P H Y S I C A L   R E V I E W   L E T T E R S

Hydrogen-Mediated Spin-Spin Interaction in ZnCoO

C. H. Park[1] and D. J. Chadi[2]

[1]*Research Center for Dielectric and Advanced Matter Physics and Department of Physics, Pusan National University,
San-30 Jangjun, Geumjung, Pusan 609-735, Korea*
[2]*NEC Laboratories America, 4 Independence Way, Princeton, New Jersey 08540, USA*

The effect of hydrogen impurities on the electronic and magnetic properties of ZnO-based diluted magnetic semiconductors is examined through first-principles pseudopotential calculations. We suggest that interstitial H can mediate a strong short-ranged ferromagnetic spin-spin interaction between neighboring magnetic impurities through the formation of a bridge bond. Results based on first-principles total-energy calculations and Monte Carlo simulations indicate that such H-mediated spin-spin interactions can lead to high temperature ferromagnetism.

Dilute magnetic semiconductors (DMS) have been extensively investigated since the discovery of ferromagnetism (FM) in InMnAs and GaMnAs [1]. Although a number of room temperature (RT) ferromagnetic semiconductors have been reported, the microscopic origins of their magnetism remain to be fully resolved. II-VI semiconductors such as ZnO are attractive DMS candidates because the solubility limit of magnetic ions is extremely high. Cobalt is the magnetic impurity most soluble in ZnO [2] and there have been many reports that, in contrast to other spin-glass or paramagnetic II-Co-VI DMS [3,4], ZnCoO (and also ZnMnO) exhibits RT-FM [2,5–7].

The origin of this phenomenon remains controversial [6–9], and it is not yet clear whether the observed FM is truly intrinsic or related to secondary phases such as magnetic clusters. Theory suggests that the double exchange interaction leading to FM in ZnCoO and ZnMnO is enhanced in the presence of a high concentration of carriers [9]. Since ZnO is very easily and naturally n doped, one expects that FM in ZnCoO should occur in combination with a high concentration of mobile carriers. However, a puzzling aspect of ZnCoO is that even though its Curie temperature can be very high, a large concentration of mobile carriers is not always observed. The measured carrier density in this material is generally not sufficiently high to lead to a strong double exchange interaction that is currently thought to be important for FM. For ZnMnO, FM is measured in the presence of n-type carriers [10], in disagreement with the prediction based on the double exchange interaction. It is noted that the magnetic properties of ZnO-based magnetic semiconductors are sensitive to growth conditions and differ from sample to sample [2,5–7,10–12]. In many ferromagnetic ZnCoO [5,7] and ZnMnO [10,12] semiconductors, the magnetization is reduced substantially at low T (around 10–50 K), and the residual FM persists up to very high T. This type of behavior is not expected from a double exchange interaction or a carrier-induced interaction. Clearly, a better understanding of the microscopic and electronic properties is needed to explain their magnetic properties.

It is well known that hydrogen is an important unintentional impurity in ZnO and should occur in significant concentrations in ZnCoO. There is considerable evidence that interstitial H is a very stable impurity and can be a major cause of the natural n-type character of ZnO as a shallow dopant [13,14]. The main purpose of this Letter is to report that H is a beneficial impurity which can directly mediate a strong short-range spin-spin interaction between magnetic ions in ZnO, and the H in large concentrations can lead to high-T FM in the absence of free carriers in ZnCoO.

Through first-principles calculations, we have investigated the interactions between H and Co ions and found that H affects the magnetic properties of ZnCoO in at least two major ways. Structurally, H drives the formation of highly stable Co dimers on nearest-neighbor Zn sites to which it binds strongly. Electronically, H opens a new channel for a strong ferromagnetic spin-spin interaction between such Co dimers that dominates over its donorlike influence on the magnetic properties. The interaction is much stronger than that expected from the double exchange interaction. The results of our theoretical studies lead us to propose that H incorporation is an effective way of generating high-T FM in ZnCoO.

