CBPF-NF-015/94

Analytical Results for Crystalline Electric Field Eigenvalues of Trivalent Rare-Earth Ions Using Computer Algebra: Application to the Magnetism of PrX_2 (X = Mg, Al, Ru, Rh, Pt)[†]

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

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

[†]Accepted for publication in the Journal of Magnetism and Magnetic Materials

[+]On leave at Massachusetts Institute of Technology, Cambridge MA 02139, USA.

Abbreviated title: Eigenvalues for Crystal Field via Computer Algebra

Abstract

The eigenvalues of the Crystalline Electric Field (CEF) Hamiltonian with cubic symmetry are analytically obtained for trivalent rare-earth ions of ground state J=5/2, 7/2, 4, 9/2, 6, 15/2 and 8, via a Computer Algebra approach. In the presence of both CEF and an effective exchange field, Computer Algebra still allows a partial factorization of the characteristic polynomial equation associated to the total Hamiltonian, a result of interest to the study of the magnetic behavior of rare-earth intermetallics. An application to the PrX_2 intermetallic compounds (X=Mg, Al, Ru, Rh, Pt) is reported.

Key-words: Crystal field; Magnetism; Rare-earth intermetallics; Algebraic computation.

PACS NUMBERS: $75.10-b$; $75.10Dg$; $71.70-d$.

1. Introduction

The Crystalline Electric Field (CEF) concept is one of the basic tenets of solid state physics. The seminal work of H. Bethe [1] opened the way to the application of symmetry operations in the construction of effective Hamiltonians and the classification of orbitals according to the irreducible representation of the point group of the site. Since that time the theory has advanced through the contributions of Stevens [2], Elliott and Stevens [3] and Judd [4], among others. Crystal field theory has become a standard tool for calculating thermal, spectroscopic, magnetic and related properties in solids. In what concern the rare earth ions (with unfilled 4f-shell), the cubic symmetrical CEF eigenvalues and eigenfunctions were systematically studied by Lea, Leask and Wolf [5] (LLW). Their results, computed numerically, were displayed in tables and graphical form and are basic in the determination of the crystal field parameters from neutron inelastic scattering data [6].

The purpose of this paper is to present a computer algebra approach to the study of crystal field of cubic symmetry. Explicit analytical results for the eigenvalues for all angular momenta J′s of interest to rare-earth ions (J=4, 6, 8, 5/2, 7/2, 9/2 and 15/2) are for the first time presented. This extends our recent work for J=4 [7]. In a further effort, we try to analyze the induced magnetic moments and magnetic order for the case where in addition to the CEF interaction, exchange between 4f magnetic ions is introduced.

An outline of the paper goes as follow: in the next section the algebraic approach is precisely defined and the eigenvalues reported; in the third section we try to extend the algebraic approach used in studying crystal field eigenvalues to the more complex problem in which, in addition to the presence of the crystal field, an effective magnetic field is applied in the (1,0,0) direction. We show that apart from the case J=15/2, the polynomial characteristic equation associated to the model Hamiltonian may be factored into simpler polynomials, which contain all the magnetic information. An application to the magnetic properties of PrX_2 (X = Mg, Al, Ru, Rh and Pt), using an algorithm developed previously [7], is performed. The fourth (and last) section summarizes the results obtained.

2. Analytical Eigenvalues of the Crystal Field Hamiltonian of Cubic Symmetry

For cubic symmetry, the CEF Hamiltonian is

$$\mathcal{H}_{cf} \;=\; B_4(O_4^o + 5O_4^4) + B_6(O_6^o - 21O_6^4) \qquad (1)$$

where O_m^n, the Stevens operators, are expressed in powers of the components J_+, J_- and J_z of the angular momentum operator [2]; B_4 and B_6 are adjustable parameters. Equation (1) applies in a coordinate system (x, y, z) which coincides with three of the fourfold symmetry axes of the crystal; z is assumed as the direction of quantization. Taking |J,m> as eigenfunctions of J_z (J and m are respectively the angular momentum

and magnetic quantum numbers), the eigenvalues of $\mathcal{H}_{cf}$ are the roots of the polynomial equation in the variable y

$$det \mid< n, J \mid \mathcal{H}_{cf} - y\delta_{n,m} \mid J, m > \;\; = \;\; 0 \tag{2}$$

Until now CEF eigenvalues have been obtained only numerically, the results displayed in tables and in graphical form, as in LLW [5]. These plots have been used in the obtention of the CEF parameters, from the analysis of inelastic neutron scattering data [6]. It is worth mentioning that for $B_6 = 0$, analytical results have been available for more than thirty years [8].

