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The synergistic character of the defect-induced magnetism in diluted magnetic semiconductors and related magnetic materials

Antonis N Andriotis\textsuperscript{1} and Madhu Menon\textsuperscript{2,3}

\textsuperscript{1} Institute of Electronic Structure and Laser, FORTH, PO Box 1527, 71110 Heraklio, Crete, Greece
\textsuperscript{2} Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506-0055, USA
\textsuperscript{3} Center for Computational Sciences, University of Kentucky, Lexington, KY 40506-0045, USA

E-mail: andriot@iesl.forth.gr and madhu@ccs.uky.edu

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Abstract

In this work, we introduce a new perspective in explaining the origin of magnetism in dilute magnetic semiconductors, carbon-based materials and other related materials. According to our proposal, the magnetism in these materials is the result of the synergistic action of defect-induced electronic processes mostly of local character which can provide magnetic moments and develop a ferromagnetic coupling among them. This synergy is realizable via appropriate codoping which appears as a general and generic approach. In the present report, we use \textit{ab initio} results to demonstrate that in a diverse sample of systems including codoped ZnO, GaN, TiO\textsubscript{2} and carbon-based materials, the ferromagnetic coupling that is developed among the doped (or defect-induced) magnetic moments results from the interaction of spin-polarized neighborhoods centered at the defect sites. Our results also give evidence that bipartite codopant configurations can further enhance the ferromagnetic features of these systems significantly.

(Some figures may appear in colour only in the online journal)

Wide classes of diverse non-magnetic materials including carbon-based materials, wide band gap semiconductors, transition metal (TM) oxides, other III–V and II–VI materials and others, have been found to exhibit magnetism in the presence of defects. (In the following the term \textit{defect} will be used to denote any structural and/or topological and/or impurity-atom defects.) For the development of magnetism in these materials, the first necessary step is the presence of unpaired electrons which provide the magnetic moments (MMs) and, secondly, the coupling of these MMs magnetically. While the origin of the MMs (either of intrinsic or extrinsic type) is attributed to the presence of the defects, however, the origin of the ferromagnetic coupling (FMC) among the defects is still far from being well understood.

The underlying physics of the FMC in the above-mentioned materials has been the subject of a plethora of reports, especially in the case of the diluted magnetic semiconductors (DMSs). The majority of the proposed explanations is focused on processes related to the magnetic impurity cations; that is, the central role is attributed to their mediated cationic interaction, which is traditionally explained in terms of the double exchange, or the superexchange, or the p–d exchange interaction etc and mainly within the atomic orbital description (see for example [1] and references therein).

Our work, on the other hand, demonstrates that the FMC is mainly associated with electronic processes that are localized within neighborhoods centered on the codopant (defect) sites. Each of these neighborhoods includes the...
codopant and its first nearest neighboring (1nn) anions, with the latter playing a crucial role in establishing the FMC. As will be demonstrated in the present work, the development of magnetism in these materials can be attributed to the overlap of spin-polarized molecular orbitals (MOs) with contributions from the anions surrounding the codopants. Although these anion polarizations could lead to a local delocalization (of finite range) of the polarized anionic spin density, a carrier mediated interaction picture does not seem to be a significant contributor to FMC.

Based on *ab initio* calculations that were carried out within the MO picture, we were able to identify several common features accompanying the development of the magnetic features in all these materials. Among them, electronic processes like charge transfers, the formation of localized electronic configurations around the defects and remote MO delocalization were found to underlie the appearance of magnetism. Our results have shown that the defect-induced magnetism is significantly enhanced if more than one type of defect is simultaneously present in any of these materials [2–8]. In the case of two codopants, for example, the defect-induced magnetism appears to be the result of the synergistic action of the codopants, one of which is responsible for the development of MMs and the other for their FMC. This view is entirely different from that according to which the codoping is considered as a possible way to tailor the position and the occupancy of the Fermi energy, \((E_F)\), of the DMSs [9–14].

The synergistic action of two codopants (defects) takes place as follows: the defects consisting of the one codopant type provide the MMs which can either be of extrinsic type (i.e. provided by magnetic impurities) or of intrinsic type (i.e. resulting from hybridization of the dopant and host orbitals). The defects of the other codopant type contribute to the FMC among the MMs. This is attributed to the coupling between spin-polarized MOs consisting of MO-parts confined in the neighborhoods centered around the sites at which the MMs are located. More interestingly, bipartite configurations of alternate codopant pathways (of the form \(\ldots ABABABA\ldots\)) were found to facilitate the delocalization of the spin-polarized MOs and enhance the appearance of the induced magnetism.

