

Topical Review

Codoping induced enhanced ferromagnetism in diluted magnetic semiconductors

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**Abstract**

The experimentally observed d^0 -magnetism and its subsequent attribution to the presence of structural and topological defects has opened the way for engineering the magnetic properties of diluted magnetic semiconductors (DMSs) and transition metal oxides (TMOs). Doping and codoping constitute the most commonly used processes (either experimentally or theoretically) for developing and studying this type of defect-induced magnetism. The focus of the present review is to highlight the basic features of the defect magnetism which have been observed over diverse systems, while emphasizing the local, holistic and synergistic response of the host materials to their doping and investigating their role in the development of the magnetic coupling (MC) that is developed among the magnetic dopants. *Ab initio* computational results elucidate the local aspects of the MC (charge and spin transfers between dopants and their first nearest neighboring anion ligands) and their relation with holistic processes which are reflected in the band structure, and the shifts of both the d - and p -band centers of the doped material (compared to the undoped one). In view of these results the MC between the magnetic dopants is framed within the newly proposed successive spin polarization and the defect-induced defect-mediated models. The similarities found in the magnetic characteristics between the codoped DMSs/TMOs and the magnetic multilayer systems lends further support to these models which introduce new contributions to the MC that are competitive with the existing classical ones (superexchange, double exchange, s - d & p - d couplings etc).

Keywords: magnetism, co-doping, first principles methods, electronic structure

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

1. Introduction

The recent discovery of magnetism in a variety of diverse non-magnetic materials (e.g. ZnO and rhombo-

hedral- C_{60} (Rh- C_{60}) polymers) containing defects, has challenged conventional thinking about the microscopic origin of magnetism in general. Especially intriguing is the case of materials which do not exhibit occupied valence d electrons which are traditionally associated with magnetism.

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Since the early investigations of magnetism in d^0 materials [1–6], a consensus has emerged in attributing this magnetism to the presence of defects. Furthermore, the most recent and outstanding works on diluted magnetic semiconductors (DMS) showed that the **magnetic properties are not exclusively related to the presence of the magnetic ions but strongly determined by the defects** [7]. These can be intrinsic (e.g. any structural and/or topological defects) or extrinsic (e.g. any impurity atoms or radicals) or a combination of them [1, 7–9]. Soon, the implementation and the management of defects were considered powerful tools for inducing and tailoring magnetic features in classes of systems of great technological interest which are not magnetic otherwise. These systems include; DMS, transition metal oxides (TMOs), carbon based materials (graphene ribbons, irradiated carbon), ordinary oxides (e.g. CaO [5, 10], HfO [6, 11], etc).

The development of defect magnetism in these materials appears to be a two step process. During the first step, unpaired electrons are introduced which provide the magnetic moments (MMs); this is one of the roles that is attributed to the defects. In the second step the magnetic coupling (MC) among the MMs is developed. While the origin of the MMs (either intrinsic or extrinsic) is undoubtedly attributed to the presence of the defects, the origin of the MC among the MMs is still far from being well understood despite the plethora of reported experimental and theoretical investigations and the models proposed [12–28]. This is illustrated with various levels of computational approximations (see section 2).

Defect states and formation of impurity bands induce dramatic alterations in the band structure of the wide band gap or semiconducting host materials and may turn them into metals. Unavoidably, in this case, the magnetism of metallic DMSs and doped TMOs was attributed to carrier mediated processes (Ruderman–Kittel–Kasuya–Yosida (RKKY), double exchange, p – d and s – d exchange) and the factors they affect them (see reference [12] and references therein). On the other hand, in the case of non-metallic DMSs and doped TMOs, the corresponding MC between two magnetic dopants was attributed to the mediation of an anion (or a *radical* made of a codopant and its surrounding anions) [29, 30]. The observation that magnetic features in non-metallic DMSs and doped TMOs are found even for dopant concentrations below the percolation threshold [31, 32] led to the proposal of various models for its justification [27, 28].

The codoping (i.e. the simultaneous doping of a material by two or more dopants) introduces a new concept in both the experimental and theoretical investigation of the defect magnetism. **Codoping appears as a number of cooperative processes undertaken by the codopants which have been labeled defect-induced defect-mediated (DIDM) model** [1, 33–41] (see section 3). Codoping focuses mainly on the local aspects of the magnetism which manifests itself within bipartite dopant conformations (see section 3.4) introducing new contributions to the MC, namely the *successive spin polarization* (SSP) (see section 4.1) and the *successive superexchange* (SSX) (see section 4.2) model ones.

The DIDM magnetism is associated with a synergistic (see section 3.3) and holistic response of the defected host to the presence of defects (see section 3.2), which is manifested in the energy shifts of the system's d -band and p -band centers which affect the energy band gap (see section 3.5). Additionally, there exists a plethora of results indicating that the MC among the intrinsic or extrinsic MMs takes the form of an interaction among spin-polarized molecular units which is facilitated by the formation of the hosted bipartite codopant structures (see section 4). The universality of the proposed mechanism is further supported by the earlier results obtained from diverse systems as will be discussed in the following relevant sections.

2. Proposed theoretical model descriptions

A large number of models have been proposed in an effort to understand the origin of the defect-induced magnetism, the type of the magnetic interactions and the establishment of the long range MC. The proposed models can be allocated in two major classes. The one, puts emphasis on the local aspects of the magnetic behavior and is usually limited in the description of the magnetic interaction between two or three magnetic defects in a given host. This is traditionally explained within the single electron approximation and/or the atomic orbital (AO) description in terms of the double exchange, or the superexchange, or the p – d and sp – d exchange interaction etc (see for example reference [12] and references therein). The second class takes a step further and examines the development of long range magnetic interactions in terms of the defect induced delocalization of the defect states and model approximations (e.g. charge carrier mediation, Korringa–Kohn–Rostocker coherent potential approximation (KKR–CPA) [42–46], Heisenberg model, etc).

Both classes of the proposed theories employ single reference (SR) model descriptions, i.e. theories which use one Slater determinant to describe the electronic structure of the ground state. In addition to that theories proposed to explain the magnetic interaction between two magnetic dopants make use of multi-reference approaches which will be referred to as configuration interaction (CI) models [47].

2.1. Multi reference model approximations

The CI approaches include various levels of computational approximations to the e – e correlations as, for example, the restricted open-shell Hartree Fock [48], the complete active space self-consistent field [49, 50], multiconfiguration coupled electron pair approximation [51] and others commonly applied in small cluster calculations.

From the widely referenced simplified applications of the multi-reference model approximations used in the description of magnetic interactions, worthy of mention are the *kinetic exchange* interaction models, i.e. the McConnell models [52, 53], the Ovchinnikov's spin polar-

ization model [54], the orbital ordering and the excitonic models [55], the s – d coupling, the superexchange model of Zener–Anderson–Hasegawa [56–59], etc.

More precisely, the organic McConnell ferromagnets [52, 53] are described by a superposition of neutral and charge-transfer molecular orbitals (MOs), while the spatial orbital ordering systems are described in terms of the ground and lower excited states as modified by induced intramolecular Jahn–Teller distortions and cooperative Jahn–Teller interactions [60, 61] (see also section 4.4). Much later, Roth [55] based on van Vleck’s observation [62] that the presence of orbital degeneracy is important in the occurrence of ferromagnetism, demonstrated that this is, in fact, possible for a narrow d -band Hubbard model [63] with two degenerate orbital states at half filling. For this model Roth showed that a spatial ordering of the orbitals is energetically favorable in the form of two sublattices with the one predominantly of the orbital states and the other for the spins to line up ferromagnetically. This model was exploited by Kawamoto [60, 61] in an effort to explain the s – p ferromagnetism of tetra-dimethyl-amino-ethylene C_{60} (TDAE- C_{60}).

The intense computational requirements of the multi-reference schemes have so far limited their applicability in electronic structure calculations. As a result this is a task that is almost exclusively left to models employing SR descriptions.

2.2. Single reference model theories

Even though the exchange coupling among lone electron spins is successfully described within the CI models ([52–54, 64, 65]), the success of the *ab initio* density functional theory (DFT) at the level of the generalized gradient approximation (GGA) or that of a hybrid DFT (for example, the Heyd–Scuseria–Ernzerhof hybrid functional [66, 67]) to address partially filled MOs has proved to be much more efficient in describing in a satisfactory way the electron delocalization and the associated charge and spin density accumulations induced by the defects.

DFT calculations have shown to be more reliable when the ground state of the system is spatially non-degenerate and the chosen exchange and correlation functional used is adequate. For spatially degenerate states, it is well known that the CI description cannot satisfactorily be replaced by a SR model. Therefore, the superexchange coupling between two magnetic dopants can no longer be described by a simple Lande-splitting [51].

From a computational point of view the *ab initio* SR-DFT solutions are based on periodic boundary conditions and a suitable approximation of the exchange and correlation potentials. Due to their nature these procedures have no direct relationship with the dependence of the magnetic features of the doped system on the concentration of the magnetic impurities except for some long range effects derived from the periodic boundary conditions and the chosen size of the unit supercell. Therefore, they are unavoidably limited to the investigation of the local features focusing on the hybridization processes, the orbital couplings, the orbital delocalization etc,

in relation with the electronic structure of the host material (see section 3.1).

Nevertheless, SR models formed the basis in formulating the extension of DFT applicability beyond its local limitations. This has contributed significantly to our understanding of fundamental aspects of magnetism in general through well elaborated theories and models like those of Stoner [68, 69], the RKKY [70–72], the band magnetism approaches [12], the KKR–CPA [42–46, 73], the Heisenberg model (see for example reference [74]), the dynamical mean field theory (MFT) [75], etc. This was also facilitated by computational schemes beyond the DFT/GGA as, for example, the time-dependent perturbation theory, suitable self-interaction corrected [76] or Hubbard- U corrected (GGA + U) [77–80] DFT schemes.

2.3. Semi-empirical models

Along with the development of *ab initio* theories, empirical and semi-empirical models were also proposed to describe and interpret the defect-induced magnetic phenomena. These models usually make use of system dependent parametrization.

