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

Tomasz Dietl1, 2, 3

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

Puzzling disagreement between photoemission and optical findings in magnetically doped GaN and ZnO is explained within a generalized alloy theory. The obtained results show that the strong coupling between valence-band holes and localized spins gives rise to a mid-gap 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.

Recent progress in the understanding of carrier-controlled ferromagnetic semiconductors such as Ga1−xMnxAs and p-type Cd1−xMnxTe relies on a large extent on comprehensive optical, magneto-optical, photoemission, and x-ray absorption (XAS) studies, which provide mutually consistent information on exchange couplings between the band states and the localized spins as well as on the positions of 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 (DMS) and diluted magnetic oxides (DMO). Here, according to photoemission and XAS works, the relevant Mn2+/Mn3+ level resides in the valence band in both GaN and ZnO, similarly to the case of arsenides, tellurides, and selenides. Furthermore, the evaluated magnitude of the p-d exchange energy βN0 shows the expected enhancement (due to a stronger p-d hybridization in nitrides and oxides) to the values of −1.6 eV in Ga1−xMnxN and to −2.7 eV or −3 eV in Zn1−xMnxO, significantly over the value of −1 eV, typical for other DMS. By contrast, optical and magneto-optical studies appear to reveal the presence of Mn3+/Mn4+ level in the band gap of both GaN and ZnO. Moreover, the determined values of βN0 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 Ga1−xMnxN leads to βN0 = +1.4 ± 0.3 eV, if the s-d exchange integral αN0 = 0.2 ± 0.1 eV is assumed, though the probed charge state may differ from that examined by photoemission. Similarly, the study of magnetoluminescence of bound excitons in Zn1−xMnxO implies |βN0| ≈ 0.1 eV. Interestingly, the contradiction in question is not limited to Mn-based nitrides and oxides – it is also rather evident for Zn1−xCo2O3, where βN0 = −3.4 eV according to XAS and in agreement with the chemical trends, while a thorough investigation of the free exciton splitting results in βN0 ≈ −0.6 eV or 1 eV, depending on the assumed ordering of the valence band subbands.

In this paper 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 magnetic impurity are met. We then calculate the spectral density A(ω) of the band-edge states by a generalized alloy theory and show that in the strong coupling limit A(ω) exhibits two maxima corresponding to the bonding and anti-bonding states, respectively. We identify the former as the deep band-gap hole trap observed optically, while the latter as the position of the band-edge, and thus of the free exciton, renormalized in a non-trivial way by the hole coupling to the system of randomly distributed magnetic impurities. As we demonstrate, our model makes it possible to explain the reversed sign and the reduced magnitude of the apparent βN0, 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.

The description of exciton splittings in the works referred to above 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 bands’ splitting proportional to the relevant bare exchange integral and magnetization of the subsystem of magnetic ions. However, while this approach describes very well the giant exciton splittings in the tellurides it has already been called into question in the case of Cd1−xMnxS. In this system, unexpected dependencies of the band-gap and of the apparent exchange
integral $\beta^{(app)}$ on $x$ have been explained by circumvent-
ing VCA and MFA either employing a non-perturbative Wigner-Seitz-type model \[12\] or by generalizing to DMS the alloy theory \[13\]. 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 $U_c$ 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 the radius $b$ one obtains \[12\] \[13\],

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

where the bare valence band offset $W N_0 = dE_k(x)/dx$, $S$ 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 \[3, 14\]. Furthermore, we note that the value of $b$ lies presumably between the anion- and cation-cation distance, $\sqrt{3}a_0/4 \lesssim b \lesssim a_0/\sqrt{2}$. Hence, for Cd$_{1-x}$Mn$_x$Te, where $S = 5/2$, $m^*/m_0 = 0.65$ and $W N_0 = -0.63$ eV \[13\] 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 $W N_0 = 0.5$ eV \[12\] 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 \[12\] \[13\].

