Ferromagnetism in ZnO with (Mn,Li) codoping*

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(Received 19 April 2012; revised manuscript received 11 September 2012)

First-principles calculations were performed to investigate the magnetic properties of Zn(Mn,Li)O based on the Perdew–Burke–Ernzerhof form of the generalized gradient approximation. Antiferromagnetic (AFM) ordering is the ground state in Mn-doped ZnO system without the codopant of Li, while seven different geometrical configurations of Zn(Mn,Li)O prefer stable ferromagnetic (FM) ordering. We found that dopant Li can effectively change the magnetic coupling in the ZnMnO system. The Curie temperature (T_C) of FM ordering depends on the geometric configuration, and the highest T_C is about 1388 K. The FM stabilization is greatly affected by Mn–Mn distance rather than by the position of dopant Li. We propose that dopant Li mediates FM coupling through a double exchange interaction or an RKKY interaction when Li is located, respectively, near or far from Mn ions.

Keywords: density functional theory, ferromagnetism, Curie temperature

PACS: 71.15.Mb, 75.50.Pp **DOI:** 10.1088/1674-1056/22/3/037102

1. Introduction

Diluted magnetic semiconductors (DMSs) are the most promising materials for spintronic applications because designers can use both the spin and the charge properties of electrons to overcome some of the limits of traditional microelectronics. Finding DMSs with room temperature (RT) ferromagnetism (FM) would be significant to the applications of such devices. ZnO has a direct wide band gap (3.35 eV) and a large excitonic binding energy (60 meV), and was predicted to be a promising host material to achieve DMS with Curie temperature (T_C) above room temperature.[1] In practice, doping 3d transition-metals (TMs) in host semiconductor material is an effective way to obtain DMSs. TMs are usually highly soluble in ZnO, and magnetic dopants can be introduced into it without precipitating out into secondary phases or metallic clusters. These properties have stimulated extensive studies of TM (Cr, Mn, Fe, Co, Ni, Cu) doped ZnO.[2–6] Nonmetal elements can also result in ferromagnetism in ZnO.[7,8] However, theoretical conclusions cannot explain such phenomena observed in experiments and the origin of the FM has not been well understood.

Mn has been widely used in doping ZnO.[9–11] However, the related results are rather controversial. Jayakumar *et al.*[12] reported that room temperature FM was observed in polycrystalline samples of Mn-doped ZnO, while Jung *et al.*[13] obtained low Curie temperature (45 K) FM in $Zn_{0.7}Mn_{0.3}O$ synthesized by laser MBE, and Lawes *et al.*[14] found no magnetic ordering down to $T = 2$ K in polycrystalline ZnO with Mn substituted. These experimental results indicate that FM ordering is sensitive to sample preparation conditions, and that defects may play an important role in the magnetic behaviors observed in these materials. Theoretical studies have concluded that antiferromagnetism (AFM) ordering is the stable ground state in Mn-doped ZnO without defects and other codopants.[15–17] A possible approach to change a Mn-doped ZnO system from AFM to FM with high T_C is codoping additional carrier inducers. In C[17,18] and N[16,19] codoped-ZnMnO, FM ordering was significantly stabilized and T_C was above room temperature. Besides the nonmetal codopants, Al[20,21] and Ga[15] can provide electrons, while Li[22,23] and Cu[15] can provide holes in a ZnO-doped system. In (Mn,Al)-codoped ZnO,[21] Al greatly enhances FM ordering and the obtained magnetic moments are close to the ideal value.

Among the codopants mentioned above, it is worth noting that the ionic radius of Li^+ (0.76 Å) is close to that of ion Zn^{2+} (0.74 Å) Thus Li ion substitution would probably not introduce structural distortion. Li contributes its 2s electron to adjacent O, subsequently induces a hole, and results in a p-type ZnO. Recently, Yi *et al.*[23] fabricated Li-doped ZnO film using pulsed laser deposition and reported that when Li doping concentration increased beyond 4 at%, the film switched from n-type to a p-type behavior, and it remained p-type until the Li doping concentration reached 13 at%. An experimental study by Jayakumar *et al.*[12] revealed that codoping Li in ZnMnO does not improve the ferromagnetic characteristics, while first-principles studies by Gopal *et al.*[3] and Zhu *et al.*[15] showed significant enhancement of ferromagnetism when Li is codoped in ZnMnO. These inconsistent results call for an extensive and thorough further investigation of

*Project supported by the National Natural Science Foundation of China (Grant No. 61102024), the Fundamental Research Funds for the Central Universities of China (Grant No. 2012RC0401), and BUPT Excellent Ph.D. Students Foundation, China (Grant No. CX201114).

