Molecular spin-orbit interaction for d^5 ions in covalent crystals: Spin-lattice coupling coefficients of Mn^{2+} in II-VI compounds

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A very detailed ligand-field (LF) model is developed to account for the increase of one or two orders of magnitude of the spin-lattice coupling coefficients (SLCC) of Mn^{2+} in the common cation series ZnS, ZnSe, ZnTe, and CdTe. First, an overall LF model shows that the SLCC's are correctly given for all studied compounds by a second-order perturbation scheme involving twice the molecular spin-orbit interaction acting between the fundamental state $^6A_1$ and the three excited states $^4T_1$ at lower energy. This model gives the contributions to the SLCC's of the strain-induced variations of the electrostatic field of the crystal, of the ligand-ligand and metal-ligand group overlaps, and of the molecular spin-orbit interaction. Second, a new analysis of the LF model gives the strain-induced variations of the splitting of the states $^4T_1$, of the monoelectronic molecular wave functions, and of the orbital operator of the molecular spin-orbit interaction. Finally, by expressing the SLCC's as a linear combination of quadratic terms in the spin-orbit constants ζ_M of the electrons d of the metal and ζ_L of the electrons p of the ligands and bilinear terms in $\zeta_M\zeta_L$, it is shown that the terms in ζ_M^2 are approximately identical for all compounds, while the terms in $\zeta_M\zeta_L$ which are partly compensated by the terms in ζ_L^2 become preponderant when passing from ZnS to ZnSe, ZnTe, and CdTe. These results account for the observed roughly linear dependence of the SLCC's on ζ_L for the common cation series ZnS, ZnSe, and ZnTe and show that molecular spin-orbit interaction is essential to analyze spin-orbit-dependent spectroscopic constants when the ratio ζ_L/ζ_M is greater than unity.

I. INTRODUCTION

For d^5 ions, the theory of the spin-lattice coupling coefficients (SLCC's) has long been developed in great detail in the framework of the classical[1] and relativistic[2,3] crystal-field (CF) model. A covalent model for the SLCC's of d^5 ions has been developed by Sharma, Das, and Orbach[4] and used to interpret the SLCC's of Mn^{2+} in oxides, fluorides, and chlorides. They showed that covalency effects were not preponderant in these compounds with respect to the overall contribution of several mechanisms involving the classical crystal-field model.

Experimental values for the SLCC's of d^5 ions in II-IV and III-V compounds show that they so strongly depend on the nature of the ligands that these early theories have to be reconsidered in order to determine the predominant mechanisms contributing to the SLCC's.

The experimental values show that the SLCC's G_{11} and G_{44}, which describe the coupling to E strains and T_2 strains, respectively, can differ by almost two orders of magnitude for Mn^{2+} in ZnS ($G_{11}=-0.02$ cm^{-1}, $G_{44}=0.20$ cm^{-1}),[5] ZnSe ($G_{11}=0.34$ cm^{-1}, $G_{44}=-0.02$ cm^{-1}),[6] ZnTe ($G_{11}=0.80$ cm^{-1}, $G_{44}=-0.36$ cm^{-1}),[7] and CdTe ($G_{11}=0.46$ cm^{-1}, $G_{44}=-0.51$ cm^{-1}),[7] and that the signs of G_{11} and G_{44} depend on the ligands. For Mn^{2+} in GaP ($G_{11}<0.1$ cm^{-1}, $G_{44}<0.1$ cm^{-1}),[8] and for Fe^{3+} in GaAs ($G_{11}=1.4$ cm^{-1}, $G_{44}=-2.2$ cm^{-1}),[8] GaP ($G_{11}=-7.74$ cm^{-1}, $G_{44}=5.87$ cm^{-1}),[8] and InP ($G_{11}=-2.8$ cm^{-1}, $G_{44}=2.4$ cm^{-1}),[8] the experimental values are as scattered as for Mn^{2+} in II-VI compounds.

This strong dependence on the ligands clearly indicates that the fairly well-known theory of the SLCC's in the framework of the crystal-field model can only fail to account for experimental values in II-VI and III-V compounds. As a corollary, the reasons for why the CF model approximately works in exceptional cases, as for Mn^{2+} and Cr^+ in ZnS, are not clear.

More precisely, in the case of Mn^{2+} in II-VI compounds which will be considered here, the Blume-Orbach[1] and relativistic[2] CF models give the preponderant contributions to the SLCC's and predict that G_{11} and G_{44} are almost identical for all II-VI compounds. Therefore we will take as a reference for the theoretical values of G_{11} and G_{44}, as given by the CF models, those obtained in ZnS, that is; $G_{11}=-0.26$ cm^{-1} and $G_{44}=0.15$ cm^{-1}.

In order to tentatively relate the experimental values of the SLCC's to constants intervening in covalent models, we have represented the SLCC's and the Landé g factors [2.0022 for ZnS,[9] 2.0051 for ZnSe,[10] 2.0106 for ZnTe,[11] 2.0067 for CdTe (Ref. 7)] in terms of the spin-orbit coupling constant ζ_L of the electrons p of the ligands[12] ($\zeta_L=384$ cm^{-1} for S, 1650 cm^{-1} for Se, and 4200 cm^{-1} for Te) (see Fig. 1). Surprisingly enough, the dependence
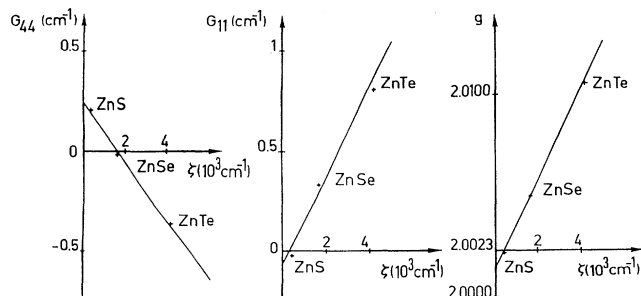
FIG. 1. Representation of the SLCC's and Landé g factors of Mn in ZnS, ZnSe, and ZnTe in terms of the spin-orbit constant of the ligand.

of the SLCC's and g factors on ζ_L is almost linear for ZnS, ZnSe, and ZnTe while the g factors and SLCC's are given by a second-order perturbation scheme involving the molecular spin-orbit interaction only once (and the Zeeman interaction) for the g factors but twice this interaction for the SLCC's.

