Diluted Ferromagnetic Semiconductors – Theoretical Aspects

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1 INTRODUCTION

The family of diluted magnetic semiconductors (DMS) encompasses standard semiconductors, in which a sizable portion of atoms is substituted by such elements, which produce localized magnetic moments in the semiconductor matrix. Usually, magnetic moments originate from 3d or 4f open shells of transition metals (TMs) or rare earths (REs) (lanthanides), respectively, so that typical examples of DMS are $Cd_{1-x}Co_xSe$, $Ga_{1-x}Mn_xAs$, $Pb_{1-x}Eu_xTe$ and, in a sense, Si:Er. A strong spin-dependent coupling between the band and localized states accounts for outstanding properties of DMS. This coupling gives rise to spin-disorder scattering, giant spin splittings of the electronic states, formation of magnetic polarons, and strong indirect exchange interactions between the magnetic moments, the latter leading to collective spin glass, antiferromagnetic, or ferromagnetic spin ordering. Owing to the possibility of controlling and probing magnetic properties by the electronic subsystem or vice versa, DMS have been successfully employed to address a number of important questions concerning the nature of various spin effects in various environments and at various length and timescales. At the same time, DMS exhibit a strong sensitivity to the magnetic field and temperature as well as constitute important media for generation of spin currents and for manipulation of localized or itinerant spins by, for example, strain, light, electrostatic, or ferromagnetic gates. These properties, complementary to both nonmagnetic semiconductors and magnetic metals, open doors for application of DMS as functional materials in spintronic devices.

Extensive studies of DMS started in 1970s, particularly in the group of Robert R. Gałązka in Warsaw, when appropriately purified Mn was employed to grow bulk II–VI Mn-based alloys by various modifications of the Bridgman method (Gałązka, 1978). Comparing to magnetic semiconductors, such as Eu chalcogenides (e.g., EuS) and Cr spinels (e.g., $CdCr_2Se_4$) investigated earlier (Nagaev, 1983), DMS exhibited smaller defect concentrations and were easier to dope by shallow impurities. Accordingly, it was possible to examine their properties by powerful magneto-optical and magnetotransport techniques (Dietl, 1994; Gałązka, 1978, 1981; Furdyna and Kossut, 1988; Awschalom and Samarth, 2002). Since, in contrast to magnetic semiconductors, neither narrow magnetic bands nor long-range magnetic ordering affected low-energy excitations, DMS were named semimagnetic semiconductors. More recently, research on DMS have been extended toward materials containing magnetic elements other than Mn as well as to III–VI, IV–VI (Bauer, Pascher and Zawadzki, 1992), and III–V (Matsukura,

Handbook of Magnetism and Advanced Magnetic Materials. Edited by Helmut Kronmüller and Stuart Parkin. Volume 5: *Spintronics and Magnetoelectronics*. ISBN: 978-0-470-02217-7.

Ohno and Dietl, 2002) compounds as well as group IV elemental semiconductors and various oxides (Prellier, Fouchet and Mercey, 2003). In consequence, a variety of novel phenomena had been discovered, including effects associated with narrow bands and magnetic phase transformations, making the borderline between properties of DMS and magnetic semiconductors more and more elusive.

A rapid progress of DMS research in 1990s stemmed, to a large extent, from the development of methods of crystal growth far from thermal equilibrium, primarily by molecular-beam epitaxy (MBE) but also by laser ablation. These methods have made it possible to obtain DMS with the content of the magnetic constituent beyond thermal equilibrium solubility limits (Ohno, 1998). Similarly, the doping during MBE process allows one to increase substantially the electrical activity of shallow impurities (Haury *et al*., 1997; Ferrand *et al*., 2001). In the case of III–V DMS (Matsukura, Ohno and Dietl, 2002), in which divalent magnetic atoms supply both spins and holes, the use of the low-temperature MBE provides thin films of, for example, $Ga_{1-x}Mn_xAs$ with x up to 0.08 and the hole concentration approaching $10^{21}\,cm^{-3}$, in which ferromagnetic ordering is observed up to 170 K (Wang *et al*., 2005). Remarkably, MBE and processes of nanostructure fabrication, make it possible to add magnetism to the physics of semiconductor quantum structures. Particularly important are DMS, in which ferromagnetic ordering was discovered, as discussed here and in the chapter **Ferromagnetic Semiconductors, Volume 5**.

Owing to novel functionalities (Ohno *et al*., 2000) and theoretical expectations (Dietl *et al*., 2000), an enormous activity has been directed to developing diluted ferromagnetic semiconductors sustaining ferromagnetic order up to high temperatures (Dietl, 2005; Liu, Yun and Morkoç, 2005) as well as to describing their properties theoretically (Jungwirth *et al*., 2006a). In fact, a ferromagnetic response, often persisting up to above room temperature, has been detected in a number of semiconductor and oxide thin layers doped with minute amount of magnetic ions (Dietl, 2005; Liu, Yun and Morkoç, 2005). As known, a highly sensitive SQUID magnetometer is necessary to detect the corresponding small signals, which are often inferior to those coming from typical remanent fields, sample holders, substrates, or residual magnetic nanoparticles originating from nominally nonmagnetic source materials or processing procedures. In rather rare cases, the ferromagnetic signal of DMS layers could univocally be assigned to precipitates of a known ferromagnetic or ferrimagnetic material. In few other cases, its magnitude has been greater than that evaluated from the nominal concentration of magnetic ions. More often, however, the ferromagnetic response of the layer coexists with paramagnetic characteristics, indicating that only a fraction of magnetic spins remains correlated at high temperatures.

A particularly important question that arises in this context is whether at the length scale appropriately greater than the mean distance between magnetic ions a spatially uniform ferromagnetic spin order is a real ground state of ferromagnetic DMS. Actually, the existence and the role of spatially nonuniform ferromagnetic spin order was an important theme in research on both magnetic semiconductors (Nagaev, 1983) and colossal magnetoresistance oxides (Dagotto, Hotta and Moreo, 2001). Nanoscale phase separation effects that were invoked to explained pertinent properties of those materials may *a priori* be even more relevant in ferromagnetic DMS, in which carrier correlation and electrostatic disorder associated with ionized impurities coexist with alloy disorder in the magnetic sublattice. We recall in this context that uncoupled nanoscale ferromagnetic regions of the volume V give rise to macroscopic ferromagnetic signatures, such as spontaneous magnetization and magnetic hysteresis, below the blocking temperature (e.g., Shinde *et al*., 2004), $T_B = KV/[k_B \ln(t_{lab}/\tau)]$, where K is the density of the magnetic anisotropy energy, and $\ln(t_{lab}/\tau) \approx 25$ for a typical ratio of a relevant spin-flip relaxation time τ to the time of hysteresis measurements, t_{lab}.

In the remaining part of this review, we focus on semiconductors which under doping with TM or RE become ferromagnetic but *remain* in the initial crystal structure or, in the other words, do not undergo any *crystallographic* phase separation. Therefore, the ferromagnetism of DMS considered here does not result simply from the precipitation of any known ferromagnetic or ferrimagnetic material. In particular, in the next section, we describe the present theoretical understanding of DMS showing *uniform* ferromagnetic order, such as (Ga,Mn)As or heavily doped p-(Zn,Mn)Te, in which interactions between randomly distributed magnetic ions are mediated by delocalized holes in the valence band. We then turn to DMS, in which a competition between long-range ferromagnetic and short-range antiferromagnetic interactions and/or the proximity to the localization boundary lead to the *electronic* nanoscale phase separation into areas of differing spin orders. Finally, we discuss, in some detail, systems exhibiting the *chemical* nanoscale phase separation into regions with a small and a large concentration of magnetic atoms, respectively.