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Zn(Mn,Li)O.

Thus, the main motivation of the present work is to extend previous calculations by investigating seven different geometrical configurations with an emphasis on the magnetic properties of the Zn(Mn,Li)O system. We describe our model and computational details and then present the calculated results and discussions. Finally we summarize our conclusions.

2. Method and model

The calculations are implemented using the Cambridge serial total energy package (CASTEP) code, which is based on density functional theory and the plane-wave pseudopotential method.[24] The electron exchange-correlation energy is described in the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) approach. A periodic 2×2×2 wurtzite supercell of ZnO containing 32 atoms is employed and the supercell is kept at a constant volume. After several runs of geometric optimization for intrinsic ZnO with different cutoff energies, 460 eV is chosen as a suitable parameter. The valence-electron configurations employed are Zn ($3d^{10}4s^2$), O ($2s^22p^4$), Mn ($3d^54s^2$) and Li ($1s^22s^1$). For Brillouin zone integration, the Monkhorst-Pack k-point sampling used for pure ZnO and ZnMnLiO alloy are 7×7×4 and 4×4×2, respectively. The optimization of the supercell is considered to be successful when the following parameters are satisfied: maximum energy change is 2×10^{-5} eV/atom, maximum force is 0.05 eV/Å, maximum stress is 0.1 GPa and maximum displacement tolerance is 0.002 Å.

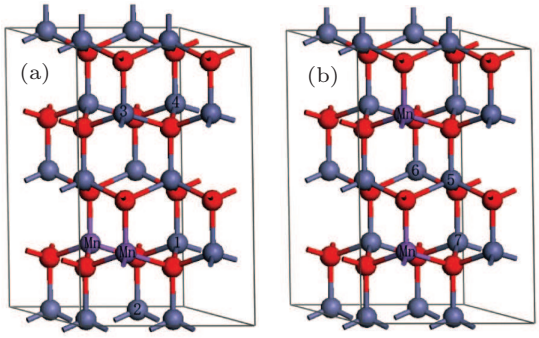


Fig. 1. (color online) A wurtzite 2×2×2 ZnO supercell with two Mn ions separated into (a) near group and (b) far group. The positions of Li ions in the seven different configurations are labeled by numerals.

In the case of Mn-doped ZnO, two Zn atoms are replaced to produce a dopant concentration of 12.5%. In Zn(Mn,Li)O, another Zn atom is replaced by introducing 6.25% additional concentration. There are a large number of geometrical configurations of relative positions of one Li ion and two Mn ions in a 2×2×2 ZnO supercell. We restrict configurations to the following seven: (1) near group: two Mn ions separated by one oxygen along the *ab* plane, (2) far group: two Mn ions separated by –O–Zn–O complexes along the *c* axis. The near group contains four different configurations and the other three belong to the far group, as shown in Fig. 1. For each configuration, we calculate parallel and antiparallel spin alignments between Mn ions, which correspond to FM and AFM orderings, respectively. We use the energy difference between AFM and FM orderings ($\Delta E = E_{\rm AFM} - E_{\rm FM}$) to indicate magnetic stability. $\Delta E > 0$ means that the FM ordering is more stable than AFM ordering and vice versa.

3. Results and discussion

3.1. Optimization of the Zn(Mn,Li)O structure

In this section, the structural geometry optimizations of intrinsic ZnO and Zn(Mn,Li)O are investigated systematically. All calculations are based on a pure ZnO model, which is a hexagonal wurtzite structure in the $P6_3mc$ space group with lattice constants $a = b = 3.249$ Å, $c = 5.202$ Å and $c/a = 1.601$. After the optimization of intrinsic ZnO, lattice constants become larger by 0.9% in *a* and *b* and 2.22% in *c* with respect to the original constants, and the optimization does not change the hexagonal structure.

