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Fast Track Communication

Successive spin polarizations underlying a new magnetic coupling contribution in diluted magnetic semiconductors

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Abstract

We propose a new type of magnetic coupling (MC) that is found in diluted magnetic semiconductors (DMSs). The origin of this is found to be the result of charge transfer processes followed by successive spin polarizations (SSPs) along successive cation–anion segments which include the impurities. The basic process underlying the SSP-based MC (SSP-MC) is the sharing of a single spin orbital by two neighboring impurities. As such, it can be considered as a *localized double exchange* as it is not mediated by free carriers. SSP-MC can be either ferromagnetic (SSP-FMC) or antiferromagnetic (SSP-AFMC) and, as demonstrated here, the SSP-FMC can be significantly enhanced via codoping; it can act in competition with superexchange and/or double and/or *p–d* exchange interactions. While the SSP-MC is not directly related to the magnitude of the magnetic moments of the impurities, it depends strongly on the energy difference of the host and impurity *d*-band centers, the difference of their electronegativities and rather weakly on the coupling interactions between them as well as between the cations and their mediating anions. The validity of the proposed SSP-MC as a new type of magnetic coupling is demonstrated by *ab initio* results for DMSs, namely ZnO, GaN, GaP, TiO₂ and MoS₂ monodoped (with Co, Cu and Mn) and codoped (with Co–Cu–Co and Mn–Cu–Mn).

Keywords: first principles calculations, molecular dynamics, molecular magnetism

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

In many recent reports, it has been pointed out that the spin-polarization of the anions which are first nearest neighbors, (1 nn), to magnetic cations/impurities, (the latter substituting cations in host materials of diluted magnetic semiconductors (DMSs)), play a crucial role in the development of the ferromagnetic coupling (FMC) among the magnetic impurities [1–9].

It has been observed that the spin-polarizations induced by the magnetic impurities/dopants, M_i , on their ν 1 nn anions, A_ν , can lead to anionic magnetic moments, μ_A , which align

themselves in direction either parallel or antiparallel to that of the magnetic moment of the parent impurity, μ_{M_i} . In view of this observation, a new type of magnetic interaction among the magnetic impurities in a DMS is proposed which can be seen as a two step process. The first step involves those processes which establish the charge state and the spin polarization of the anions which are neighboring the magnetic impurities. These processes create complexes (considered to be as a type of *radicals*) $M_i A_\nu$ each of which consists of a magnetic impurity M_i and its surrounding 1 nn anions, A_ν . The second step

involves those processes which lead to the interaction among the radicals $M_i A_v$ and the development of the FMC among them [1, 8].

Given the creation of the radicals $M_i A_v$, the MC among them based on induced spin-polarizations by the impurities can be understood as follows: let $M_1 A_v$ be the radical centered on M_1 and neighboring the $M_2 A_v$, one centered on M_2 sharing with it an anion A^* . It can then be argued that the direction of the spin polarization of M_2 relative to that of M_1 will be dictated greatly by the polarization induced on the anion A^* by M_1 . In fact, if M_2 is the same as M_1 , then M_1 and M_2 will be coupled ferromagnetically since both of them have to induce the same type of polarization (parallel or antiparallel) on A^* . If, on the other hand, M_1 is different than M_2 , the spin polarization of A^* will take on the characteristics of the stronger of the polarizations induced on it by the two neighboring impurities M_1 and M_2 . This results in the SSP-MC between M_1 and M_2 to be either FM or AFM. Thus, this new type of the MC is developed as the result of the outcome of successive spin polarizations (SSP) induced on neighboring anions and cations [1–4].

It is apparent that the SSP-based MC (SSP-MC) relies on the effectiveness of the created radicals $M_i A_v$ (e.g. on how bound the polarized anions feel to their 1 nn cation, that is, on the strength of the induced polarization by each M_i on A_v). As will be shown, the SSP-FMC is in opposition to the superexchange and adds to the double exchange and other types of magnetic interactions. However, the SSP-FMC is different than the widely known magnetic interactions and acts parallel with them in a complimentary way and can take place for magnetic dopant concentrations which can be below the percolation threshold.