2 SPATIALLY UNIFORM FERROMAGNETIC DMS

2.1 Overview

Since for decades, III–V semiconductor compounds have been applied as photonic and microwave devices, the discovery of ferromagnetism first in (In,Mn)As (Ohno *et al*.,

1992) and then in (Ga,Mn)As (Ohno *et al*., 1996) came as a landmark achievement. In these materials, substitutional divalent Mn ions provide localized spins and function as acceptor centers that provide holes which mediate the ferromagnetic coupling between the parent randomly distributed Mn spins (Dietl, Haury and Merle d'Aubigné, 1997; Matsukura, Ohno, Shen and Sugawara, 1998; Jungwirth, Atkinson, Lee and MacDonald, 1999). In another technologically important group of semiconductors, in II–VI compounds, the densities of spins and carriers can be controlled independently, similar to the case of IV–VI materials, in which hole-mediated ferromagnetism was discovered already in the 1980s (Story, Gałązka, Frankel and Wolff, 1986). Stimulated by the theoretical predictions (Dietl, Haury and Merle d'Aubigné, 1997), search for carrier-induced ferromagnetism in II–IV materials containing Mn was undertaken. Experimental studies conducted with the use of magneto-optical and magnetic methods led to the discovery of ferromagnetism in 2D (Haury *et al*., 1997) and 3D (Ferrand *et al*., 2001) II–VI Mn-based DMS doped by nitrogen acceptors.

Since magnetic properties are controlled by band holes, an appealing possibility is to influence the magnetic ordering isothermally, by light or by the electric field, which affect the carrier concentration in semiconductor quantum structures. Such tuning capabilities of the materials systems in question were put into the evidence in (In,Mn)As/(Al,Ga)Sb (Koshihara *et al*., 1997; Ohno *et al*., 2000) and modulation-doped p-(Cd,Mn)Te/(Cd,Mg,Zn)Te (Haury *et al*., 1997; Boukari *et al*., 2002) heterostructures. Actually, these findings can be quantitatively interpreted by considering the effect of the electric field or illumination on the hole density under stationary conditions and, therefore, on the Curie temperature in the relevant magnetic layers. Interestingly, according to experimental findings and theoretical modeling, photocarriers generated in II–VI systems by above barrier illumination destroy ferromagnetic order in the magnetic quantum well residing in an undoped (intrinsic) region of a p–i–p structure (Haury *et al*., 1997; Boukari *et al*., 2002) but they enhance the magnitude of spontaneous magnetization in the case of a p–i–n diode (Boukari *et al*., 2002). Furthermore, the current-induced magnetization reversal was demonstrated in submicron pillars of (Ga,Mn)As/GaAs/(Ga,Mn)As (Chiba *et al*., 2004; Elsen *et al*., 2006). Spin-polarized current was also shown to displace magnetic domain walls in (Ga,Mn)As with the easy axis perpendicular to the film plane (Yamanouchi, Chiba, Matsukura and Ohno, 2004, 2006).

Guided by the growing amount of experimental results, including informative magnetic resonance (Szczytko *et al*., 1999; Fedorych, Hankiewicz, Wilamowski and Sadowski, 2002) and photoemission (Mizokawa *et al*., 2002; Rader *et al*., 2004; Hwang *et al*., 2005) studies, a theoretical model of the hole-controlled ferromagnetism in III–V, II–VI, and group IV semiconductors containing Mn was proposed (Dietl *et al*., 2000, 2001). These materials exhibit characteristics specific to both charge transfer insulators and strongly correlated disordered metals. Moreover, complexities specific to strongly correlated systems coexist in DMS with features exhibited by heavily doped semiconductors and semiconductor alloys, such as Anderson–Mott localization (Dietl, 1994), defect generation by self-compensation mechanisms (Dietl, Ohno and Matsukura, 2001; Mašek and Máca, 2001; Yu *et al*., 2002), and the breakdown of the virtual-crystal approximation (Benoit à la Guillaume, Scalbert and Dietl, 1992). Nevertheless, the theory built on p–d Zener's model of carrier-mediated ferromagnetism and on either Kohn-Luttinger's kp (Dietl *et al*., 2000; Dietl, Ohno and Matsukura, 2001; Abolfath, Jungwirth, Brum and MacDonald, 2001) or multiorbital tight-binding (Vurgaftman and Meyer, 2001; Sankowski and Kacman, 2005; Timm and MacDonald, 2005) descriptions of the valence band in tetrahedrally coordinated semiconductors has qualitatively, and often quantitatively, described thermodynamic, micromagnetic, transport, and optical properties of DMS with delocalized holes (Dietl, 2004; Jungwirth *et al*., 2006a; Sankowski, Kacman, Majewski and Dietl, 2006a), challenging competing theories. It is often argued that owing to these studies (Ga,Mn)As has become one of the best-understood ferromagnets. Accordingly, this material is now serving as a testing ground for various *ab initio* computational approaches to strongly correlated and disordered systems.

2.2 Magnetic impurities in semiconductors

A good starting point for the description of DMS is the Vonsovskii model, according to which the electron states can be divided into two categories: (i) localized magnetic d or f shells and (ii) extended band states built up of s, p, and sometimes d atomic orbitals. The former give rise to the presence of local magnetic moments and intracenter optical transitions. The latter form bands, much alike as in the case of nonmagnetic semiconductor alloys. Indeed, the lattice constant of DMS obeys the Vegard low, and the energy gap E_g between the valence and the conduction band depends on x in a manner qualitatively similar to nonmagnetic counterparts. According to the Anderson model, the character of magnetic impurities in solids results from a competition between (i) hybridization of local and extended states, which tends to delocalized magnetic electrons and (ii) the on-site Coulomb interactions among the localized electrons, which stabilizes the magnetic moment in agreement with Hund's rule.

Figure 1 shows positions of local states derived from 3d shells of TM impurities with respect to the band energies

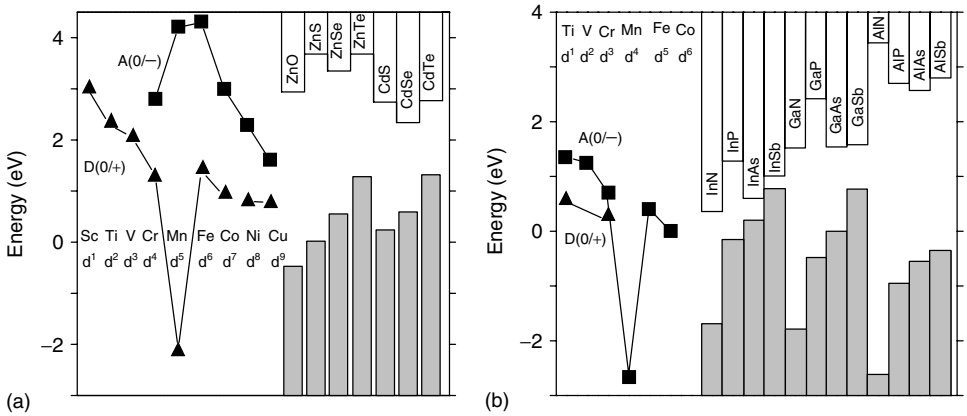

Figure 1. Approximate positions of transition-metal levels relative to the conduction and valence band edges of II–VI (a) and III–V (b) compounds. By triangles the d^N/d^{N-1} donor and by squares the d^N/d^{N+1} acceptor states are denoted. (Adapted from Langer, Delerue, Lannoo and Heinrich, 1988 and Zunger, 1986.)

of the host II–VI and III–V compounds. In Figure 1, the levels labeled 'donors' denote the ionization energy of the magnetic electrons ($TM^{2+} \rightarrow TM^{3+}$or $d^n \rightarrow d^{n-1}$), whereas the 'acceptors' correspond to their affinity energy ($TM^{2+} \rightarrow TM^{1+}$or $d^n \rightarrow d^{n+1}$). The difference between the two is the on-d-shell Coulomb (Hubbard) repulsion energy U in the semiconductor matrix. In addition, the potential introduced by either neutral or charged TM can bind a band carrier in a Zhang-Rice-type singlet or hydrogenic-like state, respectively. Such bound states are often experimentally important, particularly in III–V compounds, as they correspond to lower energies than the competing d-like states, such as presented in Figure 1.