In the present work, we present results for representative systems of wide band semiconductors and TM-oxides, all codoped with TM cations for demonstrating our proposed synergistic action picture of the defect-induced defect-mediated explanation for the origin of magnetism in these materials. Furthermore, we also compare these results with our previous results on carbon-based materials containing structural defects for demonstrating the generic feature and the universality of the proposed mechanism. All our results have been obtained using the density functional theory (DFT) in the generalized gradient approximation (GGA) and the Perdew–Burke–Ernzerhof (PBE) functional augmented by including Hubbard–U corrections (GGA + \(U\)) based on Dudarev's approach [15] as implemented in the Vienna *ab initio* Simulation Package (VASP) [16, 17]. We have used \(U = U_{d,\text{Ti}} = 9.26\) eV for rutile TiO\(_2\) for the Ti(3d) which reproduced the experimental gap (3.0 eV) and \(U_{d,\text{Cr}/\text{Co}} = 5.5\) eV for Cr and Co codopants. For ZnO and GaN, we used \(U_{d,\text{Zn}} = 10.5\) eV; \(U_{d,\text{Ga}} = 6.5\) eV, \(U_{p,\text{O}} = 7.0\) eV and \(U_{p,\text{N}} = 4.25\) eV, while \(U_{d,\text{Mn}} = 5\) eV was used for Mn. Large unit cells were employed for our host materials. Both ZnO and GaN are taken to be in the wurtzite structure using a supercell containing 108 and 192 atoms, respectively. TiO\(_2\) is taken to be in rutile structure using a supercell of 192 atoms. Co and Cu atoms were used as codopants in ZnO, while for GaN and TiO\(_2\), we used the codopant pairs (Co, Cu) and (Mn, Cu). All codopants substituted cationic sites. Up to five dopant atoms were used for ZnO and up to seven for GaN and TiO\(_2\). A \(2 \times 2 \times 2\) \(\Gamma\)-centered pack of \(k\)-vectors was used and all structures were fully optimized (including cell optimization) without any symmetry constraints. Magnetic moments of all the atoms in the unit cells were obtained by integrating the difference of (spin-up minus spin-down) electron density of states within the atomic volumes as outlined in the VASP code. The values of the magnetic moments thus obtained were then mapped onto a collinear (up or down) representation as shown by the arrows in figures 1–3.

The wide band gap materials considered in this work are ZnO, GaN and TiO\(_2\), all codoped with TM cations Co, Cu and Mn. In figures 1 and 2 (showing a plot of magnetization values) we present a close up view of the neighborhood of the codopants of the codoped wide band gap systems: Zn(Co, Cu)O, Ga(Co, Cu)N and Ga(Mn, Cu)N. In these systems, the codopants (Co, Cu) or (Mn, Cu) substitute cationic lattice sites of the host materials. Our emphasis is focused on the anionic induced spin polarization. As can be observed in figure 1, there is an induced spin polarization on the anions which is parallel to that of the inducing cations except in the case of Mn in GaN. In the case of Zn(Co, Cu)O, all induced magnetic moments are parallel to those of the magnetic impurities (Co). As a result, polarized spin density can be delocalized locally around the codopants. Similar local delocalization is found in the case of Ga(Mn, Cu)N although in this case the Cu and the N anions surrounding the Mn cations are spin-polarized anti-parallelly to Mn cations. On the other hand, in the case of Ga(Co, Cu)N we do not observe the formation of a local delocalization of polarized spin density. Instead, we see that N anions which are bonded to both Co and Cu retain the same polarization experience by the Cu atoms. As a result, the Co cations are found with 1nn anions polarized either parallelly (to Co) or anti-parallelly. However, there appears to be a common characteristic underlying all these pictures. That is, the ions of the *mediating segments* (O–Cu–O and N–Cu–N) of all the codopant configurations shown in figure 1 exhibit spin polarization along the same direction, giving rise to a coupling of neighboring codopant neighborhoods.

