

## $^{57}\text{Fe}$ Mössbauer study of $R_2\text{Fe}_{17}$ and $R_2\text{Fe}_{17}\text{N}_x$ ( $R=\text{Ce}$ and $\text{Sm}$ )

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Using  $^{57}\text{Fe}$  Mössbauer spectroscopy, magnetic and structural properties of the rare earth iron intermetallic compounds and their nitrides,  $\text{Ce}_2\text{Fe}_{17}$ ,  $\text{Ce}_2\text{Fe}_{17}\text{N}_x$ ,  $\text{Sm}_2\text{Fe}_{17}$  and  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ , have been investigated.  $^{57}\text{Fe}$  Mössbauer spectra obtained can be decomposed into 4 different subspectra corresponding to 4 different Fe sites, namely 6c, 9d, 18f and 18h. From the temperature dependence of hyperfine field, an increase of Curie temperature and enhancement of Fe magnetic moments have been observed by the nitridation for both compounds. The change in spin-structure of  $\text{Ce}_2\text{Fe}_{17}$  has been found at  $110\pm 10$  K, but for a nitride  $\text{Ce}_2\text{Fe}_{17}\text{N}_{3.12}$  and Sm-compounds the spin structure does not show any change. Site occupation problems of interstitial nitrogen and the thermal stability of these nitrides have been discussed.

## 1. INTRODUCTION

It was found that the Curie temperatures ( $T_c$ ) at around room temperature of rare earth iron intermetallic compounds,  $R_2\text{Fe}_{17}$  ( $R$ =rare earth elements), increase up to around 673 K after nitridation [1-2]. Many researchers in the world have been paid attention to these intermetallic compounds and their nitrides. In a technological point of view these nitrides are good candidate as a hard permanent magnetic material which has a possibility to overcome the well-known Nd-Fe-B permanent magnets. As an academic interest, it is important to understand how the interstitial nitrogen atoms play and affect the magnetic properties in these compounds.

In this investigation, we have made  $^{57}\text{Fe}$  Mössbauer measurements for two kinds of  $R_2\text{Fe}_{17}$  compounds and their nitrides; namely  $\text{Ce}_2\text{Fe}_{17}$ ,  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$ ,  $\text{Sm}_2\text{Fe}_{17}$  and  $\text{Sm}_2\text{Fe}_{17}\text{N}_{3.12}$ . It is known [3] that  $T_c$  of  $\text{Ce}_2\text{Fe}_{17}$  shows maximum increase by a nitridation up to 700 K from around 220 K comparing other compounds. Nitride of  $\text{Sm}_2\text{Fe}_{17}$  has been known as only one compound with a uniaxial magnetic anisotropy which is essential for the hard permanent magnetic materials.

Nitride specimens have been prepared by the

annealing of mother alloys in  $\text{N}_2$  gas atmosphere and the nitrogen contents are from 2.8 to 3.12 determined from the weight change after nitridation.

$^{57}\text{Fe}$  Mössbauer spectra have been obtained at the temperature range from 10 K to 704 K for Ce-compounds and from 10 K to 300 K for Sm-compounds. Mössbauer spectra obtained can be decomposed into 4 different subspectra corresponding to 4 different Fe sites, namely 6c, 9d, 18f and 18h sites.

$^{57}\text{Fe}$  Mössbauer measurements suggest that the spin-structure of  $\text{Ce}_2\text{Fe}_{17}$  changes from fan-type canted-ferrimagnet to helical antiferromagnet at  $110\pm 10$  K and subsequent transition to paramagnet at  $222\pm 3$  K. On the other hand, the nitride  $\text{Ce}_2\text{Fe}_{17}\text{N}_{3.12}$  has a spin-structure of collinear ferromagnet from 10K until  $704\pm 2$  K. Interstitial nitrogen atoms induce the collinear ferromagnetic spin-arrangement and enhance a magnetic moment of Fe that is proportional to a magnitude of magnetic hyperfine field at Fe nucleus. For Sm-compounds there is no such change in spin-structure, but the increase in Curie temperature and the enhancement of magnetic moments of Fe atoms have been also observed by the nitridation.

