

The magnetic properties of rare earth-Pd₃ phases

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The magnetic properties of rare earth-Pd₃ phases

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Abstract. Magnetic measurements from 1.5 to 300 K on the complete series of Cu₃Au-type RPd₃ phases have been made. LaPd₃ and LuPd₃ are diamagnetic at room temperature. CePd₃ shows Pauli-type paramagnetism indicative of a nonmagnetic virtual bound state. PrPd₃ and NdPd₃ are affected at low temperatures by the presence of the crystal field. The magnetic properties of SmPd₃ and EuPd₃ are determined by the energy levels of the lowest multiplet. GdPd₃ and (possibly) TbPd₃ become antiferromagnetic at 7.5 and 2.5 K respectively. DyPd₃-ErPd₃ obey the Curie law. The magnetic properties of these phases are discussed in relation to crystal field effects and a possible band structure.

1. Introduction

The magnetic behaviour of rare earth intermetallic compounds is of fundamental interest. Compounds of the general formula RM₃ (where R represents the rare earth metal) occur in several different structures but indium and palladium combine with the rare earth metals to form a complete series of Cu₃Au-type phases. The RPd₃ compounds are metallic in nature and probably form congruently from the melt. Their lattice parameters (Harris and Raynor 1965a) indicate that all the compounds (except cerium) contain trivalent rare earth atoms, and magnetic measurements (Gardner *et al.* 1971) confirm this. The magnetic properties of RIn₃ compounds have been reported previously (Buschow *et al.* 1969) and the results will be compared with those we have obtained for RPd₃ compounds. The magnetic susceptibility of the RIn₃ compounds suggested that most of them become antiferromagnetic above 4 K, with Néel temperatures ranging from 6 K for ErIn₃ to 45 K for GdIn₃, and this has been confirmed for a number of the compounds by neutron diffraction measurements (Arnold and Nereson 1969, Nereson and Arnold 1970). For these compounds good agreement was obtained between the variation of the Curie-Weiss θ (or the Néel temperature) with the de Gennes factor $(g - 1)^2 J(J + 1)$. This relationship was derived (de Gennes 1962) by assuming that the exchange interaction is constant along the series, is described by a predominantly indirect exchange interaction between localized 4f moments via the conduction electrons and can be treated using a molecular field approximation. The RPd₃ series seems to be quite different in that only GdPd₃ (and possibly TbPd₃) appears to be antiferromagnetic above 1.5 K and the variation of the Curie-Weiss θ does not follow the de Gennes factor. Since the exchange interaction is so weak in these compounds it is possible to examine more clearly the effects of the crystal field on the rare earth ions.

Some of the R-Pd alloys also form a fcc RPd₄ phase. Magnetic susceptibility measurements have been made on two of these, namely ScPd₄ and YPd₄.

2. Sample preparation and apparatus

An approximate form for the Pd-R phase diagram based on the investigation of Pd-Ce

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by Thomson (1967) is shown in figure 1. The RPd_3 phase forms congruently from the melt and the diagram shows that it should be possible to prepare single-phased samples. The dotted line represents a possible peritectoid phase at the RPd_4 composition which appears in some but not all of these alloy systems. There is evidence from x rays, for example, of a discrete fcc phase at the composition corresponding to YPd_4 (Harris and Norman 1968).

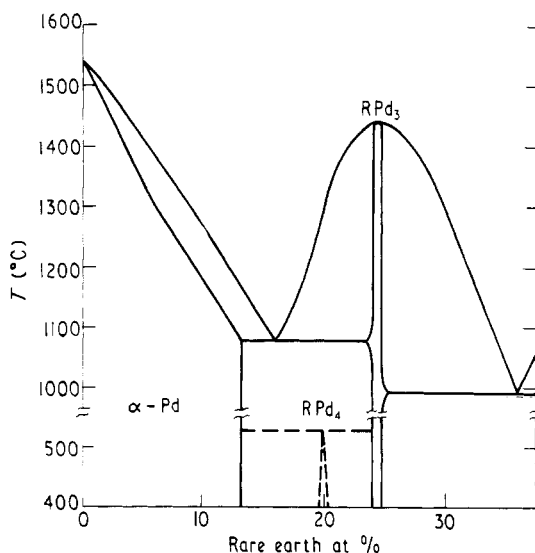


Figure 1. An approximate form of the Pd-R phase diagram.

The samples used in the magnetic measurements were prepared by argon arc melting appropriate amounts of the constituent elements. The rare earth metals and the palladium were obtained from Johnson-Matthey and were of the highest purity available. The analyses provided by Johnson-Matthey showed that all of the rare earths contained approximately 0.02 wt% of other base metals; Pr, Nd, Gd, Er and Y contained ~0.1 wt% of tantalum, Lu contained 0.5 wt% Ta but tantalum was not detected in the other elements; the total rare earth impurities were <0.01 wt% for La, Ce, and Sc, <0.1 wt% for the remainder except Eu where it was <1.0 wt%.

The arc melted buttons were weighed and the weight losses corresponded to changes in the nominal composition (25% of the rare earth component) of $\pm 0.5\%$. The Sm, Tm and Yb samples showed much larger weight losses which were probably due to the volatilization of the rare earth component but this had been allowed for in the starting weights of the constituents. Metallographic examination of the arc melted buttons showed that they were in the single phase condition but before making any measurements each button was given an homogenizing anneal at 900°C for one week. The composition of several of the alloys was checked using standard chemical techniques ('wet analysis') which determines the rare earth content to within $\pm 0.4\%$. It was observed that all of the analysed compositions agreed with the nominal compositions within the experimental errors.

Powders for x ray diffraction were prepared by grinding part of the arc melted buttons in an agate mortar and re-annealing for 2 h at 900°C. The powders were then mounted in a Philips Debye-Scherrer camera (11.483 cm diam) and exposed to Cu $K\alpha$ radiation. The lattice spacings were derived from the diffraction patterns using an extrapolation technique for the elimination of systematic errors (Nelson and Riley 1945) and are given in table 1.

The magnetic measurements have been made using the Faraday method in the temperature region 1.5 to 300 K. The results were corrected, when necessary, for ferromagnetic

Table 1 Measured properties of R Pd₃ compounds

RE	Lattice Parameter (kX) (± 0.0002)	T_N (K)	θ (K)	μ_{eff}^\dagger	χ_g (295) ($\mu\text{emu/g}$)
La	4.2267	—	—	—	-0.242
Ce	4.1195	—	—	—	2.76 ± 0.15
Pr	4.1300	1.05^\ddagger	0 (-7)	3.69 (3.4)	10.90
Nd	4.1181	—	-5 (1)	3.50 (3.4)	10.91
Sm	4.0982	—	complex	—	2.00
Eu	4.0869	—	complex	—	10.10
Gd	4.0813	7.5 ± 0.5	1.5 ± 1.0 (3)	8.03 (8.0)	56.7
Tb	4.0691	(2.5 ± 1.0)	1 ± 1 (3)	9.61 (9.3)	83.0
Dy	4.0612	—	0 ± 1 (2)	10.51 (10.1)	96.7
Ho	4.0538	—	0 ± 1 (4)	10.38 (9.3)	93.4
Er	4.0460	—	0 ± 1 (0)	9.40 (9.5)	76.1
Tm	4.0391	0.20^\ddagger	— (-1)	— (7.5)	—
Yb	4.0283	—	— 0	— (4.3)	—
Lu	4.0277	—	—	—	-0.128

† The determination of μ_{eff} involves a possible error in composition of $\pm 0.4\%$. The observed χ values have been corrected for a matrix diamagnetism of $-0.15 \mu\text{emu/g}$ in deriving these values of μ_{eff} (see text).

