Semimagnetic Semiconductors in Magnetic Fields

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1. Introduction

In this paper we will review recent work on II-VI compounds containing Mn: Hg$_{1-x}$Mn$_x$Te, Hg$_{1-x}$Mn$_x$Se, Cd$_{1-x}$Mn$_x$Te, Cd$_{1-x}$Mn$_x$Se. From many points of view these materials, called semimagnetic semiconductors (SMSC), are very similar to the well-known systems such as Hg$_{1-x}$Cd$_x$Te and Cd$_{1-x}$Zn$_x$Te. In particular, over a wide range of compositions they crystallize in zinc-blende (HgMnTe, HgMnSe, CdMnTe) or wurtzite (CdMnSe) structure, they exhibit relatively low deviation from stoichiometry, low concentration of intrinsic defects, and they can be made either n-type or p-type by intentional doping or by appropriate annealing. At first sight, their band structure is the same as that of other II-VI compounds. In particular there is a wide conduction band of s-type symmetry (of p-type in the zero-gap case) and there is a wide p-like valence band. Briefly, they exhibit typical semiconducting properties and, consequently, we have access to their structure through the most powerful techniques that have been developed to study the canonical semiconductors. However, using these techniques, especially those which involve the presence of a magnetic field, we quickly realize that the properties of SMSC are not at all similar to those of other II-VI compounds. If we want to find a reference point they are in some aspects, similar to those observed in magnetic semiconductors [1], examples being exchange-induced splitting of bands and the formation of magnetic polarons. Of course, all this is due to the presence of the half-filled 3d$^5$ shell of Mn and thus due to the presence of localized spins. In fact, early EPR [2] and magnetic susceptibility [3] studies of Mn in II-VI materials have shown that $g_{Mn} = 2$ and the total spin $|S| = 5/2$, just as in the free Mn atom.

Our review, of course, does not cover all aspects of SMSC. In particular, we omit important problems of crystal growth and characterization, possible applications, details of theoretical models. For further information and further references to original papers we refer readers to other review articles already available [4].

2. Band Structure

The starting point for the description of the band structure of SMSC is the Vonsovskii model. According to that model one assumes that electrons can be divided into two groups.
The first consists of band electrons from the bonding and antibonding \( sp^3 \) orbitals. The energy structure of extended states in SMSC resembles that of other II-VI compounds, implying in particular the applicability of the virtual crystal approximation to the description of band states in the alloys in question. The energy gap is direct and located in the center of the Brillouin zone. The gap is either zero or narrow in mercury compounds (Fig.1), or wide in cadmium compounds (Fig.2), and smoothly increases with Mn concentration. The latter property is observed in gaps away from the \( \Gamma \) point [16, 17]. The gap and Mn concentration can be independently changed in quaternary compounds, e.g. \( CdHgMnTe \) [18].

![Graph 1](energy_gap.png)

**Fig.1** Energy gap in \( Hg_{1-x}Mn_xTe \) (\( x[3, 6, 7, 8, 9] \)) and in \( Hg_{1-x}Mn_xSe \) (\( x[10, 9] \)) at 4.2K.

![Graph 2](exiton_energy.png)

**Fig.2** Free exciton energy in \( Cd_{1-x}Mn_xTe \) (\( x[1, 12, 13] \)) and \( Hg_{1-x}Mn_xSe \) (\( x[14, 15] \)). Straight lines are drawn through experimental points.

![Graph 3](photoemission.png)

**Fig.3** Shape of the photoemission spectra in \( CdMnTe \) [19] and in \( CdTe \) [20]. Energy is calculated from the top of the valence band. Arrows denote Mn(3d) and Cd(4d) bands.

![Graph 4](reflectivity.png)

**Fig.4** Reflectivity in \( Cd_{1-x}Mn_xTe \). Arrows denote structures attributed to transitions from and on 3d5 Mn shell (after [17]).
The second group comprises localized electrons from the half-filled 3d shell of Mn. These electrons, according to photoemission studies in CdMnTe [19], are about 6eV below the top of the valence band (Fig.3).

