Ferromagnetism of magnetic semiconductors—Zhang-Rice limit

T. Dietl(a), F. Matsukura(a,b), and H. Ohno(b)
(a) Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, PL-00-686 Warszawa, Poland
(b) Laboratory for Electronic Intelligent Systems, Institute of Electrical Communication, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan
(Dated: September 13, 2001)

It is suggested that p-d hybridization contributes significantly to the hole binding energy $E_h$ of Mn impurities in III-V compounds, leading in an extreme case to the formation of Zhang-Rice-like small magnetic polarons. The model explains both strong increase of $E_h$ and evolution of Mn spin-resonance spectrum with the magnitude of valence-band offsets. For such a structure of Mn impurity in III-V materials, possible models accounting for the recently determined Curie temperature of about 940 K in a compensated Ga$_{0.91}$Mn$_{0.09}$N are discussed.

Recent theoretical suggestions [1, 2] that ferromagnetic ordering may persist above room temperature in (Ga,Mn)N and related materials have triggered considerable fabrication efforts [3, 4, 5], which have culminated in the determination of Curie temperature $T_C \approx 940$ K for a film of a compensated Ga$_{0.91}$Mn$_{0.09}$N grown by molecular-beam epitaxy (MBE) [6]. In order to put this result in an appropriate perspective we note that the magnetic ion density is about twenty times smaller in Ga$_{0.91}$Mn$_{0.09}$N compared to Co, which has the highest known value of $T_C = 1400$ K. This adds a new dimension to capabilities of GaN-based structures, whose importance in photonics and high-power electronics has already been proven. While further experimental studies of this new ferromagnetic system will certainly lead to developments that are unforeseen today, it is already important to model the physical environment, in which the ferromagnetism is observed as well as to indicate parameters that are controllable experimentally, and which account for the magnitudes of $T_C$ and remanent magnetization.

In this work, we demonstrate that the high $T_C$ value quoted above is consistent with the expectations of the mean-field Zener model of the carrier-mediated ferromagnetism, which was elaborated earlier by us and co-workers [1, 2]. We then examine various assumptions and approximations of the model exploring recent developments in the field of magnetic semiconductors [3, 4, 5, 6, 7, 8]. In particular, by a detail tracing of properties of Mn impurity across the ensemble of III-V semiconductors we suggest that Zhang-Rice (ZR) small magnetic polarons are formed in GaN:Mn. We then propose that delocalization of these polarons may drive the ferromagnetic transition in p-(Ga,Mn)N. We also note that if the d$^5$/d$^6$ level resides in the gap and the concentration of donors is greater than that of Mn, double exchange involving the upper Hubbard d-band may account for ferromagnetism of n-(Ga,Mn)N.

Figure 1 presents $T_C$ of wurzite Ga$_{1-x}$Mn$_x$N calculated according to the model [1, 2] and for material parameters discussed in detail previously [4]. The data are shown for magnetization perpendicular to the c axis of the wurzite structure, which is found to be the easy plane in (Ga,Mn)N for the displayed values of the Mn and hole concentrations. As seen, $T_C$ of 940 K is expected for the hole concentrations about four times smaller than the Mn concentration $x$ in Ga$_{0.91}$Mn$_{0.09}$N. Such a value of $T_C$ is consistent with that deduced from magnetization measurements at 0.1 T between 300 and 750 K [6].

We begin the discussion of various features of theory [1, 2] by recalling that according to the mean-field Zener model [13], the properties of the system consisting of localized spins and itinerant carriers can be obtained by minimizing the total free energy with respect to the spin magnetization $M$. It is assumed [1, 2] that the Mn ions substitute the cations, and are in the 3d$^5$ S = 5/2 configuration, whereas the holes reside in the valence band, which is described by the disorder-free $k$·$p$-Kohn-Luttinger theory for tetrahedrally coordinated semiconductors. The p-d exchange between the two subsystems, the Kondo interaction, is incorporated to the $k$·$p$ scheme within the molecular-field and virtual crystal approximations, whereas the hole-hole exchange interaction is treated in terms of Landau’s Fermi liquid theory. The hole free energy, not ground state energy, is adopted for the evaluation of $T_C$ [4, 5], an ingredient significant quantitatively in the high temperature regime, such as that covered by the data in Fig. 1.