‡ E. Bucher, K. Andres and A. S. Cooper (to be published). The values in brackets in columns 4 and 5 are taken from Hutchens *et al.* (1971).

contamination by making susceptibility measurements in five fields, ranging from 5 to 13 kOe, and determining the 'corrected' susceptibility from an extrapolation of a χ^{-1}/H plot to infinite field (the Honda-Owen method). This correction was significant at room temperature only for the samples of low susceptibility, namely ScPd₃, ScPd₄, YPd₃, YPd₄, LaPd₃ and LuPd₃, and the presence of ferromagnetic impurities lead to an error of $\sim 1\%$ in the corrected values. The correction was applied at all temperatures in a satisfactory manner except, possibly, for YPd₄ (see §3.1.). YPd₄ and several of the RPd₃ samples, including GdPd₃, showed the appearance of a ferromagnetic impurity phase with a Curie temperature ~ 10 –20 K. However, in all cases, except YPd₄, we were able to prepare a further sample which was not contaminated, and the results agreed, within experimental error, with the 'corrected' results obtained for the contaminated sample. The impurity phase was always less than 5% of such samples as it was not observed in the x ray examinations. Its significance magnetically depended on the applied field. For example at 4.2 K the impurity phase produced in 400 Oe $\sim 30\%$ of the magnetization of the contaminated GdPd₃ sample but in 19 kOe its effect was less than 1% (see §3.5.). These magnitudes are typical of the effects observed in the other contaminated RPd₃ samples. The Honda-Owen correction is based on a linear M - H relation for the matrix and an impurity magnetization which saturates in fields lower than the measuring fields. It is clearly difficult to resolve the two contributions using this method of correction, if the impurity does not saturate in low fields and/or if the M - H curve of the matrix is nonlinear. In such cases it is essential to examine samples from different preparations.

3. Results

3.1. Pd₃ - Sc, Y, La, Lu and Pd₄ - Sc, Y.

Phases based on Sc, Y, La and Lu were investigated in order to determine the effects of elements with no localized moment but with the same outer electron configuration as the rare earth elements on the susceptibility of palladium. The addition of Sc, Y, La, or Lu to Pd lowers its strongly paramagnetic room temperature susceptibility and for the addition

of up to 10% Sc and Y the reduction follows the same curve as a function of electron/atom ratio as Pd–Ag alloys (Hoare *et al.* 1953, Harris and Norman 1968, 1970), if Ag and Sc etc. are assumed to have valences of 1 and 3 respectively. This kind of behaviour has been observed previously for the addition of other transition metals, namely Zr, Mo, V, Nb and Ta (Kudielka-Artner and Argent 1962). If further addition of Sc and Y followed precisely the behaviour of silver, diamagnetism would occur in these systems at 17% addition. In fact, as can be seen in figure 2, alloys containing 20% additions of Sc and Y are paramagnetic at room temperature with the susceptibility of ScPd_4 slightly larger than that of

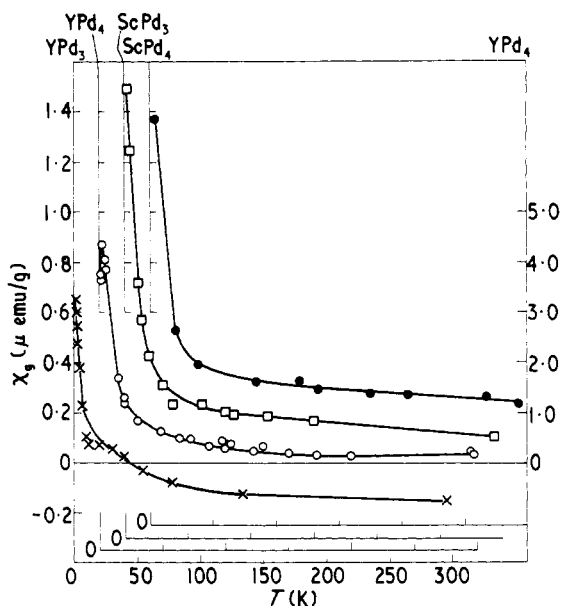


Figure 2. Gram-susceptibility (χ_g) as a function of temperature for: \square ScPd_3 ; \bullet ScPd_4 ; \times YPd_3 ; \circ YPd_4 . The ordinates are displaced in order to separate the curves, and the scale for YPd_4 is on the right of the figure.

YPd_4 . For 25% additions, although ScPd_3 is paramagnetic at room temperature, YPd_3 is clearly diamagnetic. These differences in behaviour between Sc and Y and the trend suggested by Pd–Ag alloys are presumably connected with the different diamagnetic contributions and band structures of these systems. Similar differences were observed at the higher electron/atom ratios by Kudielka-Artner and Argent (1962) and none of their alloys became diamagnetic at electron/atom ratios less than 0.5. Furthermore it can be seen in figure 2 that the susceptibility of all of these phases increases with decrease of temperature. YPd_4 increases markedly compared with the others and shows a maximum in susceptibility at ~ 3 K. The maximum and the increase in susceptibility is probably due to the presence of impurities in the sample—iron or rare earths. These impurities cause the samples to become extremely weak ferromagnets at ~ 10 K which suggests that iron impurities may be responsible. It may well be that the maximum in YPd_4 is due to an improper correction for this weak ferromagnetism.

Figure 3 shows the susceptibility of LaPd_3 and LuPd_3 . Both of these phases are weakly diamagnetic at room temperature but become paramagnetic at low temperatures, again due to the presence of rare earth/iron impurities in the alloys. From the behaviour of these systems we decided to correct the observed susceptibilities of alloys containing rare earth elements for a diamagnetic background of $-0.15 \mu \text{ emu/g}$, a value which is very similar to that of silver ($-0.180 \mu \text{ emu/g}$) and gold ($-0.143 \mu \text{ emu/g}$).

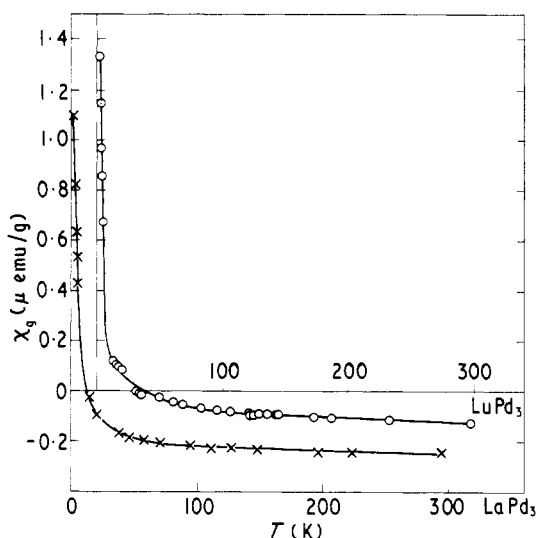


Figure 3. χ_g as a function of temperature for: \times LaPd₃; \circ LuPd₃. The ordinates are displaced in order to separate the curves.