Equation (2) is dealt with using REDUCE, a well known computer language, for J= 5/2, 7/2 , 4, 9/2, 6, 15/2 and 8. REDUCE is also employed in factoring the corresponding polynomials (of degree 2J + 1). It turns out, surprisingly, that the eigenvalues of H_{cf} are analytically expressible in terms of B_4 and B_6.

In what follows we list the CEF eigenvalues for different J's; the labels $\Gamma's$, which characterize the symmetry nature of the CEF orbitals [9], are those used by LLW [5].

Eigenvalues of the Crystal Field Hamiltonian for J integer:

J= 4 (Pr^{3+} , Pm^{3+}), F_6=1260

$$\begin{aligned} E(\Gamma_1) &= 4(7b_4 - 20b_6) \\ E(\Gamma_3) &= 4(b_4 + 16b_6) \\ E(\Gamma_4) &= 2(7b_4 + 2b_6) \\ E(\Gamma_5) &= -2(13b_4 + 10b_6) \end{aligned}$$

J= 6 (Tb^{3+}, Tm^{3+}), F_6=7560

$$\begin{aligned} E(\Gamma_1) &= -2(63b_4 - 8b_6) \\ E(\Gamma_2) &= 22(3b_4 + 8b_6) \\ E(\Gamma_3) &= 6(19b_4 - 8b_6) \\ E(\Gamma_4) &= -8(12b_4 - b_6) \\ E(\Gamma_5^{(1)}) &= 4(5b_4 - 5b_6 - M) \\ E(\Gamma_5^{(2)}) &= 4(5b_4 - 5b_6 + M) \\ M^2 &= 421b_4^2 + 126b_4b_6 + 784b_6^2 \end{aligned}$$

J= 8 (Ho^{3+}), F_6 = 13860

$$\begin{aligned} E(\Gamma_1) &= 8(49b_4 - 8b_6) \\ E(\Gamma_3^{(1)}) &= 4(7b_4 + 22b_6 - G) \\ E(\Gamma_3^{(2)}) &= 4(7b_4 + 22b_6 + G) \\ E(\Gamma_4^{(1)}) &= 2(49b_4 + 58b_6 - 12N) \\ E(\Gamma_4^{(2)}) &= 2(49b_4 + 58b_6 + 12N) \\ E(\Gamma_5^{(1)}) &= -2(91b_4 + 82b_6 + 4M) \end{aligned}$$

$$
\begin{aligned}
E(\Gamma_5^{(2)}) &= -2(91b_4 + 82b_6 - 4M) \\
G^2 &= 6601b_4^2 + 2492b_4b_6 + 5476b_6^2 \\
N^2 &= 126b_4^2 - 49b_4b_6 + 5476b_6^2 \\
M^2 &= 364b_4^2 - 1183b_4b_6 + 1054b_6^2
\end{aligned}
$$

Eigenvalues of the Crystal Field Hamiltonian for J semi-integer

J= 5/2 (Ce^{3+}, Sm^{3+})

$$
\begin{aligned}
E(\Gamma_7) &= -4b_4 \\
E(\Gamma_8) &= 2b_4
\end{aligned}
$$

J= 7/2 (Yb^{3+}), $F_6 = 1260$

$$
\begin{aligned}
E(\Gamma_7) &= -6(3b_4 + 2b_6) \\
E(\Gamma_6) &= 2(7b_4 - 10b_6) \\
E(\Gamma_8) &= 2(b_4 + 8b_6)
\end{aligned}
$$

J= 9/2 (Nd^{3+}), $F_6 = 2520$

$$
\begin{aligned}
E(\Gamma_6) &= 4(49b_4/5 - 16b_6) \\
E(\Gamma_8^{(1)}) &= -49b_4/5 + 16b_6 - M \\
E(\Gamma_8^{(2)}) &= -49b_4/5 + 16b_6 + M \\
M^2 &= 721b_4^2 + 1568b_4b_6 + 1360b_6^2
\end{aligned}
$$

J= 15/2 (Dy^{3+}, Er^{3+}), $F_6 = 13860$

$$
\begin{aligned}
E(\Gamma_6) &= 2(147b_4 - 20b_6) \\
E(\Gamma_7) &= -26(b_4 + 12b_6)
\end{aligned}
$$

