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On the Nature of the Magnetism-Promoting States in Dilute Magnetic Semiconductor and Oxide Thin Films

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Ferromagnetic (FM) ordering is observed in intermediate and wide gap dilute magnetic semiconductors as well as in oxides. While the interpretation of the experimental results is often clouded by the existence of non-homogeneous and non ideal nanostructures related to the fact that impurity concentration tends to far exceed the thermodynamic solubility limit, a general physical picture as to the physical origin of the FM interactions has emerged. We discuss the physical mechanism of ferromagnetism mediated by the carriers. We show that what stabilizes the FM spin arrangement is the energy-lowering due to interaction between partially occupied states in the band gap, localized on different transition atoms. These partially occupied states are hybrids between the d impurity band states and host vacancy orbitals, never host-like states as imagined in model Hamiltonian approaches. The theory uses both the model and first principle approach and can be applied to various types of systems such as dilute magnetic semiconductors [(Ga, Mn)As, (Ga, Mn)N, etc.] and oxides [(Ti, Co)O_2, (Zn, Mn)O, etc.] as well as nanodevices prepared of these materials.

Keywords: Magnetism, Superconductors, Impurities, Exchange Interaction, Dilute Magnetic Semiconductors, Dielectrics.

1. INTRODUCTORY REMARKS

Dilute magnetic semiconductors and dielectrics (DMS and DMD, respectively) as potential materials for spintronics and optoelectronics arouse interest of experimentalists since early 90-es. Twenty years of intense studies of dilute magnetic semiconductors and dielectrics (DMS and DMD, respectively) resulted in establishing a unified picture of the nature of indirect exchange interaction between magnetic ions. It is now clear that both universal features characteristic of all zinc blende and wurtzite compounds and particular properties of specific materials should be taken into account in explanation of the puzzling phenomenon of high T_C ferromagnetism of dilute alloys. The universal trends are related to the nature of chemical bonds between transition metal (TM) ions and the host electrons in valence and conduction bands in these materials.[1,2] Mechanisms of indirect magnetic interaction are also universal: neighboring magnetic ions virtually exchange theirs spin via available empty levels provided by the host environment. These mediating states may be different in intermediate gap DMS, wide gap DMS, and oxide based DMD. In this paper we briefly survey these mechanisms and show that the universal features prevail over the differences in mediating entities.

Studies of the chemical trends in transition metal (TM) doped III–V semiconductors in a dilute doping limit[1,2] have shown that these trends are determined by the strong *d*–*p* hybridization between the 3*d*-orbitals of TM ion and the *p*-orbitals of its nearest anion neighbors. The ensuing states of a single 3*d* impurity are determined by the relative location of the atomic 3*d* levels of TM ions and the center of gravity of the heavy hole valence band. This disposition results in two types of impurity-related states: the bonding, TM localized "Crystal Field Resonance" (CFR) and the antibonding state called "Dangling Bond Hybrid" (DBH),[9] in which the TM *d*-state hybridizes with the vacancy-like dangling bonds. The relevant partially occupied DBH or CFR orbitals are necessarily in the gap (being partially occupied) and invariably contain significant 3*d* character, not just host like character. *The basic mechanism of ferromagnetism is the interaction between two or more partially occupied DBH's or CFR's located on different* 3*d sites in the lattice.* In this case, the ferromagnetic spin arrangement leads to energy lowering (ground state) since more spins are occupying the bonding than the antibonding states.[3,4] In a given host semiconductor, the energetic positions of CFR and DBH vary in a systematic way with the atomic number of the TM.[1–4] On the other hand, considering different III–V semiconductors such as

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GaN–GaP–GaAs–GaSb with their valence band maximum (VBM) aligned according to their band offsets, the positions of the DBH-CFR levels are approximately constant, as shown in Refs. [3, 5]. Thus the fundamental cause of FM in such systems is the formation of $3d$-like impurity states in the gap (DBH or CFR) containing $3d$ character and the interaction of such states when partially occupied. While earlier on it was suggested that the host-like-states might be causing this FM, there is now compelling experimental and theoretical evidence that it is the impurity states with $3d$ signature that carry this effect.[6]