In this paper we present a ligand-field (LF) model for the SLCC's G_{11} of Mn^{2+} in the common cation series ZnS, ZnSe, ZnTe, and CdTe. Although it has long been shown that LF models give accurate multielectronic wave functions to account for spectroscopic constants of the fundamental state of d^n ions in covalent crystals as the g factors,[12] it has only recently been demonstrated that it can also account for optical constants in stressed crystals as the orbit-lattice coupling coefficients[13] (OLCC's) which describe the coupling of excited states to uniaxial stresses and the SLCC's.

The calculations will be restricted to E strains (symmetry D_{2d}) for the following reasons:

(i) A direct test of the validity of our method for obtaining the multielectronic wave functions in symmetry D_{2d} was previously checked when computing the OLCC's to E strains of the states $^4T_1$ and $^4T_2$ of Mn^{2+} in ZnS and ZnSe.[13] Such a test for wave functions in symmetry C_{3v} corresponding to T_2 strains is not possible, because the OLCC's to T_2 strains cannot be measured due to a relatively strong Jahn-Teller coupling to E vibrational modes.

(ii) The interpretation of the SLCC's to T_2 strains is complicated by the piezoelectric effect and by eventual displacements of the sublattices not described by the stress tensor.

In Sec. II we present the molecular orbitals in symmetry T_d and D_{2d} as given by the LF model for Mn^{2+} in ZnS, ZnSe, ZnTe, and CdTe.

In Sec. III we briefly recall the LF model which was previously used to compute the SLCC's of Mn^{2+} in ZnS and ZnSe.[14] The molecular spin-orbit interaction is defined first. Then we present the second-order perturbation scheme between the fundamental state $^6A_1$ and the multielectronic states $^nT_1$ ($n = 4$ and 6) and indicate that the main contribution arises from the three orbital states $^4T_1$, at lower energy. This overall self-consistent model gives the SLCC's in terms of a few constants or parameters, such as the metal-ligand distance, the charges of the

metal and ligands, the cubic-field parameter, and a constant describing the crystal electric field.

In Sec. IV we present a new analysis of the LF model which clearly shows the physical processes contributing to the SLCC's. It is first shown that the contribution due to the strain-induced splitting of the relevant orbital triplet states $^4T_1$ can be separated from the contributions of the strain-induced variations of the monoelectronic wave functions and of the molecular spin-orbit interaction. Then a very detailed analysis is made of the uniaxial stress effect on the monoelectronic molecular wave functions and on the molecular spin-orbit interaction.

The theoretical results are compared to experiments in Sec. V. First, the SLCC's are computed by using the overall LF model as given in Sec. III. Second, an analysis of the SLCC's is made in terms of the spin-orbit coupling constants of the metal and ligands. Next, following the procedure given in the preceding section, a very detailed analysis is presented of the strain-dependent spin-orbit interaction, multielectronic orbital triplet states, and monoelectronic wave functions.

II. MOLECULAR ORBITALS IN SYMMETRY T_d AND D_{2d}

The molecular orbitals are chosen as linear combinations of the atomic orbitals $3d$, $4p$, and $4s$ of Mn and the valence orbitals ns and np (with $n = 3$ for sulfur, $n = 4$ for selenium, and $n = 5$ for tellurium). The correction for ligand-ligand overlap and group overlap integrals in symmetry D_{2d} (and T_d) is given in Ref. 13.

As has long been known, the main problem of LF models for impurities in crystals is to correctly account for the influence of the crystal on the cluster. The essential difference between our LF model and previous ones lies in the way of accounting for the electrostatic field of the crystal. While previous models considered the electrostatic field of the nearest neighbors of the metal only, we include in our model the diagonal and off-diagonal elements of the electrostatic field due to the nearest neighbors of the ligands (see Ref. 14). Furthermore, the electrostatic field of the remaining ions of the crystal is included by approximating it as its contribution to the Madelung constant (C_{mad}).

The most striking effects of including the electric field of distant ions are to reduce the electric charge of the metal and to permit fitting of the experimental values of the OLCC's and, as it will be shown in the following, of the SLCC's by allowing slight variations of C_{mad}.

The valence state ionization energies E_{VSI} have been calculated by the method of Basch, Viste, and Gray[15] for Mn and from the atomic energy levels given by Moore[16] for the ligands. The relevant E_{VSI}'s in K cm^{-1} are given in terms of the charge Q_L of the ligands by

$$E_{\text{VSI}}(3s) = -1.77Q_L^2 + 74Q_L + 166 ,$$

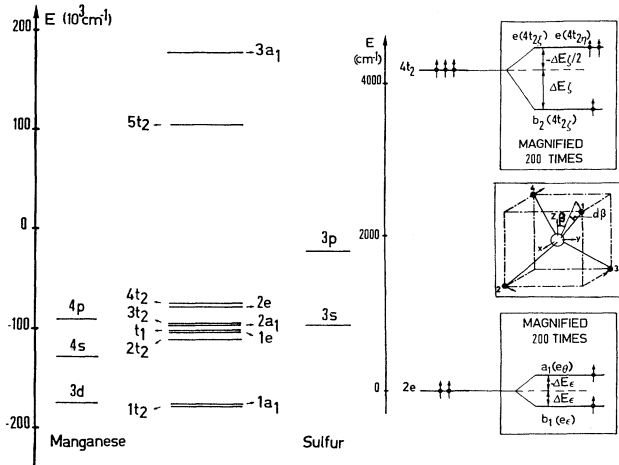$$E_{\text{VSI}}(3p) = 7.95Q_L^2 + 84Q_L + 93$$

for the electrons of sulfur,

FIG. 2. One-electron molecular energy levels of Mn^{2+} in symmetry T_d and strain-induced splitting of the monoelectronic orbitals $2e$ and $4t_2$ (the energies are those obtained for ZnS). The angle $d\beta$ defining the strains of symmetry E_θ is given in the inset.

$$E_{VSI}(4s) = 6.9Q_L^2 + 91Q_L + 168 \ ,$$

$$E_{VSI}(4p) = 6.9Q_L^2 + 73Q_L + 87$$

for the electrons of selenium, and

$$E_{VSI}(5s) = 3.73Q_L^2 + 98Q_L + 167 \ ,$$

$$E_{VSI}(5p) = 7.40Q_L^2 + 76Q_L + 89$$

for the electrons of tellurium.

