

Invited Lecture

FIRST-PRINCIPLES STUDY OF MATERIALS FOR SPINTRONICS APPLICATIONS

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We report the density-functional-theory calculations of the exchange interactions and Curie temperature for a series of III-V, II-VI diluted magnetic semiconductors (DMS) and Co-based half-metallic full Heusler alloys. The calculation of the exchange parameters is based on the frozen-magnon approach. The Curie temperature is calculated within the mean-field approximation to the classical Heisenberg Hamiltonian. For DMS we focus the discussion on the role of the holes in the establishing the ferromagnetic order in various systems. Our calculations of the exchange interactions for Heusler alloys show that in this system the inter-sublattice exchange interactions play the main role in the thermodynamics of the system.

1. INTRODUCTION

An important current problem on the way to the practical use of the spin-transport in semiconductor devices is the design of the materials that make possible the injection of spin-polarized electrons into a semiconductor at room temperature. The most promising classes of materials are the diluted magnetic semiconductors (DMS) and half-metallic Heusler alloys. A strong interest to the DMS was attracted by the observation¹ in Ga_{0.947}Mn_{0.053}As of the ferromagnetism with the Curie temperature (T_c) as high as 110 K. Half-metallic Heusler alloys have been intensively studied theoretically^{2,3,4} and experimentally^{5,6,7} as possible sources of spin-polarized carriers for spintronics applications. Among the properties useful for the spintronics are high Curie temperature, high electron spin polarization at the Fermi level, small lattice mismatch with compound semiconductors.

To design materials with Curie temperature higher than room temperature the knowledge of physical mechanisms governing the exchange interactions in DMS is of primary importance. The theoretical works on the ferromagnetism in the DMS systems can be separated into two groups. The first group models the problem with an effective Hamiltonian containing experimentally determined parameters. This part of the studies is

recently reviewed in Refs. (8, 9, 10). Different assumptions concerning the energy position and the role of the 3d states of the magnetic impurities are formulated.

The second group of theoretical studies is based on the parameter-free calculations within the density functional theory (DFT) (see, e.g., reviews Refs. (11, 12) and more recent work Refs. (13, 14, 15, 16, 17)).

In this paper we report DFT calculations for a number of III-V, II-VI DMS and Co-based half-metallic full Heusler alloys. To develop a general platform for discussion of various systems we focus on the role of the holes in the magnetism of DMS. First, we reexamine the importance of the holes for establishing the long-range ferromagnetic order. Then we discuss the properties of the holes that are relevant for the ferromagnetic ordering and consider quantitative characterization of these properties.

The DMS part of the calculations is performed within the local density approximation (LDA) to the DFT. For the Heusler alloys we used generalized gradient approximation (GGA) for the exchange correlation potential.

2. CALCULATIONAL TECHNIQUE

The calculational scheme is discussed in Refs. (13, 14, 18) to which the reader is referred for more details. The DMS studies are based on DFT calculations for supercells of semiconductor crystals with one cation atom replaced by a Mn atom. The size of the supercell determines the Mn concentration. Most of the calculations are performed for the zinc-blende crystal structure of the semiconductor matrix.

To calculate the interatomic exchange interactions we use the frozen-magnon technique and map the results of calculation of the total energy of the helical magnetic configurations

$$\mathbf{e}_n = (\cos(\mathbf{q}\mathbf{R}_n) \sin \theta, \sin(\mathbf{q}\mathbf{R}_n) \sin \theta, \cos \theta) \quad (1)$$

onto a classical Heisenberg Hamiltonian

$$H_{cl} = - \sum_{i,j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j \quad (2)$$

where J_{ij} is an exchange interaction between two Mn sites (i, j) and \mathbf{e}_i is the unit vector pointing in the direction of the magnetic moment at site i , \mathbf{R}_n are the lattice vectors, \mathbf{q} is the wave vector of the helix, polar angle θ gives the deviation of the moments from the z axis.

