Magnetic Semiconductors

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Introduction: diluted magnetic semiconductors

As discussed in accompanying lectures, today's research on spin electronics involves virtually all material families, the most mature being studies on magnetic metal multilayers, in which spin-dependent scattering and tunnelling are being successfully applied in reading heads of high density hard-discs and in magnetic random access memories (MRAM). However, in the context of spintronics [1] particularly promising are ferromagnetic semiconductors [2] since they combine complementary resources of ferromagnetic and semiconductor material systems. One of the relevant questions is to what extend the powerful methods developed to manipulate the carrier concentration and spin polarisation in semiconductor quantum structures could serve to tailor the magnitude and orientation of magnetisation produced by spins localized on magnetic ions. Another important issue concerns the elaboration of methods of injecting and transporting spin currents, which may ultimately leads to control over single spins in solid state environment.

Already early studies of Cr spinels as well as of rock-salt Eu- and Mn-based chalcogenides led to the observation of a number of outstanding phenomena associated with the interplay between ferromagnetic cooperative phenomena and semiconducting properties [3]. A strong spin-dependent (exchange) coupling between the band carriers and spins localized on the magnetic atoms accounts for outstanding properties of these materials. This coupling gives rise to strong indirect exchange interactions between the localized moments as well as to giant spin-splittings of the electronic states, which is proportional to magnetisation of the spins. However, studies of these ferromagnetic semiconductors were hampered by difficulties in material preparation and relatively low Curie temperatures (T_C), typically below 100 K. Somewhat later, research on diluted magnetic semiconductors (DMSs) was initiated [4]. This family of materials encompasses standard semiconductors, in which a sizable portion of atoms is substituted by such elements that produce localized magnetic moments in the semiconductor matrix. Usually, magnetic moments originate from 3d or 4f open shells of transition metals or rare earths (lanthanides), respectively, so that typical examples of DMSs 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 DMSs. Extensive studies of DMSs started in the late 70's when appropriately purified Mn was employed to grow bulk II-VI Mn-based alloys by various modifications of the Bridgman method. Comparing to the magnetic semiconductors investigated earlier, II-VI DMSs exhibited smaller defect concentrations and were easier to dope by shallow impurities. Accordingly, it was possible to examine various novel spin phenomena by powerful magnetooptical and magnetotransport techniques developed to study the standard semiconductors. Disappointingly, however, the dominant interactions between the localized magnetic moments turned out to be antiferromagnetic. This, together with the randomness of magnetic ion distribution, resulted in disordered spin orientations in the absence of an external magnetic field, even at the lowest achievable temperatures.

A recent rapid progress of DMS research that started in 90's has stemmed, to a large extend, from the development of crystal growth methods 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. Similarly, the doping during MBE process allows one to increase substantially the electrical activity of shallow impurities. In the case of III-V compounds, in which divalent magnetic atoms supply both spins and holes, the use of the low-temperature molecular beam epitaxy (LT MBE) provides thin films of, e.g., $Ga_{1-x}Mn_xAs$ with x up to 0.07 and the hole concentration in excess of 10^{20} cm^{-3}.

The discovery of ferromagnetism in Mn-based zinc-blende III-V compounds [5], such as (Ga,Mn)As, followed by the prediction [6] and observation of ferromagnetism in p-type II-VI materials [7,8], such as (Zn,Mn)Te:N, allows one to explore the physics of previously not available combinations of quantum structures and ferromagnetism in semiconductors. This aspect of ferromagnetic III-V and II-VI diluted magnetic semiconductors (DMS) will be outlined here together with indications of models aiming at explaining the nature of ferromagnetism in these materials.

Carrier-controlled ferromagnetism

It is well established that Mn is divalent in II-VI compounds and assumes the high spin d^5 configuration characterized by $S = 5/2$. Here, Mn ions neither introduce nor bind carriers, but give rise to the presence of localized spins. For low carrier densities, II-VI DMS are paramagnetic but neighbour Mn-Mn pairs are antiferromagnetically blocked owing to short-range super-exchange interactions. However, this antiferromagnetic coupling can be overcompensated by ferromagnetic interactions mediated by band holes [6-8]. In III-V compounds, Mn atoms when substituting trivalent metals supply both localized spins and holes, so that extrinsic co-doping is not necessary to generate the carrier-mediated spin-spin interaction [2,5,9].

The role of band carriers in promoting ferromagnetic ordering between localized spins was already noted by Zener in '50s in the context of magnetic metals. This ordering can be viewed as driven by the lowering of the carriers energy associated with their redistribution between spin subbands, split by the exchange coupling to the localised spins. A more detailed quantum treatment indicates, however, that the sign of the interaction between localised spin oscillates with their distance according to the celebrated Ruderman-Kittel-Kasuya-Yosida (RKKY) model. Because of the large density of states and spin-dependent hybridisation between anion p and magnetic d states, the carrier-mediated spin-spin interaction is particularly strong in the presence of the holes in tetrahedrally coordinated DMS. Interestingly, this carrier-mediated Zener/RKKY ferromagnetism is enhanced by exchange interactions within the carrier liquid, so that the Stoner mechanism contributes to the magnitude of the Curie temperature in these systems.

A question arises how the character of the spin-spin interactions changes if the hole concentration becomes so small that the material is on the insulator side of the metal-to insulator transition (MIT). According to the scaling theory of the Anderson-Mott MIT at distances smaller than the localization radius (which diverges right at the MIT), the states retain metallic character, so that the Zener/RKKY is predicted to be valid [6]. Recent studies of the interaction energy of nearest neighbour Mn pairs by inelastic neutron scattering in (Zn,Mn)Te [10] confirm this expectation.

