

Interaction between band electrons and transition-metal ions in diluted magnetic semiconductors

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We present a theoretical study of the effective exchange interaction arising from the hybridization between the valence-band states and the localized d orbitals of a transition-metal impurity in a II-VI semiconductor. The irreducible tensor method is used to deduce the effective Hamiltonian in the manifold of the ground multiplet of a $3d^n$ ion in a tetrahedral crystal field. There is no coupling in the cases of Sc^{2+} and Ti^{2+} ions. For Mn^{2+} , Fe^{2+} , and Co^{2+} the coupling reduces to the usual spin-exchange Kondo Hamiltonian, in agreement with experiments; the observed increase of the exchange parameter $|N_0\beta|$ from Mn to Fe to Co in a given host is also explained. In the cases of V^{2+} , Cr^{2+} , Ni^{2+} , and Cu^{2+} additional coupling terms involving the orbital degrees of freedom are obtained; these predict drastic modifications of the valence-band splitting in a magnetic field.

I. INTRODUCTION

Semimagnetic or diluted magnetic semiconductors (DMS) are typically solid solutions of II-VI compounds: $A_{1-x}^{II}M_xB^{VI}$, where $A^{II} = \text{Cd, Zn, Hg}$, $B^{VI} = \text{Te, Se, S}$, and M is a transition metal. Mn-based DMS have been investigated most extensively. The Fe- and Co-based ones have been synthesized and studied more recently. The spectacular magneto-optical properties of the Mn-based DMS were early interpreted¹ in terms of the Kondo-like exchange Hamiltonian of the form $-J\mathbf{s}\cdot\mathbf{S}$, for the coupling between the band electron spin \mathbf{s} and the Mn^{2+} ion spin \mathbf{S} , with the Hund's rule value $S = \frac{5}{2}$. The same Hamiltonian is used for describing transport properties and bound magnetic polarons. A mean-field analysis of combined magnetorefectivity and magnetization measurements yields accurate values of the exchange parameter in wide-gap DMS.² Generally speaking, the exchange parameter for the conduction-band minimum $N_0\alpha$ is positive (ferromagnetic) and of order 0.2 eV, whereas that for the valence-band maximum $N_0\beta$ is negative (antiferromagnetic) and of order 1.0 eV. We³ have accounted for these features in the following manner. The relatively small $N_0\alpha$ corresponds to the ordinary exchange integral of the Coulomb potential between a conduction-band electron and the Mn d electrons. On the other hand, $N_0\beta$ is dominated by the effective exchange arising from the hybridization between the valence-band states and the localized d orbitals. The Schrieffer-Wolff transformation⁴ was used to quantitatively relate $N_0\beta$ to the Anderson⁵ hybridization parameter V_{kd} and the energy of the d level below the valence-band maximum. These ideas have been further developed by Larson *et al.*⁶ Recently, we have studied⁷ the variation of the ion-carrier exchange parameters with the wave vector \mathbf{k} in the Brillouin zone. Hass⁸ provides a review of theoretical works on magnetic interactions in Mn-based DMS.

Let us now recall that the Schrieffer-Wolff formula for the hybridization-induced effective exchange Hamiltonian corresponds to the case of an orbitally nondegenerate

localized level occupied by a single electron. It remains valid⁹ for the S -state ion Mn^{2+} thus justifying its use in Mn-based DMS. But, in the case of other transition metal ions such as Fe^{2+} or Co^{2+} with nonzero orbital angular momentum, in addition to the spin exchange, orbital coupling terms¹⁰ were *a priori* expected. Experimental data¹¹ in Fe- and Co-based DMS are, however, found to be consistent with the simple Kondo Hamiltonian. Moreover, in passing from Mn to Fe to Co in a given host lattice, $N_0\alpha$ varies little, but $|N_0\beta|$ shows a systematic increase.

Theoretically, in the DMS context, Blinowski *et al.*¹² have studied the hybridization-induced hole-ion coupling in the cases of Cr^{2+} and Fe^{2+} in tetrahedral symmetry within a straightforward perturbation approach. They indeed find that the orbital couplings are quenched in the 5E ground multiplet of Fe^{2+} . More recently, Masek¹³ have reported CPA-based spin-polarized band calculations showing an increase of effective $|N_0\beta|$ from Mn to Co in ZnSe.

In the present work we treat the ion-carrier coupling in the general case of a $3d$ transition metal impurity in a II-VI semiconductor. First of all, the conduction-band minimum is known to belong to the representation a_1 of the tetrahedral point group T_d . As a result, even in the case of non- S -state ions, only spin-exchange coupling is allowed. Moreover, there is no hybridization between a_1 states and the d orbitals. Thus $N_0\alpha$ arises from direct exchange only, which is not expected to vary significantly with the number of electrons in the d shell,¹⁴ in agreement with experiments. We shall, therefore, focus our attention on the hole-ion coupling. The direct exchange part, i.e., the contribution of the exchange integral between the anion p -like valence-band states and the transition-metal d orbitals, is expected to be relatively small, because it is mostly off site. So, we study only the effective coupling arising from hybridization. Our approach is based on group theory and similar to that of Hirst¹⁰ for metallic alloys. We derive the effective Hamiltonian in the second order of V_{kd} and express it in terms

of irreducible tensors in the manifold of the ground multiplet of the ion in tetrahedral crystal field.

In Sec. II we treat the general case of the stable ionic configuration $3d^n$, with $n=1,2,\dots,9$. Section III specializes in the cases Mn^{2+} , Fe^{2+} , and Co^{2+} , where the coupling is shown to reduce to the spin-exchange Kondo form. In Sec. IV the results for the cases of V^{2+} , Cr^{2+} , Ni^{2+} , and Cu^{2+} are written in terms of spin and orbital angular momenta. Moreover, we examine the influence of the orbital coupling terms on the valence-band Zeeman splitting. In Sec. V we account for the observed increase of $|N_0\beta|$ from Mn to Fe to Co in a given host. Finally, some concluding remarks are presented in Sec. VI.

II. EFFECTIVE HAMILTONIAN IN THE GENERAL CASE

We assume tetrahedral (T_d) symmetry and neglect spin-orbit splitting in deriving the effective Hamiltonian. The transition-metal ion ($3d^n$) is treated in the intermediate crystal-field coupling scheme. The Hund's rule ground term (L,S) is split in the crystal field giving rise to the ground multiplet (i,S) where i is an irreducible representation of T_d . The spin-orbit interaction and also the trigonal distortion (C_{3V}) in the case of wurtzite DMS, of course, lead to further splittings. But these splittings as well as the corresponding ones in the valence band are small compared to the interconfigurational energy differences appearing in the denominators in the effective Hamiltonian (see below). Our results are, therefore, expected to be rather generally valid.