We also investigate the impact of (Mn, Li) dopants on the wurtzite structure of ZnO. Taking configuration 1 as an example, after structural geometry optimization, the lattice constants become $a = b = 3.287$ Å, $c = 5.297$ Å, which is an increase of 1.17% in *a* and *b* and 1.82% in *c* with respect to original lattice constants, and the shape of the hexagonal structure is still kept unchanged. These changes mainly result from the ionic radius of Mn^{2+} (0.83 Å) being larger than that of Zn^{2+} (0.74 Å). Of special note, we investigate the distance between the doped ions in Zn(Mn,Li)O. In the optimized configuration 1, the distance between Li ion and Mn ion is 3.27 Å, which differs from the original Zn–Zn distance (3.24 Å) by only 0.9% for the perfect ionic radius match of Li^+ (0.76 Å) and Zn^{2+} (0.74 Å).

3.2. Magnetic properties of Zn(Mn,Li)O

In Mn-doped ZnO, five different geometric configurations are calculated. In all configurations, the total energy of AFM ordering is lower than that of FM ordering, which means that AFM is always more stable than FM ordering in the $Zn_{0.875}Mn_{0.125}O$ system. In the most stable configuration, two Mn ions stay nearest in the *ab* plane and the energy of AFM ordering is about 190 meV lower than that of FM ordering. The two doped Mn ions mediate a superexchange interaction through the O ion, resulting in a stable AFM coupling. All of this shows that the ZnMnO system cannot be applied to practical DMS materials. These results are in good agreement with previous theoretical simulations.[15–17]

In the following, we study the magnetic properties of Zn(Mn,Li)O. Seven different configurations sketched in

Fig. 1 are calculated and the results of total energy are listed in Table 1. The ΔE corresponds to the thermal energy $k_B T$, and room temperature FM requires that ΔE is larger than 30 meV.[3] As shown in Table 1, the largest ΔE is 119.619 meV, in configuration 2, which can lead to ferromagnetism with the highest T_C (1388K) in the Zn(Mn,Li)O system. Figure 2(b) shows that ΔE is positive in all configurations,

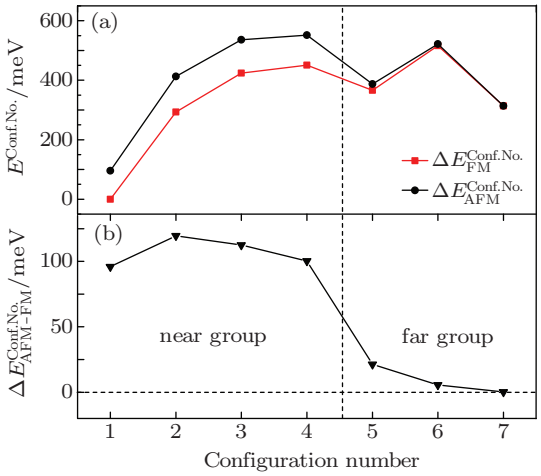


Fig. 2. (color online) (a) Total energy per supercell with AFM and FM orderings and (b) the energy differences ($\Delta E = E_{\text{AFM}} - E_{\text{FM}}$) for different geometrical configurations. The E_{FM} with the lowest total energy in configuration 1 is set to zero as an energy reference.

resulting in a more stable FM ordering in Zn(Mn,Li)O. Thus, we conclude that Li can effectively mediate FM ordering in ZnMnO system.

We define the total distance as the sum of the two distances between Li and each of the two Mn ions. In the near group, with an increase of total distance, the total energy of system becomes higher in either FM or AFM orderings. The most stable configuration has the shortest distance between Li and Mn ions, which corresponds to 95.959 meV of ΔE. It is obvious that (Mn, Li) dopants tend to form clusters rather than isolated states, which favors achieving high Curie temperature ferromagnetism.

Table 1 shows that ΔE values for the near group are much larger than those for the far group. The ΔE of each configuration in the near group is around 100 meV, while for the far group it is dramatically lower at around 20 meV. FM ordering weakly depends on the positions of codopant Li but it is greatly affected by the Mn–Mn distance. We also note that ΔE varies little for different configurations in the same group. In the near group the stability of FM ordering does not become weak when Li is located far from magnetic ions. These results show that FM stability is insensitive to the position of dopant Li, and that the effect of Li tends to be delocalized.

Table 1. Total energy of FM and AFM orderings in different geometrical configurations. The total energy difference between FM and AFM ordering equals $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$. Total distance is defined by the distance between Li and two Mn ions.

