The magnetism of rare-earth intermetallics using computer algebra: application to $PrAl_2$ and $NdAl_2$

1993 J. Phys.: Condens. Matter 5 L671

(http://iopscience.iop.org/0953-8984/5/50/003)

J. Phys.: Condens. Matter 5 (1993) L671–L676. Printed in the UK

LETTER TO THE EDITOR

The magnetism of rare-earth intermetallics using computer algebra: application to $PrAl_2$ and $NdAl_2$

R R Sobral, A P Guimarães and X A da Silva

Centro Brasileiro de Pesquisas Físicas, R Xavier Sigaud 150, 22290–180 Rio de Janeiro, RJ, Brazil

Received 23 August 1993

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 with the model is made and it is shown that, for Pr^{3+} ($J = 4$) and 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 analyse 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 neighbour 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 behaviour of different compounds.

In this paper we show results of a computer algebra approach to determine eigenvalues and magnetic moments associated with the magnetic model Hamiltonian. In particular, we make an analysis of the magnetic behaviour of the ground state and obtain an analytic expression for the critical temperature. These results are applied to the intermetallic compounds $PrAl_2$ and $NdAl_2$, 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 with the model Hamiltonian $\mathcal{H}$

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

where the Hamiltonian has two parts:

$$\mathcal{H} = \mathcal{H}_{\mathrm{cf}} + \mathcal{H}_{\mathrm{mag}}. \tag{2}$$

For cubic symmetry, the crystal field Hamiltonian can be written

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

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 others coordinate systems the form of $\mathcal{H}_{\mathrm{cf}}$ is less simple [3].

In the molecular field approximation

$$\mathcal{H}_{\mathrm{mag}} = -g\mu_{\mathrm{B}}\boldsymbol{h}\cdot\boldsymbol{J} \tag{4}$$

where $\boldsymbol{h}$ is the total magnetic field:

$$g\mu_{\mathrm{B}}\boldsymbol{h} = g\mu_{\mathrm{B}}\boldsymbol{h}_0 + \lambda_0(g-1)^2\langle\boldsymbol{J}\rangle. \tag{5}$$

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

In order to compute the magnetic moments in the x direction, $\boldsymbol{n} = (1, 0, 0)$, let us rewrite (4) as $\mathcal{H}_{\mathrm{mag}} = -g\mu_{\mathrm{B}}hJ_x$. The magnetic moments are then obtained as

$$g\mu_{\mathrm{B}}\langle i|\boldsymbol{J}\cdot\boldsymbol{n}|i\rangle \equiv -\frac{\mathrm{d}y_i}{\mathrm{d}h} = -g\mu_{\mathrm{B}}\frac{\mathrm{d}y_i}{\mathrm{d}\alpha} \tag{6}$$

where y_i are the roots of the polynomial in y generated by equation (1), $\alpha = g\mu_{\mathrm{B}}h$ and $h = \boldsymbol{h}\cdot\boldsymbol{n}$ is the molecular field acting on the 4f electrons along the direction $\boldsymbol{n}$ (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 (3), directions x, y and z, in our model, are magnetically equivalent. Actually, according to Boucherle amd Schweizer [5], at low temperature, below the Curie point, most of the RAl_2 (R = 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 $Pr^{3+}(J = 4)$ and $Nd^{3+}(J = 9/2)$, equation (1) was dealt with through computer algebra, yielding a ninth- and a tenth-degree polynomial, respectively. This was done using REDUCE, a well know 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

$$P(y, B_4, B_6, \alpha) = 0 \tag{7}$$

$$\frac{\partial P}{\partial y}\left(\frac{\mathrm{d}y}{\mathrm{d}\alpha}\right) + \frac{\partial P}{\partial \alpha} = 0. \tag{8}$$

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

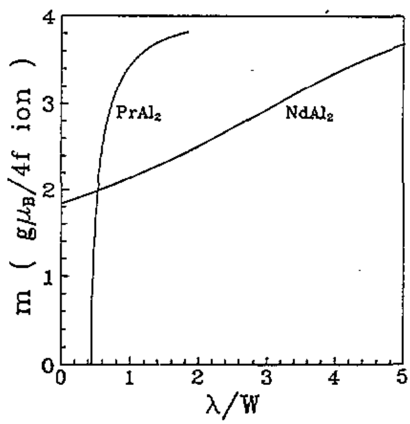

Figure 1. Magnetic moment of the ground state (in $g\mu_B$/rare-earth ion) for $PrAl_2$ and $NdAl_2$ versus λ/W, where $\lambda = (g_{eff} - 1)^2\lambda_0$. The curves were drawn using the crystal field parameters x and W given in table 1.

