PHYSICAL REVIEW B **77**, 085208 (2008)

Hole states in wide band-gap diluted magnetic semiconductors and oxides

Tomasz Dietl

Institute of Physics, Polish Academy of Science and ERATO Semiconductor Spintronics Project, Japan Science and Technology Agency, al. Lotników 32/46, PL-02-668 Warszawa, Poland and Institute of Theoretical Physics, University of Warsaw, PL-00-681 Warszawa, Poland

(Received 2 December 2007; published 25 February 2008)

Puzzling disagreement between photoemission and optical findings in magnetically doped GaN and ZnO is explained within a generalized alloy theory. The strong coupling between valence-band holes and localized spins gives rise to a midgap Zhang–Rice-like state, to a sign reversal of the apparent *p*-*d* exchange integral, and to an increase of the band gap with the magnetic ion concentration.

DOI: 10.1103/PhysRevB.77.085208 PACS number(s): 75.50.Pp, 75.20.Hr, 75.30.Et, 78.20.Ls

I. INTRODUCTION

Recent progress[1,2] in the understanding of carrier-controlled ferromagnetic semiconductors such as $Ga_{1-x}Mn_xAs$ and *p*-type $Cd_{1-x}Mn_xTe$ relies to a large extend on comprehensive magnetooptical, photoemission, and x-ray absorption (XAS) studies, which provide mutually consistent information on the exchange couplings between the band states and the localized spins as well as on the positions of the *d* bands with respect to the band edges. However, it becomes more and more apparent that this clear cut picture breaks down entirely in the case of nitride diluted magnetic semiconductors (DMSs) and diluted magnetic oxides. Here, according to photoemission[3,4] and XAS[5] works, the relevant Mn^{2+}/Mn^{3+} (d^5/d^4) level resides in the valence band in both GaN (Ref. 4) and ZnO (Refs. 3 and 5), similar to the case of arsenides, tellurides, and selenides. Furthermore, the evaluated magnitude of the *p*-*d* exchange energy βN_0 shows the expected enhancement (due to a stronger *p*-*d* hybridization[6] in nitrides and oxides) to the values of -1.6 eV in $Ga_{1-x}Mn_xN$ (Ref. 4) and to -2.7 eV (Ref. 3) or -3 eV (Ref. 5) in $Zn_{1-x}Mn_xO$, significantly over the value of -1 eV, typical for other DMS.[3–5] By contrast, optical studies seem to reveal the presence of a Mn^{2+}/Mn^{3+} level in the band gap of both GaN (Refs. 7 and 8) and ZnO.[9] Moreover, the determined values of βN_0 show either opposite sign and/or much reduced amplitude comparing to those stemming from photoemission and XAS as well as expected from the chemical trends. For instance, a detailed examination of the giant spin splitting of free excitons in $Ga_{1-x}Mn_xN$ leads to $\beta N_0 = +1.4 \pm 0.3$ eV.[10] Similarly, the study of bound excitons in $Zn_{1-x}Mn_xO$ implies $|\beta N_0| \approx 0.1$ eV.[11] The contradiction in question is not limited to Mn-based nitrides and oxides—it is also evident for $Zn_{1-x}Co_xO$, where $\beta N_0 = -3.4$ eV according to XAS and in agreement with the chemical trends,[6] while the investigation of the free exciton splitting results in $\beta N_0 \approx -0.6$ or 1 eV, depending on the assumed ordering of the valence band subbands.[12]

Here, we present arguments indicating that nitrides and oxides belong to an original and unexplored class of DMS, in which the conditions for the strong coupling between the band hole and the localized spins are met. We then calculate the spectral density $A(\omega)$ of the band-edge states and show that in the strong coupling limit $A(\omega)$ exhibits two maxima corresponding to the bonding and antibonding states, respectively. Our model makes it possible to explain the reversed sign and the reduced magnitude of the apparent βN_0, as determined by the free exciton splitting, as well as the dependence of the energy gap on the magnetic ion concentration x. In this way, we reconcile the results of photoemission, XAS, optical, and magneto-optical studies and show their consistency with the chemical trends. Furthermore, our findings provide a new piece of evidence for the inverse order of the valence subbands in ZnO as well as reconfirm that the local spin density approximation (LSDA) results in too high energetic positions of the localized *d* states.

Actually, the theory presented here has stimulated experimental studies of exciton splittings in (Ga,Fe)N.[13] The advantage of (Ga,Fe)N in the present context stems form the fact that unlike Mn, Fe in GaN is an isoelectronic impurity with the simple d^5 configuration,[14,15] allowing a straightforward interpretation of the data. Furthermore, since in GaN, in contrast to ZnO, the actual ordering of valence subbands is settled, the sign of the apparent exchange energy $N_0\beta^{(app)}$ can be unambiguously determined from polarization-resolved magnetooptical spectra. The determination of $N_0\beta^{(app)} = +0.5 \pm 0.2$ eV for (Ga,Fe)N,[13] provides a strong experimental support for the theory put forward in the present paper.

