

# Calculation of the Spin-Lattice Coefficients of $Gd^{3+}$ in $CaF_2$ Using a Point-Charge Model for the Crystalline Field

R. Calvo,\* M. C. G. Passeggi, and M. Tovar

Centro Atómico Bariloche, Comisión Nacional de Energía Atómica,  
Instituto de Física "Dr. José A. Balseiro," Universidad Nacional de Cuyo,  
San Carlos de Bariloche, Argentina

(Received 5 February 1971)

The contribution of the Blume-Orbach mechanism to the second-order spin-lattice coefficients for  $Gd^{3+}$  in cubic sites of  $CaF_2$  has been calculated with a point-charge approach for the orbit-lattice interaction. Our results,  $G_{3g}^{(2)} = -0.006 \text{ cm}^{-1}$  and  $G_{5g}^{(2)} = -0.07 \text{ cm}^{-1}$ , agree in sign with the experimental values of  $G_{3g}^{(2)} = -0.22 \text{ cm}^{-1}$  and  $G_{5g}^{(2)} = -0.11 \text{ cm}^{-1}$ . Differences in magnitude of  $G_{3g}^{(2)}$  can be understood in view of the opposite contribution of the fourth- and sixth-order terms of the orbit-lattice Hamiltonian. We conclude that the Blume-Orbach mechanism predicts values for the spin-lattice coefficients  $G_{3g}^{(2)}$  and  $G_{5g}^{(2)}$  of  $Gd^{3+}$  in  $CaF_2$  in reasonable agreement with the experimental data, and that the cubic crystalline field must be considered in any calculation of the spin-lattice parameters.

## I. INTRODUCTION

The crystalline electric fields acting on paramagnetic ions introduced as impurities in a diamagnetic lattice modify the free-ion states producing splittings and shifts of its energy levels. Their effects on the ground state are observed by electron-paramagnetic-resonance experiments (EPR) where the data are described in terms of the spin-Hamiltonian formalism.

When the crystal is deformed, e.g., by an external applied stress, an additional component of the electric field appears and originates the so-called *orbit-lattice coupling*.<sup>1</sup> From a phenomenological point of view, an effective spin formalism, similar to the spin Hamiltonian, is used to fit the experimental data. This *spin-lattice Hamiltonian*<sup>2</sup>  $H_{s1}$  couples a paramagnetic ion in a crystal with the deformations of the lattice. It reflects the local symmetry of the ion and operates on its effective spin and these deformations.

The strength of the spin-lattice interaction is given by the spin-lattice coefficients, and can be evaluated for the ground state of a paramagnetic ion through EPR experiments, where the shifts of the positions of the lines are measured as a function of an externally applied uniaxial stress.<sup>3</sup>

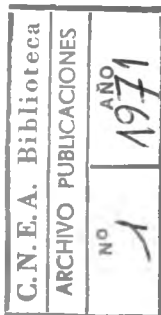
By this method several measurements of the spin-lattice coefficients for S-state ions in a cubic environment have been reported for the iron group<sup>3,4</sup> ( $3d^5$ ,  ${}^6S_{5/2}$ ,  $Mn^{2+}$ , and  $Fe^{3+}$ ) and the rare-earth group<sup>5-8</sup> ( $4f^7$ ,  ${}^8S_{7/2}$ ,  $Eu^{2+}$ , and  $Gd^{3+}$ ). The interest to study these half-filled shell ions comes from the fact that only the combined effect of the orbit-lattice interaction with the spin-orbit, spin-spin interactions, etc., can produce splittings or shifts of the ground state, and considerable efforts have been made to find which mechanisms can ex-

plain the experimental data.

A detailed account of the calculations for the iron-group ions is given by Sharma *et al.*<sup>9</sup> They consider the various mechanisms proposed by other authors,<sup>10-13</sup> including covalency and overlap corrections, and conclude that from  $Mn^{2+}$  the predominant mechanism is that originally proposed by Blume and Orbach (BO),<sup>12</sup> where the ground state  ${}^6S$  of  $Mn^{2+}$  is admixed by the spin-orbit interaction with excited states which are strongly mixed by the cubic field, providing a large contribution to the spin-lattice coefficients.

