PHYSICAL REVIEW B VOLUME 25, NUMBER 8 15 APRIL 1982

Point-charge and induced-dipole model analysis of spin-Hamiltonian parameters for Gd^{3+} doping single crystals of rare-earth-metal trichloride hexahydrates

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

(Received 31 July 1981)

Spin-Hamiltonian parameters are calculated for Gd^{3+} doping single crystals of rare-earth-metal trichloride hexahydrates $R\mathrm{Cl}_3\cdot 6\mathrm{H}_2\mathrm{O}$ (RTH): $R =$Nd, Sm, Eu, Tb, Dy, Ho, Er, and Tm, with the use of the point-charge plus induced-dipole model, with variable anisotropic tensor polarizabilities. It is found that the parameters can all be computed to be within experimental error by suitable choices of polarizability tensors. Conclusions about the polarizability values of the various ions in the RTH crystals are drawn.

I. INTRODUCTION

Although a great deal of work has been done in attempting to explain the physical origin of crystal-field parameters for rare-earth-metal ions, the theoretical results reported so far are in poor agreement with experiment.[1] It has been proposed that the observed spectra depend on various effects such as covalency and overlap, in addition to the electrostatic field of the surrounding ions. Newman[2] has listed ten such mechanisms. Many of these factors partially cancel each other. Thus, resulting theoretically computed values of the parameters are very sensitive to small changes in any one of these effects.[3,4] Recently, however, the evidence suggests that these contributions may be less important than was assumed. This conclusion arises from considerations based on models using point charges and induced dipoles. Calculations of this sort have been done by Bogomolova *et al.*,[5] Bijvank *et al.*,[6–8] and Faucher *et al.*[9] For these models, one requires the polarizabilities of the various ions in the given host lattice. References 6–9 employ isotropic polarizability tensors, while Ref. 5 uses an anisotropic polarizability tensor, but not one conforming to the symmetry of the crystal. Also, Refs. 6–8 require distortion of ionic positions. None of these references has addressed itself to an isostructural series like that of rare-earth-metal trichloride hexahydrates (RTH), and their results, while promising, do not agree well with experimental values, especially for B_2^2. For the isostructural series of RTH hosts, the only calculation that has been made for the Gd^{3+} spin-Hamiltonian parameters is solely on the basis of the point-charge model not taking into account induced dipoles; the results do not agree with the experimental values.[10]

It is the purpose of this paper to report the calculation of spin-Hamiltonian parameters for Gd^{3+} substituted in the isostructural series $R\mathrm{Cl}_3\cdot 6\mathrm{H}_2\mathrm{O}$, $R =$Nd, Sm, Eu, Tb, Dy, Ho, Er, and Tm, on the basis of a point-charge plus induced-dipole model using anisotropic tensor polarizabilities. (See Sec. IV for references with regard to the unit-cell structure of RTH.)

II. THEORY

The spin Hamiltonian of the Gd^{3+} ion for rare-earth-metal trichloride hexahydrate (RTH) hosts is given,[11,12] in the usual notation, as

$$\mathscr{H} = \mu_B \vec{\mathrm{H}}\cdot\vec{\mathrm{g}}\cdot\vec{\mathrm{S}} + \sum_{l,m} B_l^m O_l^m, l=2,4,6,\quad 0 \le m(\text{even}) \le l \tag{1}$$

where μ_B, H, g, 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. The spin-Hamiltonian parameters B_l^m are related to the crystal-field parameters A_l^m by[12]

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

where $\langle r^l \rangle$ is the expectation value of r^l over the appropriate wave function,[13] γ_l is a screening constant, and K_l is a reduced matrix element. One may write the A_l^m as follows[5,9]:

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

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 induced at the site of the ith ion. In Eq. (3), the specific harmonics required for this paper are[5]

$$Z_2^0=\frac{(3z_i^2-r_i^2)}{4r_i^2} , \tag{4a}$$

$$Z_2^2=\frac{3}{4}\frac{(x_i^2-y_i^2)}{r_i^2} , \tag{4b}$$

$$Z_4^0=\frac{1}{64}\frac{(35z_i^4-30z_i^2r_i^2+3r_i^4)}{r_i^4} , \tag{4c}$$

$$Z_4^2=\frac{5}{16}\frac{(7z_i^2-r_i^2)(x_i^2-y_i^2)}{r_i^4} , \tag{4d}$$

$$Z_4^4=\frac{35}{64}\frac{(x_i^4-6x_i^2y_i^2+y_i^4)}{r_i^4} . \tag{4e}$$

All of the sums in Eqs. (3) and (4) may be evaluated using Ewald's method[14,15] provided that one knows the values of $p_\beta(i)$. These may be found from the relation

$$p_\beta(k)=\sum_\gamma \alpha_{\beta\gamma}(k)E_\gamma(k), \quad \beta,\gamma=x,y,z \tag{5}$$

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 the ion k. The latter is composed of the monopole field $E'_\gamma(k)$ and the dipole field $E''_\gamma(k)$, i.e.,

$$E_\gamma(k)=E'_\gamma(k)+E''_\gamma(k) . \tag{6}$$

Putting (6) in (5) and inverting gives

$$\sum_{\beta=x,y,z}\alpha^{-1}_{\beta\gamma}(k)p_\beta(k)=E'_\gamma+E''_\gamma(k) . \tag{7}$$

However, one may write $E''_\gamma(k)$ as

$$E''_\gamma(k)=\sum_{k'}\sum_\beta Q_{\gamma\beta}(kk')p_\beta(k'), \quad \beta,\gamma=x,y,z \tag{8}$$

where the index k' runs over all the ions in the crystal and

$$Q_{\gamma\beta}(kk')\equiv\frac{\partial^2}{\partial x_\gamma \partial x_\beta}\frac{1}{|\vec{r}(k')-\vec{r}(k)|} . \tag{9}$$

Putting (8) in (7) gives

$$\sum_{k'}\sum_\beta[\alpha^{-1}_{\beta\gamma}(k)\delta_{kk'}-Q_{\gamma\beta}(kk')]p_\beta(k')=E'_\gamma(k) . \tag{10}$$

This set of linear equations ($3l$ in number, where l is the number of ions in the unit cell) may be solved to determine the values of $p_\beta(k)$. The quantities $Q_{\gamma\beta}(kk')$ and $E'_\gamma(k)$ have been previously determined using Ewald's method.[5]

III. APPLICATION TO RTH

A. Determination of polarizability values α

The question of what values are to be assigned to $\alpha_{\beta\gamma}(k)$ is not one to which an *ab initio* approach is currently possible.[16] Although a fair amount of work has been done on measuring and calculating polarizabilities for free atoms or ions, relatively little is known with any degree of confidence as to how these values are modified when the atom is in a molecule, and even less when the atom, or ion, is in a crystal. Nevertheless, the following guidelines may be used for a plausible calculation.

(i) Present successful semiempirical techniques, even for simple diatomic molecules, require the use of anisotropic atomic polarizabilities.[16]

(ii) The form of these tensors must conform to the symmetry of the crystal.[17] In the case of RTH (monoclinic) this requires[18] a tensor of the form

$$\begin{bmatrix}\alpha_{xx} & 0 & \alpha_{xz}\\ 0 & \alpha_{yy} & 0\\ \alpha_{zx} & 0 & \alpha_{zz}\end{bmatrix} \quad (\alpha_{xz}=\alpha_{zx}).$$

For simplicity, for the RTH hosts, this tensor will be chosen as follows (see Sec. IV for discussion):

$$\begin{bmatrix}\alpha_d & 0 & \alpha_o\\ 0 & \alpha_d & 0\\ \alpha_o & 0 & \alpha_d\end{bmatrix} .$$

(iii) The polarizability of a given atom, for example A, is not necessarily the same in different crystals.[5,16] This is the case even if the crystals form an isostructural series.

(iv) Atomic polarizabilities are not additive.[16] That is, molecular polarizabilities have been found to be less than the sum of the free-atom polarizabilities of the constituent atoms. This is also prediced by most models dealing with the polarizabilities of ions in crystals.[19] Thus one takes it to be the case that the polarizability of an ion in a crystal is less than the free-ion value.

