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*Year 2005*

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This paper originally appeared as: Peleckis, G, Wang, XL, Liu, RS and Dou, SX, Co valence and possible spin transformation in diluted magnetic semiconductors  $\text{Zn}_{1-z}\text{Mg}_z\text{Co}_{0.15}\text{O}$  and  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ , INTERMAG Asia 2005. Digests of the IEEE International Magnetics Conference, 4-8 April 2005, 283-284. Copyright IEEE 2005.

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Co VALENCE AND POSSIBLE SPIN TRANSFORMATION IN DILUTED MAGNETIC SEMICONDUCTORS Zn<sub>1-x</sub>Mg<sub>z</sub>ZO AND Zn<sub>1-x</sub>Co<sub>x</sub>O

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Introduction

Diluted magnetic semiconductors (DMS) are conventional semiconductors doped with transition metal (TM) ions that are considered as promising candidates for “spintronic” applications. ZnO is a well known direct band-gap semiconductor researched vigorously after theoretical predictions of possible room temperature ferromagnetism (FM) were published [1]. Reported experimental results on transition metal doped ZnO thin films are very controversial. Some groups observed room temperature ferromagnetism in Ni-, Co-doped thin films of ZnO [2,3], while many failed [4,5]. Also no FM was observed in polycrystalline samples [6,7]. This controversy and poor reproducibility of the data suggests that origins of ferromagnetism in TM doped ZnO are yet to be understood. Thus, in order to clarify this uncertainty, a detailed Co valence state and structural investigations are of high importance.

Experimental

Polycrystalline samples of Zn<sub>1-x</sub>Co<sub>x</sub>O (0.05 ≤ x ≤ 0.17) and Zn<sub>1-z</sub>Mg<sub>z</sub>Co<sub>0.15</sub>O (0.01 ≤ z ≤ 0.20) were prepared by “rapid oxalate decomposition” technique. Phase purity analyzed by means of x-ray diffraction technique (Philips PW-1730). Structures were refined by Rietveld refinement program. Co valence was determined by x-ray absorption near edge spectroscopy (XANES) using synchrotron irradiation (SRRC, Taipei). Magnetic properties measured with Magnetic Property Measurement System (MPMS XL, Quantum Design).

Results and discussion

Refinement results show that all samples were of hexagonal wurtzite type ZnO structure with lattice parameter *c* increasing with increase of both Co and Mg contents *x* and *z*, respectively.

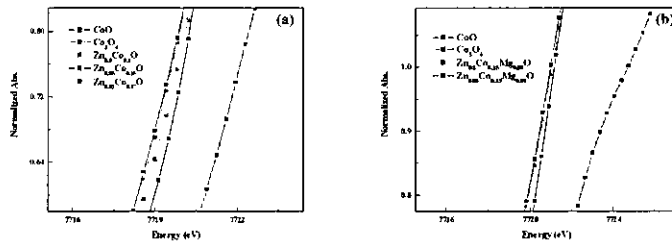


Fig. 1 Co K near-edge XAS of (a) Zn<sub>1-x</sub>Co<sub>x</sub>O and (b) Zn<sub>1-z</sub>Mg<sub>z</sub>Co<sub>0.15</sub>O oxides; CoO and Co<sub>3</sub>O<sub>4</sub> were used as reference materials for Co<sup>2+</sup> and Co<sup>3+</sup>, respectively

From Fig. 1 we can clearly see that in both cases, Co only and Mg-Co co-doped ZnO, Co valence state is 2+. This result suggests that dopant ions substitute for Zn directly, maintaining chemical stoichiometry as it is described by nominal formula. Furthermore, we can state that double exchange interaction mechanism must be excluded from discussions of origins of ferromagnetism in this system, since there is no multi-valence species of Co ion. Magnetic properties measured showed that all samples were paramagnetic, following Curie-Weiss law above 120 K. Inversed magnetic susceptibility ( $1/\chi$ ) curves as a function of temperature (*T*) are represented in Figure 2 (a,b). All Weiss temperature ( $\theta$ ) values were negative, showing that Co ions in our samples are coupled antiferromagnetically. Magnetization hysteresis measurement indicated that there is no trace of ferromagnetism. Mg doping did not incur any significant changes to magnetic properties of the material. In fact, Mg doping was found to reduce carrier density and made ZnO more insulating. Obtained from Curie-Weiss fittings at high temperature region effective magnetic moment ( $\mu_{eff}$ ) for Co is  $\mu_{eff} = 3.87 \mu_B/Co$ . This value corresponds to that of tetrahedral Co<sup>2+</sup> high spin ( $e_g^4 t_{2g}^3$ ) state. However, when fitting at  $T \rightarrow 0K$  region we observed  $\mu_{eff} = 2.82 \mu_B/Co$  indicating a possible spin state transition to Co<sup>2+</sup> low spin (LS) state. Various approaches of Co spin state estimation showed that contribution of the orbitals to the  $\mu_{eff}$  of Co in our samples is high.

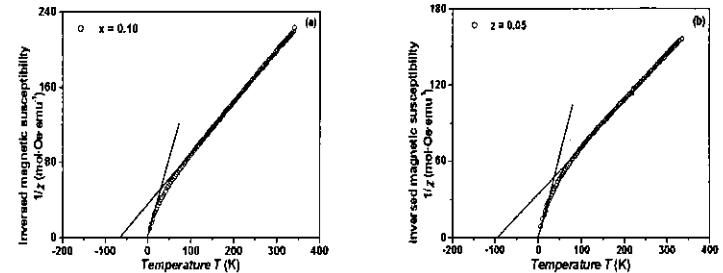


Fig. 2 Inversed magnetic susceptibility ( $1/\chi$ ) versus temperature (*T*) for (a) Zn<sub>1-x</sub>Co<sub>x</sub>O and (b) Zn<sub>1-z</sub>Mg<sub>z</sub>Co<sub>0.15</sub>O

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