Some selected results of the force constant calculations are summarized in Table III. These are not a unique set of force constants because of the many interactions that were set equal to zero and because of the arbitrary selection of a value for F_{34}. Claassen[6] has suggested using the value of F_{34} which gives a minimum value of F_{44}. However, we see no special need for this selection and have chosen to use the lowest positive value of F_{34} which gives real solutions. In Table III, values calculated for ν_6, assuming $F_{66} = F_{44}$, are also tabulated.

With a few exceptions, there are regular decreases in the force constants with increasing ion size. If pairs of isoelectronic ions are compared, it is apparent that the doubly charged ion has weaker bond-stretching and bond-bending constants than the singly charged ion. For AsF_6^- and GeF_6^{2-}, the values of f_r are lower than expected and the values of $f_{rr'}$ (opposite bond interactions) are higher. Thus it seems that, for these ions in which the fluorine atoms are beginning to overlap, there is interaction between opposite bond stretching motions which decreases the value of f_r and increases that of $f_{rr'}$. This interaction "through" the central metal ion is smaller for both the smaller and the larger ions.

Table III

Force Constants for Hexafluoride Ions (mdynes/A)

Ion	f_r	f_{rr}	$f_{rr'}$	f_α/r_0^2	$f_{\alpha\alpha}/r_0^2$	$(f_{r\alpha} - f_{r\alpha'})/r_0$[a]	ν_6 (calcd),[b] cm^{-1}
PF_6^-	4.12	0.43	0.50	0.90	0.13	0.32	402
AsF_6^-	3.72	0.26	0.50	0.58	0.10	0.00	322
SbF_6^-	3.83	0.25	0.16	0.48	0.12	0.00	294
SiF_6^{2-}	3.01	0.40	0.33	0.68	0.02	0.24	347
GeF_6^{2-}	2.71	0.31	0.40	0.47	0.08	0.00	289
SnF_6^{2-}	2.77	0.23	0.24	0.36	0.09	0.00	252

[a] Value assumed. [b] Calculated assuming $F_{66} = F_{44}$.

Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania 15213

Magnetic Properties of Intermetallic Compounds between the Lanthanides and Platinum

By W. E. WALLACE and Y. G. VLASOV[1]

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The magnetic properties are reported for a series of intermetallic compounds designated by the formula $LnPt_2$ in which Ln represents Pr, Nd, Gd, Tb, Dy, Ho, or Er. All have the C15 ($MgCu_2$) structure. Emphasis was placed on the paramagnetic region. The effective moment (μ_{eff}) for the paramagnetic $LnPt_2$ compounds is fairly close to $g\sqrt{J(J + 1)}$, the value for the free tripositive Ln ion. In $GdPt_2$ μ_{eff} exceeds this by about 2%, which is ascribed to conduction electron polarization effects. The measured μ_{eff} values indicate that Pt in the $LnPt_2$ series is nonmagnetic. Curie–Weiss behavior is observed at all temperatures down to the Curie temperature indicating a relatively weak crystal field interaction. The low moment observed for the samples in the ferromagnetic state is ascribed to failure to achieve saturation. All except $PrPt_2$ become ferromagnetic at 4.2°K. $PrPt_2$ may be a Van Vleck paramagnet at this temperature.

I. Introduction

This study is concerned with the series of intermetallic compounds represented by the formula $LnPt_2$, in which Ln is one of the seven lanthanide elements mentioned in the abstract.[2] The magnetic behavior of this group of compounds was studied earlier by Crangle and Ross,[3] but their attention was confined to the ferromagnetic state. Certain of their observations (*vide infra*) have made it desirable to extend the work to include the paramagnetic region. The present study was largely concerned with that aspect of the $LnPt_2$ compounds and in this sense parallels the work of Farrell and Wallace[4] on the isostructural and chemically similar $LnNi_2$ and $LnCo_2$ series.

Ross and Crangle[3] observed that the moment per formula unit of $LnPt_2$ in the ferromagnetic state was consistently less than gJ, the moment of the free tripositive Ln ion. Since the platinum ion is without moment in the element, it is generally assumed to be nonmagnetic in intermetallic compounds. Thus in the $LnPt_2$ compound the lanthanide is regarded as supplying all of the moment. The discrepancy between the measured moment and gJ in all cases except $GdPt_2$ was ascribed by Crangle and Ross to the quenching effect of the crystalline field. For $GdPt_2$ there was a smaller difference which, of course, cannot be ascribed to this effect. Crangle and Ross attributed it to antiferromagnetic spin polarization of the conduction electrons—that is, net spin of the conduction electrons in opposition to the spin associated with the 4f shell of the Gd ion.