Figure 2 shows the energetic position of the Mn impurity level in III-V compounds, as evaluated by various authors from measurements of optical spectra and activation energy of conductivity. A priori, the Mn atom, when substituting a trivalent metal, may assume either of two configurations: (i) d$^4$ or (ii) d$^5$ plus a weakly bound hole (d$^5$+h ≡ A$^0$). Accordingly, the experimentally determined energies correspond to either d$^4$/d$^5$ or A$^0$/A$^-$ levels. It appears to be a general consensus that the Mn acts as an effective mass acceptor (d$^5$+h) in the case of antimonides and arsenides. Such a view is supported by a relatively small Mn concentrations corresponding to the insulator-to-metal transition, which according to the Mott criterion $n^{1/3}a_B = 0.26$, points to a relatively large extension of the effective Bohr radius $a_B$. More-
over, the ESR studies of GaAs:Mn reveal, in addition to the well known spectrum of Mn d\(^5\) with the Landé factor \(g_s = 2.0\), two additional lines corresponding to \(g_a = 2.8\) and \(g_b = 6.22\), which can be described quantitatively within the \(k \cdot p\) scheme for the occupied acceptor [22, 23]. Here, the presence of a strong antiferromagnetic p-d exchange interaction between the bound hole and the Mn d-electrons has to be assumed, so that the total momentum of the complex is \(J = 1\). In agreement with the model, the additional ESR lines, in contrast to the \(g = 2.0\) resonance, are visible only in a narrow range of the Mn concentration [24], which should be greater than the concentration of compensating donors, and smaller than that at which acceptor wave functions start to overlap and to merge with the valence band. The antiferromagnetic coupling within the d\(^5\)+h complex is seen in a number of experiments, and has been employed to evaluate the p-d exchange integral \(\beta N_0 \approx -1\) eV [24] in GaAs:Mn, the value in agreement with that determined from interband magnetoabsorption in (Ga,Mn)As [20].

Importantly, the above scenario is corroborated by results of photoemission [24] and x-ray magnetic circular dichroism (MCD) studies [24, 30] in metallic or nearly metallic Ga\(_{1-x}\)Mn\(_x\)As. The latter point to the d\(^5\) Mn configuration. The former are not only consistent with such a configuration but also lead to the value of \(\beta N_0\) similar to that quoted above, \(\beta N_0 \approx -1.2\) eV [24]. Furthermore, the photoemission reveals the presence of two features in the density of states brought about by the Mn constituent: the original Mn 3d\(^5\) states located around 4.5 eV below the Fermi energy \(E_F\), and new states merging with the valence band in the vicinity of \(E_F\) [28]. These new states correspond to acceptors, as discussed above. They are derived from the valence band by the Coulomb field as well as by a local Mn potential that leads to a chemical shift in the standard impurity language, or to a valence band offset in the alloy nomenclature. The fact that transition metal impurities may produce both resonant and Coulomb states was also noted in the case of CdSe:Sc [31].

In contrast to antimonides and arsenides, the situation is much more intricate in the case of phosphides and nitrides. Here, ESR measurements reveal the presence of a line with \(g = 2.0\) only [4, 14, 32, 33], which is thus assigned to d\(^5\) (A\(^-\)) centers [14, 32, 33]. Moreover, according to a recent study carried out for a compensated n-type GaP:Mn [14], the ESR amplitude diminishes under illumination and, simultaneously, new lines appear, a part of which exhibit anisotropy consistent with the d\(^4\) configuration. This, together with the apparent lack of evidence for d\(^5\)+h states, even in p-type materials, appears to imply that Mn in the ground state possesses the d\(^4\), not A\(^0\), electron configuration [14]. This would mean that the Mn energy in Fig. 2 for GaP [14] and, therefore, for GaN [11, 12] (where the valence band is lower than in GaP) corresponds to the d\(^4\)/d\(^5\), not A\(^0\)/A\(^-\) level. Such a view seems to be supported by the \(ab\) initio computation within the local spin density approximation (LSDA), which points to the presence of the d-states in the gap of (Ga,Mn)N [2]. In this situation, the spin-spin interaction would be driven by a double exchange mechanism involving hopping of d-electrons [2, 33], as in the case of colossal magnetoresistance manganites, making the modelling leading to the results presented in Fig. 1 invalid.

