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COMMENTS AND ADDENDA

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Recalculation of the electric-field-induced g shifts for tetragonal Ce^{3+} sites in CaF_2

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We have reviewed our calculation of the electric-field-induced g-shift parameters for tetragonal Ce^{3+} sites in CaF_2 presented in an earlier paper, making use of recent spectroscopic data which were not previously available. Of the three parameters corresponding to the C_{4v} point symmetry of the site, two now agree very well with the experimental data, but one remains widely in error. This discrepancy could indicate that the first-excited doublet is closer to the ground state than it is assumed to be in the present calculation.

The C_{4v} tetragonal F^--compensated Ce^{3+} center in CaF_2 constitutes one of the simplest systems in which the linear electric-field effect (LEFE) in EPR can be studied. The odd crystal field is primarily due to the F^- ion situated along the [001] cubic axis (entirely so if distortions of the lattice are ignored). In an earlier study we measured the g-shift parameters for this center and attempted to calculate theoretical values from first principles.[1] It was, however, necessary to make certain *ad hoc* assumptions regarding the energy-level structure of the Ce^{3+} ion in CaF_2. Since this level structure has now been determined by optical methods[2] (see Fig. 1) we have revised our calculation. At the same time we have corrected some errors present in the original.

For CaF_2 the bulk dielectric constant $\epsilon = 7.36$ and the classical Lorentz field $\frac{1}{3}(\epsilon+2)\,E_{\text{app}} = 3.12\,E_{\text{app}}$, where $E_{\text{app}} = V_{\text{app}}/d$ is the field generated by a voltage V_{app} applied to parallel-plate electrodes a distance d apart. The corresponding Lorentz-field potential is given by

$$\delta V_{\text{Lor}} = 2.21\, rE_x[C_1^1(\theta,\varphi) - C_1^{-1}(\theta,\varphi)] - 3.12\, rE_z\, C_1^0(\theta,\varphi), \qquad (1)$$

where the $C_k^q(\theta,\varphi)$ are the spherical harmonics as defined in Edmonds,[3] and E_x, E_z are components of the applied field. The z axis will subsequently be taken as the C_{4v} axis, i.e., the axis along which lies the charge-compensating F^- interstitial ion. It is unnecessary to consider applied fields along the y axis since the LEFE parameter is the same for E_y as for E_x.

The change in the crystal-field potential seen by the Ce^{3+} ion when an electric field is applied is due not only to the bulk polarization of the lattice considered in Eq. (1), but also to the polarization, ionic and electronic, of the charge-compensating F^- ion. Assuming that the relative displacements of the F^- and Ce^{3+} ions are the same as those of F^- and Ca^{2+} ions in the ideal CaF_2 lattice, we can infer the ionic polarization from the low-frequency and optical dielectric constants of CaF_2, thus obtaining the induced moment[4]

$$p_{\text{ion}} = 6.4\times10^{-24} E_{\text{app}}\,\text{cm}^{-3}.$$

The electronic polarization can be estimated from tables given by Tessman, Kahn, and Shockley.[5] Allowing for the fact that the Lorentz field is taken to be the field seen by the ions listed in these tables [i.e., reintroducing the factor $\frac{1}{3}(\epsilon+2)$], we obtain the value $p_{\mathrm{el}} = 2.0\times 10^{-24} E_{\mathrm{app}}\ \mathrm{cm}^{-3}$ for the induced electronic moment of the F^- ion. Summing both moments we have

$$p_{\mathrm{tot}} = p_{\mathrm{ion}} + p_{\mathrm{el}} = 8.4\times 10^{-24} E_{\mathrm{app}}\ \mathrm{cm}^{-3}.$$

A calculation analogous to the familiar point-charge calculation can now be used to find the crystal-field potentials due to the induced dipole p_{tot}. We assume here that the F^- interstitial and the Ce^{3+} ion are located at a distance of 2.73 Å from each other at the centers of cubes formed by the F^- lattice ions. The resulting potentials added to the Lorentz-field potential[1] yield the amplitudes

$$\begin{aligned} &a_1^0 = 1.59\times 10^{-4} E_z, \quad a_1^{\pm 1} = \pm 0.78\times 10^{-4} E_x,\\ &a_2^0 = 1.24\times 10^{-5} E_z, \quad a_2^{\pm 1} = \pm 0.50\times 10^{-5} E_x, \end{aligned} \tag{2}$$

where the crystal field is written in the form $\delta V = \sum_{k,q} a_k^q C_k^q(\theta,\varphi)$. E_x, E_z are in V/cm, and the a_k^q include radial integrals and are expressed in cm^{-1} spectroscopic units. It is sufficient for the present purposes to restrict consideration to the lowest-order odd and even harmonics in the induced crystal field.