Wybourne<sup>14</sup> reported a detailed calculation of several mechanisms contributing to the axial field splitting of  $Gd^{3+}$  in the  $D_{3h}$  symmetry of the gadolinium-ethyl-sulphate crystal. His results are in agreement in magnitude with, but of opposite sign from, the experimental values and he suggests that no purely ionic model can account for the observed splitting. Recently Detrio<sup>15</sup> calculated the spin-lattice coefficients for  $Gd^{3+}$  in  $CaF_2$  using a point-charge model for the crystalline electric field and free-ion state vectors obtained by including electrostatic, spin-orbit, spin-spin, spin-other-orbit, and configuration interactions. He again obtained agreement in magnitude but opposite signs from the experimental values.<sup>5</sup> Detrio suggests that the error lies in the point-charge model used in the calculation rather than in the wave functions.

In this paper we report a calculation of the spin-lattice coefficients of  $Gd^{3+}$  in cubic positions of  $CaF_2$ . Owing to the reasonable agreement obtained by Sharma *et al.*<sup>9</sup> for  $Mn^{2+}$ , we consider the contribution coming from the BO mechanism. We obtained the values of the two second-order spin-lattice coefficients<sup>5</sup>  $G_{3g}^{(2)}$  and  $G_{5g}^{(2)}$  which correspond to  $G_{11}$  and  $G_{44}$ , respectively, as defined for the iron-group ions where only second-order coefficients



contribute.<sup>3</sup> Our estimation, performed with an effective point-charge approach for the electric field induced by the strain, gives results with the correct signs and in reasonable agreement in magnitude for the trigonal coefficients  $G_{5g}^{(2)}$ ; the value for  $G_{3g}^{(2)}$ , however, is 36 times smaller than the experimental value.<sup>5</sup> As will be discussed in Sec. IV, our results indicate that the mechanism of BO<sup>12</sup> gives a large contribution to the spin-lattice interaction, and that the effect of the cubic field is very important and should be considered in any future calculation.

## II. BLUME-ORBACH MECHANISM

The ground state of the  $Gd^{3+}$  free ion ( $4f^7$  configuration) is an orbital singlet  ${}^8S$  and the nearest excited states are  ${}^6P$ ,  ${}^6D$ ,  ${}^6F$ ,  ${}^6G$ ,  ${}^6H$ , and  ${}^6I$ . The orbital degeneracy of the excited states is removed by the cubic crystalline field of the  $CaF_2$  lattice, and they split according to the irreducible representations of the cubic group  $O_h$ .

O'Hare and Donlan<sup>16</sup> have evaluated the cubic crystalline field parameters by fitting the Hamiltonian

$$H_{\text{cub}} = B_4 [C_0^{(4)} + (\sqrt{\frac{5}{14}})(C_4^{(4)} + C_{-4}^{(4)})] \\ + B_6 [C_0^{(6)} - (\sqrt{\frac{7}{2}})(C_4^{(6)} + C_{-4}^{(6)})], \quad (1)$$

with optical data. In Eq. (1) the  $z$  axis is the  $[001]$  crystal direction, a convention which will be followed in this work. They found  $B_4 = -2160.0 \text{ cm}^{-1}$  and  $B_6 = 792.85 \text{ cm}^{-1}$ . Because the spatial part of the spin-orbit interaction transforms like  $\Gamma_4$  in  $O_h$ , only the  $\Gamma_4$  components of the excited sextuplets could be admixed to the ground state in a first-order theory.<sup>12</sup>

The energy matrix for the  $\Gamma_4$  components of the above-mentioned excited terms was then calculated using the free-ion term energies,<sup>17</sup> the Hamiltonian of Eq. (1), and the cubic  $\Gamma_4$  wave functions given by Griffith.<sup>18</sup> The reduced matrix elements inside the  $f^7$  configuration and the values for the 3- $j$  and 6- $j$  are from the tables of Nielson and Koster<sup>19</sup> and Rotenberg *et al.*,<sup>20</sup> respectively. This matrix was diagonalized, as in the calculation by BO,<sup>12</sup> because the size of the cubic field is not much smaller than the relative splitting of the terms. The eigenvectors are defined as

$$|{}^6\Gamma_{4,\alpha}, M_s\rangle = \sum_L A_{L,\alpha} |{}^6\Gamma_{4,\alpha}(L), M_s\rangle, \quad (2)$$

where  $\alpha = 1, 0, -1$ ;  $|{}^6\Gamma_{4,\alpha}(L), M_s\rangle$  is the  $\Gamma_{4,\alpha}$  component corresponding to the  ${}^6L$  term ( $L = P, F, G, H, H_b$ , and  $I$ , where  $a$  and  $b$  indicate the two states belonging to the  ${}^6H$  term which transform like  $\Gamma_4$ ), and  $M_s$  is the  $z$ -axis projection of the total-spin quantum number. The resulting eigenvalues and eigenvectors are given in Table I.

