Chapter 1
Basic Consequences of $sp-d$ and $d-d$ Interactions in DMS

Jan A. Gaj and Jacek Kossut

Abstract In this introductory chapter, we describe the basic features of diluted magnetic semiconductors. We focus on giant Zeeman splitting of excitons and related giant Faraday rotation. We show that the spin splitting is proportional to the magnetization and develop a simple model, making use of virtual crystal and mean field approximations, describing the energy states in the presence of magnetic field in diluted magnetic semiconductors having moderate and narrow gaps between the valence and conduction bands. We discuss limitations of this model description and mention cases, which make a more refined theories necessary. We introduce and discuss $sp-d$ exchange interaction constants, show the trends existing in their values in the family of II–VI DMSs. We finally discuss the $d-d$ exchange interaction, which is responsible for magnetic properties of the materials in question and show how to conveniently parametrize the magnetization.

1.1 Introduction

This chapter presents the most important experimental features that distinguish a diluted magnetic semiconductor from materials containing no magnetic ions. To achieve this goal, we select the most typical material as an example that we shall use to illustrate our considerations here, referring to other diluted magnetic semiconductors only rather sporadically. With this intention, let us define a dilute magnetic semiconductor as a substitutional ternary alloy of II–VI semiconductor compounds, such as CdTe, where part of the cations in the Cd sublattice are replaced (at random) by transition metal ions. Why do II–VI compounds represent the simple case?
Namely, transition metal ions may, and often do, form centers that are neutral with respect to the background crystalline lattice, i.e., there are no excess electric charges localized on them. This is in contrast to III–V-based diluted magnetic semiconductors, where a typical situation is that the doping transition metal ion is also a charged center. Why CdTe, in particular? First its lattice structure is that of zinc blende so that complications of the wurtzite or rocksalt case can be left for more in-depth going parts of the book. Second, the band gap of CdTe is intermediate in width, so, again, complications related to the narrow gap semiconductors do not have to be accounted for (we shall mention them here only relatively briefly) and neither do anomalies associated with the extremely wide band gap situation have to be worried about (those are left for the next chapter).

Again, limiting ourselves to simple cases, we shall, unless otherwise stated, think about Manganese when saying “a transition metal ion”. The simplicity of Manganese stems from the fact that its electronic $d$-shell is half-filled, the orbital momentum of the $d$-shell vanishes while the spin has a maximum, for transition metal series, possible value of $5/2$, and the ground state of $d$-electrons represents a spin singlet. Thus, the archetypal diluted magnetic semiconductor is a ternary Cd$_{1-x}$Mn$_x$Te, where $x$ represents the molar fraction of Mn ions that replace Cd ions. Again, to keep things as simple as possible we shall here envisage then that the $d$-electrons of manganese are considerably more localized spatially than the $s$- and $p$-electrons (that are assumed to contribute to the conduction and valence bands). Their interaction with the delocalized electrons is relatively weak (see further chapters in this volume) which substantiates, in turn, a picture in which these two electronic systems – $d$-electrons of Manganese and the delocalized $s$- and $p$-electrons – may be considered separately, to a certain extent. The weak interaction between these two electronic subsystems may be treated effectively as a spin dependent perturbation, within a combination of virtual crystal approximation and mean field approach. It is amazing how many experimental observations can be quantitatively understood with this extremely simplified view. Let us begin our encounter with diluted magnetic semiconductors by describing in a rather detailed fashion the optical phenomenon – the Faraday rotation – which turned out to be the most convincing, if not the first, experimental indication that the spin-dependent coupling between the local moments of $d$-electrons of Manganese and delocalized states forming the top of the valence and the bottom of the conduction bands (1) exists, (2) is strong enough to be easily measurable, and (3) leads to interesting consequences.

1.2 Giant Faraday and Zeeman Effects

1.2.1 Giant Faraday Effect and its Origin

1.2.1.1 Experimental Faraday Rotation Measurements

From the very beginning of the studies of Diluted Magnetic Semiconductors, the Faraday effect, i.e., a rotation of polarization plane of light propagating in a medium
along a magnetic field, attracted attention by its unusual magnitude and temperature dependence. The first Diluted Magnetic Semiconductor to reveal these striking properties was (Cd,Mn)Te [1, 2]. The Faraday rotation spectra measured in Cd$_{0.95}$Mn$_{0.05}$Te at different temperatures are shown in Fig. 1.1a and those measured at 77 K in Cd$_{1-x}$Mn$_x$Te of different Mn mole fraction $x$ values are shown in Fig. 1.1b.

The effect shown in Fig. 1.1 was measured in bulk samples with thickness of order of 1 mm in the spectral region of transparency, i.e., below the energy gap. The two striking features distinguishing (Cd,Mn)Te from semiconductors without magnetic ions are well visible: a strong temperature dependence (more than an order of magnitude between 4.2 K and 300 K) and magnitude of the effect exceeding those measured for the CdTe host crystal by more than two orders of magnitude at sufficiently low temperature. The large rotation angles made the measurements very simple: it was enough to measure a transmission spectrum in magnetic field of a sample placed between crossed polarizers. An oscillatory spectrum was obtained (Fig. 1.2), with intensity minima corresponding to rotation by multiples of $\pi$. To determine the origin of the angular scale, it was enough to measure the transmitted light intensity versus magnetic field at a selected wavelength.

To analyze the physical mechanisms behind the observed features, we shall start by recalling the basic empirical description of the Faraday effect.

1.2.1.2 Empirical Description of the Faraday Effect

As mentioned above, by the Faraday effect we understand rotation of polarization plane of light propagating along a magnetic field (Faraday configuration). In the magnetic field, the eigenmodes of the light propagation correspond to right ($\sigma^+$) and left ($\sigma^-$) circular polarizations. A linearly polarized light can be decomposed into these two circular eigenmodes (Fig. 1.3), which acquire a phase difference after traveling a distance in the medium.
Fig. 1.2 Faraday rotation of Cd$_{1-x}$Mn$_x$Te alloys can be determined by simple measurements of transmitted light intensity vs. photon energy in a given magnetic field.

Recomposing the two phase-shifted components we obtain a rotation angle $\vartheta$, which is twice smaller than their phase shift $\delta$, which, in turn, is proportional to the difference between their refraction indices and to the path $d$ traveled by the light in the sample

$$\vartheta(\omega) = \frac{\omega}{2c} d (n_+(\omega) - n_-(\omega)),$$

where $\omega$ denotes circular frequency and $c$ speed of light.

Usually, we introduce Verdet constant, i.e., rotation angle per unit thickness of the sample

$$\vartheta(\omega)/d = \frac{\omega}{2c} (n_+(\omega) - n_-(\omega)).$$ (1.1)

1.2.1.3 Sources of the Faraday Rotation

Sources of refraction index dispersion are usually found in optical transitions corresponding to light absorption (extinction) at certain frequencies. According to (1.1), we can thus look for sources of the Faraday rotation in polarization-dependent absorption, originating from optical transitions which can be affected by the magnetic field. In the case of (Cd,Mn)Te, a strong dispersion of the the Faraday rotation when the photon energy approaches the energy gap suggests an interband origin of the observed effect. This hypothesis can be verified by studying magneto-optical Kerr effect (MOKE), i.e., polarization rotation of the reflected light in the magnetic field. This has been done in [1], where the energy position of a structure observed in MOKE was shown to coincide with that of the excitonic reflectivity structure (Fig. 1.4).

An experiment revealing profound origins of the Faraday rotation was reported in a pioneering paper by Komarov et al. [2]. They showed that the Faraday rotation can...
Fig. 1.4 Comparison between reflectivity and magneto-optical Kerr rotation spectra in the interband region of Cd$_{0.95}$Mn$_{0.05}$Te shows common excitonic origin of the two effects. Reprinted with permission from [1]

Fig. 1.5 Faraday rotation of CdTe:Mn under microwave illumination, measured at photon energies 1.5 eV (1) and 1.568 eV (2). A dip at 3.3 kOe corresponds to the spin resonance of Mn$^{++}$ ions. The two curves correspond to two different wavelengths of light, whose polarization direction is monitored. Reprinted from [2] with kind permission of Springer Science and Business Media

be strongly attenuated by resonant heating of the Mn$^{++}$ ion spins using microwaves. The Faraday rotation angle measured in CdTe:Mn sample under microwave illumination, plotted versus magnetic field, (Fig. 1.5) exhibits a strong dip at the magnetic field corresponding to the spin resonance of the Mn$^{++}$ ions.

This result pinpoints the crucial role of the manganese ions in the physical mechanism of the giant Faraday rotation. The above qualitative results indicate the elements to be included in a model description of the giant Faraday rotation.