For $x \geq 0$ we have:

$$
\begin{aligned}
E(\Gamma_8^{(1)}) &= (-2/3)[67b_4 - 88b_6 + 4Msin(\theta/3 + \pi/6)] \\
E(\Gamma_8^{(2)}) &= (-2/3)[67b_4 - 88b_6 - 4Msin(\theta/3 - \pi/6)] \\
E(\Gamma_8^{(3)}) &= (-2/3)[67b_4 - 88b_6 + 4Msin(\theta/3 - \pi/2)]
\end{aligned}
$$

and for $x \leq 0$ we have

$$
\begin{aligned}
E(\Gamma_8^{(1)}) &= (-2/3)[67b_4 - 88b_6 - 4Msin(\theta/3 - \pi/2)] \\
E(\Gamma_8^{(2)}) &= (-2/3)[67b_4 - 88b_6 - 4Msin(\theta/3 + \pi/6)] \\
E(\Gamma_8^{(3)}) &= (-2/3)[67b_4 - 88b_6 + 4Msin(\theta/3 - \pi/6)]
\end{aligned}
$$

where

$$\begin{aligned} M^2 &= 14251b_4^2 + 1816b_4b_6 + 8929b_6^2 \\ \theta &= arctan\{-[-(Q^2+4P^3)]^{1/2}/Q\} \\ Q &= -(1024/27)[170072b_4^3 + 22998b_6b_4^2 + 232629b_4b_6^2 - 6686b_6^3] \\ P &= -(16/9)M^2 \\ b_4 &= F_4B_4 = Wx \\ b_6 &= F_6B_6 = W(1-|x|) \\ F_4 &= 60 \end{aligned}$$

3. Magnetic Moments of the Rare-Earth Intermetallic Compounds

The standard model used to discuss magnetic properties of cubic rare-earth intermetallics of formula RX_2 (R=rare-earth, X=non-magnetic ion) takes into account [5]: 1) the CEF interaction; 2) the effective inter-ionic exchange interaction between 4f spins. The latter, in the molecular field approximation, gives rise to the following Hamiltonian

$$\mathcal{H}_{ex} = -g\mu_B \mathbf{h}.\mathbf{J} \tag{3}$$

where g is the Landé factor, μ_B the Bohr magneton and $\mathbf{h}$ the total magnetic field:

$$g\mu_B\mathbf{h} = g\mu_B\mathbf{h}_0 + \lambda_0(g-1)^2 < \mathbf{J} > \tag{4}$$

In (4), λ_0 is the exchange parameter and $\mathbf{h}_0$ an applied magnetic field; $< \mathbf{J} >$ is the thermal average of the angular momentum operator $\mathbf{J}$.

Then, the standard model Hamiltonian, from which we derive magnetic quantities is

$$\mathcal{H} = \mathcal{H}_{cf} + \mathcal{H}_{ex} \tag{5}$$

If the eigenvalues of $\mathcal{H}$ in equation (5) are available, the magnetic moments in the $\mathbf{n}$ direction ($\mathbf{n}$ is a unit vector), are given by

$$g\mu_B < i \mid \mathbf{J}.\mathbf{n} \mid i > \equiv -\frac{dy_i}{dh} = -g\mu_B\frac{dy_i}{d\alpha} \tag{6}$$

where $h = \mathbf{h}.\mathbf{n}$ and $\alpha = g\mu_B h$.

In what follows we take $\mathbf{n} = (1,0,0)$, so that

$$\mathcal{H}_{ex} = -g\mu_B h J_x \tag{7}$$

We now make use of equation (2), substituting $\mathcal{H}$ for $\mathcal{H}_{cf}$ and obtain, using REDUCE, rather complicated polynomials of degree 2J + 1. Fortunately, REDUCE can factor most of the polynomials into simpler factors. Tables 1 and 2 show the kind of factors obtained for different J's.

Table 1

J	Factor polynomials
4	three of 2nd degree, one of 3rd degree
6	three of 3rd degree, one of 4th degree
8	two of 4th degree, one of 9th degree

Table 1: Factor Polynomials for J integer.

Table 2

J	Factor polynomials
5/2	three of 1st degree, two of 2nd degree
7/2	four of 2nd degree
9/2	two of 2nd degree, two of 3rd degree
15/2	no simple factors

Table 2: Factor Polynomials for J semi-integer.

All relevant magnetic information are contained in these factor polynomials. For J=4 and J=9/2 the factor polynomials were given in the Appendix of [7]. Let P(y,B_4,B_6,α) be one of the above mentioned factors, whose roots y_i are the energy eigenvalues.

We have

$$P(y, B_4, B_6, \alpha) = 0 \tag{8}$$

$$\frac{\partial P}{\partial y}\left(\frac{dy}{d\alpha}\right) + \frac{\partial P}{\partial \alpha} = 0 \tag{9}$$

Combining equations (8) and (9) we may solve for $dy/d\alpha$, for each root of the polynomial equation. Most of the algebra involving (8) and (9) are also done with REDUCE.