The off-diagonal matrix elements were given by Cusach's[17] approximation. The radial wave functions were those calculated by Richardson and co-workers for Mn,[18,19] by Watson and Freeman for sulfur[20] and selenium,[21] and by Roetti and Clementi for tellurium.[22]

The interatomic distances as given from crystallographic data were 2.34 Å for ZnS, 2.45 Å for ZnSe, 2.64 Å for ZnTe, and 2.81 Å for CdTe.[23] Slight variations of

these values were considered to account for the presence of Mn in the molecule.

The splitting of the monoelectronic orbitals $2e$ and $4t_2$ in symmetry D_{2d} was calculated following the procedure developed in Ref. 13, that is, by diagonalizing the matrices of the group overlaps in symmetry D_{2d} and by calculating the matrices of the energies including the E_{VSI}'s and the crystal electrostatic field expressed in symmetry D_{2d}. The one-electron molecular energy levels and the splitting of the monoelectronic orbitals $2e$ and $4t_2$ corresponding to a strain E_θ are represented in Fig. 2.

III. MODEL FOR THE SPIN-LATTICE COUPLING COEFFICIENTS

For a ^6S state, the most important term of the spin Hamiltonian describing the influence of uniaxial stress is

$$\Delta \mathcal{H}_S = \sum_{ijkl} G_{ijkl} \varepsilon_{kl} S_i S_j$$

or

$$\Delta \mathcal{H}_S = \sum_{ijkl} C_{ijkl} \sigma_{kl} S_i S_j \ ,$$

where ε is the strain tensor and σ is the stress tensor. In cubic symmetry, the tensors $\mathbf{G}$ and $\mathbf{C}$ have only two independent components G_{11}, G_{44} or C_{11}, C_{44}, which describe the coupling to strains of symmetry E_θ and T_2, respectively.

For the strain of symmetry E_θ which is considered here, G_{11} is given in terms of the matrix elements of $\Delta \mathcal{H}_S$ and ε_{33} by

$$G_{11} = \frac{\Delta E}{9 \varepsilon_{33}} \ ,$$

with

$$\Delta E = \langle S = \tfrac{5}{2}, M_S = \tfrac{5}{2} | \Delta \mathcal{H}_S | \tfrac{5}{2}, \tfrac{5}{2} \rangle - \langle \tfrac{5}{2}, \tfrac{3}{2} | \Delta \mathcal{H}_S | \tfrac{5}{2} \tfrac{3}{2} \rangle \ .$$

(ε_{33} is related to the angle $d\beta$ in Fig. 2 by $d\beta = \varepsilon_{33}/\sqrt{2}$.)

In the proposed molecular model[14] (Fig. 3) G_{11} is given by

$$G_{11} = \frac{1}{9\varepsilon_{33}} \sum_{n,u,M_S} [\langle {}^6A_1 \tfrac{5}{2} | \mathcal{H}_{SO} | {}^nT_{1u} M_S \rangle \langle {}^nT_{1u} M_S | \mathcal{H}_{SO} | {}^6A_1 \tfrac{5}{2} \rangle - \langle {}^6A_1 \tfrac{3}{2} | \mathcal{H}_{SO} | {}^nT_{1u} M_S \rangle \langle {}^nT_{1u} M_S | \mathcal{H}_{SO} | {}^6A_1 \tfrac{3}{2} \rangle]$$

$$\times \frac{1}{E({}^6A_1) - E({}^nT_{1u})} \ .$$

This expression involves states and operators which are fundamentally different from those used in CF models.

First, the fundamental state $^6A_1$ and the excited states $^nT_1$ ($n=4$ and 6) are to be computed for the strained crystal. This procedure, which severely increases the complexity of the model, is essential to account for the strain-induced variations of the group overlaps and the electrostatic field. Of course, for a symmetry lower than cubic, the orbital triplet states are split, so that the summation is performed on the components $u = x, y,$ or z of these states.

Second, the amplitude of *the molecular spin-orbit interaction* $\mathcal{H}_{SO}$ depends on interatomic distances and angles so that, in the perturbation scheme, $\mathcal{H}_{SO}$ must be calculated for a molecule MX_4 of symmetry D_{2d}. More precisely, the molecular spin-orbit interaction which has been defined by Misetich and Buch[24] can be written as

$$\mathcal{H}_{SO} = \sum_i \zeta_M(r_{iM}) l_{iM} \cdot \mathbf{s}_i + \sum_i \sum_L \zeta_L(r_{iL}) l_{iL} \cdot \mathbf{s}_i \ ,$$

where l_{iM} and l_{iL} are one-electron orbital operators for the metal and ligands, respectively. ζ_M and ζ_L are the

spin-orbit coupling constants of the electrons of the metal and ligands, respectively.[25]

$\mathcal{H}_{SO}$ can conveniently be written in terms of molecular angular momentum τ_u^i of electron i and the complex components of the spin operator[26] as

$$\mathcal{H}_{SO} = \sum_{q,i} \tau_u^i s_q^i$$

with

$$\tau_u^i = \zeta_M(r_{iM}) l_{Mu}^i + \zeta_L(r_{iL}) \Omega_u^i$$

with $u = y$ if $q = \pm 1$, and $u = z$ if $q = 0$, Ω^i being the angular momentum of electron i of the ligands.

The dependence on strain of $\mathcal{H}_{SO}$ can be explicitly put into evidence by writing in detail the angular momentum Ω^i. For example, in the case of strain E_θ defined by the angle β (see Fig. 2) we get

$$\Omega_X^i = \frac{\sin\beta}{\sqrt{2}}(l_{z1} - l_{z2} + l_{z3} - l_{z4}) + \frac{1}{\sqrt{2}}(l_{y1} + l_{y2} - l_{y3} - l_{y4})$$
$$+ \frac{\cos\beta}{\sqrt{2}}(-l_{x1} - l_{x2} + l_{x3} + l_{x4}) \, ,$$

$$\Omega_Y^i = \frac{\sin\beta}{\sqrt{2}}(l_{z1} + l_{z2} - l_{z3} - l_{z4}) + \frac{1}{\sqrt{2}}(-l_{y1} + l_{y2} - l_{y3} + l_{y4})$$
$$+ \frac{\cos\beta}{\sqrt{2}}(-l_{x1} + l_{x2} - l_{x3} + l_{x4}) \, ,$$

$$\Omega_Z^i = \cos\beta(l_{z1} - l_{z2} - l_{z3} + l_{z4}) + \sin\beta(l_{x1} + l_{x2} + l_{x3} + l_{x4}) \, .$$

