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Proceedings of the XXXV International School of Semiconducting Compounds, Jaszowiec 2006

# Comparison of Exchange Interactions in II–VI, III–V, and I–II–V Dilute Magnetic Semiconductors: Density Functional Approach

J. MAŠEK<sup>a</sup>, J. KUDRNOVSKÝ<sup>a</sup>, F. MÁČA<sup>a</sup> AND T. JUNGWIRTH<sup>b,c</sup>

<sup>a</sup>Institute of Physics, AS CR

Na Slovance 2, 182 21 Prague 8, Czech Republic

<sup>b</sup>Institute of Physics, AS CR

Cukrovarnická 10, 162 53 Prague 6, Czech Republic

<sup>c</sup>School of Physics and Astronomy, University of Nottingham

University Park, Nottingham NG7 2RD, UK

We use the coherent potential method based on the density-functional theory to compare the electronic structures and magnetic characteristics of mixed crystals (Ga,Mn)As, (Zn,Mn)Se, and Li(Zn,Mn)As. We show that, with the same degree of doping, the magnetic behavior of these materials is very similar, reflecting the similarity of their electronic structures. In particular, the superexchange in (Ga,Mn)As is as strong as in (Zn,Mn)Se and the ferromagnetic coupling in all these dilute magnetic semiconductors becomes dominant only at sufficient concentration of the holes. Remarkably, we find that ferromagnetic state appears not only in *p*-type, but also in *n*-type materials at a comparable level of doping. Although obtaining strongly *n*-type doped III–V dilute magnetic semiconductors is improbable, Li(Zn,Mn)As seems to be a promising candidate for a ferromagnetic *n*-type semiconductor.

PACS numbers: 71.15.Ap, 71.20.Nr, 71.55.Eq, 75.50.Pp

## 1. Introduction

The dilute magnetic semiconductors (DMS), e.g. III–V and II–VI compounds doped with a large amount of Mn, have been studied thoroughly in last years because of their unique magnetotransport and magneto-optical properties [1, 2]. In particular, the ferromagnetic behavior of the (III,Mn)V mixed crystals is very promising for applications in spin electronics. Real applications of the ferromagnetic DMS are, however, limited by their low Curie temperature (maximally 173 K [3]). Another limitation is connected with the fact that the ferromagnetic

coupling is assumed to be a property of only  $p$ -type doped materials. To understand and overcome these two limitations, it is necessary to analyze in more detail the main groups of DMS, i.e. II–VI and III–V materials, and to look at alternative host semiconductors.

In the II–VI DMS, such as (Cd,Mn)Te and (Zn,Mn)Se, the substitution of Mn for the host cation is isovalent and the solubility of Mn is high. Mn atoms are electrically neutral and bear magnetic moments corresponding to the total spin  $5/2$ . Without extra doping, (II,Mn)VI DMS remain intrinsic semiconductors and the exchange coupling of the local moments is dominated by antiferromagnetic (AFM) superexchange [1]. This, in combination with the random distribution of Mn atoms in the lattice, results in various disordered and frustrated magnetic phases of the II–VI DMS with zero macroscopic magnetic moment.

On the other hand, the ideal picture of the III–V DMS is such that Mn atoms substitute for trivalent cations and act as shallow acceptors, each introducing one hole into the valence band. In this case, the itinerant carriers mediate long-range Ruderman–Kittel–Kasuya–Yoshida-like (RKKY-like) exchange interaction. For realistic densities of the holes, it is ferromagnetic (FM) and sufficiently strong to dominate the total exchange interaction, resulting into alignment of all local moments [4, 5]. That is why the negative superexchange contribution to the exchange coupling in III–V DMS is assumed to be much smaller than in II–VI materials and is usually neglected in the model calculations [6]. Physically, it is explained in terms of different charge states and screening of  $\text{Mn}_{\text{Zn}}$  and  $\text{Mn}_{\text{Ga}}$  impurities. The Curie temperature  $T_c$  is expected to increase with increasing concentration of Mn and with increasing density of the holes [5]. This represents a principal obstacle in obtaining materials with high  $T_c$ , as the solubility of Mn in (Ga,Mn)As is limited due to the non-isovalent nature of  $\text{Mn}_{\text{Ga}}$ .

That is why the optimization  $T_c$  requires a detailed analysis of the exchange coupling and the Curie temperature in dependence on the Mn concentration and on the level of doping. Recent calculations [7–9] have shown that the magnetic characteristics of III–V and II–VI DMS are much closer than originally expected, including the strength of the antiferromagnetic exchange in the case of compensated materials. These calculations also indicate a possibility of ferromagnetic exchange interactions in strongly  $n$ -type doped DMS.

