Ferromagnetism in magnetically doped III-V semiconductors

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(Received October 30, 2018)

The origin of ferromagnetism in semimagnetic III-V materials is discussed. The indirect exchange interaction caused by virtual electron excitations from magnetic impurity level in the bandgap to the valence band can explain ferromagnetism in GaAs(Mn) no matter samples are degenerated or not. Formation of ferromagnetic clusters and percolation picture of phase transition describes well all available experimental data and allows to predict the Mn-composition dependence of transition temperature in wurtzite (Ga,In,Al)N epitaxial layers.

PACS numbers: 75.50.Pp; 75.50.Dd; 72.80.Ey

Electronic and optoelectronic semiconductor devices, controlled by a weak magnetic field, and electric-field controlled ferromagnetism in semiconductors promise new functionality of memory, detector 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 non-volatile storage and logic. Efficiency of spin injection depends on a quality of interfaces, and all-semiconductor structures should benefit the performance of spin-electronic devices. Recent achievement in material research resulted in ferromagnetic semiconductor material lattice-matched to III-V semiconductors: highest ever ferromagnetic critical temperature in semiconductors ($T_c = 110$ K) has been observed in metallic samples of Ga$_{1-x}$Mn$_x$As ($x = 0.053$) 

The origin of ferromagnetism in III-V materials is not well understood. The explanation of ferromagnetism by holes-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, has been found in recent articles ³.⁴.

Despite the efforts, some difficulties arise in free carrier-based explanation of ferromagnetism in GaAs(Mn). First, nonzero $T_c$ has been observed in the low-carrier concentration samples, where holes are not degenerated. Second, holes 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 $R$. In the samples under consideration in Ref. ³ this is not a case since $L$ was estimated as short due to crystal imperfections, $L \approx (5 - 6.5)$ Å whereas Mn content $x = 0.053$ corresponds to $R = 6$ Å.

Free carriers contribute to the ferromagnetism in cubic III-V samples with degenerated holes, but until now it is not clear if this contribution is responsible for high $T_c$ or not. In wide-bandgap semiconductors the degenerated free carriers can hardly be obtained and RKKY-based explanation is also under the question. Recent prediction of room temperature ferromagnetism in wide-bandgap GaN(Mn) ⁴ is based on an assumption that crystal is degenerated. However, in real p-type Mn- or Fe- doped GaN samples holes are not degenerated.

Our point is that the RKKY mechanism is not an ultimate reason of ferromagnetism and high ferromagnetic transition temperature can occur even in non-degenerate 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 ⁵). 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. ⁷). If the Fermi level is inside the band, the excitations of electrons near Fermi momentum $\hbar \mathbf{k}_F$ 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 ⁸.

In this paper 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 works no matter the sample is degenerated or not and it could also be a reason of ferromagnetism.
in GaAs(Mn) as well as in wide bandgap materials like GaN(Mn). In non-degenerated sample, where Fermi level lies in the bandgap, this mechanism is the only possible one to mediate an interaction between localized spins.

The Bloembergen-Rowland-type indirect interaction between two magnetic ions, separated by the distance \( r \), is given as

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

(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), \( m \) is the reduced electron mass in the bands under consideration, \( \Delta \) is the smallest energy gap for electron excitations, and \( K_2(y) \) is the McDonald function. The indirect exchange interaction, Eq. (1), tends to known results in two limiting cases:

a) small distances (narrow-gap semiconductors) \[10\], \( r \ll r_0 \), \( J(r) \sim 1/r^4 \),

b) large distances \[6\], \( r \gg r_0 \), \( J(r) \sim r^{-5/2} \exp(-2r/r_0) \).

In a pure semiconductor, the smallest energy gap \( \Delta \) is the bandgap. We will use the expression 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 non-degenerated \( p \)-GaAs(Mn) the smallest gap is the activation energy of a hole at Mn atom \( \Delta \simeq 113 \text{ meV} \[1\] \), the reduced mass is the valence band density of state mass \( m \simeq 0.53 m_0 \). The characteristic length for GaAs(Mn) is \( r_0 \simeq 11 \text{ Å} \).

