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*R.R. Sobral, A.P. Guimarães[†] and
X.A. da Silva*

Centro Brasileiro de Pesquisas Físicas — CBPF/CNPq
Rua Dr. Xavier Sigaud, 150
22290-180 – Rio de Janeiro, RJ – Brasil

[†]Presently on leave at the Massachusetts Institute of Technology, Cambridge
MA 02139, USA

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Abstract

The magnetism of rare earth intermetallic compounds is investigated with a model hamiltonian containing crystal field and exchange terms. An algebraic analysis of the characteristic polynomial associated to the model is made and it is shown that, for $\text{Pr}^{+3}(J = 4)$ and $\text{Nd}^{+3}(J = 9/2)$, in the case of cubic symmetry, the ninth and tenth degree polynomials are decomposed into simple factors. From these factors, analytical expressions for the crystal field eigenvalues, the magnetic moments and the critical temperatures are derived. The results are applied to PrAl_2 and NdAl_2 ; exchange parameters and effective g factors are easily obtained from crystal field, T_C , and low temperature magnetic moments data.

In order to analyze the magnetic properties of rare earth intermetallic compounds one usually starts with a model hamiltonian in which a crystal field term describes the electrostatic interaction of the 4f electrons of the rare earth ions with the neighbor charges, and an exchange term accounts for the inter-ionic spin interaction. Both terms contain adjustable parameters, which must be determined using inelastic neutron scattering data and magnetic data [1]. The computation of magnetic quantities from the model hamiltonian is usually done entirely with numerical methods, even for cubic symmetrical crystal fields and in the molecular field approximation. This, not only complicates the best fitting process, but also makes less visible the role of the model parameters in determining the magnetic behavior of different compounds.

In this paper we show results of a computer algebra approach to determine eigenvalues and magnetic moments associated to the magnetic model hamiltonian. In particular, we make an analysis of the magnetic behavior of the ground state and obtain an analytic expression for the critical temperature. These results are applied to the intermetallic compounds PrAl₂ and NdAl₂, which crystallize in the cubic Laves phase structure (C15). Using crystal field parameters, Curie temperatures and low temperature magnetic moments obtained from the literature, we calculate the exchange parameter and the effective Landé factor for these compounds.

The starting point is to obtain explicitly the characteristic polynomial associated to the model hamiltonian \mathcal{H}

$$\det | \langle J, n | \mathcal{H} - \delta_{mn} y | J, m \rangle | = 0 \quad (1)$$

where the hamiltonian has two parts:

$$\mathcal{H} = \mathcal{H}_{cf} + \mathcal{H}_{mag} \quad (2)$$

For cubic symmetry, the crystal field hamiltonian can be written

$$\mathcal{H}_{cf} = B_4 [O_4^0 + 5O_4^4] + B_6 [O_6^0 - 21O_6^4] \quad (3)$$

where B_4 and B_6 are crystal field parameters and the O_m^n are Stevens' operators, which are listed in the literature [2]; $| J, m \rangle$ are the eigenstates of J_z , for a given angular momentum J. Equation (3) is only valid in a coordinate system (x, y, z) which coincides with three of the fourfold symmetry axes of the crystal; the z axis is taken as the quantized direction. In other coordinate systems the form of \mathcal{H}_{cf} is less simple [3].

In the molecular field approximation

$$\mathcal{H}_{mag} = -g\mu_B \vec{h} \cdot \vec{J} \quad (4)$$

where \vec{h} is the total magnetic field:

$$g\mu_B \vec{h} = g\mu_B \vec{h}_0 + \lambda_0 (g-1)^2 \langle \vec{J} \rangle \quad (5)$$

In (5), g is the Landé factor, μ_B the Bohr magneton, λ_0 the exchange parameter and \vec{h}_0 is the applied field; $\langle \vec{J} \rangle$ is the thermal average of the angular momentum operator \vec{J} .

