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Stress-induced g shifts of Γ_7 levels for rare-earth ions[*]

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The angular dependence of stress-induced shifts of the gyromagnetic factor g of the Γ_7 doublets of Yb^{3+} and Dy^{3+} in CaF_2 and Er^{3+} in CeO_2 and ThO_2 have been measured in electron-paramagnetic-resonance experiments. The observed variation of the angular dependence of the g shifts is explained in terms of a phenomenological spin-lattice Hamiltonian. A microscopic theory is used to obtain a quantitative evaluation of the observed shifts using a point-charge model for the induced crystalline field. The results indicate that covalent effects and the shielding of the electric field at the impurity site are important.

I. INTRODUCTION

Data on the stress-induced changes of the gyromagnetic factor g of the Kramers doublets for rare-earth ions in cubic crystals provide useful information to test crystalline-field theories. Sroubek *et al.*[1] reported measurements of the g shifts for the Γ_7 and Γ_6 ground levels of Yb^{3+} in ThO_2 and Ho^{2+} in CaF_2 when the samples were deformed by an external uniaxial stress. They obtained a reasonable agreement between their experimental results and the predictions of a point-charge model for the crystalline field; covalent contributions, expansion of the wave functions of the ions when introduced in the crystals, and other smaller contributions are included in their model by multiplying with numerical factors the constants of the orbit-lattice Hamiltonian obtained from the point-charge model. Baker and Currel[2] measured the shift of the EPR lines corresponding to the Γ_7 doublet and some of the transitions within the Γ_8 ground quartet for $CaF_2:Dy^{3+}$. They concluded that terms with $l > 2$ are important in the stress-induced crystal field.

We felt at that moment that it would be of interest to measure the stress parameters for other rare-earth ions with a Kramers-doublet ground state and to compare the results with the existing data in order to verify systematic trends.

We report here uniaxial-stress measurements of the angular dependence of the induced g shifts for Yb^{3+} and Dy^{3+} in CaF_2 and Er^{3+} in CeO_2 and ThO_2 with the stress applied along the [110] crystal direction and the external magnetic field rotating in a plane perpendicular to the stress. Preliminary data on Dy^{3+} in CaF_2 were reported in a previous letter.[3] It is shown in this paper that the observed angular dependence of the g shifts can be explained qualitatively by a phenomenological spin-lattice Hamiltonian. A microscopic theory similar to that given by Sroubek *et al.*[1] is applied to obtain a quantitative evaluation of the observed g shifts. Using a point-charge model for the crystalline field, an order of magnitude agreement is found in most cases with the experimental values. It is shown that this agreement can be improved in all cases by considering the covalent correction to the point-charge model suggested by Sroubek *et al.*[1] and also by taking into account the shielding of the crystalline electric field.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The angular dependence of the stress induced g shifts for the Γ_7 levels of Yb^{3+} and Dy^{3+} in CaF_2 and Er^{3+} in CeO_2 and ThO_2 have been measured using the uniaxial-stress electron-paramagnetic-resonance technique.[4] The data were taken at 32 GHz for Yb^{3+} and Er^{3+} and at 9.2 GHz for Dy^{3+} with EPR systems which allow for uniaxial stress to be applied on the sample[4,5] at 4.2 °K for Er^{3+} and Dy^{3+} and at 55 °K for Yb^{3+}.

The samples were polished to a prismatic shape, where the orientation of the prism, a [110] direction, is accurately defined by the intersection of two (111) natural cleavage faces of the sample. The stress was applied along this [110] direction within an estimated error smaller than 1°. The CaF_2 crystals were supplied by Optovac Inc.; the CeO_2 crystal, kindly provided by Dr. M. Abraham, was grown by C. B. Finch at the Oak Ridge National Laboratory and the ThO_2 crystal was provided by Dr. J. Trench.

The EPR spectra of a Γ_7 doublet in a cubic crystal is described by the spin Hamiltonian

$$\mathcal{H} = g\mu_B \vec{H}\cdot\vec{S}, \tag{1}$$

where g is the isotropic gyromagnetic factor, μ_B the Bohr magneton, H is the external magnetic field and $S=\frac{1}{2}$ is the effective spin.

