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Half-metallic ferromagnetism in Cu-doped ZnO: Density functional calculations

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Half-metallic ferromagnetism in Cu-doped ZnO is predicted by accurate full-potential linearized augmented plane-wave and DMol^3 calculations based on density functional theory. A net magnetic moment of $1\mu_B$ is found per Cu. At a Cu concentration of 12.5%, total energy calculations show that the ferromagnetic state is 43 meV lower than the antiferromagnetic state and is thus predicted to be the ground state with a T_c estimated to be about 380 K. The magnetic moments are localized within the CuO$_4$ tetrahedron with ferromagnetic coupling between Cu and O. The electronic states near E_F are dominated by strong hybridization between O $2p$ and Cu $3d$ which implies that the Cu-O bond is quite covalent instead of purely ionic. We examine the interplay between the carrier density and the ferromagnetism with N codoping and oxygen vacancies where we find no apparent relation between them. Oxygen vacancies tend to destroy the ferromagnetism and therefore should be avoided during sample fabrication. We found no clustering tendency of the Cu atoms. Since there is no magnetic element in this compound, Cu-doped ZnO appears to be an unambiguous dilute magnetic semiconductor where ferromagnetic precipitate problems can be avoided.

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The possibility that the electron spin can be manipulated along with the charge degree of freedom in semiconductors has aroused great enthusiasm for so-called "spintronic" physics and its applications. Dilute magnetic semiconductors (DMS's) are proposed as spin injection sources because they can be used for seamless spin injection into semiconductors, whereas metal-semiconductor contacts suffer from low spin injection efficiency due to interface scattering. Since the possibility of high-temperature ferromagnetism (FM) in DMS's has been studied by Dietl *et al.* with the Zener model of ferromagnetism,[1] many materials have been found which display room-temperature FM.[2] Among them, ZnO-based DMS's have attracted the most attention since they become FM when doped with most of the transition-metal elements. The strong FM in these materials, however, challenges our understanding and raises two questions: (i) is the FM really intrinsic and (ii) are there really strong magnetic interactions between well-separated magnetic dopants? Unless we get clear positive answers to these questions, otherwise the usefulness of the materials is called into question. Unfortunately, as regard to the first question, it is found that various magnetic impurity phases exist in many samples;[2,3] to the second question, theoretically it is often found that the dopants often have a clustering tendency, which implies that FM may originate from nonuniform distributions of dopants.

Based on accurate first-principles electronic structure calculations, we propose Cu:ZnO as a high-T_c DMS which is free from the FM precipitate problems. We found a net magnetic moment of $1\mu_B$ per Cu and a half-metallic ground state with 100% carrier polarization that is excellent for spin injection applications. T_c is estimated to be about 380 K by the Monte Carlo simulation relation.[4] Our result is in contradiction with that of Sato and Katayama-Yoshida,[5] but agrees with the more recent work of Feng[6] and Park and Min.[7] Following our theoretical predictions,[8] room-temperature FM in Cu:ZnO has been indeed discovered recently.[9] Further, we show that the Cu dopant does not cluster, which very likely means that strong FM interactions indeed exist between well-separated dopant atoms. Moreover, we checked the possible correlation between the FM and hole density by including N codoping and oxygen vacancies, and we found that the FM seems not to be related to hole mediation. Since oxygen vacancies weaken the FM and destroy conductivity, they should be carefully avoided during sample fabrications.

The first-principles simulations were performed using the full-potential linearized augmented plane-wave (FLAPW) method[10] based on density functional theory. The muffin-tin radii of Cu, Zn, and O were chosen to be 2.3, 2.0, and 1.4 a.u., respectively, with the plane-wave basis cutoff $|\mathbf{k}+\mathbf{G}|<4.0$ a.u.$^{-1}$ and the star function cutoff of 9.0 a.u.$^{-1}$. Brillouin zone integrations were performed with the special k-point method over a $5\times5\times3$ Monkhorst-Pack mesh.[11] Convergence testings were performed, first by increasing the k point mesh to $7\times7\times5$ and then to $9\times9\times7$; we found that the total energy differs only by 10^{-5} hartree. Then we fixed the k-point mesh at $5\times5\times3$ and increased the plane-wave basis cutoff to 4.5 a.u.$^{-1}$ and 5.0 a.u.$^{-1}$; again, we found a similar very small total energy change. Thus our results are well converged. For the exchange correlation functional, we employed the local density approximation (LDA) (Hedin-Lunquist form[12]) and generalized gradient approximation (GGA) (Perdew-Burke-Ernzerhof form[13]), on pure ZnO. Both functionals gave very good lattice constants. Pure ZnO has a wurzite structure with $a=3.25$ Å and $c/a=1.60$. Our LDA results underestimated both quantities by 1.7% and 0.61%, and the GGA overestimated them by 0.86% and 0.28%, respectively. For Cu-doped ZnO, we used the GGA in our calculations.