II. THEORETICAL MODEL

The description of exciton splittings in the works referred to above[10–12] has been carried out within the time-honored virtual-crystal approximation (VCA) and molecular-field approximation (MFA), according to which the interaction of carriers and localized spins leads to a bands' splitting proportional to the relevant bare exchange integral and magnetization of the subsystem of magnetic ions. While this approach describes very well the giant exciton splittings in tellurides,[16] it has already been called into question in the case of $Cd_{1-x}Mn_xS$.[17] In this system, unexpected dependencies of the band gap and of the apparent exchange integral $\beta^{(app)}$ on x have been explained by circumventing VCA and MFA either employing a nonperturbative Wigner–Seitz-type model[17] or generalizing the alloy theory to DMS.[18] It has been found that the physics of the problem is governed by the ratio of a characteristic magnitude of the total magnetic impurity potential U to its critical value $U_c < 0$ at which a bound state starts to form. In particular, the weak coupling regime, where VCA and MFA apply, corresponds to $U/U_c \ll 1$. By modeling the total potential of the isoelectronic magnetic impurity with a square well of radius b, one obtains[17,18]

$$U/U_c = 6m^*[W-(S+1)\beta/2]/(\pi^3\hbar^2 b), \tag{1}$$

where the bare valence band offset $WN_0 = dE_v(x)/dx$, S is the impurity spin, and m^* is the effective mass of a particle with the spin $s=1/2$ assumed to reside in a simple parabolic band.

In order to evaluate U/U_c for specific materials, we adopt $\beta = -0.057$ eV nm^3, i.e., $\beta N_0 \sim a_0^{-3}$, as implied by the chemical trends.[6,19] The value of b lies presumably between the anion-cation and cation-cation distances, $\sqrt{3}a_0/4 \lesssim b \lesssim a_0/\sqrt{2}$. Hence, for Cd$_{1-x}Mn_x$Te, where $S=5/2$, $m^*/m_0 = 0.65$, and $WN_0 = -0.63$ eV (Ref. 20), we obtain $0.20 \lesssim U/U_c \lesssim 0.33$, in agreement with the notion that VCA and MFA can be applied to this system. In the case of Cd$_{1-x}$Mn$_x$S, where $m^*/m_0 = 1.0$ and $WN_0 = 0.5$ eV,[17] the coupling strength increases to $0.77 \lesssim U/U_c \lesssim 1.25$. Hence, in agreement with experimental findings, Cd$_{1-x}$Mn$_x$S represents a marginal case, in which the local spin dependent potential introduced by the magnetic ion is too weak to bind the hole, but too strong to be described by VCA and MFA.[17,18]

We argue here that even greater magnitudes of U/U_c can be expected for nitrides and oxides, as a_0 is smaller, while both m^* and W tend to be larger comparing to compounds of heavier anions. We assume $m^* = 1.3m_0$, a value expected for GaN,[21] and recall that the valence band ordering is controversial in ZnO.[22] In order to estimate W, we note that if the valence band offset is entirely determined by the p-d hybridization, W and β are related.[17] In the case of Ga$_{1-x}$Mn$_x$N, for which the Hubbard energy for the d electrons $U^{(\mathrm{eff})} = 10.4$ eV and the position of the d state with respect to the top of the valence band, $\epsilon_d^{(\mathrm{eff})} = -5.7$ eV (determined so far with an accuracy of about 1 eV),[4] we obtain $0.96 \lesssim U/U_c \lesssim 1.6$. Similarly, for Zn$_{1-x}Mn_x$O, where $U^{(\mathrm{eff})} = 9.2$ eV and $\epsilon_d^{(\mathrm{eff})} = -1.5$ eV,[5] we find $2.0 \lesssim U/U_c \lesssim 3.3$. Interestingly, the above evaluation of U/U_c remains approximately valid for other transition metal impurities, such as Fe and Co, since as long as the number of electrons in the d states of t_2 symmetry remains unchanged, the p-d hybridization energy and, hence, βS does not depend on S.[6] Although the quoted values of U/U_c are subject of uncertainty stemming from the limited accuracy of the input parameters as well as from the approximate treatment of the hole band structure, we are in the position to conclude that magnetically doped nitrides and oxides are in the strong coupling regime, $U/U_c > 1$.

We evaluate the effect of magnetic ions on a single band-edge particle ($k=0$) with the spin $s=1/2$ within a generalized alloy theory developed by Tworzydlo.[18] The theory is built for noninteracting, randomly distributed, and fluctuating quantum spins $\boldsymbol{S}$ characterized by the field-induced averaged polarization $\langle S_z(T,H)\rangle$ and neglecting the direct effect of the magnetic field H on the band states. The potential of the individual impurities is modeled[17] by the square-well potential containing both spin-dependent (exchange) and spin-independent (chemical shift) central-cell contributions, so that the theory can be applied to both magnetic and nonmagnetic alloys. The band-edge particle self-energy $\Sigma_{s_z}(\omega)$ is derived from the Matsubara formalism by summing up an infinite series of diagrams for the irreducible self-energy in the average t-matrix approximation.[18] As a result of thermal and quantum fluctuations, $\Sigma_{s_z}(\omega)$ contains weighted contributions corresponding to two spin orientations, $\Sigma_0(S)$ and $\Sigma_0(-S-1)$, according to

$$\Sigma_{s_z}(\omega) = [(S+1+2s_z\langle S_z\rangle)\Sigma_0(S) + (S-2s_z\langle S_z\rangle)\Sigma_0(-S-1)]/(2S+1). \tag{2}$$

