Ferromagnetism in Magnetically Doped III-V Semiconductors

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The origin of ferromagnetism in semimagnetic III-V materials is discussed. The indirect exchange interaction caused by virtual electron excitations from magnetic impurity acceptor levels to the valence band can explain ferromagnetism in GaAs(Mn) in both degenerate and nondegenerate samples. Formation of ferromagnetic clusters and the percolation picture of phase transition describes well all available experimental data and allows us to predict the Mn-composition dependence of transition temperature in wurtzite (Ga, In, Al)N epitaxial layers.

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Electronic and optoelectronic semiconductor devices, controlled by a weak magnetic field, and electric-field controlled ferromagnetism in semiconductors [1] promise new functionality of memory, detectors, and light-emitting sources. Possible device implementations of spin electronics are high-electron-mobility transistors, Si/Si and GaAs/Si spin-valve transistors, spin light-emitting diodes, quantum computers, and integration of nonvolatile storage and logic. Efficiency of spin injection depends on the interface quality; all-semiconductor structures should benefit the performance of spin-electronic devices. Recent achievement in materials research resulted in ferromagnetic semiconductor material lattice matched to III-V semiconductors: the highest ever ferromagnetic critical temperature in semiconductors ($T_c = 110$ K) has been observed in metallic samples of $Ga_{1-x}Mn_xAs$ ($x = 0.053$) [2,3].

The origin of ferromagnetism in III-V materials is not well understood. The explanation of ferromagnetism by hole-mediated Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction (Ref. [2]) gives theoretical critical temperature T_c pretty close to that observed experimentally. A detailed theory of the ferromagnetism based on RKKY interaction in bulk semiconductors and quantum wells can be found in Refs. [4–7]. This approach implies that the Fermi surface exists (chemical potential lies in the band). If the inverse Fermi wave number k_F^{-1} is large compared to the relevant interspin distance, one can neglect Friedel oscillations in the indirect exchange interaction Ref. [4] (Zener model). Despite the efforts, some difficulties arise in the free carrier-based explanation of ferromagnetism in GaAs(Mn). First, nonzero T_c has been observed in the low-carrier concentration samples, where the chemical potential presumably lies in the semiconductor band gap. Second, hole density in GaAs increases with Mn content; thus what we see as carrier density dependence of T_c might be the dependence on a localized spin concentration. Third, the estimation, made in Ref. [2], employs the mean-field approximation, which is valid only when the interaction radius L is much larger than the average interspin distance $\overline{R}$. In the samples under consideration in Ref. [2] this is not a case since L was estimated as short due to crystal imperfections, $L \simeq (5–6.5)$ Å, whereas Mn content $x = 0.053$ corresponds to $\overline{R} = 6$ Å.

Free carriers contribute to the ferromagnetism in cubic III-V samples with degenerate holes, but until now it is not clear if this contribution is responsible for high T_c or not. In wide band gap semiconductors the degenerate free carriers (Fermi surface) can hardly be obtained and RKKY-based explanation is also under question. A recent prediction of room temperature ferromagnetism in wide band gap GaN(Mn) [4] is based on an assumption that crystal is degenerate. However, in real p-type Mn- or Fe-doped GaN samples hole density is not enough to create the Fermi surface in the valence band (carriers are not degenerate even at $T = 0$) [8,9].

Our point is that the RKKY mechanism is not an ultimate reason of ferromagnetism and high ferromagnetic transition temperature can occur even in nondegenerate semiconductors. In this paper, we discuss the alternative mechanism of ferromagnetism in III-V materials doped with magnetic atoms. A localized spin in a crystal excites band electrons due to s-p or p-d exchange interaction and generally gives rise to three types of indirect exchange interaction between impurity spins caused by virtual excitations of band electrons. If the Fermi level lies inside an energy gap, there is a threshold for electron excitations, and the indirect exchange drops exponentially with a distance between impurities. The energy gap determines the length of the exponential decay (Bloembergen-Rowland mechanism [10]). In indirect-gap semiconductors electron excitations involve the momentum transfer $\mathbf{K}$. This modulates the exponential decay by oscillations with the period $\sim K^{-1}$ (Ref. [11]). If the chemical potential is inside the band and the Fermi level exists, the gapless excitations of electrons near k_F result in the range function that oscillates with period $\sim k_F^{-1}$ and the amplitude falling as a power of a distance. This is the long-ranged RKKY interaction [12].

In this Letter we would like to attract attention to excitations of Mn acceptors, namely, to virtual acceptor

level–valence band transitions rather than electron-hole pair excitations around Fermi level in RKKY theory. This mechanism always works, whether the sample is degenerate or not; it could also describe ferromagnetism in GaAs(Mn) as well as in wide band gap materials like GaN(Mn, Fe) where chemical potential is in the band gap and the Fermi energy is absent. In semiconductor samples, where chemical potential lies in the band gap, this mechanism is the only possible one to mediate an interaction between distant localized spins.