Hyperfine contributions have been omitted in Eq. (1) since, being at present interested in the stress-induced g shifts, we consider only the isotopes with $I=0$. Our measurements give values of the g factors in all the cases considered in agree-

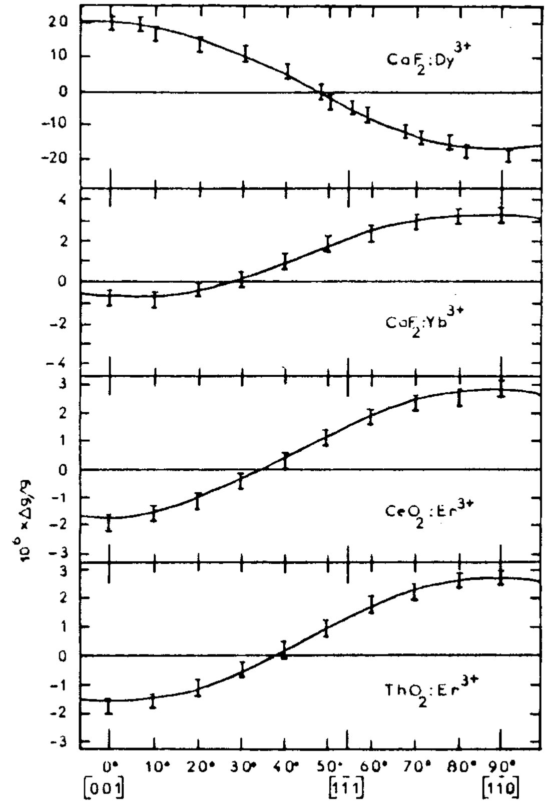

FIG. 1. Angular dependence of the g shift of Dy^{3+} and Yb^{3+} in CaF$_2$ and Er^{3+} in CeO$_2$ and ThO$_2$ under a stress P along the [110] direction.

ment with published data.[6-8]

The stress-induced g shifts $\Delta g = g(P) - g(0)$ were obtained from the measured change in resonant field of the EPR line as a function of the applied stress, for different orientations of the external magnetic field; in all the cases considered it was observed that Δg depends linearly on the applied stress. The angular dependence of $\Delta g/g$ in the (110) plane, perpendicular to the direction of the applied stress P, was measured in the four systems for P up to 600 kg/cm^2; the experimental data normalized to a value of $P = -1$ kg/cm^2 (compression) are given in Fig. 1 where the solid line gives the best fit of the data with the equation

$$\Delta g/g = A \sin^2\theta + B, \tag{2}$$

where θ is the angle between magnetic field H and the [001] direction in the (110) plane.

III. THEORY

A. Phenomenological theory

When the load is applied along the [110] direction of the crystal, three nonzero components of the strain tensor are allowed by the symmetry of the crystal.[9] They correspond to hydrostatic ϵ_{1g}, tetragonal $\epsilon_{3g,\theta}$, and trigonal $\epsilon_{5g,\zeta}$, deformations which can be expressed in terms of the strain tensor components by[9]

$$\begin{aligned}
\epsilon_{1g} &= \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}, \\
\epsilon_{3g,\theta} &= \tfrac{1}{4}(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}), \\
\epsilon_{5g,\zeta} &= \epsilon_{xy}.
\end{aligned}$$

In the spin-Hamiltonian formalism the perturbation to the Hamiltonian of Eq. (1) introduced by the deformation of the lattice is given by

$$\begin{aligned}
\mathcal{H}' = \mu_B H\{ & g_{1g}[S_z\cos\theta + \tfrac{1}{2}(S_+e^{-i\varphi} + S_-e^{i\varphi})\sin\theta]\epsilon_{1g} \\
& + g_{3g}[S_z\cos\theta - \tfrac{1}{4}(S_+e^{-i\varphi} + S_-e^{i\varphi})\sin\theta]\epsilon_{3g,\theta} \\
& + g_{5g}(S_+e^{i\varphi} - S_-e^{-i\varphi})\sin\theta\,\epsilon_{5g,\zeta}\}.
\end{aligned} \tag{3}$$

θ and φ are the polar angles of the orientation of the magnetic field; when $\vec{H}$ lies in the (110) plane, $\varphi = 135°$ and θ is the angle between $\vec{H}$ and the [001] crystal direction.

