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Relativistic contribution to the spin-lattice coupling coefficients and to the linear electric field effect for a $3d^5$ ion. Study of Mn^{++} in zinc sulfide*

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The Sandars and Beck technique of effective Hamiltonians and the Dirac-Slater wave functions have been used to calculate the second-order relativistic contribution to the spin-lattice coupling coefficients (SLCC) of a ^6S state ion in T_d and in C_{3v} symmetry. The relativistic effect is calculated for Mn^{++} in ZnS and compared to other important mechanisms contributing to the SLCC's. In this case the relativistic contribution is due primarily to the even crystal field of rank 2. The relativistic contribution is as important as the Blume-Orbach process. The spin-spin mechanism and the contribution of the equivalent even crystal field are an order of magnitude smaller. The linear electric field effect has also been treated in a relativistic scheme. We have defined an equivalent mixed-tensor operator acting in the fundamental configuration and mimicking the second-order effect of the electric field Hamiltonian and of the internal crystal field of odd parity. The relativistic electric field effect, resulting from the promotion of an electron from the $3d^5$ shell to the empty $3d^4 4p$ shell has been calculated for Mn^{++} in cubic ZnS; it was found to be negligible with respect to the classical effect.

I. INTRODUCTION

Soon after Sandars and Beck[1] defined the effective operators acting on LS-coupled relativistic states and Liberman *et al.*[2] and Waber and Cromer[3] calculated the Slater-Dirac wave functions for atoms and ions, the importance of relativistic crystal-field effects on the ground state of f^7 ions was recognized by Wybourne,[4] who has also given convenient methods to calculate some relativistic effective operators and perturbation effective operators.[4,5] The $3d^5$ ions were considered more recently by Van Heuvelen,[6] who calculated the contribution of the axial crystal-field splitting of Mn^{++} in various lattices.

Our first aim is to calculate the relativistic contribution to the spin-lattice coupling coefficients SLCC's of Mn^{++} in T_d and in C_{3v} symmetry. (This contribution was not taken into account in a previous paper[7] in which we studied experimentally and theoretically the SLCC's of this ion in stacking faults of ZnS.) Instead of calculating the $\underline{C}$ tensor related to the stress-induced terms of the spin Hamiltonian, we will evaluate the relativistic contribution to the $\underline{G}$ tensor related to the strain-induced new terms of the spin Hamiltonian and compare this contribution to the other contributions to the tensor $\underline{G}$. This procedure will permit us to avoid the hypotheses needed in the calculation of the stress-induced deformation in C_{3v} symmetry. All three possible axial sites corresponding to the axial field parameters $D = 130\times 10^{-4}$ cm^{-1}, $D = +36.4\times 10^{-4}$ cm^{-1} for Mn^{++} in stacking faults and $D = -100\times 10^{-4}$ cm^{-1} for Mn^{++} in wurtzite, will be considered.

We will then study the electronic polarization of a d^5 ion due to an external uniform electric field, using a relativistic scheme. We will first calculate an equivalent operator of rank K_{12} in spin space and of rank k_{12} in orbital space, defined by

$$W^{(K_{12}k_{12})K} = \sum_{\psi i} \frac{1}{\Delta E} \mathcal{H} |\psi_i\rangle\langle\psi_i| \mathcal{H} ,$$

and acting only on the fundamental configuration. In the above expression ΔE is the separation between the fundamental configuration and the excited configurations of odd parity. The Hamiltonian $\mathcal{H}$ is the sum of the electronic polarization and of the internal crystal field of odd parity. We will show that the main relativistic contribution comes from the following perturbation:

$$\frac{1}{E(^6S) - E(^4P)} \langle ^6S M_S | \mathcal{H}_{so} | ^4P\rangle \times \langle ^4P | W^{(1\,1)2}_{\text{equiv}} | ^6S M_{S'}\rangle .$$

The relativistic effect will be evaluated for Mn^{++} in cubic ZnS using the wave functions calculated by Liberman.

In Sec. II A we show that the effective operator corresponding to the crystal-field potential of rank 4 can be neglected and that only a mixed tensor of rank 1 for the spin and for the orbital angular momentum gives a non-negligible contribution to the "external" effects for Mn^{++}. General relations are then derived which permit the calculation of all needed matrix elements of the spin Hamiltonian owing to the relativistic effect of the crystal fields of rank 2 for a C_{3v} symmetry.

In Sec. II B the method is generalized to take into account the configurational mixing by the internal crystal field of odd parity.

The theoretical results are applied to Mn^{++} in Secs. IV and V.