In order to compute the magnetic moments in the x direction, $\vec{n} = (1, 0, 0)$, let us rewrite eq.(4) as $\mathcal{H}_{mag} = -g\mu_B h J_x$. The magnetic moments are then obtained as

$$g\mu_B \langle i | \vec{J} \cdot \vec{n} | i \rangle \equiv -\frac{dy_i}{dh} = -g\mu_B \frac{dy_i}{d\alpha} \quad (6)$$

where y_i are the roots of the polynomial in y generated by equation (1), $\alpha = g\mu_B h$ and $h = \vec{h} \cdot \vec{n}$ is the molecular field acting on the $4f$ electrons along the direction \vec{n} (a unitary vector) (see equation 5). The reason for choosing the spontaneous magnetization in the x direction is that it is the experimentally observed easy magnetic direction[4]. Of course due to the cubic symmetry of the crystal field hamiltonian (eq.(3)), directions x, y and z , in our model, are magnetically equivalent. Actually, according to Boucherle et al. [5], at low temperature, below the Curie point, most of the RAl_2 ($R = \text{rare-earth}$) exhibit a small distortion in the unit cell. This may explain why experimentally the directions $(1,0,0)$, $(0,1,0)$ and $(0,0,1)$ are not magnetically equivalent. For the cases of $\text{Pr}^{+3}(J = 4)$ and $\text{Nd}^{+3}(J = 9/2)$, equation (1) was dealt with through computer algebra, yielding a ninth and a tenth degree polynomial, respectively. This was done using REDUCE, a well known algebraic program. REDUCE also allowed the factorization of these polynomials into smaller factors. In the case of Pr^{+3} we obtained four factors: one of the third degree, and three of the second degree; for Nd^{+3} we also have four factors: two of third degree and two of second degree. They are listed in the Appendix.

These polynomials contain all the relevant magnetic information; let $P(y, B_4, B_6, \alpha)$ be one of the above mentioned factors, whose roots y_i are the energy eigenvalues.

We have

$$P(y, B_4, B_6, \alpha) = 0 \quad (7)$$

$$\frac{\partial P}{\partial y} \left(\frac{dy}{d\alpha} \right) + \frac{\partial P}{\partial \alpha} = 0 \quad (8)$$

From equations 7 and 8, we can obtain the ground state magnetic moment for each value of the exchange parameter. For the case of Pr^{+3} , the ground state is given by the lowest root of the third degree polynomial; for Nd^{+3} , the third degree polynomial with the plus sign contains the ground state. The results are shown in Figure 1 using the crystal field parameters of PrAl_2 and NdAl_2 [1]; both curves show magnetic moment reduction, relative to the free ion value. For the PrAl_2 curve, if $\lambda/W \leq 0.43$, there is no spontaneous magnetic order, although the magnetic moment of $\text{PrAl}_2(J = 4)$ saturates much earlier than that of $\text{NdAl}_2(J = 9/2)$. The initial value of the magnetic moment in the NdAl_2 curve is $(11/6)g\mu_B$.

It is worth mentioning that for $\alpha = 0$, the roots of the factor polynomials, i.e., the crystal field eigenvalues, are analytically expressed in terms of B_4 and B_6 ; they are presented in the Appendix. As far as we know, it is the first time these expressions have appeared in print; a particular solution for $B_6 = 0$ was given by Penney and Schlapp [2]. In fact, we have found that computer algebra can give analytical results for the crystal field eigenvalues of all rare earth ions [6]. Crystal field eigenvalues are usually obtained numerically and displayed in tables or in graphical form, as in Lea, Leask and Wolf [7]. These plots are used in the determination of crystal field parameters for intermetallic compounds, using inelastic neutron scattering data [8].

We will show how the factorized polynomials and their first and second derivatives can be used to obtain the energy eigenvalues of the model up to α^2 ,

$$y_i \cong y_i^0 + \left(\lim_{\alpha \rightarrow 0} \frac{dy_i}{d\alpha} \right) \alpha + \frac{1}{2} \left(\lim_{\alpha \rightarrow 0} \frac{d^2 y_i}{d\alpha^2} \right) \alpha^2 \quad (9)$$

In order to obtain the coefficients of α and α^2 in (9), we take the limit $\alpha \rightarrow 0$ of equations (7), (8) and (10)

$$\frac{\partial P}{\partial y} \left(\frac{d^2 y}{d\alpha^2} \right) + \frac{\partial^2 P}{\partial y^2} \left(\frac{dy}{d\alpha} \right)^2 + 2 \frac{\partial^2 P}{\partial y \partial \alpha} \left(\frac{dy}{d\alpha} \right) + \frac{\partial^2 P}{\partial \alpha^2} = 0 \quad (10)$$

At this point, we would like to emphasize that in order to compute the coefficients $\lim_{\alpha \rightarrow 0}(\partial P/\partial y)$, $\lim_{\alpha \rightarrow 0}(\partial P/\partial \alpha)$, etc, in (7), (8) and (10) we have to make use of the analytical expressions for the eigenvalues of the crystal field hamiltonian.