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 $\lambda/W \leqslant 0.43$, there is no spontaneous magnetic order, although the magnetic moment of $PrAl_2$ ($J = 4$) saturates much earlier than that of $NdAl_2$ ($J = 9/2$). 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 *et al* [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,

$$y_i \cong y_i^0 + \left(\lim_{\alpha\to 0} \frac{\mathrm{d}y_i}{\mathrm{d}\alpha}\right)\alpha + \frac{1}{2}\left(\lim_{\alpha\to 0} \frac{\mathrm{d}^2 y_i}{\mathrm{d}\alpha^2}\right)\alpha^2. \tag{9}$$

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

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

At this point, we would like to emphasize that in order to compute the coefficients $\lim_{\alpha\to 0}(\partial P/\partial y)$, $\lim_{\alpha\to 0}(\partial P/\partial \alpha)$, 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+}:

$$\left(\frac{\mathrm{d}y_0}{\mathrm{d}\alpha}\right)_{\alpha=0} = 0 \qquad \left(\frac{\mathrm{d}^2 y_0}{\mathrm{d}\alpha^2}\right)_{\alpha=0} = -\frac{28}{15}\frac{1}{b_4 - 6b_6}. \tag{11}$$

For Nd^{3+}:

$$\lim_{\alpha\to 0}\left(\frac{\mathrm{d}y_0}{\mathrm{d}\alpha}\right) = \frac{11}{6} \qquad \left(\frac{\mathrm{d}^2 y_0}{\mathrm{d}\alpha^2}\right)_{\alpha=0} = -\frac{8}{945}\frac{245b_4 - 47b_6}{(b_4 - b_6)(25b_4 - 3b_6)} \tag{12}$$

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), we can obtain the initial value of the magnetic moment (for $\lambda_0/W = 0$) for the $NdAl_2$ curve in the figure: the result is $\lim_{\alpha\to 0}(\mathrm{d}y_0/\mathrm{d}\alpha) = 11/6$ (in $g\mu_B$ units). Using the same procedure, we can obtain analytically the limits as $\alpha \to 0$ of $(\mathrm{d}y_i/\mathrm{d}\alpha)$ and $(\mathrm{d}^2 y_i/\mathrm{d}\alpha^2)$ of all other levels. Expressions of energy eigenvalues, up to α^2, were given by Schumacher and Hollingsworth [9] for the case $B_6 = 0$, using numerical methods. The value of the critical temperature is obtained from

$$\langle \boldsymbol{J}\cdot\boldsymbol{n}\rangle = \frac{\sum_i(-\mathrm{d}y_i/\mathrm{d}\alpha)\exp(-y_i\beta)}{\sum_i \exp(-y_i\beta)} \tag{13}$$

where the right hand side is linearized in α ($\alpha = \lambda_0(g-1)^2\langle \boldsymbol{J}\cdot\boldsymbol{n}\rangle$). 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 (A13) (see appendix) gives

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

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 $g_{\mathrm{eff}} = 0.75$. 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 1.

Table 1. Computed effective Landé 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 values characterize the nature of the crystal field ground state.

	x	W (meV)	T_C (K)	m_0 (μ_B/ion)	g_{eff}	λ_0 (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

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: (i) an algebraic approach which allows the decomposition of a complex problem into simple parts, and (ii) the development of an algorithm to obtain the magnetic moments that does not require the knowledge of the eigenfunctions. Not only does it make fitting the parameters easier, but it also gives a better understanding of the role of crystal field and exchange in determining the magnetic behaviour of different compounds. Although the present work was centred on an application to intermetallic compounds, the method is obviously not restricted to these systems. The potential of the computer algebra approach to crystal field and magnetic problems should therefore be noted.

One of the authors (RRS) acknowledges a CNPq/Brazil post-doctoral fellowship.

Appendix

Factorized polynomials:

$J = 4$

$$\begin{aligned} P_1(\Gamma_1, \Gamma_3, \Gamma_4) &= y^3 - 2y^2(23b_4 - 6b_6) + 16y\{35b_4^2 + 86b_4b_6 - 324b_6^2 - \alpha^2\} \\ &\quad - 32\{49b_4^3 + 658b_4^2b_6 - 2056b_4b_6^2 - 640b_6^3 - \alpha^2(9b_4 - 10b_6)\} \end{aligned} \tag{A1}$$

$$P_2(\Gamma_3, \Gamma_5) = -y^2 - 22y(b_4 - 2b_6) + 4\{26b_4^2 + 436b_4b_6 + 320b_6^2 + \alpha^2\} \tag{A2}$$

$$\begin{aligned} P_3^{\pm}(\Gamma_5, \Gamma_4) &= -y^2 - 2y(6b_4 + 8b_6 \pm \alpha) + 364b_4^2 + 384b_4b_6 + 80b_6^2 \\ &\quad \pm \alpha(48b_4 + 20b_6) + 3\alpha^2 \end{aligned} \tag{A3}$$

where

$$b_4 = F_4B_4 = Wx \qquad b_6 = F_6B_6 = W(1 - |x|) \qquad F_4 = 60 \qquad F_6 = 1260.$$