II. THEORY

A. Relativistic contribution of the even crystal field

The Hamiltonian governing the $3d^5$ ions will be written

$$\mathcal{H} = \mathcal{H}_0 + V_c + \mathcal{H}_{so} + \Delta V_{\text{even}} + V_{\text{odd}} + \Delta V_{\text{odd}} ;$$

$\mathcal{H}_0$ being the free-ion Hamiltonian, V_c the cubic part of the crystal field, $\mathcal{H}_{so}$ the spin-orbit interaction. ΔV_{even} is the even part of the crystal field induced, for example, by an external perturbation. This term will be studied in detail in this section. V_{odd} and ΔV_{odd} are, respectively, the odd part of the crystal field and its variation under an external perturbation. The effect of the odd fields will be studied in Sec. II B.

Using the method of Sandars and Beck,[1] it can be shown that the crystal-field operators of rank 2 and 4 acting on relativistic states can be replaced by a linear combination of mixed-tensor operators $W^{(K_1 k_1)k}$ of rank $K_1 = 0$ or 1 for spin and of rank $k_1 = 0, 1, 2, 3,$ or 4 for the orbital momentum.

For d^N configurations, the relevant $W^{(K_1 k_1)k}$ operators have been determined by Van Heuvelen[6] by using a general formula for the $b_k(K_1 k_1)$ given by Wybourne[4]:

$$\langle r^2\rangle C^{(2)} \rightarrow b_2(1\,1) W^{(1\,1)2} + b_2(1\,3) W^{(1\,3)2} + b_2(0\,2) W^{(0\,2)2} ,$$

$$\langle r^4\rangle C^{(4)} \rightarrow b_4(1\,3) W^{(1\,3)4} + b_4(0\,4) W^{(0\,4)4} .$$

In this paper, the tensors $C^{(k)}$ are related to the spherical harmonics $Y^{(k)}$ by

$$C^{(k)} = \left(\frac{4\pi}{[k]}\right)^{1/2} Y^{(k)} , \quad [k] = 2k+1 .$$

The $b_k(K_1 k_1)$ are given by[6]

$$b_2(1\,1) = \frac{12}{25\sqrt{30}}(-4R^2_{++} + 3R^2_{+-} + R^2_{--}),$$

$$b_2(1\,3) = \frac{4}{175}\,\frac{\sqrt{21}}{\sqrt{5}}\,(3R^2_{++} + R^2_{+-} - 7R^2_{--}),$$

$$b_2(0\,2) = -\frac{2}{25\sqrt{7}}(12R^2_{++} + 6R^2_{+-} + 7R^2_{--}) ,$$

$$b_4(1\,3) = \frac{4}{3\sqrt{35}}(R^4_{++} - R^4_{+-}) ,$$

$$b_4(0\,4) = \frac{2}{3\sqrt{35}}(R^4_{++} + 4R^4_{+-}) ,$$

with

$$R^k_{jj'} = \int_0^\infty F_{(nlj)} r^k F_{(nlj')}\, dr + \int_0^\infty G_{(nlj)} r^k G_{(nlj')}\, dr ;$$

F and G being, respectively, the major and the minor components of the wave functions. The usual notation + corresponds to $j = l + \frac{1}{2}$ and − corresponds to $j = l - \frac{1}{2}$.

Given the smallness of the $b_k(K_1 k_1)$ when $K_1 \neq 0$, the relativistic effect will be non-negligible only if it can lower the order of the perturbation used in the nonrelativistic theory of the external perturbation. The following calculations are performed by a perturbation method in the case of a C_{3v} symmetry. Using the A_2 and E representations of the C_{3v} symmetry group, the ground state ^6S perturbed by $\mathcal{H}_{so}$ is[7]

$$|{}^6S M_S\rangle' = |{}^6S M_S\rangle + \sum_{i=1}^{3} \frac{\alpha_i \rho}{\Delta_i}\Big[\langle (P)^4E^+ M_S - 1|\sum_j(-l^1_{1,j}s^1_{-1,j})|{}^6S M_S\rangle |{}^4_iE^+ M_S\rangle + \langle (P)^4E^- M_S + 1|\sum_j(-l^1_{-1,j}s^1_{1,j})|{}^6S M_S\rangle |{}^4_iE^- M_S + 1\rangle + \langle (P)^4A_2 M_S|\sum_j l^1_{0,j}s^1_{0,j}|{}^6S M_S\rangle |{}^4_iA_2 M_S\rangle\Big] ,$$

where ρ is the spin-orbit constant and the α_i's are the mixing parameters of the $|(P)^4T_1\rangle$ levels by $V_C \cdot \Delta_i = E(^6A_1) - E(^4_iT_1)$. It can be easily shown from the above perturbed ground state and from the effective operators that a second-order perturbation will be sufficient to calculate the matrix elements of the spin Hamiltonian. Our first aim will be to show that the mixed tensors $W^{(1\,3)k}$ with $k = 2$ or 4 give a negligible contribution with respect to that of $W^{(1\,1)2}$.

