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

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The spin-Hamiltonian parameters for Gd^{3+}-doped single crystals of RF_3 ($R =$La, Ce, Pr, and Nd) are analyzed using the linear superposition model of Newman. It is found that the parameters can be adequately described within the framework of the superposition model for values of t_2 and t_4 being 9 and 14, respectively, provided that one consider small distortions (within ± 3°) of the azimuthal angles ϕ_i of eight F^- ions nearest to Gd^{3+} in the various hosts due to the presence of the Gd^{3+} ion. The significance of the success in the application of the superposition model to the analysis of Gd^{3+} spin-Hamiltonian parameters in isostructural hosts is discussed. It is found that the zero-field splitting is a linear function of the intrinsic parameter $\bar{b}_2$ for the Gd^{3+} ion doping the various hosts.

I. INTRODUCTION

Much success has recently been achieved in the application of the superposition model to ^8S-state ions (Gd^{3+}, Eu^{2+}).[1–8] The essential idea behind the superposition model is the following: the measured spin-Hamiltonian parameters are, to a large percentage, given by covalent effects, i.e., overlap and exchange with the nearest neighbors. The normal crystal-field contributions, especially for the lower $n = 2$ rank constants b_2^m, are inherently of longer range. Thus the employment of the crystal field for calculating EPR spin-Hamiltonian parameters b_2^m is bound to fail. It has been shown that the Gd^{3+} spin-Hamiltonian parameters can be constructed from the superposition of single-ligand contributions, in the same way as the lanthanide crystal-field parameters.[9] Lately, 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.[10–12]

It is the purpose of this paper to analyze the spin-Hamiltonian parameters for Gd^{3+}-doping single crystals of RF_3($R =$La, Ce, Pr, Nd) which constitute an isostructural homologous series. The motivation has been provided by the recent availability of very accurate spin-Hamiltonian parameters as reported by Misra, Mikolajczak, and Korczak.[13] In Ref. 13 the parameters were evaluated by the application of a rigorous least-squares-fitting procedure[14] in which all resonant EPR line positions obtained for several orientations of the external magnetic field are simultaneously fitted. In addition, very accurate x-ray data are available on the RF_3 crystals to permit precise evaluation of coordination factors required in the application of the superposition model. The RF_3, being anhydrous crystals, have additional advantage in that they do not contain protons (of H_2O molecules) which defy position determination by x-ray techniques. Furthermore, since the RF_3 crystals constitute a family of homologous isostructural hosts, they appear to be ideal for the application of the superposition model, which is quite sensitive to even small changes in atomic positions. Thus one can draw definitive conclusions regarding the applicability of the superposition model to the analysis of spin-Hamiltonian parameters of Gd^{3+} doping a family of isostructural hosts, since here one is dealing with small differences in distances as one goes from one host to another in the family.

It is hoped that the present work would help towards a solution to the long-standing problem of the origin of the ground-state splitting in the ^8S-state ion Gd^{3+}.

II. EXPERIMENTAL PARAMETERS

The spin Hamiltonian consistent with the crystal structure of RF_3 hosts (see Sec. III) is in the notation of Abragam and Bleaney,[15] as follows:

$$\mathcal{H} = g\beta \vec{H}\cdot\vec{S} + \sum_{m=0,\pm 2} \tfrac{1}{3} b_2^m O_2^m + \sum_{m=0,\pm 2,\pm 4} \tfrac{1}{60} b_4^m O_4^m + \sum_{m=0,\pm 2,\pm 4,\pm 6} \tfrac{1}{1260} b_6^m O_6^m \quad . \qquad (2.1)$$

In Eq. (2.1) $\vec{H}$ is the intensity of the magnetic field, $\vec{S}$ is the spin vector of the Gd^{3+} ion ($S = \frac{7}{2}$), and the O_l^m are spin operators[15]; g and b_l^m represent the spin-Hamiltonian parameters.