1.2.1.4 Dispersion Relations

Before undertaking the search for a quantitative model, it is useful to consider dispersion relations [3], which link the real and imaginary part of the complex refraction index (refraction index and extinction coefficient, respectively): $\tilde{n}(\omega) = n(\omega) + i\kappa(\omega)$
The causality principle imposes symmetry conditions which in the presence of a magnetic field take the form

\[ n(-\omega, -B) = n(\omega, B) \quad \text{and} \quad \kappa(-\omega, -B) = -\kappa(\omega, B) \]

At \( B = 0 \) \( n \) and \( \kappa \) are thus even and odd functions of \( \omega \), respectively. This symmetry allows us to reduce the integrals in the dispersion relations to the physically meaningful range of positive frequencies, yielding the usual Kramers–Kronig form

\[ n(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega'n(\omega')d\omega'}{\omega'^2 - \omega^2} \quad \text{and} \quad \kappa(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{(n(\omega') - 1)d\omega'}{\omega'^2 - \omega^2}, \]

\( P \) denoting the principal value of the integral.

If a nonzero magnetic field is present, the above simple scheme of reducing the integrals to the range of positive frequencies does not work any more, since passing from \( \omega \) to \( -\omega \) we have to change the sign of the field at the same time, resulting in \( n \) and \( \kappa \) being neither even nor odd functions of \( \omega \). However, for \( \Delta n \) and \( \Delta \kappa \) we can write \( \Delta n(-\omega, B) = n_+(\omega, B) - n_-(\omega, B) = n_-(\omega, -B) - n_+(\omega, -B) = n_-(\omega, B) - n_+(\omega, B) = -\Delta n(\omega, B) \) and \( \Delta \kappa(-\omega, B) = \Delta \kappa(\omega, B) \), where indices + and − represent two circular polarizations of the light.

Thus, \( \Delta n \) and \( \Delta \kappa \) are odd and even functions of \( \omega \), respectively (in contrast to \( n \) and \( \kappa \) at \( B = 0 \), which are even and odd, respectively) and therefore the dispersion relations take the form

\[ \Delta n(\omega) = \frac{2\omega}{\pi} P \int_0^\infty \frac{\Delta \kappa(\omega')d\omega'}{\omega'^2 - \omega^2} \quad \text{and} \quad \Delta \kappa(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\omega'\Delta n(\omega')d\omega'}{\omega'^2 - \omega^2}. \]

The difference between this form of the dispersion relations and the standard Kramers–Kronig one is important when we are interested in a wide spectral range; in the vicinity of a narrow resonance it is negligible.

It must be stressed that the above expressions do not apply to naturally occurring optical activity of a medium with helical microscopic structure (e.g., sugar and its water solutions). Since no magnetic field is present, the usual form of Kramers–Kronig relations is valid also for the differences of real and imaginary part of the refractive index between the two circular polarizations. Another important difference between the Faraday rotation and natural optical activity concerns the sign of rotation when the propagation direction is reversed and the light passes across the sample a second time. In the case of the Faraday rotation, the polarization of the reflected light continues to turn in the same sense, producing a total rotation twice as big as in the case of a single passage, whereas for a helical medium the sense of the rotation is reversed when the light passes across the sample in the opposite direction. As a result, the total rotation vanishes (see Fig. 1.6) in the natural case.
Fig. 1.6  Polarization rotation of light passing again the same sample after reflection is enhanced in case of the Faraday rotation (a) or compensated in case of a helical medium (b)

Fig. 1.7  Extinction coefficient (left) and refraction index (right) spectra for a Lorentzian line ($\omega_0 = 1, \Gamma = 0.01$)

The difference between the two cases can be seen as a result of time reversal symmetry. Without magnetic field, the change of the light propagation direction to the opposite value corresponds to a time reversal and therefore it should bring the status of the light polarization back to the original value. In presence of a magnetic field, the time reversal symmetry would impose a sign change of the pseudovector of the magnetic field during the second passage of the light through the sample. If we keep the magnetic field unchanged, the second rotation enhances the first one instead of compensating it.

1.2.1.5 Three Types of the Faraday Rotation

As a simple example, let us consider a single Lorentzian optical transition line (Fig. 1.7). The extinction coefficient $\kappa$ and refraction index $n$ can be expressed, respectively, as imaginary and real parts of the complex refraction index $\tilde{n}(\omega) = 1 + \frac{\omega_0^2 - \omega^2}{\omega_0^2 - \omega^2 + i\omega_0 \Gamma}$, where $\omega_0$ is the resonance frequency, $2\Gamma$ is full width at half maximum (FWHM) and $A$ is an amplitude.

The Faraday rotation spectrum for such a line will differ depending on how the magnetic field influences the line parameters [4]. Usually, we think about the influence of the magnetic field on the resonance frequency (the line position), resulting in

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The chosen simplified Lorentzian form does not satisfy the symmetry conditions discussed above, therefore it can be used only close to the resonance energy.
the Faraday rotation spectrum originating from the Zeeman effect. In the low-field approximation, it reads

$$\vartheta (\omega) / d = \frac{\omega}{2c} \Delta n = \frac{\omega}{2c} A \frac{\partial n(\omega)}{\partial \omega_0} = - \frac{\omega}{2c} \Delta \omega_0 A \frac{(\omega_0 - \omega)^2 - \Gamma^2}{((\omega_0 - \omega)^2 + \Gamma^2)^2} \quad (1.2)$$

As shown in Fig. 1.8, the spectrum of the Faraday rotation is to a good approximation symmetrical related to the resonance frequency.

However, the magnetic field can also influence the line width and/or the amplitude of the line, resulting in two other different types of the Faraday rotation. The low-field analytical expressions read for the amplitude-type effect

$$\vartheta (\omega) / d = \frac{\omega}{2c} \Delta A \frac{\partial n(\omega)}{\partial A} = \frac{\omega}{2c} \Delta A \frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + \Gamma^2} \quad (1.3)$$

and for the line width type

$$\vartheta (\omega) / d = \frac{\omega}{2c} \Delta \Gamma \frac{\partial n(\omega)}{\partial \Gamma} = -\frac{\omega}{c} \Delta \Gamma A \Gamma \frac{\omega_0 - \omega}{((\omega_0 - \omega)^2 + \Gamma^2)^2} \quad (1.4)$$

As shown in Fig. 1.9, the amplitude- and linewidth-type Faraday rotation spectra have a spectral shape completely different from the Zeeman type spectrum, being approximately odd functions of detuning \( \omega - \omega_0 \).

1.2.1.6 Description of Examples of Experimental Faraday Rotation Spectra

The above examples are not as academic as they may seem to be: excitonic transitions either in bulk crystals or in quantum structures can be often described in such a simple approximation. In most cases, the simplest assumption of the Zeeman-type Faraday effect is sufficient but some interesting cases (e.g., charged excitons – see Chap. 9) may require a different description.
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An important feature of the Faraday rotation is its long range in the spectrum: it may extend quite far from the energies where the actual optical transitions (and absorption due to them) occur. Therefore, e.g., in transmission experiments on bulk crystals of macroscopic thickness, where we do not access directly the excitonic region, the measured interband Faraday rotation will be influenced not only by the 1S excitonic transition but also by transitions from a relatively large spectral range above the band gap.

1.2.1.7 Model Description of Faraday Rotation in (Cd,Mn)Te

The interpretation of the first Faraday rotation spectra measured on (Cd,Mn)Te crystals was centered on a search for the simplest model of optical transitions responsible for the obtained spectra.

When we do not approach too closely the transition energies in the Faraday rotation measurements, we can neglect the broadening of the optical transitions. In such a situation, we can ask what is the type of singularity at the transition energy. For example, in the case of a single line, the extinction coefficient \(\kappa\) can be represented by a delta-function centered at the transition energy \(\kappa(\omega) = A\delta(\omega - \omega_0)\), corresponding to a refraction index \(n(\omega) - 1 = \frac{2}{c} \frac{A\omega_0}{\omega^2}\).

The Zeeman-like Faraday rotation in the linear approximation is then

\[
\frac{\partial}{d} = \frac{\omega}{2c} \Delta n = \frac{\omega}{2c} \frac{\partial n(\omega)}{\partial \omega} = -\frac{\omega}{c} \frac{A}{\pi} \frac{\omega_0^2 + \omega^2}{(\omega_0^2 - \omega^2)^2} \Delta \omega_0. \tag{1.5}
\]

The above expression possesses a second order singularity at \(\omega \to \omega_0\). The single line can be associated with creation of the ground (1S) excitonic state or an atomic-like transition due to an impurity.

