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Ab-initio study of exchange constants and electronic structure in diluted magnetic group-IV semiconductors

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Abstract. Exchange-constants have been evaluated from first-principles in Mn-doped Ge, mainly focusing on the effects of the impurity concentration and of the arrangement of Mn-atoms in the semiconducting matrix. As expected, the Mn-concentration strongly affects the magnitude of the exchange constants (especially between Mn as first-nearest-neighbors (NNs) in the cation position). Interestingly, the arrangement of Mn atoms is found to be relevant for the behavior of the second-NN exchange-constant along the [110]-bonding direction, which shows either a strongly ferromagnetic or a marked antiferromagnetic behavior, depending on whether the interaction is mediated by a Ge or by an Mn atom, respectively. This suggests that, at least for rather high values of the doping concentration (≈10%), a detailed knowledge of the Mn positions in the host is required for a careful prediction of the exchange constants and, therefore, of the ordering Curie temperature in Mn-doped Ge. The analysis of the impurity- and host-induced effects on the exchange constants is carried out by comparing (i) Mn- and Cr-doped Ge and (ii) Mn-doped Ge and GaAs. Our findings regarding the global weak antiferromagnetism for CrGe confirm that ferromagnetism in diluted magnetic semiconductors requires the presence of holes, whereas Ge and GaAs appear rather similar as for the exchange constants, both showing strong environmental effects.

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Diluted magnetic semiconductors (DMS), i.e. mainstream semiconductors (SCs) doped with
small amounts (<10%) of transition metals (TM), have been at the center of increasing interest
(see for example [1] and references therein) since the discovery of their ferromagnetism
persisting up to ~150–200 K. However, most of the attention has been diverted toward Mn-
doped III–V semiconductors, the DMS prototype being GaMnAs; on the other hand, relatively
little interest has been devoted to Mn-doped group-IV SCs (such as MnGe and MnSi), despite
the obvious role they could play in future spintronics, mainly due to compatibility with the
current silicon-based technology.

First-principles calculations can be very helpful in addressing the nature of the exchange
coupling of TM impurities within the semiconducting matrix on the basis of the underlying
electronic structure, in terms of different hosts and of different TMs in possibly different
concentrations. In 2002, carrier-mediated ferromagnetism was detected in MnGe alloys grown
via molecular beam epitaxy (with a Curie temperature of ~100 K) and confirmed on the basis
of density functional calculations [2]. Pioneering *ab-initio* calculations were performed by
Stroppa *et al* [3]: it was shown that Mn in both Si and Ge is at the same time a source of
holes as well as of localized magnetic moment equal to about 3 $\mu_B$. The electronic structure of
MnGe alloys was found to show a half-metallic behavior and an overall ferromagnetic (FM)
coupling. A comparison among different TM as dopants for Ge revealed that Mn is indeed
the best candidate, since it grants holes that can mediate FM coupling as well as relatively
high moments [4]. While appealing from the theoretical point of view, the growth of an
Mn$_x$Ge$_{1-x}$ alloy with an appreciably homogeneous dilution of Mn [5] in the semiconducting
host was found to be a challenge: the formation of energetically competing nanoscale-sized
phases [6, 7] (in particular showing the hexagonal crystallographic phase Mn$_5$Ge$_3$ [8]) occurs
even under small concentrations of Mn and on a wide range of growth conditions (in terms
of substrate temperatures, growth rates, etc). More recently, nanoscale spinodal decomposition
was suggested to occur in Mn-doped Ge samples, with the formation of Mn-rich nanocolumns
showing a high FM ordering temperature (~400 K) [9].

In this contribution, we mainly focus on the *ab-initio* exchange-constants (obtained through
a recently implemented frozen-magnon scheme, see below) of Mn-doped Ge alloys. In fact,
despite several theoretical studies focused on either Mn-doped group IV or on first-principles
exchange-constants in DMS [10, 11] ([12] and references therein) exchange interactions in
Mn-doped Ge were only marginally investigated [13, 14]. Surprisingly, we find that there is
a strong ‘environmental’ effect: along specific crystallographic directions, the values of the exchange constant $J_{ij}$ (i.e. the Heisenberg-like magnetic interaction between Mn at sites $i$ and $j$) strongly depends on the distribution of the Mn atoms around sites $i$ and $j$. Environmental effects were also recently reported by Sato et al in DMS via a cluster-embedding method [15]. Of course, these findings imply that a careful prediction of the Curie ordering temperature requires an accurate knowledge of the real distribution of the Mn atoms in the host matrix [16, 17]. In order to have a deep understanding of the exchange constants in group-IV DMS, we focus on the dependence on (i) the concentration (by examining Mn doping varying from 12.5 up to 50%); (ii) the semiconducting host (by examining difference and similarities of Mn-doped Ge and Mn-doped GaAs) and (iii) the impurity (by examining a different behavior of Mn-doped versus Cr-doped Ge).