A straightforward calculation in this plane yields

$$\begin{aligned}
\Delta g/g = (-1/g)[& (g_{5g}\epsilon_{5g,\zeta} + \tfrac{3}{2}g_{3g}\epsilon_{3g,\theta})\sin^2\theta \\
& - (g_{1g}\epsilon_{1g} + g_{3g}\epsilon_{3g,\theta})],
\end{aligned} \tag{4}$$

where quadratic terms in the deformations have been neglected.

Equation (4) predicts the observed angular dependence of Eq. (2) and gives the values of A and B as a function of g_{1g}, g_{3g}, and g_{5g}.

B. Microscopic theory

The Hamiltonian which describes the behavior of the ground multiplet for rare-earth paramagnetic ions in a distorted cubic lattice is given by $\mathcal{H} = \mathcal{H}_{cf} + \mathcal{H}_Z + \mathcal{H}_{01}$ where $\mathcal{H}_{cf}$, $\mathcal{H}_Z$, and $\mathcal{H}_{01}$ are the cubic field, the Zeeman, and the orbit-lattice interactions, respectively.

$\mathcal{H}_{01}$ is given by[9]

$$\mathcal{H}_{01} = \sum_{n,i,\alpha,\xi} G_i^{(n,\xi)} O_{i,\alpha}^{(n,\xi)} \epsilon_{i,\alpha},$$

where the $O_{i,\alpha}^{(n,\xi)}$ are linear combinations of the nth-order Stevens operators O_n^m.[10] They transform as the α component of the Γ_i irreducible representation of O_h. G_i are the corresponding orbit-lattice coefficients and ξ stands for the cases where more than one Stevens operator transforms as Γ_i. When the stress is applied along the [110] direction and the z axis is taken as the [001] crystal direction, $\mathcal{H}_{01}$ can be written[9]

$$\begin{aligned}
\mathcal{H}_{01} = {} & [G_{1g}^{(4)}(O_4^0 + 5O_4^4) + G_{1g}^{(6)}(O_6^0 - 21O_6^4)]\epsilon_{1g} \\
& + [G_{3g}^{(2)}O_2^0 + G_{3g}^{(4)}(O_4^0 - 7O_4^4) + G_{3g}^{(6)}(O_6^0 + 3O_6^4)]\epsilon_{3g,\theta} \\
& + [G_{5g}^{(2)}O_2^2(s) + G_{5g}^{(4)}O_4^2(s) + G_{5g}^{(6,a)}O_6^2(s) \\
& + G_{5g}^{(6,b)}O_6^6(s)]\epsilon_{5g,\zeta}.
\end{aligned} \tag{5}$$

Here

$$\epsilon_{1g} = (s_{11} + 2s_{12})P, \quad \epsilon_{3g,\theta} = -\tfrac{1}{3}P(s_{11} - s_{12}) ,$$

and

$$\epsilon_{5g,\zeta} = \tfrac{1}{2}Ps_{44}$$

are the hydrostatic, tetragonal, and trigonal components of the applied deformation; P is the applied stress; and s_{11}, s_{12}, and s_{44} are the elastic constants for cubic symmetry.

The hydrostatic term in H_{01} gives no contribution inside the J ground multiplet, when only one Γ_7 doublet is present. An estimation of its effect on the g shifts taking into account the excited J multiplets leads to a negligible contribution, and was neglected in our calculations.

