^{57}Fe Mössbauer Study on Distribution and Interaction of N Interstitials in $\gamma\text{-FeN}$ Austenite and $\alpha'\text{-FeN}$ Martensite

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N atoms occupy interstitial sites in α - and γ -Fe and affect the physical and chemical properties of Fe. In order to clarify the distribution of N atoms in α - and γ -Fe and the influence upon Fe, ^{57}Fe Mössbauer measurements have been performed for Fe-N austenite and martensite. In $\gamma\text{-FeN}$ austenite, there are three kinds of Fe atoms with zero, one and two N atoms as near neighbors. An Fe atom and two near neighbor N atoms in γ -Fe constitute a N-Fe-N 180°-linear chain, although such a configuration cannot be observed in Fe-Ni-C austenite. From the amounts of these components, it was confirmed that the distribution of N atoms in γ -Fe is not random and the repulsive force acts between near neighbor N atoms. By comparison with Fe-Ni-C austenite, it became clear that the repulsive force between N atoms is weaker than that between C atoms. It was also confirmed that the martensitic transformation from γ - to α' -phase can be induced by applying the magnetic field. This phenomenon occurs at the critical magnetic field which depends on N content and increases with N content. The ^{57}Fe Mössbauer spectrum of $\alpha'\text{-FeN}$ martensite can be analyzed by four magnetic components which correspond to Fe as the first, second, third and further near neighbors of the interstitial N atom. Among them, the third near neighbor Fe shows a large hyperfine magnetic field, 36 T at room temperature, but the mean hyperfine magnetic field of $\alpha'\text{-FeN}$ martensite is nearly equal to that of α -Fe. Although the amounts of the first and second near neighbor Fe atoms can be explained by assuming that N atoms randomly occupy the O_2 sites in the bcc lattice, the amounts of the third and the further near neighbors Fe cannot. This may be because of the diffusion of N atoms to form the N-rich region in the matrix at room temperature.

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I. Introduction

It is known that N atoms occupy interstitial sites in both α - and γ -Fe. The distribution of such interstitial atoms in Fe is important from the industrial point of view. In addition, to clarify the mechanism of martensitic transformation from γ - to α' -phase and the atomic arrangement of such a diffusionless phenomenon, the interaction of interstitial atoms in α - and γ -Fe is worth studying. Thus the Fe-N alloy system has been studied by conventional ^{57}Fe Mössbauer spectroscopy, and Ron reviewed the results of the Fe-N and Fe-C systems⁽¹⁾. It has been reported that the interactions between both C atoms and N atoms in γ -Fe are repulsive forces, and the interaction between N atoms is weaker than that between C atoms⁽²⁾⁽³⁾. Oda *et al.*⁽⁴⁾ had studied Fe-9.0 at%N austenite by means of ^{57}Fe Mössbauer spectroscopy, and reported that the interaction between near neighbor N atoms is repulsive and that of the second near neighbor N atoms is attractive.

By quenching Fe-N austenite from the temperature where Fe-N austenite is stable to a lower temperature, the martensitic transformation occurs and $\alpha'\text{-FeN}$ martensite is formed. The $\alpha'\text{-FeN}$ martensite is ferromagnetic and a supersaturated solid solution of N interstitials

because of the difference in solubility between α - and γ -phases. It is known that metastable $\alpha''\text{-Fe}_{16}\text{N}_2$ precipitates from the $\alpha'\text{-FeN}$ martensite by annealing at low temperature⁽⁵⁾, and thus it is important to investigate the distribution of N atoms in the $\alpha'\text{-FeN}$ martensite and the magnetic properties in order to understand the ordering process of $\alpha''\text{-Fe}_{16}\text{N}_2$.

In this study, we performed ^{57}Fe Mössbauer measurements for Fe-N austenite and martensite in order to clarify the distribution and interaction of interstitial atoms.

II. Experimental Procedure

Fe-N austenite specimens were prepared by the following procedure. At first, α -Fe foils with the thickness of 10 μm were heated at 973 K for 1.2 ks in a gas mixture of NH_3 and H_2 . Then the foils were quenched into water and $\gamma\text{-FeN}$ austenite specimens were obtained. Austenite specimens were confirmed to be a single phase by X-ray diffraction and room-temperature Mössbauer measurements. N contents of $\gamma\text{-FeN}$ austenites were controlled by changing the pressure ratio of NH_3 and H_2 . The N contents of Fe-N austenites were determined to be 9.3 and 10.7 at%N from c/a values of martensites, which were obtained by quenching the austenites. In order to compare with Fe-N austenite, Fe-Ni-C austenite specimens (Fe-20 at%Ni-3 at%C and Fe-16 at%Ni-7 at%C) were also prepared.

