PHYSICAL REVIEW B VOLUME 46, NUMBER 19 15 NOVEMBER 1992-I

Kinetic exchange in diluted magnetic semiconductors

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(Received 23 June 1992)

Some interesting physical effects are predicted for diluted magnetic semiconductors. It is shown that the spin properties of zinc-blende-type $A^{\mathrm{II}}B^{\mathrm{VI}}$ diluted magnetic semiconductors depend crucially on the electronic configuration of the transition-metal ions. Depending on the filling of the ionic d shell, the kinetic exchange Hamiltonian evolves from antiferromagnetic to ferromagnetic Kondo-like form via more complicated forms sensitive to Jahn-Teller distortions.

I. INTRODUCTION

In metals, the spin-dependent interaction of free carriers with localized magnetic moments has been thoroughly investigated, being responsible for the spin polarization of the electron gas, which in turn leads to, e.g., the Kondo effect. Two fundamental interaction mechanisms were considered: the direct Coulomb exchange[1] and the kinetic exchange, i.e., the hybridization of the band states with localized ionic (d or f) orbitals.[2] In contrast to the former mechanism known to favor the parallel, or ferromagnetic, alignment of the interacting spins, the latter can lead to an antiferromagneticlike interaction.

Kinetic exchange may be viewed as a second-order perturbation-theory effect involving virtual transitions of an electron between the band states and the ionic orbitals.[2] An elegant derivation of the effective kinetic-exchange Hamiltonian has been given by Schrieffer and Wolff.[3] These authors applied the canonical transformation method to the Anderson Hamiltonian in the model case of one singly occupied d orbital. Subsequently, a more realistic case of five such orbitals in an S-state transition-metal ion was considered.[4] In both cases the kinetic-exchange Hamiltonian was shown to have the form of the Kondo Hamiltonian with an energy-dependent, antiferromagnetic exchange constant $J_{k,k'}$. It is worth noting, however, that the above results are subjected to change for the non-S-state transition-metal ions. As shown by Parmenter,[5] for these ions (with some empty or doubly occupied d orbitals), the Anderson Hamiltonian is not adequate.

Spin-dependent interactions of free carriers with magnetic ions were also found to play a significant role in semiconductors, being responsible for many peculiar electronic properties of magnetic[6] and diluted magnetic semiconductors (DMS's).[7] The latter are solid solutions of II-VI (or IV-VI) semiconductors with some cations replaced by transition-metal ions. In these materials, in spite of the high concentration of randomly distributed magnetic ions, all the standard notions of semiconductor physics, i.e., energy bands, effective mass, g factors, etc., proved to be valid.[8] Moreover, the separation of the effects of exchange interactions is quite straightforward in DMS's, as for each such alloy a nonmagnetic reference material can be found. Because of these features, the DMS's are particularly convenient systems for detailed studies of the exchange interactions and their physical consequences.

Evidently, the theory of exchange interactions developed for metals does not apply directly to DMS's, for which the electronic states from several bands with different Bloch functions have to be considered, the crystal-field effects and spin-orbit interactions may not be neglected, etc. Still, it has been found that the most actively studied DMS's doped with ^6S-state Mn^{2+} ions can be described by incorporating a Kondo-like Hamiltonian into effective-mass theory. Comprehensive magneto-optical studies together with band-structure computations have elucidated the microscopic origins of the exchange couplings in these DMS's, pointing to the importance of the kinetic exchange.[9]

In the last few years, a significant number of experimental results for new DMS's doped with other transition-metal ions (e.g., Fe^{2+}, Fe^{3+}, and Co^{2+}) have been accumulated.[10] For the theoretical interpretation of these results, knowledge of the effective-mass kinetic-exchange Hamiltonian appropriate for the interaction of band electrons with non-S-state magnetic ions is essential. In our previous work, we have shown, using the second-order perturbation theory, that for DMS's with ^5D-state ions additional, non-Heisenberg terms occur in the effective Hamiltonian[11] and that they can lead to new physical effects.[12]

In this paper we apply the canonical transformation method to the Parmenter Hamiltonian in order to derive the effective kinetic-exchange Hamiltonian for valence-band electrons interacting with any member of the family of transition-metal ions. Our results demonstrate a variety of possible physical situations which can be encountered and experimentally tested in DMS's with various magnetic ions: The exchange coupling can be antiferromagnetic or ferromagnetic or perturbed by non-Heisenberg terms, sensitive to Jahn-Teller distortion.

II. MODEL

We consider a band electron interacting with a single transition-metal ion having N d electrons. To account properly for the antisymmetry of the wave functions of this system of $N+1$ electrons, we use the occupation-number representation. We restrict our attention to the spin-dependent interaction resulting from hybridization of the Bloch function of the band-edge electron with ionic d orbitals. We consider the model Hamiltonian

$$\hat{H}=\hat{H}_e+\hat{H}_i+\hat{H}_{\text{hyb}}=\hat{H}_0+\hat{H}_{\text{hyb}} \ . \tag{1}$$

$\hat{H}_e$ is the effective-mass Hamiltonian for an electron in the vicinity of the high-symmetry point of the Brillouin zone:

$$\hat{H}_e=\varepsilon_p \sum_{n,k} \hat{n}_{n,k} \ . \tag{2}$$

The indexes n and k label the Luttinger states appropriate for a group of bands with energy ε_p at the degeneracy point. $\hat{n}_{n,k}$ denotes the occupation-number operator for the Luttinger state. In (2) we have omitted the k-dependent terms of the Luttinger effective-mass Hamiltonian, which do not contribute to the dominant k-independent part of the effective-mass kinetic-exchange Hamiltonian.