A very important simplification of the perturbation scheme giving G_{11} has been studied in Ref. 27, where it has been demonstrated that if the states $^6T_1$ and $^4T_1$ of the multielectronic configurations with three open shells, such as $4t_2^2 2e^2 nt_2$; $4t_2^2 2e^2 t_1$; $4t_2^2 2e^2 ne$; $4t_2^3 2ent_2$; $4t_2^3 2et_1$, are degenerate, then their contribution to G_{11} is zero so that only the three states $^4T_1$ at lower energy corresponding to the configurations with two open shells $4t_2^4 2e$, $4t_2^3 2e^2$, and $4t_2^2 2e^3$ are to be considered.

By diagonalizing the matrix of Sugano, Tanabe, and Kamimura,[28] whose elements are calculated using the Racah parameters B,C and the cubic-field parameter Dq which fit observed energies of the states $^4T_1$ at lower energy, these states can be expressed as

$$|^4T_{1u}q\rangle = a_1^q|^4T_{1u}(4t_2^4 2e)\rangle + a_2^q|^4T_{1u}(4t_2^3 2e^2)\rangle$$
$$+ a_3^q|^4T_{1u}(4t_2^2 2e^3)\rangle \, ,$$

where $q = 1$, 2, or 3 refers to one of the three states $^4T_1$ and $u = x, y$, or z.

By defining the components of the relevant multiplets $^6A_1$ and $^4T_1$ in terms of the monoelectric molecular orbitals and writing the matrix elements of the total orbital momentum as

$$\tau_u(1) = i\langle ^6A_1|\tau_u|^4T_{1u}(4t_2^4 2e)\rangle \, ,$$

$$\tau_u(2) = i\langle ^6A_1|\tau_u|^4T_{1u}(4t_2^3 2e^2)\rangle \, ,$$

$$\tau_u(3) = i\langle ^6A_1|\tau_u|^4T_{1u}(4t_2^2 2e^3)\rangle \, ,$$

then ΔE is given by the expression

$$\Delta E = \frac{1}{5}(a_1^q + a_3^q)^2 \left\{ \frac{\tau_z(1)^2}{E_z^q} - \frac{\tau_y(1)^2}{E_y^q} \right\}$$
$$+ \frac{1}{5}(a_2^q)^2 \left\{ \frac{\tau_z(2)^2}{E_z^q} - \frac{\tau_y(2)^2}{E_y^q} \right\}$$
$$+ \frac{2}{5}a_2^q(a_1^q + a_3^q) \left\{ \frac{\tau_z(t)\tau_z(2)}{E_z^q} - \frac{\tau_y(1)\tau_y(2)}{E_y^q} \right\} \, ,$$

where

$$E_u^q = E(^4T_1^q) - E(^6A_1) \, ,$$

with $u = x, y$, or z.

IV. ANALYSIS OF STRAIN-DEPENDENT STATES AND OPERATORS

A. Contributions to ΔE linear in strain

In order to get a deeper insight into the physical origin of the SLCC's we will separate ΔE into terms ΔE_1 and ΔE_2 both linear in ε_{33}. ΔE_1 is the contribution to ΔE of the strain-induced variation of the monoelectronic molecular wave functions and the strain-induced variation of the molecular spin-orbit interaction, explicitly

$$\Delta E_1 = \sum_q \frac{2}{5E^q}\{(a_1^q + a_3^q)^2\tau(1)\Delta\tau(1) + (a_2^q)^2\tau(2)\Delta\tau(2)$$
$$+ a_2^q(a_1^q + a_3^q)[\tau(1)\Delta\tau(2) + \tau(2)\Delta\tau(1)]\} \, ,$$

with

$$\tau_{(j)} = \frac{1}{2}[\tau_z(j) + \tau_y(j)] \, ,$$

$$\Delta\tau(j) = [\tau_z(j) - \tau_y(j)] \, .$$

Of course the strain-induced variation of $\mathcal{H}_{SO}$ is due to strain-induced variation of the molecular orbital momentum Ω of the ligands which intervenes in the total molecular orbital momentum τ.

ΔE_2 is the contribution due to the strain-induced splitting of the states $^4T_1$. Explicitly we get

$$\Delta E_2 = \sum_q \frac{-3\Delta E^q}{10(E^q)^2}[(a_1^q + a_3^q)^2\tau(1)^2 + (a_2^q)^2\tau(2)^2$$
$$+ 2a_2^q(a_1^q + a_3^q)\tau(1)\tau(2)] \, ,$$

with

$$E^q = \frac{1}{3}(2E_y^q + E_z^q) \, ,$$

$$\Delta E^q = \Delta E_z^q = -2\Delta E_y^q \, .$$

B. Strain-induced variation of the monoelectronic molecular wave functions

Since our model (Fig. 3) involves only the three orbital triplet states $^4T_1$ at lower energy which are issued from the configurations $4t_2^4 2e$, $4t_2^3 2e^2$, and $4t_2^2 2e^3$, the matrix elements of the molecular spin-orbit interaction are nonzero for the electrons of the orbitals $4t_2$ and $2e$ only.
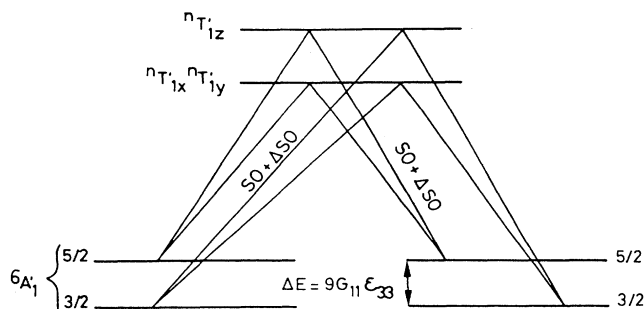
FIG. 3. Perturbation scheme for the SLCC's in symmetry D_{2d}. SO + ΔSO represent the molecular spin-orbit operator defined in Sec. III and calculated for symmetry D_{2d}. The relevant orbital triplet states $^nT_1$ are split by E_θ strains.

