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Electronic and Magnetic Properties of Co- and Mn-codoped ZnO by Density Functional Theory

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Zinc oxide crystal containing intrinsic oxygen vacancy defect as well as codoped with Mn and Co impurities is studied using density functional theory (DFT) calculations. An intra-atomic interaction term for the strongly correlated d-electrons by an unrestricted Hartree–Fock approximation (DFT+U method) is introduced to more precisely describe the system under study. The electronic and magnetic properties are investigated and discussed in detail. In particular, it is found that relative defect positions might influence the outcome if the material exhibits or not the n-type electrical conductivity.

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Zinc oxide is a wide band-gap semiconductor with a myriad of different applications in which it is a key element. The attractive features of the ZnO material include large exciton binding energy (60 meV) that permits excitonic lasing at room temperature, capability to be grown at low temperature on different substrates, piezoelectricity enabling high electromechanical coupling, and large electronegativity of the host oxygen, which allows strong p–d exchange coupling between the band carriers and localized spins. As a result, a wide range of ZnO nanostructures have been manufactured to investigate its applications in light-emitting devices,[1] varistors,[2] solar cells,[3] gas sensors,[4] field emission arrays and nanoscale biosensors.[5]

Recently, ZnO doped with transition metal (TM) ions has attracted a great deal of interest due to its magnetic properties. Such systems are called diluted magnetic semiconductors (DMS) and show permanent ferromagnetic behavior indicating a potential for use in spintronic devices.[6] Numerous works[7–15] have been reported on ZnO doped with different TM ions. Nevertheless, experimental results on TM-doped ZnO material do not converge to an explicit conclusion. The contradictory results obtained by different groups lead to debate over whether the ferromagnetism in zinc oxide is intrinsic or is due to some impurity phases or ferromagnetic precipitates. The array of seemingly contradicting experimental results as well as some lack of reproducibility has hampered practical applications of this system for electronic technology. On the other hand, there are suggestions that magnetism in ZnO is attributed to the simultaneous presence of two kinds of defects[13] forming chains of alternating effective donor and acceptor crystal sites, which could induce selective remote delocalization. Codoping also gives the possibility of using it to tailor the position and occupancy of the Fermi level of the doped DMS.[16–18] Some experimental works argue that simultaneous doping of cobalt (Co) and manganese (Mn) impurities[8,9] might allow obtaining required ferromagnetic behavior for the ZnO at room temperature, which is difficult to achieve in single doping cases. Additionally, it is known that codoping increases the solubility of dopants in ZnO,[19] which would allow more stable and lasting ferromagnetic behavior of ZnO just at room temperature. Simultaneous doping by two different specimens would also improve the conductivity of material due to the increase of the carrier mobility. Thus, there are experimental indications that Co- and Mn-codoping could be very beneficial and finally could lead to reproductive ferromagnetic behavior of the ZnO. The above mentioned experimental findings encouraged us to pursue the present research. In addition, it is known that the ZnO material normally contains oxygen vacancies as intrinsic point defects,[20] which can influence its features. This is why it is useful to take into consideration oxygen vacancy defects to study the effects of codoping.

The present work considers Co- and Mn-codoping in zinc oxide crystal already containing intrinsic oxygen vacancy defect. The research is performed at the density functional theory (DFT) level and envisages electronic, electrical and magnetic properties of the material. To the best of our knowledge no theoretical attempts have been carried out so far to study codoping in the ZnO containing oxygen vacancies.

DFT method[21] within the generalized gradient approximation (GGA)[22] scheme has been used throughout the work as it is implemented in the Vienna ab initio simulation package (VASP).[23] In this framework, valence electronic states are expanded in a set of periodic plane waves, and the interaction between the core electrons and the valence electrons is implemented through the projector augmented wave (PAW) method.[24] The following valence configurations have been exploited here: $3d^8 4s^1$ for Co, $3d^6 4s^1$ for Mn, $3d^{10} 4s^2$ for Zn and $2s^2 2p^4$ for O atoms, respectively. Perdew–Burke–Ernzerhof (PBE) developed[25] GGA functionals are used to describe the exchange–correlation interactions. Rotationally invariant approach to the GGA+U proposed by Dudarev *et al.*[26]