A simple selection rule on the mixed tensor shows that $W^{(1\,1)2}$ and $W^{(1\,3)k}$ can relate, respectively, the $(^6S)^6A_1$ and $(^4P)^4T_1$ states and the $(^6S)^6A_1$ and $(^4F)^4T_1$ states. In fact, considering only the component $\langle r^2\rangle A^0_2 C^{(2)}_0$ of the crystal field, we get

$$\langle(\tfrac{5}{2},\tfrac{5}{2})'|\,b_2(1\,1)A^0_2 W^{(1\,1)2}_0 - b_2(1\,3)A^0_2 W^{(1\,3)2}_0|\,(\tfrac{5}{2},\tfrac{5}{2})'\rangle - \langle(\tfrac{5}{2},\tfrac{3}{2})'|\,b_2(1\,1)A^0_2 W^{(1\,1)2}_0 - b_2(1\,3)A^0_2 W^{(1\,3)2}_0|\,(\tfrac{5}{2},\tfrac{3}{2})'\rangle = 2\sum_i \frac{\rho\alpha_i^2}{\Delta_i}\, b_2(1\,1)A^{(0)}_2 \frac{\sqrt{6}}{\sqrt{5}} + 2\sum_i \frac{\rho\alpha_i\beta_i}{\Delta_i}\, b_2(1\,3)A^0_2 \tfrac{6}{105} .$$

TABLE I. Matrix elements of the mixed-tensor operator $W^{(1\,1)2}$.

$W^{(1\,1)2}_0$	$^6S\ \frac{5}{2}$	$^6S\ \frac{3}{2}$	$W^{(1\,1)2}_1$	$^4P_0\ \frac{3}{2}$	$^6S\ \frac{3}{2}$	$W^{(1\,1)2}_2$	$^4P_{-1}\ \frac{3}{2}$	$^6S\ \frac{1}{2}$
$^4P_1\ \frac{3}{2}$	$\frac{1}{\sqrt{6}}$	0	$^4P_1\ \frac{3}{2}$	0	$-\frac{1}{\sqrt{5}}$	$^6S\ \frac{5}{2}$	1	0
$^4P_1\ \frac{1}{2}$	0	$\frac{1}{\sqrt{10}}$	$^6S\ \frac{5}{2}$	$-\frac{1}{\sqrt{2}}$	0	$^4P_1\ \frac{3}{2}$	0	$\frac{1}{\sqrt{10}}$
$^4P_0\ \frac{3}{2}$	0	$-\frac{2}{\sqrt{15}}$						

The first term on the right-hand side is that considered by Van Heuvelen, the second term comes from the $(^4F)^4T_1$ states. Considering R^2_{+-} as the mean value of R^2_{++} and R^2_{--}, and using the values of Waber and Cromer, we obtain

$$\frac{b_2(1\,1)}{b_2(1\,3)} = -\frac{21\sqrt{7}}{10\sqrt{2}} ;$$

for Mn^{++} in ZnS we get $[\sum(\alpha_i^2/\Delta_i)]/[\sum(\alpha_i\beta_i/\Delta_i)] = -120$; the second term is thus 720 times smaller than the first term. Therefore only the tensors $W^{(1\,1)2}$ will be considered below.

Using the matrix elements of $W^{(1\,1)2}$ as given in Table I and defining

$$K = \sum \frac{\rho\alpha_i^2}{\Delta_i} b_2(1\,1) ,$$

we get the following matrix elements of the spin Hamiltonian due to the crystal field $\Delta V_{\text{even}} = \sum_q \langle r^2\rangle A_2^q C_q^{(2)}$:

$$\langle(\tfrac{5}{2}, \tfrac{5}{2})' | \Delta V_{\text{even}} | (\tfrac{5}{2}, \tfrac{5}{2})'\rangle = +\frac{2\sqrt{5}}{\sqrt{6}} A_2^0 K ,$$

$$\langle(\tfrac{5}{2}, \tfrac{3}{2})' | \Delta V_{\text{even}} | (\tfrac{5}{2}, \tfrac{3}{2})'\rangle = -\frac{2}{\sqrt{30}} A_2^0 K ,$$

$$\langle(\tfrac{5}{2}, \tfrac{5}{2})' | \Delta V_{\text{even}} | (\tfrac{5}{2}, \tfrac{3}{2})'\rangle = -2A_2^1 K ,$$

$$\langle(\tfrac{5}{2}, \tfrac{5}{2})' | \Delta V_{\text{even}} | (\tfrac{5}{2}, \tfrac{1}{2})'\rangle = +\sqrt{2} A_2^2 K .$$