In this paper, we use (Ga,Mn)As and (Zn,Mn)Se as prototype examples of III–V and II–VI DMS and examine the effects of co-doping on the stability of the ferromagnetic state. In parallel to these two traditional systems, we consider also a new DMS Li(Zn,Mn)As that is, from the point of view of both atomic and electronic structure, very similar to the usual III–V and II–VI materials [10]. To describe the electronic structure of these mixed crystals, we use the coherent potential method (CPA) combined with the density-functional theory (cf. Ref. [11]). These electronic structure calculations are combined with the mean-field theory used to estimate the stability of the ferromagnetic state and the Curie temperature.

## 2. Curie temperature as a function of doping

In our calculations, we consider mixed crystals with a perfect zinc-blende structure and with a random distribution of Mn atoms and other impurities, used for *p*-type and *n*-type doping. In the case of (Ga,Mn)As we use  $Zn_{Ga}$  acceptors and  $Se_{As}$  and  $Si_{Ga}$  donors. The substitutional  $Li_{Zn}$  acceptors and  $Br_{Se}$  donors are assumed in (Zn,Mn)Se. In the case of Li(Zn,Mn)As, Li non-stoichiometry represented by Li vacancies (acceptors) and interstitials (donors) is used to control the type and number of carriers. These charged defects, together with Mn impurities, modify the electronic structure when introduced in concentrations of order of a few percent. The scattering on the impurities also reduces the coherence of the Bloch states. Our calculations account for both effects, neglected within the rigid-band calculations [8, 9]. We use the linear-muffin-tin-orbital implementation of the coherent-potential approach (LMTO-CPA, [11]) to calculate the configurationally averaged density of states and related spectral and thermodynamic quantities. The exchange-correlation potential is treated in the local-spin-density approximation (LSDA). More detailed analysis based on calculations including the electron correlations explicitly (LSDA+U) and microscopic tight-binding band structures will be published elsewhere.

A detailed description of the exchange interactions can be obtained by mapping of the LSDA total energy on an effective Heisenberg Hamiltonian [12]. Due to the single-site character of the CPA, it is natural to describe the strength of the exchange interactions by an effective exchange field acting on the magnetic impurity due to its magnetically polarized surrounding. Quantitatively, it is characterized by the energy  $E_{rev}$  of flipping one local moment.  $E_{rev}$  is a measure of the stability of the ferromagnetic state and can be obtained [13] from electronic structure results. It is related to the mean-field value of the Curie temperature,  $6k_B T_c = E_{rev}$ . Negative  $E_{rev}$  indicates that the ferromagnetic arrangement is unstable with respect to local rotations of the magnetic moments and that it breaks up into a disordered phase.

The dependence of  $E_{rev}$  on the concentration of the carriers is presented in Fig. 1. Without free carriers,  $E_{rev}$  is negative and shows the strength of the superexchange. It is almost the same in all three materials. With increasing number of holes (negative concentrations of carriers in Fig. 1),  $E_{rev}$  increases due to the hole-mediated ferromagnetic exchange coupling. The critical concentration of the holes, necessary to stabilize the ferromagnetic state, is proportional to the concentration  $x$  of the magnetic atoms [7].  $E_{rev}$  saturates for high hole densities.

An important and surprising feature of the calculated  $E_{rev}$  is the electron-hole symmetry. For strong *n*-type doping, the positive values of  $E_{rev}$  indicate a possibility of the ferromagnetic state in all three materials. This breaks the common prejudice that the hybridization of Mn *d*-states with the conduction band is weak and the electrons are ineffective in mediating ferromagnetic interaction in the tetrahedral semiconductors.

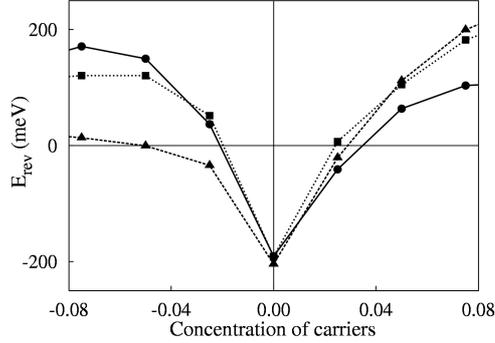


Fig. 1. Energy  $E_{\text{rev}}$  of the local spin fluctuation in ferromagnetically ordered DMS: (a)  $\text{Ga}_{0.95}\text{Mn}_{0.05}\text{As}$  (circles); (b)  $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{Se}$  (squares); (c)  $\text{LiZn}_{0.95}\text{Mn}_{0.05}\text{As}$  (triangles). Negative values of  $E_{\text{rev}}$  for low carrier concentrations indicate an instability of the ferromagnetic state.