TABLE I. Spin-Hamiltonian parameters for Gd^{3+}-doped RF_3 hosts, where R = La, Ce, Pr and Nd. All b_l^m are expressed in GHz. The errors (for all hosts) are 0.010 GHz for all b_l^m.

	NdF_3 RT	PrF_3 RT	CeF_3 RT	LaF_3 RT	LaF_3 65 K	LaF_3[a] RT	LaF_3[b] 90 K
b_2^0	0.802	0.774	0.733	0.694	0.707	0.702	0.716
b_2^2	−0.148	−0.081	−0.055	−0.083	−0.006	0.058	−0.015
b_4^0	0.019	0.017	0.018	0.016	0.015	0.015	0.017
b_4^2	0.081	0.077	0.076	0.066	0.072	−0.073	0.081
b_4^4	0.130	0.117	0.144	0.117	0.119	0.121	−0.129

[a] V. K. Sharma, J. Chem. Phys. 54, 496 (1971).

[b] D. A. Jones, J. M. Baker, and D. F. D. Pope, Proc. Phys. Soc. London 74, 249 (1959).

The Gd^{3+}-doping LaF_3-host spin-Hamiltonian parameters were first reported by Jones *et al.*[16] Sharma[17] extended the measurements to CeF_3, PrF_3, and NdF_3 hosts; however, in his choice of axes he interchanged x and y axes as chosen in Ref. 16. In both Refs. 16 and 17 the parameters were evaluated using perturbation expressions, and the absolute signs of parameters were not determined as the measurements were confined to room temperature only. Misra *et al.*[13] made extensive measurements on Gd^{3+}-doped single crystals of RF_3(R = La, Ce, Pr, Nd) at various temperatures. Not only did they determine the absolute signs of parameters, they also evaluated the parameters by the use of a rigorous least-squares-fitting procedure[14] in which all resonant line positions obtained for several orientations of the external magnetic field, both in the zx and xy planes, were simultaneously fitted and exact numerical diagonalization of the spin-Hamiltonian matrix was utilized. The error in the evaluation of parameters, which is inversely proportional to the difference between the number of line positions fitted and the number of parameters fitted,[18] was considerably reduced due to inclusion of a large number of lines (sometimes as many as 400 resonant line positions were used in the fitting[13]).

It is noted that in Ref. 17 the relative signs of the parameters b_2^0 and b_2^2 were incorrect, while in Ref. 16 the parameter b_4^4 had a negative sign. The highly accurate room-temperature parameters as reported by Misra *et al.*[13] (and which are different in magnitudes from Refs. 16 and 17) are listed in Table I. The b_6^m parameters are not listed as their inclusion does not reduce the χ-squared value of the fit by any significant amount.[13] This is in conformity with the observation that an lth order parameter represents the effect of l-particle spin correlation.[19] These will be used for comparison with the theoretical analysis presented in this paper.

III. CRYSTAL STRUCTURE

There are three crystal structures which have been proposed from x-ray measurements for RF_3 crystals. Oftdel[20] suggested a hexagonal structure having $D_{6h}^3(P6_3/mcm)$ space-group symmetry with six molecules per unit cell. Later Schlyter[21] proposed a more symmetrical hexagonal structure with a bimolecular unit cell of symmetry $D_{6h}^4(P6_3/mmc)$. More recently Mannsmann[22] and Zalkin, Templeton, and Hopkins[23] have predicted a trigonal crystal structure with a hexamolecular unit cell having $D_{3d}^4(P\bar{3}c1)$ symmetry. Andersson and Proctor,[24] from their perturbed angular correlation results, found LaF_3 structure to be hexagonal with six magnetically inequivalent La ions occupying sites of symmetry C_s, C_2, or C_{2v} in a unit cell. They proposed $C_{6v}^3(P6_3cm)$ space group for the unit cell containing six molecules. This is supported by the neutron-diffraction measurements of de Rango *et al.*[25] on LaF_3.