The supercell employed contains 32 atoms which corresponds to a $2\times2\times2$ supercell of ZnO. Two doping levels were checked: for $x=0.125$, two Zn atoms were substituted by Cu, while for $x=0.0625$ only one Zn is substituted. Most of our results were achieved for $x=0.125$ and will be compared to the $x=0.0625$ case where applicable. To make our simulations closest to the dilute doping limit, we put the two Cu atoms on positions with the largest possible distance (6.1 Å) between them in the supercell. The preferential substitution of Cu on the Zn site was confirmed by a recent experiment,[14] where no well-defined interstitial site for Cu was found. The doped structures were then optimized with respect to both the lattice constants and the atomic positions. Because the ionic radius of Cu is close to that of Zn,[15] one would not expect strong structural relaxation through Cu doping. Indeed, we found that the lattice constants changed by only −0.01 Å for a and +0.02 Å for c. The displacements of the atoms were also very small—typically 0.005 Å in magnitude. Experimentally,[14] Cu was found to occupy almost the ideal Zn site in the as-planted Cu-doped ZnO sample, until at high temperature ($>600\ ^\circ\mathrm{C}$) the Cu starts to diffuse.

For $x=0.125$, total energy comparisons between the FM and antiferromagnetic (AFM) phases show a difference of 43 meV, with the FM state being the ground state. Adapting the Heisenberg model with only nearest-neighbor exchange between Cu atoms and the relation $T_c=0.447J_1$ from Monte Carlo simulations,[4] T_c is estimated to be 380 K which is well above room temperature.

In Fig. 1, the band structure of the FM Cu-doped ZnO with $x=0.125$ shows half-metallic behavior with a half-metallic band gap of 0.3 eV; the majority-spin component is semiconducting while the minority-spin component is metallic. The carriers are thus 100% polarized which is the ideal case for spin injection applications. States near E_F are composed mostly of Cu 3d bands, hybridized strongly with the O 2p bands. Cu and its surrounding four O atoms form a $\mathrm{CuO_4}$ tetrahedron; their hybridization dominates the electronic and magnetic properties. The 2p bands from other O atoms away from the $\mathrm{CuO_4}$-distorted tetrahedron comprise the −1 eV to −5 eV region. Zn 3d states are located below E_F by more than 5 eV; hence, the $\mathrm{Zn^{2+}}$ ion is chemically inactive.

Table I displays the magnetic moment distribution in the supercell. For $x=0.125$, a total magnetic moment of $2\mu_B$ per supercell, or $1\mu_B$ per Cu atom, is found due to the half-metallicity: Cu is polarized with a magnetic moment of $0.58\mu_B$, and the four surrounding O atoms in the $\mathrm{CuO_4}$ tetrahedron are polarized with a magnetic moment of $0.04\mu_B$ for the top site O and $0.08\mu_B$ for the other three O in the basal plane. The smaller magnetic moment for the top site O is due to the distortion of the tetrahedron; the Cu-O bond is longer for the top side O than the three lying in the basal plane. The magnetic moments on Zn and other O atoms away from the $\mathrm{CuO_4}$ tetrahedron are smaller than $0.01\mu_B$ and are not listed in Table I. Summing up the magnetic moments, we found about 80% of all magnetic moments are localized within the muffin tins of Cu and O, while only $0.13\mu_B$ locate in the interstitial region. Although most of the magnetic moments are restricted within the $\mathrm{CuO_4}$ tetrahedron (as can be seen from Fig. 2), the FM coupling between Cu and its four surrounding O atoms may help extend the FM interaction to more distant atoms, thus providing an enhancement of the FM.