The zero-temperature self-energy $\Sigma_0(J)$ can be written in the form

$$\Sigma_0(J) = xN_0(vU - 16i\pi m^* UU' I\kappa' b^5/\hbar^2), \tag{3}$$

where $v = 4\pi b^3/3$, $U = U(J)$ is the potential depth for one spin orientation, $J = -S-1$, and the barrier height for the other, $J = S$, according to

$$U = -(W + J\beta/2)/v. \tag{4}$$

Similarly, $U' = U'(J)$ is the value of U corrected by the energy shift E_{vc} calculated within the VCA and MFA,

$$U' = U - E_{vc}/(vN_0), \tag{5}$$

with

$$E_{vc} = -xN_0(s_z\langle S_z\rangle\beta + W). \tag{6}$$

The magnitudes of U and $\tilde{E} = E_{vc} + \omega + i\gamma$, where γ is the intrinsic lifetime broadening taken as $\gamma = 3$ meV, determine also the dimensionless wave vectors κ and κ',

$$\kappa = b(2m^*\tilde{E}/\hbar^2)^{1/2} \tag{7}$$

$$\kappa' = b[2m^*(\tilde{E}-U)/\hbar^2]^{1/2}, \tag{8}$$

which enter to $\Sigma_0(J)$ directly and through the auxiliary variable I,

$$\begin{aligned} I = \frac{1}{12\kappa'^6}(&3(1+\Delta) + 3\kappa'^2(1+\Delta) + 2i\kappa'^3 \\ &+ 3[(i+\kappa')^2 + \Delta(\kappa'^2-1)]\cos(2\kappa') \\ &+ 3i\{\kappa'[2i(1+\Delta)+\kappa'] - 1\}\sin(2\kappa')), \end{aligned} \tag{9}$$

where

$$\Delta = i(\kappa-\kappa')\exp(i\kappa')/(\kappa\sin\kappa' + i\kappa'\cos\kappa'). \tag{10}$$

The quantity of interest is the spectral density of states,

$$A_{s_z}(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\,\frac{1}{\omega + i\gamma - \Sigma_{s_z}(\omega)}, \tag{11}$$

whose maxima provide the position of the band edge $\tilde{E}_0$ in the presence of spin and chemical disorder as a function of $\langle S_z(T,H)\rangle$. Most of the relevant experiments for magnetically doped nitrides and oxides has been carried out at low concentrations $x \lesssim 3\%$, where the effects of the interactions

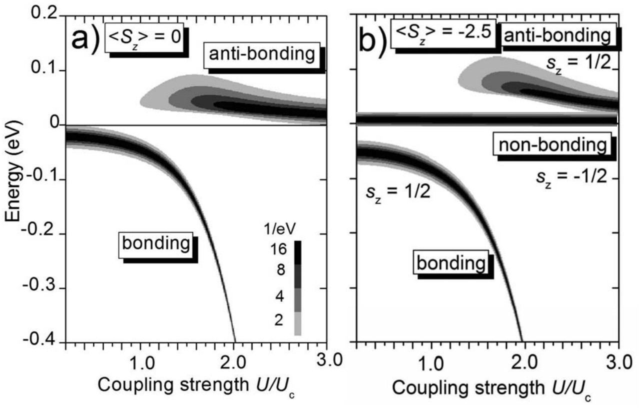

FIG. 1. Energy distribution (gray scale) of the spectral density of states $A_{s_z}(\omega)$ at the band edge ($k=0$) as a function of the coupling strength U/U_c between the spin 1/2 particle and the system of unpolarized (a) and spin-polarized (b) randomly distributed magnetic impurities. The magnitude of U/U_c is changed by the range of the impurities' potential b. The remaining material parameters are taken as $S=5/2$, $x=1\%$, $m^*=1.3m_0$, $W=0.05$ eV nm^3, and $\beta=-0.057$ eV nm^3.

among localized spins, neglected in the present approach, are not yet important. In this case, $\langle S_z(T,H)\rangle$ can be determined from magnetization measurements or from the partition function of the spin Hamiltonian for the relevant magnetic ion. For higher x, it is tempting to take into account the effects of the short-range antiferromagnetic superexchange according to the standard recipe,[16,19] i.e., via replacement of x by x_{eff} and T by $T+T_{\text{AF}}$, where $T_{\text{AF}}(x,T)>0$ and $x_{\text{eff}}(x,T)<x$. However, in the strong coupling case, this procedure is rather inaccurate as aniferromagnetically aligned pairs contribute also to the band-edge shift.