In choosing the ionic Hamiltonian $\hat{H}_i$, we adopt the spherical approximation; i.e., we neglect the direct effect of the ligand field on the d orbitals. This means that we exclude the strong crystal-field case and we attribute the crystal-field splittings in the ionic energy spectrum solely to hybridization. In the space of the many-electron states spanned by antisymmetrized products of one-electron d orbitals, the spherical ionic Hamiltonian $\hat{H}_i$ can be expressed by

$$\hat{H}_i=\varepsilon_d\hat{N}+\hat{H}_{ee} \ . \tag{3}$$

Here $\hat{N}=\sum_{m,\sigma}\hat{a}^{\dagger}_{m,\sigma}\hat{a}_{m,\sigma}$ is the operator of the number of d electrons with a common energy ε_d. The operators $\hat{a}_{m,\sigma}$ and $\hat{a}^{\dagger}_{m,\sigma}$ are annihilation and creation operators, respectively, of an electron in the d orbital with the angular momentum projection m and the spin projection σ (we put the Planck constant $\hbar=1$). We assume that they anticommute with the corresponding operators for Luttinger states; in other words, we assume that d orbitals and band states are orthogonal. $\hat{H}_{ee}$ represents the Coulomb interactions within the d shell.

In principle, $\hat{H}_i$ can be diagonalized to give the energies of all possible N-electron states. In practice, one uses for $\hat{H}_{ee}$ simplified model Hamiltonians, reproducing only the essential features of the N-electron spectrum, e.g., asserting that the fundamental term corresponds to the maximum possible value of the total spin S (Hund's rule). For a ^6S-state ion (e.g., Mn^{2+}), the simple Anderson Hamiltonian of the form $\sum_m U\hat{n}_{m\uparrow}\hat{n}_{m\downarrow}$ can be used.[4] Unfortunately, this simple Hamiltonian is not rotationally invariant (it does not commute with the angular momentum operator). This becomes crucial for non-S-state ions. In this case, however, $\hat{H}_{ee}$ can be represented by the Parmenter Hamiltonian,[11] which is spherically symmetric in both orbital and spin spaces:

$$\hat{H}_{ee}=(J-U'/2)\hat{N}+\tfrac{1}{2}(U'-J/2)\hat{N}^2-J\mathbf{S}\cdot\mathbf{S} \ . \tag{4}$$

Here U' and J are the nondiagonal Coulomb and exchange integrals, which for all orbitals are assumed to be the same. One can easily see that the last term in Eq. (4) leads to Hund's rule.

The hybridization Hamiltonian $\hat{H}_{\text{hyb}}$ permits the transitions of electrons between the Luttinger states and the localized d orbitals:

$$\hat{H}_{\text{hyb}}=\sum_{nk}\sum_{m\sigma}(V_{m\sigma,nk}\hat{a}^{\dagger}_{m\sigma}\hat{a}_{nk}+\text{H.c.}) \ , \tag{5}$$

where $V_{m\sigma,nk}=\langle m\sigma|T|nk\rangle$ is the off-diagonal matrix element of the one-electron part of the Hamiltonian. This matrix element involves the volume Ω of the crystal via the normalization factor of the Bloch function. The hybridization matrix depends on the symmetries of particular Luttinger states and on the point symmetry of the crystal potential in the range of the d-shell localization. In this paper we limit our considerations to $A^{\text{II}}B^{\text{VI}}$ diluted magnetic semiconductors with a zinc-blende-type lattice, for which both the lowest conduction band and uppermost valence bands have extremal points at the center of the Brillouin zone. The Γ_6 Luttinger states corresponding to the conduction band are essentially built of s orbitals, whereas the Γ_8 valence states involve mostly anion p orbitals. In these materials the transition-metal ions occupy cation positions with the tetrahedral symmetry. For such symmetry the hybridization matrix elements are much more important for Γ_8 than for Γ_6 bands, since in the latter they rigorously vanish at $k=0$. This is confirmed by experimental results showing no evidence of the kinetic exchange for conduction electrons. We recall here that within effective-mass theory we are interested in small k vectors only. For such wave vectors, the k dependence of the matrix elements is trivial:

$$V_{m\sigma,nk}=e^{i\mathbf{k}\cdot\mathbf{R}_I}\langle m\sigma|T|n0\rangle \ , \tag{6}$$

where $\mathbf{R}_I$ is the position vector of the ion (in the following we choose the ion at $\mathbf{R}_I=\mathbf{0}$). This comes from the fact that the periodic part of a Luttinger function is k independent and the envelope part $e^{i\mathbf{k}\cdot\mathbf{r}}$ does not vary significantly in the range of localization of the d orbitals.