3.2 CePd₃

The effective valency of the cerium atom in an alloy varies from 3 to 4 depending on the electronic state of the other component and on the atomic volume available for the cerium atom. The room temperature lattice spacings and magnetic susceptibilities of some fcc Pd–Ce solid solution alloys (Harris and Norman 1968) indicate that the cerium atoms have an effective valency of 4.0. However, in the ordered CePd₃ phase the lattice spacing indicates a valency of less than 4.0. A simple comparison of the room temperature lattice spacing of CePd₃ with those of other RPd₃ phases suggests a valency for cerium only slightly in excess of that of γ cerium (~ 3.1). Such a comparison however neglects the expansion of the palladium lattice due to the filling of the 4d states (Harris and Norman 1970) which results in a smaller contraction of the CePd₃ lattice as the result of a $3^+ \rightarrow 4^+$ change. If the lattice spacings of the solid solution alloys are extrapolated to the 25% Ce composition then a lattice spacing of 4.090 kX is obtained for CePd₃ with the Ce atoms in the 4^+ form. The lattice spacing for CePd₃ with Ce atoms in the 3^+ form can be obtained from the plot of a -spacing against the atomic diameter of the rare earth component, taking a diameter of 3.662 kX for 3^+ cerium (Speight *et al.* 1968).

Thus we calculate:

$$\text{Ce}^{4+}\text{Pd}_3 \quad a = 4.090 \text{ kX}$$

$$\text{Ce}^{3+}\text{Pd}_3 \quad a = 4.143 \text{ kX}$$

and observe

$$\text{CePd}_3 \quad a = 4.119 \text{ kX}$$

Assuming a linear variation of a -spacing with the cerium valency, then this lattice parameter corresponds to a valency of 3.45, that is, a configuration of $4f^{0.55}$. This behaviour can be contrasted with the lattice spacing data for the RIn₃ phases which clearly indicate a 3^+ state for cerium in the CeIn₃ phase (Harris and Rayner 1965 b). Furthermore the magnetic behaviour of CeIn₃ is consistent with Ce³⁺ the phase showing the theoretical value of μ_{eff} (Buschow *et al.* 1969).

Figure 4 shows the observed magnetic susceptibility of two samples of CePd₃ together with the theoretical behaviour of the free ion Ce³⁺. It can be seen that both the magnitude

and the temperature dependence of the susceptibility of both samples is much smaller than that of 3^+ cerium ions. On the other hand, if the cerium atoms were completely in the 4^+ state in CePd_3 a diamagnetic susceptibility close to that of ZrPd_3 ($-0.25 \mu\text{emu/g}$ Norman and Harris 1969) would be expected at room temperature. Thus the lattice spacing and the magnetic susceptibility data are consistent with the cerium atoms adopting an electronic configuration intermediate between 3^+ and 4^+ in the phase CePd_3 at room temperature, and hence require the f electrons to be described by a virtual bound state straddling the Fermi energy.

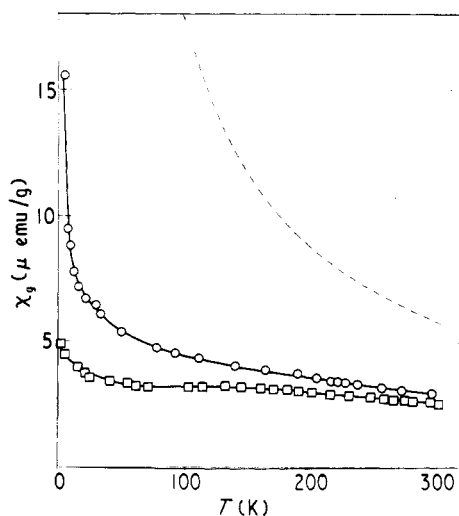


Figure 4. χ_g as a function of temperature for CePd_3 . \square Johnson-Matthey cerium; \circ 99.95% pure Koch-Light cerium; broken curve, Ce^{3+} free ion values.

The difference in the magnetic susceptibility of the CePd_3 samples prepared from Johnson-Matthey (JM) cerium ($a = 4.1195 \text{ kX}$) and Koch-Light (KL) cerium ($a = 4.1203 \text{ kX}$) is presumably accounted for by the presence of more rare earth impurities in the KL cerium. The susceptibility of the JM CePd_3 is almost independent of temperature below 200 K which suggests that the virtual bound state is non-magnetic in the Friedel-Anderson sense at low temperatures as it is in superconducting Th-Ce alloys (Huber and Maple 1970) and in cerium metal itself at pressures in excess of 10 kbar (MacPherson *et al.* 1971). In this respect it is also of interest to compare the susceptibility behaviour with that for isomorphous CeSn_3 , where the temperature dependence of the lattice parameter indicates that the cerium valence is increasing with decreasing temperature (Harris and Raynor 1965b). Here the susceptibility is found to increase slightly upon cooling, passing through a broad maximum below 200 K (Cooper *et al.* 1971). This behaviour has been associated with the magnetic to nonmagnetic transition of the $4f$ virtual bound state. On the other hand, isomorphous CePb_3 , like CeIn_3 , exhibits a linear temperature dependence of the reciprocal susceptibility down to low temperature consistent with Ce^{3+} (Cooper *et al.* 1971). Clearly, a delicate balance exists between the magnetic and non-magnetic state of the $4f$ virtual bound state of cerium, depending upon its occupation. A study of the susceptibility of these cerium compounds under pressure would be of considerable interest. Hutchens *et al.* (1971) have made susceptibility and resistivity measurements on CePd_3 and have suggested, alternatively, that a Kondo anomaly occurs.

Heat capacity measurements on CeSn_3 and CePb_3 indicate a very high density of states associated with the virtual bound state, relative to the corresponding La compounds (Cooper *et al.* 1971) with the magnetic state having the larger value. A similar situation

was also observed for metallic cerium from heat capacity measurements made at high pressure (Phillips *et al.* 1968). Thus, a comparison of the electronic heat capacities of CePd₃, LaPd₃, and ZrPd₃ could provide further useful information towards the understanding of these compounds.

3.3. PrPd₃ and NdPd₃

The inverse magnetic susceptibility of PrPd₃ and NdPd₃, corrected by $-0.15 \mu\text{emu/g}$ for the diamagnetism of the matrix are shown as a function of temperature in figures 5 and 6. χ_{gc}^{-1} can be seen to depend linearly on the temperature in the region from 50 to 250 K.

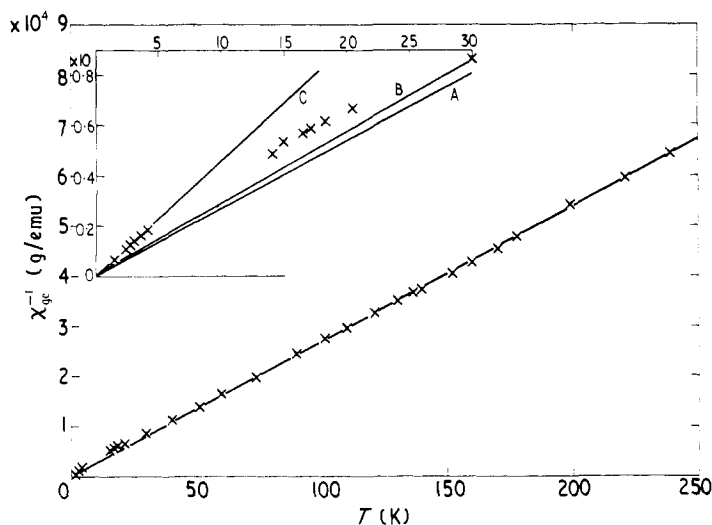


Figure 5. The reciprocal of the corrected gram susceptibility χ_{gc}^{-1} as a function of temperature for PrPd₃. The insert shows on an expanded scale the data below 30 K in relation to: A the line through the high temperature data; B the free ion slope; C the line from a Γ_5 ground state.