In symmetry D_{2d} the molecular orbitals $|nt'_2\gamma\rangle$ are

$$|nt'_2\gamma\rangle = a^d_{n\gamma}|dt_2\gamma\rangle + a^p_{n\gamma}|pt_2\gamma\rangle + a^{\sigma s}_{n\gamma}|\sigma st_2\gamma\rangle$$
$$+ a^{\sigma p}_{n\gamma}|\sigma pt_2\gamma\rangle + a^{\pi t_2}_{n\gamma}|\pi t_2\gamma\rangle + a^{\pi t_1}_{n\gamma}|\pi t_1\gamma\rangle ,$$

with $\gamma = \xi,\eta,\zeta$ for the states t_2 and $\gamma = x,y,z$ for the states t_1. $t_2\xi$, $t_2\eta$, t_1x, and t_1y correspond to the representation e of D_{2d} and $t_2\zeta,t_1z$ to the representations b_2 and b_1, respectively. Therefore, in symmetry D_{2d}, the states $t_2\xi$ and t_1x are mixed as well as the states $t_2\eta$ and t_1y. n refers to the filled levels when $n=1,2,3$, to the half-filled level when $n=4$, to the empty level when $n=5$, and to the nonbonding state t_1 in symmetry T_d when $n=6$.

By using a linear approximation to describe the strain-induced variations of the monoelectronic molecular wave functions in terms of strain of symmetry E_θ, the coefficients of the wave functions $4t_2$ can be written as

$$a^\Phi_\xi = a^\Phi_\eta = a^\Phi + \Delta a^\Phi ,$$
$$a^\Phi_\zeta = a^\Phi - 2\Delta a^\Phi ,$$

when $\Phi = d,p,\sigma s,\sigma p,\pi t_2$, and

$$a^{\pi t_1}_\xi = -a^{\pi t_1}_\eta = \Delta a^{\pi t_1} ,$$
$$a^{\pi t_1}_\zeta = \Delta a^{\pi t_1}_\zeta = 0 ,$$

when $\Phi = t_1$. The above coefficients a of the monoelectronic molecular wave functions $4t_2$ are obtained following the procedure given in Sec. II in symmetry T_d and the coefficients $a + \Delta a$ from the same procedure in symmetry D_{2d}.

In symmetry D_{2d}, the molecular orbitals $|je'\gamma\rangle$ are

$$|je'\Theta\rangle = b^d_{j\Theta}|de\Theta\rangle + b^\pi_{j\Theta}|\pi e\Theta\rangle + b^s_{j\Theta}|sa_1\rangle$$
$$+ b^{\sigma s}_{j\Theta}|\sigma sa_1\rangle + b^{\sigma p}_{j\Theta}|\sigma pa_1\rangle,$$

$$|je'\varepsilon\rangle = b^d_{j\varepsilon}|de\varepsilon\rangle + b^\pi_{j\varepsilon}|\pi e\varepsilon\rangle .$$

The index j refers to filled levels of symmetry e when $j=1$ and to the half-filled level when $j=2$; for $e'\Theta$, $j=3$ and 4 refer to the filled levels of symmetry a_1 in T_d and $j=5$ to the empty level of symmetry a_1.

In symmetry D_{2d}, the b's are of the form

$$b^\Phi_\theta = b^\Phi + \Delta b^\Phi ,$$
$$b^\Phi_\varepsilon = b^\Phi - \Delta b^\Phi ,$$

for $\Phi = d$ and π, and

$$b^\Phi_\theta = \Delta b^\Phi ,$$
$$b^\Phi_\varepsilon = \Delta b^\Phi_\varepsilon = 0$$

for $\Phi = s,\sigma s,\sigma p$. The b's are calculated following the procedure that gives the a's

C. Strain-induced variation of the molecular spin-orbit interaction

In our model which involves the states $^4T_1$ of the configuration with two open shells $4t_2$ and $2e$, the orbital components of the molecular spin-orbit interaction which intervene in ΔE_1 are given by

$$\tau(j) = \frac{i}{2}[\langle^6A_1|\tau_z|^4T_1\rangle + \langle^6A_1|\tau_y|^4T_1\rangle] ,$$

$$\tau(j) = i[\langle^6A_1|\tau_z|^4T_1\rangle - \langle^6A_1|\tau_y|^4T_1\rangle] ,$$

with

$$\tau(1) = -2a^db^d\zeta_M - (1/\sqrt{3})b^\pi[a^\pi + \sqrt{2}a^\sigma]\zeta_L ,$$

$$\tau(2) = \sqrt{2}[a^da^d - a^pa^p]\zeta_M + a^\pi[2a^\sigma - a^\pi/\sqrt{2}]\zeta_L ,$$

$$\Delta\tau(1) = 3[2b^d\Delta a^d + a^p\Delta b^p]\zeta_M$$
$$+ \sqrt{3}\,d\beta[a^\pi b^\pi/\sqrt{2} - a^\sigma b^\pi/2]\zeta_L$$
$$+ \sqrt{3}[a^\sigma\Delta b^\pi/\sqrt{2} + \sqrt{2}b^\pi\Delta a^\sigma$$
$$+ a^\pi\Delta b^\pi/2 + b^\pi\Delta a^\pi]\zeta_L ,$$

$$\Delta\tau(2) = 3\sqrt{2}[a^d\Delta a^d - a^p\Delta a^p]\zeta_M$$
$$+ 3\,d\beta[a^\pi a^\sigma/\sqrt{2} + a^\sigma a^\pi/2]\zeta_L$$
$$+ 3[a^\sigma\Delta a^\pi + a^\pi\Delta a^\sigma - a^\pi\Delta a^\pi/\sqrt{2}$$
$$- a^\sigma\Delta a^{\pi t_1}/\sqrt{3} - a^\pi\Delta a^{\pi t_1}/\sqrt{6}]\zeta_L ,$$

where $d\beta$ is the variation of the angle β (Fig. 2) giving the orientations of the local orbital angular momenta of the ligands and ζ_M and ζ_L are the spin-orbit coupling constants of the electrons $3d$ (and $4p$) of the metal and of the electrons np of the ligands, respectively.

