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# THERMAL BEHAVIOR OF TERNARY $Sm_2Fe_{17}N_x$ MAGNETS

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## Abstract

The Mössbauer spectra of $Sm_2Fe_{17}N_x$, prepared by the nitrogenation of $Sm_2Fe_{17}$ powders in an ammonia and hydrogen atmosphere, were observed at elevated temperatures to shed light on the thermal behavior of nitrogen in the compounds $Sm_2Fe_{17}N_x$. It was found that there were large differences in thermal behavior between the starting $Sm_2Fe_{17}$, crystalline $Sm_2Fe_{17}N_x$ ($x$~1.7) and amorphous $Sm_2Fe_{17}N_x$ ($x$~7).

The thermal decomposition behavior of $Sm_2Fe_{17}N_{3.2}$, developed as one of the most promising hard magnetic materials, was found to be different under different atmospheres.

Keywords: Mössbauer spectra, $Sm_2Fe_{17}N_x$

## Introduction

The compounds $Sm_2Fe_{17}N_x$ are among the most promising candidates as permanent magnets because of their strong uniaxial anisotropy. Most of the nitrogen contents ($x$) reported hither were less than 3, and the precipitation of considerable amounts of α-Fe seemed to be inevitable in the nitrogenated specimens [1]. Through nitrogenation in a mixed-gas atmosphere of $NH_3$ and $H_2$, however, we have shown that higher-purity $Sm_2Fe_{17}N_x$ with $x>3$ could be pre-

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pared. Excellent magnetic properties can be attained for the sample with $x=3.0$, the saturation magnetization being 1.57 $T$, the anisotropy field 260 kOe and the Curie temperature 746 K. For a deeper understanding of a thermal behavior of $Sm_2Fe_{17}N_x$ prepared by nitrogenation in an $NH_3+H_2$ atmosphere [3, 4], we have recorded the Mössbauer spectra of $Sm_2Fe_{17}$, $Sm_2Fe_{17}N_{3.2}$ and $Sm_2Fe_{17}N_{7.5}$ at elevated temperature in vacuum (~$10^{-3}$ Pa) and in a 95% He+5% $H_2$ atmosphere. The gases evolved from the samples in the 95% He+5% $H_2$ atmosphere were also analysed by using thermogravimetry coupled with mass spectrometer. The evolution of nitrogen atoms situated in two locations, as reported previously [5], was confirmed. It was also confirmed that the decomposition of $Sm_2Fe_{17}N_x$ is the main cause of precipitation of α-Fe.

## Experimental

A mixture of Sm and Fe metals (both of 99.9% purity), containing Sm slightly in excess of the stoichiometric ratio of 2:17 in order to exclude the existence of α-Fe in the prepared sample, was melted in an induction furnace. The cast ingot was annealed in an argon atmosphere for 15 h at 1373 K. Alloy powders with particle sizes ranging from 20 to 106 μm were obtained by roll-milling. Nitrogenation was carried out in mixed $NH_3+H_3$ gas at 738 K, followed by annealing in an argon atmosphere at 738 K.

The nitrogen content in the prepared sample was quantitatively analysed by a gas analyser (Horiba, EMGA-620).

The Mössbauer spectra were recorded between room temperature and 833 K in vacuum (~$10^{-3}$ Pa), with a transmission Mössbauer spectrometer (Austin Science Associates BSD-2400), in which a $^{57}$Co source in a Rh matrix was driven in constant acceleration mode.

The thermogravimetric data were obtained by means of the SINKU-RIKO TGD-7000 with a rate of temperature rise of 5 deg·min$^{-1}$ and evolved gas were analysed with a mass spectrometer (Nichiden-Anelva, AQA-360).

Magnetic measurements were carried out with a vibrating sample magnetometer or a loop tracer in a magnetic field up to 1.5 $T$.

