PHYSICAL REVIEW B **74**, 155201 (2006)

Crystal-field theory of Co^{2+} in doped ZnO

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(Received 20 March 2006; revised manuscript received 7 July 2006; published 2 October 2006)

We present a crystal-field theory of transition-metal impurities in semiconductors in a trigonally distorted tetrahedral coordination. We develop a perturbative scheme to treat covalency effects within the weak ligand field case (Coulomb interaction dominates over one-particle splitting) and apply it to $ZnO:Co^{2+}$ ($3d^7$). Using the large value of the charge-transfer energy Δ_{pd} compared to the p-d hoppings, we perform a canonical transformation, which eliminates the coupling with ligands to first order. As a result, we obtain an effective single-ion Hamiltonian, where the influence of the ligands is reduced to the one-particle "crystal field" acting on d-like functions. This derivation allows us to elucidate the microscopic origin of various crystal field parameters and covalency reduction factors which are usually used empirically for the interpretation of optical and electron spin-resonance experiments. The connection of these parameters with the geometry of the local environment becomes transparent. The experimentally known g values and the zero-field splitting $2D$ are very well reproduced by the exact diagonalization of the effective single-ion Hamiltonian with only one adjustable parameter Δ_{pd}. Alternatively to the numerical diagonalization we use perturbation theory in the weak-field scheme (Coulomb interaction $\gg$ cubic splitting $\gg$ trigonal splitting and spin-orbit coupling) to derive compact analytical expressions for the spin-Hamiltonian parameters that reproduce the result of exact diagonalization within 20% of accuracy.

DOI: 10.1103/PhysRevB.74.155201 PACS number(s): 75.50.Pp, 75.10.Dg, 76.30.Fc

I. INTRODUCTION

The $A^{\mathrm{II}}B^{\mathrm{VI}}$ and $A^{\mathrm{III}}B^{\mathrm{V}}$ compounds with transition-metal impurities are called diluted magnetic semiconductors (DMS). These systems are interesting both from practical and fundamental points of view. Recently, they have attracted great interest as potential materials for spintronics, the current trend of electronics, which manipulates also the spin of the carrier, not only its charge. The challenge to physicists is the highly correlated subsystem of transition-metal ions (TMI) demonstrating the peculiar interplay of the covalency and of the localized nature of d electrons.

Usually, the results of optical and electron-spin-resonance (ESR) experiments are phenomenologically described[1–3] in terms of crystal-field (CF)[4–6] theory. It considers the one-site Hamiltonian for the d shell of TMI, where Coulomb interaction and spin-orbit (SO) coupling terms are added to a one-particle CF term of unspecified nature. The CF interpretation reflects the symmetry of a TMI environment, but the values of energetic parameters are taken from experiment, and thus, say nothing about the physical interactions behind them. It concerns not only the one-particle CF terms: phenomenological reduction factors for Racah's Coulomb parameters B and C, for the orbital angular momentu; and for the SO coupling are always introduced.

Within the phenomenological CF theory, the hierarchy of interactions is well established in most complexes containing the transition-metal ion surrounded by ligands. For commonly met octahedral and tetrahedral environments, the CF terms are divided into a large cubic part and much smaller low-symmetry terms. For the $3d$ ions the SO term is one or two orders of magnitude smaller than the cubic terms. To decide the order of the interaction strength between Coulomb forces and cubic CF is much more difficult. One distinguishes the "strong" and "weak" CF cases.[7] In the strong-field approach,[5] the cubic Hamiltonian is diagonalized first, and its eigenfunctions serve as a basis for the subsequent consideration of Coulomb and remaining terms. In the weak-field approach, the many-body eigenfunctions of the single-ion Hamiltonian are exposed to the action of CF.

The Hartree-Fock molecular orbital theory enables to take into account the covalency within the strong-field approach.[5] Then, in principle, the calculation of CF parameters becomes possible, the origin of the reduction factors becomes clear, and they can be estimated. We mention here the simple analytic approach proposed in Ref. 8 for the CF parameters calculation. It is based on Harrison's parametrization of the electronic structure of solids[9] and it enables to relate the CF parameters with the structure of the TMI environment.

In the weak-field case, the account of covalency involves the Heitler-London configuration interaction (CI) approach.[5] It is much more complicated as it works with the enlarged Hilbert space of many-body functions. In this way, the description of the DMS on the energy scale of the cubic splitting (~ 0.5 eV) was achieved,[10] but more fine properties (such as magnetic anisotropy) were not obtained, and the relation of the CI approach with the phenomenological CF theory was not established.

The $A^{\mathrm{II}}B^{\mathrm{VI}}$ semiconductors crystallize in zinc-blende or wurtzite structures. In both structures, the TMI substituting for the A site has similar tetrahedral coordination. The A site has cubic point symmetry in zinc-blende structure, and trigonal symmetry in wurtzite structure. In CF theory, the cubic field of the zinc-blende structure is described by one parameter Δ, and the trigonal field (wurtzite structure) by three parameters Δ, v, v'. The deviation from cubic symmetry in wurtzite structure, though small ($\Delta \gg v, v'$), has crucial influence on the magnetic properties of TMI. The Co^{2+} ion in a trigonally distorted environment displays a large single-ion magnetic anisotropy, which strongly affects the magnetic properties of Co-based DMS.[11] The anisotropy is linear in the trigonal field parameters v and v'. The empirical determination of v and v' is difficult and ambiguous. In optical transitions they are masked by a large Δ, and various sets give a similar description;[2,12] their relation with the TMI environment structure remains unclear. It is thus highly desirable to have a microscopic model that would at least diminish the number of adjustable parameters.

One microscopic model of CF is well known and was the first one that appeared with the CF concept itself. It is the point-charge model (PCM).[4] In this model, it is possible to calculate CF both in strong- and weak-field approaches, but the CF is then strongly underestimated because the hybridization with ligands is neglected. The authors of Ref. 14 have tried to improve the PCM and proposed to modify the TMI d function in such a way that it gives the correct value of Δ within the PCM. In fact, they changed one set of parameters (CF matrix elements) to another one (those describing their Slater-type d function). In order to explain the reduction factors, they additionally introduced phenomenologically the hybridization with ligands that changes the Coulomb and SO interactions but does not contribute to the CF splitting.

Nevertheless, at the present time, any modification of the PCM cannot be accepted as a physical model of the TMI in DMS. It is not adequate even for an isolated impurity, e.g., it cannot explain the increase of cubic splitting with the increase of covalency. Nor can it be the starting point for studies of the interaction of TMI with the host valence band (p-d exchange) and between the impurities (superexchange). Both phenomena are due to the virtual hoppings of electrons between ligand and TMI described by the p-d Hamiltonian.[10]

In this paper we establish the relation between the CI approach and the phenomenology of the CF. Below we will show that the many-body perturbation theory gives the possibility to consider the d-level splitting by covalency in the weak-field case at the same level of simplicity and physical transparency as for the pure electrostatic case (PCM). Our final goal is the derivation of the effective low-energy spin-Hamiltonian, i.e., an effective Hamiltonian that describes the ground-state manifold response to the applied magnetic field. We will demonstrate with an example for the $3d^7$ ion in tetrahedral coordination that spin Hamiltonian may be derived from realistic many-body Hamiltonian by means of a set of canonical transformations.

In a first step, one eliminates the coupling with ligands: i.e., we pass from realistic p-d Hamiltonian to CF-like Hamiltonian for d ion only (Sec. II A). We find a renormalization (i.e., reduction) of Coulomb and SO parameters (Sec. II B). We generalize the ideas of Ref. 8 and give the expressions for CF parameters via d-p hopping and charge transfer energy difference. It is important to note that these expressions give the connection of CF parameters with the structure of the TMI environment (Sec. III).

Having derived the parameters for the effective CF-like Hamiltonian in Sec. III, we calculate then in a second step the zero-field splitting $2D$ and the g factors, i.e., the parameters of the low-energy spin-Hamiltonian. The basis for the crystal-field Hamiltonian of a $3d^7$ configuration including SO coupling has 120 dimensions and will be diagonalized exactly (details are given in the Appendix). It follows that we do not have to worry about the weak-field hypothesis for this effective Hamiltonian: indeed this procedure is equally valid if cubic splitting Δ and Coulomb interaction parameters B and C would be of the same order.

On the other hand, in the given case of ZnO:Co, we can alternatively obtain an analytical closed expression which connects the parameters of the microscopic Hamiltonian with the parameters of the effective spin Hamiltonian. For that purpose we use perturbation theory in the spirit of the weak-field scheme. We construct the many-body basis for a d^7 ion (Sec. IV A) and make two subsequent transformations (Sec. IV B). The first one takes into account the fact that the cubic splitting is smaller than the remaining Coulomb interaction, and the second treats the trigonal coupling as a perturbation. In the final step we take into account spin-orbit coupling in order to obtain the spin Hamiltonian observed in ESR.

