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Magnetic Characteristics of $Pr_zY_{1-z}Ni_2$ Alloys and the Nature of $PrNi_2$ at Low Temperatures[1]

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Magnetic characteristics are reported for $PrNi_2$ and a series of ternary alloys represented by the formula $Pr_zY_{1-z}Ni_2$ over the temperature range 4–300°K. All exhibit Curie–Weiss behavior for $T > 20$°K, but deviate from this behavior at lower temperatures. Ternaries with $z < 0.2$ exhibit Van Vleck paramagnetism at 4.2°K. From the limiting susceptibility the over-all crystal field splitting of the Pr^{3+} ion in $Pr_{0.1}Y_{0.9}Ni_2$ is estimated to be 98 or 141°K, depending upon whether or not the sixth-order crystal field interaction term is included. Corresponding splittings for $PrNi_2$ are estimated as 94 and 136°K. Exchange in $PrNi_2$ is treated by the molecular field approach and it is established that exchange is too weak for this material to develop a spontaneous moment at low temperature. It is thus established that $PrNi_2$ is a paramagnet at 4.2°K. Exchange is very substantial, however, so that it shows saturation effects at applied fields of 10–20 kOe. Recently computed energies and moments of the crystal field are used to interpret the magnetic properties of the several samples studied. Agreement between calculated values and experiment for the temperature dependence of susceptibility is good for ternaries in which Pr has been diluted sufficiently to render exchange insignificant. The variation of magnetization with applied field for $PrNi_2$ at 4.2°K is calculated and found to be reasonably satisfactory.

I. Introduction

In an earlier publication from this laboratory the magnetic characteristics of a large number of compounds represented by the formula $LnNi_2$ were presented.[2] Here Ln is a lanthanide element. Most of the $LnNi_2$ compounds were observed to become ferromagnetic at low temperatures; however, moments of the Ln compound were in most cases less than $gJ\mu_B$, the value expected for the free Ln ion. The discrepancy was attributed to the effect of the crystal field on the orbital angular momentum. The behavior of $PrNi_2$ was such that it was not possible to establish whether it should be more properly regarded as a ferromagnet with a strongly quenched moment or a paramagnet of the Van Vleck type with its susceptibility characteristics appreciably influenced by exchange. At the time of the earlier work the theoretical background necessary to decide between these alternatives did not exist. Recent work[3] has provided the necessary formalism, and a decision between the two alternatives can now be unambiguously made. It is the purpose of this paper to present this analysis and to clarify the nature of $PrNi_2$.

The treatment for $PrNi_2$ referred to in the preceding paragraph requires a value for E_c, the overall splitting produced by the crystal field. For a Van Vleck paramagnet which the analysis presented below shows $PrNi_2$ to be, E_c can be established from the limiting value of the susceptibility, a procedure originally described by Penney and Schlapp[4] and applied[5] to PrBi and PrSb in earlier work from this laboratory. There are complications in applying this procedure if there is appreciable exchange, as there seemed to be in the case of $PrNi_2$. (Since nickel is nonmagnetic in the $LnNi_2$ compounds, exchange originates with the lanthanide component.) Exchange, of course, can be suppressed by dilution of Pr with a magnetically inert ingredient. Yttrium was chosen as the diluent, and data have been obtained and are presented in this paper for a series of ternary alloys represented by the formula $Pr_zY_{1-z}Ni_2$. Results for alloys in which Pr has been diluted by a factor of 3 or more proved to be essential for the evaluation of E_c for $PrNi_2$ and the establishment of its magnetic nature at low temperatures.

II. Experimental Details

The $Pr_zY_{1-z}Ni_2$ samples were prepared by levitation melting under a 600-mm argon atmosphere. The samples were sealed in Vycor tubes under 600 mm of argon and annealed at 700° for 300 hr. X-Ray diffraction patterns were taken using Zr-filtered Mo Kα radiation. The lattice parameters a_0 given in Table I have an error of ± 0.005 Å.