These formulas show that ΔE_1 is the contribution due to (i) the variation of the components $3d$ and $3p$ of the metal and $np\sigma$, $np\pi$, and $np\pi t_1$ of the ligands for the monoelectronic molecular wave functions $4t_2(\xi,\eta,\zeta)$; (ii) the variation of the components $3d$ of the metal and $np\pi$ of the ligands for the nonoelectronic molecular wave functions $2e(\theta,\varepsilon)$; and (iii) the angular variation of the orientations of the local orbital angular momenta of the ligands. Numerical computations of these contributions are given in the next section.

V. RESULTS AND DISCUSSION

A. Computation of the SLCC's

The computation of the molecular orbitals was performed following the procedure given in Sec. II. The G_{11}'s were computed by using the following expressions for the spin-orbit coupling constants (in cm^{-1}) of the metal (ζ_M) and of the ligands (ζ_L):

$$\zeta_M(Mn) = 286 + 47(Q_M - 1) ,$$

$$\zeta_L(S) = 298 + 65(Q_L + 1) ,$$

$$\zeta_L(Se) = 1353 + 297(Q_L + 1) ,$$

$$\zeta_L(Te) = 3444 + 756(Q_L + 1) .$$

These formulas, which explicitly show the dependence of the spin-orbit coupling constants on the effective charge Q_M of the metal or Q_L of the ligands, were obtained by interpolating the spin-orbit coupling constants given by Blume and Watson[25] for various ionization states of the atoms. For Mn, the value $\zeta_M(Mn)$ was used both for the orbitals $3d$ and $4p$.

For ZnS:Mn the diagonalization of the matrix of Tanabe and Sugano was performed by using the sets $B = 730$ cm^{-1}, $C = 2880$ cm^{-1}, $Dq = -420$ cm^{-1},[29] and $B = 762$ cm^{-1}, $C = 2736$, cm^{-1}, $Dq = -440$ cm^{-1}.[30] For ZnSe:Mn we used the following values: $B = 740$ cm^{-1}, $C = 2740$ cm^{-1}, $Dq = -405$ cm^{-1},[30] and $B = 270$ cm^{-1} $C = 3740$ cm^{-1}, $Dq = -500$ cm^{-1}.[31] For ZnTe:Mn, absorption bands attributed to the levels $^4T_1$,[32] $^4T_2$,[33] and ^4E (Ref. 33) at lower energy have been observed at relatively high concentration in manganese. For CdTe:Mn, at high concentration in Mn, two absorption bands have been attributed to levels $^4T_1$ and $^4T_2$.[34-36] The Racah parameters for Mn in ZnTe and CdTe were chosen to be $B = 700$ cm^{-1} and $C = 2500$ cm^{-1}.

The values of the elastic stiffness constants used to calculate the C_{11}'s where those of Berlincourt, Jaffe, and Shiozawa[37] for ZnS, Lee[38] for ZnSe and ZnTe, and McSkimin and Thomas[39] for CdTe. The SLCC's of Mn^{2+} in ZnS, ZnSe, ZnTe, and CdTe have been computed for slightly varying values of the metal-ligand distance a, the Madelung constant C_{mad}, the effective charge Q_{lat} of the lattice and Q_M of the metal, and Dq. A slight increase of the value of the metal-ligand distance a has been allowed for ZnS, ZnSe, and ZnTe, while a slight decrease of the metal-ligand distance was considered for CdTe. For all compounds the values for the crystal electrostatic field due to distant neighbors (C_{mad}) were allowed to vary between 1.40 and 1.63. This variation corresponds in fact to a relatively small variation of the crystal electrostatic field of 7%.

The charges Q_{lat} of the lattice and the charges Q_M of the metal, as obtained from the self-consistent calculation of the charges, are between 0.7 and 0.9 for the lattice and between 0.74 and 1.32 for the metal. It can be remarked that the charges of the lattice are in good agreement with the values 0.91 for ZnS and 0.85 for ZnSe as obtained by Kunc from the rigid ion model.[40]

For ZnS and ZnSe, the calculated values of Dq are in

excellent agreement with the experimental values. For ZnTe and CdTe the computed Dq's are found to be approximately 300 cm^{-1}; the experimental values are not known.

The detailed contributions to C_{11} and G_{11} of the electrostatic field due to the ligands and the nearest neighbors of the ligands, the contribution of the ligand-ligand overlaps and the metal-ligand overlaps, and the contribution due to the strain-induced part of the molecular spin-orbit interaction have been computed. Except for CdTe, the contribution of the ligand-ligand overlap was found to be almost negligible with respect to the experimental values for C_{11} or G_{11}. The contribution of the metal-ligand overlap increases when passing from ZnS and ZnTe. A relatively large contribution is found for CdTe.

No simple variation of the electrostatic field and of the strain-induced part of the molecular spin-orbit interaction was found for the set ZnS, ZnSe, and ZnTe. However, for ZnS and ZnSe the contribution of the electrostatic field is partly compensated by the other contributions so that C_{11} is very sensitive to slight variations of the values of a, C_{mad}, and Q_{lat}.

For ZnS, by adding the relativistic contribution which is -2.1×10^{-8} cm/N for $Q_{lat} = 0.8$, we obtain theoretical values for C_{11} which vary from 0.85×10^{-8} to -2.16×10^{-8} cm/N. The experimental value is -0.5×10^{-8} cm/N.

For ZnSe, the relativistic contribution calculated for $Q_{lat} = 0.7$ is -2.1×10^{-8} cm/N so that the theoretical value for Q_{11} varies between 10.1×10^{-8} and 26.6×10^{-8} cm/N. The experimental value is 9.7×10^{-8} cm/N.

For ZnTe and CdTe, due to the very large value for the spin-orbit coupling constants of the ligands, C_{11} varies very fast when slightly varying the value for Q_{lat}. By choosing $Q_{lat} = 0.7$ for ZnTe and $Q_{lat} = 0.8$ for CdTe, the theoretical values for C_{11} are in good agreement with the experimental values.