In Sec. V, we apply our approach to the case of ZnO:Co and we compare the numerical diagonalization results with the perturbative formula finding reasonable agreement. We compare also our parameter set, which was calculated microscopically with the phenomenological parameter sets derived before from optics and ESR.

II. MICROSCOPIC FOUNDATION OF CRYSTAL-FIELD THEORY

A. Crystal-field Hamiltonian

In this section we show that starting from realistic p-d Hamiltonian it is possible to derive an effective single-ion Hamiltonian. The latter has the form of a classical crystal-field Hamiltonian. The crystal-field parameters acquire a clear microscopic meaning and the essential property of being calculable and connected with the structure of the TMI surroundings. The main point is the large energy separation of configurations d^n and $d^{n+1}L$ (respectively, n electrons in the d shell of the TMI and $n+1$ d electrons plus one hole in the valence band), compared with the TMI-ligand hopping.[8]

The appropriate Hamiltonian should be written in the basis of spherically symmetric functions. The basis should not necessarily coincide with the one for free ions. A more contracted basis is suitable for solids, e.g., that one of the FPLO method.[15] Without specifying it, we will assume the existence of an orthonormal basis of one-particle spherically symmetric functions localized on lattice sites. We assume also that it is a minimal basis set, i.e., one radial function suffices for the description of one electronic shell. The existence of such a basis is not explicitly proved, but there are indirect evidences in favor of it. First, the FPLO method enables to explicitly construct nonorthogonal minimal basis of localized functions. Second, Harrison succeeded in describing the electronic structure of a huge number of compounds, assuming the existence of such a basis, and empirically fitting the Hamiltonian matrix elements in this basis.[9] The Hamiltonian may be written as

$$\hat{H} = \hat{H}_d + \hat{H}_p + \hat{T}_{pd}, \tag{1}$$

where $\hat{H}_d, \hat{H}_p$ are local Hamiltonians for the TMI and ligands, respectively, and $\hat{T}_{pd}$ describes electron hoppings between the TMI and ligands. In the superposition model,[17] the contributions of separate ligands are superimposed above each other. Further on, we will give a foundation for that rule, following the lines given in Ref. 8. So, it suffices to consider the ligand at the point $(0,0,R)$. Then, the generalization to another geometry is straightforward.

In the zero-order Hamiltonian we include the diagonal one-particle terms and dominant Coulomb interaction

$$\hat{H}_0 = \epsilon_d \hat{N}_d + \epsilon_p \hat{N}_p + \hat{U}_d + \hat{U}_p, \tag{2}$$

where

$$\hat{N}_l \equiv \sum_s \sum_{m=-l}^{l} \hat{n}_{m,s}, \quad \hat{n}_{m,s} = c^{\dagger}_{m,s} c_{m,s}, \quad \hat{U}_l = \frac{A_l}{2}(\hat{N}_l^2 - \hat{N}_l),$$

ϵ_d, ϵ_p are the one-particle energies of d and p states, A_d and A_p are the corresponding Racah's parameters; the operator $c^{\dagger}_{m,s} = d^{\dagger}_{m,s}(p^{\dagger}_{m,s})$ creates an electron with the one-particle basis $d(p)$ wave function with angular momentum and spin projections m and s on the TMI and on the ligand site, respectively. In the ground state of H_0, the d shell of the TMI contains n electrons and the ligand has the closed p shell with $n_p = 6$ electrons. The hopping Hamiltonian

$$\hat{T}_{pd} = \sum_s \sum_{m=-1}^{1} t_{pdm}(d^{\dagger}_{m,s} p_{m,s} + p^{\dagger}_{m,s} d_{m,s}) \tag{3}$$

couples configurations with different numbers of d electrons. The most important is the coupling between the configurations $d^n p^6$ and $d^{n+1} p^5$. The hybridization with the conduction band depends on a second-nearest-neighbor d-s hopping matrix element and may be neglected. In the two center approximations, the hopping $\hat{T}_{pd}$ [Eq. (3)] is diagonal over the angular-momentum projection indices m and m' due to the symmetry with respect to the TMI-ligand axis. We perform a canonical transformation, which eliminates the hopping to first order

$$\hat{H}_{\text{eff}} = \exp(-\hat{W}) \hat{H} \exp(\hat{W}) \approx \hat{H} + [\hat{H}, \hat{W}] + \frac{1}{2}[[\hat{H}, \hat{W}], \hat{W}]. \tag{4}$$

We choose for this the operator $\hat{W}$ in the form

$$\hat{W} = -\frac{1}{\Delta_{pd}} \sum_s \sum_{m=-1}^{1} t_{pdm}(d^{\dagger}_{m,s} p_{m,s} - p^{\dagger}_{m,s} d_{m,s}), \tag{5}$$

where

$$\Delta_{pd} = nA_d - (n_p - 1)A_p + \epsilon_d - \epsilon_p. \tag{6}$$

With this choice of Δ_{pd}, the coupling between the $d^n p^6$ and $d^{n+1} p^5$ configurations vanishes in the first-order operator $[\hat{H}_0, \hat{W}] + \hat{T}_{pd}$. Neglecting the coupling with the high-energy $d^{n+2} p^4$ configurations in the second-order operators

$$\frac{1}{2}[[\hat{H}_0, \hat{W}], \hat{W}] = \frac{1}{2} \sum_s \sum_{m=-1}^{1} \left\{ \left(\frac{t_{pdm}}{\Delta_{pd}} \right)^2 [p^{\dagger}_{m,s} \hat{\Delta} p_{m,s} - d^{\dagger}_{m,s} \hat{\Delta} d_{m,s}] + d^{\dagger}_{m,s} \left[\frac{t_{pdm}(A_d + A_p)}{\Delta_{pd}^2} \hat{T}_{pd} \right] p_{m,s} + \text{H.c.} \right\}, \tag{7}$$

$$[\hat{T}_{pd}, \hat{W}] = 2 \sum_s \sum_{m=-1}^{1} \frac{t_{pdm}^2}{\Delta_{pd}} (d^{\dagger}_{m,s} d_{m,s} - p^{\dagger}_{m,s} p_{m,s}), \tag{8}$$

where

$$\hat{\Delta} \equiv \epsilon_d - \epsilon_p + A_d \hat{N}_d - A_p \hat{N}_p,$$

we end with the effective Hamiltonian for the $d^n p^6$ configuration

$$\hat{H}_{\text{eff}} = \hat{H}_0 + \sum_s \sum_{m=-1}^{1} \frac{t_{pdm}^2}{\Delta_{pd}} (d^{\dagger}_{m,s} d_{m,s} - p^{\dagger}_{m,s} p_{m,s}) = \epsilon_d \hat{N}_d + \hat{U}_d + \hat{H}_{CF} + \text{const}, \tag{9}$$

with

$$\hat{H}_{CF} = \sum_s \sum_{m=-1}^{1} \frac{t_{pdm}^2}{\Delta_{pd}} d^{\dagger}_{m,s} d_{m,s}. \tag{10}$$

In the last equality of Eq. (9) we have taken advantage of the fact that every state of our subspace includes the nondegenerate closed p shell of ligand for which $\langle p^6 | p^{\dagger}_{m,s} p_{m',s} | p^6 \rangle = \delta_{m,m'}$ and all terms concerning the ligand become constant. We have obtained an effective single-ion Hamiltonian [Eq. (9)] where the action of ligand has been reduced to the one-particle crystal field term $\hat{H}_{CF}$ [Eq. (10)]. Let us recall that we have assumed that

$$t_{pdm} \ll \Delta_{pd}. \tag{11}$$

Within this assumption we may neglect the terms of third and higher orders in $\hat{H}_{\text{eff}}$ in Eq. (4). It is easy to see that the second-order contributions from separate ligands simply sum up when we do subsequent transformations to remove hopping to first order between the TMI and the different ligands of the nearest surroundings. Thus, assumption (11) gives the range of validity for the superposition model in our case. Our approach also implies that besides Eq. (11), the characteristic energies of the terms in $\hat{H}_d$ not included in H_0 in Eq. (2) are also smaller than Δ_{pd}. At first this concerns the Coulomb energies

$$15B \sim 3C \ll \Delta_{pd}. \tag{12}$$

The main point here is that in addition to the one-particle energy difference, Δ_{pd} contains also the largest Coulomb parameter A_d [see Eq. (18) below].