2.3.1. DFT/GGA + U approximation. The local character of the DFT/GGA and to a lesser extent that of the (h)DFT/GGA and the fact that electron delocalization depends on the inter-site transfer integral and the strength of the on-site Coulomb correlations [64] cannot guarantee *a priori* a possible success of a (h)DFT/GGA scheme. The inadequacy of the (h)DFT/GGA to address excited states in a satisfactory way, is reflected onto its inability to predict correctly the band gaps of DMSs and TMOs.

This disadvantage of the DFT/GGA scheme has been partially overcome within the Hubbard- U corrected functional, namely the DFT/GGA + U scheme [77–80].

Within the DFT/GGA + U functional a correction term (the U -term) is incorporated as a many-body correction to overcome the underestimation of electronic correlation due to the approximate nature of the exchange–correlation functionals in the traditional single particle Kohn–Sham DFT. It provides a partial correction to the electronic self-interaction error inherent in DFT.

Initially, the U term has been applied to the metal d band [77–79, 81]. Subsequently, U terms were additionally applied to the s or p bands of the anions in order to improve the band gap and defect level descriptions of TMOs [34, 82, 83]. In some instances, a negative value of U or its equivalent has also been applied to these materials [84–86]. The reason behind this is the assumption that if a positive U adds extra Coulomb repulsion, a negative U then would add extra attraction within a band facilitating thus a better fitting of the band width [87]. Whether, in general, this would help increase the band gaps of some metal oxides and overcome the underestimation of the band gaps, is still an unresolved question.

The variety of the proposed *ab initio* implementations of the DFT/LSDA + U method [77–81, 88], despite guaranteeing the self-consistent incorporation of the U term, has not led to any substantial improvement in the estimation of the energy gap of the metal oxides if applied only on the d -electrons. This

has led to semi-empirical applications of the DFT/LSDA + U method in which the U -terms are treated as parameters which are obtained empirically by fitting to available experimental or theoretical data for band gaps and additional experimental spectral properties [34, 87, 89].

As a result, the DFT/LSDA + U approach when applied in this manner loses its *ab initio* character and therefore its predictive power.

2.3.2. Tight-binding (TB)-approximation. The tight-binding (TB) computational schemes were initially introduced as a fast and computationally efficient way to reproduce the band structures of the materials based on parameters obtained by *ab initio* methods [90–92]. Molecular dynamics based on TB approximation has been applied successfully in the description of clusters of transition metal (TM) atoms and of magnetic impurities in DMSs and TMOs [38, 93–96]. In addition to that, TM model descriptions have been proven to be very efficient in investigating the temperature stability of the materials [97] as well as the effect of temperature on the magnetic properties of clusters of TM atoms [98–100].

2.3.3. Goodenough–Kanamori rules. At a qualitative level, Goodenough and Kanamori (GK) proposed a set of rules [101–104] which have been proven highly successful in rationalizing the magnetic properties of a wide range of materials. They are based on the symmetry relations and electron occupancy of the overlapping AOs (under the assumption that the localized Heitler–London, or the valence-bond model is more representative of the chemical bonding than is the delocalized or the Hund–Mulliken–Bloch, model).

There appears to be two basic factors whose product specify the outcome of the GK-rules. The first of these is the bond type, β_{GK} , which specifies the bond type between the magnetic dopant, C_i , and its first nearest neighboring (1 nn) anions, A_i . It can take the value +1 (or –1) if the coupling between C_i and A_i is of ferromagnetic (FM) (or antiferromagnetic (AFM)) type. The second factor is the sign of the exchange coupling, J_{eff}^{sp-d} , between C_i and A_i which is taken to be positive (negative) if the orbitals bonding C_i and A_i are orthogonal (non-orthogonal). The sign of the product $J_{\text{eff}}^{sp-d} \beta_{\text{GK}}$ specifies the sign of the superexchange between the two neighboring magnetic cations C_i and C_j [101–103].

For simple cases, the GK rules readily enable the prediction of the net magnetic exchange expected for the coupling between ions. However, complications begin to arise in various situations when:

- Direct exchange and superexchange mechanisms compete with one another.
- The cation–anion–cation bond angle deviates away from 180°.
- The electron occupancy of the orbitals is non-static, it is dynamic.
- The spin–orbit coupling becomes important.

GK rules have drawn an ever lasting research interest. On the one hand, they are focused on getting a deeper understanding of the physics underlying their origin, the range of their

applicability [105–109] or cases of their violation [110, 111]. Inagaki [112] and Inagaki and collaborators [113, 114] and later Naruse and Takamori [115] proposed an orbital phase perspective of GK rules in superexchange interaction. On the other hand, GK rules proved to be a significant tool for the synthetic chemist in controlling the magnetic interactions [106, 107, 116].

Recently, we proposed a new computational method for specifying the GK-product [104, 117, 118]. It is based on the response properties of the doped system in the imposed boundary condition on magnetization density, M , of the system. Central point of the method is the calculation of the variation, $E_{\text{tot}}(M)$, of the total energy, E_{tot} , as a function of the M . The magnetization condition leads to changes in the polarization, $\Delta\mu_{\text{an}}^{\text{1nn}}$, induced by the magnetic dopants onto their 1 nn anion ligands. It was demonstrated that J_{eff}^{sp-d} can be obtained from the following formulas calculated in the limit $M \rightarrow M_{\text{opt}}$, where M_{opt} is the unbiased magnetization density of the system:

$$J_{\text{eff}}^{sp-d} \approx \frac{\lambda \beta_{\text{GK}}}{\mu_{\text{TM}}} \bigg|_{M \rightarrow M_{\text{opt}}}, \quad (1)$$

where

$$\lambda = \frac{\delta E_{\text{tot}}(M)}{\delta \Delta\mu_{\text{an}}^{\text{1nn}}(M)} \bigg|_{M \rightarrow M_{\text{opt}}}, \quad (2)$$

μ_{TM} is the MM of the magnetic dopant and $\beta_{\text{GK}} = (\Delta\mu_{\text{an}}^{\text{1nn}} \cdot \hat{\mu}_{\text{TM}}) |_{M \rightarrow M_{\text{opt}}}$ defines the bond type formed between the magnetic dopant and its 1 nn anion ligands.

2.3.4. Other empirical models. Empirical extensions of the DFT/GGA scheme by exploiting its local character have been proposed in an attempt to simulate the correct CI results. For example, the charge accumulation around a Zn vacancy in ZnO was approximated by adding an on-site potential term on the oxygen sites surrounding the vacancy [119]. Such empirical approximations are helpful in investigating the ferromagnetic coupling among the defect-induced MMs by mapping the empirically obtained exchange interactions onto the Heisenberg model. However, they do not give a thorough view of the induced magnetism and their use may not adequately address the consistency issue described by the criteria set in reference [10].

2.4. Machine learning methods

A useful practical application of the defect-induced magnetism is focused on, but not limited to, finding the optimum choice of host and dopants which could transform a chosen host (DMS or TMO) into a material with prescribed magnetic properties (e.g. strength of ferromagnetism, band gap, electron mobility, etc). This is just one of a wider class of problems which pertain to the understanding of any existing inherent correlation between structural, electronic/magnetic features of materials and the electronic properties of their constituent atoms. In practice, this problem is approached on a *trial and error* basis. A characteristic example is the band gap engineering referred to in the above (see section 3.5).



Figure 1. Proposed learning approach. Reproduced from [122]. © IOP Publishing Ltd. All rights reserved.

As an alternative to the cost and time requirements of a *trial and error* approach (either experimental or theoretical), is to use computational screening tools making use of machine learning schemes which have already impacted multiple areas such as cognitive game theory, pattern recognition, event forecasting, bioinformatics and materials science research [120–122]. The basic steps in a machine learning process are: (i) the feature selection and extraction; and (ii) the learning algorithms. In the search for new materials with specific features (as, for example, in the search of new catalysts or new magnetic DMS materials) a large set of features, called *descriptors*, which are identified through accurate *ab initio* and existing experimental results, are firstly investigated with respect to their relevance to the required property. For example, in the search for new catalysts emphasis is placed on descriptors which map the adsorption energy of reacting elements onto the catalyst. One such descriptor is the coordination number of the site of adsorption [123–125].

In the case of new DMSs, the relevance of the descriptor is firstly investigated with respect to the required property within the DMS systems formed by a host material and a chosen set of magnetic dopants. Next, the ability of the relevant descriptors to predict magnetic properties of new compounds is investigated. i.e. the past knowledge expressed in terms of the relevant *descriptors* is utilized to unravel any hidden inherent correlation between one or more given magnetic properties and the set of *descriptors*. Then, a search is performed to determine whether this correlation holds true in predicting the required magnetic properties of other (new or non-investigated yet) materials. In reference [122] Khmaissia *et al* used data from 104 systems obtained by codoping (see section 3) the hosts GaP, GaN, ZnO and CdS with two types of codopants taken from the TMs of the 3d-series. The features (descriptors) that were used included free atom properties of each host and dopant atom, namely; the atomic number, the electronegativity, the *s*–, *p*– and *d*–orbital energies, the valency and the covalent radius. Also included were the following features for each codoped system: the *d*-band center of the density of states of the *d*-orbitals of the dopants, the *p*-band center of the host anions, and the total MM per reference unit.

The proposed application of machine learning technique combined feature selection with least absolute shrinkage and selection operator regression [126] in order to enhance the

modeling of magnetism in DMS materials (see figure 1). It proved successful in identifying the top factors responsible for defect-induced magnetism in DMS by predicting the total MM of several DMS systems and confirmed that fundamental atomic features are correlated with DMS magnetism in agreement with previously reported theoretical investigations [39, 127].

3. Codoping: defect-induced defect-mediated magnetic coupling

The doping with two or more types of atoms will be referred to as codoping. A codoped host with *n* codopants of type A, *m* codopants of type B, *l* codopants of type C, and so on, will be denoted with the symbol $(A_n B_m C_l \dots)@host$. For example, the ZnO (*host*) codoped with two Co and one Cu codopants will be written as $(Co_2 Cu)@ZnO$.

