

Electronic structure of transition-metal impurities in *p*-type ZnO

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The self-interaction-corrected local spin-density approximation is used to investigate the ground-state valency configuration of transition metal (TM=Mn,Co) impurities in *p*-type ZnO. Based on total energy considerations, we find a stable localized TM²⁺ configuration for a TM impurity in ZnO if no additional hole donors are present. Our calculations indicate that the (+/0) donor level is situated in the band gap, as a consequence of which the TM³⁺ becomes more favorable in *p*-type ZnO, where the Fermi level is positioned near the top of the valence band. When codoping with N, it emerges that the conditions for the applicability of the Zener model as proposed by Dietl *et al.* [Science **287**, 1019 (2000)] are fulfilled only in the scenario where the N concentration exceeds the TM impurity concentration.

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Recently, the prediction by Dietl *et al.*¹ of room-temperature ferromagnetism in *p*-type Zn_{1-x}Mn_xO has generated considerable research activity, in both theory and experiment. So far, no conclusive experimental evidence has emerged that could either confirm or disprove the prediction. Various experimental investigations of the magnetic order in Zn_{1-x}Mn_xO give contradictory results, ranging from spin-glass behavior² and paramagnetism³ to ferromagnetism below⁴ or even above⁵ room temperature. It has also been suggested that the observed ferromagnetism might be due to the formation of secondary manganese oxide phases.⁶ The situation is quite similar for Zn_{1-x}Co_xO where there exists some experimental evidence in support of ferromagnetism,⁷ while other experiments seem to suggest antiferromagnetic behavior.^{8,9} The latest experimental studies, that we are aware of, find either no evidence for magnetic order, in Zn_{1-x}Mn_xO and Zn_{1-x}Co_xO,¹⁰ or actually suggest ferromagnetism in *n*-type transition-metal-(TM-) doped ZnO.¹¹

The theoretical description of magnetism in TM-doped ZnO centers mainly on two different methodologies. First, there is the Zener model description by Dietl *et al.*,¹ where the divalent TM impurity (Mn²⁺:*d*⁵, Co²⁺:*d*⁷) provides a localized spin, and a possible ferromagnetism originates from the RKKY-like interaction between the localized TM moments, mediated by the delocalized hole carriers. These carriers always have the character of the host valence band, and in TM-doped ZnO, they need to be introduced through additional doping—for example, by substituting some of the O atoms by N atoms. The second theoretical approach consists of describing the diluted magnetic semiconductor (DMS) in the framework of *ab initio* electronic structure calculations. Here the overlap of *d* orbitals of the neighboring TM impurities results in the formation of deep impurity band states; i.e., the *d* states are itinerant, but their character is always different from the host valence band. The exchange interaction splits the majority and minority spin bands, and depending on the density of spin-polarized states at the Fermi level, ferromagnetism based on the double-exchange mechanism

becomes theoretically possible. The magnetic properties of TM-doped ZnO have been calculated from first principles, using a wide range of different implementations, such as the Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA),¹² linear muffin-tin orbital (LMTO),¹³ projector augmented wave (PAW),⁵ and pseudopotential^{9,14,15} methods, all based on the local spin density (LSD) approximation.