The change Δg of the gyromagnetic factor is produced by a second-order perturbation process involving the orbit-lattice and Zeeman interactions. These second order g shifts for a Kramers doublet are given by

$$\frac{\Delta g}{g} = \frac{1}{\langle\Gamma_7, \alpha|\mathcal{H}_Z|\Gamma_7, \alpha\rangle} \sum_{i,s} \frac{1}{E_{\Gamma_7} - E_{\Gamma_8^{(i)}}} \times \mathrm{Re}\,[\langle\Gamma_7, \alpha|\mathcal{H}_{01}|\Gamma_{8,s}^{(i)}\rangle\langle\Gamma_{8,s}^{(i)}|\mathcal{H}_Z|\Gamma_7, \alpha\rangle - \langle\Gamma_7, \beta|\mathcal{H}_{01}|\Gamma_{8,s}^{(i)}\rangle\langle\Gamma_{8,s}^{(i)}|\mathcal{H}_Z|\Gamma_7, \beta\rangle], \tag{6}$$

where $\langle\Gamma_7, \alpha|$ and $\langle\Gamma_7, \beta|$ are the wave functions of the doublet which diagonalize the Zeeman interactions, $\langle\Gamma_{8,s}^{(i)}|$ are the wave functions of the Γ_8 quartet, where $s = \kappa, \lambda, \mu, \nu$; i stands for the case in which more than one quartet is present. $E_{\Gamma_7} - E_{\Gamma_8^{(i)}}$ is the energy difference between Γ_7 doublet and the Γ_8 quartets.

Using Eqs. (5) and (6), and symmetry properties, it is found

$$\frac{\Delta g}{g} = \frac{1}{\langle\Gamma_7, a|J_Z|\Gamma_7, a\rangle} \sum_{i,n,l} \frac{1}{E_{\Gamma_7} - E_{\Gamma_8}^{(i)}} \{[-3\langle\Gamma_8^{(i)}\nu|J_Z|\Gamma_7, a\rangle\langle\Gamma_7, a|O_{3g,\theta}^{(n,l)}|\Gamma_8^{(i)}\nu\rangle G_{3g}^{(n,l)}\epsilon_{3g,\theta} + i\langle\Gamma_8^{(i)}\mu|J_+|\Gamma_7, a\rangle\langle\Gamma_7, a|O_{5g,\zeta}^{(n,l)}|\Gamma_8^{(i)}\lambda\rangle G_{5g}^{(n,l)}\epsilon_{5g,\zeta}]\sin^2\theta + 2[\langle\Gamma_8^{(i)}\nu|J_Z|\Gamma_7, a\rangle\langle\Gamma_7, a|O_{3g,\theta}^{(n,l)}|\Gamma_8^{(i)}\nu\rangle G_{3g,\theta}^{(n,l)}\epsilon_{3g,\theta}]\}, \tag{7}$$

where $|\Gamma_7, a\rangle$ and $|\Gamma_7, b\rangle$ are the cubic-field wave functions for the doublet.

Comparing Eqs. (7) and (2) we obtain

$$B = \frac{-(s_{11} - s_{12})P}{2\langle\Gamma_7, a|J_Z|\Gamma_7, a\rangle} \sum_{i,n,l} \frac{G_{3g}^{(n,l)}}{E_{\Gamma_7} - E_{\Gamma_8^{(i)}}} \langle\Gamma_8^{(i)}\nu|J_Z|\Gamma_7, a\rangle\langle\Gamma_7, a|O_{3g,\theta}^{(n,l)}|\Gamma_8^{(i)}\nu\rangle , \tag{8a}$$

$$\tfrac{2}{3}A + B = \frac{is_{44}P}{3\langle\Gamma_7, a|J_Z|\Gamma_7, a\rangle} \sum_{i,n,l} \frac{G_{5g}^{(n,l)}}{E_{\Gamma_7} - E_{\Gamma_8^{(i)}}} \langle\Gamma_8^{(i)}\mu|J_+|\Gamma_7, a\rangle\langle\Gamma_7, a|O_{5g,\zeta}^{(n,l)}|\Gamma_8^{(i)}\lambda\rangle . \tag{8b}$$

