

Ferromagnetism and superparamagnetism of ZnCoO:H nanocrystals

Z. H. Wang,^{a)} D. Y. Geng, S. Guo, W. J. Hu, and Z. D. Zhang
Shenyang National Laboratory for Materials Science, Institute of Metal Research, and International Centre for Materials Physics, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, People's Republic of China

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ZnCoO:H nanocrystals are weak ferromagnetic at room temperature with a small coercivity and a small remanence, whereas ZnCoO nanocrystals are paramagnetic. The thermal irreversibility of zero-field cooling and field cooling magnetizations of ZnCoO:H nanocrystals corresponds to the existence of superparamagnetism due to the nanosize effect. X-ray photoelectron spectra show the incorporation of Co²⁺ ions inside the ZnO lattice without changing the wurtzite structure. Our data suggest that hydrogen can induce ferromagnetism in ZnCoO and that ferromagnetic ZnCoO:H crystals with small particle size can show the superparamagnetism. © 2008 American Institute of Physics. [DOI: 10.1063/1.2948863]

Dilute magnetic semiconductors (DMSs) have attracted much attention since the discovery of ferromagnetism in InMnAs and GaMnAs.¹ As a wide-gap II-VI oxide semiconductor, ZnO has attracted considerable attention since the possibility of ultraviolet light emitting was demonstrated.² ZnO-based materials are attractive DMS candidates because of the high solubility limit of magnetic ions. Theoretical investigations predicted that V, Cr, Fe, Co, Ni, and Mn doped ZnO should be ferromagnetic at/above room temperature.^{3,4} Experiments have been directed at producing and improving their magnetic properties.^{5,6} The control of magnetic properties through hydrogenation was demonstrated in GaMnP and GaMnN ferromagnetic semiconductors.^{7,8} Recently, the influence of hydrogen on the magnetic properties of ZnO DMS was investigated.⁹ There is considerable evidence that interstitial H can cause the natural *n*-type character of ZnO.¹⁰ However, the existence of hydrogen-induced ferromagnetism in ZnCoO is still controversial. On the one hand, it was found that ZnCoO thin films became ferromagnetic after it was hydrogenated in Ar-H₂ mixed gas.¹¹ Although Co metallic peak was observed in x-ray photoelectron spectroscopy (XPS), the ferromagnetic contribution from Co metal was not detected by magnetic circular dichroism studies.¹¹ On the other hand, the ferromagnetism was also observed at room temperature in polycrystalline ZnCoO after hydrogen reaction in Ar-H₂ at 1125 K,¹² but its origin was attributed to the presence of Co metal. In this letter, we investigate the effect of dopant H on the magnetic properties of ZnCoO nanocrystals. Magnetic measurements reveal ferromagnetic behavior with a small coercivity (H_C) and a small remanence (M_R) in ZnCoO nanocrystals after annealing in H₂. The thermal irreversibility of zero-field cooling (ZFC) and field cooling (FC) magnetizations of ZnCoO:H nanocrystals corresponds to the existence of superparamagnetism due to the nanosize effect. The XPS and x-ray diffraction (XRD) results show that Co²⁺ incorporate into the wurtzite lattice at Zn²⁺ site without presence of Co metal and cobalt oxides (such as Co₃O₄). H is strongly coupled to Co, which results in the shift of the Co $2p_{3/2}$ XPS peak of hydrogenated ZnCoO:H nanocrystals.

ZnCoO and ZnCoO:H nanocrystals were fabricated by a hydrothermal process and a subsequent annealing process at 400 °C under air and H₂, respectively. In the hydrothermal process, stoichiometric amounts of Zn(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O were first dissolved in distilled water. Then the solution was droved in Teflon-lined stainless steel autoclave and appropriate NaCO₃ solution was added as precipitator. The autoclave was sealed and maintained at 100 °C for 24 h. The powders were obtained by centrifuging the mixture after the solution was cooling down to room temperature. Finally, ZnCoO and ZnCoO:H nanocrystals were obtained by annealing the powders, respectively, in air and H₂ at 400 °C for about 2 h. The structure of the nanocrystals was characterized by means of XRD, using a D/max-γA diffractometer with Cu $K\alpha$ radiation at 50 kV and 250 mA. The size distribution, morphology, and microstructure of the nanocrystals were investigated by a high-resolution transmission electron microscope (HRTEM) (JEOL 2010EX). The nanocrystals were also characterized by XPS using Al K radiation ($h\nu = 1486.6$ eV). The magnetizations were measured by employing a superconducting quantum interference device (SQUID) (Quantum Design MPMS-7) magnetometer.

