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Defect-induced magnetism: Codoping and a prescription for enhanced magnetism

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Abstract

Recent works have given indication that the defect induced magnetism in diluted magnetic semiconductors (DMSs), transition metal oxides (TMOs) and related materials is facilitated and enhanced by codoping and the synergistic action among the codopants. In the present work, we demonstrate that the proposed defect-induced ferromagnetic coupling (FMC) exhibits the following features; *bipartition, synergy and locality* and is based on the formation and interaction among spin-polarized neighborhoods analogous to spin-polarized radicals centered at the codopant sites. The FMC is mediated by the molecular orbitals (MOs) of these *radicals* and is greatly facilitated if the codopant-centered *radicals* could form bipartite configurations within the host lattices. Within this picture, the origin of magnetism in DMSs and TMOs appears to be the synergy and the interplay between correlated spin-polarization processes that take place in a successive way within neighborhoods centered at the codopants and include their first nearest neighbors (1nn's). The proposed model can be used as a practical guide for choosing the appropriate pair of codopants for a specific semiconductor environment that can lead to the fabrication of DMSs and TMOs with enhanced magnetic properties.

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I. INTRODUCTION

Our early study of the magnetism of RhC_{60} and other carbon-based materials¹ suggested that the origin of this magnetism is the result of the synergistic action of defect-induced electronic processes, mostly of local character, which can provide magnetic moments as well as develop their ferromagnetic coupling (FMC). In particular, it was proposed that this synergy is realizable via *codoping*, ie., in the presence of two kinds of defects which have complimentary actions. That is, defects of one kind are able to provide the magnetic moments, while defects of the other kind contribute to the development of the FMC among the magnetic moments. (In the following the term *defect* will be used to denote any structural and/or topological and/or impurity-atom defects).

Contemporarily, there was experimental and theoretical evidence suggesting that the magnetism in the diluted magnetic semiconductors (DMSs) could be enhanced by *codoping*. In particular, enhanced magnetic features were observed in, among others; ZnO codoped with $(\text{Fe,Cu})^{2,3}$, $(\text{Fe,Co})^3$, $(\text{Co,Cu})^{4,5}$, $(\text{Co,Li})^{6,7}$, $(\text{Co,N})^8$, $(\text{Co,H})^9$, $(\text{Co,Al})^{10}$, $(\text{Co, O-vacancies})^{11}$, $(\text{Mn,Sn})^{12}$, $(\text{Mn,Co})^{13,14}$, $(\text{Mn,N})^{15}$, $(\text{Mn, O-vacancies})^{16}$, $(\text{Mn,C})^{17}$. Analogous findings were reported for GaN codoped with (Mn,Co) and $(\text{Cr,Mn})^{18}$; in Cr:TiO_2 and Mn:GaAs for which the magnetic enhancement was attributed to $p-d$ hopping interaction¹⁹ while in TiO_2 ²⁰ it was attributed to non-compensated $n-p$ doping²⁰, or the passivation of codopants $(\text{Mo,C})^{21}$,

Despite the numerous reports on the advantages of codoping in improving the magnetic features of the DMSs and those of the transition metal (TM) oxides (TMOs), our understanding about the origin of their magnetism is far from satisfactory. The majority of the proposed explanations is focused on processes related to a carrier mediated interaction among the cationic magnetic impurities, which is traditionally explained in terms of the double exchange, or the superexchange, the $s-d$ or the $p-d$ exchange interaction etc, either within the band or the atomic orbital description (see, for example, Ref.²² and references therein).

Our subsequent investigations seemed to reveal codoping to be a general and generic approach that underlies the appearance of magnetism in a diverse sample of systems including carbon-based materials, codoped wide band gap semiconductors and transition metal oxides (e.g., ZnO, GaN, TiO_2) as well as other III-V and II-VI materials. Further support

to this observation came from our findings that *bipartite* configurations of the codopants can improve significantly the magnetism in these materials.

This led to the suggestion^{1,23–26} that the enhanced magnetism found in bipartite codopant structures we studied [(Ti(3Co,2Cr)O₂, Ga(Co,Cu)N, Zn(Co,Cu)O and Ga(Mn,Cu)N) as well as C-based materials], is reminiscent of proposed bipartite model descriptions spanning a diverse sample of electronic processes considered to have a leading role in developing magnetic features. The models referred to in this context included the following:

Lieb²⁷: This model has found applicability in carbon based magnetic materials as demonstrated by Ovchinnikov²⁸. On the other hand, in the case of DMSs and related materials, it could be generalized by extending its applicability in the case of bipartite embedded structures. That is, in cases where the dormant bipartite structure of the original Lieb model is substituted by its *embedded* analogue in a host environment.

Roth²⁹: This model 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^{30–32}. This is found in the case of a system exhibiting 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 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^{33–35}: This model is known as the McConnell-II model and was proposed to explain the ferromagnetic charge-transfer salts. Specifically, this model predicts that an ionic (bipartite) material D^+A^- built up from positive ions of the donor molecules D and the negative ions of the acceptor A can exhibit a ferromagnetic (FM) ground state if either the donor or the acceptor molecule have a triplet neutral ground state. In such a case back charge transfer mixes the neutral triplet ground state with the triplet charge transferred state of the ionic state leading to a FM coupling.

Pairing models: These include the recently proposed two-center assisted model of blocked superparamagnetism proposed by Pemmaraju *et al.*³⁶ and that proposed by Wu *et al.*³⁷ who considered the pairing interactions between (mono)dopants as the leading processes in the development of *defect*-magnetism.

II. BASIC FEATURES OF THE FMC: BIPARTITION, SYNERGY AND LOCALITY

In addition to the bipartite feature that was traced, two additional features were also found to be common in the materials we studied. The first is the synergistic action of the codopants in establishing the FMC, and the other being the local character of the major electronic processes which seem to underlie the development of magnetism. Thus, *bipartition*, *synergy* and *locality* have been found to play dominant roles in the development of magnetism in DMSs, TMOs and related C-based materials. These features are further discussed in the following.