The  $|{}^6\Gamma_{4,\alpha}, M_s\rangle$  states are then admixed to the

$|{}^8S, M_s\rangle$  ground level by the spin-orbit interaction. To first order the admixed wave functions will be<sup>12</sup>

$$|{}^8S, M_s\rangle' = |{}^8S, M_s\rangle - \sum_{i=1}^6 \frac{A_{iP}}{\Delta_i} \zeta [a(M_s) |{}^6\Gamma_{4,1}, M_s - 1\rangle \\ + b(M_s) |{}^6\Gamma_{4,-1}, M_s + 1\rangle + c(M_s) |{}^6\Gamma_{4,0}, M_s\rangle], \quad (3)$$

where the value of the spin-orbit constant  $\zeta$  of  $Gd^{3+}$  is given in Ref. 17. The  $a(M_s)$ ,  $b(M_s)$ , and  $c(M_s)$  appearing in Eq. (3) are those defined by BO, and their values for this case were calculated using the spin-orbit reduced matrix elements given by Nielson and Koster.<sup>19</sup> We obtain

$$a(M_s) = -[\frac{1}{3}(\frac{7}{2} + M_s)(\frac{5}{2} + M_s)]^{1/2}, \quad (4a)$$

$$b(M_s) = -[\frac{1}{3}(\frac{7}{2} - M_s)(\frac{5}{2} - M_s)]^{1/2}, \quad (4b)$$

$$c(M_s) = -[\frac{2}{3}(\frac{7}{2} - M_s)(\frac{7}{2} + M_s)]^{1/2}. \quad (4c)$$

Some comments to justify Eq. (3) are important at this point. For rare-earth ions the spin-orbit interaction is stronger than the cubic crystalline field. However, in the case of an  $S$ -state ground level departures from  $L$ - $S$  coupling are absent, and, even if they are important for the excited terms, our perturbation calculation for the ground-level eigenfunctions remains valid.

### A. Tetragonal Distortion

When a force is applied along the  $[001]$  direction of the crystal, a tetragonal deformation  $\epsilon_{3g,\theta} = \frac{1}{4}(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy})$ , where the  $\epsilon_{ij}$  are the components of the strain tensor, is introduced. If the orbit-lattice Hamiltonian is expanded in terms of the deformation, the linear part introduced by this distortion is

$$\mathcal{H}_{01}^{(3g,\theta)} = \{ B_{3g}^{(2)} C_0^{(2)} \\ + B_{3g}^{(4)} [ -(\sqrt{\frac{5}{12}}) C_0^{(4)} + (\sqrt{\frac{7}{24}})(C_4^{(4)} + C_{-4}^{(4)})] \\ + B_{3g}^{(6)} [(\sqrt{\frac{7}{8}}) C_0^{(6)} + \frac{1}{4}(C_4^{(6)} + C_{-4}^{(6)})] \} \epsilon_{3g,\theta}, \quad (5)$$

where the  $B_{3g}^{(n)}$  are numerical coefficients which will be evaluated from an electrostatic model, and the linear combinations of the single-electron operators  $C_m^{(n)}$  transforming like  $\Gamma_{3g,\theta}$  are those given by Griffith.<sup>18</sup>

The matrix elements of the Hamiltonian of Eq. (5) within the states defined in Eq. (3) were calculated using the values given in Table I, the tables of Nielson and Koster<sup>19</sup> for the reduced matrix elements and symmetry arguments. We find

$$\langle {}^8S, M_s | \mathcal{H}_{01}^{(3g,\theta)} | {}^8S, M_s \rangle' = (0.084B_{3g}^{(4)} + 0.060B_{3g}^{(6)}) \\ \times \{ -\frac{1}{2}[a^2(M_s) + b^2(M_s)] + c^2(M_s) \} \epsilon_{3g,\theta} \quad (6)$$

TABLE I. Eigenvectors and eigenvalues of the cubic field of the components of the spin sextuplets of  $Gd^{3+}$  in  $CaF_2$ , transforming like  $\Gamma_4$  in  $O_h$ . The energies are referred to the ground state  $^8S_7$ .