The Bloembergen-Rowland–type indirect interaction between two magnetic ions, separated by the distance r, is given as [13]

$$J(r) = -\frac{J_{pd}^2 m^2 \Delta}{\pi^3 \hbar^4 n^2 r^2} K_2(2r/r_0), \qquad r_0 = \hbar(2m\Delta)^{-1/2}. \tag{1}$$

Here J_{pd} is the exchange interaction between free carrier and localized spin, n is the concentration of host atoms in the sublattice of substitution (cation sublattice in GaAs), $m = m_1 m_2 (m_1 + m_2)^{-1}$ is the reduced electron mass in the bands under consideration, Δ is the smallest energy gap for electron excitations, and $K_2(y)$ is the McDonald function [14]. The indirect exchange interaction, Eq. (1), tends to known results in two limiting cases: (a) small distances (narrow-gap semiconductors) [15], $r \ll r_0$, $J(r) \sim 1/r^4$, and (b) large distances [11], $r \gg r_0$, $J(r) \sim r^{-5/2} \exp(-2r/r_0)$.

Equation (1) has been derived for intrinsic semiconductor, where the smallest energy gap for electron-hole excitations Δ is the band gap. To adapt the equation for virtual excitations impurity band-valence band we use the Eq. (1) in the limit when one of the band is a narrow impurity band formed by Mn or Fe in highly doped material. In the nondegenerate p-GaAs(Mn), where chemical potential lies in the band gap between Mn acceptor level and the valence band, the smallest energy gap is the activation energy of a hole at Mn atom $\Delta \simeq 110$ meV [16]. We assume that the effective mass in the impurity band is much larger than the hole mass, so the reduced mass is equal to the valence band density of state mass $m \simeq 0.53 m_0$. The interaction radius for GaAs(Mn) is $r_0 \simeq 8$ Å.

The mean-field theory of ferromagnetic phase transition implies that the local effective magnetic field, acting on a magnetic atom, is caused by a large number of nearest magnetic atoms. In other words, the interaction radius is supposed to be much larger than the average interspin distance. As the interaction Eq. (1) is short-ranged, $r_0 \simeq \overline{R}$, the mean-field approximation cannot be used for the calculation of the ferromagnetic critical temperature T_c. Instead, we have to use the percolation approach [17]. At certain temperature, the spins, coupled by a strong exchange interaction, form a ferromagnetic cluster. The cluster size $R_{\rm cl}$ is determined by the equation $S(S+1)J(R_{\rm cl}) = k_B T$. When temperature decreases, the clusters grow in size due to coalescence, and, when a percolation threshold is reached, the "infinite" cluster penetrates the whole crystal. The percolation threshold determines the transition temperature, and it is reached when cluster size becomes $R_{\rm cl} = R_{\rm perc} \simeq \overline{R}(B_c)^{1/3}$, where B_c is a geometrical factor. In the three-dimensional random-site model, this factor is given as $B_c = 2.4$ (Ref. [18]). The ferromagnetic critical temperature follows:

$$k_B T_c = S(S+1)J(R_{\rm perc}). \tag{2}$$

The unit cell of volume $a^3/4$ (a is the lattice constant) contains one pair Ga-As, the relative Mn concentration (composition) is given as $x = N_{\rm Mn}/N_{\rm cell}$, and the average interspin distance has the form $\overline{R} = (3a^3/16\pi x)^{1/3}$. The value of the p-d exchange interaction J_{pd} is not well established; it seems to be dependent on the charge state of the Mn atom, and it was estimated as 2.5 eV [19], 3.3 eV [2], and 1.2 eV [20]. The best agreement with the experimental results we obtained with $J_{pd} = 2.8$ eV. Results of T_c calculation along with available experimental data are shown in Fig. 1. The calculations were made with the assumption that Δ and m do not depend on a composition. The real reduced effective mass, however, depends on the