A. Bipartite character

In the models described above, the bipartite character in the systems may manifest as either intrinsic or extrinsic and 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. In particular:

In carbon based materials (graphite, graphene, C₆₀-based structures, etc), the defects interrupt the perfection of the bipartition and thus provide unpaired electrons for generating the magnetic moments. Another type of defects are required to provide the FMC among the magnetic moments. As an illustration of this process we invoke the case of the C₆₀-based polymers codoped with carbon vacancies. In this material, the carbon vacancies provide the magnetic moments while the 2+2 cycloaddition bonds contribute to the establishment of the FMC among them¹.

It should be noted that the orbital ordering model, as in Lieb's description, does not require a spatial ordering. In some cases, the lattice relaxations of Jahn-Teller form are found to underlie the establishment of the bipartite structure³⁰⁻³²

In the McConnell-type systems, the intrinsic bipartite structure is modified by the charge transfer processes. The effective exchange interactions (J_{ab}) between free radicals can be considered as consisting of two major contributions, i.e.,

$$J_{ab} = J_{ab}(OO) + J_{ab}(SDP), \quad (1)$$

where $J_{ab}(OO)$ and $J_{ab}(SDP)$ denote the orbital-overlap (OO) and spin-density-product

(SDP) terms, respectively³⁸. The former is responsible for the AFM coupling contribution to J_{ab} , while the latter for the FMC contribution. Both of these terms can be approximated in terms of the single occupied molecular orbitals (SOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the radicals³⁸.

B. Defect synergy

From all these models, it becomes apparent that the defects activate potential (existing or hidden) bipartite structures and make them amenable to magnetic features. *Codoping* appears as one of the fundamental processes which provides the means to achieve this. That is, upon codoping, the codopants (defects) of the one type interrupt the (intrinsic or extrinsic) bipartite picture leading to the development of magnetic moments which can either be of extrinsic type (ie., provided by magnetic impurities) or of intrinsic type (ie., resulting from lattice relaxations or the hybridization of the dopant and host orbitals). These, in turn, can be coupled ferromagnetically with the mediating services of another type of codopant (defect)^{1,23–26}. One can, thus, invoke the existence of a dormant bipartite structure with the potential to get activated in the presence of the appropriate codopants. This appears to be a common factor in both the above listed models and in the C-based materials, the DMSs and the TMOs studied by us which were found to exhibit defect-induced magnetism. Codoping, thus, can be viewed as a generic approach to the development of magnetism in materials which exhibit potential bipartite structure. This view is entirely different from other pictures according to which the codoping has been considered as a possible way to tailor the position and the occupancy of the Fermi energy, (E_F), of the DMSs^{39–44}.

Comparing DMSs and/or TMOs with the simple ...*ABABA*... bipartite model systems described above, it can be seen that the bipartite structure of the former is a generalization of the latter in the sense that the *A*, *B* lattice sites of the simple models now take the form of clusters of atoms (A^* , B^*) in DMSs and TMOs with each cluster (A^* or B^*) centered at a codopant site and surrounded by its first nearest neighbors. As a result, the numeric parameters describing the simple models (i.e., on-site and inter-site as well as the Coulomb intra-site energies) take the form of matrices in the generalized model. The estimation of these matrices is based on the processes underlying the synergy that is provided by the codopants. In analogy with the description of the McConnell systems, these matrices may

be approximated in terms of the SOMOs and LUMOs of the clusters A^* and B^* (the *radical like* complexes) formed by each codopant and its first nearest neighbors.

The synergistic response of the codopants, is the result of electron-electron correlations which manifest themselves by electronic processes such as charge transfers, (re)hybridizations, induced spin-polarizations, etc. The key process, however, which dominates in the development of the FMC among the magnetic moments, is system specific; it depends on the symmetry of the host material, its electronic band structure, the formation of the impurity states/bands, the type of the codopants, their charge (cationic/anionic) and magnetic state, their concentration.

It is the objective of the present work to uncover the key electronic processes which are underlying the development of magnetic features in DMSs and TMOs.

C. Local character

The significance of local processes taking place in the neighborhood of the codopants towards providing a major contribution to FMC has been highlighted in various reports. For example, Ye *et al.*¹⁹ found that in the case of ZnO doped with Cu, the magnetic moments are localized within the CuO_4 tetrahedron with ferromagnetic coupling between Cu and O emerging from the hybridization of the Cu-3*d* and O-2*p* bands. Similarly, in Li doped VO_2 , the very unusual low-spin VO_2 behavior was attributed to the formation of nanosize interacting ferromagnetic spin clusters around intercalated Li ions⁴⁵. Furthermore, the localized character is inherent in the recently proposed two-center assisted model of blocked superparamagnetism proposed by Pemmaraju *et al.*³⁶. Finally, strong evidence for the inherent localized character of the FMC is provided by the McConnell magnets in which the FMC has been shown to be a property of the SOMOs and LUMOs derived from their constituent radicals.

III. PROPOSED NEW UNDERSTANDING OF THE NATURE AND ORIGIN OF THE FMC

In this section we propose a new understanding of the nature and origin of the magnetism in DMSs, TMOs and C-based materials. Our proposed explanation is based on the observed

features from an analysis of a vast amount of computational data. In the following, we explain this in the framework of locality, the synergy and the bipartition properties which were found to accompany the magnetic properties of these systems.

The local character of the FMC is mainly associated with electronic processes that are localized within neighborhoods centered on the codopant (defect) sites (the clusters A^* and B^*). Each of these neighborhoods includes the codopant and its first nearest neighboring (1nn) anions. The synergy refers to the synergistic action of the codopants which is realized with local spin-polarizations induced on the starred-clusters. The bipartition appears to enhance the synergy facilitating the development of spin polarized molecular orbitals (MOs) which exhibit contributions from the anions surrounding the codopants. In the present 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 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 of a codopant to be spin-polarized in the same direction²⁶.