The mechanism of indirect exchange is intimately related to positions of CFR and DBH impurity bands relative to valence and conduction bands of the host materials. In all the cases, magnetic ordering is possible only if the impurity band is partially occupied. Sometimes the partially filled state is DBH and sometimes CFR (but it is never a host like state that can be constructed from host effective-mass orbitals). One should distinguish between the situations where the CFR-related band is fully occupied, while the DBH-related band is partially filled and the situations, where the CFR band itself is partially filled. In both cases, the empty states serve as mediating states for the indirect FM double exchange. We will show below that both possibilities may be realized in dilute magnetic materials. Since the position of the chemical potential in the impurity band is determined as a rule by additional donor and/or acceptor states related to extra impurities or intrinsic defects of host materials, resulting Curie temperature T_C strongly depends on the fabrication method and thermal treatment of DMS and DMD. In spite of the scatter in magnetic and transport properties of available materials, one may say that these properties are based on some universal trends and mechanisms.

2. INTERMEDIATE GAP DILUTE MAGNETIC SEMICONDUCTORS

The paradigm system that combines ferromagnetism (FM) with semiconductivity involves $\mathrm{Mn}^{(2+)}$ impurity ions substituting for $\mathrm{Ga}^{(3+)}$ atoms in GaAs.[3, 7–11] Such acceptor substitution creates a hole that interacts with the local moment of d^5 Mn. This doping-induced magnetism could lead to electrical control of FM, to the potential benefit of spin-electronics (spintronics). The nature of the ferromagnetism, including its dependence on the hole concentration and on that of the Mn ions depends, however, on the physical nature of the hole state.

One view, i.e., the "*host-like hole*" model[7–10] has been that the hole resides *inside* the GaAs valence band. Such view would permit the use of the language of GaAs semiconductor physics (s–p bonding, extended wave functions, RKKY exchange; effective-mass acceptor states) in analyzing the ensuing magnetism and its dependence on concentration of the relevant species. This scenario, underlying most Model Hamiltonian treatments of the problem[8, 10] represent just a few typical cases (out of many more). It was inspired by the previously known case of isovalent Mn doping of CdTe, where, on account of the host metal atom $\mathrm{Cd}^{(2+)}$ having the same charge as the magnetic impurity ion $\mathrm{Mn}^{(2+)}$, hole formation required *additional* doping by other impurities. Such doping was accomplished by conventional hydrogen-like dopants (extended wave function in the effective mass approximation), leading to the expected host-like hole behavior underlying delocalized, effective-mass dopants.

The different, "*Impurity Band view*[3, 11] emerged from the assumption that Mn doping is unlikely to be hydrogen-like, as it introduces into GaAs a fundamentally new (d) orbital type, absent from the (s, p) host. Then it is not obvious a priori, whether the hole will carry the identity of the host or that of the impurity; and electronic structure calculations were needed to make this judgment. First principles calculations[3, 11] have shown that the hole resides in an impurity band above the host valence band. This view implies that the magnetism could not be described in the language of host semiconductor physics alone, but rather by that related to the localized d-band of Mn, hybridized with t_2 states of the host.

Recent *crucial* experimental results, discussed below, have clearly favored the impurity band model. Before discussing them, note that not all experiments are sensitive to the nature of the hole states: some experimental observables related to the (Ga, Mn)As system are not very sensitive to the nature of the hole state, and could be explained either way. Examples of such non-crucial experiments include effects reflecting predominantly the existence of local moments of Mn interacting with some background carriers in the Kohn-Luttinger s–p bands, including magneto-transport, magneto-optics, thermoelectrical effects and other phenomena related to itinerant rather than to localized carriers near the top of the valence band.

Remarkably, however, a recent *crucial* experiment[6] has settled this debate in favor of the Impurity Band view on the mechanism of FM ordering. This statement is based on measuring independently the net densities of holes and that of the Mn ions, and showing that the Fermi level resides above the valence band, inside the impurity band and that T_C is controlled by this position rather than by the density of nearly free carriers as in the host-like-hole view. A Cover Story[12] echoed this view. While explaining that "the compass is pointing in the direction of impurity band scenario," this piece[12] expressed the concern that some experimental features demonstrated by the most metallic samples are unclear as to their compliance with a particular hole model. We point out here that there are fundamental model-independent reasons for assertion that the placement of the hole in an impurity band (above the host valence band) holds both in the Mn dilute limit (on the insulating side) and in the high concentration *limit* $n_{\mathrm{Mn}} > 0.1$ (on the metallic side). These reasons are explained in what follows: (i) The Mn-induced acceptor level in III–V semiconductors is a deep acceptor-like impurity band, not

