

EXACT CALCULATION OF THE CRYSTAL-FIELD EFFECTS ON
PARAMAGNETIC CURIE TEMPERATURE IN RARE EARTH
COMPOUNDS

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The exact expression for the paramagnetic Curie temperature in rare earth crystal compounds is obtained according to the molecular field model given by Bowden et al. [1]. It is shown exactly that only the second order terms of the crystalline electric field (CEF) Hamiltonian have influence on the paramagnetic Curie temperature and only the first two CEF parameters could be unambiguously deduced from the magnetic susceptibility measurements.

1. Introduction

Usually the magnetic measurements on single crystals of rare earth compounds have shown a large anisotropy of paramagnetic susceptibility characterised by paramagnetic Curie temperatures along the principal crystalline axes, indicating significant CEF effects.

According to the modified molecular field model given by Bowden et al. [1] the values of the paramagnetic susceptibility and paramagnetic Curie temperature along principal crystalline axes can be calculated by the following equations

$$\chi_q = \frac{C}{T - \Theta_q}, \quad \Theta_q = \Theta_p - \frac{3T \{J_q^2 H_{CF}\}}{kJ(J+1)(2J+1)}, \quad q = x, y, z \quad (1)$$

where the C is the Curie constant, k is the Boltzmann constant, J is the angular momentum, H_{CF} is the CEF Hamiltonian and Θ_p is the paramagnetic Curie temperature due only to the molecular field.

These formulae show that along the three directions x, y, z and for high enough temperatures the susceptibilities follow the Curie-Weiss law and from one variation to the other there is a shift which depends on H_{CF} . From these formulae it is possible to determine the CEF parameters.

Following these considerations Zajac et al. [2] have calculated the expression of Θ_q for a CEF Hamiltonian corresponding to orthorhombic symmetry

$$H_{CF} = V_0^0 O_2^0 + V_2^0 O_2^0 + V_4^0 O_4^0 + V_4^0 O_4^0 + V_6^0 O_6^0 + V_6^0 O_6^0 + V_6^4 O_6^4 + V_6^6 O_6^6 \quad (2)$$

They have established that the Stevens operators O_2^0, O_2^2, O_4^0 and O_6^0 (and implicitly the CEF parameters V_2^0, V_2^2, V_4^0 and V_6^0) have influence on the paramagnetic Curie temperature (2) but their result is wrong¹.

2. Results and discussion

The main purpose of this paper is to calculate Θ_q using the general CEF Hamiltonian obtained according to Hutchings [3]:

$$H_{CF} = \sum_{n,m} V_n^m O_n^m(J) \quad (3)$$

where V_n^m are the CEF parameters, O_n^m are the Stevens equivalent operators and $n = 2, 4, 6, m = 0, 2, 3, 4, 6$ ($m < n$) for the rare earth ions.

The contribution can be calculated for each term of the CEF Hamiltonian (3), thus

$$\begin{aligned} \text{Tr} \{ J_z^2 O_2^0 \} &= \text{Tr} \{ J_z^2 [3J_z^2 - J(J+1)] \} \\ &= 3\text{Tr} \{ J_z^2 J_z^2 \} - J(J+1)\text{Tr} \{ J_z^2 \} \\ &= \frac{1}{10} J(J+1)(2J+1)(2J^2+2J+1) - \frac{1}{3} [J(J+1)]^2 (2J+1) \\ &= -\frac{1}{30} J(J+1)(2J+1)(2J-1)(2J+3) \end{aligned} \quad (4)$$

$$\begin{aligned} \text{Tr} \{ J_z^2 O_2^2 \} &= \text{Tr} \{ J_z^2 [3J_z^2 - J(J+1)] \} = 3\text{Tr} \{ J_z^4 \} - J(J+1)\text{Tr} \{ J_z^2 \} \\ &= \frac{1}{5} J(J+1)(2J+1)(3J^2+3J-1) - \frac{1}{3} [J(J+1)]^2 (2J+1) \\ &= \frac{1}{15} J(J+1)(2J+1)(2J-1)(2J+3) \end{aligned} \quad (5)$$

$$\begin{aligned} \text{Tr} \{ J_x^2 O_2^2 \} &= \text{Tr} \{ J_x^2 (1/2) [J_x^2 + J_y^2] \} = \text{Tr} \{ J_x^4 \} - \text{Tr} \{ J_z^2 J_y^2 \} \\ &= \frac{1}{15} J(J+1)(2J+1)(3J^2+3J-1) \\ &\quad - \frac{1}{30} J(J+1)(2J+1)(2J^2+2J+1) \\ &= -\frac{1}{30} J(J+1)(2J+1)(2J-1)(2J+3) \end{aligned} \quad (6)$$