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has been employed. The value of U parameter for the Zn $3d$ electrons ($U = 5.0$ eV) was optimized to fit basic structural and electronic features of pure ZnO crystal. We replicated fairly well the lattice parameters of the hexagonal ZnO wurtzite-type structure. Computed values of lattice parameters were found to be equal to $a = 3.239$ Å and $c = 5.198$ Å, which are close to the corresponding experimental figures.[5] Computed band-gap width for the ZnO crystal has been found to be equal to 3.1 eV. This is only slightly smaller than the corresponding experimentally available outcome (∼3.4 eV).[27] Values of U parameter for the Co and Mn atoms were taken from elsewhere:[28] $U = 5.7$ eV for Co $3d$ electrons and $U = 4.5$ eV for Mn $3d$ electrons, respectively. A cut-off kinetic energy of 540 eV has been used by converging the total energy of ZnO primitive unit cell to less than 1 meVatom^{-1}. Here Γ-centred Monkhorst–Pack (MP) grid with a 0.04 Å^{-1} separation has been applied, which corresponds to a k-point mesh of $9 \times 9 \times 5$ for the 4-atom primitive unit cell of the ZnO. The above-mentioned parameters were obtained by the atomic relaxation until all the forces were <0.01 eVÅ^{-1} and equilibrium state of the system was achieved. To study effects produced by the dopants, 4-atom primitive unit cell was expanded twenty seven times ($3 \times 3 \times 3$ extension), which resulted in a 108-atom supercell. The k-point mesh of $3\times3\times2$ maintaining the same MP grid with a 0.04 Å^{-1} separation in the reciprocal space has been exploited for integrations over the Brillouin zone for the large supercell.

One of the O atoms has been removed from the 108-atom supercell creating a neutral oxygen vacancy. Oxygen vacancy concentration equals to 1.85 mol%. Performed geometry optimization clearly indicates that defect-nearest atoms tend to move themselves towards the empty region created by the oxygen removal. The average movements for Zn and O atoms are approximately 0.17 Å and 0.05 Å, respectively. Two occupied local states within the band-gap region have been observed. Their positions are 0.99 eV (α spin) and 1.67 eV (β spin) above the valence band (VB) top, respectively, or 2.11 eV (α spin) and 1.43 eV (β spin) below the conduction band (CB) bottom, respectively. We interpret these states as localized F-type centers (two electrons trapped by an oxygen vacancy).[29–31] These results are consistent with a previous experimental spectroscopy study[32] and theoretical computations[33] conducted for the oxygen vacancies in ZnO and arguing for the presence of F centers. We would also like to state that the fact that two electrons are well localized both spatially within the oxygen vacancy region and energetically within the band-gap suggests that oxygen vacancy cannot be the origin of the n-type electrical conductivity in ZnO because a considerable optical excitation would be required to transfer the electrons from their respective local energy states towards the CB region. The origin of the n-type conductivity in undoped ZnO is rather controversial subject in Refs. [9,34] and our study supports the concept that intrinsic n-type conductivity in this material is rather due to the ubiquitous H impurity rather than oxygen vacancy defect.[35] Our point is that hydrogen is rather difficult to be detected experimentally and as a result some of its properties in oxides are attributed to other entities, hitherto oxygen vacancy.

We observe the occurrence of a local magnetic moment, 2.94 μ_B, in the region nearby to the oxygen vacancy. The magnitude of this magnetic moment is mainly due to the following contributions: 4.2 μ_B from the neighboring O atoms and −1.26 μ_B from the closest Zn atoms. This implies antiparallel alignment of electrons in the O $2p$ atomic orbitals (AOs) with respect to those in the Zn $3d$ AOs. The fact that the undoped ZnO material might show magnetism has recently also been observed in the thermal annealing experiments on pure ZnO.[36] However, our outcomes might indicate that ferromagnetism in ZnO is not of intrinsic nature since antiparallel spin alignment is observed in our computations.

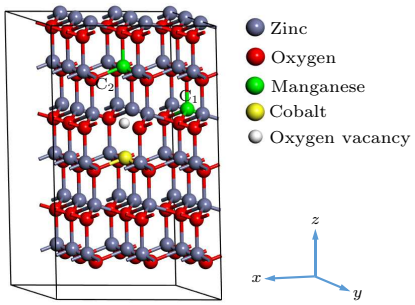

Fig. 1. Schematic diagram of relative defect positions within the ZnO crystal. C_1 and C_2 correspond to the Co atom position for the first and second configurations, respectively.