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 compared to compounds of heavier anions. We assume $m^* = 1.3m_0$ and, in order to estimate $W$, we note that if the valence band offset is entirely determined by the p-d hybridization, $W$ and $\beta$ are related \[12\]. In the case of Ga$_{1-x}$Mn$_x$N, for which the Hubbard correlation energy for the d electrons $U^{(eff)} = 10.4$ eV and the position of the d-state with respect to the top of the valence band, $\epsilon_d^{(eff)} = -5.7$ eV \[8\] (determined so-far with accuracy of about 1 eV), we arrive to $0.96 \lesssim U/U_c \lesssim 1.6$. Similarly for Zn$_{1-x}$Mn$_x$O, where $U^{(eff)} = 9.2$ eV and $\epsilon_d^{(eff)} = -1.5$ eV \[4\], we find $2.0 \lesssim U/U_c \lesssim 3.3$. Interestingly, the above evaluation of $U/U_c$ for particular materials remains valid for DMS and DMO containing other transition metals than Mn in the 2+ state as, to a first approximation, $\beta S$ does not depend on $S$ \[3\]. 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, $U/U_c > 1$, where the hole states cannot be described by VCA and MFA.

We evaluate the effect of magnetic impurities upon a single band-edge particle ($k = 0$) with the spin $s = 1/2$ by employing a generalized alloy theory developed by Tworzynski \[13\]. The theory is built for non-interacting, randomly distributed, and fluctuating quantum spins $\mathbf{S}$ characterized by the field-induced averaged polarization $\langle S_z(T, H) \rangle$. The potential of the individual impurities is modeled \[12\] by the square-well potential containing both spin-dependent (exchange) and spin-independent (chemical shift) contributions, as discussed above. The particle self-energy $\Sigma_{ss}(\omega)$ is derived from the Matsubara formalism by summing up an infinite series for the irreducible self-energy in the average t-matrix approximation (ATA) \[13\]. Because of its general applicability for various alloys, we write down the form of $\Sigma_{ss}(\omega)$ explicitly, neglecting the direct effect of the magnetic field on the band states,

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

where $\Sigma_0(J) = xN_0(vU - 16i\pi m^*U U^U I K_b^2/h^2); v = 4\pi b^2/3; U = -(W + J S/2)/v; U^U = U - E_{vc}/(vN_0); E_{vc} = -xN_0(s_\beta \langle S_z \rangle \beta + W); \Delta = i(K - \kappa')\exp(ik')/(\kappa \sin \kappa' + ik' \cos \kappa'); \kappa = b(2m^* E - h^2)/(h^2 + 2); \kappa' = b(2m^* (E - U) h^2)/(h^2 + 2); I = \{3(1 + \Delta) + 3\kappa'^2(1 + \Delta) + 2i\kappa'^3 + 3(1 + \kappa'^2 + \Delta(\kappa'^2 - 1)] \cos(2\kappa') + 3i[\kappa'(2(1 + \Delta) + \kappa') - 1] \sin(2\kappa')/(12\kappa'^2).$$

Here $\bar{E} = \omega + E_{vc} + i\gamma$, where $\gamma$ is an intrinsic life-time broadening of the $k = 0$ state, taken here to be 3 meV.

The quantity of interest is the spectral density of states,

$$A_s(\omega) = -\frac{1}{\pi} \frac{1}{\omega + i\gamma - \Sigma_{ss}(\omega)},$$

whose maxima provide the position of the band edge $E_0$.
in the presence of spin and chemical disorder as a function of $(S_z(T, H))$. Most of relevant experiments for magnetically doped nitrides and oxides has been carried out at low concentrations $x \lesssim 3\%$, where effects of interactions among localized spins, neglected in the present approach, are not yet important. In this case, $(S_z(T, H))$ can be determined from magnetization measurements or from the the partition function of spin hamiltonian for the relevant magnetic ion at given temperature $T$ and the magnetic field $H$. For higher $x$, it is tempting to take into account effects of the short-range antiferromagnetic superexchange according to the standard recipe [11, 14], i.e., via replacement of $x$ by $x_{eff}$ and $T$ by $T + T_{AF}$, where $T_{AF}(x, T) > 0$ and $x_{eff}(x, T) < x$. However, in the strong coupling case this procedure is rather inaccurate as aniferromagnetically aligned pairs contribute also to the band-edge shift.

