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Point-charge and induced-dipole model analysis of spin-Hamiltonian parameters for Gd^{3+}-doped single crystals of rare-earth trifluorides

Norman R. Lewis and Sushil K. Misra
Physics Department, Concordia University, Sir George Williams Campus,
1455 de Maisonneuve Boulevard West, Montreal, H3G 1M8 Canada

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Spin-Hamiltonian parameters are calculated for Gd^{3+}-doped single crystals of rare-earth trifluorides RF_3 (R = La,Ce,Pr,Nd), with the use of the point-charge—plus—induced-dipole model. It is found that most of the parameters can be computed to be within experimental error by suitable choices of polarizability tensors.

I. INTRODUCTION

In attempting to explain the physical origin of crystal-field parameters for rare-earth-metal ions, two basic approaches have been taken; these appear, at first sight, to be mutually contradictory. On one hand, it is argued that the observed spectra depend mainly on short-range mechanisms, such as convalency and overlap. (Newman[1,2] has listed ten effects of this sort.) On the other hand, the model based on long-range contributions due to point charges and induced dipoles (PCID) has also met with success. Calculations of this sort have been done by Bogomolova *et al.*,[3] Bijvank *et al.*,[4–6] Faucher *et al.*,[7] and more recently by Lewis and Misra[8] (hereafter referred to as LM). For the latter model, one needs polarizability tensors conforming to the symmetry of the crystal. The calculation done so far that takes this requirement into account is that of LM for the system Gd^{3+}:$RCl_3\cdot 6H_2O$ (R = Nd,Sm,Eu,Tb,Dy,Ho,Er,Tm). It was found there that, with a suitable choice of the elements of the polarizability tensor, one can compute numerical values of spin-Hamiltonian parameters within experimental errors. It is the purpose of the present paper to apply the analysis of LM (Ref. 8) (point-charge—plus—induced-dipole model) to the system Gd^{3+}:RF_3 (R = La,Ce,Pr,Nd). To this end, very accurate experimentally measured values for the spin-Hamiltonian parameters of this system have recently been reported by Misra *et al.*[9]

II. THEORY

As the theory of the PCID model can be found in LM, only an outline will be given here. The spin Hamiltonian of the Gd^{3+} ion for rare-earth trifluoride hosts is given,[9–11] in the usual notation, as

$$\mathcal{H}=\mu_B\vec{H}\cdot\overleftrightarrow{g}\cdot\vec{S}+\sum_{l}\sum_{\substack{m\ \text{even}\\ 0\leq m\leq l}} B_l^m O_l^m,\quad l=2,4,6\ , \tag{1}$$

where μ_B, $\vec{H}$, $\overleftrightarrow{g}$, $\vec{S}$, and O_l^m represent the Bohr magneton, static magnetic field, the g tensor, the ionic spin of Gd^{3+} ($=\frac{7}{2}$), and spin operators, respectively. Regarding the parameters for $m<0$, the experimental results of Ref. 9 indicate that their values are very small (of the order of experimental errors). For the particular crystal structure dealt with here (see below), they should be identically zero, from symmetry considerations. This was, indeed, verified by an explicit calculation. The spin-Hamiltonian parameters B_l^m are related to the crystal-field parameters A_l^m by[8,11]

$$B_l^m=A_l^m\langle r^l\rangle K_l\gamma_l\ , \tag{2}$$

where $\langle r^l\rangle$ is the expectation value of r^l over the appropriate wave function, γ_l is a screening constant, and K_l is a reduced matrix element. This relation is valid provided that only mechanisms which are linear in the parameters A_l^m contribute to the parameters B_l^m. There is considerable evidence that this is the case, at least for $l=2$. Examples are the results for lanthanide ethylsulphates,[12] studies on insulator data,[2] and the work of Bijvank *et al.*[4–6] Further, Newman's successful superposition model, mentioned above, is based on the validity of this assumption.[13] In this context, Newman[14] argues that a linear relationship also exists for the $l=4$ parameters. This question is further analyzed by Barnes *et al.*[15]

Given the assumption of linearity, there still exists the separate question of how it can be the case that the relative sign of B_l^m and A_l^m is different for Gd^{3+} substituted in different hosts belonging to the same isostructural series [e.g., YVO_4 and YPO_4 (Ref. 2)]. In the PCID model, as will be shown below, one writes A_l^m as a sum of point-charge contributions plus induced-dipole contributions. In many cases, these terms are of the same order of magnitude but of opposite sign. Further, the dipole term is very sensitive to the local environment. Thus it is quite possible for the resultant sum A_l^m to change sign in going from host to host in a homologous isostructural series. The term K_l in Eq. (2) is usually ascribed to those effects which contribute to the B_l^m but not to the A_l^m. These are discussed in Refs. 8 and 12. However, some mechanisms, for example, the correlation crystal field,[2,12] although incorporated in the K_l, do depend on the effect of the crystalline environment and have a contribution of opposite sign to that of other significant mechanisms. Thus it is possible that, in some cases, because of different local coordination for different members of a homologous isostructural series, either the A_l^m or the K_l in Eq. (2) change sign, thus inverting the relative sign of B_l^m and A_l^m. In any case, in the series being considered here, the relative sign does not change. As well, the case of Eq. (2) does give good results, as will be seen below.