The valence-band states at Γ are known to belong to the irreducible representation t_2 . On the other hand, localized d orbitals separate into a t_2 triplet and an e doublet, the latter lying lower in energy. By assuming that the total Hartree-Fock Hamiltonian retains the tetrahedral site symmetry, the Anderson mixing (hybridization) term can be written as ($k \approx 0$)

$$H_{\text{mix}} = \sum_{\mathbf{k},\gamma,\sigma} V_{\mathbf{k}d} c_{\mathbf{k}\gamma\sigma}^\dagger a_{\gamma\sigma} + \text{H.c.} \quad (1)$$

Here $\sigma = \frac{1}{2}(\uparrow), -\frac{1}{2}(\downarrow)$ is the z component of spin and $\gamma = 1, 0, -1$ designates the row of the irreducible representation t_2 according to the spherical harmonics basis $Y_{1\gamma}$. The operator $c_{\mathbf{k}\gamma\sigma}^\dagger$ creates an electron in the valence band and $a_{\gamma\sigma}$ in a localized orbital. Note that $V_{\mathbf{k}d}$ is assumed independent of γ . Strictly speaking, the above symmetry classification of the band states is valid only at $\mathbf{k}=0$. At the end we shall calculate the coupling at Γ . The result can, however, be used for small k values in the $\mathbf{k}\cdot\mathbf{p}$ formalism and it is convenient to keep the \mathbf{k} index at this stage.

H_{mix} describes virtual one-electron hopping processes between the valence band and the transition-metal ion. The ionic configuration $3d^n$ is assumed to be energetically stable against *real* emission into or absorption from the valence band. Usually, in II-VI semiconductors, the 2^+ ion of the transition metal corresponds to such a stable configuration. There are, however, cases like Fe in HgSe, where the 2^+ ion is a donor;¹⁵ our results could then be

used only for the stable 3^+ ion.

We shall now transform the hybridization into an effective scattering Hamiltonian between a hole and the ion by using the perturbation method.¹⁰ The hole states are described in terms of the missing electron ones. We, therefore, formulate the problem in terms of scattering between a single electron in the valence band and the impurity ion. In the second order of perturbation, the effective Hamiltonian is

$$H_n = - \sum_I \frac{H_{\text{mix}}|I\rangle\langle I|H_{\text{mix}}}{E_I - E_{\text{in}}}, \quad (2)$$

the initial state energy $E_{\text{in}} = E_0(n) + E_v$, where E_v is the energy of an electron at the valence-band maximum and $E_0(n)$ is the ground-state energy of the $3d^n$ ion. The intermediate states I are of two kinds. Those corresponding to virtual absorption have $E_I^+ = E_0(n+1)$. For virtual emission $E_I^- = E_0(n-1) + 2E_v$. The virtual excitation energies

$$E_{\text{ex}}^\pm = E_I^\pm - E_{\text{in}} \quad (3)$$

are relatively large; this is the condition of stability. By neglecting multiplet splittings in the excited configurations, the energy denominators in (2) can be taken out of the summation. We thus obtain

$$H_n = (I_n^+ + I_n^-) \sum_{\substack{\mathbf{k},\gamma,\sigma \\ \mathbf{k}',\gamma',\sigma'}} a_{\gamma\sigma}^\dagger a_{\gamma'\sigma'} c_{\mathbf{k}'\gamma'\sigma'}^\dagger c_{\mathbf{k}\gamma\sigma} - I_n^+ \sum_{\substack{\mathbf{k},\mathbf{k}' \\ \gamma,\sigma}} c_{\mathbf{k}'\gamma\sigma}^\dagger c_{\mathbf{k}\gamma\sigma} - I_n^- \sum_{\substack{\mathbf{k} \\ \gamma,\sigma}} a_{\gamma\sigma}^\dagger a_{\gamma\sigma}, \quad (4)$$

where $I_n^\pm = |V_{0d}|^2/E_{\text{ex}}^\pm$. The second term in (4) is a potential scattering one and the third term is a constant. The exchange coupling is thus contained in

$$H_n = I_n \sum_{\substack{\mathbf{k},\gamma,\sigma \\ \mathbf{k}',\gamma',\sigma'}} a_{\gamma\sigma}^\dagger a_{\gamma'\sigma'} c_{\mathbf{k}'\gamma'\sigma'}^\dagger c_{\mathbf{k}\gamma\sigma}, \quad (5)$$

where

$$I_n = |V_{0d}|^2 \left[\frac{1}{E_{\text{ex}}^+} + \frac{1}{E_{\text{ex}}^-} \right]. \quad (6)$$

In order to rewrite Eq. (5) in a symmetry invariant form we define the following mixed-symmetry irreducible tensor operators:¹⁰

$$A_{\delta\nu}^{\Delta\Sigma} = \sum_{\substack{\gamma,\sigma \\ \gamma',\sigma'}} \sqrt{\lambda(\Delta)} [-1]^{t_2-\gamma'} \begin{pmatrix} t_2 & \Delta & t_2 \\ -\gamma' & \delta & \gamma \end{pmatrix} \times \sqrt{2\Sigma+1} (-1)^{s-\sigma'} \begin{pmatrix} s & \Sigma & s \\ -\sigma' & \nu & \sigma \end{pmatrix} a_{\gamma'\sigma'}^\dagger a_{\gamma\sigma}. \quad (7)$$

Here we use Wigner's $3j$ symbol¹⁶ for the spin part with $s = \frac{1}{2}$. Clearly, $\Sigma = 0, 1$. The orbital analogue of the $3j$ symbol in tetrahedral symmetry:

$$\begin{pmatrix} a & \Delta & b \\ \alpha & \delta & \beta \end{pmatrix} = V \begin{pmatrix} a & b & \Delta \\ \alpha & \beta & \delta \end{pmatrix}, \quad (8)$$

where the V coefficients are given by Griffith.¹⁷ These are Clebsch-Gordan-like coupling coefficients with standard phase convention. $\Delta = a_1, e, t_1, t_2$ are contained in the direct product $t_2 \times t_2$; each irreducible representation appears only once, giving unique coupling coefficients. The phase symbol $[-1]^n$ is from Ref. 17. $\lambda(\Delta)$ is the degeneracy of Δ and δ is the row index. Similarly,

$$\begin{aligned} C^{k' k \Delta}_{\delta v \Sigma} &= \sum_{\substack{\gamma, \sigma \\ \gamma', \sigma'}} \sqrt{\lambda(\Delta)} [-1]^{t_2 - \gamma'} \begin{pmatrix} t_2 & \Delta & t_2 \\ -\gamma' & \delta & \gamma \end{pmatrix} \\ &\times \sqrt{2\Sigma + 1} (-1)^{s - \sigma'} \begin{pmatrix} s & \Sigma & s \\ -\sigma' & \nu & \sigma \end{pmatrix} \\ &\times c_{k' \gamma' \sigma'}^\dagger c_{k \gamma \sigma}. \end{aligned} \quad (9)$$

