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Energy-level spectra of transition-metal ions in II-VI semiconductors

Murielle Villeret and S. Rodriguez
Department of Physics, Purdue University, West Lafayette, Indiana 47907

E. Kartheuser
Institut de Physique, Université de l'Etat à Liège, Sart-Tilman, B-4000 Liège, Belgium

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We present a systematic investigation of the low-lying levels and Zeeman splittings of transition-metal ions in diluted magnetic semiconductors having the zinc-blende or the wurtzite structure. The site symmetry of the magnetic ions is T_d in the former and C_{3v} in the latter. The present formalism permits a general derivation of the energies of the levels in the lowest terms of the $(3d)^n$ configurations for all the iron-group ions including the effects of the spin-orbit coupling and Zeeman interaction up to second order. The g factors of all levels are obtained including the anisotropy of the Γ_8 states of Co^{2+} and Cu^{2+}.

I. INTRODUCTION

Diluted magnetic semiconductors[1] (DMS's) are materials obtained by alloying a II-VI compound $A^{II}B^{VI}$, where A^{II} and B^{VI} are elements of the groups II and VI of the Periodic Table of the elements, respectively, with MB^{VI}, where M is a transition-metal ion. Usually, the element M enters the structure substitutionally at A sites in the compound $A^{II}B^{VI}$. The chemical formula of the resulting compound is $A_{1-x}M_xB$, x being the atomic concentration of M. The Mn-based DMS's have, until recently, received the greatest attention. Since the ground state of Mn^{2+} is ${}^6S_{5/2}$, the crystal field has a negligible effect on its magnetic properties and isolated Mn^{2+} ions in DMS's behave as if they were free. Other doubly ionized transition-metal ions exhibit ground terms possessing orbital as well as spin degeneracies. In this paper we present a systematic investigation of these transition ions in zinc-blende and wurtzite semiconductors. In the former, the symmetry of the site of the impurity is tetrahedral (point group T_d) whereas in the latter a slight distortion along the [111] direction yields trigonal symmetry (point group C_{3v}). Excluding Mn^{2+}, all the doubly ionized iron-group ions have ground states that are either D or F terms. The values of L and S are symmetrical with respect to the half-filled $3d$ shell so that a study of ions whose shell is more than half filled yields automatically information about those for which the $3d$ shell is less than half full. However, the order of the crystal-field-split levels is reversed and the spin-orbit coupling constant λ changes sign. Therefore we need only study four of the transition-metal ions. Symmetry arguments show that, while a D term splits into a doublet Γ_3 and a triplet Γ_5 in the presence of a tetrahedral field,[2] F terms split into $\Gamma_2+\Gamma_4+\Gamma_5$. It can be shown[3] that the ground multiplet of an ion in the $(3d)^n$ configuration in a field produced by a tetrahedral arrangement of negatively charged ions is Γ_1 for $n=5$, Γ_2 for $n=2$ and 7, Γ_3 for $n=1$ and 6, Γ_4 for $n=3$ and 8, and Γ_5 for $n=4$ and 9. We expect a fundamental difference between the behavior of Fe^{2+} and Ni^{2+} on the one hand and of Co^{2+} and Cu^{2+} on the other, because while the number of electrons in the former is even, in the latter it is odd. By virtue of Kramers' theorem, all eigenstates of Co^{2+} and Cu^{2+} have even degeneracies and thus must always exhibit paramagnetism. Fe^{2+} and Ni^{2+} can have both degenerate and nondegenerate states. It turns out that, in the crystals under study, the ground states of Fe^{2+} and Ni^{2+} are nondegenerate and are, to first approximation, nonmagnetic. However, in the presence of a magnetic field, the Zeeman interaction mixes the states of the lowest term giving rise to a temperature-independent paramagnetism (Van Vleck paramagnetism).

We first develop a general formulation of the effective spin Hamiltonian of D terms in a crystal field of tetrahedral symmetry. The study includes all levels in the lowest terms of the $(3d)^n$ ($n=6$ and 9) configurations. The calculations are carried out to second order in the spin-orbit interaction and in $\mathbf{B}$ for the lowest orbital states and to first order in $\mathbf{B}$ for the excited states as functions of the spin quantum number S. Thus the present work generalizes that of Weakliem[4] who made a thorough study of the optical spectra of Ni^{2+}, Co^{2+}, and Cu^{2+} in tetrahedral sites in crystals in the absence of a magnetic field. The results are subsequently applied to the cases of Fe^{2+} and Cu^{2+}. A study of the magnetization of Fe^{2+} in CdTe is also presented. It reveals that, even in the cubic field, the magnetization $\mathbf{M}$ is anisotropic in the regime in which $\mathbf{M}$ is not a linear function of the magnetic field $\mathbf{B}$. To illustrate the effect of a trigonal distortion we obtain the temperature dependence of the differential magnetic susceptibility of Fe^{2+} in the wurtzite-structure semiconductor CdSe and determine its anisotropy in the low-temperature regime. These results are in good qualitative agreement with the experiment.[5,6] The second part of this paper is devoted to the study of F terms in a tetrahedral field. The general theory follows the same lines as that for the D terms and is applied to Co^{2+} and Ni^{2+}.

II. SPIN HAMILTONIAN FOR A D TERM IN A T_d FIELD

A. General formalism

In this subsection we derive the spin Hamiltonian of a D term in a tetrahedral environment of negatively charged ions. When $L=2$, the only significant part of the crystal potential can be expressed as

$$V_c(T_d)=\pm a[\tfrac{1}{8}(L_+^2+L_-^2)^2+\tfrac{3}{2}L_z^4-6L_z^2-\tfrac{12}{5}] \qquad (1)$$

where a is positive and the + and − signs hold for Cu^{2+} and Fe^{2+}, respectively. Here $L_\pm=L_x\pm iL_y$ and L_x, L_y, and L_z are the components of the angular momentum operator along the cubic axes **x**, **y**, and **z**. The orbital angular momentum states of the free ion are eigenvectors of L_z and are denoted by $|M_L\rangle$ ($M_L=2,1,0,-1,-2$). In the presence of the T_d field the D term splits into Γ_3 and Γ_5 with basis functions

$$\begin{aligned}\Gamma_3:\ & u_1=|0\rangle\ ,\\ & u_2=2^{-1/2}(|2\rangle+|-2\rangle)\ ;\\ \Gamma_5:\ & v_+=|-1\rangle\ ,\\ & v_0=2^{-1/2}(|2\rangle-|-2\rangle)\ ,\\ & v_-=-|1\rangle\ .\end{aligned} \qquad (2)$$

The functions u_1 and u_2 belong to the rows of the Γ_3 representation of T_d generated by $2z^2-x^2-y^2$ and $\sqrt{3}(x^2-y^2)$, respectively. The choice of phase in the wave functions v_+, v_0, and v_- is selected so that they generate the same matrix representation as $-z(y+ix)/\sqrt{2}$, xy, and $z(y-ix)/\sqrt{2}$, respectively.

We write the Hamiltonian operator of the problem as a supermatrix divided into diagonal square blocks of $2(2S+1)$ and $3(2S+1)$ dimensions corresponding to the $2(2S+1)$ $|u_i,M_S\rangle$ states ($i=1,2$; $M_S=S, S-1,\dots,-S+1,-S$) generated by the orbital Γ_3 levels and to the $3(2S+1)$ $|v_i,M_S\rangle$ ($i=+,0,-$) vectors belonging to the Γ_5 levels. We consider the Hamiltonian

$$H=H_c+H_{\text{s.o.}}+H_Z \qquad (3)$$

where H_c is the Hamiltonian of the ion in the crystal field excluding the spin-orbit coupling $H_{\text{s.o.}}=\lambda\mathbf{L}\cdot\mathbf{S}$. The term H_Z is the Zeeman energy in a magnetic field $\mathbf{B}=B\hat{\mathbf{n}}$, i.e.,

$$H_Z=\mu_B B\hat{\mathbf{n}}\cdot(\mathbf{L}+2\mathbf{S})\ . \qquad (4)$$

The expression for the Hamiltonian matrix H in the states (2) is

$$H=\begin{vmatrix} E_0(\Gamma_3)+2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S} & (\lambda\mathbf{S}+\mu_B B\hat{\mathbf{n}})\cdot\mathbf{U} \\ (\lambda\mathbf{S}+\mu_B B\hat{\mathbf{n}})\cdot\mathbf{U}^\dagger & E_0(\Gamma_5)+2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S}-(\lambda\mathbf{S}+\mu_B B\hat{\mathbf{n}})\cdot\mathbf{I}\end{vmatrix}\ . \qquad (5)$$

Here $E_0(\Gamma_3)$ and $E_0(\Gamma_5)$ are the unperturbed energies of the Γ_3 and Γ_5 states, respectively. Two new quantities **U** and **I** are introduced, their definition being

$$\langle u_\nu|\mathbf{L}|v_\kappa\rangle=\mathbf{U}_{\nu\kappa} \qquad (6)$$

and

$$\langle v_{\kappa'}|\mathbf{L}|v_\kappa\rangle=-\mathbf{I}_{\kappa'\kappa} \qquad (7)$$

($\nu=1,2$ and $\kappa,\kappa'=+,0,-$). The components of **I** obey the commutation relation $\mathbf{I}\times\mathbf{I}=i\mathbf{I}$ and can thus be treated exactly as an angular momentum operator with quantum number $I=1$.

The Schrödinger equation $H\psi=E\psi$ can be rearranged replacing the $5(2S+1)$-component vector ψ by a composite of two vectors, namely $\psi^{(3)}$ and $\psi^{(5)}$ of dimensions $2(2S+1)$ and $3(2S+1)$, respectively. The Schrödinger equation is equivalent to two coupled equations which can be solved for $\psi^{(3)}$ and $\psi^{(5)}$ by iteration keeping terms up to second order in λ and $\mu_B B$. This yields the effective spin Hamiltonians for the Γ_3 and Γ_5 states. They are

$$\begin{aligned}H(\Gamma_3)=\ & E_0(\Gamma_3)+2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S}\\ & +\frac{1}{E_0(\Gamma_3)-E_0(\Gamma_5)}\\ & \times(\lambda\mathbf{S}+\mu_B B\hat{\mathbf{n}})\cdot\mathbf{U}\mathbf{U}^\dagger\cdot(\lambda\mathbf{S}+\mu_B B\hat{\mathbf{n}})\end{aligned} \qquad (8)$$

and

$$\begin{aligned}H(\Gamma_5)=\ & E_0(\Gamma_5)+2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S}-(\lambda\mathbf{S}+\mu_B B\hat{\mathbf{n}})\cdot\mathbf{I}\\ & +\frac{1}{E_0(\Gamma_5)-E_0(\Gamma_3)}\\ & \times(\lambda\mathbf{S}+\mu_B B\hat{\mathbf{n}})\cdot\mathbf{U}^\dagger\mathbf{U}\cdot(\lambda\mathbf{S}+\mu_B B\hat{\mathbf{n}})\ .\end{aligned} \qquad (9)$$

To proceed further we express $\mathbf{U}^\dagger\mathbf{U}$ and $\mathbf{U}\mathbf{U}^\dagger$ in terms of pseudoangular momentum operators:

$$\mathbf{U}^\dagger\mathbf{U}=4\sum_i \hat{\mathbf{e}}_i\hat{\mathbf{e}}_i(1-I_i^2)+\sum_{i<j}(\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j+\hat{\mathbf{e}}_j\hat{\mathbf{e}}_i)\{I_i,I_j\} -i\sum_{i,j,k}\epsilon_{ijk}\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j I_k \tag{10}$$

and

$$\mathbf{U}\mathbf{U}^\dagger=\sum_i \hat{\mathbf{e}}_i\hat{\mathbf{e}}_i(2+\sigma_z)-3\hat{\mathbf{e}}_3\hat{\mathbf{e}}_3\sigma_z+\sqrt{3}(\hat{\mathbf{e}}_1\hat{\mathbf{e}}_1-\hat{\mathbf{e}}_2\hat{\mathbf{e}}_2)\sigma_x\ . \tag{11}$$

