

# Valencies of Mn impurities in ZnO

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## Abstract

We use the self-interaction corrected (SIC) local spin-density (LSD) approximation to investigate the groundstate valency configuration of Mn impurities in p-type ZnO. In  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ , we find the localized  $\text{Mn}^{2+}$  configuration to be preferred energetically. When codoping  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  with N, we find that four  $d$ -states stay localized at the Mn site, while the remaining  $d$ -electron charge transfers into the hole states at the top of the valence bands. If the Mn concentration  $[\text{Mn}]$  is equal to the N concentration  $[\text{N}]$ , this results in a scenario without carriers to mediate long range order. If on the other hand  $[\text{N}]$  is larger than  $[\text{Mn}]$ , the N impurity band is not entirely filled, and carrier mediated ferromagnetism becomes theoretically possible.

The design of diluted magnetic semiconductors (DMS), that apart from the well known electronic properties also have incorporated spin-functionality, is expected to play a major part in the development of the next generation of electronic devices. [1] In this respect, it is important that these materials remain ferromagnetic above room temperature. In Mn doped GaAs, where ferromagnetism is well established, the Curie temperature is  $T_C \simeq 160$  K. Ferromagnetism has been predicted theoretically to occur in a variety of Mn doped semiconductors, but there remains considerable disagreement as to the nature of the exchange mechanism and the magnetic order.

ZnO crystallizes in the hexagonal wurtzite structure (lattice constants  $a_0=3.2495$  Å, and  $c_0=5.2069$  Å). Its wide band gap, in the near UV range (3.3 eV) makes it a candidate for optoelectronic applications that rely on short wavelength light emitting diodes. As was shown by Fukumura *et al.*, [2] solubility of Mn in the ZnO matrix is relatively high ( $x \leq 0.35$ ). The various experimental investigations of the magnetic order in  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  give contradictory results, ranging from spin glass behaviour [3] and paramagnetism, [4] to ferromagnetism at room temperature [5]. The very latest

experimental study that we are aware of, finds no evidence for magnetic order, down to  $T=2$  K. [6], and it has been suggested that the previously observed ferromagnetism is due to precipitates containing manganese oxides. [7] Codoping with N has so far revealed itself to be rather elusive. [8]

With respect to theory, the agreement is that  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ , without additional carriers is not ferromagnetic. According to the Zener model approach by Dietl *et al.*, [9] ferromagnetism in DMS's originates from the RKKY-like interaction between the localized transition metal moments, and delocalized hole carriers. In Mn doped ZnO, the Mn impurities provide the localized moments, but without acceptor codoping, there are no carriers to mediate the long range interaction. Bandstructure calculations, based on the LSD approximation, [10, 12, 5, 11] find the delocalized Mn- $d$  levels to be situated in the ZnO semi-conducting gap. Without additional hole doping, the Fermi level separates a completely filled majority-spin band from a completely empty minority-spin band resulting in a spin glass state. [10].

The question as to which picture, Zener or LSD, is more appropriate to describe  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  depends on the relative strength of the on-site  $d$ - $d$  correlations which tend to localize the  $5d$ -electrons on each their site, and the gain in band formation energy that results from the electrons becoming delocalized over the crystal. In order to evaluate the actual  $d$ -electron groundstate configuration, one needs to be able to compare the total energies of the two scenarios. With the SIC-LSD approximation, used in the present work, [13, 14] delocalized and localized  $d$ -electrons are treated on an equal footing, by adding a contribution to the LSD energy functional, allowing each  $d$ -electron to localize. [15] Thus the localized mean field scenario and the delocalized bandstructure scenario can be compared, and the groundstate configuration of the Mn-ion can be deduced from the global energy minimum.