## Results and discussion

### *X-ray analysis*

Typical examples of the powder X-ray diffraction patterns of samples are shown in Fig. 1. Although the host alloy $Sm_2Fe_{17}$ was found to contain a small amount of $SmFe_3$ phase, the diffraction line of $SmFe_3$ disappeared after nitrogenation. Accordingly, we also investigated the nitrogenation of a $SmFe_3$ specimen by using the mixed gas of $NH_3$ and $H_2$, and found that $SmFe_3$ became

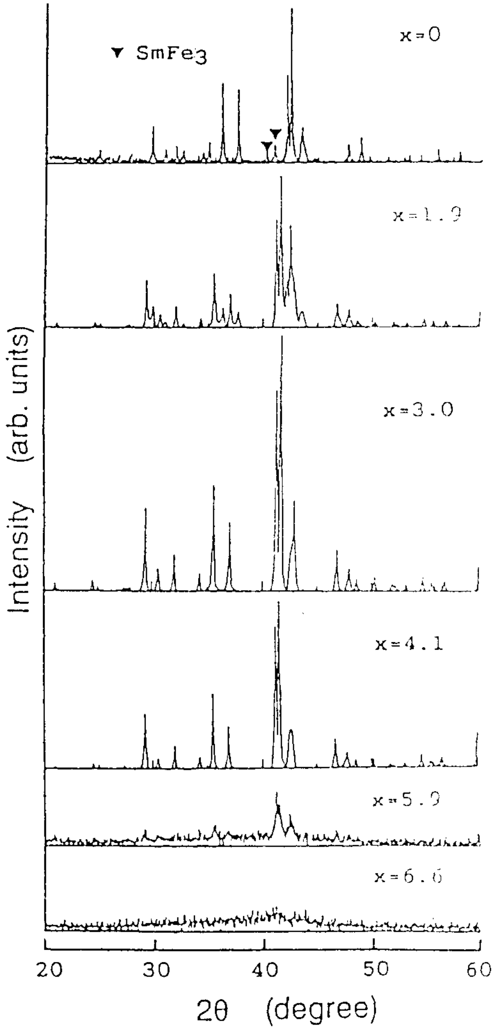

**Fig. 1** X-ray diffraction patterns of the $Sm_2Fe_{17}N_x$ powder

amorphous with the progress of nitrogen absorption. The disappearance of the diffraction line of $SmFe_3$ from the $Sm_2Fe_{17}N_x$ sample, therefore, seemed to be a result of amorphization of the $SmFe_3$ phase. All nitrogenated specimens except $x=6.6$ exhibited the same $Th_2Zn_{17}$ structure as $Sm_2Fe_{17}$. The diffraction pattern of $Sm_2Fe_{17}N_x$ ($x=1.9$) consists of two sets of diffraction lines corresponding to the single-phase specimens of $Sm_2Fe_{17}N_x$ with $x=0$ and $x=3.0$. It should be noted that the coarse powder sample with $x=1.9$ displayed only a single set of diffraction lines found in $Sm_2Fe_{17}N_{3.0}$, probably because the un-nitrogenated core was present in an inner sphere of sample particles with diameter greater than 20 μm, where the X-ray beam could penetrate. The specimen with $x=5.9$, on the other hand, showed a set of fairly broad diffraction lines with enhanced background. This specimen was demonstrated to contain a fair amount of an amorphous phase as the outer sphere of the particles. The amorphous phase prevailed in the specimen with $x=6.6$. The existence of the amorphous phase was confirmed by Mössbauer investigation [5]. Several studies concerning the site of the nitrogen atom in $Sm_2Fe_{17}N_x$ have been reported, and many authors insist that the nitrogen occupies only the 9e site [6, 7], whereas Jaswal *et al.* pointed out the possibility of the occupation by the nitrogen atom of the 18g site [8]. We concluded that the majority of the nitrogen atoms occupy the 9e site to form stable and crystalline $Sm_2Fe_{17}N_x$, and the remainder might occupy other sites in the crystal to form amorphous and paramagnetic substances as the nitrogen absorption proceeds.

### *Analysis by magnetism measurements*

Figures 2(a) and (b) show the temperature dependence of the magnetization of $Sm_2Fe_{17}N_x$ in magnetic fields of 1.0 *T* and 0.0048 *T*, respectively. The curves for the specimens with $x=1.9$ and $x=5.9$ in Fig. 2(a) reveal behavior which can be interpreted in terms of the accommodation of nitrogen atoms at two distinct sites or the presence of two substances. This conclusion is consistent with the X-ray diffraction results.