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[1] Participant in the United States–Soviet Union Cultural and Education Exchange Program and on leave from the University of Leningrad, USSR.

[2] Sm and Tm, which are usually included in such studies, were omitted because their volatility is such as to render the making of the high-melting platinum compounds very difficult. Eu and Yb are normally divalent in the metallic state and hence were omitted from this study which was concerned with tripositive lanthanides.

[3] J. Crangle and J. W. Ross, "Proceedings of the International Conference on Magnetism at Nottingham," Institute of Physics and the Physical Society, London, 1964, p 240.

[4] J. Farrell and W. E. Wallace, *Inorg. Chem.*, **5**, 105 (1966).

While most of the interpretations of the reduced moments of intermetallic compounds entail the notion of substantial crystal field quenching of the lanthanide moment,[3-11] certain experiments indicate the contrary. Bulk magnetic measurements give low moments for $DyNi_2$ and $DyNi_5$, whereas Dy^{161} Mössbauer measurements[12,13] on these two compounds indicate the free ion moment (*gJ*) for Dy. In contrast with these findings neutron diffraction measurements show definite quenching of the lanthanide moment in a number of cases, for example, in $NdCo_2$,[14] in $ErMn_2$, $TmMn_2$, and $TbNi_2$,[15] and in $LnIr_2$ compounds.[16] In view of the contradictory evidence derived from Mössbauer spectroscopy and neutron diffraction work, it is not possible to decide *a priori* whether or not the lanthanide in an intermetallic compound carries the free ion moment. In view of this it was not clear when the present investigation was begun whether the low moments observed by Crangle and Ross for the $LnPt_2$ compounds originated with low Ln moments or with Ln moments which were normal but coupled antiferromagnetically to moment-carrying Pt ions. These two possibilities should be distinguishable by magnetic susceptibility (χ) measurements in the paramagnetic region. If the low moments are a crystal field effect, predictable deviations from Curie–Weiss behavior will occur. The nature of the deviations, the details of which have been discussed elsewhere,[4,9,17] are specific with the particular lanthanide. If the low moment is due to ferrimagnetism, the effective moment obtained from the temperature dependence of χ will contain a contribution from platinum and will hence exceed that expected of the lanthanide component alone. The susceptibility work described below was undertaken to clarify the situation as regards the $LnPt_2$ compounds. This aspect of the work of course involved the paramagnetic region. Since the technique in all cases involved cooling to liquid helium temperatures, where the $LnPt_2$ compounds are ferro- (or possibly ferri-) magnetic, and making measurements as the sample warmed to room temperature, data for the ferromagnetic region were also obtained. These new data are also presented and compared with those obtained by Crangle and Ross.[3]

II. Experimental Section

Samples were prepared using techniques that are now standard for these kinds of materials.[4,18,19] Stoichiometric proportions of the component metals were fused together in high-purity Magnorite crucibles under high-purity argon. The samples were examined by standard X-ray diffraction techniques to confirm the existence of a single-phase material. Preliminary experiments showed that the compound with the C15 structure[20] ($MgCu_2$ structure) developed immediately from the melt and that annealing or further heat treatment, such as is required for the LnT_2 compound with T = Fe, Co, or Ni, is unnecessary. (From this it can be inferred that the $LnPt_2$ compounds melt congruently whereas the $LnNi_2$, etc., compounds form peritectically.) Platinum was obtained from Engelhard Industries and was of purity 99.9+%. The lanthanides (99.9% pure by the supplier's claims) were the best grades available commercially and were obtained from Research Chemicals.

The magnetic measurements were made using equipment and techniques that have been described.[4,21] Applied fields up to 21 koersteds were employed in obtaining saturation magnetizations in the ferromagnetic region. Measurements were extrapolated to infinite field by a Honda plot (magnetization varying linearly with the reciprocal of the effective field).