In the case of Mn, in which the d shell is half-filled, the d-like donor state lies deep in the valence band, whereas the acceptor level resides high in the conduction band, so that $U \approx 7\,\text{eV}$ according to photoemission and inverse photoemission studies. Thus, Mn-based DMS can be classified as charge transfer insulators, $E_g < U$. The Mn ion remains in the 2+ charge state, which means that it does not supply any carriers in II–VI materials. However, it acts as a hydrogenic-like acceptor in the case of III–V antimonides and arsenides, while the corresponding Mn-related state is deep, presumably due to a stronger p–d hybridization, in the case of phosphides and nitrides. According to Hund's rule, the total spin $S = 5/2$ and the total orbital momentum $L = 0$ for the d^5 shell in the ground state. The lowest excited state d^{*5} corresponds to $S = 3/2$ and its optical excitation energy is about 2 eV. Thus, if there is no interaction between the spins, their magnetization is described by the paramagnetic Brillouin function. In the case of other TMs, the impurity-induced levels may appear in the gap, and then compensate shallow impurities, or even act as resonant dopant, for example, Sc in CdSe, Fe in HgSe or Cu in HgTe. Transport studies of such systems have demonstrated that intersite Coulomb interactions between charged ions lead to the Efros-Shklovskii gap in the density of the impurity states, which makes resonant scattering to be inefficient in semiconductors (Wilamowski, Świątek, Dietl and Kossut, 1990). Furthermore, spin-orbit interaction and Jahn–Teller effect control positions and splittings of the levels in the case of ions with $L \neq 0$. If the resulting ground state is a magnetically inactive singlet there is no permanent magnetic moment associated with the ion, the case of Fe^{2+}, whose magnetization is of the Van Vleck type at low temperatures.

2.3 Exchange interaction between band and localized spins

The important aspect of DMS is a strong spin-dependent coupling of the effective mass carriers to the localized d electrons, first discovered in (Cd,Mn)Te (Komarov *et al.*, 1977; Gaj, Gałązka and Nawrocki, 1978) and (Hg,Mn)Te (Bastard *et al.*, 1978; Jaczyński, Kossut and Gałązka, 1978). Neglecting nonscalar corrections that can appear for ions with $L \neq 0$, this interaction assumes the Kondo form,

$$H_K = -I(\vec{r} - \vec{R}^{(i)})\vec{s}\vec{S}^{(i)} \tag{1}$$

where $I(\vec{r} - \vec{R}^{(i)})$ is a short-range exchange energy operator between the carrier spin $\vec{s}$ and the TM spin localized at $\vec{R}^{(i)}$. When incorporated to the kp scheme, the effect of H_K is described by matrix elements $\langle u_i|I|u_i\rangle$, where u_i are the Kohn-Luttinger amplitudes of the corresponding band extreme. In the case of carriers at the Γ point of the Brillouin zone in zinc-blende DMS , the two relevant matrix elements $\alpha = \langle u_c|I|u_c\rangle$ and $\beta = \langle u_v|I|u_v\rangle$ involve s-type and p-types wave functions, respectively. There are two

mechanisms contributing to the Kondo coupling (Dietl, 1981; Bhattacharjee, Fishman and Coqblin, 1983; Kacman, 2001): (i) the exchange part of the Coulomb interaction between the effective mass and localized electrons; (ii) the spin-dependent hybridization between the band and local states. Since there is no hybridization between Γ_6 and d-derived (e_g and t_{2g}) states in zinc-blende structure, the s–d coupling is determined by the direct exchange. The experimentally determined values are of the order of $\alpha N_o \approx 0.25\,\mathrm{eV}$, where N_o is the cation concentration, somewhat reduced comparing to the value deduced from the energy difference between $S1/2$ states of the free singly ionized Mn atom $3d^5 4s^1$, $\alpha N_o = 0.39\,\mathrm{eV}$. In contrast, there is a strong hybridization between Γ_8 and t_{2g} states, which affects their relative position, and leads to a large magnitude of $|\beta N_o| \approx 1\,\mathrm{eV}$. If the relevant effective mass state is above the t_{2g} level (the case of, e.g., Mn-based DMS, $\beta < 0$ but otherwise β can be positive (the case of, e.g., $Zn_{1-x}Cr_xSe$ (Mac *et al.*, 1993)).

2.4 p–d Zener model

It is convenient to apply the Zener model of carrier-controlled ferromagnetism by introducing the functional of free-energy density, $\mathcal{F}[\vec{M}(\vec{r})]$. The choice of the local magnetization $\vec{M}(\vec{r})$ as an order parameter means that the spins are treated as classical vectors, and that spatial disorder inherent to magnetic alloys is neglected. In the case of magnetic semiconductors $\mathcal{F}[\vec{M}(\vec{r})]$ consists of two terms, $\mathcal{F}[\vec{M}(\vec{r})] = \mathcal{F}_S[\vec{M}(\vec{r})] + \mathcal{F}_c[\vec{M}(\vec{r})]$, which describe, for a given magnetization profile $\vec{M}(\vec{r})$, the free energy densities of the Mn spins in the absence of any carriers and of the carriers in the presence of the Mn spins, respectively. A visible asymmetry in the treatment of the carries and of the spins corresponds to an adiabatic approximation: the dynamics of the spins in the absence of the carriers is assumed to be much slower than that of the carriers. Furthermore, in the spirit of the virtual-crystal and molecular-field approximations, the classical continuous field $\vec{M}(\vec{r})$ controls the effect of the spins upon the carriers. Now, the thermodynamics of the system is described by the partition function Z, which can be obtained by a functional integration of the Boltzmann factor $\exp(-\int \mathrm{d}\vec{r}\mathcal{F}[\vec{M}(\vec{r})]/k_B T)$ over all magnetization profiles $\vec{M}(\vec{r})$, an approach developed for bound magnetic polarons (Dietl and Spałek, 1983; Dietl, 1983), and directly applicable for spin physics in quantum dots as well. In the mean-field approximation (MFA), which should be valid for spatially extended systems and long-range spin–spin interactions, a term corresponding to the minimum of $\mathcal{F}[\vec{M}(\vec{r})]$ is assumed to determine Z with a sufficient accuracy.

If energetics is dominated by spatially uniform magnetization $\vec{M}$, the spin part of the free energy density in the magnetic field $\vec{H}$ can be written in the form (Świerkowski and Dietl, 1988)

$$\mathcal{F}_S[\vec{M}] = \int_0^{\vec{M}} \mathrm{d}\vec{M}_o \vec{h}(\vec{M}_o) - \vec{M}\vec{H} \tag{2}$$

Here, $\vec{h}(\vec{M}_o)$ denotes the inverse function to $\vec{M}_o(\vec{h})$, where $\vec{M}_o$ is the available experimentally macroscopic magnetization of the spins in the absence of carriers in the field h and temperature T. In DMS, it is usually possible to parameterize $M_o(h)$ by the Brillouin function $B_S(T, H)$ that takes the presence of intrinsic short-range antiferromagnetic interactions into account. Near T_C and for $H = 0$, M is sufficiently small to take $M_o(T, h) = \chi(T)h$, where $\chi(T)$ is the magnetic susceptibility of localized spins in the absence of carriers. Under these conditions,

$$\mathcal{F}_S[M] = \frac{M^2}{2\chi(T)} \tag{3}$$

which shows that the increase of $\mathcal{F}_S$ with M slows down with lowering temperature, where $\chi(T)$ grows. Turning to $\mathcal{F}_c[M]$ we note that owing to the giant Zeeman splitting of the bands proportional to M, the energy of the carriers, and thus $\mathcal{F}_c[M]$, decreases with $|M|$, $\mathcal{F}_c[M] - \mathcal{F}_c[0] \sim -M^2$. Accordingly, a minimum of $\mathcal{F}[M]$ at nonzero M may develop in $H = 0$ at sufficiently low temperatures signalizing the appearance of a ferromagnetic order.