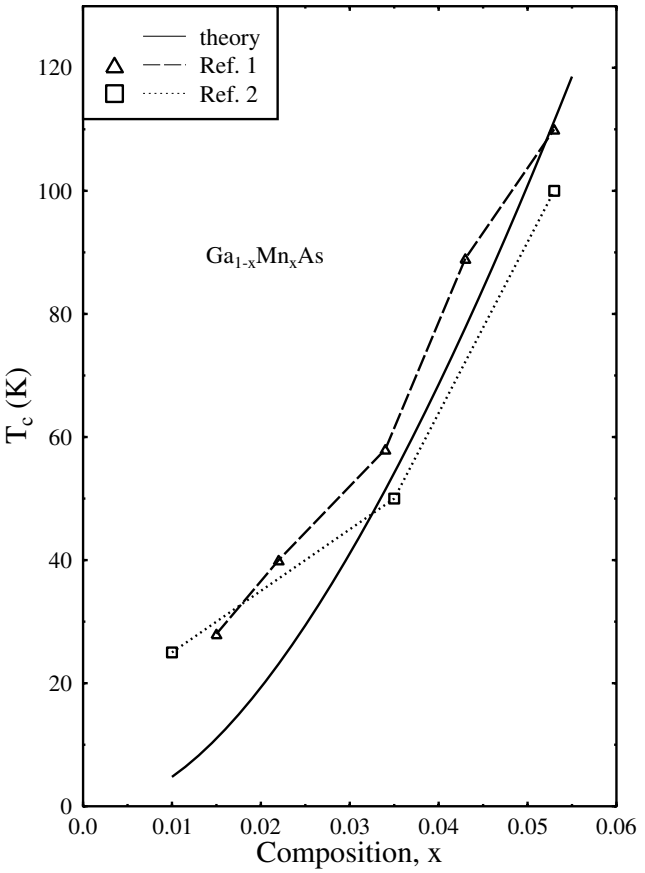

FIG. 1. Mn concentration dependence of ferromagnetic transition temperature in GaAs(Mn). Theoretical dependence (solid line) is obtained from the percolation threshold [Eq. (2)] for $J_{p\text{-}d} = 2.8$ eV, $\Delta = 0.11$ eV, $m = 0.53 m_0$.

impurity band width (Mn content). This might be a reason for the discrepancy between experimental data and the theory at small values of composition.

An increase in Mn concentration beyond $x = 0.055$ most likely causes the formation of the defects, which compensates Mn acceptors (self-compensation), and the Fermi level moves toward the conduction band and then appears to lie between the Mn acceptor level and the conduction band. At this point, the smallest gap is the energy difference between the acceptor level and the edge of the conduction band. This difference is large, which makes the exchange interaction small and T_c low [see Eq. (1)].

The prediction of the impurity band formation in GaN(Mn, Fe) was reported in Ref. [21]. In p-type group-III nitrides the acceptor levels lie in the band gap, not closer than 200–250 meV to the valence band. The average interspin distance in wurtzite GaN(Mn) is $\overline{R} = (3^{4/3}a^2c/16\pi x)^{1/3}$, where a and c are the lattice constants. P-d exchange interaction is unknown and can be estimated the same way as in Ref. [4]: the J_{pd} value in GaAs is multiplied by the ratio of cation density in wurtzite nitrides to that in cubic GaAs. This ratio is found as 1.95 (GaN), 1.45 (InN), and 2.163 (AlN). The calculations are done for $m = 0.8m_0$, and the results are shown in Fig. 2.

The transition temperature, shown in Fig. 2, is sensitive to the value of the minimum energy gap Δ. At present, there is not much information about the actual position of Mn or Fe levels in the band gap of GaN-based materials. According to local density approximation (LDA) results for cubic GaN(Fe, Mn) [22], Mn gives rise to two peaks of density of states with one portion merging with the top of the valence band. Because the accuracy of LDA results is of the order of 1 eV, experimental studies are also needed to specify the position of Mn and Fe levels in the band gap. Figure 3 illustrates the Δ dependence of T_c in wurtzite GaN.

The mechanism we discussed treats the exchange interaction as a result of virtual excitations acceptor level-valence band. This mechanism always works, whether the level is in the band gap of GaAs (neutral acceptor, $Mn^{3+} = Mn^{2+} + \text{hole}$) or in the valence band (ionized acceptor, Mn^{2+}). In the latter case the activation energy Δ is the distance between acceptor and Fermi levels both situated in the valence band. In this case the rise of the hole concentration with Mn doping decreases Δ that increases T_c in accordance with the observed data. The resonance ionized Mn^{2+} acceptors may take place in epitaxial layers and in highly doped bulk GaAs(Mn) [20,23]. However, the problem of acceptor level position and charge state of Mn in GaAs is not well understood yet. To illustrate our interpretation of the ferromagnetic phase transition we assume that the acceptor level is situated in the band gap.

Since ferromagnetic ordering appears in a crystal, a spin polarization of free carriers can reveal itself in many different experiments, no matter whether ferromagnetism is caused by free electrons or not. So the mechanism, discussed here, is not in contradiction with anomalous Hall effect [2] and magnetic dichroism in optical absorption [3], observed in GaAs(Mn).