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For ^{57}Fe Mössbauer measurements, three specimens containing α' -FeN martensite were synthesized. The N contents of the specimens were determined to be 5.8 at%, 9.3 at% and 10.7 at% from the c/a values of α' -FeN martensites obtained from X-ray diffraction measurements. To obtain martensite specimens, Fe-9.3 and 10.7 at%N austenites at room temperature were quenched into liq. He in order to induce the martensitic transformation. Fe-5.8 at%N martensite coexists with the retained austenite at room temperature after quenching from high temperature.

^{57}Fe Mössbauer measurements had been performed at room temperature in transmission geometry. The ^{57}Co in Rh was used as a γ -ray source. The velocity scale of the Mössbauer spectrum is relative to α -Fe at room temperature.

Martensitic transformation from γ -FeN austenite to α' -FeN martensite was investigated by means of a SQUID magnetometer. Magnetization of the specimen was measured with decreasing temperature from 290 to 2.0 K, and the behavior of martensitic transformation was detected from the temperature dependence of magnetization. During the M-T curve measurement, the magnetic field of 1.0 T was applied parallel to the surface of the specimen. Following the M-T curve measurement, the M-H curve of the specimen was also measured at 4.0 K to investigate the martensitic transformation under the applied magnetic field.

III. Results and Discussion

1. γ -FeN austenite

Figure 1 shows ^{57}Fe Mössbauer spectra of Fe-N austenites measured at room temperature. The Mössbauer spectra of all austenite specimens can be well-reproduced as a superposition of three paramagnetic components, one singlet (γ_0) and two doublets (γ_1 and γ_2). Mössbauer parameters of these absorption components are listed in Table 1. It must be noted that the line width of γ_2 component in Fe-10.7 at%N austenite, which is represented with (*) in Table 1, is narrower than the natural line width of ^{57}Fe first excited state (0.1940(3) mm/s). This is due to both the weak intensity of this component and the superposition of some components, and thus the linewidth may not reflect the real value. In each spectrum, isomer shift of the singlet denoted as γ_0 is smaller than those of other components; γ_1 and γ_2 . γ_2 component shows a larger isomer shift and quadrupole splitting than γ_0 and γ_1 . Fall *et al.*⁽⁶⁾ reported the analysis of Mössbauer spectra of Fe-N austenites. They analyzed the spectrum as a superposition of two singlets and three doublets with in consideration of the first and second near neighbor configurations. However, in general, the influence of the second near neighbor atom in the fcc lattice is thought to be not so important because the distance between Fe and the second near neighbor N is represented as $\sqrt{3}/2 \cdot a$ (where a as a lattice parameter of fcc lattice) and is quite longer than the distance between

Fig. 1 ^{57}Fe Mössbauer spectra of Fe-N austenites measured at room temperature. Velocity scale is relative to α -Fe at room temperature.

Table 1 Mössbauer parameters of Fe-N austenites measured at room temperature. δ is the isomer shift value, Δ is the quadrupole splitting and Γ is the full width at half maximum.

Specimen		$\delta/\text{mm} \cdot \text{s}^{-1}$	$\Delta/\text{mm} \cdot \text{s}^{-1}$	$\Gamma/\text{mm} \cdot \text{s}^{-1}$	Area (%)
Fe-9.3 at%N (10 μm)	γ_0	-0.019(2)	—	0.294(2)	43.6(3)
	γ_1	0.061(2)	0.387(2)	0.249(1)	53.0(3)
	γ_2	0.202(10)	0.617(10)	0.213(10)	3.4(3)
Fe-10.7 at%N (10 μm)	γ_0	-0.005(2)	—	0.309(2)	38.4(3)
	γ_1	0.075(2)	0.379(1)	0.257(1)	56.5(3)
	γ_2	0.174(6)	0.707(6)	0.186(5)*	5.1(3)

Fe and the near neighbor N; $a/2$. In the present study, therefore, only the near neighbor N is considered and the Mössbauer spectrum was analyzed by three components.

In the fcc lattice of γ -Fe, there are the following near neighbor environments for Fe; Fe having no near neighbor N denoted as Fe(0), Fe having one near neighbor N as Fe(1), and Fe with two near neighbor N as Fe(2) as shown in Fig. 2. According to the arrangement of interstitial atoms, however, Fe(2) can be classified into two different configurations. One is Fe(2, 180°) and the other is Fe(2, 90°). Among such Fe atoms, Fe(0) exists only in the environment of cubic symmetry and thus shows no quadrupole splitting. Therefore it is easily found that the singlet γ_0 originates from Fe(0) in γ -Fe.

The quadrupole interaction is sensitive to the local environment of the probe nucleus, and therefore quadrupole splitting $Q.S.$ ($=\Delta$) of Fe(1) should be different from that of Fe(2). Furthermore, the $Q.S.$ values of Fe(2, 180°) and Fe(2, 90°) may be different, because they have the same number of near neighbor N but the site symmetries of them are different from each other.

