Isolation and aggregation of substituent Co in ZnO:Co diluted magnetic semiconductors

Y B Zhang, M H N Assadi and S Li

School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia

E-mail: y.zhang@unsw.edu.au

Abstract

Distribution of magnetic ions in a semiconducting host is critical for the functionality of diluted magnetic semiconductors. By investigating the temperature- and field-dependent magnetization of single-phase polycrystalline ZnO:Co oxides, the substitution of Co at the Zn site is found not to occur randomly but Co ions appear to have a tendency for aggregation via oxygen with an antiferromagnetic coupling, in contrast to paramagnetic isolated free Co. The experimental findings are justified through first-principles density functional calculations based on the generalized gradient approximation. It suggests that Co dopants in ZnO:Co have a tendency towards staying close to each other along the *ab* plane.

ZnO-based diluted magnetic semiconductors (DMS) have initiated enormous scientific interest recently because of their unique spintronic properties with potential technological applications [1, 2]. Reviews of the DMS state-of-the-art emphasize the ZnO:Co system as particularly promising for applications requiring ferromagnetism near room temperature [3, 4]. Although there are tremendous works focusing on the ZnO:Co DMS [3, 4], the origin of ferromagnetism of the DMS is not clear and their properties have not been well understood yet. The existing argument on its origin mainly arises from the unknown distribution of Co in the ZnO host. The source of ferromagnetism could include the presence of secondary phases in which the Co atoms can be self-organized to be magnetically robust micro- [5] or nano- [6] crystals embedded in the host paramagnetic matrix. The Co aggregation occurs especially in either a reduction environment, such as a hydrogen atmosphere [7], or vacuum in non-equilibrium processes, such as pulsed laser ablation [5] and ion implantation [8]. Apart from the external source, the claims of intrinsic ferromagnetism from ZnO:Co remain contentious. The substituent Co ions at the Zn site can appear as a form of substitutional clusters via oxygen ions (spinodal decomposition) or be randomly substitutional (dispersed/diluted). In general, the intrinsic ferromagnetism is based on the homogeneous distribution of Co ions in the ZnO host. However, *ab initio* density functional calculations of chemical pair interactions in the ZnO:Co DMS suggest a strong tendency of clustering between Co atoms [9]. Furthermore, antiferromagnetically coupled Co pairs, in contrast to purely paramagnetic isolated Co dopants, have widely been reported [10, 11]. In this work, the precise distribution of substituent Co ions is presented in polycrystalline stoichiometric ZnO:Co oxides. The Co tendency towards aggregation via oxygen is verified experimentally by magnetization analyses and is justified by rigorous first-principles density functional calculations.

