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 "rst 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.

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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 uni"ed 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 speci"c 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

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 d-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 Mn^+ impurity ions substituting for Ga^{3+} atoms in GaAs.[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[7…10] model 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 Cd^{2+} having the same charge as the magnetic impurity ion 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,[12] 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 $n_{Mn} > 0.1$ (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

Zener-like double exchange via the impurity band[34] can
be seen in Figure 2 of that paper.

(v) Two recent experimental findings unambiguously sup-
port the statement that the d-p-hybridization is responsi-
ble not only for the Zener exchange but also for the shape
of the DOS near the top of the valence band in metal-
lic 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

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 4Ti ions with empty $3d$ shell accept two electrons from nearby O vacancies (V_O). The corresponding addition energy transforms into a CFR level $_t d^6/d^7$ below the vacancy related band $_{vac}$, 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 $(Ce, Co)O_2$[23] also support the double exchange mechanism proposed in Ref. [19].

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.

References and Notes

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