For the calculations presented in this paper the lat-

TABLE II. Room-temperature lattice constants of the rare-earth trifluorides in angstroms. [J. D. H. Donnay and G. Donnay, *Crystal Data Determinative Tables*, 2nd ed. (American Crystallographic Association, New York, 1963).]

RF_3	a	c
LaF_3	7.186	7.352
CeF_3	7.112	7.279
PrF_3	7.061	7.218
NdF_3	7.030	7.199
GdF_3	6.883	7.057

TABLE III. Positions of nine nearest-neighbor F^- ions derived from x-ray data used in superposition model fits. All angles are in degrees, all distances are in angstroms. [Positions of 3, 5, 7, and 9 ions are $(R, \theta, \phi+180°)$.] [M. Mansmann, Z. Anorg. Alleg. Chem. 331, 98 (1964); Z. Kristallogr. Kristallogeom. Kristallphys. Kristallchem. 122, 375 (1965)].

	Ions	1	2,3	4,5	6,7	8,9
	R	2.453	2.419	2.466	2.473	2.604
LaF_3	θ	0.0	118.13	90.56	69.19	150.07
	ϕ	· · ·	166.55	279.04	32.44	72.64
	R	2.427	2.394	2.442	2.448	2.578
CeF_3	θ	0.0	118.13	90.56	69.19	150.06
	ϕ	· · ·	166.54	279.04	32.45	72.65
	R	2.410	2.376	2.422	2.430	2.558
PrF_3	θ	0.0	118.13	90.56	69.19	150.08
	ϕ	· · ·	166.56	279.05	32.42	72.63
	R	2.399	2.366	2.415	2.420	2.548
NdF_3	θ	0.0	118.13	90.56	69.20	150.04
	ϕ	· · ·	166.53	279.04	32.47	72.66
	R	2.349	2.317	2.367	2.370	2.496
GdF_3	θ	0.0	118.13	90.56	69.20	150.02
	ϕ	· · ·	166.52	279.02	32.50	72.67

est x-ray results of Mansmann (D_{3d}^4) (Ref. 22) will be used. The unit-cell parameters for the various crystals are given in Table II.[26] The positions of the nearest neighbor (nine fluorine ions) to a Gd^{3+} ion are given in Table III. The D_{3d}^4 crystal structure depicting the positions of ions for LaF_3 is shown in Fig. 1.

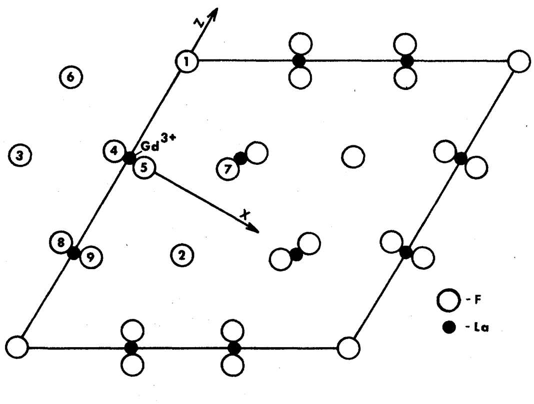

FIG. 1. D_{3d}^4 structure of LaF_3 doped with Gd^{3+}. The projection of the particles on the hexagonal cell is shown on a plane perpendicular to crystal c axis and passing through half of the La ions. The positions of z and x axes are also shown.

IV. SUPERPOSITION MODEL

A. General theory of the linear superposition model

In this model the spin-Hamiltonian parameters b_l^m can be expressed as linear superposition of single-ligand contributions

$$b_l^m = \sum_i \bar{b}_l(R_i) K_l^m(\theta_i, \phi_i) \ , \tag{4.1}$$

where $K_l^m(\theta_i, \phi_i)$ are spherical harmonic functions of rank l of polar angles θ_i, ϕ_i. For the particular case considered in this paper, one requires the following functions[8]:

$$K_2^0(\theta,\phi) = \tfrac{1}{2}(3\cos^2\theta - 1) \ , \tag{4.2}$$

$$K_2^2(\theta,\phi) = \tfrac{3}{2}\sin^2\theta\cos2\phi \ , \tag{4.3}$$

$$K_4^0(\theta,\phi) = \tfrac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3) \ , \tag{4.4}$$

$$K_4^2(\theta,\phi) = \tfrac{5}{2}(7\cos^2\theta - 1)\sin^2\theta\cos2\phi \ , \tag{4.5}$$

$$K_4^4(\theta,\phi) = \tfrac{35}{8}\sin^4\theta\cos4\phi \ . \tag{4.6}$$

In Eq. (4.1) the summation extends over the nearest-neighbor ligands of the paramagnetic ion. The $\bar{b}_l(R)$ are functions of the radial metal-ligand distance R, which are called the intrinsic parameters. They differ for different paramagnetic ions, e.g., Gd^{3+}, Mn^{2+}, Fe^{3+}, as well as for oxygen or fluorine ligands.[8,9] So far, it has been assumed that the functional form of $\bar{b}_l(R)$ obeys a single potential law

$$\bar{b}_l(R_i)=\bar{b}_l(R_0)(R_0/R_i)^{t_l} , \qquad (4.7)$$

where the power-law exponent t_l is typical of the particular system considered. In Eq. (4.7) R_0 is the reference distance and R_i is the distance of the ligand ion i. In certain cases, however, a sum of two exponents had to be taken[9]; e.g.,

$$\bar{b}_2(R)=-\alpha R^{-7}+\beta R^{-10}, \quad \alpha>\beta>0 . \qquad (4.8)$$

In other words, $\bar{b}_2$ as given by Eq. (4.8) is a sum of nearly canceling terms,[1] arising from the crystal field, the correlation crystal field,[27,28] the exchange crystal field,[5] and the relativistic crystal field.[29]

For rare-earth impurities, the assumption of linear superposition, as in Eq. (4.1), has been proven successful. For the even-more-covalently-bound transition-metal ions, consistent results were first accumulated by Newman and Siegel,[10] and were further corroborated by the work of Siegel and Müller.[11]

With the knowledge of the function $\bar{b}_l(R)$ one is able to accomplish the following: (i) an analysis of local arrangements, if the EPR parameters are known and if the symmetry is sufficiently high and (ii) predictions of the sign and magnitude of spin-Hamiltonian parameters can be made if, for a local configuration, the crystallographic data are available.

B. Application to RF$_3$ hosts

For specific application to $R\mathrm{F}_3$ hosts the following procedure was used.

1. *Determination of t_l*

The values of $t_l(l=2,4)$ were determined as follows. For a chosen value of t_l one can determine $\bar{b}_l$ in two ways. (a) From Eq. (4.1) for any host $R\mathrm{F}_3$

$$\bar{b}_l=b_l^0/P_l^0(t_l) , \qquad (4.9)$$

where

$$P_l^m(t_l)=\sum_i K_l^m(\theta_i,\phi_i)\left[\frac{R_0}{R_i}\right]^{t_l} . \qquad (4.10)$$

In writing Eq. (4.10), the relation (4.7) has been taken into account. (b) If the relation (4.7) is indeed true it should be possible to express $\bar{b}_l$ for any host in terms of that for the host Gd^{3+} [denoted as $\bar{b}_l(\mathrm{Gd})$]. The required value of the spin-Hamiltonian parameter b_2^0 can be obtained from extrapolation of the values for the other $R\mathrm{F}_3$ hosts since b_2^0 is linear in host-ion radius.[13] (This value comes out to be 0.897 GHz.) Thus

$$\bar{b}_l=\bar{b}_l(\mathrm{Gd})(R_0^{\mathrm{Gd}}/R_0^R)^{t_l} . \qquad (4.11)$$

In Eq. (4.11) R_0^{Gd} and R_0^R refer to the smallest distance between a Gd^{3+} ion and an F$^-$ ion in the GdF$_3$ and $R\mathrm{F}_3$ hosts, respectively; these are listed in Table III.