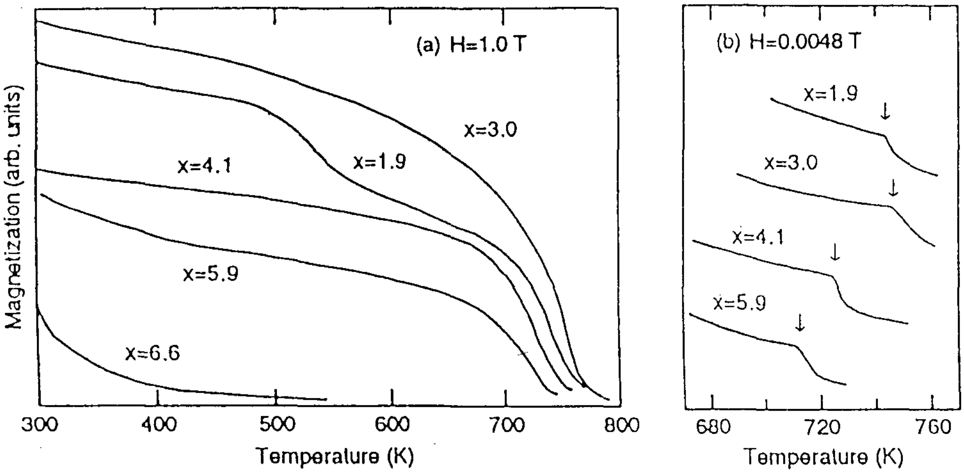

Fig. 2 Temperature dependence of magnetization of $Sm_2Fe_{17}N_x$ (a) $H=1.0$ *T* (b) $H=0.0048$ *T*

The Curie temperature was estimated from the inflection point in the curves, as indicated by the arrows in Fig. 2(b). For the specimen with $x=3.0$, we also carried out detailed measurements of magnetization as a function of magnetic field and temperature, and determined the Curie temperature by means of the Arrott plot. The value of 746 K thus obtained was in good agreement with that determined from Fig. 2(b).

The Curie temperatures are plotted as a function of $x$ in Fig. 3. The Curie temperatures are nearly independent of the value of $x$ in the region of $x$ less than 3.0, as expected from the coexistence of the two phases [9, 10]. When $x$ exceeded 3.0, the Curie temperature decreased gradually with the increase of $x$. This is probably due to the existence of the amorphous phase, clearly indicated in the X-ray diffraction pattern and confirmed in the Mössbauer spectrum [5]. This evidence explains why the $Sm_2Fe_{17}N_x$ magnets have fairly good thermal properties.

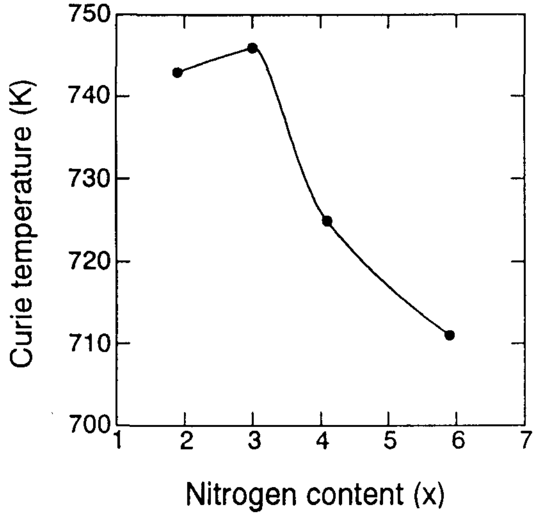

**Fig. 3** Curie temperatures *vs.* $x$ of $Sm_2Fe_{17}N_x$

### *Analysis of Mössbauer data on $Sm_2Fe_{17}$ and $Sm_2Fe_{17}N_8$*

Crystalline $Sm_2Fe_{17}N_x$ has the rhombohedral $Th_2Zn_{17}$ structure, where the iron atoms are distributed over four crystallographically nonequivalent sites: 6c, 9d, 18f and 18h.

Figure 4 shows Mössbauer spectra of $Sm_2Fe_{17}$ heated from room temperature up to 383 K in vacuum. The magnitude of the internal magnetic field ($H_{int}$) decreases with the elevation of temperature due to the decrease in super-exchange interactions between the spins in nearby iron atoms. Since the relative intensities of each subspectra did not show any variation on the elevation of temperature, it is concluded that neither the $Sm_2Fe_{17}$ crystal lattice nor the particles were destroyed up to the Curie temperature.