B. Analysis in terms of the spin-orbit coupling constants of the metal and ligands

Since the SLCC's are correctly given by a second-order perturbation scheme involving twice the molecular spin-orbit interaction, these coefficients can be expressed in terms of the spin-orbit coupling constants of the electrons d of metal and electrons p of ligands as

$$C_{11} = \alpha \zeta_M^2 + \beta \zeta_L^2 + \gamma \zeta_L \zeta_M .$$

For ZnS, ZnSe, and ZnTe the term in ζ_M^2 is approximately equal to -5×10^{-8} cm/N. For CdTe this term is approximately equal to -10×10^{-8} cm/N. For all four compounds the term in $\beta \zeta_L^2$ is negative and its modulus increases rapidly when passing from ZnS to ZnSe, ZnTe, and CdTe. The term in $\gamma \zeta_L \zeta_M$ is positive and increases rapidly when passing from ZnS to ZnSe, ZnTe, and CdTe. Therefore the C_{11}'s are primarily given by two large contributions of opposite sign. While the quadratic and bilinear terms in ζ_M and ζ_L do not critically depend on the sets of constants a, C_{mad}, Q_L, and Q_M, the overall contribution to C_{11} is very sensitive to the values determined for these constants.

The variation of the parameters β and γ for the three compounds having the same cation have been represented in Fig. 4. Finally, it is shown in Fig. 5 that C_{11} almost linearly depends on ζ_L for $\zeta_L > 300 \text{ cm}^{-1}$.

C. Analysis of the strain-dependent molecular spin-orbit interaction and multielectronic orbital triplet states

In Sec. IV A, it was shown that G_{11} is given by

$$G_{11} = \frac{1}{9\varepsilon_{33}}(\Delta E_1 + \Delta E_2) .$$

For brevity ΔE_1 will be written as

$$\Delta E_1 = S_{11}K_{11} + S_{22}K_{22} + S_{12}K_{12} ,$$

with

$$S_{11} = 2\tau(1)\Delta\tau(1) ,$$

$$S_{22} = 2\tau(2)\Delta\tau(2) ,$$

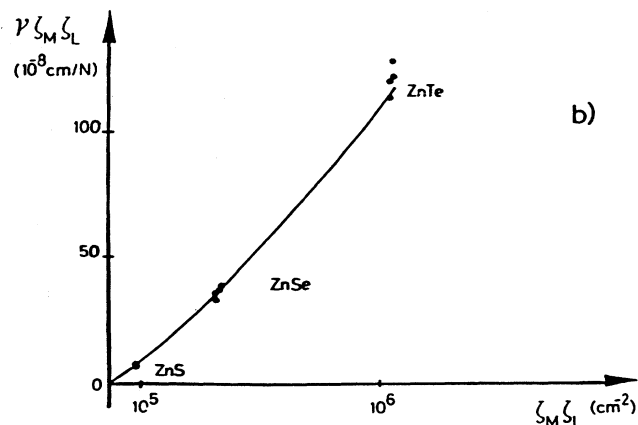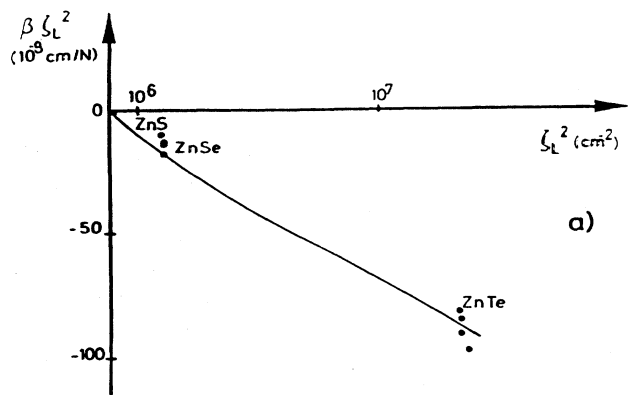$$S_{12} = \tau(1)\Delta\tau(2) + \tau(2)\Delta\tau(1) ,$$

and

FIG. 4. Contribution to C_{11} of the terms in ζ_L^2 and $\zeta_M\zeta_L$.
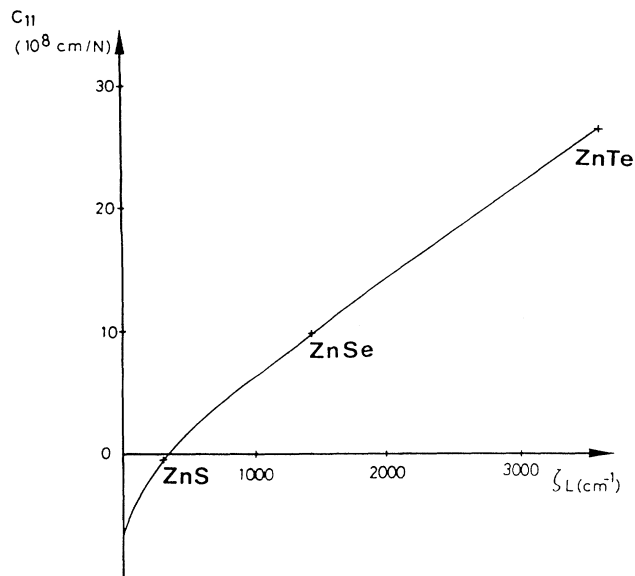
FIG. 5. Representation of the experimental values for C_{11} in terms of ζ_L.

$$K_{11} = \sum_q \frac{1}{5Eq}(a_1^q + a_3^q)^2 ,$$

$$K_{22} = \sum_q \frac{1}{5Eq}(a_2^q)^2 ,$$

$$K_{12} = \sum_q \frac{1}{5Eq}a_2^q(a_1^q + a_3^q) .$$

It is clear that the influence of the strain-dependent molecular spin-orbit interaction is described by the S's since $\tau(1)$ and $\tau(2)$ are, respectively, the matrix elements of the orbital molecular kinetic momentum between the fundamental state $^6A_1$ and the state $^4T_1$ of the configuration $4t_2^4 2e$ for $\tau(1)$ and the state $^4T_1$ of the configuration $4t_2^3 2e^2$ for $\tau(2)$. The $\Delta\tau$'s are the variations of the τ's due to a strain of symmetry E_θ.

The mixing parameters and the energies of the multielectronic orbital states $^4T_1$ as given by the diagonalization of the matrix of Tanabe and Sugano intervene in the K's, which are therefore functions of the reduced values B and C of the Racah parameters and of the cubic field parameter Dq.