Figure 1(a) presents a grey scale plot of the spectral density $A_s(\omega)$ 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 $E_0$ is obviously given by $-xN_0W$. For higher $U/U_c$, a downward shift of $E_0$ 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 is also expected within the dynamic mean-field approximation [16]. 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 [17]. This band-gap hole trap should be visible in photoionization experiments $d^5 \rightarrow d^4 + h + e$, as indeed observed in both $n$-Ga$_{1-x}$Mn$_x$N [6] and Zn$_{1-x}$Mn$_x$O [7] but assigned in those works to $d^5 \rightarrow d^4 + e$ transitions. In Ga$_{1-x}$Mn$_x$N samples, in which donors were partly compensated, intra-center excitations corresponding to this level were also detected at 1.4 eV [18] and analyzed in considerable details [6, 19, 20]. While symmetry considerations cannot discriminate between $d^5 + h$ and $d^4$ many-electron configurations, the larger crystal-field splitting and the smaller Huang-Rhys factor in Ga$_{1-x}$Mn$_x$N comparing to their values in (II,Cr)VI compounds [19, 20] point to a relatively large localization radius, expected for the $d^5 + h$ case. Our interpretation reconfirms also the limited accuracy of ab initio computations within LSDA in the case of transition metal insulators, which place the $d^4$ Mn level within the band-gap of GaN [21].

Interestingly, 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 band-edge energy $E_0$ expected within VCA and MFA. We identify this state with the actual valence band-edge for $U/U_c > 1$, whose position $E_0$ determines, e.g., the onset of interband optical transitions and the free exciton energy. In Fig. 2(a), we plot $E_0(x)$ 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 [13], Zn$_{1-x}$Mn$_x$Se [22], and Ga$_{1-x}$Mn$_x$As [14]. In contrast, for $U/U_c > 1$ the present model predicts an increase of the gap with $x$, in agreement with the data for Ga$_{1-x}$Mn$_x$N [20], Zn$_{1-x}$Mn$_x$O [23], and Zn$_{1-x}$Co$_x$O [10].

As shown in Fig. 1(b), the saturating magnetic field, such that $\langle S_z(T, H) \rangle = -2.5$, produces a downward and upward shift of the bonding and anti-bonding states (which correspond to $s_z = 1/2$), respectively, and leads to the appearance of a non-bonding state ($s_z = -1/2$), whose energy is virtually independent of $U/U_c$. Re-
FIG. 3: Dependence of the band-edge spin splitting on the spin polarization, $\Delta_\beta(\langle S_z \rangle)$ for three values of the coupling strength in comparison to the values expected within VCA and MFA, $\Delta^{VCA}_{\beta}(\langle S_z \rangle)$. Normalized apparent p-d exchange integral defined as $\Delta_\beta(-2.5)/\Delta^{VCA}_{\beta}(-2.5)$ for various combinations of the materials parameters (b).

markably, the latter resides below the anti-bonding level, which means that the character of the apparent p-d exchange changes from antiferromagnetic for $U/U_c < 1$ to ferromagnetic for $U/U_c > 1$. Extensive studies of the giant free excitons’ splitting $\Delta_x$ in Ga$_{1-x}$Mn$_x$N [8] and Zn$_{1-x}$Co$_x$O [11] demonstrated a linear dependence of $\Delta_x$ on $x$ and $\langle S_z(T,H) \rangle$, as expected within VCA and MFA. Figures 2(b) and 3(a) demonstrate that approximately linear dependence of $\Delta_x$ on $x$ and $\langle S_z(T,H) \rangle$ is predicted within the present theory, too, except for an anticrossing behavior occurring when the non-binding state is in a resonance with the non-normalized band-edge, $E_0 = 0$. Accordingly, for the sake of comparison to the experimental determinations, $\Delta_x$ can be characterized by an apparent p-d exchange integral according to $\Delta_x = -xN_0\beta_{\text{app}}(\langle S_z(T,H) \rangle)$. In Fig. 3(b), we depict the expected evolution of $\beta_{\text{app}}/\beta$ with $U/U_c$ for several values of $W$ and $m^*$. We see that our theory explains the sign reversal of $\beta_{\text{app}}$ and its reduced amplitude comparing to the $\beta$ values determined by the photoemission and XAS experiments. Our findings may imply also that the exchange coupling between the band hole and the hole on the d$^5 + h$ center is not qualitatively important in Ga$_{1-x}$Mn$_x$N as well as verify the reversed order of valence band subbands in ZnO [21].