The computational approach used in this study is based on first-principles pseudopotential total-energy calculations within the local spin density approximation [15–17]. Norm-conserving soft pseudopotentials were generated in the manner of Troullier and Martins [18,19]. An energy cutoff of 45 Ry was used for the plane wave expansions. The atomic geometry was fully optimized through the use of Hellmann-Feynman forces. A 36 atom supercell was mostly used to examine impurities and defects. For the total-energy calculations, the $(1/2, 1/2, 1/2)$ wave vector of the Brillouin zone of the supercell was used. The semicore Zn-$3d$ state orbitals were explicitly included in the calculations in order to consider the Zn-$3d$ states on an equal footing with Co-$3d$ states. The inclusion of these d states results in a shrinkage of the calculated band gap to 0.92 eV as compared to the much larger value of 1.84 eV

when the effect of d states is included only indirectly via partial core corrections [20]. The underestimation of the gap is a well known local-density approximation (LDA) error.

We first examine the energetics of H incorporation in ZnCoO. As in ZnO, interstitial H is a shallow donorlike impurity that is most stable at a bond-center (BC) site. In the wurtzite structure two types of bonds can be distinguished: a type-I bond along the c axis (BC_I) and a type-II bond along the other three bond axes (BC_{II}). We find that $H(BC_{II})$ is more stable than $H(BC_I)$ by 0.09 eV. The stable structure is similar to that obtained by Van de Walle [13]. The formation enthalpy of positively charged H at its most stable BC site is calculated from $\Omega(H^+) = E(H^+$ in ZnO$) - E($ZnO$) - \mu(H_2)/2 + E_F$. When the Fermi level E_F lies at the conduction-band minimum (CBM) or at the valence-band maximum (VBM), $\Omega(H^+)$ is calculated to be about 0.02 eV and 0.90 eV, respectively. The calculated binding energy of interstitial H in n-type ZnO is similar to that obtained by Van de Walle who used partial core correction to treat the Zn-3d states [13]. Our smaller absolute value for $\Omega(H^+)$ when E_F is at the VBM is caused by an upward shift of the VBM when Zn-3d orbitals are explicitly included in the calculations. Both results for $\Omega(H^+)$ indicate that ZnO can easily become contaminated by H.

The stability of H in ZnCoO is enhanced by the capture of its shallow donor electron by a Co-3d-t_{2g} orbital in the gap [9]. We tested various geometries for H binding to substitutional Co and also examined its binding to a Co dimer (a pair of substitutional Co ions placed at nearest-neighbor cation sites) since the concentration of dimers should be significant in $Zn_{1-x}Co_xO$ when the x is large. As in ZnO, the most stable binding site for interstitial H around a Co is at a Co-O bond-centered (BC_{II}) site, shown in Fig. 1(a). This site is 0.09 eV more stable than BC_I. The most stable antibonding (AB) configuration occurs for the AB site of a Co_{Zn} along a "c axis" type-I Co-O bond. This AB site is 0.19 eV less stable than the BC_{II} site. However, we find that in the case of a Co dimer, interstitial H is most

stable at the common antibonding position of the two Co ions, as shown in Fig. 1(b), instead of at a BC site, forming (Co-H_{AB}-Co) complex. The energy for the AB site is 0.25 eV lower than that for a BC configuration. It is also found that the binding of H^+ to a Co dimer is 0.22 eV stronger than to an isolated Co_{Zn} atom. In the (Co-H_{AB}-Co) complex, the Co-H distance is 1.64 Å and the Co-H-Co angle is 116° in the parallel spin-paired state. In the antiparallel state the Co-H bond length becomes slightly lengthened, to 1.71 Å, and the Co-H-Co angle becomes 114°. Since the deep Co-d level in a Co dimer can capture the shallow donor electron of an isolated interstitial H, we consider the reaction in which an ionized H atom is captured by the dimer to form a Co-H-Co complex:

$$H_i^+ + (Co_{Zn}\text{-dimer})^- \rightarrow (Co\text{-}H\text{-}Co)^0. \quad (1)$$
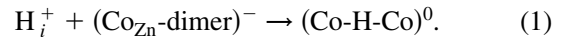
The reaction is 1.05 eV exothermic, indicating that the formation of (Co-H-Co) complexes can be significant in H-contaminated ZnCoO with high Co and H content.