The Faraday rotation due to interband transitions (excitonic effects neglected) has been calculated, e.g., by Kołodziejczak et al. [5]. Their model assumes a square root shaped absorption edge, and as a consequence, a singularity of the type of \((\omega_0 - \omega)^{-1/2}\).
If we want to propose a more realistic description of the fundamental absorption edge, including excitonic effects, the first rough approximation may take the form of a step function \( \kappa(\omega) = A \Theta(\omega_0 - \omega) \). For the Zeeman-like Faraday effect, we shall have in this case a \( \delta \)-shaped circular dichroism \( \Delta \kappa(\omega) = A\Delta \omega_0 \delta(\omega_0 - \omega) \). Using the dispersion relations, we obtain then

\[
\frac{\vartheta(\omega)}{d} = \frac{\omega}{2c} \Delta n = -\frac{\omega^2}{\pi c} \frac{A\Delta \omega_0}{\omega_0^2 - \omega^2}. \tag{1.6}
\]

The above expression contains a first-order singularity at \( \omega \rightarrow \omega_0 \).

Gaj, Gałązka, and Nawrocki [1] compared the three model expressions with results of the Faraday rotation measurements in (Cd,Mn)Te. They found that the square root edge model is the most remote from the experimental spectra, which have an intermediate form between the single line model and step function model curves. It has been found that the singularity is located at the frequency of the excitonic structure occurring in reflectivity spectra. This fact led the authors to assign the observed Faraday rotation to interband transitions, which in medium- and wide-gap semiconductors are strongly modified by presence of excitons.

An improved model based on calculations of spectral moments was shown to describe the Faraday rotation of (Cd,Mn)Te with a fair accuracy [6] (Fig. 1.10).

In this model, the spectrum of the extinction coefficient is represented by a combination of a single line and a step function.

The best currently available description of the refractive index due to interband transitions is due to Tanguy [7, 8] for bulk crystals and low-dimensional structures. The model can certainly provide a precise description of the interband Faraday rotation.

Summarizing, we identify Zeeman split interband transitions as the source of the giant Faraday rotation observed in (Cd,Mn)Te. The size of the effect implies giant Zeeman splittings of these transitions. The next challenge is to confirm experimentally the existence of the giant Zeeman effect and to describe its relation to the spin state of Mn\(^{++} \) ions. This will be done in the following sections.

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**Fig. 1.10** Model description (solid line) of the Faraday rotation data of (Cd,Mn)Te (points). After [6]
1.2.2  **Excitonic Zeeman Effect in (Cd,Mn)Te**

1.2.2.1  **Zeeman Effect Measurements**

Reliable measurements of excitonic Zeeman splitting can be obtained from measurements performed directly in the spectral region of the excitonic absorption. While reflectivity measurements do not present any special experimental difficulty, absorption (which represents the most direct probe of optical transitions) requires thin samples (below $1 \mu m$). Such samples have been first obtained from bulk DMS crystals by Twardowski [9], who was able to detect not only the excitonic ground $1s$ states but also a wealth of excited states in a magnetic field. Magnetoabsorption and magnetoreflectivity measurements on (Cd,Mn)Te at low temperatures [9, 10] revealed that the $1s$ excitonic ground state transition splits into six components: two of them visible in each circular polarization in the Faraday configuration (light propagating along magnetic field, Fig. 1.11a) and additional two visible in $\pi$ polarization ($E \parallel B$) in Voigt configuration (light propagation perpendicular to the magnetic field, Fig. 1.11b).

Typical reflectivity spectra of (Cd,Mn)Te measured at 1 T and 1.8 K in various polarizations are shown in Fig. 1.12. Two strong and two weak components are visible in circular polarizations (Faraday configuration) and two additional ones in Voigt configuration. The observed six component splitting pattern can be expressed in terms of a band-splitting scheme shown in the same figure.

1.2.2.2  **Energy Band Splitting Pattern**

The scheme shown in Fig. 1.12 assumes symmetrical splitting of the conduction band in two components and of the valence band in four equidistant components. It imposes an interdependence between the energies of the observed components: each component observed in $\pi$ polarization lies in energy in the middle between a strong and a weak components observed in the opposite circular polarizations. After experimental verification of this regularity, the Voigt configuration results were not used in further discussion, as their energies do not carry any new information. We

![Fig. 1.11](image-url)  
**Fig. 1.11** Faraday configuration (a) and Voigt configuration (b) used in magneto-optical experiments. Linear ($\sigma$ and $\pi$) and circular ($\sigma^+$ and $\sigma^-$) polarizations of respective eigenmodes indicated.
will show in the following that this splitting scheme corresponds to \( J_z \) eigenstates of the conduction and valence electrons. This means that we can associate an exciton (keeping in mind the excitonic character of the optical transitions) with each pair of exchange-split components of energy bands. Such a result is obtained by neglecting electron–hole exchange interaction which would couple excitonic states associated with various pairs of the subbands. In fact, electron–hole exchange interaction energy in CdTe and in similar compounds is typically of the order of 1 meV, very small compared to giant Zeeman splittings, which at liquid He temperatures and in a field of a few Tesla are often of the order of 100 meV. Assuming that the excitonic effects are identical for all subbands in question, the relative transition intensities can be calculated for simple interband transitions, assuming conduction wavefunctions of the form \[ \text{[11]} \]

\[
|1/2\rangle = |S\rangle \uparrow, \quad |-1/2\rangle = |S\rangle \downarrow \quad \text{(1.7)}
\]

and the valence band wavefunctions as

\[
|3/2, 1/2\rangle = \sqrt{\frac{1}{6}} (|X + iY\rangle \downarrow -2|Z\rangle \uparrow),
\]

\[
|3/2, -1/2\rangle = \sqrt{\frac{1}{6}} (|X - iY\rangle \uparrow +2|Z\rangle \downarrow)
\]

and

\[
|3/2, 3/2\rangle = \sqrt{\frac{3}{2}} |X + iY\rangle \uparrow, \quad |3/2, -3/2\rangle = \sqrt{\frac{3}{2}} |X - iY\rangle \downarrow \quad \text{(1.8)}
\]

for light- and heavy-hole bands, respectively. Six nonvanishing transition probabilities are then obtained as squares of absolute values of electric dipole matrix...
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elements between the corresponding states. Denoting the electric dipole operator $\hat{D} = (\hat{X}, \hat{Y}, \hat{Z})$, we use directly its components for linearly polarized light. In Voigt configuration (light propagation, say, along $y$ direction), the only nonvanishing interband matrix elements for $\pi$ polarization are

$$\langle 1/2 | \hat{Z} | 3/2, 1/2 \rangle = -\sqrt{2/3} \langle S | \hat{Z} | Z \rangle$$

and

$$\langle -1/2 | \hat{Z} | 3/2, -1/2 \rangle = \sqrt{2/3} \langle S | \hat{Z} | Z \rangle$$

whereas for $\sigma$ polarization only

$$\langle 1/2 | \hat{X} | 3/2, 3/2 \rangle = \sqrt{1/2} \langle S | \hat{X} | X \rangle = \langle -1/2 | \hat{X} | 3/2, -3/2 \rangle$$

and

$$\langle 1/2 | \hat{X} | 3/2, -1/2 \rangle = \sqrt{1/6} \langle S | \hat{X} | X \rangle = \langle -1/2 | \hat{X} | 3/2, 1/2 \rangle$$

(1.9)

(1.10)
do not vanish.

In the Faraday configuration, when the light propagates along magnetic field ($z$ direction), the electric dipole operator components corresponding respectively to $\sigma^+$ and $\sigma^-$ circular polarizations

$$\hat{D}^+ = \sqrt{1/2} (\hat{X} + i\hat{Y}) \quad \text{and} \quad \hat{D}^- = \sqrt{1/2} (\hat{X} - i\hat{Y})$$

(1.11)

produce nonvanishing interband matrix elements

$$\langle 1/2 | \hat{D}^+ | 3/2, -1/2 \rangle = \sqrt{1/3} \langle S | \hat{X} | X \rangle = \langle -1/2 | \hat{D}^- | 3/2, 1/2 \rangle$$

and

$$\langle 1/2 | \hat{D}^- | 3/2, 3/2 \rangle = \langle S | \hat{X} | X \rangle = \langle -1/2 | \hat{D}^+ | 3/2, -3/2 \rangle$$

(1.12)

where we used equivalence of $x$ and $Y$ direction in a cubic crystal. Remembering that the $Z$ direction is equivalent to each of them, we see that the relative intensities of all the interband optical transitions are given by the above results. We obtain thus a splitting pattern with four components in the Faraday configuration of relative intensities 6 (heavy holes) and 2 (light holes) in each circular polarization, whereas in the Voigt configuration we obtain two components of relative intensities 4 in $p$ polarization and four components: two of relative intensity 3 (heavy holes) and two of relative intensity 1 (light holes). Experimental spectra confirm qualitatively the calculated selection rules (see Fig. 1.12). The splitting pattern described here was used in the previously described model description of the Faraday rotation spectra [6]: the assumed model shape of the absorption edge was assumed to split in four components (two weak and two strong ones) active in the Faraday configuration.
The intensity ratio 1:3 of weak to strong components was assumed according to the matrix element values calculated above.

