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## Interaction and arrangement of nitrogen atoms in FCC $\gamma$ -iron

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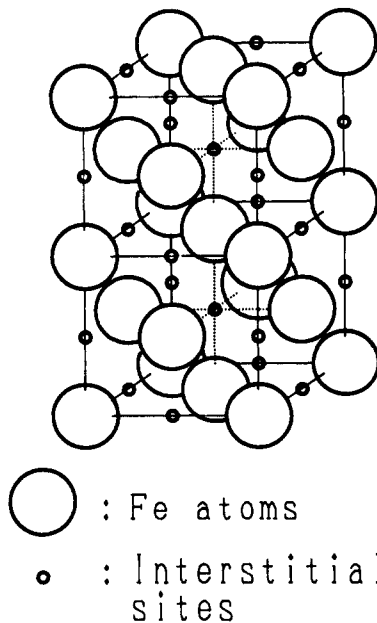
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**Abstract.** A Mössbauer effect measurement of  $^{57}\text{Fe}$  has been performed for the Fe–N austenite in order to study the interaction between nitrogen atoms and the distribution among the octahedral sites of the FCC lattice. The spectrum for Fe–N austenite is decomposed into one singlet  $\gamma_0$  and two sets of doublets  $\gamma_1$  and  $\gamma_2$  which are identified as being caused by iron atoms with different configurations of nitrogen atoms at the nearest-neighbour sites. The fractional intensities for the three components are precisely determined by taking into account the effect of the absorber thickness. It is concluded from the analysis that the interaction between the first-nearest-neighbour nitrogen atoms is strongly repulsive and that between the second nearest nitrogen is weakly attractive.

### 1. Introduction

Interstitial solid solute atoms in iron austenite, such as carbon or nitrogen, are known to occupy octahedral interstitial sites in the FCC lattice, but knowledge of the distribution of the atoms among the lattice, and of the interaction between the atoms is still insufficient. Results of activity measurements showed that the interaction between carbon atoms is repulsive in high-temperature austenite and that between nitrogen atoms is also repulsive, but not so strongly repulsive as that between carbon atoms [1, 2]. From this point of view, carbon or nitrogen atoms can be expected to occupy separate octahedral sites in the FCC lattice. However, information about the local atomic interaction between the interstitial atoms at the first neighbouring position, the second one and so on, is difficult to obtain from thermodynamic measurements.

Since the interstitial atoms occupy octahedral sites in the FCC iron lattice, an iron atom can be associated with six nearest neighbouring interstitial atoms. We will now take into account only the effect of interstitial atoms at the nearest sites, which will be an appropriate assumption in the present study of Mössbauer spectroscopy. The configurations of an iron atom and the surrounding octahedral sites in a FCC lattice are shown in figure 1. The electronic environment and, therefore, the energy levels of the  $^{57}\text{Fe}$  nucleus would be modified when interstitial atoms occupy the neighbouring sites. The Mössbauer effect measurement is a powerful method for obtaining knowledge about the environment of an atom on an atomic scale by measuring the energy level of the nucleus.



**Figure 1.** Positions of iron atoms and octahedral interstitial sites in FCC lattice.

The Mössbauer spectrum of  $^{57}\text{Fe}$  in paramagnetic austenite can be decomposed into two kinds of components [3–13]. One is a singlet which is assigned to iron atoms having no nearest interstitial atoms, and the other is a doublet assigned to those having interstitial atoms at the nearest-neighbouring sites. When an interstitial atom exists at the nearest-neighbour octahedral site of an iron atom, the cubic symmetry of the electric field at the  $^{57}\text{Fe}$  nucleus is destroyed, leading to a non-vanishing electric field gradient (EFG). As a result, the spectrum splits into a doublet. The magnitude of this quadrupole splitting (QS) depends on the type and the number of interstitial atoms. The interstitial atoms also change the electron density of the iron nucleus and, therefore, the spectrum is shifted parallel to the velocity axis. The difference between the centre of gravity of the spectrum and zero velocity is called the isomer shift (IS). The measured Mössbauer spectrum of  $^{57}\text{Fe}$  in austenite is a superposition of the spectra originating from the iron atoms in different environments [3–13].