The present authors and coworkers (Dietl *et al.*, 2000) found that the minimal Hamiltonian necessary to describe properly effects of the complex structure of the valence band in tetrahedrally coordinated semiconductors upon $\mathcal{F}_c[M]$ is the Luttinger $6 \times 6\,kp$ model supplemented by the p–d exchange contribution taken in the virtual-crystal and molecular-field approximations,

$$H_{pd} = \frac{\beta \vec{s}\vec{M}}{g\mu_B} \tag{4}$$

This term leads to spin splittings of the valence subbands, whose magnitudes – owing to the spin-orbit coupling – depend on the hole wave vectors $\vec{k}$ in a complex way even for spatially uniform magnetization $\vec{M}$. It would be technically difficult to incorporate such effects to the Ruderman-Kittel-Kasuya-Yosida (RKKY) model, as the spin-orbit coupling leads to nonscalar terms in the spin–spin Hamiltonian. At the same time, the indirect exchange associated with the virtual spin excitations between the valence subbands, the Bloembergen-Rowland mechanism, is automatically included. The model allows for strain, confinement, and was developed for both zinc-blende and wurzite materials (Dietl, Ohno and Matsukura, 2001). Furthermore, the direct influence of the magnetic field on the hole spectrum

was taken into account. Carrier–carrier spin correlation was described by introducing a Fermi-liquid-like parameter A_F (Dietl, Haury and Merle d'Aubigné, 1997; Haury *et al*., 1997; Jungwirth, Atkinson, Lee and MacDonald, 1999), which enlarges the Pauli susceptibility of the hole liquid. No disorder effects were taken into account on the ground that their influence on thermodynamic properties is relatively weak except for strongly localized regime. Having the hole energies, the free energy density $\mathcal{F}_c[\vec{M}]$ was evaluated according to the procedure suitable for Fermi liquids of arbitrary degeneracy. By minimizing $\mathcal{F}[\vec{M}] = \mathcal{F}_S[\vec{M}] + \mathcal{F}_c[\vec{M}]$ with respect to $\vec{M}$ at given T, H, and hole concentration p, Mn spin magnetization $M(T, H)$ was obtained as a solution of the mean-field equation,

$$\vec{M}(T, H) = x_{\text{eff}} N_o g \mu_B S B_S \left[\frac{g\mu_B \left(-\frac{\partial \mathcal{F}_c[\vec{M}]}{\partial \vec{M}} + \vec{H} \right)}{k_B (T + T_{AF})} \right] \quad (5)$$

where the carrier energy and entropy as well as peculiarities of the valence band structure, such as the presence of various hole subbands, anisotropy, and spin-orbit coupling, are hidden in $F_c[\vec{M}]$. Near the Curie temperature T_C and at $H = 0$, where M is small, we expect $\mathcal{F}_c[M] - \mathcal{F}_c[0] \sim -M^2$. It is convenient to parameterize this dependence by a generalized carrier spin susceptibility, which is related to the magnetic susceptibility of the carrier liquid according to $\chi_c = A_F (g^* \mu_B)^2 \tilde{\chi}_c$. In terms of $\tilde{\chi}_c$,

$$\mathcal{F}_c[M] = \mathcal{F}_c[0] - \frac{A_F \tilde{\chi}_c \beta^2 M^2}{2(g\mu_B)^2} \quad (6)$$

By expanding $B_S(M)$ for small M one arrives to the mean-field formula for $T_C = T_F - T_{AF}$, where T_F is given by

$$T_F = \frac{x_{\text{eff}} N_o S(S+1) A_F \tilde{\chi}_c(T_C) \beta^2}{3k_B} \quad (7)$$

For a strongly degenerate carrier liquid $|\epsilon_F|/k_B T \gg 1$, as well as neglecting the spin-orbit interaction $\tilde{\chi}_c = \rho/4$, where ρ is the total density of states for intraband charge excitations, which in the 3D case is given by $\rho = m^*_{DOS} k_F / \pi^2 \hbar^2$. In this case and for $A_F = 1$, T_F assumes the well-known form, derived already in 1940s in the context of carrier-mediated nuclear ferromagnetism (Fröhlich and Nabarro, 1940). In general, however, $\tilde{\chi}_c$ has to be determined numerically by computing $\mathcal{F}_c[M]$ for a given band structure and degeneracy of the carrier liquid. The model can readily be generalized to various dimensions as well as to the case, when $\vec{M}$ is not spatially uniform in the ground state, a case of spin-density waves expected in the case of 1D systems.

The same formalism, in addition to T_C and Mn magnetization $M(T, H)$, as discussed in the preceding text, provides also quantitative information on spin polarization and magnetization of the hole liquid (Dietl, Ohno and Matsukura, 2001). Furthermore, it can be exploited to describe chemical trends as well as micromagnetic, transport, and optical properties of ferromagnetic DMS (Jungwirth *et al*., 2006a). In particular, a detail theoretical analysis of anisotropy energies and anisotropy fields in films of (Ga,Mn)As was carried out for a number of experimentally important cases within the p–d Zener model (Dietl, Ohno and Matsukura, 2001; Abolfath, Jungwirth, Brum and MacDonald, 2001). The cubic anisotropy as well as uniaxial anisotropy under biaxial epitaxial strain were examined as a function of the hole concentration p. Both shape and magnetocrystalline anisotropies were taken into account. The perpendicular and in-plane orientation of the easy axis is expected for the compressive and tensile strain, respectively, provided that the hole concentration is sufficiently small. However, according to theory, a reorientation of the easy axis direction is expected at higher hole concentrations. Furthermore, in a certain concentration range the character of magnetic anisotropy is found to depend on the magnitude of spontaneous magnetization, that is on the temperature. The computed phase diagram for the reorientation transition compared to the experimental results for a (Ga,Mn)As film is shown in Figure 2. In view that theory is developed with no adjustable parameters the agreement between experimental and computed concentrations and temperature corresponding to the reorientation transition is very good. Furthermore, the computed magnitudes of the anisotropy field H_u (Dietl, Ohno and Matsukura, 2001) are consistent with the available findings for both compressive and tensile strain.

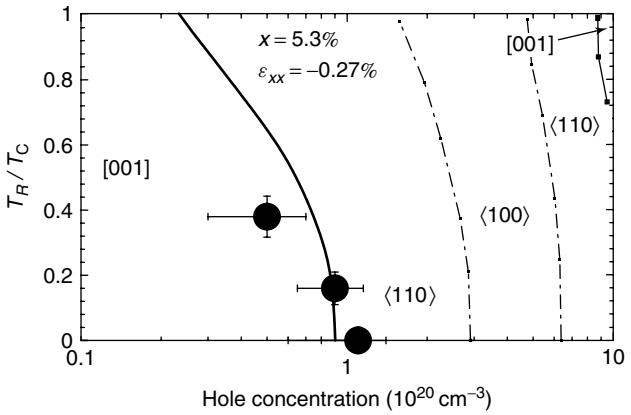

Figure 2. Experimental (full points) and computed values (thick lines) of the ratio of the reorientation to Curie temperature for the transition from perpendicular to in-plane magnetic anisotropy. Dashed lines mark expected temperatures for the reorientation of the easy axis between ⟨100⟩ and ⟨110⟩ in-plane directions. (Reproduced from Sawicki *et al*., 2005, with permission from the American Physical Society. © 2005.)

It should be emphasized that the preceding description of ferromagnetic DMS is strictly valid only in the weak coupling limit (Dietl *et al*., 2000). On going from antimonides to nitrides or from tellurides to oxides, the p–d hybridization increases. In the strong-coupling limit, the short-range part of the TM potential may render the virtual-crystal approximation and molecular-field approximation invalid (Benoit à la Guillaume, Scalbert and Dietl, 1992; Matsukura and Ohno, 2002), leading to properties somewhat reminiscent of those specific to alloys which cannot be described by the virtual crystal approximation, like Ga(As,N) (Wu, Shan and Walukiewicz, 2002). Here, dynamic mean-field approximation (DMFA) may capture relevant physics (Chattopadhyay, Das Sarma and Millis, 2001). In particular, in the strong-coupling limit, the short-range potential of the TM ion admixes to the itinerant carrier wave function a local component. This, together with quantum effects of Anderson–Mott localization, may generate modifications in optical and transport characteristics, such as an apparent increase in the carrier effective mass (Burch *et al*., 2006).

