

XMCD and photoemission investigations of the origin of room temperature ferromagnetism in Fe-doped ZnO nanoparticles

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1. Introduction

There is growing interest in diluted magnetic semiconductors (DMS), where magnetic ions are doped into the semiconductors, due to the possibility to utilize both charge and spin degrees of freedom in the same material, which allows us to design a new generation of spin electronic devices with enhanced functionalities [1-3]. Theoretical studies on the basis of Zener's *p-d* exchange model have shown that transition-metal-doped wide-gap semiconductors such as ZnO are promising candidates for room temperature ferromagnetic DMS [4,5] and a number of experiments on the ZnO-based DMS have revealed ferromagnetic properties at room temperature [6,7].

Recently, Karmakar *et al.* have reported room temperature ferromagnetism in Fe-doped ZnO nanoparticles [8]. ZnO-based DMS nanoparticles are of interest for applications in drug-targeting, high-density magnetic memory, high-frequency electronics, and high performance permanent magnets. Thus, the origin of ferromagnetism in the Fe-doped ZnO nanoparticles is very interesting not only for potential applications but also for basic science of magnetism. In Ref. [8], the ferromagnetic properties of the Fe-doped ZnO nanoparticles are proposed to originate from the Fe²⁺ - Fe²⁺ exchange interaction mediated by Fe³⁺ ions which are present on the surface of the nanoparticles. However, the origin of magnetic properties in Fe-doped ZnO nanoparticles has not been clear yet.

In this work, we have investigated the electronic structure and the magnetic properties of the Zn_{0.9}Fe_{0.1}O nanoparticles by performing x-ray absorption (XAS), x-ray magnetic circular dichroism (XMCD) and photoemission measurements.

2. Experimental details

Details of the sample preparation were described in Ref. [8]. Zn_{0.9}Fe_{0.1}O nanoparticles were prepared by the chemical pyrophoric reaction technique and structural characterization with x-ray diffraction and transmission electron microscopy were carried out, resulting in a clear nanocrystal

phase. As obtained from TEM data, the average particle size is around 7 nm, whereas broad particle size distribution exists within the sample. Magnetization measurements on the same material reveal a ferromagnetic to paramagnetic transition temperature > 450 K. XAS and XMCD measurements were performed at the Dragon Beamline BL11A of National Synchrotron Radiation Research Center (NSRRC) in the total-electron-yield mode. The monochromator resolution was $E/\Delta E > 10000$ and the circularly polarization of x-rays was ~55%. Photoemission measurements were performed at BL23-SU of SPring-8. Spectra were taken in the base pressure below 10⁻⁸ Pa at room temperature. The total resolution of the spectrometer was ~200 meV.

3. Results and discussion

Figure 1(a) shows the absorption spectra of Zn_{0.9}Fe_{0.1}O nanoparticles for the different magnetization directions (σ^+ and σ^-), the XMCD spectrum, and its integration, compared with the XMCD spectrum of Fe metal measured at room temperature [9]. The XMCD spectrum have been normalized to the maximum height of the Fe *L*_{2,3} edge XAS [$(\sigma^+ + \sigma^-)/2$] spectra as 100. The XMCD spectral line shape of the Zn_{0.9}Fe_{0.1}O nanoparticles is different from that of Fe metal. This suggests the magnetism in this sample is not due to metallic Fe clusters but due to Fe ions with localized 3*d* electrons. In the XMCD spectrum of the Zn_{0.9}Fe_{0.1}O nanoparticles, three sharp peaks around $h\nu = 708.5$, 709.5 and 710.5 eV are observed, denoted by **a**, **b** and **c**, respectively. From previous reports [10, 11], peaks **b** and **c** are assigned to Fe³⁺ at the tetrahedral *T_d* and octahedral *O_h* sites, respectively. For peak **a**, it is expected to be attributed not only to *T_d* Fe²⁺ but also to *O_h* Fe³⁺ from a soft x-ray resonant photoemission study (not shown). Figure 1(b) shows the XMCD spectrum of the Zn_{0.9}Fe_{0.1}O nanoparticles in comparison with those of γ -Fe₂O₃ nanoparticles, where Fe³⁺ ions are both at the *T_d* and *O_h* sites [10], and Fe₃O₄, where Fe³⁺ at *T_d*, *O_h* and Fe²⁺ at *O_h* coexist [12]. The XMCD spec-