There have been several studies of Fe–C and Fe–N alloys by Mössbauer spectroscopy. As for Fe–C austenite it is generally accepted that carbon atoms are separately distributed among the octahedral sites in the FCC lattice and, therefore, that there exists a repulsive interaction between the carbon atoms [3, 4, 8, 12, 13]. This evidence agrees well with the results of thermodynamical experiments [1, 2]. The formation of the  $\text{Fe}_8\text{C}$  type long-range order due to this repulsive interaction has been suggested [12, 13], although another study exists which reports a random distribution of carbon atoms [5]. Most of the previously reported Mössbauer spectra for Fe–C austenite show similar shape parameters [3–5, 10, 12, 13]. The value of the QS for iron atoms with one carbon atom in the first-nearest-neighbour shell was measured to be about  $0.63 \text{ mm s}^{-1}$ . The difference in isomer shift (IS) is small ( $0.04 \text{ mm s}^{-1}$ ) between the iron atoms with and without carbon atoms at the first-nearest-neighbour site.

As for the Fe–N austenite, the QS of the doublet is in the range  $0.29\text{--}0.36 \text{ mm s}^{-1}$  which is quite small compared with that of the Fe–C system [6–11]. By analysing the

component ratio of the measured spectra, it has been presumed that nitrogen atoms are randomly distributed [6, 8, 9]. The difference in the IS between the doublet and the singlet has been reported to be about  $0.075 \text{ mm s}^{-1}$  [7].

We report in this paper the result of a precise Mössbauer effect study for Fe–N austenite in order to clarify the distribution of nitrogen atoms and the interaction energy between the first- and second-nearest-neighbour nitrogen atoms.

## 2. Experimental procedure

Fe–N foil samples,  $5 \mu\text{m}$  and  $10 \mu\text{m}$  thick, were prepared by nitriding pure iron films in a mixture of  $\text{NH}_3$  and  $\text{H}_2$  gas at a temperature of 923 K. In order to avoid the formation of a martensite phase, and to detect the effect of nitrogen atoms clearly, the nitrogen concentration in the austenite phase was increased to 9.0 at.% (2.4 wt%). The composition of the alloy was determined by x-ray diffraction, by using the well known relationship [14] between the peak position and the nitrogen concentration in solid solution. No ferromagnetic component was found in the Mössbauer spectrum, as expected in this alloy, since the  $M_s$  temperature at which the martensitic transformation begins is lower than room temperature in this alloy composition.

Mössbauer absorption spectra were measured at room temperature using a  $^{57}\text{Co}$  source for 14.4 keV  $\gamma$  rays with an intensity of 500 MBq. The velocity scale of the spectrum was calibrated with an  $\alpha$ -iron reference absorber. Isomer shifts are given with respect to  $\alpha$ -iron.

The absorption intensity of the Mössbauer spectrum is a non-linear function of the specimen thickness. As the absorber thickness increases, the intensity shows a tendency to be suppressed from a linear relation [15]. For a thick specimen, therefore, the apparent fractional intensity for a strong component is less than the true value for the component and vice versa for a weak one.

In order to correct for the effect of thickness and to determine the true fraction of the spectrum component, we measured the spectra for the same specimen with different thicknesses. The thickness of the absorber was changed from 5 to  $20 \mu\text{m}$  by changing the number of piled foils. The spectrum measured at each thickness was least-square fitted by a superposition of Lorentzian curves. The linewidths were assumed to be the same and were varied simultaneously. The fractional intensity of each Lorentzian curve was obtained as a function of thickness. Using this function, the true component ratio was estimated by a method described in the next section.

## 3. Experimental results and analysis

A Mössbauer spectrum for a  $20 \mu\text{m}$  thick Fe–9.0 at.%N austenite specimen is shown in figure 2. This spectrum is decomposed into one singlet ( $\gamma_0$ ) and two doublets ( $\gamma_1$  and  $\gamma_2$ ) given as full curves in the figure. The  $\gamma_2$  component was not detected in previous studies [3, 7, 8], but was found in the precise measurement performed by the present authors [10]. The fitting parameters are listed in table 1. The value of the QS of  $\gamma_2$  was  $0.72 \text{ mm s}^{-1}$  which is nearly twice as large as that of  $\gamma_1$  ( $0.39 \text{ mm s}^{-1}$ ). The IS increases going from  $\gamma_0$  via  $\gamma_1$  to  $\gamma_2$ . The values of IS and QS for  $\gamma_0$  and  $\gamma_1$  agree well with previously reported values [3, 7, 8].