III. Results and Discussion

The data shown in Figures 1–4 are representative of the measurements made. Results obtained for all seven compounds were generally similar except that saturation is more rapidly approached for $GdPt_2$. The Gd compound is magnetically softer than the other compounds since Gd is in an S state and hence is essentially free of magnetocrystalline anisotropy. From Figures 1–3 it is clear that χ for the $LnPt_2$ compounds at room temperature is independent of field.

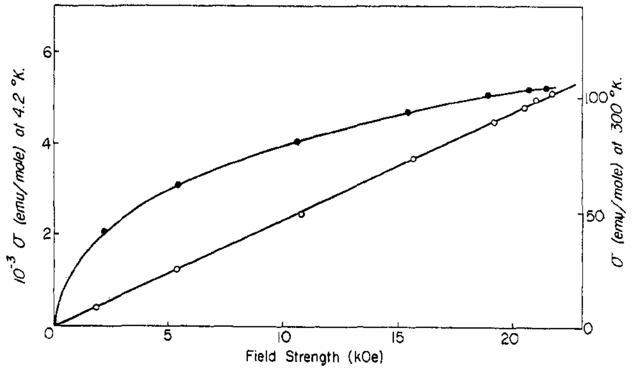

Figure 1.—Magnetization (σ) *vs.* applied field for $PrPt_2$ at 4.2°K (●) and 300°K (○).

Curie–Weiss behavior is observed for all compounds above the Curie temperature. For $PrPt_2$, but not for the others, the magnetization measured at 4.2°K leads to a χ in agreement with that expected from the Curie–Weiss plot (see Figure 4). From this it appears that at 4.2°K the Pr compound, like $PrNi_2$, may not be ferromagnetic but instead may be a Van Vleck paramagnet. It has recently become clear that these paramagnets show saturation effects[10,22] such as are indicated in the liquid helium data in Figure 1. Thus the use of the data to derive a Curie temperature[23] while

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(23) The procedure employed is the customary one of extrapolating a (magnetization)^2 *vs.* temperature plot to zero magnetization.

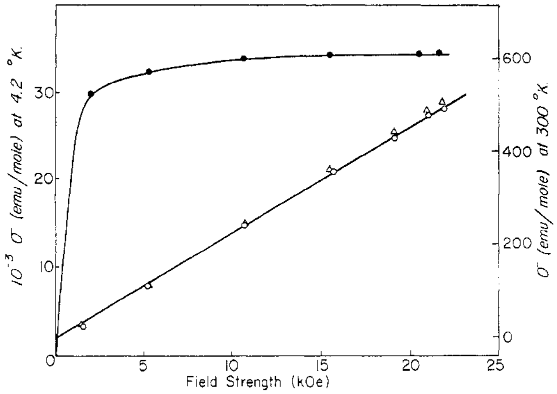

Figure 2.—Magnetization (σ) *vs.* applied field for $GdPt_2$ at 4.2°K (●) and two samples at 300°K (○, △).

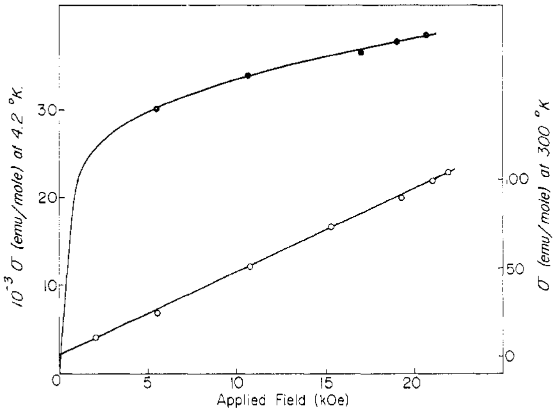

Figure 3.—Magnetization (σ) *vs.* applied field for $HoPt_2$ at 4.2°K (●) and 300°K (○).