In the present work, we will analyze the two step processes which lead to the SSP-FMC (or the SSP-AFMC) in DMSs and demonstrate that this new type of magnetic interaction can be considered as a *localized double exchange*. Towards this objective, we are following a route that is radically opposite to the commonly used approach. That is, instead of investigating the electronic processes around different magnetic impurities (e.g. the $3d$ series) in a given host (e.g. ZnO), we investigate and compare the electronic processes that follow the substitution of host-cations by a given impurity in various host materials.

Step-1 processes: The stability and behavior of the complex (radical) $M_i A_v$ within the given semiconductor host depends on some key factors some of which characterize the properties of the atoms involved in a particular DMS and some others characterize the structure of the host system. The relevant *atomic* and *crystal* properties include, the point group symmetry at the sites of the magnetic impurities, the energy position of the magnetic-impurity bands relative to those of the valence band of the host, the relative valency of the magnetic impurity with respect to that of the host atom it substitutes, the band filling factors, the relative strength of the crystal field splitting with respect to that of the exchange splitting in the magnetic impurity. Most of these factors underlie the (re)hybridization of the host and impurity bands and the charge transfer between host and impurity

atoms. Additionally, they can also specify the expected spin-polarization that will be induced on the anions neighboring the magnetic impurities and characterize magnetic type model interactions between neighboring magnetic impurities (double exchange, p - d exchange, superexchange, etc [10]).

Step-2 processes: It is apparent that the processes leading to a particular type of the SSP-MC (i.e. FM or AFM) depend greatly on the outcome of the step-1 processes which specify the status of the radicals $M_i A_v$. Whether the subsequent $M_i A_v$ - $M_j A_v$ interactions will be dominated by localized electronic configurations (e.g. superexchange) or delocalized ones (e.g. double exchange) depends largely on the electronic configuration of the radicals $M_i A_v$. This will be demonstrated in the following, while comparing the SSP-MC with the well known exchange model interactions.

SSP-MC versus Double Exchange: In contradistinction to Double exchange, the SSP-MC is not based on a *delocalized* carrier-mediated model interaction; (i) it is a *local* one as it refers to localized electronic processes, (ii) it does not involve delocalized free electron carriers, and (iii) it may lead to a FMC or an AFMC. SSP-MC becomes pronounced mainly in the coupling of non-isovalent magnetic cations but its appearance is not ruled out in the case of isovalent cations.

SSP-MC versus Superexchange: Comparing the electronic processes underlying the SSP-MC with those of the superexchange interaction, it is observed that in the latter case two interacting magnetic cations share one electron pair of the filled electronic valence shell of the anion they are sharing. On the other hand, in the SSP-MC the sharing involves just one partially filled valence spin orbital which satisfies the dictated spin polarizations induced on the mediating anion by its neighboring cations, (see figure 5 and discussion below). The resulting spin-polarization of the mediated anion is determined by its coupling features, its band fillings and the energetics of the bonding orbitals that it forms with the d -orbitals of its neighboring cations. If the cations sharing the same anion are of the same type, the SSP-MC leads to a FM coupling between the cations in contradistinction to the superexchange which promotes the AFM coupling.

*Results from ab initio calculations*³: in table 1 we present new *ab initio* results along with previously reported ones for the coupling type (FM or AFM) between 1 nn magnetic cations (denoted as C–C coupling) and between magnetic cations and their 1 nn anions (C–A coupling). As observed in table 1, a pair of 1 nn Co-ions or Mn-ions is found to couple ferromagnetically (i.e. the C–C coupling is FM) in all the five host semiconductors that we investigated, namely the ZnO, GaN, GaP, TiO₂ and MoS₂. On the other hand, the C–A coupling is found to be mostly FM for Co and mostly AFM for Mn in these host materials. The same picture of the C–A coupling is also found in systems with only one substitutional magnetic impurity (Co or Mn)⁴.

³ Our results were obtained by employing the VASP code [14–16] at the levels of the generalized gradient approximation (GGA) and the GGA+U of the density functional theory (DFT) as described in [1].

⁴ Results for the polarization behavior of the rest of the $3d$ elements in ZnO and GaN have been presented recently in [1].