The issue how various corrections to the mean-field p–d Zener model (Dietl *et al*., 2000) affect theoretical values of T_C was recently examined in some detail for (Ga,Mn)As (Brey and Gómez-Santos, 2003; Timm and MacDonald, 2005; Jungwirth *et al*., 2005; Popescu *et al*., 2006) with the conclusions that the overall picture remains quantitatively valid. Figure 3 shows one of the recent theoretical modelings of T_C in comparison to experimental findings for (Ga,Mn)As (Jungwirth *et al*., 2005). These results confirm, in particular, that T_C values above 300 K could be achieved in $Ga_{0.9}Mn_{0.1}As$ if such a large magnitude of the substitutional Mn concentration could be accompanied by a corresponding increase of the hole density (Dietl *et al*., 2000).

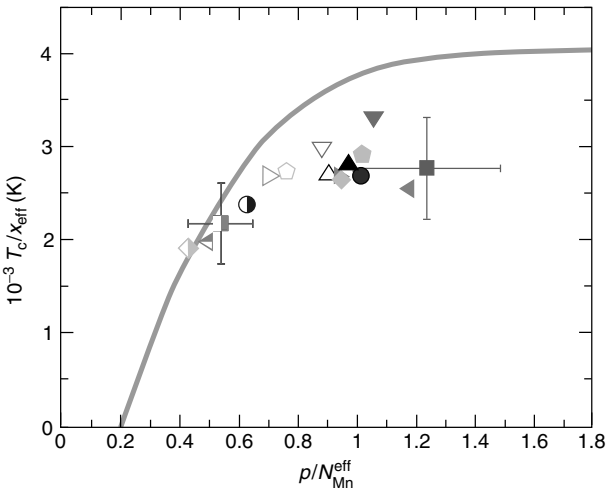

Figure 3. Experimental Curie temperatures versus hole density p relative to effective concentration of Mn moments, $N_{Mn} = 4x_{eff}/a_o^3$, where x_{eff} is the content of Mn in the substitutional positions and a_o is the lattice constant. Gray line is theoretical computed within the tight-binding and coherent potential approximations. (Reproduced from Jungwirth *et al*., 2005, with permission from the American Physical Society. © 2005.)

2.5 Theory of modulated structures of diluted ferromagnetic semiconductors

The discovery of carrier-induced ferromagnetism in zinc-blende III–V and II–VI compounds has made it possible to consider physical phenomena and device concepts for previously unavailable combinations of quantum structures and magnetism in semiconductors. Indeed, it has already been demonstrated that various modulated structures of (Ga,Mn)As show functionalities relevant for spintronic devices including spin injection of holes (Ohno *et al*., 1999; Young *et al*., 2002) and electrons (Kohda *et al*., 2001, 2006; Johnston-Halperin *et al*., 2002), interlayer coupling (Chiba *et al*., 2000; Sadowski *et al*., 2002), exchange bias (Eid *et al*., 2005), giant magnetoresistance (GMR) (Chiba *et al*., 2000), tunneling magnetoresistance (TMR) (Tanaka and Higo, 2001; Mattana *et al*., 2003; Chiba, Matsukura and Ohno, 2004), tunneling anisotropic magnetoresistance (TAMR) (Ruster *et al*., 2005; Giddings *et al*., 2005), and domain-wall resistance (Tang *et al*., 2004; Chiba *et al*., 2006).

Because of paramount importance of interfaces as well of Rashba and Dresselhaus terms, spin properties of modulated semiconductor structures cannot be meaningfully modeled employing a standard kp theory. Accordingly, an empirical multiorbital tight-binding theory of multilayer structures has been developed (Oszwałdowski, Majewski and Dietl, 2006; Sankowski and Kacman, 2005; Sankowski, Kacman, Majewski and Dietl, 2006a,b). The employed procedure describes properly the carrier dispersion in the entire Brillouin zone and takes into account the presence of magnetic ions in the virtual-crystal and molecular-field approximations. Furthermore, since the phase coherence and spin diffusion lengths are comparable in these devices and, moreover, they are typically longer than the length of the active region, the formulation of spin transport model in terms of the Boltzmann distribution function f for particular spin orientations is not appropriate. Recently, theory that combines a Landauer-Büttiker formalism with tight-binding approximation has been developed (van Dorpe *et al*., 2005; Sankowski, Kacman, Majewski and Dietl, 2006a,b). In contrast to the standard kp method (Petukhov, Chantis and Demchenko, 2002; Brey, Fernández-Rossier and Tejedor, 2004), this theory, in which $sp^3d^5s^*$ orbitals are taken into account, describes properly the interfaces and inversion symmetry breaking as well as the band dispersion in the entire Brillouin zone, so that the essential for the spin-dependent tunneling Rashba and

Dresselhaus terms as well as the tunneling via $\vec{k}$ points away from the zone center are taken into account.

The approach in question, developed with no adjustable parameters, provided information on sign of the interlayer coupling (Sankowski and Kacman, 2005), explained experimentally observed large magnitudes of both electron current spin polarization up to 70% in the (Ga,Mn)As/n-GaAs Zener diode (van Dorpe *et al*., 2005) and TMR of the order of 300% in a (Ga,Mn)As/GaAs/(Ga,Mn)As trilayer structure (Sankowski, Kacman, Majewski and Dietl, 2006b), as shown in Figure 4. Furthermore, theory reproduced a fast decrease of these figures with the device bias as well as it indicated that the magnitude of TAMR should not exceed 10% under usual strain conditions and for hole densities corresponding to the metal side of the metal-to-insulator transition (MIT) (Sankowski, Kacman, Majewski and Dietl, 2006a). A similar model was employed to examine an intrinsic domain-wall resistance in (Ga,Mn)As (Oszwałdowski, Majewski and Dietl, 2006).

3 NONUNIFORM FERROMAGNETIC DMS – ELECTRONIC NANOSCALE PHASE SEPARATIONS

3.1 Effects of competing magnetic interactions

A number of effects has been identified, which may lead to deviations from a simple ferromagnetic spin order in carrier-controlled diluted ferromagnetic semiconductors even if the spatial distribution of magnetic ions is uniform. In particular, spin-density waves appear to be in the ground state in the case of 1D systems (Dietl, Cibert, Ferrand and Merle d'Aubigné, 1999). Another proposal involves canted ferromagnetism stemming from a nonscalar form of spin–spin interactions, brought about by spin-orbit coupling (Zaránd and Jankó, 2002), though a large value of saturation magnetization in (Ga,Mn)As indicates that the effect is not large (Jungwirth *et al*., 2006b). Finally, a competition between long-range ferromagnetic interactions and intrinsic short-range antiferromagnetic interactions (Kępa *et al*., 2003) may affect the character of magnetic order (Kechrakos, Papanikolaou, Trohidou and Dietl, 2005). It appears that the effect is more relevant in II–VI DMS than in III–V DMS where Mn centers are ionized, so that the enhanced hole density at closely lying Mn pairs may compensate antiferromagnetic interactions (Dietl, Ohno and Matsukura, 2001).