III. RESULTS AND COMPARISON TO EXPERIMENTAL FINDINGS

We now present expectations of the theory exposed in the previous section as well as discuss its relevance *vis-à-vis* experimental results. Figure 1(a) shows a gray scale plot of the spectral density $A_{s_z}(\omega)$ as a function of the coupling strength in the absence of spin polarization, $\langle S_z\rangle=0$, so that the spin degeneracy is conserved, $A_{1/2}(\omega)=A_{-1/2}(\omega)$. In the weak coupling limit, $U/U_c \ll 1$, the band-edge position $\tilde{E}_0$ is obviously given by $-xN_0W$. For higher U/U_c, a downward shift of $\tilde{E}_0$ is visible, particularly rapid for $U/U_c>1$, when the magnetic ion potential is strong enough to bind a hole, even if the magnetic ion is an isoelectronic impurity. Such an effect has also been revealed within the dynamic mean-field theory[23] and, recently, by a numerical diagonalization of the alloy problem.[24] The small magnetic polaron formed in this way, reminiscent of the Zhang–Rice singlet, will be built also of k states away from the Brillouin zone center, as discussed previously.[25] In the case when magnetic impurities act as dopants, the case of Mn in III-V compounds, the effects discussed here enhance the corresponding binding energy.

The presence of the band-gap hole traps introduced by the magnetic ions will lead to strong hole localization in p-type samples. In the n-type case, in turn, these charge transfer states should be visible in photoionization experiments. Indeed, if there is no hole on a magnetic impurity, a photon can transfer an electrons from surrounding bonds to the conduction band leaving a trapped hole behind, $d^n \to d^n+h+e$. The corresponding subgap absorption was indeed observed in both n-Ga$_{1-x}$Mn$_x$N (Refs. 7 and 8) and Zn$_{1-x}$Mn$_x$O (Ref. 9) but assigned in those works to $d^5 \to d^4+e$ transitions. We propose here that the corresponding photoionization processes are $d^5 \to d^5+h+e$. Furthermore, in Ga$_{1-x}$Mn$_x$N samples, in which the net concentration of compensating donors was sufficiently small, intracenter excitations Mn→Mn* were detected at 1.4 eV,[26] and analyzed in considerable details.[8,27,28] While symmetry considerations cannot discriminate between the d^5+h and d^4 many-electron configurations of the Mn ions, the larger crystal-field splitting and the smaller Huang–Rhys factor in Ga$_{1-x}$Mn$_x$N, compared to their values in (II,Cr)VI compounds,[27,28] point to a relatively large localization radius, as expected for the d^5+h configuration[25] advocated here. This interpretation reconfirms also the limited accuracy of *ab initio* computations within LSDA in the case of transition metal impurities, which place the d^5/d^4 Mn level within the band gap of GaN.[29]

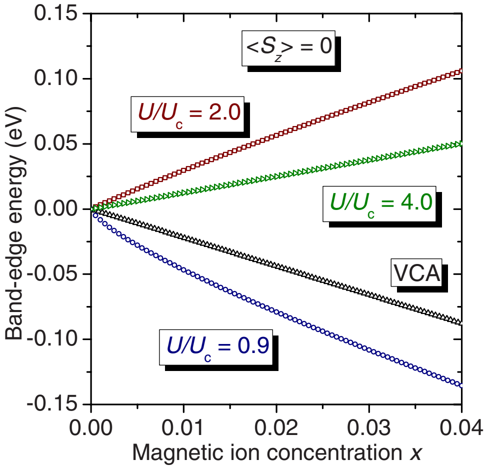

FIG. 2. (Color online) Dependence of band-edge energy $\tilde{E}_0$ on the concentration of magnetic impurities x for three values of the coupling strength U/U_c in comparison to the expectations within VCA and MFA (denoted as VCA) for material parameters of Fig. 1.

As seen in Fig. 1(a), when U/U_c increases beyond 1, the spectral density is gradually transferred from the bonding state discussed above to an antibonding state appearing above the bandedge energy E_0 expected within VCA. We identify this state with the actual valence band edge for $U/U_c>1$, whose position $\tilde{E}_0$ determines, e.g, the onset of interband optical transitions and the free exciton energy. In Fig. 2, we plot $\tilde{E}_0(x)$ for $U/U_c<1$ and $U/U_c>1$ in comparison to the VCA and MFA expectations. We see that if $U/U_c<1$, the correction to VCA and MFA leads to a reduction of the band gap with x, as observed in Cd$_{1-x}$Mn$_x$S (Ref. 18) and Zn$_{1-x}$Mn$_x$Se.[30] In contrast, for $U/U_c>1$ our model predicts an increase of the gap with x, in accord with the data for Ga$_{1-x}$Mn$_x$N,[28] Zn$_{1-x}$Mn$_x$O,[31] and Zn$_{1-x}$Co$_x$O.[12]

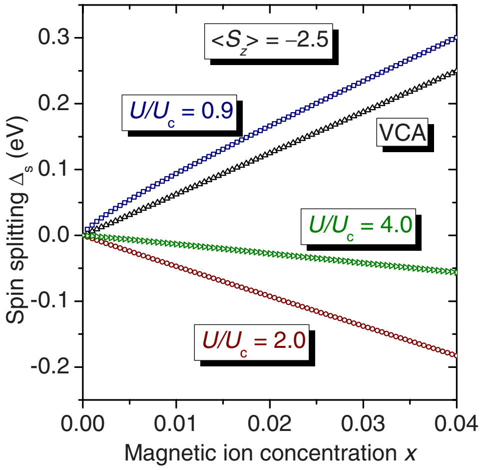

FIG. 3. (Color online) Dependence of spin splitting Δ_s on the concentration of magnetic impurities x for three values of the coupling strength in comparison with the values expected within VCA and MFA (denoted as VCA) for material parameters of Fig. 1.