Here $\hat{\mathbf{e}}_1=\hat{\mathbf{x}}$, $\hat{\mathbf{e}}_2=\hat{\mathbf{y}}$, $\hat{\mathbf{e}}_3=\hat{\mathbf{z}}$, $\{u,v\}=uv+vu$, and ϵ_{ijk} is the antisymmetric Levi-Cività tensor density in three dimensions. $\sigma_x,\sigma_y,\sigma_z$ are the usual Pauli matrices which are introduced as a convenient representation of operators having matrix elements between the twofold degenerate Γ_3 orbital states. The terms which do not contain σ_x, σ_y, or σ_z are to be understood as direct products of the matrix shown by the unit matrix in two dimensions. Using Eqs. (10) and (11) we can write explicitly the expressions for $H(\Gamma_5)$ and $H(\Gamma_3)$. It is convenient to write these operators in the form

$$H(\Gamma_\nu)=H_0(\Gamma_\nu)+H_1(\Gamma_\nu)+H_2(\Gamma_\nu) \tag{12}$$

where $\nu=3,5$. The operator $H_0(\Gamma_\nu)$ is independent of the magnetic field $\mathbf{B}$. $H_1(\Gamma_\nu)$ and $H_2(\Gamma_\nu)$ are the linear and quadratic terms in $\mathbf{B}$, respectively. Use of Eqs. (8), (11), and (12) yields the Hamiltonian for the Γ_3 states

$$H_0(\Gamma_3)=E_0(\Gamma_3)+\frac{\lambda^2}{E_0(\Gamma_3)-E_0(\Gamma_5)}\times\left[2\mathbf{S}\cdot\mathbf{S}+(\mathbf{S}\cdot\mathbf{S}-3S_z^2)\sigma_z+\frac{\sqrt{3}}{2}(S_+^2+S_-^2)\sigma_x\right], \tag{13}$$

$$H_1(\Gamma_3)=2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S}+\frac{2\mu_B B\lambda}{E_0(\Gamma_3)-E_0(\Gamma_5)}\times\left[2\hat{\mathbf{n}}\cdot\mathbf{S}+(\hat{\mathbf{n}}\cdot\mathbf{S}-3n_zS_z)\sigma_z+\frac{\sqrt{3}}{2}(n_+S_++n_-S_-)\sigma_x\right], \tag{14}$$

and

$$H_2(\Gamma_3)=\frac{(\mu_B B)^2}{E_0(\Gamma_3)-E_0(\Gamma_5)}\times\left[2+(1-3n_z^2)\sigma_z+\frac{\sqrt{3}}{2}(n_+^2+n_-^2)\sigma_x\right]. \tag{15}$$

Here $n_\pm=n_x\pm i n_y$. The Hamiltonian operators for the Γ_5 states are given by

$$H_0(\Gamma_5)=E_0(\Gamma_5)-\lambda\mathbf{I}\cdot\mathbf{S}+\frac{\lambda^2}{E_0(\Gamma_5)-E_0(\Gamma_3)}\left[\mathbf{S}\cdot\mathbf{I}-4\sum_i S_i^2I_i^2+4\mathbf{S}\cdot\mathbf{S}+\sum_{i<j}\{S_i,S_j\}\{I_i,I_j\}\right], \tag{16}$$

$$H_1(\Gamma_5)=\mu_B B\left[2\hat{\mathbf{n}}\cdot\mathbf{S}-\hat{\mathbf{n}}\cdot\mathbf{I}+\frac{8\lambda}{E_0(\Gamma_5)-E_0(\Gamma_3)}\left[\mathbf{S}\cdot\hat{\mathbf{n}}-\sum_i S_in_iI_i^2+\tfrac{1}{4}\sum_{i<j}(S_in_j+S_jn_i)\{I_i,I_j\}\right]\right], \tag{17}$$

and

$$H_2(\Gamma_5)=\frac{4(\mu_B B)^2}{E_0(\Gamma_5)-E_0(\Gamma_3)}\times\left[1-\sum_i n_i^2I_i^2+\tfrac{1}{2}\sum_{i<j}n_in_j\{I_i,I_j\}\right]. \tag{18}$$

A further simplification can be obtained if we eliminate the sums over $i<j$ in the above expressions. For that purpose, we use the following identities:

$$2\sum_i S_i^2I_i^2+\sum_{i<j}\{S_i,S_j\}\{I_i,I_j\}=2(\mathbf{I}\cdot\mathbf{S})^2+\mathbf{I}\cdot\mathbf{S}\ , \tag{19}$$

$$\sum_{i<j}(S_in_j+S_jn_i)\{I_i,I_j\}+2\sum_i S_iI_i^2n_i-\{\mathbf{S}\cdot\mathbf{I},\mathbf{I}\cdot\hat{\mathbf{n}}\}=0\ , \tag{20}$$

and

$$(\hat{\mathbf{n}}\cdot\mathbf{I})^2=\sum_i n_i^2I_i^2+\sum_{i<j}n_in_j\{I_i,I_j\}\ . \tag{21}$$

We use Eqs. (19)–(21) and introduce the operators

$$\tilde{Q}=(2S_z^2-S_x^2-S_y^2)(2I_z^2-I_x^2-I_y^2)+3(S_x^2-S_y^2)(I_x^2-I_y^2)=6\sum_i S_i^2I_i^2-2\mathbf{S}\cdot\mathbf{S}\mathbf{I}\cdot\mathbf{I} \tag{22}$$

and

$$Q=(2n_zS_z-n_xS_x-n_yS_y)(2I_z^2-I_x^2-I_y^2)+3(n_xS_x-n_yS_y)(I_x^2-I_y^2)=6\sum_i n_iS_iI_i^2-4\hat{\mathbf{n}}\cdot\mathbf{S} \tag{23}$$

to write $H(\Gamma_5)$ as

$$H_0(\Gamma_5)=E_0(\Gamma_5)-\lambda\mathbf{I}\cdot\mathbf{S}+\frac{\lambda^2}{E_0(\Gamma_5)-E_0(\Gamma_3)}\times[2\mathbf{S}\cdot\mathbf{I}+2(\mathbf{S}\cdot\mathbf{I})^2-\tilde{Q}]\ , \tag{24}$$

$$H_1(\Gamma_5)=\mu_B B\left[2\hat{\mathbf{n}}\cdot\mathbf{S}-\hat{\mathbf{n}}\cdot\mathbf{I}+\frac{2\lambda}{E_0(\Gamma_5)-E_0(\Gamma_3)}(\{\mathbf{S}\cdot\mathbf{I},\mathbf{I}\cdot\hat{\mathbf{n}}\}-Q)\right], \tag{25}$$

and

$$H_2(\Gamma_5)=\frac{(\mu_B B)^2}{E_0(\Gamma_5)-E_0(\Gamma_3)}\left[4-6\sum_i n_i^2 I_i^2+2(\hat{\mathbf{n}}\cdot\mathbf{I})^2\right]. \tag{26}$$

The results derived thus far hold for any value of S. To find the eigenvalues of the Hamiltonians $H(\Gamma_3)$ and $H(\Gamma_5)$ we need to specify the spin quantum number so that we now make the distinction between Fe^{2+} and Cu^{2+}. In order to solve the Schrödinger equations, we make the assumption that the spin-orbit coupling is stronger than the Zeeman interaction. The validity of this hypothesis is discussed later but this assumption usually holds for a large range of values of the magnetic induction $\mathbf{B}$. Thus we first study the spectrum of $H_0(\Gamma_\nu)$ $(\nu=3,5)$ which includes the effect of the spin-orbit coupling. We diagonalize this term up to second order in λ. We then proceed to the analysis of the effect of an external magnetic field. We regard the Zeeman Hamiltonian as a perturbation on the levels split by the spin-orbit coupling. A few general results can be derived by using the theory of group representations. The form of the Zeeman splitting depends on the number n of electrons contained in the unfilled $3d$ shell. An important difference in behavior arises depending on whether this number is even or odd. If the ion contains an even number of electrons, its states are classified according to the irreducible representations of the single point group T_d. The only invariant linear in $\mathbf{B}$ is of the type $\mathbf{I}\cdot\mathbf{B}$. An example of such a behavior is Fe^{2+} which contains six electrons. In this case, the Zeeman energy is written as $g\mu_B B\hat{\mathbf{n}}\cdot\mathbf{I}$ and the g factors are isotropic. However, when the number of electrons in the $(3d)^n$ configuration is odd, we recall that, according to Kramers' theorem, all states are, at least, doubly degenerate. Consequently we must work not with the single group T_d as before but with the double group $\bar{T}_d$. We then have a splitting of the crystal-field states into Γ_6, Γ_7, or Γ_8 levels. The matrix representation of the Zeeman Hamiltonian for the doublets (Γ_6,Γ_7) can be written as

$$H_Z^{(6,7)}=\tfrac{1}{2}g^{(6,7)}\mu_B B\hat{\mathbf{n}}\cdot\sigma \tag{27}$$

where σ is the Pauli matrix. In the double group $\bar{T}_d$, there are two invariants linear in $\mathbf{B}$, namely $\mathbf{B}\cdot\mathbf{J}$ and $\sum_i B_i J_i^3$ so that the Zeeman energy for a Γ_8 state reads

$$H_Z^{(8)}=g_1\mu_B B\hat{\mathbf{n}}\cdot\mathbf{J}+g_2\mu_B B\sum_i n_i J_i^3 \tag{28}$$

where $\mathbf{J}$ is the angular momentum operator for $J=\frac{3}{2}$. Thus the g factor is anisotropic. We see that group theory predicts qualitatively the form of the Zeeman interaction. However, this information must be supplemented by a quantitative evaluation of the g factors.

B. Application to Fe^{2+} and Cr^{2+}

The value of the spin quantum number for Fe^{2+} and Cr^{2+} is $S=2$. The lowest multiplet of Fe^{2+} is the orbital doublet $^5\Gamma_3$. The difference in energy between the $^5\Gamma_5$ and $^5\Gamma_3$ states is denoted by Δ where $\Delta=6a$ so that $E_0(^5\Gamma_5)=\Delta$, taking $E_0(^5\Gamma_3)=0$. We first investigate the effect of the spin-orbit coupling on the $^5\Gamma_3$ orbital states. The spin states of Fe^{2+} belong to the representation $D_+^{(2)}$ which reduces to $\Gamma_3+\Gamma_5$ in the field of T_d symmetry. When we take the spin-orbit coupling into account, we expect, from group-theoretical arguments, a splitting of the lowest orbital states into $\Gamma_3\times(\Gamma_3+\Gamma_5)=\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4+\Gamma_5$.