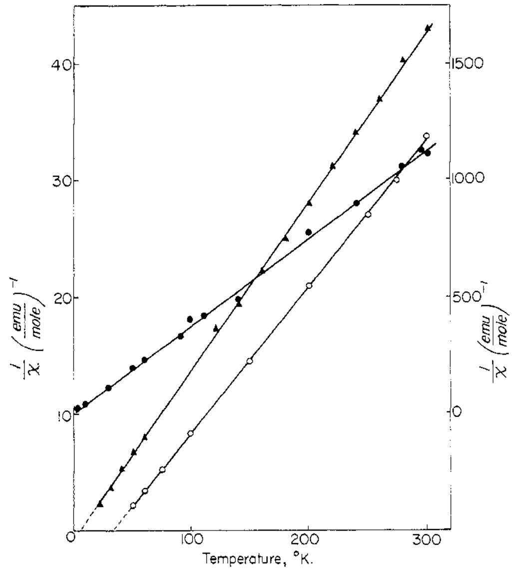

Figure 4.—Inverse susceptibility *vs.* temperature for $PrPt_2$ (●), $GdPt_2$ (○), and $HoPt_2$ (▲). The scale at the right applies to $PrPt_2$; that at the left to the other two compounds. For $HoPt_2$ $2(1/\chi)$ has been plotted.

formally indicating a transition temperature of reasonable magnitude may actually be unwarranted for $PrPt_2$. The other compounds are free of this complication and clearly become ferromagnetic (or possibly ferrimagnetic) at 4.2°K.

Derived data for all of the $LnPt_2$ compounds are given in Table I. For the ferromagnetic region the results are in accord with the observations of Crangle and Ross in that the measured moments are well below gJ, the value for the free tripositive ion. However, the two sets of measurements in most instances differ appreciably. This may reflect the different modes[24] of preparation of the samples which in previous studies of lanthanide intermetallics have been observed to influence their magnetic behavior.[4,25,26]

The effective moment in the paramagnetic region is close to that expected for a free Ln^{3+} ion in all cases. The measured moment exceeds the free ion moment only for $GdPt_2$. However, in this case μ_{eff} is well within the range of effective moments observed for elemental Gd,[27] Gd solid solution systems,[27–29] and Gd intermetallics in which it is certain the partner metal is nonmagnetic. GdAg is an example of the latter. For it Walline and Wallace observed[18] an effective moment of 8.57 μ_B. It is generally believed that the excess Gd moment over 7.94 μ_B in such cases results from conduction electron effects.[30] Comparison of the measured μ_{eff} with $g\sqrt{J(J+1)}$ for the several compounds confirms that Pt is nonmagnetic in this series and excludes the possibility presented in the Introduction that the low moments measured below T_c were a consequence of ferrimagnetism. This being the case, it does not follow, however, that involvement of crystal field quenching has been established. Strong crystal field quenching will in cases in which the ground crystal field state is a singlet (for example, Ln = Pr, Tb, and Ho) completely inhibit magnetic ordering[5,9,10,17] and the sample will become a Van Vleck paramagnet instead. Except for $PrPt_2$, whose status as noted above is in doubt, this clearly does not happen. For a weaker crystal field, but one which is still strong compared to exchange, quenching will be apparent at relatively high temperatures where the samples are paramagnetic and significant deviations from Curie–Weiss behavior will become apparent.[4,9,17] This does not occur with any of the compounds studied from which one must conclude that the crystal field interaction is relatively weak, at least as compared to exchange, in all cases except possibly $PrPt_2$. The discrepancies between the measured moments and gJ are quite large, and hence imply strong quenching and a relatively strong interaction with the crystal field. However, this possibility as noted earlier is excluded by the paramagnetic results. Thus one must conclude that the low measured moments obtained in the ferromagnetic region are most likely an artifact. The extrapolation from 21 koersteds to infinite field

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(24) Crangle and Ross prepared their samples by an arc-melting technique. Compounds prepared in this way suffer a more drastic quenching than those prepared by crucible melting.

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TABLE I

MAGNETIC CHARACTERISTICS OF $LnPt_2$ COMPOUNDS[a]

	Ferromagnetic results				Paramagnetic results		
	Measured moment, μ_B per formula unit						
	This study	Crangle and Ross	Calcd moment, gJ	T_c, °K	μ_{eff}, μ_B per formula unit	$g\sqrt{J(J+1)}$	θ, °K
$PrPt_2$	1.60 (21)	1.67	3.20	13.5	3.43 ± 0.05^b	3.58	0
$NdPt_2$	2.11 (10)	1.60	3.27	10	3.60	3.62	0
$GdPt_2$	6.28 (2)	6.77	7.00	46.5	8.10 ± 0.05^b	7.94	32
$TbPt_2$	7.08 (13)	6.67	9.00	26	9.61	9.72	17
$DyPt_2$	6.40 (8)	7.34	10.00	25	10.58 ± 0.01^b	10.60	7
$HoPt_2$	8.88 (13)	7.65	10.00	19	10.60	10.60	2
$ErPt_2$	7.48 (20)	7.26	9.00	15	9.50	9.60	1