By symmetry, one finds that the crystal Hamiltonian couples the Γ_8 Luttinger states only with the three one-electron d states belonging to the t_{2g} representation of the point group T_d. The hybridization Hamiltonian H_{hyb} can be then expressed in the form

$$\begin{aligned}\hat{H}_{\text{hyb}}&=\sum_{m_L\sigma}[\hat{M}_{m_L\sigma}\hat{a}^{\dagger}_{m_L\sigma}+\text{H.c.}] \ , \\ \hat{M}_{m_L\sigma}&=(V/\Omega^{1/2})\sum_{m_Jk}(2+2\sigma m_L)^{1/2}\delta_{m_L+\sigma,m_J}\hat{a}_{m_Jk} \ ,\end{aligned} \tag{7}$$

where $m_L=-1,0,1$ labels the three t_{2g} ionic orbitals and can be considered as the projection of the fictitious orbital angular momentum $\mathbf{L}$ with $l=1$. $m_J=-\frac{3}{2}$, $-\frac{1}{2}$, $\frac{1}{2}$, and $\frac{3}{2}$ are the corresponding projections of the fictitious angular momentum $\mathbf{J}$ with $j=\frac{3}{2}$ commonly used for the

Γ_8 Luttinger states. V is a single hybridization constant, which can be related to Slater-Koster interatomic matrix elements (see, e.g., Ref. 9).

III. CANONICAL TRANSFORMATION

In the canonical transformation method, one expresses the second-quantized Hamiltonian $\hat H = H(\hat a,\hat a^\dagger)$ in terms of new operators $\hat c$ and $\hat c^\dagger$ ($\hat c = e^{-\hat O}\hat a e^{\hat O}$) obeying the same anticommutation relations as $\hat a$ and $\hat a^\dagger$. The desired properties of the new functional form $\bar H(\hat c,\hat c^\dagger)$ of the Hamiltonian $\hat H$,

$$\bar H(\hat c,\hat c^\dagger)=e^{\hat O}H(\hat c,\hat c^\dagger)e^{-\hat O} , \tag{8}$$

can be assured by an appropriate choice of the anti-Hermitian operator $\hat O$.

For our Hamiltonian (1), we require $\bar H(\hat c,\hat c^\dagger)$ not to contain terms linear in the hybridization constant V; i.e., we have to find $\hat O$ satisfying the condition

$$[H_0(\hat c,\hat c^\dagger),\hat O]=H_{\text{hyb}}(\hat c,\hat c^\dagger) . \tag{9}$$

Then the second order in the V part of the Hamiltonian (8) is given by

$$H_2(\hat c,\hat c^\dagger)=\tfrac{1}{2}[\hat O,H_{\text{hyb}}(\hat c,\hat c^\dagger)] . \tag{10}$$

For reasons which will become clear later on, in the following we consider separately the cases of ions with $N \geq 5$ and $N \leq 5$ electrons.

For $N \leq 5$, we choose the operator $\hat O$ satisfying Eq. (9) in the form

$$\hat O=\sum_{m_L\sigma}\hat M^\dagger_{m_L\sigma}\{\hat\eta_\sigma\hat c_{m_L\sigma}+\hat\vartheta_\sigma\hat c_{m_L-\sigma}\}-\text{H.c.} , \tag{11}$$

where

$$\begin{aligned}
&\hat\eta_\sigma=(\hat\Delta_N-2\sigma J\hat S_z)[\hat\Delta_N(\hat\Delta_N+J)-J^2\mathbf{S}\cdot\mathbf{S}]^{-1} ,\\
&\hat\vartheta_\sigma=-J\hat S_{-2\sigma}[\hat\Delta_N(\hat\Delta_N+J)-J^2\mathbf{S}\cdot\mathbf{S}]^{-1} ,\\
&\hat\Delta_N=\varepsilon_p-\varepsilon_d-J-(U'-J/2)\hat N .
\end{aligned} \tag{12}$$

The spin-raising ($\hat S_{+1}$) and -lowering ($\hat S_{-1}$) operators have the form

$$\hat S_{-2\sigma}=\sum_{m_L=1,0-1}\hat c^\dagger_{m_L-\sigma}\hat c_{m_L\sigma}+\sum_{i=1,2}\hat c'^\dagger_{i-\sigma}\hat c'_{i\sigma} . \tag{13}$$

We denote by $\hat c'_{i\sigma}$ ($i=1,2$) the transformed annihilation operators of electrons with the spin projection σ in the e_g one-electron orbitals.

With such a canonical transformation operator $\hat O$, we get from (10) the effective Hamiltonian (compare Ref. 3)

$$H_2=H'_0+H_{\text{ch}}+H_{p\text{-}d} . \tag{14}$$

The term H'_0, involving no band-electron creation and annihilation operators, represents the hybridization-induced tetrahedral corrections to the ionic Hamiltonian H_i, which in our model are responsible for the crystal-field splittings, i.e., the energy difference between t_{2g} and e_g one-electron states. The next term describes the high-energy processes, changing the number of d electrons by 2, and will be disregarded. The kinetic-exchange Hamiltonian $H_{p\text{-}d}$ describes the scattering of a band electron on an impurity ion. In contrast to the simple case discussed by Schrieffer and Wolff in Ref. 3, here there is no clear-cut separation into spin-independent and -dependent parts of this term:

$$\begin{aligned}
H_{p\text{-}d}=\tfrac{1}{2}\sum_{\substack{m'_L\sigma'\\ m_L\sigma}}\hat M^\dagger_{m'_L\sigma'}\hat M_{m_L\sigma}\{&\hat c^\dagger_{m_L\sigma}(\hat\eta_{\sigma'}+\hat\eta_\sigma)\hat c_{m'_L\sigma'}+\hat c^\dagger_{m_L\sigma}\hat\vartheta_{\sigma'}\hat c_{m'_L-\sigma'}+\hat c^\dagger_{m_L-\sigma}\hat\vartheta_{-\sigma}\hat c_{m'_L\sigma'}+\hat\eta_{\sigma'}\hat c_{m'_L\sigma'}\hat c^\dagger_{m_L\sigma}\\
&+\hat c_{m'_L\sigma'}\hat c^\dagger_{m_L\sigma}\hat\eta_\sigma+\hat\vartheta_{\sigma'}\hat c_{m'_L-\sigma'}\hat c^\dagger_{m_L\sigma}+\hat c_{m'_L\sigma'}\hat c^\dagger_{m_L-\sigma}\hat\vartheta_{-\sigma}\} .
\end{aligned} \tag{15}$$

For $N \geq 5$, we choose

$$\hat O'=\sum_{m_L\sigma}\hat M^\dagger_{m_L\sigma}\{\hat c_{m_L\sigma}\hat\eta'_\sigma+\hat c_{m_L-\sigma}\hat\vartheta'_\sigma\}-\text{H.c.} , \tag{16}$$

with

$$\begin{aligned}
&\hat\eta'_\sigma=(\Delta'_N-2\sigma J\hat S_z)[\Delta'_N(\Delta'_N-J)-J^2\mathbf{S}\cdot\mathbf{S}]^{-1} ,\\
&\hat\vartheta'_\sigma=-J\hat S_{-2\sigma}[\Delta'_N(\Delta'_N-J)-J^2\mathbf{S}\cdot\mathbf{S}]^{-1} ,\\
&\Delta'_N=\Delta_N+U' ,
\end{aligned} \tag{17}$$

and, by calculating the commutator (10), we get

$$\begin{aligned}
H_{p\text{-}d}=\tfrac{1}{2}\sum_{\substack{m_L\sigma\\ m'_L\sigma'}}\hat M^\dagger_{m'_L\sigma'}\hat M_{m_L\sigma}\{&\hat c_{m'_L\sigma'}(\hat\eta'_{\sigma'}+\hat\eta'_\sigma)\hat c^\dagger_{m_L\sigma}+\hat c_{m'_L-\sigma'}\hat\vartheta'_{-\sigma'}\hat c^\dagger_{m_L\sigma}+\hat c_{m'_L\sigma'}\hat\vartheta'_\sigma\hat c^\dagger_{m_L-\sigma}+\hat\eta'_\sigma\hat c^\dagger_{m_L\sigma}\hat c_{m'_L\sigma'}\\
&+\hat c^\dagger_{m_L\sigma}\hat c_{m'_L\sigma'}\hat\eta'_{\sigma'}+\hat c^\dagger_{m_L\sigma}\hat c_{m'_L-\sigma'}\hat\vartheta'_{-\sigma'}+\hat\vartheta'_\sigma\hat c^\dagger_{m_L-\sigma}\hat c_{m'_L\sigma'}\} .
\end{aligned} \tag{18}$$

IV. KINETIC EXCHANGE

We consider a sequence of transition-metal ions with $N=1,2,\ldots,9$ electrons in the d shell (Fig. 1). The kinetic-exchange Hamiltonian describing the interaction of the low-energy Γ_8-band electron with a given transition-metal ion is derived by restricting the Hamiltonian $H_{p\text{-}d}$ to the subspace of the lowest-energy states of the ion. In our model the ion is described by the sum of the free-ion Hamiltonian H_i and the hybridization-induced spin-independent cubic Hamiltonian H_0'. Therefore the lowest-energy states of the ion are the Hund states, i.e., the states with the maximum value of the total spin S [$S=N/2$ for $N=\leq 5$ and $S=(10-N)/2$ for $N\geq 5$]. In these states the number of singly occupied one-electron d orbitals is equal to $2S$. We note here that the annihilation or creation of an electron in an initially singly occupied orbital leads to the decrease of the total spin of the d shell by one-half. This implies that the annihilation of an electron in the Hund state for $N\leq 5$ produces also a Hund state for $N-1$ electrons. In contrast, for $N\geq 5$, the creation of an electron in the Hund state gives a Hund state for $N+1$ electrons. Now one can see that our choice of operators $\hat{O}$ in Eqs. (11) and (16) guarantees that the operators $\hat{\eta}$ and $\hat{\vartheta}$ in (15) and (18) act only on Hund states (for N and $N-1$ electrons in the case $N\leq 5$ and for N and $N+1$ electrons for $N\geq 5$). Then the inverse operators entering the definitions of η and ϑ reduce to c-numbers. This does not mean that we neglected the virtual processes involving the electron creation for $N\leq 5$ and annihilation for $N\geq 5$. In fact, all the expected energy denominators will be recovered in the kinetic-exchange constants B_N and C_N appearing in the final results.