The values of the orbit-lattice coefficients $G_i^{(n,l)}$ defined in Eq. (5) have to be obtained in order to evaluate Eqs. (8a) and (8b) for the different systems. Using the point-charge model of Sroubek *et al.*[1] we obtain for these coefficients the following expressions:

$$\begin{aligned}
G_{3g}^{(2)} &= -\tfrac{16}{3}\alpha_J e^2 e_{\mathrm{eff}} \frac{\langle r^2\rangle}{R^3} f_{3g}^{(2)}, & f_{3g}^{(2)} &= 0.787;\\
G_{3g}^{(4)} &= \tfrac{20}{27}\beta_J e^2 e_{\mathrm{eff}} \frac{\langle r^4\rangle}{R^5} f_{3g}^{(4)}, & f_{3g}^{(4)} &= 1.443;\\
G_{3g}^{(6)} &= \tfrac{7}{9}\gamma_J e^2 e_{\mathrm{eff}} \frac{\langle r^6\rangle}{R^7} f_{3g}^{(6)}, & f_{3g}^{(6)} &= 0.833;\\
G_{5g}^{(2)} &= \tfrac{16}{3}\alpha_J e^2 e_{\mathrm{eff}} \frac{\langle r^2\rangle}{R^3} f_{5g}^{(2)}, & f_{5g}^{(2)} &= 0.787;\\
G_{5g}^{(4)} &= \tfrac{100}{9}\beta_J e^2 e_{\mathrm{eff}} \frac{\langle r^4\rangle}{R^5} f_{5g}^{(4)}, & f_{5g}^{(4)} &= 1.189;\\
G_{5g}^{(6,a)} &= -\tfrac{35}{9}\gamma_J e_{\mathrm{eff}} \frac{\langle r^6\rangle}{R^7} f_{5g}^{(6,a)}, & f_{5g}^{(6,a)} &= 1.088;\\
G_{5g}^{(6,b)} &= -\tfrac{77}{27}\gamma_J e^2 e_{\mathrm{eff}} \frac{\langle r^6\rangle}{R^7} f_{5g}^{(6,b)}, & f_{5g}^{(6,b)} &= 0.531;
\end{aligned} \tag{9}$$

the factors $f_i^{(n,l)}$ take into account the sum over four spheres of ligands; $f_i^{(n,l)} = 1$ if only nearest neighbors are considered. The α_J, β_J, and γ_J are the Stevens multiplicative factors for rare-earth ions; e_{eff} is the effective charge of the ligands in units of the electronic charge. The values $\langle r^n\rangle$ are given by Freeman and Watson.[11] R is the paramagnetic ion-ligand distance.

Numerical values of B and $\tfrac{2}{3}A + B$ can be obtained from Eqs. (8a), (8b), and (9) and from data on the cubic-field splittings. For each of the studied systems we obtain the material that follows.

1. $CaF_2 : Yb^{3+}$ and $ThO_2 : Yb^{3+}$

Yb^{3+} is a $4f^{13}\,{}^2F_{7/2}$ ion; its wave functions in a cubic crystalline field are given by Lea, Leask, and Wolf[12] (LLW). From Eqs. (8a) and (8b) we obtain, for $Yb^{3+} : CaF_2$,

$$B = (-0.2108\, G_{3g}^{(2)} + 25.30\, G_{3g}^{(4)} + 354.2\, G_{3g}^{(6)}) \times 10^8,$$

$$\tfrac{2}{3}A + B = (-1.290\, G_{5g}^{(2)} - 4.838\, G_{5g}^{(4)}$$

$$+33.87\, G_{5g}^{(6,a)} + 101.6\, G_{5g}^{(6,b)}) \times 10^{8}. \qquad (10)$$

A value $E_{\Gamma_7} - E_{\Gamma_8} = 604\ \mathrm{cm}^{-1}$ for this case, reported by Baker *et al.*[13] was used to evaluate Eq. (10).