The above-mentioned competition between the long-range RKKY merely ferromagnetic interaction and short-range merely antiferromagnetic superexchange was shown to affect in a nontrivial way magnetic properties of modulation-doped p-type (Cd,Mn)Te quantum wells (Kechrakos, Papanikolaou, Trohidou and Dietl, 2005). In this system, the temperature T_C at which spontaneous spin splitting of electronic levels appears as well as its temperature dependence (Haury *et al*., 1997; Kossacki *et al*., 2000, 2002; Boukari *et al*., 2002) follow predictions of a simple mean-field Zener-like model of ferromagnetism (Dietl, Haury and Merle d'Aubigné, 1997). A reasonable accuracy of the MFA in this low-dimensional system was linked to the long-range

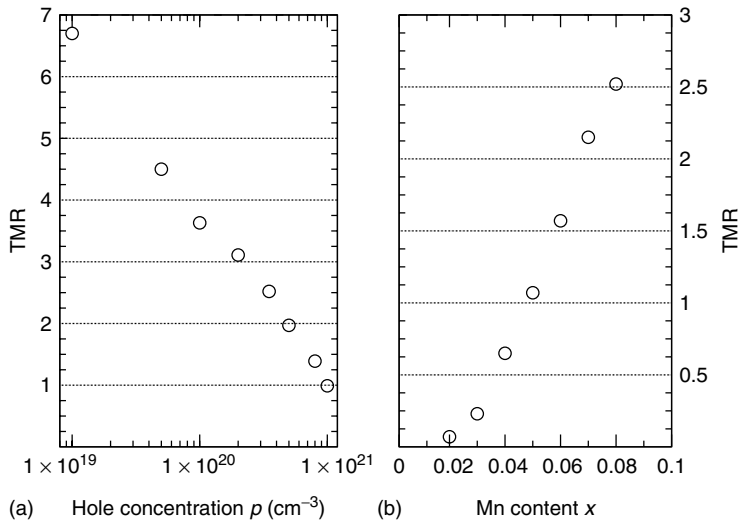

Figure 4. Difference in resistance for antiparallel and parallel magnetization orientations normalized by resistance for parallel orientation for tunneling structures p-$Ga_{1-x}Mn_xAs$/GaAs/p-$Ga_{1-x}Mn_xAs$ as a function of: (a) hole concentration p (for $x = 0.08$); (b) Mn content x (for $p = 3.5 \times 10^{20}\,\mathrm{cm}^{-3}$) in the limit of small bias voltage. (Reproduced from Sankowski, P. *et al*., 2006, with permission from Elsevier. © 2006.)

character of the ferromagnetic interactions as well as to the combined effects of spin-orbit interaction and confinement that lead to the Ising-type universality class (Haury *et al*., 1997). At the same time, however, wide hysteresis loops and the associated spontaneous macroscopic magnetization in zero magnetic field, which are expected within this model (Lee, Jungwirth and MacDonald, 2002), have not been observed. Instead, according to polarization-resolved photoluminescence measurements, the global spin polarization of the carrier liquid increases slowly with the external magnetic field along the easy axis, reaching saturation at a field by a factor of 20 greater than what could be accounted for by demagnetization effects (Kossacki *et al*., 2000, 2002).

In order to explain this behavior, Monte Carlo simulations were employed (Kechrakos, Papanikolaou, Trohidou and Dietl, 2005), in which the Schrödinger equation was solved at each Monte Carlo sweep. Such a model is capable to assess the influence of magnetization fluctuations, short-range antiferromagnetic interactions, disorder, magnetic polaron formation, and spin-Peierls instability on the carrier-mediated ferromagnetism in two-dimensional electronic systems. It has been found that the determined critical temperatures and hystereses are affected in a nontrivial way by the presence of short-range antiferromagnetic interactions, as shown in Figure 5. In particular, the antiferromagnetic interactions decrease T_C less than expected within the MFA. However, the presence of competing interactions reduces strongly the remanence and the coercive field. It appears that in order to satisfy both ferromagnetic and antiferromagnetic spin couplings in an optimum way, the system breaks into nanoscale ferromagnetic domains, so that the global magnetization averages to zero. At the same time, the magnitude of the external magnetic field that can align these domains is set by the strength of the antiferromagnetic interactions, not by demagnetization or magnetic anisotropy energies.

3.2 Effects of Anderson–Mott localization

Similar to other doped semiconductors, p-type DMS undergo MIT, when an average distance between the carriers becomes 2.5 times greater than the Bohr radius. The insulator regime can be reached not only by reducing the acceptor density but also by increasing the concentration of compensation donors or by depleting the film of holes either by electrostatic gates or by charge transfer to surface states or to neighbor undoped layers. In has been found that, in contrast to charge transport characteristics, the Curie temperature, like other thermodynamic properties, does not show up any critical behavior on crossing the MIT (Matsukura, Ohno, Shen and Sugawara, 1998; Ferrand *et al*., 2001).

Two competing models have been put forward in order to explain the existence of ferromagnetic order on the insulator side of the MIT. According to the magnetic polaron scenario (Durst, Bhatt and Wolff, 2002; Kaminski and Das Sarma, 2002) the holes stay localized by the individual parent acceptors, so that their localization length corresponds to the Bohr radius, usually diminished – particularly in the strong-coupling regime – by the hole interaction with the short-range part of the TM potential. In such a case, the ferromagnetic transition can be viewed as the percolation threshold of bound magnetic polarons.

Another scenario was put forward by the present author and coworkers (Dietl, Haury and Merle d'Aubigné, 1997; Dietl *et al*., 2000; Ferrand *et al*., 2001). Within this model, the hole localization length, which diverges at the MIT,

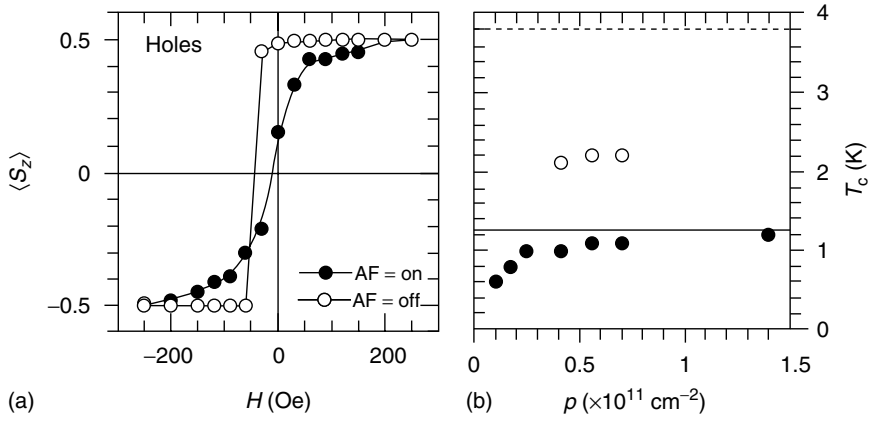

Figure 5. (a) Upper branch of the magnetization hysteresis loop of hole spins in a $Cd_{0.96}Mn_{0.04}Te$ quantum well at $T = 0.7T_C$, where T_C is the Curie temperature, as determined by Monte Carlo simulations neglecting (open symbols) an taking into account (full symbols) the presence of antiferromagnetic interactions. The sheet hole density is $p = 0.41 \times 10^{11}\,cm^{-2}$. (b) The simulated dependence of T_C on p. Horizontal lines are the mean-field results neglecting (dashed line) and taking into account (solid line) antiferromagnetic interactions. (Reproduced from Kechrakos *et al*., 2005, with permission from the American Physical Society. © 2005.)

remains much greater than an average distance between the acceptors for the experimentally important range of the hole densities. Accordingly, the holes can be regarded as delocalized at the length scale relevant for the coupling between magnetic ions. Hence, the spin–spin exchange interactions are effectively mediated by the itinerant carriers, so that the p–d Zener or RKKY model can be applied also on the insulator side of the MIT. At the same time, however, large mesoscopic fluctuations in the local value of the density of states are expected near the MIT. As a result, nanoscale phase separation into paramagnetic and ferromagnetic regions takes place below and in the vicinity of the apparent Curie temperature. The paramagnetic phase persists down to the lowest temperatures in the locations that are *not* visited by the holes or characterized by a low value of the blocking temperature T_B defined in Introduction. The ferromagnetic order develops in the regions, where the carrier liquid sets long-range ferromagnetic correlation between the randomly distributed TM spins. According to this model, the portion of the material encompassing the ferromagnetic bubbles, and thus the magnitude of the saturated ferromagnetic moment, grows with the net acceptor concentration, extending over the whole sample on the metallic side of the MIT.