The origin of the electric field gradient is not only the asymmetry of the local environment but also the spatial distribution of 3d electrons of the probe atom itself. Therefore it seems difficult to determine the local configu-

Fig. 2 Configuration of interstitial N atoms around Fe in γ -Fe.

ration of atoms around Fe and distinguish Fe(2, 180°) and Fe(2, 90°) only from quadrupole splitting.

The isomer shift is the other parameter obtained by Mössbauer spectroscopy, which reflects the s -electron density at the nucleus, and also sensitive to the environment of the probe nucleus, because s -electron density at the nucleus is affected by the chemical bonding with other atoms or ligands around the probe nucleus. For example, isomer shift of Fe in both γ' -Fe₄N and ϵ -Fe_xN increases with increasing number of near neighbor N⁽⁷⁾. In these nitrides, N atoms occupy the octahedral interstitial sites, whose situation is the same as that in γ -FeN austenite. As shown in Table 1, the isomer shift of the component in γ -FeN austenite increases in sequence of γ_0 , γ_1 , and γ_2 . Therefore the number of near neighbor N atoms seems to increase in this order. In addition, with increasing N content, the area ratios of γ_1 and γ_2 increase and that of γ_0 decreases. From these results, it can be concluded that γ_0 , γ_1 , and γ_2 correspond to Fe having zero, one and two N atoms as the near neighbors. However, the local environment of γ_2 ; Fe(2, 180°) or Fe(2, 90°), cannot be determined from the isomer shift.

In order to discuss the local environment of Fe which corresponds to γ_2 , the hybridization between Fe 3d and N 2p will be considered.

3d electrons of Fe distribute between the coordinate axes ($d_{x^2-y^2}$, d_{xy} , d_{yz} and d_{zx}) or along the z -axis ($d_{3z^2-r^2}$). On the other hand, 2p electrons of N lie along the coordinate axis. Therefore, in the case of the hybridization between Fe and two N atoms in γ -Fe, $d_{3z^2-r^2}$ orbital seems appropriate for the hybridization with 2p orbitals of two N atoms, and thus the 180°-linear chain of the N-Fe-N configuration will be formed. Thus, according to the spatial distribution of Fe 3d and N 2p electrons, the Fe(2, 180°) configuration is favorable for the hybridization between one Fe and two N.

In the Fe-N system, there is a stable fcc compound; γ' -Fe₄N. In γ' -Fe₄N, Fe atoms constitute a fcc lattice and the N atom occupies the octahedral interstitial sites which are located at the center of the unit cell. In this compound, there are two kinds of Fe sites; one has zero and the other has two N atoms called Fe 0 and Fe 2 as the near neighbors. The local environment of Fe 2 in γ' -Fe₄N is the same as Fe(2, 180°) shown in Fig. 2. Thus, the short range order of Fe(2, 180°) is thought to be more stable than Fe(2, 90°) in γ -Fe. If the Fe(2, 180°) configuration is formed in austenite and it develops to the long-range order over the lattice with increasing N content, the phase transformation from γ -FeN austenite to γ' -Fe₄N will occur and γ' -Fe₄N is formed as a stable compound.

From the discussion mentioned above, the γ_2 component observed in austenite may correspond to the Fe(2, 180°) configuration.

As mentioned above, the origin of the electric field gradient is both the charge of other atoms or ligands and that of the probe atom itself, and it is not clear that which is the dominant. However, by assuming here that the electric field gradient at the probe nucleus results only from the point charge of other atoms which are located at the near neighbor site of Fe in the fcc lattice, $Q.S.$ of Fe(0), Fe(1), Fe(2, 180°) and Fe(2, 90°) will be considered.

Assuming that one N atom in the near neighbor site creates the electric field gradient q at the Fe nucleus, the magnitude of the quadrupole splitting $Q.S.$ observed in the paramagnetic spectrum is as follows:

$$Q.S. = \frac{1}{2} e^2 |q| Q \left(1 + \frac{\eta^2}{3} \right)^{1/2} \quad (1)$$

where

$$eq = V_{zz}, \quad \eta = \frac{V_{xx} - V_{yy}}{V_{zz}}. \quad (2)$$

e is the charge of electron; Q is the nuclear quadrupole moment; and V_{xx} , V_{yy} and V_{zz} are diagonal terms of the electric field gradient tensor. When the Fe atom does not have any N neighbor and is located at the cubic symmetry, the quadrupole splitting of Fe(0) is

$$Q.S.(Fe(0)) = 0. \quad (3)$$

When only one N atom is located at the direction of the z -axis, the quadrupole splitting of Fe(1) can be represented as follows:

$$Q.S.(Fe(1)) = \frac{1}{2} e^2 |q| Q. \quad (4)$$

On the other hand, there are two types of Fe(2) which has two near neighbor N atoms. They can be classified by the angle of N-Fe-N bond; one is 90° (Fe(2, 90°)) and the other is 180° (Fe(2, 180°)). As Oda *et al.* discussed⁽⁴⁾, $Q.S.$ of Fe(2, 90°) and Fe(2, 180°) are represented as follows by assuming that the electric field gradient arising from two N atoms can be simply superimposed:

$$Q.S.(Fe(2, 90^\circ)) = -\frac{1}{2}e^2|q|Q \quad (5)$$

$$Q.S.(Fe(2, 180^\circ)) = e^2|q|Q. \quad (6)$$

From the comparison to $Q.S.(Fe(1))$, it is found that quadrupole splitting of $Fe(2, 90^\circ)$ has the opposite sign and the same magnitude of $Q.S.(Fe(1))$. Unfortunately, it is difficult to classify these two local environments from the paramagnetic spectrum. On the other hand, $Q.S.$ of $Fe(2, 180^\circ)$ is twice that of $Fe(1)$. As shown in Table 1, $Q.S.$ of γ_2 is almost twice of that of γ_1 . Therefore, the discussion mentioned above also suggests that γ_2 is the absorption due to $Fe(2, 180^\circ)$.

Therefore, it can be concluded that $Fe(2, 90^\circ)$ configuration does not exist in γ -FeN austenite and the absorption components, γ_0 , γ_1 , and γ_2 , result from $Fe(0)$, $Fe(1)$, and $Fe(2, 180^\circ)$. This conclusion implies that the distribution of N atoms in γ -Fe is not random.

Figure 3 shows the room-temperature ^{57}Fe Mössbauer spectra of Fe-Ni-C austenites in order to compare with the results of Fe-N austenite. The Mössbauer spectrum of Fe-Ni-C austenite can be analyzed as a superposition of two paramagnetic components γ_0 and γ_1 . The γ_2 component cannot be observed in the spectra. It must be noted that the γ_0 component in Fe-Ni-C austenite shows

slight asymmetry and has a broad line width compared with the γ_1 component. This may be due to the influence of Ni atoms in the substitutional near neighbor sites⁽⁸⁾. Because of such asymmetry, the γ_0 component cannot be reproduced by a single Lorentz line, and thus the component was analyzed as a superposition of some lines and the mean value of the positions of lines was defined as the isomer shift δ . The Mössbauer parameters obtained from Fe-Ni-C austenites are listed in Table 2.

In Fe-Ni-C austenite, only the γ_0 and γ_1 components can be observed and the γ_2 component cannot be seen. Therefore, there is no Fe atom which has two C atoms as a near neighbor. This is quite different from Fe-N austenite. Such a difference between Fe-N and Fe-Ni-C austenites implies the difference in the distribution of such interstitial atoms in γ -Fe.

The distribution of interstitial N and C will be discussed here. In order to explain the relative areas of γ_0 , γ_1 and γ_2 in Fe-N and Fe-Ni-C austenites in view of the configuration of interstitial atoms, three kinds of distribution models are considered as Oda *et al.* suggested⁽⁴⁾, (a) interstitial atoms distribute randomly in γ -Fe, (b) the repulsive force acts between the first and second near neighbor interstitial atoms, (c) the repulsive force acts only between the near neighbor interstitial atoms. According to the calculations of Oda *et al.*⁽⁴⁾, the probability of each atomic configuration was calculated as follows:

By using

$$P = \frac{x}{1-x} \quad (7)$$

where x is the N content of the alloy $Fe_{1-x}N_x$ and assuming all N the atoms occupy the octahedral interstitial sites in the fcc lattice, the probability of Fe having n N atoms as the near neighbors in the model-(a) was calculated as follows:

$$I_{Fe(n)} = {}_6C_n p^n (1-p)^{6-n}. \quad (8)$$

In the model-(b), the fraction of each Fe atom was calculated as follows:

$$\begin{aligned} I_{Fe(0)} &= 1 - 6p \\ I_{Fe(1)} &= 6p \\ I_{Fe(2)} &= I_{Fe(3)} = \dots = 0. \end{aligned} \quad (9)$$

Calculations of the probabilities in model-(c) were performed by following equations:

Fig. 3 ^{57}Fe Mössbauer spectra of Fe-Ni-C austenites measured at room temperature. Velocity scale is relative to α -Fe at room temperature.

Table 2 Mössbauer parameters of Fe-Ni-C austenites measured at room temperature. δ is the isomer shift value, Δ is the quadrupole splitting and Γ is the full width at half maximum.