For the chosen axially symmetric geometry, the crystal field is diagonal with respect to the angular momentum projection m. For the general relative positions of TMI and ligands the $\hat{H}_{CF}$ will have the form[8]

$$\hat{H}_{CF} = \sum_{s} \sum_{m,m'=-2}^{2} V_{mm'} d^{\dagger}_{m,s} d_{m',s}, \tag{13}$$

$$V_{mm'} = \sum_{i} \{ b_4(R_i) A_{mm'} Y_4^{m-m'}(\theta_i,\phi_i) + b_2(R_i) B_{mm'} Y_2^{m-m'}(\theta_i,\phi_i) + b_0(R_i)\delta_{mm'} \}, \tag{14}$$

where

$$A_{mm'} = (-1)^{m'} \frac{5\sqrt{4\pi}}{27} C^{224}_{-m'm} C^{224}_{00},$$

$$B_{mm'} = (-1)^{m'} \frac{\sqrt{4\pi}}{5} C^{222}_{-m'm} C^{222}_{00},$$

the $C^{j_1j_2J}_{m_1m_2} = \langle j_1 j_2 m_1 m_2 | JM = m_1 + m_2 \rangle$ are the Clebsch-Gordan coefficients (see, e.g., Refs. 3 and 16) and the Y_l^m are the spherical harmonics. The coefficients

$$b_k(R_i) = \frac{2k+1}{5} \left\{ \frac{t^2_{pd\sigma}}{\Delta_{pd}} + \left[2 - \frac{k(k+1)}{6} \right] \frac{t^2_{pd\pi}}{\Delta_{pd}} \right\}, \tag{15}$$

depend only on the nature of ligand and TMI and on the distance between them; the standard notations $m = \sigma, \pi$ in Eq. (15) correspond to $m = 0, \pm 1$, respectively. The summation in Eq. (14) goes over the ligand spherical coordinates R_i, θ_i, ϕ_i. In the spirit of the superposition model,[17] the physical and geometrical information is separated in Eq. (14). Note that in the general case the summation in Eq. (13) runs over all d states.

The idea to use Harrison's parametrization for the calculation of hybridization contribution to CF and to Eq. (15) was first proposed in Ref. 8 from perturbative approximate diagonalization of the *mean-field one-particle part* of the p-d Hamiltonian. In this scheme the Δ_{pd} has the meaning of the Hartree-Fock energies difference

$$\Delta_{pd,HF} = \varepsilon_{d,HF} - \varepsilon_{p,HF}, \tag{16}$$

$$\varepsilon_{l,HF} = \epsilon_l + A_l(n_l - 1). \tag{17}$$

In this sense the approach of Ref. 8 is close to the strong CF scheme.

In the spirit of the strong CF scheme, another approach was developed in Ref. 18. There, the Coulomb electron-electron interaction is taken into account *after* the diagonalization of the one-particle mean-field Hamiltonian. It is thus rewritten in terms of eigenfunctions of cubic CF. The applicability of Racah's parametrization of Coulomb integrals is then questioned. In DMS, the strong CF scheme fails. It is unable to explain the position of the incomplete d shell below the Fermi level, because the mean-field neglects the configuration interaction. The weak CF scheme is free from such difficulties and our considerations show the way to account for covalency in this scheme. Concluding this remark, let us mention that comparing Eqs. (6), (16), and (17) we see that

$$\Delta_{pd} = \Delta_{pd,HF} + A_d. \tag{18}$$

This relation explains why the TMI d level having the Hartree-Fock mean-field energy lower than the ligand p level (e.g., $\varepsilon_{d,HF} = -17.77$ eV for Co is lower than $\varepsilon_{p,HF} = -16.77$ eV for oxygen[9]) remains incompletely filled. As we mentioned in the Introduction, the difference between strong and weak CF schemes reflects the difference of Hartree-Fock and Heitler-London ways of accounting for the covalency, our consideration being close to the Heitler-London approach.

B. Renormalization of Coulomb, spin-orbit, and Zeeman terms

In the phenomenological CF theory, the covalency is accounted for by the introduction of reduction factors for Racah's parameters B, C and for orbital angular-momentum matrix elements. The orbital moment appears in the spin-orbit interaction $\hat{H}_{SO}$ and in the Zeeman term

$$\hat{H}_Z = \mu_B (g_s \hat{\mathbf{S}} + \hat{\mathbf{L}}) \mathbf{B}, \tag{19}$$

where $g_s = 2.0023$ is the Landé's factor and μ_B is the Bohr's magneton.

The canonical transformation [Eq. (4)] changes the many-body basis of the problem. For the sake of consistency we should transform every additional term of the Hamiltonian as well as any observable. The covalency reduction factors naturally occur as a result of the canonical transformation of the corresponding operators. The total spin operator $\hat{\mathbf{S}}$ commutes with the canonical transformation operator $\hat{W}$ [Eq. (5)] and remains unchanged. Let us now demonstrate the appearance of an orbital reduction factor k ($\hat{L} \to k\hat{L}$, $k < 1$) for the spin-orbit term. We begin with the canonical transformation of annihilation operators and with the ligand situated at $(0,0,R)$,

$$\tilde{d}_{m,s} \approx d_{m,s} + [d_{m,s}, \hat{W}] + \frac{1}{2}[[d_{m,s}, \hat{W}], \hat{W}] = \left(1 - \frac{1}{2}\lambda_m^2\right) d_{m,s} - \lambda_m p_{m,s},$$

$$\tilde{p}_{m,s} \approx \left(1 - \frac{1}{2}\lambda_m^2\right) p_{m,s} + \lambda_m d_{m,s}, \tag{20}$$

where $\lambda_m = t_{pdm}/\Delta_{pd}$. The apparent similarity of Eqs. (20) with a molecular-orbital expression should not mislead the reader. We recall that it works only in the subspace of $d^n p^6$ and $d^{n+1} p^5$ configurations and Δ_{pd} [Eq. (6)] depends on the number of d and p electrons n, n_p.

Substituting the transformed annihilation and creation operators into the second quantization expression for an operator, we immediately obtain its transformed version. The spin-orbit operator acquires the form

$$\begin{aligned}\hat{H}_{SO} &= \frac{\xi_{d,0}}{2}\sum_{m,m',s,s'}\tilde{d}^{\dagger}_{m,s}\mathbf{L}^{d}_{m,m'}\boldsymbol{\sigma}_{s,s'}\tilde{d}_{m',s'}\\ &\quad+\frac{\xi_{p,0}}{2}\sum_{m,m',s,s'}\tilde{p}^{\dagger}_{m,s}\mathbf{L}^{p}_{m,m'}\boldsymbol{\sigma}_{s,s'}\tilde{p}_{m',s'}\\ &\approx\frac{\xi_{d,0}}{2}\sum_{m,m',s,s'}\left(1-\frac{1}{2}\lambda_m^2\right)d^{\dagger}_{m,s}\mathbf{L}^{d}_{m,m'}\\ &\quad\times\boldsymbol{\sigma}_{s,s'}\left(1-\frac{1}{2}\lambda_{m'}^2\right)d_{m',s'}\\ &\quad+\frac{\xi_{p,0}}{2}\sum_{s,s'}\sum_{m,m'=-1}^{1}\lambda_m\lambda_{m'}d^{\dagger}_{m,s}\mathbf{L}^{p}_{m,m'}\boldsymbol{\sigma}_{s,s'}d_{m',s'},\end{aligned}\tag{21}$$

where $\mathbf{L}^{p(d)}_{m,m'}$ is the angular-momentum matrix vector for a $L=2(d)$ or $L=1(p)$ particle; $\boldsymbol{\sigma}$ is the Pauli matrix vector. The spin-orbit coupling value $\xi_{d(p),0}$ is the free-ion (ligand) one (see below). For the light ligands (e.g., oxygen) $\xi_{p,0} \ll \xi_{d,0}$, and this term is usually neglected.

For the ligand situated in the point with spherical coordinates (φ,θ,R) in crystallographic coordinates, we should first go to the local coordinate system $X'Y'Z'$ with the Z' axis pointing towards the ligand. The rotation is described by three Euler angles $\{\alpha=\varphi,\ \beta=\theta,\ \gamma=0\}$ and the operators in the two systems are related by the linear transformation

$$d'_{m,s}=\sum_{m_1}D_{m_1,m}(\alpha,\beta,\gamma)d_{m_1,s}.\tag{22}$$

The matrices $D_{m_1,m}(\alpha,\beta,\gamma)=R^{(2)}_{m_1,m}(\alpha,\beta,\gamma)$ describe the transformation of spherical harmonics between two coordinate systems.[16] After a canonical transformation in the local coordinate system according to Eqs. (20), we perform a backward rotation and obtain

$$\begin{aligned}\tilde{d}_{m,s}&=\sum_{m_1}D_{m_1,m}(0,-\theta,-\varphi)\tilde{d}'_{m_1,s}=d_{m,s}+\sum_{m_1}D_{m_1,m}(0,-\theta,-\varphi)\\ &\quad\times\left[-\lambda_{m_1}p_{m_1,s}-\frac{\lambda^2_{m_1}}{2}\sum_{m_2}D_{m_2,m_1}(\varphi,\theta,0)d_{m_2,s}\right].\end{aligned}\tag{23}$$

The summation over all ligands will give the final expression for $\tilde{d}_{m,s}$. Generally it is very complicated, but for highly symmetric surroundings, it recovers a form similar to Eq. (20). For example, for the tetrahedrally coordinated TMI we have

$$\begin{aligned}\tilde{d}_{t_{2g},s}&=\left(1-\frac{2}{3}\lambda_\sigma^2-\frac{4}{9}\lambda_\pi^2\right)d_{t_{2g},s}-\sqrt{\frac{4}{3}\lambda_\sigma^2-\frac{8}{9}\lambda_\pi^2}\,p_{t_{2g},s},\\ \tilde{d}_{e_g,s}&=\left(1-\frac{4}{3}\lambda_\pi^2\right)d_{e_g,s}-\frac{2\sqrt{6}}{3}\lambda_\pi p_{e_g,s},\end{aligned}\tag{24}$$

where the operator $d_{\Gamma,s}$ annihilates the electron in the state which transforms according to the irreducible representation $\Gamma=e_g,t_{2g}$; $m=\sigma,\pi$ again means $m=0,\pm 1$. Instead of operators $p_{m,s}$, an admixture of symmetric combinations of ligand orbitals enters Eqs. (24).