Contemporary experimental and theoretical evidence suggested that the magnetism in the DMSs could be enhanced by *codoping*. In particular, enhanced magnetic features were observed in, among others; ZnO codoped with (Fe, Cu) [24, 25], with (Fe, Co) [25], (Co, Cu) [128, 129], (Co, Li) [20, 21], (Co, N) [130], (Co, H) [131], (Co, Al) [19], (Co, O-vacancies) [16], (Mn, Sn) [14], (Mn, Co) [15, 23], (Mn, N) [132], (Mn, O-vacancies) [18], (Mn, C) [133], (Gd, O-vacancies) [134]. Analogous findings were reported for GaN codoped with (Mn, Co) and (Cr, Mn) [135]; in $(Cr)@TiO_2$, $(Co)@TiO_2$ [136] and $(CoTi)@TiO_2$ [137]; in $(Mn)@GaAs$, for which the magnetic enhancement was attributed to *p*–*d* hopping interaction [138–141], while in TiO_2 [142] it was attributed to non-compensated *n*–*p* doping [142], or the passivation of codopants (Mo, C) [143]. Similar studies were extended to TM dichalcogenides (namely MX_2 , with *M* = Mo, W and *X* = S, Se, Te) in the search of materials suitable for spintronics and valleytronics applications [144–153].

Codoping theories are generally centered around the local aspect of the MC (see section 3.1). An important aspect of the codoping involves holistic (see section 3.2) and synergistic (see section 3.3) set of processes between two main types of mutually dependent responses of the system to its (co)doping. The first one refers to the rehybridization of the AOs associated with the defects themselves (e.g. impurity atoms, vacancies)

and those of the surrounding the defect ligands [154, 155] and characterized by many features which have local character (for example, inter- and intra-atomic charge redistributions). The other group of processes has a long range character and leads to the MC among the MMs; they depend crucially on the induced charge transfers, the remote MO delocalization and the remote MO overlaps [156].

Many reports point to the evidence that the defects activate potential (existing or hidden) bipartite structures (see section 3.4) and make them amenable to magnetic features as found in a wide range of materials and model approximations [52–55, 60, 61, 157–159]. Codoping appears as one of the fundamental processes which provides the means to exploit and achieve this. 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. This appears to be a common factor in many systems studied including carbon based materials, DMSs and TMOs, which were found to exhibit defect-induced magnetism.

The holistic character of the codoping process is basically reflected in the band gap changes an undoped material undergoes upon its magnetic codoping (see section 3.5). This dictates one of the practical aspects of codoping, namely the gap engineering in the search of materials with predetermined energy gap values.

It thus appears that codoping can be viewed as a generic approach which can justify the defect induced magnetism in a diverse set of non-magnetic systems. This view is entirely different from those views according to which the codoping has been considered as a possible way to tailor the position and the electron density, $\rho(E_F)$, at the Fermi energy, (E_F), of the (co)doped systems [160–165] considering, thus, the defect magnetism as a consequence of the Stoner magnetism. Certainly, the hybridization processes could lead to a possible enhancement of $\rho(E_F)$ and could add a contribution to the development of magnetism especially in combination with the impurity band spin-split model [27].

It appears that the location of the Fermi level within the impurity band plays a crucial role in determining the Curie temperature through determining the degree of localization of the impurity band holes [27, 166]. Despite these findings the Fermi level engineering does not provide an answer about the way the MC is developed among the magnetic dopants/defects, a feature that is also missing from the description of the holistic band picture of magnetism. The models proposed so far (see section 4) based on the codoping concept have taken upon themselves the job of illuminating the local aspect of the MC as will be exemplified in this section.

Taking into account the synergistic aspect of the codoping, the magnetism developed in a codoped system has been named DIDM magnetism. In a series of recent publications, it has been demonstrated that codoping leads to the development of magnetic features in a variety of diverse non-magnetic wide band gap semiconductors, including DMSs, TMOs, III–V, II–VI, carbon based materials [1, 33–38] and TM-dichalcogenides [167]. In view of the codoping concept,

the DIDM magnetism in DMSs and TMOs is linked to the previously proposed theories of magnetic organic salts and carbon based materials [168].

3.1. Local aspects of the magnetic coupling

The defect induced MC has been shown to be well correlated with those system features which characterize the neighborhood of the magnetic dopants. Of particular interest are the relative difference of the free atomic electronegativities, $E_{N,j}$, and that of the d -band centers, $d_{c,j}$, of the d -bands of dopants with respect to those of the host elements (where j indicates the referenced atom). These features also dictate those factors which underlie the sp - d MC, J_{eff}^{sp-d} , between the d -band of the TM-dopant and the sp -band of the host anions. J_{eff}^{sp-d} plays a multiple role in understanding the magnetic features of a material. Among others, it contributes to the estimation of the interdopant coupling (in terms of the GK rules, see section 2.3.3) as well as the quantification of the Curie temperature, T_c , (recall $T_c \approx (J_{\text{eff}}^{sp-d})^2 * \chi_h$, where χ_h is the hole concentration [153]).

More precisely, J_{eff}^{sp-d} exhibits dependence on:

- The MM, $\mu_A^{X,\text{host}}$, of a dopant A in the presence or not of a codopant X in the specific *host*. (In the absence of any codopant, X is taken to be the host cation; for example, for the (Co)@GaN, we denote the MM of Co as $\mu_{\text{Co}}^{\text{Ga,GaN}}$).
- The MMs, $\mu_{\text{an},A}^{i,\text{host}}$, $i = 1, N$ induced by a magnetic dopant A onto its N first nearest neighboring (1 nn) host anions, *an*, in the specific *host*.
- The bond type, $\beta_{\text{GK}} = \hat{\mu}_{\text{an},A}^{i,\text{host}} \cdot \hat{\mu}_A^{X,\text{host}}$ where $\hat{\mu}_{\text{an},A}^{i,\text{host}}$ and $\hat{\mu}_A^{X,\text{host}}$ are the unit vectors along $\mu_{\text{an},A}^{i,\text{host}}$ and $\mu_A^{X,\text{host}}$ respectively. β_{GK} can take the values +1 or –1 depending on whether the MC between the d -band of the dopant and the sp -band of the host anions is FM or AFM respectively. The bond type, β_{GK} , plays a significant role in the GK rules (section 2.3.3) for predicting the inter-dopant coupling [101–104].

The relative difference in the electronegativity and the d -band center of the dopants with respect to those of the host atoms varies along the 3d-series of the TM dopants. This variation dictates the type of the bond type β_{GK} (see figure 2) and the value of both the $\mu_A^{X,\text{host}}$ and $\mu_{\text{an},A}^{i,\text{host}}$, $i = 1, N$ (see figure 3).

These observations can be identified as various trends linking the properties of the free atoms which constitute the dopant-radical (i.e. the dopant along with its 1 nn anion ligands) with properties of the doped system. In particular:

- It was found that the bond type and the charge transfer processes from and toward the magnetic dopants as well as the charge redistribution within them depend on whether the magnetic dopant belongs to the early or the late 3d-series of the TM metals. This indicates, on the one hand, a dependence on the dopant's d -band filling [39, 170] and, on the other hand, on how far its d -band center is from the Fermi level; a factor which is correlated with the degree of its localization [171, 172].

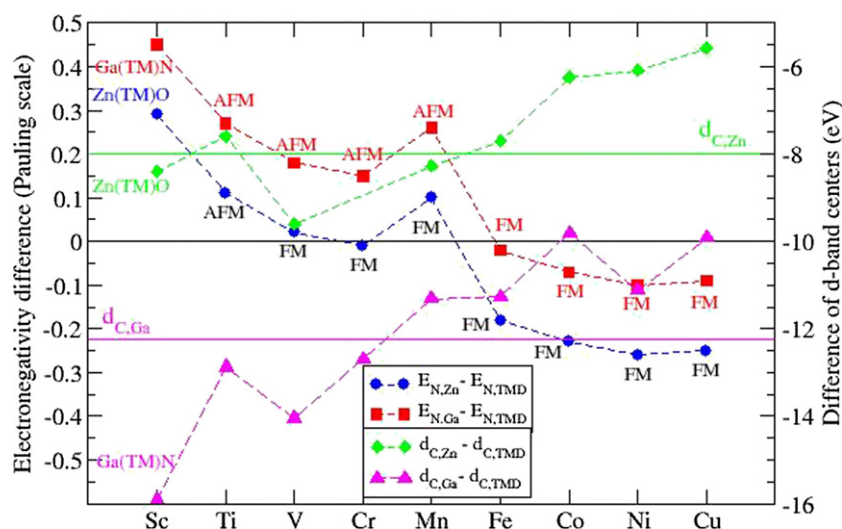


Figure 2. *Ab initio* results [169] showing the observed correlation between the bond type β_{GK} (FM or AFM) and the relative difference (with respect to the host cations) of both the electronegativity and the d -band center of the $3d$ -TM-substitutional-dopants, (TMD), (shown on the horizontal axis) in ZnO and GaN. Blue circles (red squares) denote the electronegativity differences in ZnO (GaN) (tabulated Pauling electronegativities were used). Green diamonds (magenta triangles) denote the corresponding d -band center differences in ZnO (GaN). Solid green (magenta) line denotes the $d_{\text{Zn,ZnO}}^{\text{Ga,GaN}}$ ($d_{\text{Ga,GaN}}^{\text{Zn,ZnO}}$). Reproduced from [39]. © IOP Publishing Ltd. All rights reserved.