Specimen		$\delta/\text{mm}\cdot\text{s}^{-1}$	$\Delta/\text{mm}\cdot\text{s}^{-1}$	$\Gamma/\text{mm}\cdot\text{s}^{-1}$	Area (%)
Fe-20 at%Ni-3 at%C	γ_0	-0.04(1)	—	*	79.8(8)
	γ_1	0.004(6)	0.665(5)	0.247(3)	20.2(8)
	γ_2	—	—	—	0.0
Fe-16 at%Ni-7 at%C	γ_0	-0.038(1)	—	*	65.45
	γ_1	0.011(1)	0.680(1)	0.283(1)	35.55
	γ_2	—	—	—	0.0

Fig. 4 The distribution of N atoms in Fe-N austenite obtained from the observed ^{57}Fe Mössbauer spectra and from the calculations by three distribution models.

$$\begin{aligned}
 I_{\text{Fe}(2,180^\circ)} &= 3p^2 \\
 I_{\text{Fe}(2,90^\circ)} &= 0 \\
 I_{\text{Fe}(1)} &= 6p(1-p) \\
 I_{\text{Fe}(0)} &= 1 - I_{\text{Fe}(2,180^\circ)} - I_{\text{Fe}(1)}.
 \end{aligned}
 \quad (10)$$

In Figs. 4 and 5, the relative areas of each component observed and calculated from the above distribution models are shown for Fe-N and Fe-Ni-C austenites.

In the case of Fe-N austenite, it is clear from the figures that the model-(a) and (b) cannot explain the experimental results, and the relative area calculated from model-(c) shows good agreement with the experimental results. Although, Oda *et al.* concluded that the interaction between the second near neighbor N atoms is attractive, it becomes clear that the interaction between N atoms is repulsive which can act only between the near neighbor N atoms. The interaction between the second near neighbor N atoms may be repulsive or may not act.

On the contrary to Fe-N austenite, the Mössbauer spectrum of Fe-Ni-C austenite consists of two components γ_0 and γ_1 , and the γ_2 component which corresponds to Fe having two interstitial atoms as the near neighbors was not observed. In the case of carbon interstitials, we have to consider the effects of the additional constituent atom, Ni. However, the effect of Ni in fcc Fe-Ni-C austenite is too small to induce appreciable changes in isomer shift and quadrupole interaction on the near neighbor Fe but broadens the linewidth of the paramagnetic absorption peak. Ni atoms in fcc Fe-Ni are randomly distributed and we can assume the effect of Ni on the interaction be-

Fig. 5 The distribution of C atoms in Fe-Ni-C austenite obtained from the observed ^{57}Fe Mössbauer spectra and from the calculations by three distribution models.

tween carbon interstitials is negligibly small. From Fig. 5, it is also clear that the experimental results can be explained only by model-(b) in which the strong repulsive force is assumed. Therefore, it is concluded that the repulsive force acts on both first and second near neighbor C atoms in $\gamma\text{-Fe}$.

As mentioned above, it is suggested that the interactions between N atoms and C atoms in $\gamma\text{-Fe}$ are different from each other. Although the repulsive force between C atoms is strong and acts between first and second near neighbor atoms, the repulsive force between the N atoms is not so strong that it can act only between the first near neighbors. Such an interaction between the N atoms results in the short-range ordering of Fe and N atoms like the N-Fe-N 180° -linear chain; ($\text{Fe}(2, 180^\circ)$) in fcc Fe-N austenite, and this may be the origin of $\gamma'\text{-Fe}_4\text{N}$. On the other hand, there is no fcc compound like Fe_4C in the Fe-C system, and this is because that the repulsive force between C atoms is stronger than that between the N atoms.

Figure 6 shows the isomer shift and quadrupole splitting obtained from Fe-N and Fe-Ni-C austenites as a function of the number of near neighbor atoms. With increasing number of near neighbor atoms, isomer shifts of both Fe-N and Fe-Ni-C austenites increase. Fe-N austenite shows a larger isomer shift than Fe-Ni-C austenite. The increase in the isomer shift means the decrease in the s -electron density at ^{57}Fe nucleus. Gielen⁽⁹⁾ attributed such a difference in isomer shift to the difference in the bonding state between Fe and these interstitial atoms. He suggested that C atoms contribute electrons to

Fig. 6 Mössbauer parameters of Fe-N and Fe-Ni-C austenites as a function of the number of nearest neighbor atoms measured at room temperature.

the Fe 4s band and N atoms leave Fe in the $3d^7$ state. However, it seems not clear yet.

Isomer shift values of both Fe-N and Fe-Ni-C austenites rise by the increase in the amount of interstitial atoms. This is due to the expansion of the lattice volume by increasing the number of interstitial atoms. Due to such a variation of the lattice volume, Fe d -electron is localized and then the shielding effect becomes strong. Therefore the s -electron density at the Fe nucleus becomes small. This is the origin of the increase in the isomer shift with an increase in amounts of interstitial atoms.