We define the constant B_N:

$$B_N=(V^2/2S)[(E_N^S-E_{N-1}^{S-1/2}-\varepsilon_p)^{-1}+(E_N^S+\varepsilon_p-E_{N+1}^{S-1/2})^{-1}]\,, \tag{19}$$

where E_N^S denotes the unperturbed energy of the d shell with N electrons and total spin S:

$$E_N^S=(\varepsilon_d+J-U'/2)N+\tfrac{1}{2}(U'-J/2)N^2-JS(S+1)\,. \tag{20}$$

B_N collects the contributions from all virtual transitions, changing the occupation of the initially singly occupied orbitals.

In an empty orbital, the creation of an electron, as well as the annihilation of an electron from a doubly occupied orbital, can produce virtual states with two values of the total spin, $S+\frac{1}{2}$ and $S-\frac{1}{2}$, having different energies. Such processes contribute to the constant C_N:

$$C_N=\frac{V^2}{2S+1}[(E_N^S\pm\varepsilon_p-E_{N\pm1}^{S+1/2})^{-1}-(E_N^S\pm\varepsilon_p-E_{N\pm1}^{S-1/2})^{-1}]\,, \tag{21}$$

where the upper sign corresponds to $N<5$ and the lower sign to $N>5$.

Both constants B_N and C_N are negative if only the state of N d electrons and one band electron is energetically stable. They depend on four parameters: the three parameters of the Parmenter model, i.e., $\varepsilon_d-\varepsilon_p$, U', and J, and the hybridization constant V. These parameters can, in principle, be inferred for each DMS from experimental data, e.g., in a way similar to that reviewed by Fujimori for the case of Anderson Hamiltonian.[13]

A. $N=5$

In an ^6S-state ion with $N=5$ d electrons (e.g., Mn^{2+}), all the orbitals are singly occupied, so that $C_5=0$. In this case the kinetic-exchange Hamiltonian obtained from either Eq. (15) or (18) has the following antiferromagnetic Kondo-like matrix form

$$H_{\text{ex}}=-(1/\Omega)2B_5\mathbf{S}\cdot\mathbf{J}\,. \tag{22}$$

Here J_i and S_i are matrices representing the ith com-

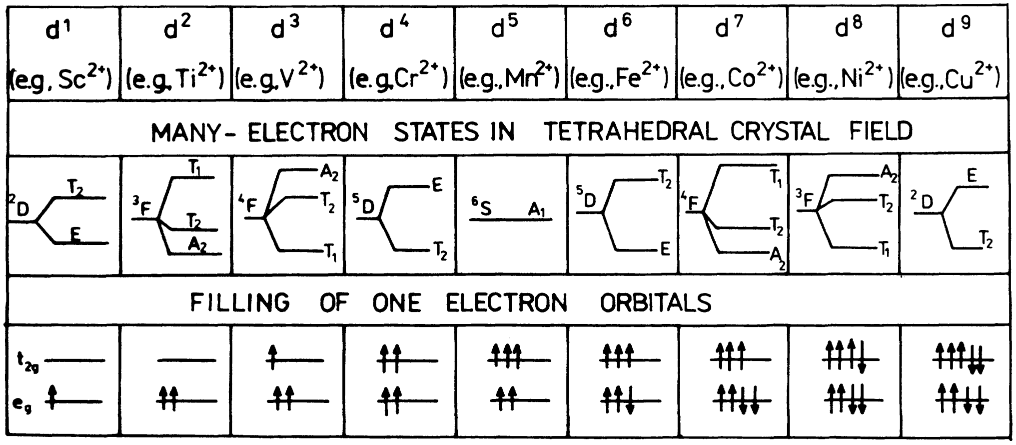

FIG. 1. Low-energy orbital states and the filling of one-electron d orbitals for transition-metal ions in a tetrahedral environment (in the intermediate crystal-field case).

ponent of the fictitious angular momentum $j=\frac{3}{2}$ and the ionic spin, respectively.

Summing up the thermodynamical average of (22) (multiplied by $e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_l}$, over randomly distributed magnetic ions in DMS's, one gets the well-known diagonal-in-k one-electron mean-field kinetic-exchange Hamiltonian for a Γ_8-band electron:

$$H_{\text{ex}}=-xN_0(\beta/3)\langle S_{\parallel}\rangle J_{\parallel}\ , \tag{23}$$

where xN_0 is the concentration of magnetic ions, $\langle S_{\parallel}\rangle$ is the thermodynamical average of the impurity spin component along the external magnetic field. $J_{\parallel}$ can be easily diagonalized by an appropriate rotation of the Luttinger basis. $\beta=6B_5$ is the conventionally used exchange constant.[14]

B. $N=6$ and 7

The d shell in free ions with $N\neq 5$ electrons has a nonvanishing orbital momentum. The cubic Hamiltonian H_0' lifts the orbital degeneracy by increasing the energy of the three t_{2g} orbitals hybridizing with Γ_8-band states as compared to the two e_g orbitals. The many-electron ground orbital states are the doublet E for $N=6$ and the singlet A_2 for $N=7$. In these states all the t_{2g} orbitals are singly occupied just as in the $N=5$ case, the sixth and seventh electrons occupying e_g orbitals. As a result, the kinetic-exchange Hamiltonians, derived from Eq. (18), for Γ_8-band electrons interacting with Fe^{2+} ($N=6$) or Co^{2+} ($N=7$) ions in their ground orbital states are given by (23) with B_5 replaced by B_6 and B_7, respectively.