The values of $\bar{b}_2$ as determined from Eqs. (4.9) and (4.11) will hereafter be referred to as $\bar{b}_2(A)$ and $\bar{b}_2(B)$, respectively. In order to find the best t_2 value for the entire $R\mathrm{F}_3$ family considered (R =La, Ce, Pr, and Nd), the function

$$E(t_2)=[\bar{b}_2(A)-\bar{b}_2(B)]/\bar{b}_2(B) \qquad (4.12)$$

was computed for different values of t_2 for each $R\mathrm{F}_3$ host. The resulting $E(t_2)$ values are plotted in Fig. 2, from which it is clear that the minima for $E(t_2)$ for the various hosts are found in the range $t_2=9\pm1$. Thus a value of $t_2=9$ will hereafter be used for further considerations. Table IV contains a

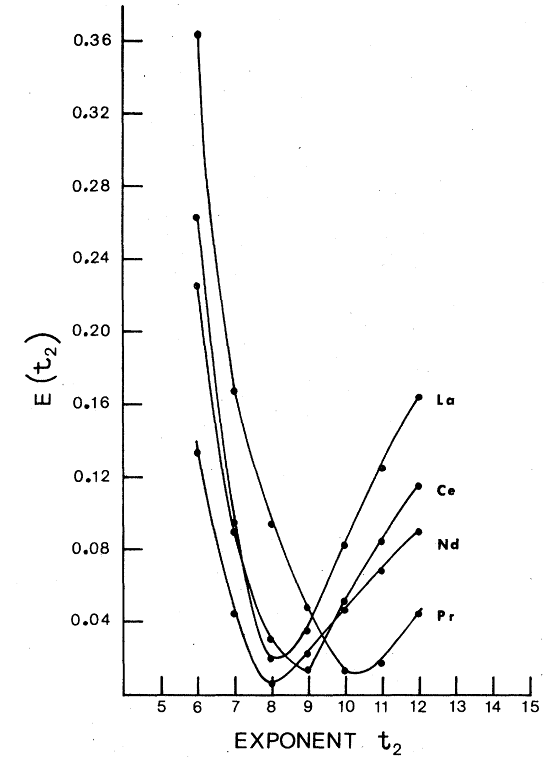

FIG. 2. Plot of $E(t_2)$ as a function of t_2 in various $R\mathrm{F}_3$ hosts, R =La, Ce, Pr, Nd. [For definition of $E(t_2)$ see Sec. IV, Eq. (4.12).]

TABLE IV. Values for $\bar{b}_2$ and $\bar{b}_4$ parameters as a function of the power-law exponent for Gd^{3+} in NdF_3 without distortions. All b_n^m are expressed in GHz.

t_n	b_0^0/P_2^0	b_2^2/P_2^2	b_4^0/P_4^0	b_4^2/P_4^2	b_4^4/P_4^4
1	3.510	0.743	0.0155	0.0349	0.0216
2	4.855	1.175	0.0159	0.0322	0.0218
3	7.473	2.627	0.0163	0.0300	0.0220
4	14.730	−14.764	0.0167	0.0283	0.0222
5	129.293	−2.019	0.0171	0.0269	0.0224
6	−21.231	−1.107	0.0176	0.0258	0.0226
7	−10.307	−0.774	0.0180	0.0248	0.0228
8	−7.022	−0.601	0.0185	0.0240	0.0230
9	−5.446	−0.495	0.0190	0.0234	0.0232
10	−4.526	−0.424	0.0195	0.0228	0.0234
11	−3.925	−0.372	0.0200	0.0224	0.0236
12	−3.505	−0.333	0.0205	0.0220	0.0238
13	−3.197	−0.303	0.0211	0.0216	0.0240
14	−2.963	−0.279	0.0216	0.0214	0.0242
15	−2.781	−0.259	0.0222	0.0211	0.0244
16	−2.636	−0.242	0.0228	0.0209	0.0246
18	−2.434	−0.216	0.0241	0.0207	0.0250
20	−2.291	−0.196	0.0255	0.0205	0.0254
22	−2.192	−0.181	0.0269	0.0204	0.0257
24	−2.124	−0.169	0.0285	0.0204	0.0261
26	−2.079	−0.158	0.0302	0.0205	0.0265