These observations, while not ruling out the possibility of carrier mediated coupling (e.g. double exchange, superexchange etc) among the magnetic cations, demonstrate that the FMC accommodates additional significant contributions derived from localized spin polarizations of the anions. In other words, the spin polarization of an anion appears to be the outcome of the fields produced by its neighboring cationic ligands. In turn, the polarized anion contributes
to the formation of spin-polarized MOs with simultaneous contributions from similarly spin-polarized neighborhoods which are not necessarily in neighboring positions to each other. It is the coupling among these MOs which underlies the development of the FMC [8]. In this view, the non-magnetic codopants play a multi-modal role; they become hybridized (with their surrounding ions) as well as spin polarized themselves and, in turn, spin polarize their first nn anions. This facilitates the development of delocalized spin-polarized MOs over a more extended range. In this picture it is not necessary to have all the 1nn anions to a codopant to be spin polarized in the same direction (see figure 1).

Figure 3. Supercell consisting of 192 atoms of Ti(3Co, 2Cr)O$_2$ used in our calculations showing spin-polarized neighborhoods. The Co (Cr) atoms are shown in blue (violet). The O anions are shown in red.

Results for the codoped TM-oxide Ti(3Co, 2Cr)O$_2$ are presented in figure 3 in which Co and Cr codopants substitute Ti sites and form a bipartite pathway and surrounded by spin-polarized neighborhoods. It is apparent that the codopants induce impurity levels in the gap which lead to a large reduction of the energy gap, namely from 3.13 to 0.57 eV. As seen in the DOS (figure 4) the impurity levels show a strong hybridization between the codopant d-states and the anion p-states. The ground state is FM in the coupling of the Co$_i$ atoms which exhibit magnetic moments $\mu_{\text{Co}_i}$, $i = 1, 2, 3$ as follows: $\mu_{\text{Co}_1} = 3.176$, $\mu_{\text{Co}_2} = 3.055$, $\mu_{\text{Co}_3} = 1.816$ in Bohr magnetons ($\mu_B$). Correspondingly, the Cr$_j$, $j = 1, 2$ atoms exhibit magnetic moments $\mu_{\text{Cr}_1} = -0.004$ and $\mu_{\text{Cr}_2} = 2.220 \mu_B$.

All the anions which are nn to the codopants experience an induced spin polarization which does not exhibit a specific trend (spin-up or spin-down). Its direction depends on the polarization of the nearby codopants. We thus recover the picture that we found in the case of Ga(4Co, 3Cu)N shown in figure 2.

Strong evidence has been found for a strong dependence of the induced polarization on the impurity configuration and, in particular, on whether the Co–Cr–Co segments are on the same lattice plane, namely, the (210) and/or the (210) planes,
or not (see figure 5 top panel). In particular, if the Co–Cr–Co segment is not on the same plane, then the Co’s are found to have equal magnetic moments and are ferromagnetically coupled through the Cr cation with the latter exhibiting no spin polarization. In this case the FMC appears to take place via the spin-polarized anions which are common neighbors to both Co and Cr with all anions being parallelly polarized to Co’s. This is reminiscent of a similar result found in the case of the Co–Cu–Co segment in ZnO in which the Co–Co interaction becomes ferromagnetic if the mediating Cu atom is not polarized [4]. On the other hand, if the segment Co–Cr–Co lies on the same plane, the Co’s are still ferromagnetically coupled but do not exhibit equal magnetic moments, while the mediating Cr cation attains strong spin polarization parallel to that of the Co’s. In this case however, the spin polarization of the anions can be parallel or anti-parallel to that of the Co’s.

As shown in figure 5, the directionality of the participating bonding orbitals strongly affects the exhibited spin polarization of the anions leading to its strong dependence on the geometry of the configuration of the codopants. In particular, if the anion-mediated bonding involves an off-plane orbital \((d_{x^2-y^2})\) of the one codopant and an in-plane orbital \((d_{x^2-y^2})\) of the other codopant, then the spin polarization of the anion is parallel to the codopants. On the other hand, when the bonding involves in-plane orbitals from both codopants neighboring the Cr, the spin polarization of the mediating anion is anti-parallel to one of the codopants. In the case in which all the codopants bond to each other using one off-plane and one in-plane d-orbital in a bipartite configuration, (of the alternate form \(\text{Co}_{\alpha-}\text{Cr}_{\beta-}\text{Co}_{\gamma-}\text{Cr}_{\delta-}\text{Co}_{\alpha'}\)), as shown schematically in the right panel of figure 5, the system shows enhanced ferromagnetism with values \(\mu_\alpha = 3.030\), \(\mu_\beta = 3.200\) and \(\mu_\gamma = 3.050\) \(\mu_B\) for the Co atoms and \(\mu_\lambda = 2.050\) and \(\mu_\mu = 2.220\) \(\mu_B\) for Cr atoms. In this case anions which are polarized anti-parallelly to the magnetic cations exhibit very small magnetic moments compared to those of the parallelly polarized anions.