C. $N=1$ and 2

For such ions in a tetrahedral environment, the ground orbital states are E for $N=1$ (e.g., Sc^{2+}) and A_2 for $N=2$ (e.g., Ti^{2+}). In these cases one gets from (15) the kinetic-exchange Hamiltonian in the form

$$H_{\text{ex}}=(1/\Omega)2C_N\mathbf{S}\cdot\mathbf{J}\ . \tag{24}$$

In contrast to (22), only the constants C_N enter the final result, because in the ground orbital states of $N=1$ and 2 ions e_g orbitals are occupied, whereas all the t_{2g} orbitals are empty. The Hamiltonian (24) has a ferromagnetic character. This comes from the fact that virtual states of $N+1$ electrons on the d shell with spin $S+\frac{1}{2}$ have lower energy than those with $S-\frac{1}{2}$ spin. This time the mean-field Hamiltonian for a random distribution of magnetic ions has the form

$$H_{\text{ex}}=-xN_0(\gamma/3)\langle S_{\parallel}\rangle J_{\parallel}\ . \tag{25}$$

The estimate of the positive constant $\gamma=-6C_N$ indicates that in Γ_8 bands the ferromagnetic kinetic exchange for both Sc and Ti, although weaker than the antiferromagnetic one for DMS's with Mn^{2+} ions, should still dominate over the direct Coulomb exchange.[15]

In an earlier paper,[11] primarily concerned with kinetic exchange for ions with $N=4$, 5, and 6 d electrons, we speculated also about other transition-metal ions. The naive intuitions based on the use of the Anderson Hamiltonian led us to an erroneous conclusion about the absence of kinetic exchange for $N=1$ and 2. This conclusion has also been reached by Bhattacharjee,[16] who reconsidered the problem addressed in Ref. 11 by applying the irreducible-tensor method to the Anderson Hamiltonian.

In all cases A, B, and C, the occupations of all three t_{2g} orbitals were identical. For all other transition-metal ions, some of the t_{2g} orbitals are singly occupied, whereas the remaining ones are empty (for $N<5$) or doubly occupied (for $N>5$). In this situation both types of virtual processes (contributing to B_N and C_N, respectively) should thus be important, with different relative weight, for different ions. The ground states of all these ions are either T_1 or T_2 orbital triplets (Fig. 1). It is now convenient to introduce a fictitious angular momentum operator $\mathbf{L}$ (with $l=1$) and to choose the eigenvectors of its z component L_z as the basis vectors for these orbital triplets (see the Appendix). The fictitious angular momentum operator $\mathbf{L}$ will appear in the effective kinetic-exchange Hamiltonians coupled with the operators $\mathbf{S}$ and $\mathbf{J}$, in addition to the Kondo-like term proportional to $\mathbf{S}\cdot\mathbf{J}$.

D. $N=3$ and 8

The ground orbital states for both V^{2+} ($N=3$) and Ni^{2+} ($N=8$) are the T_1 triplets (see Fig. 1). In the former the three d electrons occupy two e_g and one t_{2g} one-electron orbitals. The latter can be obtained from the S-like A_1 orbital configuration of the Mn^{2+} ion by adding three electrons also into two e_g and one t_{2g} orbital. For both cases we have obtained very similar kinetic-exchange Hamiltonians, which differ only by the sign of one term:

$$H_{\text{ex}}=(1/\Omega)\{[(C_N-B_N)\cdot\mathbf{J}\mp(C_N+B_N)(\mathbf{J}-[\hat{H}_Q+\mathbf{L}\cdot\mathbf{J},\mathbf{L}-\mathbf{J}]_+)]\cdot\mathbf{S}-D_N(\hat{H}_Q+\mathbf{L}\cdot\mathbf{J})\}\ , \tag{26}$$

with the upper sign for $N=3$ and the lower for $N=8$ ions. Here

$$D_N=(S+1)C_N+SB_N \tag{27a}$$

and the operator

$$\hat{H}_Q=(\mathbf{L}\cdot\mathbf{J})^2+\tfrac{1}{2}\mathbf{L}\cdot\mathbf{J}-\tfrac{1}{3}l(l+1)j(j+1) \tag{27b}$$

has the form of an electric quadrupole-quadrupole interaction.

The first term in (26), which involves the spin operator $\mathbf{S}$ of the ion, represents the modification of the Kondo-like Hamiltonian by the $\mathbf{L}\cdot\mathbf{J}$ coupling. The second term represents a new type of interaction of the band electron with the magnetic ion that depends only on the orbital state of the ion.