Configuration No.	Total distance/Å	E_{FM}/meV	E_{AFM}/meV	ΔE/meV	Magnetic moments
1	6.536	0	95.959	95.959	4.300
2	7.834	293.006	412.625	119.619	4.320
3	11.546	423.723	536.236	112.513	4.330
4	12.515	451.004	551.306	100.302	4.320
5	6.419	366.056	387.419	21.363	4.300
6	9.222	516.342	521.936	5.594	4.330
7	9.490	313.404	313.632	0.228	4.310

To illuminate the origin of induced ferromagnetism, the density of state (DOS) of Zn(Mn,Li)O is investigated. We focus on the description of the DOS in four configurations of the near group. Figure 3 shows the partial DOS of Mn d and Li s states of these configurations with FM ordering.

In configuration 1, as shown in Fig. 3(a), Li is located near Mn ions and we can clearly observe that both Mn d and Li s states are from -7.0 to 0 eV. Around the Fermi level, strong hybridization between Mn d and Li s states is obvious from -2.0 to 1.0 eV. The doped holes can hop into the Mn d states to stabilize FM ordering. The FM ordering is mediated through a double exchange interaction between the Mn ions and holes induced by dopant Li. Stabilization of FM ordering mediated by the double exchange interaction has also been observed in several other systems, such as the (Mn,N)-codoped ZnO system[16] and the (Ni, Li)-codoped ZnO system.[25]

In configurations 2–4, Li is located relatively far away from Mn ions, and the overlap between Mn d and Li s states seems to disappear. The doped holes cannot hop into the Mn d orbits, and the double exchange mechanism is not effective. As ΔE in these configurations is never less than 100 meV, an indirect exchange mechanism must exist to stabilize the FM ordering. Considering that the stabilization of FM ordering is insensitive to the position of Li and the effect of Li tends to be delocalized, we refer to the RKKY exchange interaction to explain the observed FM stabilization.

According to RKKY theory,[26–28] itinerant carriers are first spin polarized by local spin-polarized electrons of magnetic impurities and then interact with neighboring magnetic impurities. As a result, the spins of magnetic impurities couple

together through the itinerant carriers, i.e., RKKY interaction. The s-type holes induced by Li are relatively small near the Fermi level, and it does not impact the shape of total density of states much. We found almost the same shape of the total density of states in the valence bands of undoped ZnO and ZnO with Li impurity states. This means that holes introduced by Li doping are delocalized and serve as itinerant carriers.[29] RKKY interaction has two characters: (1) The magnetic coupling is mediated by itinerant carriers, so this kind of interaction requires high concentration of free carriers. (2) The magnetic interaction displays oscillation as a function of distance between magnetic elements. RKKY theory has been used successfully to explain the origin of FM stabilization in several systems.[30,31] In (Co,Al)-codoped ZnO,[30] RKKY interaction has been used to explain the lowered kinetic energy of the FM states when the double exchange interaction is weak.

In configurations 2–4, as shown in Figs. 3(b)–3(d), the appearances of Mn d and Li s states are similar. In these configurations, the Li ion is located relatively far away from Mn ions and no hybridization between Mn d and Li s states is observed. The effect of Li tends to be delocalized and the induced holes act as itinerant carriers. Mn ions couple with each other through polarized itinerant holes resulting in a stable FM ordering. In Zn(Mn,Li)O, when the distance between Li ion and Mn ions is rather small, double exchange is the dominant mechanism for the origin of FM ordering. When the Li ion is far away from Mn ions, FM stabilization is attributable to the RKKY interaction via itinerant holes in the valence band. In our calculations we have two different Mn–Mn distances. (The near group one is 3.1 Å and the far group one is 5.3 Å.) RKKY interaction shows oscillating magnetic couplings as a function of the Fermi wave number and the distance between magnetic elements. The distance when AFM first appears is mainly determined by the Fermi wave number. We can obtain the Fermi wave number based on the hole carrier density.[9] We have obtained the shortest distance for which AFM first appears according to the concentration of free carriers, and it is 6.72 Å. For those configurations in which Mn–Mn distance is less than 6.72 Å, FM coupling is more stable and magnetic interaction gets weak drastically with the Mn–Mn distance increasing. With the Mn–Mn distance changing from 3.1 Å to 5.3 Å, ΔE changes from 120 meV to 20 meV, and this is consistent with the RKKY model. In addition, we note that when Li is far away from Mn ions, such as configuration 4 (ΔE is 100.302 meV), FM is slightly more stable than it is in the nearest configuration 1 (ΔE is 95.959 meV). The indirect RKKY interaction is even slightly stronger than the double exchange interaction in (Mn,Li)-codoped ZnO.