For $ThO_2: Yb^{3+}$ using $E_{\Gamma_7} - E_{\Gamma_8} = 630\ \mathrm{cm}^{-1}$, we obtain[1]

$$B = (-0.0903\, G_{3g}^{(2)} + 10.84\, G_{3g}^{(4)} + 151.8\, G_{3g}^{(6)}) \times 10^{8},$$

$$\tfrac{2}{3} A + B = (-0.5241\, G_{5g}^{(2)} - 1.965\, G_{5g}^{(4)} + 13.76\, G_{5g}^{(6,a)} + 41.27\, G_{5g}^{(6,b)}) \times 10^{8}. \qquad (11)$$

2. $CaF_2 : Dy^{3+}$

Dy^{3+} is a $4f^{9}\ {}^{6}H_{15/2}$ ion; its degeneracy breaks down in a cubic crystalline field into three Γ_8 quartets and two doublets Γ_6 and Γ_7.

For the energy differences between the Γ_7 doublet and the Γ_8 quartets we used the values[6,14]

$$E_{\Gamma_7} - E_{\Gamma_8^{(1)}} = 7.35\ \mathrm{cm}^{-1},$$

$$E_{\Gamma_7} - E_{\Gamma_8^{(2)}} = -66.0\ \mathrm{cm}^{-1},$$

$$E_{\Gamma_7} - E_{\Gamma_8^{(3)}} = -553\ \mathrm{cm}^{-1}.$$

Again, the cubic-field wave functions of Dy^{3+} in CaF_2 were taken from LLW[12] for $x = 0.6$. We obtain

$$B = (-33.87\, G_{3g}^{(2)} + 18970\, G_{3g}^{(4)} + 356800\, G_{3g}^{(6)}) \times 10^{8},$$

$$\tfrac{2}{3} A + B = (175.0\, G_{5g}^{(2)} - 15715\, G_{5g}^{(4)} - 232600\, G_{5g}^{(6,a)} - 317700\, G_{5g}^{(6,b)}) \times 10^{8}. \qquad (12)$$

These values differ slightly from those previously reported by us where less accurate data on the cubic-field splittings were used.[3]

3. $CeO_2 : Er^{3+}$ and $ThO_2 : Er^{3+}$

Neither the cubic-field splittings of $CeO_2: Er^{3+}$ nor the elastic constants for CeO_2 are known well enough so it was necessary to estimate those parameters.

A value $x = -0.4$, suggested from data on Er^{3+} in other cubic crystals[7] was used to obtain the corresponding wave functions. Measurements of a T_1 Orbach process[15] for Er^{3+} in CeO_2 gave the value $E_7 - E_8^{(1)} = -93\ \mathrm{cm}^{-1}$, which with $x = -0, 4$ gives $E_{\Gamma_7} - E_{\Gamma_8^{(2)}} = -710\ \mathrm{cm}^{-1}$ and $E_{\Gamma_7} - E_{\Gamma_8^{(3)}} = -770\ \mathrm{cm}^{-1}$. Using these values together with Eqs. (8a) and (8b) we obtain

$$B = (-3.22\, G_{3g}^{(2)} + 668.4\, G_{3g}^{(4)} + 29\,200\, G_{3g}^{(6)}) \times 10^{8};$$

$$\tfrac{2}{3} A + B = (-10.93\, G_{5g}^{(2)} + 333.9\, G_{5g}^{(4)} - 38\,410\, G_{5g}^{(6,a)} - 3450\, G_{5g}^{(6,b)}) \times 10^{8}. \qquad (13)$$

For the elastic constants of CeO_2, values were taken as equal to those measured for the isomorphous ThO_2 crystal.[16] For Er^{3+} in ThO_2 the energy difference between the Γ_7 doublet and the Γ_8 quartet gives the value $E_{\Gamma_7} - E_{\Gamma_8^{(1)}} = -60\ \mathrm{cm}^{-1}$,[17] which with $x = -0.4$ gives $E_{\Gamma_7} - E_{\Gamma_8^{(2)}} = -460\ \mathrm{cm}^{-1}$ and $E_{\Gamma_7} - E_{\Gamma_8^{(3)}} = -500\ \mathrm{cm}^{-1}$.