Although these anion polarizations could lead to a *local delocalization* (i.e., of finite range), this does not seem to lead to a significant contribution to FMC. Thus, our findings, while not ruling out the possibility of remote MO-overlap and/or the carrier mediated coupling (e.g., double exchange, superexchange, $p - d$ exchange, etc) among the magnetic cations, demonstrate that the FMC accommodates additional significant contributions derived from localized spin-polarizations of the anions belonging to neighboring codopants.

A. Computational details

We performed extensive calculations for representative systems that included ZnO, GaN and TiO₂ codoped with various pairs of codopants. 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 approach⁴⁶ as implemented in the Vienna Ab-initio Simulation Package (VASP)^{47,48}. We use $U=U_{d,Ti}=9.26$ eV for rutile TiO₂ for the Ti(3d) which reproduced the experimental gap (3.0 eV^{49,50}) and $U_{d,Cr/Co}=5.5$ eV for Cr and Co codopants. For ZnO and GaN, we used $U_{d,Zn}=10.5$ eV; $U_{d,Ga}=6.5$ eV, $U_{p,O}=7.0$ eV and

$U_{p;N}=4.25$ eV, while $U_{d;Mn}=5$ 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 (see Fig. 1). TiO_2 is taken to be in rutile structure using a supercell consisting 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 5 dopant-atoms were used for ZnO and up to 7 for GaN and TiO_2 . A $2\times 2\times 2$ Γ -centered pack of \mathbf{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 specified by the covalent radii of the elements) as outlined in the VASP code. More computational details can be found in Refs.^{1,23–26,51–53}.

B. Anion polarization

As stated in the above, the polarization of the anions is a key ingredient in the development of magnetism. This is dictated to a large extent by the cation to which the anions are first nearest neighbors (1nn) and the local symmetry in the neighborhood of the cation. The latter dictates the hybridization of the anionic and cationic electronic orbitals, while the former dictates the rehybridization processes that take place within the tetrahedron centered on the cation and surrounded by its 1nn.

From our *ab initio* calculations it was found that isolated Co and Cu dopants, acting as substitutional cationic impurities in ZnO, induce spin polarization on their 1nn O-anions. This leads their 1nn anions to align their magnetic moments parallel to that of the dopant (see Fig. 2a). Similar behavior was found when Cu and Co act as isolated substitutional impurities in GaN. That is, they polarize their 1nn N-anions so that their magnetic moments align parallel with respect to that of the dopants (Fig. 2c). In contradistinction with Cu and Co, Mn acting as a substitutional impurity in GaN, polarizes its 1nn N-anions in an anti-parallel way (Fig. 2c). In the case of codoping in which the codopants are found in neighboring tetrahedra, the polarization induced on the 1nn of the codopants may retain the picture of the isolated dopants only if there is compatibility of the induced polarizations on their common 1nn anions. That is, as far as each codopant develops a strong bonding

with its 1nn anions and can support the polarization that induces on them acting alone. Otherwise, the anion that is common to two codopants may attain a spin direction which it finds energetically more favorable(Fig. 2b). It is thus apparent that the strength of the anion-dopant bond plays a key role in the outcome of the direction of the spin-polarization of the anion which is common to two codopants. As will be discussed in the following, the polarization of this common anion can dictate the orientation of the magnetic moments of the neighboring codopants.

C. Coupling among spin-polarized neighborhoods

Let us compare the codopant-mediated interaction between two Co atoms in the following two cases:



and



that is, in segment-3 the mediated segment is $O - Cu - O$ while in segment-2 the mediation takes place by only one Cu atom.

In the case of segment-2, the $Co - Co$ interaction depends on the intersite (hopping) integral, t , the on site energies of the electrons and the total number of valence electrons. These parameters specify the electronic structure of the segment and offer a rough estimate of the total electronic energy of the ground state (assumed to be the sum of occupied electronic states) and, therefore, can specify which of the FM or the AFM state will be the energetically more favorable state.

The situation is much more different in the case of the mediating segment-3 (Fig. 2b). In this case, the key role underlying the mediated $Co - Co$ interaction should be sought in the electronic processes that take place in the segment



connecting the Co-cations. Due to the induced spin-polarization experienced by the O-atoms because of their neighboring with the Co atoms, the Cu atom is found with first nn's which are spin polarized. The question that arises then is whether the spin-polarized Cu-O₄ complex can be energetically stable while accommodating the O-atoms with parallel,

antiparallel or randomly oriented magnetic moments. It is apparent that if the Cu-O₄ complex can accommodate O-atoms with parallel (antiparallel) magnetic moments, the coupling between the Co-atoms will be (in both cases) FM. This type of exchange interaction can be considered as a sort of generalized double-exchange/superexchange that we have termed *grand double-exchange/superexchange interaction*⁵².

As noted in the above, in ZnO doped with Cu, the magnetic moments are localized within the CuO₄ tetrahedron with ferromagnetic coupling between Cu and O¹⁹. The FM Co–Co interaction in Zn(Co,Cu)O may then be explained as follows, assuming that the codopants form segments of the form shown in Fig. 2a: One Co atom, to be denoted as Co_1 , spin-polarizes its 1nn O-anions which align their magnetic moments parallelly to that of Co_1 . One of these O-anions is 1nn to Cu as well. However, all O-anions which are 1nn to Cu favor their FM alignment with Cu¹⁹ and, therefore, their FM alignment with the other 1nn O-atoms to Cu. One of these 1nn of Cu is also 1nn of the other Co atom, to be denoted as Co_2 . Due to the fact that Co spin-polarizes its 1nn-anions ferromagnetically, it is the polarization of this O-atom induced by Co_1 (via Cu), that *dictates* the direction of the magnetic moment of Co_2 . Thus, Co_2 becomes aligned ferromagnetically with respect to Co_1 in order to retain the energetics within the CuO₄ tetrahedron. It is apparent however, that the proposed picture for the ferromagnetism is the result of the interplay between the energetics that take place in the nearby CuO₄ and the CoO₄ tetrahedra.