Co- and Mn-codoping has been carried out for the ZnO material already containing an oxygen vacancy defect. Twelve different configurations have been taken into consideration by situating Co and Mn atoms at different distances from the oxygen vacancy and also considering distinct Co-Mn inter-atomic separations. We also initially considered both parallel (ferromagnetic) and antiparallel (antiferromagnetic) alignments of electrons on the Co $3d$ and Mn $3d$ AOs. After careful geometry optimization of all systems we arrived at two configurations, which showed lowest total energies and thus can be considered as energetically favorable to be detected experimentally. The features of these two cases will be analyzed in the following.

The first configuration, also showing the lowest total energy, corresponds to the following inter-atomic separations (Fig. 1): 2.99 Å between Co and Mn impurities, 1.85 Å between oxygen vacancy and Co atom and finally 1.81 Å between oxygen vacancy and Mn impurity. The second configuration, showing 1.1 eV higher energy compared to that of the first configuration, shows the following final geometry (Fig. 1): 2.59 Å between the dopants, 0.56 Å between oxygen

vacancy and Co atom and finally 2.03 Å between oxygen vacancy and the Mn atom. As one can notice, Co impurity in the second configuration moves itself towards the empty vacancy site by a considerable amount.

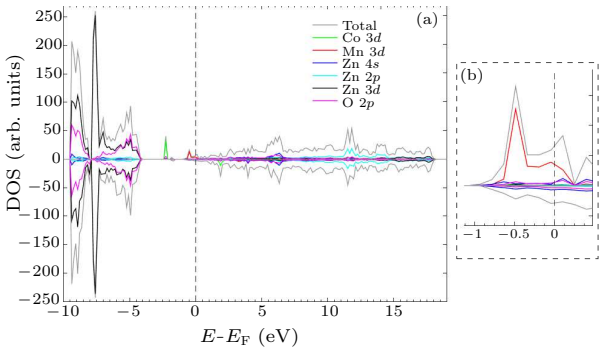

Fig. 2. (a) DFT+U computed total and partial DOS for the codoped ZnO material in the case of the first configuration. Local occupied in-gap states as well as n-type electrical conductivity have been observed. Vertical line denotes the Fermi level ($E_{\rm F}$). (b) Zoom of the DOS between -1.0 eV and 0.5 eV clearly indicating the area between the CB bottom and the Fermi level, which corresponds to free conducting electrons.

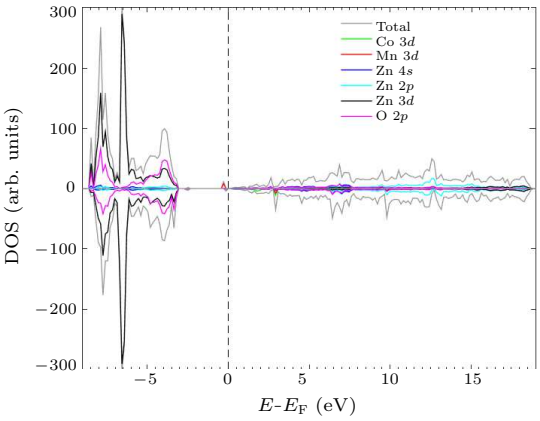

Fig. 3. DFT+U computed total and partial DOS for the codoped ZnO material in the case of the second configuration. Local occupied in-gap states have been observed. Vertical line denotes the Fermi level ($E_{\rm F}$).

Density of state (DOS) pattern depicted for the first configuration (Fig. 2) displays a possibility that codoping procedure might induce the n-type electrical conductivity in the material, which is a common feature of impurity-doped ZnO.[37] The area between the CB bottom and the Fermi level with a wave function mainly due to the Mn 3d AOs corresponds to free electrons; i.e., the solid can be treated for this case as a polarizable continuum with conducting electrons moving through the lattice. Additionally, a local occupied state has been found within the band-gap region. This state is situated roughly 1.8 eV above the upper VB edge and is composed predominantly of the Co 3d states with a considerable admixture of the O 2p AOs. Apparently, this state can be attributed to the localized F-type center. DOS for the second configuration (Figure 3) also shows a local occupied state within the band-gap region. However, the situation of this state is only 0.2 eV below the CB edge and apparently small excitation can lead to the electron transfer to the CB and subsequent n-type conductivity. Anyway, the electrical properties for the second configuration are quite different from those of the first configuration where free electrons are already present in the CB without any extra electron transitions. Therefore, we consider conductivity in the second configuration as semiconductor conductivity with high resistivity.