Using the values of the unperturbed energies $E_0(\Gamma_i)$ and the fact that $S=2$, Eq. (13) yields

$$H_0(^5\Gamma_3)=-\frac{\lambda^2}{\Delta}(12+\Omega) \tag{29}$$

where the operator Ω is given by

$$\Omega=(12-3S_z^2)\sigma_z+\frac{\sqrt{3}}{2}(S_+^2+S_-^2)(\sigma_++\sigma_-), \tag{30}$$

where $\sigma_+|u_2\rangle=|u_1\rangle$ and $\sigma_-|u_1\rangle=|u_2\rangle$. In the states $|u_{1,2},M_S\rangle$ $(M_S=2,1,0,-1,-2)$ this operator is a 10×10 matrix. The diagonalization of Ω is considerably simplified observing that only a few of its elements are nonzero. We denote the states by $|M_S^{\pm}\rangle$ where $+$ and $-$ stand for u_1 and u_2, respectively. Consider, for example, the state $|0^+\rangle$. This state is connected to $|2^-\rangle$ and $|-2^-\rangle$ only, through the operators $S_+^2\sigma_-$ and $S_-^2\sigma_-$. In the same way $|0^-\rangle$ is connected to $|2^+\rangle$ and $|-2^+\rangle$, whereas $|1^+\rangle$ and $|-1^-\rangle$ on the one hand and $|1^-\rangle$ and $|-1^+\rangle$ on the other are mixed by Ω. Therefore the 10×10 matrix reduces to two 3×3 and two 2×2 submatrices. The diagonalization of the latter is straightforward and yields the energies $-24\lambda^2/\Delta$, $-18\lambda^2/\Delta$, $-12\lambda^2/\Delta$, $-6\lambda^2/\Delta$, and 0 for the Γ_1, Γ_4, Γ_3, Γ_5, and Γ_2 levels, respectively.[7,8] We note that the lowest levels of Fe^{2+} are equidistant and that the ground state is a singlet Γ_1. Since it is nondegenerate, Fe^{2+} in a crystalline environment will only show Van Vleck paramagnetism at the lowest temperatures.

We now investigate the effect of a magnetic field on the levels just obtained. From Eqs. (14) and (15) the terms in the Hamiltonian in first and second order in the magnetic field $\mathbf{B}$ are

$$H_1(^5\Gamma_3)=2\mu_B B\left[\hat{\mathbf{n}}\cdot\mathbf{S}-\frac{\lambda}{\Delta}\left[2\hat{\mathbf{n}}\cdot\mathbf{S}+(\hat{\mathbf{n}}\cdot\mathbf{S}-3n_zS_z)\sigma_z+\frac{\sqrt{3}}{2}(n_+S_++n_-S_-)\sigma_x\right]\right] \tag{31}$$

and

$$H_2({}^5\Gamma_3)=-\frac{(\mu_B B)^2}{\Delta}\left[2+(1-3n_z^2)\sigma_z+\frac{\sqrt{3}}{2}(n_+^2+n_-^2)\sigma_x\right] . \quad (32)$$

We write these two operators in the basis generated by the wave functions that diagonalize the spin-orbit coupling. The Γ_1, Γ_4, Γ_3, Γ_5, and Γ_2 levels originating from the ${}^5\Gamma_3$ states are further split in the presence of a magnetic field. The linear terms in B, which only occur for the Γ_4 and Γ_5 levels, are characterized by first-order Zeeman energies $\mu_B B(1+2\lambda/\Delta)\hat{\mathbf{n}}\cdot\mathbf{I}$ for Γ_4 and $\mu_B B(1-6\lambda/\Delta)\hat{\mathbf{n}}\cdot\mathbf{I}$ for Γ_5. The quadratic contributions to the energies are diagonalized using a unitary transformation making $\hat{\mathbf{n}}\cdot\mathbf{I}$ diagonal. They are listed in Table I.

We note that the energy eigenvalues depend on the orientation of the magnetic field with respect to the crystal axes through the function $f(\hat{\mathbf{n}})$ defined by

$$f(\hat{\mathbf{n}})=n_y^2n_z^2+n_z^2n_x^2+n_x^2n_y^2 . \quad (33)$$

This function is the anisotropic part of the cubic harmonic of order 4 and takes the values 0, $\frac{1}{3}$, and $\frac{1}{4}$ for $\hat{\mathbf{n}}$ parallel to the $\langle 100\rangle$, $\langle 111\rangle$, and $\langle 110\rangle$ directions. These values are local extrema of f, $\frac{1}{3}$ being an absolute maximum and 0 an absolute minimum. As we shall see, this leads to an anisotropy in the magnetization $\mathbf{M}$ in the nonlinear region of the curve $\mathbf{M}$ versus $\mathbf{B}$. The differential susceptibility $\chi_D=(\partial M/\partial B)_{B=0}$ is, of course, isotropic.

The above perturbation approach is valid only when the Zeeman interaction is small compared to the splitting $6\lambda^2/\Delta$ of the spin-orbit-split ${}^5\Gamma_3$ states. Thus it holds for magnetic fields less than $6\lambda^2/\Delta\mu_B$. This is of order 500 kG for iron in CdTe for which we use the following estimates: $\lambda=-100\ \text{cm}^{-1}$ and $\Delta=2500\ \text{cm}^{-1}$.

TABLE I. Second-order contributions in B to the energies of the ${}^5\Gamma_3$ multiplet of Fe^{2+}. The coefficients of $\Delta(\mu_B B)^2/\lambda^2$ and of $(\mu_B B)^2/\Delta$ are given for all states in the ${}^5\Gamma_3$ multiplet.

Level	I_n	$\Delta(\mu_B B)^2/\lambda^2$	$(\mu_B B)^2/\Delta$
Γ_1		$-\frac{4}{3}$	-2
Γ_4	-1	$-\frac{1}{4}(1+6f)$	$-(1+3f)$
	0	$3f$	$-2(2-3f)$
	1	$-\frac{1}{4}(1+6f)$	$-(1+3f)$
Γ_3		$-\frac{4}{3}(1-3f)^{1/2}$	-2
		$\frac{4}{3}(1-3f)^{1/2}$	-2
Γ_5	-1	$\frac{1}{4}(1+6f)$	$-3(1-f)$
	0	$-3f$	$-6f$
	1	$\frac{1}{4}(1+6f)$	$-3(1-f)$
Γ_2		$\frac{4}{3}$	-2

The higher multiplet of Fe^{2+}, namely, ${}^5\Gamma_5$, is split by the spin-orbit coupling into $\Gamma_5\times(\Gamma_3+\Gamma_5)=\Gamma_1+\Gamma_3+2\Gamma_4+2\Gamma_5$. The energies of these levels are given by the eigenvalues of $H_0(\Gamma_5)$. From Eq. (24) we get

$$H_0({}^5\Gamma_5)=\Delta-\lambda\left[1-2\frac{\lambda}{\Delta}\right]\mathbf{S}\cdot\mathbf{I}+2\frac{\lambda^2}{\Delta}(\mathbf{S}\cdot\mathbf{I})^2-\frac{\lambda^2}{\Delta}\tilde{Q} . \quad (34)$$

To determine the eigenvalues and eigenvectors of $H_0(\Gamma_5)$ we proceed in the following manner. Since $\mathbf{I}$ and $\mathbf{S}$ transform as angular momentum operators, we define

$$\mathbf{F}=\mathbf{I}+\mathbf{S} . \quad (35)$$

The components of $\mathbf{F}$ obey the same commutation rules as those of $\mathbf{I}$ and $\mathbf{S}$. In the case of Fe^{2+}, we combine an angular momentum $I=1$ with the angular momentum $S=2$ so that F takes the values 1, 2, or 3. The eigenvalues of $\mathbf{F}\cdot\mathbf{F}$ are $F(F+1)$ and the quantity $\mathbf{I}\cdot\mathbf{S}$ is

$$\mathbf{I}\cdot\mathbf{S}=\tfrac{1}{2}[F(F+1)-I(I+1)-S(S+1)] \quad (36)$$

in the representation generated by the states

$$|F,M_F\rangle=\sum_{M_S,M_I}|M_S,M_I\rangle\langle M_S,M_I|F,M_F\rangle \quad (37)$$

where $M_I=1,0,-1$, $M_S=2,1,0,-1,-2$, and $M_F=F, F-1,\dots,-F+1, -F$. $\langle M_S,M_I|F,M_F\rangle$ is a Clebsch-Gordan coefficient. To diagonalize $H_0(\Gamma_5)$ we also need the matrix elements of $\tilde{Q}$. These are evaluated in Appendix A, for a general value of S. We now apply these results to the case of Fe^{2+} ($S=2$). We find that the energies of the spin-orbit-split levels are $\Delta+3\lambda+(18\lambda^2/5\Delta)$, $\Delta+\lambda+(6\lambda^2/\Delta)$, $\Delta+\lambda+(12\lambda^2/\Delta)$, $\Delta-2\lambda+(12\lambda^2/5\Delta)$, $\Delta-2\lambda+(12\lambda^2/\Delta)$, and $\Delta-2\lambda+(24\lambda^2/\Delta)$ corresponding to Γ_5, Γ_4, Γ_3, Γ_5, Γ_4, and Γ_1 levels, respectively.

The effect of a magnetic field $\mathbf{B}$ on these levels is obtained in first-order perturbation theory. The calculation

TABLE II. g factors for Fe^{2+} and Cu^{2+}.

Fe^{2+}			Cu^{2+}			
T_d	Level	g	Level	$g^{(6,7)}$	g_1	g_2
Γ_3	Γ_1					
	Γ_4	$1+2\lambda/\Delta$				
	Γ_3		Γ_8		$\frac{7}{3}+(\lambda/3\Delta)$	$-\frac{4}{3}-(4\lambda/3\Delta)$
	Γ_5	$1-6\lambda/\Delta$				
	Γ_2					
Γ_5	Γ_5	$\frac{7}{2}+(18\lambda/5\Delta)$				
	Γ_4	$\frac{3}{2}-(2\lambda/\Delta)$	Γ_7	-2		
	Γ_3					
	Γ_5	$\frac{3}{2}-(12\lambda/5\Delta)$				
	Γ_4	$\frac{1}{2}-(4\lambda/\Delta)$	Γ_8		$-9\lambda/\Delta$	$4\lambda/\Delta$
	Γ_1					

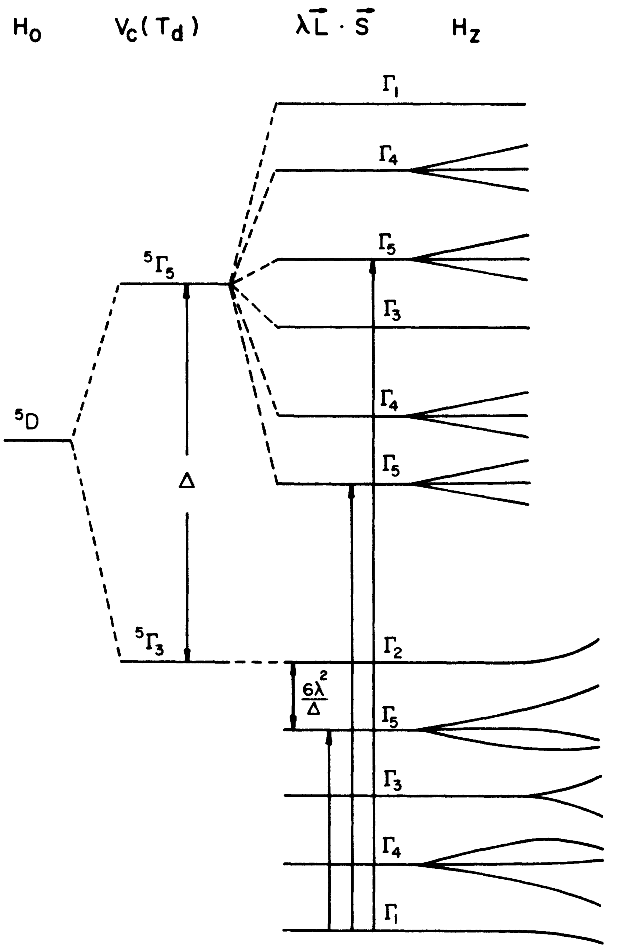

FIG. 1. Schematic diagram of the energy levels of Fe^{2+} in a tetrahedral potential. From left to right we show the splittings of the ^5D term of the free ion caused by the crystal field, the spin-orbit interaction, and the Zeeman energy H_Z in an external magnetic field. We assume that $V_c(T_d) > \lambda\mathbf{L}\cdot\mathbf{S} > H_Z$.

is carried out using the results of Appendix B and the g factors are listed in Table II. Figure 1 shows schematically the energy levels of Fe^{2+} in a tetrahedral field taking into account the spin-orbit coupling and the Zeeman energy in an external magnetic field.