Quadrupole splitting of Fe-N austenite increases with increasing number of near neighbor N atoms. In addition, it is clear from the figure that the quadrupole splitting resulting from one C atom is larger than that from one N atom. Such a difference in the magnitude of quadrupole splitting may be due to the difference in the charge state of interstitial atoms in γ -Fe. The C atom in γ -Fe was reported as positively charged⁽¹⁰⁾⁽¹¹⁾. On the other hand, some investigations suggested that N atom in γ -Fe is negatively charged⁽¹²⁾⁽¹³⁾. Comparing to N atom, C atom may cause a large change in its charge state. This may result in the larger quadrupole splitting in Fe-Ni-C austenite than that of Fe-N austenite. The strong repulsive force between the C atoms compared with that between N atoms also implies such a difference in the charge states of C and N in γ -Fe.

Fig. 7 M-T curves of Fe-N austenites measured with decreasing temperature.

2. Martensitic transformation from γ - to α' -phase

Figure 7 shows the results of magnetization measurements for γ -FeN austenites with N 9.3 and 10.7 at%N. Measurements were done with decreasing temperature under the magnetic field of 1.0 T. While γ -FeN is paramagnetic at room temperature and antiferromagnetic at low temperature, α' -FeN martensite is a ferromagnet. Therefore, the martensitic transformation from the γ to α' -phase and the transition temperature (M_s) can be found by detecting the change in the magnetization by using SQUID. With decreasing temperature from 290 K, the magnetization does not vary and is almost zero at first. With a further decrease of the temperature, the values of the magnetization rise up sharply below a certain critical temperature. Such an increase in the magnetization suggests the martensitic transformation from antiferromagnetic γ -austenite to ferromagnetic α' -martensite. The temperature at which the martensitic transformation starts (M_s) depends on the N content of austenite. From the figure, M_s temperature can be deduced to be 150 K for Fe-9.3 at%N and 100 K for Fe-10.7 at%N.

The increase of the magnetization implies the increase in the amount of α' -FeN martensite. From the figure it can be found that the increase in the magnetization of Fe-10.7 at%N specimens becomes insignificant below 40 K, and therefore the martensitic transformation finishes at 40 K. The same tendency can be observed at 30 K for the Fe-9.3 at%N specimen. Therefore the temperature at which the martensitic transformation finishes (M_f) also depends on the N content of γ -FeN austenite, and these are deduced to be 30 K for 9.3 at%N and 40 K for 10.7 at%N.

With increasing N content, M_s of Fe-N austenite decreases and M_f increases. Martensitic transformation in Fe-9.3 at%N can occur in a wide temperature range compared with Fe-10.7 at%N. This is due to the stability of both γ -FeN and α' -FeN, and γ -FeN becomes more stable with increasing N content. The amounts of the retained γ -FeN austenite depends on the N content.

Figure 8 shows the results of M-H curve measurements

Fig. 8 M-H curves of Fe-N martensites measured at 4.0 K.

at 4.0 K following the M-T curve measurements shown in Fig. 7 by using a SQUID magnetometer. With increasing applied magnetic field, the magnetization of the specimen is once saturated, and then suddenly increases by a further large magnetic field. After applying the magnetic field up to 5.0 T, the magnetization was measured again with decreasing magnetic field from 5.0 T. The magnetization does not show the discontinuity as observed with increasing magnetic field. Therefore such an abrupt change in the magnetization reflects the increase in the amount of α' -FeN martensite. Consequently, these results suggest the martensitic transformation of the retained austenite induced by the applied magnetic field.

For Fe-10.7 at%N austenites, the martensitic transformation occurred at two different magnetic fields, 4.0 T for the specimens #2 and #4, and 4.4 T for #1 and #3. Such a discrepancy in the critical magnetic field for Fe-10.7 at%N austenites may be due to the difference in the shape and/or volume of these specimens. From the relative change in the magnetization, the amount of α' -FeN martensite in Fe-10.7 at%N specimens increases by about 40–55% by applying the magnetic field higher than the critical field.

On the other hand, the critical magnetic field for Fe-9.3 at%N austenite is deduced to be 3.6 T and smaller than that of Fe-10.7 at%N. This is because that γ -FeN austenite becomes unstable with decreasing the N content. The amount of α' -FeN martensite in Fe-9.3 at%N specimen may increase by about 25% by the induced martensitic transformation.

There are many investigations for the field-induced martensitic transformation in the alloy systems of Fe-Ni-Cr, Fe-Ni-C, Fe-Ni-Mn etc. However, report on such a phenomenon in Fe-N system is not so many. Koyano *et al.*⁽¹⁴⁾ reported the martensitic transformation of Fe-9.8 at%N austenite induced by the magnetic field investigated by means of magnetization and X-ray diffraction measurements. They reported the continuous growth of the diffraction peaks due to α' -martensite with increasing the applied magnetic field up to 17 T. In this study, however, the martensitic transformation is found to be induced by the critical magnetic field.