Both the Zener model description and the LSD-based *ab initio* calculations are in agreement regarding the crucial role played by additional hole carriers in the ferromagnetism of Zn_{1-x}(TM)_xO, while the electronic state of the TM impurity and, consequently, the mechanism behind the long-range magnetic interaction differ qualitatively between the two descriptions. The description of the TM *d* states, as either localized at the Mn/Co sites or bandlike delocalized throughout the crystal, depends on the relative importance of the on-site correlations on the one hand and the kinetic energy on the other. Since the LSD approximation ignores exchange and correlation effects beyond those of the homogeneous electron gas, it cannot account for the on-site localization of correlated electrons by the local Coulomb repulsion. The LSD introduces an unphysical self-interaction of an electron with itself, which is insignificant for extended band states, but considerable for atomiclike states. In the self-interaction-corrected (SIC) LSD both localized and delocalized states are treated on an equal footing by subtracting from the LSD energy functional a self-interaction contribution of each *d* electron, thus enhancing its localized nature.^{16,17} Such a localization of a *d* state at the impurity site gives rise to a gain in SIC (localization) energy, but simultaneously results in the loss of any possible band formation energy. By studying various valency configurations of the TM ion, realized when treating some of the *d* electrons as localized and allowing the remainder to hybridize, one can find both the global energy minimum and the ground-state configuration of localized orbitals.¹⁸ Here we assume that the ground-state spin and orbital moments of the TM *d* orbitals are governed by Hund's rules.

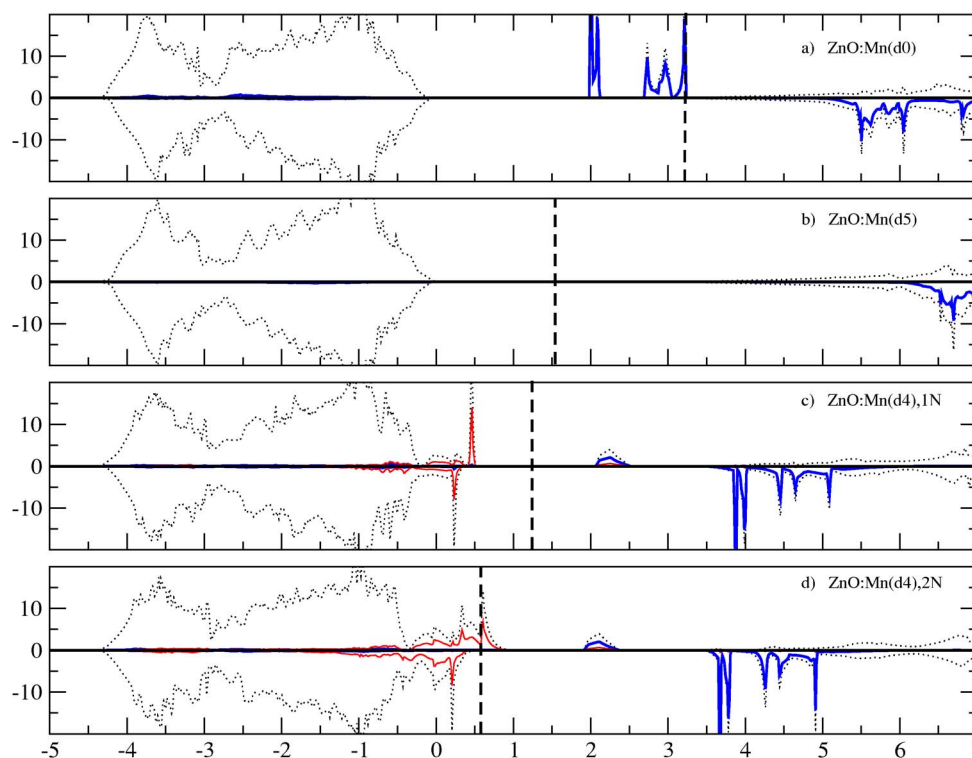


FIG. 1. (Color online) Total DOS as a function of energy, in states per eV, of $\text{Zn}_{15/16}\text{TM}_{1/16}\text{O}_{1-y}\text{N}_y$: (a) LSD configuration, $y=0$, (b) TM^{2+} configuration, $y=0$, (c) TM^{3+} configuration, $y=1/16$, and (d) TM^{3+} configuration, $y=2/16$. The thin dotted black, thick blue (black), and thin red (dark grey) lines represent the total, TM d -projected, and N p -projected densities of states, respectively. The energy is given relative to the valence-band maximum, with the Fermi level indicated by the black dashed line.