1.2.2.3 Magnetization Measurements

A next step in the analysis of the magnetooptical results is to describe quantitatively the relation between the giant Zeeman effect and the spin state of the magnetic ions, proved qualitatively in [2]. It was done by comparing the giant Zeeman splitting with the magnetization of the crystal. As CdTe is known to be diamagnetic [12], the magnetization of a (Cd,Mn)Te crystal is at low temperature dominated by the alignment of the magnetic moments of the Mn\(^{++}\) ions. A series of magnetization measurements was performed on (Cd,Mn)Te samples with Mn mole fraction values \(x\) ranging from 0.005 to 0.3. Typical results are shown in Fig. 1.13.

At low field magnetization of all the samples increases linearly, showing at higher fields a tendency to saturation, most pronounced for the most dilute samples. For such samples, the magnetization can be fairly well described by a Brillouin function, characteristic for a system of noninteracting spins

\[
B_S(\xi) = \frac{2S + 1}{2S} \cth \left( \frac{2S + 1}{2S} \xi \right) - \frac{1}{2S} \cth \left( \frac{1}{2S} \xi \right),
\]

(1.13)

where in our case \(S = 5/2\) is Mn spin value. An empirical description valid for any Mn composition at pumped Helium temperatures up to about five Tesla can be obtained [13] by introducing two empirical parameters: effective spin saturation

![Fig. 1.13](image-url) Magnetization of (Cd,Mn)Te crystals of various Mn mole fraction \(x\) values (indicated in %). With increasing \(x\) a tendency to saturation at higher field weakens. Reprinted with permission from [13]
value $S_0$ and a temperature correction $T_0$. The magnetization, expressed as mean spin value per Mn ion, takes then the form

$$\langle S_z \rangle = S_0 B_S \left( \frac{g \mu_B S B}{k_B (T - T_0)} \right), \quad (1.14)$$

where $g = 2$ is Mn gyromagnetic factor, $\mu_B$, $k_B$ and $T$ are Bohr magneton, Boltzmann constant, and temperature respectively. The parameters $S_0$ and $T_0$ depend on Mn mole fraction $x$ of the alloy – this dependence was discussed in [14]. This magnetization behavior is related to ion–ion $d-d$ interaction, and will be discussed in Sect. 1.4.

### 1.2.2.4 Zeeman Splittings vs. Magnetization

The splitting of the strong components visible in reflectivity (such as the ones in Fig. 1.12) was plotted versus magnetization measured under approximately the same experimental conditions. The results are shown in Fig. 1.14.

Magnetization is presented in Fig. 1.14 as mean Mn spin value per unit cell

$$x \langle S_z \rangle = \frac{M}{N_0 g \mu_B}. \quad (1.15)$$

where $N_0$ is the number of unit cells per unit volume.

In this way, results obtained in samples with different $x$ values can be directly compared. The points obtained at different magnetic fields for samples with seven

![Fig. 1.14 Splitting of the "strong" (heavy hole) exciton component of (Cd,Mn)Te crystals of various Mn mole fraction values (indicated in %) vs. magnetization. Reprinted with permission from [13]](image-url)
different $x$ values form a unique linear dependence (represented by the straight line). This proportionality of the Zeeman splittings to the magnetization is a general property of a large part of DMS, with energy gap values around 1 or 2 eV. It will be interpreted in what follows in terms of ion-carrier $sp$–$d$ interaction described in the mean field approximation. Narrow gap DMS (e.g., (Hg,Mn)Te) and large gap ones (such as (Zn,Mn)O) do not obey this rule for different reasons. Their peculiarities will be discussed in Sect. 1.5 and Chap. 2, respectively.

1.2.3 Mean Field Approximation, Ion-carrier ($sp$–$d$) Exchange Integrals in (Cd,Mn)Te

We shall describe the influence of magnetic ions on the charge carriers in terms of $s$–$d$ (for the conduction band) or $p$–$d$ (for the valence band) exchange interaction. In fact its nature is purely electrostatic (see, e.g., Ashcroft & Mermin [15]), but it can be expressed by a scalar product of the interacting spins. In the form known as Heisenberg Hamiltonian [16]

$$\hat{H} = -\sum_i J(r - R_i)\sigma \cdot S_i,$$

where $\sigma$ and $S_i$ denote (vector) spin operators of the carrier and $i$-th magnetic ion, respectively, the magnetic ion being placed at the position characterized by the $R_i$ lattice vector. $J$ is an effective operator acting on the carrier’s spatial coordinates. The physical origin of the $sp$–$d$ interaction in DMS is discussed in detail in Chap. 3.

While describing the influence of the carrier–ion interaction on the properties of a semimagnetic semiconductor with a moderate energy gap it is important to keep in mind the relative numbers: we have usually to do with a number of magnetic ions comparable to the total number of atoms in the crystal, while the number of carriers is smaller by orders of magnitude; the material is often semi-insulating and the only carriers are those created by light. A delocalized, itinerant carrier interacts usually with a great number of magnetic ions. This disparity makes the influence of the carriers on the magnetic ions negligible, justifying the most commonly used approach: an external magnetic field aligns the magnetic ions, which in turn act on carriers via ion–carrier interaction. This action has been described successfully in the mean field approximation, where the spin operators of magnetic ions have been replaced by their thermal average. Furthermore, the mean field approximation is usually completed by the virtual crystal approximation, restoring crystal periodicity: the random distribution of magnetic ions and host cations over the cation sublattice is replaced by a periodical structure with artificial cations possessing properties of the host cation and the magnetic ion, averaged using occupation probabilities as 

---

3 Semiconductors or their structures containing large density of free carriers possess different properties, which are not discussed here.
weights. Within these approximations the carrier-ion Hamiltonian becomes

\[ \hat{H} = -N_0 \alpha x \sigma_z \langle S_z \rangle \]  

(1.17)

for the conduction electrons and

\[ \hat{H} = -N_0 \beta x \sigma_z \langle S_z \rangle \]  

(1.18)

for the valence band carriers, where \( N_0 \) denotes number of unit cells per unit volume, \( \alpha = \langle S | J | S \rangle \) and \( \beta = \langle X | J | X \rangle \) are exchange integrals for the conduction- and valence-electrons, respectively. This form of the Hamiltonian applied to the states at \( \Gamma \)-point of the Brillouin zone produces a splitting of the conduction band in two components of opposite spins separated by \( \Delta E_c = |N_0 \alpha x \langle S_z \rangle| \) and a splitting of the valence band in four equidistant components with the external ones split by \( \Delta E_v = |N_0 \beta x \langle S_z \rangle| \). Since in low \( x \) limit, the substances in question are paramagnetic, a non-vanishing magnetization can be obtained by applying the magnetic field. Acting on the conduction- and valence-band states, this field will modify the wavefunctions of the carriers, produce Landau quantization, usual spin splittings, etc. These effects are of primary importance in narrow gap materials, but in moderate- and wide-gap semiconductors often they may be neglected compared to the giant spin splitting due to ion–carrier interaction. In such an approximation, we can still apply the notion of the wavevector and consider unperturbed bands except for the exchange splittings (Fig. 1.15).

In the case of Mn\(^{++}\) ions possessing no orbital magnetic moment, the thermal average \( g \mu_B N_0 \langle S_z \rangle \) represents the magnetization per magnetic ion and \( g \mu_B N_0 x \langle S_z \rangle \) represents the magnetization per cation.

Considering nonvanishing wavevectors (kinetic energies non-negligible with respect to the exchange splittings) within the above approximations, Gaj, Ginter, and Gałązka [17] obtained a fairly complicated band structure as a result of combined carrier-ion exchange- and \( k \cdot p \) interactions.