The magnetic properties of ZnCoO and ZnCoO:H nanocrystals with about 10% Co were investigated by SQUID. Figure 1 shows the ZFC and FC magnetization curves of the ZnCoO and ZnCoO:H nanocrystals between 5 and 300 K at a magnetic field of 500 Oe. The ZFC and FC curves of the ZnCoO nanocrystals fit well each other [Fig. 1(a)]; it is clear that the ZnCoO nanocrystals show the paramagnetic behavior at 300 K [also see the inset of Fig. 1(a)]. The Néel temperature T_N of cobalt oxides is not observed in the magnetization curves of ZnCoO, indicating to the absence of cobalt oxides (such as Co₃O₄). The bifurcation between ZFC and FC curves of ZnCoO:H nanocrystals indicates a large thermal irreversibility with the onset near 300 K, which is characterized as the existence of superparamagnetism above room temperature, due to the nanosize effect. The magnetic hysteresis loop observed for ZnCoO:H at 300 K is shown in the inset of Fig. 1(b). However, the coercivity H_C and the remanence M_R of ZnCoO:H are very small, which suggest also that it will become superparamagnetism at higher temperatures. It was reported that the superparamagnetism in TiCoO films was caused by Co cluster with size of

^{a)}Electronic mail: zhwang@imr.ac.cn.

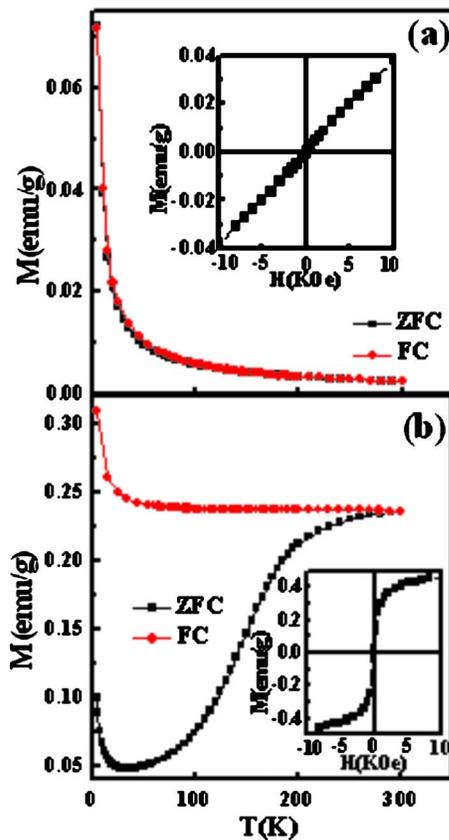


FIG. 1. (Color online) ZFC and FC magnetization curves of (a) ZnCoO and (b) ZnCoO:H nanocrystals from 5 to 300 K. Insets are the magnetic hysteresis loops of ZnCoO and ZnCoO:H at 300 K.

8–10 nm.¹³ The superparamagnetism takes place at room temperature for Co particles with sizes of about 12 nm.¹⁴ In the present case, the size of the ZnCoO:H nanocrystals is ranged from 10 to 30 nm, as revealed in the HRTEM image (Fig. 2). The interplanar distance is 0.247 nm, corresponding to the (101) lattice plane of hexagonal ZnO-type structure. However, the hysteresis loops of ZnCoO:H at different temperatures [represented in Fig. 3 and also the inset of Fig. 1(b)] are different with those of the TiCoO films.¹³ It is clear that the hysteresis loops at 300 and 200 K of our ZnCoO:H are almost same, except the slight bigger H_C and M_R at 200 K [see the Fig. 3(b)]. The hysteresis loop at 5 K of our ZnCoO:H shows comparatively small H_C and M_R , compared with the previous data for hydrogenated ZnCoO polycrystal-

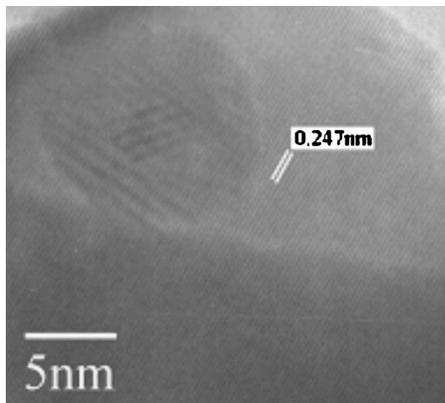


FIG. 2. HRTEM image of ZnCoO:H nanocrystals with interplanar distance of 0.247 nm.

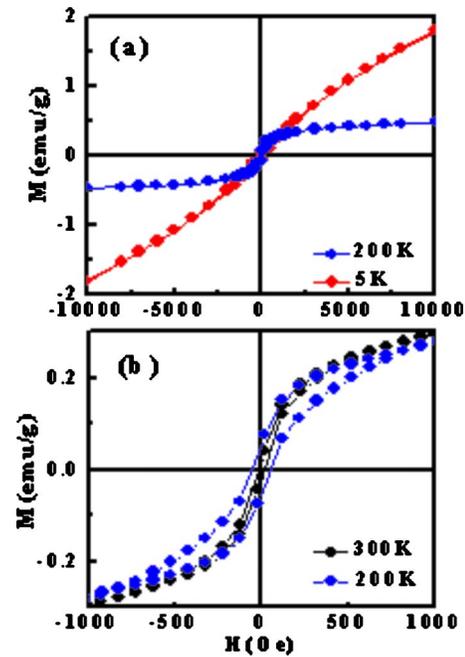


FIG. 3. (Color online) Magnetic hysteresis loops of ZnCoO:H nanocrystals at 200 and 5 K. Inset shows the low field part of the hysteresis loops at 300 and 200 K.