Within the Heisenberg model (2) the energy of frozen-magnon configurations can be represented in the form

$$E(\theta, \mathbf{q}) = E_0(\theta) - \sin^2 \theta J(\mathbf{q}) \quad (3)$$

where E_0 does not depend on \mathbf{q} and $J(\mathbf{q})$ is the Fourier transform of the parameters of the exchange interaction between pairs of Mn atoms:

$$J(\mathbf{q}) = \sum_{j \neq 0} J_{0j} \exp(i\mathbf{q}\mathbf{R}_{0j}) \quad (4)$$

Performing back Fourier transformation we obtain the parameters of the exchange interaction between Mn atoms:

$$J_{0j} = \sum_{\mathbf{q}} \exp(-i\mathbf{q}\mathbf{R}_{0j}) J(\mathbf{q}) \quad (5)$$

The Curie temperature is estimated in the mean-field (MF) approximation

$$k_B T_{MF}^C = \frac{2}{3} \sum_{j \neq 0} J_{0j} \quad (6)$$

We use a rigid band approach to calculate the variation of exchange parameters and Curie temperature with respect to electron occupation. We assume that the electron structure calculated for a DMS with a given concentration of the 3d impurity is basically preserved in the presence of defects. The main difference is in the occupation of the bands and, respectively, in the position of the Fermi level.

The Heusler alloys have several magnetic atoms per unit cell. In this case the exchange parameters are divided into two groups: inter-sublattice (Mn-Co) and intra-sublattice (Mn-Mn, Co-Co). The intra-sublattice exchange parameters are calculated as discussed above. The generalization of the frozen-magnon approach to the case of inter-sublattice interactions is discussed in Ref.23. The Curie temperature of a many-sublattice system is estimated as a solution of a matrix problem.²³

3. RESULTS FOR (GaMn)As, (GaCr)As, (GaFe)As

Next we consider calculations for three III-V DMS: (GaMn)As, (GaMn)As and (GaFe)As. Figure 1 presents the DOS of the systems for the impurity concentration of 3.125%. For comparison the GaAs DOS is shown. In the case of (GaMn)As the replacement of one Ga atom in the supercell of GaAs by a Mn atom does not change the number of spin-down states in the valence band. In the spin-up channel there are, however, five additional energy bands which are related to the Mn 3d states. Since there

are five extra energy bands and only four extra valence electrons (the atomic configurations of Ga and Mn are $4s^2 4p^1$ and $3d^5 4s^2$) the valence band is not filled and there appear unoccupied (hole) states at the top of the valence band. There is exactly one hole per Mn atom.

In (GaCr)As, the Cr 3d states assume a higher energy position relative to the semiconductor-matrix states than the Mn 3d states in (GaMn)As. As a result, the spin-up impurity band is separated from the valence band and lies in the semiconducting gap of GaAs. This impurity band contains three energy bands. Since Cr has one electron less than Mn, only one third of the impurity band is occupied: the occupied part contains one electron per Cr atom and there is place for further two electrons.

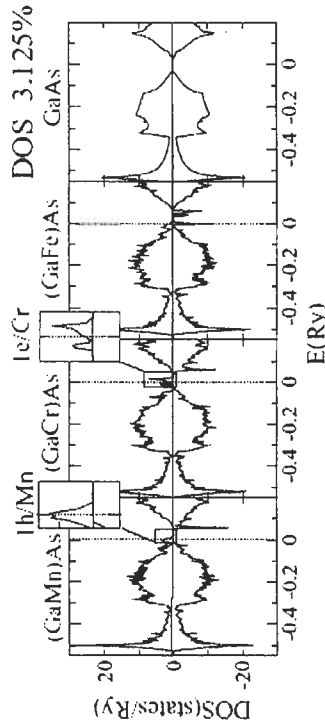


Fig. 1. The spin-resolved DOS for (GaMn)As, (GaCr)As, (GaFe)As. For comparison the DOS of GaAs is shown. The concentration of Mn is 3.125%. Upper part of the graph shows spin-up DOS. The inserts zoom the important energy regions about the Fermi level. In (GaMn)As there is one hole per Mn atom. In (GaCr)As there is one electron per Cr atom in the impurity band.

