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Introduction

1.1 Introduction

Both ferromagnetic and paramagnetic dilute magnetic semiconductors (DMS) are currently of interest in the context of spintronics and spin optoelectronics. These technologies combine the merits of semiconductor-electronic and magneto-electronic devices [1, 2].

Magnetoresistance measurements on DMS are well established techniques to analyze the interplay of electronic and magnetic properties in dilute magnetic semiconductors. So far spin-dependent scattering was applied successfully for the interpretation of transport measurements in ferromagnetic metallic GaMnAs random alloys, where the ferromagnetic coupling can be explained by a Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism [3, 4, 5]. However, these theories are no longer applicable for semiconducting samples in the paramagnetic phase (e.g. obtained by annealing at elevated temperatures) or DMS materials which even show segregation of clusters. The RKKY-based theories are limited to metallic random GaMnAs alloys where disorder effects can be neglected to a first approximation. Recently hybrid systems formed out of ferromagnetic clusters embedded in a paramagnetic host matrix raised particular attention [6, 7, 8, 9]. They are considered as possible candidates for the creation of spintronic devices working at room temperature. Along with this interest, there is the need to find a proper theoretical model for the description of the material and transport properties of this highly complex material class, e.g. beyond the the scope of (microscopic) RKKY theories. It is the aim of this work to show that the transport properties of the matrix material and of the hybrid structures can be described taking into account disorder aspects as a major issue. The (macroscopic) description we use is rather empirical, but it may serve as a first step towards a microscopic theory.

We start by introducing a network model for the description of the magnetotransport in p-type dilute magnetic semiconductors in the paramagnetic phase. The model is based on a simplified description of the valence-band structure and the acceptor state of the DMS. Band filling effects, magnetic-field splitting of the band states due to the p-d exchange interaction as well as effects of magnetic-field independent disorder are accounted for. We do not include carrier-carrier interactions other than those responsible for the local magnetism of the Mn ions. Despite the exclusion of many-body effects[1] in the bands, positive as well as negative MR effects are predicted by the model [10] which show a qualitative agreement with experiments on paramagnetic p-type DMS [11, 12]. The model is adopted to the quantitative description of Mn doped GaAs which serves as the archetypal dilute magnetic semiconductor. As a physical by-catch on the way towards a fundamental description of this material (from the limit of a very dilute Mn incorporation over annealed samples which show segregation trends to the other limit of paramagnetic/ferromagnetic hybrid samples), an alternative explanation of a non-Arrhenius temperature dependence of the resistivity is given. It is clearly shown that in contrast to common oppinion a non-Arrhenius temperature dependence is not inevitably indicative of hopping transport. This rather fundamental conclusion is not limited to the special choice of dilute magnetic semiconductors.
In chapter 3 the model is extended to provide a quantitative description of a series of annealed $Ga_{0.98}Mn_{0.02}As$ samples. It also serves for the first systematic theoretical study of the magnetotransport properties of $Ga_{1-x}Mn_xAs/MnAs$ hybrid structures in chapter 5. The first part of this work ends with a prediction for the design of hybrid structures tailored to show strongly enhanced magnetoresistance effects for possible future spintronic applications.

1.2 Dilute magnetic semiconductors – an overview

A dilute magnetic semiconductor is a semiconductor with a small (dilute) fraction of magnetic ions incorporated on lattice sites. Due to the exchange interaction between the localized spins of the magnetic ions and the spins of the free carriers they exhibit unusual magnetic properties. Two major classes of DMS are wide-gap (II,Mn)VI and (III,Mn)V alloys [13, 14, 15]. The magnetism of such DMS will strongly depend on the Mn content, the electronic configuration of the Mn ion and on the degree of doping. While in

[1] As a matter of fact, whenever in the following 'many-body effects' are claimed to be excluded, all many-body effects are neglected except the p-d exchange interaction which is expressly included.

