p-d exchange interaction for *3d* transition-metal impurities in II-VI semiconductors

T. Mizokawa and A. Fujimori

Department of Physics, University of Tokyo, Bunkyo-ku, Hongo 7-3-1, 113 Japan

We have investigated the exchange interaction between the localized d electrons of $3d$ transition-metal impurities and the delocalized host band electrons in II-VI semiconductors based on the configuration-interaction scheme. The exchange constant $N\beta$ in the Kondo-type effective Hamiltonian is evaluated from Ti to Ni. For Mn, Fe, and Co, $N\beta$ is negative (antiferromagnetic), and is in good agreement with experimental values. The exchange coupling of the Ti impurity is predicted to be positive (ferromagnetic) due to Hund's coupling. For V, Cr, and Ni, in which orbital degrees of freedom is important, the sign of $N\beta$ depends on the Jahn-Teller distortion. [S0163-1829(97)09135-2]

I. INTRODUCTION

In diluted magnetic semiconductors, interaction between the localized d electrons of magnetic impurities and the delocalized host band electrons causes interesting magnetic and optical properties. In particular, the strong magneto-optical effect in II-VI semiconductors with substitutional $3d$ transition-metal impurities has attracted much interest, and has been extensively studied.[1] In II-VI semiconductors, the conduction band is mainly formed by the s orbitals of the cation, and the valence band by the p orbitals of the anion. The exchange interaction between the s electrons in the conduction band and the d electrons of the transition-metal impurities is derived from the direct exchange. On the other hand, the exchange interaction between the p electrons in the valence band and the d electrons is mainly determined by p-d hybridization.[1-3] When the magnetic moments of the transition-metal impurities are aligned in a strong magnetic field, the valence and conduction bands are split through the exchange interaction. The band splitting has been observed in free-exciton spectroscopy. The exchange constant $N\beta$ between the $3d$ electrons and the Bloch electrons at the host valence-band maximum has been obtained experimentally.[1]

A Kondo-type effective Hamiltonian with a p-d exchange interaction can be derived from the Anderson impurity Hamiltonian by means of the Schrieffer-Wolf transformation.[4] Therefore, it is possible to estimate the exchange constants once the electronic-structure parameters in the Anderson impurity model are determined. The exchange constants for the II-VI diluted magnetic semiconductors with Mn, Fe, and Co impurities, in which the orbital degree of freedom is not important, have been evaluated along this line and are in good agreement with the experimental results.[2,3,5] Bhattacharjee[6] investigated the exchange constants for various $3d$ transition-metal impurities in II-VI semiconductors by using the Schrieffer-Wolf transformation and considering the orbital degrees of freedom. However, in this model, intra-atomic exchange interaction or Hund's coupling, which would play an important role in some transition-metal ions, is not included. Recently, ferromagnetic p-d exchange interaction was observed in Cr-based II-VI diluted semiconductors,[7] indicating the importance of the intra-atomic exchange interaction.

In this paper, we present an expression for $N\beta$ in the configuration-interaction scheme and evaluate $N\beta$ for the transition-metal impurities from Ti to Ni using the Anderson impurity model, in which the intra-atomic exchange interaction is included. We employ the electronic-structure parameters of the Anderson impurity model obtained by a configuration-interaction analysis of d-d optical-absorption spectra, photoemission spectra, and donor-acceptor ionization energies.[5]

II. MODEL AND METHOD

The Anderson impurity Hamiltonian is given by

$$H = H_p + H_d + H_{pd}, \tag{1}$$

$$H_p = \sum_{k,\sigma} \epsilon_k^p p_{k,\sigma}^+ p_{k,\sigma}, \tag{2}$$

$$
\begin{aligned}
H_d ={}& \epsilon_d \sum_{m,\sigma} d_{m,\sigma}^+ d_{m,\sigma} + u \sum_m d_{m,\uparrow}^+ d_{m,\uparrow} d_{m,\downarrow}^+ d_{m,\downarrow} \\
&+ u' \sum_{m \neq m'} d_{m,\uparrow}^+ d_{m,\uparrow} d_{m',\downarrow}^+ d_{m',\downarrow} \\
&+ (u' - j') \sum_{m > m',\sigma} d_{m,\sigma}^+ d_{m,\sigma} d_{m',\sigma}^+ d_{m',\sigma} \\
&+ j' \sum_{m \neq m'} d_{m,\uparrow}^+ d_{m',\uparrow} d_{m,\downarrow}^+ d_{m',\downarrow} \\
&+ j \sum_{m \neq m'} d_{m,\uparrow}^+ d_{m',\uparrow} d_{m',\downarrow}^+ d_{m,\downarrow},
\end{aligned}
\tag{3}
$$