¹The very fresh work by Nowotny and Zajac [8] communicated to us after submission of this paper, already corrects their earlier results [2]

$$\text{Tr} \{ J_y^2 O_2^2 \} = -\text{Tr} \{ J_z^2 O_2^2 \} = \frac{1}{30} J(J+1)(2J+1)(2J-1)(2J+3) \quad (7)$$

$$\text{Tr} \{ J_z^2 O_2^2 \} = \text{Tr} \{ J_z^2 (1/2) [J_x^2 + J_y^2] \} = \text{Tr} \{ J_z^2 J_x^2 \} - \text{Tr} \{ J_z^2 J_y^2 \} = 0 \quad (8)$$

and

$$\text{Tr} \{ J_q^2 O_n^m \} = 0, \quad q = x, y, z, \quad m > 2, \quad n > 2 \quad (9)$$

To demonstrate the relation (9) we give below a few examples of calculations.

Example 1.

$$\begin{aligned} \text{Tr} \{ J_z^2 O_4^0 \} &= \text{Tr} \{ J_z^2 [35J_z^4 - 30J(J+1)J_z^2 + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2] \} \\ &= 35\text{Tr} \{ J_z^6 \} - [30J(J+1) - 25]\text{Tr} \{ J_z^4 \} - [6J(J+1) - 3J^2(J+1)^2] \text{Tr} \{ J_z^2 \} \\ &= \frac{5}{3} J(J+1)(2J+1)(3J^4+6J^3-3J+1) \\ &\quad - \frac{1}{3} J(J+1)(2J+1)(6J^2+6J-5)(3J^2+3J-1) \\ &\quad + \frac{1}{3} J(J+1)(2J+1)(3J^4+6J^3-3J^2-6J) = 0 \end{aligned} \quad (10)$$

Example 2.

$$\begin{aligned} \text{Tr} \{ J_z^2 O_4^2 \} &= \text{Tr} \{ J_z^2 (1/4) \\ &\quad \times [(7J_z^2 - J(J+1) - 5)(J_x^2 + J_y^2) + (J_x^2 + J_y^2)(7J_z^2 - J(J+1) - 5)] \} \\ &= \text{Tr} \{ J_z^2 [(7J_z^2 - J(J+1) - 5)(J_x^2 - J_y^2)] \} \\ &= 7\text{Tr} \{ J_x^4 J_z^2 \} - 7\text{Tr} \{ J_z^2 J_x^2 J_y^2 \} - [J(J+1) + 5](\text{Tr} \{ J_x^4 \} - \text{Tr} \{ J_x^2 J_y^2 \}) \\ &= (1/30) J(J+1)(2J+1) \times \\ &\quad \times [6J^4 + 12J^3 + 14J^2 + 8J - 5 - (J-1)(J+2)(2J^2+2J-5)] - \\ &\quad - (1/30) [J(J+1) + 5] J(J+1)(2J+1) [2(3J^2+3J-1) - (2J^2+2J+1)] \end{aligned} \quad (11)$$

Obviously we have

$$\text{Tr} \{ J_x^2 O_4^2 \} = \text{Tr} \{ J_z^2 O_4^2 \} = 0 \quad (12)$$

and

$$\begin{aligned} \text{Tr} \{ J_z^2 O_4^4 \} &= \text{Tr} \{ J_z^2 [(7J_z^2 - J(J+1) - 5)(J_x^2 - J_y^2)] \} \\ &= 7\text{Tr} \{ J_z^2 J_x^2 \} - 7\text{Tr} \{ J_z^2 J_y^2 \} - [J(J+1) + 5](\text{Tr} \{ J_z^2 J_x^2 \} - \text{Tr} \{ J_z^2 J_y^2 \}) \\ &= 0 \end{aligned} \quad (13)$$