The same mechanism can be proposed to justify the ferromagnetism in Ga(Mn,Cu)N, Ga(Co,Cu)N and Ti(Cr,Cu)O₂^{53–55}. As stated in Sec. IIIB, contrary to the case of Zn(Co,Cu)O, in Ga(Mn,Cu)N the Mn-induced spin-polarization on its 1nn N-atoms is such that the magnetic moment of Mn is aligned antiparallelly with respect to that of the induced magnetic moments on its 1nn N-atoms as shown schematically in segment 5 and Fig. 2c.

$$Mn - N - Cu - N - Mn \quad (5)$$

Despite this difference, it is found that in the CuN₄ unit the Cu-atom and its 1nn N-atoms are spin-polarized ferromagnetically in a compatible way with the spin-polarizations that take place within the MnN₄ units. On the other hand, in the case of AFM Mn-Mn coupling between the Mn-atoms of segment 5, it is found that all the atoms of the CuN₄ unit exhibit no-spin polarization. Furthermore, our results have shown that the strength of the FMC is found to depend on the way the codopant segments are developed and oriented within the

host lattices⁵³.

The above proposed picture for the FMC in DMSs and TMOs has similarity with what was proposed for the FMC among Co-atoms adsorbed in graphene vacancies⁵⁶.

The case of Ga(Co,Cu)N is even more interesting. As shown in segment-6 and Fig. 2b,



the 1nn N-anions of each Co-cation are not all polarized along the same direction. In particular, the N-anions which are common to both Co and Cu prefer the orientation induced by the Cu-cation. Thus, the Cu-cation appears FM aligned with all its 1nn while the Co-cations have 1nn with mixed orientations.

While these results demonstrate the role the local energetics (those within the tetrahedra centered on the codopants) play in the development of the exchange coupling between the magnetic cations, they also indicate the importance of the compatibility of the spin-polarizations that are induced by the specific codopant pairs.

It is worth noting that the single anion mediated interaction between two magnetic cations (as, for example, in the segment $Mn - O - Mn$) leads in many cases to their AFM coupling, while the corresponding interaction between these two magnetic cations turns to be FM if mediated by a codopant segment (as, for example, in the segment $Mn - O - Cu - O - Mn$ of Fig. 2c). It is thus observed that the effect of the codopant (the Cu atom in this example) is to reduce or eliminate the superexchange interaction and replace it with a generalized exchange interaction which, instead of being mediated by a single O-anion, is now mediated by a cluster of O-anions surrounding a cationic codopant. In the former case (ie, in $Mn - O - Mn$), the spin of the orbital of the mediated O-anion, which makes a bond to the Mn-cation, dictates the polarization direction of the Mn. That is, the spin-up O(p)-orbital makes a bond with a spin-up Mn cation orbital and the spin-down O(p)-orbital bonds to a spin-down Mn cation orbital (superexchange). On the other hand, in the latter case, all O-anions surrounding the Cu-cation all have the same spin-polarization and, therefore, they make bonds to Mn atoms of the same polarization (provided that bonding orbitals of the magnetic impurity are available for bonding as in the case of Mn).

IV. APPLICABILITY OF THE PROPOSED MODEL

The proposed model, while providing an explanation for the development and the origin of magnetism in DMSs, TMOs and C-based materials, can also provide a means for choosing the most appropriate pairs of codopants that can induce enhanced magnetic features in these materials. It is apparent from segments 3, 5 and 6 that enhanced ferromagnetism can be expected if the codopant-induced spin-polarizations on the host anions are parallel among themselves and at the same time there is compatibility between the polarizations induced by a chosen codopant pair. The prescription this leads to is very simple. Choose codopant-pairs which induce parallel spin-polarization on their 1nn-anions in a given host and, while at the same time the codopants are able to develop parallel alignment among themselves within the given host environment. Such a choice can be facilitated by taking into account the available bonding electrons of the codopants and their ability to bond to the anions of the given host. This is exemplified in Fig. 3 for the (Mn,Cu) pair of codopants in GaN.

It is apparent from Fig. 3 that in GaN the Mn-cation will bond to one of its 1nn N-anions through a sharing of one of its e_g electrons. Due to intra-atomic exchange the d -electrons of the Mn are all spin-polarized parallelly (Hund's rule). As a result, the shared e_g electron of Mn dictates the spin-polarization of the bonding electron of the N-anion (Mn's 1nn) and through which it dictates the spin-polarization of the bonding electron of the other codopant which, now has to be able to provide bonding electrons with the proper spin-polarization to the N-anion which is common to both codopants. This type of analysis can help us in choosing the optimum pair of codopants. The reasoning proposed suggests that the (Co,Cu) pair should be more efficient for codoping GaN than the (Mn,Cu) pair because the former pair leads to FM alignment of the codopants, in contradistinction to the AFM alignment of the (Mn,Cu) pair. This, in fact, has been justified by our *ab initio* calculations according to which the magnetic moment per unit cell of the Ga(2Co,Cu)N ($7.41 \mu_B$) is found to be greater than that of Ga(2Mn,Cu) ($5.85 \mu_B$). This is despite the fact that the magnetic moments of the Mn-cations are much larger than those of the Co-cations⁵⁴.