$$H_{pd} = \sum_{k,m,\sigma} V_{k,m}^{pd} d_{m,\sigma}^+ p_{k,\sigma} + \text{H.c.} \tag{4}$$

Equation (2) represents the Hamiltonian for the anion p electrons of the host semiconductor, where k labels the wave vector in the first Brillouin zone. Equation (3) describes the Hamiltonian for the $3d$ electrons of the transition-metal impurity, in which σ and m are indices for the spin and orbital, respectively, and the intra-atomic $3d$-$3d$ Coulomb interac-

tion is expressed by Kanamori parameters u, u', j, and j'.[8] We have to assume relationships $u' = u - 2j$ and $j' = j$ in order to retain the rotational invariance in real space of the Coulomb term. The hybridization between the $3d$ orbitals and the host band states is expressed by Eq. (4). The multiplet-averaged charge-transfer energy is defined by $\Delta \equiv E(d^{n+1}\underline{L}) - E(d^n)$, where $\underline{L}$ denotes a hole in the host valence band and $E(d^n\underline{L}^m)$ is the center of gravity of the $d^n\underline{L}^m$ multiplet. The multiplet-averaged Coulomb interaction is defined by $U \equiv E(d^{n-1}) + E(d^{n+1}) - 2E(d^n)$, which is given by $u - 20/9j$. These two parameters have a relationship $\Delta = \epsilon_d - \epsilon_p + nU$, where ϵ_p is the center of the host valence band. The charge-transfer and Coulomb interaction energy defined with respect to the lowest term of each multiplet are denoted as Δ_{eff} and U_{eff}, respectively.

Because of the p-d hybridization term, a hole created at the valence-band maximum can hybridize with $3d$ orbitals. In the configuration-interaction picture, the lowest $d^n\underline{L}_0$ configuration, where $\underline{L}_0$ denotes the hole at the valence-band maximum, hybridizes with the d^{n-1} and $d^{n+1}\underline{L}_0^2$ configurations. The energy difference between the lowest terms of $d^n\underline{L}_0$ and $d^{n+1}\underline{L}_0^2$ is given by δ_{eff}, which is defined by $\Delta_{\text{eff}} - W_V/2$. Here W_V is the width of the host valence band contributing to the hybridization term, and is fixed at 2 eV. This is because a tight-binding model calculation has shown that the upper 2 eV of the valence band contributes mainly to the hybridization term, although the total widths of the valence bands of ZnS and ZnSe are 4–5 eV.[5] The lowest term of d^{n-1} is larger by $U_{\text{eff}} - \delta_{\text{eff}}$ than that of $d^n\underline{L}_0$. The Bloch state at the valence-band maximum located at the Γ point hybridizes only with $3d$ orbitals with t_2 symmetry. The transfer integral $V_{0,t2}^{pd}$ is given by $\frac{1}{3}(pd\sigma) - \frac{2\sqrt{3}}{9}(pd\pi)$. Using the electronic-structure parameters Δ, U, $(pd\sigma)$, and $(pd\pi)$ obtained from the configuration-interaction calculation for the d-d optical-absorption and photoemission spectra, we can calculate $N\beta$'s for the $3d$ transition-metal impurities in the second order of perturbation on the hybridization term.[2,3,5]