(v) The polarizability (units Å^3) of an atom is roughly equal to the cube of the atomic radius.[20]

(vi) It has been found in the study of the electric field effect (EFE) (Ref. 21) that a large effect is observed when the substituted paramagnetic ion is small in relation to the cation it displaces. According to Ref. 21, in which one uses an isotropic polarizability tensor (the magnitude of diagonal elements will hereafter be referred to as scalar polarizability), it is reasonable to associate this as resulting from an increase in the scalar polarizability with decreasing difference in the host rare-earth-ion radius $(r_R)^4$ and the Gd^{3+} ion radius $(r_{Gd})^4$. If this is the case, then a plot of the rare-earth-ion polarizability versus $\Delta r(\equiv r_R - r_{Gd})$ should have a negative slope for $r_R > r_{Gd}$. For the rare-earth ions used in the calculation, the free-ion polarizabilities are as follows (in units of Å^3) (Ref. 22): Nd (1.23), Sm (1.11), Eu (1.06), Tb (0.97), Dy (0.94), Ho (0.90), Er (0.86), and Tm (0.83). Those for chlorine and oxygen are (Ref. 23) Cl^- (2.97, also reported 3.05 and 3.53), O^{2-} (3.88). No value is available for H^+, although the molecular polarizability of the H_2 molecule is given by Birge[16] as 0.79 Å^3, so the polarizability for H^+ should be about 0.40 Å^3. Note that the symbol H^+ in this context does not denote a proton. The hydrogen is bonded covalently to the oxygen and thus has an effective fractional charge as is discussed below. Hence, to speak of the polarizability of H^+ is to refer to the deformability of the electron cloud (molecular orbital) in which the hydrogen is situated.

B. Charge distribution on water molecules

In dealing with the water molecules in RTH, one needs to know the values of the charges on the hydrogen and oxygen ions. The charge distribution is not uniquely known. Therefore, for the present calculations, the charges $-2\eta|e|$ and $\eta|e|$ were chosen for the oxygen and hydrogen ions; here $|e|$ is the magnitude of the electrons's charge. Good results were obtained for $\eta=0.21$. This compares with the result of Burns[24] who took $\eta=0.30$ to reproduce the value of the dipole moment in gaseous H_2O.

C. Second-order parameters

For the second-order parameters B_2^0 and B_2^2 one requires the values of $\langle r^2\rangle$, K_2, and γ_2 [see Eq. (2)]. For Gd^{3+}, $\langle r^2\rangle = 0.785a_0^2$ (Ref. 13) (a_0 is the atomic unit, equal to 0.53 Å). For a pure S ground state, $K_2=0$; however, owing to mixing of states, this quantity is not zero. Wybourne[25] has shown that there exists considerable admixture of $L\neq 0$ character into the ground state. In particular, one obtains

$$K_2 = -\frac{12}{5}\frac{|e|\xi^3}{W_P^2 W_D}\langle r^2\rangle + \frac{16|e|\xi}{245 W_P}\langle R^2\rangle \ . \quad (11)$$

In Eq. (11) $\xi(=1534\ \text{cm}^{-1})$ (Ref. 26) is the one-electron spin-orbit coupling parameter, $W_P(=32\,200\ \text{cm}^{-1})$ (Ref. 25) and $W_D(=40\,000\ \text{cm}^{-1})$ (Ref. 27) are the energy separations between the ground state $^8S_{7/2}$ and the excited states $^6P_{7/2}$ and $^6D_{7/2}$, respectively, and $\langle R^2\rangle = -0.07a_0^2$.[28] The first term in Eq. (11) is associated with the coupling mechanism proposed by Hutchison *et al.*,[29] and the second term is due to relativistic effects.[30] The quantity $\gamma_2(=0.33)$ (Ref. 31) measures the screening due to the $5s^2p^6$ electrons.

D. Fourth-order parameters

For the fourth-order parameters (B_4^0, B_4^2, and B_4^4) the value for K_4 (see Sec. II) is not known. However, one may determine the values for A_4^l ($l=0,2,4$) using the same polarizabilities for each ion as were used for the second-order parameters. Having done this, it was found that good results were achieved by taking $B_4^l = cA_4^l$ ($l=0,2,4$), where $c=3.254\times 10^{-5}$ Å^4 is the same for all hosts and is independent of l.

