p (K)$
$NdPd_3B$	3.54	-12.0
$PrPd_3B$	3.54	-13.0
$TbPd_3B$	9.76	-11.0
$DyPd_3B$	10.73	-7.8
$ErPd_3B$	9.74	-5.0
$TmPd_3B$	7.76	-4.0
$NdRh_3B$	3.75	-7.0
$PrRh_3B$	3.80	-18.0
$TbRh_3B$	9.77	5.0
$DyRh_3B$	10.69	4.0
$ErRh_3B$	9.64	5.0

consequence of the temperature independent contribution arising due to narrow multiplet separation of Sm^{3+} ion.

Introduction of non magnetic boron in the RPd_3 compounds, besides expanding the lattice, will also change the electron concentration in the conduction band. Since RKKY interaction responsible for magnetic ordering in rare earth compounds is electron concentration-dependent, any change in the latter would be expected to modify the exchange interaction between the rare earth ions. Examples exist in literature where such effects have been found. For instance while the moment carrying trivalent rare earths RAI_2 order ferromagnetically (except $CeAl_2$), the compound $EuAl_2$ in which Eu is divalent and, therefore, contributes one electron less to the conduction band, is

antiferromagnetic (Wallace 1973). In the pseudobinary $\text{Eu}_x\text{La}_{1-x}\text{Al}_2$ a reversal in the magnetic coupling from antiferromagnetic to ferromagnetic with increasing x , which alters the electron concentration, is observed (Mader and Wallace 1968). Similarly while GdAg and GdIn order antiferromagnetically with Neel temperatures of 145 K and 28 K respectively, the pseudobinary solutions $\text{GdAg}_x\text{In}_{1-x}$ exhibit ferromagnetism for $0.8 < x < 0.3$ with Curie temperature increasing with increasing x (Sekizawa and Yasukochi 1966). The dependence of exchange interaction on the electron concentration can be understood from the formula

$$\theta_p = -\frac{3\pi Z^2 |J(0)|^2}{k_B E_F} S(S+1) \sum_i F(2k_F r_i), \quad (1)$$

where θ_p is the paramagnetic Curie temperature, Z is the average number of conduction electrons per atom, $2J(0)$ is the exchange interaction constant between the rare earth spin S and conduction electron spin s , E_F is the Fermi energy and $F(x) = (x \cos x - \sin x)/x^4$. In the molecular field approximation θ_p is identical with the magnetic ordering temperature. The sign of $F(x)$ determines the kind of magnetic order that develops: antiferromagnetic if sum is positive and ferromagnetic if the sum is negative. With the increase in electron concentration, *i.e.* an increase in Z and hence in k_F (assuming crystal structure remains the same) x increases and $F(x)$ shows an oscillatory behaviour from positive to negative values.

In order to see if the addition of boron is accompanied with any electron concentration effects, magnetic behaviour of GdPd_3 and GdPd_3B was studied down to liq. He temperature. The compound GdPd_3 was chosen because it is the only compound in the RPd_3 series that orders magnetically above 4.2 K (Gardner *et al* 1972). Figure 7 shows the magnetisation as a function of temperature in GdPd_3 and GdPd_3B . In an external field of 4 kOe magnetisation of GdPd_3 shows a sharp singularity at ~ 6 K which corresponds to an antiferromagnetic ordering in this compound. No such feature is observed in GdPd_3B which continues to remain paramagnetic down to 4.2 K. These observations show that the addition of boron modifies the exchange interaction

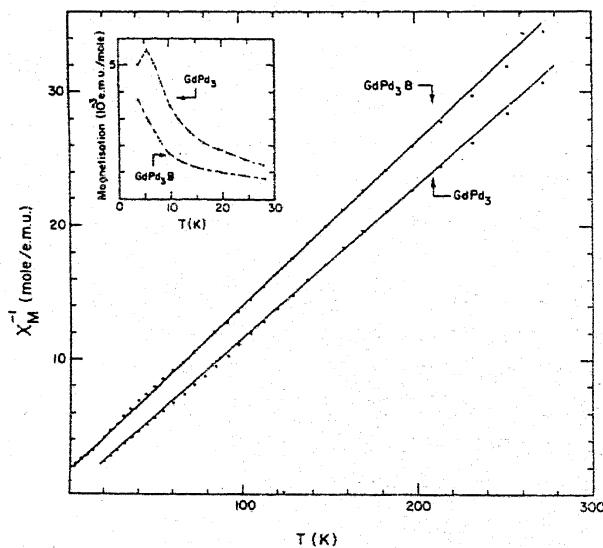


Figure 7. The inverse susceptibility of GdPd_3 and GdPd_3B as a function of temperature. The inset shows the temperature dependence of magnetization (in a field of 4 kOe).

between the rare earth ions either due to lattice expansion, or by changing electron concentration or a combination of both. Extension of magnetisation below 4.2 K may, perhaps, show evidence of magnetic ordering in GdPd_3B .