Table 1. *Ab initio* DFT/SGGA+U results for the type of coupling (FM or AFM) between 1 nn magnetic cations (C–C) and between magnetic cations and their 1 nn anions (C–A) examined for Co, Cu, Mn substitutional impurities in five host semiconducting materials, namely ZnO, GaN, GaP, TiO₂ and MoS₂. The alignment of the magnetic moments of the codopants is indicated by the set of three arrows. In all calculations (unless otherwise specified) we used the following U -parameters (in eV): $U_{d,Co} = U_{d,Cu} = U_{d,Mn} = 5.5$, $U_{d,Zn} = 10.5$, $U_{d,Ti} = 9.26$, $U_{d,Mo} = 0.0$, $U_{d,Ga} = 6.5$, $U_{p,P} = -14.25$, $U_{p,N} = 4.25$, $U_{p,O} = 0.0$ in the case of TiO₂ and $U_{p,O} = 7.0$ in the case of ZnO.

Impurities	Magnetic Coupling in Host Materials									
	ZnO		GaN		GaP		TiO ₂		MoS ₂	
	C–C	C–A	C–C	C–A	C–C	C–A	C–C	C–A	C–C	C–A
Co		FM		FM		No polarization		FM		FM/AFM
Co–Co	FM ^a	FM	FM	FM	FM	AFM	FM	AFM	FM	FM/AFM ^b
Co–Cu–Cu	↑↓↑ ↑↑↑ ^c	FM	↑↓↑	FM	↑↑↑	FM	↑↑↑	FM	↑↑↑	FM
Cu		FM		FM		No polarization		FM	FM ^d	FM
Mn		AFM		AFM		AFM		AFM		AFM
Mn–Mn	AFM	FM	FM	AFM	FM	AFM	FM	AFM	FM	AFM
Mn–Cu–Mn	↑↓↑	FM	↑↓↑	FM/AFM ^e	↓↓↓ ↑↑↑	AFM AFM ^f	↑↓↑	AFM	↑↓↑	AFM

^aFor $U_{d,Co} < 5.5$, the C–A interaction becomes AFM.

^bFor $U_{d,Co} < 5.5$, the C–A interaction is FM.

^c $U_{d,Co} = 0.0$.

^dResult for Cu–Cu in MoS₂.

^e $U_{d,Mn} = U_{d,Cu} = 3.5$.

^f $U_{d,Mn} = U_{d,Cu} = 6.5$.

The aim of the present work is to uncover those electronic processes which are underlying the development of the SSP-MC. To achieve this we check the potentiality of each of the step-1 and step-2 processes in contributing to the SSP-MC.

Model approximation: We start by considering the effect of the participating atom properties within a simplified tight binding (TB) model. This model allows us to estimate the dependence of the spin character and the energies of the bonding and antibonding orbitals of an anion A on the properties of the cations M_i and M_j that it couples along the segment $M_i - A - M_j$. More precisely, we consider the p -orbital, p_A , of an anion-A forming bonding/antibonding orbitals with the d_i and d_j orbitals, correspondingly, of two neighboring magnetic impurities M_i and M_j . If for a particular spin orientation σ , $\epsilon_{p,A}^{0,\sigma}$, $\epsilon_{d,M_i}^{0,\sigma}$ and $\epsilon_{d,M_j}^{0,\sigma}$ are the corresponding orbital energies and $V_{pd_i}^{0,\sigma}$, $V_{pd_j}^{0,\sigma}$ and $V_{d_i d_j}^{0,\sigma}$ are the corresponding coupling interactions⁵, we can obtain the approximate bonding/antibonding spin-orbital energies solving the following equation for the model Hamiltonian H_{model}^σ :

$$H_{\text{model}}^\sigma - E = \begin{pmatrix} \epsilon_{d,M_i}^{0,\sigma} - E & V_{pd_i}^{0,\sigma} & V_{d_i d_j}^{0,\sigma} \\ V_{pd_i}^{0,\sigma} & \epsilon_{p,A}^{0,\sigma} - E & V_{pd_j}^{0,\sigma} \\ V_{d_i d_j}^{0,\sigma} & V_{pd_j}^{0,\sigma} & \epsilon_{d,M_j}^{0,\sigma} - E \end{pmatrix} = 0. \quad (1)$$

Solving equation (1) we can see how the spin-orbital energies, $\epsilon_{p,A}^\sigma$ of A are varied as the spin-orbital energy of M_i and its coupling $V_{pd_i}^{0,\sigma}$ changes, while $\epsilon_{d,M_j}^{0,\sigma}$ of the host cation M_j remains constant. From this, one may find whether a spin up or spin down p_A orbital is energetically more favorable to be occupied. Solutions of equation (1) are plotted in figure 1.