The single-phase polycrystalline stoichiometric ZnO:Co oxides were prepared by conventional solid state reaction, a thermal equilibrium process. The experimental details were published elsewhere [12]. X-ray photoelectron spectroscopy measurements showed that the Co content of the polycrystalline ZnO:Co oxides corresponded to the nominal one at the limit of accuracy and the Co ion in the doped ZnO is substitutional in the $+2$ formal oxidation state [13]. Figure 1(a) shows the field dependence of magnetization at 5 K for $Zn_{1-x}Co_xO$ (x = 0.02, 0.05, 0.0625 and 0.10) polycrystalline samples. No hysteresis was detected, showing no ferromagnetic ordering even at such a low temperature. M increased almost linearly with the applied external field, demonstrating typical paramagnetic behavior. However, M decreased as x increased in a particular applied magnetic field. This is contradictory to the paramagnetic behavior
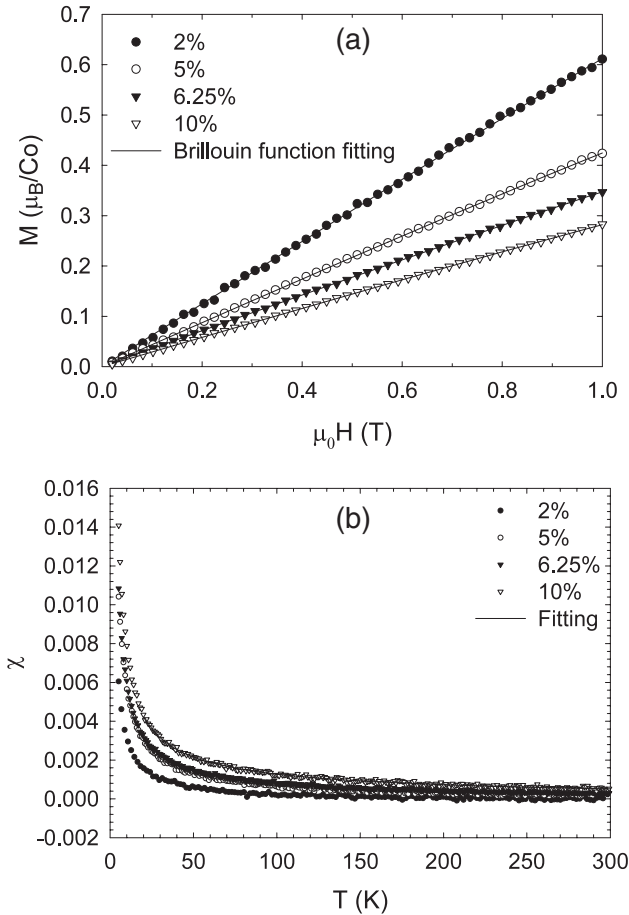
Figure 1. (a) The field dependence of magnetization at 5 K for $Zn_{1-x}Co_xO$ ($x = 0.02, 0.05, 0.0625$ and 0.10) polycrystalline samples. The solid lines correspond to the fits using a Brillouin function. (b) Magnetic susceptibility as a function of temperature for $Zn_{1-x}Co_xO$ ($x = 0.02, 0.05, 0.0625$ and 0.10) polycrystalline samples. The solid lines are fits to the function $(\chi = C_1/T + C_2/(T + \theta) + k)$.

Table 1. Results of fitting magnetic susceptibility versus temperature curves to the function ($\chi = C_1/T + C_2/(T + \theta) + k$) and magnetization versus magnetic field curves to a Brillouin function for $Zn_{1-x}Co_xO$ ($x = 0.02, 0.05, 0.0625$ and 0.10) polycrystalline samples.

	x			
	0.02	0.05	0.0625	0.10
C_1 (K)	0.035	0.043	0.043	0.064
C_2 (K)	0.001	0.034	0.050	0.122
k ($\times 10^{-4}$)	-1.2	-0.5	-0.1	-0.1
θ (K)	19.8	17.7	28.7	88.8
$f(C_1)$	0.966	0.539	0.451	0.354
$f(C_2)$	0.034	0.461	0.549	0.646
μ_{eff} from C_1 (μ_B)	4.04	3.82	3.74	4.07
μ_{eff} from C_2 (μ_B)	3.87	3.66	3.66	4.16

that the concentration of a paramagnetic Co^{2+} ion was lower than the nominal one, especially at a higher Co doping level x where a higher fraction of aggregated Co ions exists with antiferromagnetic coupling.

Figure 1(b) presents magnetic susceptibility as a function of temperature for $Zn_{1-x}Co_xO$ ($x = 0.02, 0.05, 0.0625$ and 0.10) polycrystalline samples. The data were acquired on warming from 5 to 300 K in an external field of 0.5 T after cooling in zero field (ZFC). $\chi \rightarrow \infty$ as $T \rightarrow 0$, which also signifies free Co spins. Therefore, both sets of substituent Co spins and a diamagnetic background from ZnO are incorporated to fit the magnetization versus temperature curves from 20 to 300 K as no magnetic ordering above $T = 20$ K [17]. One set of Co spins is completely isolated and free without any nearest neighbors, and thus follows an ideal paramagnetic behavior. The other set of Co spins with at least one nearest neighbor is antiferromagnetically coupled. The diamagnetic background k includes the contribution from ZnO. Therefore, the total χ is given as $\chi = C_1/T + C_2/(T + \theta) + k$. The Curie constant C (C_1 or C_2) is given by $C = \mu_0\mu_{eff}^2 n/3k_B$, where μ_0 is a magnetic constant, μ_{eff} is the effective magnetic moment, n is the number of the isolated free Co ions (for C_1) or aggregated Co ions (for C_2) per unit volume and k_B is the Boltzmann constant.