However, there is a chain of arguments which calls the above interpretation into question. First, guided by photoemission results for II-VI compounds [28] one expects that the energy of the d\(^4\)/d\(^5\) level will vary little between
arsenides and nitrides. This implies that this level should reside in the valence band of GaN despite the 1.8 eV valence band offset between GaN and GaAs. The resulting contradiction with the LSDA findings can be removed by noting that in the case of strongly correlated 3d electrons, a semi-empirical LSDA+U approach is necessary to reconcile the computed and photoemission positions of states derived from the Mn 3d shell in (Ga,Mn)As [28, 47].

Second, it is known that the p-d hybridization, in addition to producing the exchange interaction, can contribute to the hole binding energy $E_b$ [28, 48]. We take the hole wave function as a coherent superposition of p-states of anions adjacent to Mn [28]. Assuming the p-orbitals to be directed towards the ion Mn we find that the $T_2$ state has 30% lower energy than that corresponding to the mutually parallel p-orbitals. This shows that not only Kohn-Luttinger amplitudes from the Γ point of the Brillouin zone are involved. In order to evaluated $E_b$, a square-well spherical potential $U(r) = U\Theta(b - r)$ is assumed [28], whose depth $U$ is determined by the p-d hybridization taking into account the above mentioned arrangement of the p-orbitals,

$$U = \frac{5}{8\pi} \frac{\beta N_0}{1.04} \left( 1 - \frac{\Delta e_{\text{eff}}}{U_{\text{eff}}} \right) \left( \frac{a_p}{b} \right)^3.$$ (1)

Here, the values of $\beta N_0$ are taken from Ref. [28]: $\Delta e_{\text{eff}}$ is the distance of $d^5/d^6$ level to the top of the valence band, which is evaluated to be 2.7 eV in (Ga,Mn)As [27], and is assumed to be reduced in other compounds by the corresponding valence band offsets (Fig. 2), and $U_{\text{eff}} = 7$ eV is the correlation energy of the 3d electrons [27, 46]. Finally, $b/a_p$ is the well radius in the units of the lattice constant, and should lie in-between the cation-anion and cation-cation distance, $\sqrt{3}a_o/4 < b < a_o/\sqrt{2}$. It turns out that in the case of GaN:Mn the hole is bound by Mn, even in the absence of the Coulomb potential, $E_b = 1.0$ eV for $b = 0.46a_o$. This demonstrates rather convincingly that a large part of $E_b$ originates indeed from the p-d interaction, indicating that the Zhang-Rice (ZR) limit [28, 39] is reached in these systems. The formation of ZR small magnetic polarons invoked here has a number of important consequences which are now discussed.

We begin by arguing that when the ZR polarons are formed, the $d^5$ and $d^6$ states acquire virtually the same Landé factor $g = 2.0$. Quite generally, the role of the intra-atomic spin-orbit splitting $\Delta_o$ diminishes with the carrier kinetic energy, and thus with $E_b$. An upper limit of orbital-momentum corrections to the Mn Landé factor, $\Delta g = g - g_S$ can thus be evaluated by considering non-magnetic acceptors, for which $E_b$ is typicaily smaller than that of Mn. In the wurzite GaN, the orbital momentum is quenched by the uniaxial crystal field, and the Landé factors of GaN:Mg are close to two, $g_{\parallel} = 2.07$ and $g_{\perp} = 1.99$ [14]. Hence, for the $d^5$-h state in wz-GaN:Mn, where the total spin $S_p = 2$, we obtain $\Delta g = (g_S - g_h)/6 \approx -0.01$. In cubic materials, in turn, the total momentum $J_p = 1$ and $\Delta g = 3/4$ for deep $d^5$-h states $E_b$ [22, 23], in agreement with the ESR findings for GaAs:Mn [24, 25, 26]. We note, however, that the Jahn-Teller effect should be particularly strong in the case of ZR polarons. The corresponding lowering of local symmetry will lead to the quenching of orbital momentum, especially in compounds with a relatively small value of $\Delta_o$. Hence, also in the cubic nitrides and phosphites, $S_p = 2$ and thus $\Delta g \approx 0$. Interestingly, by exploiting the hole interaction with host nuclear spins, it becomes possible to tell $d^5$ and $d^6$-h states despite their similar Landé factors [33].