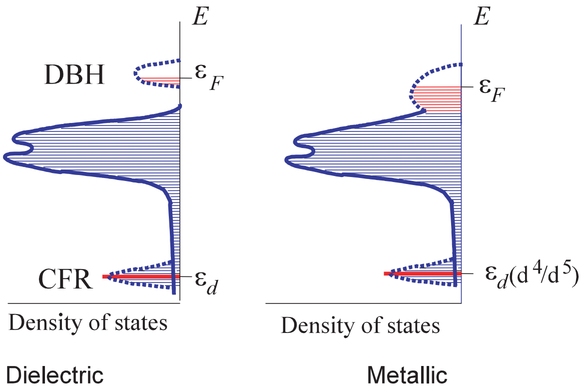

Fig. 1. Density of electron states in the dielectric (left) and metallic (right) phases of (Ga, Mn)As. Two impurity-related peaks in DOS form a covalent pair CFR (related to the Mn(d^4/d^5) level)-DBH (impurity band above the top of the valence band). Only the $t_2$partial contribution in the heavy hole band DOS is schematically shown. The CFR/DBH structure originated from the local d–p bonding survives at any level of doping.

effective-mass like. These are DBH states, i.e., vacancy-like dangling bonds hybridizes with the TM 3d states (see Fig. 1). The chemical trends mentioned above unequivocally point to the d–p hybridization, rather than hydrogen-like acceptors, as the principal mechanism of formation of acceptor levels and impurity bands. Critically, Mn in GaAs, creates a DBH state outside the host valence band (inside the gap). The fact that this level is only 0.1 eV above the VBM does not imply that this is a shallow, host-like level, since its wave function is indeed composed from a multitude of k-points (unlike effective-mass or $\boldsymbol{k}\cdot\boldsymbol{p}$ description) and contains d-character, absent from the host crystal. In the more extreme case of Mn in GaN, where the CFR acceptor level is very deep in the gap (1.4 eV above the VBM) and cannot possibly lead to ionizeable free holes, the magnetism clearly cannot be described by the host-like hole s–d-exchange theory[13] with inter-site spin exchange (see also discussion in Ref. [14]).

(ii) The model of impurity potential used in the $\boldsymbol{k}\cdot\boldsymbol{p}$ approach to deduce a delocalized nature of the Mn states is not appropriate for the 3d impurities. Reference [13] attempted to describe Mn in GaAs by means of a square well potential interacting with the host bands. In the presence of many such wells the bound state spreads out, creating an impression of a host-like resonance impurity state. This approach relies also on the RKKY mechanism to account for the FM interaction, which has been shown to be inadequate.[15, 16] The numerical calculations[17] indicate an absence of oscillations typical of RKKY mechanism. The description of resonance impurity scattering by means of potential scattering[13] is misleading because it lacks the d-orbital nature of the real Mn state with its specific Mn 3d orbital energy. In turn, the d–p hybridization mechanism [(i) above] with its correct Mn 3d orbital energy places the state outside the host bands and is robust, in the sense that it cannot be significantly modified by any kind of screening, or disorder effects. In fact, disorder cannot destroy the local chemical bonds. The immediate consequence of this fact is that even for high Mn concentration, on the metallic side, where the impurity band is merged with the valence band and there is no gap for charge transport, the top of this impurity band is still formed by strongly hybridized d–p orbitals (see Fig. 1).

(iii) *The impurity band picture correctly describes the dependence of* T_C *on the carrier concentration*: In accordance with the above picture, the Fermi level is pinned in the impurity band region of strong d–p hybridization both in insulating and metallic states. This impurity band modifies the host crystal density of states (DOS) generating a Lorentzian-like impurity band above the host valence band maximum. This DOS is responsible for the details of the hole-mediated Zener double exchange[18] as shown in Refs. [14, 19]. Strong correlation of the d-electrons (Hund rule) plays in this case a crucial rule.