⁵ The parameters of the model Hamiltonian are taken from [17] $V_{d_i d_j}^{0,\sigma}$ is taken to be vanishingly small.

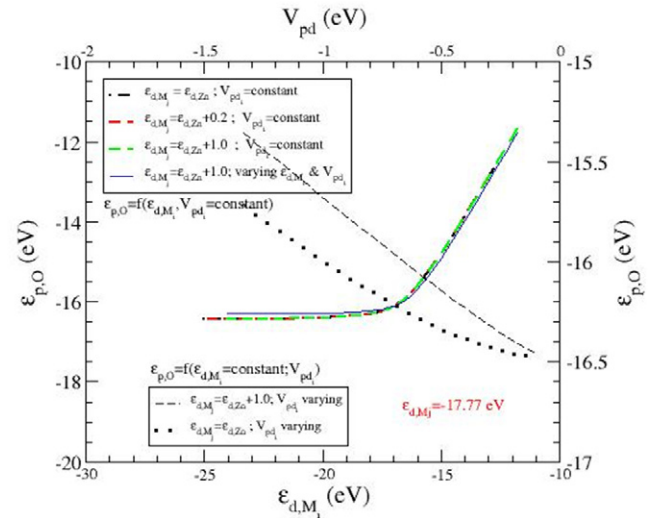


Figure 1. Variation of the spin-up orbital energies $\epsilon_{p,O}^\sigma$ of the O-anion (in the segment Zn–O– M_i) as the magnetic dopant orbital energy ϵ_{d,M_i}^σ and/or its coupling interaction $V_{pd_i}^0$ is changed as obtained using equation (1). Curves with shifted $\epsilon_{d,ZnO}^\sigma$ orbital energies simulate spin-down case.

According to figure 1, the energy position of $\epsilon_{p,A}^\sigma$ does not change if $\epsilon_{d,M_i}^{0,\sigma}$ (i.e. the orbital energy of the dopant) is smaller than $\epsilon_{d,M_j}^{0,\sigma}$ (i.e. the orbital energy of the host atom); it does change, however, dramatically as $\epsilon_{d,M_i}^{0,\sigma}$ shifts to higher energy than $\epsilon_{d,M_j}^{0,\sigma}$. These observations indicate that small exchange and/or crystal orbital splittings will not affect the energy position of $\epsilon_{p,A}^\sigma$ in an appreciable way. On the other hand, the interactions $V_{pd_i}^{0,\sigma}$ and $V_{pd_j}^{0,\sigma}$ act more or less equally well on $\epsilon_{p,A}^\sigma$, while significant variation of $\epsilon_{p,A}^\sigma$ is found for relatively small changes of either $V_{pd_i}^{0,\sigma}$ or $V_{pd_j}^{0,\sigma}$. It is

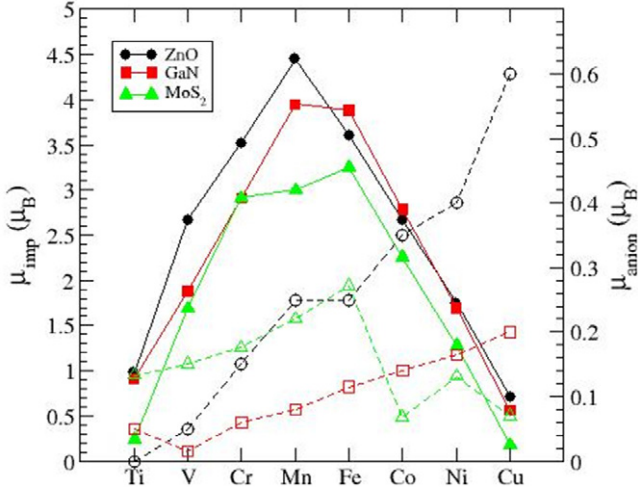


Figure 2. Variation of (i) the magnetic moment of a substitutional impurity in ZnO, GaN and MoS₂ (solid symbols) and (ii) the induced magnetic moments on the anions which are 1 nn to the impurities (open symbols).

apparent that equation (1) introduces higher order terms in the expression for $\epsilon_{p,A}^\sigma$ compared to that obtained on the basis of the 1st order perturbation in $|V_{pd_i}^{0,\sigma}|^2$ [10].