In (GaFe)As the number of valence electrons is by one larger than in (GaMn)As. Simultaneously, the Fe 3d states assume lower energy position with respect to the semiconductor matrix than Mn 3d states. As a result, the spin-down Fe 3d states become partly occupied. There are carriers in both spin-channels. In Fig. 2 we show calculated mean-field Curie temperatures. For (GaMn)As and (GaCr)As we obtained rather similar results at least for realistic impurity concentrations below 15%. In the case of (GaFe)As there is a clear trend to antiferromagnetism. (GaCr)As and (GaFe)As are not yet sufficiently studied experimentally. For (GaMn)As our result of high Curie temperature for

low Mn concentrations is in good correlation with experiment. Our estimation of the Curie temperature is substantially higher than the early experimental value of 110 K for $\text{Ga}_{0.947}\text{Mn}_{0.053}\text{As}$. However, later measurements¹⁹ on samples with less uncontrolled defects gave higher Curie temperature of 150 K that is closer to our estimation.

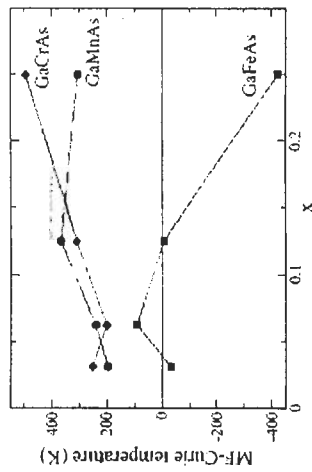


Fig. 2. The mean-field Curie temperature. The negative values of the Curie temperature reveal the prevailing antiferromagnetic exchange interactions and instability of the ferromagnetic state.

An important issue in DMS on the GaAs basis is the presence of donor defects, in particular As_{Ga} antisites, compensating part of the holes. Thus the number of holes per Mn atom is usually smaller than one. To study this effect we performed calculations for varied band occupation. An increase of band occupation leads to a decrease of the number of holes and vice versa. The results are shown in Fig. 3. In the case that all energy bands are either completely filled or empty [these are the point of $n = 1$ for (GaMn)As and the points $n = -1$ and $n = 2$ for (GaCr)As (Fig. 3)] the antiferromagnetic interatomic exchange interactions always prevail. This agrees with the picture of Anderson's antiferromagnetic superexchange. In (GaMn)As there is a clear trend to decreasing T_c for hole number less than the nominal value of one. In Fig. 4 we show the Curie temperature as a function of Mn concentration for different numbers of holes per Mn atom. For the case of $n = 0.6$ (that is 0.4 hole per Mn atom) the calculated Curie temperatures are close to the experimental values.

In (GaCr)As the situation is different. Because of a decreased number of valence electrons the impurity band can accept two further electrons per Cr atom and is far from

the full occupation. As a result the donor defects do not exert in this case the strong influence obtained for (GaMn)As: One compensating electron makes (GaMn)As

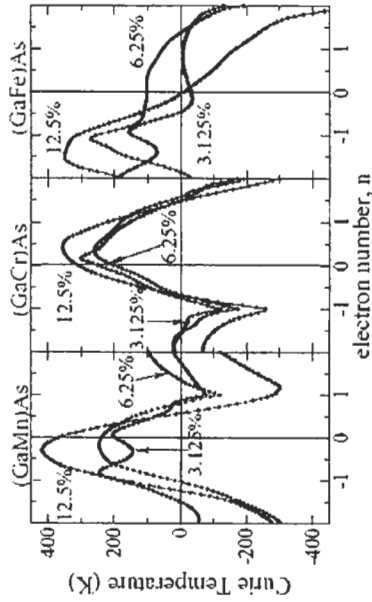


Fig.3. The Curie temperature as a function of the electron number, n is the number of the excess electrons (or missing electrons for negative values) per magnetic impurity atom. The nominal electron number corresponds to $n=0$. In all cases of completely filled electron bands (kinks on the curves) the prevailing exchange interactions are antiferromagnetic.