These matrix elements are all that is needed in the case of a C_{3v} symmetry. The A_2^q's must be calculated in the axis system: $\vec{z}$ along the c axis and $\vec{x}$ in a mirror plane. In the case of a T_d symmetry it is sometimes more convenient to perform the calculation with $\vec{x}, \vec{y}, \vec{z}$ along the [100], [010], and [001] crystallographic axes. The above relations are valid in this case since only ^4P states intervene.

B. Relativistic contribution of the odd crystal field

Since 1959, when Rohrlich[8,9] first considered the influence of configuration interactions in atomic spectroscopy by using Racah's formalism, many authors have considered the problem using more elaborate schemes.[10–13] In 1967, Wybourne[14] studied configuration interactions and performed perturbation summations involving spin-independent and spin-dependent one-particle tensor operators. A variant of the commutative properties of the orbital operators which he used will be relevant in the following relativistic treatment of the effect of configurations interactions.

In the study of external effects, it is convenient to separate the Hamiltonian corresponding to the crystal field of odd parity $\mathcal{H}_{\text{odd}}$ in two parts,

$$\mathcal{H}_{\text{odd}} = V_{\text{odd}} + \Delta V_{\text{odd}} ,$$

V_{odd} being the internal crystal field of odd parity for the free crystal and ΔV_{odd} being either the pressure-induced crystal field of odd parity or the new term $\mathcal{H}_E = \sum_i e\vec{E}\cdot\vec{r}_i$ which must be added to the Hamiltonian of an ion subjected to a uniform electric field.

In order to calculate the equivalent operator

$$W_{\text{equiv}} = \sum_{\psi_i} \frac{1}{E_0 - E_i} (V_{\text{odd}} + \Delta V_{\text{odd}}) | \psi_i\rangle \times \langle\psi_i | (V_{\text{odd}} + \Delta V_{\text{odd}}) ,$$

we will assume that the fundamental configuration is well separated from the excited configurations, so that $E_0 - E_i \approx \Delta E$ for all states $|\psi_0\rangle$ of the fundamental configuration and all states $|\psi_i\rangle$ of the excited configuration. This is evidently a crude approximation, however it does allow us to perform conveniently the summation on all $|\psi_i\rangle$'s.

In the second-quantization formalism, an operator such as $r^k C^{(k)}$ can be written

$$r^k C^{(k)} = -\sum_{n,l,j} \sum_{n',l',j'} [k]^{-1/2} [q^\dagger(n, l, j) \times q(n', l', j')]^{(k)} \langle nlj \| r^k C^{(k)} \| n'l'j'\rangle ,$$

where the components $q^\dagger(n, l, j, m)$ of the tensor operator $q^\dagger$ of rank j are defined by

$$q^\dagger(n, l, j, m) | 0\rangle = | n, l, j, m\rangle ,$$

$|0\rangle$ being the vacuum state and $|n, l, j, m\rangle$ the state of a single relativistic electron defined by the quantum numbers n, l, j and by the component m of j. The tensor operator q is defined in terms of the adjoint of the creation operator by[15]

$$q(n', l', j', m') = (-1)^{j'-m'}[q^\dagger(n', l', j', -m')]^* .$$

In order to simplify the notation, we will represent the set of quantum numbers (n, l, j) by α, and we will use primed letters for electrons belonging to different configurations.

The general term S,

$$S = \sum_{\psi_i} \langle \psi_0 | r^{k_1} C^{(k_1)} | \psi_i \rangle \langle \psi_i | r^{k_2} C^{(k_2)} | \psi_0' \rangle ,$$

will be evaluated in the jj coupling scheme using the following commutative properties of the operators $q^\dagger q$[13,14]

$$\{[q^\dagger(\alpha)q(\alpha')]^{(k_1)}[q^\dagger(\alpha'')q(\alpha''')]^{(k_2)}\}_Q^{(K)} - \{(-1)^{k_1+k_2-K}[q^\dagger(\alpha'')q(\alpha''')]^{(k_2)}[q^\dagger(\alpha)q(\alpha')]^{(k_1)}\}_Q^{(K)}$$