III. RESULT AND DISCUSSION

The configurations which contribute to the p-d exchange interaction are summarized in Fig. 1, and the calculated $N\beta$'s are listed in Table I for the various transition-metal impurities. In Mn^{2+}, Fe^{2+}, and Co^{2+} impurities, where the t_2 orbitals are half-filled, only those ligand holes whose spins

are antiparallel to that of the transition-metal impurity can be transferred into the unoccupied t_2 orbitals. Configurations thus allowed are shown in Fig. 1(a). As a result, the p-d exchange is antiferromagnetic. The exchange constant $N\beta$ for the Mn^{2+}, Fe^{2+}, and Co^{2+} impurities is given by[2,3]

$$N\beta = -\frac{16}{S}\left(\frac{1}{-\delta_{\text{eff}} + U_{\text{eff}}} + \frac{1}{\delta_{\text{eff}}}\right)\left(\frac{1}{3}(pd\sigma) - \frac{2\sqrt{3}}{9}(pd\pi)\right)^2. \quad (5)$$

U_{eff} is $u + 4j$, $u + 3j$, and $u + 2j$, and the magnitude of the local spin S is $\frac{5}{2}$, 2, and $\frac{3}{2}$ for the Mn^{2+}, Fe^{2+}, and Co^{2+} impurities, respectively. The $N\beta$ values for $Cd_{1-x}Mn_xY$ (Y = S, Se, and Te) evaluated using the above parameters are -1.3, -1.1, and -0.9 [5], in good agreement with the experimental results -1.8, -1.11, and -0.88 for Y = S, Se, and Te, respectively.[1] The $N\beta$ values for the Mn^{2+}, Fe^{2+}, and Co^{2+} impurities in ZnSe are calculated to be -1.1, -1.3, and -2.3 eV, respectively, using the parameters listed in Table I. These values are also in agreement with the experimental values -1.31, -1.74, and -2.2 for Mn^{2+}, Fe^{2+}, and Co^{2+} impurities in ZnSe.[9]

Recently, it was reported that the exchange constant $N\beta$ for Cr^{2+} in ZnSe is positive, that is, the spin of the Cr^{2+} ion and that of the hole in the host valence band couple ferromagnetically.[7] In the Cr^{2+} impurity, a ligand hole whose spin is parallel as well as antiparallel can be transferred to the unoccupied t_2 orbitals. As a result, ferromagnetic and antiferromagnetic terms coexist in the p-d exchange interaction. Configurations which contribute to the p-d exchange in the Cr^{2+} impurity are shown in Fig. 1(b). The Cr^{2+} impurity, where the t_2 orbitals are partially occupied, undergoes a Jahn-Teller distortion, making the evaluation of $N\beta$ complicated. The exchange constant is sensitive to the populations of the unoccupied xy, yz, and zx orbitals in the t_2 subshell. Here we assumed that the populations of the CrY_4 tetrahedra compressed along the x, y, and z directions are equal, that is, the populations of the Cr sites with unoccupied xy, yz, and zx orbitals, respectively, are $\frac{1}{3}$.[10,11] It has also been assumed that the magnitude of the Jahn-Teller splitting is negligibly small compared with δ_{eff} to evaluate the exchange constant. $N\beta$'s for the Cr^{2+} impurities in ZnS and ZnSe thus calculated are -0.5 and $+0.8$ eV, respectively, as shown in Table I. Here it should be noted that the difference between the two hosts is derived from the difference in δ_{eff} and not from that in the Jahn-Teller distortion. The positive $N\beta$ value for the Cr^{2+} impurity in ZnSe is

TABLE I. Exchange constant $N\beta$ for $3d$ transition-metal impurities in ZnS and ZnSe (in eV). The values of u and δ_{eff} have been taken from Ref. 5. The Kanamori parameter j is fixed to the values of free ions.

	u	j	δ_{eff}	ZnS $N\beta$	expt.	δ_{eff}	ZnSe $N\beta$	expt.
Ti^{2+}	3.72	0.55	2.4	$+0.8$		1.9	$+1.0$	
V^{2+}	4.32	0.59	2.1	-3.1		1.6	-0.8	
Cr^{2+}	5.02	0.68	0.9	-0.5	$+0.6$ (Ref. 12)	0.4	$+0.8$	$+0.85$ (Ref. 7)
Mn^{2+}	5.58	0.71	4.2	-1.3		3.7	-1.1	-1.31 (Ref. 9)
Fe^{2+}	6.30	0.81	2.9	-1.5		2.4	-1.3	-1.74 (Ref. 9)
Co^{2+}	6.97	0.89	1.9	-2.2		1.4	-2.3	-2.2 (Ref. 9)
Ni^{2+}	7.58	0.94	0.7	-6.0		0.2	-20.0	