For the ground state energy level we have, for Pr^{+3} :

$$\left(\frac{dy_0}{d\alpha} \right)_{\alpha=0} = 0; \quad \left(\frac{d^2 y_0}{d\alpha^2} \right)_{\alpha=0} = -\frac{28}{15} \frac{1}{b_4 - 6b_6} \quad (11)$$

For Nd^{+3} :

$$\lim_{\alpha \rightarrow 0} \left(\frac{dy_0}{d\alpha} \right) = \frac{11}{6}; \quad \left(\frac{d^2 y_0}{d\alpha^2} \right)_{\alpha=0} = -\frac{8}{945} \frac{245b_4 - 47b_6}{(b_4 - b_6)(25b_4 - 3b_6)} \quad (12)$$

where b_4 and b_6 are related to B_4 and B_6 (see Appendix). In obtaining (11) and (12) we have assumed that the crystal field ground states of Pr^{+3} and Nd^{+3} are Γ_3 and Γ_6 , respectively; these are the cases of PrAl_2 and NdAl_2 . Using (6), (11) and (12) we can obtain the threshold value of λ_0 ($\lambda_c/W = 0.433$) for the PrAl_2 curve in Figure 1. Also, using (6), (9) and (12), obtain the initial value of the magnetic moment (for $\lambda_0/W = 0$) for the NdAl_2 curve in the Figure: the result is $\lim_{\alpha \rightarrow 0}(dy_0/d\alpha) = 11/6$ (in $g\mu_B$ units). Using the same procedure, we can obtain analytically the limits as $\alpha \rightarrow 0$ of $(dy_i/d\alpha)$ and $(d^2 y_i/d\alpha^2)$ of all other levels. Expressions of energy eigenvalues, up to α^2 were given by Schumacher and Holligsworth [9] for the case $B_6 = 0$, using numerical methods. The value of the critical temperature is obtained from

$$\langle \vec{J} \cdot \vec{n} \rangle = \frac{\sum_i (-dy_i/d\alpha) \exp(-y_i \beta)}{\sum_i \exp(-y_i \beta)} \quad (13)$$

where the right hand side is linearized in α ($\alpha = \lambda_0(g-1)^2 \langle \vec{J} \cdot \vec{n} \rangle$). An expression for T_C in the case of Pr^{+3} compounds is given in the Appendix.

Using the crystal field parameters and the experimental value of T_C given in the review by Purwins and Leon [1] for PrAl_2 , the expression (A.13) (see Appendix) gives

$$(g_{eff} - 1)^2 \frac{\lambda_0}{W} = 1.55 \quad (14)$$

This result, together with the value of the moment $m_0 = 2.8\mu_B$ for the ion Pr^{+3} in PrAl_2 [1], allows, using the curve for PrAl_2 in the Figure, the determination of $g_{eff} = 0.75$. Again, using (14), $\lambda_0 = 24.23$ meV. A similar procedure was followed for Nd^{+3} in NdAl_2 . The results for PrAl_2 and NdAl_2 are given in Table I.

To summarize, we want to stress the two basic contributions of this work to the study of the magnetism of $4f$ systems with crystal field interactions: 1) an algebraic approach which allows the decomposition of a complex problems into simple parts, and 2) the development of an algorithm to obtain the magnetic moments that does not require the knowledge of the eigenfunctions. Not only it makes it easier the fitting the parameters, but

it also gives a better understanding of the role of crystal field and exchange in determining the magnetic behavior of different compounds. Although the present work was centered on an application to intermetallic compounds, the method is obviously not restricted to these systems. The potentialities of computer algebra approach to crystal field and magnetic problems should therefore be noted.

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A - APPENDIX

Factorized polynomials:

$J = 4$

$$P_1(\Gamma_1, \Gamma_3, \Gamma_4) = y^3 - 2y^2(23b_4 - 6b_6) + 16y\{35b_4^2 + 86b_4b_6 - 324b_6^2 - \alpha^2\} - 32\{49b_4^3 + 658b_4^2b_6 - 2056b_4b_6^2 - 640b_6^3 - \alpha^2(9b_4 - 10b_6)\} \quad (\text{A.1})$$

$$P_2(\Gamma_3, \Gamma_5) = -y^2 - 22y(b_4 - 2b_6) + 4\{26b_4^2 + 436b_4b_6 + 320b_6^2 + \alpha^2\} \quad (\text{A.2})$$

$$P_3^\pm(\Gamma_5, \Gamma_4) = -y^2 - 2y(6b_4 + 8b_6 \pm \alpha) + 364b_4^2 + 384b_4b_6 + 80b_6^2 \pm \alpha(48b_4 + 20b_6) + 3\alpha^2 \quad (\text{A.3})$$

where

$$\begin{aligned} b_4 &= F_4 B_4 = Wx \\ b_6 &= F_6 B_6 = W(1 - |x|) \\ F_4 &= 60 \\ F_6 &= 1260 \end{aligned}$$