$$= [k_1, k_2]^{1/2}\Big[\delta(\alpha', \alpha'')(-1)^{j+j'''+K}\begin{Bmatrix} k_1 & k_2 & K \\ j''' & j & j' \end{Bmatrix}[q^\dagger(\alpha)q(\alpha''')]_Q^{(K)}$$

$$+ \delta(\alpha, \alpha''')(-1)^{j'+j''+k_1-k_2}\begin{Bmatrix} k_1 & k_2 & K \\ j'' & j' & j \end{Bmatrix}[q^\dagger(\alpha'')q(\alpha')]_Q^{(K)}\Big], \quad [k_1, k_2] = (2k_1+1)(2k_2+1) .$$

S can now be calculated by using the closure theorem $\sum |\psi_i\rangle\langle\psi_i| = 1$ and by coupling the tensors $C^{(k_1)}$ and $C^{(k_2)}$. It can be easily shown that three types of configuration interactions exist in the case of a single open shell. They correspond to (i) the promotion of an electron of the l^N shell to an empty l' shell, (ii) the promotion of an electron of the closed $l'^{\,4l'+2}$ shells to the l^N shell, and (iii) the promotion of an electron from filled to empty shells. This last interaction will not be considered, since it shifts equally all levels of the ion.

Explicitly the equivalent operator

$$S_{\text{equiv}} = \sum_{\psi_i} r^{k_1} C^{(k_1)} | \psi_i \rangle \langle \psi_i | r^{k_2} C^{(k_2)} ,$$

is given by

$$S_{\text{equiv}} = -\sum (-1)^{j_1+j_2+K+Q+\Phi}\begin{pmatrix} k_1 & k_2 & K \\ q_1 & q_2 & -Q \end{pmatrix}\begin{Bmatrix} k_1 & k_2 & K \\ j_2 & j_1 & j' \end{Bmatrix}\langle nlj_1 \| r^{k_1} C^{(k_1)} \| n'l'j' \rangle \langle n'l'j' \| r^{k_2} C^{(k_2)} \| nlj_2 \rangle$$

$$\times [q^\dagger(nlj_1)q(nlj_2)]_Q^{(K)} .$$

The mechanism (i) described above corresponds to $\Phi = 0$; $\Phi = 1$ corresponds to case (ii).

Now writing S_{equiv} in terms of operators acting on relativistic (nl) states,[16,17] we get

$$S_{\text{equiv}} = -\sum (-1)^{j_1+j_2+K+Q+\Phi}\begin{pmatrix} k_1 & k_2 & K \\ q_1 & q_2 & -Q \end{pmatrix}\begin{Bmatrix} k_1 & k_2 & K \\ j_2 & j_1 & j' \end{Bmatrix}\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & K_{12} \\ l & l & k_{12} \\ j_1 & j_2 & K \end{Bmatrix}$$

$$\times \langle nlj_1 \| r^{k_1} C^{(k_1)} \| n'l'j' \rangle \langle n'l'j' \| r^{k_2} C^{(k_2)} \| nlj_2 \rangle [j_1, j_2]^{1/2}[K_{12}, k_{12}]^{1/2}[q^\dagger(nl)q(nl)]^{(K_{12}\,k_{12})K}_{Q} ,$$

where the sum is over $j_1, j_2, n', l', j', K_{12}, k_{12}, K, Q$. The $3j$, $6j$, and $9j$ symbols are those defined by Rotenberg *et al.*[18]

III. SLCC'S OF Mn^{++} IN C_{3v} SYMMETRY

When only second-order terms in S are considered, the new terms of the spin Hamiltonian induced by external stresses can be written[7,19]

$$\Delta\mathcal{H} = \sum_{i,j} S_i \delta D_{ij} S_j + \sum_{i,j} S_i \delta g_{ij} H_j .$$

Since δg_{ij} is generally negligible for d^5 ions, only the tensor D_{ij} will be considered below. This symmetric rank-4 tensor[20,21] can be expressed either in terms of the internal stresses or in terms of strains. In order to avoid calculating the strains from the applied pressure, we will use the following form of $\Delta\mathcal{H}$:

$$\Delta\mathcal{H}_{\text{strain}} = (\underline{G} \times \underline{\epsilon} \times \underline{S})_{\text{contracted}}$$

$\underline{\epsilon}$ is the strain tensor, and $\underline{S}$ is a rank-2 tensor in

TABLE II. Contribution of the Blume-Orbach (BO) mechanism, and of the relativistic effect to the SLCC's of Mn^{++} in sited AS and PN and in wurtzite. Numerical values are given in units of cm^{-1} per unit strain.