The values given in table 1 for the effective moments μ_{eff} and the Curie-Weiss temperatures θ have been derived from this linear region. Table 1 also shows, for comparison, the values obtained by Hutchens *et al.* (1971); within experimental error their quoted values of μ_{eff} and θ agree with ours except for HoPd₃. The inserts in these figures, which show the low temperature results on an expanded scale, reveal significant departures from the line drawn through the high temperature data. This behaviour suggests that the effects of a crystal field on the ground level are important but the onset of magnetic ordering is not indicated in either sample above 1.5 K. Butcher (private communication) has made magnetic measurements on PrPd₃ below 1 K and has observed the onset of antiferromagnetic ordering at 1.05 K). The inverse susceptibility of PrPd₃ shows no signs of becoming constant as in the isostructural PrIn₃ (Bushow *et al.* 1969) indicating that the ground state in PrPd₃, unlike PrIn₃ is not a singlet.

A useful summary of some basic data on the RPd₃ phases is given in table 2. The ground level given assumes that the rare earth ions behave as 3^+ . The energy of the first excited level in the lowest multiplet is taken from the table of experimental values given by Aarås and Colvin (1961), except for EuPd₃ where the value is our best value (see 3.4). The last column gives the susceptibility at 295 K calculated using the Van Vleck theory (1932) so as to include all the contributions from the lowest multiplet and should be compared with the simple ground level susceptibility given in column 7 of table 2. It can be seen that the higher levels modify the susceptibilities of PrPd₃ and NdPd₃ by only $\sim 2\%$ at 295 K because of

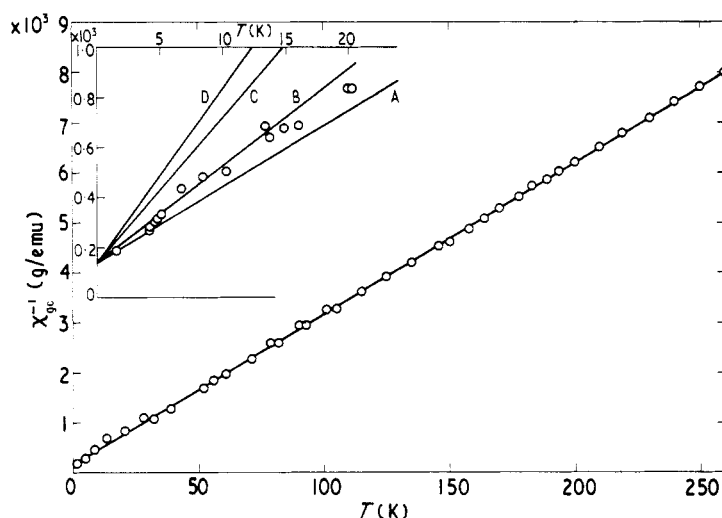


Figure 6. The reciprocal of the corrected gram susceptibility χ_{gc}^{-1} as a function of temperature for NdPd₃. The insert shows on an expanded scale the data below 20 K in relation to: A the line through the high temperature data, and the lines from the ground states: B $\Gamma_8^{(1)}$; C $\Gamma_8^{(2)}$; D Γ_6 converging at $T = 0$ K.

the relatively large energy separation of the first excited level and the strong paramagnetism of the ground level.

The degeneracy of the free ion ground level is removed by the crystalline field acting at each rare earth ion site in a manner determined by the symmetry of the charge distribution on its neighbours. In the RPd₃ structure the rare earth ions are situated at the corners of a simple cubic lattice, that is, each R ion has 6 R neighbours at a distance a , and the Pd ions are at the centres of the cube faces, so that each R ion has 12 Pd ions at a distance $a/\sqrt{2}$.

Table 2 Basic data on R Pd₃ compounds

RE	MW	4f ⁿ	Free ion Ground level	+ Crystal Field Ground state	$g_J \{J(J+1)\}^{\frac{1}{2}}$	χ_g^s (295) (μ emu/g)	Energy of 1st Excited level (K)	χ_g^{vv} (295) (μ emu/g)
La	458.1	0	1S_0	—	0	—	—	—
Ce	459.3	1	$^2F_{5/2}$	Γ_8	2.54	5.93	3242	6.03
Pr	460.1	2	3H_4	$\Gamma_5 (\Gamma_3)$	3.58	11.79	3124	12.00
Nd	463.4	3	$^4J_{9/2}$	$\Gamma_8^{(1)} (\Gamma_6)$	3.62	11.97	2918	12.33
Sm	469.6	5	$^6H_{5/2}$	Γ_8	0.85	0.644	1580	2.14
Eu	471.2	6	7F_0	—	0	0	477 (1250)	10.20
Gd	476.4	7	$^8S_{7/2}$	—	7.94	56.04	—	56.04
Tb	478.1	8	7F_6	$\Gamma_3 (\Gamma_5)$	9.72	83.77	2990	84.02
Dy	481.7	9	$^6H_{15/2}$	Γ_8	10.65	99.71	4605	—
Ho	484.1	10	5J_8	Γ_5	10.61	98.46	7267	—
Er	486.5	11	$^4J_{15/2}$	$\Gamma_6 (\Gamma_8)$	9.58	79.96	11500	—
Tm	488.1	12	3H_6	$\Gamma_3 (\Gamma_5)$	7.56	49.63	11900	—
Yb	492.2	13	$^2F_{7/2}$	$\Gamma_7 (\Gamma_8)$	4.54	17.72	14800	—
Lu	494.2	14	1S_0	—	0	—	—	—

(i) Crystal field states are based on point charge model with 12-fold co-ordination of negative charges or 6-fold co-ordination of positive charges. State given first would be lowest if only 4th degree term were present. 1. and 2 are non-magnetic singlets, 3 is a non-magnetic doublet, 4 and 5 are triplets with isotropic splitting factor and behave like $S = 1$, 6 and 7 are doublets (isotropic), 8 is a complex quartet.

(ii) The value in brackets for Eu in column 7 is the energy of the second excited level.

Thus each rare earth ion is at a site of cubic point symmetry in 12 fold co-ordination with the nearest Pd ions and 6 fold co-ordination with the nearest R ions. The splitting of the ground level is determined by the sign and magnitude of the charge at the neighbouring sites (Lea *et al.* 1962). In the case of Pr, if a point charge model is applicable and the crystalline field from the Pd ions predominates, the ground state becomes Γ_5 or Γ_3 , depending on the ratio of the fourth- to sixth-order terms, if the Pd ions are negatively charged and Γ_1 if the Pd ions are positively charged (Low and Offenbacher 1965). On the other hand if the crystalline field from the 6 neighbouring R³⁺ ions predominates the ground state will again be Γ_5 or Γ_3 (Lea *et al.* 1962). The states Γ_1 and Γ_3 are non-magnetic whereas Γ_5 is magnetic. The low temperature magnetic behaviour of PrPd₃ (see insert) clearly indicates that Γ_5 is the lowest state, that is, the fourth order term predominates and either the Pd ions are negatively charged or the crystal field from the rare earth neighbours is predominant, the latter being the more probable.