$J = 9/2$

$$P_1^\pm(\Gamma_6, \Gamma_8^1, \Gamma_8^2) = y^3 - y^2(98b_4 - 32b_6 \pm 3\alpha/2) - y\{34832b_4^2 - 3136b_4b_6 \pm 1022b_4\alpha + 3152b_6^2 \pm 144b_6\alpha + 61(\alpha/2)^2\} + 3\{1020768b_4^3 + 281344b_4^2b_6 \pm 60312b_4^2\alpha - 128576b_4b_6^2 \pm 3808b_4b_6\alpha + 3402b_4(\alpha/2)^2 - 23552b_6^3 \mp 4104b_6^2\alpha - 64b_6\alpha^2 \pm 21(\alpha/2)^3\} \quad (\text{A.4})$$

$$P_2^\pm(\Gamma_8^1, \Gamma_8^2) = -y^2 - 2y(49b_4 - 16b_6 \pm \alpha/2) + 3\{5208b_4^2 + 3136b_4b_6 \pm 77b_4\alpha + 368b_6^2 + 5(\alpha/2)^2\} \quad (\text{A.5})$$

where

$$\begin{aligned} b_4 &= \frac{F_4 B_4}{5} = \frac{Wx}{5} \\ b_6 &= F_6 B_6 = W(1 - |x|) \\ F_4 &= 60 \\ F_6 &= 2520 \end{aligned}$$

Roots of the crystal field hamiltonian:

$J = 4$

$$E(\Gamma_1) = 4(7b_4 - 20b_6) \quad (\text{A.6})$$

$$E(\Gamma_3) = 4(b_4 + 16b_6) \quad (\text{A.7})$$

$$E(\Gamma_4) = 2(7b_4 + 2b_6) \quad (\text{A.8})$$

$$E(\Gamma_5) = -2(13b_4 + 10b_6) \quad (\text{A.9})$$

$J = 9/2$

$$E(\Gamma_6) = 4(49b_4 - 16b_6) \quad (\text{A.10})$$

$$E(\Gamma_8^1) = -49b_4 + 16b_6 - M \quad (\text{A.11})$$

$$E(\Gamma_8^2) = -49b_4 + 16b_6 + M \quad (\text{A.12})$$

$$M = \{5(3605b_4^2 + 1568b_4b_6 + 272b_6^2)\}^{1/2}$$

Expression relating T_C to crystal field and exchange parameters for $J = 4$.

$$\frac{\lambda}{W} = \frac{e^{-\beta E(\Gamma_1)} + 2e^{-\beta E(\Gamma_3)} + 3e^{-\beta E(\Gamma_4)} + 3e^{-\beta E(\Gamma_5)}}{c_1 e^{-\beta E(\Gamma_1)} + c_2 e^{-\beta E(\Gamma_3)} + c_3 e^{-\beta E(\Gamma_4)} + c_4 e^{-\beta E(\Gamma_5)}} \quad (\text{A.13})$$

where

$$c_1 = -\frac{20}{21(7x - 6)}$$

$$c_2 = \frac{8(49x - 64)}{15[(7x - 6)(9x - 14)]}$$

$$c_3 = -\frac{(2227x - 702)}{280[(7x - 6)(2x + 3)]} + 2\beta\left(\frac{1}{2}\right)^2$$

$$c_4 = \frac{5(25x - 78)}{24[(2x + 3)(9x - 14)]} + 2\beta\left(\frac{5}{2}\right)^2$$