Site occupation problems of interstitial nitrogen in these compounds and the stability of these nitrides have been also presented.

## 2. EXPERIMENT

Powder specimens of Ce- and Sm-compounds are prepared in Hiroshima University. Average size of the specimen powder was ranged from 0.005 to 0.1 mm in diameter. Quantity of nitrogen in nitride was determined by the weight change after a nitridation and chemical formulas of the specimen were determined to be  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$  and  $\text{Sm}_2\text{Fe}_{17}\text{N}_{3.12}$ , respectively. Nitridation was performed by the annealing of the mother alloy,  $\text{Ce}_2\text{Fe}_{17}$  and  $\text{Sm}_2\text{Fe}_{17}$ , for 12 hours at 748 K in  $\text{N}_2$  gas under a pressure of about 30 atm. These powder specimens were used as an absorber of the  $^{57}\text{Fe}$  Mössbauer experiments. A 925 MBq  $^{57}\text{Co}$  in Rh was used as a source and transmitted gamma-rays through the specimen were accumulated in a 1024 channel of the memory controlled for the multiscaler mode by personal computer. Temperature dependence of the Mössbauer spectra from 10 K to 300 K was measured using a continuous-flow type low temperature cryostat, Oxford CF500. For the measurements above 300 K the electric furnace operated under vacuum was used and the temperature was controlled with an error within 0.5 K by personal computer.

## 3. RESULTS AND DISCUSSION

### 2.1. $\text{Ce}_2\text{Fe}_{17}$ and $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$

Results from X-ray diffraction analysis show that the crystal structure of powder specimen is  $\text{Th}_2\text{Zn}_{17}$ -type rhombohedral structure and their lattice parameters are  $a=8.51 \text{ \AA}$  and  $c=12.4 \text{ \AA}$  for  $\text{Ce}_2\text{Fe}_{17}$ ,  $a=8.75 \text{ \AA}$  and  $c=12.8 \text{ \AA}$  for  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$ , respectively. Figure 1(a) shows a typical paramagnetic  $^{57}\text{Fe}$  Mössbauer spectrum of  $\text{Ce}_2\text{Fe}_{17}$  at 300 K. Spectrum consists of 4 components having 4 different Mössbauer parameters; those are quadrupole splitting (QS) and isomer shifts (IS), although the spectral shape is nearly asymmetric doublet. Each component is attributed to the Fe atoms which occupy non-equivalent structural sites; namely 6c, 9d, 18h and 18f. Intensity ratio corresponds to the ratio in number of sites occupied by Fe atoms and is fairly agree to 2:3:6:6 for the components; 6c, 9d, 18h and 18f. Figure 2(a) and 2(b) show  $^{57}\text{Fe}$  Mössbauer spectra of  $\text{Ce}_2\text{Fe}_{17}$  (a)