(iv) In GaAs:Mn films the Fermi level position depends on the ratio between the substitution and interstitial Mn-related defects, and the optimum concentration corresponds to half-filling of the impurity band. Thus, the dependence of T_C on the effective carrier concentration x dependence is the “dome-shaped” function observed in experiment (Ref. [6] Fig. 1). This type of dependence follows from the model calculations[14, 19] and first-principles supercell calculations[3] based on the mechanism of d–p-hybridized CFR-DBH states, and therefore on the pinning of these states to the universal energy scale (the valence band offset). A dome-like dependence $T_C(x)$ obtained within the model of impurity ferromagnetism due to the

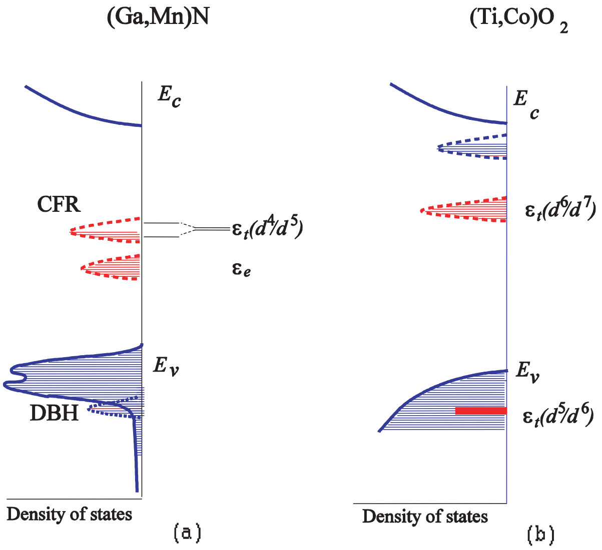

Fig. 2. (a) Density of electron states in (Ga, Mn)N. CFR states Mn(d^4/d^5) form an impurity band in the middle of the gap: d_e-related band is fully occupied, and d_{t2} band is partially occupied in partially compensated samples. DBH impurity band is deep in the valence band. (b) Density of electron states in (Ti, Cr)O$_2$, where the localized states related to oxygen vacancies form a band below the bottom of conduction band of the host material (see text for further explanation).

Zener-like double exchange via the impurity band[14] can be seen in Figure 2 of that paper.

(v) Two recent experimental findings unambiguously support the statement that the *d–p*-hybridization is responsible not only for the Zener exchange but also for the shape of the DOS near the top of the valence band in metallic ferromagnetic (Ga, Mn)As. These are the dome-shaped $T_C(x)$ (Ref. [6], Fig. 1), and the absence of Drude peak in the infrared conductivity of "metallic" samples (Ref. [20], Fig. 10), (Ref. [21], Figs. 1 and 3), which indicates the absence of free charge carriers at the Fermi level in the samples.

(vi) The mechanism of *d–p* hybridized hole states above the top of the valence band provides guidelines for optimization of devices fabricated from FM semiconductors. There are some important practical consequences of the change of FM model from host-like hole to impurity band hole: (a) one should look for the fabrication and annealing regimes, which favor the optimal half-filling of Mn-related impurity band; (b) the narrower is the band, the higher T_C is expected. To make this band narrower, fabrication of heterostructures with spatially quantized impurity bands may be useful.

3. WIDE GAP DILUTE MAGNETIC SEMICONDUCTORS

Due to the general chemical trends stabilizing the ionization energies TM(+/0) and TM(0/−) relative to the ionization threshold,[1,2] the acceptor levels for the most of TM impurities in the wide-gap semiconductors like GaP and GaN are of CFR nature. However, in the specific case of Mn, the acceptor level in the gap is DBH-like in GaP but CFR-like in GaN.

In the latter case the positions of corresponding impurity bands are determined by the addition energy $E(d^4/d^5)$ for the electrons with e and t_2 orbitals in the $3d$ shell of Mn ion[22] (Fig. 2). First principle calculations for (Ga, Mn)P[3,23,24] (see also (Ga,Cu)P with the addition energy $E(d^9/d^{10})$[25]) and Ga(Mn)N[3,11,24,26–28] support these expectations. One may say that due to *d–p* hybridization the Mn ions in GaN are in an intermediate valence state