There are two combined factors decisive of the electron-induced ferromagnetism in the investigated materials: (i) First of all, the exchange coupling is connected with the central part of the Brillouin zone. We find that, contrary to the  $\Gamma$ -point, the hybridization of the states around it quickly arises with increasing wave vector due to changes of the orbital composition of the band and due to relaxed selection rules for the hybridization out of the  $\Gamma$ -point. (ii) Because of their favorable orbital composition, also the side minima can be involved in the hybridization with Mn  $d$ -states at high electron densities. Let us notice that the final width of spectral lines effectively reduces their distance from the bottom of the conduction band in the disordered systems so that, in  $(\text{Ga},\text{Mn})\text{As}$  and  $\text{Li}(\text{Zn},\text{Mn})\text{As}$ , the side minima become populated at the considered degree of doping.

### 3. Non-stoichiometric $\text{Li}(\text{Zn},\text{Mn})\text{As}$

The atomic arrangement in a half-ionic compound  $\text{LiZnAs}$  is derived from the zinc-blende structure formed by covalently bonded Zn cations and As anions. The valence and the lowest conduction bands, mostly built of Zn and As related states, have the same structure as the energy bands in GaAs. Also the band gap 1.61 eV is close to the value for GaAs [10]. Li atoms occupy the tetrahedral interstitial positions  $\text{T}(\text{As}_4)$  and their bonding is much weaker [10]. They provide electrons to satisfy the charge neutrality and to fill the valence band, and their non-stoichiometry decides about the type of carriers in the material.

Because of the valency reasons, it is natural to assume that Mn atoms substitute for Zn and that the mixed crystals  $\text{Li}(\text{Zn},\text{Mn})\text{As}$  can be easily formed. Indeed, the calculations of the formation energy of  $\text{Mn}_{\text{Zn}}$  show that it remains negative in a wide range of Mn concentrations  $x$  and does not depend much on

the Li non-stoichiometry [14]. This means that, in contrast to (Ga,Mn)As, there are no apparent limits for solubility of Mn in Li(Zn,Mn)As.

On the other hand, the Li non-stoichiometry can be used to control the number of carriers in the mixed crystal. It can be realized by four defects, namely Li vacancies, Li atoms filling the other tetrahedral interstitial position  $T(\text{Zn}_4)$ , and the antisite defects  $\text{Li}_{\text{Zn}}$  and  $\text{Zn}_{\text{Li}}$ . The vacancies and  $\text{Li}_{\text{Zn}}$  are acceptors, interstitial Li and  $\text{Zn}_{\text{Li}}$  act as donors. Because of their high formation energies, Li vacancies and  $\text{Zn}_{\text{Li}}$  impurities are unlikely to be formed, so that the density of the carriers is determined by the incorporation of the excess Li [14].

The interplay between substitutional  $\text{Li}_{\text{Zn}}$  and interstitial  $\text{Li}_{\text{int}}$  is treated in the same way as the problem of  $\text{Mn}_{\text{Ga}}$  and  $\text{Mn}_{\text{int}}$  in (Ga,Mn)As [7, 15]. With a given total amount of Li, the partial concentrations  $x_s$  and  $x_i$  of  $\text{Li}_{\text{Zn}}$  and  $\text{Li}_{\text{int}}$  can be obtained from the compositional dependence of their formation energies,  $E_s(x_s, x_i)$  and  $E_i(x_s, x_i)$ , by using the condition  $E_s(x_s, x_i) = E_i(x_s, x_i)$ . The solution shows that always  $x_s < x_i$  and that the preferential formation of  $\text{Li}_{\text{int}}$  is further enhanced in mixed crystals with a higher content of Mn. In this way, the strong  $n$ -type doping of Li(Zn,Mn)As DMS seems to be attainable.

#### 4. Conclusions

Using density-functional CPA calculations of the electronic structures of (Ga,Mn)As, (Zn,Mn)Se, and Li(Zn,Mn)As DMS with variable type and degree of doping, we point out the similar magnetic behavior of these materials. In particular, we have shown the importance of the superexchange in III-V DMS and, consequently, a critical carrier density necessary to stabilize FM state.

We have also demonstrated a general tendency to ferromagnetism in strongly  $n$ -type doped III-V, II-VI, and I-II-V DMS. The electron-mediated FM coupling is caused by two combined effects, namely by strong hybridization of the conduction band states around the  $\Gamma$ -point, and by population of the side minima of the conduction band in the strongly doped disordered materials that also hybridize with the  $d$ -states.

Although sufficiently high electron density can be hardly achieved in (Ga,Mn)As, we showed that the electron-mediated ferromagnetism may be realized in Li(Zn,Mn)As by introducing more Li into the empty interstitial positions. Also the solubility of Mn is predicted to be substantially larger in LiZnAs than in GaAs.

#### Acknowledgments

This work was done within the project AVOZ1-010-0520 of the AS CR. The financial support was provided by the Academy of Sciences of the Czech Republic (grant No. A1010214) and by COST Project OC150-P19.

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