Bushchow *et al.* (1969) have considered the crystalline field effect in PrIn₃ from all lattice sites within 10 Å of a Pr³⁺ ion. They have assumed the presence of a positive point charge $Z = +3e$ at both the Pr and In sites. They state that the charges at the Pr sites give rise mainly to fourth-order contributions but that the indium sites give rise to both fourth- and sixth-order contributions. Clearly in PrIn₃ the contributions from the indium sites predominates so that Γ_1 is lowest. Buschow *et al.* (1969) were unable to determine the overall crystal field splitting Δ from the susceptibility data alone since it depends on the ratio of the fourth- to sixth-order terms. However, they concluded that it probably lies between 172 and 394 K. Clearly the weaker positive, or possibly negative charge at the Pd site accounts for the completely different low temperature magnetic properties of PrIn₃ from PrPd₃. We estimate that the crystal field splitting is about 100 K in PrPd₃.

The observation given above for Pr that a 12-fold co-ordination of negative charges produces the same ground state from the free ion J manifold as a 6-fold co-ordination of positive charges is in fact true for all of the rare earth ions. (Bleaney 1964). However, in the point charge model the ratio of the sixth to the fourth order term is 6.5 times as large for the 12-fold co-ordination compared with 6-fold co-ordination. Thus a detailed analysis of the states would resolve the kind of crystal field present but this is not possible from magnetic measurements alone.

Magnetic measurements give information about the ground state and in table 2 column 5 we list the ground states determined from a point charge model for a 12-fold co-ordination of negative charges (or 6-fold co-ordination of positive charges). Any modification to these states caused by the predominance of the sixth-order term over the fourth-order term is given in brackets.

In the insert in figure 6 the magnetic behaviour of $\Gamma_8^{(1)}$, $\Gamma_8^{(2)}$ and Γ_6 (the superscripts refer to the states given by Lea *et al.* 1962) are indicated. It can be seen that at low temperatures the behaviour is closer to $\Gamma_8^{(1)}$ than Γ_6 suggesting that the fourth-order terms are more important in NdPd₃ than the sixth-order ones. The observed points for NdPd₃, unlike PrPd₃, do not tend to pass through 0 K suggesting the presence of a small anti-ferromagnetic exchange interaction in NdPd₃.

3.4. SmPd₃ and EuPd₃

The magnetic behaviour of SmPd₃ is determined not only by the effects of the crystal field on the ground level but also by the structure of the lowest multiplet (⁶H). The positions of the levels corresponding to different values of J within the lowest multiplet of Sm³⁺ are given in table 3 (Gobrecht 1937). These levels are split by the crystal field. The point charge model for a 12-fold co-ordination of negative charges predicts that ⁶H_{5/2} will split into $\Gamma_8 + \Gamma_7$ (only a fourth degree term is involved) and ⁶H_{7/2} into $\Gamma_8 + \Gamma_7 + \Gamma_6$. In the insert in figure 7 the Curie-Weiss type behaviour from the free ion, pure Γ_8 and pure Γ_7 ground states is illustrated. It can be seen that the low temperature data clearly reject a Γ_7 ground state in agreement with the predictions of the point charge model. Furthermore,

Table 3 Energy levels of the lowest multiplet (⁶H) of Sm³⁺

J	5/2	7/2	9/2	11/2	13/2	15/2
E (K)	0	1580	3310	5180	7200	9500

these experimental results show that it is necessary to include the effects of a small exchange interaction. The molecular field approximation using only the spin-dependent contribution has been applied and in figure 7 the experimental results are compared with a calculated curve. The calculated curve shown corresponds to the level separations given in table 3, a crystal field splitting of 150 K between Γ_8 and Γ_7 in the lowest level and zero in the second level and exchange equivalent to a Curie-Weiss θ of -3 K.

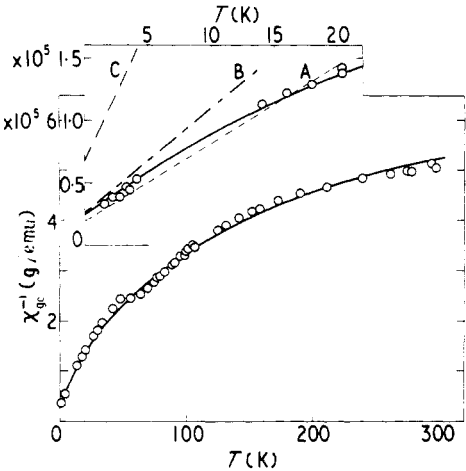


Figure 7. The reciprocal of the corrected gram susceptibility χ_{gc}^{-1} as a function of temperature for SmPd₃. The curves line through the points has been calculated. The insert shows on an expanded scale the data below 20 K in relation to the calculated curve and Curie-Weiss ($\theta = -3$ K) lines for: A the free ion; B a Γ_8 ground state; C a Γ_7 ground state.

Mössbauer measurements (Wickman *et al.* 1968, Harris and Longworth 1971) and lattice parameter measurements (Harris and Raynor 1965a) indicate that europium is present as Eu³⁺ in EuPd₃. The lowest multiplet is therefore ⁷F and some previously determined values of the energies of the seven levels are given in table 4. The lowest level is a singlet

Table 4 Energy levels (in K with reference to ⁷F₀) of the lowest multiplet (⁷F) of Eu³⁺

J/E	1	2	3	4	5	6	A (K)
(i)	430	1580	2730	4170	5610	7340	-2.81
(ii)	460	1350	2590	4100	5740	7340	-1.06
(iii)	480	1330	2590	4100	5750	7340	0.19
(iv)	530	1610	2890	4330	5793	7375	3.57
(v)	477	1330	—	—	—	—	0
(vi)	477	1250	—	—	—	—	0

- (i) Gobrecht (1937) values determined from spectroscopic measurements.
- (ii) Judd (1956) calculated values.
- (iii) Van Vleck (1947) values are based on a minor extrapolation from the spectroscopically determined levels of Sm³⁺.
- (iv) Chang and Gruber (1964) optically determined values.
- (v) and (vi) see text.

so that the magnetic behaviour of EuPd₃ is determined mainly by the energies of the excited levels. A crystal field has no effect on ⁷F₀ or ⁷F₁ but a fourth-degree field would split ⁷F₂ into $\Gamma_3 + \Gamma_5$. This splitting would have a small effect only on the results at our highest temperatures and will not be considered. Thus although the effect of the crystal field on the magnetic susceptibility may be neglected the modification due to the exchange interaction could be important.

