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Some Inadequacies in Theories of Dilute Magnetic Semiconductors

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Abstract

Two theoretical approaches to dilute magnetic semiconductors (DMS) are visited in light of experimental results and interactions indicating their insufficiency. *Model Hamiltonian theory* of DMS appears unrealistic in guessing the leading magnetic interaction, while *first principle calculations* appear to lose information in using exact pseudo potentials on computation package without worrying of magnetic interaction between impurity and host crystal.

Introduction

Transition-metal (TM)-doped diluted magnetic semiconductors (DMS) have recently attracted both experimentalists and theorists to their potential use in new nanostructured devices and new technologies. The spin and charge based electronics, known asspintronics, is an emerging potential branch of science and technology that provides, for instance, a way to create fully spin-polarized currents in novel devices. It is an endeavour of electrical control of spin based (magnetic) effects. Excluding magnetite like magnetic semi-conductors in which all of the ions have non-zero spins, the most recent focus has been on developing magnetism in nonmagnetic semiconductor hostsby doping a small amount of magnetic transition-metal ions or some defects. Although the existence of room temperature ferromagnetism (FM) in transition metal (TM)-doped oxides has been reported, the origin of the FM is still controversial. Magnetism arises as the electrons in a material collectively align their spins. In a ferromagnetic sample, there is an imbalance between the occupancy of spin-up and spin-down states; such a collective spin alignment leads to a macroscopic spontaneous magnetization that persists up to a Curie temperature T_C.There are indications that the FM in crystalline samples comes from different sources, metallic clusters, secondary phases, or is due to a free carrier-mediated mechanism in the bulk. The presence of oxygen vacancies in oxide semiconductors is systematically related to the observed ferromagnetic state. Magnetic nanoparticles exhibit a rich variety of

interesting phenomena such as superparamagnetism, spin-glass and coercivity enhancement, which are usually related to the finite size and surface effects [1].

The situation in thefieldof theory of synthesis of nanostructured particles, explanations and predictions of their useful properties is almostdangling, thoughtheoretical methods have greatly influenced experiment in search of the semiconductor electronics based on magnetism and, thus, the development of spintronics. One, as such, must be realizing the limitations and strengths of theoretical approaches which exhibit diffusion like steps in progress, instead of military precision.

Theories

The theoretical works on the ferromagnetism in the DMS systems can be separated into two groups. The first group uses a *model Hamiltonian* for the problem, with the Hamiltonian containing experimentally determined parameters. Review of this approach may be seen in ref [2- 4].Assumptions concerning the energy position and the 3d impurity states, and various exchange interactions – potential, kinetic, super, double, RKKY, Bloembergen-Rowland and others – are used to describe the properties of the system. Most of the model-Hamiltonian studies assume the presence of holes as important for ferromagnetism of DMS.

The second group of theoretical studies is based on the parameter-free*first principle calculations*employing the density functional theory (DFT)[5-11]. In these calculations, every electron state is involved in effective exchange interaction with all other electron states [18], intermixing and affecting different types of exchange interactions. It is, however, very useful to relate the DFT results to the results of the model-Hamiltonian treatments in an endeavour to find out the leading exchange mechanisms responsible for the establishing of the long range spin alignment.

Experiments

The *first experiments* on dilute magnetic semiconductors focused on host semiconductors with *narrow band gaps*, such as GaAs, InAs and other doped III-V semiconductors. For instance, when doped with manganese, divalent manganesesubstitutes for trivalent host, thus releasing *holes*.These holes are said to collectively align the Mn^{2+}spins resulting in ferromagnetism. But to observe it, the sample must beat a temperature below its transition temperature, T_C. Ferromagnetism in GaMnAs cannot, however, be observed at room temperature; its transition temperature was low and sample had to be cooled for observation of the effect. Low temperature characterizations were positive.To enhance magnetization per unit magnetizing field, increment in manganese proportion indefinitely could not go beyond a limit, because by adding more Mn impurity atoms, some of these occupy interstitial sites or form some clustered phases, thereby inhibiting a global ferromagnetic order. Thus, a low transition temperature and small ferromagnetism in GaMnAs and other doped III-V semiconductors, could not prove technologically useful. For this reason, the second experimental phase started.

The *second phase* of experiments considered *wide band gap* hosts.The possibilityof high transition temperature and susceptibility were expected in oxides; doping common insulators like CaO, ZnO, In_2O_3, GaN, and HfO_2stared. These materials have the additional feature of being optically transparent medium, with optoelectronic potential. Theory, during these developments, in many cases preceded experiments and influenced the type of systems that were studied. Research in the III-V hosts became almost neglected.