It can be shown that the mixed tensors A and C have the following symmetry properties. In the orbital space, they transform as the δ th row of the irreducible representation Δ of T_d . In the spin space, they transform as the angular momentum eigenfunction $J = \Sigma$ and $J_z = \nu$. Moreover, any bilinear operator $a_{\gamma' \sigma'}^\dagger a_{\gamma \sigma}$ can be written as a linear combination of $A_{\delta v \Sigma}^{\Delta \Sigma}$ and similarly for the band-state operators. We thus obtain

$$H_n = I_n \sum_{\substack{\Delta, \delta \\ \Sigma, \nu \\ k', k}} (A_{\delta v \Sigma}^{\Delta \Sigma})^\dagger C^{k' k \Delta}_{\delta v \Sigma}. \quad (10)$$

This symmetry invariant form is, however, written in terms of one-electron orbitals and has to be projected onto the n -electron ground multiplet. The latter is spanned by the states $|i, \mu; S, M\rangle$, where μ denotes the row of the irreducible representation i and M is the z component of the total spin S . Let us define the irreducible tensors $B_{\delta v \Sigma}^{\Delta \Sigma}$ in this subspace by

$$\begin{aligned} \langle i, \mu'; S, M' | B_{\delta v \Sigma}^{\Delta \Sigma} | i, \mu; S, M \rangle \\ = \sqrt{\lambda(\Delta)} [-1]^{i - \mu'} \begin{pmatrix} i & \Delta & i \\ -\mu' & \delta & \mu \end{pmatrix} \\ \times \sqrt{2\Sigma + 1} (-1)^{S - M'} \begin{pmatrix} S & \Sigma & S \\ -M' & \nu & M \end{pmatrix}. \end{aligned} \quad (11)$$

The symmetry invariant effective Hamiltonian can then be written as

$$H_n^{i, S} = \sum_{\substack{\Delta, \delta \\ \Sigma, \nu \\ k', k}} I(n, i, \Delta, \Sigma) (B_{\delta v \Sigma}^{\Delta \Sigma})^\dagger C^{k' k \Delta}_{\delta v \Sigma}. \quad (12)$$

In fact, Eq. (12) as such is more general than Eq. (10). Note that Δ must be contained in $i \times i$. Thus, for the one-dimensional representations $i = A_1$ (Mn^{2+}) and A_2 (Co^{2+}), the only allowed Δ is A_1 .

Now, we resort to Eq. (10) for calculating the coupling constants. The Wigner-Eckart theorem and its analogue

for T_d tell us that, in the subspace (i, S) , the matrix elements of the irreducible tensor A are proportional to those of B :

$$\begin{aligned} \langle i, \mu'; S, M' | A_{\delta v \Sigma}^{\Delta \Sigma} | i, \mu; S, M \rangle \\ = \alpha(\Delta, \Sigma) \langle i, \mu'; S, M' | B_{\delta v \Sigma}^{\Delta \Sigma} | i, \mu; S, M \rangle. \end{aligned} \quad (13)$$

The proportionality constant $\alpha(\Delta, \Sigma)$, related to "reduced matrix elements," depends on i and S and can be calculated through one nonvanishing matrix element of $A_{\delta v \Sigma}^{\Delta \Sigma}$. Finally, our effective coupling Hamiltonian is

$$H_n^{\text{eff}} = I_n \sum_{\substack{\Delta, \delta \\ \Sigma, \nu \\ k', k}} \alpha(\Delta, \Sigma) (B_{\delta v \Sigma}^{\Delta \Sigma})^\dagger C^{k' k \Delta}_{\delta v \Sigma}. \quad (14)$$

In order to calculate $\alpha(\Delta, \Sigma)$ we need to know the one-electron amplitudes in the n -electron ground state. We proceed as follows. The stretched state $L_z = L$, $S_z = S$ of the Hund's rule ground term L, S is a single Slater determinant. It is obtained by filling the $3d$ shell in the following order: $m = 2, 1, 0, -1, -2$ with spin up ($\sigma = +\frac{1}{2}$) for the first five electrons, and then spin down ($\sigma = -\frac{1}{2}$) for the rest of them. Thus

$$|L, L_z = L; S, M = S\rangle = \prod_{\sigma, m} d_{m\sigma}^\dagger |0\rangle. \quad (15)$$

Here $|0\rangle$ is the vacuum state and the product is over the occupied orbitals. The states $|L, L_z; S, S\rangle$ for $L_z < L$ are then deduced by applying the step-down operator

$$L^- = L_{\uparrow}^- + L_{\downarrow}^-, \quad (16a)$$

with

$$L_{\sigma}^- = \sum_m [(2+m)(2-m+1)]^{1/2} d_{m-1, \sigma}^\dagger d_{m\sigma} \quad (16b)$$

and properly normalizing after each step. Now, in the intermediate crystal-field scheme, the orbital states $|i, \mu\rangle$ are known linear combinations of $|L, L_z\rangle$ (see the Appendix). We thus obtain the spin-stretched states $|i, \mu; S, S\rangle$ in terms of the creation operators $d_{m\sigma}^\dagger$. The latter are simply related to the operators in tetrahedral symmetry:

$$\begin{aligned} d_{2\sigma} &= \frac{a_{e\epsilon\sigma} + a_{t_2 0\sigma}}{\sqrt{2}}, \quad d_{1\sigma} = -a_{t_2 \bar{1}\sigma}, \quad d_{0\sigma} = a_{e\theta\sigma}, \\ d_{\bar{1}\sigma} &= a_{t_2 1\sigma}, \quad d_{\bar{2}\sigma} = \frac{a_{e\epsilon\sigma} - a_{t_2 0\sigma}}{\sqrt{2}}. \end{aligned} \quad (17)$$

The resulting n -electron states $|i, \mu; S, S\rangle$ are listed in the Appendix. $\alpha(\Delta, \Sigma)$ is then deduced from Eq. (13) by calculating a diagonal matrix element of $A_{\delta v \Sigma}^{\Delta \Sigma}$. Note that the t_2 index on the operators, a , is implicit in Eq. (7). In the case of $\Delta = T_2$ the diagonal matrix element vanishes and an off-diagonal one is used.