By using the above fitting the values of C_1 and C_2 can be obtained. The fraction of the isolated free Co spins $f(C_1)$ has been obtained from Brillouin function fitting of M versus H at 5 K. Consequently μ_{eff} for isolated free Co spins is computed from the value of C_1. Thus the fraction of aggregated Co spins $f(C_2)$ and its μ_{eff} could be determined from the value of C_2. Table 1 summarizes the values obtained from curve fitting M versus H and χ versus T. $f(C_1)$ was found to decrease from 96.6% (for $x = 0.02$), via 53.9% (for $x = 0.05$) and 45.1% (for $x = 0.0625$), to 35.4% (for $x = 0.10$). It is noted that $f(C_1)$ is very close to the fraction of magnetically active Co ions, x_{eff}/x, reported by Yoon *et al* [18]. μ_{eff} for the isolated free Co spins was determined to be 4.04, 3.82, 3.74 and 4.07 μ_B for $x = 0.02, 0.05, 0.0625$ and 0.10, respectively. It is interesting to note that the values are very close to the theoretical value (spin only) of 3.87 μ_B for Co^{2+} ions [19].

of free Co spins. It implies that the M was contributed by distinct substituent Co spins, namely the isolated free spins and the aggregated spins with antiferromagnetic coupling via oxygen [14, 15]. As x increases, the fraction of Co ions that belong to antiferromagnetic coupling increases, leading to the reduction of M. This is in agreement with the previous reports by Risbud *et al* [14] and Lawes *et al* [15]. However, in their work the distribution of Co ions in the ZnO host is assumed to be random. Even the abundance of Co dopants on Zn substitutional sites in various clustered configurations using Behringer's equations for the hcp lattice was employed to explain the field dependence of magnetization [11]. Actually Behringer's equations are also based on a purely statistical model [16]. Recently initial experimental [13] and theoretical [9] results show that the Co distribution in ZnO was not random. To clarify this, the experimental magnetization versus field curves have been fitted using a Brillouin function shown in figure 1(a). The total angular momentum J is assumed to be 1.5 for a Co^{2+} in a high-spin state. The fraction of the isolated free Co spins can be obtained from the fitting. Results clearly indicate

k for $x = 0.02$ is -1.2×10^{-4}, which is comparable to the diamagnetic χ of pure ZnO [20]. These agreements reinforce the validity of our method to describe the magnetic behavior of $Zn_{1-x}Co_xO$. Using the obtained $f(C_1)$ above for the isolated free Co spins, $f(C_2)$ was determined to increase significantly from 3.4% to 46.1% as x increases slightly from 0.02 to 0.05. Then it enhances to 54.9% and 64.6% for $x = 0.0625$ and 0.10. Using C_2 obtained from the curve fitting with our experimental results, μ_{eff} for aggregated Co spins was 3.87, 3.66, 3.66 and 4.16 μ_B for $x = 0.02$, 0.05, 0.0625 and 0.10, respectively. The μ_{eff} fluctuates within a reasonable limit to the theoretical spin-only value for the Co^{2+} spins. As x increases from 0.05 to 0.10, the Curie–Weiss temperature increased from 17.7 to 88.8 K, indicating that the effective Co–Co exchange constant in the aggregated Co ions enhances as well. When the substitution of Co at the Zn site is assumed to be random, $f(C_2)$ was predicted to be approximately 18% and 34% for $x = 0.05$ and 0.10, respectively [14]. Therefore, the experimentally determined fraction of aggregated Co spins is much higher than that which could be predicted theoretically based on random substitution of Co at the Zn site. Only 53.9% and 35.4% are isolated Co ions for $x = 0.05$ and 0.10, respectively. This strongly indicates that the tendency for Co ions to aggregate is greater than the statistical effect of random substitution.