The substitution of Zn by Cu is a p-type doping. In Table I we also present the net charge variation in the muffin tins and in the interstitial region. The hole numbers are obtained by subtracting the number of electrons of Cu-doped ZnO from that of the pure ZnO. It is apparent that the substitution of Zn by Cu actually has a very limited effect on the electron numbers at the substitutional site. In fact, the charge redistribution mostly happens in the interstitial region instead of inside the muffin tins. Although it was proposed that Cu stays in the 2+ state when doped into ZnO,[6] the hole numbers in Table I indicate that the chemical valence of Cu is fractional and lies between 1+ and 2+ due to strong Cu-O covalency. Since the loss of the electrons on the Cu site is

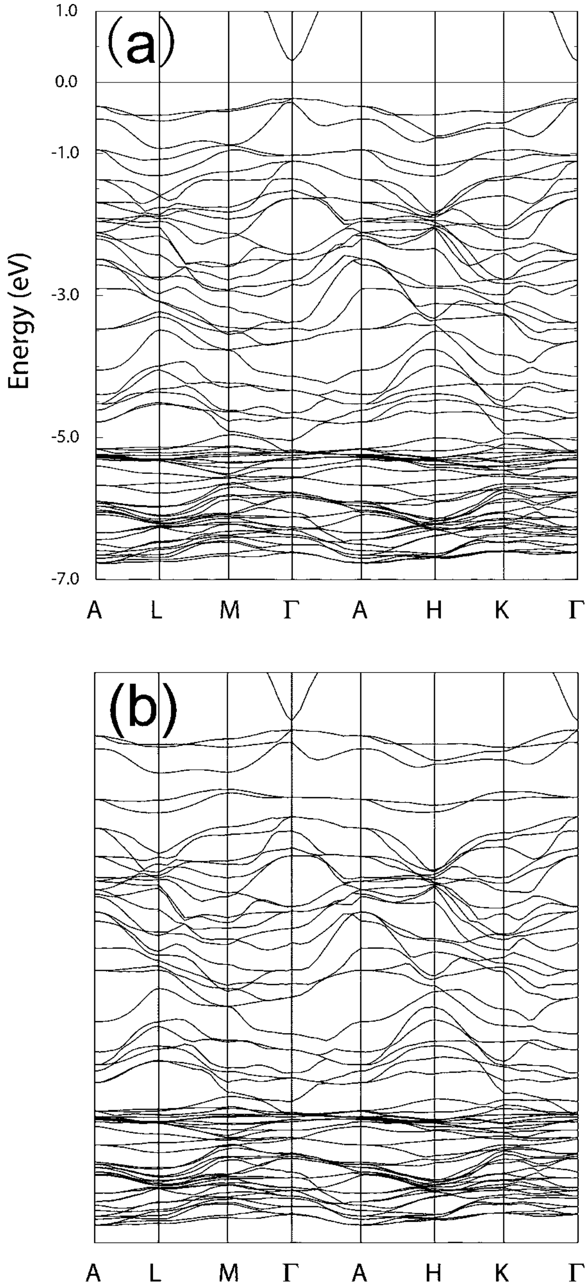

FIG. 1. Band structure of 0.125 Cu-doped ZnO. Half-metallicity is shown for (a) the majority-spin channel to be semiconducting while (b) the minority-spin channel is metallic. The Fermi level is set to 0.0 eV

TABLE I. Hole (unit: e) and magnetic moment (unit: μ_B) distributions for the ferromagnetic state with $x=0.0625$, the ferromagnetic state with $x=0.125$, and the antiferromagnetic state with $x=0.125$.

	FM ($x=0.0625$)	FM ($x=0.125$)	AFM ($x=0.125$)
Cu	0.18 (0.58)[a]	0.19 (0.58)	0.19 (0.56)
O (in CuO_4):			
Top site	—(0.04)	0.01 (0.04)	0.01 (0.04)
Basal plane	—(0.09)	0.01 (0.08)	0.02 (0.09)
Zn and other O	—(—)	—(—)	—(—)
Interstitial	0.82 (0.05)	1.63 (0.13)	1.62 (—)

[a] Quantities outside and inside the parentheses are the hole numbers and magnetic moments, respectively.

only about 0.19, the Cu chemical valence is actually closer to 1+ than 2+. This may explain why the x-ray absorption spectroscopy measurements[16] found a chemical valence of 1+ for Cu. Because the Cu-O bond in Cu-doped ZnO is largely covalent (as can also be seen from the strong hybridization between the O $2p$ and Cu $3d$ bands in Fig. 1), a purely ionic description of ZnO:Cu is not appropriate.