The relative coupling constants $\alpha(\Delta, \Sigma)$ are presented in Table I. Note that values for the trivial case $\Delta = A_1$, $\Sigma = 0$ are not shown.

It can be seen that the hybridization does not lead to any coupling for $n = 1$ (Sc^{2+}) and $n = 2$ (Ti^{2+}), because the hybridizing t_2 subshell is empty in the ionic ground

TABLE I. Coupling constants $\alpha(\Delta, \Sigma)$ for $3d^n$ ions.

n	L	S	i	$\alpha(A_1, 1)$	$\alpha(E, 0)$	$\alpha(E, 1)$	$\alpha(T_1, 0)$	$\alpha(T_1, 1)$	$\alpha(T_2, 0)$	$\alpha(T_2, 1)$
1	2	$\frac{1}{2}$	E	0	0	0	0	0	0	0
2	3	1	A_2	0	0	0	0	0	0	0
3	3	$\frac{3}{2}$	T_1	$\sqrt{8/5}$	$\sqrt{18/5}$	$\sqrt{2/5}$	$\frac{7}{10}\sqrt{2}$	$\frac{7}{6}\sqrt{2/5}$	$\frac{9}{10}\sqrt{2}$	$3/\sqrt{10}$
4	2	2	T_2	$\sqrt{5}$	$-\sqrt{5/2}$	$-\sqrt{5/2}$	$\sqrt{5/2}$	$\sqrt{5/2}$	$-\sqrt{5/2}$	$-\sqrt{5/2}$
5	0	$\frac{5}{2}$	A_1	$\sqrt{21/5}$	0	0	0	0	0	0
6	2	2	E	$\sqrt{15/2}$	0	0	0	0	0	0
7	3	$\frac{3}{2}$	A_2	$\sqrt{10/3}$	0	0	0	0	0	0
8	3	1	T_1	$\frac{9}{5}$	$\frac{3}{5}\sqrt{3/2}$	$-\frac{3}{5}$	$\frac{7}{10}\sqrt{3/2}$	$-\frac{7}{10}$	$\frac{9}{10}\sqrt{3/2}$	$-\frac{9}{10}$
9	2	$\frac{1}{2}$	T_2	1	-1	1	1	-1	-1	1

state. On the other hand, for $n = 5$ (Mn^{2+}), 6 (Fe^{2+}), and 7 (Co^{2+}) the t_2 subshell is half filled and the only non-trivial coupling rank is $\Delta = A_1$, $\Sigma = 1$. This is, in fact, the spin-only Kondo Hamiltonian, as shown in Sec. III. The remaining cases, namely, V^{2+} , Cr^{2+} , Ni^{2+} , and Cu^{2+} , are more interesting; there are couplings involving the orbital degrees of freedom.

III. THE CASES OF Mn^{2+} , Fe^{2+} , AND Co^{2+}

The effective Hamiltonian reduces to

$$H_n^{\text{eff}} = I_n \alpha(A_1, 1) \sum_{\mathbf{k}, \mathbf{k}'} (B^{A_1 \frac{1}{2}})_{\nu}^{\dagger} C^{\mathbf{k}' \mathbf{k}} A_1 \frac{1}{\nu}. \quad (18)$$

Now,

$$\begin{aligned} \langle i, \mu'; S, M' | (B^{A_1 \frac{1}{2}})_{\nu} | i, \mu; S, M \rangle \\ = \frac{\delta_{\mu' \mu}}{\sqrt{\lambda(i)}} \sqrt{3} (-1)^{S-M'} \begin{bmatrix} S & 1 & S \\ -M' & \nu & M \end{bmatrix}. \end{aligned} \quad (19)$$

Thus, the orbital part of B can be represented by a normalization constant. The spin part is clearly proportional to the familiar first-rank spherical tensor $O_{\nu}^{(1)}(\mathbf{S})$ given by

$$O_0^{(1)}(\mathbf{S}) = S_z, \quad O_{\pm 1}^{(1)}(\mathbf{S}) = \mp S^{\pm} / \sqrt{2}. \quad (20)$$

Thus,

$$B^{A_1 \frac{1}{2}} = c_i O_{\nu}^{(1)}(\mathbf{S}). \quad (21)$$

We calculate c_i through the diagonal matrix element for $M = S$,

$$c_i = \left[\frac{3}{\lambda(i)} \right]^{1/2} \begin{bmatrix} S & 1 & S \\ -S & 0 & S \end{bmatrix} / S. \quad (22)$$

However, for the three cases in hand ($n = 5, 6, 7$), we have

$$\alpha(A_1, 1) = \left[\frac{\lambda(i)}{2} \right]^{1/2} \begin{bmatrix} S & 1 & S \\ -S & 0 & S \end{bmatrix}^{-1}. \quad (23)$$

Thus,

$$H_n^{\text{eff}} = I_n \frac{\sqrt{3}}{\sqrt{2}} \frac{1}{S} \sum_{\mathbf{k}, \mathbf{k}'} (O_{\nu}^{(1)}(\mathbf{S}))_{\nu}^{\dagger} C^{\mathbf{k}' \mathbf{k}} A_1 \frac{1}{\nu}. \quad (24)$$

Writing out the tensor operators explicitly,

$$\begin{aligned} H_n^{\text{eff}} = \frac{I_n}{2S} \sum_{\mathbf{k}, \mathbf{k}'} \left[S^{-} c_{\mathbf{k}' \gamma \uparrow}^{\dagger} c_{\mathbf{k} \gamma \downarrow} \right. \\ \left. + 2S_z \sum_{\sigma} \sigma c_{\mathbf{k}' \gamma \sigma}^{\dagger} c_{\mathbf{k} \gamma \sigma} + S^{+} c_{\mathbf{k}' \gamma \downarrow}^{\dagger} c_{\mathbf{k} \gamma \uparrow} \right]. \end{aligned} \quad (25)$$

This is the Kondo Hamiltonian with the exchange parameter

$$J_{\mathbf{k} \mathbf{k}'} = -I_n / S. \quad (26)$$

In the usual notation, $\beta = J_{00}$. Thus,

$$\beta = - \left[\frac{1}{2S} \right] 2 |V_{0d}|^2 \left[\frac{1}{E_{\text{ex}}^{+}} + \frac{1}{E_{\text{ex}}^{-}} \right]. \quad (27)$$

In fact, this is a generalization of the Schrieffer-Wolff formula. The normalization factor ($1/2S$) was previously obtained in the case of Mn^{2+} in spherical symmetry.⁹ We shall see the importance of this factor in Sec. V.

