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Superposition model analysis of spin-Hamiltonian parameters for Gd^{3+} in rare-earth metal trichloride hexahydrates

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The second-order spin-Hamiltonian parameters for Gd^{3+}-doped single crystals of $R\mathrm{Cl}_3 \cdot 6\mathrm{H}_2\mathrm{O}$ (R = Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm) are analyzed using the linear superposition model of Newman. It is found that, in order to explain satisfactorily the observed values of the parameters, the model requires different values of t_2 for different hosts; these values are linear in the host-ion radius. Further, the analysis enables one to decouple the metal-ligand distance effects from other factors which influence t_2. A similar result is found for $\bar{b}_2$.

I. INTRODUCTION

Considerable success has been achieved in the application of the superposition model to ^8S-state ions (Gd^{3+}, Eu^{2+}).[1–8] The original motivation for the use of the model for the present calculations was the following. It was taken to be the case that the measured spin-Hamiltonian parameters were, to a large extent, determined by short-range effects such as covalency and overlap. However, the crystal-field contributions A_l^m are inherently of longer range, especially for $l=2$. Thus it was argued that the simple employment of crystal-field parameters A_l^m, for calculating EPR spin-Hamiltonian parameters b_l^m (via A_l^m), is bound to fail. It has recently been shown by Misra *et al.*[9] that the Gd^{3+} spin-Hamiltonian parameters can be constructed directly from the superposition of single-ligand contributions, in the same way as the lanthanide crystal-field parameters.[9] Misra *et al.*[9] applied the model to Gd^{3+} doping $R\mathrm{F}_3$ (R = La, Ce, Pr, Nd). They found that good agreement with experiment was obtained if one introduced small angular distortions of the positions of the neighbors nearest to Gd^{3+}. Previously, attempts have been made to apply the superposition model to the analysis of ^6S Mn^{2+} or Fe^{3+} spin-Hamiltonian parameters with some success.[10–13]

It is the purpose of this paper to analyze the spin-Hamiltonian parameters for Gd^{3+}-doping single crystals of $R\mathrm{Cl}_3 \cdot 6\mathrm{H}_2\mathrm{O}$ (hereafter RTH), where R = Nd, Sm, Eu, Tb, Dy, Ho, Er, and Tm, which form an isostructural homologous series. Precise experimental values for these spin-Hamiltonian parameters have been reported by Misra and Sharp[14] and by Misra *et al.*[15] The structure and position parameters required for the present calculations for RTH were taken from Marezio *et al.*[16] and the unit-cell parameters for RTH are listed in Ref. 17. Since the RTH constitute an isostructural family containing rare-earth ions whose ionic radii are both larger and smaller than the substituted Gd^{3+} ion, they are ideal for testing the superposition model as this model is quite sensitive to atomic positions, which change as one goes from host to host in the family. However, no attempt has been made to include distortion for the RTH hosts. It is hoped that the present work would contribute towards clarifying the apparently persistent problem of the origin of the ground-state splitting of ^8S-state ions.

II. SUPERPOSITION MODEL

A. Theory

In this model, the spin-Hamiltonian parameters b_l^m can be expressed as a linear superposition of single-ligand contributions[1–5]

$$b_l^m = \sum_i \bar{b}_l(R_i) K_l^m(x_i,y_i,z_i) \ . \qquad (1)$$

In particular, for $l=2$, one has

$$K_2^0(x_i,y_i,z_i) = \frac{(3z_i^2 - R_i^2)}{R_i^2} \ , \qquad (2)$$

$$K_2^2(x_i,y_i,z_i) = \tfrac{3}{2}(x_i^2 - y_i^2)/R_i^2 \ . \qquad (3)$$

In Eq. (1), the summation extends over the nearest neighbors of the paramagnetic ion. For RTH, the positions (x_i,y_i,z_i) of the nearest neighbors (six O^{2-}, in this case) are given in Table I. The $\bar{b}_l(R_i)$ are called intrinsic parameters; these are functions of the radial metal-ligand distance R_i. They differ for different paramagnetic ions, e.g., Gd^{3+}, Mn^{2+}, Fe^{3+}, as well as for different ligands (e.g., O^{2-}, F^-). Conventionally, it has been assumed that $\bar{b}_l(R_i)$ is a function of the form[1–5]