For pure ZnO in the wurtzite structure, we find that applying SIC-LSD—namely, treating the Zn $3d$ electrons as localized—results in an energy gap of $E_g=3.7$ eV, as compared to the smaller LSD value $E_g=1.8$ eV and in relatively good agreement with the experimental value $E_g=3.4$ eV. In the LSD approximation, the d bands are situated too high in energy, at the bottom of the valence band, and the ensuing unphysical level repulsion with the O p bands shifts the latter closer to the conduction bands, resulting in the reduced band gap.¹⁹ By SI (self-interaction)-correcting the d states, they become atomic like and occur at lower energy, which is a considerably better representation of their actual electronic structure in ZnO. Often the SIC-LSD leads only to a partial improvement of energy gaps, as it deals with the SI of the filled d states in the valence band but, unlike the GW approximation, it does not improve the description of the excited d states in the conduction band. In ZnO, however, all ten d states are filled and best described as self-interaction corrected (localized), while the LSD approximation is adequate for the valence band, which explains the good agreement between our results and the experimental value for the energy gap. We should note here that the ZnO ground-state scenario, with all the d electrons localized by the SI, results in valence and conduction bands that are very similar to those obtained when treating the d electrons as core electrons. In the latter scenario, the energy gap is $E_g=3.4$ eV. Given this similarity and the considerable computational effort associated with describing all the Zn d in the supercell as SI corrected, we opted for describing these states as core like in our calculations.

Fukumura *et al.*²⁰ were able to fabricate epitaxial thin films of DMS $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x \leq 0.35$), indicating a high solubility of Mn in the ZnO matrix and showing that the Mn ions occupy the Zn sites without changing the wurtzite structure. It was similarly shown that a large amount of Co can be substituted for Zn in ZnO, without any impurity phase appearing in the wurtzite structure.²¹ Attempts to incorporate significant amounts of N into ZnO have so far not been very successful. It should be noted here that in this work we assume a given concentration of TM impurities and codopants of ZnO, to study their interactions. The questions as to whether and how these concentrations can be achieved lie outside the scope of this study. In our calculations, $\text{Zn}_{1-x}\text{TM}_x\text{O}$ is realized by substituting a single Zn atom by either Mn or Co, in a $(2 \times 2 \times 2)$ supercell consisting of 16 ZnO formula units. In Fig. 1(a), we show the density of states (DOS) of Mn-doped ZnO, as calculated within the LSD approximation—i.e., when all the d states are treated as band states. The O p states make up most of the broadband situated below 0 eV. The exchange splitting separates the d manifold [thick blue (online) line] into a completely filled majority band and an empty minority band. The DOS of the LSD scenario for Co doping (not shown) is quite similar to Fig. 1(a), except for the fact that the two additional d electrons are now accommodated in the minority band. Based on the position of the Fermi level, it has been suggested that $\text{Zn}_{1-x}\text{Co}_x\text{O}$, but not $\text{Zn}_{1-x}\text{Mn}_x\text{O}$, is ferromagnetic, with the magnetic order being mediated by the double-exchange mechanism.¹² In contrast, calculations by Spaldin¹⁴ seem to indicate that ferromagnetism is unlikely to occur in either

TABLE I. Columns 2–5, total energy (with respect to the TM^{2+} configuration) in eV, of $\text{Zn}_{15/16}\text{TM}_{1/16}\text{O}_{1-y}\text{N}_y$ for TM^{2+} , TM^{3+} , TM^{4+} , and LSD configurations, with $\text{TM}=\text{Mn}$ or Co and $y=0, 1/16$, and $2/16$. Column 6, the Fermi level (with respect to the VBM) as obtained in the TM^{3+} configuration. Column 7, the donor level (+/0) with respect to the VBM (given in eV).