This finding is consistent with UV reflectivity measurements (Fig.4), a structure around 10eV being attributed to the transitions from the 3d^5 level to a point in the conduction band away from the center of the Brillouin zone [17] (with an uncertainty concerning crystal field splitting of the final state. 3d^4; crystal field parameters can be estimated by analysing the intra 3d^5 absorption band observed near 2.2eV [12]). The same measurements reveal a structure around 4eV. This structure may be attributed to the transitions from the valence band on the 3d^5 level which, when occupied (3d^6), lies above the valence band because of a strong Coulomb repulsion between d-electrons of opposite spins. The above measurements result in a picture for the density of states, which is very schematically presented in Fig.5. According to that picture, the stability of the magnetic moment is due to the localized character of the 3d^5 Mn shell and a large intratomic correlation energy for d-electrons, U=10eV. The important feature of that picture is also a large distance of d-levels from the Fermi level. This a posteriori explains why the band structure near the Fermi level and K,β parameters of the materials in question are so similar to those of Mn-less II-VI compounds.

![Schematic picture for the density of states in II-VI compounds containing Mn. Arrows mark energy gap E₀ and correlation energy U (after [17])]

However, it should be noted that there is some information which may indirectly indicate that the mixing of d-levels and band states does not play a negligible role. First, one observes a strong modification and broadening of the UV reflectivity spectra in comparison with other II-VI alloys [16,17]. Second, the p-d exchange integral is relatively large β/Ω = -1eV and about two times larger than the s-d integral α/Ω = 0.5eV (for definition of symbols see next section). This is probably hard to interpret without allowing for the p-d hybridization.

3. Exchange Interaction

There is, of course, a Coulomb interaction between the two electron systems described in the previous section. A part of this interaction depends both on the spin of the band electron and the total spin localized on the Mn ion. It is assumed that this spin-dependent part of the interaction, the exchange interaction, can
be taken into account by completing a hamiltonian of the problem in question with the Heisenberg term:
\[ H' = -J(\hat{S} - \hat{S}_i) \cdot \hat{S}_j \tag{1} \]
where \( J \) is the short range exchange operator acting on a one-electron orbital part of a band electron wave function; \( \hat{S} \) is the spin operator of a band electron; \( \hat{S}_i \) is the total spin operator of a Mn ion located at the point \( R_i \). As is usual in the study of magnetic materials, this is the basic hamiltonian for further discussion.

4. Exchange-Induced Splitting of the Effective Mass States in a Magnetic Field

4.1 General remarks

The exchange-induced corrections to an effective mass electron energy are calculated within the framework of the molecular field approximation and the first order perturbation theory (if necessary generalized for degenerate or closely lying bands). The former approximation leads to the interaction of the Ising form:
\[ H' = -2J \langle S_z \rangle \sum_{i} J(\hat{S} - \hat{S}_i) \tag{2} \]
where the \( z \)-axis is chosen along the average value of the spin \( \langle S_z \rangle \) and the summation runs over all Mn ions in the crystal. We see that in the absence of a magnetic field or spontaneous magnetization there are no exchange corrections to electron energy. If, however, a magnetic field is applied there appears a nonvanishing spin polarization along the magnetic field, and for electrons in a simple s-like band the corrections, according to the first order perturbation theory, are given by: \( E_s = \frac{\alpha}{N_0} \langle S_z \rangle \) for "spin down" and "spin up" electrons, respectively. Here \( N_0 \) is the concentration of Mn ions and \( \alpha = \langle s \rangle \) is the exchange integral, where the integration is over the unit cell volume \( \Omega \). Therefore, the exchange interaction produces an additional spin-splitting \( E_s = \frac{\alpha}{N_0} \langle S_z \rangle \) with \( \gamma \)-factor given by:
\[ \gamma = \frac{\alpha \chi}{N_0 \mu_B} \tag{3} \]
where we used the standard relations between \( \langle S_z \rangle \), magnetization \( M \), and magnetic susceptibility \( \chi : M = -N_0 \mu_B \langle S_z \rangle \), \( \chi = N \mu / M \).
Inserting a typical value of the exchange integral \( \alpha / \Omega = 0.5 \text{ eV} \) and a typical value of \( \chi \) at low temperatures \( \chi = 4 \times 10^{-4} \text{emu} \) (i.e. magnetic permeability \( \mu = 1.005 \)) into (3), we find \( \gamma \) as large as 100.