$$\bar{b}_l(R_i) = \bar{b}_l(R_0)(R_0/R_i)^{t_l} \ . \qquad (4)$$

Here, R_0 is the average metal-ligand distance for all

TABLE I. Positions of the six nearest oxygen ions for the series RTH. For a given host the coordinates (Å) for three ions are given (relative to Gd^{3+} taken as origin). Those for the other three are given by $(-x, -y, z)$. r is the magnitude of the radius vector.

Host	Ion	x	y	z	r
Nd	1	2.053	1.074	−0.693	2.418
	2	−1.588	0.159	1.804	2.409
	3	0.037	−2.236	0.968	2.436
Sm	1	2.133	0.948	−0.688	2.433
	2	−1.580	0.253	1.790	2.401
	3	−0.122	−2.229	0.961	2.431
Eu	1	2.161	0.882	−0.686	2.433
	2	−1.572	0.302	1.785	2.398
	3	−0.189	−2.226	0.958	2.431
Tb	1	2.090	0.994	−0.684	2.413
	2	−1.575	0.214	1.779	2.386
	3	−0.058	−2.219	0.955	2.417
Dy	1	2.097	0.964	−0.682	2.406
	2	−1.568	0.235	1.774	2.379
	3	−0.087	−2.214	0.952	2.411
Ho	1	2.098	0.941	−0.679	2.397
	2	−1.560	0.248	1.768	2.371
	3	−0.105	−2.205	0.949	2.403
Er	1	2.114	0.905	−0.679	2.397
	2	−1.555	0.274	1.768	2.371
	3	−0.145	−2.202	0.949	2.402
Tm	1	2.124	0.866	−0.677	2.391
	2	−1.546	0.301	1.763	2.364
	3	−0.182	−2.194	0.946	2.396

the nearest neighbors in the entire series. In previous applications of the superposition model (e.g., Ref. 9) to homologous series, the parameter $\bar{b}_l(R_0)$ was taken to be different for different hosts, whereas t_l was assumed to be the same for all members of a given series. It is presently not clear whether or not intrinsic parameters for a given ligand are transferable to other crystals of different structure.

B. Application to RTH

For a given host, $\bar{b}_2[\equiv \bar{b}_2(R_0)]$ can be written in two ways; i.e.,

$$\bar{b}_2(A) \equiv b_2^0/P_2^0(t_2) \tag{5}$$

or

$$\bar{b}_2(B) \equiv b_2^2/P_2^2(t_2) \ , \tag{6}$$

where b_l^m are experimental parameters and

$$P_l^m(t_l) \equiv \sum_i \left(\frac{R_0}{R_i}\right)^{t_l} K_l^m(x_i,y_i,z_i) \ . \tag{7}$$

Consistency of the model requires that

$$\bar{b}_2(A) = \bar{b}_2(B) \ , \tag{8}$$

or, equivalently, that

$$E(t_2) \equiv [\bar{b}_2(A) - \bar{b}_2(B)]/\bar{b}_2(A) = 0 \ . \tag{9}$$

The value of $E(t_2)$ for each host in the RTH series was calculated for various values of t_2. It was found that, for each host, there is a particular value of t_2 for which $E(t_2)$ is effectively zero. For this value of t_2, one immediately gets the corresponding value of $\bar{b}_2$. The results are given in Table II.

TABLE II. Values of t_2 and $\bar{b}_2$ for which $E(t_2) = 0$. [See Eq. (9) in text.]

Host	t_2	$\bar{b}_2$ (GHz)
Nd	0.166	3.106
Sm	−13.050	−2.228
Eu	−17.412	−1.964
Tb	−3.943	−2.851
Dy	−5.704	−2.796
Ho	−5.701	−2.870
Er	−10.247	−2.772
Tm	−12.244	−2.784

III. ANALYSIS

A. t_2 values

First, it is noted from Table II that all the values for t_2, except for one, are negative. One would anticipate *a priori* that they should be positive (ions farther away contributing less), but there is no absolute restriction that need be so. Indeed, Edgar and Newman[18] have reported $t_2 < 0$ for CaF_2 and Buzaré *et al.*[19] have reported $t_4 < 0$ for $RbCaF_3$.