To test the dependence of our data on the Cu concentration, we repeated the calculations for $x=0.0625$; the results are also listed in Table I. The total magnetic moment is still $1\mu_B$ per Cu and the system keeps its half-metallic character; the muffin-tin magnetic moments and hole numbers are not much affected by decreasing the doping level, showing that the interplay between dopants is still very small at $x=0.125$, and so we expect the results to be similar in the dilute doping limit. In the interstitial region, the magnetic moment and hole number decrease monotonically with respect to the Cu concentration. For $x=0.125$, another comparison is made between FM and AFM in Table I, where the only noticeable difference is that the magnetic moment in the interstitial region becomes zero, of course. These data suggest that the polarization of the atoms and the orbital occupancies are mostly determined by the local chemical environment and are not much affected by the presence of another Cu 6.1 Å away. Since there is no appreciable charge transfer between the two Cu atoms with the addition of the second Cu to the supercell, the direct d-d correlation between Cu atoms may be small which could imply an indirect exchange mechanism being responsible for the ferromagnetism.

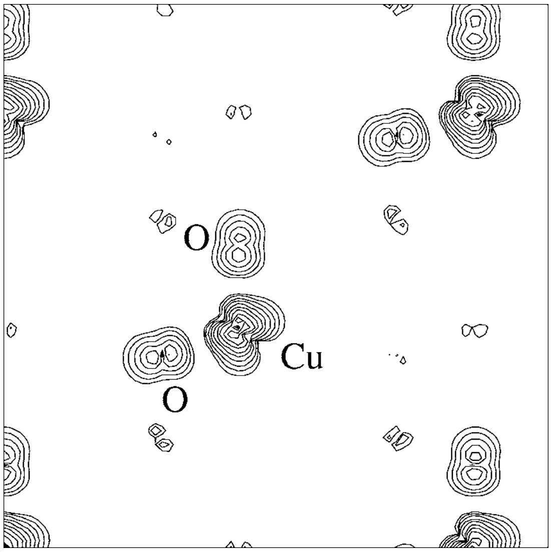

FIG. 2. Spin density distribution in the $x=0.125$ FM state of Cu-doped ZnO. Most of the spin density is localized within the CuO_4 tetrahedron.

That Cu-doped ZnO has a FM ground state agrees with the prediction by Park and Min:[7] with the LDA linear maffin-tin orbital atomic sphere approximation (LMTO-ASA) method they obtained half-metallicity and a Cu magnetic moment of $0.81\mu_B$, but when taking into account the on-site Coulomb repulsion U and spin-orbit coupling, the Cu magnetic moment increased to $1.85\mu_B$. The inclusion of U enabled consideration of a strong correlation effect of the Cu $3d$ states. However, since there is no experimental evidence to support the strong correlation or any measurement of the value of U, the performance of this LDA+U treatment is unknown. Further, the authors found that putting in a possible Jahn-Teller (JT) distortion drives the system into a more stable insulating state, quenches the orbital moment, and enhances the Cu spin magnetic moment to $0.99\mu_B$.

To test the possibility of a JT distortion, we initialized a random perturbation of the atomic positions and redid the structural relaxation without assuming any symmetry. The result showed no sign of the proposed JT distortion. The calculations were then repeated by use of DMol[3], another widely used first-principles package,[17] with the special k-point mesh increased to $9\times9\times7$. Again, we did not find a structural distortion reported in Ref. 7. A third testing was performed by manually rotating the CuO_4 tetrahedron as proposed in Ref. 7. When the structure was allowed to relax to equilibrium, we found that the distorted CuO_4 tetrahedron always rotates back with the three basal plane oxygen atoms returning to the same z plane. Therefore, the proposed rotated CuO_4 tetrahedron is found to be unstable in our calculations. Experimentally, however, it is believed that a dynamical JT effect should be included to successfully explain the paramagnetic susceptibility of Cu:ZnO.[18] This discrepancy between theory and experiment may be due to the fact that the experiment measured the paramagnetic phase, while our calculations consider the ferromagnetic phase. The strong Cu-O covalency in our calculations does not support the pure ionic description of Cu dopant as a $3d^9$ system and so does not favor the JT distortion. Our result is consistent with that of Luo and Martin[19] who performed comparative calculations to check possible JT distortions in Mn:GaAs and Mn:GaN. While in Mn:GaN there is indeed a JT distortion due to the localized feature of the Mn $3d$ states, no appreciable effect is found in Mn:GaAs since the Mn $3d$ states strongly hybridize with the As $4p$ states.