IV. THE CASES OF V^{2+} , Cr^{2+} , Ni^{2+} , AND Cu^{2+}

Here the effective Hamiltonian given by Eq. (14) contains coupling terms of rank $\Delta = A_1, E, T_1, T_2$ and $\Sigma = 0, 1$. Thus, the orbital degrees of freedom of the ion are coupled to those of the valence-band electron, with or without spin exchange. In order to understand the significance of the new terms, it is once again useful to express the irreducible tensors in terms of more conventional operators in the ground-state manifold of the ion. In addition to the spherical tensors of rank 1 in Eq. (20), we shall use those of rank 0 and 2:

$$O_0^{(0)}(\mathbf{j}) = 1, \quad (28a)$$

$$O_0^{(2)}(\mathbf{j}) = \frac{1}{2} [3j_z^2 - j(j+1)], \quad (28b)$$

$$O_{\pm 1}^{(2)}(\mathbf{j}) = \mp \frac{\sqrt{3}}{\sqrt{8}} [j_z j^{\pm} + j^{\pm} j_z], \quad (28c)$$

$$O_{\pm 2}^{(2)}(\mathbf{j}) = \frac{\sqrt{3}}{\sqrt{8}} (j^{\pm})^2. \quad (28d)$$

Let us now write the mixed double tensor B as a product of orbital and spin parts:

$$B_{\delta v}^{\Delta \Sigma} = P_{\delta}^{\Delta}(\mathbf{L}) Q_{v}^{\Sigma}(\mathbf{S}). \quad (29)$$

The spin part can be written as

$$Q_{v}^{\Sigma}(\mathbf{S}) = r^{(\Sigma)} O_{v}^{(\Sigma)}(\mathbf{S}), \quad (30)$$

where

$$r^{(\Sigma)} = \sqrt{2\Sigma+1} \begin{bmatrix} S & \Sigma & S \\ -S & 0 & S \end{bmatrix} / S^{\Sigma}. \quad (31)$$

The orbital tensors for $i = T_1$ or T_2 are given by

$$P^{A_1}(\mathbf{L}) = \frac{1}{\sqrt{3}}, \quad (32a)$$

$$P_{\delta}^{T_1}(\mathbf{L}) = \beta_L(T_1) O_{\delta}^{(1)}(\mathbf{L}), \quad (32b)$$

$$P_{\theta}^E(\mathbf{L}) = \beta_L(E) O_{\theta}^{(2)}(\mathbf{L}), \quad (32c)$$

$$P_{\epsilon}^E(\mathbf{L}) = \beta_L(E) \frac{1}{\sqrt{2}} [O_2^{(2)}(\mathbf{L}) + O_{-2}^{(2)}(\mathbf{L})], \quad (32d)$$

$$P_0^{T_2}(\mathbf{L}) = \beta_L(T_2) \frac{1}{\sqrt{2}} [O_2^{(2)}(\mathbf{L}) - O_{-2}^{(2)}(\mathbf{L})], \quad (32e)$$

$$P_{\pm 1}^{T_2}(\mathbf{L}) = \beta_L(T_2) [\pm O_{\mp 1}^{(2)}(\mathbf{L})]. \quad (32f)$$

Thus, $\Delta = T_1$ corresponds to the orbital angular momentum, while the $\Delta = E$ and $\Delta = T_2$ terms are proportional to the electric quadrupole moment. For $L = 2$ (Cr^{2+} and Cu^{2+}),

$$\beta_2(T_1) = -\frac{1}{\sqrt{2}}, \quad \beta_2(E) = -\frac{\sqrt{2}}{3\sqrt{3}}, \quad \beta_2(T_2) = \frac{\sqrt{2}}{3\sqrt{3}}, \quad (33)$$

and for $L = 3$ (V^{2+} and Ni^{2+}),

$$\beta_3(T_1) = -\frac{\sqrt{2}}{3}, \quad \beta_3(E) = \frac{\sqrt{2}}{6\sqrt{3}}, \quad \beta_3(T_2) = -\frac{2\sqrt{2}}{3\sqrt{3}}. \quad (34)$$

At $\Gamma(\mathbf{k}' = \mathbf{k} = 0)$, by assuming p -type wave functions, the valence-band irreducible tensor C can be similarly written as a product

$$C^{0 \ 0 \Delta \ \Sigma} = P_{\delta}^{\Delta}(l) Q_{v}^{\Sigma}(s), \quad (35)$$

with $l = 1$, $s = \frac{1}{2}$, and

$$\beta_1(T_1) = \frac{1}{\sqrt{2}}, \quad \beta_1(E) = \frac{\sqrt{2}}{\sqrt{3}}, \quad \beta_1(T_2) = \frac{\sqrt{2}}{\sqrt{3}}. \quad (36)$$

Finally, the effective Hamiltonian is given by

$$\begin{aligned} H_n^{\text{eff}} = & I_n (\gamma_1 \alpha(A_1, 1) \mathbf{s} \cdot \mathbf{S} + [\gamma_0 \alpha(T_1, 0) + 3\gamma_1 \alpha(T_1, 1) \mathbf{s} \cdot \mathbf{S}]) \frac{1}{\sqrt{2}} \beta_L(T_1) l \cdot \mathbf{L} \\ & + [\gamma_0 \alpha(E, 0) + 3\gamma_1 \alpha(E, 1) \mathbf{s} \cdot \mathbf{S}] \frac{1}{2\sqrt{6}} \beta_L(E) \{ (3l_z^2 - 2)[3L_z^2 - L(L+1)] + 3(l_x^2 - l_y^2)(L_x^2 - L_y^2) \} \\ & + [\gamma_0 \alpha(T_2, 0) + 3\gamma_1 \alpha(T_2, 1) \mathbf{s} \cdot \mathbf{S}] \frac{\sqrt{3}}{2\sqrt{2}} \beta_L(T_2) \\ & \times [(l_x l_y + l_y l_x)(L_x L_y + L_y L_x) + (l_y l_z + l_z l_y)(L_y L_z + L_z L_y) + (l_z l_x + l_x l_z)(L_z L_x + L_x L_z)], \end{aligned} \quad (37)$$