Second, the way in which t_2 varies (Table II) depends on whether the ionic radius, r, of the corresponding rare-earth host is greater or less than that of the substituted Gd^{3+} ion ($r_{Gd} = 0.938$ Å). This may be seen from Fig. 1 where plots of t_2 vs r give separate straight lines in the two regions: $r < r_{Gd}$ and $r > r_{Gd}$. If one now considers R_N [$= R_N(i)$], the distance of the nearest O^{2-} ion from Gd^{3+} for a given host, one finds that a plot of r vs R_N for the various hosts (see Fig. 2) gives two separate straight lines of slightly different slopes if the cases $r < r_{Gd}$ and $r > r_{Gd}$ are considered separately. Thus, plots of t_2 vs R_N also give separate straight lines as shown in Fig. 3. If one considers the t_2 vs R_N equations for these lines, as determined by a least-squares fit, one finds {defining $t_<$ [$= t_<(i)$] as being values of t_2 for

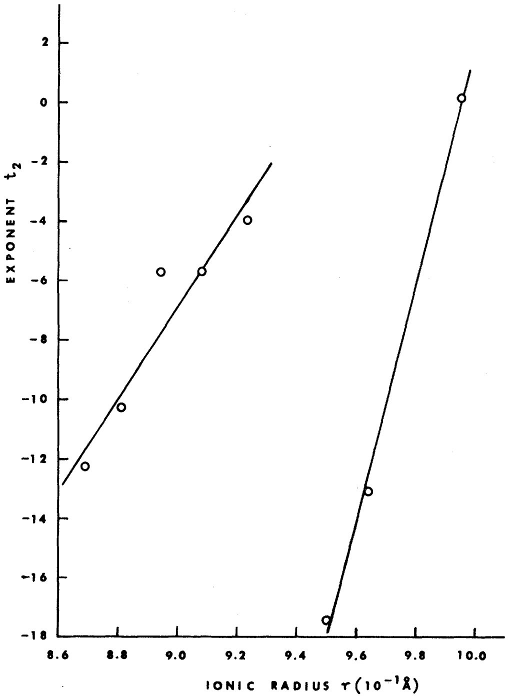

FIG. 1. Graph of the values of t_2, as determined from Eq. (9), vs the host-ion radius $r(10^{-1}$ Å). The cases $r < r_{Gd}$ and $r > r_{Gd}$ are plotted separately. The values for r are taken from K. N. R. Taylor and M. I. Davey [*Physics of Rare Earth Solids* (Chapman and Hall, London, 1972), p. 8].

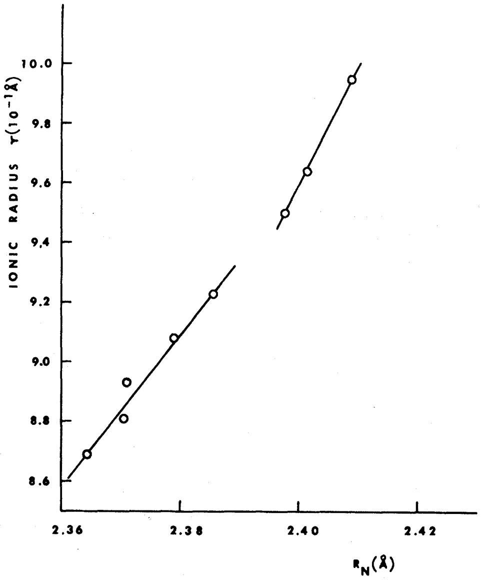

FIG. 2. Graph of the host-ion radius $r(10^{-1}$ Å) vs R_N(Å). R_N is defined in Sec. III A. The cases $r < r_{Gd}$ and $r > r_{Gd}$ are plotted separately.