Fig. 9 ^{57}Fe Mössbauer spectra of Fe-10.7 at%N measured at room temperature. (a) Austenite, and (b), (c) martensite. Velocity scale is relative to α -Fe at room temperature.

By annealing α' -FeN martensite, α'' -Fe₁₆N₂ is formed. This compound was reported to have a giant magnetic moment which is larger than that of α -Fe⁽¹⁵⁾. Because of the large amount of retained austenite, it is difficult to obtain the single phase and bulk α'' -Fe₁₆N₂ by annealing of α' -FeN martensite. N content of α'' -Fe₁₆N₂ is 11.1 at%. With increasing the N content of γ -FeN austenite, γ -FeN austenite becomes stable and it becomes difficult to obtain large amount of α' -FeN martensite. The magnetic field-induced martensitic transformation may be available to prepare bulk α'' -Fe₁₆N₂.

3. α' -FeN martensite

Figure 9(a) shows a room-temperature ^{57}Fe Mössbauer spectrum of Fe-10.7 at%N austenite. This specimen was quenched into *liq.* He in order to induce the martensitic transformation, and then the Mössbauer spectrum was measured at room temperature. The observed Mössbauer spectrum is shown in Fig. 9(b). The spectrum consists of paramagnetic and magnetic components. The former absorption is due to retained austenite, and the latter is due to ferromagnetic martensite. Because of the high N content, γ -FeN becomes stable and thus a large amount of γ -FeN austenite is retained in the specimen. To discuss the spectrum of martensite in detail, the spectrum of α' -FeN martensite is shown in Fig. 9(c) which is the same as that in Fig. 9(b) but vertically expanded. ^{57}Fe Mössbauer spectrum of Fe-10.7 at%N martensite can be analyzed as a superposition of four magnetic components. These components originate from four kinds of Fe atoms which are located in different environments in the bct lattice of

α' -martensite.

In Fig. 10 are shown ^{57}Fe Mössbauer spectra of α' -FeN martensites with different N contents (5.8 at%, 9.3 at%, and 10.7 at%). All the spectra of these specimens consist of four magnetic components, and their absorption intensities vary with N content. Mössbauer parameters of α' -FeN martensites obtained from spectral analysis are listed in Table 3. There are some interpretations on these four magnetic components in the Mössbauer spectrum of α' -FeN martensite. DeCristofaro and Kaplow⁽¹⁶⁾ suggested that these four magnetic components correspond to Fe atoms as the first, second, third and further near neighbors of the N atom. Rochegude and Foct⁽¹⁷⁾ also

Fig. 10 ^{57}Fe Mössbauer spectra of α' -FeN martensites measured at room temperature. Velocity scale is relative to α -Fe at room temperature.

analyzed the Mössbauer spectrum of α' -FeN martensite in the same manner as did DeCristofaro and Kaplow. On the other hand, Fall *et al.*⁽¹⁸⁾ analyzed the Mössbauer spectrum by using seven magnetic subspectra; Fe with two N atoms as near neighbors, two kinds of Fe with one N atom as near neighbor and the Fe-N direction is parallel or perpendicular to the (001) plane, and four kinds of Fe atoms with zero near neighbor N and the second near neighbor N from zero to four. However, the observed spectra of α' -FeN martensite in the present work are rather broad and it seems difficult to analyze them reasonably as superpositions of seven magnetic subspectra as Fall *et al.* reported. It seems appropriate to analyze the spectrum by four magnetic components with different FWHM, which correspond to Fe as the first, second, third, and further near neighbor of the N atom.

Among four magnetic components, only one component, which corresponds to Fe as a third neighbor of the N atom, shows a large hyperfine magnetic field of about 36 T at room temperature. This hyperfine magnetic field is larger than that of α -Fe. Hyperfine magnetic fields of other three components are nearly equal to or smaller than that of α -Fe. Therefore, the mean hyperfine magnetic field of α' -FeN martensite is not so large and almost the same as that of α -Fe.

The α' -FeN martensite has a bct structure in which the c -axis is longer than the a -axis. This is because that the interstitial N atoms occupy one of the three interstitial sites, O_z site. DeCristofaro and Kaplow⁽¹⁴⁾ reported the Mössbauer spectrum of Fe-2.83 mass%N fresh martensite measured at 80 K. The Mössbauer spectrum could be analyzed as a superposition of four magnetic components corresponding to Fe atoms mentioned above, and their relative intensities could be explained by the distribution model assuming that the N atoms randomly occupy the O_z sites in the bct lattice. The relative area of each component obtained here is compared with the model calculation suggested by DeCristofaro and Kaplow⁽¹⁵⁾. The relative intensities obtained from the Mössbauer spectra are plotted with the results of model calculation in Fig. 11. It is clear from the figure that the

Table 3 Mössbauer parameters of α' -FeN martensite measured at room temperature. H_{int} is the magnitude of the hyperfine magnetic field, δ is the isomer shift value, Δ is the quadrupole splitting and Γ is the full width at half maximum.