[a] gJ and $g\sqrt{J(J+1)}$ are the free ion moments for tripositive lanthanide ions in their ground states in the ferromagnetic and paramagnetic states, respectively. The measured moment is the value extrapolated to infinite field and 0°K. The extrapolation to infinite field is made from 21 koersteds assuming linearity of magnetization with $1/H$ (a Honda plot). As noted in the text, these fields are probably too low, except for $GdPt_2$, to achieve true saturation. T_c is the Curie temperature measured at 19 koersteds. θ is the Weiss constant. The numbers in parentheses in column 2 indicate the size of the extrapolation (in per cent of the saturation value) from 21 koersteds to infinite field. Thus at 21 koersteds $GdPt_2$ is 98% saturated whereas $PrPt_2$ is only 79% saturated. Moments were extrapolated from 4.2 to 0°K assuming applicability of the Brillouin function. [b] These numbers refer to differences in μ_{eff} observed for two different $LnPt_2$ samples.

seems valid since magnetization appears to be linear with $1/H$. However, in actuality it must be invalid. Probably much higher fields are needed to achieve saturation in all samples except $GdPt_2$. Measurements on the other compounds are needed at fields extending to 100 koersteds or more, or other types of measurements, such as neutron diffraction work or Mössbauer experiments, are needed to assess properly the Ln moment.[31]

The elemental lanthanides exhibit a variety of magnetic structures. As examples, the Dy moments between 85 and 178°K are arranged in a flat spiral; below 20°K a conical arrangement of moments exists in Ho.[32] Saturation, *i.e.*, collinearity of moments with applied field, of these metals in polycrystalline form is achieved with great difficulty if at all because of their strong anisotropy (*i.e.*, crystal field forces). Saturation requires a field sufficiently powerful to disrupt completely their magnetic structures. It seems likely that the Ln moments in the $LnPt_2$ compounds exist in some complex (*i.e.*, noncollinear arrangement) structure and it is this which makes them so difficult to saturate. This viewpoint is reinforced by the Mössbauer work of Nowik, *et al.*[33] They infer from their measurements that Dy in $DyPt_2$ is carrying the free ion moment. Yet bulk magnetic measurements (Table I) for $DyPt_2$ indicate only 64% of that of the free ion. These observations taken together leave little doubt that the magnetic structure at least of $DyPt_2$ is noncollinear, a conclusion which should be examined by appropriate neutron diffraction work. Gd is free of anisotropy, since it is in an S state. It saturates comparatively easily. The smallness of its moment may indicate a small deviation from a collinear magnetic structure but is more likely due to the antiferromagnetic coupling of the conduction electrons referred to above.

In regard to the low moments observed for the ferromagnetic region an additional possibility merits comment, namely, that there is antiferromagnetic coupling of lanthanide moments. This could involve ions only on the lanthanide sublattice (the A positions) or on both sublattices (A and B positions) if there was disorder so that Ln and Pt ions were interchanged. It is not possible to establish directly, that is, by X-ray work, whether this interchange occurs in the $LnPt_2$ compounds because the X-ray scattering power of the lanthanides and Pt is so nearly the same. However, in other more favorable cases, *e.g.*, in isostructural $MgCu_2$, it has been found[34] that the interchange of the A- and B-type ions is negligible, presumably because the 22.5% difference in radii represents too great a size disparity. From this one concludes that disorder in the $LnPt_2$ compounds, which have the same radius ratio, is insignificantly small. Hence one needs only consider interactions involving ions on the lanthanide sublattice.

The systematics of lanthanide coupling in Laves phase compounds are well understood and have been discussed at length elsewhere.[9] Lanthanide spin vectors always couple ferromagnetically because of the nature of the interactions. Hence one cannot ascribe the low moments to antiferromagnetic coupling of the Ln moments. Apart from this, however, the numbers given in column 2, Table I, make it equally unlikely that antiferromagnetism is involved. With $HoPt_2$, for example, one would have to postulate a structure in which about 10% of the Ho ions were aligned counter to the remaining 90%. The existence of any such magnetic structure is extremely unlikely.

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