The odd components $a_1^q(\theta,\varphi)\, C_1^q(\theta,\varphi)$ contribute to the LEFE by mixing the $4f$ manifold of Ce^{3+} with other manifolds of opposite parity. The resulting higher-order perturbations are treated by finding an "equivalent even field" δV_{EEF} which, once derived, can be used in the same way as the even components $a_2^q\, C_2^q(\theta,\varphi)$ in calculations involving only the ground manifold of states.[6] The crystal-field parameters for this equivalent even field are given by

$$a_\kappa^\rho(E) = -\frac{2}{\bar{E}_{ug}} \sum_{K,Q} (-1)^\rho A_K^Q a_k^q \begin{pmatrix} K & k & \kappa \\ Q & q & -\rho \end{pmatrix} \eta_{\mathrm{EEF}}, \tag{3}$$

where $\bar{E}_{ug}$ is the mean separation between the ground state and the opposite-parity manifold, the A_K^Q are parameters belonging to the odd portion of the normal crystal field (i.e., the crystal field which is present before the electric field is applied), η_{EEF} is a numerical factor of the order of unity, and the term adjacent to this is the Wigner $3j$ symbol. For the present purpose we consider mixing between the $4f$ manifold and the $5d$ manifold only (Fig. 1). We shall also take only the first term in the odd field due to the F^- ion. This requires an estimate for the amplitude A_1^0 in the normal crystal field. A point-charge calculation gives the value $A_1^0 = 7790\ \mathrm{cm}^{-1}$. The remaining parameters are $\bar{E}_{ug} = 43\,340\ \mathrm{cm}^{-1}$ and $\eta_{\mathrm{EEF}} = 1.17$ and yield the equivalent-even-field parameters

$$\begin{aligned} &a_2^0(E) = -2.4\times 10^{-5} E_z,\\ &a_2^{\pm 1}(E) = \pm 1.0\times 10^{-5} E_x, \end{aligned} \tag{4}$$

the units being the same as in Eq. (2).

It can be seen from (2) and (4) that the induced even field and the equivalent even field are roughly comparable. Adding them together we obtain

$$\begin{aligned} &\bar{a}_2^0 = -1.20\times 10^{-5} E_z,\\ &\bar{a}_2^{\pm 1} = \pm 1.5\times 10^{-5} E_x, \end{aligned} \tag{5}$$

for the total even-field potentials. These amplitudes can now be used to estimate the g-shift parameters T_{zxx}, T_{zzz}, and T_{xzx}, which occur in the LEFE spin Hamiltonian $\mathcal{H}_{\mathrm{elec}} = \mu_B E_{ijk} E_i H_j S_k$. It can be shown by perturbation theory that

$$\begin{aligned} T_{zxx} &= 4g_J \sum_i \frac{1}{E_i} \mathrm{Re}(\langle\psi^+|J_x|\psi_i\rangle\langle\psi_i|\delta V_z|\psi^-\rangle),\\ T_{zzz} &= 4g_J \sum_i \frac{1}{E_i} \mathrm{Re}(\langle\psi^+|J_z|\psi_i\rangle\langle\psi_i|\delta V_z|\psi^+\rangle),\\ T_{xxz} &= 4g_J \sum_i \frac{1}{E_i} \mathrm{Re}(\langle\psi^+|J_x|\psi_i\rangle\langle\psi_i|\delta V_x|\psi^+\rangle),\\ T_{xzx} &= 4g_J \sum_i \frac{1}{E_i} \mathrm{Re}(\langle\psi^+|J_z|\psi_i\rangle\langle\psi_i|\delta V_x|\psi^-\rangle), \end{aligned} \tag{6}$$

where $\delta V_z = \bar{a}_2^0\, C_2^0(\theta,\varphi)$, $\delta V_x = \bar{a}_2^1\, C_2^1(\theta,\varphi) + \bar{a}_2^{-1} C_2^{-1}(\theta,\varphi)$,

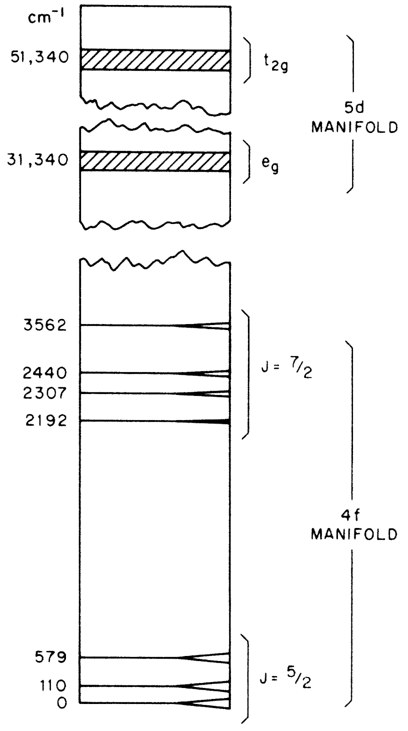

FIG. 1. Levels of the tetragonal Ce^{3+} center in CaF_2 derived from spectroscopic data (Ref. 2). The mean value $\bar{E}_{ug}$ of the interval between the ground state and the $5d$ manifold is $43\,340\ \mathrm{cm}^{-1}$.