E. $N=4$ (e.g., Cr^{2+}) and $N=9$ (e.g., Cu^{2+})

In these two cases (with the ground-state triplets T_2), the occupations of the one-electron orbitals t_{2g} hybridizing with the band states, when interpreted in terms of holes, are identical with the occupation of these orbitals by electrons in cases $N=8$ and 3, respectively. The Hamiltonian H_{ex} obtained for DMS's doped with Cr^{2+} and Cu^{2+} ions can be written in the form

$$H_{\mathrm{ex}}=(1/\Omega)\{[(C_N-B_N)\cdot\mathbf{J}\pm(C_N+B_N)(\mathbf{J}+[\hat{H}_Q-\mathbf{L}\cdot\mathbf{J},\mathbf{L}+\mathbf{J}]_+)]\cdot\mathbf{S}+D_N(\hat{H}_Q-\mathbf{L}\cdot\mathbf{J})\}\ , \tag{28}$$

(with the upper sign corresponding to the Cr^{2+} ion). Equation (28) could be also deduced from Eq. (26) by exploiting the rules of electron-to-hole transformation.

In order to examine the effect of kinetic-exchange interactions on the properties of Γ_8-band electrons in cases D and E, we have to sum up the thermodynamical averages of the single-ion Hamiltonians for a random distribution of magnetic ions. In contrast to the Hamiltonians discussed in cases A, B, and C, (26) and (28) depend crucially on the orbital state of the ion. This makes them sensitive to Jahn-Teller distortions, spin-orbit interaction, and the external magnetic field, which are lifting the orbital degeneracy of the ground state.

In Ni^{2+}, the strong spin-orbit interaction and, in Cu^{2+}, the dynamic Jahn-Teller effect make the orbital composition of the low-energy states depend strongly on the magnetic field.[17] Therefore the calculations of the thermodynamical averages of the single-ion Hamiltonians (26) and (28) cannot be reduced to the calculations of the averages of the ionic spin component $S_{\parallel}$.

The V^{2+} and Cr^{2+} ions in $A^{\mathrm{II}}B^{\mathrm{VI}}$ compounds are known to undergo a strong static Jahn-Teller effect (trigonal and tetragonal, respectively[18,19]). Even in this simplest case, when the fictitious angular momentum of each ion is totally quenched, the form of the mean-field kinetic-exchange interaction has a nontrivial dependence on the relative number of ions with the distortions along different equivalent crystallographic axes, as well as on the direction and magnitude of the external magnetic field. Still, if none of the possible equivalent directions of the Jahn-Teller distortions is privileged (so that, in average, the cubic symmetry is conserved), the mean-field exchange Hamiltonian in the high-magnetic-field limit has a simple form.

For DMS's with V^{2+} ions, we get the ferromagnetic mean-field exchange Hamiltonian

$$H_{\mathrm{ex}}=xN_0(2C_3)\langle S_{\parallel}\rangle J_{\parallel}\ , \tag{29}$$

similar to those for DMS's doped with Sc^{2+} or Ti^{2+} ions.

For DMS's with Cr^{2+} ions, we obtain the antiferromagnetic Hamiltonian

$$H_{\mathrm{ex}}=-xN_0\tfrac{2}{3}(2B_4-C_4)\langle S_{\parallel}\rangle J_{\parallel}\ . \tag{30}$$

This time the Hamiltonian is similar to those obtained in the cases of Mn^{2+}, Fe^{2+}, and Co^{2+} ions, but with the exchange constant $\frac{2}{3}(2B_N-C_N)$ reduced as compared to $2B_N$.

In the opposite limit, with all distortions along the same crystallographic axis, the cubic symmetry is broken and the form of the Hamiltonian depends on the direction of the external magnetic field.

For DMS's with V^{2+} ions (trigonal Jahn-Teller effect) with all distortions and the magnetic field along the [111] axis, we get, for an arbitrary magnitude of the field,

$$\begin{aligned}H_{\mathrm{ex}}=&\,xN_0D_4(\tfrac{5}{4}-J_{\parallel}^2)\\&-xN_0 2\langle S_{\parallel}\rangle J_{\parallel}[B_3(\tfrac{9}{4}-J_{\parallel}^2)+C_3(\tfrac{5}{4}-J_{\parallel}^2)]\ .\end{aligned} \tag{31}$$

Similarly, for DMS's with Cr^{2+} ions (the tetragonal case), with the distortions and magnetic field along the [001] axis, we obtain

$$\begin{aligned}H_{\mathrm{ex}}=&\,xN_0D_4(\tfrac{5}{4}-J_{\parallel}^2)\\&+xN_0 2\langle S_{\parallel}\rangle J_{\parallel}[C_4(\tfrac{9}{4}-J_{\parallel}^2)+B_4(\tfrac{5}{4}-J_{\parallel}^2)]\ .\end{aligned} \tag{32}$$

The first term in (31) and (32) leads to the concentration-dependent zero-field splitting at $k=0$ between the $m_J=\pm\frac{3}{2}$ and $\pm\frac{1}{2}$ Γ_8 bands with a different band ordering for Cr^{2+} and V^{2+}. The terms proportional to $\langle S_{\parallel}\rangle$ give unusual patterns of the Γ_8 band Zeeman splittings. For the $m_J=\pm\frac{3}{2}$ bands, the expected splitting is antiferromagnetic ($\propto B_4$) for Cr^{2+} and ferromagnetic ($\propto C_3$) for V^{2+}. In contrast, for $m_J=\pm\frac{1}{2}$, the order of the bands is reversed—the splitting is ferromagnetic ($\propto B_4+2C_4$) for Cr^{2+} and antiferromagnetic for V^{2+} ($\propto 2B_3+C_3$). These effects should show up in exciton magneto-optical transitions in strained DMS's doped with these ions.