As shown in Fig. 1(b), in the presence of the magnetic field, such that $\langle S_z(T,H)\rangle = -2.5$, a considerable reorganization of the level positions takes place. The spin polarization of the magnetic ions generates a downward and upward shift of the bonding and antibonding states (both corresponding to $s_z = 1/2$) and leads to the appearance of a nonbonding state ($s_z = -1/2$), whose energy is virtually independent of U/U_c. Remarkably, the latter resides below the antibonding level, which means that the effect of the p-d exchange on the extended states changes from antiferromagnetic for $U/U_c < 1$ to ferromagnetic for $U/U_c > 1$. Interestingly, this sign reversal of spin splitting of extended states, appearing when the coupling strength is large enough to produce bound states, can also be inferred from Fig. 1 of Ref. 24, where the alloy Hamiltonian was diagonalized numerically.

Extensive studies of the giant free excitons' splitting Δ_s in $Ga_{1-x}Mn_xN$,[10] $Zn_{1-x}Co_xO$,[12] and $Ga_{1-x}Fe_xN$ (Ref. 13) demonstrated a linear dependence of Δ_s on x and $\langle S_z(T,H)\rangle$, as expected within VCA and MFA. Figures 3 and 4 demonstrate that an approximately linear dependence of Δ_s on x and $\langle S_z(T,H)\rangle$ is predicted within the present theory, too, except for an anticrossing behavior occurring when the nonbonding state is in a resonance with the non-normalized band edge, $E_0 = 0$. Accordingly, for the sake of comparison to the experimental determinations, Δ_s can be characterized by an apparent p-d exchange integral according to $\Delta_s = -xN_0\beta^{(\mathrm{app})}\langle S_z(T,H)\rangle$. In Fig. 5, we depict the expected evolution of $\beta^{(\mathrm{app})}/\beta$ with U/U_c for several values of W and m^*. We see that in the strong coupling regime, $U/U_c > 1$, our theory implies the sign reversal of $\beta^{(\mathrm{app})}$ and its reduced amplitude in comparison to the β values determined from photoemission and XAS experiments.

The ferromagnetic sign and the reduce magnitude of the p-d exchange integral $\beta^{(\mathrm{app})}$ were observed in (Ga,Fe)N.[13] Similar findings were reported for (Ga,Mn)N,[10] though a direct comparison to our theory is hampered by the presence of holes on Mn ions, which may contribute to the apparent exchange interactions between the carriers and localized spins.[32] Significantly reduced magnitudes of $|\beta^{(\mathrm{app})}|$ were also found in (Zn,Co)O and (Zn,Mn)O.[11,12] The sign of $\beta^{(\mathrm{app})}$ depends on the assumed valence subband ordering. The positive sign of $\beta^{(\mathrm{app})}$, as implied by our theory, points to the inverted subband ordering in ZnO, in agreement with the *ab initio* studies of the spin-orbit splitting in ZnO.[22]

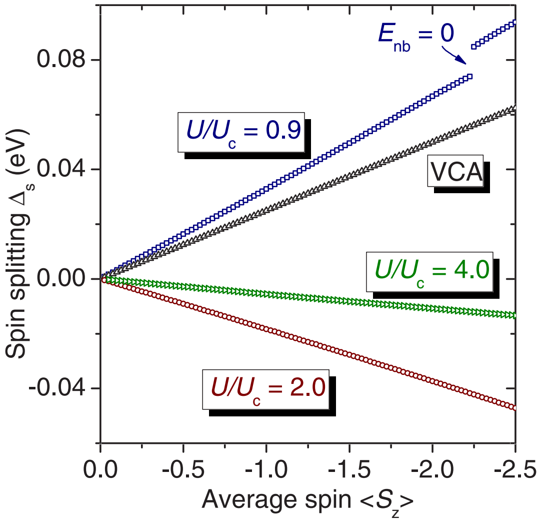

FIG. 4. (Color online) Dependence of the band-edge spin splitting on the spin polarization of magnetic impurities, $\Delta_s(\langle S_z\rangle)$ for three values of the coupling strength in comparison with the values expected within VCA and MFA, and $\Delta_s^{VCA}(\langle S_z\rangle)$ for material parameters of Fig. 1.