2. Structural and computational details

We have carried out first-principles calculations within the density functional theory using the generalized gradient approximation (GGA) [18] to the exchange–correlation potential. The all-electron full-potential linearized augmented plane-wave (FLAPW) [19] method in the FLEUR implementation [20] was used, choosing muffin-tin radius equal to 2.25 for Mn, Ge, As, Cr and to 2.31 for Ga. A cut-off of 3.6 au was used in the plane-wave expansion and the Monkhorst–Pack [21] method was used to select the special $k$-points for the Brillouin-zone sampling (up to about 280 $k$-points in the smallest zincblende unit-cell). Due to the failures of bare GGA in predicting the correct semiconducting behavior for pure Ge, we used the LDA + $U$ (or GGA + $U$) approach [22] and added a Hubbard $U$ on Ge p states (forcing the density matrix to be fixed so as to fully occupy the p-bands). In fact, although the GGA + $U$ approach is generally used for systems with strongly correlated electrons, it was successfully applied to SCs [23] to partially correct the deficiencies of a bare GGA treatment even in SCs. A value of $U = 2$ eV was found to reproduce the correct experimental band gap in pure Ge ($E_{\text{gap}} \sim 0.65$ eV) and was consistently applied in all the simulations (i.e. in CrGe and GaMnAs—on the As p-states).

In order to investigate the behavior of Mn-doped Ge at finite temperatures, we start from the assumption that the system can be described by a Heisenberg Hamiltonian,

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} \mathbf{M}_i \cdot \mathbf{M}_j.$$  \hspace{1cm} (1)

The magnetic moments localized on the lattice sites $i$ and $j$ are considered as classical vectors $\mathbf{M}_i$, with the assumption that their magnitudes $M$ are constant. The exchange interaction between the magnetic moments is described by the pair interaction $J_{ij}$. Using the frozen-magnon approach, as implemented in the FLEUR code [20, 24], we calculated the $J_{ij}$ coefficients for several different concentrations and atom arrangements.

Let us now give some structural details of the simulated structures. First of all, since we aim at a comparison between MnGe and the mainstream GaMnAs (where Mn substitutes for Ga), we put Mn only on the ‘cationic’ site with reference to the host zincblende-like structure with two inequivalent atoms per unit-cell (and not diamond-like structure, with two equivalent atoms per unit-cell).

In order to simulate both concentration and environmental effects, we considered the following systems, each containing one Mn atom (located in the origin) per unit cell: (i)
Figure 1. Unit cells (marked with straight lines): (a) $x = 50\%$, (b) $\delta$-layer, $x = 25\%$, (c) $\delta$-layer, $x = 12.5\%$, (d) ‘Mn [110]-rows’, $x = 12.5\%$ and (e) ‘simple cubic’, $x = 12.5\%$. Mn and Ge atoms are denoted by green and gray spheres.

