

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

Victor Fleurov¹, Konstantin Kikoin¹ and Alex Zunger²

¹Raymond and Beverly Sackler Faculty of Exact Sciences, School of Physics and Astronomy,
 Tel-Aviv University, Tel-Aviv 69978, Israel

²University of Colorado, Boulder, Colorado 80309, USA

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)O₂, (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. Mechanisms of indirect magnetic interaction are also universal: neighboring magnetic ions virtually exchange their 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 d 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 d signature that carry this effect.

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

Delivered by Publishing Technology to: Victor Fleurov
IP: 132.66.129.76 On: Thu, 23 Jul 2015 08:15:29
Copyright: American Scientific Publishers

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

(v) Two recent experimental findings unambiguously support the statement that the 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 vs 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 p hybridized hole states above

decomposition of dopant, diffusion and implantation pro-the extended electronic states of oxygen vacancies favor "les, etc. Even in carefully checked conditions, where theformation of a long-range magnetic order with high precipitation of parasitic phases and aggregation of superat small enough concentration of magnetic ions (see also paramagnetic clusters with excessive concentration of TMRef. [50]). The •charge transfer ferromagnetismZ model ions are prevented or at least controlled, one cannot get proposed for (Ti, Fe)Oin Ref. [46] in fact follows along rid of this generic feature of oxide DMD materials. the same lines.

We restrict ourselves to the discussion of the systems Experimental "ndings for (Ce, Co)O also support where a consensus about intrinsic nature of ferromagnetism the double exchange mechanism proposed in Ref. [19] exists.³³ For example it was claimed that (Ti, Fe)Othin "lms prepared by pulsed-laser deposition •are de"nitely not superparamagnetic.⁴² Having this in mind we have chosen two families of DMD, namely ZnO and TiO₂ 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, Co)O samples the magnetic ordering effect is less distinct than in poor quality "lms. Film thickness, degree of inhomogeneity in spatial distribution of magnetic dopants, thermal treatment regime, codoping with other impurities, all these factors in"uence the magnetic properties of DMD. The empirical trends in this multifactor in"uence are not completely revealed yet. Here we will not describe all these trends. Instead, we intend to project these empirical "ndings 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 polarons³² and/or excitons⁴⁸ 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- δ} Co _{δ} O⁴⁹ 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- δ} Co _{δ} O₂ 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 ϵ_d^6/d^7 below the vacancy related band ϵ_{vac} , which is only partially "lled due to the electron transfer from O vacancies to Co ions. As a result the complexes ([Co...V]) are formed, and double exchange mediated by

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 materials and inhomogeneous superparamagnetic thin films with columnar nanoclusters piercing through samples should be treated as potential elements of nano-devices combining semiconductor transport properties with strong magnetic response characteristic for transition metal ions.

References and Notes

1. A. Zunger, *Solid State Physics*, edited by F. Seitz, H. Ehrenreich, and D. Turnbull, Acad. Press, New York, 1966, Vol. 39, p. 276.
2. K. A. Kikoin and V. N. Fleurov, *Transition Metal Impurities in Semiconductors*, World Sci., Singapore, 1991.