The most important result of our study is that when H is located between two nearest-neighbor Co_{Zn} atoms to form a (Co-H_{AB}-Co) complex, it induces a strong ferromagnetic spin-spin interaction between the Co atoms. We find that the parallel spin pairing state of (Co-H_{AB}-Co) is highly more stable (by 0.21 eV) than the antiparallel spin-paired state. The large energy difference indicates that the H-induced spin-spin interaction is strong enough to lead to room T FM. The H-induced ferromagnetic spin pairing together with the strong tendency of H to bind to a Co dimer indicates that high-T FM in ZnCoO can be achieved through H incorporation. Another remarkable feature is that H in a Co-H-Co complex creates a deep level and it does not contribute, therefore, to carrier transport. This provides an explanation for the low carrier concentration in ZnCoO. Both of these results can be understood by examining the electronic and magnetic properties of H in ZnCoO. Figures 2(a) and 2(b) show the total electronic and spin densities around a spin-parallel aligned (Co-H_{AB}-Co) complex. It is to be noted that the spin on H is opposite to that of the two Co ions, indicating that H is spin-polarized and the hydrogenic orbital is coupled to the minority spin orbital of Co_{Zn}. An examination of the electronic structure reveals the way in which the parallel spin configuration is stabilized. In the parallel spin-paired state, the energy level of the hydrogenic state lies deeply (by 2.22 eV) below the highest occupied Co-e_g level [21]. As shown in Fig. 2(c), the H atom combines with two Co-3d-t_{2g} minority spin orbitals, forming a *bridge bond*. The bridge bond is stable only when the spins of the two Co ions are parallel. In the antiparallel spin-paired state, the hydrogenic state arises from a coupling of a H-s and a Co-t_{2g} orbital, as shown in Fig. 2(d), and the level is located 0.65 eV below the Co-e_g state. The electronic energy is, therefore, far lower in the parallel spin-paired state. The *bridge-bond-mediated d-d* coupling stabilizes the parallel spin state.
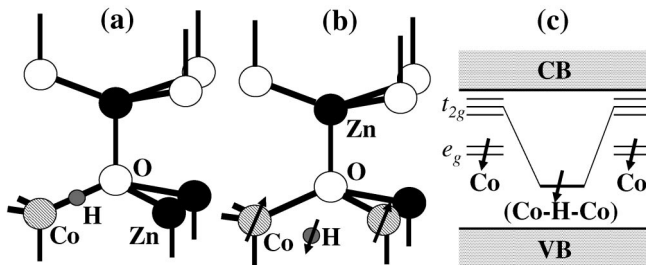