Equations (8) and (9) can be used to expand the model eigenvalues up to α^2. The procedure has already been discussed in [7] and it allows the determination of the coefficients α and α^2 in terms of the parameters of the model (see Appendix for the case J=4). These coefficients had been previously obtained by Schumacher and Holligsworth [10] for the case $B_6 = 0$, using numerical methods. From the expansion of the eigenvalues we can obtain the expression of the Curie temperature as a function of the model parameters. Table 3 shows the values of λ_0 and g_{eff} obtained for PrX_2, using the values of T_C, CEF parameters and low temperature magnetization measurements given in the literature [6, 11, 12, 13]. Again, the case of X=Al is reproduced for comparison.

Table 3

	x	W(mev)	$T_c(K)$	$m_o(ion/\mu_B)$	g_{eff}	λ_o	Jg_{eff}	Γ_i
$PrMg_2^{(a)}$	0.671	-0.345	10.0	2.00	0.633	9.36	2.53	Γ_3
$PrAl_2^{(b)}$	0.739	-0.329	33.0	2.80	0.747	24.23	2.99	Γ_3
$PrRu_2^{(c)}$	0.680	-0.330	33.9	1.73	0.481	6.65	1.92	Γ_3
$PrRh_2^{(c)}$	0.930	-0.350	7.9	1.16	0.302	3.03	1.21	Γ_1
$PrPt_2^{(c)}$	0.930	-0.380	7.7	1.52	0.397	3.90	1.59	Γ_1

Table 3: Computed effective Landé factors (g_{eff}) and exchange parameters (λ_0) for PrX_2 compounds. In (a) the CEF data are from [6]; T_C and m_0 are from [13]; in (b) the CEF data, T_C and m_0 are taken from [11] and in (c) the CEF data are taken from [6], m_0 and T_C from [12]. CEF parameters refer to x and W (LLW notation) defined at the end of section 2.

4. Conclusions

The main contribution of this paper is the use of Computer Algebra in dealing with CEF eigenvalues and magnetic quantities of interest to the rare-earth intermetallic compounds. We think that the analytical results obtained for the first time for the CEF eigenvalues and the expansion of the eigenvalues of the total Hamiltonian up to second order of the effective magnetic field may give insights not available in the usual numerical treatment. In section 3 we have tried to show how Computer Algebra can facilitate the analysis of the characteristic equation associated to the total model Hamiltonian through the decomposition of a complex problem (a polynomial of the degree 2J+1) into simple parts (factor polynomials of lower degree). We have also developed a simple algorithm to obtain magnetic information from these factorized polynomials. The parametrization of magnetic quantities of some PrX_2 compounds (see Table 3) illustrates this procedure. In our opinion the Computer Algebra approach applied to CEF (not only cubic symmetric) and magnetic related problems may present potentialities far beyond the simple examples treated in this paper.

Acknowledgement

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

Appendix

Eigenvalues of the combined CEF and magnetic model Hamiltonian, for J=4, up to α^2 ($\alpha = g\mu_B h$).

$$
\begin{aligned}
E(\Gamma_1) &= 4(7b_4 - 20b_6) + \frac{10\alpha^2}{21(b_4 - 6b_6)} \\
E(\Gamma_3^{(1)}) &= 4(b_4 + 16b_6) - \frac{14\alpha^2}{15(b_4 - 6b_6)} \\
E(\Gamma_3^{(2)}) &= 4(b_4 + 16b_6) + \frac{2\alpha^2}{3(5b_4 + 14b_6)} \\
E(\Gamma_4^{(1)}) &= 2(7b_4 + 2b_6) - \frac{\alpha}{2} + \frac{7\alpha^2}{32(5b_4 + 3b_6)} \\
E(\Gamma_4^{(2)}) &= 2(7b_4 + 2b_6) + \frac{16\alpha^2}{35(b_4 - 6b_6)} \\
E(\Gamma_4^{(3)}) &= 2(7b_4 + 2b_6) + \frac{\alpha}{2} + \frac{7\alpha^2}{32(5b_4 + 3b_6)} \\
E(\Gamma_5^{(1)}) &= -2(13b_4 + 10b_6) - \frac{5\alpha}{2} - \frac{7\alpha^2}{32(5b_4 + 3b_6)} \\
E(\Gamma_5^{(2)}) &= -2(13b_4 + 10b_6) - \frac{2\alpha^2}{3(5b_4 + 14b_6)} \\
E(\Gamma_5^{(3)}) &= -2(13b_4 + 10b_6) + \frac{5\alpha}{2} - \frac{7\alpha^2}{32(5b_4 + 3b_6)}
\end{aligned}
$$

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