Figure 6 represents $\tau(1)$ and $\tau(2)$ in terms of the spin-orbit coupling constants ζ_L of the ligands for ZnS, ZnSe, and ZnTe. It shows that $\tau(1)$ increases from -500 cm^{-1} for $\zeta_L = 0$ to approximately -200 cm^{-1} for $\zeta_L = 3600$ cm^{-1}, while $\tau(2)$ decreases from 380 cm^{-1} for $\zeta_L = 0$ to -1150 cm^{-1} for $\zeta_L = 3600 \text{ cm}^{-1}$. [We can remark that for $\zeta_L = 0$, the ratio $\tau(1)/\tau(2) = -b^d\sqrt{2}/a^d = -\sqrt{2}$.]

Except for ZnS, $\Delta\tau(2)$ was found to be negligible with respect to $\Delta\tau(1)$. $\Delta\tau(1)$ is represented in terms of ζ_L for ZnS, ZnSe, and ZnTe in Fig. 7.
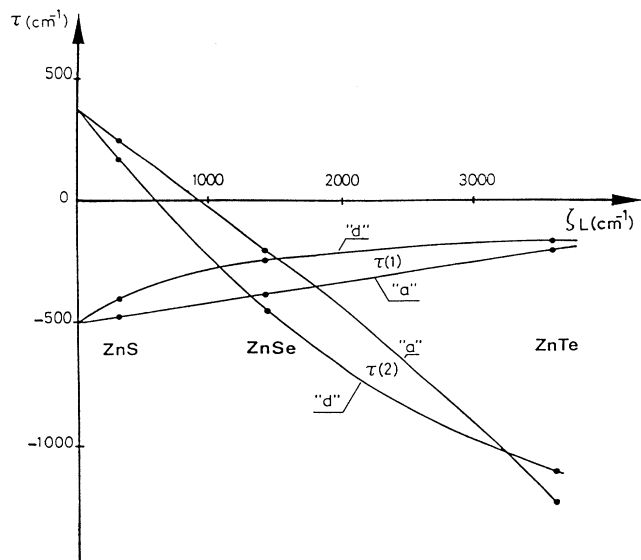
FIG. 6. Matrix elements $\tau(1)$ and $\tau(2)$ of the molecular spin-orbit interaction in terms of ζ_L. a and d indicate that the calculations were performed for two sets of values of the metal-ligand distance a, the energy of Madelung C_{mad}, the effective charge Q_{lat} of the lattice and Q_M of the metal, and Dq.

FIG. 7. Variation $\Delta\tau(1)$ of the matrix elements of the molecular spin-orbit operator due to a unit strain of symmetry E_θ.

D. Contributions of the strain-induced variations of the monoelectronic wave functions, of the energy levels, and of the molecular spin-orbit interaction

For the studied compounds, detailed computations have been performed of the contributions to C_{11} proportional to ζ_M^2, ζ_L^2, and $\zeta_M\zeta_L$ due to (i) the strain-induced variations of the wave functions Δt_2^d, Δ_e^d, and Δt_2^p of the metal; (ii) the strain-induced variations of the wave functions Δt_2^σ, Δt_2^π, Δt_1^π, and Δe^π of the ligands; (iii) the strain-induced splitting of the orbital triplet states $^4T_1$; and (iv) the strain-induced variation of the molecular spin-orbit coupling.

For ZnS, the contributions due to the variations of the wave functions of the metal, of the ligands, and of the molecular spin-orbit interaction are very roughly of the same order of magnitude. For ZnSe and ZnTe, the contribution due to the variation of the wave functions of the metal is negligible. For all compounds the contribution due to the variation of the wave function of the antibonding state t_1 is important, as well as the contribution due to the variation of the molecular spin-orbit interaction.

VI. CONCLUSION

By studying the SLCC's C_{11} of Mn^{2+} in the common metal series ZnS, ZnSe, and ZnTe, and also CdTe, it has been shown that the SLCC's primarily depend on the molecular spin-orbit interaction which involves the electrons p of the ligands as soon as the spin-orbit coupling
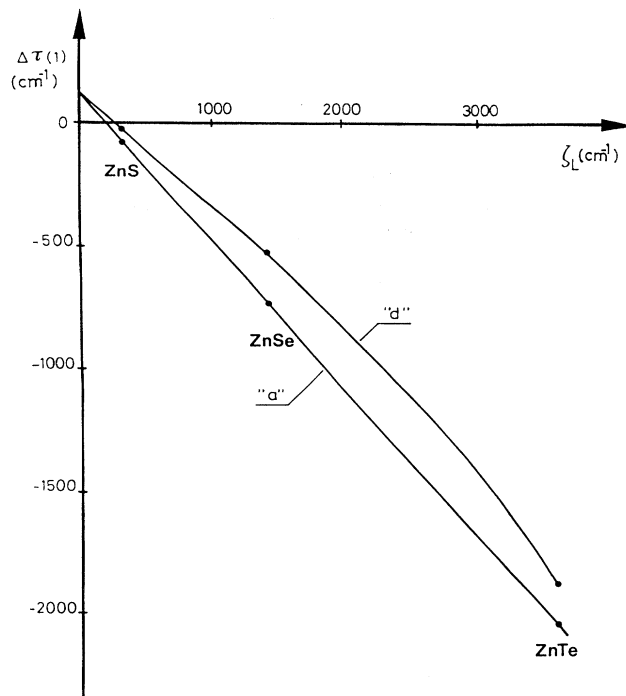
constant of the ligands is greater than the spin-orbit coupling constant of Mn^{2+}.

Second, it has been shown that the SLCC's C_{11} for ZnS, ZnSe, and ZnTe depend almost linearly on ζ_L when $\zeta_L > \zeta_M$. This linear dependence was not evident a priori since in our model the SLCC's are given by a second-order perturbation scheme involving twice the molecular spin-orbit interaction. The almost linear dependence on ζ_L is due to the fact that the terms in ζ_L^2 are partly compensated by the terms in $\zeta_M\zeta_L$ which are not linear in ζ_L. Therefore a simple phenomenological analysis of the experimental value for which the terms in ζ_M^2 would be (correctly) considered as constants and the terms in $\zeta_M\zeta_L$ as linear in ζ_L would underestimate these terms and overestimate the terms in ζ_L^2 at least for ZnTe.

More generally, this very detailed study of the molecular spin-orbit interaction indicates that the physical constants which depend on the spin-orbit interaction either to the first order or to higher orders in a perturbation scheme should be very sensitive to the spin-orbit interaction of the electrons of the ligands as soon as $\zeta_M < \zeta_L$.

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