Another report on the FM in Cu-doped ZnO was made by Feng[6] with the semiempirical B3LYP hybrid density functional, in which the nonlocal Hartree-Fock exchange is mixed into the GGA. This resulted in a magnetic moment on Cu of $0.75\mu_B$, with a total energy difference of 130 meV between FM and AFM at a Cu-Cu distance of 5.2 Å. Similar to the LDA+U treatment in Ref. 17, the nonlocal Hartree-Fock exchange term also included considerations of a possible strong correlation effect. However, the mixing parameter in the B3LYP hybrid functional is actually not universal but system dependent. On the other hand, in the work of Sato and Katayama-Yoshida[5] by the Korringa-Kohn-Rostoker (KKR) Green function method based on the LDA combined with the coherent potential approximation (CPA), they reported no magnetic moment on Cu and concluded that Cu-doped ZnO is nonmagnetic. The reason for this discrepancy is unknown. It is possible that their simulated doping level ($x=0.25$) is too high so that the short-range AFM superexchange interaction becomes stronger and neutralizes the FM interaction.

Since the origin of the FM in DMS's in still under debate, it is interesting to see how a different carrier density affects the strength of the magnetic interaction in Cu:ZnO. We check two situations corresponding to increased and decreased hole density. A higher hole density is simulated by the substitution of one oxygen by nitrogen, while by creating one oxygen vacancy the holes are totally eliminated. In both cases, the related O site locates away from the CuO_4 tetrahedron in order to avoid much disturbance to the Cu-O bonds. The O-to-N substitution increases the total magnetic moments in the supercell to $3\mu_B$ with the FM state still being the ground state. The total energy difference is 44 meV between FM and AFM states which does not change much by N codoping. On the other hand, by creating an O vacancy, we still got an FM ground state which is substantially weakened; the FM and AFM total energy difference drops to 26 meV. These studies imply that the FM seems not to be related to the hole density.

In fact, the oxygen vacancy can be more harmful to the FM if located within the CuO_4 tetrahedron, since removing one O atom from the CuO_4 tetrahedron results in the breaking of one Cu-O bond, which should have a stronger effect on the magnetic properties. Indeed, the relevant Cu atom is found to be depolarized, and the system becomes a paramagnetic metal. When we move the O vacancy from outside of the CuO_4 tetrahedron to inside, the total energy decreases by 0.7 eV. Therefore, the O vacancy prefers to be attached to the Cu dopant and tends to destroy the FM. Besides, as n-type defects, O vacancies provide impurity electrons which could neutralize the p-type carriers and destroy the conductivity by Cu doping—an effect called defect compensation. Therefore, it is important in the experiments to keep a high oxygen pressure during sample fabrication in order to avoid the formation of the O vacancies.

Further, we considered the possibility of Cu clustering by varying the Cu-Cu distance. The first calculation was done by moving the two Cu atoms in the supercell from 6.1 Å to a closer distance of 5.7 Å; the total energy is found to increase by 68 meV. In our second calculation, the two Cu atoms were placed even closer so that they connect to the same O atom. A huge total energy increase (5.7 eV) is found which definitely disfavors this structure. We thus conclude that there is no tendency for Cu clustering in Cu-doped ZnO.

In summary, our accurate first-principles simulations predict Cu-doped ZnO to be a half-metallic dilute magnetic semiconductor. The ferromagnetism emerges from the hybridization of the Cu $3d$ and O $2p$ bands. There is no close relation between the ferromagnetism and hole density. Compared to conventional DMS's, Cu:ZnO does not contain any magnetic ion; neither is any compound with (Cu,Zn,O) ferromagnetic. Therefore, Cu:ZnO is free of ferromagnetic precipitate problems. With the unambiguous intrinsic ferromagnetism and the 100% spin polarization of the carriers, we expect Cu-doped ZnO to be a useful DMS, both in applications and in theoretical studies of the ferromagnetism in DMS's.

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