antiferromagnetic whereas the Curie temperature of (GaCr)As changes only weakly. On the other hand, the acceptor defects influence strongly the Curie temperature of (GaCr)As: a decreasing number of valence electrons below the nominal value marked by $n=0$ in Fig. 3 leads to a fast decrease of the interatomic exchange parameters resulting in the change of the sign of the parameters and in the transition from ferromagnetic to antiferromagnetic exchange interactions. At $n=-1$ the impurity band becomes empty that corresponds to the strongest antiferromagnetic interactions (minimum of T_c in Fig. 3). The result for (GaFe)As differ drastically from the results for both (GaMn)As and (GaCr)As. Here, already for nominal electron number ($n=0$) the antiferromagnetic interactions become stronger than ferromagnetic. The reasons for this are a small number of the holes in the spin-up channel and a very narrow impurity band in the spin-down channel.

Summarizing, our calculations show that the partial occupation of the energy bands is essential for the formation of ferromagnetic order.

4. (ZnCr)Te

In this Section we discuss the study of the II-VI DMS (ZnCr)Te. A strong interest to this system is attracted by the recent experiment by Saito et al²¹ who detected the ferromagnetism of $Zn_{0.8}Cr_{0.2}Te$ with the Curie temperature of 300 K, together with magneto-optical evidence in favour of an intrinsic (i.e., hole mediated) mechanism of ferromagnetism.

The cations in II-VI semiconductors have one additional valence electron compared to the cations in III-V systems. Therefore the replacement of a cation atom by a Mn atom is not expected to result in partially filled bands. The situation changes in the case of Cr doping since one Cr atom has one valence electron less than one Mn atom.

We performed calculations for $Zn_{0.75}Cr_{0.25}Te^{22}$ and found a number of features similar to the properties of (GaMn)As. The calculated DOS is shown in Fig. 5a. The system is half-metallic. There is exactly one hole per Cr atom in the spin-up valence band.

The calculated Curie temperature is shown in Fig. 5b. The decreasing number of holes leads to a transition from ferromagnetic to antiferromagnetic exchange interactions. As expected, the doping with Mn does not result in partially filled bands. Correspondingly (ZnMn)Te is antiferromagnetic for nominal number of valence electrons. Remarkable that $T_c(n)$ curves for (ZnCr)Te and (ZnMn)Te are similar with the major difference consisting

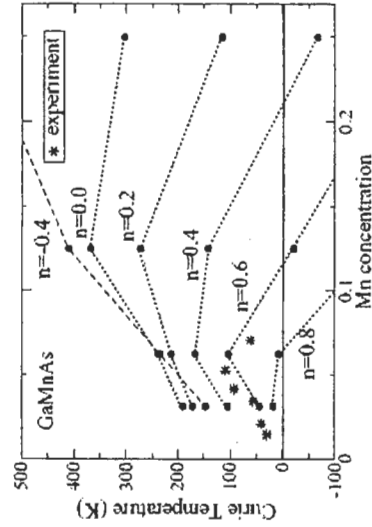


Fig. 4. The Curie temperature of (GaMn)As as a function of Mn concentration for different numbers of holes. The experimental values are taken from Ref. (20).

in the shift by one along the axis of band occupation. This result shows the validity of the rigid band model for qualitative considerations.