$$\epsilon_{p,A}^\sigma = \epsilon_{p,A}^{0,\sigma} + \frac{|V_{pd_i}^{0,\sigma}|^2}{\epsilon_{p,A}^{0,\sigma} - \epsilon_{d,M_i}^{0,\sigma}}. \quad (2)$$

Analyzing further our *ab initio* results (shown in figure 2), it is observed that the magnitude of the induced magnetic moments on the anions surrounding the magnetic impurities does not correlate with the magnitude of the magnetic moments of the magnetic impurities (absolute values are compared). As shown in figure 2, while the magnetic moment of the substitutional impurity follows the well known *d*-band filling variation, the induced magnetic moments on the anions which are 1 nn to the magnetic impurities follow a rather monotonic variation with the atomic number of the impurity (except in MoS₂). This indicates that the magnitude of the magnetic moment of the impurity is not a dominant factor underlying the SSP-MC. Instead, charge transfer processes seem to have a major contribution, especially in cases of non-isovalent impurities.

Factors underlying the charge transfer processes: *Ab initio* results for the transferred charge q_O that is developed on the O-anions which are 1 nn to a TM-dopant (TMD) in ZnO are shown in figure 3. As shown in figure 3, q_O changes from positive to negative values as the TMD changes from the early to the late 3*d* series. It is apparent from figure 3 that the trend in this relationship (q_O, TMD) does not change as the U -value, $U_{d,\text{TMD}}$, used for the *d*-orbitals of the TMD is changed. It is worth noting that the relationship between q_O and the corresponding magnetic moment, μ_O , of the O-anions is linear as shown in the inset of figure 3.

Investigating further the factors underlying the charge transfer between the TMD and its 1 nn anions, we find that q_O (and, correspondingly, μ_O) show a strong dependence on two synergistic key factors which appear to dictate the polarization status of the anions which are 1 nn to the TMDs. These are:

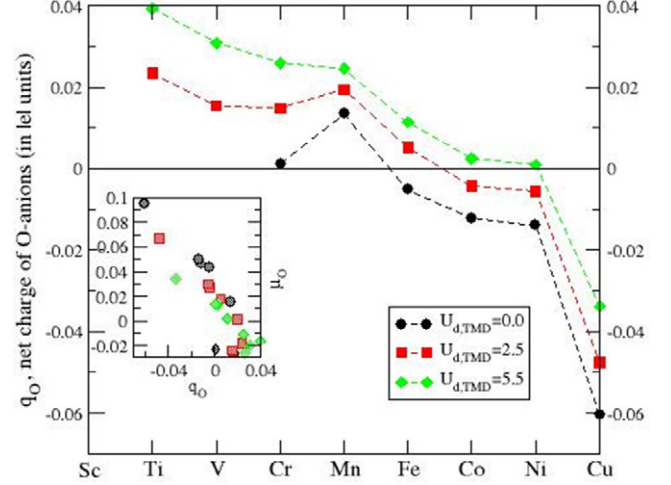


Figure 3. The transferred charge q_O (shown by solid symbols) on the O-anions which are 1 nn to TMDs in ZnO as obtained by *ab initio* calculations using three different $U_{d,\text{TMD}}$ values. No charge transfer or induced moments were found in the case of the Sc-dopant. The corresponding (q_O, μ_O) relationship is shown in the inset.

- The electronegativity, $E_{N,\text{TMD}}$, of the TMD as compared to that of the host cations, $E_{N,\text{host}}$, and,
- The strength of the O–TMD bond.

The relative value of $E_{N,\text{TMD}}$ with respect to $E_{N,\text{host}}$, dictates the direction of the charge transfer processes which will take place between the O-anion and its neighboring dopant and host cations. On the other hand, the charge transfer processes are facilitated by the bonding features provided by the TMDs. Among the latter is their electron DOS at the Fermi energy, E_F , as revealed by the observed correlation (not shown) between μ_O and the position of the *d*-DOS or approximately that of the *d*-band center, $d_{C,\text{TMD}}$, of the TMD relative to E_F or relative to the *d*-band center of the host cations $d_{C,\text{host}}$.⁶

The observed correlation between the set of the key factors ($E_{N,\text{TMD}}$, $E_{N,\text{host}}$, $d_{C,\text{TMD}}$, $d_{C,\text{host}}$) and the spin polarization (FM or AFM) of the anions which are 1 nn to TMDs in GaN is shown in figure 4. A similar picture is obtained in the case of TMDs in ZnO (not shown). From figure 4 the following exhibited trend is apparent: as the difference ($E_{N,\text{TMD}} - E_{N,\text{host}}$) changes sign or as $d_{C,\text{TMD}}$ becomes greater than $d_{C,\text{host}}$, the induced spin polarization on the anions which are 1 nn to the TMDs changes from the FM to the AFM alignment with respect to that of the parent TMD. These results are consistent with those of the model Hamiltonian in equation (1).