TABLE I. g values and the parameters B_{ij} for Ce^{3+} in tetragonal sites in CaF_2. The B_{ij} denote shifts in g^2 as defined in Ref. 7. They are given in units of 10^{-9} (V/cm)$^{-1}$. The calculated values are based on the assumption that the ground doublet has the form $0.912\,|\frac{5}{2},\ \pm\frac{5}{2}\rangle + 0.410\,|\frac{5}{2},\ \pm\frac{3}{2}\rangle$. The state-mixing parameters are obtained by making a best fit to the experimental g values.

	$g_\parallel$	$g_\perp$	B_{33}	B_{31}	B_{15}
Expt	3.038	1.396	68	−16	5.5
	±0.003	±0.002	±10	±3	±1
Calc	3.13	1.43	83	−19	55

$g_J = \frac{6}{7}$ is the Landé g for the lowest $J=\frac{5}{2}$ manifold of Ce^{3+} states, $\psi^{\pm}$ are the states of the ground doublet, ψ_i are the remaining $J=\frac{5}{2}$ states, and E_i are the energy separations. (State mixing between the $J=\frac{5}{2}$ and $J=\frac{7}{2}$ manifolds can also occur, of course, and will result in small modifications to the values calculated above.) The three $J=\frac{5}{2}$ doublets can be expanded in the form

$$\begin{aligned} \psi^{\pm} &= a\left|\tfrac{5}{2},\ \pm\tfrac{5}{2}\right\rangle + b\left|\tfrac{5}{2},\ \pm\tfrac{3}{2}\right\rangle && \text{(ground state)}, \\ \psi_2^{\pm} &= \left|\tfrac{5}{2},\ \pm\tfrac{1}{2}\right\rangle && (E_2 = 110\ \mathrm{cm}^{-1}), \\ \psi_3^{\pm} &= a\left|\tfrac{5}{2},\ \pm\tfrac{5}{2}\right\rangle - b\left|\tfrac{5}{2},\ \pm\tfrac{3}{2}\right\rangle && (E_3 = 579\ \mathrm{cm}^{-1}), \end{aligned} \tag{7}$$

where the values $a=0.912$, $b=0.410$ give a best fit to the experimental ground-state g values. Substituting in Eqs. (7) we thus obtain the results $T_{zxx} = -6.8\times10^{-9}$ (V/cm)$^{-1}$, $T_{zzz} = 13.6\times10^{-9}$ (V/cm)$^{-1}$, $T_{xxz} = -1.4\times10^{-9}$ (V/cm)$^{-1}$, $T_{xzx} = 42.4\times10^{-9}$ (V/cm)$^{-1}$. It will be noticed that $T_{xxz} \neq T_{xzx}$. This is a consequence of the representation chosen in Eqs. (7), i.e., a representation in terms of magnetic eigenstates quantized with respect to the C_{4v} axis. This representation is not in any way unique but merely happens to be the most convenient one to use here. (It also yields a symmetric g matrix. A representation giving the result $T_{xxz} = T_{xzx}$ would do so at the price of rendering the g matrix asymmetric.)

Experimental measurements of the electric-field-induced frequency shifts do not lead directly to the g-shift parameters T_{ijk} but give shifts in a matrix A_{ij} which describe[7] the quantity g^2. Since it is not possible to separate out T_{xxz} and T_{xzx} from these measurements, we shall make the comparison between theory and experiment in terms of the g^2-shift parameters B_{ij}. In the case of C_{4v} point symmetry there are three such parameters related to the g-shift parameters by the equations[8]

$$\begin{aligned} &B_{31} = 2g_\perp T_{zxx}, \quad B_{33} = 2g_\parallel T_{zzz}, \\ &B_{15} = g_\perp T_{xzx} + g_\parallel T_{xxz}. \end{aligned} \tag{8}$$

From the T_{ijk} calculated above and from the experimental g values we obtain the B_{ij} shown in Table I.