For the interpretation of the excitonic optical spectra, it is enough to limit oneself to the vicinity of the \( \Gamma \)-point. Using the approximations mentioned above (negligible e-h exchange interaction and constant exciton binding energy), we can express

![Fig. 1.15 Conduction- and valence bands of a typical moderate gap II–VI semimagnetic semiconductor in the vicinity of \( \Gamma \) point, split by exchange interaction (a schematical representation)
excitonic Zeeman splitting as differences of the corresponding band splittings. By plotting, thus obtained, excitonic Zeeman splittings versus the magnetization we obtain straight lines in excellent agreement with experimental data (see Fig. 1.14), with the slope determined by exchange integrals. Thus for the “strong” components observed in the Faraday configuration (heavy hole exciton), the Zeeman splitting in the mean field approximation (Fig. 1.12) is

\[ \Delta E_e = E_- - E_+ = N_0(\beta - \alpha)x\langle S_z \rangle \] (1.19)

where indices $-$ and $+$ denote circular polarizations (please note that $\langle S_z \rangle$ is negative). For the “weak” components (light hole exciton), the splitting is

\[ \Delta E_e = E_- - E_+ = N_0(\beta/3 + \alpha)x\langle S_z \rangle. \] (1.20)

Such plots have been shown to be common for various Mn mole fraction values. They supply reliable values of exchange integrals. In (CdMn)Te, commonly accepted values are $N_0\alpha = 0.22$ eV and $N_0\beta = -0.88$ eV for the conduction- and valence-band, respectively [13].

### 1.2.4 Giant Zeeman Effect in Narrow Gap Materials

In the beginning of 1970s, narrow gap semiconductors such as HgTe or HgSe and also ternary compounds with Cadmium, e.g., (Hg,Cd)Te were studied quite extensively because of their applications in infrared detectors. Therefore, narrow gap semiconductors (or even those with an inverted band gap) made of Mercury chalcogenides with Manganese were in fact among the first semimagnetic crystals studied in an extensive way. The interest in those compounds stemmed, at least partly, from the fact that Morrissy [18] in his Ph.D. work had observed anomalously high electron mobility in (Hg,Mn)Te. Narrow gap semiconductors represent a slightly more complicated case than (Cd,Mn)Te discussed above because proximity of the conduction and topmost valence bands precludes their separate consideration. In fact, the smallest set of states to be included in the calculation consists of four states: $s$-like conduction (light hole, in the case of inverted band structure), $p$-like valence band states (heavy and light holes degenerate at $I$ point of the Brillouin zone, or heavy hole and conduction band states in the case of the inverted band structure) and $p$-like spin orbit split-off band. Away from the zone center, these states are considerably intermixed due to $k \cdot p$ interaction. Therefore, the description of the coupling of magnetic ions with, say, the conduction band will involve not only terms proportional to $\alpha$ but also due to $\beta$ exchange integrals.

Since the basic method of investigation of these compounds involved either the interband magnetoabsorption [19, 20] or observation of Shubnikov de Haas oscillation of the magnetoconductivity [21, 22], therefore, all relevant calculations had to be done in the presence of an external magnetic field. It was realized fairly early that
the modifications of the band structure of (Hg,Mn)Te upon doping with Mn were spin dependent. A very clear demonstration of this fact is shown in Fig. 1.16, which shows the spin and Landau splittings of nonmagnetic (Hg,Cd)Te and magnetic (Hg,Mn)Te having comparable energy gaps.

While the Landau splitting is essentially identical in both compounds (as it is ruled by the width of the gap, the momentum matrix element being very similar in most II–VI semiconductors), the spin splitting is very much different, being, moreover, temperature dependent in the case of Mn-containing samples. Because of narrow band gap, and therefore, small effective mass of conduction electrons ($\varepsilon_0 \sim 1/m^*$), the Landau quantization cannot be neglected. Technically, one has to diagonalize two $4 \times 4$ matrices each being a sum of “nonmagnetic” matrix due to $k \cdot p$ interaction and that due to $sp-d$ interaction: $h^a_L + h^a_S$ and $h^b_L + h^b_S$.

The form of these matrices depends, of course, on the choice of the basis functions. Here, we have used the basis states given by $|\{1/2\}, 3/2 \rangle, |3/2, 1/2 \rangle, |1, 1 \rangle_{so}$ and $|\{1/2\}, 3/2 \rangle, |3/2, -1/2 \rangle, |3/2, -3/2 \rangle, |1/2, 1/2 \rangle, |1/2, -1/2 \rangle_{so}$ defined above in the case of the conduction and valence band states (heavy and light holes, (1.7)–(1.8)) together with

$| -1/2 \rangle_{so} = -\sqrt{3/5}(|X-iY \uparrow -2|Z \downarrow), \ |1/2 \rangle_{so} = \sqrt{1/5}(|X+iY \downarrow +2|Z \uparrow)$

to additionally describe the presence of the spin–orbit split-off valence band. This choice results in

$$H_L + H_S = \begin{pmatrix} h^a_L & 0 \\ 0 & h^b_L \end{pmatrix} + \begin{pmatrix} h^a_S & 0 \\ 0 & h^b_S \end{pmatrix},$$

![Fig. 1.16](image-url) The sum of cyclotron splitting of the first Landau levels in the conduction and heavy hole valence bands $h_2^2$ and the sum spin splitting of the same subbands $s_c(1)$ measured directly in magnetoabsorption in (Hg,Mn)Te (solid symbols) and (Hg,Cd)Te (empty symbols) for various crystal compositions (and therefore various band gaps $\varepsilon_0$) at 2 T. Note that the cyclotron splitting follows the same trend in both materials, and is temperature independent between 4.4 K and 2 K, while the spin splitting is considerably larger in (Hg,Mn)Te, where it shows temperature dependence. Reprinted with permission from [19]
where \( h_{a;b}^{a} \) represent four-dimensional Luttinger–Kohn (or Pidgeon and Brown) matrices [23,24] that describe the Landau levels within the general \( k \cdot p \) approach in the presence of an external magnetic field in narrow gap semiconductors and whose terms depend on the energy gap, spin–orbit splitting energy, momentum matrix element and four parameters that describe interactions with bands more remote than the four (doubly degenerate) bands of \( \Gamma_6, \Gamma_8, \) and \( \Gamma_7 \) symmetries that are taken into account explicitly. The matrices \( h_{a;b}^{a} \) (also \( 4 \times 4 \) dimensional) represent additions due to \( sp-d \) interaction and may be written explicitly as [25]

\[
\begin{align*}
\begin{pmatrix}
a & 0 & 0 & 0 \\
0 & 3b & 0 & 0 \\
0 & 0 & -b & -2i\sqrt{2}b \\
0 & 0 & i2\sqrt{2}b & b \\
\end{pmatrix} \quad \text{and} \quad \\
\begin{pmatrix}
-a & 0 & 0 & 0 \\
0 & -3b & 0 & 0 \\
0 & 0 & b & 2i\sqrt{2}b \\
0 & 0 & -i2\sqrt{2}b & -b \\
\end{pmatrix}
\end{align*}
\]

with \( a = \frac{1}{2} N_0 x_\alpha \langle S_z \rangle \) and \( b = \frac{1}{e} N_0 x_\beta \langle S_z \rangle \).

Let us notice that even in the simplest approximation (virtual crystal + mean field) the terms proportional to the magnetization appear not only on the diagonal of those matrices but also mix somewhat the light hole and spin–orbit split-off band. Fortunately, strong spin–orbit interaction in HgTe-based crystals and similar compounds makes this mixing a negligible effect. Small band gap combined with a strong spin–orbit interaction in mercury chalcogenides result in huge \( g \)-factors describing the spin splitting of the band states even in absence of magnetic ions. Nevertheless, inclusion of Mn in, say, HgTe leads to a truly huge \( g \)-factors that can sometimes exceed the orbital Landau splitting, which adds to the difficulty in proper identification of the optical transition lines. Numerous crossings of the various bands, occurring when the external magnetic field is varied, can be expected (and indeed are observed). One has to mention at this point that these are, in the present approximation, true crossings without any tendency of “quantum repulsion” or self-avoiding behavior. An illustration of the discussed behavior is shown in Fig.1.17.

