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 Fe$^{2+}$ - Fe$^{3+}$ exchange interaction mediated by Fe$^{3+}$ 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 polarized x-rays was $\sim 55\%$. 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 $\sim 200$ 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 ($\sigma^+$ and $\sigma^-$), 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 3d 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 Fe$^{3+}$ at the tetrahedral $T_d$ and octahedral $O_h$ sites, respectively. For peak a, it is expected to be attributed not only to $T_d$ Fe$^{3+}$ but also to $O_h$ Fe$^{3+}$ 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 $\gamma$-Fe$_2$O$_3$ nanoparticles, where Fe$^{3+}$ ions are both at the $T_d$ and $O_h$ sites [10], and Fe$_3$O$_4$, where Fe$^{3+}$ at $T_d$, $O_h$ and Fe$^{2+}$ at $O_h$ coexist [12]. The XMCD spec-
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magnetism in this sample exists, the contribution ap-

nanoparticles is mainly originated from the

<truncate>Fe$_3$O$_4$, which displays the overlapping contributions from the Fe$^{3+}$ and Fe$^{2+}$ sites, is different from that of the Zn$_{0.9}$Fe$_{0.1}$O nanoparticles. Moreover, Fe$_2$O$_4$ 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 Zn$_{0.9}$Fe$_{0.1}$O nanoparticles is nearly identical to that of the $\gamma$-Fe$_2$O$_3$ nanoparticles where XMCD signals are due to only Fe$^{3+}$ sites. This indicates that the magnetism in the Zn$_{0.9}$Fe$_{0.1}$O nanoparticles is mainly originated from the $T_d$ Fe$^{3+}$ and $O_h$ 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 $\gamma$-Fe$_2$O$_3$ and nonstoichiometric ZnFe$_2$O$_4$ has been reported [13], it is possible that the room temperature ferromagnetism in this sample may be due to the superexchange coupling between $O_h$ Fe$^{3+}$ and $T_d$ 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 $T_d$ Fe$^{3+}$ and $O_h$ Fe$^{3+}$ ions within this sample. We discuss here the various possibilities for the presence of the $T_d$ Fe$^{3+}$ and $O_h$ Fe$^{3+}$ ions. One possible reason for the presence of Fe$^{3+}$ ions in the spinel structure is the segregation of spinel ferri-

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magnet with $T_c = 860$ K [12], which is way beyond 450 K.

\textbf{References}


\section*{4. Conclusions}

In summary, we have performed XAS and XMCD and photoemission measurements on the Zn$_{0.9}$Fe$_{0.1}$O nanoparticles DMS, which exhibit ferromagnetic properties at room temperature. The XAS and XMCD spectra show multiple structures derived from a Fe$^{2+}$-Fe$^{3+}$ mixed-valent state. From the similarity of the XMCD spectral line shape to that of $\gamma$-Fe$_2$O$_3$, $O_h$ Fe$^{2+}$-O-$T_d$ 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 Zn$_{0.9}$Fe$_{0.1}$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.

\section*{Acknowledgements}

This work was supported by a Grant-in-Aid for Scientific Research in Priority Area “Spin Current: Its Creation and Control” (19048012) from MEXT, Japan. The experiments at SPring-8 were performed under the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (proposal no. 2007B3825). We thank T. Koide and D. Asakura for useful discussion and comments.