$J = 9/2$

$$\begin{aligned} P_1^{\pm}(\Gamma_6, \Gamma_8^1, \Gamma_8^2) &= y^3 - y^2(98b_4 - 32b_6 \pm 3\alpha/2) \\ &\quad - y\{34\,832b_4^2 - 3136b_4b_6 \pm 1022b_4\alpha + 3152b_6^2 \pm 144b_6\alpha \\ &\quad + 61(\alpha/2)^2\} + 3\{1\,020\,768b_4^3 + 281\,344b_4^2b_6 \pm 60\,312b_4^2\alpha \\ &\quad - 128\,576b_4b_6^2 \pm 3808b_4b_6\alpha + 3402b_4(\alpha/2)^2 \\ &\quad - 23\,552b_6^3 \mp 4104b_6^2\alpha - 64b_6\alpha^2 \pm 21(\alpha/2)^3\} \end{aligned} \tag{A4}$$

$$\begin{aligned} P_2^{\pm}(\Gamma_8^1, \Gamma_8^2) &= -y^2 - 2y(49b_4 - 16b_6 \pm \alpha/2) + 3\{5208b_4^2 + 3136b_4b_6 \\ &\quad \pm 77b_4\alpha + 368b_6^2 + 5(\alpha/2)^2\} \end{aligned} \tag{A5}$$

where

$$b_4 = \frac{F_4B_4}{5} = \frac{Wx}{5} \qquad b_6 = F_6B_6 = W(1 - |x|) \qquad F_4 = 60 \qquad F_6 = 2520.$$

Roots of the crystal field Hamiltonian:

$J = 4$

$$E(\Gamma_1) = 4(7b_4 - 20b_6) \tag{A6}$$
$$E(\Gamma_3) = 4(b_4 + 16b_6) \tag{A7}$$
$$E(\Gamma_4) = 2(7b_4 + 2b_6) \tag{A8}$$
$$E(\Gamma_5) = -2(13b_4 + 10b_6) \tag{A9}$$

$J = 9/2$

$$E(\Gamma_6) = 4(49b_4 - 16b_6) \tag{A10}$$
$$E(\Gamma_8^1) = -49b_4 + 16b_6 - M \tag{A11}$$
$$E(\Gamma_8^2) = -49b_4 + 16b_6 + M \tag{A12}$$
$$M = \{5(3605b_4^2 + 1568b_4b_6 + 272b_6^2)\}^{1/2}.$$

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

$$\frac{\lambda}{W} = \frac{e^{-\beta E(\Gamma_1)} + 2e^{-\beta E(\Gamma_3)} + 3e^{-\beta E(\Gamma_4)} + 3e^{-\beta E(\Gamma_5)}}{c_1 e^{-\beta E(\Gamma_1)} + c_2 e^{-\beta E(\Gamma_3)} + c_3 e^{-\beta E(\Gamma_4)} + c_4 e^{-\beta E(\Gamma_5)}} \tag{A13}$$

where

$$c_1 = -\frac{20}{21(7x-6)} \qquad c_2 = \frac{8(49x-64)}{15[(7x-6)(9x-14)]}$$

$$c_3 = -\frac{(2227x-702)}{280[(7x-6)(2x+3)]} + 2\beta\left(\frac{1}{2}\right)^2 \qquad c_4 = \frac{5(25x-78)}{24[(2x+3)(9x-14)]} + 2\beta\left(\frac{5}{2}\right)^2$$

$$E(\Gamma_1) = 4(27x-20) \qquad E(\Gamma_3) = -4(15x-16)$$

$$E(\Gamma_4) = 2(5x+2) \qquad E(\Gamma_5) = -2(3x+10)$$

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

References

[1] Purwins H G and Leon A 1990 *Adv. Phys.* **39** 309
[2] Penney W G and Schlapp R 1932 *Phys. Rev.* **41** 194
[3] Fischer G and Herr A 1986 *Phys. Status. Solidi* b **136** 103
[4] Eyers A, Alke A, Leson A, Kohake D and Purwins H G 1982 *J. Phys. C: Solid State Phys.* **15** 2459
[5] Boucherle J X and Schweizer J 1981 *J. Magn. Magn. Mater.* **24** 308
[6] Sobral R R *et al* 1994 to be published
[7] Lea K R, Leask M J M and Wolf W P 1962 *J. Phys. Chem. Solids* **23** 1381
[8] Greidanus F J A M, de Jongh L J, Huiskamp W J, Furrer A and Buschow K H J 1982 *Crystalline Electric Field Effects in f-electron Magnetism* ed R P Guertin, W Suski and Z Zolmerek (New York: Plenum) p 13
[9] Schumacher D P and Hollingsworth C A 1966 *J. Phys. Chem. Solids* **27** 749