Variation of the spin splitting with the temperature leads to a spectacular phenomenon in the oscillatory magnetotransport experiment (Shubnikov de Haas oscillations). The oscillation, crudely speaking, arise because the Fermi level crosses the (oscillatory) density of states as the Landau levels are pushed up by the magnetic field in those samples. While the period of the oscillations of the magnetoresistance is determined by the ratio of the Fermi energy and Landau splitting, the amplitude usually increases with the field. As a function of the temperature, the amplitude is usually quickly suppressed because of an increased role of various modes of scattering of the charge carriers. In fact, the rate of the amplitude decrease with the temperature can be used as a method of extraction of the value of the effective mass from such data. The method works, however, if both the mass and the spin splitting themselves are only weakly temperature dependent. Unfortunately, this is not the case of the \( g \)-factor now since it is a sensitive function of the temperature via the term containing the magnetization. Therefore, a temperature may exist, at which the spin splitting equal half of the cyclotron splitting. Under such conditions, one
Fig. 1.17 Calculated spin split Landau levels in the conduction band of (Hg,Mn)Te (containing $x = 0.02$ Mn) and one, topmost Landau level belonging to the heavy hole set (denoted by $b_{v}(-1)$) at two temperatures: 4 K (upper panel) and 36 K (lower panel). Note that at 4 K the band gap opens only at elevated magnetic fields (above, approximately 8 T). Broken line shows the position of the Fermi level and the open symbols mark the observed maxima of the resistivity in the Shubnikov de Haas oscillation experiments. Note that at the higher temperature the peak indicated by the arrow splits in two components. The lines cross without showing an anticrossing behavior since the corresponding states do not mix. Reprinted with permission from [22]

expects the amplitude of the Shubnikov de Haas oscillations to vanish. In fact, theoretical expression for the amplitude of contains a factor $\cos(\pi g m^*/2m_0)$, which vanishes whenever the argument is equal to an odd multiple of $\pi/2$. With $g$ being a strong function of the temperature this indeed may happen in an available temperatures range in diluted magnetic semiconductors. An example of such behavior is shown in Fig. 1.18. Sometimes several “spin-splitting zeros” of the amplitude are observed (c.f. [26]).
Fig. 1.18  The amplitude of the Shubnikov de Haas oscillations in (Hg,Mn)Te \((x = 0.02)\) showing a clear spin-splitting zero. The solid line was calculated using the model described above and inserting the resulting values of the \(g\)-factor \(g\) and effective mass \(m^*\) to the expression \(\cos(\pi g m^*/2m_0)\). Reprinted with permission from [21].

![Graph of amplitude vs. T (K)](image1)

Fig. 1.19  Thermo-oscillation in magnetotransport of \(n\)-type doped (Hg,Mn)Te \((x = 0.009)\) at several constant magnetic fields as a function of the sample temperature. The arrows show the calculated points of coincidence of the Fermi level and bottoms of the Landau levels in the conduction band. Reprinted with permission from [27].

![Graph of Δp/p vs. T (K)](image2)

In the case of an inverted band gap material (say, in (Hg,Mn)Te with less than about 7 molar percent of Mn, \(x < 0.07\)), the initial upward shift of the heavy hole subband can even lead to an effective closure of the gap making the compound a half-metal. Of course, when the magnetic field increases and the magnetization saturates, the “normal” huge \(g\)-factor overcomes the \(sp−d\)-induced modification and the band ordering returns to that observed in ordinary nonmagnetic narrow gap materials. Noticeably, the position of the band states becomes, via the magnetization, sensitive to the temperature at moderate fields. Thus, a phenomenon termed thermooscillations was predicted and recorded (see Fig. 1.19) in magnetotransport experiments [27].

Similar analysis can be done in the case of other narrow gap semimagnetic compounds such as PbTe:Mn [28, 29] and Cd₃As₂:Mn [26] and related compounds.
Determination of the \( sp-d \) exchange constants in narrow gap materials is much less reliable than that in wide band gap semiconductors. This is related to the fact that the analysis is done simultaneously for at least four bands together with determination of such parameters as momentum matrix element, the band gap (which is a strong function of \( x \)), and the higher band Luttinger parameters, the latter often not known with a very high precision even in starting nonmagnetic end-point materials, such as HgTe.

1.3 Values of \( sp-d \) Exchange Integrals

1.3.1 Experimental Determination

As discussed above, the interband magnetoabsorption or magnetoreflectivity combined with magnetization measurements represent the basic experimental tool used for determination of \( sp-d \) exchange integrals. However, other methods are also useful.

1.3.1.1 Photoluminescence in Magnetic Field

The optical transitions used in magnetoabsorption can be also exploited in photoluminescence (PL). However, several phenomena limit the applicability of the PL measurements, especially in bulk crystals. Photoluminescence often originates from recombination of localized excitons. In such cases, the approximation discussed in Sect. 1.4 of negligible influence of the carriers on the magnetic ions may no longer be valid, leading to creation of bound magnetic polarons (BMP), discussed in Chap. 8. Another limitation occurs in case of excitons bound to neutral centers, such as a neutral acceptor (\( A^0X \) state). These states contain a pair of identical carriers (holes for \( A^0X \)) in a singlet spin state, which cannot profit from the exchange with the magnetic ions within their range. As a result, destabilization of such bound excitons occurs at sufficient magnetization [30]. This is similar to the destabilization, which occurs in QWs for charged excitons (trions). The properties of doped DMS quantum wells are discussed in detail in Chap. 10. The effects mentioned above make the mean field expressions (1.19) and (1.20) inapplicable. However, if the BMP or 2D carrier gas effects are negligible (at magnetization values high enough) and at the same time, the magnetization is below destabilization value, (1.19) and/or (1.20) can be used. This possibility is particularly valuable in microphotoluminescence mapping, where the Zeeman shift measured in a moderate field range can be fitted with modified Brillouin function (1.14) and used to determine local magnetic ion concentration [31].
1.3.1.2 Spin Flip Raman Scattering

Excitonic magnetooptics provides information on combinations of exchange splitting of conduction- and valence-bands. These splittings can be measured separately in spin-flip Raman scattering (SFRS).

Figure 1.20 shows a scheme of a typical SFRS event. A photon gives a part of its energy to a carrier, inducing its transfer to another spin state. The spin flip energy, equal within the mean field approximation to the Zeeman splitting of the conduction band, can be determined from SFRS spectrum as Stokes shift, i.e. energy difference between the energies of the incident and scattered photons. In \( n \)-type DMS such as (Cd,Mn)Se, spin flip Raman scattering (SFRS) is useful for determination of \( s-d \) exchange integral values, as demonstrated first by Nawrocki et al. [32]. Raman scattering selection rules favor Voigt configuration (light propagation perpendicular to the magnetic field). Typical SFRS experiments are performed in backscattering geometry with crossed linear polarizations of incident and scattered light. By tuning the incident light photon energy slightly below the energy gap, a resonant enhancement of the scattered light intensity can be obtained. SFRS spectra obtained in such experiments [32] are shown in Fig. 1.21.

The Stokes shift shown in inset exhibits to a first approximation a Brillouin-like behavior expected in the mean field approximation. However, a non-zero electron spin flip energy at zero field shows clearly that the mean field model is not fully applicable. This behavior originates from magnetic polaron effects, discussed in Chap. 8. The only case known so far of SFRS results describable within the mean field approximation is represented by (Cd,Fe)Se. These experiments were first performed by Heiman et al. [33]. Figure 1.22 shows clearly the proportionality of the Stokes shift to magnetization, in contrast with the results obtained on (Cd,Mn)Se.

Such experiments determine the conduction band exchange integral \( \alpha \) from the coefficient of the proportionality. In case of materials where magnetic polaron effects are present, the slope should be measured at higher field values, where they are no longer significant.

1.3.1.3 Knight Shift

Another way of circumventing the difficulty in determination of \( sp-d \) integrals created by high carrier concentration is related to the initial idea of Furdyna (see Introduction). Free carriers can influence electron paramagnetic resonance (EPR)
Fig. 1.21 Raman scattering spectra of CdMnSe is indicated configuration. Energy shift vs. magnetic field shown in inset. Reprinted with permission from [32].

Fig. 1.22 Conduction electron spin flip energy for (Cd,Fe)Se represented vs. magnetization obeys well the mean field approximation, as opposed to (Cd,Mn)Se (bound magnetic polaron effects). Reprinted with permission from [33].
of magnetic ions. This modification can be expressed in the form of a variation of effective gyromagnetic factor with carrier concentration – see Fig. 1.23.

Story et al. [34] have shown that this modification, known under the name of Knight shift, can be used for determination of both sign and absolute value of carrier-ion exchange integrals in (Pb,Mn)Te and (Sn,Mn)Te. The modification of the effective $g$-factor can be explained by the presence of the effective magnetic (exchange) field $B_{\text{eff}}$ of the carriers, acting on spins of magnetic ions. This field is proportional to the spin polarization and the density $n$ of the carriers.

$$B_{\text{eff}} = \frac{J n \langle \sigma_z \rangle}{g \mu_B},$$

and adds to or subtracts from the external magnetic field, leading to an enhancement or decrease of the effective $g$ factor, depending on the sign of carrier-ion coupling constant $J$.