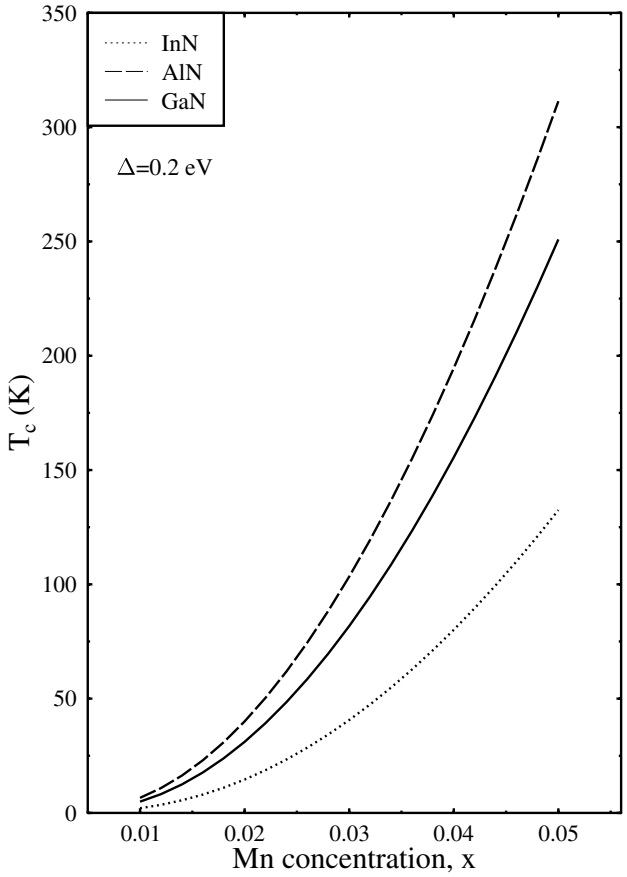

FIG. 2. Theoretical transition temperature in wurtzite group III-nitrides doped with Mn [Eq. (2)], $\Delta = 0.2$ eV, $m = 0.8m_0$. Exchange constants are discussed in the text.

The contribution to the indirect exchange interaction, we discuss in the paper, is quite general and may take place in other than III-V materials if proper positions of magnetic impurity levels provide an effective interspin coupling. As for the percolation mechanism of the ferromagnetic phase transition, however, its extrapolation to the II-VI materials is not straightforward due to the superexchange-induced antiferromagnetic coupling between magnetic atoms separated by a small distance.

In conclusion, we have discussed the specific contribution to the indirect exchange interaction in III-V-cubic and wurtzite materials that is caused by virtual impurity level–valence band electron excitations. As the indirect exchange interaction is short-ranged, the mean-field theory is not valid and we use a more adequate percolation picture of a phase transition. The contribution we calculated can explain ferromagnetism in GaAs(Mn) and possible ferromagnetism in wide band gap materials. As far as the absolute value of T_c is concerned, it depends on the values of p-d exchange interaction J_{pd} and the energy

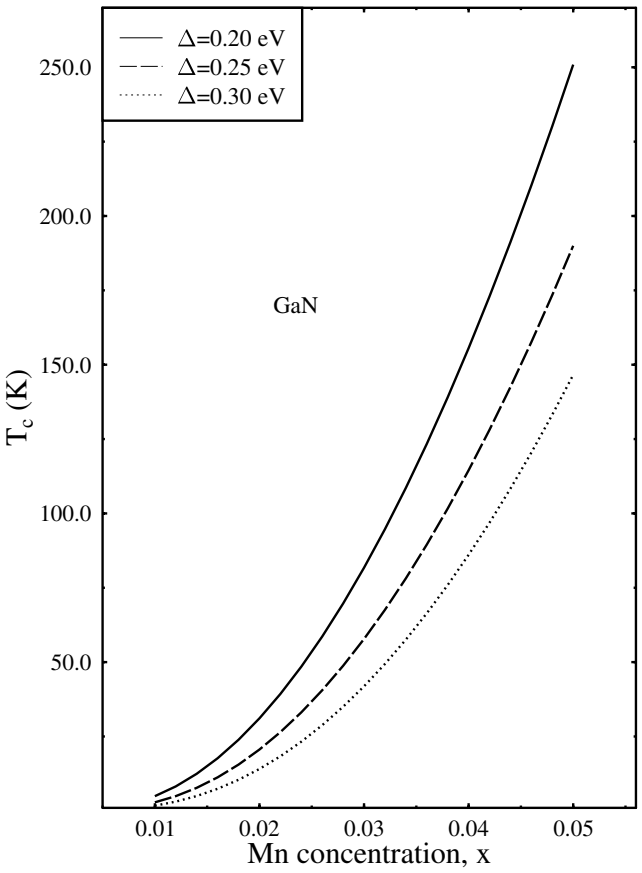

FIG. 3. Concentration dependence of the transition temperature [Eq. (2)] in GaN(Mn, Fe) for different values of the activation energy Δ.

gap between impurity and band electron levels Δ, which are uncertain to some extent, especially for the GaN material system. Further progress in understanding impurity ferromagnetism in III-V materials will depend mostly on growth and magnetic characterization of epitaxial layers GaN-InN-AlN(Mn, Fe), and further experimental studies of GaAs(Mn).

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