$Zn_{1-x}Co_xS$ (a)

t_2 e

δ_{eff} $-\delta_{eff} + u + 2j$

$N\beta = -16/S[1/3(pd\sigma) - 2\sqrt{3}/9(pd\pi)]^2[1/\delta_{eff} + 1/(-\delta_{eff} + u + 2j)]$

$Zn_{1-x}Fe_xS$

t_2 e

δ_{eff} $-\delta_{eff} + u + 3j$

$N\beta = -16/S[1/3(pd\sigma) - 2\sqrt{3}/9(pd\pi)]^2[1/\delta_{eff} + 1/(-\delta_{eff} + u + 3j)]$

$Zn_{1-x}Mn_xS$

t_2 e

δ_{eff} $-\delta_{eff} + u + 4j$

$N\beta = -16/S[1/3(pd\sigma) - 2\sqrt{3}/9(pd\pi)]^2[1/\delta_{eff} + 1/(-\delta_{eff} + u + 4j)]$

$Zn_{1-x}Cr_xS$ (b)

t_2 e

δ_{eff}

$\delta_{eff} + 4j$

$\delta_{eff} + 6j$ $-\delta_{eff} + u' - j$

$N\beta = 16/S[1/3(pd\sigma) - 2\sqrt{3}/9(pd\pi)]^2$
$\times 1/3[1/\delta_{eff} - 1/(\delta_{eff} + 4j)]$
$+ 16/S[1/3(pd\sigma) - 2\sqrt{3}/9(pd\pi)]^2$
$\times 2/3[-1/(\delta_{eff} + 6j) - 1/(-\delta_{eff} + u' - j)]$

$Zn_{1-x}Ti_xS$ (e)

t_2 e

δ_{eff} $\delta_{eff} + 2j$

$N\beta = 16/S[1/3(pd\sigma) - 2\sqrt{3}/9(pd\pi)]^2[1/\delta_{eff} - 1/(\delta_{eff} + 2j)]$

$Zn_{1-x}Ni_xS$ (c)

t_2 e

$-\delta_{eff} + u' - j$

$-\delta_{eff} + u' + j$

δ_{eff} $-\delta_{eff} + u' + 3j$

$N\beta = 16/S[1/3(pd\sigma) - 2\sqrt{3}/9(pd\pi)]^2$
$\times 1/3[1/(-\delta_{eff} + u' - j) - 1/(-\delta_{eff} + u' + j)]$
$+ 16/S[1/3(pd\sigma) - 2\sqrt{3}/9(pd\pi)]^2$
$\times 2/3[-1/\delta_{eff} - 1/(-\delta_{eff} + u' + 3j)]$

$Zn_{1-x}V_xS$ (d)