where

$$\gamma_0 = [2(2S+1)]^{-1/2}, \quad (38a)$$

$$\gamma_1 = \sqrt{2} [3(2S+1)(S+1)S]^{-1/2}, \quad (38b)$$

We shall now examine the consequences of the orbital coupling terms in Eq. (37) on the magneto-optical properties of a DMS. In order to calculate the contribution of the effective Hamiltonian to the valence-band splitting in a magnetic field in the mean-field approximation, we need to evaluate the expectation values of the band operators l, s and their products in the band states $|jm\rangle$. On the other hand, the expectation values of the ionic operators have to be calculated in the eigenstates of the Zeeman Hamiltonian including the spin-orbit interaction and then thermally averaged. We shall report such calculations in a subsequent paper. Here we consider a simple analytical limit that reveals the importance of the orbital coupling terms. It is the limit of high magnetic field, when the ionic Zeeman Hamiltonian is much larger than the spin-orbit Hamiltonian. Then the ionic eigenstates in the field are given by $|i, \mu; S, M\rangle$. In a zinc-blende DMS the Γ_8 valence band splits into four components ($m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$) with the energies

$$\begin{aligned} E_m = & N_0 x I_n \left[\alpha(A_1, 1) \gamma_1 \langle M \rangle \left[\frac{m}{3} \right] + \alpha(T_1, 0) \gamma_0 \langle \mu \rangle \left[\frac{m}{3} \right] + \alpha(T_1, 1) \gamma_1 \langle \mu \rangle \langle M \rangle^{\frac{1}{2}} (m^2 - \frac{3}{4}) \right. \\ & \left. + \alpha(E, 0) \gamma_0 \langle \mu^2 - \frac{2}{3} \rangle^{\frac{1}{2}} (m^2 - \frac{5}{4}) + \alpha(E, 1) \gamma_1 \langle \mu^2 - \frac{2}{3} \rangle \langle M \rangle^{\frac{3}{2}} m (m^2 - \frac{23}{12}) \right]. \end{aligned} \quad (39)$$

TABLE II. The effective coupling induced valence-band Zeeman splitting in the high-field saturation limit: subband energies $E_m/(N_0x)$ in different cases.

m (subband)	V^{2+}	Cr^{2+}	$Mn^{2+}, Fe^{2+}, Co^{2+}$	Ni^{2+}	Cu^{2+}
$-\frac{3}{2}$	$-\frac{1}{20}I_3$	$-\frac{1}{3}I_4$	$\frac{1}{2}I_n$	$\frac{3}{10}I_8$	$\frac{1}{6}I_9$
$-\frac{1}{2}$	$-\frac{1}{15}I_3$	$\frac{1}{3}I_4$	$\frac{1}{6}I_n$	$\frac{1}{60}I_8$	$-\frac{1}{6}I_9$
$+\frac{1}{2}$	$\frac{1}{12}I_3$	0	$-\frac{1}{6}I_n$	$-\frac{7}{30}I_8$	$\frac{1}{6}I_9$
$+\frac{3}{2}$	$-\frac{1}{5}I_3$	$-\frac{1}{3}I_4$	$-\frac{1}{2}I_n$	$\frac{3}{20}I_8$	$\frac{1}{6}I_9$

Here $\langle \dots \rangle$ means thermal average and N_0x is the number of transition-metal ions per unit volume. The expectation value of the ionic Zeeman Hamiltonian

$$\langle i, \mu; S, M | H_Z | i, \mu; S, M \rangle = \mu_B B (2M + \langle i\mu | L_Z | i\mu \rangle). \quad (40)$$

For $L=2$ (Cr^{2+} and Cu^{2+})

$$\langle i\mu | L_Z | i\mu \rangle = -\mu \quad (41a)$$

and for $L=3$ (V^{2+} and Ni^{2+})

$$\langle i\mu | L_Z | i\mu \rangle = -\frac{3}{2}\mu. \quad (41b)$$

Thus the ground state in all cases corresponds to $\mu=+1$ and $M=-S$. Using these values in Eq. (37) we obtain the valence-band splitting in the saturation limit ($T \rightarrow 0$). The results are presented in Table II. The case of s-S coupling ($Mn^{2+}, Fe^{2+}, Co^{2+}$) is also shown for comparison. Notice the drastic modification of subband ordering and the reduced overall splitting in the cases of V^{2+} , Cr^{2+} , Ni^{2+} , and Cu^{2+} . It should be kept in mind that these results represent only the contribution of hybridization-induced coupling; neither the direct effect of the field nor the potential exchange contribution has been taken into account. Above all, the condition $\mu_B B > \lambda$ (spin-orbit coupling) probably situates B as high as 100 T in the cases of V^{2+} and Cr^{2+} . The spin-orbit coupling is much stronger in Ni^{2+} and Cu^{2+} . Calculations of valence-band splitting in the usual experimental field range will be reported elsewhere.¹⁸ The results presented here, however, illustrate the drastic influence of the orbital coupling terms on the valence-band splitting.

In comparing different cases in Table II, one should note that the coefficient I_n will vary with the ion in a given host compound. However, from V^{2+} through Co^{2+} the energy denominators concern only the majority-spin t_2 subshell, and we do not expect a large variation of I_n (see Sec. V). On the other hand, in the cases of Ni^{2+} and Cu^{2+} , the minority-spin level is also involved, and I_n might be quite different. We can say that in the saturation limit the overall splitting will decrease systematically from Mn to Cr to V in a given host.

V. COMPARISON WITH EXPERIMENTS

So far, apart from the more familiar Mn-based DMS, experimental data are available in Fe- and Co-based DMS

only. Magnetization and magneto-optical data in these systems have been successfully analyzed in terms of the simple spin-exchange Kondo Hamiltonian for the band-ionic coupling. This is in agreement with our results. Appropriate effective g factors have been used to determine the exchange parameters $N_0\alpha$ and $N_0\beta$. See Ref. 11 for a list of carrier-ion exchange parameters in different Mn-, Fe-, and Co-based DMS. As expected, $N_0\alpha$ representing the on-site direct potential exchange varies little with the transition metal. But $|N_0\beta|$ increases strongly from Mn to Fe to Co in a given host crystal. In order to discuss this variation, we rewrite Eq. (27) in a more familiar form. First of all, in the tight-binding model for the valence band⁶

$$V_{0d} = \frac{4}{\sqrt{N_0}} V_{pd} \quad (42)$$

where V_{pd} is the real-space hopping amplitude from the transition metal d orbital to a neighboring anion p orbital. Next, we resort to the effective one-electron (Hartree-Fock) level scheme for the energy denominators. $E_{ex}^-(E_{ex}^+)$ corresponds to virtual emission from (absorption into) a singly occupied t_2 orbital at ϵ_d so that

$$E_{ex}^- = E_v - \epsilon_d, \quad E_{ex}^+ = \epsilon_d + U_{eff} - E_v \quad (43)$$

in the usual notations. Thus, finally,

$$N_0\beta = - \left[\frac{1}{2S} \right] 32 V_{pd}^2 \left[\frac{1}{E_v - \epsilon_d} + \frac{1}{\epsilon_d + U_{eff} - E_v} \right]. \quad (44)$$

This formula was previously used in Mn-based DMS.⁸ We have shown its validity in Mn-, Fe-, and Co-based DMS.