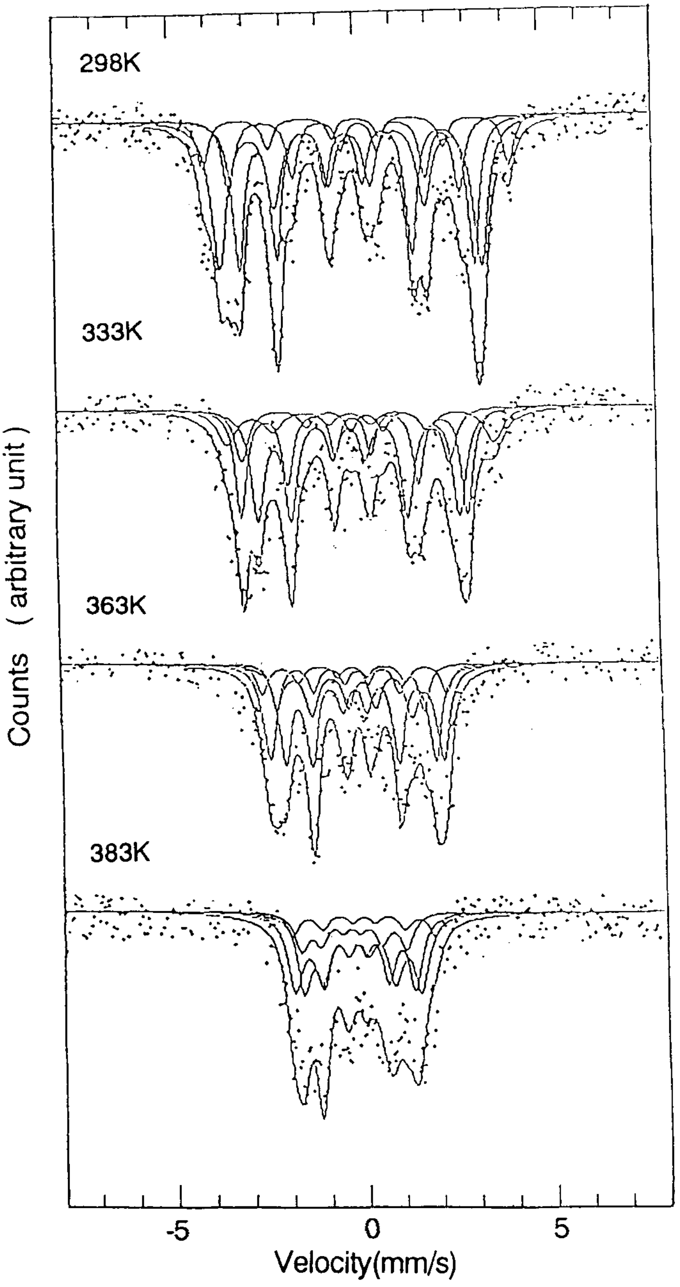

**Fig. 4** Variation of Mössbauer spectra of $Sm_2Fe_{17}$ by the elevation of temperature in vacuum ($10^{-3}$ Pa)

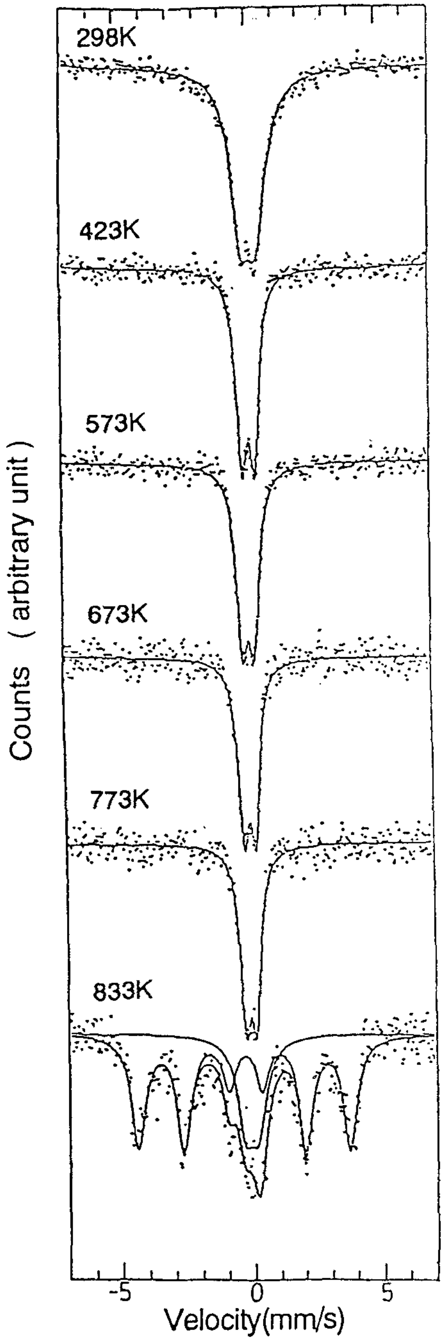

**Fig. 5** Variation of Mössbauer spectrum of $Sm_2Fe_{17}N_8$ by the elevation of temperature in vacuum ($10^{-3}$ Pa)

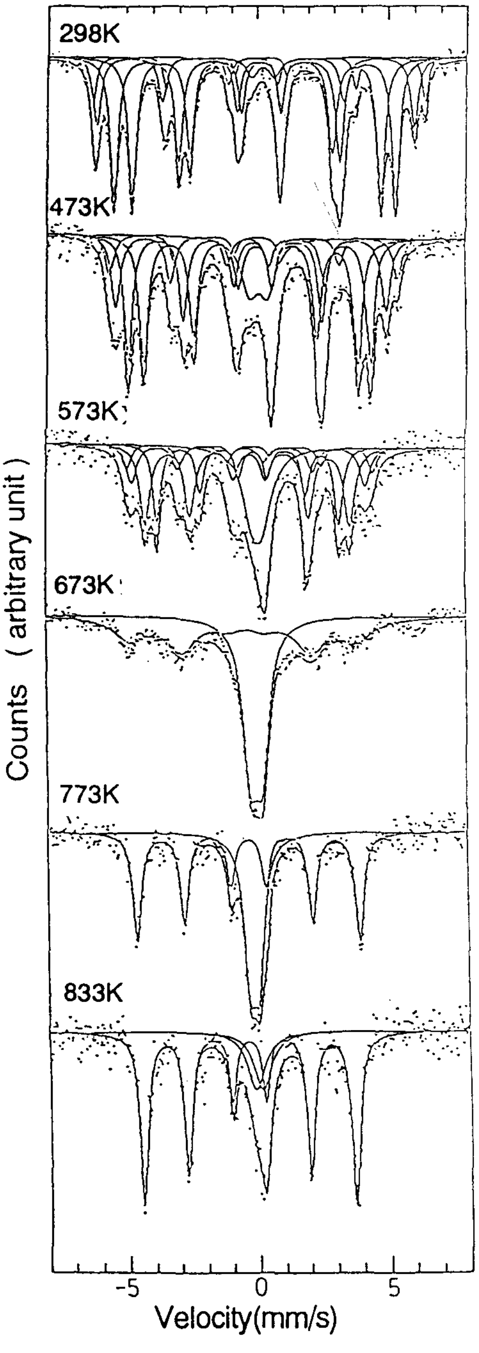

**Fig. 6** Variation of Mössbauer spectra of $Sm_2Fe_{17}N_{3.2}$ by the elevation of temperature in vacuum ($10^{-3}$ Pa)

The Mössbauer spectrum of amorphous $Sm_2Fe_{17}N_8$, produced by the excess intrusion of nitrogen atoms into the crystal of $Sm_2Fe_{17}$, is shown in Fig. 5. The amorphous phase was stable up to 773 K, and decomposed at 773~873 K. The decomposition was associated with the evolution of nitrogen. The decomposition reaction of $Sm_2Fe_{17}N_8$ was presumed to occur as follows, because no peaks appeared in the Mössbauer spectrum other than those α-Fe:

$$Sm_2Fe_{17}N_8 \rightarrow 2SmN + 17\alpha\text{-}Fe + 3N_2 \text{ (reaction 1)}$$

The reaction of $Sm_2Fe_{17}N_8$ with oxygen which may be present in the vacuum atmosphere of $10^{-3}$ Pa may well be negligible because sufficient nitrogen is present to form SmN. The paramagnetic or amorphous phase of $Sm_2Fe_{17}N_8$ decomposed into α-Fe above 773~833 K, releasing nitrogen. The mass spectrometrical analysis of the evolved gas reported previously [5] suggested that all the nitrogen atoms in the amorphous phase were located in similar physico-chemical sites and were loosely bound in the crystal lattice. The oxidation reactions of samarium and iron were not taken into account, with regard to the results obtained by thermogravimetric analysis of the same sample in a helium atmosphere [5].

