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Ferromagnetism of magnetic semiconductors: Zhang-Rice limit

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It is suggested that p-d hybridization contributes significantly to the hole binding energy E_b of Mn acceptors in III-V compounds, leading in an extreme case to the formation of Zhang-Rice-like small magnetic polarons. The model explains both the strong increase of E_b and the evolution of a Mn spin-resonance spectrum with the magnitude of valence-band offsets. The high Curie temperature above room temperature is shown to be in accordance with the mean-field Zener model.

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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,[3–8] which have resulted in the observations of high-temperature ferromagnetism in this compound by a number of groups.[6–8] This adds a 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 both T_C and remanent magnetization.

In this work, we demonstrate that the high T_C, up to the highest reported value of 940 K,[8] 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.[1,9] We then examine various assumptions and approximations of the model exploring recent developments in the field of magnetic semiconductors.[2,10–14] In particular, by a detailed tracing of properties of the Mn impurity across the ensemble of III-V semiconductors, we suggest that Zhang-Rice small magnetic polarons are formed in GaN:Mn. We then propose that delocalization of these polarons may drive the ferromagnetic transition in (Ga,Mn)N.

Figure 1 presents T_C of wurzite (Ga,Mn)N calculated according to the model[1,9] and for material parameters discussed in detail previously.[9] The results 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, a T_C of 940 K is expected for hole concentrations about four times smaller than the Mn concentration x in $\mathrm{Ga_{0.91}Mn_{0.09}N}$. Such a value of T_C is consistent with that deduced from magnetization measurements at 0.1 T between 300 and 750 K.[8]

We begin the discussion of various features of theory[1,9] by recalling that according to the mean-field Zener model,[15] the properties of a 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[1,9] that the Mn ions substitute the cations, and are in the $3\mathrm{d}^5 S=5/2$ configuration, whereas the holes reside in the valence band, which is described by the disorder-free $\mathbf{k}\cdot\mathbf{p}$ Kohn-Luttinger theory for tetrahedrally coordinated semiconductors. The p-d exchange between the two subsystems, the Kondo interaction, is incorporated to the $\mathbf{k}\cdot\mathbf{p}$ 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,[1,9] 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, in respect to valence-band edges,[16] as evaluated by various authors[13,17–23] 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). Accordingly, the experimentally determined energies correspond to either d^4/d^5 or d^5+h/d^5 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 the relatively small Mn concentrations leading 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. Moreover, the ESR studies of GaAs:Mn reveal, in addition to the well known spectrum of

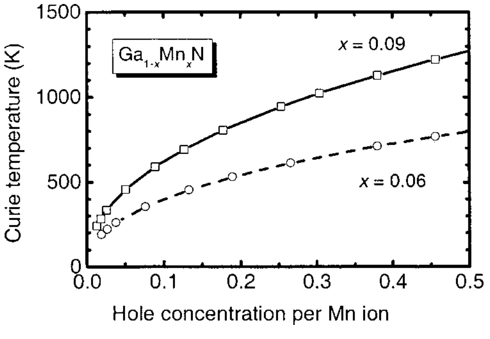

FIG. 1. Curie temperature of wurzite $\mathrm{Ga_{1-x}Mn_xN}$ according to the mean-field Zener model (Refs. 1 and 9) calculated as a function of the ratio of the hole and Mn concentrations, $x_h=p/xN_o$.

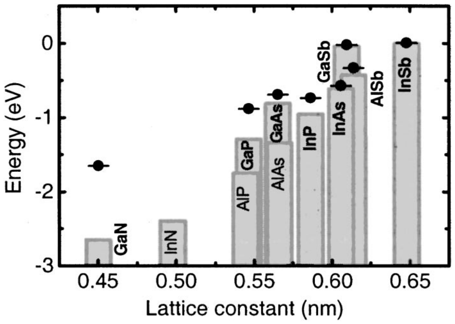

FIG. 2. Experimental energies of Mn levels in the gap of III-V compounds according to Refs. 13 and 17–23 in respect to valence-band edges, whose relative positions are taken from Ref. 16.

Mn d^5 with the Landé factor $g_{Mn}=2.0$, two additional lines corresponding to $g_1=2.8$ and $g_2\approx 6$,[24–26] which can be described quantitatively within the $\boldsymbol{k}\cdot\boldsymbol{p}$ scheme for the occupied acceptor.[24,25] 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[26] that should be greater than the concentration of compensating donors, and smaller than that at which acceptor wave functions start to overlap and 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 in GaAs:Mn,[27] the value in agreement with that determined from interband magnetoabsorption in (Ga,Mn)As.[28]

Importantly, the above scenario is corroborated by results of photoemission[29,30] and x-ray magnetic circular dichroism studies[31,32] in metallic or nearly metallic (Ga,Mn)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 βN_0 similar to that quoted above: $\beta N_0\approx -1.2$ eV.[29] 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 states merging with the valence band in the vicinity of E_F.[30] These 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.[33]

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,[4,17,34–36] which is thus assigned to d^5 centers.[4,17,34,35] Moreover, according to a detailed study carried out for a compensated n-type GaP:Mn,[17] 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, seems to imply that Mn in the ground state possesses a d^4, not a d^5+h, electron configuration.[17] This would mean that the Mn energy in Fig. 2 for GaP (Ref. 17) and, therefore, for GaN (Refs. 13 and 14), where the valence band is lower than in GaP, corresponds to the d^4/d^5, not $(d^5+h)/d^5$ level. Such a view appears to be supported by the *ab initio* computation within the local-spin-density approximation (LSDA), which points to the presence of 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,[2,37] as in the case of colossal magnetoresistance manganites, making the modeling 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[38] 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. This conclusion is supported by most recent K-edge near-edge x-ray-absorption fine-structure studies, which point to $+2$ valency of Mn in (Ga,Mn)N.[39] 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.[30,40]

