Magnetic reversal in Mn$_{4-x}$Ni$_x$N films measured via X-ray magnetic dichroism

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1 Introduction

Ferrimagnets have attracted increasing attention for their applications to spintronics devices. There are some ferrimagnets possessing a magnetic (angular momentum) compensation point since their key feature is that the magnetic moments of their sublattices are aligned antiparallel to each other. Spin transfer torque (STT) and spin orbit torque (SOT) are composed of a flux of angular momentum carried by an incoming spin current and absorbed by the magnetization. In ferrimagnets close to the angular momentum compensation point, the switching is eased and the critical current densities decrease, and thus this can be applied to current-induced domain wall motion (CIDWM) assisted by STTs and SOTs. Thus far, there have been many studies on ferrimagnets consisting of both transition-metal and rare-earth (RE) elements. For instance, a domain wall velocity of 1.3 km/s assisted by both STTs and SOTs has been achieved in Gd$_{0.2}$Co$_{0.8}$ at 260 K [1]. However, there have been no reports of ferrimagnets without RE elements possessing a compensation temperature close to room temperature (RT). Under such circumstances, we have focused on RE-free ferrimagnet Mn$_x$N films [2-4].

Figure 1 shows the crystal structure of Mn$_x$N. The corner and face-centered atomic sites are labelled as I and II, respectively. The II sites are further divided into IIA and IIB sites in the presence of magnetization (arrow in Fig. 1). N atoms are at the body-centered sites. Neutron diffraction measurement shows the magnetic moments of the Mn atoms in bulk Mn$_N$ to be 3.53 $\mu_B$ at I sites and $-0.89 \mu_B$ at II sites with the easy magnetization axis along the [111] direction [5,6], where $\mu_B$ is the Bohr magneton. Mn$_x$N films have perpendicular magnetic anisotropy (PMA) with relatively a large magnetic anisotropy constant of approximately $10^3$ J/m$^3$. We have recently achieved a velocity of approximately 900 m/s with a current density of $1.2 \times 10^{12}$ A/m$^2$ at RT [7], which is a record velocity for CIDWM only by STT. Thus, mixed crystal nitride films based on Mn$_x$N are expected to have both PMA with low saturation magnetization ($M_S$) and a compensation point, leading to more efficient domain wall motion. Compared with Mn$_{N}$, Mn$_{4-x}$Ni$_x$N films have shown an anomalous decrease in $M_S$ of 45% at $x = 0.1$ and 75% at $x = 0.25$, while the PMA is preserved. It is noted that the tensile stress is present in the Mn$_{4-x}$Ni$_x$N films with PMA. We further concluded that Mn$_{4-x}$Ni$_x$N films have a magnetic compensation composition at RT because the signs of the anomalous Hall resistivity and $M_S$ temperature dependences were different between $x = 0.1$ and 0.25 [8].

The latter two trends were also similar to those of Mn$_{4-x}$In$_x$N and Mn$_{4-x}$Sn$_x$N, in which Mekata demonstrated the existence of a magnetic compensation point [9]. However, the magnetic structures and preferential occupation sites of Ni atoms in Mn$_{4-x}$Ni$_x$N epitaxial films are not yet known. X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) are powerful techniques for determining element-specific electronic structures.

In this work, we performed XAS and XMCD measurements on Mn$_{4-x}$Ni$_x$N ($x = 0.1, 0.25$) epitaxial films, and proposed a model describing the magnetic moments of Ni and Mn atoms below and above the Ni magnetic compensation composition in Mn$_{4-x}$Ni$_x$N films.