FIG. 1. (a) Atomic geometry of a Co-O bond-centered H [H_{BC}-Co] and (b) the most stable geometry of H bound to a Co dimer (Co-H_{AB}-Co) complex. (c) The energy diagram for a (Co-H-Co) complex in the spin-parallel state shows that the hydrogenic level is located deep below the Co-e_g level.
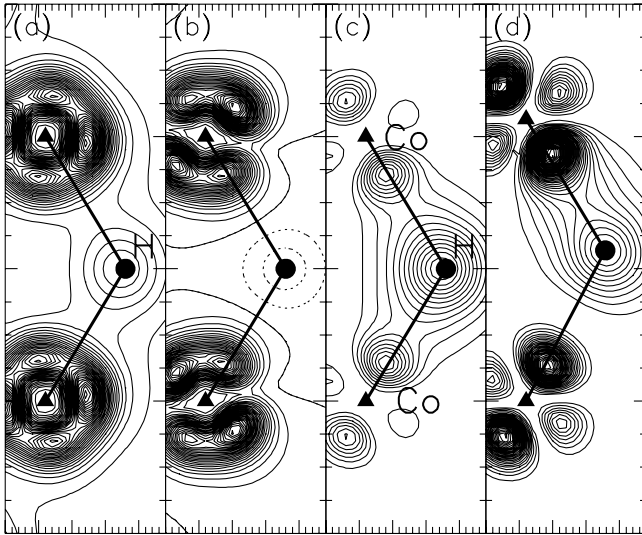
FIG. 2.   Contour graphs of (a) the total electron density and (b) the spin density around a Co-H_{AB}-Co complex defect are shown on a plane including the Co dimer and the H atom. The graph for the minority spin density is shown by the dotted lines. (c) The hydrogenic states arising from the interaction between H and the minority spin state of Co-t_{2g} in the parallel spin-paired state and (d) in the antiparallel spin-paired state are shown. The increments between contour lines are 100 electrons for (a), 50 electrons for (b), and 2 electrons for (c)–(d) per 36 atom supercell.

The large binding energy of H to a Co dimer can be further understood to arise from a large reduction in the electronic energy resulting from the transfer of an electron from the t_{2g} level of Co_{Zn}^{-} to the deep hydrogenic level. Since the hydrogenic level of the (Co-H_{AB}-Co) complex is deep and stable in a neutral charge state, H does not contribute to electrical conductivity. When coupled to a Co dimer the contamination of ZnCoO by H does not automatically lead to free (electron) carriers or to the electronic occupation of the uppermost Co-t_{2g} levels.

In order to obtain further support for the idea that strong H-induced ferromagnetic spin-spin interactions in (Co-H_{AB}-Co) complexes can lead to high-T FM, we have simulated the temperature (T) dependence of the magnetization of disordered ZnCoO through Monte Carlo (MC) simulations. We employed a Heisenberg-type Hamiltonian $H_{ij} = -JS_iS_j$. The parameter J was determined from the results of our calculations, i.e., the 0.21 eV energy difference between the spin-parallel and antiparallel states for nearest-neighbor cation Co spins and 0.002 eV for second-nearest Co_{Zn} dimers. The H-induced dimerization of Co ions in the wurtzite lattice was taken into account by a random distribution of Co atoms, in which a significant fraction of Co atoms were dimerized, and all Co dimers were assumed to capture H atoms which then induce strong spin-spin interactions. The concentration of H relative to Co is described in the inset of Fig. 3(a). The computational

results on the T dependence of the magnetization (from the average value of the Co spin) for $Zn_{0.75}Co_{0.20}O$ and $Zn_{0.85}Co_{0.15}O$ are shown in Fig. 3(a). Percolation of Co dimers leads to a long-range interaction, resulting in high-T FM [22]. It can be seen that the curve is similar to that from experimental data in Refs. [5,7]. Since the spin-exchange interaction is locally enhanced between nearest-neighbor Co ions and also in the Co-H-Co complex, the magnetization at high-T is finite. The results of our calculations for the Co alloy ratio dependence of the average spin near room T are shown in the inset of Fig. 3(a). The average spin of Co increases as the Co alloy ratio x becomes larger than 0.05, indicating the percolation behavior. Percolation of strong spin-spin interactions leading to ferromagnetic ordering requires a high concentration of Co. The magnetization is enhanced at low T. At high T, only the percolated clusters connected via strong nearest-neighbor interactions mediated by H contribute to the magnetization, and smaller clusters which contribute to the magnetization at low T are averaged out.