IV. FITTING PROCEDURE AND RESULTS

Using the expressions (2)–(4) and (10) of Sec. II, the spin-Hamiltonian parameters for the Gd^{3+} ion doping the various RTH hosts were computed so as to be in agreement with the experimental values for all the hosts. (The structure and position parameters required for RTH were taken from Ref. 32 and the rare-earth unit-cell parameters from Ref. 33.)

The considerations of Sec. III A were used to estimate the trial values for $\alpha_{\beta\gamma}(k)$. When these were substituted into Eq. (10) of Sec. II, taking

$\eta = 1$, it was found that the magnitudes of the dipole sums for B_2^0 and B_2^2 were large and of opposite sign, compared to their counterparts for the point-charge sums. The value of η was then reduced. The effect of this was to greatly reduce the magnitude of the dipole contributions while giving a relatively small change in the point-charge contributions. By further reduction of η it was thus possible to reduce the dipole values to such an extent that they, plus the point-charge values, were in approximate agreement with experiment. The polarizability values were then adjusted so as to bring the results to within experimental error.

It was found that the polarizabilities (α_d) listed in Table I gave values of B_2^0, B_2^2, and B_4^0 within the limits of experimental error for all hosts. For all ions it was assumed, for simplicity, that for any given RTH crystal, $\alpha_d \equiv \alpha_{xx} (= \alpha_{yy} = \alpha_{zz})$. The α_d values were allowed to vary from host to host so as to give the best fit to the experimental parameters. Although some simplification has been made in choosing all diagonal elements to be the same, for a given ion this still represents an improvement over previous choices in that nonzero off-diagonal elements $\alpha_0 \equiv \alpha_{xz} (= \alpha_{zx})$ are also taken into account. For a given ion, the same value of α_0 has been chosen for all the hosts. The best values for α_0 were found to be 0.00, 0.34, 2.22, and 0.031 Å^3 for any rare-earth (R^{3+}), chlorine (Cl^-), oxygen (O^{2-}), and hydrogen (H^+) ions, respectively. Plots of α_d vs Δr are given in Fig. 1. On the basis of these, the computed values for B_2^0 and B_2^2 are listed in Table II, and those for B_4^0, B_4^2, and B_4^4 are in Table III.

TABLE I. Polarizabilities (α_d) for the various ions in RTH hosts (Å^3).

Host	R	Cl^-	O^{2-}	H^+	r (10^{-2} Å)
Nd	0.85	2.68	3.79	0.414	+5.7
Sm	0.75	3.18	3.79	0.441	+2.6
Eu	0.70	3.44	3.79	0.460	+1.2
Tb	0.65	2.69	3.79	0.416	−1.5
Dy	0.63	2.72	3.79	0.415	−3.0
Ho	0.62	2.73	3.79	0.408	−4.4
Er	0.59	2.91	3.79	0.412	−5.7
Tm	0.58	3.05	3.79	0.412	−6.9

V. DISCUSSION

The polarizability values of Table I are consistent with (iv) of Sec. III A in that these values are considerably smaller than the free-ion values. For H^+, the values are in the range 0.420±0.030 Å^3, to be compared with the crude free-ion estimate of 0.40 Å^3 given in Sec. III. For Cl^-, the values are within 3.04±0.40 Å^3; this is to be compared with the reported free-ion values of 2.97,

TABLE II. Second-order spin-Hamiltonian parameters b_l^m (GHz). Note: $b_2^m = B_2^m / 3$; experimental error $= \pm 0.01$ GHz.