$$E(\Gamma_1) = 4(27x - 20)$$

$$E(\Gamma_3) = -4(15x - 16)$$

$$E(\Gamma_4) = 2(5x + 2)$$

$$E(\Gamma_5) = -2(3x + 10)$$

$$\beta = \frac{1}{k_B T_C}$$

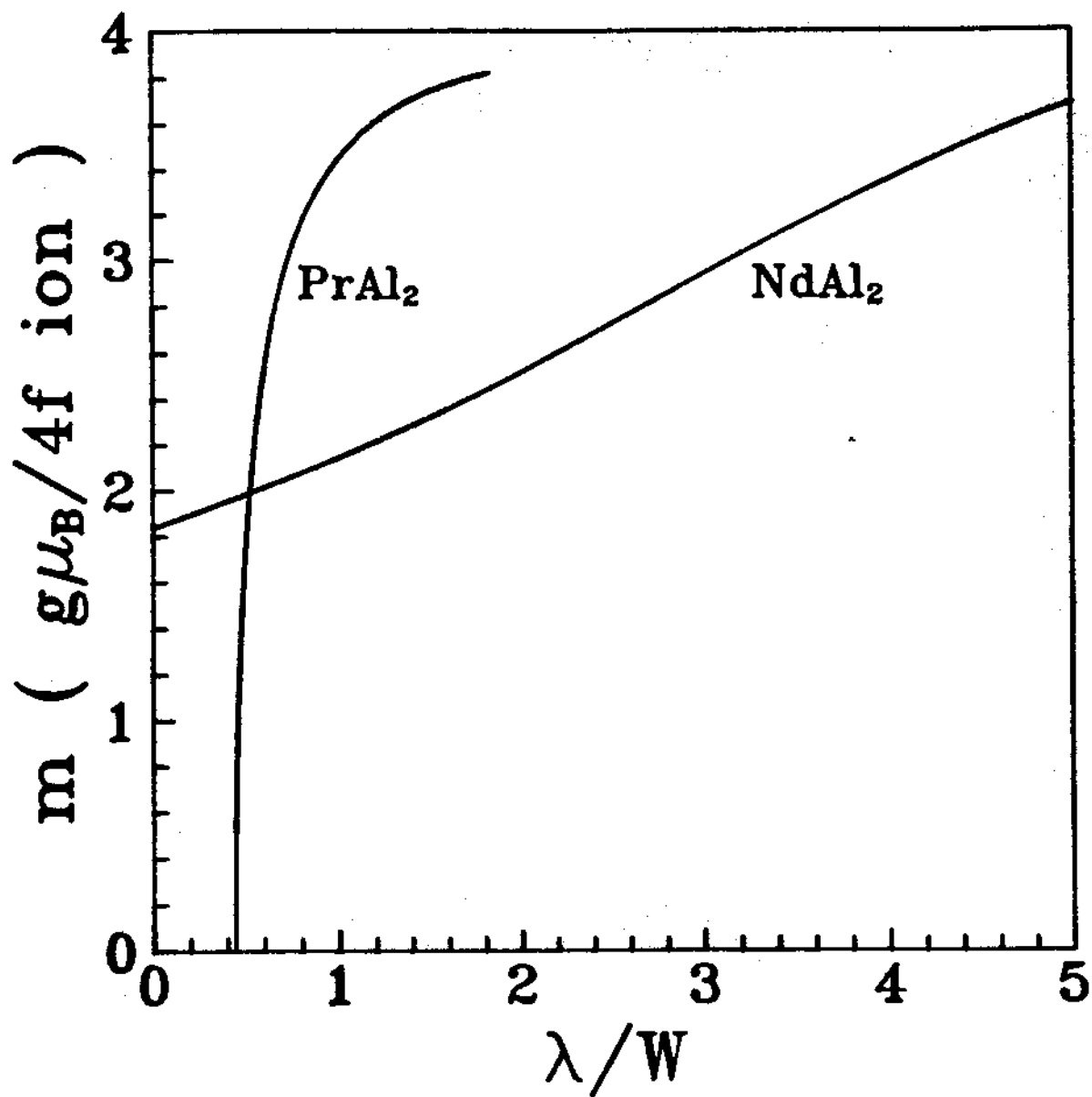
Captions

Fig. 1. Magnetic moment of the ground state (in $g\mu_B/\text{rare-earth ion}$) for PrAl_2 and NdAl_2 versus λ/W , where $\lambda = (g_{eff} - 1)^2\lambda_0$. The curves were drawn using the crystal field parameters x and W given in Table I.

Table I. Computed effective Lande's factors (g_{eff}) and exchange parameters (λ_0) for PrAl_2 and NdAl_2 . The crystal field parameters x and W , the critical temperature T_C and the low temperature magnetic moments m_0 are taken from [1]. The Γ 's characterize the nature of the crystal field ground state.

Tab.I

	x	$W(\text{meV})$	$T_C(K)$	$m_o(\mu_B/\text{ion})$	g_{eff}	$\lambda_o(\text{meV})$	Γ_i
PrAl_2	0.739	-0.329	33.0	2.80	0.75	24.23	Γ_3
NdAl_2	-0.370	0.161	65.0	2.45	0.68	7.47	Γ_6



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