The magnetic behaviour of Eu³⁺ has been considered previously by Arais and Colvin (1964) for the compound Eu₂O₃. They used the energy levels derived by Judd (1956) (line (ii) table 4) and obtained excellent agreement with their data from 300 to 1300 K. However, at $T = 0$ K the observed value is $\sim 25\%$ larger than the value calculated from these levels. Huang and Van Vleck (1969) invoked roughly equal contributions from the effects of a crystalline field (assuming lattice distortion) and isotropic exchange effects in order to explain the discrepancy. The magnetic behaviour of europium metal, on the other hand, has not, as yet, received a satisfactory explanation (Bozorth and Van Vleck 1960, Colvin *et al.* 1961).

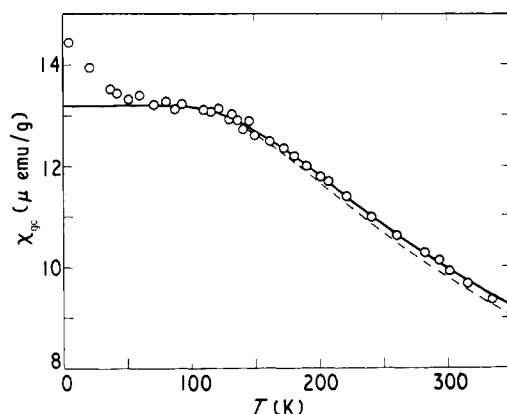


Figure 8. The corrected gram susceptibility of EuPd₃ as a function of temperature. Experimental values, O. Calculated values from table 4: broken curve, column (v); full curve, column (vi).

It is interesting to compare our experimental measurements made up to 340 K (figure 8) with theory. Now the susceptibility is given by (Wolf and Van Vleck 1960, De Wijn *et al.* 1967)

$$\chi = \chi_0 + \chi_{ex} \quad (1)$$

$$\chi_0 = \frac{N\mu_B^2}{\sum \exp(-E_J/kT)} \sum_J \left(\frac{g^2 J(J+1)}{3kT} + \alpha \right) (2J+1) \exp(-E_J/kT) \quad (2)$$

$$\chi_{ex} = \frac{2N\mu_B^2}{\sum \exp(-E_J/kT)} \times \frac{\left[\sum_J \{g(g-1)J(J+1)/(3kT) + \alpha\} (2J+1) \exp(-E_J/kT) \right]^2}{1 - \{2A/\sum \exp(-E_J/kT)\} \sum_J \{(g-1)^2 J(J+1)/(3kT) + \alpha\} (2J+1) \exp(-E_J/kT)} \quad (3)$$

E_0, E_1 are the energies (in K) of ⁷F₀ and ⁷F₁, and A (in K) is related to the spin dependent exchange interaction. (The effects of the crystalline field on ⁷F₁, considered by Huang and

Van Vleck (1969) have been neglected since we are assuming cubic symmetry). At $T = 0$ K the expressions (2) and (3) become

$$\chi_0 = \frac{8N\mu_B^2}{k(E_1 - E_0)} = \frac{3}{E_1 - E_0} \quad (4)$$

$$\chi_{ex} = \frac{128N\mu_B^2 A}{k^2(E_1 - E_0)^2} = \frac{48A}{(E_1 - E_0)^2} \quad (5)$$

An examination of the contributions to the susceptibility at 350 K shows that it is almost entirely determined by the energies of the levels 7F_0 , 7F_1 and 7F_2 with 77% of the susceptibility originating from 7F_0 and 7F_1 .

Since the ground level (7F_0) is a singlet a temperature independent susceptibility is expected at low temperatures. The experimental points on the other hand show that χ_{gc} is still increasing at the lowest measured temperature. We ascribe this increase below 50 K to either the presence of Eu^{2+} or other rare earth ion impurities in the sample. The increase would correspond to 0.1% of the europium ions being divalent. On correcting the data for this contribution the remaining χ is temperature independent below 90 K and has a value of $13.20 \mu \text{ emu/g}$ at 0 K. From this value and equations (1), (4) and (5) A may be calculated if we substitute published values of $E_1 - E_0$ (table 4 (i)–(iv)) or alternatively A may be assumed to be zero and $E_1 - E_0$ determined (table 4(v) (vi)). From the value of θ obtained for GdPd_3 we would not expect A to exceed 0.5 K, which puts the energy of 7F_1 at 477 ± 10 K, relative to 7F_0 .

Using equations (1)–(3) and these calculated values of A all the given energy schemes table 4 (i)–(iv) produce calculated susceptibilities which are too low at room temperature. By lowering the energy of 7F_2 a good fit with the data can be obtained from all of the energy schemes. Since the data is incapable of resolving between the various energy schemes modified by exchange we do not show all the calculated curves. Indeed the effects of exchange are so small that an equally good fit to the data may be made with zero exchange interaction, by adjusting the energy of 7F_2 . Two such calculated curves using the energy schemes (v) and (vi) are shown in figure 8. These curves clearly demonstrate the effects on the high temperature results of a small change in the energy of 7F_2 .

3.5. GdPd_3

The inverse corrected magnetic susceptibility of GdPd_3 passes through a clear minimum value at 7.5 ± 0.5 K as shown in figure 9 insert (i), suggesting the onset of antiferromagnetism. The straight line drawn through the results obtained above this temperature (see the main figure) leads to values of $\mu_{\text{eff}} = 8.03$ and $\theta = 1.5 \pm 1.0$ K (table 2). The magnetization behaviour has been investigated in fields up to 43 kOe at 4.2 K and in three fields at 1.5 K and the results are shown in figure 9 insert (ii). It can be seen that there is only a slight increase in magnetization with decrease of temperature from 4.2 K to 1.5 K in the three fields examined. For comparison with these results the Brillouin function at 4.2 K (see A) and 1.5 K (see B) are also plotted. It can be seen immediately that the magnetization behaviour of GdPd_3 , particularly at 1.5 K, is strongly depressed below that expected from the Brillouin function suggesting the presence of an antiferromagnetic exchange interaction. Despite the fact that Hutchens *et al.* (1971) obtain values of μ_{eff} and θ which agree closely with the above values there is a considerable discrepancy in the results obtained at low temperatures. Hutchens *et al.* (1971) report measurements below 25 K in a field of 400 Oe and below 200 K in a field of 19 kOe. The magnetization values in 400 Oe at all temperatures and in 19 kOe down to 4 K are larger than those calculated from the Brillouin function, by a factor of two at 20 K and four at 10 K in 400 Oe and by $\sim 50\%$ at 10 K in 19 kOe. One would have anticipated that the value in 19 kOe at ~ 2.5 K would have

closely approached the saturation value of ~ 39100 emu/mol yet it is marked low, even lying below the Brillouin value. We think that the somewhat excessive values in 400 Oe indicate the presence of a ferromagnetic impurity in their sample (see § 2).