We note that the spectrum of Cr^{2+} is deduced from that of Fe^{2+} by reversing the order of the states split by the crystalline field and by changing the sign of the spin-orbit coupling constant λ which is negative for Fe^{2+} and positive for Cr^{2+}.

We illustrate the preceding considerations with a study of the magnetization of Fe^{2+} ions embedded in a zinc-blende-structure semiconductor. The magnetization of a system containing n Fe^{2+} ions per unit volume is given by

$$M = nk_B T \frac{\partial}{\partial B} \ln Z \tag{38}$$

where Z is the partition function. The energies depend on the orientation of the magnetic field relative to the crystal axes through the function f leading to an anisotropy of the magnetization M. However, at sufficiently low magnetic fields when the magnetization is linear in $\mathbf{B}$, this anisotropy disappears because there is no term linear in $\mathbf{B}$ containing f and the terms quadratic in $\mathbf{B}$ containing f occur in pairs of equal magnitudes and opposite signs. This is, of course, expected from general con-

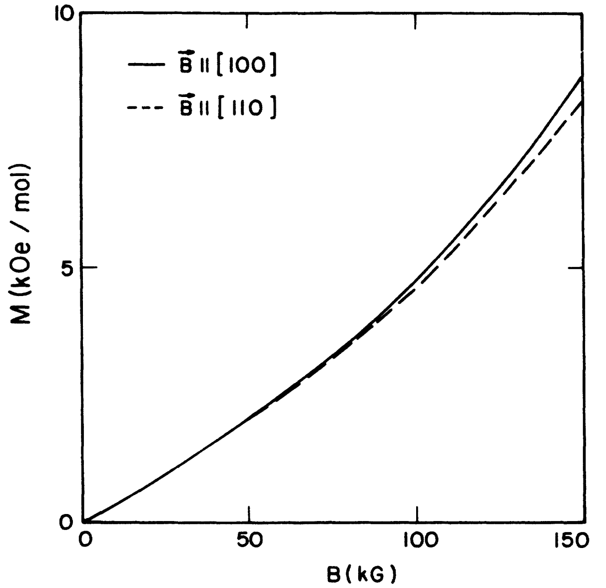

FIG. 2. Magnetization of $Cd_{1-x}Fe_xTe$ per mole of Fe as a function of the external magnetic field B at a temperature $T = 77$ K. The following parameters were used: $\lambda = -100$ cm^{-1}, $\Delta = 2500$ cm^{-1}. Note the anisotropy of M in the nonlinear region of the curves.

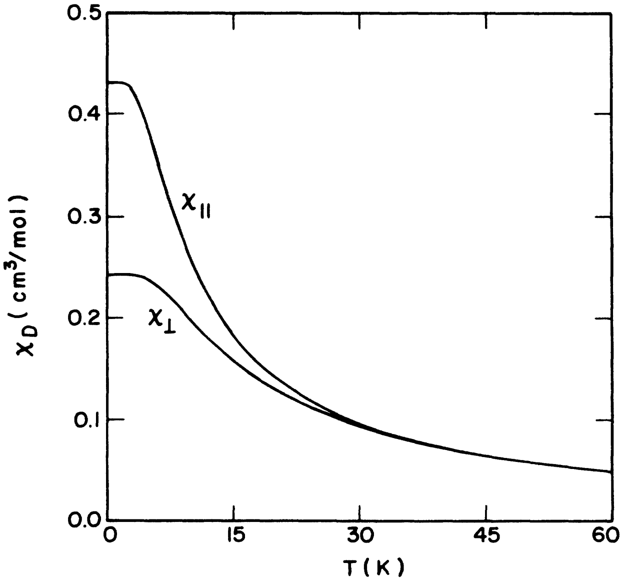

FIG. 3. Magnetic susceptibility of $Cd_{1-x}Fe_xSe$ as a function of temperature for small x and weak magnetic fields. The curves are obtained using $\lambda = -81$ cm^{-1} and $\Delta = 2680$ cm^{-1} taken from Ref. 5. The energy separation of the $\Gamma_2(C_{3v})$ and $\Gamma_3(C_{3v})$ is selected to be $3W = 7.5$ cm^{-1} to yield agreement with the experimental data (Ref. 6). $\chi_\parallel$ and $\chi_\perp$ are the differential magnetic susceptibilities when $\mathbf{B}$ is parallel and perpendicular to the trigonal axis, respectively.

TABLE III. Energy eigenvalues of the $^5\Gamma_3$ states of Fe^{2+} in a field of symmetry C_{3v} including terms to second order in the magnetic field $\mathbf{B}\|\hat{\zeta}$.

C_{3v}	Energy eigenvalue
Γ_1	$-24\lambda^2\Delta^{-1}-8\mu_B^2B_\zeta^2(6\lambda^2\Delta^{-1}-2W)^{-1}$
Γ_2	$-18\lambda^2\Delta^{-1}-2W+8\mu_B^2B_\zeta^2(6\lambda^2\Delta^{-1}-2W)^{-1}-\mu_B^2B_\zeta^2\Delta/3\lambda^2$
Γ_3	$-18\lambda^2\Delta^{-1}+W-\mu_BB_\zeta(1+2\lambda\Delta^{-1})-4\mu_B^2B_\zeta^2(6\lambda^2\Delta^{-1}-W)^{-1}-\mu_B^2B_\zeta^2\Delta/12\lambda^2$
	$-18\lambda^2\Delta^{-1}+W+\mu_BB_\zeta(1+2\lambda\Delta^{-1})-4\mu_B^2B_\zeta^2(6\lambda^2\Delta^{-1}-W)^{-1}-\mu_B^2B_\zeta^2\Delta/12\lambda^2$
Γ_3	$-12\lambda^2\Delta^{-1}+4\mu_B^2B_\zeta^2(6\lambda^2\Delta^{-1}-W)^{-1}-4\mu_B^2B_\zeta^2(6\lambda^2\Delta^{-1}+W)^{-1}$
Γ_1	$-6\lambda^2\Delta^{-1}-2W-8\mu_B^2B_\zeta^2(6\lambda^2\Delta^{-1}+2W)^{-1}+\mu_B^2B_\zeta^2\Delta/3\lambda^2$
Γ_3	$-6\lambda^2\Delta^{-1}+W-\mu_BB_\zeta(1-6\lambda\Delta^{-1})+4\mu_B^2B_\zeta^2(6\lambda^2\Delta^{-1}+W)^{-1}+\mu_B^2B_\zeta^2\Delta/12\lambda^2$
	$-6\lambda^2\Delta^{-1}+W+\mu_BB_\zeta(1-6\lambda\Delta^{-1})+4\mu_B^2B_\zeta^2(6\lambda^2\Delta^{-1}+W)^{-1}+\mu_B^2B_\zeta^2\Delta/12\lambda^2$
Γ_2	$8\mu_B^2B_\zeta^2(6\lambda^2\Delta^{-1}+2W)^{-1}$

siderations. Clearly, this anisotropy becomes small in the low- and high-temperature limits, but at intermediate temperatures and sufficiently high magnetic fields, it is possible to have nonlinear contributions to M from the Γ_4, Γ_3, and Γ_5 states. Figure 2 shows an example of this behavior. This figure has been drawn for $Cd_{1-x}Fe_xTe$ at 77 K using the following parameters: $\lambda=-100\ \text{cm}^{-1}$ and $\Delta=2500\ \text{cm}^{-1}$. At 150 kG we expect an anisotropy in M of 5%.

In wurtzite semiconductors the symmetry is trigonal rather than tetrahedral. The trigonal distortion which affects the energy levels and the magnetic properties of the system is described by the additional potential

$$V(C_{3v})=-b(2-L_\zeta^2)-c(\tfrac{7}{12}L_\zeta^4-\tfrac{31}{12}L_\zeta^2+\tfrac{6}{5}) \tag{39}$$

where L_ζ is the component of $\mathbf{L}$ along the trigonal axis. As an example we investigate the magnetic susceptibility of Fe^{2+} in a wurtzite semiconductor, such as CdSe.

The differential magnetic susceptibility is defined by

$$\chi_D=nk_BT\lim_{B\to 0}[Z^{-1}(\partial^2Z/\partial B^2)-Z^{-2}(\partial Z/\partial B)^2]\ . \tag{40}$$

We take into account the contributions of the states arising from the lowest orbital multiplet of Fe^{2+}, namely, $^5\Gamma_3$. We calculate the energy levels of the $^5\Gamma_3$ states using second-order perturbation theory and assuming that the Zeeman splitting is smaller than the separation between the levels caused by the trigonal field. The results, including all the levels within the lowest orbital states, are displayed in Tables III and IV for $\mathbf{B}$ parallel and perpendicular to the trigonal axis $\hat{\zeta}$, respectively. In these tables, $\Delta=6a$ is the crystal-field parameter and $3W=2|(3b-c)\lambda|/\Delta$ is the energy splitting of the $\Gamma_2(C_{3v})$ and $\Gamma_3(C_{3v})$ states originating from the $\Gamma_4(T_d)$ level of the lowest orbital state. Figure 3 shows the temperature dependence of the differential magnetic susceptibility of $Cd_{1-x}Fe_xSe$. We note that the susceptibilities when $\mathbf{B}$ is either parallel or perpendicular to $\hat{\zeta}$ differ considerably below 10 K in good qualitative agreement with experimental results.[5,6] To obtain an insight into the physical effect responsible for this behavior we consider only the three lowest states of Fe^{2+} in a trigonal field, namely Γ_1, Γ_2, and Γ_3 (see Fig. 4). The Zeeman interaction giving rise to the Van Vleck paramagnetism mixes the Γ_1 and Γ_2 states when $\mathbf{B}$ is parallel to $\hat{\zeta}$ and the Γ_1 and Γ_3 states when $\mathbf{B}$ is perpendicular to this axis. The energy of the ground state Γ_1 is then

$$E_0(B)=-(24\lambda^2/\Delta)-8\mu_B^2B_\zeta^2[(6\lambda^2/\Delta)-2W]^{-1}$$
$$-8\mu_B^2B_\perp^2[(6\lambda^2/\Delta)+W]^{-1}\ . \tag{41}$$

TABLE IV. Energy eigenvalues of the $^5\Gamma_3$ states of Fe^{2+} in a field of symmetry C_{3v} including terms to second order in the magnetic field $\mathbf{B}\perp\hat{\zeta}$.