Specifically, in the PCID model, the A_l^m are written as

$$A_l^m = -|e| \sum_i q_i \left[\frac{Z_l^m(r_i)}{r_i^{l+1}} \right] - |e| \sum_i \vec{p}_i \cdot \vec{\nabla} \left[\frac{Z_l^m(r_i)}{r_i^{l+1}} \right] . \quad (3)$$

The index i runs over all the ions in the crystal, r_i ($\equiv |\vec{r}_i|$) is the magnitude of the radius vector of the ith ion with respect to the substituted Gd^{3+} ion taken as origin, $|e|$ is the magnitude of the charge on the electron, q_i is the valence of the ith ion, and $\vec{p}_i$ [$\equiv p_\beta(i);\beta=x,y,z$] is the dipole moment vector, induced at the site of the ith ion. The Z_l^m are spherical harmonics (listed in LM). The sums in Eq. (3) may be evaluated by Ewald's method,[16,17] provided that one knows the values of $p_\beta(i)$. These may be found from the relation

$$p_\beta(k) = \sum_\gamma \alpha_{\beta\gamma}(k) E_\gamma(k), \quad \gamma = x,y,z \quad (4)$$

where $\alpha_{\beta\gamma}(k)$ is the polarizability tensor of ion k, and $E_\gamma(k)$ ($\gamma=x,y,z$) are the components of the total electric field at the site of ion k. The values of $E_\gamma(k)$ may also be found by Ewald's method.[16,17]

The question of what polarizabilities to assign in the use of Eq. (4) has been discussed in detail in LM. The predominant consideration is that the form of the tensor must conform to the symmetry of the crystal.[18] In the case of RF_3(hexagonal[9]) this required a tensor of the form[19]

$$\alpha = \begin{bmatrix} \alpha_o & 0 & 0 \\ 0 & \alpha_o & 0 \\ 0 & 0 & \alpha_e \end{bmatrix} \quad (5)$$

at the site of both the rare-earth-metal and fluoride ions. Here $\alpha_o = \alpha_{11} = \alpha_{22}$ and $\alpha_e = \alpha_{33}$. [Note that hexagonal symmetry requires the off-diagonal components (α_{ij}, $i \neq j$) to be zero.] The subscripts in Eq. (5) allude to the fact that RF_3 is birefringent. That is, the optical index of refraction as measured along the z axis (n_e) is different from that measured along the x or y axis (n_o). (The "e" and "o" refer to the so-called "extraordinary" and "ordinary" rays.) The polarizabilities are crudely related to these indexes of refraction by the Lorentz relation.[7] Since the measured values of n_o and n_e for any RF_3 differ by less 0.5%,[20] it will be assumed, for the present calculations, that one may take $\alpha_e = \alpha_o$ for all the rare-earth-metal ions in the crystal. Furthermore, it is noted that the polarizability of a given ion is not necessarily the same in different crystals,[21] and that the polarizability of an ion in a crystal may be different from its free-ion value.

These considerations were used in the employment of Eqs. (2)–(4) to calculate the spin-Hamiltonian parameters B_2^m ($m=0,2$) and B_4^m ($m=0,2,4$), for RF_3 ($R=$La,Ce,Pr,Nd). The various crystal structures which have been proposed for RF_3 are discussed in Ref. 9. The unit cell used for this calculation has symmetry D_{6h}^3 ($P6_3/mcm$). Details regarding unit-cell parameters are given in Refs. 22 and 23.

In the computation one would normally need values for the polarizability of the fluorine ion (F^-) for each of the four hosts in the series (always taking $\alpha_o = \alpha_e$) and for R^{3+} ($R=$La,Ce,Pr,Nd). However, for the crystal structure being used, it is known *a priori*, from symmetry, that the electric

TABLE I. Polarizabilities (Å^3) used for Eq. (5).

Host	$\alpha(F^-)$
La	0.0168
Ce	0.0163
Pr	0.0159
Nd	0.0157

TABLE II. Second-order spin-Hamiltonian parameters b_l^m (GHz). Note that $b_2^m = 3B_2^m$ and the experimental error is ±0.01 GHz.