t_2 e

δ_{eff}

$\delta_{eff} + 3j$

$\delta_{eff} + 5j$ $-\delta_{eff} + u' - j$

$N\beta = 16/S[1/3(pd\sigma) - 2\sqrt{3}/9(pd\pi)]^2$
$\times 2/3[1/\delta_{eff} - 1/(\delta_{eff} + 3j)]$
$+ 16/S[1/3(pd\sigma) - 2\sqrt{3}/9(pd\pi)]^2$
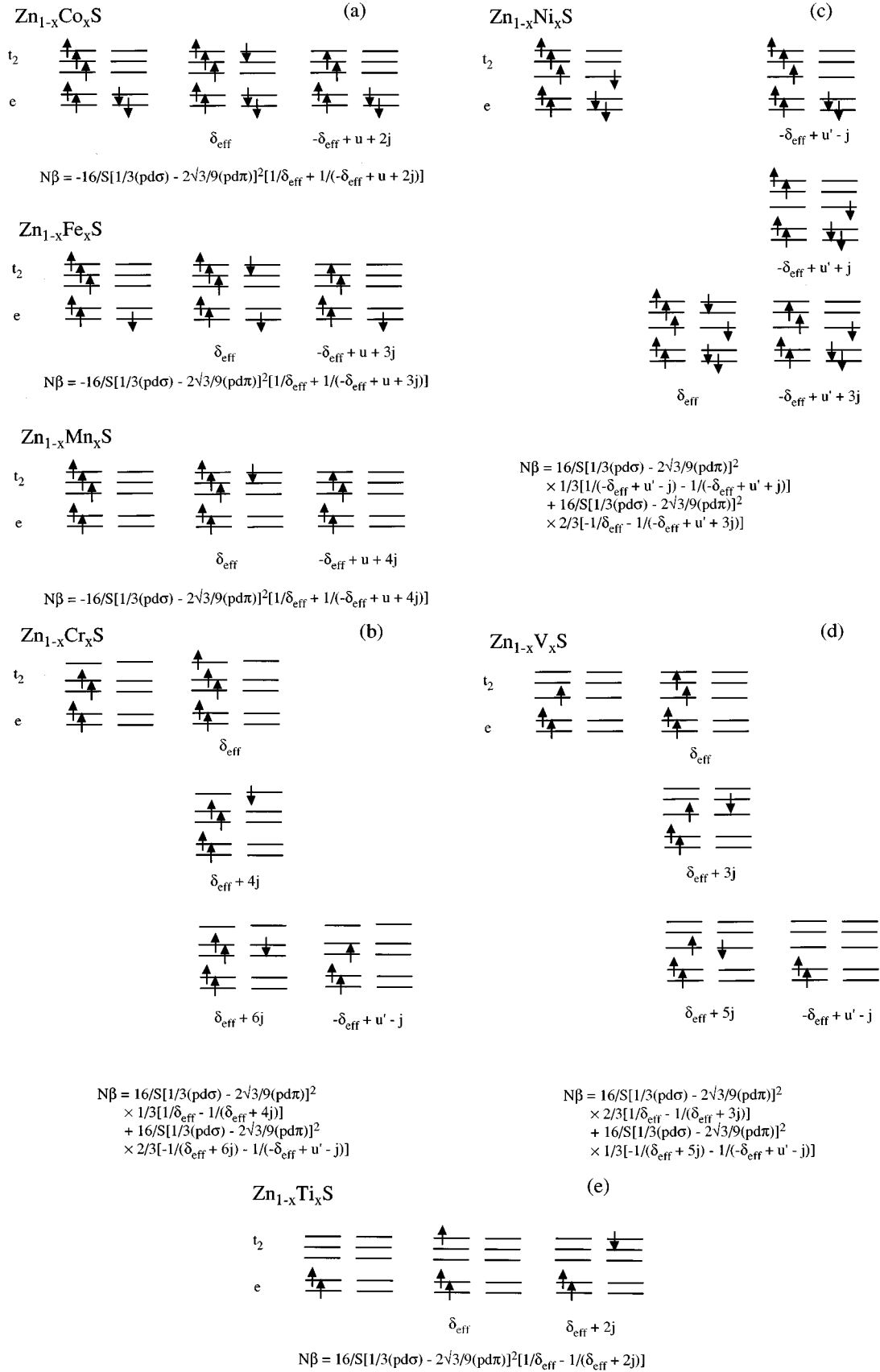$\times 1/3[-1/(\delta_{eff} + 5j) - 1/(-\delta_{eff} + u' - j)]$

FIG. 1. Configurations which contribute to the *p-d* exchange interaction in the second order of the hybridization term for (a) $Zn_{1-x}Co_xS$, $Zn_{1-x}Fe_xS$, and $Zn_{1-x}Mn_xS$, (b) $Zn_{1-x}Cr_xS$, (c) $Zn_{1-x}Ni_xS$, (d) $Zn_{1-x}V_xS$, and (e) $Zn_{1-x}Ti_xS$. The configurations for the ground state (d^n), affinity states (d^{n+1}), and ionization states (d^{n-1}) are shown on the left, middle, and right, respectively, below which the energy difference between the ground state and each affinity or ionization state is shown.

