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Magnetism and clustering in Cu doped ZnO

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The influence of defect charge state on the magnetism of Cu doped ZnO as well as the Cu defects clustering have been investigated by the first-principles calculations. We demonstrate that *p*-type ZnO:Cu could have ferromagnetic (FM) property, but *n*-type ZnO:Cu would not have local magnetic moment. Furthermore, the neutral substitutive Cu defects are found to be favorable in clustering, which maintains the FM ordering. © *2008 American Institute of Physics*.

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The possibility to utilize both charge and spin degrees of freedom into semiconductor devices has spawned a new field of electronics known as "spintronics."[1,2] Room-temperature diluted magnetic semiconductors (DMS) are intensively requested for the spintronic application nowadays. Recently, Cu doped semiconductors (such as ZnO, GaN, TiO_2 etc) have been shown to be ferromagnetic (FM) from both first-principles calculations[3–6] and experiments.[7–10] Among these alloys, ZnO attracts most interests since it was predicted as one of the most promising materials for room-temperature DMS,[11] in addition to its versatile properties in piezoelectric, optical, and semiconducting fields.[12]

Much of the experimental work on the magnetism of oxide and nitride semiconductors has been controversial, and ZnO:Cu is not an exception. Particularly, the magnetic moments per Cu atom are dispersedly distributed. In addition to the dispersedly reported magnetic moment, there exists discrepancy on whether *n*-type or *p*-type is beneficial to the ferromagnetism in the ZnO:Cu sample. Buchholz *et al.*[8] pointed out that *p*-type ZnO:Cu was FM but *n*-type ZnO:Cu was non-FM. Conversely, Hou *et al.*[13] reported *n*-type ZnO:Cu was FM and the magnetic moment decreased with the electrons concentration due to the nitrogen doping. More recently, Keavney *et al.*[14] also found FM in *p*-type ZnO:Cu and non-FM in *n*-type ZnO:Cu sample. However, they find no dichroic signal consistent with FM originating from any of Cu, O, and Zn ions, leaving the magnetism in ZnO:Cu a mystery.

From the theoretical point of view, earlier work[15] found that ZnO doped with 25% Cu showed a non-FM ground phase. Subsequently, it was found in the 12.5% Cu-doped ZnO that the FM state was favored when doped Cu atoms were well separated, but the antiferromagnetic (AFM) state became more stable for a pair of close Cu atoms.[16] Recently, Ye *et al.*[3] and Huang *et al.*[4] both found that ZnO:Cu had strong FM interaction when two Cu atoms were even closely separated. Meanwhile, Ye *et al.*[3] showed that there was no tendency for Cu clustering in ZnO:Cu, in clear contrast with the experimental report of Cu planar clustering.[17] While above theoretical work presented interesting magnetic properties in ZnO:Cu, the charge state effect of Cu defects in ZnO was not considered. It has been demonstrated that the charge state of transition metal defects has significant impact on the magnetic properties in the magnetic semiconductors.[18] Particularly, the controversy of FM in ZnO:Cu has involved its conductivity types (*p*-type versus *n*-type). Therefore, there is no reason to neglect the impact of charge state of Cu defects in ZnO:Cu.

In this work, we find that Cu atoms in ZnO are likely in the form of ${Cu_{Zn}}^0$ (i.e., Cu^{2+}) or ${Cu_{Zn}}^-$ (i.e., Cu^{1+}) when Cu is the dominant defects in ZnO sample. The calculation shows that Cu^{2+} or Cu^{3+} possesses of local magnetic moment, while Cu^{1+} and Cu^0 do not. Moreover, our calculated defect formation energy shows that Cu presents as Cu^0 or Cu^{1+} in *n*-type sample and presents as Cu^{2+} or Cu^{1+} in weak *p*-type sample. Thus, *n*-type ZnO:Cu would not show FM, while *p*-type ZnO:Cu could have FM property. A strong tendency of Cu–O–Cu clustering is shown from the study of a series of configurations for a pair of Cu atoms in a 72 atom supercell. We have also investigated the possibility of clustering for three Cu ions in ZnO and found that in-plane trimer are favorable to form with FM ordering.

Our first-principles calculations have been carried out with the spin polarized density functional theory and the PW91 generalized gradient approximations formulas[19] for the exchange and correlation functional. A plane-wave basis set and the projector augmented wave potentials[20] are employed as implemented in the Vienna *ab initio* simulation package (VASP).[21,22] An energy cutoff of 500 eV is used throughout the calculations. Brillouin zone integrations are performed with the special *k*-point method over a 3×3×3 Monkhorst–Pack mesh for a 72 atom supercell. The theoretically calculated equilibrium lattice parameters of wurtzite ZnO, $a=3.282$ Å and $c=5.265$ Å, are employed, and the internal coordinates are fully relaxed throughout this work.