Codoping: Our proposed SSP-FMC has been found to be enhanced by suitable codoping. This can be understood by looking at the exchange coupling along the $M_i - A - N_k - A - M_j$ segment where N_k denotes the codopant (see figure 6). For pronounced enhancement of the SSP-FMC in the codoped case the codopant N_k has to attain itself spin-polarization and spin-polarize its 1 nn anions in a complimentary way to

⁶ The comparison of $d_{C,\text{TMD}}$ with respect to $d_{C,\text{host}}$ can be used for the ZnO and GaN hosts since in these cases the $d_{C,\text{host}}$ is located much deeper than the $d_{C,\text{TMD}}$ for all the 3*d*-TMDs and does not change upon substituting a Zn or, correspondingly, a Ga atom by a single TMD.

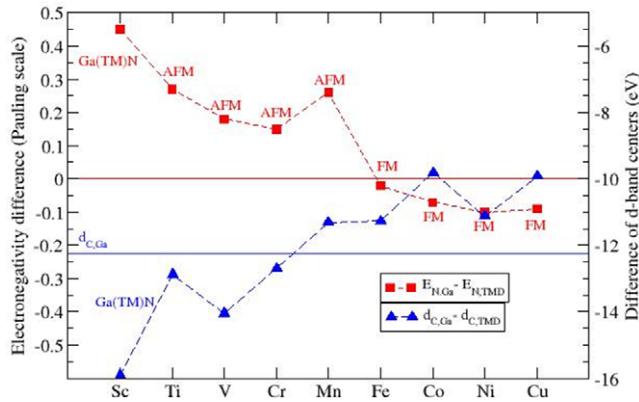


Figure 4. Results showing the observed correlation between both the electronegativity and the d -band center of the $3d$ -TM-substitutional-dopants in GaN with the spin polarization (FM or AFM) of their 1 nn anions. Red squares denote the difference between the electronegativity of each one of the TM-dopants and that of the host cation (Ga). (Electronegativities were obtained from tabulated data). Blue triangles denote the difference between the d -band center of the projected d -DOS of Ga and that of the $3d$ -dopants in GaN. Solid blue line denotes the $d_{C,Ga}$. The $d_{C,TMD}$ and $d_{C,host}$ as well as anion-polarization results were obtained by *ab initio* calculations as described in [1].

both M_i and M_j . That is, the exchange coupling between N_k and its 1 nn anions and cations (i.e. the C–C and C–A couplings along the segment $M_i - A - N_k - A - M_j$) to be all of FM type. Such cases appear in ZnO and GaN (figure 6) with both codoped with Co and Cu. In these systems both codopants polarize their 1 nn anions in such a way so as to have the anion magnetic moments align in parallel with those of the codopants. This may be considered as the one dimensional analog of layered magnetic compounds [11, 12]. There appear cases, however, where one codopant does not act in a complimentary way with the other codopant. In these cases, the total magnetic moment of the codoped system may be found to be smaller than the corresponding value of the monodoped case (case of Mn monodoped and Mn–Cu–Mn codoped in TiO_2 , shown in table 2). It has also been found that in some cases the type of the C–A polarization depends on the choice of the U -parameters that are used for the dopants. This is because the U -parametrization could change the ordering of the spin orbitals and, as a result, could affect the outcome of the successive spin polarizations. However, it does not change the concept, the idea, about the nature and origin of the proposed SSP-MC.

SSP-FMC is facilitated by charge transfer processes and opposes superexchange. This is shown schematically in figure 5 for two example cases. In the first we consider two 1 nn Co atoms mediated by an O-atom in ZnO. Superexchange can be naturally developed between the Co cations as the O-anion can share one electron pair of its complete p -shell with the Co cations. As a result, AFM coupling is developed between the Co cations. On the contrary, in the case of the SSP-FMC, one of the electrons provided by the oxygen’s electron pair can be shared by the two Co cations leading to a FM coupling between them. The SSP-FMC is facilitated by the charge transfer processes which leave the mediating O-anion with unpaired spins with the latter manifesting as the magnetic moment of

Table 2. *Ab initio* results for the total magnetic moments per unit cell for monodoped and codoped DMSs obtained within the DFT/SGGA+U method. U -parameters as in caption of table 1 unless specified.