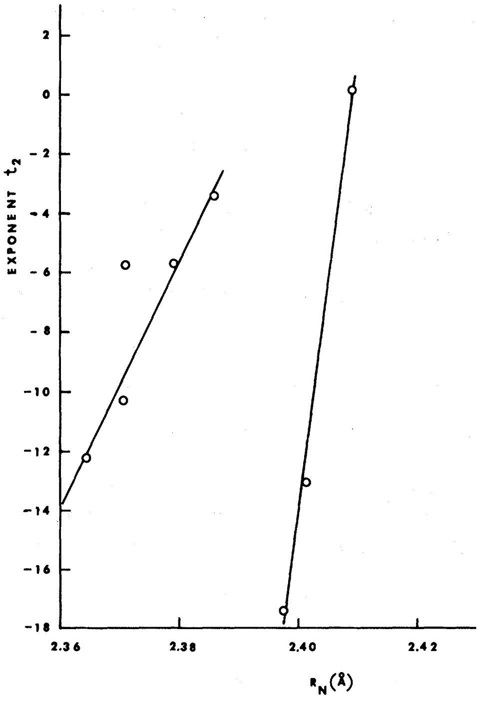

FIG. 3. Graph of the values of t_2, as determined from Eq. (9), vs R_N(Å). R_N is defined in Sec. III A. The values for those hosts whose ionic radii are less than that of Gd^{3+} are plotted separately.

which $r < r_{\mathrm{Gd}}$, and similarly for $t_>$}:

$$t_< = 391.345(R_N - 2.395) \ , \tag{10}$$

$$t_> = 1631.126(R_N - 2.409) \ . \tag{11}$$

The numbers in the brackets in Eqs. (10) and (11) have an average value of 2.402 Å. It is of interest to compare this with the value of R_0 for RTH, which is 2.404 Å. One may then approximate Eqs. (10) and (11) as

$$t_{\gtrless} = k_{\gtrless}(R_N - R_0) \ . \tag{12}$$

Equation (12) has the advantage that it decouples the variation of t_2 from metal-ligand distance effects, thus enabling one to concentrate on other factors which give rise to the specific value of $k_{\gtrless}$. It could also explain why, for some series,[9] success has been obtained by taking t_2 to be roughly constant, whereas for RTH there is a wide variation from host to host. For example, in the application of the method of Sec. II B to $\mathrm{Gd^{3+}}$:$R\mathrm{F_3}$ (R = La, Ce, Pr, Nd),[9] the values found for t_2 were in the range 9 ± 1 (as accomplished by allowing distortion of ionic positions); as for the average change in the value of $R_N - R_0$ (of undistorted lattice) in going from host to host, it was about 25%. In the present case (RTH), the corresponding average change is about 65%.

It is also clear that $k_{\gtrless}$ depend on whether the ligands are free to relax toward the substituted $\mathrm{Gd^{3+}}$ ion ($\Delta r = r - r_{\mathrm{Gd}} > 0$) or whether they are being forced away ($\Delta r < 0$).

B. $\bar{b}_2$ values

From Table II it is seen that the value of $\bar{b}_2$, for $\Delta r < 0$, is constant; i.e., $\bar{b}_2(\Delta r < 0) = 2.8146 \pm 0.0368$ GHz with an average deviation from the mean of 1.3%. For $\Delta r > 0$, it is seen from Fig. 4 that $\bar{b}_2(\Delta r > 0)$ varies linearly with the host-ion radius. Hence, it will also vary linearly with R_N. The relation, from a least-squares fit, is

$$\bar{b}_2(\Delta r > 0) = -106.475(R_N - 2.380) \ . \tag{13}$$

The number in the bracket may be compared with the average value of R_N for the various hosts, $\bar{R}_N = 2.385$ Å. Hence, one may put Eq. (13) as

$$\bar{b}_{2>} = C_>(R_N - \bar{R}_N) \ , \tag{14}$$

and similarly, for $\Delta r < 0$,

$$\bar{b}_{2<} = C_< \ . \tag{15}$$

Equations (14) and (15) indicate that one is also able to separate out the distance dependence of $\bar{b}_2$ from other effects.