Investigating further our proposed model, we show in Table I the spin-polarizations of the 3d TM-series along with the spin-polarization they induce on their 1nn anions if these TMs are used as substitutional impurities in ZnO and GaN. From this Table it can be observed that the 3d-TMs substituting Zn in ZnO induce spin-polarization on their 1nn

which is parallel to their own. Exception appears to be the Ti dopant. In GaN, on the other hand, we find, in agreement with Ref.⁵⁷, that TMs of the early (late) 3d-series, used as substitutional impurities for Ga, induce spin-polarization that is antiparallel (parallel) to theirs. In Fig. 4 we present magnetization density isosurfaces for the two types of induced spin-polarizations, represented by Ga(Ni)N and Ga(V)N.

From the results of Table I, and based on spin-polarizations, it can be expected that the codopant pairs (TM,Cu) of Cu with any of the late 3d TM-elements could be more suitable for producing DMSs based on ZnO, while the use of the (TM,Cu)-pairs for codoping GaN is not expected to be as effective due to the anti-parallel polarizations of TM and Cu. Furthermore, the results of Table I also suggest that codoping of GaN with the codopant pairs (Fe,Cu) and (Ni,Cu) could lead to a similar behavior to that obtained with the (Co,Cu) pair, while doping GaN with (V,Cu) or (Cr,Cu) is expected to give similar results as the codoping with (Mn,Cu).

It should be emphasized that the above criteria can constitute the basis for a first screening among possible pair of codopants. However, the relative orientation of the magnetic moments of a codopant pair (M,N) is a delicate interplay of energetically competing processes as explained below. In particular, in addition to the spin-polarization induced by the codopants on their ν 1nn anions, X, key factors which dictate the magnetic interaction between the codopants are the hybridization and the charge transfer experienced by the codopants within the given host and, in particular, within the tetrahedra MX_ν and NX_ν . These processes depend on the distance between the MX_ν and NX_ν neighborhoods. If the MX_ν radical is a neighbor to NX_ν , the direction of the spin polarization of N relative to that of M (or vice versa) depends (as stated in the above) on the spin-polarization that will be adopted by the anion X^* which is common to both M and N. This in turn depends on the hybridization and the relative stability and the energetics of the available spin-configurations of the $MX^*X_{\nu-1}$ and $NX^*X_{\nu-1}$ complexes within the given host. The energetic competition between these processes determine the eventual line-up of the hybridized levels of the $MX^*X_{\nu-1}$ and $NX^*X_{\nu-1}$ complexes.

Let us take the system Zn(Co,Cu)O as an example. In ZnO, both Co and Cu have similar behavior (see Table I); they induce magnetic moments on their 1nn anions which are parallel to their own. This then leads to the expectation that neighboring CoO_4 and CuO_4 tetrahedra (complexes/radicals) will all have their magnetic moments parallel (FM

interaction). However, this is not always the case and it may happen that Co and Cu have their magnetic moments aligned anti-parallelly (AFM interaction). This is because of the nearly filled d -orbitals of Cu and the fact that in this case the spin-up and spin-down configurations of the Cu^{2-q} cation ($0 \leq q < 1$), are almost isoenergetic for large enough q -values. In addition to this observation one also needs to consider the criteria that the hybridization energy levels of the CuO^*O_3 complex should be lined-up with the corresponding ones of the CoO^*O_3 complex. It is the energy difference between these two processes ie, the line-up of the hybridization levels and the spin-flip of the $\text{Cu}^{2-q}\text{O}^*\text{O}_3$ complex that specify the relative orientation of the magnetic moments of neighboring Cu and Co codopants. This is the reason why the magnetic coupling of the CoO_4 and CuO_4 tetrahedra may be found in either FM or AFM within the DFT/SGGA+U theory, as one varies the Hubbard-U parameter for the $\text{Cu}(3d)$ -electrons.

V. ANALYZING FURTHER THE RESULTS OF TABLE I

Comparing the direction of the induced spin-polarization of the 1nn anions of the codopants, in both ZnO and GaN (shown in Table I), it is noted that this is correlated with the electronegativity, E_N , of the codopants thus underlying the role of the charge transfer processes which follow the doping. In particular, regarding the doped ZnO, it is observed that $E_N(\text{Zn})$ is almost equal to or smaller than $E_N(X)$ where X is a TM of the $3d$ -series with the exception of Ti, which appears to spin-polarize its 1nn anions anti-parallelly. For all the other $3d$ cations it is observed that they spin-polarize their 1nn-anions parallelly. It is worth noting that, in cases for which $E_N(\text{Zn})$ is approximately equal to that of the TM-dopant, the magnetic moments of the 1nn O-anions are almost zero. This can be attributed to the minimal charge transfer which allows the O-anions to keep their p -shells closed (O-anions are doubly negatively charged). As $E_N(\text{Zn})$ becomes smaller than $E_N(X)$, the magnetic moments of the O-anions which are 1nn to the dopants increase possibly due to a charge transfer.

Analogous picture can be seen in the case of the GaN host. That is, $E_N(\text{Ga})$ appears greater (smaller) than that of the early (late) $3d$ -TMs and, correspondingly, the early $3d$ -TMs induce anti-parallel (parallel) spin-polarization on their 1nn N-anions.

It is apparent that the magnetic moments of the dopants are related to their d -filling

factor as shown in Fig. 5. In Fig. 5, we have also included results for the magnetic moments obtained from codoped systems. As can be observed, the magnetic moments of monodoped and codoped systems are almost equal. This indicates that the magnetic moment of each dopant is mainly the result of local processes which take place in the neighborhood of the dopant thus supporting the *locality* aspect of the magnetic features of DMSs discussed in section II C.

Furthermore, we observe in Fig. 5 some variation trends for the magnetic moments which reflect their dependence on the semiconductor host. These trends are described as follows:

$$\mu_{early-TM}^{ZnO} > \mu_{early-TM}^{GaN} \quad (7)$$

and

$$\mu_{late-TM}^{ZnO} < \mu_{late-TM}^{GaN}, \quad (8)$$

where μ_X^H denotes the magnetic moment of the X-dopant in the H-host. These trends can be attributed to the *d*-filling status of the dopants and the fact that in ZnO, the dopants have to relinquish two electrons, while in GaN they loose three.