Impurities	Magnetic Moments				
	$\mu_{u,cell}$ (μ_B)				
	ZnO	GaN ^a	GaP	TiO ₂	MoS ₂
Co–Co	5.90	1.22	4.08	2.27	4.28
Co–Cu–Co	4.71	7.41	6.00	7.16	5.38
		6.64 ^b			
Mn–Mn	3.69	7.59	7.81	5.91	4.90
Mn–Cu–Mn	8.27	5.85	0.41	3.81	4.26
			8.38 ^c		

^a $U_{d,Co} = 3.5$; $U_{d,Cu} = 3.5$.

^b $U_{d,Co} = 5.5$; $U_{d,Cu} = 0.0$.

^c $U_{d,Mn} = U_{d,Cu} = 6.5$.

the anion. It is this charge transfer that makes the branches of the superexchange sharing processes non-equivalent. On the other hand, the one spin-electron sharing of the SSP-FMC achieves symmetric processes towards its neighboring Co-cations that make it competitive to superexchange sharing processes. Very small charge transfer that may be developed between the dopants and their 1 nn anions in some systems could explain the contradicting results that have been reported for the type of the exhibited magnetic coupling. Characteristic example is the Co-doped ZnO, for which some groups are claiming FMC coupling and others AFM coupling. It appears that structural defects occurring in growth processes as well as computational technical details (e.g. relaxation effects, size of unit cell used in the calculations, level of DFT approximation used, etc) may also affect the outcome of the interplay between the various coupling processes that act simultaneously in a particular system. The SSP-FMC picture becomes more pronounced as the charge transfer processes become stronger, developing large induced magnetic moments. This is the case of the interaction that is developed along the Co–O–Cu segment shown in figure 5. As both Co and Cu induce magnetic moments on their 1 nn anions with directions parallel to their own, the Co–Cu coupling is strongly FM. On the contrary, in the case of the segment Mn–N–Cu (case of the codoped GaN), the Mn–Cu magnetic coupling is AFM because Mn (correspondingly, Cu) induces magnetic moments on its 1 nn N-anions with direction antiparallel (correspondingly parallel) to its own.

In view of figure 5, the SSP-MC appears as a *localized double exchange* process as it is mediated by localized spin orbitals participating in simultaneous local charge transfer processes analogous to the *localized RKKY* coupling that was proposed in explaining the magnetic coupling in binary metallic clusters [13].

Conclusion: We have demonstrated that the proposed SSP-MC, which has been found in DMSs, can be considered as the result of charge transfer processes followed by successively induced spin polarizations both taking place in the neighborhoods of the magnetic and non magnetic impurities. The processes underlying the SSP-MC are not directly related to the magnitude of the magnetic moments of the impurities but