Another important consequence of the ZR polaron formation is the shift of the Mott critical concentration towards rather high values. According to the known relation between $E_b$ and $a_{\parallel} (1)$, the critical hole concentration is $p_c = 4 \times 10^{19} \text{cm}^{-3}$ in (Ga,Mn)As and at least an order of magnitude greater in (Ga,Mn)N, if no shallower acceptors are present. According to the two-fluid model [1], corroborated by experimental results [23, 42, 43], only a part of spins orders ferromagnetically in the insulator phase. The Mn spins are ordered in space regions, in which weakly localized holes reside [1, 3]. This can be the case of the ferromagnetic Ga$_{0.91}$Mn$_{0.09}$N sample [1], whose spontaneous magnetic moment constitutes only about 20% of the value expected for $x = 0.09$ and $S = 5/2$. Remarkably, the disorder in Mn positions seems to shift $T_C$ to higher values in such a case [1], presumably even above those display in Fig. 1. On the other hand, corrections to molecular- and mean-field approximations tend to lower $T_C$ values [3, 11]. While our work provides a background for detail studies of these effects, we expect that the corresponding corrections will not be qualitatively significant. Indeed, the short-range potential of Eq. 1 is still relatively weak: our $|\beta|$ corresponds to $J_{pd} = 0.054 \text{ eVnm}^3$ and $J = 0.5$ eV of Refs. [8, 10], respectively.

It might appear from Fig. 1 that a further enhancement of $T_C$ would be possible by increasing the hole concentration $p$. Actually, however, if $p \rightarrow xN_0$ (i.e., $x_h \rightarrow 1$), the antiferromagnetic portion of the carrier-mediated (RKKY) interaction will reduce $T_C$ [43] and eventually drive the system towards a spin-glass phase [44]. Thus, it seems that the compensation by donors, despite introducing an additional disorder, constitutes the important ingredient of ferromagnetism in Mn-based III-V compounds [15].

Finally, we note that if indeed, as we advocate here, the $d^5/d^6$ state resides in the valence band, the $d^5/d^6$ level may lie below the bottom of the conduction band. If this
is the case, and the concentration of donors is greater than that of Mn, double exchange involving the d\(^6\) electrons may account for ferromagnetism of n-(Ga,Mn)\(N\). We note in this context that because of the anomalous (spin) Hall effect [12], a possible coexistence of p-type and n-type regions in compensated semiconductors [13], and the presence of strong electric fields due to lack of inversion symmetry, the evaluation of the carrier type and concentration from transport measurements is by no means straightforward in thin films of wz-(Ga,Mn)\(N\).

In summary, according to the discussion presented in this paper, while the Mn substitutional impurities act as shallow acceptors characterized by the Bohr radius spacing over tens of Å in antimonides, in the case of lighter anions the hole becomes tightly localized. In the extreme case, such as GaN:Mn, the Zhang-Rice-like magnetic polarons are formed. At sufficiently high Mn concentrations, the holes tend to delocalize and can then mediate long-range correlation between the Mn ions. In an over-compensated material this correlation may be transmitted by d\(^6\) electrons, if the corresponding upper Hubbard band resides below the bottom of the conduction band.

We thank J. Blinowski, P. Kacman, M. Kamińska, and A. Twardowski for valuable discussions. The work in Poland was supported by State Committee for Scientific Research, Grant No. 2-P03B-02417, and Foundation for Polish Science.

[46] Because of compensation, the values of x determined in Ref. 9 from saturation values of magnetization assuming S = 2 are somewhat overestimated.