TABLE I. Cartesian coordinates of the CoO$_4$ tetrahedron using the lattice parameters a=3.2427 Å, c=5.1948 Å, and δ=0.0076 of the host lattice ZnO (Ref. 19).

	x/a	y/a	z/c
Co	0	0	0
O$_1$	$\frac{1}{\sqrt{3}}$	0	$-\frac{1}{8}+\delta$
O$_2$	$-\frac{1}{2\sqrt{3}}$	$\frac{1}{2}$	$-\frac{1}{8}+\delta$
O$_3$	$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2}$	$-\frac{1}{8}+\delta$
O$_4$	0	0	$\frac{3}{8}+\delta$

In the ground state of the tetrahedrally coordinated d^7 ion, the t_{2g} states are filled (by holes) and only the nondiagonal matrix element of angular momentum $\langle t_{2g}|\hat{L}|e_g\rangle$ enters the expression of the spin-Hamiltonian parameters. It means that we may substitute

$$\hat{L}\rightarrow k\hat{L},\tag{25}$$

$$k=\left(1-\tfrac{2}{3}\lambda_\sigma^2-\tfrac{4}{9}\lambda_\pi^2\right)\left(1-\tfrac{4}{3}\lambda_\pi^2\right)\approx\left(1-\tfrac{2}{3}\lambda_\sigma^2-\tfrac{16}{9}\lambda_\pi^2\right),\tag{26}$$

in the Zeeman term (19) and

$$\xi_{d,0}\rightarrow\xi_d=k\xi_{d,0},\tag{27}$$

in the spin-orbit term.

The matrix elements of the Coulomb interaction that were not included in H_0 [Eq. (2)] acquire prefactors that are the product of four terms $\left(1-\frac{1}{2}\lambda_m^2\right)$. Therefore, the reduction factors for the Coulomb interaction may differ from those of SO and angular-momentum terms. Nevertheless, an approximate estimate may be done by multiplying the free-ion Racah's parameters B_0 and C_0 with k^2 from Eq. (26), i.e.,

$$B_0\rightarrow B=k^2B_0,\quad C_0\rightarrow C=k^2C_0.\tag{28}$$

Such an approach is completely sufficient for the given case of ZnO:Co since the lowest ^4F multiplet is well separated from the higher multiplets and, correspondingly, the parameters of the effective spin-Hamiltonian (g factors and zero-field splitting) are not very sensitive to B and C (see Sec. V below).

III. CRYSTAL-FIELD THEORY FOR THE TETRAHEDRALLY COORDINATED d^7 ION

The effective single-ion Hamiltonian derived in the previous sections reads

$$\hat{H}_{\text{eff}}=\hat{H}_{\text{Coul}}+\hat{H}_{CF}+\hat{H}_{SO}+\hat{H}_Z.\tag{29}$$

The Coulomb interaction within the d shell $\hat{H}_{\text{Coul}}$ will not be written down explicitly since it is diagonal in the many-body basis corresponding to the weak-field scheme. In our approach, the CF parameters are connected with the local environment of the TMI (see Table I and Fig. 1 for the ZnO:Co example).

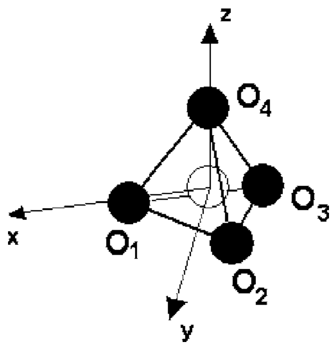

FIG. 1. CoO_4 tetrahedron.

It is convenient to choose the zero of energy from the condition Tr $V_{m,m'}=5\Sigma_i b_0(R_i)=0$. The term $\hat{H}_{CF}$ in Eq. (13) may be split into cubic and trigonal parts,

$$\hat{H}_{CF}=\hat{H}_{\text{cub}}+\hat{H}_{\text{trig}}, \tag{30}$$

since the ideal tetrahedron with $\frac{c}{a}=\sqrt{\frac{8}{3}}$ and $\delta=0$ is identical to cubic symmetry. In reality, however, $\frac{c}{a}$ deviates from the ideal value and $\delta\neq 0$. The trigonal field is described by three parameters. There exist several different systems of notation in the literature and we will use here the parameters Δ, v, and v' like Koidl[2] and MacFarlane[12] (see also Ref. 13). They are defined as a parametrization of the crystal-field matrix elements $V_{mm'}$ [Eq. (13)] in the one-particle basis of the trigonal coordinate system (the z axis is the threefold axis pointing towards O_4),

$$|x\rangle=\sqrt{\frac{2}{3}}|x^2-y^2\rangle-\sqrt{\frac{1}{3}}|zx\rangle,$$

$$|y\rangle=-\sqrt{\frac{2}{3}}|xy\rangle-\sqrt{\frac{1}{3}}|zy\rangle,$$

$$|z\rangle=|z^2\rangle,$$

$$|v\rangle=\sqrt{\frac{1}{3}}|x^2-y^2\rangle+\sqrt{\frac{2}{3}}|zx\rangle,$$

$$|w\rangle=-\sqrt{\frac{1}{3}}|xy\rangle+\sqrt{\frac{2}{3}}|zy\rangle, \tag{31}$$

where we have the usual real d-basis functions constructed out of the complex basis functions $|l\rangle=d^{+}_{l\sigma}|0\rangle$ on the right-hand side. The three basis functions $|x\rangle$, $|y\rangle$, and $|z\rangle$ build up the t_{2g} representation of the cubic group and $|v\rangle$, $|w\rangle$ span up the e_g subspace. The one-particle crystal-field matrix elements are given in this basis by

$$V_{zz}=\frac{2}{5}\Delta-\frac{2v}{3},$$

$$V_{xx}=V_{yy}=\frac{2}{5}\Delta+\frac{v}{3},$$

$$V_{vv}=V_{ww}=-\frac{3}{5}\Delta,$$

$$V_{xv}=v'. \tag{32}$$

The relationship between the Δ, v, and v' parameters with the Stevens equivalent operators and other parametrizations used in the literature can be found in the Appendix.

If we substitute the ligand coordinates from Table I into $V_{mm'}$ in Eq. (14) and then transform them into the trigonal crystal-field parameters, we obtain

$$\Delta=-\frac{5}{27}\left\{b_4(R_1)\frac{72(z_1^2a^2-z_1^4)-3a^4+20\sqrt{6}z_1a^3}{24R_1^4}-b_4(R_4)\right\},$$

$$v=\frac{b_4(R_1)}{9R_1^4}\left\{\frac{20}{7}\left[3(z_1^2a^2-z_1^4)-\frac{a^4}{8}\right]-\frac{5\sqrt{6}z_1a^3}{6}\right\}-\frac{20}{63}b_4(R_4)$$
$$-\frac{3}{14}\left[b_2(R_1)\frac{6z_1^2-a^2}{R_1^2}+2b_2(R_4)\right],$$

$$v'=\frac{5b_4(R_1)}{9R_1^4}\left\{\frac{\sqrt{2}}{7}\left[3(z_1^2a^2-z_1^4)-\frac{a^4}{8}\right]-\frac{\sqrt{3}z_1a^3}{12}\right\}$$
$$-\frac{\sqrt{2}}{9}b_4(R_4)+\frac{\sqrt{2}}{14}\left[b_2(R_1)\frac{6z_1^2-a^2}{R_1^2}+2b_2(R_4)\right], \tag{33}$$

where z_i is the z coordinate of the ligand O_i; $R_1=\sqrt{a^2/3+z_1^2}$, $R_4=z_4$ are the corresponding distances.