To justify this experimental finding and identify the preferred particular positions of the Co substitution in ZnO, total energy calculations using first-principles density functional theory were performed using the CASTEP program [21] with the generalized gradient approximation and plane wave pseudopotential (PWP) approach. The energy cutoff E_{cut} of 800 eV and a Monkhorst–Pack k-point grid of $3 \times 3 \times 1$ were used for all calculations on a 32-atom ZnO host supercell ($2a \times 2a \times 2c$). The lattice constants were fixed while all atoms were allowed to relax within convergence thresholds of 0.1 eV $Å^{-1}$ for maximum force and 5×10^{-5} eV/atom for the maximum energy change. As closely related configurations were to be optimized and their calculated total energies E_{tot} compared, a finite basis set correction scheme was applied to all calculations. Errors associated with finite E_{cut} which might affect E_{tot} and the magnitude of acting forces on atoms in the supercell are significantly reduced and more reliable geometry optimizations are conducted via this correction. $dE_{tot}/d \ln E_{cut}$ is the only required parameter for this correction. It is also an indicator of how reasonably the computational settings were chosen. In current work $dE_{tot}/d \ln E_{cut}$ was calculated by using three total energies with three successive E_{cut} of 790, 795 and 800 eV for initial structure of all configurations. In all cases $dE_{tot}/d \ln E_{cut}$ was smaller than 1 meV/atom, indicating a very good convergence for E_{tot} as a function of chosen E_{cut} and k-point sampling grid.

Figure 2 shows a 32-atom ZnO supercell in which two of the Zn are substituted with Co. As a result the chemical formula of our supercell is $Zn_{14}Co_2O_{16}$, which is equivalent to a Co concentration of 12.5% ($Zn_{0.875}Co_{0.125}O$). Since two Co are essential for study of spin alignment in the supercell, the $Zn_{14}Co_2O_{16}$ system was chosen to investigate the distribution of Co in the ZnO host. The experimental lattice parameters of $a = 3.2527$ Å and $c = 5.2046$ Å were employed [12].
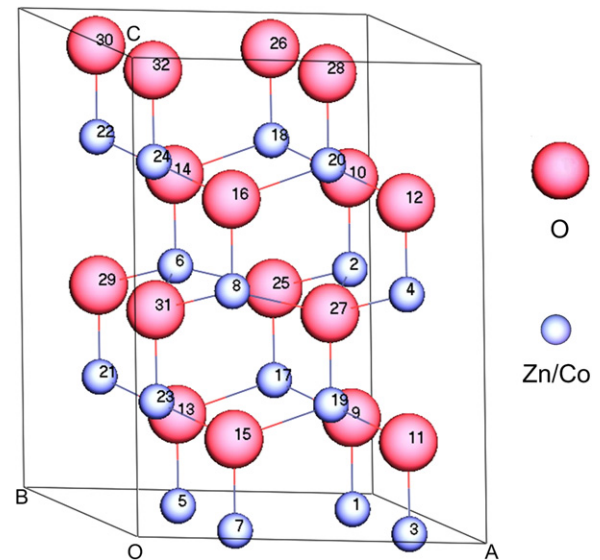

Figure 2. A 32-atom $2 \times 2 \times 2$ ZnO supercell with lattice sites labeled.
(This figure is in colour only in the electronic version)