It is still a formidable task, even in nonmagnetic semiconductors, to describe quantitatively effects of both disorder and carrier–carrier correlation near the Anderson–Mott transition. However, there is a growing amount of experimental results indicating that the model outlined in the previous paragraph is qualitatively correct. In particular, for samples on the insulator side of MIT, the field dependence of magnetization shows the presence of superimposed ferromagnetic and paramagnetic contributions in both (Ga,Mn)As (Oiwa *et al*., 1997) and p-(Zn,Mn)Te (Ferrand *et al*., 2001). Interestingly, the paramagnetic component is less visible in the anomalous Hall effect data, presumably because it probes merely the regions visited by the carriers (Ferrand *et al*., 2001). At the same time, colossal negative magnetoresistance is observed, leading to the field-induced insulator-to-metal transition in samples with the appropriate acceptor densities (Ferrand *et al*., 2001; Katsumoto *et al*., 1998). The enhanced conductance in the magnetic field can be linked to the ordering of ferromagnetic bubbles and to the alignment of the spins in the paramagnetic regions. Remarkably, the corresponding effects have recently been found in modulation-doped quantum well of (Cd,Mn)Te, where no localization of carriers by individual ionized impurities and, thus, no formation of bound magnetic polarons is expected (Jaroszyński *et al*., 2005). The question whether the holes bound by individual acceptors or rather the holes residing in weakly localized states mediate ferromagnetism in DMS on the insulating side of the MIT was also addressed by inelastic neutron scattering in (Zn,Mn)Te:P (Kępa *et al*., 2003). In that work, the difference in the nearest-neighbor Mn pairs exchange energy J_1 in the presence and in the absence of the holes was determined. The hole-induced contribution to J_1 was found to be by a factor of 4 smaller than that calculated under the assumption that the holes reside on individual acceptors. By contrast, if the hole states are assumed to be metallic-like at length scale of the nearest-neighbor distance, the calculated value is smaller than the experimental one by a factor of 1.5, a discrepancy well within combine uncertainties in the input parameters to theory and experimental determination.

4 NONUNIFORM FERROMAGNETIC DMS – CHEMICAL NANOSCALE PHASE SEPARATIONS

4.1 Spinodal decomposition

It is well known that phase diagrams of a number of alloys exhibit a solubility gap in a certain concentration range. This may lead to spinodal decomposition into regions with a low and a high concentration of particular constituents. If the concentration of one of them is small, it may appear in a form of coherent nanocrystals embedded by the majority component. For instance, such a spinodal decomposition is known to occur in the case of (Ga,In)N (Farhat and Bechstedt, 2002), where In-rich quantum-dot-like regions are embedded by an In-poor matrix. However, according to the pioneering *ab initio* work of van Schilfgaarde and Mryasov (2001) and others (Sato, Katayama-Yoshida and Dederichs, 2005) particularly strong tendency to form nonrandom alloy occurs in the case of DMS: the evaluated gain in energy by bringing two Ga-substitutional Mn atoms together is $E_d = 120\,\text{meV}$ in GaAs and 300 meV in GaN, and reaches 350 meV in the case of Cr pair in GaN (van Schilfgaarde and Mryasov, 2001).

Since spinodal decomposition does not usually involve a precipitation of another crystallographic phase, it is not easy detectable experimentally. Nevertheless, its presence was found by transmission electron microscopy (TEM) (Moreno *et al*., 2002; Yokoyama, Yamaguchi, Ogawa and Tanaka, 2005) in (Ga,Mn)As, where coherent zinc-blende Mn-rich (Mn,Ga)As nanocrystals led to the apparent Curie temperature up to 360 K (Yokoyama, Yamaguchi, Ogawa and Tanaka, 2005). Furthermore, coherent hexagonal and diamond-type Mn-rich nanocrystals were detected by spatially resolved X-ray diffraction in (Ga,Mn)N (Martinez-Criado *et al*., 2005) and by TEM in (Ge,Mn) (Bougeard, Ahlers, Trampert and Abstreiter, 2006), respectively.

In view of typically limit solubility of magnetic atoms in semiconductors, it may, therefore, be expected that such a

spinodal decomposition is a generic property of a number of DMS. Owing to the high concentration of the magnetic constituent, the nanocrystals form in this way order magnetically at a relatively high temperature T_m, usually much greater than room temperature. Obviously, either ferromagnetic or ferrimagnetic nanocrystals possess a nonzero magnetic moment. Interestingly enough, nanocrystals in which antiferromagnetic interactions dominate can also show a nonzero magnetic moment owing to the presence of uncompensated spins at their surface, whose relative magnitude grows with decreasing nanocrystal size (Trohidou, Zianni and Blackman, 2002).

As an example we consider (Zn,Cr)Se (Karczewski *et al*., 2003) and (Zn,Cr)Te (Saito, Zayets, Yamagata and Ando, 2003), which show (Karczewski *et al*., 2003; Kuroda *et al*., 2005) the well-known superparamagnetic behavior (Shinde *et al*., 2004; Goswami *et al*., 2005), indicating that the system is to be viewed rather as an ensemble of noninteracting ferromagnetic particles than a uniform magnetic alloy. In such a case the temperature dependencies of magnetization and magnetic susceptibility are described by four distinguished temperatures: T_m, the blocking temperature T_B that corresponds to a maximum of zero-field cooled magnetization; the apparent Curie temperature $T_C^{(app)}$ of the composite material, and the Curie–Weiss temperature Θ characterizing a weighted magnitude of the exchange interactions between the Cr spins within the nanocrystal. A maximum value of $T_C^{(app)} \approx 320\,\mathrm{K}$ is obtained for (Zn,Cr)Te with x_{Cr} above the percolation limit for 3D, $x \approx 0.2$.

These remarkable observations can readily be interpreted under the assumption that the relevant magnetic nanoparticles are built of a metallic zinc-blende CrTe or Cr-rich (Zn,Cr)Te characterized by $T_m \approx 320\,\mathrm{K}$ and by the lattice constant imposed by a paramagnetic semiconductor host, either ZnTe or (Zn,Cr)Te with a rather small Cr concentration. This conjecture is consistent with *ab initio* computations (Zhao and Zunger, 2005) predicting zinc-blende CrTe to be a ferromagnetic half-metal as well as with experimental results for CrTe in a bulk NiAs-type structure for which $T_m \equiv T_C = 340 \pm 10\,\mathrm{K}$ (Ohta, Kanomata, Kaneko and Yoshida, 1993). Within this scenario, for small ferromagnetic nanocrystals we expect $T_B < T_C^{(app)} < T_C$, T_B being proportional to a mean nanoparticle volume V, $T_B \approx KV/(25k_B)$, where K is the density of the magnetic anisotropy energy. Similarly, $T_C^{(app)}$ provides information on the upper bound of the V distribution. Furthermore, we note that broken magnetic bonds at the nanocrystal surface reduce the Curie–Weiss temperature Θ from its anticipated value for large V, $\Theta_{max} \geq T_C$.

It is, therefore, legitimate to suppose that coherent nanocrystals with a large concentration of magnetic constituent account for high apparent Curie temperatures detected in a number of DMS. This model explains, in particular, a long staying puzzle about the origin of ferromagnetic response in DMS, in which an average concentration of magnetic ions is below the percolation limit for the nearest neighbor coupling and, at the same time, the free-carrier density is too low to mediate an efficient long-range exchange interaction. Remarkably, the presence of magnetically active nanocrystals leads to an enhanced magneto-optical (Yokoyama, Yamaguchi, Ogawa and Tanaka, 2005) and magnetotransport (Shinde *et al*., 2004; Ye *et al*., 2003) properties. This opens doors for various applications of such hybrid systems provided that methods for controlling nanocrystal characteristics and distribution would be elaborated. So far, the most rewarding method of self-organized growth of coherent nanocrystals or quantum dots has exploited strain fields generated by lattice mismatch at interfaces of heterostructures (Stangl, Holý and Bauer, 2004). Remarkably, it becomes possible to fabricate highly ordered three-dimensional dot crystals under suitable spatial strain anisotropy (Stangl, Holý and Bauer, 2004). A further progress in this direction is particularly timely as it could result in the development of high-density 3D memories and spatial light modulators for advanced display technologies. A new method of self-organized growth has recently been proposed by the present author (Dietl, 2006). In this approach, long-range Coulomb forces serve to control the aggregation of alloy constituents.