VI. CONCLUSION

The codoping considered as a mean for enhancing the magnetic feature of DMSs has been discussed in a number of reports recently^{2,3,15,58–63} and a number of models have been proposed for the origin of the FMC among the magnetic impurities. The proposed models vary depending on the nature of the codopants which can be either a pair of cationic dopants or a pair consisting of one cationic and one anionic dopant. The case of cationic codopants can be further divided into two cases; namely one in which both the cationic codopants exhibit inherent magnetic moments (e.g., Co/Fe) and another in which one codopant exhibits an inherent magnetic moment and the other does not (e.g., Co/Cu, Fe/Cu, Co/Al, etc).

For the cationic codoping of ZnO, as pointed out by Kittilstved^{40,63}, there is a common feature which appears as the key property underlying the development of the FMC in all of the proposed models. This is the strong electronic coupling between the magnetic ions and the partially delocalized charge carriers at the Fermi level, namely, the dopant-defect hybridization. The free carriers (electrons or holes) may arise due to the donors or to anionic

nonstoichiometry (as, for example, oxygen vacancies, V_O , in ZnO). The proposed carrier mediated exchange coupling is expected to overcome the superexchange interaction that may develop between the codopants through an anion. In some models the carrier mediated exchange interaction is recognized either as of the Ruderman-Kittel-Kasuya-Yosida (RKKY) type or of a direct exchange type⁵⁸. However, the carrier mediated FMC is still a subject of considerable debate and instead an alternate model of the impurity band ferromagnetism via a double exchange^{2,3,64} interaction has been proposed. Finally, the $p-d$ exchange interaction between carriers and Mn atoms has also been proposed in the case of a cation/anion pair of codopants $Zn(Mn,N)O$ ¹⁵.

In the present work, we are proposing a new model for explaining the development of the FMC. The present results show 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^{1,23–26,51,52}. In all these materials, the proposed defect-induced defect-mediated mechanism is realizable through a codoping procedure. The proposed codoping mechanism can be considered as 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 spin-polarized neighborhoods (tetrahedra) analogous to spin-polarized radicals. These are centered at the codopant sites. The FMC is mediated by the MOs of these *radicals* and is greatly facilitated if the codopants could form bipartite configurations within the host lattices. Within this picture, the origin of magnetism in DMSs and TMOs appears to be the interplay between correlated spin-polarization processes that take place in a successive way within neighborhoods centered at the codopants and include their 1nn's. The model proposed by us can be used as a practical guide for choosing the appropriate pair of codopants for a specific semiconductor environment that can lead to the fabrication of DMSs and TMOs with enhanced magnetic properties.

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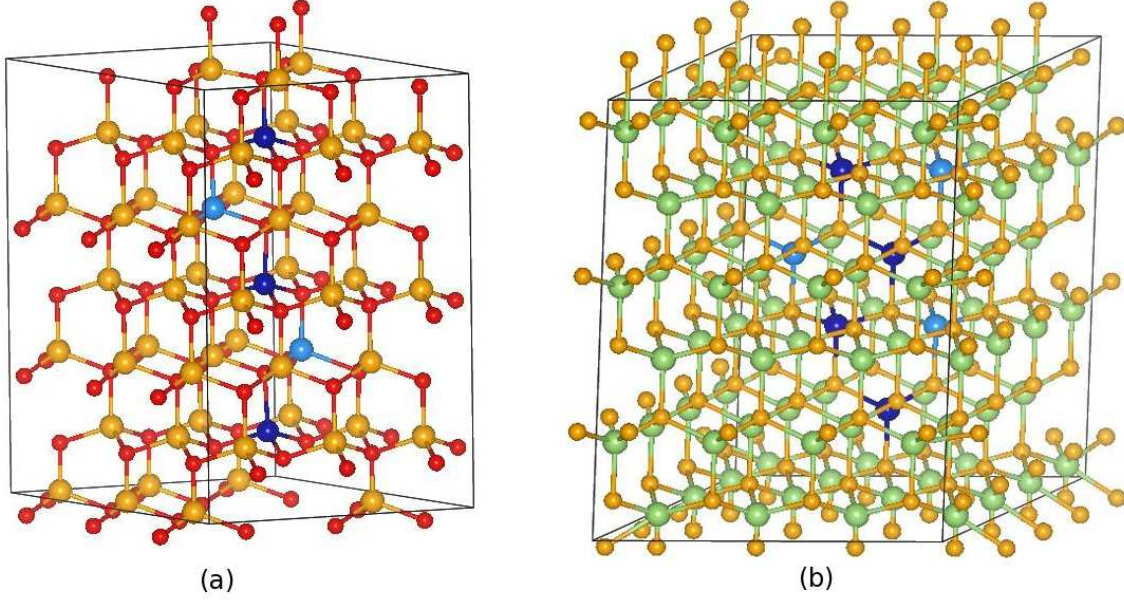


FIG. 1: Supercells used in our calculations for codoped ZnO and GaN systems. (a) Relaxed structure of 108 atom $\text{Zn}(\text{3Co},\text{2Cu})\text{O}$ supercell with a Co-Cu-Co-Cu-Co chain of nearest neighboring codopants over successive Zn planes. The Zn atoms are shown in yellow and O in red. The Co atoms are colored dark blue, while Cu are in light blue. (b) Relaxed structure of 192 atom $\text{Ga}(\text{4Co},\text{3Cu})\text{N}$ supercell with codopants forming a bipartite lattice. The Ga atoms are shown in green and N in yellow. Coloring of Co and Cu atoms are the same as in (a).