‘zincblende’ structure (in which all the cations are replaced by Mn, $x = 50\%$, 2 atoms per unit-cell), (ii) ‘$\delta$-layer’, $x = 25\%$ (in which a tetragonal unit-cell with 4 atoms per unit-cell simulates a [001]-ordered superlattice where one of every four layers is fully replaced by Mn atoms); (iii) ‘$\delta$-layer’, $x = 12.5\%$ (in which a tetragonal unit-cell with 8 atoms per unit-cell simulates a [001]-ordered superlattice where one of every eight layers is fully replaced by Mn atoms); (iv) ‘Mn [110]-rows’, $x = 12.5\%$ (in which an orthorhombic unit-cell with 8 atoms per unit-cell contains alternating rows of Mn and Ge running along the [110] axis), (v) ‘simple cubic’ (SC), $x = 12.5\%$ (a cubic unit-cell with 8 atoms per unit-cell). Structures (i)–(v) are schematically shown in figure 1. Our simulations for relatively large Mn concentrations are meaningful with respect to a realistic comparison with experiments [9], recently reporting Mn-rich regions in Ge (i.e. concentration close to MnGe$_2$). Although relevant for comparison with some experiments [2, 5], where the dopant Mn concentration is of the order of a few per cent, calculations for lower concentration of Mn (i.e. larger unit-cells) were not performed, since they would, with the method used here, be computationally too heavy. For DFT simulations performed for low Mn concentrations, we refer the reader to the extensive discussion reported in [13]. We note, however, that we do not expect qualitative changes of the obtained behavior of the exchange interactions at lower concentrations, since the bandwidth of the impurity band depends on the Mn concentration $c$ as $\sqrt{c}$, changing slowly as the concentration drops.

3. Hybridization between TM d states and SC valence band

Let us now recall the mechanism that leads to an efficient hybridization between Mn 3d states with the SC valence band (cf figure 2). Let us start with an Mn atom showing its 3d levels split...
in minority and majority due to exchange; when put in a tetrahedral environment (such as that of an Mn impurity in an SC) there is a further crystal-field splitting into doubly degenerate $e_g$ levels and triply degenerate $t_{2g}$ levels. Now let us consider the interaction of Mn states with electronic states on the semiconducting side. From the symmetry point of view, $e_g$ cannot mix well with any of the relevant SC states and remain more or less ‘non-bonding’ even in DMS; on the other hand, $t_{2g}$ states strongly interact with (say) Ge p states, by forming a bonding–antibonding set of states. In particular, when counting the available electrons (7 - $d^5 - s^2$ from Mn and 4 - $s^2 - p^2$ from the group-IV atom) and available states, we end up with a diluted magnetic group-IV semiconductor, with a local moment of 3 Bohr magnetons and two holes in the majority triply-degenerate antibonding $t_{2g}$ level that crosses the Fermi energy. In the minority spin-channel, the bonding $t_2$ (non-bonding $e$) level is fully occupied (empty) so that a gap is formed, at the origin of the well-known half-metallic behavior (i.e. 100% spin-polarized electrons at the Fermi level, $E_F$).

Incidentally, we note that, according to a similar mechanism, in the case of Cr-doped Ge, we expect a local moment of 2 $\mu_B$ (with the majority $e_g$ states as highest occupied level) and no-holes in the $t_{2g}$ level, whereas in the case of Mn-doped GaAs case, we expect a high moment of 4 $\mu_B$ with one hole in the $t_{2g}$ level.

4. Mn-doped Ge: environmental and concentration effects

The exchange constants were evaluated for all the systems studied and the results are reported in figure 3 versus the $R/a$ ratio, where $R$ is the Mn–Mn distance and $a$ is the experimental cubic lattice constant ($a_{Ge} = 5.658 \text{ Å}$). In order to facilitate the discussion reported below, we denote as $J_1$, $J_2$, $J_3$ and $J_4$ the exchange constants for the first ‘cation’ nearest-neighbor (NN) (along the [110]-direction, $R = a/\sqrt{2}$), the second NN (along the [100]-direction, $R = a$), the
Figure 3. The effects of different concentrations and atom arrangements on the magnetic interaction constants $J_{ij}$: $x = 12.5\%$, Mn δ-layer (filled blue circles), $x = 12.5\%$, Mn-rows (filled red diamonds), $x = 12.5\%$, Mn in a simple cubic lattice (filled green squares), $x = 25\%$, Mn δ-layer (filled purple up-triangles), $x = 50\%$, zincblende-like MnGe (filled yellow left-triangles). Inset: notation for the exchange constants $J_1$, $J_2$, $J_3$ and $J_4$ in a zincblende MnGe lattice.

third NN (along the [112]-direction, $R \sim 1.22a$) and the fourth NN (along the [110]-direction, $R = \sqrt{2}a$), respectively (see inset in figure 3). A careful look at the arrangements of Mn in the different unit-cells (cf figure 1) shows that, of course, there is not a couple of Mn between which to evaluate the corresponding exchange constant at all the distances (for example, in the ‘simple cubic’ case, there is no reported first NN $J_1$ because there are no Mn separated by $\sqrt{2}a$).