	Sites AS		Sites PN		Wurtzite	
	BO mechanism	Relativistic effect	BO mechanism	Relativistic effect	BO mechanism	Relativistic effect
$G_{11}+G_{12}$	+0.31544	+0.29300	+0.31544	+0.29300	+0.31544	+0.29300
$G_{11}-G_{12}$	+0.32221	+0.14643	+0.32221	+0.14643	+0.26824	+0.14643
G_{13}	−0.28949	−0.43670	−0.29547	−0.29303	−0.31088	−0.43670
G_{51}	+0.44154	+0.51796	+0.44154	+0.51796	+0.44802	+0.69837
G_{44}	−0.15345	−0.36528	−0.15105	−0.28976	−0.09613	−0.36528
G_{15}	+0.44940	+0.51760	+0.43963	+0.51760	+0.39839	+0.69790

S. The evaluation of $\underline{G}$ will permit a direct comparison between the relativistic and classical contributions.

For a $3d^5$ ion in a C_{3v} symmetry site the relativistic contribution to the G_{ij}'s of the pressure-induced crystal field $A_2^q\langle r^2\rangle C_q^{(2)}$ is given by

$$(G_{11}+G_{12})_{\epsilon_{11}\neq 0} = -\frac{\sqrt{6}}{3\sqrt{5}}(A_2^0)_{\epsilon_{11}\neq 0}K\,,$$

$$(G_{11}-G_{12})_{\epsilon_{11}\neq 0} = +\frac{4\sqrt{2}}{\sqrt{40}}(A_2^2)_{\epsilon_{11}\neq 0}K\,,$$

$$(G_{13})_{\epsilon_{33}\neq 0} = -\frac{1}{\sqrt{30}}(A_2^0)_{\epsilon_{11}\neq 0}K\,,$$

$$(G_{51})_{\epsilon_{11}\neq 0} = -\frac{1}{\sqrt{5}}(A_2^1)_{\epsilon_{11}\neq 0}K\,,$$

$$(G_{44})_{\epsilon_{13}\neq 0} = -\frac{\sqrt{5}}{10}(A_2^1)_{\epsilon_{13}\neq 0}K\,,$$

$$(G_{15})_{\epsilon_{13}=0} = +\frac{\sqrt{2}}{\sqrt{40}}(A_2^2)_{\epsilon_{13}\neq 0}K\,.$$

The indices $\epsilon_{ij\neq 0}$ mean that the pressure-induced crystal field must be calculated by taking into account only the strain ϵ_{ij}. The calculation of the crystal field must be performed in the axis system—$\vec{z}$ along the optical axis, $\vec{x}$ in a mirror plane.

The calculation of the relativistic contribution to the G_{ij}'s has been performed for Mn^{++} in ZnS wurtzite and for Mn^{++} in two stacking faults, denoted by AS and PN.[22] (The sites denoted AS possess six second neighbors forming a trigonal antiprism and one third neighbor on the [111] axis, the sites denoted PN possess six second neighbors forming a trigonal prism without a third neighbor on the [111] axis.) The parameter $K=-(56.22\times10^{-6})a_0^2$ (a_0 is the first Bohr radius) has been calculated from $\rho=300\ cm^{-1}$, $\sum_i(\alpha_i^2/\Delta_i)=44.09\times10^{-6}$ cm, $b_2(1\,1)=-0.0485a_0^2$ (see Ref. 6). The results are given in Table II. The relativistic effect is compared to the classical Blume-Orbach effect. The results show clearly that the relativistic effect is as important as the Blume-Orbach effect which gives the preponderant contribution when only classical effects are considered. (The spin-spin mechanism, the contribution of the equivalent even crystal fields, the Sharma-Das-Orbach effect, and higher-order effects have been studied in great detail in Ref. 7.)