	Mn^{2+}	Mn^{3+}	Mn^{4+}	Mn^{7+}	$\epsilon_F (d^4)$	$\text{Mn}(+/0)$
$y=0$	0.00	0.52	1.10	3.01	3.22	2.70
$y=1/16$	0.00	-1.77	-1.18		1.28	3.04
$y=2/16$	0.00	-1.20	-1.15		0.60	1.80
	Co^{2+}	Co^{3+}	Co^{4+}	Co^{9+}	$\epsilon_F (d^6)$	$\text{Co}(+/0)$
$y=0$	0.00	0.64	1.34	5.66	3.51	2.87
$y=1/16$	0.00	-1.59	-0.94		1.06	2.64
$y=2/16$	0.00	-1.73	-1.51		0.54	2.27

compound, unless carriers are added. When treating the TM d states as localized, within the SIC-LSD approximation, an altogether different picture emerges, as can be seen from Fig. 1(b). The SIC localizes the TM d electrons in atomiclike orbitals and consequently shifts the corresponding d states below the valence band, giving rise to a wide energy band gap.

In Table I, the total energies for $\text{Zn}_{15/16}\text{Mn}_{1/16}\text{O}$ (row 2) and $\text{Zn}_{15/16}\text{Co}_{1/16}\text{O}$ (row 6) have been calculated for three different localized scenarios (columns 2, 3, and 4), as well as the LSD configuration (column 5). All energies are with respect to energy of the divalent configuration, with a negative (positive) value indicating that the corresponding configuration is energetically more (less) favorable. We find that the global energy minima are obtained when treating all the TM impurity d states in ZnO as localized, where the preferred configurations are respectively Mn^{2+} , with five localized d electrons, and Co^{2+} , with seven localized d electrons. For both dopants the energy difference between the divalent and LSD scenarios is more than 3 eV, indicating that d electron localization results in an overall gain in SIC energy that far outweighs any corresponding loss in hybridization energy. The divalent ground-state configuration is in agreement with experimental observation both for Mn^{22} and Co^{23} . Given the fact that in the divalent scenario of Fig. 1(b) there are no available hole carriers to mediate the interaction between the localized spins, we conclude that neither $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ nor $\text{Zn}_{1-x}\text{Co}_x\text{O}$ will be ferromagnetic.

As can be seen from Table I, rows 3 and 7, p -doping $\text{Zn}_{15/16}\text{TM}_{1/16}\text{O}$, by substituting one O with one N atom, has a major effect on the ground-state valency configuration of the TM impurity. The global energy minimum is now obtained for the trivalent TM^{3+} state. Nitrogen, having one p electron fewer than O, acts as an acceptor when introduced into ZnO, with the corresponding acceptor level situated near the top of the valence band²⁴ [Fig. 1(c)]. Since one of the previously localized d states becomes delocalized in the TM^{3+} configuration, the corresponding electron charge transfers into the N acceptor state, leaving behind an empty d band, situated at approximately 2 eV above the valence band maximum (VBM) for the Mn-doped case shown in Fig. 1(c). Again the situation is very similar for $\text{Zn}_{15/16}\text{Co}_{1/16}\text{O}_{15/16}\text{N}_{1/16}$, where the empty d state is situated

at approximately 1.5 eV above the VBM. The energy gain, resulting from the charge transfer and hybridization in the TM^{3+} configuration, is obviously large enough to overcome the corresponding loss in SIC (localization) energy with respect to the TM^{2+} configuration. The Fermi level is situated in the gap above the completely filled acceptor states, indicating that the compensation is complete and that there are no carriers left to mediate the magnetic order.