3. RRh_3B compounds

3.1 Synthesis and structure

In the beginning of this paper we mentioned that alloys of the formula CeRh_3B_x could be formed. This observation together with the fact that alloys of the composition RPd_3B_x exist for all R prompted us to investigate whether single phase RRh_3B_x alloys could be synthesised. It was found that RRh_3B compounds, do indeed, form for all rare earths R. The x-ray diffraction patterns of RRh_3B compounds (figure 8) are similar to those of RPd_3B compounds. Therefore, presumably RRh_3B compounds also crystallise in the anti-perovskite or filled AuCu_3 type structure. It may be noted that while the parent RPd_3 compounds exist for all R, such is not the case with RRh_3 compounds. The latter form only for R = Ce (AuCu₃ type structure) and La, Sm, Nd and Gd (hexagonal CeNi₃ type structure) (Iandelli and Palenzona 1979). The non-metallic element boron, therefore, has the effect of stabilising the cubic RRh_3B phase. In fact, while our experimental investigations were on, we came across instances in the literature where complex metallic phases are stabilised by atoms like C, B, N, Si etc (Stadelmaier 1979). The alloys of composition RRh_3C_x ($x \sim 1$) for all R also exist in the perovskite structure (Holleck 1971), thus strengthening our conclusions, reached independently by us, about the crystal structure of RRh_3B compounds.

In contrast to RPd_3B_x alloys where $0 < x \leq 1$, it appears that RRh_3B_x compounds do not form below a certain minimum concentration of boron (CeRh_3B_x being an exception). Thus for $x = 0.5$ no perovskite formation was observed for R = La, Nd and Er. Though, this was not tested for other rare earths we believe similar considerations should hold. We have not determined the minimum value of x for which RRh_3B_x alloys can be stabilised.

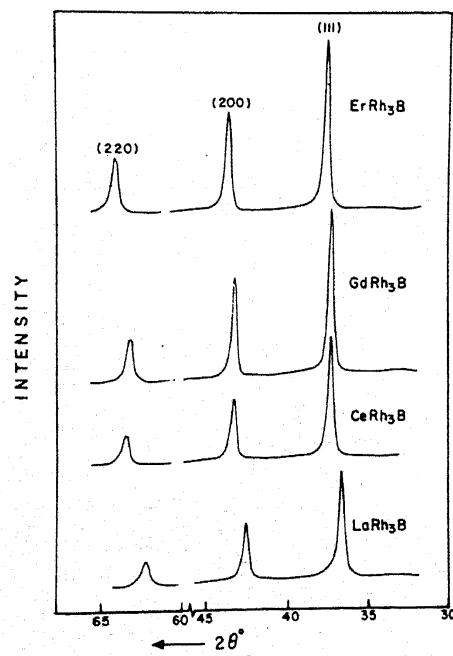


Figure 8. The x-ray diffraction patterns of some RRh_3B (R = La, Ce, Gd and Er) compounds. These patterns can be indexed on the basis of a cubic unit cell.

3.2 Magnetic susceptibility and ^{151}Eu Mössbauer measurements

The lattice constants of RRh_3B compounds are plotted in figure 9. With the exception of CeRh_3B , the usual lanthanide contraction with no anomaly in the lattice parameter is observed. This points out the trivalent character of rare earth ions in these compounds. This has been verified from susceptibility measurements carried out on some of these compounds in the temperature range 300 to 77 K. The χ^{-1} vs T plots are shown in figures 10 and 11. For SmRh_3B χ^{-1} vs T is non-linear for reasons similar to those given for SmPd_3B . The effective paramagnetic moments (very close to free ion value) and paramagnetic Curie temperatures are listed in table 2.

In case of EuRh_3B , the trivalence of Eu has been confirmed from ^{151}Eu Mössbauer spectroscopy. A single Mössbauer absorption with isomer shift of 2.4 ± 0.1 mm/sec, characteristic of trivalent Eu in metallic environments, is observed at 300 K (figure 12). There is no change in isomer shift on lowering the temperature to 88 K.