We also examined the H-mediated spin-spin interaction in ZnMnO. ZnMnO is predicted to be ferromagnetic in the
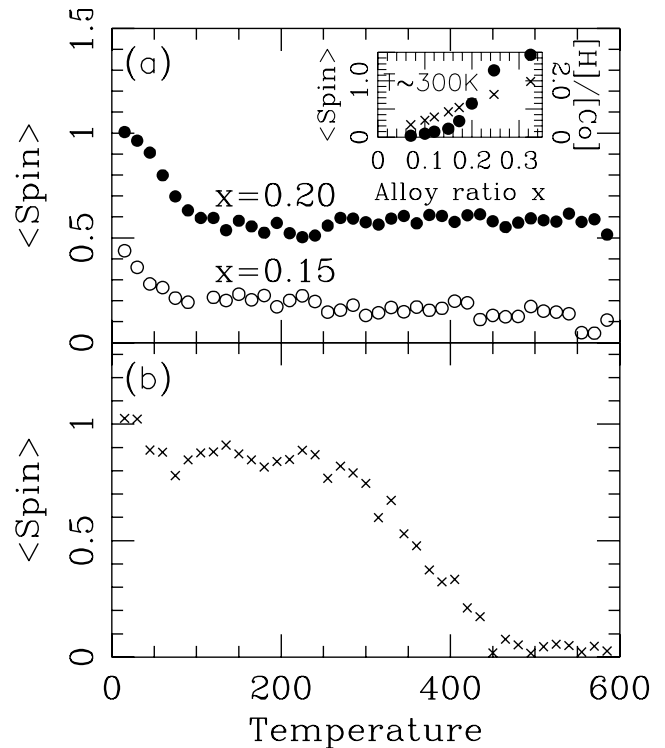

FIG. 3.   (a) The average Co spin magnitude in $Zn_{1-x}Co_xO$ derived from MC simulations for $x = 0.15$ and 0.20, assuming H-enhanced spin-spin interactions. In the inset, the results of calculations for the Co alloy ratio dependence of the average spin (circle) near room T and the concentration of H relative to Co, [H]/[Co], (x) are shown. (b) The average Co spin value in $Zn_{1-x}Co_xO$ arising from the double exchange interaction between Co spins as derived from MC simulations for $x = 0.20$.

presence of p-type carriers based on the double exchange interaction, while FM is observed in the presence of n-type carriers [10]. It is found that since the H-mediated coupling of t_{2g}-3d levels brings the hydrogenic level below the e_g level, the hydrogenic state can induce a spin-spin interaction even in ZnMnO:H. It is calculated that the spin-parallel state of the (Mn-H$_{AB}$-Mn) geometry is more stable by 0.26 eV than the antiparallel state, indicating that the H effect is important also for FM in ZnMnO. This provides an explanation for the fact that the reported magnetic properties of ZnMnO are similar to those of ZnCoO, especially for the temperature dependence of the magnetization [5,7,10–12]. The hydrogenic state is calculated to lie 0.05 eV below the CBM. This provides an explanation for n-type conduction in ZnMnO [10]. The spin splitting of the Mn-3d levels are much larger than those of Co-3d, and the energy level of the minority spin state of Mn-3d is located much higher in the band gap, compared to that of Co. This makes the hydrogenic state in ZnMnO to lie close to the conduction band. The H effect in another II-VI semiconductor, ZnCoS, was also examined. Since the atomic and electronic structures are similar to those in ZnCoO, a correspondingly strong H-mediated spin-spin interaction is expected in ZnCoS. It is calculated that the spin-parallel state of (Co-H$_{AB}$-Co) is 0.10 eV more stable than the antiparallel state. This indicates that the H-enhanced spin interactions can occur in other II-VI semiconductors when a high concentration of H between magnetic impurities can be achieved.

The strong spin-spin interaction induced by interstitial H is specific to hydrogen. Even though Li is electronically similar to H in having only one electron in a chemically active s orbital, it does not form the bridge-bond coupling of two d orbitals, and the stable binding site for Li is significantly displaced from that for H. Therefore its effect on the magnetic properties of ZnCoO is very different. We tested the spin-spin interaction induced by interstitial Li at a common antibonding site of a Co dimer and found that the *antiparallel* state is 0.05 eV more stable than the parallel spin-paired state.