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.[41,42] We take the hole wave function in this charge transfer state as a coherent superposition of p-states of anions adjacent to Mn.[41] Assuming the p orbitals to be directed toward the Mn ion, we find that the T_2 state has 30% lower energy than that corresponding to the mutually parallel p orbitals. This shows that the Kohn-Luttinger amplitudes away from the Γ point of the Brillouin zone are also involved. In order to evaluated E_b, a square-well spherical potential $V(r)=V_o\Theta(b-r)$ is assumed,[42] whose depth V_o is determined by the p-d hybridization, taking into account the above-mentioned arrangement of the p orbitals:

$$V_o=\frac{5}{8\pi}\frac{\beta N_0}{1.04}\left(1-\frac{\Delta_{eff}}{U_{eff}}\right)\left(\frac{a_o}{b}\right)^3. \tag{1}$$

Here the values of βN_0 are taken from Ref. 9; Δ_{eff} is the distance of d^4/d^5 level to the top of the valence band, which is evaluated to be 2.7 eV in (Ga,Mn)As,[29] and is assumed to be reduced in other compounds by the corresponding valence-band offsets (Fig. 2), and $U_{eff}=7$ eV is the correlation energy of the $3d$ electrons.[29,38] Finally, b/a_o is the well radius in 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 indeed originates from the p-d interaction, indicating that the Zhang-Rice (ZR)

limit[41,42] is reached in these systems. Obviously, however, a combination of self-consistent first-principles electronic calculations[43] with the LDA+U method[44] is expected to provide a more quantitative evaluation of the relevant energies.

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^5+h states acquire virtually the same g factor of $g=2.0$. Quite generally, the role of the intra-atomic spin-orbit splitting Δ_o diminishes with the carrier kinetic energy, and thus with E_b. An upper limit of the hole orbital-momentum contribution to the g factor of the d^5+h complex, $\Delta g = g - g_{Mn}$ can thus be evaluated by considering non-magnetic acceptors, for which E_b is typically smaller than that of Mn. In wurzite GaN, the orbital momentum is quenched by the uniaxial crystal field, and the effective Landé factors of holes bound to Mg in GaN are close to two: $g_h^{\parallel}=2.07$ and $g_h^{\perp}=1.99$.[45] Hence, for the d^5+h state in noncubic GaN:Mn, where the total spin $S_p=2$, we obtain $\Delta g = (g_{Mn}-g_h)/6 \approx -0.01$. In cubic materials, in turn, the total momentum $J_p=1$ and $\Delta g \approx 1$ for deep d^5+h states,[24] in agreement with the ESR findings for GaAs:Mn.[24–26] We note, however, that the Jahn-Teller effect should be particularly strong in the case of ZR polarons. The corresponding lowering of the local symmetry will lead to a quenching of the orbital momentum, especially in compounds with a relatively small value of Δ_o. Hence, in cubic nitrides and phosphides, $S_p=2$ and thus $\Delta g \approx 0$. Interestingly, by exploiting the hole interaction with host nuclear spins, it may become possible to distinguish d^5 and d^5+h states despite their similar effective Landé factors.[36] In particular, the presence of the hole can lead to an additional broadening of the Mn hyperfine sextet.[46]

Another important consequence of the the ZR polaron formation is the shift of the Mott critical concentration toward rather high values. According to the known relation between E_b and a_B,[11] the critical hole concentration is $p_c = 4 \times 10^{19}$ 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,[31,47,48] only a part of the spins orders ferromagnetically in the insulator phase. The Mn spins are ordered in space regions, in which weakly localized holes reside.[1,11] This can be the case of the ferromagnetic $Ga_{0.91}Mn_{0.09}N$ sample,[8] 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,[11] presumably even above those displayed in Fig. 1. On the other hand, corrections to molecular- and mean-field approximations tend to lower T_C values.[10,12] While our work provides a background for detailed 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 $J_{pd} = 0.054$ eV nm^3 and $J=0.5$ eV of Refs. 10 and 12, 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 Ruderman-Kittel-Kasuya-Yosida interaction will reduce T_C,[1,10,12,48] and eventually drive the system towards a spin-glass phase.[49] 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. However, once the material becomes *n* type, in a sense that the Fermi level resides in the conduction band and the Mn d^6 upper Hubbard band is yet not occupied, according to both theoretical modeling[50] and experimental results for *n* type systems,[51] no ferromagnetism is expected above 1 K. Hence an indication of ferromagnetism detected in *n*-(Ga,Mn)N at higher temperatures[5] is challenging.

In summary, the values of ionization energies collected here indicate that Mn acts as effective mass acceptor in III-V compounds, whose chemical shift is small in antimonides but gradually increases on going through arsenides and phosphides to nitrides. By generalizing the Zhang-Rice model for the case of tetrahedrally coordinated semiconductors, this chemical trend is shown to result from the growing contribution of *p*-*d* hybridization to the hole binding energy. This hybridization also leads to the strong *p*-*d* exchange interaction between the Mn spins and the holes in the valence band. It is demonstrated that for the resulting magnitude of the exchange coupling, the high values[6–8] of T_C can be explained by the mean-field Zener model which allows for the wurzite structure and weak degeneracy of the hole liquid. In more general terms, within this model, large magnitudes of T_C result from the strong spin coupling within the ZR polaron and the efficient transfer of spin information due to the relatively large extent of the *p*-wave functions. Obviously, however, further experimental work is needed to elucidate a possible role of precipitates of various Mn-Ga and Mn-N compounds as well as of defect complexes involving Mn.

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