Chapter 2
Successive Spin-Correlated Local Processes Underlying the Magnetism in Diluted Magnetic Semiconductors and Related Magnetic Materials

Antonis N. Andriotis
Institute of Electronic Structure and Laser, Greece

Madhu Menon
University of Kentucky, USA

ABSTRACT

Recent works have suggested that the defect induced magnetism in Diluted Magnetic Semiconductors (DMSs), Transition Metal Oxides (TMOs) and related materials is facilitated and enhanced by codoping and the synergistic action between the codopants. In the present work we demonstrate that the proposed defect synergy is the result of the interplay among correlated spin-polarization processes which take place in a successive way in neighborhoods centered at the codopants and include their first nearest neighbors. These processes result in a reduction in the superexchange coupling which in turn causes an enhancement in the ferromagnetic coupling (FMC) among the magnetic dopants. The proposed FMC is demonstrated using ab initio calculations of the electronic properties of codoped ZnO, GaN and TiO2.

1. INTRODUCTION

The origin of magnetism in the technologically important class of the diluted magnetic semiconductors (DMSs) and the transition metal oxides (TMOs) is an unresolved issue and has been the subject of an ongoing debate. While the experimental information in many cases provides contradictory results, the theoretical approaches fail to give a conclusive answer for systems exhibiting magnetic features at dopant concentrations below the percolation threshold.

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Adding to the problem is the appearance of magnetism in carbon-based materials which lack the presence of d-electrons and/or of dopants of inherent magnetic moments. In these materials, the development of magnetism had to be associated with their inherent properties resulting from structural modifications and imperfections. However, the presence of a single type of structural conformations that could be considered as potential candidates which can provide magnetic moments (as, for example, the presence of carbon vacancies), proved not to be sufficient to explain the appearance of magnetism.

The recent works on the magnetism of Rh-C60 and other carbon-based (Cbased) materials (Andriotis, Menon, Sheetz, & Chernozatonskii, 2003) led to the proposal that the origin of this magnetism is the result of the simultaneous presence of two types of defects. That is, it was proposed that the magnetism in the C-based materials is the result of the synergistic action of defect-induced electronic processes, mostly of local character, which can provide magnetic moments and develop their ferromagnetic coupling (FMC). In particular, it was shown that this synergy is realizable via codoping (Andriotis, Lisenkov, & Menon, 2011; Andriotis & Menon, 2011, 2012) ie., in the simultaneous presence of two kinds of defects which can act in a complimentary way. Specifically, while the defects of one kind are able to provide mainly the magnetic moments, defects of the other kind contribute mainly to the development of the FMC among the magnetic moments. Thus, according to this proposal, the magnetism of the C-based materials is a defect-induced defect-mediated process that is realizable via codoping. (In the following, the term defect will be used to denote any structural and/or topological and/or impurity-atom defects).

Based on our proposed defect-induced defect-mediated approach to the magnetism of the C-based materials, we investigated whether this model approach is applicable in the case of DMSs and TMOs. This idea was further supported by contemporary experimental evidence which demonstrated that the magnetism in DMSs could be enhanced by codoping. In particular, enhanced magnetic features were observed in ZnO codoped with (Fe,Cu)(Han et al., 2002; Park & Min, 2003), (Fe,Co)(Park & Min, 2003), (Co,Cu)(Naeem, Hasanain, Afgan, & Rumaiz, 2008; H. T. Lin et al., 2004), (Co,Li)(Jayakumar, Gopalakrishnan, & Kulshreshtha, 2006; Y. H. Lin, Ying, Li, Wang, & Nan, 2007), (Co,N)(Assadi, Zhang, & Li, 2009), (Co,H)(Shin et al., 2012), (Co,Al)(Chattopadhyay & Natha, 2010), (Co, O-vacancies)(Pemmaraju, Archer, Sanchez-Portal, & Sanvito, 2007), (Mn,Sn)(Norton et al., 2003), (Mn,Co)(Behan et al., 2008; Duan, Rao, Wang, Yu, & Wang, 2008), (Mn,N)(Wang, Sun, Jena, & Kawazoe, 2004), (Mn, Ovacancies)(Mi, Bai, Liu, & Sun, 2007) and (Mn,C)(Yadav, Sanyal, & Mookerjee, 2009). Analogous findings were reported for other TMOs as well as for III-V and II-VI materials as, for example, in GaN codoped with (Mn,Co) and (Cr,Mn)(Santos, Marques, Teles, & Ferreira, 2010); in Cr:TiO2 and Mn:GaAs(Ye & Freeman, 2006); in TiO2(Zhu et al., 2009; Gai, Li, Li, Xia, & Wei, 2009) etc.

Despite the numerous reports on the advantages of codoping in improving the magnetic features of the DMSs and those of the TMOs, our understanding about the origin of their magnetism is far from satisfactory. The majority of the proposed explanations so far is based on the proposed traditional exchange interaction processes including; the double exchange, the superexchange, the s−d exchange or the p − d hopping exchange interaction (Ye & Freeman, 2006), the non-compensated n − p doping(Zhu et al., 2009), the passivation of codopants (Mo,C)(Gai et al., 2009), etc. These model interactions map leading configuration interaction terms onto atomic spin-orbital description terms (see, for example, Ref. (Sato et al., 2010) and references therein). By their nature. these descriptions are focused on processes related to the interactions among the magnetic impurity cations; ie., the central role is attributed to their direct and/or mediated cationic interaction.

In this Chapter, we present our work to uncover the key electronic processes which underlie the development of magnetic features in DMSs and TMOs.