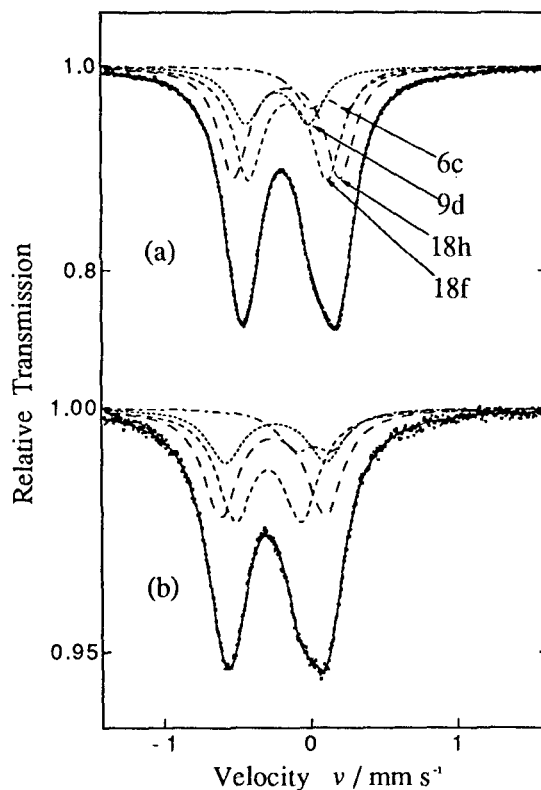


Figure 1.  $^{57}\text{Fe}$  Mössbauer spectra of (a)  $\text{Ce}_2\text{Fe}_{17}$  at 300 K and (b)  $\text{Sm}_2\text{Fe}_{17}$  at 423 K.

and  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$  (b) ordered magnetically at 10 K. Spectra are rather complex shape but can be decomposed into 4 different magnetically split sextets corresponding to 4 different Fe sites, albeit a fit is not excellent. Analyses of the spectra were performed also using 7 and 10 components taking accounts of the dipole field contribution for each Fe sites. Seven component model corresponds to the case that the magnetic moments lie along one of the orthohexagonal axis, and ten components model corresponds to the case that the magnetic moments of Fe lie in the basal plane and couple ferromagnetically. For the calculation of dipole fields at each Fe sites, the magnitudes of magnetic moments are assumed for Ce(6c), Fe(6c), Fe(9d), Fe(18f) and Fe(18h) to be  $-0.20, 1.94, 1.36, 1.46$  and  $1.60 \mu_B$ , respectively, whose values were estimated from the results from magnetization measurement [4] and Mössbauer hyperfine fields obtained from 4 components analysis in present investigation. Structural parameters were assumed to be  $a=8.51 \text{ \AA}$

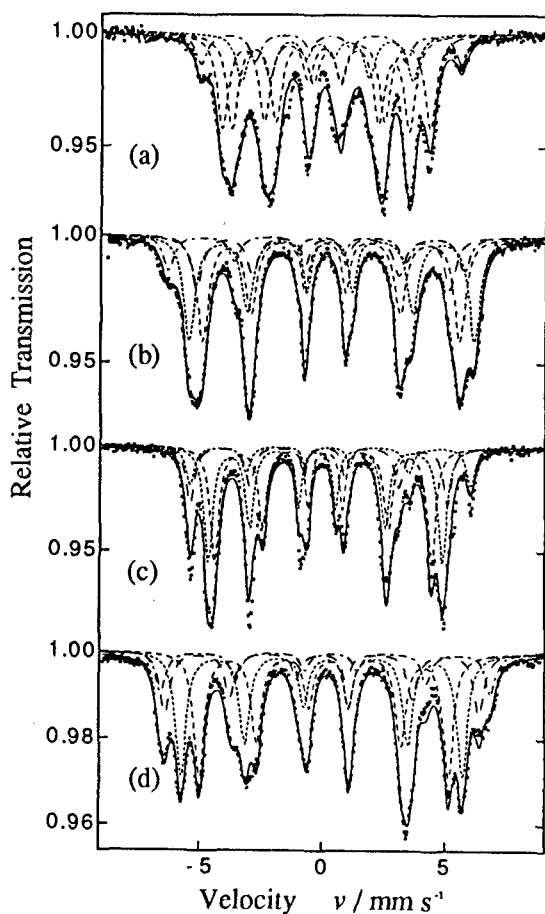


Figure 2. Typical  $^{57}\text{Fe}$  Mössbauer spectra at 10 K, (a)  $\text{Ce}_2\text{Fe}_{17}$ , (b)  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$ , (c)  $\text{Sm}_2\text{Fe}_{17}$  and  $\text{Sm}_2\text{Fe}_{17}\text{N}_{3.12}$ , respectively.