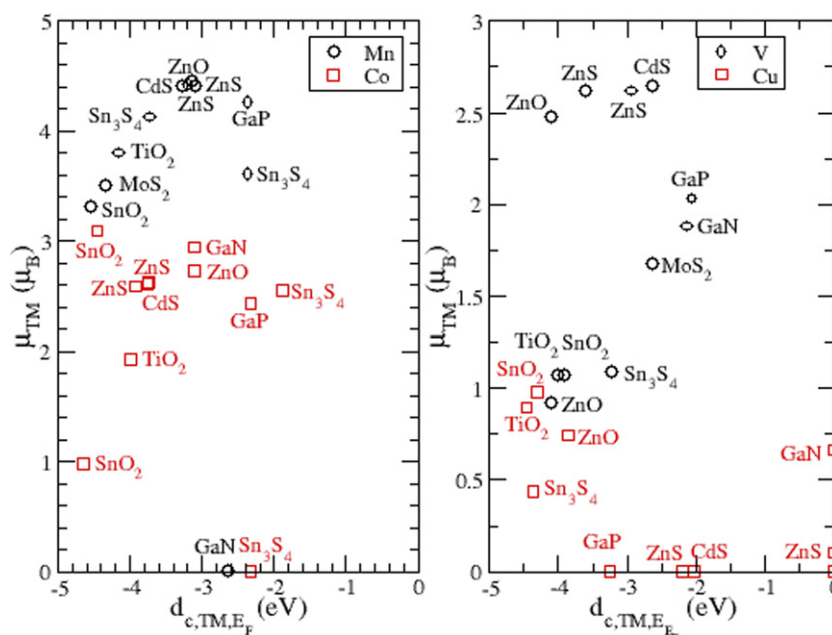


Figure 3. Correlation ($\mu_{\text{TM}}^{\text{TM,host}}$, $d_{\text{c, TM}}^{\text{TM,host}}$) between the MM $\mu_{\text{TM}}^{\text{TM,host}}$ of single 3d-TM dopants in various (indicated) hosts and their corresponding d -band center, $d_{\text{c, TM}}^{\text{TM,host}}$. Left panel for TM = Mn, Co; right panel for TM = V, Cu. The slope $\frac{\delta\mu_{\text{TM-dop}}^{\text{host}}}{\delta d_{\text{c, TM-dop}}^{\text{host}}}$ can be positive (as for Mn, Co) or negative (as for V and Cu) depending on the dopant and the host material. Reprinted with permission from [127]. Copyright (2017) American Chemical Society.

- The MM $\mu_A^{X,\text{host}}$ of an A-codopant (in the presence or not of a codopant X) is found to correlate well with its corresponding d -band center, $d_{c,A}^{X,\text{host}}$ (see figure 3), as well as with the p -band center, $p_{c,\text{an}}^{A,X}$, of the anions of the host in the presence or not of X codopants [127] (see figure 4 and also the right panel of figure 9). The dependence of $\mu_{\text{an},A}^{i,\text{host}}$ on dopant's valency (dopant type) and the host material is shown in figure 5 [170].
- The electronegativities of the free atoms constituting the dopant-radical were found to be well correlated with the development of $\mu_{A_i;\text{TM}}^{\text{host}}$ $i = 1, M$ through a universal relationship [173]. Furthermore, it was proposed that dopants with weaker electronegativity than that of the anions in the host semiconductor should be used to produce magnetic semiconductors by anion substitutional doping with $2p$ light elements, as these lead to longer

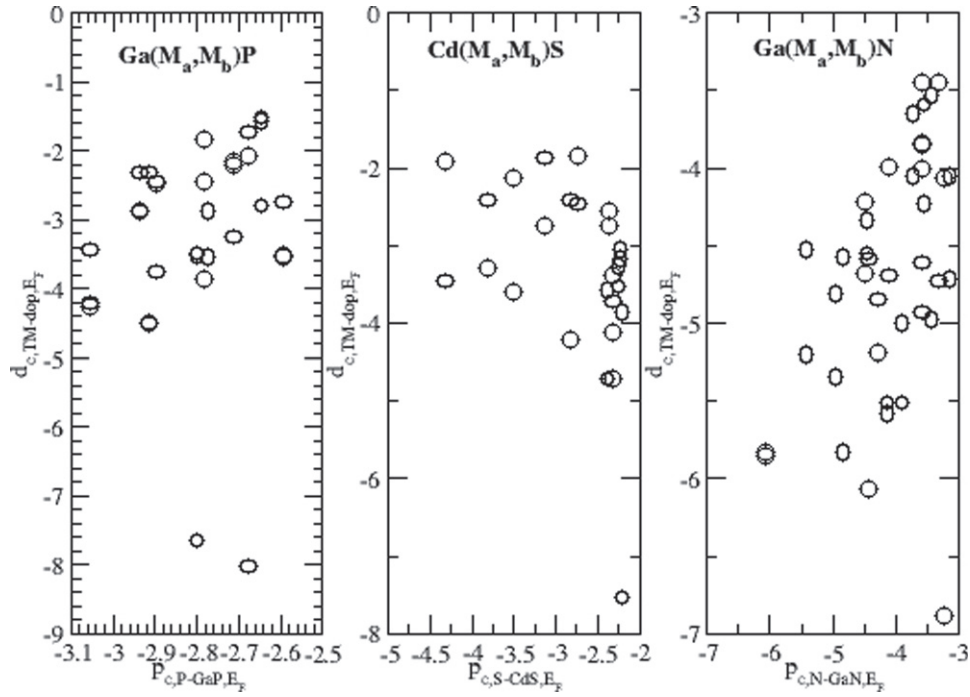


Figure 4. Correlation between $d_{c,M_{\alpha}}^{M_{\beta},\text{host}}$ and $p_{c,an}^{M_{\alpha},M_{\beta}}$, for the hosts GaP, CdS and GaN, codoped with M_{α} and M_{β} atoms both being 3d-TM codopants. It is worth noting that the average slope ($\frac{\partial d_{c,M_{\alpha}}^{M_{\beta},\text{host}}}{\partial p_{c,an}^{M_{\alpha},M_{\beta}}}$) can be positive or negative depending on the host material. Reprinted with permission from [127]. Copyright (2017) American Chemical Society.

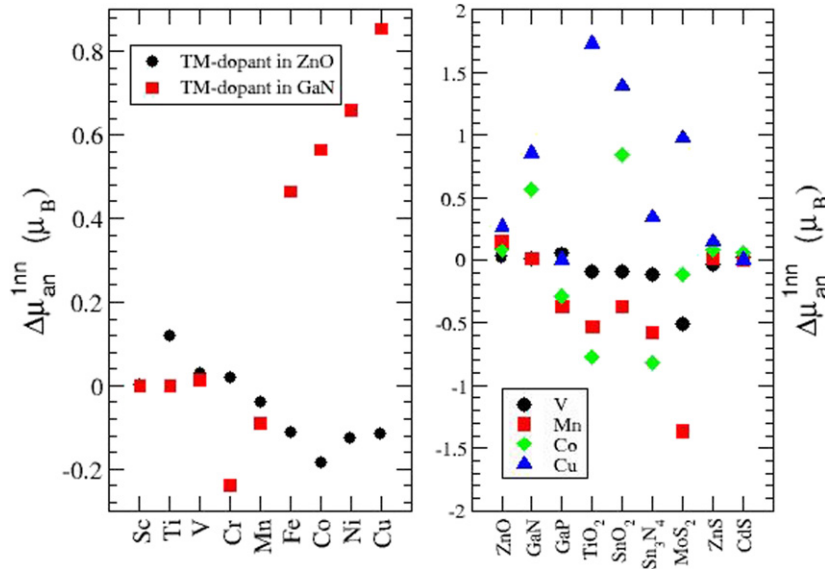


Figure 5. Results indicating the dependence of $\Delta\mu_{an}^{1nn} = \sum_{i=1}^N \mu_{an,A}^{i,\text{host}}$ (the polarization induced by a dopant onto its N 1 nn anion ligands) on host material and dopant type (A). (Left) $\Delta\mu_{an}^{1nn}$ induced by 3d-TM dopants, (shown on the horizontal axis) in ZnO and GaN. (Right) $\Delta\mu_{an}^{1nn}$ induced by V, Mn, Co and Cu in various hosts indicated on the horizontal axis. Reproduced from [170]. © IOP Publishing Ltd. All rights reserved.

anion–cation bond lengths and, therefore, localized MMs [174].

- The trend for the bond type β_{GK} , i.e. the polarization type (FM or AFM) of the MMs $\mu_{an,A}^{i,\text{host}}$, $i = 1, N$, induced by a magnetic dopant A onto its N 1 nn anion ligands relative to the polarization of $\mu_A^{X,\text{host}}$, i.e. that of their parent

dopant, has been obtained and shown to have the tendency to be AFM (correspondingly, FM) if A belongs to the early (correspondingly, late) 3d-TM series. This, however, is not a universal trend and β_{GK} may depend on the host material. There is also some evidence that this correlation could be affected by the level of the

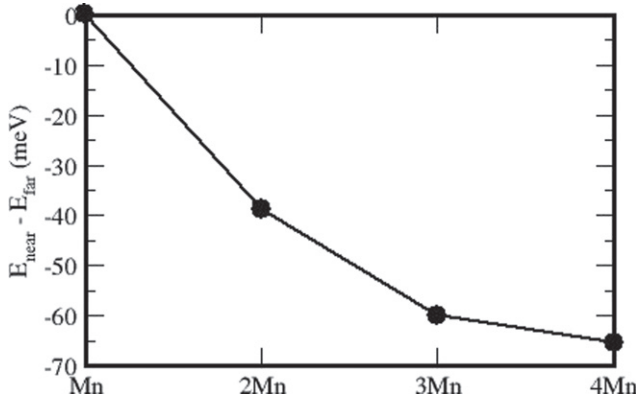


Figure 6. Calculated energy difference, $\Delta E = E_{\text{near}} - E_{\text{far}}$, for substitutional $n\text{Mn}$ atoms in ZnO. E_{near} (E_{far}) is the total energy per unit cell of neighboring (far away from each other) $n\text{Mn}$ dopants ($n = 2, 3, 4$) in ZnO. The negative energy difference indicates that Mn atoms prefer to cluster together. Reprinted (figure) with permission from [37], Copyright (2011) by the American Physical Society.

computational approximations used in the evaluation of the projected spin densities of the dopant's anion ligands [39, 169, 175, 176]. Nevertheless, the type of the MC (FM or AFM) between $\mu_A^{\text{X,host}}$ and $\mu_{\text{an,A}}^{\text{i,host}}$, is of fundamental importance for the conclusions to be drawn since it specifies the bond type β_{GK} which plays a fundamental role in the theory of GK-rules and the determination of J_{eff}^{sp-d} (see, section 2.3.3).

There is strong evidence that β_{GK} is a property of the *radical* formed by the TM-dopant and its 1 nn anion ligands. In particular, it was shown that Cu in ZnO induces $\mu_{\text{an,Cu}}^{\text{i,ZnO}}$, $i = 1, N$ which are aligned parallel to $\mu_{\text{Cu}}^{\text{Zn,ZnO}}$ [140]. It is this intra-radical feature, i.e. that of the dopant and its 1 nn anions, which dictates the inter-dopant MC as anticipated by Goodenough and Kanamori (section 2.3.3).