	Site	H_{int}/T	$\delta/\text{mm}\cdot\text{s}^{-1}$	$\Delta/\text{mm}\cdot\text{s}^{-1}$	$\Gamma/\text{mm}\cdot\text{s}^{-1}$	Area (%)	$\langle H_{\text{int}} \rangle/\text{T}$
Fe-5.8 at%N	1st NN of N	29.4(1)	0.07(9)	-0.22(2)	0.44(1)	11(1)	33.2(1)
	2nd NN of N	32.0(5)	0.11(7)	-0.01(1)	0.44(1)	20(1)	
	3rd NN of N	35.8(2)	0.10(7)	-0.06(2)	0.44(1)	15(1)	
	further	33.7(1)	0.02(3)	0.042(6)	0.44(1)	54(1)	
Fe-9.3 at%N	1st NN of N	29.7(1)	0.07(3)	-0.122(7)	0.411(6)	20(1)	33.2(1)
	2nd NN of N	32.1(1)	0.16(3)	-0.014(6)	0.411(6)	26(1)	
	3rd NN of N	36.3(1)	0.09(3)	-0.055(8)	0.411(6)	19(1)	
	further	34.3(1)	0.04(2)	0.073(5)	0.411(6)	35(1)	
Fe-10.7 at%N	1st NN of N	29.6(1)	0.07(3)	-0.093(6)	0.442(6)	24(1)	33.0(1)
	2nd NN of N	32.0(1)	0.18(3)	-0.015(6)	0.442(6)	27(1)	
	3rd NN of N	36.7(1)	0.09(4)	-0.052(8)	0.442(6)	19(1)	
	further	34.3(1)	0.05(3)	0.074(6)	0.442(6)	50(1)

Fig. 11 The observed and calculated probabilities of the components in α' -FeN martensites.

relative intensities of the first and second near neighbor Fe show good agreement with the results of model calculation. The observed and calculated intensities of the third and further near neighbor do not agree. The probability to find the third neighbor Fe is much less than the calculated one by assuming the random distribution. On the contrary, the probability to find the further near neighbor Fe is larger than the calculated one, which may be due to the local short-range concentration fluctuations of N atoms. This may be because of the diffusion of interstitial N atoms in the host lattice. In this experiment, Mössbauer measurements have been done at room temperature. It is known that only 0.4 at% of N atoms can be solved in α -Fe, and thus α' -FeN martensite is a super-saturated solid solution of the N atoms. Such excessive N atoms can easily be diffused to form the second phases in α' -FeN martensite. Compared with the calculation, the intensity of the third near neighbor Fe is small, but that of the further near neighbor Fe is large. From this result, N atoms which are randomly distributed at O_z sites in the bct lattice may diffuse and gather to make the ordered arrangement of N atoms. Such a diffusion of N atoms may result in the formation of α'' -Fe₁₆N₂.

IV. Summary

^{57}Fe Mössbauer study of Fe-N austenite has been performed to investigate the distribution and interaction of N atoms in γ -Fe and to compare with those of C atoms. The Mössbauer spectra of Fe-N austenites can be analyzed as a superposition of the three paramagnetic components, γ_0 , γ_1 and γ_2 , having zero, one and two N atoms as near neighbors. Among them, the γ_2 component corresponds to the configuration of a N-Fe-N 180°-linear chain. It can be confirmed that N atoms are not distribut-

ed randomly in γ -Fe and the interaction between the first near neighbor N atoms is repulsive. By comparison with the Fe-Ni-C austenite, it was found that the repulsive force between N atoms in γ -Fe is weaker than that between C atoms.

By means of the magnetization and ^{57}Fe Mössbauer measurements, the martensitic transformation and α' -FeN martensite were investigated. With increasing N content, M_s of FeN austenite decreases and M_f increases. It was confirmed that the martensitic transformation from γ -FeN austenite to α' -FeN martensite can be induced by applying the critical magnetic field which depends on N content. This phenomenon is available to obtain the bulk specimen of metastable α'' -Fe₁₆N₂. ^{57}Fe Mössbauer spectra of α' -FeN martensites could be analyzed by the four magnetic components which correspond to Fe as the first, second, third, and further near neighbor of the N atom. Among them, the third near neighbor Fe atom shows the hyperfine magnetic field of about 36 T, which is larger than that of α -Fe. However, the mean hyperfine magnetic field of α' -FeN martensite is nearly equal to that of α -Fe. From the relative areas of absorption components, the distribution of N atoms in α' -FeN austenite was discussed. The distribution model that N atoms randomly occupy O_z sites in α' -FeN martensite, cannot explain the experimental results, especially the amounts of the third and further near neighbor Fe. This may be because of the diffusion of N atoms to form the N-rich region in matrix α' -FeN at room temperature.

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