Host	Parameter index	Point charge	Dipole	Total	Experiment (Ref. 34)	Difference
Nd	20	−0.8074	2.6655	1.8580	1.8550	+0.0030
	22	1.4600	−2.5186	−1.0585	−1.0650	+0.0065
Sm	20	−0.8088	2.6752	1.8664	1.8640	+0.0024
	22	1.5398	−2.6572	−1.1174	−1.1120	−0.0054
Eu	20	−0.7848	2.6412	1.8564	1.8540	+0.0024
	22	1.5367	−2.6809	−1.1442	−1.1500	+0.0058
Tb	20	−0.8081	2.6862	1.8781	1.8820	−0.0039
	22	1.5489	−2.7406	−1.1917	−1.1910	−0.0007
Dy	20	−0.8078	2.6834	1.8756	1.8830	−0.0074
	22	1.5574	−2.7758	−1.2183	−1.2280	+0.0097
Ho	20	−0.8157	2.7038	1.8881	1.8900	−0.0019
	22	1.5656	−2.8068	−1.2412	−1.2410	−0.0002
Er	20	−0.8240	2.6754	1.8514	1.8430	+0.0084
	22	1.5653	−2.8428	−1.2275	−1.2760	−0.0015
Tm	20	−0.8237	2.7083	1.8846	1.8800	+0.0046
	22	1.5691	−2.8744	−1.3053	−1.3110	+0.0057

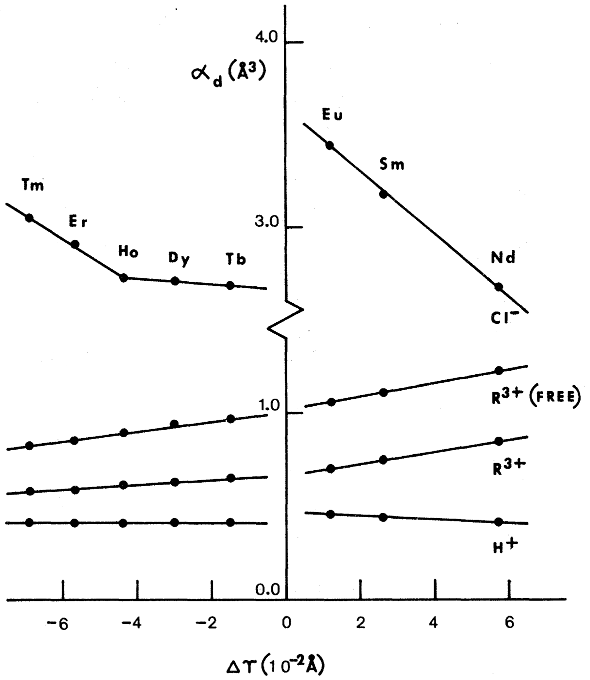

FIG. 1. Graph showing polarizability α_d (Å^3) for chlorine (Cl^-), hydrogen (H^+), and rare-earth (R^{3+}) ions in the isostructural series of RTH as a function of Δr (10^{-2} Å) (defined in Sec. III A). Also shown are the free-ion polarizabilities (Ref. 22) for the rare-earth ions.

3.05, 3.53 Å^3.[23] For O^{2-} the value is 3.79 Å^3 as compared to the free-ion value of 3.88 Å^3.[23] For the rare-earth hosts, all values are considerably smaller than their free-ion counterparts and show approximately the same trends as the free-ion values, except as discussed below. With regard to the changes in α_d as the host lattice is varied, one sees that for $r_R > r_{\rm Gd}$, both Cl^- and H^+ have a negative slope when the α_d's are plotted versus Δr. This is what one would expect according to Ref. 21.

For the rare-earth ions, for $r_R > r_{\rm Gd}$, the slope for α_d vs Δr is less than that for the free-ion polarizabilities plotted against Δr. Thus one finds that the polarizabilities of the rare-earth ions in the RTH crystals decrease with r in the same way as they do in the free-ion state. However, in the RTH crystals the polarizabilities, α_d, decrease less quickly than they do for the free ions; this is in accordance with (vi) of Sec. III A. Thus, taking this factor into account, it can be seen from Fig. 1 that the slopes (α vs Δr) for R^{3+}, Cl^-, and H^+ exhibit the same trend for $r_R > r_{\rm Gd}$. For $r_r > r_{\rm Gd}$, the trends are similar in that the slopes for R^{3+}, Cl^-, and H^+ all have the same sign as the slopes for $r > r_{\rm Gd}$, but the magnitudes of the slopes for $r > r_{\rm Gd}$ are smaller for all three graphs.