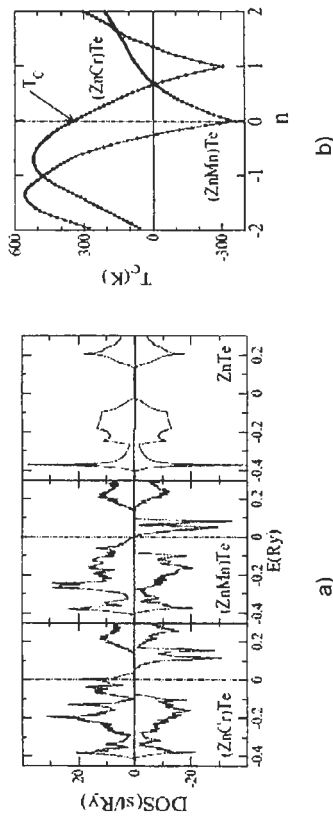


Fig. 5: a) The DOS of $Zn_{0.75}Cr_{0.25}Te$ and $Zn_{0.75}Mn_{0.25}Te$. For comparison the DOS of $ZnTe$ is shown. b) The Curie temperature of $(ZnCr)Te$ and $(ZnMn)Te$ as a function of the electron number.

5. HEUSLER ALLOYS: Co_2MnX (X=Si, Ge, Sn)

In this Section we discuss the study of the Co-based half-metallic full Heusler alloys focusing on the consequent account for the exchange interactions between the atoms of different magnetic sublattices.

We present in Fig. 6 the GGA spin-projected total density of states of Co_2MnX . The majority spin channel is strongly metallic, while the minority spin channel shows a semiconducting gap around the Fermi level, E_f , except in Co_2MnSn . The Mn atom carries the largest magnetic moment ($\sim 3 \mu_B$), while Co has a moment of $\sim 1 \mu_B$. The X atom is antiferromagnetically coupled to Mn and Co atoms. The total magnetic moment in Co_2MnSi and Co_2MnGe is $5 \mu_B$, which indicates half-metallic behavior. On the other hand Co_2MnSn is found to be nearly half-metallic with magnetic moment slightly higher than $5 \mu_B$.

The calculated Heisenberg exchange parameters are presented in figure 7. The calculations show that the closeness of the experimental Curie temperatures is the consequence of the similarity of the exchange interactions. We obtain a very weak dependence of the exchange interactions on the type of the X atom.

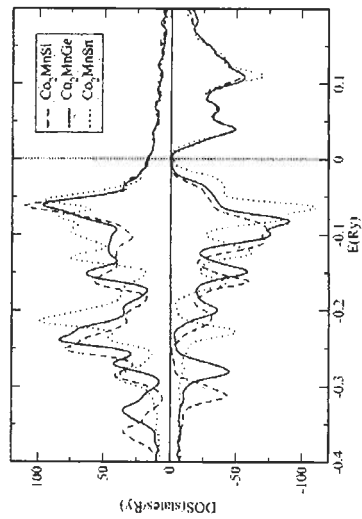


Fig. 6. Spin-projected total density of states of Co_2MnX (X=Si, Ge, Sn)