Of course, a more quantitative theory has to take into account the direct influence of magnetic field on electron states, \( k \cdot p \) interaction between bands, symmetry of bands, spin-orbit interaction [21, 22, 23, 24] and in the case of excitons [25, 26] or impurities [27] - appropriate Coulomb interactions. Clearly, all the above factors are very important but they do not affect the main property of the alloys in question: in SMSC there are large exchange-induced spin splittings which reflect the temperature and magnetic-field dependence of the magnetization.

For an \( S \)-state ion (such as the Mn-1con in the ground 3d\(^5\) state) the exchange coupling is determined by two nonvanishing and independent matrix elements: \( \alpha = \langle s \rangle \) and \( \beta = \langle s \rangle \) [26]. They are to be determined by experiment, the typical values obtained being \( \alpha / \Omega = 0.5 \text{ eV} \), \( \beta / \Omega = -1 \text{ eV} \) [29].
4.2 Spectroscopic Observations

In this section we will discuss the spectroscopic evidence for the exchange-enhanced spin splitting of Landau levels, shallow impurities, and excitons.

In narrow gap SMCs (HgMnTe, HgMnSe), due to large $\omega_c\tau$ and small exciton corrections, the positions of magnetic sublevels (spin-split Landau levels) can be accurately determined by interband [6,9,21,30] and intraband [31,32] magnetooptics. Fig. 6 shows the sum of cyclotron energies of electrons and light holes, and the spin splitting of the first Landau level in the conduction band, as obtained from interband magnetooptics in HgCdTe and HgMnTe [21]. The cyclotron energy for a given value of $E_c$ is similar in both materials indicating similar value of $k\cdot p$ parameters. The spin splitting is however much larger in HgMnTe than in HgCdTe because of the exchange interaction in the former material. For the sample Hg$_{0.97}$Mn$_{0.03}$Te ($E_c = -150$ meV) the spin splitting in 2T is as large as 20 meV, which corresponds to $g_s=170$. Furthermore, spin splitting in HgMnTe is temperature dependent, which reflects the temperature dependence of the magnetization.

![Diagram](https://via.placeholder.com/150)

**Fig. 6** Sum of the cyclotron energy of electrons and light holes $E_k$ and spin splitting of the first Landau level in the conduction band, $s_{c(1)}$ as a function of energy gap in HgCdTe (○ △) and in HgMnTe (● ■). Solid lines are drawn through experimental points and can be reproduced by the exchange-modified Pidgeon-Brown model (after [21]).

**Fig. 7** Stokes shift in Cd$_{0.95}$Mn$_{0.05}$Se at 1.6K. Note the large value of shift, saturation in high fields, and non-zero value in zero field (after [33]).

In Fig. 7 we see the magnetic-field dependence of the energy difference between incoming and scattered light (Stokes shift) in Cd$_{0.95}$Mn$_{0.05}$Se at 1.6K [33]. In CdMnSe at low temperatures excitons are localized on donors and thus the Stokes shift is a direct measure of the Zeeman splitting of a donor level. Again, the splitting is very large and tends to saturation in high fields reflecting the saturation of the Mn spin polarization.

Finally, we turn to the exchange-induced splitting of excitons in CdMnTe [23,25,26,34,35]. In Fig. 8 the energy difference $\Delta E$ between the stronger components of the free exciton observed in
magnetoreflection up to 51 in the $g$- and $g'\neq 0$ configuration is plotted as a function of mean spin value, $N_g <S_g>$ [35]. The latter value has been deduced from direct magnetization measurements. The strict proportionality of $|g|$ and $N_g <S_g>$ implies that the assumptions of the model are basically correct and that the exchange integrals are composition independent.

4.3 Influence on Transport Phenomena

4.3.1 Quantum Transport

The unusual temperature dependence of the positions of magnetic sublevels strongly influences the Shubnikov-de Haas effect. In narrow gap SMSR with temperature-independent electron concentration and mobility, one observes the following effects. First, temperature dependence of the positions of oscillation maxima [10, 22, 36]. Second, in constant magnetic field, oscillations of magnetoresistance as a function of temperature [37]. This is because temperature variations induce transitions of the magnetic sublevels through the Fermi level. Third, nonmonotonic dependence of the Shubnikov-de Haas oscillation amplitude on temperature [10, 22] (see Fig. 9).