The importance of the nondiagonal matrix element between e_g and t_{2g} states, v', was first pointed out in Refs. 12 and 20 and will be outlined in the following, but it was not thoroughly treated in the standard textbooks.[3] Hopping integrals t_{pdm} have been calculated from Harrison's table.[9] Then all the CF parameters depend only on one value: Δ_{pd}. Its determination is complicated by the fact that the Coulomb repulsion A_d is partially screened in semiconductors and it differs much more from free-ion value than B and C. That is the reason why we have used Δ_{pd} as an adjustable parameter. After the determination of its value from experimental knowledge of cubic parameter Δ, the other parameters v and v' are determined by geometry.

For the spin-orbit and Zeeman terms we have

$$\hat{H}_{SO}=\frac{\xi_d}{2}\sum_{m,m',s,s'}d^{\dagger}_{m,s}\mathbf{L}_{m,m'}\boldsymbol{\sigma}_{s,s'}d_{m',s'}, \tag{34}$$

$$\hat{H}_Z=\mu_B(g_s\hat{\mathbf{S}}+k\hat{\mathbf{L}})\mathbf{B}. \tag{35}$$

Here ξ_d is the renormalized spin-orbit coupling and k is approximately given by Eq. (26); $\hat{\mathbf{S}}$ and $\hat{\mathbf{L}}$ are, respectively, the total spin and orbital angular-momentum operators. Within the ^4F term, H_{SO} may be rewritten as

$$\hat{H}_{SO,^4F}=\lambda\hat{\mathbf{S}}\hat{\mathbf{L}} \quad \text{with } \lambda=-\xi_d/3. \tag{36}$$

IV. SPIN HAMILTONIAN FOR THE GROUND-STATE MANIFOLD

As it was already noted in the Introduction, this second step of our calculation can be performed exactly by numerical diagonalization of the effective single-ion Hamiltonian (29) once we have determined all its parameters (see the Appendix). In that sense it is not restricted to the weak-field case. In addition to the numerical diagonalization, we derive below an analytic perturbative formula, which is valid in the weak-field case of ZnO:Co.

A. Many-body basis

For a while let us neglect the spin-orbit coupling. Then the total spin S and total angular momentum L are conserved, because Coulomb interaction is rotationally invariant and does not depend on spin. The ground state for seven d electrons (three holes) is $|^4F\rangle$ with $L=3$, $S=3/2$ and it is $(2L+1)(2S+1)=28$-fold degenerate. The eigenfunctions are $|L,M,m_s\rangle$, M being the momentum projection on z axis and m_s being the total spin projection. For $M=3$ and $m_s=\frac{3}{2}$ we have

$$\left|3,3,\frac{3}{2}\right\rangle = d_{0\uparrow}^{\dagger}d_{1\uparrow}^{\dagger}d_{2\uparrow}^{\dagger}|\text{vac}\rangle.$$

Acting on this state by the $\hat{L}_-$ operator we obtain successively

$$\left|3,2,\frac{3}{2}\right\rangle = d_{-1\uparrow}^{\dagger}d_{1\uparrow}^{\dagger}d_{2\uparrow}^{\dagger}|\text{vac}\rangle,$$

$$\left|3,1,\frac{3}{2}\right\rangle = \left(\sqrt{\frac{2}{5}}d_{-2\uparrow}^{\dagger}d_{1\uparrow}^{\dagger}d_{2\uparrow}^{\dagger} + \sqrt{\frac{3}{5}}d_{-1\uparrow}^{\dagger}d_{0\uparrow}^{\dagger}d_{2\uparrow}^{\dagger}\right)|\text{vac}\rangle,$$

$$\left|3,0,\frac{3}{2}\right\rangle = \sqrt{\frac{1}{5}}(2d_{-2\uparrow}^{\dagger}d_{0\uparrow}^{\dagger}d_{2\uparrow}^{\dagger} + d_{-1\uparrow}^{\dagger}d_{0\uparrow}^{\dagger}d_{1\uparrow}^{\dagger})|\text{vac}\rangle, \text{ etc.}$$

Under the action of cubic crystal field this level splits into one singlet and two triplets. Then the basis functions may be labeled as $|3,\chi,\tilde{m},m_s\rangle$, where $\chi=A_2,T_2,T_1$ denotes the representation of the cubic group and $\tilde{m}$ is the projection of a fictive angular momentum within each manifold. We have

$$|3,A_2,0,m_s\rangle = -\frac{\sqrt{5}}{3}|3,0,m_s\rangle + \frac{\sqrt{2}}{3}(|3,3,m_s\rangle - |3,-3,m_s\rangle),$$

$$|3,T_2,\pm 1,m_s\rangle = \frac{1}{\sqrt{6}}|3,\mp 2,m_s\rangle \pm \sqrt{\frac{5}{6}}|3,\pm 1,m_s\rangle,$$

$$|3,T_2,0,m_s\rangle = \frac{1}{\sqrt{2}}(|3,3,m_s\rangle + |3,-3,m_s\rangle),$$

$$|3,T_1,\pm 1,m_s\rangle = \mp\sqrt{\frac{5}{6}}|3,\mp 2,m_s\rangle + \frac{1}{\sqrt{6}}|3,\pm 1,m_s\rangle,$$

$$|3,T_1,0,m_s\rangle = -\frac{2}{3}|3,0,m_s\rangle - \frac{1}{3}\sqrt{\frac{5}{2}}(|3,3,m_s\rangle - |3,-3,m_s\rangle). \qquad (37)$$

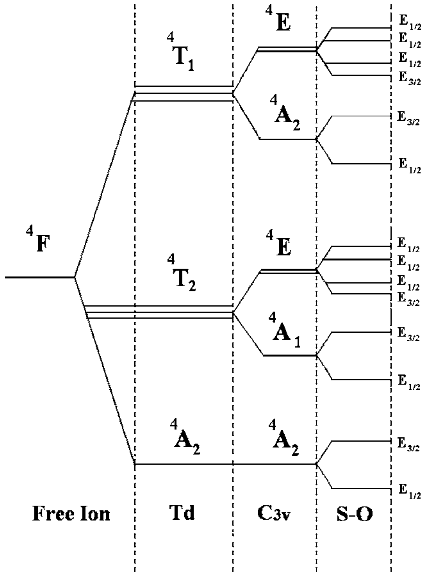

FIG. 2. Qualitative splitting due to the cubic field, followed by the trigonal crystal field and by the SO effect.

The trigonal field splits the triplets into doublets and singlets and also couples the states of different manifolds with equal $\tilde{m}$. This is schematically shown in Fig. 2. The lowest excited level is ^4P with $L=1$, $S=3/2$,

$$\left|1,1,\frac{3}{2}\right\rangle = \left(\sqrt{\frac{3}{5}}d_{-2\uparrow}^{\dagger}d_{1\uparrow}^{\dagger}d_{2\uparrow}^{\dagger} - \sqrt{\frac{2}{5}}d_{-1\uparrow}^{\dagger}d_{0\uparrow}^{\dagger}d_{2\uparrow}^{\dagger}\right)|\text{vac}\rangle,$$

$$\left|1,0,\frac{3}{2}\right\rangle = \sqrt{\frac{1}{5}}(d_{-2\uparrow}^{\dagger}d_{0\uparrow}^{\dagger}d_{2\uparrow}^{\dagger} - 2d_{-1\uparrow}^{\dagger}d_{0\uparrow}^{\dagger}d_{1\uparrow}^{\dagger})|\text{vac}\rangle, \text{ etc.}$$

In the free ion it is separated by energy $15B$ from the ground state. The cubic field couples the states $|1,M,m_s\rangle$ and $|3,T_1,\tilde{m},m_s\rangle$ with $\tilde{m}=M$. The trigonal field also has matrix elements between $|3,A_2,\tilde{m},m_s\rangle$, $|3,T_2,\tilde{m},m_s\rangle$, and $|1,\tilde{m},m_s\rangle$ states that are proportional to v and v', thus they are much smaller.

B. Perturbation theory

From the parameter values discussed below, it will become clear that we are in the regime where $15B \gg \Delta \gg v, v', \lambda$. In the strong cubic crystal-field case (i.e., when $\Delta \gg 15B$) a perturbative formula for zero-field splitting $2D$ and the gyromagnetic factors $g_{\parallel}$ and $g_{\perp}$ was developed by MacFarlane.[12,20] But it is not adequate in the present situation. Now, we can define four small values $\frac{\Delta}{(15B)}$, $\frac{v}{\Delta} \sim \frac{v'}{\Delta} \sim \frac{\lambda}{\Delta}$. In fact, we have $15B \gg \Delta$, and the value $\Delta/15B$ being almost of the same order of magnitude as v/Δ, then the ratio

$$\frac{\upsilon}{15B} = \frac{\upsilon}{\Delta}\frac{\Delta}{15B}$$

can be considered as an order of magnitude smaller than $\Delta/15B$. This justifies the application of the weak crystal-field approach.