Firstly, we notice that the interaction is generally short-ranged, characteristic for DMS. A striking feature is that the only interactions which are essentially different from zero are the ones between an Mn atom with its first and (in some cases) second Mn neighbor along the [110]-direction and they are predominantly FM, in agreement with the previous studies [13]. As evident from figure 3, exchange constants for distances $R > a\sqrt{2}$ are negligible and will therefore not be discussed in the following. As already noted in different works, the exchange constants show a markedly anisotropic behavior [25] and they are much stronger along the [110]-direction, which—in zincblende-like SCs—is the direction along which the bonding chains are oriented and is consistent with the aforementioned p–d hybridization. Before we move to the discussion of the environmental effects, we remark that the electronic structure and related exchange constants might be affected by the treatment of correlations beyond the standard LDA/GGA. For small/medium band gap semiconductors, the introduction of the Hubbard $U$ on Mn d states generally strengthens the damping of the exchange parameters with distance (recall that the damping arises due to half-metallicity and this increases due to larger band gap in the minority spin-channel within LDA + $U$ [13]). Moreover, as argued in [11], the hole properties are affected by the introduction of beyond-LDA correlations: there is a strong
increase in the hole localization and decreased p–d hybridization. For a careful discussion of the effects on the exchange constants and related Curie temperatures, we refer the reader to [11]–[13].

As for the environmental effects, let us now focus on the case of \( x = 12.5\% \), since it remarkably shows the dramatic consequences on the exchange-interaction of the arrangement of dopant atoms in the host matrix. For \( J_1 \) and \( J_2 \), the values of the exchange constants appear rather independent of the arrangement of the Mn atoms, confirming what was already known by the previous studies [14], i.e. that the first NN \( J_1 \) is strongly FM (see similar values for \( x = 12.5\% \) for \( \delta \)-layer and ‘Mn-rows’) and that the second NN \( J_2 \) is very small (see similar values for \( x = 12.5\% \) in all the three considered arrangements). However, when looking at \( J_4 \) (i.e. the fourth NN \( J_4 \), i.e. the second one along the \([110]\)-direction), we observe that there can be two different situations: the sequence of atoms connecting the two Mn separated by \( \sqrt{2}a \) and along the \([110]\)-bonding direction is (\( a \)) Mn–Ge–Ge–Ge–Mn (i.e. the middle cationic position is occupied by a Ge atom) or (\( b \)) Mn–Ge–Mn–Ge–Mn (i.e. the middle cationic position is occupied by another Mn atom). As shown in figure 3, this difference induces dramatic changes: when the interaction is mediated via a Ge atom (case \( a \)), it is strongly FM (see both the \( x = 12.5\% \) systems denoted as ‘Mn-rows’ and ‘Mn’ (simple cubic), whereas it turns to be strongly antiferromagnetic (AFM) when the interaction is mediated via an Mn atom (case \( b \), cf the \( x = 12.5\% \) systems denoted as ‘Mn-rows’ and \( \delta \)-layer). The origin of this FM-versus-AFM behavior is not easy to disentangle; in fact, it involves fourth NN interactions and common models to describe exchange mechanisms are therefore not particularly adequate, since they generally focus on first-NN interactions and seldom do they take into account environmental effects.

Let us now turn to the concentration dependence of the exchange constants.

As already pointed out for the diluted case (\( x = 12.5\% \)), only \( J_\text{s} \) for \( R \) smaller than \( \sim 1.5a \) are relevant. Furthermore, due to the magnetic screening, the range of the magnetic interactions becomes even shorter with an increasing concentration of Mn atoms, and for the case of zincblende structure, it is limited to the first neighbors only.