### *Analysis of Mössbauer data of $Sm_2Fe_{17}N_{3.2}$*

The Mössbauer spectrum of $Sm_2Fe_{17}N_{3.2}$ at elevated temperatures at $10^{-3}$ Pa is shown in Fig. 6. Elevation of the temperature up to 673 K not only decreases

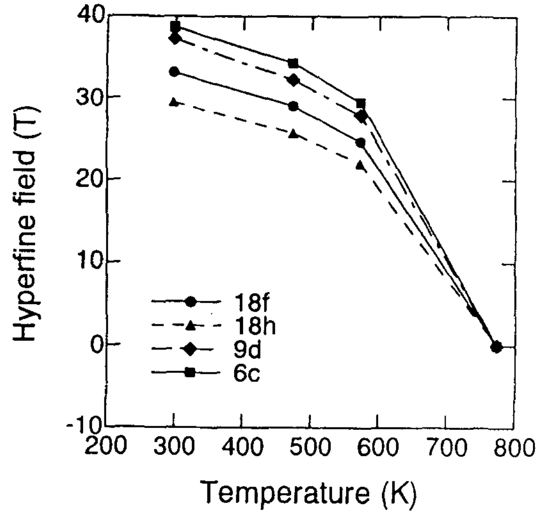

**Fig. 7** Variation of hyperfine fields for each crystallographically inequivalent Fe site of $Sm_2Fe_{17}N_{3.2}$ as a function of temperature

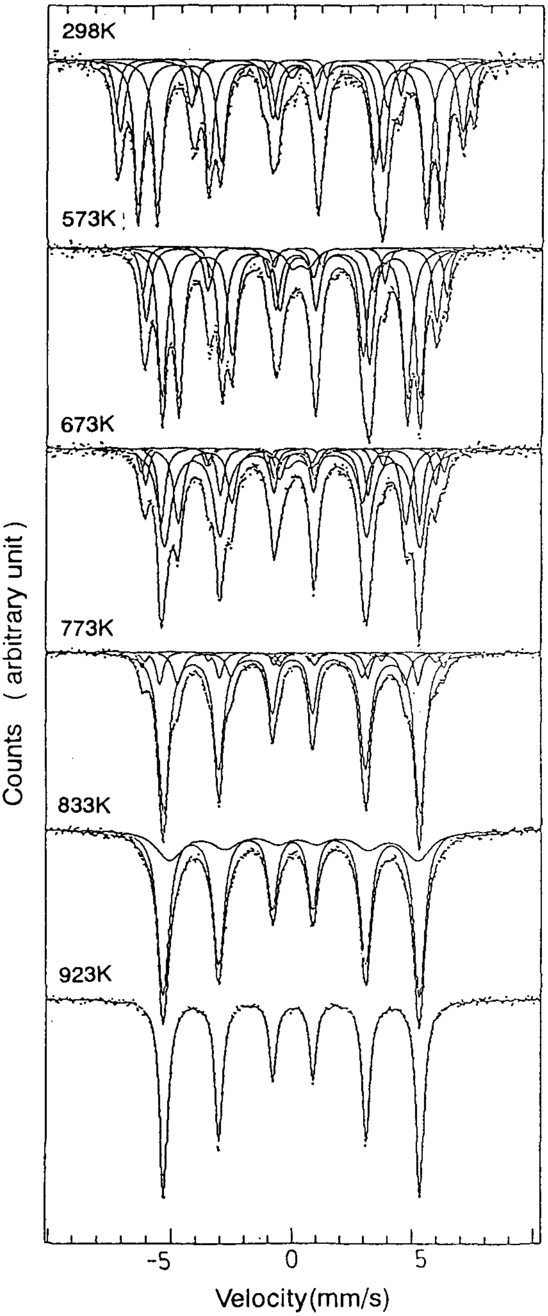

**Fig. 8** Variation of Mössbauer spectrum of $Sm_2Fe_{17}N_{3.2}$ by the elevation of temperature in (95% He+5% $H_2$, $10^5$ Pa) atmosphere