listing of $\bar{b}_l$ values ($l=2,4$) for different m as obtained from the relation

$$\bar{b}_l = b_l^m / P_l^m(t_l) \qquad (4.13)$$

for the host NdF_3. From Table IV it is clear the the $\bar{b}_2$ value as obtained for $m=2$ from Eq. (4.13) is almost one-tenth that obtained for $m=0$. In order to bring these two values closer together one should consider distortion of ϕ_i values; this is done in Sec. IV B 2.

Since the $\bar{b}_4$ values as determined from Eq. (4.13) for $m=0$ do not exhibit sharp minima or maxima as a function of t_4, as is seen from Table IV, t_4 was chosen to have such a value that for it the $\bar{b}_4$ values as determined from Eq. (4.13) for $m=0,2,4$ lie closest to each other. This value turns out to be $t_4=14$. Thus t_4 will hereafter be chosen to have the value 14.

2. *Determination of local distortions*

In order to bring closer together the two $\bar{b}_2$ values as obtained for $m=0$ and 2 from Eq. (4.2), one should consider distortion in the positions of ions due to the presence of the Gd^{3+} impurity in RF_3 hosts. It is noted from Eqs. (4.2)–(4.6) that if one were to vary only the ϕ_i values then only the $\bar{b}_l$ values, as determined from Eq. (4.13), for $m \neq 0$ will vary. With this in mind, the ϕ_i values for the eight nearest neighbors 2–9, as given in Table III, relative to that for the nearest-neighbor number 1 (Table III) were varied in the hope that such variation would bring agreement between the $\bar{b}_l$ values as obtained from Eq. (4.13) for different m values. Reasonably close $\bar{b}_2$ values (for different m) are found for variations of ϕ_i within ±3°. The results are listed in Table V. For $\bar{b}_2$ values the agreements are within 0.18%, 0.54%, 0.01%, and 0.13% for LaF_3, CeF_3, PrF_3, and NdF_3 hosts, respectively.

The particular deviations $\Delta\phi_i$ as indicated in Table IV were used to calculate the coordination factors $P_l^m(t_l)$. With these $P_l^m(t_l)$ values and the experimentally determined spin-Hamiltonian parameters the $\bar{b}_l$

TABLE V. The angular distortions $\Delta\phi_i$ ($i=2,8$) to bring close together the $\bar{b}_2$ values as obtained from b_2^0 and b_2^2. $\Delta\bar{b}_2$ represents the percent difference $[\bar{b}_2(m=2)-\bar{b}_2(m=0)] \times [100/\bar{b}_2(m=0)]$. $\bar{b}_l$ are expressed in GHz. The a's indicate the deviations used for theoretical calculations of parameters b_l^m as given in Table VII.