These results indicate that the FMC among the magnetic cations in Ti(3Co, 2Cr)O₂ is mediated by the spin-polarized anions whose spin polarization appears to be affected by electronic processes which take place within the prisms which surround the magnetic cations. It is these processes which specify the (direction of the) spin polarization of the anions which, in turn, mediate the FMC. The interaction between the prisms surrounding the ferromagnetically coupled codopants appears to be facilitated by anions (polarized either parallelly or anti-parallelly to the magnetic cations) which contribute to the formation of delocalized spin-polarized MOs over the defect neighborhoods.

The key feature for the appearance of magnetism in all these materials we studied appears to be the synergistic action of more than one electronic processes. These may differ from system to system as they depend on the possible (re)hybridizations, charge transfers, Jahn–Teller effects, induced polarizations, crystal-field and exchange splittings etc. However, there are two basic features which are common to all. The first is the cooperative nature of the processes that are induced by the different defects. The second is the potential of the bipartite codopant configurations to enhance the defect-induced magnetism. This is quite pronounced in the case of Ti(3Co, 2Cr)O₂ as illustrated in figure 5.

It is worth noting that the bipartite codopant structure found in the systems we studied (Ti(3Co, 2Cr)O₂, Ga(Co, Cu)N, Zn(Co, Cu)O and Ga(Mn, Cu)N) is analogous to that proposed by Roth [18] and used later by Kawamoto to explain the ferromagnetism in the TDAE-C₆₀ and layered perovskite-type materials [19–21]. That is, we find the case of a system exhibiting a narrow d- or impurity band and spatial orbital ordering which, by its nature, has the potential to favor a FM ground state. The distinguishing feature of our...
model compared to the models described above is the nature and origin of the model parameters (intra- and inter-particle interactions) that specify the bipartite structure.

An analogous picture was also found to be developed in codoped carbon-based (C-based) materials in which the bipartite structure is of inherent nature. In these materials a defect type that interrupts the intrinsic bipartite picture can lead to the development of unpaired electrons which, in turn, can be coupled ferromagnetically with the mediating services of another type of defect [2, 3, 5, 6, 8]. One can, thus, invoke the existence of a dormant bipartite structure which has the potential to become activated in the presence of the appropriate codopants and this appears to be a common factor in the studied systems which can exhibit defect-induced magnetism.

All our results indicate that codoping leading to the formation of alternate codopant configurations results in Lieb-type bipartite systems with the dormant bipartite structure substituted by their embedding in a host environment. So Lieb’s theorem [22] could, in principle, be applicable. In the present paper we describe the physical processes which are associated with the development of the bipartite structure and appear to be responsible for establishing the ferromagnetic features.

Along the lines of a synergistic approach to the development of magnetism in these materials and strong support for our proposed theory, one may consider the recently proposed two-center model mechanism for ferromagnetism by Pemmaraju et al [23] and the work of Wu et al [24] who considered the pairing interactions between (mono)dopants as the leading processes in the development of defect-magnetism.

In conclusion, the present results allow us to claim that our interpretation links the defect-induced magnetism in DMSs (diluted magnetic semiconductors) and TMOs (transition metal oxides) to the previously proposed theories of magnetic organic salts and carbon-based materials [2–8]. In all these materials, the proposed defect-induced defect-mediated mechanism is realizable through a codoping procedure. The proposed codoping mechanism can be considered a general and generic approach that can be used to justify the defect-induced magnetism in a diverse set of non-magnetic systems. The FMC that the proposed model introduces is based on the formation and interaction among MOs which have simultaneous contributions from neighborhoods which include codopant ions. The FMC thus developed can be greatly enhanced if the codopants form bipartite configurations within the host lattices.

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References

[1] Sato K et al 2010 Rev. Mod. Phys. 82 1633