Comparison of the theoretical and experimental values in Table I indicates that two parameters agree surprisingly well but the third is wrong by a factor of 10. There are, of course, many places in the calculation where approximations have been made which could lead to discrepancies. Taking the difference between the ionic radii[9] of Ce^{3+} and Ca^{2+} into account, one might, for instance, reduce the estimate for the relative displacement of the F^- interstitial and the Ce^{3+} ion, making it somewhat less than the relative displacement of Ca^{2+} and F^- ions inferred from the dielectric constant. The force on Ce^{3+} due to the electric field is, on the other hand, larger than the force on Ca^{2+}. If these two effects are allowed for by postulating a net $\alpha:1$ increase in the relative displacement there will be an $\alpha:1$ increase in p_{ion} and, since p_{el} is small, an increase $\simeq \alpha:1$ in p_{tot} also. The crystal-field parameters a_2^q will be increased by the same factor, but the effect on the a_1^q would be several times smaller since these parameters are largely determined by the long-range Lorentz field. The total even-field perturbations in Eqs. (5) will approximately be changed to $\overline{a}_2^0 = -(2.4 - 1.2\,\alpha)\times10^{-5}E_z$ and $\overline{a}_2^{\pm1} = \pm(0.5 + 1.0\,\alpha)\times10^{-5}E_x$. The final values for B_{31}, B_{33} are then proportional to $\overline{a}_2^0$, and the final value for B_{15} is proportional to $\overline{a}_2^{\pm1}$. Clearly, however, there is no reasonable choice of α which would give a significantly better fit to the results.

Other assumptions which might be reviewed concern the exclusion of the A_3^0 harmonic in the odd field and of the harmonics a_3^q in the induced field from the calculation of the equivalent-even-field amplitudes $a_2^q(E)$. Estimates show that the contributions due to these harmonics are an order of magnitude smaller than the main contribution considered here, partly because the amplitudes vary as a higher power of the radial distance and partly because the long-range Lorentz field no longer enters. Consideration of mixing between the $J=\frac{5}{2}$ and $J=\frac{7}{2}$ manifolds is also unlikely to affect the result significantly, at least not in comparison with possible errors in the *ad hoc* assumptions which are made in estimating the crystal fields. The question remains, therefore, as to the primary origin of the large discrepancy between the theoretical and experimental values for B_{15}.

It is conceivable here that the error may arise from the use of the point-charge model without corrections for screening, and without any attempt to introduce covalency effects. The relevant corrections can be considerable as shown by Burns,[10] and it is perhaps surprising in view of this that such good agreement is obtained for two of the three coefficients. An alternative possibility is that there is an appreciable error in the value assumed for the energy of the first excited state. According to Ref. 2 this level was not observed directly in fluorescence, as was the 579-cm^{-1} level, but was inferred via calculations involving the other $4f$ levels, the only direct experimental evidence being that it must lie above 50 cm^{-1}. The coefficients B_{31}, B_{33} are not affected by the position of this level but B_{15} depends strongly on it. A value of 65 cm^{-1} would bring about agreement between our calculated and experimental values. It would of course be unreasonable to attribute the entire discrepancy to this one cause,[11] in view of the weaknesses inherent in the crystal-field model that we have used, but there is at least some independent evidence supporting our calculated conclusion that the B_{15} parameter is exceptionally sensitive to changes in the lattice constant such as might be expected to alter the level spacings. For the corresponding tetragonal Ce^{3+} site in BaF_2, B_{15} is $\simeq 6\times$ larger than in CaF_2, whereas B_{31} and B_{33} are less than twice as large. Unfortunately, no optical data exist for the $BaF_2:Ce$ system so we cannot at present make a detailed comparison with the $CaF_2:Ce$ case.

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[1] A. Kiel and W. B. Mims, Phys. Rev. B 6, 34 (1972).

[2] W. J. Manthey, Phys. Rev. B 8, 4086 (1973).

[3] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, N. J., 1957), pp. 22–25.

[4] $p_{\text{ion}} = [3(\epsilon - \epsilon_{\text{opt}})E_{\text{app}}]/[4\pi N_F(\epsilon_{\text{opt}} + 2)]$, where N_F is the number of F^- ions per cm^3 in CaF_2, and ϵ_{opt} is the square of the refractive index.

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

[6] A. Kiel, Phys. Rev. 148, 247 (1966).

[7] W. B. Mims, Phys. Rev. 140, A531 (1965).

[8] Since $g_\perp = g_{xx}$, $g_\parallel = g_{zz}$, the parameter B_{15} is intrinsically symmetric with respect to the subscripts of the operator $H_j S_k$ in the spin Hamiltonian. It is also independent of the representation adopted.

[9] Ce^{3+} may be as much as 8% larger than Ca^{2+}, according to tables given by R. D. Shannon and C. T. Prewitt, Acta Crystallogr. B 25, 925 (1969).

[10] G. Burns, J. Chem. Phys. 42, 377 (1965).

[11] The author of Ref. 2 agrees (private communication) that there could be considerable latitude in the 110-cm^{-1} assignment, although not necessarily enough to yield agreement between the theoretical and calculated values of B_{15}.