$$\Psi = \cos\theta d^5 + \sin\theta d^4 P \tag{1}$$

where P is a molecular orbital formed by a superposition of the atomic *p*-orbitals centered on pnictogen ions P or N in the nearest vicinity of the Mn impurity. (It applies also to the other FM impurities in semiconductors.) An impurity band arises due to overlap between the "*p*-tails" of the corresponding impurity states. As a result of this overlap the specific mechanism of indirect exchange between Mn ions in partially occupied impurity band arises.[14] The distance between the two partner ions involved in indirect exchange should be optimized in such a way that the hybridization splitting of two levels in the pair pushes one of these levels below the chemical potential μ and leaves the second one above μ (see Fig. 2). Then the Zener-type FM double exchange[18] between the mixed states of the Mn ions mediated by pnictogen orbitals orients their spins mutually parallel. If the concentration of such pairs is high enough, a long range FM order arises in the dilute alloy (see below a more detailed discussion). As a result the Curie temperature depends on the concentration x of excess dopants or acceptors responsible for the position of the chemical potential μ in the impurity band, $T_C \sim \Delta(x)$, where $\Delta(x)$ is the overlap integral weighted with the impurity distribution. It is clear that the optimal position of the chemical potential for the maximal T_C is in the middle of impurity band and $T_C(x)$ should be a dome-like function with a maximum at the optimal doping. Such dependence has been really observed experimentally in GaP.[29] Numerical calculations also support this picture.[28]

A puzzling feature of DMS, shared with the wide-gap DMD, is the fact that the long range FM order occurred at impurity concentration seemingly well below that for the percolation threshold in cubic or wurtzite lattices.[30] A few explanations to this effect have failed. The magnetic polaron model[31] (see reviews in Refs. [32, 33]) for the explanation of the puzzle is not relevant to the wide-gap (Ga,Mn)N. The chemical potential in this system is pinned around the $E(d^4/d^5)$ level in the middle of the gap and the classical Zener double exchange mechanism is realized. A plausible explanation[34] is that even though the nominal average impurity concentration is below percolation, the sample is not homogeneous and exhibits some microstructure whereby the entire impurity concentration is located in *parts of the sample*, exceeding percolation threshold in that domain.

4. WIDE GAP DILUTE MAGNETIC OXIDES

During the last decade, the room temperature ferromagnetism was announced in many transition metal doped oxides. Among these materials are (Zn, Mn)O and (Zn, Co)O,[35–37] (Sn, Cr)O_2,[38] (Ti, Co)O_2, (Ti, Cr)O_2,[36] (Ce, Co)O_2[39–43] and other. There is also a vast literature on the possibility of FM ordering in *undoped* non-stoichiometric oxides without transition metal impurities. The formation of these non-equilibrium thin films has been modeled numerically (see, e.g., Ref. [44]). It was shown that these systems are unstable against phase separation. As a result, self-organized "seaweed-like" nanostructures form magnetic clusters responsible for superparamagnetism with hysteretic features. We do not consider here undoped oxides and refer the reader to the critical discussion in Ref. [45].

The same pitfall, however, emerges for TM doped oxides. These materials are unstable against various heterogeneities, namely, precipitation of other crystallographic phases, phase separation in host material, spinodal decomposition of dopant, diffusion and implantation profiles, etc. Even in carefully checked conditions, where the precipitation of parasitic phases and aggregation of superparamagnetic clusters with excessive concentration of TM ions are prevented or at least controlled, one cannot get rid of this generic feature of oxide DMD materials.

We restrict ourselves to the discussion of the systems where a consensus about intrinsic nature of ferromagnetism exists.[33] For example it was claimed that (Ti, Fe)O_2 thin films prepared by pulsed-laser deposition "are definitely not superparamagnetic."[46] Having this in mind we have chosen two families of DMD, namely ZnO and TiO_2 doped with iron group ions (V, Cr, Mn, Fe, Co). As mentioned above the key feature of the available DMD materials is a strong sensitivity of their magnetic properties to the quality of samples and preparation techniques. It was noticed, in particular in Ref. [47], that in the most perfect (Ti, Cr)O_2 samples the magnetic ordering effect is less distinct than in poor quality films. Film thickness, degree of inhomogeneity in spatial distribution of magnetic dopants, thermal treatment regime, codoping with other impurities—all these factors influence the magnetic properties of DMD. The empirical trends in this multifactor influence are not completely revealed yet. Here we will not describe all these trends. Instead, we intend to project these empirical findings on the microscopic picture of dielectric materials without free carriers but with strong imperfections, which on the one hand may mediate the long-range magnetic ordering of transition metal ions and on the other hand trigger phase separation and formation of magnetic precipitates. This is a direct indication that uncontrollable defects may play principal part in the formation of ferromagnetic order.