C_{3v}	Energy eigenvalue
Γ_1	$-24\lambda^2\Delta^{-1}-8\mu_B^2B_\perp^2(6\lambda^2\Delta^{-1}+W)^{-1}$
Γ_2	$-18\lambda^2\Delta^{-1}-2W-\mu_B^2B_\perp^2[(3W)^{-1}+4(6\lambda^2\Delta^{-1}+2W)^{-1}+(12\lambda^2\Delta^{-1}+3W)^{-1}]$
Γ_3	$-18\lambda^2\Delta^{-1}+W+\mu_B^2B_\perp^2[(3W)^{-1}-2(6\lambda^2\Delta^{-1}-W)^{-1}-(\Delta/6\lambda^2)]$
	$-18\lambda^2\Delta^{-1}+W+\mu_B^2B_\perp^2[8(6\lambda^2\Delta^{-1}+W)^{-1}-2(6\lambda^2\Delta^{-1}-W)^{-1}-(\Delta/6\lambda^2)-(12\lambda^2\Delta^{-1}-3W)^{-1}]$
Γ_3	$-12\lambda^2\Delta^{-1}+\mu_B^2B_\perp^2[-4(6\lambda^2\Delta^{-1}-2W)^{-1}+2(6\lambda^2\Delta^{-1}-W)^{-1}-2(6\lambda^2\Delta^{-1}+W)^{-1}]$
	$-12\lambda^2\Delta^{-1}+\mu_B^2B_\perp^2[4(6\lambda^2\Delta^{-1}+2W)^{-1}+2(6\lambda^2\Delta^{-1}-W)^{-1}-2(6\lambda^2\Delta^{-1}+W)^{-1}]$
Γ_1	$-6\lambda^2\Delta^{-1}-2W+\mu_B^2B_\perp^2[(12\lambda^2\Delta^{-1}-3W)^{-1}+4(6\lambda^2\Delta^{-1}-2W)^{-1}-(3W)^{-1}]$
Γ_3	$-6\lambda^2\Delta^{-1}+W+\mu_B^2B_\perp^2[(12\lambda^2\Delta^{-1}+3W)^{-1}+(\Delta/6\lambda^2)+2(6\lambda^2\Delta^{-1}+W)^{-1}-8(6\lambda^2\Delta^{-1}-W)^{-1}]$
	$-6\lambda^2\Delta^{-1}+W+\mu_B^2B_\perp^2[(\Delta/6\lambda^2)+(3W)^{-1}+2(6\lambda^2\Delta^{-1}+W)^{-1}]$
Γ_2	$8\mu_B^2B_\perp^2(6\lambda^2\Delta^{-1}-W)^{-1}$

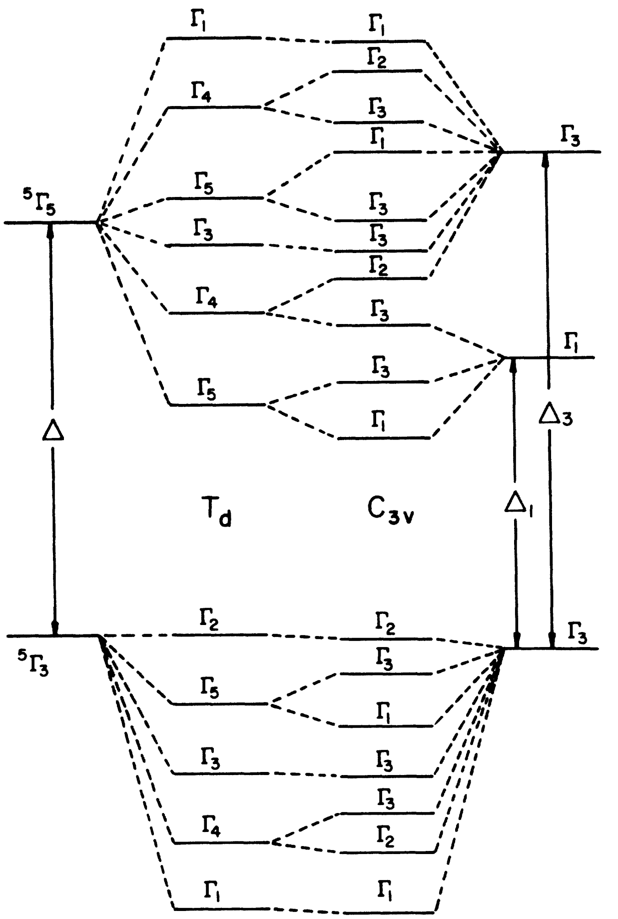

FIG. 4. Schematic diagram of the energy levels of Fe^{2+} in T_d and C_{3v} fields taking into account the spin-orbit interaction.

If n is the number of Fe^{2+} ions per unit volume,

$$\chi_{\parallel}=-(n/B_{\zeta})(\partial E_0/\partial B_{\zeta})=16n\mu_B^2[(6\lambda^2/\Delta)-2W]^{-1} \tag{42}$$

and

$$\chi_{\perp}=-(n/B_{\perp})(\partial E_0/\partial B_{\perp})=16n\mu_B^2[(6\lambda^2/\Delta)+W]^{-1} . \tag{43}$$

Thus $\chi_{\parallel}>\chi_{\perp}$ and a fit of $\chi_{\parallel}/\chi_{\perp}$ to the experimental result extrapolated to 0 K allows us to determine the value of W. We estimate[6] that $W\simeq 2.5\ \mathrm{cm}^{-1}$ for $\lambda=-81\ \mathrm{cm}^{-1}$ and $\Delta=2680\ \mathrm{cm}^{-1}$ appropriate to $\mathrm{Cd}_{1-x}\mathrm{Fe}_x\mathrm{Se}$. These parameters have been used in Fig. 3 which gives the behavior of $\chi_{\parallel}$ and $\chi_{\perp}$ as functions of the temperature T.

C. Application to the cases of Cu^{2+} and Sc^{2+}

Cu^{2+} has a spin quantum number $S=\frac{1}{2}$. As a consequence, it is very easy to investigate the effect of the spin-orbit coupling on its crystal-field-split states. In contrast to the case of iron, the lowest multiplet of Cu^{2+} is $^2\Gamma_5$ so that we take here $E_0(^2\Gamma_5)=0$. We now use $\Delta=6a$ to designate the difference in energy between the $^2\Gamma_3$ and $^2\Gamma_5$ states, i.e., $E_0(^2\Gamma_3)=\Delta$. A spin $S=\frac{1}{2}$ state belongs to the representation Γ_6 of T_d so that the $^2\Gamma_5$ state splits into $\Gamma_5\times\Gamma_6=\Gamma_7+\Gamma_8$ whereas the $^2\Gamma_3$ state becomes a Γ_8 level when the spin is introduced. For $S=\frac{1}{2}$, $\{S_i,S_j\}=0$, with $i\neq j$, and $S_x^2=S_y^2=S_z^2=\frac{1}{4}$. Equation (16) yields

$$H_0(^2\Gamma_5)=-\lambda\mathbf{I}\cdot\mathbf{S}-\frac{\lambda^2}{\Delta}\mathbf{I}\cdot\mathbf{S}-\frac{\lambda^2}{\Delta} . \tag{44}$$

As in the case of iron we introduce a new "angular momentum" operator

$$\mathbf{F}=\mathbf{I}+\mathbf{S} . \tag{45}$$

Now F takes the values $\frac{1}{2}$ and $\frac{3}{2}$. $\mathbf{I}\cdot\mathbf{S}$ is calculated from Eq. (36) and takes the values $\frac{1}{2}$ if $F=\frac{3}{2}$ and -1 if $F=\frac{1}{2}$. Therefore the eigenvalues of $H_0(^2\Gamma_5)$ are $-(\lambda/2)-(3\lambda^2/2\Delta)$ for the Γ_8 state and λ for the Γ_7 state. Since $\lambda<0$, the Γ_7 state lies below Γ_8. The Γ_8 wave functions are $\psi_{3/2}=v_+\alpha$, $\psi_{1/2}=3^{-1/2}v_+\beta+(\frac{2}{3})^{1/2}v_0\alpha$, $\psi_{-1/2}=3^{-1/2}v_-\alpha+(\frac{2}{3})^{1/2}v_0\beta$, $\psi_{-3/2}=v_-\beta$ where α and β correspond to spin up and spin down, respectively, and the subscript in the wave function indicates the row of the representation Γ_8 to which it belongs. The Γ_7 functions are $\chi_{1/2}=(\frac{2}{3})^{1/2}v_+\beta-3^{-1/2}v_0\alpha$ and $\chi_{-1/2}=-(\frac{2}{3})^{1/2}v_-\alpha+3^{-1/2}v_0\beta$.

The g factors corresponding to these two states are determined using the results of Appendix B and Eqs. (25), (27), and (28). They are listed in Table II. It is interesting to note that the Zeeman splittings of the fourfold level, characterized by $g_1=-9\lambda/\Delta$ and $g_2=4\lambda/\Delta$, are small compared to those usually encountered and in comparison to those of the $^2\Gamma_3=\Gamma_8$ state. Using the properties of $\mathbf{S}$ and Eq. (13), we find that for the $^2\Gamma_3$ states, the Hamiltonian $H_0(^2\Gamma_3)$ is

$$H_0(^2\Gamma_3)=\Delta+\frac{3\lambda^2}{2\Delta} \tag{46}$$

where it is understood that the quantity on the right-hand side is multiplied by the unit matrix in four dimensions. The appropriate eigenvectors are $\phi_{3/2}=-u_2\beta$, $\phi_{1/2}=u_1\alpha$, $\phi_{-1/2}=-u_1\beta$, $\phi_{-3/2}=u_2\alpha$.

With $S=\frac{1}{2}$, the Hamiltonian $H_1(^2\Gamma_3)$ [see Eq. (14)] becomes

$$H_1(^2\Gamma_3)=2\mu_B B\left[\left[1+2\frac{\lambda}{\Delta}\right]\hat{\mathbf{n}}\cdot\mathbf{S}+\frac{\lambda}{\Delta}(\mathbf{S}\cdot\hat{\mathbf{n}}-3S_z n_z)\sigma_z\right.$$
$$\left.+\frac{\sqrt{3}}{2}\frac{\lambda}{\Delta}(S_+n_+ + S_-n_-)\sigma_x\right] . \tag{47}$$

The matrix of $H_1(^2\Gamma_3)$ in the eigenfunctions above is

$$H_1(^2\Gamma_3)=\begin{bmatrix} -n_z\left[1+4\frac{\lambda}{\Delta}\right] & -\sqrt{3}\frac{\lambda}{\Delta}n_- & 0 & -\left[1+\frac{\lambda}{\Delta}\right]n_+ \\ -\sqrt{3}\frac{\lambda}{\Delta}n_+ & n_z & -\left[1+3\frac{\lambda}{\Delta}\right]n_- & 0 \\ 0 & -\left[1+3\frac{\lambda}{\Delta}\right]n_+ & -n_z & -\sqrt{3}\frac{\lambda}{\Delta}n_- \\ -\left[1+\frac{\lambda}{\Delta}\right]n_- & 0 & -\sqrt{3}\frac{\lambda}{\Delta}n_+ & n_z\left[1+4\frac{\lambda}{\Delta}\right] \end{bmatrix} \tag{48}$$

We know from group-theoretical arguments that the Zeeman Hamiltonian for a Γ_8 state can be written in the form (28). Direct comparison between (28) and (48) yields the values of g_1 and g_2 for the higher Γ_8 state of the Cu^{2+} ground term. We find $g_1=\frac{7}{3}+\lambda/3\Delta$ and $g_2=-\frac{4}{3}-4\lambda/3\Delta$.

Figure 5 shows the energy-level diagram of Cu^{2+} in a T_d field, taking into account the spin-orbit coupling and the effect of an external magnetic field. A similar diagram is expected for Sc^{2+} except that Γ_3 is then the lowest level and the spin-orbit coupling constant λ has a positive value.