IV. LINEAR ELECTRIC FIELD EFFECT IN EPR FOR Mn^{++} IN T_d SYMMETRY

The spin Hamiltonian of an ion subjected to an external uniform electric field is given by[23–25]

$$\mathcal{H}_E=\sum_{i,j,k}R_{ijk}E_iS_jS_k+\sum_{i,j,k}T_{ijk}E_iH_jS_k$$
$$+\text{higher-order terms.}$$

The tensor $\underline{R}$ describing the linear electric field effect is nonzero only if the ion is located in noncentrosymmetric sites. The tensor $\underline{T}$ and the tensors corresponding to the higher-order terms in $\vec{E}$, $\vec{H}$, or $\vec{S}$ will not be studied here. In fact their contributions to the displacements of the absorption lines are generally negligible when compared to that of the linear effect.[26]

The Hamiltonian is obtained simply by adding $\mathcal{H}_E=\sum_i e\vec{E}\cdot\vec{r}_i$ to the Hamiltonian of Sec. II A. The terms ΔV_{odd} and ΔV_{even} of the Hamiltonian of Sec. II A must now be interpreted as being due to the ionic polarization. We will consider calculating only the linear effect in E caused by the electronic polarization of the ion. Neglecting the piezoelectric effect is a correct approximation for Mn^{++} in ZnS, since its effect is only $\frac{1}{15}$ of the electronic effect.[27] We will also neglect all ionic displacements not described by the piezoelectric tensor. Using the theory developed by Kiel and Mims for loose ions[28–30] and, in particular, for Mn^{++} in various scheelites, it can be easily demonstrated that this last approximation is certainly valid for Mn^{++} substituted for Zn^{++}.

The equivalent operator corresponding to the composition of V_{odd} and $\mathcal{H}_E$ can be easily obtained from the last relation in Sec. III B. Expanding the reduced matrix elements and introducing the mixed-tensor operators $W^{(K_{12}k_{12})K}$, we get the following general expression for W_{equiv}:

$$W_{\mathrm{equiv}}=\sum_{j_1,j_2}\sum_{n',l',j'}\sum_{K_{12},k_{12},K,Q,k_1,k_2}(-1)^{2j_1+j_2+j'+K+Q+\Phi}[j_1,j_2,j'][K_{12},k_{12}]^{1/2}$$
$$\times\begin{pmatrix}k_1 & k_2 & K\\ q_1 & q_2 & -Q\end{pmatrix}\begin{Bmatrix}\frac{1}{2} & \frac{1}{2} & K_{12}\\ l & l & k_{12}\\ j_1 & j_2 & K\end{Bmatrix}\begin{Bmatrix}k_1 & k_2 & K\\ j_2 & j_1 & j'\end{Bmatrix}\begin{pmatrix}j_1 & k_1 & j'\\ \frac{1}{2} & 0 & -\frac{1}{2}\end{pmatrix}\begin{pmatrix}j' & k_2 & j_2\\ \frac{1}{2} & 0 & -\frac{1}{2}\end{pmatrix}$$
$$\times R(j_1,j',j_2)\,W^{(K_{12}k_{12})}{}^{K}_{Q}\,A^{q_1}_{k_1}A^{q_2}_{k_2}\;,$$

where

$$R(j_1,j',j_2)=\int_0^\infty[F(nlj_1)r^{k_1}F(n'l'j')+G(nlj_1)r^{k_1}G(n'l'j')]\,dr\int_0^\infty[F(n'l'j')r^{k_2}F(nlj_2)$$
$$+G(n'l'j')r^{k_2}G(nlj_2)]\,dr\;.$$

The relativistic effect corresponding to the promotion of an electron of the $3d^5$ shell to an empty $4p$ shell will now be calculated explicitly. This interaction corresponds to Fig. 1(a). In the axis system $\vec{x}\parallel[100]$, $\vec{y}\parallel[010]$, and $\vec{z}\parallel[001]$, the odd crystal field is given by

$$V_{\mathrm{odd}}=\langle r^3\rangle A^2_3(C^{(3)}_2-C^{(3)}_{-2})\;.$$

For an applied electric field parallel to the $\vec{z}$ axis, $\mathcal{H}_E$ can be written

$$\mathcal{H}_E=\langle r\rangle A^0_1C^{(1)}_0\;,$$

with $A^0_1=eE$. Having shown in Sec. II A that the equivalent operator $W^{(1\,3)2}_{\mathrm{equiv}}$ gives a negligible contribution to the relativistic effect, we will calculate only the equivalent operator $W^{(1\,1)2}_{\mathrm{equiv}}$, thus getting

$$W^{(1\,1)2}_{\mathrm{equiv}}=b_2(1\,1)_{\mathrm{equiv}}(W^{(1\,1)2}{}_{2}-W^{(1\,1)2}{}_{-2})\;,$$

with

$$b_2(1\,1)_{\mathrm{equiv}}=\frac{\sqrt{2}}{875\sqrt{3}\sqrt{5}}[48R(\tfrac{5}{2},\tfrac{3}{2},\tfrac{5}{2})-18R(\tfrac{3}{2},\tfrac{3}{2},\tfrac{5}{2})$$
$$+32R(\tfrac{5}{2},\tfrac{3}{2},\tfrac{3}{2})-12R(\tfrac{3}{2},\tfrac{3}{2},\tfrac{3}{2})$$
$$-50R(\tfrac{5}{2},\tfrac{1}{2},\tfrac{3}{2})]A^2_3A^0_1\;.$$