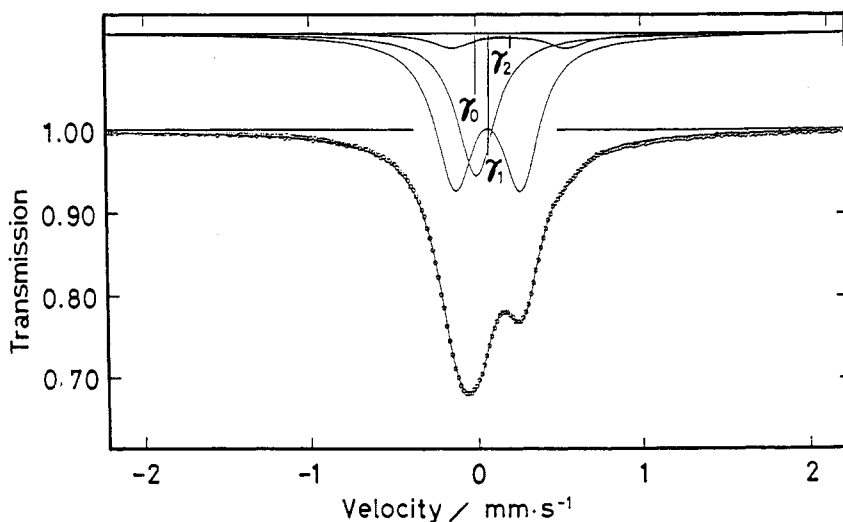


Figure 2. A Mössbauer spectrum for 20  $\mu\text{m}$  thick Fe-9.0 at.%N austenite, together with the decomposed components.

Table 1. The Mössbauer parameters for the spectrum of Fe-9.0 at.%N austenite (20  $\mu\text{m}$  thickness).

Specimen	Component	is (mm s <sup>-1</sup> )	qs (mm s <sup>-1</sup> )	Intensity <sup>a</sup> (%)	Width <sup>b</sup> (mm s <sup>-1</sup> )
Fe-9.0 at.%N (2.4 wt%N)	$\gamma_0$	0.01	—	31.4	0.139
	$\gamma_1$	0.08	0.39	62.6	0.139
	$\gamma_2$	0.20	0.72	6.0	0.139

<sup>a</sup> Apparent fraction of intensity for a thick specimen (20  $\mu\text{m}$ ).

<sup>b</sup> Apparent Lorentzian width simultaneously varied for fitting the spectrum.

The results of precise measurements of intensities for the specimens 5, 10, 15 and 20  $\mu\text{m}$  thick are shown in figure 3. The intensity of the strong component is seen to decrease relatively as the thickness increases and vice versa for the weak ones. For the values of is and qs, no dependence on thickness was seen. On the other hand, the value of the linewidth had positive correlation with thickness from 0.12 mm s<sup>-1</sup> for the 5  $\mu\text{m}$  thick absorber to 0.14 mm s<sup>-1</sup> for the 20  $\mu\text{m}$  one. The linewidth of a 5  $\mu\text{m}$   $\alpha$ -Fe reference absorber was 0.11 mm s<sup>-1</sup>.

In figure 4 the variation of the apparent fractional intensities obtained by curve fitting of Lorentzian functions to the measured spectrum is shown as a function of the absorber thickness. The true fractional intensities for each component ratio at zero thickness can be obtained in the following way.

A single Mössbauer absorption peak centred at zero velocity can be expressed on the basis of the resonant absorption theory by a function:

$$P(\varepsilon) = \exp(-\mu_A t_A) \frac{2}{\pi\Gamma} \int_{-\infty}^{\infty} dE \left[ \exp\left(-T \frac{(\Gamma/2)^2}{E^2 + (\Gamma/2)^2}\right) \times \exp(-\mu_s t_s) \left( \frac{N(\Gamma/2)^2}{(E + \varepsilon)^2 + (\Gamma/2)^2} \right) \right]$$

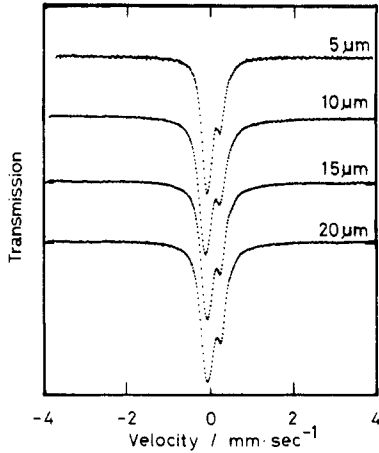


Figure 3. The dependence of the spectra of Fe-9.0 at.%N austenite on the thickness of absorber.