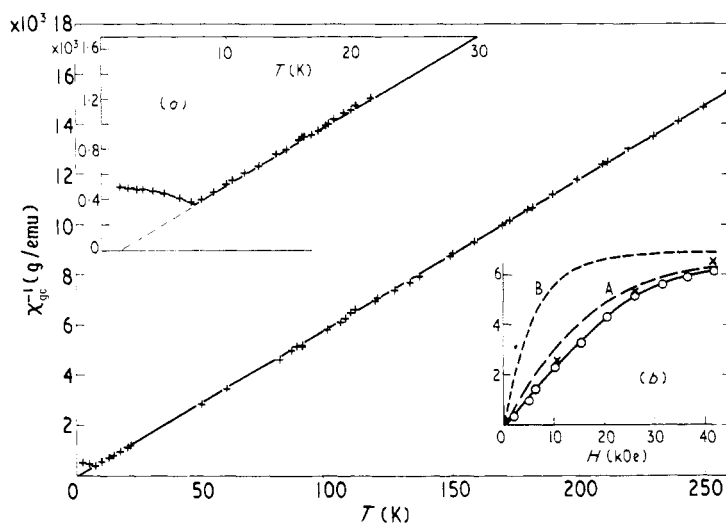


Figure 9. The reciprocal of the corrected gram susceptibility χ_{gc}^{-1} of GdPd₃ as a function of temperature. Insert (a) shows the behaviour below 30 K on an expanded scale. Insert (b) shows the magnetization (in $\mu_B/\text{Gd atom}$) at ~ 4.2 K: $\times 1.5$ K; as a function of applied field. Curves A and B represent the Brillouin function at 4.2 K and 1.5 K respectively.

This disagreement in low temperature magnetization results shows that the samples of GdPd₃ prepared in the two laboratories are different and that the difference may be due to the presence of a significant amount of impurity phase with a Curie temperature ~ 20 K in the sample of Hutchens *et al.* (1971). As stated previously (see § 2) we have measured several samples of GdPd₃ obtained from different preparations and our results have proved consistent.

3.6. TbPd₃

The inverse corrected magnetic susceptibility of TbPd₃ as a function of temperature from 1.3 – 250 K is shown in figure 10. The results above 5 K can be fitted by a straight line corresponding to $\mu_{eff} = 9.61$ and $\theta = 1 \pm 1$ K. Below 5 K (see insert in figure 10) the inverse susceptibility becomes nearly constant and it is possible that there is a shallow minimum. This behaviour fails to distinguish between the alternatives of the onset of antiferromagnetism below 5 K or the effects of a crystal field. The latter can readily account for the observed behaviour since the point charge model predicts (Lea *et al.* 1962) that, provided the 4th degree is predominant, the order of states will be $\Gamma_3 + \Gamma_5^{(1)} + \Gamma_2 + \Gamma_3^{(2)} + \Gamma_4 + \Gamma_1$ with the lowest state being the non magnetic doublet Γ_3 . Thus at very low temperatures the inverse susceptibility will become constant. However, if the overall splitting in the crystal field is small (~ 100 K) the close proximity of the magnetic triplet $\Gamma_5^{(1)}$ would permit the observed appearance of temperature dependent behaviour by 4 K. A comparison of the minima observed in GdPd₃ and TbPd₃ suggests that the crystal field explanation may be the more appropriate. However, Mössbauer measurements (Longworth, private communication) on an alloy containing 1 at % tin show that TbPd₃ is ordered below ~ 5 K.

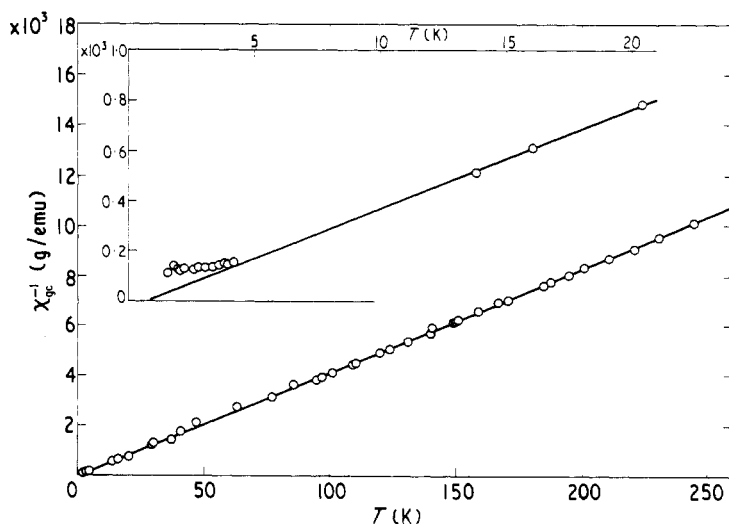


Figure 10. The inverse gram susceptibility χ_{gc}^{-1} of $TbPd_3$ as a function of temperature. The insert shows the behaviour below 20 K on an expanded scale.

3.7. $DyPd_3$, $HoPd_3$ and $ErPd_3$

The inverse corrected susceptibilities of $DyPd_3$, $HoPd_3$ and $ErPd_3$ as functions of temperature are shown in figure 11. All of the data obtained for $DyPd_3$ above 1.5 K can be fitted by a straight line corresponding to $\mu_{eff} = 10.51$ and $\theta = 0 \pm 1$ K. There is no evidence of either antiferromagnetism or crystal field effects. However, the latter may be present since the point change model predicts that the lowest state will be the complex magnetic quartet $\Gamma_8^{(3)}$ with $\Gamma_8^{(2)}$ in close proximity. If the overall crystal field splitting is small the scatter in the data may well obscure the effects of a crystal field in this particular case.

The data for $HoPd_3$ above 15 K can be fitted by a straight line corresponding to $\mu_{eff} = 10.38$ and $\theta = 0 \pm 1$ K. Below 15 K the data departs from the straight line in a manner suggesting that the effects of the crystal field are important. The point change model predicts that the lowest state will be $\Gamma_5^{(1)}$ with the non-magnetic $\Gamma_3^{(1)}$ as the nearest state. Thus, the effect of the crystal field is expected to be more evident for this phase.

The data for $ErPd_3$ above 3 K can be fitted by a straight line corresponding to $\mu_{eff} = 9.40$ and $\theta = 0 \pm 1$ K. Below 3 K the data appears to deviate significantly from the straight line suggesting the presence of crystal field effects. For Er^{3+} the point change model predicts that the lowest state will be Γ_6 but $\Gamma_8^{(3)}$ will be in close proximity. Thus one would expect smaller effects for $ErPd_3$ than $HoPd_3$ but bigger than for $DyPd_3$. These qualitative conclusions are in agreement with the data.

3.8. $TmPd_3$ and $YbPd_3$

Measurements on these two systems have so far been unsatisfactory. The samples have either contained more than one phase, sometimes with a high ferromagnetic ordering temperature as in the case of $TmPd_3$ or proved deficient in the rare earth element due to large losses from evaporation when melting as in $YbPd_3$. The results on $YbPd_3$ however clearly show a well-defined moment on the Yb atoms which is consistent with the 3^+ state of Yb in this phase indicated by the lattice spacing results (Harris and Raynor 1965a). It is unfortunate that the samples of these two phases have proved unsatisfactory, as it would