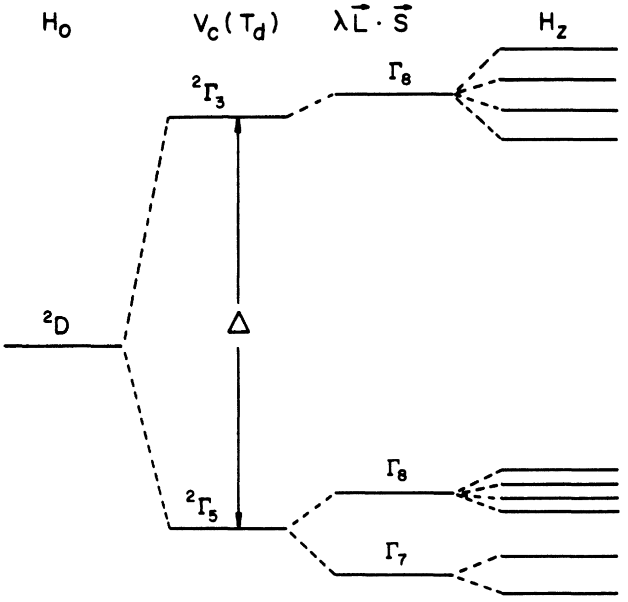

FIG. 5. Schematic diagram of the energy levels of Cu^{2+} in a T_d field taking into account the spin-orbit coupling and the Zeeman interaction.

III. THEORETICAL STUDY OF *F* TERMS IN A TETRAHEDRAL FIELD

A. General formalism

Having completed the study of *D* terms in a tetrahedral crystal field we now turn to the investigation of the behavior of *F* terms in the same potential. This applies to the four ions Ti^{2+}, V^{2+}, Co^{2+}, and Ni^{2+}. However, their spin quantum numbers *S* differ. As in Sec. II, we first develop the general theory of *F* terms in a T_d field including the effect of the spin-orbit coupling and the Zeeman interaction and subsequently particularize it to each individual case. When $L=3$, the crystal potential reads

$$V_c(T_d)=\pm a[\tfrac{1}{8}(L_+^2+L_-^2)^2+\tfrac{3}{2}L_z^4-12L_z^2-12] \tag{49}$$

where the upper sign holds for Co^{2+} and the lower sign for Ni^{2+}. We describe the orbital states of the free ion in terms of the eigenvectors of L_z which we denote by $|M_L\rangle$ ($M_L=3,2,1,0,-1,-2,-3$). The eigenvectors of the *F* term in the crystal field (49) and their symmetry characterization are

$$\Gamma_2\text{:}\quad \beta=2^{-1/2}(|2\rangle-|-2\rangle)\;; \tag{50a}$$

$$\Gamma_5\text{:}\quad \epsilon_+=(\tfrac{5}{8})^{1/2}|-1\rangle-(\tfrac{3}{8})^{1/2}|3\rangle\;,$$

$$\epsilon_0=2^{-1/2}(|2\rangle+|-2\rangle)\;,$$

$$\epsilon_-=(\tfrac{5}{8})^{1/2}|1\rangle-(\tfrac{3}{8})^{1/2}|-3\rangle\;; \tag{50b}$$

$$\Gamma_4\text{:}\quad \delta_+=-(\tfrac{3}{8})^{1/2}|1\rangle-(\tfrac{5}{8})^{1/2}|-3\rangle\;,$$

$$\delta_0=|0\rangle\;,$$

$$\delta_-=-(\tfrac{3}{8})^{1/2}|-1\rangle-(\tfrac{5}{8})^{1/2}|3\rangle\;. \tag{50c}$$

The wave functions ϵ_+, ϵ_0, and ϵ_- are selected so that they belong to rows of the irreducible representation Γ_5 of T_d generated by the functions $-(x+iy)/\sqrt{2}$, z, and $(x-iy)/\sqrt{2}$. In a similar way, δ_+, δ_0, and δ_- generate the irreducible representation Γ_4 identical to that whose basis functions are $-(\kappa_x+i\kappa_y)/\sqrt{2}$, κ_z, and

$(\kappa_x - i\kappa_y)/\sqrt{2}$ with $\kappa_x = x(y^2 - z^2)$, $\kappa_y = y(z^2 - x^2)$, and $\kappa_z = z(x^2 - y^2)$.

The spin Hamiltonian of the system is obtained in a manner similar to that of Sec. II. The Hamiltonian of Eq. (3) is rewritten as a $[7(2S+1)]\times[7(2S+1)]$ supermatrix in the vectors $|\mu, M_S\rangle$ where μ is any one of the orbital states (50) and $M_S = S, S-1, \ldots, -S+1, -S$ is an eigenvalue of the projection of the spin $\mathbf{S}$ on the $\hat{\mathbf{z}}$ axis. The Schrödinger equation in matrix form with entries in the order given above for μ and M_S reads

$$\begin{bmatrix} Q_2 & P & 0 \\ P^\dagger & Q_5 & R \\ 0^\dagger & R^\dagger & Q_4 \end{bmatrix} \begin{bmatrix} \psi^{(2)} \\ \psi^{(5)} \\ \psi^{(4)} \end{bmatrix} = E \begin{bmatrix} \psi^{(2)} \\ \psi^{(5)} \\ \psi^{(4)} \end{bmatrix} \tag{51}$$

where 0 is the zero matrix of dimensions $(2S+1)\times 3(2S+1)$ and $\psi^{(2)}$, $\psi^{(5)}$, and $\psi^{(4)}$ are wave functions having $2S+1$, $3(2S+1)$, and $3(2S+1)$ components, respectively. To fix the ideas we take Γ_2 as the lowest state, an arbitrary assumption for the purpose of the description of our procedure. However, it can be shown that the Γ_5 state always lies between Γ_2 and Γ_4. The square matrices Q_2, Q_5, and Q_4 are obtained calculating the matrix elements of the Hamiltonian (3) and are given by

$$Q_2 = E_0(\Gamma_2) + 2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S} , \tag{52}$$

$$Q_5 = E_0(\Gamma_5) + 2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S} + \tfrac{1}{2}(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}})\cdot\mathbf{I} , \tag{53}$$

and

$$Q_4 = E_0(\Gamma_4) + 2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S} - \tfrac{3}{2}(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}})\cdot\mathbf{I} \tag{54}$$

where $E_0(\Gamma_i)$ are the energies of the unperturbed crystal-field-split states and $\mathbf{I}$ is the angular momentum matrix for $I=1$, introduced earlier in the study of D terms. Finally, the $(2S+1)\times[3(2S+1)]$ and $[3(2S+1)]\times[3(2S+1)]$ matrices P and R are given by

$$P = (\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}})\cdot\mathbf{V} \tag{55}$$

and

$$R = \tfrac{1}{2}(\tfrac{15}{2})^{1/2}(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}})\cdot\mathbf{W} . \tag{56}$$

The matrices $\mathbf{V}$ and $\mathbf{W}$ are given by

$$\mathbf{V} = 2\left[-\frac{\hat{\mathbf{x}} + i\hat{\mathbf{y}}}{\sqrt{2}}, \hat{\mathbf{z}}, \frac{\hat{\mathbf{x}} - i\hat{\mathbf{y}}}{\sqrt{2}} \right] \tag{57}$$

and

$$\mathbf{W} = i\sqrt{2}(\hat{\mathbf{x}}\{I_y, I_z\} + \hat{\mathbf{y}}\{I_z, I_x\} + \hat{\mathbf{z}}\{I_x, I_y\}) . \tag{58}$$

Equation (51) is equivalent to three coupled relations which can be solved for the wave functions $\psi^{(i)}$ ($i = 2,5,4$) by iteration keeping terms up to second order in λ and $\mu_B B$. In this way we obtain the Hamiltonians for the Γ_2, Γ_5, and Γ_4 states. They are

$$H(\Gamma_2) = E_0(\Gamma_2) + 2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S} + \frac{1}{E_0(\Gamma_2) - E_0(\Gamma_5)}(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}})\cdot\mathbf{V}\mathbf{V}^\dagger\cdot(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}}) , \tag{59}$$

$$\begin{aligned} H(\Gamma_5) = {} & E_0(\Gamma_5) + 2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S} + \tfrac{1}{2}(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}})\cdot\mathbf{I} + \frac{15}{8}\frac{1}{E_0(\Gamma_5) - E_0(\Gamma_4)}(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}})\cdot\mathbf{W}\mathbf{W}^\dagger\cdot(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}}) \\ & + \frac{1}{E_0(\Gamma_5) - E_0(\Gamma_2)}(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}})\cdot\mathbf{V}^\dagger\mathbf{V}\cdot(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}}) , \end{aligned} \tag{60}$$

and

$$H(\Gamma_4) = E_0(\Gamma_4) + 2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S} - \tfrac{3}{2}(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}})\cdot\mathbf{I} + \frac{15}{8}\frac{1}{E_0(\Gamma_4) - E_0(\Gamma_5)}(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}})\cdot\mathbf{W}^\dagger\mathbf{W}\cdot(\lambda\mathbf{S} + \mu_B B\hat{\mathbf{n}}) \tag{61}$$

where we used the explicit expressions of the matrices Q_2, Q_5, Q_4, P, and R. To proceed further, we follow the same line of reasoning as in Sec. II and express the products $\mathbf{W}\mathbf{W}^\dagger$, $\mathbf{W}^\dagger\mathbf{W}$, $\mathbf{V}\mathbf{V}^\dagger$, and $\mathbf{V}^\dagger\mathbf{V}$ in terms of the components of the pseudoangular momentum $\mathbf{I}$, i.e.,

$$\mathbf{W}\mathbf{W}^\dagger = \mathbf{W}^\dagger\mathbf{W} = 2\sum_i \hat{\mathbf{e}}_i\hat{\mathbf{e}}_i I_i^2 - \sum_{i<j}(\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j + \hat{\mathbf{e}}_j\hat{\mathbf{e}}_i)\{I_i, I_j\} - i\sum_{i,j,k}\epsilon_{ijk}\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j I_k , \tag{62}$$

$$\mathbf{V}\mathbf{V}^\dagger = 4\sum_i \hat{\mathbf{e}}_i\hat{\mathbf{e}}_i , \tag{63}$$

and

$$\mathbf{V}^\dagger\mathbf{V}=4\sum_i \hat{\mathbf{e}}_i\hat{\mathbf{e}}_i(1-I_i^2)-2\sum_{i<j}(\hat{\mathbf{e}}_i\hat{\mathbf{e}}_j+\hat{\mathbf{e}}_j\hat{\mathbf{e}}_i)\{I_i,I_j\}+2i\sum_{i,j,k}\epsilon_{ijk}\hat{\mathbf{e}}_i\hat{\mathbf{e}}_jI_k \ . \tag{64}$$

Use of Eqs. (59) and (63) yields the spin Hamiltonian for the Γ_2 orbital singlet

$$H(\Gamma_2)=E_0(\Gamma_2)+2\mu_B B\hat{\mathbf{n}}\cdot\mathbf{S}+\frac{4\lambda^2\mathbf{S}\cdot\mathbf{S}}{E_0(\Gamma_2)-E_0(\Gamma_5)}+\frac{8\mu_B B\lambda}{E_0(\Gamma_2)-E_0(\Gamma_5)}\hat{\mathbf{n}}\cdot\mathbf{S}+\frac{4(\mu_B B)^2}{E_0(\Gamma_2)-E_0(\Gamma_5)} \ . \tag{65}$$