(II,Mn)VI compounds the Mn is built in isoelectronically on group II cation sites, in (III,Mn)V alloys the Mn ions are incorporated on cation sites acting as acceptors. In particular the intrinsic correlation of transport and magnetic properties in the III-Mn-V semiconductors aroused the interest of researchers [16, 17, 18, 19]. The most prominent and best studied representative of the (III,Mn)V alloys is $Ga_{1-x}Mn_xAs$. In ideal $Ga_{1-x}Mn_xAs$ the Mn ions are spatially randomly incorporated on Ga sites Mn_{Ga} acting as acceptors [20], whilst the half filled Mn 3d-shell provides $S = \frac{5}{2}$ localized magnetic moments [21]. Since (II,Mn)VI compounds exhibit paramagnetic behavior up to very high Mn contents, the combination of free holes and large localized magnetic moments yields ferromagnetism in $Ga_{1-x}Mn_xAs$ alloys. An Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism is considered to be responsible for the origin of ferromagnetism in this material. This is where the ferromagnetic coupling between the localized Mn spins is mediated by the free holes in the valence band [3, 22, 23, 24, 25]. Even though GaAs:Mn shows a paramagnetic phase down to very low temperatures in the dilute regime, possible Curie temperatures above room temperature are predicted theoretically for higher Mn contents [26, 27]. However, the highest Curie temperature realized experimentally so far in this alloy system is $T_C = 173\,K$ [28].

For temperatures above T_C the magnetization of dilute magnetic semiconductor alloys is usually described by a modified Brillouin function accounting for residual magnetic coupling between the magnetic ions. In paramagnetic (II,Mn)VI alloys (where the magnetic properties are determined solely by superexchange between Mn ions) the residual coupling is reflected by the temperature dependence of the susceptibility, the inverse susceptibility follows a linear Curie-Weiss temperature dependence at higher temperatures, but shows a clear down bend when the temperature decreases [29, 30, 31, 32, 33]. This behavior shows the temperature-induced change of the magnetic coupling. The origin of this unusual behavior is the formation of antiferromagnetically coupled nearest-neighbor Mn spins at low temperatures which break up with increasing temperature [31]. It is worth noting that somewhat similar effects may be anticipated for the magnetization of (III,Mn)V alloys above T_C, leading to a Curie-Weiss parameter Θ which will depend on the sample properties as well as on temperature. A detailed study of the influence of Θ on the magnetotransport properties of a $Ga_{1-x}Mn_xAs$ alloy and a first attempt to clarify its dependence on the beforehand mentioned sample properties as well as on temperature by comparison with experimental data is given in chapter 3.

Possible DMS-based designs consist either of ferromagnetic DMS [13], paramagnetic DMS [34, 35, 36, 37] or paramagnetic-ferromagnetic hybrid structures [38]. (Ga,Mn)As/MnAs is a typical example of such a hybrid structure. In this hybrid, ferromagnetic MnAs clusters are embedded in a paramag-

netic $Ga_{1-x}Mn_xAs$ host matrix. Several current studies show that DMS-based hybrid systems exhibit large positive and negative magneto-resistance (MR) effects. Examples are the MR behavior of $Ga_{1-x}Mn_xAs$/MnAs [39, 40, 41], of GaAs/ErAs [42], of GaAs:Mn/MnSb [43, 44] and of $Ge_{1-y}Mn_y$:$Mn_{11}Ge_8$ [45]. However, so far the microscopic mechanisms are not at all understood because the galvano-magnetic properties of such granular ferromagnetic hybrid systems depend strongly on the electronic transport properties of the paramagnetic matrix material, the magnetic properties of the clusters and on the interaction of the electronic states of the host matrix with the ferromagnetic clusters. Of course, one essential prerequisite for understanding the galvano-magnetic properties of the hybrids are detailed experimental and theoretical studies of the transport in the paramagnetic DMS materials which act as host matrix for the clusters.

Multiple magneto-transport experiments were reported on wide-gap DMS alloys covering n-type $Cd_{1-x}Mn_xTe$ [46] and $Cd_{1-x}Mn_xSe$ [47] and more recently p-type DMS such as $Zn_{1-x}Mn_xTe$:N [11] and paramagnetic $Ga_{1-x}Mn_xAs$ [12]. It is worth noting that already the paramagnetic DMS alloy alone (i.e. without clusters) exhibits positive as well as negative MR effects [11, 12, 46, 47, 48]. However, these are different from those in the corresponding hybrids [41]. The unusual MR effects of the paramagnetic DMS are commonly explained by the interplay of band filling, magnetic-field induced tuning of the band structure, carrier-carrier interactions and quantum corrections [48, 49, 50, 51, 52, 53]. As an example, the influence of the magnetic-field induced tuning of the alloy disorder on the galvano-magnetic properties of DMS was included so far only in the magnetic polaron picture [54]. It arises due to fluctuations in the Mn concentration which, in an applied magnetic field, lead to local fluctuations of the Mn-induced band splitting. Magnetic-field tuning of alloy disorder is a well known feature of DMS [55, 56, 57, 58]. On the other hand, it is well established that disorder in crystalline semiconductor alloys and even more in amorphous semiconductors has a considerable impact on the transport properties [59].