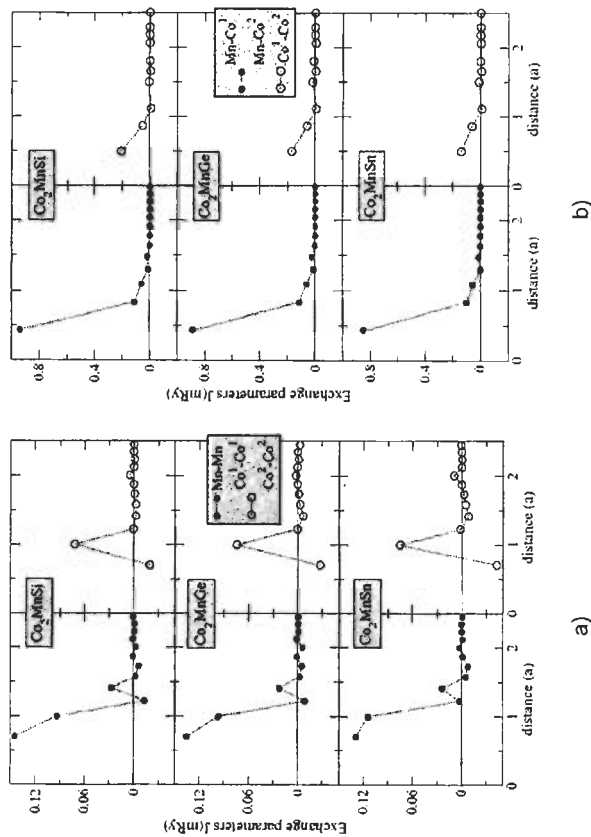


Fig. 7. Inter-atomic Heisenberg exchange parameters of Co_2MnX (X=Si, Ge, Sn): a) Intra-sublattice Mn-Mn (left side) and $Co-Co^1$ (Co^2-Co^2) (right side) exchange interactions, b) Inter-sublattice Mn- Co^1 (Mn- Co^2) (left side) and Co^1-Co^2 (right side) exchange interactions. The distances are given in the units of the lattice constant.

Considering the Mn–Mn interactions (Fig. 7a) we notice that in Co_2MnSi and Co_2MnGe the interaction with the coordination spheres from the first to second is positive. The third one is negative and very small. The interaction with the first and second coordination spheres is stronger than with the following ones. The interaction with the fourth sphere is small and positive. The interaction with further coordination spheres is very weak.

In Co_2MnSn the Mn–Mn interaction with the first sphere decreases and with second sphere increases compared with Co_2MnSi and Co_2MnGe . On the other hand, the interaction with the third sphere becomes very small and positive. The remaining interactions are very similar to Co_2MnSi and Co_2MnGe .

For Co–Co intra-sublattice exchange interactions we obtain a linear dependence of interactions on the X atom along the Si–Ge–Sn column in the Periodic Table. The interaction with the first coordination sphere is negative and with the second sphere is positive. The interaction with further coordination spheres is very weak.

The inter-sublattice Mn–Co and Co^1 – Co^2 interactions behave differently. Very strong interactions take place only between nearest neighbors, the interaction quickly decrease for further coordination spheres and become very small at the fourth nearest neighbor. Although Mn atoms carry large magnetic moments, the Mn–Mn interaction is found to be less important than Mn–Co interaction.

TABLE I: Mean–field estimation of the Curie temperature for Co_2MnX (X=Si, Ge, Sn). The experimental Curie temperatures are taken from Ref.24.

	$T_c^{\text{Mn–Mn[MFA]}}(K)$	$T_c^{\text{[MFA]}}(K)$	$T_c^{\text{[Exp]}}(K)$
Co_2MnSi	234	870	985
Co_2MnGe	225	822	905
Co_2MnSn	265	790	829

The interatomic exchange parameters are used to evaluate the Curie temperature. If only the Mn–Mn interactions are taken into account we obtain values shown in the second column of Table I. The comparison of the Curie temperatures calculated with the use of

the Mn–Mn exchange parameters only with experimental Curie temperatures shows strong difference between theory and experiment. In all three cases the error is about 70%. Account for inter–sublattice interactions improves the agreement with experimental T_c values cardinally (Table I). This shows that the Co moment provides a magnetic degree of freedom, which plays a crucial role in the thermodynamics of the system.

6. CONCLUSIONS

We have systematically studied exchange interactions and Curie temperatures for a series of III–V and II–VI diluted magnetic semiconductors and Co-based half-metallic full Heusler alloys within the parameter–free density functional theory. The Curie temperature of both classes of systems is calculated within the mean–field approximation to the classical Heisenberg Hamiltonian. Good agreement with experiments is obtained.

We focus the discussion on the role of the holes in the establishing the ferromagnetic order in various DMS. Our calculations of the exchange interactions for Heusler alloys showed that in this system the inter-sublattice exchange interactions play the main role in the thermodynamics of the system. The contribution of the Mn–Co inter–sublattice interactions into Curie temperature reaches here the value of 70%.

ACKNOWLEDGEMENT

The support from Bundesministerium für Bildung und Forschung is acknowledged.

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