The formation enthalpies for extrinsic Cu doping and intrinsic defects at different charge state are calculated with a single Cu atom in a 3×3×2 supercell consisting of 72 atoms according to[23]

$$\Delta H_f^{(\alpha,q)} = E(\alpha,q) - E(0) + \sum_{\alpha} n_a(\Delta\mu_\alpha + \mu_\alpha^{\text{solid}}) + q(E_{\text{VBM}} + E_F), \qquad (1)$$

where $E(\alpha,q)$ and $E(0)$ are the total energy of the supercell with and without defect α. Here $(\Delta\mu_\alpha+\mu_\alpha^{\text{solid}})$ is the absolute value of the chemical potential of atom α. $\mu_\alpha^{\text{solid}}$ is the chemical potential of the elemental solid. Also, n_α is the number of

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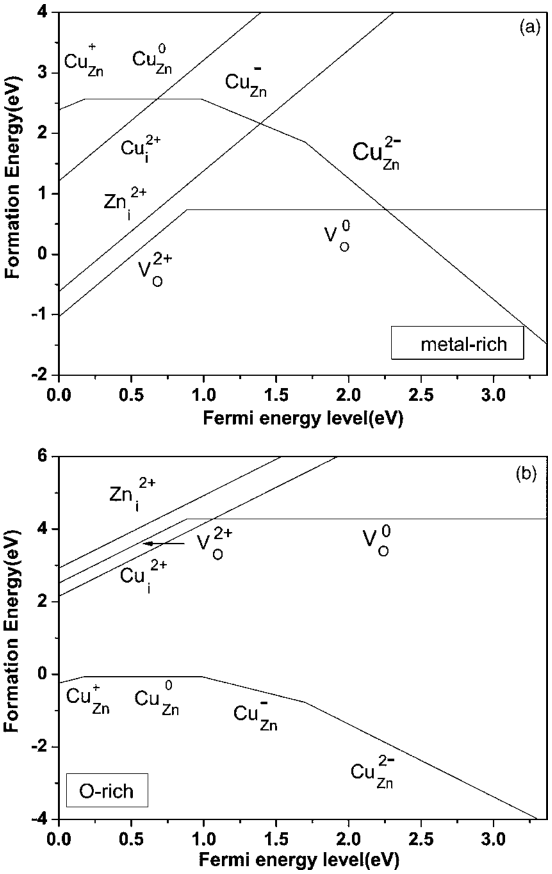

FIG. 1. The calculated defect formation energy as a function of E_F under (a) Cu-rich and Zn-rich conditions and (b) oxygen-rich conditions. The charge states of the defects are marked accordingly. Here, the experimental gap of ZnO, $E_g=3.37$ eV, is adopted.

atoms for each defect; $n_\alpha=-1$ if an atom is added, while $n_\alpha=1$ if an atom is removed. $E_{\rm VBM}$ represents the energy of the valance band maximum (VBM) of the defect-free system and E_F is the Fermi energy relative to the $E_{\rm VBM}$.

Figure 1 shows the formation energies of substitutive and interstitial Cu defects in ZnO and the main intrinsic defects under the metal-rich and oxygen-rich conditions. Under the metal-rich condition, we set $\Delta\mu_{\rm Cu}=0$ and $\Delta\mu_{\rm Zn}=0$, i.e., the sample is in equilibrium with metal Cu and metal Zn. Under the oxygen-rich condition, we set $\Delta\mu_{\rm O}=0$ and $\mu_{\rm O}$ is referred to the O chemical potential in molecule $\rm O_2$. Correspondingly, $\Delta\mu_{\rm Zn}$ is derived from $\Delta\mu_{\rm Zn}+\Delta\mu_{\rm O}=\Delta H_f(\rm ZnO)$, and $\Delta\mu_{\rm Cu}$ is the maximum Cu chemical potential under the condition of $2\Delta\mu_{\rm Cu}+\Delta\mu_{\rm O}\leqslant\Delta H_f(\rm Cu_2O)$. The defect charge states of Cu are marked in Fig. 1. The transition energy levels of Cu defect are located at 0.18, 0.98, and 1.70 eV, respectively. Our calculated transition level of $\rm Cu^{2+}/Cu^{1+}$ at 0.98 eV is also in consistent with the emission peak in the photoluminescence spectra of ZnO:Cu at 525 nm (2.36 eV) (Ref. 24) or 510 nm (2.43 eV),[25] which is expected to be induced by the transition between the conduction band minimum ($E_g=3.37$ eV) and the transition level at 0.98 eV.