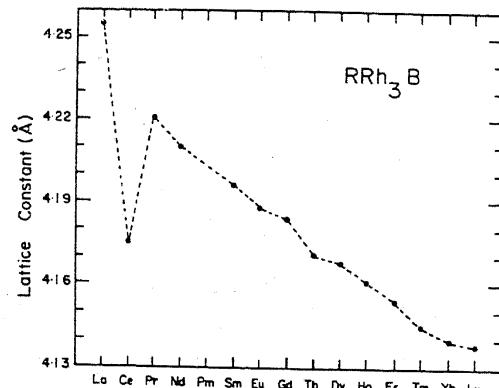


Figure 9. The lattice parameter of RRh_3B (R = rare earth) compounds.

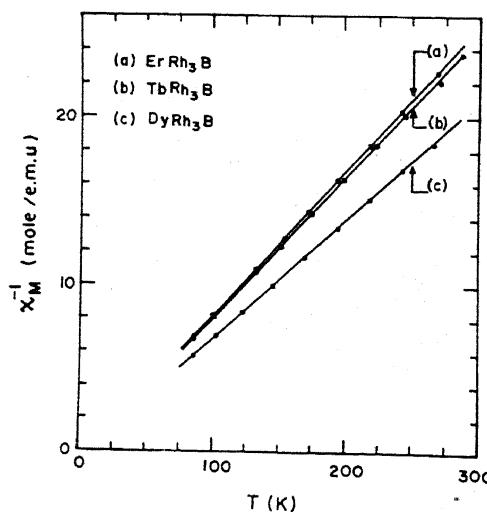


Figure 10. Inverse susceptibility as a function of temperature in RRh_3B (R = Er, Tb and Dy) compounds.

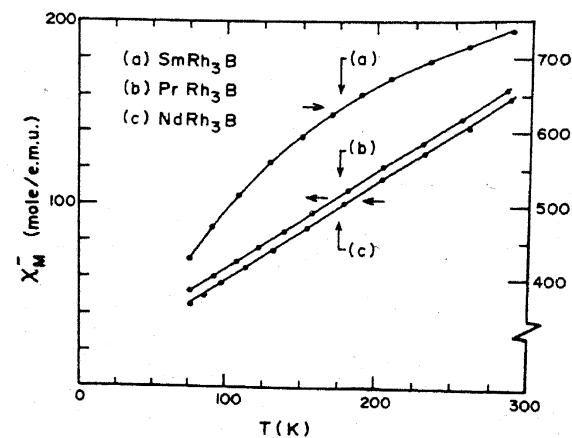


Figure 11. Inverse susceptibility vs temperature of RRh_3B (R = Sm, Pr and Nd) compounds.

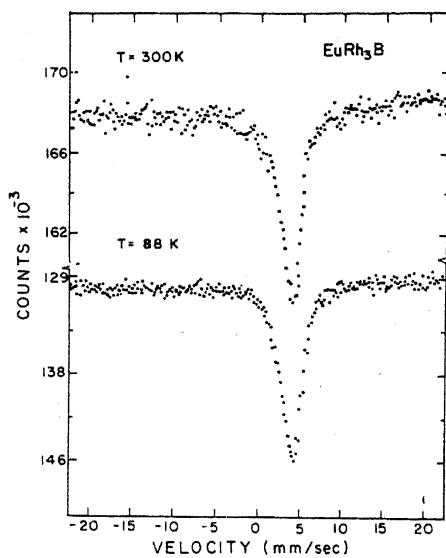


Figure 12. ^{151}Eu Mössbauer spectrum of EuRh_3B at 300 and 88 K.

4. Silicon addition to RPd_3 compounds

From the structural considerations of the RPd_3 unit cell mentioned above, we concluded that the small boron atoms in the RPd_3B_x alloys occupy the interstitial vacant body-centred position. It was, therefore, natural to investigate whether other non-metallic elements could be introduced in the RPd_3 lattice. In this direction we tried the synthesis of RPd_3Si_x alloys for $\text{R} = \text{La, Ce}$ and Eu only. It was found that like boron, silicon can also be alloyed with RPd_3 compounds. However, the atomic percentage of silicon that can be dissolved into RPd_3 lattice is far less than that of boron. Only up to $x \sim 0.3$, single phase cubic alloys were obtained for RPd_3Si_x composition. This may be related to the relatively larger atomic volume of silicon compared to that of boron. From volume filling considerations alone it may not be possible to accommodate as many number of silicon atoms as boron. The addition of silicon, like boron, to parent RPd_3 compound leads to lattice expansion. Results of magnetic susceptibility and ^{151}Eu Mössbauer spectroscopy on CePd_3Si_x and EuPd_3Si_x , where a valence change of Ce and Eu ions is observed on alloying with Si, are presented elsewhere (Malik *et al* 1982; Dhar *et al* 1983).

Carbon addition to RPd_3 compounds was also tried and it was found that carbon cannot be alloyed with RPd_3 compounds.

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