The geometrically possible configurations of two substituent Co were identified in the $2 \times 2 \times 2$ ZnO supercell. The two Co can be either isolated with different distances or paired to be a dimer intermediated by one O where they can lie on either the ab plane or c direction. In configuration 1, the Zn sites 17 and 6 are replaced by Co with a shortest distance of 3.209 Å in the $2 \times 2 \times 2$ ZnO supercell, while in configuration 2, Co substitute the Zn sites 17 and 19 with a distance of 3.253 Å. In configuration 3 the two Co sites are 17 and 8 with a distance of 4.569 Å while they are 17 and 18 with a distance of 5.205 Å in configuration 4. Finally in configuration 5 the sites 17 and 24 are substituted with Co with a furthest distance of 6.137 Å. For each configuration the calculation was performed once when electronic spin alignment of the Co was fixed parallel (ferromagnetic state) and once again when the electronic alignment was fixed antiparallel (antiferromagnetic state). E_{FM} and E_{AFM} represent total energy per supercell for ferromagnetic and antiferromagnetic states, respectively, while ΔE_{AFM-FM} is their difference per Co defined as $(E_{AFM} - E_{FM})/2$. In order to make the total energy comparison among different configurations tractable and illustrative E_{AFM} for configuration 5 having a furthest Co distance with unrelaxed ionic coordinates was chosen as an energy reference. It means that all energies calculated for other configurations, either unrelaxed or relaxed, were shifted accordingly. It should be noted that ΔE_{AFM-FM} is not affected by the shift. E_{AFM} for different $Zn_{14}Co_2O_{16}$ geometry configurations with unrelaxed or relaxed ionic coordinates is presented in figure 3(a) and ΔE_{AFM-FM} in figure 3(b). For each configuration, E_{AFM} is lower than E_{FM} for both unrelaxed and relaxed ionic coordinates. E_{AFM} and ΔE_{AFM-FM} for relaxed ionic coordinates is always slightly lower than those for the unrelaxed one. Since the lower the energy is, the more stable that configuration is, it is clearly observed that a strong tendency towards forming Co dimers exists. Configurations 3,
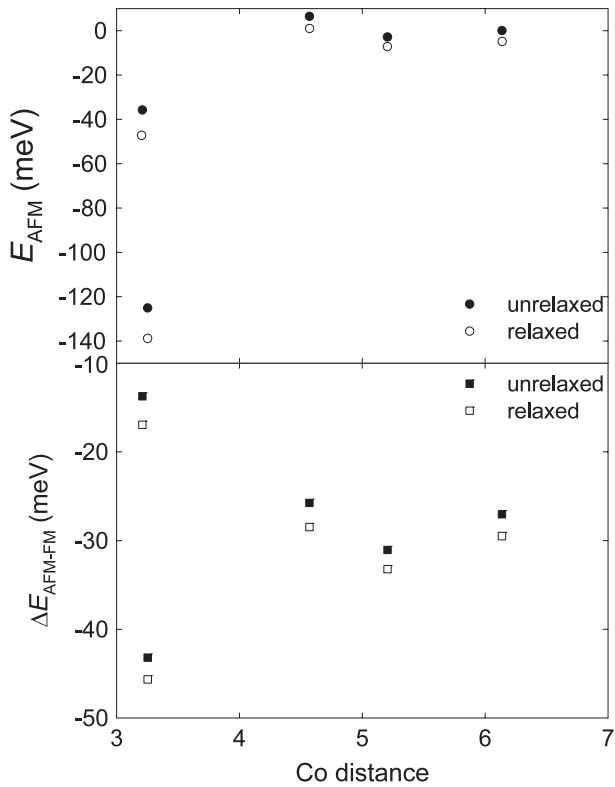
3

Figure 3. (Top) Total energy per supercell for an antiferromagnetic state (E_{AFM}) of the $Zn_{14}Co_2O_{16}$ structure with unrelaxed or relaxed ionic coordinates. E_{AFM} for the configuration having a furthest Co distance with unrelaxed ionic coordinates was chosen as an energy reference. (Bottom) The difference in total energy per Co between antiferromagnetic and ferromagnetic states (ΔE_{AFM-FM}) for different $Zn_{14}Co_2O_{16}$ geometry configurations where the ionic coordinates are either unrelaxed or relaxed.

4 and 5 with isolated Co dopants all stand in the higher energy region in AFM. As two Co move next to each other via an O when the Co are paired along the c direction or ab plane, configuration 1 becomes more stable by around 47 meV for the relaxed structure and configuration 2 significantly stabilizes by approximately 139 meV. This is in agreement with the report that the AFM coupling is much more enhanced for paired Co ions aligned along the ab plane than that for those aligned along the c direction [22]. 3d orbitals of the paired Co ions along the ab plane effectively interact with a mediating O 2p orbital. Since the interacting lobes of Co d and O p orbitals form an angle of 34.56°, both dp π and dp σ interactions exist between the O and two neighboring Co atoms. However, for the paired Co ions along the c direction, weak dp π-type interactions exist between the O and one of the two neighboring Co atoms, significantly reducing the magnitude of the electron (or hole) transfer matrix element, while the d orbital of the other Co atom strongly interacts with the O p orbital via the dp σ-type coupling. Therefore the most stable configuration occurs when the paired Co dimer is along the ab plane. In this configuration, a strong AFM electronic ground state of $\Delta E_{AFM-FM} = 46$ meV/Co was predicted, which is large enough to lead to antiferromagnetism with no doubt. ΔE_{AFM-FM} was found to drop to around 30 meV

per Co when the Co are isolated from each other. The thermal energy $k_B T$ suggests that in these configurations the antiferromagnetism is not stable. It is interesting to note that the AFM coupling is even less stable when the paired Co dimer is along the c direction. It is concluded that generally Co dopants tend to aggregate rather than stay isolated where their magnetic interaction may be paramagnetic. The most stable configuration was predicted where two Co are paired via one O along the ab plane. This new understanding may be used to explain some phenomena in Co-substituted ZnO in a different way. It may help to clarify the low value of the Co magnetic moment widely obtained from experiments by considering the competition between the ferromagnetic interaction of isolated Co ions mediated by the free or localized carriers and the antiferromagnetic superexchange coupling of the aggregated Co ions.