It should be noted that clustering of dopants may also happen which could affect the stability and the magnetic behavior of the material. This is illustrated in figure 6 where it can be seen that clustering of Mn dopants in ZnO is favored [37, 132, 177], while the magnetic configuration of the dopants is non-FM.

3.2. Holistic response to defects

In addition to the local processes (e.g. charge and spin transfers and/or redistributions), which accompany the presence of an defect, the host material can also undergo a holistic transition in the presence of defects. This is manifested in the band structure changes induced by the codopants. For example, for the Cu-doped GaN we find that when codoped with TMs of the 3d-series the band gap of (CuX)@GaN increases from zero and attains saturation at the value of 0.5 eV for X belonging to the late 3d-series [127]. (See section 3.5)

Furthermore, it was found that codoping induces a shift in the *p*-band center of the anions as a result of the relocation of the valence band maximum (VBM) of the host material. This, in turn, pulls the *d*-band center of the *d*-bands of the codopants relative to E_F thus affecting the value of the MM,

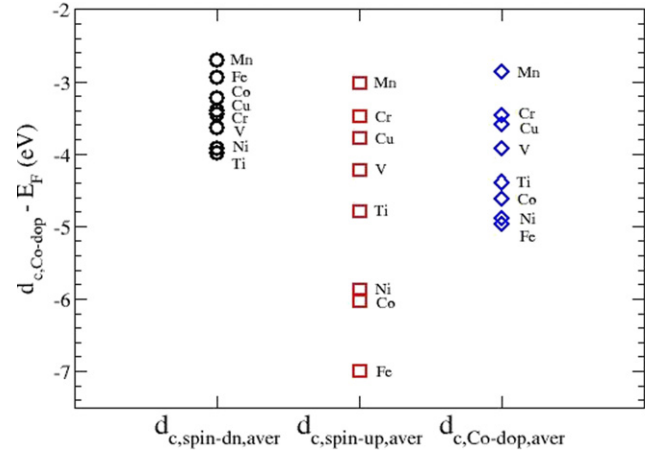


Figure 7. Averages of the spin resolved *d*-band centers $d_{\text{c,Co-dop}}^{\text{X,host}}$ and $d_{\text{c,Co-dop}}^{\text{X,host}}$ for the spin-up and spin-down total *d*-band, respectively, of the systems (CoX)@GaN, X = 3d-TM as indicated near the symbols. Reproduced from [41]. © IOP Publishing Ltd. All rights reserved.

$\mu_A^{\text{X,host}}$, which changes as the *d*-band center of the dopants moves away from (nearer to) E_F (see figure 3) thus becoming less (more) delocalized [41].

Most of the observed features can be understood as resulting from the development of bonding and antibonding orbitals formed between the *d*-orbitals, d_A , of the dopants and the orbitals, d_X , of the X-codopants. In fact, the bonding energy, $E_{\text{AX}}^{\text{bond}}$, resulting from the hybridization of d_A and d_X coupled through the interaction V_{AX} is given by the following TB-derived equation [92] (see section 2.3.2):

$$E_{\text{AX}}^{\text{bond}} = \frac{\epsilon_{d_A} + \epsilon_{d_X}}{2} - \left\{ \left(\frac{\epsilon_{d_A} - \epsilon_{d_X}}{2} \right)^2 + V_{\text{AX}}^2 \right\}^{1/2}. \quad (3)$$

In the case of $|V_{\text{AX}}| \ll 1$, equation (3) takes the following form:

$$E_{\text{AX}}^{\text{bond}} = \begin{cases} \epsilon_{d_X} - \frac{V_{\text{AX}}^2}{\epsilon_{d_A} - \epsilon_{d_X}} & \epsilon_{d_A} > \epsilon_{d_X} \\ \epsilon_{d_A} - \frac{V_{\text{AX}}^2}{\epsilon_{d_X} - \epsilon_{d_A}} & \epsilon_{d_A} < \epsilon_{d_X} \end{cases}, \quad (4)$$

where ϵ_{d_A} and ϵ_{d_X} are the free atom *d*-orbital energies of the A and X codopants.

Equation (4) describes a trend found in the codoped systems. In particular, it has been shown that for Cu in a particular host, it was found (as expected) that $E_{\text{CuX}}^{\text{bond}} (\approx d_{\text{c,Cu}}^{\text{X,host}} \approx \epsilon_{d_X})$ is a decreasing function of the X = 3d-TM codopant, because for Cu we have: $\epsilon_{d_{\text{Cu}}} > \epsilon_{d_X} \forall X \in [3d - \text{TM}]$. Correspondingly, the results for $d_{\text{c,Mn}}^{\text{X,GaN}}, d_{\text{c,Mn}}^{\text{X,GaP}}, d_{\text{c,V}}^{\text{X,GaN}}$ exhibit an increasing and a decreasing part joined at $\epsilon_{d_X} = \epsilon_{d_A}$, A = Mn, V. Exceptions to this trend (as, for example, found in the behavior of $d_{\text{c,Co}}^{\text{X,GaP}}$) could be eliminated if equation (4) was spin resolved, in other words, applied separately for each spin state. This was found necessary because in some cases the spin resolved *d*-states exhibit band centers differing substantially from each other [41] (see figure 7).

3.3. Synergistic processes

The magnetism, which appears to be common to all codoped materials, is the result of the synergistic cooperation and action of the codopant pairs (or *complexes* or *radicals*) facilitated by the host material. This multiple and holistic synergy manifests itself through electronic processes such as charge transfers, (re)hybridizations, induced spin-polarizations, the development of the long range MC, etc.

All these key processes have strong dependence on the characteristics of the hosting system and the type of the codopants. They depend on the lattice symmetry of the host material, its electronic band structure, the type of the codopants, their charge (cationic/anionic) and magnetic state as well as their concentration, the level of orbital hybridization, etc.

Despite its system dependence, the recipe for creating defect induced defect mediated (DIDM) ferromagnetism appears to be quite general [35]. The required basic step is to find two *synergistic codopants or radicals*, one for providing the unpaired electrons (this dopant can be an extrinsic magnetic atom/radical or an intrinsic topological defect, e.g. a vacancy) and the other for facilitating the FMC (the second codopant can be a substitutional atom/radical or a defect). For example, in DMSs and TMOs, the 3d-TM magnetic impurities play a dominant role in the development of magnetism by providing the MMs. On the other hand, in carbon based materials, which are devoid of *d*-electrons, this role could be undertaken by their structural and topological defects (vacancies) (in the absence of 3d magnetic impurities) [1, 22]. A striking example is the case of the magnetic Rh-C₆₀ for which the carbon vacancies and the 2 + 2 cycloaddition bonds were proposed to be the synergistic codopant-pair responsible for its magnetism [1, 33, 168]. Furthermore, defect-induced *d*⁰ magnetism has been attributed to the synergy of grain boundaries and defect complexes (made of host cation substitution and/or host cation and/or anion vacancies) in ZnO [178–180].

In many cases the synergy is attributed to *local* charge and spin density transfers which are dictated by a dopant or a dopant-complex and the availability of these transfers to be accommodated by the orbitals of the dopant complexes [6, 27, 137, 181]. Nevertheless, there is no consensus for the origin of the synergistic action of the codopants toward the development of the MC among their magnetic moments. In particular, the MC between two Co-atoms in ZnO or in GaN in the presence of a Cu codopant is attributed to the spin polarization of Cu [3, 33–35, 37, 39, 169, 176] which is the localized analogue of the spin polarization of the free electrons which mediate the RKKY interaction [70–72]. For the same system, in the presence of oxygen vacancies O_V, the interaction between two Co atoms is found to be AFM [16]) and becoming almost isoenergetic to their FM configuration in the presence of Cu-codopants [34]. This indicates that Cu-codopants, acting as acceptors, cannot contribute to an FM coupling in a way analogous to that of a donor-type codopant (hydrogen) [16]. As Lin *et al* [21], demonstrated experimentally, the substitution of Cu by Li enhances the (Co)@ZnO-ferromagnetism leading them to suggest that in (Co, Li)@ZnO the Li-codopants

may be inducing an indirect exchange in the form of the bound magnetic polaron (MP) [27, 28]. For the same (Co, Li)@ZnO system, Sluiter *et al* [17], proposed that the Li codopants induce charge transfers which result in the enhancement of the MMs of the Co-ions while bringing their *d*-states closer to the optimal values for double exchange.

In section 4 the long range MC is discussed in terms of SSPs coupling magnetic codopants and host anions.

3.4. Forming bipartite and pairing conformations

Study of various codoped systems (such as (Co₃Cr₂)@TiO₂, (CoCo)@GaN, (CoCu)@ZnO, (MnCu)@GaN and carbon based materials) has revealed the synergy between the codopants as seen within the formation of bipartite dopant configurations. These are reminders of the proposed bipartite model descriptions spanning a diverse sample of electronic processes considered to have a leading role in developing magnetic features. The most notable among these models are the following:

- Neel's bipartite two sublattice AFM model; the AFM lattice by its very nature is bipartite (see, for example, reference [182] and references therein).
- The two-fluid model according to which itinerant electrons are converted into singly occupied impurity states which become phase separated from the itinerant electron phase upon increasing the disorder [183, 184]. As an example application of this model we point to the polaronic model of indirect exchange via shallow donors (treated in a two-sublattice mean-field approximation) [27].
- Lieb's model [157]: this model has found applicability in magnetic carbon based materials as demonstrated by Ovchinnikov [54].
- Roth's model [55, 185, 186]: this is known as the *orbital ordering model* and was subsequently used by Kawamoto to explain the ferromagnetism in the TDAE-C₆₀ and layered perovskite-type materials [60, 61, 158]. The distinguishing feature among these models is the nature and origin of the model parameters (intra- and inter-particle interactions) that specify the bipartite (orbital ordering) structure.
- McConnell's model [52, 53, 159, 187]: this model was proposed to explain the FM charge-transfer ionic salts in which either the positive (donor) or the negative (acceptor) molecule have a triplet neutral ground state allowing back charge transfer that mixes the neutral triplet ground state with the triplet charge transferred state.
- Pairing models [16, 188]: in these models, the pairing interactions between dopants (assisted or not by a codopant) are proposed as leading processes in the development of *defect*-magnetism. It was suggested that, if the pairing interactions lead to antibonding states which are not filled, these become associated with MMs which could be mutually coupled either antiferromagnetically or ferromagnetically. The latter case becomes possible if the antibonding pairing states hybridize with the lowest