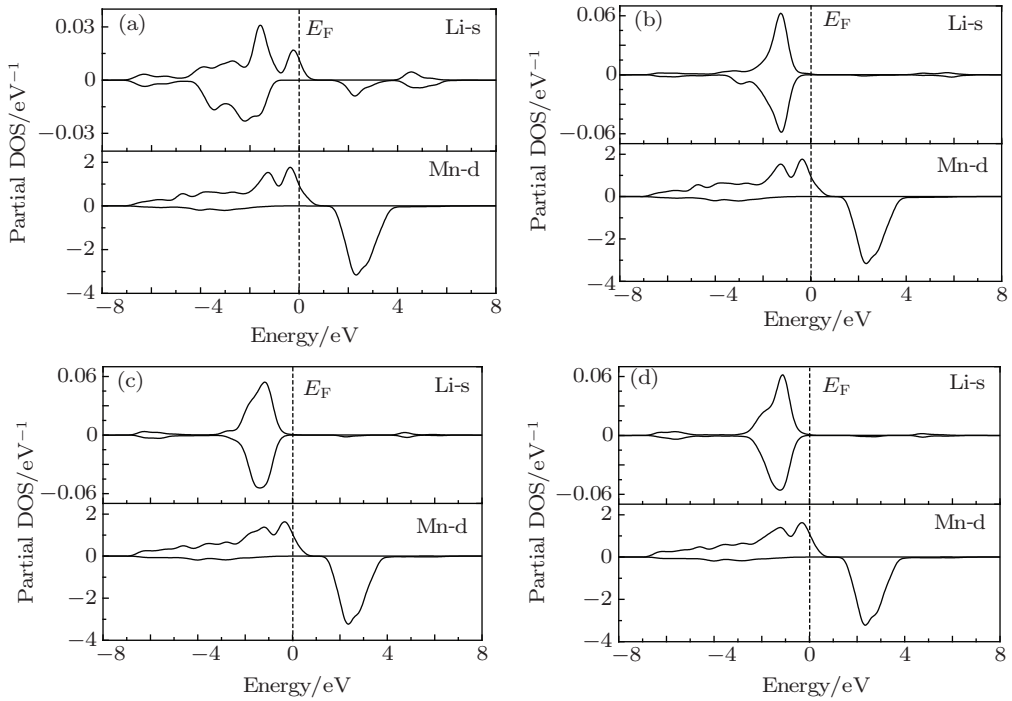


Fig. 3. The partial DOS of Mn d and Li s states in (a) configuration 1, (b) configuration 2, (c) configuration 3, and (d) configuration 4 with FM ordering.

As mentioned above, the Mn–O–Mn structure usually leads to a direct superexchange and an AFM coupling is favored. We examined the PDOS of Mn and O atoms before and after Li doping. There is not a large difference in PDOS. The O-mediated exchange interaction is not enhanced after Li-doping. Actually, only when double exchange or RKKY interaction dominates over superexchange is FM possible. The existing different types of magnetic interaction compete with

each other and finally show a specific FM or AFM coupling. Compared with (Mn,N)-codoped ZnO[16] dominated by the double exchange mechanism, (Mn,Li)-copdoped ZnO mediated by the long-ranged RKKY interaction is more favorable for practical DMS applications. The double-exchange interaction is very short-ranged due to the exponential decay of the impurity wave function in the gap.[32] The short-ranged interaction may lead to AFM ordering in some cases, while long-ranged interaction tends to form FM coupling.

4. Conclusions

In summary, using first principles, we calculated the magnetic properties of Zn(Mn,Li)O. AFM ordering is the ground state in Mn-doped ZnO, while seven different geometric configurations in Zn(Mn,Li)O all prefer a more stable FM ordering. The element Li can alter the ZnMnO system from AFM to FM ground state and the Curie temperature of FM is above room temperature. Total energy results indicate that the Mn–Mn distance plays an important role in the FM stabilization. A mechanism of (Mn,Li)-codoped ZnO is proposed, and we found that dopant Li mediates FM coupling via a double exchange interaction or an RKKY interaction when Li is located, respectively, near or far from Mn ions.

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