Although we are dealing with several types of inhomogeneous distributions of Mn atoms and the environmental effects are pronounced, due to the high dopant concentrations and the aforementioned short range of the magnetic interactions, we attempt a mean-field evaluation of the Curie temperature, \( T_{\text{MF}}^C = M^2 \sum_j J_{0j}/3 \), where \( M \) stands for the magnetic moment of Mn and \( J_{0j} \) for an interaction of an Mn atom at a fixed site \( 0 \) with another Mn atom at site \( j \). For comparison, we have also evaluated the Curie temperature of MnGe in zincblende structure using the Monte Carlo method and obtained a value of approx 1000 K. The mean-field result, \( T_{\text{MF}}^C = 1370 \) K, is, as expected, somewhat higher than the one obtained by the Monte Carlo method, but from the mean-field calculations valuable information about the trends can still be extracted. We further remark that—for the zincblende case—our results (both for the exchange constants as well as Curie temperatures within mean-field) are in qualitative agreement with those reported in [26] and the small differences (such as higher \( T_{\text{c}} \) in our work) can be attributed to the introduction of the Hubbard-\( U \) on the Ge-p states as well as to differences in the implementation method (ASW in [26] and FLAPW in the present work). An interesting result is that the dependence of \( T_{\text{MF}}^C \) seems to follow a square-root behavior with \( n \), i.e. the number of the first Mn neighbours on the cation (fcc) sublattice. This is shown in figure 4, where the \( \sqrt{n} \)-fit is plotted with a dashed line (we should note here that in the case of a (simple cubic (SC) Mn-sublattice, the ground state we find is a non-collinear one, so that in this case \( T_{\text{MF}}^C = 0 \). The square-root behavior is reminiscent of the work by Sato et al [27], who investigated

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Figure 4. Mean field $T_C$ versus the number of Mn first neighbors on the cation sublattice $n$. The dashed line represents the $\sqrt{n}$-fit.

Mn-doped III–V semiconductors within a double-exchange model. According to their findings and the general idea of double-exchange, the $t_{2g}$ impurity band at the Fermi level broadens upon increasing the concentration of Mn atoms and this broadening stabilizes the ferromagnetism, with an energy gain proportional to the bandwidth of the impurity band. Sato et al showed, using tight-binding description, that this $t_{2g}$ bandwidth is proportional to the square root of the concentration of Mn atoms, $\sqrt{c}$, which finally leads to a $\sqrt{c}$-dependence of the calculated mean-field Curie temperature $T_C^{MF}$. A similar mechanism could be at play here, where the concentration $c$—due to the short-rangedness of the $J$s—is replaced by the number of NN, $n$.

5. Dependence on dopant: Cr versus Mn doping in Ge

Let us now examine a different dopant: instead of Mn, we will consider Cr impurities in Ge. One electron less in this case means that the antibonding majority $t_{2g}$ states (figure 2) are now empty and the Fermi level lies energetically below them and just above the filled majority $e_g$ states. The density of states (DOS) of FM Cr-doped Ge for the case of 25% cation sublattice doping with rows along the [110]-direction is shown in figure 5. For comparison, the DOS of Mn-doped Ge with the same atom arrangement is also shown with a dashed line. The positive values of the DOS represent the majority-spin DOS and the negative ones, the minority-spin DOS.

The bands in the two cases seem to be just rigidly shifted with respect to each other, the difference being that the Fermi level in Cr-doped Ge lies between two peaks in the majority-spin direction, in the region of very low DOS. In this case, no energy is gained through the broadening of the (unoccupied) antibonding $t_{2g}$ majority states and the Zener exchange which
stabilizes ferromagnetism in the case of the Mn dopant (see also discussion below) plays no role here. An AFM ground state is stabilized instead, possibly through the super-exchange interaction. This is also reflected in the calculated values of the exchange parameters $J_{ij}$ (figure 6), which are much weaker and have the opposite sign of the ones characterizing Mn interactions in the same atom arrangement. It is often said, in other words, that ferromagnetism in DMS is hole-mediated. The example we considered here confirms that the presence of the holes at the Fermi level (i.e. partially filled $t_{2g}$ bands crossing the Fermi level) is necessary for stabilizing ferromagnetism in these materials.

6. Dependence on host: Mn-doping of Ge versus GaAs

In order to have a better understanding of the exchange constants in TM-doped group-IV SCs, we compare the exchange coupling constants in Mn-doped Ge and Mn-doped GaAs, each with 1 Mn over 8 atoms per unit cell and considering two different arrangements of the dopant atoms: the ‘δ-layer’ and ‘TM rows along [110]’. In both the SCs, Mn d states are positioned lower with respect to the main semiconducting valence band than, for instance, in larger-gap SC such as GaN, where the Mn d states are located above the valence band of the host. Thus, we expect the FM exchange to present partially Zener p–d character, at variance with Mn-doped GaN, where the double-exchange prevails. Therefore, still in the framework of generally short-ranged $J_s$ in DMS, in both the Ge and GaAs cases, we expect somewhat longer ranged interactions compared to Mn-doped GaN, where the exchange interaction is very strong for first-NNs but decays very fast as the Mn–Mn distance increases. We note that the double-exchange character of the interaction in Mn-doped Ge is enhanced by the Hubbard $U$ applied on the p-states of Ge, pushing them to lower energies.

