HIGH ENERGY XAFS STUDIES OF THE Sm: K-EDGE IN $Sm_2Fe_{17}N_x$ COMPOUNDS

$Sm_2Fe_{17}N_x$ compounds (x=0~3) are relatively new hard magnetic materials. Upon introduction of three nitrogen atoms into Sm_2Fe_{17}, the Curie temperature increases dramatically from 398 K to 752 K [1]. The saturation magnetization of $Sm_2Fe_{17}N_3$ is comparable to that of $Nd_2Fe_{14}B$, while its uniaxial magnetic anisotropy is three times larger.

Several studies have been performed on the change of the crystal structure of $Sm_2Fe_{17}N_x$ compounds due to the absorption of nitrogen atoms [2]. The crystal structure of Sm_2Fe_{17} is rhombohedral Th_2Zn_{17} -type (R3m) and the lattice expands more than 6% to accommodate three nitrogen atoms at the interstitial site. Two possible sites – $9e$ and $18g$ sites – are inferred from the results of the powder neutron diffraction studies of $Pr_2Fe_{17}N_x$, $Nd_2Fe_{17}N_x$ and $Y_2Fe_{17}N_x$. Several XAFS studies [3-5] were carried out at room temperature on the L_3-edge of samarium atom and on the K-edge of iron atom in Sm_2Fe_{17} and $Sm_2Fe_{17}N_x$ (x = 2.8 ±1.0). The XANES spectra of the Sm L_3 edge indicate that the Sm valence was not changed upon nitrogenation. Furthermore, the XANES spectra of the Fe K-edge of Sm_2Fe_{17}, $Sm_2Fe_{17}N_x$ and α-Fe indicate that the environment of iron atoms in the $Sm_2Fe_{17}N_x$ was intermediate between its anionic state in Sm_2Fe_{17} and its covalent state in α-Fe. Also, a small edge shift occurred, implying that some charge transfer had occurred between the nitrogen and iron atoms. On the other hand, the magnetically-oriented powder EXAFS spectra of the Sm L_3-edge suggested that the distance between samarium and iron atoms is expanded by nitrogenation, and the interstitial site of the nitrogen atoms in $Sm_2Fe_{17}N_x$ is the $9e$ site.

The study of the structural change in the intermediate nitrogen concentration (0 < x < 3) in $Sm_2Fe_{17}N_x$ compounds is important in order to clarify the mechanism of the change in magnetic properties by nitrogenation. These studies have not yet been performed, except on the lattice parameters and the unit cell volume. We carried out XAFS studies on the Sm K-edge in $Sm_2Fe_{17}N_x$ (x= 0.0, ≤0.1, 0.5, 2.0 and 3.0) at room temperature [6] in order to obtain more precise structural data. In the case of Sm L_3-edge, the results were limited by the presence of the Fe K-edge at k=10.2 $Å^{-1}$.

A Sm_2Fe_{17} alloy was prepared by the high frequency induction-melt method. First, nitrogenation was carried out under N_2 gas at 1 atm pressure and 400 °C for several hours. After that, we exchanged the gas from N_2 to Ar, and annealing was performed continuously under Ar gas at 1 atm pressure and 400 °C for a few days. From the results of the preliminary X-ray powder diffraction measurements, a few % α-Fe was mixed in $Sm_2Fe_{17}N_x$ (x ≤ 0.1, 0.5 and 2.0).

XAFS investigation was carried out at beamline **BL01B1**. Measurements were made on the Sm K-edge (46.834 keV) using the transmission mode with an Si(511) adjustable inclined double-crystal monochromator. The incident and transmitted X-ray intensities were monitored with ionization chambers filled with Kr gas. The estimated energy resolution was about 4 eV.
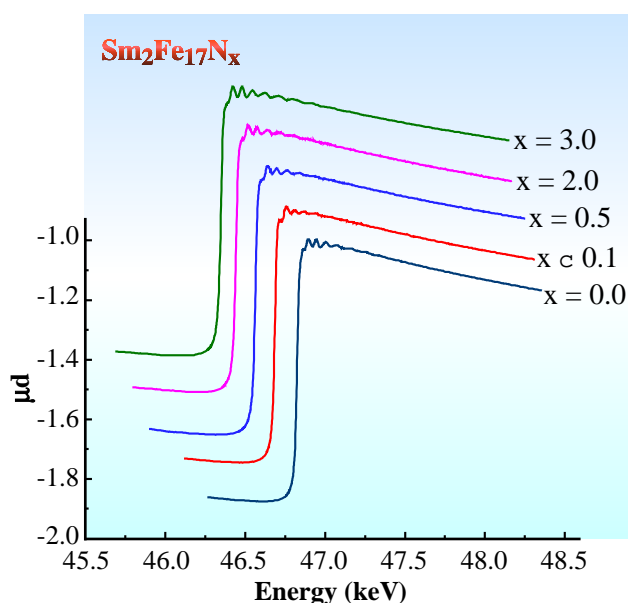

Fig. 1. Observed XAFS spectra at the Sm K-edge (46.836 keV) for $Sm_2Fe_{17}N_x$(x= 0.0, ≤ 0.1, 0.5, 2.0 and 3.0). The origin of each spectrum is shifted [6].