Example 3.

$$\begin{aligned} & \text{Tr} \{ J_x^2 O_6^2 \} \\ &= \text{Tr} \{ J_x^2 [33J_x^4 - (18J(J+1) + 123) J_x^2 + J^2(J+1)^2 + 10J(J+1) + 102] \\ & \quad \times (J_x^2 - J_y^2) \} \\ &= 33 (\text{Tr} \{ J_x^4 J_x^4 \} - \text{Tr} \{ J_x^2 J_x^4 J_y^2 \}) \\ & \quad - [18J(J+1) + 123] (\text{Tr} \{ J_x^4 J_x^2 \} - \text{Tr} \{ J_x^2 J_x^2 J_y^2 \}) \\ & \quad + [J^2(J+1)^2 + 10J(J+1) + 102] (\text{Tr} \{ J_x^4 \} - \text{Tr} \{ J_x^2 J_y^2 \}) = 0 \end{aligned} \quad (14)$$

because we have:

$$\text{Tr} \{ J_x^4 J_x^4 \} = \frac{1}{210} J(J+1)(2J+1)(2J^6 + 6J^5 + 14J^4 + 18J^3 + J^2 - 7J + 1) \quad (15)$$

$$\text{Tr} \{ J_x^2 J_x^4 J_y^2 \} = \frac{1}{630} J(J+1)(2J+1)(J-1)(J+2)(2J^4 + 4J^3 - 19J^2 - 21J + 12) \quad (16)$$

$$\text{Tr} \{ J_x^4 J_x^2 \} = \frac{1}{210} J(J+1)(2J+1)(6J^4 + 12J^3 + 14J^2 + 8J - 5) \quad (17)$$

$$\text{Tr} \{ J_x^2 J_x^2 J_y^2 \} = \frac{1}{210} J(J+1)(2J+1)(J-1)(J+2)(2J^2 + 2J - 5) \quad (18)$$

$$\text{Tr} \{ J_x^4 \} = \frac{1}{15} J(J+1)(2J+1)(3J^2 + 3J - 1) \quad (19)$$

$$\text{Tr} \{ J_x^2 J_y^2 \} = \frac{1}{30} J(J+1)(2J+1)(2J^2 + 2J + 1) \quad (20)$$

The algebraic evaluation in a systematic way in the manner illustrated in the examples given above has shown the validity of the relation (9) for all n , $m > 2$ and $q = x, y, z$.

From equations (1) via relations (4-9) we obtain the following expressions for the paramagnetic Curie temperature

$$\Theta_x = \Theta_P + \frac{(2J-1)(2J+3)}{10k} (V_2^0 + V_2^2) \quad (21)$$

$$\Theta_y = \Theta_P + \frac{(2J-1)(2J+3)}{10k} (V_2^0 - V_2^2) \quad (22)$$

$$\Theta_z = \Theta_P - \frac{(2J-1)(2J+3)}{5k} V_2^0 \quad (23)$$

$$\Theta_P = \frac{1}{3} (\Theta_x + \Theta_y + \Theta_z) \quad (24)$$

3. Conclusions

The formulae (21-25) have been frequently used in literature for the calculation of the CEF parameters when the Hamiltonian (3) is only approximated in the second term [4], [5], [6], [7]. In this paper we have shown that the contribution of the 4th and 6th order CEF parameters in formulae (21-24) is zero for the elementary symmetry reasons involved by the model used in calculation.

It is obvious that only the first two CEF parameters can be determined in this way from the experimental values of paramagnetic Curie temperatures using the relations

$$V_2^0 = \frac{5k(\Theta_x + \Theta_y - 2\Theta_z)}{3(2J-1)(2J+3)}, \quad V_2^2 = \frac{5k(\Theta_x - \Theta_y)}{(2J-1)(2J+3)} \quad (25)$$

For a uniaxial crystal $V_2^2 = 0$ we then have $\Theta_x = \Theta_{\parallel}$ and $\Theta_z = \Theta_y = \Theta_{\perp}$.

The above analysis corrects the results obtained by Zajac and Maczjak in [2] and shows that in the given model only the second order terms in the CEF Hamiltonian will contribute to Θ_q besides the anisotropic exchange interactions [4].

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