In order to make the connection between the localization-delocalization picture and the terminology used in describing doping in semiconductors, we need to analyze the ionization levels of the TM impurities. To avoid confusion we introduce a notation that is better suited for describing neutral and charged impurities, i.e., $(\text{ZnO}:\text{TM}^v, q)$, where v and q refer, respectively, to the valency and the charge state of the impurity. In the neutral-charge state the substitutional TM impurity can either assume the divalent configuration, $\text{TM}^{2+} \equiv (\text{ZnO}:\text{TM}^{2+}, 0)$, which does not introduce states in the gap, or the trivalent configuration, $\text{TM}^{3+} \equiv (\text{ZnO}:\text{TM}^{3+}, 0)$, which is about 0.5–1.5 eV higher in energy (see Table I, columns 2 and 3) and has an occupied electron d state in the gap. This electron can be transferred to the conduction band, depending on the Fermi level position, ionizing the TM impurity into the positive charge state $(\text{ZnO}:\text{TM}^{3+}, +)$. Thus, with respect to substitutional Co or Mn in the $\text{Zn}^{2+}\text{O}^{2-}$ matrix, the delocalization process, $(\text{ZnO}:\text{TM}^{2+}, 0) \rightarrow (\text{ZnO}:\text{TM}^{3+}, +) + e^-$, results in a deep donor level (+/0) in the band gap, which can be illustrated by calculating the formation energy E_f of the neutral and the positively charged TM impurity using²⁵

$$E_f(\text{ZnO}:\text{TM}^v, q) = E_{\text{tot}}(\text{ZnO}:\text{TM}^v, q) - E_{\text{tot}}(\text{ZnO}) - \mu_{\text{Zn}} + \mu_{\text{TM}} + q\epsilon_F. \quad (1)$$

Here μ_{Zn} and μ_{TM} are the respective chemical potentials and ϵ_F is the Fermi level (with respect to VBM). Although the absolute formation energies depend on the chemical potentials, here we will discuss the relative values that depend only on the total energy differences between the various TM valency configurations. The total energy of the positive charge state $E_{\text{tot}}(\text{ZnO}:\text{TM}^{3+}, +)$ is estimated by subtracting the one-electron energy of the gap state from the total energy of the neutral $(\text{ZnO}:\text{TM}^{3+}, 0)$ configuration.²⁶ The relative

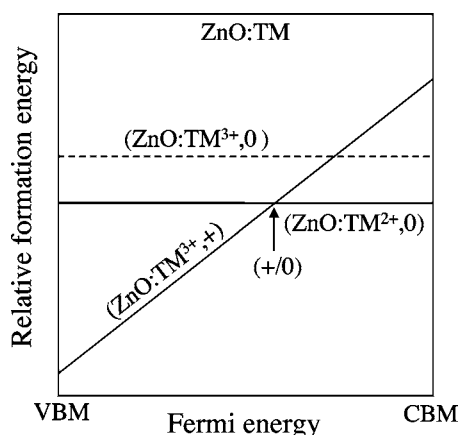


FIG. 2. Schematic plot of the formation energy as a function of Fermi energy for ZnO:TM illustrating the link between the localization-delocalization picture and the transition-metal donor ionization level in the band gap. Only the (+/0) between the positively charged TM^{3+} and the neutral TM^{2+} valence configuration is indicated.

formation energies as a function of the Fermi energy are schematically plotted in Fig. 2. For the charged impurity configuration ($\text{ZnO:TM}^{3+}, +$) the formation energy is determined by the position of the Fermi level, as follows from Eq. (1) and as indicated by the skew line. The neutral-charge configurations ($\text{ZnO:TM}^{3+}, 0$) and ($\text{ZnO:TM}^{2+}, 0$) are indicated by the horizontal dashed and solid lines, respectively. The donor transition level (+/0) is defined by the Fermi energy above which the TM impurity is in the divalent configuration and below which it is in the positively charged trivalent configuration. Since the neutral-charged ($\text{ZnO:TM}^{3+}, 0$) has a gap state in the high-energy part of the band gap and since for $\text{TM}=\text{Mn/Co}$ it is situated only 0.52/0.64 eV above the neutral ($\text{ZnO:TM}^{2+}, 0$) configuration, the donor transition level (+/0) is also situated in the gap. It is interesting to note that in the SIC-LSD picture, the doping of TM impurities into ZnO results in the donor level (+/0) being situated in the gap, as is also found experimentally,²⁷ as a result of two competing valence configurations ($\text{ZnO:TM}^{2+}, 0$) and ($\text{ZnO:TM}^{3+}, +$). Without N codoping, in both $\text{Zn}_{15/16}\text{Mn}_{1/16}\text{O}$ and $\text{Zn}_{15/16}\text{Co}_{1/16}\text{O}$, the Fermi level is situated above the donor level (respectively, columns 7 and 6 in Table I), which explains the stability of the localized TM^{2+} configuration. With N codoping (rows 3, 4 and 7, 8), the additional acceptor state lowers ϵ_F , energetically favoring the TM^{3+} configuration. This is in contrast to Dietl's Zener-model description, where it is assumed that the ground-state configuration remains Mn^{2+} , based on the argumentation that the (+/0) level is situated below the VBM.²⁸