A number of theoretical models have been put forward, which assume that the exchange in these systems can be mediated by various types of defect such as, magnetic polarons[32] and/or excitons[48] bound to the magnetic impurities. Magnetic polaron mechanism assumes an antiferromagnetic interaction between magnetic impurities and a shallow state due to some defect, say vacancy. Therefore two magnetic impurities orient antiparallel to the polaron and, hence, parallel, i.e., ferromagnetically ordered, with respect to each other. It means that magnetic properties of the electrons bound to the mediating defects are crucial for this mechanism. However as shown by calculations in $Zn_{1-x}Co_xO$[49] singly charged vacancies prefer to dissociate into neutral and doubly charged vacancies and become magnetically neutral.

The indirect double exchange mechanism proposed in Ref. [19] for $Ti_{1-x}Co_xO_2$ takes this dissociation into account explicitly. Co ions substituting Ti^{4+} ions with empty $3d$ shell accept two electrons from nearby O vacancies (V_O). The corresponding addition energy transforms into a CFR level $\varepsilon_t(d^6/d^7)$ below the vacancy related band ε_{vac}, which is only partially filled due to the electron transfer from O vacancies to Co ions. As a result the complexes ([Co–V_O]) are formed, and double exchange mediated by the extended electronic states of oxygen vacancies favors formation of a long-range magnetic order with high T_C at small enough concentration of magnetic ions (see also Ref. [50]). The "charge transfer ferromagnetism" model proposed for (Ti, Fe)O_2 in Ref. [46] in fact follows along the same lines.

Experimental findings for (Ce, Co)$O_{2-\delta}^{39}$ also support the double exchange mechanism proposed in Ref. [19]. Like in the case of DMS the Curie temperature is sensitive to the carrier concentration: the dependence $T_C(x)$ is described by a dome-like function[19] with a maximum for a half-filled band ε_{vac}. In the films codoped with other shallow donors,[3, 8] second polaronic band of donor origin appears.[51] This band retains its localized nature similarly to the heavily doped p-type (Ga,Mn)As discussed above, and the second maximum of $T_C(x)$ emerges at high donor concentration.[33, 50]

In principle, other defects are capable of serving as such mediators. Magnetic properties (if any) of these mediating states are irrelevant. Magnetically neutral mediators are even preferable. This mechanism is in fact a modification of the double exchange mechanism discussed above in connection with the intermediate and wide gap DMS.[14]

5. CONCLUSIONS

It is now becoming clear from recent experimental findings together with the fundamental quantum-mechanical properties of TM ions in III–V semiconductor hosts and oxides unambiguously point out to the localized nature of carriers mediating indirect exchange in DMS and DMD. Localized hole states involved in the double exchange between Mn^{3+} ions in p type (Ga, Mn)As and (Ga, Mn)P are formed mainly by impurity related dangling bond hybrids (DBH). Mn ions in a wide gap (Ga, Mn)N or (Ga, Co)N form crystal field resonances (CFR) as a mid gap states. If the defect related band is partially occupied, these ions are in the mixed valence state, and the indirect magnetic interaction is similar to the classical Zener double exchange in TM oxides. Dilute magnetic oxides are usually fabricated in the form of annealed thin films with quenched distribution of defects (as a rule, oxygen vacancies). These vacancies bound in complex defects with TM ions create defect bands below the bottom of conduction band and mediate the indirect exchange between magnetic ions. Figures 1, 2 illustrate all three types of electronic spectra in DMS and DMD.

In all three cases, the presence of unfilled states in the defect bands is crucially important for realization of long-range magnetic interaction. Firstly, the characteristic radii of carriers involved in the indirect exchange are large compared with lattice spacing in the host matrix, so that the long-range magnetic order arises at unusually small concentration of magnetic impurities. Secondly, the Curie temperature depends on the concentration of additional dopants, and the optimum doping level corresponding to the maximal T_C exists for all three types of dilute magnetic materials.

Since the long-range magnetic order arises only at concentrations well above the thermodynamic solubility limit for TM impurities in specially prepared thin films, the possibility of magnetic nanocluster formation in these films should be taken into account. Both the homogeneous ferromagnetic materias and inhomogeneous superparamagnetic thin films with columnar nanoclusters piercing through samples should be treated as potential elements of nanodevices combining semiconductor transport properties with strong magnetic response characteristic for transition metal ions.

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