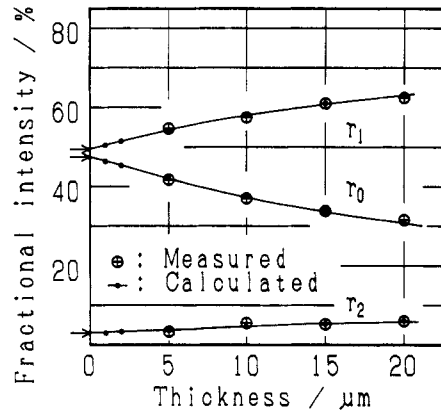


Figure 4. The apparent fractional intensities as functions of the thickness of absorber obtained by curve fitting of Lorentzian functions to both measured and calculated spectra.

where  $\varepsilon$  is the Doppler energy of the  $\gamma$  ray and  $\Gamma$  is the natural width of the 14.4 keV excited level of  $^{57}\text{Fe}$ ;  $t_A$  and  $t_s$  are the thickness of absorber and source, respectively;  $\mu_A$  and  $\mu_B$  are the absorption coefficient for each material.  $T$  is the effective thickness of absorber given by

$$T = nt_A \sigma f$$

where  $n$ ,  $t_A$ ,  $\sigma$  and  $f$  are the number density of  $^{57}\text{Fe}$  nuclei, thickness, Mössbauer cross section and recoilless fraction of the absorber, respectively. By using this function, a spectrum with multi-components can be written in the following formula:

$$P_{\text{tot}}(\varepsilon, f, t_A) = \exp(-\mu_A t_A) \frac{2}{\pi\Gamma} \int_x^{-\infty} dE \left( \exp[-p(E)] \times \exp(-\mu_s t_s) \frac{N(\Gamma/2)^2}{(E + \varepsilon)^2 + (\Gamma/2)^2} \right)$$

in which

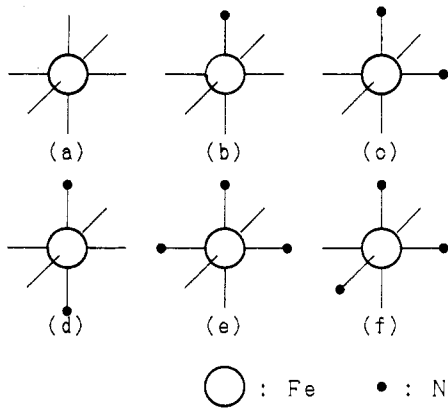
$$p(E) = \sum_i T_i \frac{(\Gamma/2)^2}{(E - IS_i)^2 + (\Gamma/2)^2} \quad (\text{singlet})$$

$$+ \sum_j \frac{T_j}{2} \left( \frac{(\Gamma/2)^2}{(E - IS_j - QS_j/2)^2 + (\Gamma/2)^2} + \frac{(\Gamma/2)^2}{(E - IS_j + QS_j/2)^2 + (\Gamma/2)^2} \right) \quad (\text{doublet}).$$

Here,  $T_i$  is the effective thickness of the  $i$ th component given by

$$T_i = I_i n t_A \sigma f$$

where  $I_i$  is the fractional intensity of the  $i$ th component. We assume that the recoilless fraction for each component is the same.



**Figure 5.** Possible coordinations of nitrogen atoms around iron in FCC lattice: (a) Fe(0); (b) Fe(1); (c) Fe(2, 90°); (d) Fe(2, 180°); (e) and (f) two types of configurations of Fe(3).

First, a set of spectra with different thickness was calculated by substituting assumed ratios of the intensities  $I_i$ , etc, together with the experimental values of IS and QS for each component to the above formula. Then, the calculated spectra were decomposed into three components by assuming Lorentzian shapes of peaks, in the same way as was done for the measured spectra. The assumed fractions  $I_i$ , etc, were varied until the calculated intensities corresponded to the experimentally derived ones for each thickness.

