Interstitial Mn in (Ga,Mn)As: Hybridization with Conduction Band and Electron Mediated Exchange Coupling

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We investigate theoretically the possibility of n-type DMS based on III–V materials with Mn impurities in interstitial instead of substitutional positions, and discuss some situations when this can happen. We show that the d-states at interstitial Mn atoms in (Ga,Mn)As hybridize with both valence and conduction bands. The hybridization is strong enough to establish an indirect ferromagnetic coupling of the Mn magnetic moments mediated either by holes or by conduction electrons. Moreover, the Curie temperatures estimated within the mean-field theory are comparable with T_c obtained for conventional materials with the same concentration of Mn_{Ga}.

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1. Introduction

Dilute magnetic semiconductors (DMS) are derived from ordinary semiconductors by introducing a large amount (up to a few molar percent) of magnetic impurities. In the case of Mn-doped III–V semiconductors such as $Ga_{1-x}Mn_xAs$ most of the Mn atoms occupy regular cation positions, Mn_{Ga}, and act as acceptors [1]. In this way, Mn impurities not only bear magnetic moments but also supply holes that mediate a long-range ferromagnetic exchange coupling of the local moments. A minor part of Mn atoms occupy interstitial positions, Mn_{int}, and act as compensating double donors [2, 3]. The partial concentration x_i of Mn_{int} in

the as-grown materials is around $x/6$, which is sufficient to reduce the number of holes to one half. As a result, the ferromagnetic interaction becomes weaker. Besides the charge compensation, Mn_{int} tend to form antiferromagnetically coupled pairs with Mn_{Ga} [4, 5] and reduce the total magnetization.

In some cases, however, the number of Mn_{int} can exceed the number of Mn atoms in the regular positions. This is e.g. the case of GaAs–$Ga_{1-x}Mn_xAs$ hetero- and superstructures in which Mn_{int} are able to diffuse across the interface into GaAs while Mn_{Ga} remain fixed in their original positions. An enhanced concentration of the Mn_{int} may be expected also in the sub-surface region of $Ga_{1-x}Mn_xAs$ layers in the intermediate stage of the annealing. Finally, the balance of Mn_{Ga} and Mn_{int} is sensitive to the nature of the host material, as demonstrated recently in the case of (Ga,Mn)(As,P) [6], and it may turn in favor of Mn_{int}. Such tendency has been indicated theoretically for (Al,Ga,Mn)As mixed crystals [6].

It is important to know more about unusual materials with Mn atoms located preferentially in interstitial rather than in substitutional positions. The crucial question is how the d-states of Mn_{int} hybridize with the valence and conduction bands of GaAs and whether this hybridization is sufficient to stabilize the ferromagnetic order. It is the aim of this paper to analyze the hybridization within the frame of a tight-binding model, and to use density-functional calculations to obtain a realistic estimate of the exchange coupling between Mn_{int}.

2. Exchange coupling and the Curie temperature of GaAs doped with interstitial Mn

The magnetic interactions in DMS are characterized by the Kondo exchange constant J_{pd} and by the Curie temperature T_c. Within the mean-field approximation, J_{pd} is represented by a splitting of the spin-polarized valence band, $\Delta E_{val} = E_{val,\downarrow} - E_{val,\uparrow} = 4x/a^3 J_{pd}S$, where x is the concentration of Mn impurities, S their spin, and a the lattice constant. The Curie temperature is related to the energy E_{rev} required to flip just one local moment in otherwise perfectly ordered ferromagnetic state, $6k_BT_c = E_{rev}$.

Both ΔE_{val} and E_{rev} can be obtained from the coherent-potential approximation (CPA) description of the electronic structure of (Ga,Mn)As. We combine the CPA with the density-functional theory within the linear muffin-tin orbital method [7] and calculate the spin-polarized electronic structure for three series of (Ga,Mn)As: (i) GaAs doped with Mn_{Ga}, (ii) GaAs doped with Mn_{int} in the $T(As_4)$ positions, and (iii) GaAs doped with Mn_{int} in the $T(Ga_4)$ positions.

Figure 1 shows the Curie temperature as a function of Mn concentration for the three above-mentioned geometries. The values of T_c are similar for all considered kinds of Mn impurities. Neither the local bonding nor the type of carriers mediating the kinetic exchange seems to be of a special importance for the ferromagnetism, at least within the mean field approximation.

Also the calculated exchange constants J_{pd} for Mn in substitutional, $T(As_4)$, and $T(Ga_4)$ positions are close one to another (–144 meV nm^3, –135 meV nm^3,
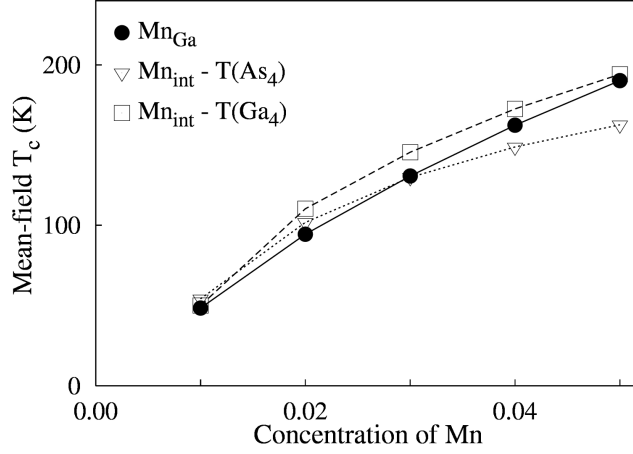
Fig. 1. Curie temperature for three bonding geometries of Mn.

and -111 meV nm^3). The closeness of the first two values reflects the fact that Mn impurity has in both cases As neighbors. The third value is lower because the contribution of Ga states to the valence band is smaller than the contribution of As states.