Theory pointed towards oxides, carbides or nitrides, the wide band gap binary compounds, as systems that will show high-T_C ferromagnetism. Wide band gap metal oxides (ZnO, HfO_2), nitrides (GaN), and carbides based on dilute transition metal impurities such as Mn, however, exhibited low transition temperature, as the Mn acceptor level becomes more localized and contributing to lower and lower T_C as one moves up the group V in periodic table of elements from arsenic to nitrogen.

Another important feature appeared during experiments. Magnetism was observed even without magnetic impurity.Simple structural defects such as *cation vacancies* [12-15] or *carbon* or *nitrogen impurities* [16-18] also exhibitedferromagnetism in wide band gap insulators.

Interactions

Many theories appeared in the development pushing transition temperature upward, predicting systems and, in many cases, diverting the experimentalists. It appears in order to look into the framework of theories and assumptions therein and compare them with the groundreality.

We first see systems exhibiting magnetism as per experiments and underlying *interactions*. Ultimately theory has to incorporate these and proceed.

Ultra dilute samples: In the early phase of experimental investigations during 1980s [19, 20], the experimental methods produced samples containing 10^{21}–10^{23} impurities/$m^3$with large impurity-impurity separations, and hence almost no impurity-impurity interactions. These are called ultra-dilute samples. In such cases, a number of intriguing physical phenomena such as *self-regulatingresponse* [21, 22], the *vacuum pinning rule* and *exchange-correlation negative U* [23] were revealed due to coexisting localized 3*d* impurity states, but such systems revealed no ferromagnetism. The reason was understood: ferromagnetic ordering requires the individual magnetic impurity ions to be close enough to one another so as to interact and produce global ordering of spins and this implieda larger concentration.

Dilute samples: Increasing concentration of impurities requires thermodynamic approval and is subject to mechanical strength of sample obtained after doping. The 3*d*-impurities in semiconductors have such a low value of thermodynamically allowed solubility limit that no long range spin alignment is expected. However, using non-equilibrium growth techniques such as very low-temperature molecular beam epitaxy, and others, impurity concentration of a few orders of magnitude as10^{26} dopants/m^3, or higher, has become possible. Such *dilute samples* can be prepared.

Dilute samples of magnetic ions in semiconductors, such as GaAs: Mn [24, 25], lead to ferromagnetism with relatively high Curie temperatures of around 100 K. The

doping of a 3d impurity is combination of two processes, first the removal of a host Ga atom, leaving behind *cation vacancy state* (dangling bondsof t(p) symmetry) and second, the placement of a 3*dimpurity atom* in its place, superposing the *impurity orbital* of the 3*d* atom having t(d) symmetry as well as nonbonding e(d) symmetry. The interaction between these states leads to a bonding state and an anti-bonding state; the partial occupancy, which is responsible for unbalanced spins, andhence ferromagnetism, lies in the *higher* of these states. The basic driving force of this form of ferromagnetism of 3*d* impurities in III-V semiconductors is the energy stabilization ensuing from the interaction between partially occupied hybrid orbitals located on different impurity sites [26].

In wide band gap semiconductors, a proper combination of defect-impurity- host crystal leads to a hole-carrying (partially occupied) level, centered about this defect or impurity site. A ferromagnetic spin arrangement results due to energy stabilizationby their interactions.

Theoretical insufficiency

Theories of model Hamiltonian and first principle calculations guided the search for the particular defect-impurity- host combinations in many instances [27-30], but were themselves based on simplified interactions and assumptions.

In *model Hamiltonian* approach, certain interaction between ions in semiconductor is postulated, and thereby other interactions that may be important, are excluded. RKKY model assumes that spin-polarized 3d impurity ions interact in the same way as nuclei interact through mediation of conduction electrons in metals. It also assumes that host crystal is almost unperturbed by presence of impurity ions.

The *first principle calculation* considers fundamental electronic structure of host-impurity system. It assumes that magnetic effects emerge as a result of solution of many- electron Hamiltonian incorporating electron-ion and electron- electron interaction. It just ignores magnetic interactions at the very outset. DFT approximations do not guess any impurity effect on particular host crystal. It uses exact pseudo potentials on preset computer packages without questioning exactness of these pseudo potentials. It several times creates high transition temperatures and ferromagnetism due to false occupancy that are not observed.

Conclusion

Electronic structure calculations and model Hamiltonian being powerful tools, theorist must look for the types of interactions that are indeed realistic, at the outset, to construct safe and simpler Hamiltonians and results may be used as guide for somenew theoretical models.

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