4.2 Controlling spinodal decomposition by interion coulomb interactions

It is well known that in most DMS the levels derived from the open d or f shells of magnetic ions reside in the band gap of the host semiconductor (Dietl, 2002). This property of magnetic ions has actually been exploited for a long time to fabricate semi-insulating materials, in which carriers introduced by residual impurities or defects are trapped by the band-gap levels of magnetic impurities. The essential ingredient of the proposal in question (Dietl, 2006) is the observation that such a trapping alters the charge state of the magnetic ions and, hence, affect their mutual Coulomb interactions. Accordingly, codoping of DMS with shallow acceptors or donors modifies E_d and thus provides a mean for the control of ion aggregation. Indeed, the energy of the Coulomb interaction between two elementary charges residing on the nearest-neighbor cation sites in the GaAs lattice is 280 meV. This value indicates that the Coulomb interaction can preclude the aggregation, as the gain of energy associated with the bringing two Mn atoms in (Ga,Mn)As is $E_d = 120\,\mathrm{meV}$.

It is evident that the model in question should apply to a broad class of DMS as well to semiconductors and insulators, in which a constituent, dopant, or defect can exist

in different charge states under various growth conditions. As important examples we consider (Ga,Mn)N and (Zn,Cr)Te, in which remarkable changes in ferromagnetic characteristics on codoping with shallow impurities have recently been reported (Reed *et al*., 2005; Ozaki *et al*., 2005). In particular, a strong dependence of saturation magnetization M_s at 300 K on codoping with Si donors and Mg acceptors has been found (Reed *et al*., 2005) for (Ga,Mn)N with an average Mn concentration $x_{Mn} \approx 0.2\%$. Both double exchange and superexchange are inefficient at this low Mn concentration and for the midgap Mn level in question. At the same time, the model of nanocrystal self-organized growth in question explains readily why M_s goes through a maximum when Mn impurities are in the neutral Mn^{3+} state, and vanishes if codoping by the shallow impurities makes all Mn atoms to be electrically charged.

It has also been found that $T_C^{(app)}$ depends dramatically on the concentration of shallow N acceptors in (Zn,Cr)Te. Actually, $T_C^{(app)}$ decreases monotonically when the concentration x_N of nitrogen increases, and vanishes when x_{Cr} and x_N become comparable. This supports the model as in ZnTe the Cr state (Godlewski and Kamińska, 1980) resides about 1 eV above the nitrogen level (Baron, Saminadayar and Magnea, 1998). Accordingly, for $x_N \approx x_{Cr}$ all Cr atoms become ionized and the Coulomb repulsion precludes the nanocrystal formation. At the same time, the findings are not consistent with the originally proposed double exchange mechanism (Ozaki *et al*., 2005), as undoped ZnTe is only weakly p type, so that T_C should be small for either $x_N \approx 0$ and $x_N \approx x_{Cr}$, and pick at $x_N \approx x_{Cr}/2$, not at $x_N \approx 0$.

Finally, we mention the case of Mn doped GaAs, InAs, GaSb, and InSb. In those materials, owing to a relatively shallow character of Mn acceptors and a large Bohr radius, the holes reside in the valence band. Thus, the Mn atoms are negatively charged, which – according to our model – reduces their clustering, and makes it possible to deposit, by low-temperature epitaxy, a uniform alloy with a composition beyond the solubility limit. Codoping with shallow donors, by reducing the free-carrier screening, will enhance repulsions among Mn, and allow one to fabricate homogenous layers with even greater x_{Mn}. On the other hand, codoping by shallow acceptors, along with the donor formation by a self-compensation mechanism (Yu *et al*., 2002), will enforce the screening and, hence, lead to nanocrystal aggregation.

5 SUMMARY

The findings discussed here demonstrate that a number of pertinent properties of spatially uniformed carrier-controlled diluted ferromagnetic semiconductors and their heterostructures can be understood qualitatively, if not quantitatively, by the present theory. The accumulated data point clearly to the importance of spin-orbit interactions in the physics of hole-mediated ferromagnetism in semiconductors. These interactions control the magnitude of the Curie temperature, the saturation value of the magnetization, the anomalous Hall effect as well as the character and magnitude of magnetic and transport anisotropies. A growing amount of evidences shows that under various conditions the spatial distribution of carriers and/or magnetic ions is by no means uniform. The nanoscale phase separation can be driven either by randomness in the carrier and spin subsystems or by limited solubility of TMs in the host semiconductor, which leads to spinodal decomposition into regions with a small and a large concentration of the magnetic constituent. Interestingly, by manipulating the charge state of magnetic ions, it becomes possible to control the spinodal decomposition. This constitutes an appealing avenue toward self-organized coherent epitaxy of magnetic nanocrystals over a wide range of their dimensions. It is expected that further works will indicate how to tailor nanocrystal size dispersion and spatial distribution. In this context, engineering of local strains by exploiting various combinations of dopants and hosts may turn out to be of relevance. The self-organized growth mode in question (Dietl, 2006) is rather universal – it applies to dopants exhibiting a solubility gap, and different charge states that are stable under the growth conditions. The existence of this nano-assembling mechanism, as exemplified here by the case of (Zn,Cr)Te and (Ga,Mn)N codoped with shallow impurities, explains outstanding properties of a broad class of composite DMS, and offer prospects for exploiting their novel functionalities. In particular, the nanocrystals, rather than the host, are shown to account for ferromagnetic signatures in magnetic and magneto-optical characteristics of these systems. These findings imply also that today's *ab initio* methods of computational materials science, assigning the high-temperature ferromagnetism of, for example, (Zn,Cr)Te (Bergqvist *et al*., 2004; Fukushima, Sato, Katayama-Yoshida and Dederichs, 2004) to the uniform diluted alloy, overestimate substantially long-range ferromagnetic correlation, presumably because effects of Mott–Hubbard and Anderson–Mott localization of paramount importance in the case of the narrow d band are implicitly disregarded in the codes developed so far. It thus appears that delocalized or weakly localized valence band holes are necessary to transmit magnetic information between the diluted spins (Dietl *et al*., 2000; Jungwirth *et al*., 2006a). In addition to (Ga,Mn)As, (Zn,Mn)Te:N, and related systems, recent indications of ferromagnetism in p-(Ga,Mn)N (Edmonds *et al*., 2005; Sarigiannidou *et al*., 2006) and p-(Ga,Mn)P (Scarpulla *et al*., 2005) appear to support this conclusion. However, in those and other experimentally relevant cases, nonuniformity associated with hole localization is seen to affect strongly ferromagnetic properties. It is still

to be found out experimentally whether nitrides, oxides or diamond containing 5% of randomly distributed magnetic impurities and more than 3×10^{20} valence band holes/cm^3 show ferromagnetic ordering above the room temperature.

ACKNOWLEDGMENTS

This work was supported in part by ERATO Semiconductors Spintronics Project of Japan Science and Technology Agency, by NANOSPIN E. C. project (FP6-2002-IST-015728), by Humboldt Foundation, and carried out in collaboration with M. Sawicki, K. Osuch, H. Przybylińska, M. Kiecana, A. Lipińska, and P. Kossacki in Warsaw, as well as with groups of H. Ohno in Sendai, S. Kuroda in Tsukuba, K. Trohidou in Athens, J. Cibert and D. Ferrand in Grenoble, J. Jaroszyński and D. Popović in Tallahassee, L. Molenkamp in Würzburg, B. Gallagher in Nottingham, and A. Bonanni in Linz.

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