From the SIC-LSD calculations it follows that the band description of the d states does not fully account for the correct electronic structure of the $\text{Zn}_{1-x}\text{M}_x\text{O}$ ground state, even when codoped with N. But also the Zener model, with hole carriers mediating the magnetic interaction between lo-

calized spins residing on TM^{2+} ions, is not a true representation of the groundstate, due to the fact that the $\text{TM}(+/0)$ donor level is situated above the N acceptor levels which therefore are fully compensated by the delocalized d electron. There are no hole carriers in either $\text{Zn}_{15/16}\text{Mn}_{1/16}\text{O}_{15/16}\text{N}_{1/16}$ or $\text{Zn}_{15/16}\text{Co}_{1/16}\text{O}_{15/16}\text{N}_{1/16}$, and carrier-mediated ferromagnetism can therefore not occur. It seems plausible that increasing the concentrations of the dopants [TM] and [N] will not change the overall picture of fully compensated acceptor states, as long as $[\text{TM}]=[\text{N}]$. However, the qualitative picture changes considerably if we increase the relative amount of N impurities—i.e., if $[\text{N}] > [\text{TM}]$. Substituting two of the O atoms by N, but with a single TM impurity in the 32-atom ZnO supercell, we find that, contrary to what one might expect, overdoping with N does not result in a further delocalization—i.e., a transition from $\text{TM}^{3+} \rightarrow \text{TM}^{4+} + e^-$. From Table I we see that the TM^{3+} configuration gives the lowest total energy, for both $\text{Zn}_{15/16}\text{Mn}_{1/16}\text{O}_{14/16}\text{N}_{2/16}$ (column 3, row 4) and $\text{Zn}_{15/16}\text{Co}_{1/16}\text{O}_{14/16}\text{N}_{2/16}$ (column 3, row 8). The additional N impurity is thus not compensated by TM d electrons and, from the corresponding DOS [Fig. 1(d)], we find that this results in an impurity band at the top of the valence band, which is now only partially filled. It is most noticeable that, since these hole states coexist simultaneously with the localized spins on the TM^{3+} impurities, the conditions for the applicability of the Zener model are fulfilled in this scenario. In order to determine whether the ferromagnetic ordering of the magnetic impurities is energetically preferred, SIC-LSD total energy calculations for different magnetic configurations will need to be performed. On the other hand, since codoping with N has revealed itself to be a rather difficult undertaking,²⁹ the condition $[\text{N}] > [\text{TM}]$ constitutes a considerable hurdle with regard to actually synthesizing these DMS.

In summary, we have studied the electronic structure and different valency configurations of Co and Mn impurities in p -type ZnO using the SIC-LSD *ab initio* method. From total energy considerations we find that the TM d states remain localized if no additional hole donors are present. The TM^{3+} becomes more favorable in p -type ZnO, which leads us to conclude that the Zener model like carrier-mediated ferromagnetism, as proposed by Dietl *et al.*¹ can only possibly be realized when the N codoping exceeds the concentration of the TM impurities.

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