The praseodymium and yttrium used were obtained from the Research Division of the Nuclear Corp. of America, Phoenix, Ariz. Both metals were stated to be 99.9% pure. The 99.999% pure nickel was obtained from the United Mineral and Chemical Corp., New York, N. Y.

Magnetic measurements were made between 4.2 and 300°K with field strengths up to 21 kOe, using the Faraday method. Details have been given in earlier publications from this laboratory.[5,6]

III. Results and Discussion

Results are largely summarized in Figures 1 and 2 and in Table I. Reciprocal susceptibility data, shown for $Pr_{0.1}Y_{0.9}Ni_2$, are typical of $PrNi_2$ and the other ternaries studied. All displayed Curie–Weiss behavior at high temperatures with deviations in the direction of the temperature-independent Van Vleck type of paramagnetism below 20°K. The magnetization of $PrNi_2$ at 4.2°K (Figure 2) shows a tendency toward satura-

(1) This work was supported through a grant from the Army Research Office, Durham, N. C.

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

(3) (a) W. E. Wallace, F. Kissell, E. Segal, and R. S. Craig, *J. Phys. Chem. Solids*, in press; (b) K. H. Mader, E. Segal, and W. E. Wallace, *ibid.*, in press.

(4) W. G. Penney and R. Schlapp, *Phys. Rev.*, **41**, 194 (1932).

(5) T. Tsuchida and W. E. Wallace, *J. Chem. Phys.*, **43**, 2087, 2885 (1965).

(6) R. A. Butera, R. S. Craig, and L. V. Cherry, *Rev. Sci. Instr.*, **32**, 708 (1961).

TABLE I
MAGNETIC CHARACTERISTICS OF $PrNi_2$ AND $(Pr,Y)Ni_2$ TERNARIES

	a_0, Å	$10^3\chi_M$, emu/mol of Pr (300°K)	μ_{eff}, μ_B	θ, °K	χ, emu/mol of Pr (0°K extrp)
$PrNi_2$	7.288	5.30	3.60	−1	0.222
$Pr_{0.5}Y_{0.5}Ni_2$	7.243	5.54	3.72	−7	0.222
$Pr_{0.2}Y_{0.8}Ni_2$	7.203	5.36	3.67	−12	0.125
$Pr_{0.1}Y_{0.9}Ni_2$[a]	7.191	5.40	3.59	−12	0.087
YNi_2	7.186	0.18	Pauli paramagnet		

[a] Magnetic data corrected for YNi_2.

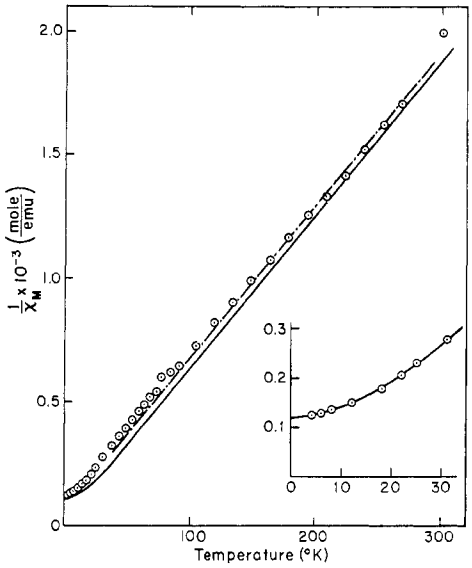

Figure 1.—Plot of $1/\chi$ *vs.* T for $Pr_{0.1}Y_{0.9}Ni_2$. Points give the experimental results measured at 18.4 kOe, corrected for $Y_{0.9}Ni_{1.8}$. The line is computed from eq 3 regarding the crystal field interaction as pure fourth order. The dashed line is the corresponding calculation with sixth-order contribution equal to that found by Bleaney[7] for Pr and by Mader, Segal, and Wallace[3] for isostructural $PrAl_2$. E_c, the over-all crystal field splitting, is taken to be 134°K if the interaction is pure fourth order or 94°K if the sixth-order contribution is included. Calculated results for low temperatures (inset) are insignificantly different for the two cases; for clarity only the pure fourth-order results are shown.

tion. The Weiss constant becomes more negative as Pr is replaced with Y, indicating, as expected, a weakening of ferromagnetic exchange.