In summary, the approach put forward here allows one to reconcile the findings of photoemission, XAS, optical, and magneto-optical measurements accumulated over recent years for the magnetically doped nitrides and oxides. In view of our results, these systems form an outstanding class of materials, in which a number of concepts developed earlier for DMS has to be revised. In particular, the strong hole localization discussed here, along with the issues of self-compensation and solubility, need to be overcome in order to observe the hole-mediated ferromagnetism in nitrides and oxides.

This work was supported in part by and 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, Materials Today 9(11), 18 (2006).
[2] T. Mizokawa, T. Nambu, A. Fujimori, T. Fukumura, and M. Kawasaki, Phys. Rev. B 65, 085209 (2002).
[3] 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).
[4] J. Okabayashi, K. Ono, M. Mizuguchi, M. Oshima, S. S. Gupta, D. D. Sarma, T. Mizokawa, A. Fujimori, M. Yui, C. T. Chen, et al., J. Appl. Phys. 95, 3573 (2004).
[5] J. Blinowski, P. Kacman, and T. Dietl, Proc. Mat. Res. Soc. Symp. 690, F6.9.1 (2002); cond-mat/0201012.
[6] 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).
[7] K. R. Kittilstved, W. K. Liu, and D. R. Gamelin, Nature Materials 5, 291 (2006).
[8] W. Pacuski, D. Ferrand, J. Cibert, J. A. Gaj, A. Golnik, P. Kossacki, S. Martec, E. Sarigiannidou, and H. Mariette, cond-mat/0703041.
[9] E. Przedziecka, E. Kamińska, M. Kiecana, M. Sawicki, L. Klopotowski, W. Pacuski, and J. Kossut, Solid State Commun. 139, 541 (2006).
[10] W. Pacuski, D. Ferrand, J. Cibert, C. Deparis, J. A. Gaj, P. Kossacki, and C. Morhain, Phys. Rev. B 73, 035214 (2006).
[11] J. A. Gaj, R. Planét, and G. Fishman, Solid State Commun. 29, 435 (1979).
[12] C. Benoit à la Guillaume, D. Scalbert, and T. Dietl, Phys. Rev. B 46, 9853(R) (1992).
[13] J. Tworzydlo, Phys. Rev. B 50, 14591 (1994); Solid State Commun. 94, 821 (1995); Acta Phys. Polon. A 88, 655 (1995).
[14] T. Dietl, H. Ohno, and F. Matsukura, Phys. Rev. B 63, 195205 (2001).
[15] T. Wojtowicz, M. Kutrowski, M. Surna, K. Kopałko, G. Karcewski, J. Kossut, M. Godlewski, P. Kossacki, and Nguyen The Khoi, Appl. Phys. Lett. 88, 3326 (1996).
[16] A. Chattopadhyay, S. D. Sarma, and A. J. Millis, Phys. Rev. Lett. 87, 227202 (2001).
[17] T. Dietl, F. Matsukura, and H. Ohno, Phys. Rev. B 66, 033203 (2002).
[18] 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, Appl. Phys. Lett. 81, 5159 (2002).
[19] A. Wolos, A. Wyszmolek, M. Kaminska, A. Twardowski, M. Bockowski, I. Grzegory, S. Porowski, and M. Potemski, Phys. Rev. B 70, 245202 (2004).
[20] S. Martec, 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).
[21] 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. Kanou, et al., Phys. Rev. B 72, 115209 (2005).
[22] R. B. Bylsma, W. M. Becker, J. Kossut, U. Dobsa,
D. Yoder-Short, Phys. Rev. B 33, 8207 (1986).
[23] T. Fukumura, Z. Jin, A. Ohtomo, H. Koinuma, and M. Kawasaki, Appl. Phys. Lett. 75, 3366 (1999).
[24] W. R. L. Lambrecht, A. V. Rodina, S. Limpijumnong, B. Segall, and B. K. Meyer, Phys. Rev. B 65, 075207 (2002).