lines with the presence of Co metal.¹² One of the characters of the magnetization at 5 K of our ZnCoO:H is that it is unsaturated at the high magnetic field. Just on the contrary, the hysteresis loops of TiCoO and (La, Sr)TiO₃ films exhibit a large H_C and M_R at 5 K, due to the presence of ferromagnetic Co nanoparticles, and the magnetization could be saturated below 2 T.^{13,15} Furthermore, the saturation magnetization of our ZnCoO:H at 300 K is much smaller than that induced by Co reported in ZnCoO.¹² It is understood that, in our case, the superparamagnetism could not be induced by Co clusters (see also XRD and XPS analysis below). The FC magnetization of ZnCoO:H decreases rapidly with increasing temperature up to 40 K and the residual ferromagnetism persists up to room temperature.

The typical XRD patterns of ZnCoO and ZnCoO:H with about 10% Co concentration are shown in Fig. 4(a). It is shown that the wurtzite structure of ZnO is unchanged by the Co doping and/or the H addition. Furthermore, any secondary phase such as Co clusters or cobalt oxides could not be detected in the XRD patterns. Crystallite sizes of ZnCoO and ZnCoO:H nanocrystals were 12–15 and 20–28 nm, respectively, as calculated by using the Scherrer formula. It is shown that the size is increased after annealing in H₂.

The XPS was used to study Co ions in the ZnCoO and ZnCoO:H nanocrystals. As shown in Fig. 4(b), the charge-shifted spectra were corrected using the adventitious C1s photoelectron signal at 284.6 eV. The energy difference between Co2p_{3/2} and Co2p_{1/2} is 15.54 eV (or 15.72 eV), corresponding to ZnCoO (or ZnCoO:H). The energy difference for the existence of Co as metal clusters should be 15.05 eV, while that for Co surrounded by oxygen should be 15.5 eV.^{16,17} Therefore, in our nanocrystals, the formation of Co clusters could be ruled out. The big energy difference in ZnCoO:H was due to the H addition. The spectra in Fig. 4(b) could be divided into four peaks (p_1 , p_2 , p_3 , and p_4). The positions of peaks p_1 and p_3 are similar to that of CoO corresponding to Co2p_{3/2} and Co2p_{1/2}, respectively. How-

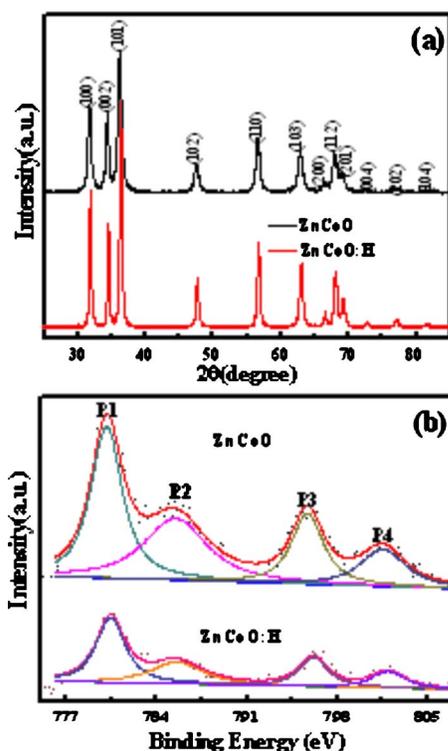


FIG. 4. (Color online) (a) XRD and (b) XPS patterns of ZnCoO and ZnCoO:H nanocrystals at room temperature.

ever, the Co $2p$ signals of ZnCoO:H are shifted to a higher energy level by 0.4–0.6 eV, and the full width at half maximum of those peaks is broader than that of ZnCoO. It is known that the energy of Co–O bonding is 780.1 eV and the binding energy is increased to 781 eV when Co binds to hydrogen.^{11,18} It means that the H addition affects the Co states in Co–O bonding. Peaks $p2$ and $p4$ correspond to the shake-up satellite lines of $p1$ and $p2$, respectively, which reflects the fact that Co $^{2+}$ would incorporate into the wurtzite lattice at the Zn $^{2+}$ sites.¹¹ The XPS and XRD data for ZnCoO:H provide evidence for a significant amount of the Co–H coupling. The magnetic properties further indicate that the hydrogen can enhance the ferromagnetic spin-spin interaction in the ZnCoO:H nanocrystals. It can be concluded from the discussions above that room temperature DMS with small particle size can show superparamagnetism at higher temperatures.

In summary, we have investigated the effect of hydrogen on the magnetic properties of ZnCoO nanocrystals. No secondary phase is observed for ZnCoO and ZnCoO:H nanocrystals with about 10% cobalt concentration. The ferromagnetism is significantly enhanced by the hydrogen addition to ZnCoO, according to the ZFC and FC magnetizations and the hysteresis loops. The evidences for the existence of superparamagnetism are characterized.

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