![Fig. 1: Crystal structure of Mn$_x$N. Face-centered sites (II) can be further divided into IIA and IIB sites with magnetization (arrow).](image-url)
3 Results and Discussion

Figures 2(a)(e) and 2(b)(f) show the XAS and XMCD spectra of Mn$_{1.9}$Ni$_{0.1}$N and Mn$_{3.75}$Ni$_{0.25}$N at the Ni $L_{2,3}$ and Mn $L_{2,3}$ absorption edges, respectively. Figures 2(c) and 2(d) are those for Ni$_3$FeN and NiFe$_2$N at the Ni $L_{2,3}$ absorption edges, respectively. Concerning the XAS spectra of Mn$_{1.9}$Ni$_{0.1}$N and Mn$_{3.75}$Ni$_{0.25}$N films in Figs. 2(a) and 2(b), only the sharp main peaks appear at the $L_2$ edge (852–853 eV) and the $L_2$ edge (870 eV). In contrast, we see shoulders in the XAS spectrum of Ni-rich Ni$_3$FeN films in Fig. 2(c) [10].

![Fig. 2: XAS (blue) and XMCD (black) spectra in (a)(e) Mn$_{1.9}$Ni$_{0.1}$N films and (b)(f) Mn$_{3.75}$Ni$_{0.25}$N films at Ni-$L_{2,3}$ and Mn-$L_{2,3}$ absorption edges, respectively. (c) and (d) are those for Ni$_3$FeN and NiFe$_2$N films at Ni-$L_{2,3}$ absorption edges.

Such shoulders are observed approximately 2 eV above the Ni $L_{2,3}$ main peaks, and are reported for other antiperovskite ferromagnetic nitrides such as Fe$_2$N and Co$_2$N films above the Fe (Co) $L_{2,3}$ main peaks [11,12]. These are interpreted to originate from the electric dipole transition from the metal 2$p$ core level to the hybrid state between the orbitals of the N 2$p$ and metal 3$d$ at II sites. These results indicate that the objective element is at II sites [11]. However, we don’t see these shoulders in the XAS spectrum of NiFe$_2$N films in Fig. 2(d). It is reported that in Ni$_3$Fe$_2$N, the preferential sites of Ni atoms determined by XAS measurements agree well with those obtained via Mössbauer measurements and first-principles calculations based on the configuration-dependent total energy [10]. Thus, we have a reasonable confidence in the results obtained for Mn$_{1.9}$Ni$_{0.1}$N as well. From these results, it can be safely stated that Ni atoms preferentially occupy the I sites in Mn$_x$N when $x \leq 0.25$. In addition to the shoulders mentioned above, Figs. 4(a)–4(d) show other distinct satellites marked as A and A’. Satellites A and A’ are observed at approximately 7 eV above the Ni $L_1$ and $L_2$ edges. We initially considered their origin to be the hybrid state between the Ni 3$d$ and O 2$p$ orbitals. However, these are rather close to the satellite positions reported for the Ni $L_{2,3}$ edges of Ni$_3$Fe$_2$N.

In contrast to XAS spectra, the XMCD spectra for Ni are simple. The peak signs are opposite at the $L_{2,3}$ edges between Mn$_{1.9}$Ni$_{0.1}$N and Mn$_{3.75}$Ni$_{0.25}$N in Figs. 2(a) and 2(b). Thus, the directions of magnetic moments of Ni(I) in Mn$_{3.9}$Ni$_{0.1}$N films are different with that in Mn$_{3.75}$Ni$_{0.25}$N with respect to magnetizations. Regarding satellites B in Figs. 4(a)–4(d), it has been found only experimentally. This can be understood by considering that satellite B results from the interaction between the final-state multiplets described with $2p^3 3d^7$ and $2p^2 3d^{10}$. Although no distinct satellite is observed in the XMCD spectra above the Ni $L_2$ edges, it has been experimentally confirmed elsewhere [13]. We conclude that the satellite intensity is weak owing to the small atomic ratio of Ni, and that the satellites are buried in background signals.

We next move on to the XAS and XMCD spectra of Mn$_{3.9}$Ni$_{0.1}$N (Fig. 4(e)) and Mn$_{3.75}$Ni$_{0.25}$N films (Fig. 4(f)) at the Mn $L_{2,3}$ absorption edges. Shoulders marked by arrows and satellites (C,C‘) are observed at approximately 2 eV and 3.5 eV, respectively, above the Mn $L_{2,3}$ main peaks of the Mn$_{1.9}$Ni$_{0.1}$N and Mn$_{3.75}$Ni$_{0.25}$N films. Note that similar features were observed in the XAS spectra of Mn-related oxides such as MnFe$_2$O$_4$ [14], and are characterized by the final state multiplets of the $2p^3 3d^7$ configuration from a highly localized Mn$^{2+}$ ground state.