Host	Parameter index	Calculated	Experiment (Ref. 9)	Difference
La	20	0.685	0.693	0.008
	22	−0.074	−0.085	−0.011
Ce	20	0.737	0.735	−0.002
	22	−0.090	−0.084	−0.006
Pr	20	0.770	0.773	0.003
	22	−0.081	−0.081	0.000
Nd	20	0.802	0.795	−0.007
	22	−0.146	−0.149	−0.003

field at the rare-earth-metal sites is identically zero. Thus in the present case, only the fluorine polarizabilities are required. As a first estimate, the free-ion value[24] (0.76 Å^3) is used. It is found that, in order to get agreement with experimental values, the value for the polarizabilities of the various F$^-$ ions had to be decreased. The results are presented in Table I. On the basis of this, the computed values for B_2^0 and B_2^2 are given in Table II, and those for B_4^0, B_4^2, and B_4^4 are given in Table III. The values for B_2^0, B_2^2, and B_4^0 agree with experimental values within experimental limits. On the other hand, the B_4^2 and B_4^4 values do not fully agree with experimental ones; this might be because such high-order parameters are extremely sensitive to distortions of the ionic positions; these distortions are not considered in this paper.

III. ANALYSIS

It is noted that the values obtained for the polarizability of the F$^-$ ion ($\sim$0.016 Å^3) are rather small compared to the reported free-ion value (0.760 Å^3). However, such a low value may be consistent with the predictions of the shell model[25–27] of polarizability. In this model the anion polarizability may be expressed as[25]

$$\alpha_- = \frac{(n_- e + D)^2}{k_- + A} . \tag{6}$$

Here n_- is the effective number of outer-shell electrons participating in the polarization process, k_- is the shell-core spring constant, A is a shell-shell spring constant, and D is an exchange-charge parameter related to orbital-overlap effects. For F$^-$ the value of n_- has been reported to be as low as 0.9 (Ref. 26) and that for D/e as -0.1 (Ref. 25). The values for k_- and A for F$^-$ have been given as 5100 N/m and 100 N/m, respectively.[26] Using these, the value for α_- is found to be 0.028 Å^3, which is of the same order of magnitude as that found in the present work (PCID model). While the values of the shell-model parameters are highly uncertain, they do show that a low "in-crystal polari-

TABLE III. Fourth-order spin-Hamiltonian parameters b_l^m (GHz). Note that $b_4^m = 60B_4^m$ and the experimental error is ±0.01 GHz.

Host	Parameter index	Calculated	Experiment (Ref. 9)	Difference
La	40	0.019	0.016	−0.003
	42	0.043	0.074	0.031
	44	−0.063	0.125	0.188
Ce	40	0.020	0.016	−0.004
	42	0.045	0.085	0.040
	44	−0.057	0.169	0.226
Pr	40	0.021	0.016	−0.005
	42	0.047	0.083	0.036
	44	−0.053	0.117	0.170
Nd	40	0.021	0.018	−0.003
	42	0.047	0.105	0.058
	44	−0.050	0.128	0.178

zability" value for F^- is not implausible.

There is, however, another way to interpret the present results in terms of polarizability values which are close to the free-ion value. This can be seen to be true if one introduces off-diagonal terms in the polarizability tensor, which presumably arise due to distortions of ionic positions. Then the polarizability tensor becomes of the form given below if the distortion reduces the local symmetry to monoclinic and/or triclinic[19]:

$$\alpha = \begin{bmatrix} \alpha_o & \alpha_x & 0 \\ \alpha_x & \alpha_o & 0 \\ 0 & 0 & \alpha_e \end{bmatrix} \tag{7}$$

(where $\alpha_o = \alpha_e$, as discussed previously). Then it follows that, in the equations for the dipole moment, one uses, instead of $\alpha_o \simeq 0.016$, the relation

$$\alpha^1 \equiv \alpha_o - \frac{\alpha_x^2}{\alpha_o} \simeq 0.016 \; . \tag{8}$$

Clearly, α_o *can* now be of the order of the free-ion value ($\alpha_x \sim \alpha_o$). [In the computational method being used here one needs only the value of α^1 as given by (8). Thus it cannot predict α_o and α_x separately.]

IV. CONCLUSION

The above results reinforce the conclusion of LM that it is possible to explain the crystal-field splitting of Gd^{3+} using a polarizable dipole model. It is noted that the distortion of ionic positions could play a significant role. Thus further computation along the present line should consider taking into account the distortions quantitatively.

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