We will proceed in three steps that may be regarded as three subsequent canonical transformations of our Hamiltonian similar to Eq. (4). First, we eliminate the coupling with ${}^4P$ states retaining only the order $\Delta/15B$ (the explicit use of a weak CF scheme). Then only the states $|3,T_1,\tilde{m},m_s\rangle$ acquire an admixture

$$|T_1,\tilde{m},m_s\rangle = |3,T_1,\tilde{m},m_s\rangle + \frac{\langle 1,\tilde{m},m_s|\hat{H}_{CF}|3,T_1,\tilde{m},m_s\rangle}{(E_{T_1 0} - E_{P0})}|1,\tilde{m},m_s\rangle, \quad (38)$$

where

$$\frac{\langle 1,\tilde{m},m_s|\hat{H}_{CF}|3,T_1,\tilde{m},m_s\rangle}{(E_{T_1 0} - E_{P0})} \simeq \frac{2}{5}\frac{\Delta}{15B} \equiv \kappa_P.$$

We thus obtain an effective Hamiltonian acting in the ${}^4F$ subspace. In the next step we consider the perturbation due to the trigonal field with the small parameters $\frac{\upsilon}{\Delta}$ and $\frac{\upsilon'}{\Delta}$. In the following we will use the first-order ground-state wave function of the approximately diagonal crystal-field Hamiltonian,[21] i.e.,

$$|\psi_0\rangle = |A_2,0,m_s\rangle \approx |3,A_2,0,m_s\rangle - \kappa_0|T_1,0,m_s\rangle, \quad (39)$$

as well as the excited states

$$|T_2,0,m_s\rangle \approx |3,T_2,0,m_s\rangle,$$

$$|T_2,\pm 1,m_s\rangle \approx |3,T_2,\pm 1,m_s\rangle \mp \kappa_2|T_1,\pm 1,m_s\rangle,$$

$$|T_1,0,m_s\rangle_t \approx |T_1,0,m_s\rangle + \kappa_0|3,A_2,0,m_s\rangle,$$

$$|T_1,\pm 1,m_s\rangle_t \approx |T_1,\pm 1,m_s\rangle \pm \kappa_2|3,T_2,\pm 1,m_s\rangle, \quad (40)$$

where

$$\kappa_0 \equiv \frac{\upsilon'\sqrt{10}}{5(E_{T_1 0} - E_{A_2})}(1 + 2\kappa_P) \simeq \frac{\upsilon'\sqrt{10}}{9\Delta}(1 + 2\kappa_P),$$

$$\kappa_2 \equiv \frac{\upsilon + 2\upsilon'\sqrt{2}}{2\sqrt{5}(E_{T_1 1} - E_{T_2 1})} + \frac{\kappa_P}{\sqrt{5}(E_{T_1 1} - E_{T_2 1})}\left(\upsilon - \frac{3\sqrt{2}}{2}\upsilon'\right).$$

The corresponding energies are

$$E_{A_2} \approx -\frac{6\Delta}{5},$$

$$E_{T_2 0} \approx -\frac{\Delta}{5} + \frac{\upsilon}{3},$$

$$E_{T_2 1} \approx -\frac{\Delta}{5} - \frac{\upsilon}{6},$$

$$E_{T_1 0} \approx \frac{3\Delta}{5} + \frac{3\upsilon}{5} + \frac{4\upsilon'\sqrt{2}}{5} - \frac{4}{5}\frac{\Delta^2}{75B},$$

$$E_{T_1 1} \approx \frac{3\Delta}{5} - \frac{3\upsilon}{10} + \frac{\upsilon'\sqrt{2}}{210} - \frac{4}{5}\frac{\Delta^2}{75B}. \quad (41)$$

Then we consider the spin-orbit interaction as a perturbation with respect to the crystal-field Hamiltonian. We thus obtain the usual formulas for the g factor and the anisotropy D,

$$g_{\mu\nu} - g_s = -2\lambda k \Lambda_{\mu\nu}, \quad (42)$$

$$D = -\lambda^2(\Lambda_{zz} - \Lambda_{xx}), \quad (43)$$

where

$$\Lambda_{\mu\nu} = \sum_{n \neq 0} \frac{\langle \psi_0|\hat{L}^\mu|n\rangle\langle n|\hat{L}^\nu|\psi_0\rangle}{E_n - E_0}, \quad (44)$$

with $E_0 = E_{A_2}$ and λ is defined in Eq. (36). These are the parameters appearing in the effective spin $\left(S=\frac{3}{2}\right)$ Hamiltonian

$$H_{\text{spin}} = \mu_B g_\parallel B_z S_z + \mu_B g_\perp(B_x S_x + B_y S_y) + D\left[S_z^2 - \frac{1}{3}S(S+1)\right]. \quad (45)$$

Let us note that all energy denominators appearing in $\Lambda_{\mu\nu}$ [Eq. (44)] are of the order of cubic splitting Δ. Thus, the perturbation theory requires the SO coupling to fulfill $\lambda \ll \Delta$. But λ may be of the same order of magnitude as υ and υ'. The operator $\hat{L}_z$ couples the ground state only with $|T_2,0,m_s\rangle$,

$$\hat{L}_z|A_2,0,m_s\rangle = (2 + \kappa_0\sqrt{5})|T_2,0,m_s\rangle,$$

then

$$\Lambda_{zz} = \frac{4(1 + \kappa_0\sqrt{5})}{(E_{T_2 0} - E_{A_2})}.$$

For $\hat{L}_x = (\hat{L}_+ + \hat{L}_-)/2$ we have

$$\hat{L}_x|A_2,0,m_s\rangle = \frac{1}{2}\left\{-2\sqrt{2}(|T_2,1,m_s\rangle - |T_2,-1,m_s\rangle) - \kappa_0\left[-\frac{3\sqrt{2}}{2}(|T_1,1,m_s\rangle + |T_1,-1,m_s\rangle) - \sqrt{\frac{5}{2}}(|T_2,1,m_s\rangle - |T_2,-1,m_s\rangle)\right]\right\},$$

and

$$\Lambda_{xx} \simeq \frac{4\left(1 - \frac{\kappa_0\sqrt{5}}{2}\right)}{(E_{T_2 1} - E_{A_2})}.$$

The anisotropy constant appears only in the third order (second order of spin orbit and first order of trigonal field)

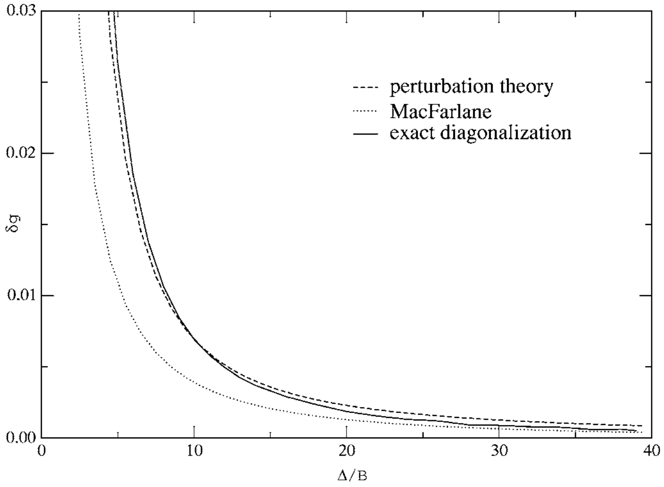

FIG. 3. Comparison between our perturbation theory (46) for the weak-field case (dashed line), the result derived by MacFarlane (Ref. 12) in the strong-field case (dotted) and the exact diagonalization calculation for $\delta g = g_\perp - g_\parallel$ (full line).

$$D \approx \frac{4\lambda^2}{\Delta}\left(\frac{\upsilon}{2\Delta} - \frac{3\kappa_0\sqrt{5}}{4}\right) \approx \frac{\lambda^2}{\Delta}\left[2\frac{\upsilon}{\Delta} - \frac{10\sqrt{2}}{3}\frac{\upsilon'}{\Delta}(1+2\kappa_P)\right].$$

The final results are

$$D = \frac{\lambda^2}{\Delta}\left[2\frac{\upsilon}{\Delta} - \frac{10\sqrt{2}}{3}\frac{\upsilon'}{\Delta}\left(1+\frac{4}{75}\frac{\Delta}{B}\right)\right],$$

$$g_\parallel = g_s - \frac{8\lambda}{\Delta}k\left[1 - \frac{\upsilon}{3\Delta} + \frac{5\sqrt{2}}{9\Delta}\upsilon'\left(1+\frac{4}{75}\frac{\Delta}{B}\right)\right],$$

$$g_\perp = g_s - \frac{8\lambda}{\Delta}k\left[1 + \frac{\upsilon}{6\Delta} - \frac{5\sqrt{2}}{18\Delta}\upsilon'\left(1+\frac{4}{75}\frac{\Delta}{B}\right)\right]. \qquad (46)$$

An alternative perturbative formula for zero-field splitting $2D$, which is valid in the present situation, was derived by Mao-Lu and Min-Guang.[14] However, our result is much more compact than theirs [Eqs. (5)–(9) of Ref. 14 take one page and a half] and, correspondingly, more practicable. We have checked that the difference between the compact formulas (46) and the result given in Ref. 14 is very small and can be neglected in numerical applications.