Although H can induce a strong spin-spin interaction suitable for high-T FM in ZnCoO, the possibility of FM through the double exchange interaction resulting from the presence of extra electrons in the Co-3d-t_{2g} band cannot be excluded. When there is just one extra electron per two Co ions, the parallel spin-paired state of two nearest Co$_{Zn}$ ions is more stable by 0.08 eV than the antiparallel spin-paired state due to the double exchange interaction in the t_{2g} band [9]. If the Co$_{Zn}$ are placed onto second-nearest cation sites, the energy difference is reduced to 7 meV. The calculated temperature dependence of the magnetization using these calculated spin-interaction energies [see Fig. 3(b)] is simi-

lar to experimental data showing that the T_c of ZnCoO is about 300 K (see Refs. [2,6]). More details will be provided later. Some groups have shown that ZnCoO exhibits high-T FM, while others have failed to observe it. The rate of H contamination and the concentration of donorlike defects can provide an explanation for these complicated magnetic properties.

[1] H. Munekata *et al.*, Phys. Rev. Lett. **63**, 1849 (1989); F. Matsukura *et al.*, Phys. Rev. B **57**, R2037 (1998); H. Ohno *et al.*, Phys. Rev. Lett. **68**, 2664 (1992); T. Dietl *et al.*, Science **287**, 1019 (2000); T. Dietl, Semiconductor and Technology **17**, 367 (2002).

[2] K. Ueda, H. Tabata, and T. Kawai, Appl. Phys. Lett. **79**, 988 (2001).

[3] *Diluted Magnetic Semiconductors*, edited by J. K. Furdyna and J. Kossut, Semicond. Semimet. Vol. 25 (Academic, New York, 1988).

[4] W. Mac *et al.*, Phys. Rev. Lett. **71**, 2327 (1993); V. Ladizhansky *et al.*, Phys. Rev. B **60**, 8097 (1999); M. Zielinski *et al.*, Phys. Rev. B **63**, 35202 (2001).

[5] H.-J. Lee *et al.*, Appl. Phys. Lett. **81**, 4020 (2002).

[6] W. Prellier *et al.*, Appl. Phys. Lett. **82**, 3490 (2003).

[7] K. Rode *et al.*, J. Appl. Phys. **93**, 7676 (2003).

[8] Z. Jin *et al.*, Appl. Phys. Lett. **78**, 3824 (2001).

[9] K. Sato and H. Katayama-Yoshida, Jpn. J. Appl. Phys., **39**, L555 (2000); Semicond. Sci. Technol. **17**, 367 (2002).

[10] Y. W. Heo *et al.*, Appl. Phys. Lett. **84**, 2292 (2004).

[11] T. F. Fukumura *et al.*, Appl. Phys. Lett. **78**, 958 (2001).

[12] D. P. Norton *et al.*, Appl. Phys. Lett. **82**, 239 (2003).

[13] C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000); E. V. Lavrov, J. Weber, F. Borrnert, C. G. Van de Walle, and R. Helbig, Phys. Rev. B **66**, 165205 (2002).

[14] S. J. F. Cox *et al.*, Phys. Rev. Lett. **86**, 2601 (2001); D. M. Hofmann *et al.*, Phys. Rev. Lett. **88**, 045504 (2002); Y. Strzhermechny *et al.*, Appl. Phys. Lett. **84**, 2545 (2004).

[15] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[16] J. Ihm *et al.*, J. Phys. C **12**, 4409 (1979).

[17] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[18] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 8861 (1991).

[19] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[20] S. G. Louie *et al.*, Phys. Rev. B **26**, 1738 (1982).

[21] By the LDA calculations, the electronic level of Co-3d orbital is overestimated by the strong self-interaction effect.

[22] A. L. Efros, Phys. Rev. Lett. **68**, 2208 (1992).