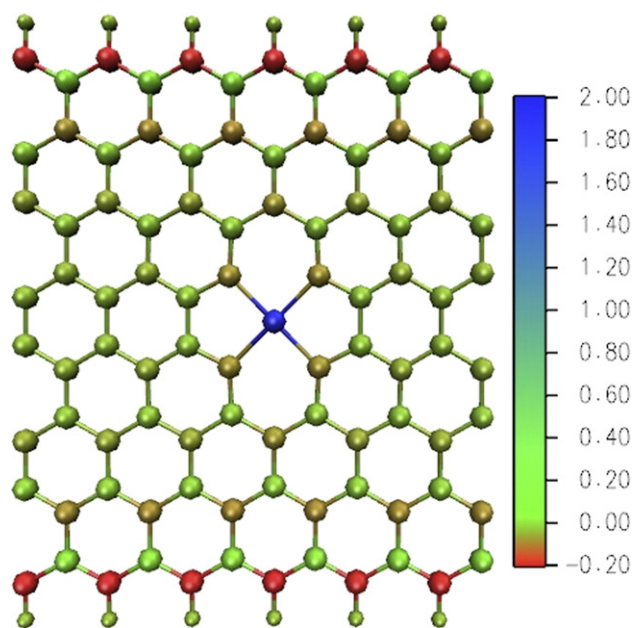


Figure 8. Figure showing the MMs of the lowest energy configuration for Co substituted in a carbon double vacancy in graphene nanoribbon. One of the pairs of the four nearest neighbor (nn) C atoms, namely the upper pair, become polarized with polarization direction opposite to that of Co. This pair, in turn, dictates the bipartite arrangement of MMs of the upper part (above the Co-level) of the graphene ribbon. Similarly, the influence of the Co atom causes the lower pair of nn C atoms to polarize opposite to it and dictate the bipartite arrangement of MMs of the lower part. The overall effect is to cause the lower edge of the graphene ribbon to become spin polarized in the same direction (ferromagnetically aligned) as the upper edge. Reprinted (figure) with permission from [175], Copyright (2012) by the American Physical Society.

conduction band states of the host lattice and broaden into resonances causing the conduction band and the spin density to spread over the pairs and the neighboring host atoms [188, 189].

- The oscillatory exchange coupling developed between thin FM layers separated by a non-FM (metallic) layer (the spacer) [185, 186]. This has surprising similarities with the DIDM magnetism (see section 4.1).

The formation of defect configurations of bipartite character (which does not require a spatial ordering and can be intrinsic or extrinsic) in the codoped systems appears to be of crucial importance by providing the appropriate background environment in which the *codoping-defects* can act to promote the development of magnetism. For example, in many of carbon based materials (graphene, C_{60} -based structures, etc), the bipartite character is intrinsic. In view of this, a Co-dopant in a graphene nanoribbon interrupts the regular bipartite structure of the pristine graphene, transforming it into two separate bipartite structures, one above and one below the Co atom [175] as a result of the spin polarization induced by the Co onto its 1 nn carbon ligands. (See figure 8). Pair of codopants can be also facilitated by the framework of the bipartite lattice to form bipartite chains of the codopants which could contribute to the establishment of the FMC among them. This, for example, is the case of the

defect pair (carbon vacancies and 2 + 2 cycloaddition bonds) chains which were identified as contributing to the observed magnetism in Rh- C_{60} [1].

Similar appears to be the case of the formation of bipartite codopant chains in DMS and TMO hosts as, for example, the bipartite chains:

$$\dots \text{Ga-N-Mn-N-Cu-N-Mn-N-Ga} \dots \quad (5)$$

formed by Mn and Cu codopants in GaN. These form the building blocks for the development of long range inter-dopant MC as will be discussed in sections 4.1 and 4.2. Interestingly, the bipartite pair chains are reminiscent of, on the one hand, the characteristics of the layered magnetic materials [185, 186] (see section 4.1.3) and, on the other hand, the McConnell's theory [53, 159] of magnetism of the charge-transfer organic salts.

3.5. Codoping and band gap engineering

The tremendous potentiality of the doping, derives from its possibility for enabling injection into a material either charge carriers (holes or electrons) or impurity atoms and impurity complexes (magnetic or non-magnetic) or even compound-dopants [190–202].

It should be noted that the doping with impurity atoms/complexes/compounds is associated with the development of impurity states formed within the energy band gap, thereby causing a shift of either the edges of the energy band gap and/or the Fermi level. As a result these processes have rendered doping as a powerful tool for engineering the band gap, especially that of the wide band gap materials. For example, it was experimentally demonstrated that in $(\text{GaN})_{1-x}(\text{ZnO})_x$ the gap value varies from 2.446 eV for $x = 0.0$ (GaN case) to 0.921 eV for $x = 0.5$ and finally approaching (after a small oscillation) the value of 1.568 for $x = 1$ (ZnO case [195, 203]), in agreement with the corresponding theoretical results [194, 198, 202]. This holistic response of a host to its doping is also found in the case of DMSs and TMOs doped with magnetic dopants as manifested by the reduction of their energy band gaps (compared to the undoped values) (see figure 9).

The non-intentional modification of the energy gap (in the case of magnetic doping), does not differ in origin from that of the intentional one which is employed, for example, in the search of new materials suitable for photoelectrochemical water splitting in the process for green energy (H_2) production [195, 198, 204–208]. That is, to bring the band gap to a value of ≈ 1.5 eV with band edges straddling the redox potentials of H_2O [122, 198, 202, 206, 207, 209–214]. Relevant to these problems is the specification of the band edges with respect to vacuum which appears to be a challenging theoretical problem. Theoretically, the band edges are usually obtained with empirical or semi-empirical methods. In particular, TB method is used to obtain firstly the position of the VBM within Harrison's method [92, 210], while the position of the conduction band minimum (CBM) is obtained by adding the energy gap value (experimental or theoretical) to the position of the VBM. In another approach, the CBM is identified firstly, in terms of the material's affinity energy [202, 212, 213], while

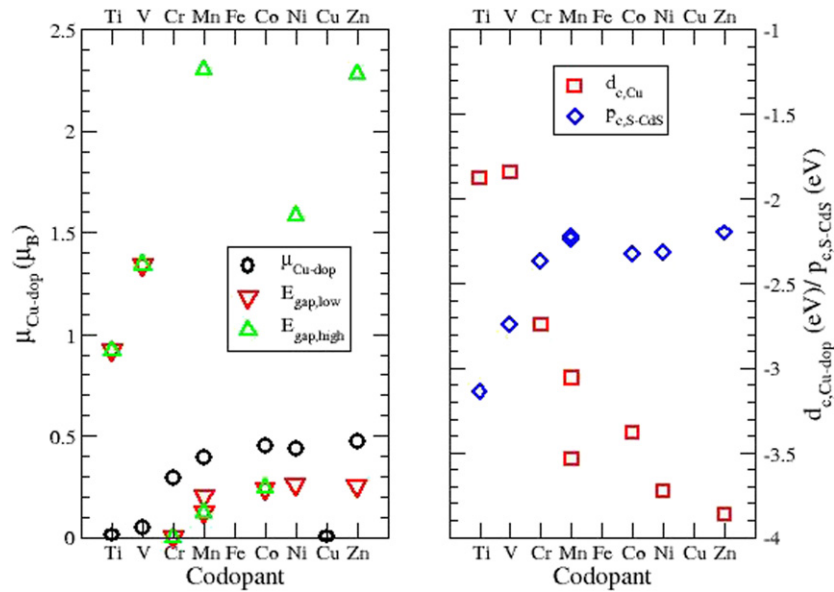


Figure 9. The $\mu_{\text{Cu}}^{\text{X,CdS}}$ (left) and $d_{\text{c,Cu}}^{\text{X,CdS}}$ (right) of Cu-dopants in $(\text{CuX})@\text{CdS}$, $\text{X} = 3d\text{-TM}$. Additionally, in the left panel we include the variation of the corresponding energy gaps for spin-up and spin-down electrons (indicated as low/high spins), while in the right panel we included the variation of the p -band center, $p_{\text{c,S}}^{\text{Cu,X}}$, of the S-anions upon codoping. Reproduced from [41]. © IOP Publishing Ltd. All rights reserved.

the VBM is obtained by subtracting the energy gap from the value of the CBM.

Experimental evidence derived from the intentional doping confirms the effect of the electronegativity of the dopants in band gap engineering. In particular, it was found that larger electronegativity mismatch between dopant and host atoms results in greater band gap reduction for the same amount of dopant concentration. For example, at 1.5% of N substitution in GaAs results in ≈ 220 meV band reduction, while 1.52% of N substitution in GaSb results in ≈ 320 meV band reduction [215]. This reaffirms the corresponding findings of the underlying electronegativity effect in the charge transfer processes observed in magnetic doping.

Analogous properties and similar nature are also encountered in the doping by donor-acceptor pairs, e.g. (N, Al) [205]. This is further supported by the observations in N-doped and (C, S) codoped TiO_2 materials, which shows that codoping utilizing the mediation of a double-hole coupling of dopants could lead to the formation of fully filled impurity bands lying above the VBM thus resulting in a much more effective band gap reduction than that induced by monodoping or conventional donor-acceptor codoping [189].

From a theoretical perspective, the band gap reduction is associated with electronic processes such as the conduction band anticrossing [216, 217] and valence band anticrossing [218–222] as well as the orbital rehybridization. The latter is due to the shift of the Fermi energy within an impurity band formed at the edge of the VBM. The former can be the result of strong coupling between the VBM states (respectively, the CBM ones) and those of the dopant. For example, antibonding pairing states, facilitated by lattice structure relaxations, hybridize with the lowest conduction band states of the host lattice and broaden into resonances causing the conduction

band and the spin density to delocalize over the pairs and the neighboring host atoms [188, 189, 198].

In addition to the gap changes upon doping, one also observes additional changes in the band structure around E_F that gives rise to interesting magnetic features in the doped materials transforming them into potential candidates for spintronics applications [223–228]. These include half metals [229–235], half semiconductors [231, 232], 2D-bipolar materials [230, 236, 237] etc.