Host	$\bar{b}_2(m=0)$	$\Delta\bar{b}_2$ (%)	$\Delta\phi_2$	$\Delta\phi_3$	$\Delta\phi_4$	$\Delta\phi_5$	$\Delta\phi_6$	$\Delta\phi_7$	$\Delta\phi_8$	$\Delta\phi_9$
LaF_3	−4.457	0.18	−2°	−2°	−1°	3°	3°	3°	1°	1°
CeF_3	−4.879	0.54	$-3^{\circ a}$	$-2^{\circ a}$	$0^{\circ a}$	$-1^{\circ a}$	$2^{\circ a}$	$3^{\circ a}$	$-1^{\circ a}$	$-1^{\circ a}$
			−3°	−2°	0°	−1°	3°	2°	−1°	−1°
Prf_3	−4.936	0.01	−3°	−2°	−1°	−1°	1°	3°	−1°	0°
			$-3^{\circ a}$	$-2^{\circ a}$	$-1^{\circ a}$	$-1^{\circ a}$	$1^{\circ a}$	$3^{\circ a}$	$0^{\circ a}$	$-1^{\circ a}$
NdF_3	−5.472	0.13	0°	0°	−3°	−2°	3°	3°	−1°	3°
			0°	0°	−3°	−2°	3°	3°	3°	−1°
			$0^{\circ a}$	$0^{\circ a}$	$-2^{\circ a}$	$-3^{\circ a}$	$3^{\circ a}$	$3^{\circ a}$	$-1^{\circ a}$	$3^{\circ a}$
			0°	0°	−2°	−3°	3°	3°	3°	−1°

TABLE VI. The values of $\bar{b}_l$ (in GHz) as obtained for different m values using the deviations $\Delta\phi_i$ given by Table V.

	$\bar{b}_2$		$\bar{b}_4$		
Host	$m=0$	2	0	2	4
LaF_3	−4.457	−4.465	0.018	0.018	0.031
CeF_3	−4.879	−4.853	0.020	0.020	0.035
PrF_3	−4.936	−4.935	0.019	0.020	0.026
NdF_3	−5.472	−5.479	0.022	0.021	0.025

values for different m's were computed; these values are listed in Table VI. Finally, using the average $\bar{b}_l$ value, as obtained from $\bar{b}_l$ values for different m's and the coordination factors taking into account the particular deviations $\Delta\phi_i$, as listed in Table IV, the spin-Hamiltonian parameters were calculated. These theoretical values are listed in Table VII, which also contains the experimental values. It is seen from Table IV that, taking into account the experimental error of ±0.010 GHz for each b_l^m parameter, the agreement of $b_2^0, b_2^2, b_4^0, b_4^2$ theoretically calculated values with those determined experimentally is perfect. As for the b_4^4 values, the agreement for the PrF_3 and NdF_3 hosts is perfect within experimental errors, whereas those for the LaF_3 and CeF_3 experimental and theoretical values can be considered reasonably close.

In order to see the relationship of the intrinsic parameter b_2^0 with the zero-field splitting, these two quantities are plotted in Fig. 3. It is seen that the zero-field splitting is linear in $\bar{b}_2$ values within experimental error. Since the zero-field splitting is also linear in host-ion radius,[13] it is then concluded that $\bar{b}_2$ is also linear in host-ion radius.

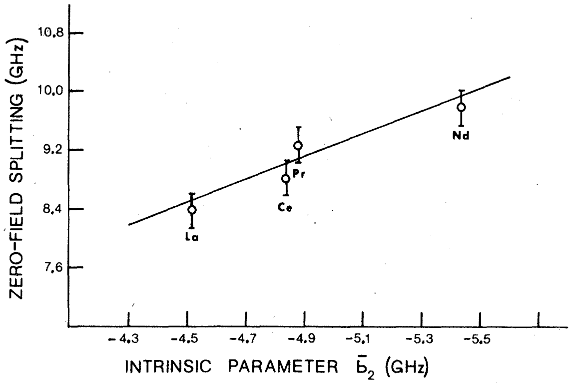

FIG. 3. Plot of the zero-field splittings for the various RF_3 hosts, as a function of the host intrinsic parameter $\bar{b}_2$. (Here the zero-field splitting means the differences in the energies corresponding to magnetic quantum numbers $\pm\frac{1}{2}$ and $\pm\frac{7}{2}$ for the Gd^{3+} ion doping the various hosts in zero magnetic field.)