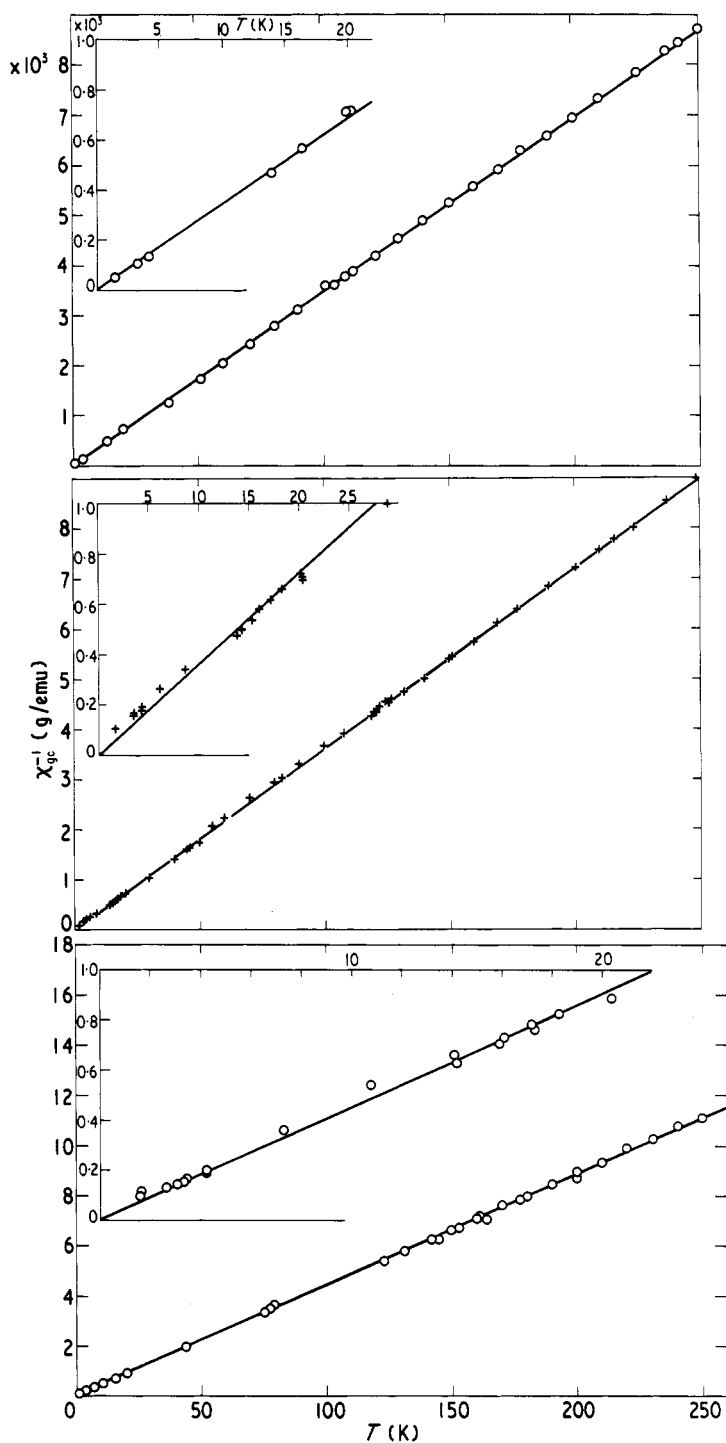


Figure 11. The inverse corrected gram susceptibilities χ_{gc}^{-1} of (a) DyPd₃; (b) HoPd₃; (c) ErPd₃ as functions of temperature. The inserts show the behaviour below 20 K on an expanded scale for DyPd₃ and ErPd₃ and below 30 K for HoPd₃.

have been valuable to compare the results on these two systems with the other compounds. However, Bucher, Andres and Cooper (to be published) have prepared a sample of TmPd_3 and observed that it becomes antiferromagnetic at $T_N = 0.20$ K and Hutchens *et al.* (1971) have obtained values of μ_{eff} for TmPd_3 and YbPd_3 which are close to the theoretical values and low values of θ (see table 1).

4. Discussion

The magnetic behaviour of the RPd_3 compounds clearly shows that the effects of the crystal field are stronger than the magnetic interactions. In fact, the magnetic interactions are almost an order of magnitude weaker than in any other rare earth Cu_3Au type compound investigated. Thus compare the susceptibility measurements (Buschow *et al.* 1969) and neutron diffraction measurements (Arnold and Nereson 1969, Olsen *et al.* 1970, Nereson and Arnold 1970) which have shown that the Néel temperatures of DyIn_3 , TbIn_3 , HoIn_3 , DyPt_3 , TbPt_3 and DyTi_3 are 24, 37, 11.5, 13, 20.5 and 11 K respectively.

Buschow *et al.* (1969) showed that the variations in Néel temperature and Curie-Weiss θ as a function of atomic number for the RIn_3 compounds was similar to the de Gennes factor $(g - 1)^2 J(J + 1)$. This factor was derived (de Gennes 1962) from a molecular field treatment of the Ruderman and Kittel (1954) coupling between the rare earth moments and a system of conduction electrons, and we would have anticipated that this would be the origin of the predominant exchange interaction in the RPd_3 compounds. However, it is immediately obvious that this description does not fit the behaviour of either T_N or θ as a function of atomic number. This is perhaps not surprising since in a series where the exchange interaction is low the crystal field will have modified the ground state to such an extent that a free ion approximation will be invalid. Nereson and Arnold (1970) stated that the RPt_3 compounds varied according to the de Gennes factor on the basis of the Néel temperatures of TbPt_3 and DyPt_3 respectively, which were roughly 0.5 of the values for the corresponding RIn_3 compounds. However the much stronger exchange interaction for these RPt_3 compounds may account for this differing behaviour from the RPd_3 compounds.

Of more fundamental interest is the question of why the exchange interaction is so low for the RPd_3 series. This may be directly connected with the band structure of these compounds. The diamagnetic susceptibility of YPd_3 , LaPd_3 and LuPd_3 indicates that there can be very few d electrons at the Fermi surface and thus the d-band of palladium must be filled. The d states associated with the rare earth atoms are presumably sufficiently removed in energy that the three valence electrons from the rare earth atoms are associated with broad s-p bands so that the resulting density of states is small and comparable with that of silver†, and the Pauli paramagnetism is compensated by the diamagnetism of the core electrons. It seems reasonable therefore to conclude that these compounds have such a weak interaction because there is a very low density of states. Specific heat measurements on this series would undoubtedly provide a useful check on this suggestion. An alternative explanation may simply be that the indirect exchange interaction is low in these compounds. Thus the magnitude and sign of the interaction depends on the lattice spacing and the number of conduction electrons/atom. However, a worthwhile estimate of its magnitude for the RPd_3 compounds calls for detailed knowledge of the Fermi surface, which is unfortunately not available. If a spherical Fermi surface is assumed then a free electron analysis, similar to Mattis (1965), to calculate θ (or T_N) as a function of the number of conduction electrons predicts low values of θ for about 0.75 conduction electrons/atom.

Errors in the observed value of μ_{eff} are due to errors in composition as well as measurement. We estimate an overall error of $\leq 2\%$. By comparing the values of μ_{eff} in table 1 and table 2 it can be seen that there is no significant departure of the observed value of μ_{eff}

† In the CsCl type RAg compounds the exchange interaction is large and follows the de Gennes factor (Pierre 1970).

from the theoretical value indicating that crystal field effects are not significant in the temperature range from which μ_{eff} has been deduced and also that any conduction electron polarisation is less than 1%.

It should be possible to determine the complete energy level diagram and hence deduce the crystal field parameters from the inelastic neutron spectra (Turberfield *et al.* 1971). Such measurements are already in progress (Wedgwood private communication).

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Note added in proof. Specific heat measurements (J M Machado da Silva, private communication) reveal a well defined magnetic anomaly in TbPd₃ at 3.8 K.

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