Manipulations of magnetisation

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 structures. Such tuning capabilities of the materials systems in question were put into the evidence in (In,Mn)As/(Al,Ga)Sb [11,12] and modulation doped p-(Cd,Mn)Te/(Cd,Mg,Zn)Te [7,13] 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 modelling, photocarriers generated by above barrier illumination destroy ferromagnetic order in the magnetic quantum well residing in an undoped (intrinsic) region of a p-i-p structure [7,13] but they enhance the magnitude of spontaneous magnetisation in the case of a p-i-n diode [13].

For the valence band states, whose periodic part of the Bloch functions contain spin components mixed up by the spin-orbit interaction, the exchange splitting does not depend only on the product of the p-d exchange integral and the Mn magnetisation but also on the magnitude and direction of the hole wave-vector, confinement, and strain. In particular, both experimental and theoretical results demonstrate that the orientation of the easy axis in respect to the film plane depends on whether the epitaxial strain is compressive or tensile [9]. Hence, magnetic anisotropy and thus easy axis direction and domain structure [14], can be manipulated by appropriate layout of the layer sequence, as epitaxial growth of DMS films in question is usually pseudomorphic. Furthermore, magnetic anisotropy at given strain is predicted to vary with the degree of the occupation of particular hole subbands. This, in turn, is determined by the ratio of the valence band exchange splitting to the Fermi energy, and thus, by the magnitude of spontaneous magnetisation, which depends on temperature. Such a temperature-induced switching of the easy axis direction has recently been detected in samples with appropriately low hole densities [15]. A related sensitivity of the easy axis direction to the carrier concentration constitutes a novel method enabling to control the magnetisation direction locally by a system of electrostatic gates.

Spin injection

A number of groups is involved in the development of devices capable of injecting spins into a non-magnetic semiconductor. Obviously, owing to a high degree of spin polarisation and resistance matching ferromagnetic semiconductors constitute a natural material of choice here. Typically, a p-i-n light emitting diode structure is employed, in which the p-type spin injecting electrode is made of a ferromagnetic semiconductor. In this particular experiment for the (Ga,Mn)As/GaAs/(In,Ga)As/n-GaAs diode [16], the degree of circular polarisation is examined for light emitted in the growth direction. In this Faraday configuration, simple selection rules are obeyed for radiative recombination between the electron and heavy hole ground state subbands. Since the easy axis is in plane, a field of a few kOe is necessary to align the magnetisation and thus to produce a sizable degree of light polarisation. Importantly, the injection of spin polarised electrons, using Zener or Esaki tunnelling from p-type (Ga,Mn)As electrode into n-type GaAs, was also realized.

Quantum Hall ferromagnet

The above results demonstrate rather convincingly the decisive role of the valence band holes in setting on the ferromagnetic ordering in these systems, a conclusion corroborated by studying the Curie temperature T_C as a function of compensation in epitaxial films of (Ga,Mn)As and as a function of the acceptor concentration in p-(Zn,Mn)Te. At the same time, in agreement with theoretical predictions, no ferromagnetic ordering was detected above 1 K in heavily doped n-type (Zn,Mn)O [17]. However, according to experimental results presented in Fig. 3, for an appropriate combination of an external magnetic field and gate voltage that controls electron concentration, an Ising ferromagnetic ground state with T_C up to 2 K can be observed in high-quality modulation-doped n-(Cd,Mn)Te/(Cd,Mg)Te heterostructures [18]. The quantum Hall ferromagnetism shows up when two partly filled Landau levels with opposite spin directions are brought into a coincidence. This Stoner-like instability of the carrier liquid appears due to the enhancement of the density of states in two-dimensional systems in quantising magnetic fields. Incidentally, Landau level crossings occur in such structures due to the enlargement of electron spin-splitting by the s-d exchange interaction with the Mn spins.

Summary and outlook

Extensive studies of ferromagnetic semiconductor heterostructures have lead to the observation of a number of spin phenomena. Some of them, such as spin injection as well as giant and tunnelling magnetoresistance, are familiar from parallel studies of magnetic multilayers. Other effects, like isothermal driving of the system between ferromagnetic and paramagnetic phases by the electric field or by the photon flux in the direction that can be selected by an appropriate design of the structure, appear unique to ferromagnetic semiconductors. These striking effects offer new tools for patterning magnetic nanostructures as well as for information writing and processing, beyond the heating effects of light exploited in the existing magneto-optical memories. Obviously, however, while the potential of ferromagnetic semiconductors can already be exploited for the development of quantum information hardware, their practical applications in classical information systems have to be preceded by progress in the synthesis of a functional material with T_C surpassing comfortably the room temperature. Following the theoretical suggestion [9], a number of oxide and nitride-based DMS, containing Mn or other magnetic elements, has been obtained, which indeed show indications of ferromagnetism at room temperature [19]. However, a further progress in this field requires development of growth and characterization methods that enable a better control over solubility limits, self-compensations, phase segregations, and precipitations of other compounds.

On the theoretical side, it appears that double- and super-exchange, rather than the Zener/RKKY mechanism, may account for ferromagnetism is systems containing magnetic elements other than Mn. Since ferromagnetic DMS combine intricate properties of charge-transfer insulators and strongly correlated disordered metals with the physics of defect and band states in heavily doped semiconductors, despite important advances in theoretical understanding of these systems, their description from first principles may take some time. With no doubt, search for functional ferromagnetic semiconductor nanostructures and their theoretical modelling have evolved into an important branch of today's materials science and condensed matter physics.

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