Finally, we also note that the ferromagnetic character of $\beta^{(\mathrm{app})}$ was reported for (Ga,Mn)As in both impurity[33] and metallic limit.[34] While the results in the metallic range are readily explained by the Moss–Burstein shift,[34] the present theory elucidates how the presence of bound states, produced here partly by the Mn Coulomb potential, results in the ferromagnetic sign of $\beta^{(\mathrm{app})}$ for the extended valence-band states, though exchange interactions between band carriers

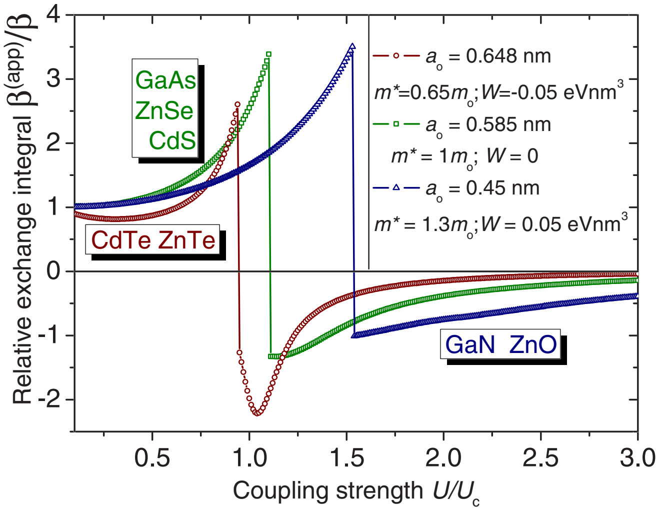

FIG. 5. (Color online) Normalized apparent p-d exchange integral defined as $\Delta_s(-2.5)/\Delta_s^{VCA}(-2.5)$ for various combinations of the materials parameters.

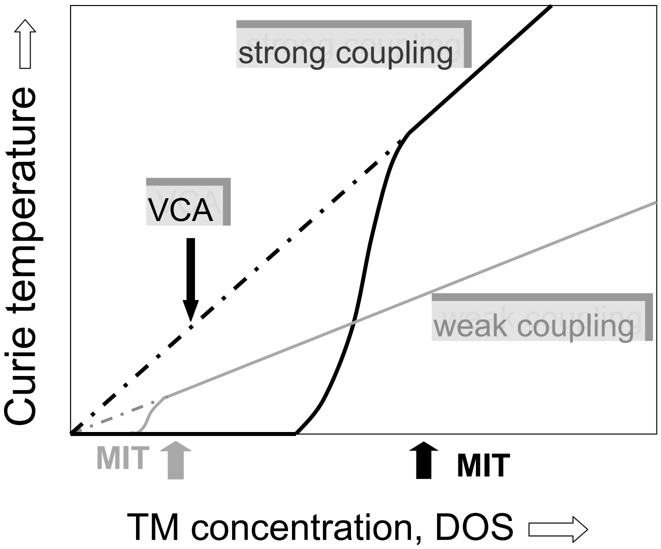

FIG. 6. Schematic dependence of the Curie temperature T_C on the concentration of magnetic impurities and density of hole states at the Fermi level for a weak and a strong coupling. Higher values of T_C are predicted within VCA and MFA for the strong coupling. However, the region, where the holes are localized and do not mediate the spin-spin interaction is wider in the strong coupling case.

and the localized hole[32] have to be considered in a quantitative description of the data.

IV. CONCLUSIONS AND OUTLOOK

In summary, our findings make it possible to trace changes in electronic states on going from the weak to the strong coupling regime. Similar to other cases in which bound states appear, such as the Kondo effect or superconductivity, the system properties cannot be described by perturbation theory.

In view of the results presented above, DMS in the strong coupling regime form an outstanding class of materials, in which a number of concepts developed earlier for these compounds has to be revised. In particular, a simple relation between *sp*-*d* exchange integrals and splitting of extended states breaks down qualitatively in this regime. The approach put forward here allows one to reconcile the findings of photoemission, XAS, optical, and magneto-optical measurements carried out for magnetically doped nitrides and oxides. Furthermore, our results help to settle the issue of valence subband ordering in ZnO.

Our results, in line with photoemission findings, imply that *d* levels of transition metal impurities reside at about 2 eV lower than implied by DFT computations within LSDA. This issue is now being considered by many groups, and various computation schemes are proposed to improve the reliability of first principles methods in the case of DMS.[35]

The formalism presented in this paper may serve also for describing nonmagnetic diluted alloys such as $GaAs_{1-x}N_x$, where isoelectronic N impurities form bound states, particularly under hydrostatic pressure. The relevant experimental results for such systems are often analyzed in terms of the so-called band anticrossing model.[36] It is assumed within this model that the impurities introduce a resonant level and that the coupling strength of this level to the relevant band is proportional to x. The resulting band diagram is then similar to that of Fig. 1(a). Thus, our theory of the carrier coupling to the system of randomly distributed isoelectronic impurities provides a microscopic explanation how the anticrossing behavior and related properties emerge.