V. SUMMARY

In this paper we considered the kinetic-exchange interactions in zinc-blende $A^{\mathrm{II}}B^{\mathrm{VI}}$ diluted magnetic semiconductors doped with various $3d$ ions. To account for the intrashell electron correlations, we used the Parmenter Hamiltonian. By generalizing the Schrieffer-Wolff canonical transformation to the case of the Parmenter Hamiltonian, we derived the kinetic-exchange Hamiltonians for Γ_8 electrons interacting with different transition-metal ions. For Mn^{2+}, Fe^{2+}, and Co^{2+} the antiferromagnetic, whereas for Sc^{2+} and Ti^{2+} the ferromagnetic Kondo-like Hamiltonians were obtained. For ions with the ground orbital triplet, we found the kinetic exchange to contain extra terms dependent on the orbital state of the ion. This makes the kinetic exchange sensitive to the Jahn-Teller effect. It was shown within the mean-field approximation that new physical effects should be expected for diluted magnetic semiconductors containing other than Mn^{2+}, Fe^{2+}, or Co^{2+} transition-metal ions.

ACKNOWLEDGMENTS

We would like to thank Professor T. Dietl for many valuable discussions and comments. This work was partially supported by the Grant No. KBN-2-09-28-91-01.

APPENDIX: LOW-ENERGY STATES FOR TRANSITION-METAL IONS

We specify the orthonormal bases spanning the subspaces of the lowest-energy many-electron states for subsequent transition-metal ions in the tetrahedral crystal environment. For each ion we write down explicitly only the states $|\alpha, m_S = 2\sigma S\rangle$ with the maximum absolute value of the spin projection (α stands here for the orbital quantum numbers). All other states can be generated by using the formula

$$|\alpha, m_S\rangle = (\hat{S}_{-2\sigma})^{S-2\sigma m_S} |\alpha, 2\sigma S\rangle \times \left[\frac{(S+2\sigma m_S)!}{(2S)!(S-2\sigma m_S)!} \right]^{1/2} . \tag{A1}$$

$N=1$, orbital doublet E ($i=1,2$):

$$|i, m_S = \sigma\rangle = c'^{\dagger}_{i\sigma} |0\rangle \ ;$$

$N=2$, orbital singlet A_2:

$$|m_S = 2\sigma\rangle = c'^{\dagger}_{1\sigma} c'^{\dagger}_{2\sigma} |0\rangle \ ;$$

$N=3$, T_1 triplet ($m_L = 1, 0, -1$):

$$|m_L, m_S = 3\sigma\rangle = c^{\dagger}_{m_L\sigma} c'^{\dagger}_{1\sigma} c'^{\dagger}_{2\sigma} |0\rangle \ ;$$

$N=4$, T_2 triplet ($m_L = 1, 0, -1$):

$$|m_L, m_S = 4\sigma\rangle = (-1)^{m_L+1} c_{-m_L\sigma} |m_S = 5\sigma\rangle \ ,$$

where $|m_S = 5\sigma\rangle$ is the state of the half-filled d shell; $N=5$, A_1 singlet:

$$|m_S = 5\sigma\rangle = c^{\dagger}_{1\sigma} c^{\dagger}_{0\sigma} c^{\dagger}_{-1\sigma} c'^{\dagger}_{1\sigma} c'^{\dagger}_{2\sigma} |0\rangle \ ;$$

$N=6$, E doublet ($i=1,2$):

$$|i, m_S = 4\sigma\rangle = c'^{\dagger}_{i-\sigma} |m_S = 5\sigma\rangle \ ;$$

$N=7$, A_2 singlet:

$$|m_S = 3\sigma\rangle = c'^{\dagger}_{1-\sigma} c'^{\dagger}_{2-\sigma} |m_S = 5\sigma\rangle \ ;$$

$N=8$, T_1 triplet ($m_L = 1, 0, -1$):

$$|m_L, m_S = 2\sigma\rangle = 2\sigma c^{\dagger}_{m_L-\sigma} c'^{\dagger}_{1-\sigma} c'^{\dagger}_{2-\sigma} |m_S = 5\sigma\rangle \ ;$$

$N=9$, T_2 triplet ($m_L = 1, 0, -1$):

$$|m_L, m_S = \sigma\rangle = (-1)^{m_L+1/2-\sigma} c_{-m_L-\sigma} |m_S = 0\rangle \ ,$$

where $|m_S = 0\rangle$ is the state of the completely filled d shell:

$$|m_S = 0\rangle = 2\sigma c^{\dagger}_{1\sigma} c^{\dagger}_{0\sigma} c^{\dagger}_{-1\sigma} c'^{\dagger}_{1\sigma} c'^{\dagger}_{2\sigma} c^{\dagger}_{1-\sigma} c^{\dagger}_{0-\sigma} c^{\dagger}_{-1-\sigma} c'^{\dagger}_{1-\sigma} c'^{\dagger}_{2-\sigma} |0\rangle \ .$$

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