For a quantitative comparison with experiments, we focus on $Cd_{1-x}M_xSe$ with $M=Mn, Fe, Co$, because photoemission data are available in these systems. A preliminary report of the present discussion has been included in Ref. 19; the sources of experimental data are cited therein. The experimental $N_0\beta$ values are -1.238 , -1.450 , and -1.883 eV, respectively, for $M=Mn, Fe, Co$. Photoemission data suggest the following values for $E_v - \epsilon_d$: 3.4, 3.7, and 3.5 eV, respectively. These correspond to the majority-spin occupied states. In the Fe- and Co-based systems, photoemission also indicates occupied minority-spin level at 0.5 and 0.8 eV, respectively, below the valence-band maximum. According to the U, U', J model of Kanamori, discussed by Hass,⁸ the

difference between the minority- and majority-spin levels is then $4J = 3.2$ eV for Fe and $3J = 2.7$ eV for Co. On the other hand, $U_{\text{eff}} = U + 4J$, $U + 3J$, and $U + 2J$ for Mn, Fe, and Co, respectively. Thus, if we assume the same U and J values for all, starting from the estimated U_{eff} value⁶ of 7.6 eV for Mn, we estimate $U_{\text{eff}} = 6.8$ and 5.9 eV, respectively, for Fe and Co. With the above $E_v - \varepsilon_d$ and U_{eff} values and the appropriate S values, comparison between formula (44) and experimental $N_0\beta$ yields the V_{pd} values: 0.6, 0.55, and 0.5 eV respectively for Mn-, Fe- and Co-based systems. These are in excellent agreement with Harrison's scaling rule,²⁰ $V_{pd} \propto (r_d^3/d^7)^{1/2}$, if we assume the bond length d to be constant. (The tabulated values²⁰ of the d -shell radius r_d are 0.86, 0.80, and 0.76 Å, respectively.) This quantitative agreement between our analysis and experiment, however, should not be taken too seriously. There are considerable uncertainties in the interpretation of photoemission spectra, and, in particular, in the estimated values of U_{eff} . Moreover, no extended x-ray-absorption fine-structure spectroscopy information is as yet available on the bond length in Fe- or Co-based DMS.

Let us emphasize the following points. Contrary to previous interpretation²¹ the hybridization parameter V_{pd} decreases from Mn to Fe to Co, due to the decreasing d -shell radius. The resulting decrease of $|N_0\beta|$ is more or less compensated by the increase coming from reduced U_{eff} values. The normalization factor ($1/2S$) in Eq. (44), ignored previously, is thus crucial for explaining the large increase of $|N_0\beta|$ from Mn to Fe to Co.

VI. CONCLUDING REMARKS

Starting from the Anderson mixing (hybridization) Hamiltonian we have derived the effective coupling between a valence-band electron and a transition-metal ion in the stable configuration $3d^n$. The effective Hamiltonian is expressed in terms of tensor operators in the manifold of the ground-state multiplet of the ion in tetrahedral crystal field. In the cases of Sc^{2+} and Ti^{2+} there is no hybridization-induced coupling, because the hybridizing t_2 subshell is empty. Thus, Sc- and Ti-based DMS would be interesting test systems. In the cases of Mn^{2+} , Fe^{2+} , and Co^{2+} with half-filled t_2 level the effective coupling reduces to spin exchange only, in agreement with experiments. The Schrieffer-Wolff formula for the exchange parameter is found to be multiplied by a normalization factor $1/2S$. It is crucial for explaining the observed increase of $|N_0\beta|$ from Mn to Fe to Co in a given host. Quantitative comparison between theory and experiment in $\text{Cd}_{1-x}\text{M}_x\text{Se}$ shows that the hybridization parameter

V_{pd} decreases as M goes from Mn to Fe to Co, in accordance with Harrison's scaling rule. This result contradicts the interpretation by other authors based on the unmodified Schrieffer-Wolff formula.

In the cases of V^{2+} , Cr^{2+} , Ni^{2+} , and Cu^{2+} , in addition to the spin-exchange term, there are orbital couplings with or without spin exchange. We have investigated the influence of these additional terms on the Zeeman splitting of the valence band in a zinc-blende DMS in the high-field saturation limit. We find drastic modifications of subband ordering and reduced overall splitting as compared to the simple spin-exchange model. A theoretical study of the valence-band splitting in the field range of typical magneto-optical experiments is in progress and will be reported elsewhere.¹⁸ However, the unusual limiting behavior predicted here should encourage experimental studies in new DMS systems.

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APPENDIX: IONIC GROUND STATES IN T_d

The orbital states $|i, \mu\rangle$ are known linear combinations of $|L, L_z\rangle$, and listed below.

For $L = 2$ ($n = 1, 4, 6, 9$),

$$|E, \theta\rangle = |2, 0\rangle, \quad (\text{A1})$$

$$|E, \varepsilon\rangle = \frac{1}{\sqrt{2}}(|2, 2\rangle + |2, -2\rangle), \quad (\text{A2})$$

$$|T_2, 1\rangle = |2, -1\rangle, \quad (\text{A3})$$

$$|T_2, 0\rangle = \frac{1}{\sqrt{2}}(|2, 2\rangle - |2, -2\rangle), \quad (\text{A4})$$

$$|T_2, -1\rangle = -|2, 1\rangle. \quad (\text{A5})$$

For $L = 3$ ($n = 2, 3, 7, 8$),

$$|A_2\rangle = \frac{1}{\sqrt{2}}(|3, 2\rangle - |3, -2\rangle), \quad (\text{A6})$$

$$|T_1, 1\rangle = -\frac{\sqrt{5}}{\sqrt{8}}|3, -3\rangle - \frac{\sqrt{3}}{\sqrt{8}}|3, 1\rangle, \quad (\text{A7})$$

$$|T_1, 0\rangle = |3, 0\rangle, \quad (\text{A8})$$

$$|T_1, -1\rangle = -\frac{\sqrt{5}}{\sqrt{8}}|3, 3\rangle - \frac{\sqrt{3}}{\sqrt{8}}|3, -1\rangle. \quad (\text{A9})$$