The findings presented here shed also some light on the question[37] concerning the influence of the strong coupling effects on the carrier-mediated ferromagnetism in DMS. It is obvious that the enhanced hole binding energy will shift the metal-insulator transition (MIT) to higher hole concentrations. As sketched in Fig. 6, this will result in a corresponding displacement of the onset of ferromagnetism, in accord with the notion that delocalized or weakly localized holes are necessary for the existence of efficient spin-spin interactions between diluted spins.[38,39] A twofold smaller value of the Curie temperature T_C in $Ga_{0.94}Mn_{0.06}P$ in comparison to $Ga_{0.94}Mn_{0.06}As$,[40] and T_C as low as 8 K in $Ga_{0.94}Mn_{0.06}N$,[41] reflects an increase of hole localization on going from arsenides to phosphides and nitrides.

Another interesting question, relevant also to (Ga,Mn)As,[42] concerns the nature of hole states on the metallic side of the MIT. We supplement the previous detail discussion[42] of this issue by one comment: The appearance of a metallic phase means that screening of impurity potentials by the carrier liquid has washed out bound states. We claim, therefore, that the anticrossing behavior of Fig. 1 will disappear in the metallic regime. Accordingly, VCA and MFA can serve for the description of the ferromagnetic phase, as sketched in Fig. 6. At the same time, many body interactions will shift the band rigidly down in energy, according to theory of band-gap narrowing. The above considerations mean that the high-temperature ferromagnetism can appear in oxides and nitrides containing a few percent of randomly distributed magnetic ions, provided that the hole density would be sufficiently high to reach the MIT.

ACKNOWLEDGMENTS

This work was supported in part by the EC project NANOSPIN (FP6-2002-IST-015728). I would like to thank A. Bonanni, F. Matsukura, H. Ohno, and W. Pacuski for valuable discussions.

[1] T. Dietl and H. Ohno, Mater. Today **9**, 18 (2006).

[2] T. Jungwirth, J. Sinova, J. Mašek, J. Kucera, and A. H. MacDonald, Rev. Mod. Phys. **78**, 809 (2006).

[3] T. Mizokawa, T. Nambu, A. Fujimori, T. Fukumura, and M. Kawasaki, Phys. Rev. B **65**, 085209 (2002).

[4] J. I. Hwang, Y. Ishida, M. Kobayashi, H. Hirata, K. Takubo, T. Mizokawa, A. Fujimori, J. Okamoto, K. Mamiya, Y. Saito *et al.*, Phys. Rev. B **72**, 085216 (2005).

[5] J. Okabayashi, K. Ono, M. Mizuguchi, M. Oshima, S. S. Gupta, D. D. Sarma, T. Mizokawa, A. Fujimori, M. Yuri, C. T. Chen *et al.*, J. Appl. Phys. **95**, 3573 (2004).

[6] J. Blinowski, P. Kacman, and T. Dietl, *Spintronics*, MRS Symposia Proceedings No. 690 (Materials Research Society, Pittsburgh, 2002), p. F6.

[7] T. Graf, S. T. B. Goennenwein, and M. S. Brandt, Phys. Status Solidi B **239**, 277 (2003).

[8] A. Wolos, M. Palczewska, M. Zajac, J. Gosk, M. Kaminska, A. Twardowski, M. Bockowski, I. Grzegory, and S. Porowski, Phys. Rev. B **69**, 115210 (2004).

[9] K. R. Kittilstved, W. K. Liu, and D. R. Gamelin, Nat. Mater. **5**, 291 (2006).

[10] W. Pacuski, D. Ferrand, J. Cibert, J. A. Gaj, A. Golnik, P. Kossacki, S. Marcet, E. Sarigiannidou, and H. Mariette, Phys. Rev. B **76**, 165304 (2007).

[11] E. Przeździecka, E. Kamińska, M. Kiecana, M. Sawicki, Ł. Kłopotowski, W. Pacuski, and J. Kossut, Solid State Commun. **139**, 541 (2006).

[12] W. Pacuski, D. Ferrand, J. Cibert, C. Deparis, J. A. Gaj, P. Kossacki, and C. Morhain, Phys. Rev. B **73**, 035214 (2006).

[13] W. Pacuski, P. Kossacki, D. Ferrand, A. Golnik, J. Cibert, M. Wegscheider, A. Navarro-Quezada, A. Bonanni, M. Kiecana, M. Sawicki, and T. Dietl, Phys. Rev. Lett. **100**, 037204 (2008).

[14] A. Bonanni, M. Kiecana, C. Simbrunner, T. Li, M. Sawicki, M. Wegscheider, M. Quast, H. Przybylinska, A. Navarro-Quezada, R. Jakiela, A. Wolos, W. Jantsch, and T. Dietl, Phys. Rev. B **75**, 125210 (2007).

[15] E. Malguth, A. Hoffmann, W. Gehlhoff, O. Gelhausen, M. R. Phillips, and X. Xu, Phys. Rev. B **74**, 165202 (2006), and references cited therein.

[16] J. A. Gaj, R. Planel, and G. Fishman, Solid State Commun. **29**, 435 (1979).

[17] C. Benoit à la Guillaume, D. Scalbert, and T. Dietl, Phys. Rev. B **46**, 9853(R) (1992).

[18] J. Tworzydlo, Phys. Rev. B **50**, 14591 (1994); Solid State Commun. **94**, 821 (1995); Acta Phys. Pol. A **88**, 655 (1995).