the hyperfine field of $Sm_2Fe_{17}N_{3.2}$, but also increases the intensity of the paramagnetic doublet (near 0.34 mm/s). It is suggested that a major proportion of the amorphous peak of $Sm_2Fe_{17}N_{3.2}$ is due to the thermal fluctuation of finer particles causing superparamagnetism. The amorphous phase decomposed to α-Fe above 773 K. The variations in the hyperfine fields ($H_{int}$) of each Fe site as a function of temperature are shown in Fig. 7. At room temperature, the 6c dumbbell site had the largest hyperfine fields (38.7 *T*), whereas the 18 h site had the smallest (29.4 *T*). The corresponding values at 573 K were 29.4 *T* and 21.9 *T*, respectively. Figure 8 shows the thermal variation in the Mössbauer spectrum of $Sm_2Fe_{17}N_{3.2}$ annealed in a 95% He+5% $H_2$ ($10^5$ Pa) atmosphere. The peak intensity of the doublet was not increased by the rise of temperature.

In order to obtain experimental evidence that the nitrogen atoms are located in two different sites, evolved gases from $Sm_2Fe_{17}N_{3.2}$ were introduced into a mass spectrometer coupled to the thermal analysis apparatus filled with 95% He+5% $H_2$ ($10^5$ Pa) gas.

### *Mass spectrometric analysis of evolved gas*

Nitrogen was evolved from $Sm_2Fe_{17}N_x$ at 793~993 K and at 993~1043 K, as shown in Fig. 9. The evolution of nitrogen from $Sm_2Fe_{17}N_{1.7}$ at ~1013 K and at

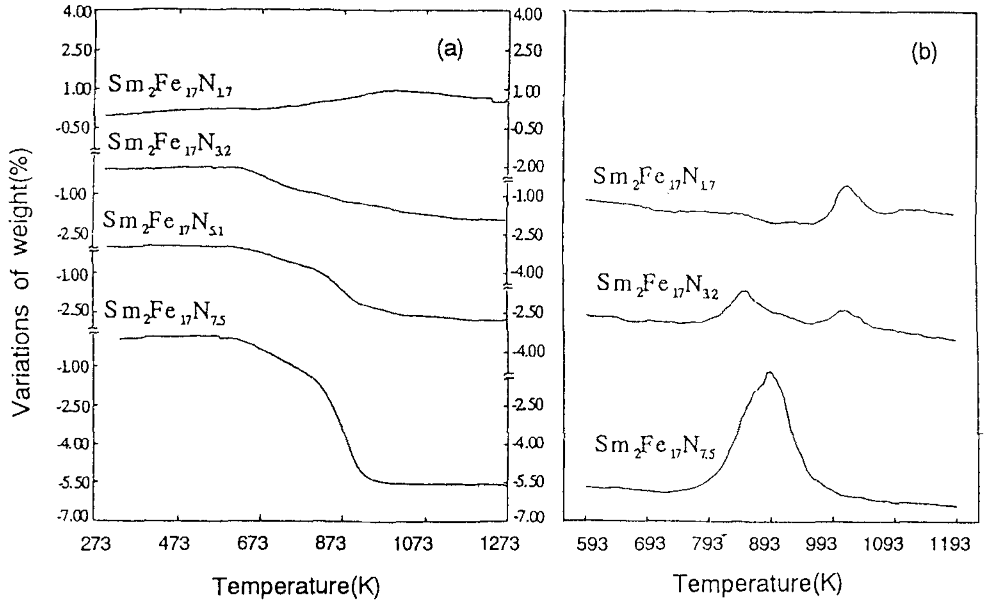

Fig. 9 (a) Variation of weight of $Sm_2Fe_{17}N_x$ by the elevation of temperature in (95% He+5% $H_2$, $10^5$ Pa) atmosphere (heating rate: 5 deg·min$^{-1}$)
(b) Variation of mass spectral peak intensity of $N_2$ by the elevation of temperature in (95% He+5% $H_2$, $10^5$ Pa) atmosphere (heating rate: 5 deg·min$^{-1}$)

~893 K from $Sm_2Fe_{17}N_{7.5}$ strongly suggested that the nitrogen atoms were accommodated in two different locations. We concluded that the difference in nitrogen evolution temperatures is good evidence of the existence of nitrogen atoms in two states. These results confirmed the anticipation that the nitrogen atoms exist in two sites, one being tightly bound to the 9e site and the other being relatively loosely bound at a different distorted lattice site, possibly attributed to amorphous $Sm_2Fe_{17}N_x$. The loosely bound nitrogen atoms may be evolved at about 793 K, as shown for $Sm_2Fe_{17}N_{7.5}$ in Fig. 9, following the decomposition reaction 2b. Nitrogen tightly bound to be 9e site was evolved at above 993 K, as shown for $Sm_2Fe_{17}N_{1.7}$ by the thermogravimetric data and the mass spectrometric thermal analysis data (Fig. 9) following the second step shown in reaction 2a. Since SmN and $Fe_2N$ are considered to be among the most stable nitrides of samarium and iron, Fig. 9 suggests that the evolution of nitrogen in the first and second stages may be proof of the following thermochemical processes:

$$Sm_2Fe_{17}N_x \rightarrow \left|\begin{array}{l} \rightarrow 2SmN + (x-2)Fe_2N + (21-2x)\alpha\text{-}Fe \rightarrow \\ \quad 2SmN + 17\alpha\text{-}Fe + 1/2(x-2)N_2 \ \text{(crystalline, reaction 2a)} \\ \\ \rightarrow 2SmN + 17\alpha\text{-}Fe + 1/2(x-2)N_2 \ \text{(crystalline, reaction 2b)} \end{array}\right.$$

It can be concluded that the nitrogen atoms are introduced into the two locations in the mixture of crystalline and amorphous phases if $x$ is more than 2.3. The higher the value of $x$, the more amorphous phase or the finer the compounds of $Sm_2Fe_{17}N_x$ present [5], and the more $N_2$ is evolved at around 893 K.

The elevation of the background to above 700 K for $Sm_2Fe_{17}N_x$ ($x<2.3$) could be due to the formation of $Sm_2O_3$, following the thermochemical reaction of the crystalline phase:

$$\begin{array}{l} Sm_2Fe_{17}N_x + 3/4O_2 \rightarrow SmN + 1/2Sm_2O_3 + (x-1)Fe_2N + (19-2x)\alpha\text{-}Fe \\ \rightarrow SmN + 1/2Sm_2O_3 + 17\alpha\text{-}Fe + (x-1)N \ \text{(crystalline, reaction 3)} \end{array}$$

## Conclusions

The internal magnetic field of $Sm_2Fe_{17}$ decreases with the elevation of temperature because of the decrease in super-exchange interactions among the spins of the iron atoms. The ferromagnetic $Sm_2Fe_{17}N_{3.2}$ transforms to a paramagnetic amorphous compound above 673 K and then decomposed into α-Fe in vacuum ($10^{-3}$ Pa) at around 773 K, whereas it transforms directly to α-Fe above 573~773 K in a 95% He+5% $H_2$ ($10^5$ Pa) atmosphere. Paramagnetic $Sm_2Fe_{17}N_{7.5}$ is stable in vacuum ($10^{-3}$ Pa) up to 773 K and decomposed into α-Fe above 773 K. The thermogravimetric, mass spectrometric, thermal analytical and Mössbauer spectrometric studies revealed that $Sm_2Fe_{17}N_x$ synthesized by nitrogenation of $Sm_2Fe_{17}$ in mixed gas atmospheres of ammonia and hydrogen in various ratios have two possible locations for accommodating nitrogen atoms in the particle of $Sm_2Fe_{17}N_x$ ($x>2.3$). The outer layer of the $Sm_2Fe_{17}N_x$ particles, exposed to nitrogen atoms, are richer in nitrogen than 2.3, preferably forming an amorphous phase, while the core of the $Sm_2Fe_{17}N_x$ particles is poorer in nitrogen than 2.3, preferably forming a crystalline phase.

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**Zusammenfassung** — Zur Klärung des thermischen Verhaltens von Stickstoff in $Sm_2Fe_{17}N_x$-Verbindungen wurde bei höheren Temperaturen das Mössbauer-Spektrum von $Sm_2Fe_{17}N_x$ aufgenommen, wobei die Verbindung aus $Sm_2Fe_{17}$ durch Nitrierung in Wasserstoffatmosphäre hergestellt wurde. Man fand, daß erhebliche Differenzen zwischen dem thermischen Verhalten des Ausgangsstoffes $Sm_2Fe_{17}$, kristallinem $Sm_2Fe_{17}N_x$ ($x$~1.7) und amorphem $Sm_2Fe_{17}N_x$ ($x$~7) bestehen.

Für unterschiedliche Atmosphären fand man unterschiedliches thermisches Zersetzungsverhalten von $Sm_2Fe_{17}N_{3.2}$, entwickelt als eines der vielversprechendsten harten magnetischen Materialien.