Regarding the off-diagonal elements α_0 (same for all hosts), the value of zero is found for all the rare earths. This is reasonable since the free-ion value is rather small to begin with, and also the $4f$ electrons are screened by the outer ($n = 5$) shell. For Cl^- the value of 0.34 Å^3 is small compared to the free-ion value. One would expect this value to be small because Cl^- is a closed-shell configuration and is thus relatively less susceptible to an asymmetric distortion.

For O^{2-}, the value of 2.33 Å^3 for the off-diagonal element α_0 is of the same order of magnitude as α_d; this may be expected in that O^{2-} has two covalent bonds with the hydrogens and thus is not in an isotropic state. Hence it will respond in a skewed fashion to an external field because of the constraints imposed by these bonds and because its electron cloud is asymmetrical to begin with. For H^+, the value of 0.031 Å^3 is small; this is because α_d for H^+ is small. However, α_0 for H^+ is nonzero due to covalent bonding.

The experimental values for B_4^2 and B_4^4 are somewhat uncertain.[34] Also, these values are extremely sensitive to the ionic positions. Thus when ionic distortions, caused by the introduction of Gd^{3+} guest ions, are taken into account the computed values can be found to agree with the experimental ones. This paper does not, however, take such distortions into account.

It may be argued that for each host one is fitting three data points (B_2^2, B_2^2, and B_4^0) with three parameters ($\alpha_{R^{3+}}$, $\alpha_{\rm Cl^-}$, and $\alpha_{\rm H^+}$). However, the fit is not in the nature of a least-squared fit or a purely empirical fit where one does an arbitrary search. This arises because the values of α_d, α_0 are fairly strictly limited according to the considerations of Sec. III, and are found to be compatible with these constraints. Namely, the values correlate with the free-ion values, they vary linearly with Δr, and the slopes are consistent with those described in (vi) of Sec. III A.

VI. CONCLUSIONS

It is well known that the point-charge model alone does not explain the observed spin-Hamiltonian parameters.[10] The results of this paper support the conclusion of Bijvank *et al.*[6–8] and

TABLE III. Fourth-order spin-Hamiltonian parameters b_l^m (10^{-2} GHz). Note: $b_4^m = B_4^m/60$; experimental error = ±0.01 GHz.

Host	Parameter index	Point charge	Dipole	Total	Experiment (Refs. 12 and 34)	Difference
Nd	40	−3.07	−0.221	−3.30	−3.30	0.00
	42	−0.319	3.69	3.37	3.50	0.13
	44	−6.84	0.559	−6.28	−1.40	−4.88
Sm	40	−3.11	−0.246	−3.36	−3.50	0.14
	42	−1.32	3.51	2.20	2.30	−0.10
	44	−5.32	0.863	−4.46	1.00	−4.56
Eu	40	−3.12	−0.248	−3.37	−3.40	0.031
	42	−1.75	3.11	1.56	3.40	−1.84
	44	−4.73	0.870	−3.86	0.40	−4.26
Tb	40	−3.15	−0.253	−3.40	−3.70	0.298
	42	−0.940	3.75	2.81	2.40	0.412
	44	−5.79	0.782	−5.00	−0.40	−4.60
Dy	40	−3.17	−0.258	−3.43	−3.50	0.073
	42	−1.15	3.73	2.58	3.10	−0.519
	44	−5.46	0.785	−4.68	−0.50	−4.18
Ho	40	−3.19	−0.265	−3.46	−3.30	−0.156
	42	−1.31	3.80	2.49	5.20	−2.71
	44	−5.23	0.767	−4.46	−3.30	−1.16
Er	40	−3.19	−0.267	−3.46	−3.60	0.140
	42	−1.59	3.72	2.14	9.20	−7.06
	44	−4.85	0.797	−4.06	6.90	11.0
Tm	40	−3.21	−0.273	−3.49	−3.50	0.014
	42	−1.88	3.69	1.81	5.40	−3.59
	44	−4.45	0.814	−3.64	3.10	−6.74

of Faucher *et al.*[9] that a polarizable dipole model can explain the crystal-field splitting of Gd^{3+} and other rare-earth ions with the proviso that one must employ an anisotropic polarizability tensor. The fact that this approach gives excellent results does not mean that effects such as overlap and covalency do not play any role. Rather, it is likely that the effect of such mechanisms is built into the polarizability tensor in that it is modified as one goes from one host to the other. Detailed microscopic calculations of such effects are not currently feasible.