When doping ZnO with Mn, the Mn ions occupy the Zn site without changing the wurtzite structure. [2] For our initial calculations, we consider a (2x2x2) supercell consisting of 8 ZnO unit cells, with a single Zn substituted by Mn. Changing the valency configuration of the Mn ion in  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ , from localized  $\text{Mn}^{2+}$  to delocalized  $\text{Mn}^{7+}$ , enables us to study the resulting changes in electronic structure, and to compare the corresponding total energies. The main graph in Fig. 1 shows the density of states (DOS), as obtained in the localized scenario, i.e. keeping five  $d$ -electrons on the Mn ion localized. The inset in the same figure shows the DOS, as obtained in the LSD approximation, i.e. with the Mn  $d$  electrons delocalized. The main difference

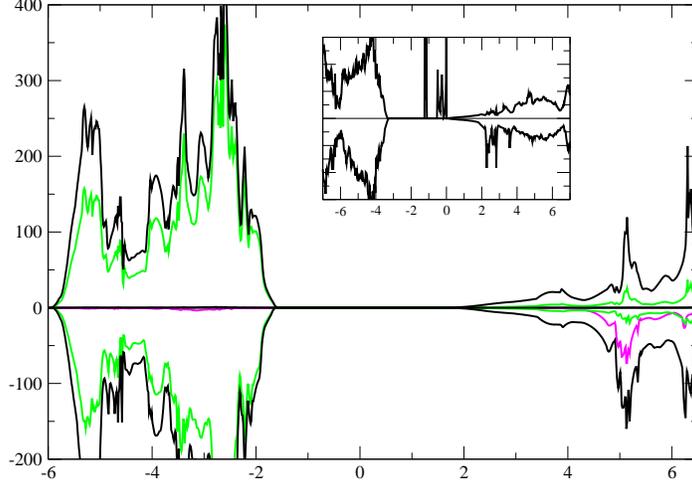


Figure 1: Total DOS, in states per eV, of  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ , with Mn respectively in the divalent  $\text{Mn}^{2+}$  configuration (main graph), and the delocalized  $\text{Mn}^{7+}$  configuration (inset). The black, purple, and green lines represent the total,  $d$ -projected, and  $p$ -projected densities of states respectively. The energies are in eV, with the Fermi energy at zero.

between the two plots, is that the band features, which in the delocalized scenario are situated just below the host conduction edge, have disappeared in the SI corrected scenario. The LSD picture is in good agreement with the previously mentioned *ab-initio* calculations. However, comparing the total energy for both scenarios, we find that the localized  $\text{Mn}^{2+}$  configuration is energetically favoured over the LSD scenario by more than 3 eV. Localizing the Mn  $3d$ 's on each their site thus results in an overall gain in SIC energy that far outweighs any corresponding loss in hybridization energy. The  $\text{Mn}^{2+}$  valency groundstate configuration is in agreement with experimental observation, [16] and would seem to support the Zener model rather than the band picture.

As was stated earlier, theory predicts ferromagnetism to occur in Mn-doped ZnO, only if additional hole carriers are introduced. In the Zener model the holes guarantee the communication between the localized sites, whilst according to the bandstructure calculations, due to the hole states, the majority spin-band is only partially filled, and the ferromagnetic double-exchange becomes strong enough to overcome the anti-ferromagnetic super-exchange. [10] We p-dope  $\text{Zn}_{15/16}\text{Mn}_{1/16}\text{O}$  by substituting a single O atom with N. Gradually delocalizing the Mn  $d$ -electrons, we find that the global