in good agreement with the experimental value $+0.85$.[7] $N\beta$ for the Cr^{2+} impurity in ZnS, however, becomes negative because δ_{eff} of Cr^{2+} in ZnS is large compared with that of Cr^{2+} in ZnSe, which disagrees with the experimental result.[12] Since the exchange constant is given by the difference between the ferromagnetic and antiferromagnetic contributions, and the ferromagnetic term is proportional to $1/\delta_{eff}$, the sign of $N\beta$ is sensitive to δ_{eff}. $N\beta$ of Cr^{2+} in ZnS becomes positive if we reduce δ_{eff} by 0.3 eV. The sign of the exchange constant is also sensitive to the populations of the xy, yz, and zx orbitals. If all the CrY_4 tetrahedra are compressed along the z direction, that is, if the xy orbital is unoccupied at all the Cr sites, $N\beta$ of Cr^{2+} in ZnS is estimated to be $+2.46$ eV.

V^{2+} and Ni^{2+} impurities, where the t_2 orbitals are partially filled, should also be accompanied by the Jahn-Teller distortion. Under the same assumption that the populations of the tetrahedra elongated along the x, y, and z directions are equal, the p-d exchange constants are expressed as shown in Figs. 1(c) and 1(d). The V^{2+} impurity is expected to show the same behavior as the Cr^{2+} impurity because the t_2 subshell is less than half filled. However, $N\beta$ for V^{2+} thus calculated is negative, as listed in Table I. This is because δ_{eff} of V^{2+} is much larger than that of Cr^{2+} in ZnSe.

For Ti^{2+}, where the t_2 orbitals are empty, ligand holes can be transferred into the t_2 orbitals irrespective of their spin direction. As shown in Fig. 1(e), the configuration obtained by the transfer of the ligand hole whose spin is parallel to the Ti^{2+} spin is stabilized by the intra-atomic exchange interaction j. Therefore the p-d exchange constant for Ti^{2+} becomes positive, as listed in Table I. It is very interesting to check the prediction for the p-d exchange constant, especially for the positive value of Ti^{2+}.

IV. CONCLUSION

In conclusion, we have evaluated the p-d exchange constant $N\beta$ in the II-VI diluted magnetic semiconductors with the various $3d$ transition-metal impurities ranging from Ti^{2+} to Ni^{2+}. For Mn^{2+}, Fe^{2+}, and Co^{2+}, $N\beta$'s are negative and are in good agreement with the experimental values. The exchange constant for $Zn_{1-x}Cr_xSe$ is calculated to be positive reproducing the experimental result. For Ti^{2+}, Hund's coupling plays an important role, and the exchange constant is also predicted to be positive.

[1] J. K. Furdyna, J. Appl. Phys. **64**, R29 (1988), and references therein.
[2] B. E. Larsson, K. C. Hass, H. Ehrenreich, and A. E. Carlsson, Phys. Rev. B **37**, 4137 (1988).
[3] K. C. Hass, in *Semimagnetic Semiconductors and Diluted Magnetic Semiconductors*, edited by M. Averous and M. Balkanski (Plenum, New York, 1991), p. 59.
[4] J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966).
[5] T. Mizokawa and A. Fujimori, Phys. Rev. B **48**, 14 150 (1993).
[6] A. K. Bhattacharjee, Phys. Rev. B **46**, 5266 (1992).
[7] W. Mac, Nguyen The Khoi, A. Twardowski, J. A. Gaj, and M. Demianiuk, Phys. Rev. Lett. **71**, 2327 (1993).
[8] J. Kanamori, Prog. Theor. Phys. **30**, 275 (1963).
[9] A. Twardowski, H. J. M. Swagten, and W. J. M. de Jonge, in *II-VI Semiconductor Compounds*, edited by M. Jain (World Scientific, Singapore, 1993), p. 227, and references therein.
[10] W. Mac, A. Twardowski, P. J. T. Eggenkamp, H. J. M. Swagten, Y. Shapira, and M. Demianiuk, Phys. Rev. B **50**, 14 144 (1994).
[11] A. K. Bhattacharjee, Phys. Rev. B **49**, 13 987 (1994).
[12] W. Mac, A. Twardowski, and M. Demianiuk, Phys. Rev. B **54**, 5528 (1996).