[19] T. Dietl, H. Ohno, and F. Matsukura, Phys. Rev. B **63**, 195205 (2001).

[20] T. Wojtowicz, M. Kutrowski, M. Surma, K. Kopalko, G. Karczewski, J. Kossut, M. Godlewski, P. Kossacki, and Nguyen The Khoi, Appl. Phys. Lett. **68**, 3326 (1996).

[21] See, B. Santic, Semicond. Sci. Technol. **18**, 219 (2003).

[22] W. R. L. Lambrecht, A. V. Rodina, S. Limpijumnong, B. Segall, and B. K. Meyer, Phys. Rev. B **65**, 075207 (2002).

[23] A. Chattopadhyay, S. Das Sarma, and A. J. Millis, Phys. Rev. Lett. **87**, 227202 (2001).

[24] R. Bouzerar, G. Bouzerar, and T. Ziman, Europhys. Lett. **78**, 67003 (2007).

[25] T. Dietl, F. Matsukura, and H. Ohno, Phys. Rev. B **66**, 033203 (2002).

[26] Y. Korotkov, J. M. Gregie, and B. W. Wessels, Appl. Phys. Lett. **80**, 1731 (2002); T. Graf, M. Gjukic, M. S. Brandt, and M. Stutzmann, *ibid.* **81**, 5159 (2002).

[27] A. Wolos, A. Wysmolek, M. Kaminska, A. Twardowski, M. Bockowski, I. Grzegory, S. Porowski, and M. Potemski, Phys. Rev. B **70**, 245202 (2004).

[28] S. Marcet, D. Ferrand, D. Halley, S. Kuroda, H. Mariette, E. Gheeraert, F. J. Teran, M. L. Sadowski, R. M. Galera, and J. Cibert, Phys. Rev. B **74**, 125201 (2006).

[29] see, e.g., A. Titov, X. Biquard, D. Halley, S. Kuroda, E. Bellet-Amalric, H. Mariette, J. Cibert, A. E. Merad, G. Merad, M. B. Kanoun *et al.*, Phys. Rev. B **72**, 115209 (2005).

[30] R. B. Bylsma, W. M. Becker, J. Kossut, U. Debska, and D. Yoder-Short, Phys. Rev. B **33**, 8207 (1986).

[31] T. Fukumura, Z. Jin, A. Ohtomo, H. Koinuma, and M. Kawasaki, Appl. Phys. Lett. **75**, 3366 (1999).

[32] C. Śliwa and T. Dietl, arXiv:0707.3542 (unpublished).

[33] J. Szczytko, W. Mac, A. Stachow, A. Twardowski, P. Becla, and J. Tworzydlo, Solid State Commun. **99**, 927 (1996).

[34] J. Szczytko, W. Mac, A. Twardowski, F. Matsukura, and H. Ohno, Phys. Rev. B **59**, 12935 (1999).

[35] see, e.g., M. Wierzbowska, D. Sánchez-Portal, and S. Sanvito, Phys. Rev. B **70**, 235209 (2004); T. C. Schulthess, W. M. Temmerman, Z. Szotek, W. H. Butler, and G. M. Stocks, Nat. Mater. **4**, 838 (2005); P. Gopal and N. A. Spaldin, Phys. Rev. B **74**, 094418 (2006); M. Toyoda, K. Sato, and H. Katayama-Yoshida, Physica B **376**, 647 (2006).

[36] J. Wu, W. Shan, and W. Walukiewicz, Semicond. Sci. Technol. **17**, 860 (2002), and references cited therein.

[37] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand,Science **287**, 1019 (2000); T. Dietl, H. Ohno, and F. Matsukura, Phys. Rev. B **63**, 195205 (2001); F. Popescu, C. Şen, E. Dagotto, and A. Moreo, *ibid.* **76**, 085206 (2007), and references cited therein.

[38] T. Dietl, A. Haury, Y. Merle d'Aubigné, Phys. Rev. B **55**, R3347 (1997).

[39] T. Dietl, J. Phys. Soc. Jpn. (to be published).

[40] M. A. Scarpulla, B. L. Cardozo, R. Farshchi, W. M. Hlaing Oo, M. D. McCluskey, K. M. Yu, and O. D. Dubon, Phys. Rev. Lett. **95**, 207204 (2005).

[41] E. Sarigiannidou, F. Wilhelm, E. Monroy, R. M. Galera, E. Bellet-Amalric, A. Rogalev, J. Goulon, J. Cibert, and H. Mariette, Phys. Rev. B **74**, 041306(R) (2006).

[42] T. Jungwirth, J. Sinova, A. H. MacDonald, B. L. Gallagher, V. Novák, K. W. Edmonds, A. W. Rushforth, R. P. Campion, C. T. Foxon, L. Eaves, E. Olejník, J. Mašek, S.-R. Eric Yang, J. Wunderlich, C. Gould, L. W. Molenkamp, T. Dietl, and H. Ohno Phys. Rev. B **76**, 125206 (2007); H. Ohno and T. Dietl, J. Magn. Magn. Mater. (to be published).