1.3.1.4 Peculiarities of Large Gap Materials

Large gap semiconductors, such as those based on ZnO (3.4 eV) or GaN (3.5 eV), contain typically light anion elements. Therefore the spin–orbit splitting of the valence band is in such materials much smaller than, say, in CdTe. Furthermore, large effective masses lead to strong excitonic effects, in particular to large electron–hole exchange interaction. Both these effects modify the dependence of the excitonic
Basic Consequences of \( sp-d \) and \( d-d \) Interactions in DMS

energies on the magnetization, making it strongly nonlinear. In addition, small interatomic distances in these materials enhance the carrier–ion exchange interaction, which may lead to creation of electronic states bound to iso electronic magnetic impurities. Because of all these effects, determination of \( sp-d \) exchange integrals in large gap DMS is by far more complex than the simple procedures described here. The peculiarities of large gap DMS are discussed in detail in Chap. 2.

1.3.2 Numerical Values of \( sp-d \) Exchange Integrals, Chemical Trends

The procedure described in 1.2.3 has been applied to many other semimagnetic semiconductors resulting in determination of the \( sp-d \) exchange constants. The obtained values are collected in Table 1.1. It is interesting to note positive values of valence band \( p-d \) constant in Cr-containing alloys. The origin of this interesting result was discussed, e.g., by Blinowski and Kacman [50].

The mechanisms leading to those values are discussed in Chap. 3 by Merkulov and Rodina further in this volume. For more numerical values, the reader is referred to Landolt-Bornstein tables [51, 52]. Let us mark here only the trend that while \( \alpha \) is relatively stable (with possible exception of narrow gap (Hg,Mn)Te and

<table>
<thead>
<tr>
<th>Compound</th>
<th>( N_0\alpha ) [eV]</th>
<th>( N_0\beta ) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cd,Mn)Te [13]</td>
<td>0.22</td>
<td>−0.88</td>
</tr>
<tr>
<td>(Cd,Mn)Se [35]</td>
<td>0.23</td>
<td>−1.27</td>
</tr>
<tr>
<td>(Cd,Mn)S [36]</td>
<td>0.22</td>
<td>−1.8(^a)</td>
</tr>
<tr>
<td>(Zn,Mn)Te [37]</td>
<td>0.19</td>
<td>−1.09</td>
</tr>
<tr>
<td>(Zn,Mn)Se [38]</td>
<td>0.26</td>
<td>−1.31</td>
</tr>
<tr>
<td>(Be,Mn)Te [39]</td>
<td></td>
<td>−0.34/−0.4(^c)</td>
</tr>
<tr>
<td>(Cd,Fe)Te [40]</td>
<td>0.30</td>
<td>−1.27</td>
</tr>
<tr>
<td>(Cd,Fe)Se [41]</td>
<td>0.26</td>
<td>−1.53</td>
</tr>
<tr>
<td>(Zn,Fe)Se [42]</td>
<td>0.22</td>
<td>−1.74</td>
</tr>
<tr>
<td>(Zn,Co)Te [43]</td>
<td>0.31</td>
<td>−3.03</td>
</tr>
<tr>
<td>(Cd,Co)Se [44]</td>
<td>0.28</td>
<td>−1.87</td>
</tr>
<tr>
<td>(Zn,Cr)Se [45]</td>
<td>0.2(^b)</td>
<td>+0.95</td>
</tr>
<tr>
<td>(Zn,Cr)Te [45]</td>
<td>0.2(^b)</td>
<td>+4.25</td>
</tr>
<tr>
<td>(Zn,Cr)S [45]</td>
<td>0.2(^b)</td>
<td>+0.62</td>
</tr>
<tr>
<td>(Cd,Cr)S [46]</td>
<td>0.22</td>
<td>+0.48</td>
</tr>
<tr>
<td>(Hg,Mn)Te [47, 48]</td>
<td>0.4</td>
<td>−0.6(^d)</td>
</tr>
<tr>
<td>(Hg,Mn)Se [49]</td>
<td>0.4</td>
<td>−0.7(^d)</td>
</tr>
</tbody>
</table>

\(^a\)High \( x \) value (see Sect. 1.4)  
\(^b\)Assumed typical value  
\(^c\)Light/heavy hole value  
\(^d\)We reversed the sign of the original determination to stay consistent with the convention adopted in this volume
(Hg,Mn)Se), $\beta$ varies considerably: the smaller the ionic radii of the host compound the greater is the value of $\beta$. This trend (see Chap. 2) will break down in the case of semiconductor hosts with extremely large forbidden energy gap, i.e., those involving BeTe, ZnO, and GaN. Here, we quote only the value determined for (Be,Mn)Te.

### 1.3.3 Zeeman Effect for Excitons Above the Fundamental Energy Gap

Twardowski et al. [53] reported studies of excitons in (Cd,Mn)Te involving holes from the spin–orbit split-off valence band at energies about 2.5 eV ($E_0 + \Delta_0$ in the Fig. 1.24). The measured Zeeman splitting was described in terms of the same $sp-d$ interaction constants as for the transitions at the fundamental energy gap. These measurements allowed the authors to determine also a precise value of the spin–orbit splitting $\Delta_0$ of the CdTe valence band, equal 0.948 eV.

Zeeman effect was also studied for transitions at the $L$-point of the Brillouin zone. These studies were initiated by Dudziak et al. [55] in 1982. The first quantitative results have been obtained on (Cd,Mn)Te by Ginter et al. [56]. Coquillat et al. [54] have performed measurements for (Zn,Mn)Te and (Hg,Mn)Te. In all cases, the measured splittings were much smaller than the width of the reflectivity structures. Therefore only some kind of averaged splitting values was possible to obtain by polarization modulation techniques (Fig. 1.25).

The splitting values of the $E_1$ transition were found to be proportional to those measured at $\Gamma$ point ($E_0$ transition), and therefore to the magnetization (see Fig. 1.26), in agreement with the mean field approximation.

The splittings in question were found to be considerably smaller than those measured at the center of the Brillouin zone. An attempt to compute Zeeman splittings at the $L$ point in terms of a tight binding model [56] suggested two reasons for the observed reduction: reduction of splittings of the energy bands and relaxation of selection rules, both due to mixing between the conduction- and valence-band wavefunctions. However, they calculated a reduction smaller than that measured.

![Fig. 1.24](Image) Scheme of optical transitions in the Brillouin zone of (Cd,Mn)Te
Fig. 1.25 Typical setup for modulation magnetoreflectivity measurements, where light reflected from the sample (S) placed in a superconducting coil (C) passes through a photoelastic modulator (PM) and is analyzed in a monochromator (M). Reprinted from [54]

Fig. 1.26 Splitting of the $E_1$ reflectivity structure in Zn$_{1-x}$Mn$_x$Te at 4.5 K vs. that of the two strong components of the $E_0$ structure, after Coquillat et al. [54]; $x = 0.02$ (crosses) and 0.17 (circles)

experimentally. To explain the difference, a $k$-dependence of the $p-d$ exchange integral was postulated. Besides, the calculations predicted for $E_1$ and $E_1 + \Delta_1$ transitions (involving two valence band components split by spin–orbit interaction) splittings identical in absolute value and opposite in sign (see Fig. 1.27). This result has been confirmed by experimental data [54] and later by a more realistic calculation performed by Bhattacharjee [57].

Dependence of $sp-d$ interaction on wave vector in quantum wells has been also reported by Mackh et al. [58]. It was deduced from Zeeman effect results in short period (Cd,Mn)Te/(Cd,Mg,Mn)Te superlattices.

The confinement-induced reduction of giant Zeeman splittings was analyzed theoretically by Bhattacharjee [59], who explained qualitatively the results of Mackh et al. and predicted much stronger effects in quantum dots.
Fig. 1.27  Positive and negative values of Zeeman splitting measured in Hg$_{1-x}$Mn$_x$Te for $E_1$ and $E_1 + \Delta_1$ transitions, respectively. Mn mole fraction $x = 0.05$ (crosses) and 0.2 (circles). After Coquillat et al. [54]

1.4  Beyond the Mean Field Approximation

That the mean field approximation is of limited applicability became evident fairly early in the course of investigation of diluted magnetic semiconductors. Namely, the attempts to determine the $sp-d$ exchange constants in CdS doped with minute amounts of Mn showed that these constants were (a) anomalously large and (b) strongly depended on the Mn molar fraction present in the crystal [60]. It was shown by Dietl [61] that this is a consequence of an increased probability of the presence of the $s$ or $p$-like carriers in the vicinity of a magnetic ion.