1.3 The transport model

According to the transport theory of Drude in a system which is considered to be isotropic the resistivity ρ and the conductivity $\nu = \frac{1}{\rho}$ can be represented in terms of carrier density n and carrier mobility μ as

$$\rho = \frac{1}{n \cdot q \cdot \mu} \tag{1.1}$$

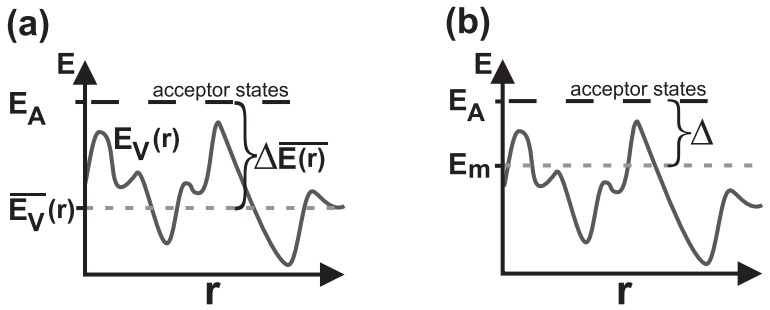

Fig. 1.1. For a doped semiconductor with a spatially disordered valence-band edge it holds $\Delta < (E_A - \overline{E_V}(r))$ (a) shows the energy spacing $\overline{\Delta E}(r)$ between the average valence-band edge $\overline{E_V}(r)$ (dashed grey line) and the acceptor level E_A. (b) illustrates the activation energy $\Delta = (E_A - E_m)$ given by the energy spacing between the acceptor energy E_A and the mobility edge E_m (dashed grey line).

where q denotes the carrier's charge. In the framework of a semiclassical transport description the mobility μ can be decomposed as $\mu = \frac{q \cdot \tau}{m^\star}$ where τ represents the average time between two scattering events and $m^\star$ is the effective mass. The density of carriers in a semiconductor[2] is given by

$$n = \int_{-\infty}^{E_V} N(E) F^h(E) dE \tag{1.2}$$

where E_V is the band-edge energy-level of the unperturbed valence band, $N(E)$ is the density of states in the valence band and $F^h(E)$ is the Fermi distribution of holes. Usually this direct current resistivity ρ in doped semiconductors can be simplified and represented by an Arrhenius temperature dependence

$$\rho = \tilde{\rho} \cdot exp(\Delta / k_\mathrm{B} T) \tag{1.3}$$

where $\tilde{\rho}$ is a pre-exponential factor, Δ is the activation energy and k_B is the Boltzmann constant. A detailed analysis of the validity of such a simplification depending on specific material parameters is given in chapter 2.

Disorder in the transport dominating band of a semiconductor can be taken into account e.g. by a modification (a disorder-dependent reduction) of the mobility. It is obvious that the mean free path (herewith τ) gets reduced with increasing spatial fluctuations of the potential. Also the carrier density gets affected by disorder. Besides a change of the position of the Fermi level,

[2] Since $Ga_{1-x}Mn_xAs$ that is in the focus of this work is a p-type semiconductor, we leave here the general description and concentrate on a semiconductor with hole transport in the valence band.

due to the fluctuations of the local valence-band edge $E_V(r)$, holes on acceptor states do not have to be activated to the spatial average of the valence-band edge $\overline{E_V}(r)$ but merely to an energy level E_m, the so-called mobility edge. As illustrated in Fig. 1.1 the required activation energy Δ is given by $\Delta = (E_A - E_m)$. It holds $\Delta < (E_A - \overline{E_V}(r))$. Descriptions of the transport properties in (doped) disordered semiconductors following this approach can be found e.g. in [59, 60, 61] as well as in [10] where a comparison with the alternative description given in the following is presented. Another attempt to handle a transport description in the presence of disorder is to separate a given disordered system into a number of subsystems which are so small, that inside each single subsystem the influence of disorder can be neglected. The transport properties of each of these ordered subsystems can be calculated according to Eqn. 1.1 and 1.2. The members of this ensemble of subsystems have to be connected somehow to represent the physical realities and the macroscopic transport variables of the global system have to be derived.