![Fig. 8](image-url) **Fig. 8** Free exciton splitting in Cd$_{1-x}$Mn$_x$Te as a function of mean spin value deduced from magnetization. Solid line is theoretical (after [35]).

![Fig. 9](image-url) **Fig. 9** Amplitude of Shubnikov-de Haas oscillations as a function of temperature in Hg$_{0.9}$Mn$_{0.1}$Te. Solid line is theoretical (after [22]).

The latter effect can be easily explained [38] if we note that the amplitude is determined by the ratio of the distance between magnetic sublevels to their broadening. In particular, the maximum in Fig. 9 at 2.5K means that the distance between the magnetic sublevels has reached its maximum value $\hbar \omega_c$ and thus spin-splitting is equal to $n \hbar \omega_c$, $n$ being an integer ($n=2$ in this particular case). The minimum at 74K occurs because spin-splitting has been reduced to $\hbar \omega_c$ and thus the distance between the magnetic sublevels has its minimum value $\hbar \omega_c$. 
4.3.2 Hopping Conductivity

In n-CdMnSe, with $N_D = 10^{16} - 10^{17} \text{cm}^{-3}$ and a donor binding energy $E_D = 25 \text{meV}$, a magnetic field below 5T does not cause shrinking of donor wave functions in a degree sufficient to affect magnetoresistance in the hopping region. In spite of this, one observes a large and complex magnetoresistance [39] (absent in CdSe, see Fig.10). The negative magnetoresistance in high fields is attributed to the presence of a magnetic polaron [39] (see next section). Several mechanisms can under certain circumstances lead to the positive magnetoresistance [40]. First, increasing magnetic field makes the spin-flip transitions less effective because of large energy distance between spin-down and spin-up states in a magnetic field. The spin-flip transitions in SMS can be originated in the exchange-induced hopping, spin and energy for the hops being taken from the magnetic subsystem.

Second, magnetic field lifts the spin degeneracy of donor levels, and the form of the electron distribution function in the impurity band changes. Thus, assuming constant number of electrons and density of states, we have a change (increase) of the Fermi energy. Third, the field dependence of the energy of the donor level is sensitive to the distance from other occupied donors when taking into account the exchange interaction between electrons on the neighbouring donors. This may lead to increase of the width of the impurity band in a magnetic field.

The exchange interaction affects in an interesting way the hopping conductivity in narrow-gap p-type SMS [27]. In $B \gg 3T$ the exchange-enhanced splitting shifts the top valence-band magnetic sublevel $b_v(-1)$ from the other levels to a distance larger than the acceptor binding energy $E_a$. Therefore, in spite of a small magnetic field ($\gamma = \hbar v_F / B << 1$), we can construct the ground state acceptor wave function from the $b_v(-1)$ wave function. In the wave function thus obtained the longitudinal radius $a_{1L}$ is only slightly affected by the magnetic field, but the transverse radius is now determined by the magnetic length $\lambda$. Thus the mag-
netic field extends the acceptor wave function ($\lambda B = 3a^*$ in 3T) leading to a giant negative magnetoresistance, as indeed observed in p-type Hg$_{1-x}$Mn$_x$Te, $x = 0.15$, in the hopping conductivity region [27,41].

5. Magnetic Polaron

So far we have considered the influence of the exchange on the effective mass states. On the other hand, each Mn ion is in a molecular field produced by effective-mass electrons. The mutual interaction between these subsystems leads, under some conditions, to nonvanishing spin polarization of both subsystems even in the absence of magnetic field, the loss of entropy being outweighed by the lowering of the system energy.