4. Model approximations within codoping

The MC that is developed among the magnetic dopants in DMSs, TMOs, TM-dichalcogenides, carbon based materials, etc, has various contributions as referred to in section 2. The present review is focused on the newly proposed contributions related to codoping and the DIDM magnetism. These are the SSP (section 4.1) and the successive superexchange (section 4.2) Model contributions. Reference is also made to the carrier mediated MC (section 4.3) and the aspect of the molecular description (section 4.4).

It is worth mentioning that one of the basic issues of the defect-induced MC discussed in the present work is the spin polarization of the host anions which are 1 nn ligands of the magnetic defects. They mediate the MC among the dopants. The anion polarization is a manifestation of d^0 -MMs and hence that of the resulting d^0 -magnetism (in the absence of magnetic dopants) as discussed in references [1, 134, 238]. However, in the presence of magnetic dopants, the observed magnetism is more general than a pure d^0 -magnetism; it involves MC contributions like the superexchange, double exchange, etc, possibly mediated in some cases by d^0 -MMs (spin-polarized anions).

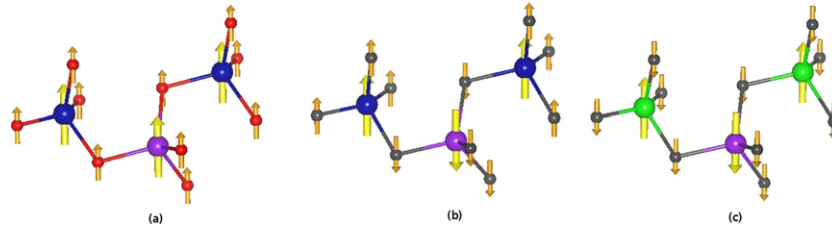


Figure 10. A close up view of the spin-polarized portions of (a) (CoCu)@ZnO, (b) (CoCu)@GaN and (c) (MnCu)@GaN in their FM configurations. The codoping Co, Cu and Mn as well as the host anions N and O atoms are colored in blue, violet, green, black and red, respectively. Copyright © 2016, IGI Global.

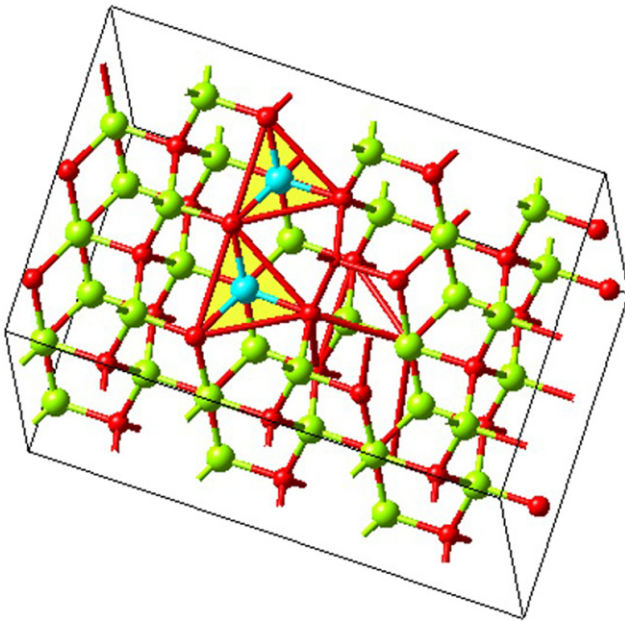


Figure 11. Tetrahedral neighborhoods around magnetic dopants within a unit cell of ZnO wurtzite structure in which two neighboring Zn atoms were replaced by Co atoms (shown in turquoise). Zn and oxygen atoms are shown in green and red color, respectively. The two tetrahedra share a common O-atom. Copyright © 2016, IGI Global.

4.1. Successive spin polarization (SSP) model

The SSP model suggests a possible way of how a long range MC can be developed among the magnetic (co)dopants. This is proposed in terms of the local magnetic interactions based on the mediating role of the dopant's anion ligands in the development of the MC among the dopants in DMSs and TMOs [3, 33–35, 37, 39, 41, 127, 169, 170, 175, 176, 239]. The emphasis is centered on the notion that the spin polarization induced by a dopant on its 1 nn anion ligands could dictate the magnetic behavior of a nearby dopant thus invoking a new and competitive MC contribution adding to the list of all possible ones.

According to this model, the long range MC results from SSP processes induced by the dopants on their 1 nn anion ligands forming segments of compatibly spin polarized dopants (see figure 10) [240]. The anion mediation is attributed to inherent properties of the *complex* (or the *radical*), formed by the dopant and its 1 nn anion ligands (see figure 11)

[240], namely those properties which characterize the strength, $J_{\text{eff}}^{sp-d}(\text{TM} - \text{an})$, which describes the MC between the *sp*-band of the host anions, an, and the *d*-band of the TM dopants (section 3.1).

Three example applications of the SSP-based MC between magnetic dopants will be discussed below. In particular, we will discuss the propagation of the MC in the monodoped systems, the codoped systems and the magnetic multilayers.

4.1.1. Monodoped systems. According to the SSP-model, in monodoped DMSs and TMOs, e.g. in $(\text{Co}_n)\text{GaN}$, $n = 2, 3, \dots$, the dopant Co_i induces spin polarization on its 1 nn nitrogen atoms which are thus aligned along the same (FM) or opposite (AFM) direction relatively to the orientation of the MM, $\mu_{\text{Co}_i}^{\text{Ga,GaN}}$ of Co_i as dictated by the exchange coupling $J_{\text{eff}}^{sp-d}(\text{Co}-\text{N})$ between Co and N [33–35, 37, 39, 140, 169, 176, 241]. When another Co_j atom finds itself in the neighborhood of the Co_iN_4 radical, the spin polarization of the nitrogen atom, N^* , which is common to both Co_i and Co_j will dictate the orientation of the $\mu_{\text{Co}_j}^{\text{Ga,GaN}}$ because the N^*-Co_j coupling is dictated by the dynamics of the radical (i.e. Co_jN_4) i.e. by the $J_{\text{eff}}^{sp-d}(\text{Co}-\text{N})$. As a result $\mu_{\text{Co}_j}^{\text{Ga,GaN}}$ aligns itself parallel to $\mu_{\text{Co}_i}^{\text{Ga,GaN}}$ i.e. Co_i and Co_j are ferromagnetically coupled. This inter-dopant MC is propagated successively along the Co radicals which come close together.

The described successive spin mediated interdopant FM coupling would have been the only coupling contribution in the absence of any other coupling mechanisms which favor, say, the AFM coupling between the two Co's. One major factor which determines whether the successive spin mediated FM coupling will prevail over all other mechanisms depends on the strength of $J_{\text{eff}}^{sp-d}(\text{TM}-\text{an})$, i.e. the exchange coupling between the *d*-band of the dopant and the *sp*-band of the host anions (see section 3.1).

The SSP-based MC is found to be enhanced in the case of the Co-doped graphene (see section 3.4 and figure 8) as in this case the SSP process is superimposed on the dynamics of the bipartite structure of graphene [175].

4.1.2. Codoped systems. Codoping is one way to override the outcome of the various coupling mechanisms in favor of the SSP contribution, i.e. to dope the host with two or more synergistic dopants. As an example, it is assumed that the system $(\text{Co}_n)\text{GaN}$ discussed in the above, is codoped with Cu

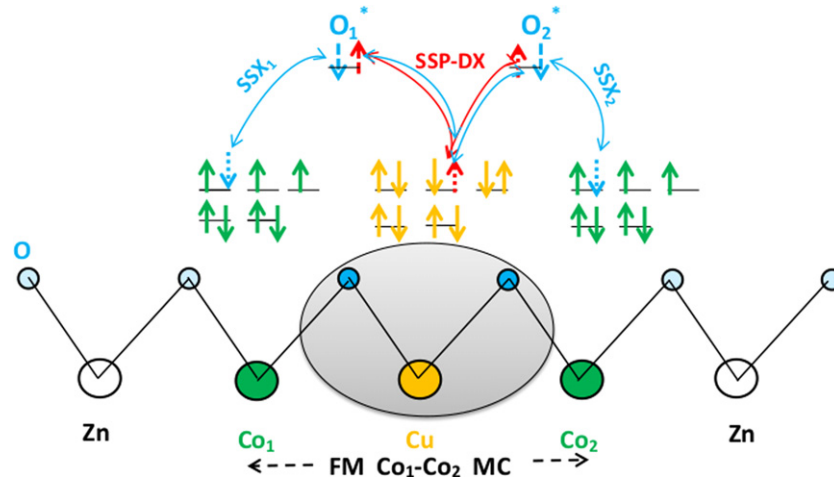


Figure 12. Schematic representation of part of the system $(\text{Co}_2\text{Cu})@\text{ZnO}$ focused in the neighborhood of the codopant complex Co_2Cu . The successive superexchange interactions SSX_1 and SSX_2 (between $\text{Co}_1\text{--O--Cu}$ and Cu--O--Co_2 , respectively) are shown in blue color, while the SSP double exchange interaction, SSP-DX , is shown in red color. The superposition of these interactions lead to the FM $\text{Co}_1\text{--Co}_2$ MC between two Co atoms (Co_1 and Co_2) mediated by a Cu-cation in ZnO and similarly in other hosts. Reproduced from [40]. © IOP Publishing Ltd. All rights reserved.

dopants. In this, a Cu dopant (*radical*) found in the neighborhood of two Co *radicals*, say Co_i and Co_j , could mediate the coupling between them by sharing with them common N^* ligands. Provided that $J_{\text{eff}}^{sp-d}(\text{Cu--N})$ is large enough, all the N anions which are 1 nn to the Cu dopant will have the same spin polarization as dictated by the dynamics of the radical CuN_4 (see figure 10). As a result, the common N^* anions (between Co and Cu dopants) will impose the same spin polarization on Co_i and Co_j thus providing a mediated FM coupling between them [34–37, 104, 117, 176].

It can be surmised that the SSP-derived MC is based on the dynamics of the radicals which are formed by each dopant and its 1 nn host anion ligands, (i.e. the corresponding J_{eff}^{sp-d} (dopant-anion) couplings) and highlights the local aspects of the MC which, in fact, is found to decay rapidly beyond the 1 nn. It is, however, part of the holistic response of the host to its doping as this is reflected in the system's holistic electronic properties (shifts of *d*- and *p*-band electron DOSs, implicit relationships between charge and spin accumulations, changes of the band gap, etc).