Using the values together with Eqs. (8a) and (8b) we obtain

$$B = (-4.99\, G_{3g}^{(2)} + 1036.0\, G_{3g}^{(4)} + 45\,260\, G_{3g}^{(6)}) \times 10^{8},$$

$$\tfrac{2}{3} A + B = (-16.93\, G_{5g}^{(2)} + 517.6\, G_{5g}^{(4)} - 59\,535\, G_{5g}^{(6,a)} - 5347\, G_{5g}^{(6,b)}) \times 10^{8}. \qquad (14)$$

IV. DISCUSSION

Our experimental values $\frac{2}{3}A + B$ for $CaF_2: Yb^{3+}$, $CeO_2: Er^{3+}$, $ThO_2: Er^{3+}$, and $CaF_2: Dy^{3+}$ together with the ones reported by Sroubeck *et al.* for $ThO_2: Yb^{3+}$ are given in Table I.

The contributions of the second-, fourth-, and sixth-order crystalline-field terms obtained from Eqs. (10)–(14) with $e_{\mathrm{eff}} = -1$ for CaF_2 and $e_{\mathrm{eff}} = -2$ for ThO_2 and CeO_2 are also shown in the table.

An order-of-magnitude agreement of the experimental data with the prediction of the point-charge model is obtained in all cases, except for $\frac{2}{3}A + B$ of Dy^{3+} in CaF_2.

In this point-charge model we have neglected the contributions of the shielding of the crystalline field, which are important for second-order terms that are reduced by a factor of $\frac{1}{2}$.[18] Covalent contributions as discussed by Bleaney[19] and Sroubek *et al.*[1] can produce an enhancement of the fourth- and sixth-order terms; in order to improve the agreement between the experimental and the calculated values of $\frac{2}{3}A + B$ and B on Table I, both effects should be considered.

The importance of shielding effects is evident

TABLE I. Experimental and calculated values for $\frac{2}{3}A + B$ and B.

	Experimental $10^6\,(\frac{2}{3}A + B)$	Calculated $10^6\,(\frac{2}{3}A + B)$	Experimental $10^6 B$	Calculated $10^6 B$
$CaF_2:Yb^{3+}$	2.10 ± 0.12	$5.15 - 0.26 + 0.01 + 0.01 = 4.91$	-0.60 ± 0.06	$-0.84 + 0.11 - 0.01 = -0.74$
$ThO_2:Yb^{3+}$	1.80[a]	$3.85 - 0.18 + 0.005 + 0.005 = 3.68$	-0.32 ± 0.09[a]	$-0.66 + 0.08 - 0.01 = -0.59$
$CeO_2:Er^{3+}$	1.29 ± 0.10	$7.74 - 1.12 - 0.35 - 0.01 = 6.26$	-1.68 ± 0.05	$-2.28 - 0.18 - 0.04 = -2.50$
$ThO_2:Er^{3+}$	1.27 ± 0.10	$10.8 - 1.46 - 0.42 - 0.02 = 8.90$	-1.80 ± 0.05	$-3.17 - 0.23 - 0.05 = -3.45$
$CaF_2:Dy^{3+}$	-4.8 ± 0.6	$165.4 - 39.9 - 0.6 - 0.3 = 124.6$	20.1 ± 0.3	$32.0 + 3.9 - 0.1 = 35.8$

[a] Reference 1.

when second-order contributions dominate. An overestimation of $\frac{2}{7}A+B$ and B is obtained with the point-charge model. This happens for all the cases except for $\frac{2}{7}A+B$ of $CaF_2:Dy^{3+}$ where covalent effects can be important because fourth order contribution are relatively large. As a final remark it should be noted that by applying an homogeneous uniaxial stress, the induced deformations are completely specified by the symmetric strain (ϵ_{ij}) tensor, with components transforming as basis for the Γ_{1g}, Γ_{3g}, Γ_{5g} reps of the cubic group O_h. Therefore, the discrepancies between the experiments and the theoretical results cannot be explained by assuming that some effects of cluster rotation of Γ_{4g} symmetry[20,21] were also present in $\mathcal{H}'$.

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