As the interaction is short-ranged, the mean field approximation is not helpful for the calculation of the ferromagnetic critical temperature \( T_c \). Instead, we have to use the percolation approach \[12\]. At certain temperature, the spins, coupled by a strong exchange interaction, form a ferromagnetic cluster. The cluster size \( R_{cl} \) is determined by the equation \( S(S+1)J(R_{cl}) = k_B T \). 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 \( R_{cl} = R_{perc} \simeq (B_c)^{1/3} \), where \( B_c \) is a geometrical factor. In the three-dimensional random-site model, this factor is given as \( B_c = 2.4 \) (Ref. \[13\]). The ferromagnetic critical temperature follows:

\[
k_B T_c = S(S+1)J(R_{perc}).
\]

(2)

The composition dependence of \( T_c \) comes from the average interspin distance, which in GaAs(Mn) has the form \( R_c = (3n^3/16\pi x)^{1/3} \). We used \( p-d \) exchange interaction \( J_{pd} = 2.5 \text{ eV} \[14\] \). Results of \( T_c \) calculation along with available experimental data are shown in Fig. 1.

Increase in Mn concentration beyond \( x = 0.055 \) most likely causes compensation, the Fermi level moves toward the conduction band and then appears to lie between the Mn acceptor level and a 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, that makes the exchange interaction small and \( T_c \) low (see Eq. (1)).

![FIG. 1. Mn concentration dependence of ferromagnetic transition temperature in GaAs(Mn).](image1)

![FIG. 2. Ferromagnetic transition temperature in wurtzite group III-Nitrides doped with Mn.](image2)
The prediction of the impurity band formation in GaN(Mn,Fe) was reported in Ref. [4]. In p-type group-III Nitrides the acceptor levels lie in the bandgap, not closer than 200-250 meV to the valence band. The average interspin distance in wurtzite GaN(Mn) is \( R = (3^{1/3} a^2 c/16\pi x)^{1/3} \), 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 densities in wurtzite GaN and cubic GaAs. This ratio is found as 1.95 (GaN), 1.45 (InN), and 2.163 (AlN). The calculations are done for \( m = 0.8 m_0 \), and the results are shown in Fig. 2.

![FIG. 3. Concentration dependence of the transition temperature for different values of the energy gap.](image)

The transition temperature, shown in Fig. 2, is sensitive to the value of the minimum energy gap \( \Delta \). At present, there is no much information about actual position of Mn or Fe levels in the bandgap of GaN-based materials. According to local density approximation (LDA) results for cubic GaN (Fe,Mn) [1], Mn gives rise to two peaks of density of states with one portion merging with 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 bandgap. Fig. 3 illustrates the \( \Delta \)-dependence of \( T_c \) in wurtzite GaN.

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 [3] and magnetic dichroism in optical absorption [3], observed in GaAs(Mn).

In conclusion, we have discussed the specific contribution to 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 more adequate percolation picture of phase transition. The contribution we calculated can explain ferromagnetism in GaAs(Mn) and possible ferromagnetism in wide bandgap materials. As far as absolute value of \( T_c \) is concerned, it depends on the values of \( p-d \) exchange interaction \( J_{pd} \) and the energy gap between impurity and band electron levels \( \Delta \), which are uncertain to some extent, especially for GaN material system. Further progress in understanding of impurity ferromagnetism in III-V materials will depend mostly on growth and magnetic characterization of epitaxial GaN-InN-AlN(Mn,Fe), and further experimental studies of GaAs(Mn).

We acknowledge J. Barnaš for reading the manuscript and useful comments. V.L. thanks H. Morkoc for fruitful discussions. V.D. is grateful to U. Krey for stimulating discussions and P. Bruno for the encouragement.

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