Magnetic impurities give rise to local magnetic moments within the material. In the case of the first configuration, the Co atom contributes 4.63 $\mu_{\rm B}$ and Mn impurity contributes 3.61 $\mu_{\rm B}$ towards the total magnetic moment of the supercell. These contributions are mainly due to the 3d electrons of both elements. Additionally, about 0.14 $\mu_{\rm B}$ are due to the defect-nearest O 2p electrons. Thus the total magnetic moment of the first configuration is equal to 8.38 $\mu_{\rm B}$. The second configuration has somewhat larger total magnetic moment, being equal to 9.15 $\mu_{\rm B}$, which is mainly due to the Co atom (4.62 $\mu_{\rm B}$) and the Mn atom (4.12 $\mu_{\rm B}$), respectively. The admixture of the nearest O atoms (0.41 $\mu_{\rm B}$) is also larger compared with that obtained for the first configuration. One can see that ferromagnetic ordering has been found in both the energetically feasible cases. Obviously, magnetic dopants can be considered as the origin of ferromagnetism in DMS ZnO samples. We would like to state that we cannot compare directly computationally obtained values of magnetic moments to the available experimental data for the ZnO crystal since experimental methodology and measurement conditions have too much influence on the experimental magnetic moments. It is also necessary to clear up that usually a given sample possesses a number of mixed magnetic phases, which compete between themselves reducing considerably the true value of magnetic moment. However, we can compare our results to the sum of magnetic moments for free Mn^{2+} ion, $\sim$5 $\mu_{\rm B}$,[38] and free Co^{2+} ion, $\sim$3 $\mu_{\rm B}$,[38] which gives $\sim$8 $\mu_{\rm B}$ for the dopant pair and is very close to our computed values. In our minds, magnetism and electronic properties are related between themselves,; i.e., there is the hybridization effect between electrons on the impurity 3d AOs and those on the neighboring O 2p AOs. It is also important to note that the lowest energy configuration provides the n-type electrical conductivity, meaning that the coupling mechanism of magnetic moments has been activated through the interaction between conduction electrons. Thus we suggest that the origin of the magnetism in the codoped ZnO material can be at least for some defect spatial configurations described by the Ruderman–Kittel–Kasuya–Yosida (RKKY) model.[39–41] However, depending on the relative defect-defect distances, other plausible explanations are possible. The same is truth with respect to the electrical conductivity traits. Both metallic n-type conductivity (configuration 1) and semiconductor conductivity (configuration 2) are options, de-

pending on the relative impurity-impurity as well as impurity-vacancy positions. The fact that the energy difference between the configurations described here is only 1.1 eV implies that both of the cases might occur simultaneously in a given sample, which is also confirmed experimentally.[42] Although we do not study separately single impurity doping, the configurations corresponding to impurity-impurity relative distance of 6 Å and larger may be considered as doping of single (not interacting) Co and Mn impurities. We can state that such configurations are not energetically stable since their energies are at least 25 eV higher compared with the equilibrium configurations discussed in the present study. Additionally, such single doping configurations tend to display antiparallel (antiferromagnetic) alignment between electrons in the Mn 3*d* and Co 3*d* AOs. Apparently, codoping provides stability for the system and lasting ferromagnetism.

In conclusion, Co and Mn codoping in ZnO leads to ferromagnetism whereas intrinsic oxygen vacancy defect produces a local magnetic moment while it does not conduct towards the permanent ferromagnetic behavior of the material. This was confirmed by our DFT+U computations considering a number of different Mn-Co-vacancy spatial configurations. We hope that these outcomes can contribute to better understanding of the origin of ferromagnetism in ZnO. Relative positions between defects in the crystalline lattice are of high significance since, depending on it, one might have different electrical features. In particular, n-type conductivity has been obtained when the impurity-vacancy distance is close to 1.8 Å for both dopants whereas the semiconductor behavior has been found in the case of one impurity (Co atom) situated very close to the empty vacancy site. It is also worth mentioning that oxygen vacancies do not produce the n-type electrical conductivity, instead they lead to the formation of localized F centers.

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