Another example of a DMS object that could not be understood in terms of mean field approach was magnetic polaron [32,62]. Going further it is now very likely that quasi zero-dimensional quantum dots containing many Mn ions represent a polaron-like entity and thus are also not describable in terms of a simple mean field approach. In fact, Wojnar [63] used a very similar model to successfully describe photoluminescence spectra from Mn-containing CdTe quantum dots (muffin tin model) that previously was applied to the case of acceptor bound magnetic polarons [64, 65]. The most striking consequences of the usually neglected terms of the interaction Hamiltonian is that the energy of formation of the polaron is strongly dependent on (thermal) fluctuation of the magnetization in the region penetrated by the mobile carrier wave function.

Finally, anomalies in temperature dependence of the energy gap itself (observed in (Cd,Mn)Te [66] and ZnMnSe [67]) were interpreted due to higher order perturbation (and, thus, due to $\langle S_x \rangle$ and $\langle S_y \rangle$) by the $sp-d$ interaction. Again, the contribution may be expressed in terms of the magnetic susceptibility.
1.5 Ion–ion (d–d) Exchange Interaction

The magnetic moments localized on substitutitional transition metal ions in diluted magnetic semiconductors may interact not only with delocalized valence and conduction band carriers that we have dealt with so far. They, of course, may also interact between each other either indirectly or directly. All the collective magnetic phenomena are, of course, caused by interactions between those microscopic magnetic moments. The most important of these interactions is the exchange interaction. It is also purely electrostatic by nature (see, e.g., Ashcroft and Mermin), and can have several underlying mechanisms. In the simplest case, it can be described by a spin Hamiltonian containing scalar products of the interacting spins. In this simple isotropic case in 3D space the corresponding Hamiltonian is called Heisenberg Hamiltonian and for two interacting spins $S_1$ and $S_2$ can be written as follows

$$\hat{H} = -J \mathbf{S}_1 \cdot \mathbf{S}_2,$$

where $J$ denotes here the interaction strength; its positive sign corresponds to a tendency to parallel alignment (i.e., ferromagnetic) of the two spins. The exchange interaction can be either direct (then $J$ is always positive) or mediated by some states residing between the two interacting magnetic moments: bond electrons, free carriers etc. Then, the sign of $J$ can be such that an antiparallel (antiferromagnetic) alignment of neighboring spins may be more favorable. Usually, the exchange interaction is relatively short-ranged and it often suffices to limit oneself to spins occupying nearest neighboring sites neglecting interaction between those that are further apart. The case of antiferromagnetic exchange interactions may bring in a qualitatively new situation when not all spins can be aligned in a way that is energetically most favorable. The phenomenon is called frustration and the simplest example is that of three spins occupying a triangular lattice. While each two can be aligned antiferromagnetically, the third will always be ferromagnetic (i.e., configured energetically not favorably) to one of the first two. Formation of the spin glass is likely under such conditions. Indeed, a behavior characteristic for spin glasses is often observed when studying susceptibility or specific heat of diluted magnetic semiconductors [68]. The spin glasses in themselves are very interesting objects. For example, they exhibit intensive behavior of the dynamics of the localized spins [69]. For the sake of this discussion it will suffice, however, to envisage the collection of the localized spins as just giving rise to a static magnetization. This is, within the mean field/virtual crystal approximation, all that is needed to calculate the near the band gap modification of the band structure induced by the presence of the transition metal ions in our materials.

Another issue that is related to the mechanism of the interaction is the question how quickly it disappears with growing distance between the two interacting ions. The issue was studied for a variety of diluted magnetic semiconductors in [70], where it was found that the observed trends sometimes deviate from the predicted dependence $\exp(-r^2/a)$ found by Larson et al. [71] in the theory assuming superexchange as the main contributor to $J$. The deviations may indicate that
other mechanism apart from the superexchange (e.g., Bloembergen–Rowland mechanism) are also present. In any case, the interaction strength drops down rather quickly and it is not a bad approximation to limit ourselves to interaction between nearest neighbors only. Experimentally, it is also observable that the smaller is the distance between cations occupying nearest neighbor sites in the crystalline lattice the greater is the value of \( J \). So the interaction constant increases in the family of, say, Zn chalcogenides with Mn as one goes from tellurides down to sulfides. The superexchange theory provides a natural explanation of this trend: hybridization between \( p \)-states of the mediating anions is greater when the distance between atoms in the lattice is smaller. For the same reason, also the compressive strain which may arise in certain superlattices involving diluted magnetic semiconductors leads to a small increase of the strength of the exchange interaction.

As mentioned, very often to interpret various phenomena in DMSs, one needs only the values of magnetization that result from a parameterization of experimental values of the magnetization. One of the convenient parametrizations was already mentioned above in this chapter (see Sect. 1.2.2). While strictly speaking, the parametrization has no strict derivation it is intuitively understandable. \( T_0 \) is directly related to \( J \) (and can be approximately expressed with the help of high temperature series expansion [72]), while \( x_0 \) (smaller that actual \( x \)) defined as \( x_0 = S_0 x / S \) reflects the fact that only a fraction of localized spins contributes to the magnetization; a part of localized spins is frozen by strong and predominantly antiferromagnetic interactions. In the crudest approximation (valid only in a limited range of small Mn molar fractions), \( x_0 \approx x (1 - x) (1 - x)^{12} \) provided that the crystal structure is that of fcc zinc blende type. An experimentally established values of \( x_0 \) and \( T_0 \) are collected in [73] for Cd\(_{1-x}\)Mn\(_x\)Te.

To determine the real values of the inter ion exchange interaction \( J \), there are two methods that are especially accurate and therefore worth mentioning. The first makes use of magnetization steps observed in, e.g., optical measurements in strong magnetic fields, strong enough to disrupt the antiferromagnetic coupling between a pair of nearest neighboring Mn ions. The field when magnetic contribution to the energy becomes equal to that of the coupling is reflected by a relatively sudden increase of the magnetization and is observable as a step of, say, observed exciton transition line. The mechanism of formation of up to five steps is schematically depicted in Fig. 1.28.

Another accurate method of determination of \( J \) makes use of inelastic scattering of neutrons by pairs of interacting magnetic ions [75]. Of course, fitting of various models to the measured susceptibility and specific heat do provide also information concerning the value of \( J \), however, this is (1) model dependent and (2) usually less reliable. For a tabulation of variously determined values of \( J \) the reader is referred to the existing compilations [51, 52]. Let it suffice to say here that \( J \) in bulk CdMnTe for nearest neighboring Mn ions amounts to about 6–10 K while for next nearest neighboring ions it is smaller, 1–2 K. Similarly, in ZnMnTe which has a smaller lattice parameter, those two exchange constants are, respectively 10 K and 0.6 K, as determined by the magnetization step method. Note that there is often a difference
Fig. 1.28 Upper panel: energy spectrum of the triplet state of antiferromagnetically interacting (via the Heisenberg interaction) pair of localized magnetic moments as a function of an external magnetic field. The spin singlet with $m = 0$ does not contribute to the magnetization (lower panel) and at low field the latter is given only by those moments which do not have a nearest neighbor. With the field increasing the higher states with nonvanishing $m$ become the ground state of the pair and their contribution to the magnetization manifests itself as a sudden-step like feature in the magnetization. Taken from [74]

by a factor of 2 in the definition of $J$, as is the case of the former determination, and therefore – differences in quoted values.

From the theoretical side the question of the inter-ion exchange interaction was addressed by Larson et al. [71]. The conclusion of that work was that in typical DMS materials the dominating channel of exchange coupling is that of superexchange, and proportional to hybridization of the valence band electrons with $d$-states localized on transition metal substituting the host cations. Thus, one expects that $J$ is proportional to $\beta^2$. Indeed trends of this type are observed experimentally [76].

In a very concentrated case MnTe-rich materials seldom exists in zinc blende form, but tend to have nickel arsenide structure. However, by use of molecular beam epitaxy, one can grow cubic zinc blende MnTe as well. In such a form, it is also antiferromagnetic and the arrangement of localized spins in such a case is discussed in detail in Chap. 12 of this volume.

We have so far assumed that the localized spin–spin interaction is of Heisenberg form. That the Dzialoshinsky–Moriya interaction (involving a cross product of spins), although much weaker in strength, is present can be inferred from EPR
(electron paramagnetic resonance) experiments reported by Samarth and Furdyna [77]. In most of the cases, this more complicated interaction can be safely neglected.

Finally, let us mention that when the band carriers are particularly abundant in the material an indirect coupling between two localized spins is possible as shown in lead salt-containing DMSs by Story et al. [78]. In fact, this specific interaction is of central interest in “newer” III–V-based diluted magnetic semiconductors and is a source of hopes of applications of these latter materials in semiconductor spintronics.

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