To check the applicability of our perturbation theory (46) we compared it with the exact diagonalization (see the Appendix). We fixed the parameters (in inverse centimeters) $\upsilon=54$, $\upsilon'=-213$, $C=3148$, $B=804$, $k=0.85$, and $k\xi_{d,0}=481$ to those values, which we derived for Co^{2+} in ZnO (see Sec. V) and varied Δ/B to display the different regimes. As one can see from Fig. 3, the difference of g factors $\delta g = g_\perp - g_\parallel$ from our formula compares well with the exact diagonalization for Δ/B up to 15. Therefore, we can certainly apply it to the case of Co^{2+} in ZnO where Δ/B is roughly 5 and where there are considerable deviations for MacFarlanes formula.[12] On the other hand, the exact diagonalization converges towards MacFarlanes formula for large values of Δ/B.

V. APPLICATION TO ZnO:Co

We apply our theory to the calculation of spin-Hamiltonian parameters for Co impurity in zinc oxide. As input, we need the following parameters of $\hat{H}$ [Eq. (1)]: (i) the structure of the Co environment given in Table I, (ii) the charge transfer energy Δ_{pd} [Eq. (18)], (iii) the free-ion spin-orbit coupling $\xi_{d,0} \approx 567$ cm^{-1} (see, e.g., Table 7.6 of Ref. 3), and (iv) the Racah's parameters $B_0 \approx 1115$ cm^{-1} and $C_0 \approx 4366$ cm^{-1} (from Table 7.5 of Ref. 3).

As was mentioned above, we calculate the hopping integrals that enter $\hat{H}$ [Eqs. (1) and (3)] from Harrison's expressions[9]

$$t_{pdm}(R) = \eta_{pdm}\frac{\hbar^2 r_d^{3/2}}{mR^{7/2}}, \quad \eta_{pd\sigma} = -2.95, \quad \eta_{pd\pi} = 1.36, \qquad (47)$$

where the value $r_d = 0.76$ Å for the Co ion. The distance R is measured in angstroms and t_{pdm} in electron volts (1 eV $= 8065.5$ cm^{-1}). This gives, e.g., for $t_{pd\sigma}(R_4) \approx 1.34$ eV. The coefficients b_k [Eq. (15)] are inversely proportional to the charge-transfer energy Δ_{pd}. We choose the $\Delta_{pd} \approx 3.6$ eV $\approx 28\,800$ cm^{-1} so that the cubic splitting Δ [Eqs. (33)] is equal to the experimentally determined value[2] $\Delta = 4070$ cm^{-1}. Then, the trigonal CF parameters $\upsilon \approx 54$ cm^{-1} and $\upsilon' \approx -213$ cm^{-1} are unambiguously determined by the Co environment via Eqs. (33) and *are not* additionally adjusted. The SO and angular-momentum reduction factor $k \approx 0.85$ was *calculated* from Eq. (26). This gives the spin-orbit coupling $\xi_d = k\xi_{d,0} \approx 481$ cm^{-1}, $\lambda = -\xi_d/3 \approx -160$ cm^{-1} very close to the values met in the literature (and adjusted empirically): $\xi_d = 450$ cm^{-1} in Ref. 12 and $\xi_d = 430$ cm^{-1} in Ref. 2. From our above consideration, we have seen that the reduction factors for Coulomb interaction may differ from those of SO and angular-momentum terms. Nevertheless, an order-of-magnitude estimate may be done as $B \approx k^2 B_0 \approx 804$ cm^{-1} and $C \approx k^2 C_0 \approx 3148$ cm^{-1}. We adopt these values for our calculations. The agreement with the experimentally adjusted values $B = 750$ cm^{-1}, $C = 3500$ cm^{-1} of MacFarlane[12] is very good, keeping in mind the roughness of the estimate. We should also note that the influence of the B and C parameters on the calculated g factors and the zero-field splitting $2D$ is rather small. So, using instead of our estimations for B and C the values of MacFarlane (and keeping all the other parameters constant) leads to $2D = 4.882$, $g_\parallel = 2.230$, and $g_\perp = 2.256$, quite close to the results listed in Table II.

The parameters of the ground-state spin-Hamiltonian [Eq. (45)] obtained by the exact diagonalization of single-ion Hamiltonian $\hat{H}_{\text{eff}}$ [Eq. (29)] are shown in Table II. Note that our sign convention for the crystal-field parameters corresponds to the electron representation in contrast to the hole representation used in Refs. 2 and 12. The agreement with purely empirical approaches, where all parameters are fitted to experiment, is very good. We also show the parameters for the excited state.

Table III compares the spin-Hamiltonian parameters obtained by an analytic perturbative approach [Eqs. (46)] with

TABLE II. Measured ESR (Ref. 11) and magneto-optic (Ref. 23) data, compared to those calculated from CF theory with empirical parameters (Refs. 2 and 12) or estimated from our approach. $2D$ ($2D'$) and g (g') are the values for the ground (excited) state. The energy unit is inverse centimeter. In the empirical CF theory (Refs. 2 and 12) all the seven parameters listed in the upper part of the table are used as fitting parameters, whereas they are microscopically calculated in our approach fixing only the cubic CF splitting Δ to the experimental value.

	Koidl[a]	MacFarlane[b]	Present work	Experiment
v	–120	–400	54	
v'	–320	–350	–213	
Δ	4000	4000	4070	4070[a]
B	760	750	804	
C	3500	3500	3148	
k	1	0.8	0.85	
$k\xi_{d,0}$	430	450	481	
$2D$	5.44	5.41	4.91	5.52[c]
$g_{\parallel}$	2.24	2.20	2.23	2.236[c]
$g_{\perp}$	2.28	2.23	2.26	2.277[c]
$2D'$	21.4	90.3	5.8	38[a]
$g'_{\parallel}$	2.85	3.36	4.22	3.52[d]
$E_{^2E\bar{E}}—E_{^4A\bar{E}}$	15171	15050	14381	15123[d]

[a] Reference 2.
[b] Reference 12.
[c] Reference 11.
[d] Reference 23.

the results of the exact diagonalization and experiment. We see that the analytic results lie within 15% of accuracy. For the phenomenological parameter set of Koidl[2] the accuracy is about 20%.[11] The reason is that in our set the absolute values of trigonal parameters are smaller than for the set of Ref. 2 and the cubic splitting is the same, thus the perturbation theory for our set converges better. The main reason for the deviation from exact diagonalization is our neglect of the interaction with the ^2G term that violates the Hund's rule, but nevertheless lies rather low in energy, just above the ^4P term (see Table IV). This deviation is remarkable for $2D$, but much less for the g factors.

VI. CONCLUSION

We have shown that Harrison's parametrization of the electronic structure of solids[9] may be successfully applied to the calculation of spin-Hamiltonian parameters [Eq. (45)] for TMI impurities in semiconductors [Eqs. (46)]. It is especially useful for the description of low-symmetry paramagnetic centers as it provides the connection between CF parameters and the geometry of TMI surroundings [Eqs. (33)]. Thus, the number of empirically adjustable parameters is substantially reduced.

TABLE III. ESR data as calculated from the numerical diagonalization and the perturbation theory using the calculated crystal-field parameters.

	Experiment	Diagonalization	Perturbation theory
$2D$	5.52	4.91	4.31
$g_{\parallel}$	2.24	2.23	2.25
$g_{\perp}$	2.28	2.26	2.28

TABLE IV. Coulomb energy depending on the multiplet.

Term	Coulomb energy
^4F	$3A-15B$
^4P	$3A$
^2G	$3A-11B+3C$
^2H	$3A-6B+3C$
^2P	$3A-6B+3C$
^2F	$3A+9B+3C$
$^2D, {}^2D'$	$3A+5B+5C\pm\sqrt{(193B^2+8BC+4C^2)}$

We have demonstrated that the physical reason for the possibility to apply the CF concept to TMI in semiconductors is the strong Coulomb repulsion within the d shell. It provides the large value of charge-transfer energy Δ_{pd} [Eqs. (6) and (18)] even in the case when the mean-field energy of the d level falls into the valence band. We have given the explicit form of the canonical transformation [Eqs. (4) and (5)] of the many-body Hamiltonian [Eq. (1)] and basis functions, which exploits this strongly correlated feature of the TMI subsystem [Eq. (11)], and provides the effective single-ion Hamiltonian [Eq. (9)]. The latter connects the CF Hamiltonian with the geometry of local surroundings of the impurity and with the parameters of the electronic structure [Eqs. (13)–(15)]. The transformation [Eqs. (4) and (5)] accounts for the covalency in the weak CF case within the Heitler-London configuration-interaction approach. When applied to the spin-orbit, Zeeman and Coulomb terms, it renormalizes their parameters by covalency.