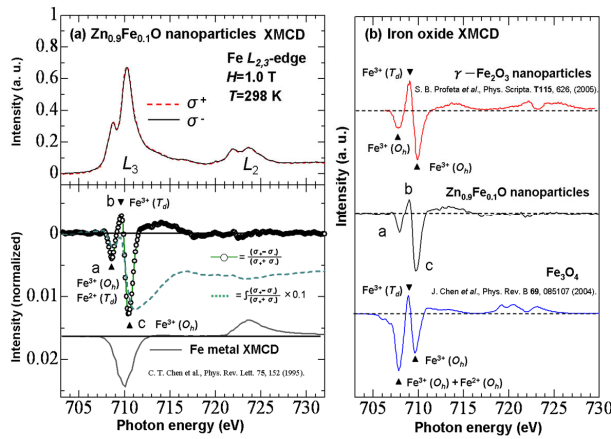


Fig. 1. Fe $L_{2,3}$ x-ray absorption spectra $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$ nanoparticles at 298 K in a magnetic field of 1 T. (a) XAS (σ^+ and σ^-), XMCD and its integration compared with XMCD spectrum of Fe metal [9]. The XMCD spectrum have been normalized to the maximum height of the Fe $L_{2,3}$ edge XAS [$(\sigma^+ + \sigma^-)/2$] spectra as 100 (b) XMCD spectrum of $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$ nanoparticles compared with the XMCD of $\gamma\text{-Fe}_2\text{O}_3$ [10] and Fe_3O_4 [11].

trum of Fe_3O_4 , which displays the overlapping contributions from the Fe^{3+} and Fe^{2+} sites, is different from that of the $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$ nanoparticles. Moreover, Fe_3O_4 is a ferrimagnet with $T_c = 860$ K [12], which is way beyond 450 K. On the other hand, the spectral line shape of the $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$ nanoparticles is nearly identical to that of the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles where XMCD signals are due to only Fe^{3+} sites. This indicates that the magnetism in the $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$ nanoparticles is mainly originated from the $T_d \text{Fe}^{3+}$ and $O_h \text{Fe}^{3+}$ sites. Although the contribution from the Fe^{2+} ions to the magnetism in this sample exists, the contribution appears to be small. Considering that room temperature ferromagnetism (ferrimagnetism) in the spinel ferrite structure such as the $\gamma\text{-Fe}_2\text{O}_3$ and nonstoichiometric ZnFe_2O_4 has been reported [13], it is possible that the room temperature ferromagnetism in this sample may be due to the superexchange coupling between $O_h \text{Fe}^{3+}$ and $T_d \text{Fe}^{3+}$ via O in the spinel structure.

Usually, if Fe ions are present at the substitutional site in the ZnO crystal, the valence state of Fe would be +2. However, our XMCD result confirms the presence of $T_d \text{Fe}^{3+}$ and $O_h \text{Fe}^{3+}$ ions within this sample. We discuss here the various possibilities for the presence of the $T_d \text{Fe}^{3+}$ and $O_h \text{Fe}^{3+}$ ions. One possible reason for the presence of Fe^{3+} ions in the spinel structure is the segregation of spinel ferrite such as the $\gamma\text{-Fe}_2\text{O}_3$ and nonstoichiometric ZnFe_2O_4 at the surface region of the particles. Indeed, Shim *et al.* has reported that the ferromagnetism in Fe- and Cu-codoped ZnO is originated from the secondary phase, nanocrystalline ZnFe_2O_4 with inverted spinel structure, while the majority of Fe ions substituted into the ZnO lattice appears to remain magnetically inert [14]. However, Karmakar *et al.* has suggested that the presence of Fe_3O_4 , Fe_2O_3 and

ZnFe_2O_4 in this sample as secondary phases is excluded from EPR and Mossbauer studies [8]. The other reason for the presence of the Fe^{3+} ions in the spinel structure is that the particle surface may have structures different from a bulk-terminated one. If the valence state of Fe changes from 2+ to 3+ due to defects such as surface vacancies and/or surface oxidation, the crystal field may no longer possess tetrahedral symmetry [8, 15]. Indeed, the ligand hybridization and surface reconstruction of nanocrystals capped by organic ligands has been reported [15]. Although we cannot give a definite answer, the presence of $O_h \text{Fe}^{3+}$ is speculated to be correlated with surface effects.

4. Conclusions

In summary, we have performed XAS and XMCD and photoemission measurements on the $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$ nanoparticles DMS, which exhibit ferromagnetic properties at room temperature. The XAS and XMCD spectra show multiple structures derived from a $\text{Fe}^{2+}\text{-Fe}^{3+}$ mixed-valent state. From the similarity of the XMCD spectral line shape to that of $\gamma\text{-Fe}_2\text{O}_3$, $O_h \text{Fe}^{3+}\text{-O-}T_d \text{Fe}^{3+}$ superexchange interaction is proposed to occur in the spinel structure, resulting in a ferrimagnet with large magnetization. There is a possibility that the room temperature ferromagnetism in the $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$ nanoparticles is originated from the segregation of spinel ferrite-like structure. However, the presence of the spinel structure may be due to surface effects and not due to a secondary phase. Our study indicates that the surface structure of the particles is important in understanding the magnetic properties of nanoparticle DMSs.

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