In SMC the spontaneous magnetization produced by the above mechanism has so far been found to occur within the Bohr radius of occupied impurity states (bound magnetic polaron BMP), as evidenced by observation of zero-field splitting of impurity states in bound exciton luminescence studies in p-type CdMnTe [42] and spin-flip Raman scattering measurements in n-CdMnSe [33] (see Fig.7). The formation of BMP strongly reduces hopping conductivity through an increase of hopping activation energy and a decrease of the Bohr radius of an occupied donor. The negative magnetoresistance in a large field in n-CdMnSe can thus be attributed to the vanishing of BMP, occurring if all the Mn spins are polarized by an external magnetic field (see Fig.11). A similar effect occurs in p-type HgMnTe [27].

![Fig.11](image1.png)  ![Fig.12](image2.png)

Fig.11 Ratio of min. and max. resistivity in magnetic field in n-CdMnSe at 1.5K [39] (see Fig.10). The calculated ratio of resistivity without and with magnetic polaron [40]. Here polaron binding energy is identified with half of spin splitting in zero magnetic field [33] (see Fig.7); magnetizations from [35] are used.

Fig.12 Critical temperature in Cd$_{1-x}$Mn$_x$Te as obtained from the broadening of the EPR line & [46], low field magnetic susceptibility [45] ($B=1.5\text{mT}, f=0$)$\Delta$ [47] ($B=4\text{mT}, f=36\text{Hz}$), and elastic neutron scattering $\circ$[48].
6. Magnetic Structure

The dominant spin-spin coupling in SMSC is believed [43,44] to originate from an indirect exchange interaction produced by virtual interband excitations induced by the exchange (1), i.e. so-called Bloembergen and Rowland mechanism.

The phase diagram of \( Cd_{1-x}Mn_xTe \) [45] is shown in Fig.12. For \( x_0 \leq 0.17 \) no phase transition is observed because of the short range and antiferromagnetic sign of the interaction, and the disorder in the magnetic system (some broadening of the EPR line is however seen at low temperatures [46], which may be indicative of the onset of a contribution from the long range dipole-dipole interaction). Above \( x_0 \geq 0.17 \) the spin-glass phase occurs as is shown by the cusps in the low field magnetic susceptibility and the linear temperature dependence of the specific heat [45]. Interestingly enough, the spin-glass phase is due to purely antiferromagnetic interactions and not to a competition between ferro and antiferro interactions as is the case in canonical spin-glasses. Finally, for \( x=0.6 \) an antiferromagnetic ordering takes place, as is demonstrated most directly by a maximum in the magnetic susceptibility and in the specific heat [45] as well as by elastic neutron scattering [48].

7. Final Remarks

From the above discussion we see that II-VI compounds containing Mn do not exhibit the key feature of magnetic semiconductors: the influence of narrow bands and critical phenomena (related to the well defined phase transition) on their behaviour. This makes these materials very interesting from the point of view of semiconductor properties. They possess all features of a typical and simple semiconductor with one difference: the exchange interaction. Consequently one can study, say, the amplitude of the SDH effect, excited states of excitons, hopping conductivity... by affecting independently spin and orbit. In addition, these materials form an interesting class of disordered magnetic systems. In this review we have limited our considerations to HgMnTe, HgMnSe, CdMnTe, CdMnSe. However, the family of materials with similar properties is quite large and contains other II-VI compounds (eg. ZnMnTe [49]) with other magnetic ions (eg. HgFeTe [50]) as well as, for instance, IV - VI, and II - V compounds with Mn (eg. FeMnTe [51], (CdMn)\(_3\)As\(_2\) [52]).

The above arguments have lead R.R. Gałążka [4] to propose a separate name for the family of materials exhibiting the properties mentioned above: semimagnetic semiconductors. This name seems to be appropriate not only because it is simple and thus facilitates communication, but also because it correctly reflects the absence of several characteristic features of magnetic semiconductors and simultaneously stresses the excellent semiconducting properties of the family.
Acknowledgements

The extensive study of II-VI compounds with Mn was initiated by Dr. R.R. Gałążka and most of the results presented above have been obtained by teams headed by him and Prof. Z. Kossoński. The author is also indebted to the authors of most of the papers listed below for many valuable discussions. A part of this paper was prepared during the author's stay at Munich Technical University and Osaka University. It is a pleasant duty to thank Prof. F. Koch, Prof. S. Narita, and S. Takeyama for their hospitality.

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