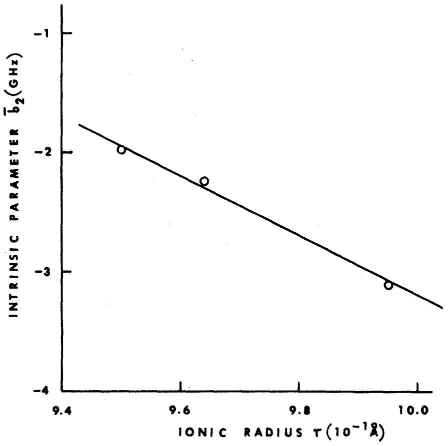

FIG. 4. Graph of the intrinsic parameter $\bar{b}_2$(GHz), as determined via Eq. (9), vs the host-ion radius r(10^{-1} Å) for those hosts for which $r > r_{\mathrm{Gd}}$.

C. b_2^m values

Taking into account that $\bar{b}_2(R_0)$ is host (R) dependent, it may be written as $\bar{b}_2(R,R_0)$. Defining $\delta_i \equiv R_i - R_0$, Eqs. (1) and (4) may be expressed as

$$b_2^m = \sum_i \bar{b}_2(R,R_0)\left(1 - \frac{\delta_i}{R_i}\right)^{t_2} K_2^m(i) \ . \tag{16}$$

Clearly $|\delta_i|/R_i \ll 1$. Hence, Eq. (16) may be approximated

$$b_2^m = \sum_i \bar{b}_2(R,R_0)\left(1 - t_2\frac{\delta_i}{R_i}\right) K_2^m(i) \ . \tag{17}$$

Define now

$$\delta_{\bar{N}} \equiv R_N - \bar{R}_N \tag{18}$$

and

$$\delta_{N_0} \equiv R_N - R_0 \ . \tag{19}$$

Combining Eqs. (17)–(19) with Eqs. (12), (14), and (15) gives

$$b_2^m = \sum_i C_{\gtrless}\delta_{\bar{N}}\left[1 - k_{\gtrless}\delta_{N_0}\left(\frac{\delta_i}{R_i}\right)\right] K_2^m(i) \ . \tag{20}$$

Equation (20) is to be understood as being two equations, one for $\Delta r > 0$ and one for $\Delta r < 0$. For the later case one takes $\delta_{\bar{N}} = 1$ [see Eq. (15)]. Substituting for δ_i, and rearranging gives

$$b_2^m = \sum_i \left[C_{\gtrless}\delta_{\bar{N}}(1 - k_{\gtrless}\delta_{N_0}) + C_{\gtrless}\delta_{\bar{N}}k_{\gtrless}\delta_{N_0}\left(\frac{R_0}{R_i}\right)\right] K_2^m(i) \tag{21}$$

or

$$b_2^m = \sum_i \left[A + B\left(\frac{R_0}{R_i}\right)\right] K_2^m(i) \ , \tag{22}$$

where

$$A = C_{\gtrless}\delta_{\bar{N}}(1 - k_{\gtrless}\delta_{N_0}) \ , \tag{23}$$

$$B = C_{\gtrless}\delta_{\bar{N}}(k_{\gtrless}\delta_{N_0}) \ . \tag{24}$$

It is to be noted that Eqs. (22)–(24) refer to a homologous series in that R_0 and $\bar{R}_N$ are averages over a series. These equations can, however, be employed for a single host since one can calculate these averages for the series to which the host belongs if one knows the crystal-structure and unit-cell parameters.

IV. CONCLUSIONS

It has been shown that, for the RTH hosts, it is possible to explain the observed spin-Hamiltonian parameters using the superposition model. Further, the superposition model can be formulated in such a way as to decouple the metal-ligand distance dependence from the parameters $\bar{b}_2$ and t_2. This enables one to carry out further analysis to relate these parameters to other factors. For example, very recent work[20] indicates that the ligand polarizability has a distance dependence similar to that described in this paper. Further detailed analysis is required to make a definitive correlation between the long-range electrostatic and the nearest-neighbor superposition effects.

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