Our calculations indicate that the ZnO:Cu system containing $\rm Cu_{Zn}{}^{+}$ (i.e., $\rm Cu^{3+}$) or $\rm Cu_{Zn}{}^{0}$ (i.e., $\rm Cu^{2+}$) is found to possess magnetic moments of $2\mu_B$/Cu and $1\mu_B$/Cu, respectively.[26] However, the system is found to be nonmagnetic when the Cu defects stay in ZnO as $\rm Cu_{Zn}{}^{-}$ (i.e., $\rm Cu^{1+}$), or $\rm Cu_{Zn}{}^{2-}$ (i.e., $\rm Cu^{0}$).This could be expected from the electronic configuration of Cu. The configuration of $\rm Cu^{3+}$ is corresponding to $3d^84s^0$, while $\rm Cu^{2+}$ is corresponding to $3d^94s^0$. $\rm Cu^{1+}$ or $\rm Cu^0$ does not possess of any local magnetic moment since its d electrons are fully filled at the configuration of $3d^{10}4s^0$ or $3d^{10}4s^1$ correspondingly. It is well known that ZnO is easy to form n-type intrinsic defects such as oxygen vacancies ($V_{\rm O}$) and zinc interstitials ($\rm Zn_{\it i}$), and thus E_F is likely to stay above the midgap intrinsically. As shown in Fig. 1, the Fermi level may not move to the p-type region to form $\rm Cu_{Zn}{}^{0}$ under metal-rich condition, due to the low formation energy of n-type intrinsic defects such as $\rm Zn_{\it i}$ and $V_{\rm O}$. However, under O-rich condition, substituting Cu defect clearly has the lowest formation energy. When the doping concentration of Cu increases, substituting $\rm Cu^{1+}$ or $\rm Cu^0$ helps the p-type conductivity of ZnO and the Fermi level would shift toward p-type region until the transition level of $\rm Cu^{2+}/Cu^{1+}$ as a result of overall charge neutrality.[27] The ratio of $\rm Cu^{2+}/Cu^{1+}$ will be determined by the chemical potential of Cu and other growth condition since the negative charged $\rm Cu_{Zn}{}^{-}$ defects will be neutralized by the positive charged $\rm Zn_{\it i}$ and $\rm Cu_{\it i}$ defects. Thus, most of Cu would be in the oxidation state of +2 or +1 in the ZnO:Cu sample as E_F is pinned around $\rm Cu^{2+}/Cu^{1+}$ under O-rich condition. This is in consistent with the experiment observation that Cu is in a mixed oxidation state of +1 or +2 from the x-ray photoelectron spectroscopy in which the samples show the large resistivity[7,28] and the ratio of $\rm Cu^{2+}/Cu^{1+}$ would increase after N incorporation (p-type defect) into the sample.[28] It is clear from our theoretical calculations that n-type ZnO:Cu is non-FM and p-type ZnO:Cu could be FM. This supports

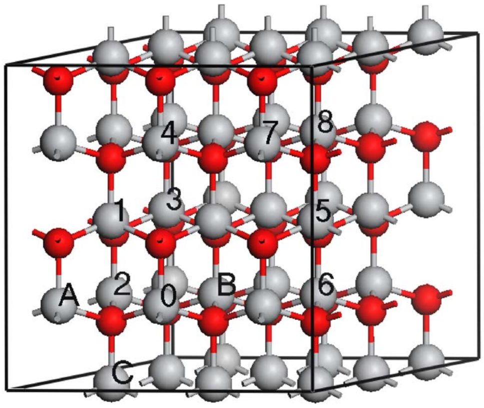

FIG. 2. (Color online) The schematic 72 atom supercell used in the calculations. The gray and red balls stand for Zn and O atoms, respectively.