For the Γ_4 and Γ_5 triplets we write

$$H(\Gamma_\nu)=H_0(\Gamma_\nu)+H_1(\Gamma_\nu)+H_2(\Gamma_\nu) \tag{66}$$

where $\nu=4,5$ and the subscripts 0,1,2 indicate the power of **B** in the expression. We have

$$H_0(\Gamma_5)=E_0(\Gamma_5)+\frac{\lambda}{2}\mathbf{S}\cdot\mathbf{I}+\frac{15}{4}\frac{\lambda^2}{E_0(\Gamma_5)-E_0(\Gamma_4)}[\tfrac{2}{3}\tilde{Q}+\tfrac{4}{3}\mathbf{S}\cdot\mathbf{S}-(\mathbf{S}\cdot\mathbf{I})^2]+\frac{4\lambda^2}{E_0(\Gamma_5)-E_0(\Gamma_2)}[\mathbf{S}\cdot\mathbf{S}-(\mathbf{S}\cdot\mathbf{I})^2-\mathbf{S}\cdot\mathbf{I}] \ , \tag{67}$$

$$H_1(\Gamma_5)=\mu_B B\left[2\hat{\mathbf{n}}\cdot\mathbf{S}+\tfrac{1}{2}\hat{\mathbf{n}}\cdot\mathbf{I}+\frac{15}{4}\frac{\lambda}{E_0(\Gamma_5)-E_0(\Gamma_4)}(\tfrac{2}{3}Q+\tfrac{8}{3}\hat{\mathbf{n}}\cdot\mathbf{S}-\{\mathbf{S}\cdot\mathbf{I},\,\mathbf{I}\cdot\hat{\mathbf{n}}\})+\frac{4\lambda}{E_0(\Gamma_5)-E_0(\Gamma_2)}(2\hat{\mathbf{n}}\cdot\mathbf{S}-\{\mathbf{S}\cdot\mathbf{I},\,\mathbf{I}\cdot\hat{\mathbf{n}}\})\right] \ , \tag{68}$$

and

$$H_2(\Gamma_5)=(\mu_B B)^2\left[\frac{15}{8}\frac{1}{E_0(\Gamma_5)-E_0(\Gamma_4)}\left[4\sum_i n_i^2I_i^2-2(\hat{\mathbf{n}}\cdot\mathbf{I})^2\right]+\frac{4}{E_0(\Gamma_5)-E_0(\Gamma_2)}[1-(\hat{\mathbf{n}}\cdot\mathbf{I})^2]\right] \tag{69}$$

for the Γ_5 triplet and

$$H_0(\Gamma_4)=E_0(\Gamma_4)-\tfrac{3}{2}\lambda\mathbf{S}\cdot\mathbf{I}+\frac{15}{4}\frac{\lambda^2}{E_0(\Gamma_4)-E_0(\Gamma_5)}[\tfrac{2}{3}\tilde{Q}+\tfrac{4}{3}\mathbf{S}\cdot\mathbf{S}-(\mathbf{S}\cdot\mathbf{I})^2] \ , \tag{70}$$

$$H_1(\Gamma_4)=\mu_B B\left[2\hat{\mathbf{n}}\cdot S-\tfrac{3}{2}\hat{\mathbf{n}}\cdot\mathbf{I}+\frac{15}{4}\frac{\lambda}{E_0(\Gamma_4)-E_0(\Gamma_5)}(\tfrac{2}{3}Q+\tfrac{8}{3}\hat{\mathbf{n}}\cdot\mathbf{S}-\{\mathbf{S}\cdot\mathbf{I},\mathbf{I}\cdot\hat{\mathbf{n}}\})\right] \ , \tag{71}$$

and

$$H_2(\Gamma_4)=\frac{15}{4}\frac{(\mu_B B)^2}{E_0(\Gamma_4)-E_0(\Gamma_5)}\left[\sum_i n_i^2I_i^2-\sum_{i<j}n_in_j\{I_i,I_j\}\right] \ , \tag{72}$$

for the Γ_4 states. Here we have used Eqs. (19)–(23).

The results given so far are valid for any value of S and apply to Co^{2+} as well as to Ni^{2+}. The explicit evaluation of the eigenvalues and eigenvectors of the Hamiltonians derived above requires the specification of the spin quantum number S and, hence, the specialization to either the case of Co^{2+} or that of Ni^{2+}. As earlier we make the assumption that the spin-orbit coupling is stronger than the Zeeman interaction.

B. Application to the cases of Co^{2+} and V^{2+}

The ground term of Co^{2+} has a spin quantum number $S=\frac{3}{2}$ and the ground multiplet is the orbital singlet Γ_2. Therefore, with $E_0(\Gamma_2)=0$, we write $E_0(\Gamma_5)=\Delta=30a$ and $E_0(\Gamma_4)=9\Delta/5$. From Eq. (65), the Hamiltonian for the ground state of Co^{2+} is

$$H(^4\Gamma_2)=-15\frac{\lambda^2}{\Delta}+2\mu_B B\left[1-4\frac{\lambda}{\Delta}\right]\hat{\mathbf{n}}\cdot\mathbf{S}-\frac{4(\mu_B B)^2}{\Delta} \tag{73}$$

so that, in a purely tetrahedral site, the g factor is isotropic and equal to $2-(8\lambda/\Delta)$. Replacing $E_0(\Gamma_i)$ by its value we get, from Eqs. (67) and (70), the Hamiltonians for the Γ_5 and Γ_4 triplets, namely,

$$H_0(^4\Gamma_5)=\Delta+\frac{\lambda}{2}\mathbf{S}\cdot\mathbf{I}-\frac{75}{16}\frac{\lambda^2}{\Delta}[\tfrac{2}{3}\tilde{Q}+\tfrac{4}{3}\mathbf{S}\cdot\mathbf{S}-(\mathbf{S}\cdot\mathbf{I})^2]+\frac{4\lambda^2}{\Delta}[\mathbf{S}\cdot\mathbf{S}-(\mathbf{S}\cdot\mathbf{I})^2-\mathbf{S}\cdot\mathbf{I}] \tag{74}$$

and

$$H_0(^4\Gamma_4)=\tfrac{9}{5}\Delta-\tfrac{3}{2}\lambda\mathbf{S}\cdot\mathbf{I}+\frac{75}{16}\frac{\lambda^2}{\Delta}[\tfrac{2}{3}\tilde{Q}+\tfrac{4}{3}\mathbf{S}\cdot\mathbf{S}-(\mathbf{S}\cdot\mathbf{I})^2] \ . \tag{75}$$

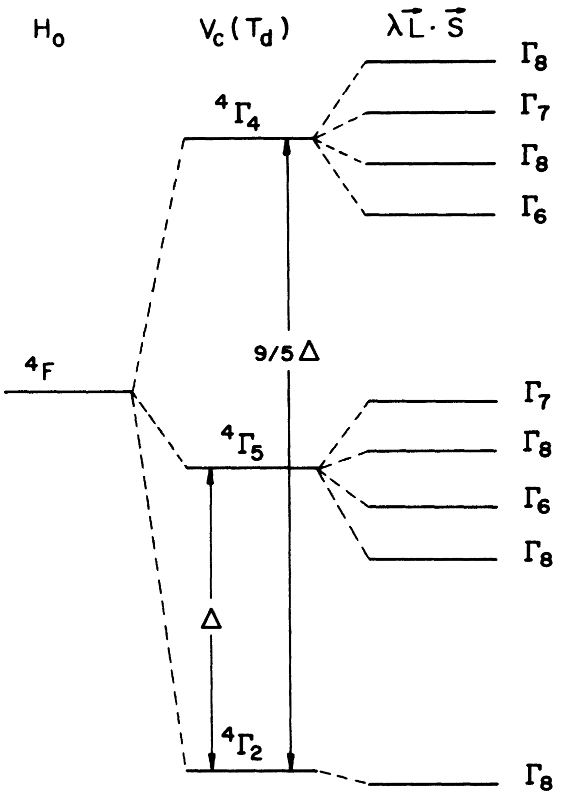

FIG. 6. Schematic diagram of the energy levels of Co^{2+} taking into account the spin-orbit coupling.

The spin states belong to the representation Γ_8 of T_d and the states $^4\Gamma_5$ and $^4\Gamma_4$ split into $\Gamma_6+\Gamma_7+2\Gamma_8$ under the influence of the spin-orbit coupling whereas the Γ_2 ground state becomes Γ_8. Note that all these states are at least doubly degenerate in agreement with Kramers' theorem since Co^{2+} has an odd number of electrons in the incomplete $3d$ shell.

We now evaluate the expectation value of the Hamiltonians (74) and (75) in the $|F,M_F\rangle$ representation using the results of Appendix A. We find that the energies of the levels originating from the $^4\Gamma_5(T_d)$ state are $\Delta+3\lambda/4-(1305\lambda^2/64\Delta)$, $\Delta+3\lambda/4-(225\lambda^2/64\Delta)$, $\Delta-\lambda/2+(15\lambda^2/4\Delta)$, and $\Delta-5\lambda/4-(225\lambda^2/64\Delta)$ for Γ_8, Γ_6, Γ_8, and Γ_7, respectively. For the $^4\Gamma_4(T_d)$ states we find $(9\Delta/5)+15\lambda/4+(225\lambda^2/64\Delta)$, $(9\Delta/5)+3\lambda/2+(45\lambda^2/4\Delta)$, $(9\Delta/5)-9\lambda/4+(225\lambda^2/64\Delta)$, and $(9\Delta/5)-9\lambda/4+(1305\lambda^2/64\Delta)$ corresponding to Γ_6, Γ_8, Γ_7, and Γ_8 levels, respectively. Our results are in agreement with those of Ryskin, Natadze, and Kazanskii.[9] Figure 6 shows the energy-level scheme of Co^{2+} in a field of tetrahedral symmetry including the effect of the spin-orbit coupling on the crystal-field-split states. The diagram of levels of V^{2+} is obtained from that of Co^{2+} by reversing the order of the states and changing the sign of the spin-orbit coupling constant λ, i.e., by reversing the order of the spin-orbit-split states as well. The g factors for Co^{2+} are anisotropic and are given in Table V.

C. Application to the cases of Ni^{2+} and Ti^{2+}

Ni^{2+} is a doubly ionized ion having spin quantum number $S=1$ in its ground term. The Γ_4 state is the lowest multiplet of Ni^{2+} in a field of tetrahedral symmetry. Hence, we take $E_0(\Gamma_4)=0$, $E_0(\Gamma_5)=\Delta$ so that $E_0(\Gamma_2)=9\Delta/4$. Equations (70), (67), and (65) yield

$$H_0(^3\Gamma_4)=-\tfrac{3}{2}\lambda\mathbf{S}\cdot\mathbf{I}-\frac{15}{4}\frac{\lambda^2}{\Delta}[\tfrac{1}{3}\tilde{Q}+\tfrac{8}{3}-(\mathbf{S}\cdot\mathbf{I})^2]\ , \tag{76}$$

$$\begin{aligned}H_0(^3\Gamma_5)=&\ \Delta+\frac{\lambda}{2}\mathbf{S}\cdot\mathbf{I}+\frac{15}{4}\frac{\lambda^2}{\Delta}[\tfrac{1}{3}\tilde{Q}+\tfrac{8}{3}-(\mathbf{S}\cdot\mathbf{I})^2]\\&-\frac{16\lambda^2}{5\Delta}[2-(\mathbf{S}\cdot\mathbf{I})^2-\mathbf{S}\cdot\mathbf{I}]\ ,\end{aligned} \tag{77}$$

and

$$\begin{aligned}H(^3\Gamma_2)=&\ \tfrac{9}{4}\Delta+\frac{32}{5}\frac{\lambda^2}{\Delta}+2\mu_B B\left(1+\frac{16}{5}\frac{\lambda}{\Delta}\right]\hat{\mathbf{n}}\cdot\mathbf{S}\\&+\frac{16}{5}\frac{(\mu_B B)^2}{\Delta}\ .\end{aligned} \tag{78}$$

TABLE V. g factors for Ni^{2+} and Co^{2+}.

