A report on the magnetic order of transition-metal δ-doped cubic ZnO

I. Galanakis\textsuperscript{1, a)}
Department of Materials Science, School of Natural Sciences, University of Patras, GR-26504 Patra, Greece

Preliminary results on the properties of transition-metal (Ti, V, Cr, Mn, Fe, Co, Ni) δ-doped ZnO are reported. Using \textit{ab-initio} electronic structure calculations the magnetic order is studied assuming both the cubic rock-salt and zinc-blende structures for ZnO. The ground state magnetic order is found to depend strongly on the transition-metal atom.

ZnO is a well-known wide-band semiconductor crystalizing in the wurtzite (WZ) structure.\textsuperscript{1} When grown as a thin film the lattice structure adopted is the cubic analog the zinc-blende (ZB) structure, while a pressure of about 6 GPa induces the cubic rock-salt (RS) structure.\textsuperscript{1} Both cubic structures have similar lattice constants (4.47 Å for the ZB and 4.25 Å for the RS). Both can be viewed in general as a fcc lattice with four sites as basis distributed along the diagonal in equidistant positions. In both structure the Zn atoms occupy the origin of the unit. In the RS the oxygen atoms are located at the middle of the diagonal and in reality they bridge the Zn atoms being positioned in the middle of the line connecting the nearest-neighboring Zn atoms being located in the same (001) layer with them. In the ZB structure the oxygen atoms occupy the second site along the diagonal and they create a pure O (001) layer which lies in-between two successive pure (001) Zn layers. Finally we should remark that the WZ and RS structures are similar since the Zn and O atoms show similar electronic properties in both structures; only the width of the bands in the density of states (DOS) is somewhat smaller in the WZ structure.

ZnO has started to attract considerable consideration in spintronic/magneto-electronic research since it was discovered that the occurrence of Zn/O antisites or defects can lead to the appearance of magnetism.\textsuperscript{2} Moreover the case of transition-metal impurities has been widely studied\textsuperscript{3} (especially Co and Mn impurities) but contradictory results are found in literature both within the experimental and theoretical articles and thus the appearance of magnetic order in ZnO diluted magnetic semiconductors still remains an open issue.\textsuperscript{4–7} In this report we present preliminary results on the transition-metal δ-doped cubic ZnO structures. We have considered a tetragonal 1×1×2 unit cell and along the (001) direction we have substituted one Zn layer with a transition-metal layer; thus if we neglect the oxygens we have one transition-metal layer followed by three Zn layers which is repeated along the (001) direction. Within the transition metal layer we have considered both ferromagnetic (FM) and antiferromagnetic (AFM) coupling of the nearest-neighboring transition-metal atoms and we have calculated the total energies of the considered magnetic configuration. To perform the calculations we have employed the full-potential nonorthogonal local-orbital minimum-basis band structure scheme (FPLO)\textsuperscript{8} within the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof formulation.\textsuperscript{9} Moreover in the reciprocal \textbf{k}-space we considered a 12×12×6 grid in the Brillouin zone to perform the integrals calculations. The Zn 3\textit{d} states were treated as valence states and they result in a narrow band low in energy with respect to the other valence states.

\begin{table}[h]
\centering
\caption{Calculated atom-resolved spin magnetic moments ($\mu_B$) for the transition-metal atoms for the two cubic structure under study (ZB and RS) for the cases of magnetic coupling taken into account.\textsuperscript{a)}
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{X} & \textbf{AFM} & \textbf{FM} & \textbf{AFM} & \textbf{FM} \\
\hline
\textbf{Ti} & 0.000 & - & 1.163 & - \\
\textbf{V} & 2.027 & 2.736 & 2.668 & 2.615 \\
\textbf{Cr} & 3.237 & - & 3.787 & 3.743 \\
\textbf{Mn} & - & 4.701 & - & 4.640 \\
\textbf{Fe} & 3.523 & 3.759 & 3.751 & - \\
\textbf{Co} & 2.474 & 2.655 & 2.515 & - \\
\textbf{Ni} & 1.308 & 1.575 & 1.658 & - \\
\hline
\end{tabular}
\label{tab:1}
\end{table}

\begin{table}[h]
\centering
\caption{Energy difference in eV. 2nd and 3rd column are the differences between the ZB and the RS ($\Delta E_{ZB-RS}$) structure in both the FM and AFM configurations; positive value means that the RS structure is favored while negative means that the ZB is favored. 4th and 5th column are the differences between the AFM and the FM ($\Delta E_{AFM-FM}$) orderings in both the ZB and RS structures; positive value means that the FM configuration is favored while negative means that the AFM is favored. The last column denotes which is the stable ground state. Dashes correspond to the case where the $\Delta E$s cannot be computed since they involve not-converged calculations.\textsuperscript{a)}
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{X} & $\Delta E_{ZB-RS}$ & $\Delta E_{AFM-FM}$ & \textbf{Stable} \\
\hline
\textbf{AFM} & \textbf{FM} & \textbf{ZB} & \textbf{RS} & \textbf{Ground State} \\
\hline
\textbf{Ti} & +0.511 & - & - & AFM-RS \\
\textbf{V} & +0.933 & +0.109 & +0.425 & -0.398 & AFM-RS \\
\textbf{Cr} & +0.474 & - & - & -0.304 & AFM-RS \\
\textbf{Mn} & - & -0.624 & - & - & FM-ZB \\
\textbf{Fe} & -1.342 & - & -0.242 & - & AFM-ZB \\
\textbf{Co} & -1.601 & - & -0.204 & - & AFM-ZB \\
\textbf{Ni} & -0.068 & +0.380 & - & - & FM-ZB \\
\hline
\end{tabular}
\label{tab:2}
\end{table}