$i$	$L$	Eigenvectors $A_{i,L}$					$\Delta_i$ ( $cm^{-1}$ )	
		$^6P$	$^6F$	$^6G$	$^6H_a$	$^6H_b$		$^6I$
1		0.9660	-0.0082	0.0254	-0.0069	0.0	-0.2571	33413
2		-0.0106	0.9138	0.4023	-0.0474	-0.0001	-0.0279	54660
3		-0.0237	-0.4047	0.9108	-0.0766	-0.0001	0.0161	53168
4		-0.0023	0.0115	0.0892	0.9956	0.0010	-0.0269	60146
5		-0.0	0.0	0.0001	-0.0010	1.0000	0.0001	60073
6		0.2573	0.0313	0.0057	0.0258	-0.0	0.9655	35673

in units of  $cm^{-1}$ .

The experimental data can be fitted with a spin-lattice Hamiltonian which contains second- and fourth-order operators in the effective spin.<sup>5</sup> For a tetragonal deformation it can be written as

$$H_{s1}^{(3\epsilon, \theta)} = [G_{3\epsilon}^{(2)} O_2^0 + G_{3\epsilon}^{(4)} (O_4^0 - 7O_4^4)] \epsilon_{3\epsilon, \theta}, \quad (7)$$

where the  $O_n^m$  are the Stevens operators and  $G_{3\epsilon}^{(2)}$

and  $G_{3\epsilon}^{(4)}$  are the second- and fourth-order spin-lattice coefficients, respectively. When Eqs. (6) and (7) are compared using the values given in Eqs. (4a)–(4c), it is seen that the BO mechanism predicts the same tensorial dependence in  $M_s$  as that of the second-order terms in  $H_{s1}$ . We find

$$G_{3\epsilon}^{(2)} = (-0.028B_{3\epsilon}^{(4)} - 0.020B_{3\epsilon}^{(6)}) \times 10^{-4} cm^{-1}. \quad (8)$$

### B. Trigonal Distortion

A trigonal distortion appears when a stress is applied along the  $[111]$  crystal direction. In this case  $\mathcal{H}_{01}$  is

$$\mathcal{H}_{01}^{(5\epsilon, \zeta)} = (1/\sqrt{2}) \{B_{5\epsilon}^{(2)} (C_2^{(2)} - C_{-2}^{(2)}) + B_{5\epsilon}^{(4)} + B_{5\epsilon}^{(6,a)} (C_2^{(6)} - C_{-2}^{(6)}) + B_{5\epsilon}^{(6,b)} (C_6^{(6)} - C_{-6}^{(6)})\} \epsilon_{5\epsilon, \zeta}, \quad (9)$$

case  $\mathcal{K}$

where  $\epsilon_{5\epsilon, \zeta} = \epsilon_{xy}$ . The corresponding  $H_{s1}$  is<sup>5</sup>

$$H_{s1}^{(5\epsilon, \zeta)} = \{G_{5\epsilon}^{(2)} (1/2i) (S_+^2 - S_-^2) + G_{5\epsilon}^{(4)} (1/4i) [(7S_+^2 - S(S+1) - 5) (S_+^2 - S_-^2) + (S_+^2 - S_-^2) (7S_-^2 - S(S+1) - 5)]\} \epsilon_{5\epsilon, \zeta}. \quad (10)$$

Along the same lines as for the tetragonal distortion, we find, comparing Eqs. (9) and (10),

$$G_{5\epsilon}^{(2)} = i [0.00025B_{5\epsilon}^{(2)} - 0.0242B_{5\epsilon}^{(4)} + 0.0966B_{5\epsilon}^{(6,a)} - 0.0200B_{5\epsilon}^{(6,b)}] \times 10^{-4} cm^{-1}. \quad (11)$$