	Ni^{2+}		Co^{2+}			
T_d	Level	g	Level	$g^{(6,7)}$	g_1	g_2
Γ_4	Γ_1		Γ_6	$\frac{13}{3}+(75\lambda/8\Delta)$		
	Γ_4	$\frac{1}{4}-(15\lambda/4\Delta)$	Γ_8		$\frac{16}{15}+(65\lambda/4\Delta)$	$-5\lambda/\Delta$
	Γ_3		Γ_7	$1-(75\lambda/8\Delta)$		
	Γ_5	$\frac{1}{4}+(15\lambda/4\Delta)$	Γ_8		$\frac{5}{2}+(435\lambda/16\Delta)$	$-\frac{6}{5}-(45\lambda/4\Delta)$
Γ_5	Γ_4	$\frac{5}{4}-(15\lambda/4\Delta)$	Γ_8		$\frac{35}{6}-(435\lambda/16\Delta)$	$-\frac{14}{5}+(45\lambda/4\Delta)$
	Γ_3		Γ_6	$\frac{7}{3}+(75\lambda/8\Delta)$		
	Γ_5	$\frac{5}{4}-(53\lambda/20\Delta)$	Γ_8		$\frac{8}{5}-(33\lambda/4\Delta)$	$5\lambda/\Delta$
	Γ_2		Γ_7	$3-(75\lambda/8\Delta)$		
Γ_2	Γ_5	$2+(32\lambda/5\Delta)$	Γ_8		$2-(8\lambda/\Delta)$	0

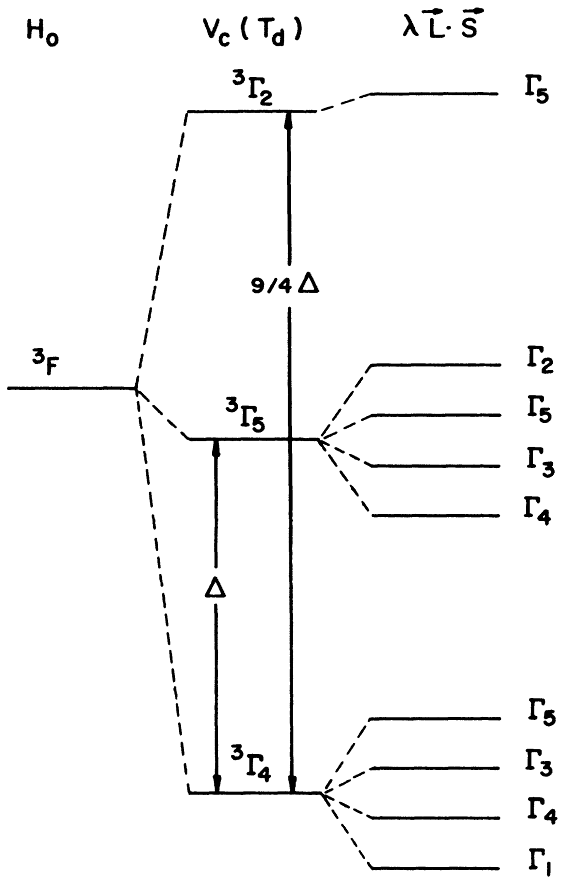

FIG. 7. Schematic diagram of the energy levels of Ni^{2+} in a tetrahedral crystal field including spin-orbit coupling.

The spin states of Ni^{2+} belong to $D_{+}^{(1)} \equiv \Gamma_4$ and the Γ_4 and Γ_5 states split into $\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5$ and $\Gamma_2+\Gamma_3+\Gamma_4+\Gamma_5$, respectively, whereas the Γ_2 level becomes Γ_5 when the spin-orbit coupling is taken into account.

The energies of the spin-orbit-split states are easily determined from Appendix A and Eqs. (76) and (77). We find that the Γ_1 ground state has energy 3λ while the Γ_4, Γ_3, and Γ_5 levels of the lowest multiplet of Ni^{2+} have energies $3\lambda/2-(15\lambda^2/4\Delta)$, $-3\lambda/2-(45\lambda^2/4\Delta)$, and $-3\lambda/2-(15\lambda^2/4\Delta)$. The levels originating from $^3\Gamma_5$ have energies $\Delta-\lambda$, $\Delta-\lambda/2-(53\lambda^2/20\Delta)$, $\Delta+\lambda/2+(45\lambda^2/4\Delta)$, and $\Delta+\lambda/2+(15\lambda^2/4\Delta)$ for the Γ_2, Γ_5, Γ_3, and Γ_4 states, respectively. Ni^{2+} having an even number of electrons in the incomplete $3d$ shell has g factors that are isotropic. Their values are shown in Table V. Figure 7 represents the energy levels of Ni^{2+} in a crystal field of tetrahedral symmetry in the presence of spin-orbit coupling. We note that the lowest state of Ni^{2+} is a Γ_1 singlet so that this ion will exhibit Van Vleck paramagnetism at the lowest temperatures, for reasons similar to those occurring in the iron-based semiconductors. In contrast, Ti^{2+}, whose energy diagram is obtained from that of Fig. 7 reversing the order of the levels, has a Γ_5 triplet as its ground state and, hence, exhibits a standard temperature-dependent paramagnetism.

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APPENDIX A: MATRIX ELEMENTS OF $\tilde{Q}$

We evaluate here the matrix elements of the operator $\tilde{Q}$ defined in Eq. (22). This operator can be conveniently rewritten as

$$\tilde{Q}=(3S_z^2-\mathbf{S}\cdot\mathbf{S})(3I_z^2-\mathbf{I}\cdot\mathbf{I})+\tfrac{3}{4}(S_+^2+S_-^2)(I_+^2+I_-^2) \tag{A1}$$

and its matrix elements in the $|F,M_F\rangle$ representation are obtained from

$$\langle F,M_F'|\tilde{Q}|F,M_F\rangle=\sum_{M_S',M_I'}\sum_{M_S,M_I}\langle F,M_F'|M_S',M_I'\rangle \times\langle M_S',M_I'|\tilde{Q}|M_S,M_I\rangle \times\langle M_S,M_I|F,M_F\rangle\,. \tag{A2}$$

We disregard matrix elements connecting different values of F because the degeneracy of the states $F=S-1$, S, $S+1$ is already lifted in first-order perturbation theory by the term proportional to $\lambda\mathbf{S}\cdot\mathbf{I}$ in the Hamiltonians (24), (67), and (70).

To evaluate the matrix elements of $\tilde{Q}$ in the $|F,M_F\rangle$ representation we first carry out the summation over M_I, keeping in mind the fact that $M_S+M_I=M_F$. Use of Clebsch-Gordan coefficients[10] corresponding to the addition of any angular momentum operator S with an angular momentum $I=1$ then yields, for the diagonal matrix elements,

$$\langle F=S-1,\,M_F|\tilde{Q}|F=S-1,\,M_F\rangle=\frac{1}{2S(2S+1)}[21M_F^4+3M_F^2(5-6S^2+6S)+S(5S^3+6S^2+7S+6)]\,, \tag{A3}$$

$$\langle F=S,\,M_F|\tilde{Q}|F=S,\,M_F\rangle=\frac{1}{2S(S+1)}[-21M_F^4-3M_F^2(5-6S^2-6S)+S(-5S^3-10S^2+S+6)]\,, \tag{A4}$$

and

$$\langle F=S+1, M_F|\tilde{Q}|F=S+1, M_F\rangle = \frac{1}{(2S+1)(2S+2)}[21M_F^4-3M_F^2(7+6S^2+18S)+S(5S^3+14S^2+19S+10)] \ . \tag{A5}$$

In a similar way, the only nonvanishing off-diagonal matrix elements are found to be

$$\langle F=S-1, M_F\pm4|\tilde{Q}|F=S-1, M_F\rangle$$

$$=\frac{3}{4S(2S+1)}\{[S^2-(M_F\pm1)^2][S^2-(M_F\pm2)^2][S^2-(M_F\pm3)^2](S\pm M_F)(S\mp M_F-4)\}^{1/2} \ , \tag{A6}$$

$$\langle F=S, M_F\pm4|\tilde{Q}|F=S, M_F\rangle$$

$$=-\frac{3}{4S(S+1)}\{(S\mp M_F)[S^2-(M_F\pm1)^2][S^2-(M_F\pm2)^2][S^2-(M_F\pm3)^2](S\pm M_F+4)\}^{1/2} \ , \tag{A7}$$

and

$$\langle F=S+1, M_F\pm4|\tilde{Q}|F=S+1, M_F\rangle$$

$$=\frac{3}{2(2S+1)(2S+2)}\{(S\mp M_F)[(S\mp M_F)^2-1][S^2-(M_F\pm2)^2](S\pm M_F+3)(S\pm M_F+4)(S\pm M_F+5)\}^{1/2} \ . \tag{A8}$$

APPENDIX B: MATRIX ELEMENTS OF S, I, and Q IN THE $|F,M_F\rangle$ REPRESENTATION

This appendix is devoted to the evaluation of the matrix elements of the operators that are needed in the study of the Zeeman Hamiltonians (25), (68), and (71). By virtue of the Wigner-Eckart theorem, we have

$$\langle F,M_F'|\mathbf{V}|F,M_F\rangle = \frac{\langle F,M_F|\mathbf{V}\cdot\mathbf{F}|F,M_F\rangle}{F(F+1)}\langle F,M_F'|\mathbf{F}|F,M_F\rangle \tag{B1}$$

for any vector operator **V**. This allows us to find the matrix elements of the operators **S** and **I**. We have

$$\langle F,M_F'|\mathbf{S}|F,M_F\rangle = \frac{F(F+1)+S(S+1)-I(I+1)}{2F(F+1)} \times\langle F,M_F'|\mathbf{F}|F,M_F\rangle \tag{B2}$$

and

$$\langle F,M_F'|\mathbf{I}|F,M_F\rangle = \frac{F(F+1)-S(S+1)+I(I+1)}{2F(F+1)} \times\langle F,M_F'|\mathbf{F}|F,M_F\rangle \ . \tag{B3}$$

The matrix elements of the operator Q defined in Eq. (23) are also needed. Since we know, from group-theoretical arguments, the form of the Zeeman Hamiltonian [see Eqs. (27), (28)], it is sufficient to consider the magnetic field to be oriented in a specific direction, say $\hat{\mathbf{z}}$, so that $\hat{\mathbf{n}}=(0,0,1)$ and the operator Q becomes

$$Q=2S_z(3I_z^2-\mathbf{I}\cdot\mathbf{I}) \ . \tag{B4}$$

Its matrix elements are

$$\langle F,M_F'|2S_z(3I_z^2-\mathbf{I}\cdot\mathbf{I})|F,M_F\rangle = \sum_{M_S,M_I}|\langle F,M_F|M_S,M_I\rangle|^2 2M_S[3M_I^2-I(I+1)]\delta_{M_F'M_F} \ . \tag{B5}$$

We first perform the summation over $M_I = 1, 0, -1$ and use the expression for the Clebsch-Gordan coefficients. We find

$$\langle F=S-1, M_F|2S_z(3I_z^2-\mathbf{I}\cdot\mathbf{I})|F=S-1, M_F\rangle = 2M_F\frac{3M_F^2-S^2+3S+1}{S(2S+1)}, \quad \text{(B6)}$$

$$\langle F=S, M_F|2S_z(3I_z^2-\mathbf{I}\cdot\mathbf{I})|F=S, M_F\rangle = 2M_F\frac{S^2+S-1-3M_F^2}{S(S+1)}, \quad \text{(B7)}$$

and

$$\langle F=S+1, M_F|2S_z(3I_z^2-\mathbf{I}\cdot\mathbf{I})|F=S+1, M_F\rangle = 2M_F\frac{3M_F^2-3-S^2-5S}{(S+1)(2S+1)}. \quad \text{(B8)}$$

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[1] See, for example, *Diluted Magnetic Semiconductors* in *Semiconductors and Semimetals,* edited by J. K. Furdyna and J. Kossut (Academic, Boston, 1988), Vol. 25.

[2] The group-theoretical notation for the point groups and the corresponding irreducible representations follows G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (M.I.T. Press, Cambridge, MA, 1966).

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