The $2J + 1$ degenerate ground-state multiplet is decomposed by a cubic crystal field into Γ_1, Γ_4, Γ_3, and Γ_5 states.[4,7] The occurrence of Van Vleck paramagnetism indicates that the singlet Γ_1 state is the ground state, as suggested by Bleaney.[7] Penney and Schlapp[4] drew attention to the fact that the over-all splitting can be established from χ_0, the limiting value of the susceptibility at low temperatures. Application of their procedure to $PrNi_2$ seemed at the outset inappropriate in view of the results in Figure 2. These data cast doubt on the validity of regarding $PrNi_2$ as a Van Vleck paramagnet. $Pr_{0.1}Y_{0.9}Ni_2$, however, shows a magnetization which is linearly dependent on field strength and behaves in every way as an ideal Van Vleck paramagnet. The Penney–Schlapp formalism leads to a

(7) B. Bleaney, *Proc. Roy. Soc.* (London), **A276**, 28 (1963).

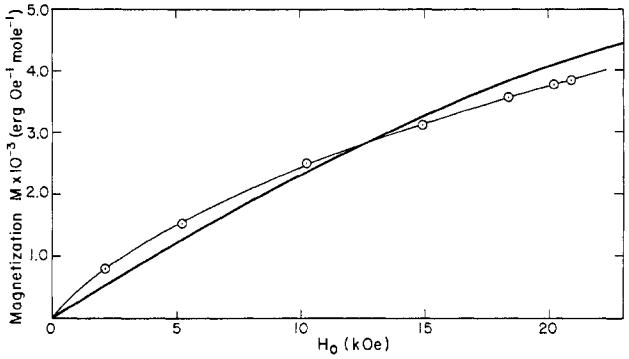

Figure 2.—Magnetization *vs.* applied field for $PrNi_2$ at 4.2°K. Points are experimental. The heavy line is computed from eq 6. The effect of ferromagnetic exchange is treated by the molecular field approach with λ, the molecular field constant, taken to be 7 Oe^2 mol/erg. E_c is the same as for the calculations shown in Figure 1. Results calculated with and without the sixth-order contribution are insignificantly different.

relationship between χ_0 and E_c, the over-all crystal field splitting, given as

$$E_c = 12.34/\chi_0 \quad (1)$$

Here χ_0 is the molar susceptibility in ergs per oersted and E_c is expressed in degrees Kelvin. The treatment leading to eq 1 neglects the sixth-order contribution to the interaction with the crystal field. Lea, Leask, and Wolf[8] have treated the case in which the sixth-order term is included; however, they confined attention to the zero (magnetic) field case. Segal[9] has made calculations which include the influence of both the sixth-order term and magnetic field. For this case the expression corresponding to eq 1 is

$$E_c = 8.86/\chi_0 \quad (2)$$

This is the relationship if the sixth-order contribution is the same as found for elemental Pr and $PrAl_2$, which is isostructural with the $Pr_zY_{1-z}Ni_2$ alloys. E_c for $Pr_{0.1}Y_{0.9}Ni_2$ is calculated to be 141 and 98°K from eq 1 and 2, respectively. The $1/\chi$ *vs.* temperature behavior computed from the fundamental Van Vleck equation

$$\chi = \frac{N\sum_i \mu_i \exp(-E_i/kT)}{H \qquad Q} \quad (3)$$

is shown in Figure 1. In eq 3 μ_i and E_i are moments and energies of the ith crystal field state, N is the Avogadro number, and Q is the partition function. For the pure fourth-order case the μ_i's were taken from the calculations of Penney and Schlapp; the corresponding data with the sixth-order terms included were taken from the calculations of Segal.[9] Good agreement with experiment is achieved in either case.