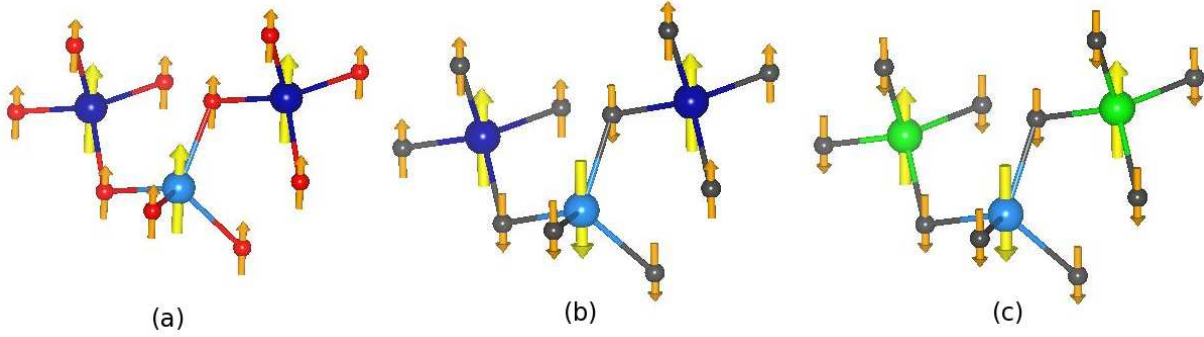


FIG. 2: A close up view of the spin polarized portions of (a) $\text{Zn}(\text{Co},\text{Cu})\text{O}$, (b) $\text{Ga}(\text{Co},\text{Cu})\text{N}$ and (c) $\text{Ga}(\text{Mn},\text{Cu})\text{N}$ in their ferromagnetic configurations. The Co atoms are colored dark blue, while Cu are in light blue. The Mn atoms are shown in green, O in red and N in gray.

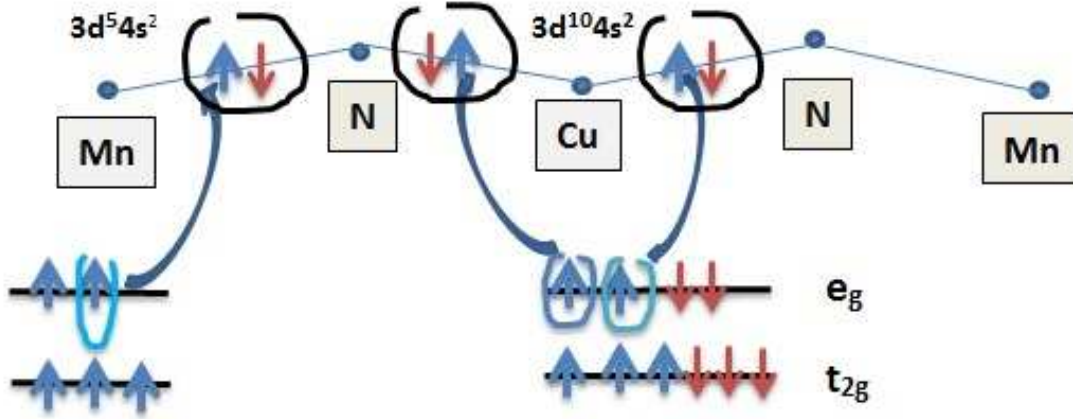


FIG. 3: Proposed mechanism for FMC in codoped DMSs. Example case: $\text{Ga}(\text{Mn,Cu})\text{N}$. Mn (as it does not have available spin-down d -electrons) gives one of its spin-up e_g electrons to N which has to give up one of its spin-down sp^3 electrons in order to form a Mn-N covalent bond. Due to the fact that Cu forms covalent N-Cu bonds with all its 1nn with the latter exhibiting parallel spin-polarization among themselves, all sp^3 N-electrons have to attain the same (spin-down) polarization. This forces Cu to give up its spin-up e_g electrons to form N-Cu covalent bonds thus leaving Cu with a spin-down orientation (see Fig. 1c).