The present calculations indicate that the spin-Hamiltonian parameters can be calculated theoretically to explain satisfactorily the observed values on the basis of point charges plus induced dipoles, provided that one chooses the polarizability tensors of the various ions appropriately.

---

[1] D. J. Newman and W. Urban, Adv. Phys. 24, 793 (1975).

[2] D. J. Newman, Adv. Phys. 20, 197 (1971).

[3] H. A. Buckmaster, R. Chatterjee, and Y. H. Shing, Can. J. Phys. 50, 991 (1972).

[4] K. N. R. Taylor and M. I. Darey, *Physics of Rare Earth Solids* (Chapman and Hall, London, 1972), p.36.

[5] G. A. Bogomolova, L. A. Bumagina, A. A. Kaminskii, and B. Z. Mankin, Fiz. Tverd. Tela (Leningrad) 19, 2439 (1977).

[6] E. J. Bijvank and H. W. den Hartog, Bull. Mag. Res. 2, 165 (1980).

[7] E. J. Bijvank and H. W. den Hartog, Phys. Rev. B 22, 4121 (1980).

[8] E. J. Bijvank and H. W. den Hartog, Phys. Rev. B 22, 4133 (1980).

[9] M. Faucher, J. Dexpert-Ghys, and P. Caro, Phys. Rev.

B 21, 3689 (1980).

[10] S. K. Misra and P. Mikolajczak, J. Mag. Res. 35, 87 (1979).

[11] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[12] S. K. Misra and G. R. Sharp, Phys. Status Solidi B 75, 607 (1976).

[13] A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962).

[14] P. P. Ewald, Ann. Phys. (Leipzig) 64, 253 (1921).

[15] S. K. Misra and N. R. Lewis, J. Chem. Phys. 71, 1033 (1979).

[16] R. R. Birge, J. Chem. Phys. 72, 5312 (1980).

[17] A. P. Cracknell, *Group Theory in Solid State Physics* (Taylor and Francis, London, 1975), p.11.

[18] G. S. Koerber, *Properties of Solids* (Prentice-Hall, Englewood Cliffs, 1962).

[19] B. G. Dick, Jr. and A. W. Overhauser, Phys. Rev. 112, 90 (1958).

[20] A. Cohen, Phys. Lett. 68, 166 (1979).

[21] W. B. Mims, *The Linear Electric Field Effect in Paramagnetic Resonance* (Clarendon, Oxford, 1976).

[22] K. M. S. Saxena and S. Fraga, J. Chem. Phys. 57, 1800 (1972).

[23] J. R. Tessman, A. H. Kahn, and W. Schockley, Phys. Rev. 92, 890 (1953).

[24] G. Burns, Phys. Rev. 128, 2121 (1962).

[25] B. G. Wybourne, Phys. Rev. 148, 317 (1966).

[26] B. R. Judd and I. Lindgren, Phys. Rev. 122, 1802 (1961).

[27] A. G. Malkhomek and V. S. Korolkov, Opt. Spektrosk. 25, 104 (1968).

[28] M. T. Hutchings, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1964), Vol. 16, p.227.

[29] C. A. Hutchison, B. R. Judd, and D. F. D. Pope, Proc. Phys. Soc. London Sect. B 70, 1514 (1957).

[30] B. G. Wybourne, J. Chem. Phys. 43, 4506 (1966).

[31] B. Williamson and W. C. Hommels, Phys. Status Solidi A 10, 183 (1972).

[32] M. Marezio, H. A. Plettinger, and W. H. Zachariasen, Acta Crystallogr. 14, 234 (1961).

[33] S. K. Misra and G. R. Sharp, J. Phys. C 10, 897 (1977).

[34] S. K. Misra, P. Mikolajczak, and M. Jalochowski Phys. Rev. B 24, 3729 (1981).