The E_c value obtained for $Pr_{0.1}Y_{0.9}Ni_2$ can be used to establish the nature of $PrNi_2$ at low temperatures. It is first appropriate to correct the value by a point charge calculation to allow for the change in the inter-

(8) K. R. Lea, M. J. M. Leask, and W. P. Wolf, *J. Phys. Chem. Solids*, **23**, 1381 (1962).

(9) E. Segal, ref 3 and unpublished calculations.

atomic distances in $PrNi_2$ as compared to the ternary. Distances in the former are slightly larger and E_c for $PrNi_2$ is estimated[10] to be 136°K for the pure fourth-order case or 94°K if the sixth-order contribution is included.

As noted in the Introduction it has not been possible to establish until now whether $PrNi_2$ is a paramagnet or a ferromagnet in the liquid helium range. The magnetization-field data (Figure 2) suggest the latter, but the moment is very low compared to the value expected for the free Pr^{3+} ion. The type of analysis which has recently been applied[3] to $PrAl_2$ and $(Pr,Y)Al_2$ and $(Pr,La)Al_2$ can also be employed with $PrNi_2$. Each crystal field state has a moment, which at low fields varies linearly with H

$$\mu_i = a_i + b_iH \tag{4}$$

H, the effective field, is the sum of H_0, the applied field, and λM, the molecular field contribution. Magnetization M is obtained from the expression

$$M = \frac{A + BH_0}{Q - B\lambda} \tag{5}$$

Here $A = \Sigma_i a_i \exp(-E_i/kT)$, $B = \Sigma_i b_i \exp(-E_i/kT)$, and λ is the molecular field constant. Q and B are both functions of temperature. Elsewhere[3] it has been shown that the Curie temperature (*i.e.*, the temperature below which spontaneous magnetization appears) corresponds to the condition that the denominator vanishes. λ can be evaluated from the Weiss constant, θ, which is known[3,4] to be made up of two contributions—one due to the crystal field interaction and the other the result of exchange. From the difference in θ for $PrNi_2$ and $Pr_{0.1}Y_{0.9}Ni_2$ or $Pr_{0.2}Y_{0.8}Ni_2$, the exchange contribution can be established to be 11°K. $\lambda = 11/1.62$ for Pr^{3+} ions, which gives $\lambda = 7$ Oe² mol/erg. With this value of λ, one can investigate the value of $Q - 7B$ at various temperatures. Using values for b_i and E_i given elsewhere[3] it is found that $Q - B\lambda$ is nonvanishing at all temperatures. Thus it is concluded that $PrNi_2$ remains paramagnetic to the lowest measured temperatures.

Since $PrNi_2$ at 4.2°K is a paramagnet, curvature in Figure 2 is of interest. The molar magnetization can be evaluated from the expression

$$M = \frac{N\sum_i \mu_i \exp(-E_i/kT)}{Q} \tag{6}$$

In this expression μ_i, E_i, and Q are all functions of the effective field, $H_{eff} = H_0 + \lambda M$. The μ_i and E_i values needed to evaluate M in eq 6 are available[3,9] in terms of the parameter E_c, which, as noted above, is taken to be 136 or 94°K, depending upon whether or not the interaction is pure fourth order. M is obtained for various values of H_{eff} and then the value of H_0 to produce this effective field is computed from $H_0 = H_{eff} - \lambda M$. The computed results are shown in Figure 2 along with the experimental data. Both show a nonlinear variation of M with H. The curvature in the calculated result is an outgrowth of the varying polarizability of the ground state with field strength. The ground-state moment increases essentially linearly with field up to 20 kOe, the deviation from linearity being less than 1%. Above 30 kOe the deviation rapidly increases. The curvature in Figure 2 is primarily a consequence of exchange. The field is enhanced by the λM term so that for $H_0 = 20$ kOe the applied field is in excess of 50 kOe.

The agreement between calculated and observed results in Figure 2 can be considered to be reasonable. The differences are due to general inadequacies of the molecular field approach in regard to the details of exchange.

(10) These estimates are supported by heat capacity measurements by M. Dixon, M. Aoyagi, R. S. Craig, and W. E. Wallace, which are to be published.