4.1.3. Magnetic multilayers. The SSP derived MC found in codoped DMSs and TMOs appears to be similar in nature to the observed oscillatory exchange coupling between successive 3*d* TM FM layers separated by a non-ferromagnetic metal layer (spacer).

According to the experimental findings of Samant *et al* [186] concerning the magnetic features of the Co/Cu multilayers the polarization of the Cu spacer is found to be concentrated near the Co interface. Its *d* component is parallel to that of Co and is almost entirely of spin character. It has a value of less than $0.05 \mu_B$ per Cu atom which varies as the inverse of the width of the spacer. Furthermore, the coupling between the Co layers is FM. From parallel theoretical investigation it was found that the sum of the Cu *s* and *p* spin moments at the Co–Cu interface, are opposite in sign to the Cu *d* moments. This difference in the behavior of the Cu spacer

in the Co/Cu multilayers from the corresponding one of the Cu codopant in $(\text{Co}_2\text{Cu})@\text{GaN}$ is striking and suggests the influence of the dimensionality and/or substrate/host dependence of J_{eff}^{sp-d} .

The proposed justification for the enhanced Cu *d* moment near the Co/Cu interface is attributed by Samant *et al* [186] to the considerable hybridization of the Cu and Co *d* orbitals near their interface and the development of *d* holes per Cu atom as its separation from the Co layers decreases.

It is apparent that the magnetic features found for the Co/Cu multilayers are mapped uniquely onto those of the corresponding codoped system, codoped with the same type of codopants (e.g. Co and Cu) within possible discrepancies due to the host-induced contributions.

4.2. Successive superexchange (SSX) model

The SSP-derived FM coupling (section 4.1) between two 1 nn magnetic dopants of the same type, namely M_1 and M_2 , is operated by just one host anion, A^* , which has the potential to dictate the same spin polarization on M_1 and M_2 . However, this is not always the case and the coupling can be found to be AFM as the result of other dominating MCs (e.g. superexchange [12]). Nevertheless, when a TM codopant, M_X , is interjected between M_1 and M_2 , the AFM coupling may turn to FM [33–37, 156, 169, 175, 176]. The role of M_X is still to mediate the coupling between M_1 and M_2 by letting one of its *d*-electrons to be shared by two of its own anion-ligands, namely the A_1^* and A_2^* , which are, respectively, common to the $(\text{M}_X\text{--M}_1)$ and $(\text{M}_X\text{--M}_2)$ pairs. Each of the pairs $(\text{M}_X\text{--M}_i)$, $i = 1, 2$, is coupled via a superexchange AFM coupling, SSX_i , $i = 1, 2$ (see figure 12). A *d*-electron of the M_X is shared between A_1^* and A_2^* forming an FM SSP Double Exchange coupling, SSP – DE, between them in a way analogous to the formation of the double exchange. As a result, each of the two anions A_i^* , $i = 1, 2$ will contribute a spin orbital of the same type in forming the corresponding

superexchange SSX_{*i*}, *i* = 1, 2 couplings leaving the dopants M_{*i*}, *i* = 1, 2, polarized along the same direction, i.e. coupled ferromagnetically.

The SSX mechanism is exemplified in the case of the codoped (Co₂Cu)@ZnO system and is schematically shown in figure 12 [40] illustrating the successive superexchange couplings with each one of the M₁ = Co₁ and M₂ = Co₂ dopants through common O-anions (O₁^{*} and O₂^{*}).

It is worthwhile to notice the difference between the SSP and the SSX-derived couplings. More precisely, in the former case, the MM, $\mu_{\text{COSP}}^{\text{host}} = 3 \mu_{\text{B}}$, while in the latter case $\mu_{\text{COSP}}^{\text{host}}$ could take values between 2 and 3 μ_{B} .

4.3. Carrier mediated magnetism

Free carriers (electrons or holes) in DMSs and doped-TMOs contribute to the MC among the magnetic dopants as mediating agents. They form the basis of Zener's double exchange model [56, 57] which in turn has been used as the basis for generalizations and extensions [12, 27, 242–244].

Due to the charge carriers, the magnetic interaction ($\mu_{\text{dop}}^{\text{X,host}} \cdot \mathbf{s}$), which is developed between the MM of the dopant, $\mu_{\text{dop}}^{\text{X,host}}$, and the spin, \mathbf{s} , of the carrier, perturbs the carrier wave functions in the following two pronounced ways:

- It polarizes the free carriers. The RKKY interaction is the result of this polarization (perturbation) at the level of the second order perturbation approximation [70–72].
- It drives one or more free carriers into hydrogenic orbits around the defects forming what is known as MPs. These in turns act as codopants mediating the MC among the magnetic dopants [6, 27, 28].

Both processes, i.e. the spin polarization of the carriers and the formation of the MPs, correspond to higher electron-correlation terms which are usually approximated within various perturbational schemes such as the RKKY picture [70–72] and the standard MFT [15, 75, 245–249].

For carrier densities less than $1.3 \times 10^{18} \text{ cm}^{-3}$, the doped specimens exhibit an insulating phase (I-phase), while for carrier densities greater than 10^{20} cm^{-3} the specimens have a metallic phase (M-phase). Interestingly, both insulating and metallic phases exhibit magnetic features. It has been argued that when the range of carrier densities is between $1.3 \times 10^{18} \text{ cm}^{-3}$ and 10^{20} cm^{-3} , the specimens are not magnetic [15, 27, 248]. However, Xu *et al.*, have reported the observation of a strong positive (negative) magnetoresistance for carrier concentrations smaller (greater) than 10^{19} cm^{-3} .

The magnetism of the M-phase is generally explained along the standard MFT for DMSs [15, 75, 245–249]. According to this theory, the exchange is maximized when the ratio $\frac{n_{\text{c}}}{n_{\text{i}}}$ (that of the carriers n_{c} to the magnetic ions n_{i}) is between 0.3 and 0.5. More precisely, the localization of the carrier wave function depends crucially on the carrier concentration, n_{c} , through which the mean distance, r , between carriers is specified. According to the theory of the *n*-type semiconductors [15, 166, 248], the critical concentration n_{c} at which the metal–insulator transition takes place is determined from the relation $r = a_{\text{B}}$, where a_{B} is the effective

Bohr radius. From the relations: $n_{\text{c}} = \left(\frac{3}{4\pi a_{\text{B}}^3}\right)^{1/3}$ one obtains $n_{\text{c}}^{1/3} a_{\text{B}} = 0.24$ [249].

In the absence of extra carriers as, for example, in the (Co)@ZnO case, the MC could be mediated by the delocalized Zn(4*s*) and Co(4*s*) electrons which form the conduction bands. The derived AFM MC, between the magnetic dopants in this case has local (intrinsic) character and should be distinguished from the carrier mediated coupling which can be considered as being of non-local (extrinsic) character.

The AFM coupling found between the Co dopants (in (Co)@ZnO) within DFT can be turned into FM by codoping the system with extra carriers. However, the onset of ferromagnetism is not correctly described. This is attributed to the limitations of the DFT/GGA or DFT/GGA + *U* approaches (i.e. band gap, energetics of the impurity band estimations etc), which hamper the validity of the conclusions of the band description of magnetism [85].

4.4. Molecular orbital description of the effective exchange interaction

As referred to in the multi-reference model approximations (see section 2.1), kinetic exchange models employ the MO description of the MC. A characteristic example is the calculation of the effective exchange interaction, J_{eff} , between free organic radicals exhibiting non-zero-spin states as proposed by Yamaguchi *et al* [52, 53, 187, 250]. Such a description resolves the MC into its two major contributions, namely the one due to charge transfers and the other to spin density transfers. In particular, according to this approximation, J_{eff} has two major contributions; the overlap-orbital (OO) denoted as $J_{\text{eff,OO}}$ and the spin-density-product one denoted as $J_{\text{eff,SDP}}$. The former ($J_{\text{eff,OO}}$) is dominated by the charge transfers (among the frontier singly occupied molecular orbital (SOMO) and its associated unoccupied molecular orbital, and contributes an AFM term—the overlap between SOMOs leads to AFM coupling; the other, $J_{\text{eff,SDP}}$, owes its origin to the spin transfers induced by spin-polarization and adds up an FM term. In most of the cases $J_{\text{eff,OO}}$ outweighs $J_{\text{eff,SDP}}$. It is thus clear that charge transfer and spin localization processes are in a sense the prerequisites for establishing MC within the MO description.

The MO-based models are usually computationally demanding calculations and are mostly applied to small systems (molecules, clusters).

5. Conclusion

In the present review, we have attempted to summarize the basic inherent components of the problem associated with the defect-induced magnetism in monodoped and codoped DMSs and TMOs. Among the identified components of the problem, we have discussed its local and, at the same time, its holistic aspect as well as its synergistic and bipartite features.

Theoretical and experimental evidence have been presented in elucidating the characteristics of each of the identified components of this problem. Furthermore, emphasis has been placed in the local aspects of the problem and the way they propagate and form long range magnetic interactions. We have brought attention to the newly proposed models for the MC propagation, namely the (SSP) and the (SSX) models. Both of these models are found to promote the FM coupling via the codoping process through the synergy of simultaneous two or more dopants. The resultant magnetism can be attributed to the result of defect-induced defect-mediating (DIDM) doping process i.e. the synergy among the codopants.

We have also demonstrated that the dynamics of the DIDM magnetism is facilitated by any existing inherent bipartite lattice structure and, therefore, retains similarities with model descriptions of magnetic phenomena covering large groups of systems like the DMS, TMO, TM-dichalcogenides, carbon based materials, magnetic multilayers, etc.

The holistic aspect of the defect-induced and/or the DIDM magnetism is found to be reflected in the changes of the band structure (band gap) and the relative position of the *d*- and *p*-band electron DOS of the system with respect to the Fermi level, E_F . These, in turn, affect both the intrinsic and extrinsic magnetic features (MMs, DOS at E_F , spin polarization processes) of the system.

The present review sheds a new light onto the coupled and implicit electronic processes which adds new contributions to the development of the MC among the dopants and provides a valuable addition to the existing efforts to fully understand the nature of the magnetism in DMSs and doped TMOs.

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