V. DISCUSSION

The analysis presented in this paper has departed from the conventional procedure of obtaining $\bar{b}_2$, in which one first obtains the intrinsic parameter $\bar{A}_2$ from the crystal-field parameter A_2^0 and then uses the ratio of $b_2/A_2 = -3\times10^{-4}$ as obtained by Newman and Urban in various salts.[1] Here one directly computes $\bar{b}_2$ using the procedure described in Sec. IV. The procedure for deriving the value of t_2 is thus correspondingly different.

It is noted that the values of t_2 and t_4 as derived in this paper are considerably larger from those previously otained in other hosts, e.g., Gd^{3+}-doped CaF_2, SrF_2, BaF_2,[8,30] Gd^{3+}-doped lanthanide ethyl sulfate nonahydrates.[31] (Of course in CaF_2, SrF_2, and BaF_2 the Gd^{3+} ion is replacing doubly charged Ca^{2+}, Sr^{2+}, or

TABLE VII. The values of theoretical and experimental spin-Hamiltonian parameters b_l^m(GHz). The angular deviations as given in Table V have been used for theoretical parameters. The $\bar{b}_l$ values used for theoretical parameters which are the averages of values for different m's are also given. (Expt. stands for experimental value, while Theor. stands for theoretical value.)

	LaF_3		CeF_3		PrF_3		NdF_3	
	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
b_2^0	0.694	0.695	0.733	0.731	0.774	0.744	0.802	0.803
b_2^2	−0.083	−0.083	−0.055	−0.055	−0.081	−0.081	−0.148	−0.148
b_4^0	0.016	0.020	0.018	0.022	0.017	0.019	0.019	0.020
b_4^2	0.066	0.083	0.076	0.096	0.077	0.084	0.081	0.087
b_4^4	0.117	0.084	0.144	0.104	0.117	0.097	0.130	0.118
$\bar{b}_2$	−4.461		−4.866		−4.934		−5.476	
$\bar{b}_4$	0.022		0.025		0.022		0.022	

Ba^{2+} ions; thus for these hosts there are additional effects due to charge compensation.) However, if the overlap model does indeed take into account effects other than the electrostatic effects, such large values are not unreasonable, in view of large powers, e.g., 6 and 12, of interionic distances, occurring in Leonard-Jones potential describing the cohesive energy.[32] At any rate, the values of t_2 and t_4 are in conformity with those found for Fe^{3+}.[11,33,34] Furthermore, the large value of t_2 found here is in contradiction with the hypothesis of Newman and Urban[1] that $\bar{b}_2$ is a sum of nearly canceling terms from the crystal field, correlation crystal field,[27,28] the exchange crystal field,[5] and the relativistic crystal field[29] [Eq. (4.8)].

In almost all the previous applications of the superposition model to Gd^{3+} spin-Hamiltonian parameters the crystal symmetry had been such that the parameter b_2^2 was identically zero, unlike the situation with the $R\mathrm{F}_3$ hosts considered in this paper. Thus the application of the superposition model to $R\mathrm{F}_3$ hosts has subjected this model to a more rigorous test in that here one should have the same value for $\bar{b}_2$ as obtained from the parameters b_2^0 and b_2^2. The fact that it is possible to do so with small distortions of angular positions establishes the validity of this model.

Using the $\bar{b}_l$ values as function of host-ion radius as found in this paper, it should be possible to estimate the spin-Hamiltonian parameters for Gd^{3+} doping other $R\mathrm{F}_3$ hosts not investigated experimentally so far.

VI. CONCLUSION

It has been possible to satisfactorily account for the spin-Hamiltonian parameters for Gd^{3+} doping $R\mathrm{F}_3$ single crystals within the framework of the superposition model. (Of course, for testing the validity of the superposition model one should have very accurate experimental parameters available, which is true for the $R\mathrm{F}_3$ hosts considered here.) It is hoped that the analysis presented in this paper on isostructural hosts would bring further understanding of the zero-field splitting of Gd^{3+} ion. Towards this end, further attempts should be made to analyze the spin-Hamiltonian parameters of Gd^{3+} doping other isostructural hosts, using the procedure adopted in this paper on the application of the superposition model.

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