\textsuperscript{a)}Electronic mail: galanakis@upatras.gr
FIG. 1. Density of state (DOS) of the Ti atom in the various cases under study. Note that the Fermi energy is set to zero. Positive (negative) DOS values correspond to the spin-up (spin-down) states. In the AFM cases the DOS of the second Ti atom has the two spin-bands exchanged.

In table I we have gathered the spin magnetic moments of the transition metal atoms for both ZB and RS structures. We do not present the induced spin magnetic moments for the Zn and O atoms since they are almost negligible with respect to the transition metal atoms. Wherever no number is given, are the cases where convergency could not be achieved. For Ti we were able to converge only the AFM configurations but only in the RS structure magnetism was present. As shown in Fig. 1, the AFM-ZB is a usual metal while in the AFM-RS case around the Fermi level we get only spin-up states and the compound is in reality a half-metal since the Zn and O atoms (not presented here) show an almost semiconducting behavior. The later is also the ground state as can be deduced from Table II where we present the energy differences between the various configurations.

When the $\delta$-doping is of vanadium character we were able to converge all cases as shown in Table I with large spin magnetic moments which approach the ideal $3\mu_B$ of the isolated single V impurity with the exception of AFM-ZB. The later case as shown by the DOS is Fig. 2 is the only case where a small weight around the Fermi level is also present in the spin-down band structure. The most stable structure as can be deduced from Table II is the AFM-RS structure as for the Ti-case, which should be robust since the Fermi level is located after a high-intensity pick in the spin-up DOS crossing a low of the spin-up DOS. Cr shows similar behavior to V although we were not able to converge the FM-ZB case. Again for the two magnetic orderings of the RS we get spin magnetic moments approaching the ideal $4\mu_B$ of the isolated single Cr impurity and the AFM-RS is the ground state as shown in Table II. DOS in Fig. 2 shows similar trends to the V one although almost states corresponding to the one extra electron are occupied in the spin-up DOS.

In the case of Mn, we were able to converge only the FM solutions for both RS and ZB structures with very large Mn atomic spin magnetic moments; they approach the $5\mu_B$ of the isolated Mn impurity. The most stable is the FM-ZB structure and not the RS one showing a different behavior with respect to the early-transition metal $\delta$-doping. As shown in Fig. 3 the FM-ZB is in reality a ferromagnetic semiconductor while the FM-RS is a special case of spin-gapless semiconductor since the top of the spin-up valence touches the bottom of the spin-down conduction band exactly at the Fermi level.

As we substitute Fe(Co,Ni) for Mn we start populating also spin-down states. and the atomic spin magnetic moments decrease by about $1\mu_B$ as we move from Mn to Fe and then to Co and Ni since we increase the number of valence electrons by one. In all three Fe-, Co- and Ni-cases we were not able to converge the FM-RS structure and the ground state was found among the two magnetic ZB configurations as for the Mn-case (FM-ZB for Fe and Co and FM-ZB for Ni). As shown in Fig. 4 the cases of Fe, Co and Ni $\delta$-doping in the ground ZB structure should not be stable since the Fermi level crosses intense spin-down picks.

To conclude using first-principles calculations we present preliminary results on the magnetic ordering in
FIG. 3. Similar to Fig. 1 for the Mn δ-doped system under study.

the case of transition-metal δ-doping in cubic zinc-blende (ZB) and rock-salt (RS) structures. The ZB is expected to represent also the phenomena occurring in the ground wurtzite structure. When the doping is of Fe, Co and Ni character we expect the resulting structure to be unstable. Mn doping leads to stable ferromagnetic coupling while in all three Ti, V and Cr doping-cases the antiferromagnetic RS structure is favored. Mn-based systems are magnetic semiconductors while the rest of the early transition metal atoms (Ti, V, Cr) results in half-metallic behavior. Further calculations using more dense grids in the reciprocal space as well as calculations including the on-site Coulomb correlations (Hubbard U) are programmed to be performed as the next step. Especially on-site correlations should play a decisive role since it has been already shown that even in bulk ZnO the electronic properties are altered when the former are included, and the effect is even larger in transition-metal doped ZnO.11,12

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FIG. 4. Similar to Fig. 1 for the Fe, Co and Ni δ-doped systems under study.

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