### III. EVALUATION OF ORBIT-LATTICE INTERACTION IN POINT-CHARGE APPROACH

The values given in Eqs. (8) and (11) for  $G_{3\epsilon}^{(2)}$  and  $G_{5\epsilon}^{(2)}$  were calculated using only the energies of the free-ion terms, the spin-orbit interaction constant, and the cubic field parameters of the  $Gd^{3+}$  ion in the  $CaF_2$  lattice, which are known from optical data.<sup>16,17</sup> It remains now to estimate values for the orbit-lattice Hamiltonian parameters  $B_i^{(n)}$ . To do that, we have used a point-charge model, in a first-nearest-neighbors approach, valid for the  $n=4$  and  $n=6$  terms of  $\mathcal{H}_{01}$ , which gives the main contribution to Eqs. (8) and (11). For a cubic coordination of  $F^-$  ions around the impurity we find

$$B_{3\epsilon}^{(2)} = -\frac{32}{3} \frac{e^2 e_{\text{eff}} \langle r^2 \rangle}{R^3},$$

$$B_{5\epsilon}^{(2)} = -\frac{32}{9} (\sqrt{3}) i \frac{e^2 e_{\text{eff}} \langle r^2 \rangle}{R^3},$$

$$B_{3\epsilon}^{(4)} = -\frac{64}{27} (\sqrt{15}) \frac{e^2 e_{\text{eff}} \langle r^4 \rangle}{R^5},$$

$$B_{5\epsilon}^{(4)} = \frac{80}{9} (\sqrt{5}) i \frac{e^2 e_{\text{eff}} \langle r^4 \rangle}{R^5},$$

$$B_{3\epsilon}^{(6)} = \frac{32}{9} (\sqrt{14}) \frac{e^2 e_{\text{eff}} \langle r^6 \rangle}{R^7},$$

$$B_{5\epsilon}^{(6,a)} = -\frac{16}{27} (\sqrt{210}) i \frac{e^2 e_{\text{eff}} \langle r^6 \rangle}{R^7},$$

$$B_{5\epsilon}^{(6,b)} = -\frac{16}{81} (\sqrt{462}) i \frac{e^2 e_{\text{eff}} \langle r^6 \rangle}{R^7}, \quad (12)$$

where the  $F^-$  ions are supposed to be a point charge  $ee_{\text{eff}}$  at a distance  $R$  from the  $\text{Gd}^{3+}$  ion.

The quantities appearing in Eq. (12) were evaluated, as in BO, from the experimental values of the cubic field parameters. In the point-charge approach  $B^{(4)}$  and  $B^{(6)}$  defined in Eq. (1) are

$$B^{(4)} = \frac{28}{9} \frac{e^2 e_{\text{eff}} \langle r^4 \rangle}{R^5}, \quad B^{(6)} = -\frac{16}{9} \frac{e^2 e_{\text{eff}} \langle r^6 \rangle}{R^7}.$$

Then

$$\frac{e^2 e_{\text{eff}} \langle r^4 \rangle}{R^5} = -694 \text{ cm}^{-1}$$

and

$$\frac{e^2 e_{\text{eff}} \langle r^6 \rangle}{R^7} = -446 \text{ cm}^{-1}.$$

With those values and using Eqs. (12), we find

$$B_{3g}^{(4)} = 6370 \text{ cm}^{-1}, \quad B_{5g}^{(4)} = -13790i \text{ cm}^{-1},$$

$$B_{3g}^{(6)} = -5930 \text{ cm}^{-1},$$

$$B_{5g}^{(6,a)} = 3830i \text{ cm}^{-1}, \quad B_{5g}^{(6,b)} = 1890i \text{ cm}^{-1}.$$

$B_{3g}^{(2)}$  and  $B_{5g}^{(2)}$  cannot be evaluated by this approach, but  $B_{3g}^{(2)}$  does not contribute to Eq. (8), and a direct estimation of  $B_{5g}^{(2)}$  shows that its contribution to  $G_{5g}^{(2)}$  in Eq. (11) can be neglected.

This semiempirical evaluation of the orbit-lattice Hamiltonian parameters avoids making assumptions about the real values of  $R$ , which can be altered by the local distortions of the lattice, of  $\langle r^4 \rangle$  and  $\langle r^6 \rangle$ , which are known only for the free ion, and of  $e_{\text{eff}}$ , which depends on the polarization and spatial charge distribution of the ligands ions. Covalent and other effects could yield different contributions for the cubic field than for the orbit-lattice parameters, and then our values for the  $B_i^{(n)}$  should be taken as a very rough estimation of the orbit-lattice coupling.