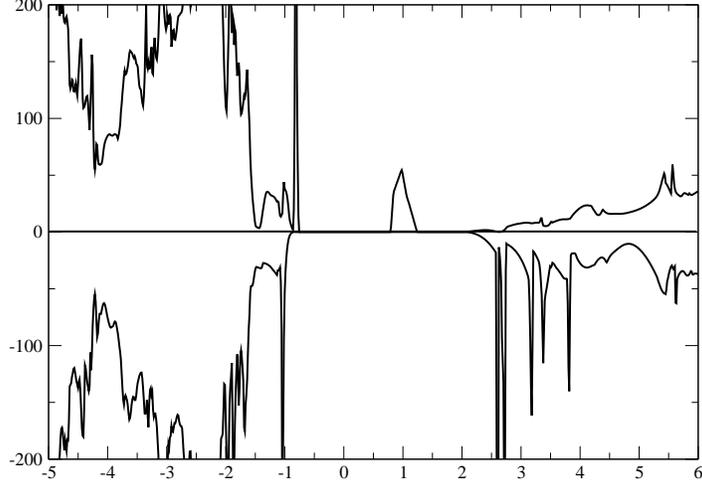


Figure 2: Total DOS (in states per eV) of  $\text{Zn}_{1-x-y}\text{Mn}_x\text{N}_y\text{O}$  in the trivalent  $\text{Mn}^{3+}$  configuration. The energies are in eV, with the Fermi energy at zero .

energy minimum is now obtained in the trivalent  $\text{Mn}^{3+}$  with four localized  $d$ -electrons. The resulting DOS for the groundstate configuration is shown in Fig. 2. The narrow, exchange-split peak, at the top of the valence band originates from the  $p$ -orbitals of the N-impurity. Compared to the O which it substitutes, N has one less occupied  $p$ -orbital, and in the scenario with 5 localized Mn  $d$ -electrons, this impurity peak would remain partially unoccupied. In the actual groundstate configuration, one of the otherwise localized  $d$ -states gains sufficient energy, through hybridization and charge transfer to overcome the corresponding loss in SIC energy, and prefers to delocalize, which results in the valence band being completely filled, and the Fermi level being situated in the band gap, below the delocalized Mn- $d$  peak. From the SIC-LSD calculations it thus follows that neither the itinerant nor the localized scenarios represent the groundstate of  $\text{Zn}_{15/16}\text{Mn}_{1/16}\text{O}_{15/16}\text{N}_{1/16}$  and that there are no hole carriers in the actual trivalent groundstate. Alternatively to N doping, we also considered P and C as possible hole donors, but also in this case the  $\text{Mn}^{2+}$  groundstate configuration is not realized.

The question arises to what degree the delocalization depends on the proximity of the Mn and N dopants. In order to determine the effect of the Mn-N distance on the preferred valency configuration of the Mn ion, we calculated the total energies for different scenarios, where the N impurity is substituting an O atom, situated at increasing distances from the Mn impurity. It turns out, that the trivalent configuration remains energetically most favourable, in all three cases, however we notice that the

energy difference between the divalent and trivalent configuration,  $E(\text{Mn}^{2+})-E(\text{Mn}^{3+})$ , decreases from the nearest neighbour scenario to the furthest away neighbour scenario. Overall, the lowest total energy is obtained for Mn and N substituting two neighbouring Zn and O sites, which might be an indication that the Mn ions will tend to cluster around the N impurity.

Even though the codoping with N readily removes one electron from the otherwise localized Mn- $d$  manifold, the resulting oxidation state is stable with respect to an increase in N concentration. Comparing the total energies of  $\text{Zn}_{15/16}\text{Mn}_{1/16}\text{O}_{14/16}\text{N}_{2/16}$  for respectively the  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Mn}^{4+}$  configurations, we find the  $\text{Mn}^{3+}$  configuration with four localized  $d$ -electrons to be energetically most favourable. In this scenario, the Fermi level is situated in the now only partially filled, N impurity band at the top of the valence band, and the coexistence of both localized spins from the  $\text{Mn}^{3+}$  and hole states in the valence bands, makes ferromagnetism, as proposed in the Zener model, theoretically possible.

In conclusion, we have studied the electronic structure of Mn impurities in ZnO. With no additional carriers, we find the localized  $\text{Mn}^{2+}$  to be energetically most favourable. When codoping with N, the  $\text{Mn}^{3+}$  configuration is realized, and ferromagnetism mediated by hole carriers becomes possible if the N concentration is larger than the Mn concentration.

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