We have applied this theory to the Co impurity in ZnO. We have adjusted only one parameter of our starting p-d Hamiltonian [Eq. (1)], which acts in an energy scale of several eV. In the result, we have fairly well reproduced a number of measurable quantities available from ESR and optical experiments. Note that these values reflect the tiny features of electronic structure (magnetic anisotropy, Zeeman splitting), which have the scale of several cm^{-1}. The results indicate that the proposed theory catches the essential physics of TMI in semiconductors.

ACKNOWLEDGMENTS

The authors would like to thank A. Stepanov, A. S. Moskvin, M. D. Kuzmin, M. Richter, I. Opahle, S.-L. Drechsler, D. Ferrand, and J. Cibert for many useful discussions. In part, this work was supported by NATO Collaborative Grant No. CBP.NUKR.CLG 981255. R.O.K. also acknowledges support from the DFG project No. 436/UKR/17/8/05.

APPENDIX: EXACT DIAGONALIZATION FOR $3d^3$ ($3d^7$)

In this section we detail the numerical calculations of the exact diagonalization for three particles on a $3d$ level. The case of interest, namely, $3d^7$ can be obtained from the former using a particle-hole transformation.

The number of states for three particles on a d level is $10\times 9\times 8/3! = 120$. These states can be labeled by the usual quantum numbers for total spin and angular momentum, we thus obtain different multiplets: ^4F for which $S=\frac{3}{2}$, $L=3$; this multiplet contains $(2S+1)(2L+1)=28$ different states. We also have $^4P(S=\frac{3}{2}, L=1)$, $^2H(S=\frac{1}{2}, L=5)$, $^2G(S=\frac{1}{2}, L=4)$, $^2F(S=\frac{1}{2}, L=3)$, ^2D and $^2D'(S=\frac{1}{2}, L=2)$, and finally, $^2P(S=\frac{1}{2}, L=1)$. This basis will be noted $\{|\alpha\rangle = |S,L,M,m_s,\epsilon\rangle\}$; the last quantum number ϵ is needed to distinguish states belonging to the two multiplets ^2D and $^2D'$.

The $\{|\alpha\rangle\}$ basis is the natural one for the Coulomb interaction as well as the Zeeman Hamiltonian; however, another basis emerges when writing the one-body part of the Hamiltonian, namely, the crystal-field and spin-orbit terms. Let us denote by $\{|i\rangle, i=1,\ldots,10\}$, the basis for one electron on a d level. i is an index for the (m_l,σ) state, where m_l and σ are the momentum and spin quantum numbers. We can construct a new basis of 120 states $\{|n\rangle = |ijk\rangle = c_i^\dagger c_j^\dagger c_k^\dagger |\text{vac}\rangle,\ i<j<k:1,\ldots,10,\ n:1,\ldots,120\}$ where $|\text{vac}\rangle$ is the empty d level.

The complete Hamiltonian has been written in Eq. (29). The Coulomb part is diagonal in the $\{|\alpha\rangle\}$ basis, and Table IV gives the different energy values. Contrary to MacFarlane's work[12] where the Zeeman Hamiltonian is treated in a perturbative manner, it is here diagonalized on the same foot as the other terms. In the $\{|\alpha\rangle\}$ basis, the Zeeman Hamiltonian is block diagonal, and the nonzero matrix elements just connect states by $\hat{L}_{+(-)}$ or $\hat{S}_{+(-)}$. The crystal-field Hamiltonian is the sum of the cubic and trigonal parts. The one-particle matrix elements of $\hat{H}_{CF}$ [Eq. (13)] may also be expressed in terms of Stevens equivalent operators[3]

$$\hat{H}_{\text{cub}} = -\frac{2}{3}B_4^0(\hat{O}_4^0 - 20\sqrt{2}\hat{O}_4^3), \quad \hat{H}_{\text{trig}} = B_2'\hat{O}_2^0 + B_4'\hat{O}_4^0, \tag{A1}$$

corresponding to a d^1 configuration. The Stevens operators are given by

$$\hat{O}_4^0 = 35\hat{L}_z^4 - 30L(L+1)\hat{L}_z^2 + 25\hat{L}_z^2 - 6L(L+1) + 3L^2(L+1)^2,$$

$$\hat{O}_4^3 = \frac{1}{4}\{\hat{L}_z(\hat{L}_+^3 + \hat{L}_-^3) + (\hat{L}_+^3 + \hat{L}_-^3)\hat{L}_z\},$$

$$\hat{O}_2^0 = 3\hat{L}_z^2 - L(L+1), \tag{A2}$$

where the operators $\hat{L}_z$, $\hat{L}_+$, or $\hat{L}_-$ are *one-particle* operators.

In analytic calculations we have used the $\{|\alpha\rangle\}$ basis and for the d^7 configuration the crystal-field Hamiltonians [Eqs. (A1)] have to be used with the parameters

$$\tilde{B}_4^0 = -\frac{B_4^0}{5}, \quad \tilde{B}_4' = -\frac{B_4'}{5}, \quad \tilde{B}_2' = \frac{B_2'}{5}. \tag{A3}$$

The parameters Δ, v, and v', previously defined in Eqs. (32), are connected with the Stevens parameters by

$$B_4^0 = -\frac{\Delta}{120} - \frac{1}{360}\left(v + \frac{3\sqrt{2}}{2}v'\right),$$

$$B_4' = -\frac{1}{140}\left(v + \frac{3\sqrt{2}}{2}v'\right),$$

$$B_2' = \frac{v - 2\sqrt{2}v'}{21}. \tag{A4}$$

Using Eqs. (33) we obtain

$$\tilde{B}_4^0 = -\frac{\sqrt{6}}{2880}b_4(R_1)\frac{z_1a^3}{R_1^4},$$

$$\tilde{B}_4' = -\frac{1}{140}\left\{b_4(R_1)\frac{7\sqrt{6}z_1a^3 + 72(z_1^4 - z_1^2a^2) + 3a^4}{216R_1^4} + \frac{b_4(R_4)}{9}\right\},$$

$$\tilde{B}_2' = -\frac{1}{210}\left\{b_2(R_1)\frac{6z_1^2 - a^2}{R_1^2} + 2b_2(R_4)\right\}, \tag{A5}$$

where z_i is the z coordinate of the ligand O$_i$; $R_1 = \sqrt{a^2/3 + z_1^2}$, $R_4 = z_4$ are the corresponding distances. For completeness we also give here the relation with another parameter set, which is often met in the literature

$$Dq = 12B_4^0, \quad D\tau = 12B_4', \quad D\sigma = -3B_2'. \tag{A6}$$

This set is used, e.g., in Ref. 14.

The crystal-field Hamiltonian is easily written in the one-particle basis $\{|i\rangle, i=1,\ldots,10\}$, where one evaluates the matrix elements $H_{ij}^{CF} = \langle i|H_{\text{CF}}|j\rangle$. Then the matrix elements of the CF Hamiltonian can be written in the three-particle basis $\{|n\rangle = |ijk\rangle\}$ as follows:

$$\begin{aligned}
\langle k'j'i'|H_{CF}|ijk\rangle = {} & H_{i'i}^{CF}(\delta_{j'j}\delta_{k'k} - \delta_{j'k}\delta_{k'j}) \\
& - H_{i'j}^{CF}(\delta_{j'i}\delta_{k'k} - \delta_{j'k}\delta_{k'i}) \\
& + H_{i'k}^{CF}(\delta_{j'i}\delta_{k'j} - \delta_{j'j}\delta_{k'i}) \\
& - H_{j'i}^{CF}(\delta_{i'j}\delta_{k'k} - \delta_{i'k}\delta_{k'j}) \\
& + H_{j'j}^{CF}(\delta_{i'i}\delta_{k'k} - \delta_{i'k}\delta_{k'i}) \\
& - H_{j'k}^{CF}(\delta_{i'i}\delta_{k'j} - \delta_{i'j}\delta_{k'i}) \\
& + H_{k'i}^{CF}(\delta_{i'j}\delta_{j'k} - \delta_{i'k}\delta_{j'j}) \\
& - H_{k'j}^{CF}(\delta_{i'i}\delta_{j'k} - \delta_{i'k}\delta_{j'i}) \\
& + H_{k'k}^{CF}(\delta_{i'i}\delta_{j'j} - \delta_{i'j}\delta_{j'i}),
\end{aligned}$$

where δ is the Kronecker symbol. The spin-orbit term [Eq. (34)] is also easily written in the one-particle basis $\{|i\rangle\}$, then in the three-particle one $\{|ijk\rangle\}$, using the preceding expansion.

At this stage we have some part of the total Hamiltonian written in the $\{|\alpha\rangle\}$ basis and the other one in the $\{|ijk\rangle\}$ basis. To perform the numerical diagonalization, the last quantity needed is the transformation matrix to connect these two bases. The transformation basis is a kind of Clebsch-Gordan coefficient matrix for three particles constrained by the Pauli principle.

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