and  $c=12.4 \text{ \AA}$ . Results obtained show that the number of Fe sites increases to 7 and 10 sites with the different dipole fields although the expected Mössbauer spectra show non-split broad lines depending on the different Fe sites. A neutron diffraction study [4] shows that the spin-structure of  $\text{Ce}_2\text{Fe}_{17}$  is helical structure at 140 K. Helical spin-structure with wave vector  $0.037 \text{ \AA}^{-1}$  propagating along  $c$  axis causes the many different magnitudes of the dipole field at Fe sites, which was 60 different one only for 18f site when the magnetic moments lie in basal plane. From the above models we constructed Mössbauer spectra expected by the different contributions of the dipole field and the resultant spectra can be analyzed fairly by using the 4 different components with different broad

widths. From the above analysis, the Mössbauer parameters (magnitude of the hyperfine fields ( $H_i$ ), QS and IS) were determined from 10 K up to 700 K for  $\text{Ce}_2\text{Fe}_{17}$  and its nitride  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$ . Figure 3 (a) shows the temperature dependence of averaged  $H_i$  for  $\text{Ce}_2\text{Fe}_{17}$  and  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$ . An enhancement of  $H_i$  extrapolated to 0 K which corresponds to the saturation magnetic moment of Fe and an increase of the magnetic transition temperature after nitridation are clearly shown in Fig. 3.

It is noteworthy to add one observation that at  $110 \pm 10 \text{ K}$  the  $H_i$  of  $\text{Ce}_2\text{Fe}_{17}$  shows appreciable deviation from its smooth temperature dependence. That is most probably due to the change in spin-structure from fan-type canted ferrimagnet to helical antiferromagnet. As shown in Fig. 3 (a), such spin-structure change occurred at  $110 \pm 10 \text{ K}$  and Néel temperature was determined to be  $222 \pm 3 \text{ K}$  for  $\text{Ce}_2\text{Fe}_{17}$ . On the other hand, the temperature dependence of  $H_i$  for nitride  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$  shows no such deviation and smooth curve till above 700 K. It is interpreted that this substance has collinear ferromagnetic spin-structure. Curie temperature of  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$  was determined to be  $704 \pm 2 \text{ K}$ . Quite large increase of the magnetic transition temperature is interpreted by the change of the spin structure by nitridation.

A spectrum at 300 K obtained from  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$  consists of two sets of the components. Since the one component is due to the paramagnetic  $\text{Ce}_2\text{Fe}_{17}$  and the other are due to the superposition of magnetically split sextets rising from the nitride, this  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$  specimen is a mixture of two phases, namely  $\text{Ce}_2\text{Fe}_{17}$  and its nitride  $\text{Ce}_2\text{Fe}_{17}\text{N}_3$  in which the N atoms occupy completely 9e sites. Above 600 K, the nitride  $\text{Ce}_2\text{Fe}_{17}\text{N}_{2.8}$  decomposes and the Mössbauer spectra show clearly the existence of the  $\alpha$ -Fe components whose contribution increases as an increase of the temperature and annealing periods in vacuum.

## 2.2. $\text{Sm}_2\text{Fe}_{17}$ and $\text{Sm}_2\text{Fe}_{17}\text{N}_{3.12}$

Structures of  $\text{Sm}_2\text{Fe}_{17}$  and its nitride  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  were reported  $\text{Th}_2\text{Zn}_{17}$  type and same as those of Ce-compounds. Lattice parameters obtained for similar specimen with present investigation were determined as  $a=8.48 \text{ \AA}$ ,  $c=12.41 \text{ \AA}$  for  $\text{Sm}_2\text{Fe}_{17}$  and  $a=8.74 \text{ \AA}$ ,  $c=12.65 \text{ \AA}$  for