#### IV. RESULTS AND DISCUSSION

Using the orbit-lattice parameters calculated in Sec. III and Eqs. (8) and (11), we find

$$G_{3g}^{(2)}(\text{theor}) = -0.006 \text{ cm}^{-1},$$

$$G_{5g}^{(2)}(\text{theor}) = -0.07 \text{ cm}^{-1}.$$

The experimental values of these spin-lattice strain coefficients are obtained from the values of the stress coefficients measured by Calvo *et al.*,<sup>5</sup> using the elastic constants of the  $\text{CaF}_2$  crystal<sup>21</sup>:

$$G_{3g}^{(2)}(\text{expt}) = -0.22 \text{ cm}^{-1}, \quad G_{5g}^{(2)}(\text{expt}) = -0.11 \text{ cm}^{-1}.$$

It is seen that the signs of both coefficients predicted by our calculation are correct, but the magnitude obtained for  $G_{3g}^{(2)}$  is about 36 times smaller than the experimental value, and that obtained for

$G_{5g}^{(2)}$  is slightly smaller than the experimental value.

In our calculation, the main contributions to  $G_{3g}^{(2)}$  and  $G_{5g}^{(2)}$  come from the mixture of the  ${}^6P$  states with the  ${}^6G$  and  ${}^6I$  terms (see Table I) induced by the fourth- and sixth-order cubic crystal fields, respectively. The resulting  ${}^6P$  states are admixed to the  ${}^8S$  ground state by the spin-orbit interaction; when an axial field is induced by the strain, fourth- and sixth-order terms of the orbit-lattice interaction will give contributions to the spin-lattice coefficients, which are mainly proportional to the admixtures of the  ${}^6P$  with the  ${}^6G$  and  ${}^6I$  terms due to the cubic field. For  $G_{5g}^{(2)}$  the fourth- and sixth-order terms of Eq. (9) contribute in the same direction, as is seen in Eq. (11) using Eq. (12). This is not the case for  $G_{3g}^{(2)}$ , where the fourth- and sixth-order contributions have opposite signs and are comparable in magnitude as indicated by Eqs. (8) and (12). Then, within our rough estimation of the orbit-lattice parameters, we can expect agreement with the experimental data only for  $G_{5g}^{(2)}$ , as is the case in our calculation.

We have only considered the contribution to the spin-lattice interaction coming from the mechanism proposed by BO<sup>12</sup> for  $\text{Mn}^{2+}$ . However, as pointed out in Sec. I, Wybourne has proposed several other mechanisms<sup>14</sup> which should be considered in an evaluation of the spin-lattice interaction. Detrio,<sup>15</sup> in his calculation of the spin-lattice coefficients for  $\text{Gd}^{3+}$  in  $\text{CaF}_2$ , uses free-ion state vectors obtained by diagonalizing simultaneously the spin-orbit, spin-spin, spin-other-orbit, and configuration interactions, and he found that the main contribution to the spin-lattice interaction comes from second-order terms in  $\mathcal{H}_{01}$ . The disagreement in sign obtained by both authors is attributed to the inadequacy of the ionic model. Probably further improvement in the calculation of the spin-lattice coefficients of an S-state ion could be obtained by considering the effect of the covalent mixing of the  $4f$  and, more important, the  $5p$  shells, as was done by Watson and Freeman<sup>22</sup> in the calculation of the crystal field splittings of  $\text{Tm}^{2+}$ .

Newman<sup>23</sup> has advanced the hypothesis that the dominant contribution to the zero-field-splitting parameter of  $\text{Gd}^{3+}$  in axial symmetry comes from charge-conjugation-invariant components of the crystal field. At present no numerical evaluation of this mechanism exists.

Our calculation shows that, even within the weakness of the point-charge approach, the cubic crystalline field acting on the  $\text{Gd}^{3+}$  ion is very important and should be considered in obtaining the ground-state wave functions.

We think that it would be very interesting to measure the  $B_i^{(n)}$  parameters of  $\mathcal{H}_{01}$  by uniaxial-stress optical experiments; these values could provide a direct check of the model.