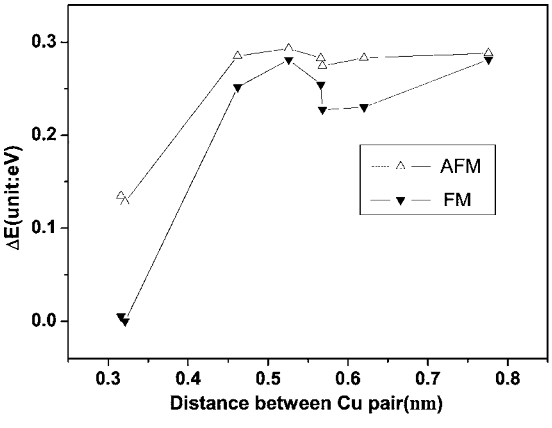

FIG. 3. The relative energies of eight different configurations as the pair distance changes for both AFM and FM phases. The total energy of configuration 2 under FM state is set to zero as a reference.

TABLE I. The total energies (in meV) of the three Cu atoms doped ZnO, relative to the lowest energy in the considered configurations. The configuration labeled with "—" is found to transit to the other magnetic phase spontaneously. The sites 0, 1, 2, A, B, and C are shown in Fig. 2.

	Closely separated				Well separated
Configurations	0-2 plus A	0-2 plus C	0-2 plus 1	0-2 plus B	0-2 plus 8
Ferrimagnetic	—	—	—	137	419
FM	0	18	61	68	369

the experiment observation from Refs. 8 and 14 but is in contradiction with results from Ref. 13. It is suggested that the reported *n*-type FM ZnO:Cu samples need more careful characterizations.

In order to get a clear picture on the clustering and magnetic property in ZnO:Cu, we have done a systematic calculations for two ${\rm Cu_{Zn}}^0$ defects in a $3\times3\times2$ supercell (Fig. 2).[29] One Cu is put at a Zn lattice site (marked 0 in Fig. 2), and the other Cu atom is put at positions 1–8 of the Zn lattice site according to the order of Cu–Cu distance. This gives eight different configurations, where configuration n denotes for the Cu pair of $(0,n)$.

We find that configuration 2 with FM ordering has the lowest total energy, and the relative energies of the eight different configurations are shown in Fig. 3. Obviously, the magnetic coupling of ZnO:Cu is dominated by short ranged interatomic exchange interactions and shows a directional dependence. The energy difference between FM and AFM is similar for configurations 1 and 2, but significantly drops for the other configurations. The interaction via hopping along $[1\bar{1}00]$ (configuration 6) and $[\bar{1}2\bar{1}1]$ (configuration 7) direction lowers the total energy of the FM phase significantly. They are both orientated along the $\langle110\rangle$ direction as denoted in the three-axis coordinates.

Figure 3 indicates that the Cu pair in ZnO has a clear clustering tendency for both FM and AFM phases. The possibility of further clustering of three Cu (i.e., ${\rm Cu_{Zn}}^0$) atoms is considered in a 72 atoms ZnO supercell. Local structures based on the FM phase of configuration 2, the most stable Cu pair are constructed for the possible three atoms clustering: four closely separated structures (configuration 2 plus site 1, A, B, or C in Fig. 2) and one well separated structure (configuration 2 plus site 8 in Fig. 2). Calculated results are listed in Table I for both the FM and ferrimagnetic (spin of the other Cu site is opposite to that of configuration 2) phases. We find that the FM phase of configuration 2 plus A structure is energetically favored. The AFM phases of the closely separated configurations are spontaneously transited to the FM phases except for the case of configuration 2 plus B. For the well-separated configuration, FM phase is also found to be stable with its energy lower than the ferrimagnetic phase by 50 meV. The well-separated configuration is unstable by 369 meV in comparison with the case of configuration 2 plus A.[30] Thus, it is demonstrated that the Cu defects has a tendency to form clusters, with the FM ordering maintained. This is consistent with the experimental observation of Cu planar clustering,[17] but in sharp contrast with the results of Ye *et al.*[3] which is done in a 32 atom supercell.

In summary, we have investigated the influence of defect charge state on the magnetism and the Cu clustering in Cu-doped ZnO by the first-principles calculations. It is shown that the FM coupling is favored between the substitutive Cu ions at +2 or +3 oxidation state, which are only available in the *p*-type samples. The Cu^{1+} and Cu^0 defects would form in *n*-type samples, but would not possess any local magnetic moments. Thus, the reported FM *n*-type ZnO:Cu samples may need careful characterization. Clustering of Cu defects is found to be energetically favorable with the FM ordering maintained. A dimmer and an in-plane trimer in FM ordering are found to be stable for 2 and 3 Cu atoms clustering, respectively.

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[30] We also calculate the configuration 2 plus site A and configuration 2 plus site 8 in a 108 atom supercell. The results show no remarkable difference with that obtained from the 72 atom supercell.