1.3.1 General limitation of the approach

There is, however, one problem with the used description which should not be concealed: Apart from the issue of finding the correct subsystem size which represents the disorder in the system (discussed in detail in section 1.4.1), one should keep in mind, that there exists a lower boundary of this subsystem size. For subsystem sizes below this boundary the transport properties have to be described quantum mechanically [62, 63]. Finding the exact value of this lower boundary and its connection to parameters of the system is a field of current research [64]. Therefore we follow a very pragmatic route and hope that all subsystem sizes of use are large enough - an assumption that indeed does not make the treatment of the given problem simple but at least drastically simplifies it compared to the universal approach[3].

1.3.2 The magnetoresistance

The material system we analyze is the magnetic semiconductor $Ga_{1-x}Mn_xAs$ which in this work is in the main described in its paramagnetic phase. The obtained results form a basis of the study of so-called paramagnetic-ferromagnetic hybrid structures built out of a $Ga_{1-x}Mn_xAs$ host matrix with embedded ferromagnetic MnAs clusters as shown in chapter 5. Discussed in

[3] "It would mean that the only possibility that remains is to describe the whole universe at once by using one huge Hilbert space. It goes without saying that such an approach will lead to many other problems" [63].

more detail in section 1.3.3 the interaction of the localized magnetic moments of the Mn-ions with an external magnetic field and their exchange interaction with the valence-band states lead to a strong spin-selective splitting of the valence band. According to this local variations of the carrier densities n as well as a modified mobility μ arise due to the magnetic field induced disorder effects. These modifications of quantities appearing in Eqn. 1.1 cause a noticeable change of the resistivity. To access the magnetic fields influence on the resistivity the macroscopic observable magnetoresistance (MR) is introduced

$$\mathrm{MR} = \frac{\rho_m - \rho_0}{\rho_0}, \tag{1.4}$$

ρ_m is the resistivity in the presence of an external magnetic field while ρ_0 is the resistivity at zero field. Negative values of MR represent a resistivity that decreases in the presence of an external magnetic field (in other words the conductivity increases). The lower boundary of the magnetoresistance for $\rho_m \leq \rho_0$ is given by MR$= -1$. For positive values of the MR the opposite situation holds with $\rho_m < \rho_0$ and no general upper boundary exists.

1.3.3 Interaction with an external magnetic field

In this section the interaction of a DMS with an external magnetic field $\mathbf{H}$ is described briefly. For all further considerations the magnetic field is taken as a weak perturbation and eigenvalues of the system Hamilton operator for $\mathbf{H} = 0$ are assumed to be known i.e. the band structure in the absence of an external magnetic field is given. For simplicity the energy gets normalized by the value of the unperturbed valence-band edge using $E_V = 0$ at $\mathbf{H} = 0$. Starting point is the magnetic part $\mathcal{H}_\mathrm{m}$ of the single-particle system Hamilton operator $\mathcal{H}$ describing the interaction between a free carrier with spinoperator $\mathbf{s}$, an external magnetic field $\mathbf{H} = (0, 0, H)$ oriented in z-direction and the system of magnetic ions with spinoperators $\mathbf{S}_i$

$$\begin{aligned}&\mathcal{H}_\mathrm{m}(\mathbf{s}, \mathbf{S_i}) = \\ &\underbrace{\mathcal{H}_\mathrm{L} + g\mu_\mathrm{B}\mu_0 \mathbf{s}\cdot\mathbf{H}}_{I} \underbrace{- 2\sum_i J_i \mathbf{S_i}\cdot\mathbf{s}}_{II} + \underbrace{g'\mu_\mathrm{B}\mu_0\mathbf{H}\sum_i \mathbf{S_i} - \sum_{i\neq j} J'_{i,j}\mathbf{S_i}\cdot\mathbf{S_j}}_{III}.\end{aligned} \tag{1.5}$$

Part I describes the diamagnetic Landau quantization by $\mathcal{H}_\mathrm{L}$ and the contribution of the paramagnetic Zeeman splitting as for a pure diamagnetic material. In part II the exchange interaction between the carrier and the localized magnetic ions is taken into account while part III covers the interaction between the magnetic ions and the external field as well as the interaction among the