Additional information about the effectiveness of the BO mechanism to the spin-lattice interaction for the  $f^7$  configuration could be obtained from calculations of  $G_3^{(2)}$  and  $G_5^{(2)}$  for  $\text{Eu}^{2+}$  in  $\text{CaF}_2$ , and  $\text{Gd}^{3+}$  in  $\text{CaO}$ . These coefficients have been measured,<sup>5,6</sup> and the values for  $\text{Gd}^{3+}$  in the octahedral coordination of the  $\text{CaO}$  have opposite signs from those found for  $\text{Gd}^{3+}$  in a cubic environment; this change could be related with the different signs of the fourth-order cubic field parameters for those co-

ordinations. Unfortunately no optical data exist for those systems.

Oseroff and co-workers<sup>8,24</sup> have observed a variation with temperature of the spin-lattice coefficients of  $\text{Gd}^{3+}$  in  $\text{ThO}_2$  and  $\text{CeO}_2$  which cannot be explained with the change of the elastic constants. This variation should indicate that dynamic effects due to the orbit-lattice coupling contribute to the spin-lattice interaction. This effect will be discussed in a forthcoming paper.

\*Member of the Carrera del Investigador Científico, Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

<sup>1</sup>J. H. Van Vleck, *J. Chem. Phys.* **7**, 72 (1939); *Phys. Rev.* **57**, 426 (1940).

<sup>2</sup>See, for example, D. K. Ray, T. Ray, and P. Rudra, *Proc. Phys. Soc. (London)* **87**, 485 (1966).

<sup>3</sup>E. Feher, *Phys. Rev.* **136**, A145 (1964).

<sup>4</sup>R. Calvo, Z. Sroubek, R. S. Rubins, and P. Zimmermann, *Phys. Letters* **27A**, 143 (1968).

<sup>5</sup>R. Calvo, R. A. Isaacson, and Z. Sroubek, *Phys. Rev.* **177**, 484 (1969).

<sup>6</sup>J. W. Hopson and A. W. Nolle, *Bull. Am. Phys. Soc.* **13**, 885 (1968).

<sup>7</sup>C. M. Bowden and J. E. Miller, *J. Phys. Chem. Solids* **30**, 1661 (1969).

<sup>8</sup>S. B. Oseroff, R. Calvo, and C. Fainstein, *Phys. Letters* **32A**, 393 (1970).

<sup>9</sup>R. R. Sharma, T. P. Das, and R. Orbach, *Phys. Rev.* **149**, 257 (1966); **155**, 338 (1967); **171**, 378 (1968); R. R. Sharma, *ibid.* **176**, 467 (1968).

<sup>10</sup>M. H. L. Pryce, *Phys. Rev.* **80**, 1107 (1950).

<sup>11</sup>H. Watanabe, *Progr. Theoret. Phys. (Kyoto)* **18**, 405 (1957).

<sup>12</sup>M. Blume and R. Orbach, *Phys. Rev.* **127**, 1587 (1962).

<sup>13</sup>R. Orbach, T. P. Das, and R. R. Sharma, in *Proceedings of the International Conference on Magnetism, Nottingham*, 1964 (The Institute of Physics and the Physical Society, London, 1965), p. 330.

<sup>14</sup>B. G. Wybourne, *Phys. Rev.* **148**, 317 (1966).

<sup>15</sup>J. A. Detrio, *Bull. Am. Phys. Soc.* **15**, 335 (1970).

<sup>16</sup>J. M. O'Hare and V. L. Donlan, *Phys. Rev.* **185**, 416 (1969).

<sup>17</sup>B. R. Judd, H. M. Crosswhite, and H. Crosswhite, *Phys. Rev.* **169**, 130 (1968).

<sup>18</sup>J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge U. P., New York, 1961).

<sup>19</sup>C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the  $p^n$ ,  $d^n$  and  $f^n$  Configurations* (MIT Press, Cambridge, Mass., 1963).

<sup>20</sup>M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols* (MIT Press, Cambridge, Mass., 1959).

<sup>21</sup>H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7, p. 214.

<sup>22</sup>R. E. Watson and A. J. Freeman, *Phys. Rev.* **156**, 251 (1967).

<sup>23</sup>D. J. Newman, *Chem. Phys. Letters* **6**, 288 (1970).

<sup>24</sup>S. B. Oseroff and R. Calvo (unpublished).