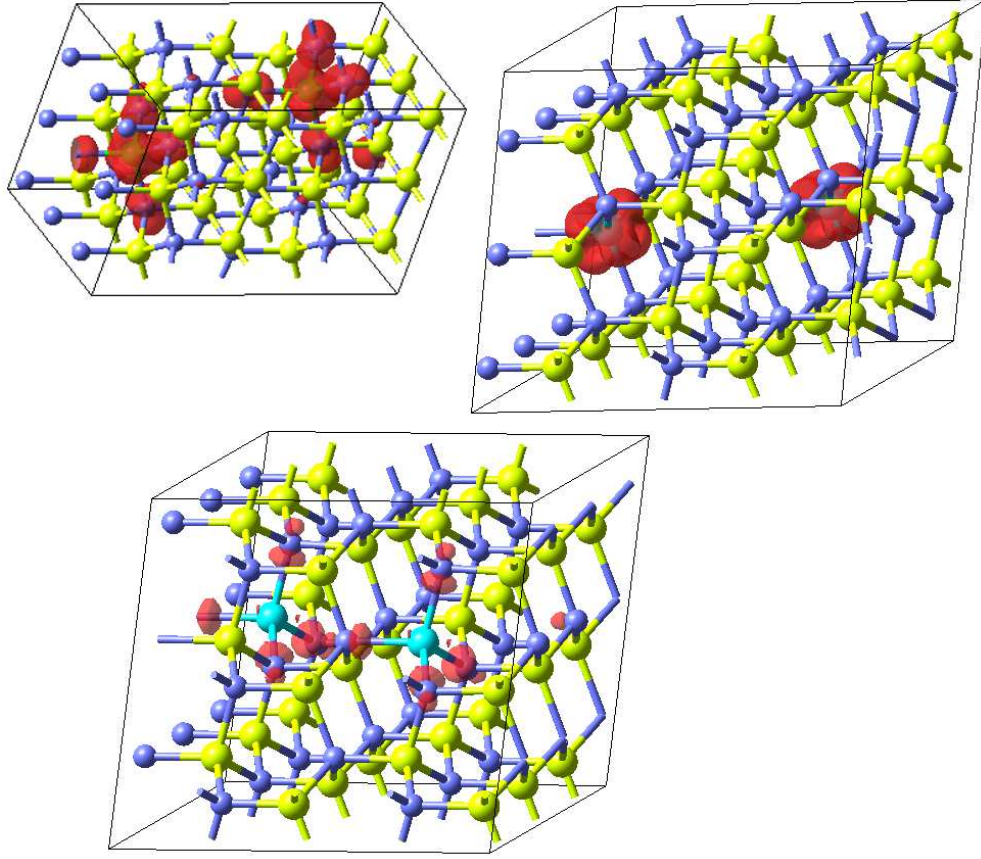


FIG. 4: Magnetization density isosurfaces for two systems which exhibit parallel (top left panel) and anti-parallel (top right and bottom panels) spin-polarizations. Clockwise from top left: Ga(2Ni)N (at $0.05 e/\text{\AA}^3$); Ga(2V)N (at $0.07 e/\text{\AA}^3$); Ga(2V)N (at $-0.02 e/\text{\AA}^3$).

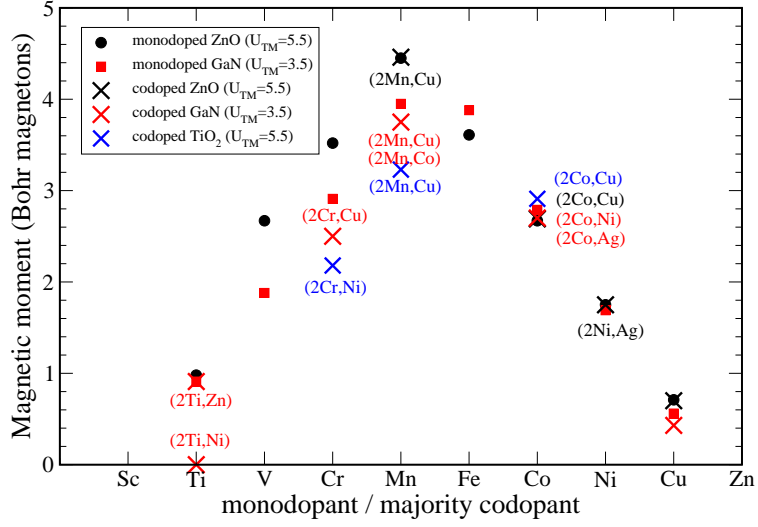


FIG. 5: Magnetic moments of transition metals (TM) used as substitutional monodopants or codopants in ZnO, GaN and TiO₂. It can be seen that $\mu_{early-TM}^{ZnO} > \mu_{early-TM}^{GaN}$ and $\mu_{late-TM}^{ZnO} < \mu_{late-TM}^{GaN}$. Codopants are indicated in parentheses. The results were obtained within the DFT/SGGA+U functional using U-values as indicated in the legend.

ZnO			GaN	
Dopant	Spin-polarization of dopant vs. 1nn anions	Mag. moment (μ_B)	Spin-polarization of dopant vs. 1nn anions	Mag. moment (μ_B)
Ti	anti-parallel	$\mu_{Ti_1} = \mu_{Ti_2} = 0.98$ $\mu_O \in [-0.01, 0.01]$	anti-parallel	$\mu_{Ti_1} = \mu_{Ti_2} = 0.91$ $\mu_N \in [-0.01, 0.00]$
V	parallel	$\mu_{V_1} = \mu_{V_2} = 2.67$ $\mu_O \in [0.0, 0.01]$	anti-parallel	$\mu_{V_1} = \mu_{V_2} = 1.88$ $\mu_N \in [-0.02, 0.01]$
Cr	parallel	$\mu_{Cr_1} = \mu_{Cr_2} = 3.52$ $\mu_O \in [0.00, 0.02]$	anti-parallel	$\mu_{Cr_1} = \mu_{Cr_2} = 2.91$ $\mu_N \in [-0.07, -0.05]$
Mn	parallel	$\mu_{Mn_1} = \mu_{Mn_2} = 4.45$ $\mu_O \in [0.02, 0.03]$	anti-parallel	$\mu_{Mn_1} = \mu_{Mn_2} = 3.95$ $\mu_N \in [-0.10, -0.06]$
Fe	parallel	$\mu_{Fe_1} = \mu_{Fe_2} = 3.61$ $\mu_O \in [0.02, 0.03]$	parallel	$\mu_{Fe_1} = \mu_{Fe_2} = 3.88$ $\mu_N \in [0.11, 0.12]$
Co	parallel	$\mu_{Co_1} = \mu_{Co_2} = 2.67$ $\mu_O \in [0.03, 0.04]$	parallel	$\mu_{Co_1} = \mu_{Co_2} = 2.79$ $\mu_N \in [0.13, 0.15]$
Ni	parallel	$\mu_{Ni_1} = \mu_{Ni_2} = 1.75$ $\mu_O \in [0.03, 0.05]$	parallel	$\mu_{Ni_1} = \mu_{Ni_2} = 1.69$ $\mu_N \in [0.16, 0.17]$
Cu	parallel	$\mu_{Cu_1} = \mu_{Cu_2} = 0.71$ $\mu_O \in [0.04, 0.08]$	parallel	$\mu_{Cu_1} = \mu_{Cu_2} = -0.56$ $\mu_N \in [-0.25, -0.14]$

TABLE I: Magnetic moments on isolated dopants and induced spin-polarization on their surrounding 1nn anions in ZnO and GaN hosts.