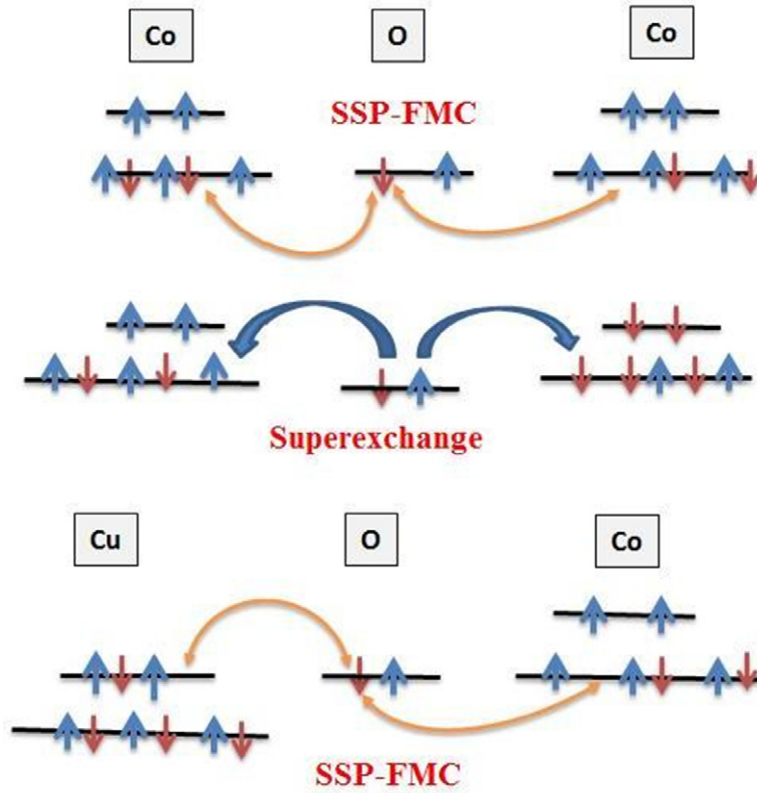


Figure 5. Pictorial view of the SSP-FMC and the superexchange interactions.

depend strongly on the charge transfer between the impurities and their 1 nn anions. In particular, it has been demonstrated that the status of the polarization state induced by substitutional TMDs on their 1 nn anions in ZnO and GaN is dictated by the electronegativity and the d -band center of the TMDs in these hosts. In particular, it was shown that in these systems as the difference $(E_{N,TMD} - E_{N,host})$ changes sign or as $d_{C,TMD}$ becomes greater than $d_{C,host}$, the induced spin polarization on the anions which are 1 nn to the TMDs changes from the FM to the AFM alignment with respect to that of the parent TMD.

The present results provide further support to our observations and our proposed model for the origin of magnetism in DMSs and TMOs according to which the induced spin polarization of the anions which are 1 nn to the TMDs in DMSs and doped TMOs emerges as a fundamental factor for the development and enhancing the magnetism in these materials. This is because the spin-polarization of the anions neighboring the TMDs dictates the spin polarization of neighboring TMDs along segments of the form $(co)dopant-anion-(co)dopant-anion-(co)dopant-etc$ within DMS or TMO hosts (see [1] and references therein). The FM coupling among the TMDs can be described as a double exchange process mediated by localized electron orbitals.

The SSP-FMC may be significantly enhanced via codoping. It is apparent, however, that the strength and the type (FM or AFM) of the magnetic coupling depends on the outcome of all the competitive processes (e.g. superexchange) that act simultaneously in a given system.

The present work elucidates the physics underlying this new mechanism and the origin of the magnetic coupling in

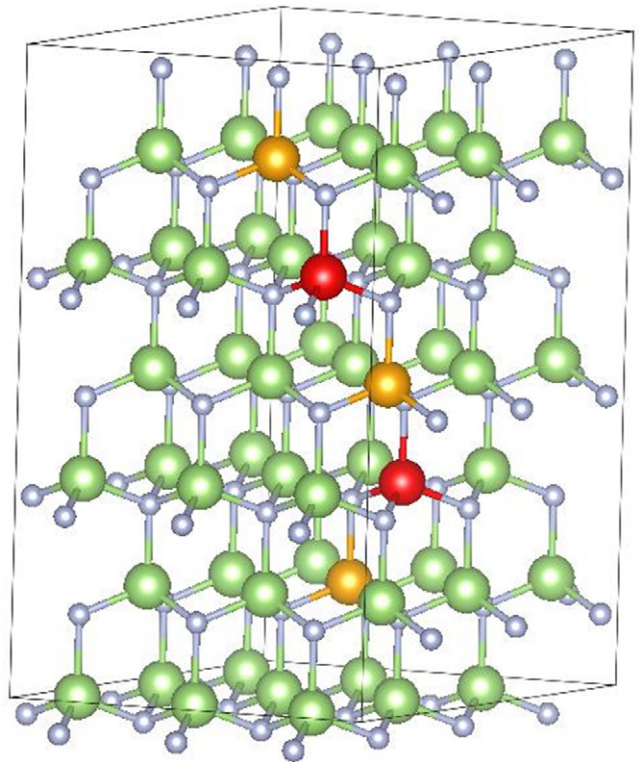


Figure 6. Figure showing codoped $M_i - A - N_k - A - M_j$ segment in GaN with M_i and $M_j = \text{Co}$ (yellow) and $N_k = \text{Cu}$ (red).

DMSs and TMOs by assigning it to the basic features of the electronic properties of hosts and dopants.

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