The XMCD spectra of these films also show some complexity. The signs of the XMCD signals around the Mn $L_3$ edge are positive, negative, and positive from low to high photon energy in Mn$_{3.9}$Ni$_{0.1}$N. The superposition of spectra with different signs indicates that the magnetic moments of Mn(I) and Mn(II) are aligned antiparallel to each other. In our previous studies on Fe$_2$N films, the transition metals at the II site exhibit localized (itinerant) states supported by the first-principles calculation using the all-electron full-potential linearized augmented-plane-wave (FLAPW) method and Fermi’s golden rule with E1 transitions [15]. Similar calculation results are also supported for Mn$_x$N by the FLAPW calculation [16]. Therefore, the XMCD spectra of Mn$_{1.9}$Ni$_{0.1}$N and Mn$_{3.75}$Ni$_{0.25}$N films can also be viewed as an overlap of such localized and itinerant components characterized by features α and β, respectively, with opposite signs. In
Mn$_{1.8}$Ni$_{0.2}$N, the broad positive peak (b) near 642 eV likely originates from Mn(II) atoms because of the hybridization between Mn(II) 3d and N 2p orbitals. In contrast, the sharp negative peak (a) near 640 eV likely comes from Mn(I), which is remote from N, and therefore entails less hybridization. Note that the signs of the XMCD signals near the Mn $L_3$ absorption edges are negative, positive, and negative from low to high photon energy in Mn$_{1.8}$Ni$_{0.2}$N, which is the opposite of the results obtained for the Mn$_{3.8}$Ni$_{0.2}$N films. We ascribe this to magnetization reversal at both I and II sites. It is also notable that the XMCD signal at the Ni $L_3$ absorption edge has the opposite sign of the sharp peak for the Mn $L_3$ edge at 640 eV regardless of x, and has the same sign as that of the broad spectrum at 642 eV. The former mainly comes from Mn(I) atoms and the latter from Mn(II) atoms. Thus, the magnetic moments of Ni(I) always align in parallel with those of Mn(II) or in antiparallel with those of Mn(I) in the studied range of x.

On the basis of these discussions, we conclude that the preferential occupation site of Ni is the I site in Mn$_{x}$Ni$_{1-x}$N thin films, and that the magnetic moments of Ni atoms are parallel to those of Mn(II). As mentioned in Fig. 1, Mn$_{x}$N is a ferrimagnetic material in which the magnetic moments of the Mn(I) atoms are aligned parallel to the magnetic field $H$ and antiparallel to the moments of the Mn(II) atoms. The magnetic moments of the Mn(I) sites thus determine the direction of $M_S$. For $x = 0.1$, some Mn(I) atoms are replaced with Ni atoms, and the magnetic moments of the Ni(I) atoms are parallel to those of Mn(II). This results in a net decrease in $M_S$ [8], and the Mn(I) atoms still determine the direction of $M_S$. When x is increased further to 0.25, more Mn(I) atoms are replaced with Ni atoms to the extent where the sum of the magnetic moments aligned antiparallel to magnetic field becomes greater than that of those aligned parallel to it. In this state, the net magnetization and magnetic field are antiparallel, causing an unstable Zeeman energy state. Thus, all magnetic moments need to flip to achieve the stable state. As a result, the magnetic moments of the Mn(II) sites determine the direction of $M_S$ at $x = 0.25$. Therefore, we can safely state that the magnetic compensation occurs at a value of x between 0.1 and 0.25.

Acknowledgement
This work was supported by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (Nos. 19K04499, 19K21954, and 19KK0104). The XMCD experiment was performed at beam line BL-16A of KEK-PF with the approval of the Photon Factory Program Advisory Committee (Proposal No. 2018P011).

References

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