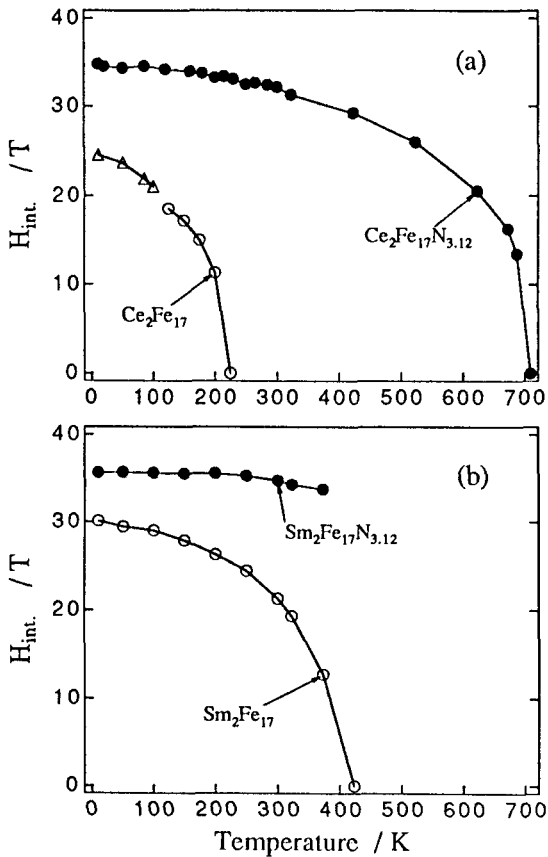


Figure 3. Averaged hyperfine fields  $H_i$  obtained from (a) Ce- and (b) Sm-compounds as a function of temperatures.

$Sm_2Fe_{17}N_{3.1}$  [5]. Figure 1 (b) shows the paramagnetic  $^{57}Fe$  Mössbauer spectrum of  $Sm_2Fe_{17}$  at 423 K and shows an essentially same spectral shape with  $Ce_2Fe_{17}$  at 300 K. It implies that the Mössbauer parameters QS and IS at Fe sites in paramagnetic Sm-compound are nearly same with those of the paramagnetic Ce-compound, not depending on the difference in the rare earth elements. However, the Mössbauer spectra obtained from Sm-compounds at 10 K show magnetically split spectra and rather different shape from Ce-compounds as shown in Fig. 2 (b) and 2 (c). It is suggested that the exchange interactions and the magnitude of saturation magnetic moments in Sm-compounds differ from those of Ce-compounds. Mössbauer spectrum obtained for  $Sm_2Fe_{17}N_{3.12}$  at 300 K not-shown in Fig. 2 consists of definitely distinguishable 4 kinds of sextets corresponding to 4 Fe sites; namely 6c, 9d, 18f and 18h. Temperature

dependencies of the averaged  $H_i$  were determined from 10 K to 423 K for  $Sm_2Fe_{17}$  and  $Sm_2Fe_{17}N_{3.12}$  and are shown in Fig. 3(b). Smooth changes of  $H_i$  as a function of temperature indicate no-change in spin-structure in the above temperature range and suggest the colinear ferromagnetic alignment of Fe in Sm-compounds. Figure 3 shows the enhancement of magnitude in hyperfine fields at 0 K corresponding to the saturation magnetic moments of Fe atoms in Sm-compound and appreciable increase of the Curie temperature, albeit not determined for the nitride, by the nitridation. All of the Mössbauer spectra were able to analyze using 4 different kinds of sextets corresponding to different 4 Fe sites. It means that the nitrogen atoms occupy completely 9e sites and the nitrogen content in the specimen must be  $Sm_2Fe_{17}N_3$ . Since the result from analysis of nitrogen content was  $Sm_2Fe_{17}N_{3.12}$  by the weight change, the extra nitrogen contents 0.12 might be attributed to the nitrogen at surface and along grain-boundaries.

### 3. SUMMARY

$^{57}Fe$  Mössbauer measurements have been performed for  $Ce_2Fe_{17}$ ,  $Ce_2Fe_{17}N_{2.8}$ ,  $Sm_2Fe_{17}$  and  $Sm_2Fe_{17}N_{3.12}$  from 10 K to 704 K using powder specimens. Spectra obtained can be decomposed into 4 different subspectra corresponding to 4 different Fe sites; 6c, 9d, 18f and 18h, in these compounds. From the temperature dependence of hyperfine fields, increase of the magnetic ordering temperatures and the enhancement of Fe magnetic moments have been observed by the nitridation of both compounds. A change in spin structure, the site occupation problems and their thermal stability have been discussed for these compounds.

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