3. Hybridization of Mn d-states with the Bloch states

To analyze the hybridization of the d-states at Mn atoms in various positions with the band states of the host semiconductor we use a tight-binding method. Schematically, the Hamiltonian matrix consists of four blocks, describing the bands of the host semiconductors (H_{bb}), additional states at the Mn impurities (H_{aa}), and their hybridization (H_{ba}),

$$H = \begin{pmatrix} H_{bb} & H_{ba} \\ H_{ba}^+ & H_{aa} \end{pmatrix}. \tag{1}$$

H_{bb} is, as usual, represented in the sp^3-basis appropriate for the valence and the lowest conduction bands [8]. The off-diagonal hybridization matrix H_{ba} is constructed according to the Slater–Koster formulae and parameterized according to the Harrison rules [9]. Finally, with respect to the low concentration of Mn, we can neglect any interatomic matrix elements of H_{aa} and represent this part of the Hamiltonian only by atomic levels of the extra states (Mn d-states for Mn$_{\text{Ga}}$, a complete set of s-, p-, and d-states for Mn$_{\text{int}}$).

To estimate the strength of hybridization of a particular Bloch state with Mn d-states we find a unitary matrix $U_{bb}(k)$ that diagonalizes H_{bb} and construct a partly diagonalized total Hamiltonian $\tilde{H} = U^{-1}HU$ by using the unitary transformation

$$U = \begin{pmatrix} U_{bb}(k) & 0 \\ 0 & I \end{pmatrix}. \tag{2}$$

Clearly, the matrix elements of $\tilde{H}_{ba}(k) = U_{bb}^{-1}(k)H_{ba}(k)$ define the hybridization of a particular Bloch state with the d-states. It should be pointed out that the k-dependence of $\tilde{H}_{ba}(k)$ reflects both k-dependent form factors in $H_{ba}(k)$ and varying orbital composition of the bands.

We characterize the strength of this hybridization by using a single quantity

$$\eta_n(k) = \Big[\sum_m |(\tilde{H}_{ba}(k))_{nm}|^2 \Big]^{1/2} \tag{3}$$

with summation running over the d-states.

The results for the two uppermost valence bands and for the lowest conduction band are summarized in Fig. 2 comparing $\eta_n(k)$ for Mn in the regular cation position, and in two inequivalent tetrahedral interstitial positions $T(As_4)$ and $T(Ga_4)$, respectively. In the center of the Brillouin zone, the d-states hybridize with the valence bands and the strength of the hybridization is almost the same for Mn_{Ga} and for Mn_{int} in the $T(As_4)$ positions. The hybridization does not change much in the physically relevant part of the Brillouin zone around the Γ-point. It should be mentioned, however, that $\eta_v(k)$ diminishes in the L-point for the non-degenerate valence band from symmetry reasons. The reduced value
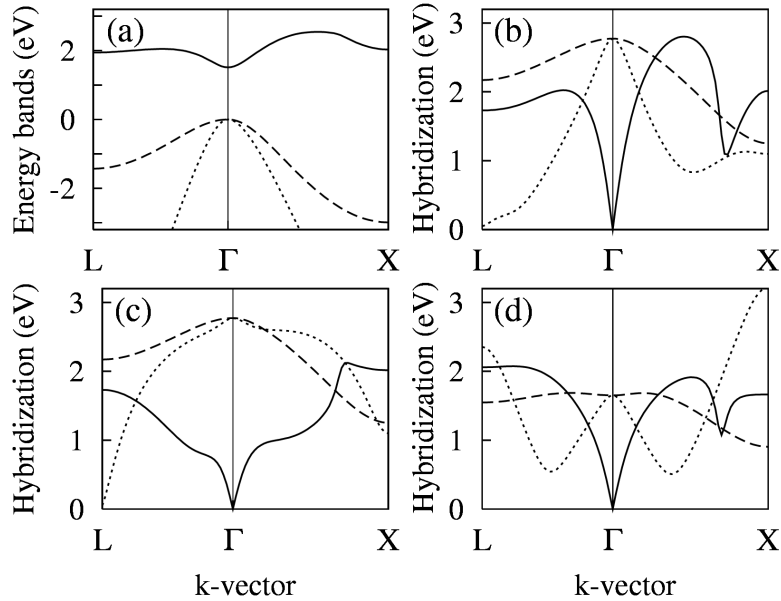

Fig. 2. Hybridization $\eta_n(k)$ of Mn d-states with the highest valence bands (dashes and dotted lines) and with the lowest conduction band (solid line): (a) energy dispersion of the respective bands in GaAs, hybridization for Mn_{Ga} (b), Mn_{int} in $T(As_4)$ (c), Mn_{int} in $T(Ga_4)$ (d).

and different shape of $\eta_v(k)$ for Mn_{int} in the $T(Ga_4)$ positions results from the contribution of Ga orbitals to the valence band.

The hybridization with the conduction band is more complicated. It starts from zero in the Γ-point and shows apparent bending at the point where the orbital composition changes due to interaction with another conduction band. The most important feature is that $\eta_c(k)$ arises quickly with increasing wave vector and, in all three cases, becomes comparable to $\eta_v(0)$ for sufficiently strong doping. As shown recently [10, 11], this is the mechanism leading to the ferromagnetic exchange coupling in n-type DMS with the substitutional Mn. We see now that this is also the case of n-type DMS with Mn_{int}.

It should be pointed out that, in contrast to the n-type III–V DMS with the substitutional Mn, the systems with Mn_{int} could be realized, e.g. on the basis of (Al,Ga)As. A more detailed theoretical analysis of systems with Mn_{int} and of their growth from the point of view of formation energies will be published elsewhere.

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