Sm K-edge XAFS spectra of $Sm_2Fe_{17}N_x$ (x= 0.0, $\leq$ 0.1, 0.5, 2.0 and 3.0) are shown in Fig. 1. The origin of each XAFS spectrum is shifted. Good XAFS signals were observed, despite the existence of blunt edge jumps ($\sim$ 50 eV) and reduction of the EXAFS signal at higher energy. The structure above the absorption edge changed with nitrogen content as shown in Fig. 2. Results of Sm L-edge XANES and Fe K-edge XANES studies by Capehart et al. [5] imply that the structure indicated by an arrow in Sm_2Fe_{17} is due to the $1s\rightarrow6p$ transition, because samarium is trivalent in both Sm_2Fe_{17} and $Sm_2Fe_{17}N_{2.8}$ and the $6p$ band is unoccupied. Although a clear peak is observed in x $\leq$ 0.1 compound, it becomes obscure with the increase of nitrogen content. Since the $1s\rightarrow6p$ transition is forbidden, this structure cannot be observed in L_3-edge XANES. It is inferred that the interstitial nitrogen atom directly changes the electrical state of the samarium atom.

The XAFS oscillation ($\chi(k)$) and the radial distribution function ($\phi(r)$) indicate that the local structures around the samarium atom were changed upon nitrogenation. Figure 3 shows the XAFS oscillation ($\chi(k)$) for $Sm_2Fe_{17}N_x$ (x=0.0, 2.0 and 3.0). The period of each XAFS oscillation becomes shorter with increasing numbers of nitrogen atoms. The Sm-Fe distance expanded monotonously upon nitrogenation and most of the expansion in lattice parameters and unit cell volume did not occur as previously indicated by X-ray diffraction studies. In order to clarify the precise nitrogen-induced local structural changes around the samarium atom in $Sm_2Fe_{17}N_x$ compounds by nitrogenation, further experiments will be conducted.

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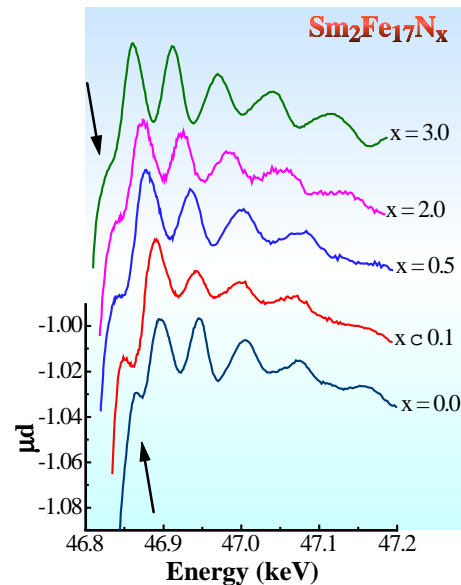
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Fig. 2. Enlargement of the edge region of the spectra. The structure indicated by arrow changes by nitrogenation [6].
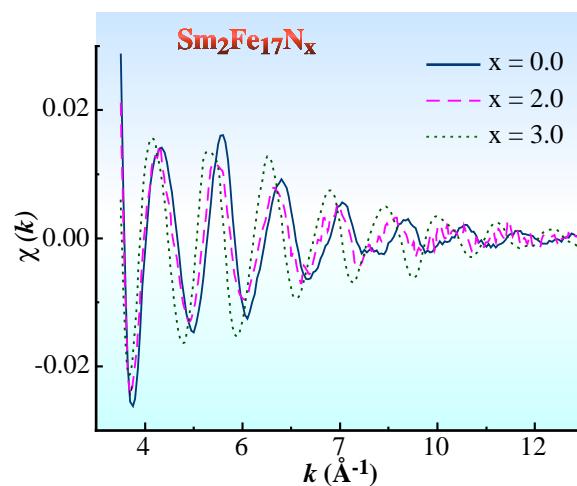

Fig. 3. XAFS oscillations $\chi(k)$ in $Sm_2Fe_{17}N_x$ [6].

References

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