Figure 5. Total DOS of Cr- (solid lines) and Mn-doped (dashed red lines) Ge, 12.5% doping, rows along [110].
Figure 6. Exchange constants in Cr- (black circles) and Mn-doped (red diamonds, values divided by 10) Ge. In Mn-doped Ge, hole-mediated Zener p–d and double-exchange stabilize ferromagnetism, while super-exchange makes the ground state of Cr-doped Ge AFM.

As shown in figure 7, there are several issues that are worth discussing when comparing Mn-doped Ge and GaAs: (i) the first-NN exchange constant is much larger (by about a factor of two) in Ge with respect to GaAs. This is in agreement with what was previously found for zincblende compounds MnAs and MnGe [26] and attributed to the more efficient mediation by the group-IV versus group-V sp atoms of an FM Mn–Mn short-range interaction. As far as the second-NN along the [110]-direction is concerned, the comparison between Ge and GaAs is strongly affected by the specific Mn arrangements: as already pointed out, $J_2$ through the Mn atom in the cation sublattice shows an AFM behavior. In Ge, however, $J_2$ is strongly AFM, whereas in GaAs it is still AFM, but substantially negligible. On the other hand, when the $J_2$ interaction goes through an sp atom in the cation sublattice and it is strongly FM, it is substantially equal for Ge and GaAs. Therefore, we expect a global behavior of Mn-doped Ge and GaAs to be rather similar in terms of Curie temperatures. For the ‘$\delta$-layer’ and for the ‘[110]-rows’, we have not tried to estimate the ordering temperatures via a Monte Carlo approach; indeed, due to the basically two-dimensional and one-dimensional characters of the Mn arrangements in the digital and TM-rows structures, long-range ferromagnetism within the bare Heisenberg model should be forbidden according to the Mermin–Wagner theorem. In order to achieve a long-range ordering, one should include in the model Hamiltonian an anisotropy term, which goes beyond the scope of the present work.
7. Conclusions

First-principles simulations have been carried out for TM-doped Ge, mainly focusing on the exchange interactions calculated by means of the frozen-magnon approach. Our results show that, at least for relatively high concentrations (of the order of 10%), there is a strong ‘environmental’ effect: some of the exchange coupling constants strongly depend on the specific arrangement of the surrounding Mn atoms. In particular, we find that the second-NN interaction along the [110]-crystallographic axis is strongly FM if the [110]-atomic chain that connects the two interacting Mn atoms is composed of a sequence Mn–sp–sp–sp–Mn, whereas it shows an AFM behavior when the sequence is as Mn–sp–Mn–sp–Mn. These findings are particularly relevant in the prediction and optimization of the resulting Curie temperature of a DMS: engineering the arrangement of the dopant atoms in the host matrix so as to maximize the number and strength of FM interactions opens the way toward a promising increase of the resulting Curie temperature.

The comparison between Cr- and Mn-doped Ge shows that most of the Cr–Cr interactions have a weak overall AFM character, consistent with the general argument that ferromagnetism in DMS is hole-mediated and, therefore, the lack of holes (as happens in the semiconducting Cr-doped Ge) destroys the FM interaction. Furthermore, Mn-doped Ge and GaAs appear rather similar: both show a strong ‘environmental’ effect in the second-NN interaction along the [110]-direction. Ge shows a much stronger NN FM interaction, whereas the second-neighbor interaction through an Mn in the cationic positions in GaAs appears ‘less’ AFM than in Ge.

Figure 7. Exchange constants in Mn-doped semiconductors for $x = 12.5\%$: MnGe with Mn δ-layer (filled blue circles), MnGe for Mn-[110]-rows (filled red diamonds), GaMnAs with Mn δ-layer (empty blue triangles) and GaMnAs with Mn-[110]-rows (empty red squares).
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