In conclusion, the magnetization of single-phase polycrystalline $Zn_{1-x}Co_xO$ ($x = 0.02, 0.05, 0.0625$ and 0.10) oxides has been systematically studied. The temperature dependence of magnetization can be fitted with a paramagnetic Curie term from spins of isolated free Co, an antiferromagnetic Curie–Weiss term from spins of paired Co in nearest-neighbor positions via oxygen ions and a diamagnetic constant. Results show that the substitution of Co at the Zn site does not occur randomly but Co ions appear to have a tendency for aggregation. By investigating five geometrically distinct configurations first-principles density functional calculations based on the generalized gradient approximation support that Co dopants have a tendency towards staying close to each other via oxygen along the ab plane with an antiferromagnetic coupling.

References

[1] Liu C, Yun F and MorKoc H 2005 *J. Mater. Sci.: Mater. Electron.* **16** 555
[2] Pan F, Song C, Liu X J, Yang Y C and Zeng F 2008 *Mater. Sci. Eng.* R **62** 1
[3] Prellier W, Fouchet A and Mercey B 2003 *J. Phys.: Condens. Matter* **15** R1583
[4] Chambers S A, Droubay T C, Wang C M, Rosso K M, Heald S M, Schwartz D A, Kittilstved K R and Gamelin D R 2006 *Mater. Today* **9** 28
[5] Kim J H, Kim H, Kim D, Ihm Y E and Choo W K 2002 *J. Appl. Phys.* **92** 6066
[6] Park J H, Kim M G, Jang H M, Ryu S and Kim Y M 2004 *Appl. Phys. Lett.* **84** 1338
[7] Deka S and Joy P A 2006 *Appl. Phys. Lett.* **89** 032508
[8] Norton D P, Overberg M E, Pearton S J, Pruessner K, Budai J D, Boatner L A, Chisholm M F, Lee J S, Khim Z G, Park Y D and Wilson R G 2003 *Appl. Phys. Lett.* **83** 5488
[9] Sanyal B, Knut R, Granas O, Iusan D M, Karis O and Eriksson O 2008 *J. Appl. Phys.* **103** 07D131
[10] Sati P, Deparis C, Morhain C, Schafer S and Stepanov A 2007 *Phys. Rev. Lett.* **98** 137204

[11] Ney A, Ollefs K, Ye S, Kammermeier T, Ney V, Kaspar T C, Chambers S A, Wilhelm F and Rogalev A 2008 *Phys. Rev. Lett.* **100** 157201

[12] Zhang Y B, Sritharan T and Li S 2006 *Phys. Rev. B* **73** 172404

[13] Zhang Y B and Li S 2008 *Appl. Phys. Lett.* **93** 042511

[14] Risbud A S, Spaldin N A, Chen Z Q, Stemmer S and Seshadri R 2003 *Phys. Rev. B* **68** 205202

[15] Lawes G, Risbud A S, Ramirez A P and Seshadri R 2005 *Phys. Rev. B* **71** 045201

[16] Behringer R E 1958 *J. Chem. Phys.* **29** 537

[17] Kolesnik S, Dabrowski B and Mais J 2002 *J. Supercond.* **15** 251

[18] Yoon S W, Cho S-B, We S C, Yoon S, Suh B J, Song H K and Shin Y J 2003 *J. Appl. Phys.* **93** 7879

[19] Kittel C 1986 *Introduction to Solid State Physics* (New York: Wiley) p 406

[20] Kane M H, Shalini K, Summers C J, Varatharajan R, Nause J, Vestal C R, Zhang Z J and Ferguson I T 2005 *J. Appl. Phys.* **97** 023906

[21] Clark S J, Segall M D, Pickard C J, Hasnip P J, Probert M I J, Refson K and Payne M C 2005 *Z. Kristallogr.* **220** 567

[22] Lee E-C and Chang K J 2004 *Phys. Rev. B* **69** 085205