We express the spin-stretched states $|i, \mu; S, M = S\rangle$ of the ground multiplet in terms of effective one-electron operators. (The method is explained in Sec. II.)

$$3d^1(\text{Sc}^{2+}): |E, \theta; \frac{1}{2}, \frac{1}{2}\rangle = a_{e\theta\uparrow}^\dagger |0\rangle, \quad (\text{A10})$$

$$|E, \varepsilon; \frac{1}{2}, \frac{1}{2}\rangle = a_{e\varepsilon\uparrow}^\dagger |0\rangle, \quad (\text{A11})$$

$$3d^2(\text{Ti}^{2+}): |A_2; 1, 1\rangle = a_{e\theta\uparrow}^\dagger a_{e\varepsilon\uparrow}^\dagger |0\rangle, \quad (\text{A12})$$

$$3d^3(\text{V}^{2+}): |T_1, 1; \frac{3}{2}, \frac{3}{2}\rangle = \frac{2}{\sqrt{5}} a_{t_2, 1\uparrow}^\dagger a_{e\varepsilon\uparrow}^\dagger a_{e\theta\uparrow}^\dagger |0\rangle + \frac{1}{2\sqrt{5}} a_{t_2, 0\uparrow}^\dagger a_{t_2, 1\uparrow}^\dagger a_{e\theta\uparrow}^\dagger |0\rangle + \frac{\sqrt{3}}{2\sqrt{5}} a_{t_2, 1\uparrow}^\dagger a_{t_2, 0\uparrow}^\dagger a_{e\varepsilon\uparrow}^\dagger |0\rangle, \quad (\text{A13})$$

$$|T_1, 0; \frac{3}{2}, \frac{3}{2}\rangle = \frac{2}{\sqrt{5}} a_{t_2 0 \uparrow}^\dagger a_{e \epsilon \uparrow}^\dagger a_{e \theta \uparrow}^\dagger |0\rangle - \frac{1}{\sqrt{5}} a_{t_2 \bar{1} \uparrow}^\dagger a_{t_2 1 \uparrow}^\dagger a_{e \theta \uparrow}^\dagger |0\rangle, \quad (\text{A14})$$

$$3d^4(\text{Cr}^{2+}): |T_2, 1; 2, 2\rangle = a_{t_2 0 \uparrow}^\dagger a_{t_2 1 \uparrow}^\dagger a_{e \epsilon \uparrow}^\dagger a_{e \theta \uparrow}^\dagger |0\rangle, \quad (\text{A15})$$

$$|T_2, 0; 2, 2\rangle = a_{t_2 \bar{1} \uparrow}^\dagger a_{t_2 1 \uparrow}^\dagger a_{e \epsilon \uparrow}^\dagger a_{e \theta \uparrow}^\dagger |0\rangle, \quad (\text{A16})$$

$$3d^5(\text{Mn}^{2+}): |A_1; \frac{5}{2}, \frac{5}{2}\rangle = a_{t_2 \bar{1} \uparrow}^\dagger a_{t_2 0 \uparrow}^\dagger a_{t_2 1 \uparrow}^\dagger a_{e \epsilon \uparrow}^\dagger a_{e \theta \uparrow}^\dagger |0\rangle, \quad (\text{A17})$$

$$3d^6(\text{Fe}^{2+}): |E, \theta; 2, 2\rangle = a_{e \theta \downarrow}^\dagger |A_1; \frac{5}{2}, \frac{5}{2}\rangle, \quad (\text{A18})$$

$$|E, \epsilon; 2, 2\rangle = a_{e \epsilon \downarrow}^\dagger |A_1; \frac{5}{2}, \frac{5}{2}\rangle, \quad (\text{A19})$$

$$3d^7(\text{Co}^{2+}): |A_2; \frac{3}{2}, \frac{3}{2}\rangle = a_{e \theta \downarrow}^\dagger a_{e \epsilon \downarrow}^\dagger |A_1; \frac{5}{2}, \frac{5}{2}\rangle, \quad (\text{A20})$$

$$3d^8(\text{Ni}^{2+}): |T_1, 1; 1, 1\rangle = \left[\frac{2}{\sqrt{5}} a_{t_2 1 \downarrow}^\dagger a_{e \epsilon \downarrow}^\dagger a_{e \theta \downarrow}^\dagger + \frac{1}{2\sqrt{5}} a_{t_2 0 \downarrow}^\dagger a_{t_2 1 \downarrow}^\dagger a_{e \theta \downarrow}^\dagger + \frac{\sqrt{3}}{2\sqrt{5}} a_{t_2 \bar{1} \downarrow}^\dagger a_{t_2 0 \downarrow}^\dagger a_{e \epsilon \downarrow}^\dagger \right] |A_1; \frac{5}{2}, \frac{5}{2}\rangle, \quad (\text{A21})$$

$$|T_1, 0; 1, 1\rangle = \left[\frac{2}{\sqrt{5}} a_{t_2 0 \downarrow}^\dagger a_{e \epsilon \downarrow}^\dagger a_{e \theta \downarrow}^\dagger - \frac{1}{\sqrt{5}} a_{t_2 \bar{1} \downarrow}^\dagger a_{t_2 1 \downarrow}^\dagger a_{e \theta \downarrow}^\dagger \right] |A_1; \frac{5}{2}, \frac{5}{2}\rangle, \quad (\text{A22})$$

$$3d^9(\text{Cu}^{2+}): |T_2, 1; \frac{1}{2}, \frac{1}{2}\rangle = a_{t_2 0 \downarrow}^\dagger a_{t_2 1 \downarrow}^\dagger a_{e \epsilon \downarrow}^\dagger a_{e \theta \downarrow}^\dagger |A_1; \frac{5}{2}, \frac{5}{2}\rangle \quad (\text{A23})$$

$$|T_2, 0; \frac{1}{2}, \frac{1}{2}\rangle = a_{t_2 \bar{1} \downarrow}^\dagger a_{t_2 1 \downarrow}^\dagger a_{e \epsilon \downarrow}^\dagger a_{e \theta \downarrow}^\dagger |A_1; \frac{5}{2}, \frac{5}{2}\rangle. \quad (\text{A24})$$

Notice the crystal-field configuration mixing in the cases of V^{2+} and Ni^{2+} .

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