In T_d symmetry, the tensor $\underline{\mathrm{R}}$ has only one independent component[20,21] so that in the axis system defined above, the spin Hamiltonian takes the form

$$\mathcal{H}_E=iRE\frac{\sqrt{2}}{\sqrt{3}}(O^{(2)}_{-2}-O^{(2)}_{+2})\;,$$

the $O^{(k)}_q$'s are the tensor operators defined by Thornley and Smith.[31] R is given by

$$R=\frac{i}{E\sqrt{10}}\langle(\tfrac{5}{2},\tfrac{5}{2})'|\textstyle\sum e\vec{\mathrm{E}}\cdot\vec{\mathrm{r}}|(\tfrac{5}{2},\tfrac{1}{2})'\rangle\;.$$

Using the general relations of Sec. II A, we get

$$R=\frac{i}{E\sqrt{5}}\sum\frac{\rho\alpha_i^2}{\Delta i}b_2(1\,1)_{\mathrm{equiv}}\epsilon_{\mathrm{eff}}A^2_3A^0_1\frac{1}{\Delta E}\;,$$

where ϵ_{eff} is the effective dielectric constant. The

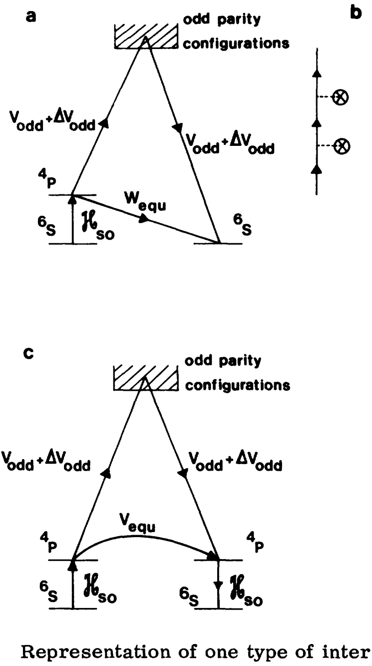

FIG. 1. Representation of one type of interaction intervening in the relativistic effect of odd crystal field. The scheme (a) shows the equivalent operator W_{equiv} coupling the fundamental configuration to the excited configurations $d^4\,4p$, $d^4\,4f$, etc.; (b) represents the graph describing the promotion of an electron from the fundamental configuration to an empty configuration, ⊗ represents the crystal-field operator; and (c) gives the classical configuration interaction described in Refs. 7 and 27.

introduction of $\epsilon_{\rm eff}$ relating the internal and applied electric field permits us to obtain R directly in terms of the applied electric field.

The Slater-Dirac wave functions for Mn^{++} determined by Liberman *et al.*[32] were used to calculate the needed radial integrals. Taking only into account the major components of the radial wave functions (the contribution of the minor components of the wave functions is at least three orders of magnitude inferior to that of the major components) we get $b_2(1\,1)_{\rm equiv}/A_3^2A_1^0 = 0.00041 a_0^4$. For Mn^{++} in cubic ZnS we have $\epsilon_{\rm eff} = 3.9$ (this value being given by the Clausius-Mosotti formula) and $A_3^2 = -0.02193\, ie^2/2a_0^4$. These values give $R = 0.0013$ G/kV mm^{-1} which is $\frac{1}{70}$ of the experimental value $|R_{\rm expt}| = 0.09$ G/kV mm^{-1}.[27] The relativistic contribution to the linear electric field effect on Mn^{++} in ZnS is thus negligible when compared to the classical contribution: $R_{\rm class} = 0.038$ G/kV mm^{-1}.[27]

V. CONCLUSION

The calculations performed for the SLCC's of Mn^{++} in C_{3v} symmetry show that the relativistic contribution enhances considerably the importance of crystal potentials of rank 2. This confirms the previous results obtained by Wybourne[4] and Van Heuvelen.[6] The study of the linear electric field effect has shown that for Mn^{++} the relativistic part of the electronic polarization gives a negligible contribution to the tensor $\underline{R}$. This result is in disagreement with previous semiquantitative studies of this effect.[33] Finally, the relativistic effect most likely could be of importance in evaluating the ionic contribution to the linear electric field effect of loose ions.

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