The values of the consistent fractional intensities to reproduce the experimentally derived ones for each thickness will give the true component ratios. Although the shape of the spectra deviates largely from a superposition of Lorentzian curves for the case of a thick absorber, it should be noted that the same decomposition procedure is applied to both experimental and theoretical spectra for the same absorber thickness. The absolute values of the fractional intensities for each thickness give no physical meanings, instead the consistent fractional intensities at zero thickness are essentially important.

From this procedure, the true component ratios were obtained as:

$$I_{\gamma 0} = 0.473 \quad I_{\gamma 1} = 0.496 \quad I_{\gamma 2} = 0.031$$

where the recoilless fraction of each component was assumed to be 0.75 [16].

## 4. Discussion

### 4.1. Identification of the components

The local environment of an iron atom in FCC iron can be classified as shown in figure 5 (a) Fe(0), with no nitrogen atom at the nearest octahedral interstitial sites; (b) Fe(1), with one nitrogen atom; (c) Fe(2, 90°), with two nitrogen atoms placed at the two adjacent neighbouring sites; (d) Fe(2, 180°), with two nitrogen atoms placed at the opposite nearest sites of iron; (e) and (f) Fe(3), two types of configurations with three atoms. It should be noted that the symmetries of an iron with more than three nitrogen atoms, i.e. Fe(4), Fe(5) and Fe(6) are the same as those of Fe(2), Fe(1) and Fe(0), respectively.

The Mössbauer spectrum of paramagnetic austenite can be decomposed into a single peak and two doublet peaks as already mentioned. The splitting of the peak is due to the quadrupole interaction between the quadrupole moment of iron nucleus and the

electric field gradient (EFG) at the nucleus. The quadrupole interaction can be written as

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

Here,  $q$  is defined by

$$eq = V_{zz}$$

where  $V_{zz}$  is the main axis of the EFG tensor, and  $\eta$  is the asymmetry parameter,  $\eta = (V_{xx} - V_{yy})/V_{zz}$ .

When there is no nitrogen atom in the surroundings of an iron atom, the electrostatic field around the iron atom is cubic symmetrically and, therefore,

$$V_{xx} = V_{yy} = V_{zz}.$$

By taking into account the requirement of  $V_{xx} + V_{yy} + V_{zz} = 0$  (Laplace equation), we obtain,

$$V_{xx} = V_{yy} = V_{zz} = 0$$

which leads to  $Qs(\text{Fe}(0)) = 0$ , the singlet peak.

In the case of an iron atom with a nitrogen atom placed at the nearest interstitial site on the  $z$ -axis:

$$V_{zz} = eq \quad V_{xx} = V_{yy} = -eq/2 \quad \eta = 0.$$

Then,

$$Qs(\text{Fe}(1)) = e^2 |-q| Q/2.$$

When two nitrogen atoms are placed at the nearest-neighbouring sites along the  $x$ - and  $y$ -axes (the  $\text{Fe}(2, 90^\circ)$  configuration) by assuming that EFG can be superimposed, as in the case of point charge approximation, we obtain

$$\begin{aligned} \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix} &= \begin{pmatrix} eq & 0 & 0 \\ 0 & -eq/2 & 0 \\ 0 & 0 & -eq/2 \end{pmatrix} + \begin{pmatrix} -eq/2 & 0 & 0 \\ 0 & eq & 0 \\ 0 & 0 & -eq/2 \end{pmatrix} \\ &= \begin{pmatrix} eq/2 & 0 & 0 \\ 0 & eq/2 & 0 \\ 0 & 0 & -eq \end{pmatrix} \end{aligned}$$

and the asymmetry parameter  $\eta = 0$ . Then,

$$Qs(\text{Fe}(2, 90^\circ)) = e^2 |q| Q/2.$$

In this case, the sign of EFG is opposite to that for  $\text{Fe}(1)$ , but the magnitude is the same. It is not possible to distinguish the two components except for the measurement with an external magnetic field [10, 15, 17].



In the case when two nitrogen atoms are placed at the two opposite nearest-neighbour sites of the iron atom (Fe(2, 180°)), the effect of the two nitrogen atoms is additive and then

$$QS(\text{Fe}(2, 180^\circ)) = e^2 |q| Q.$$

The splitting is expected to be twice as large as in the case for Fe(1) or Fe(2, 90°) [10, 15, 17].

From these considerations, the three components in the measured spectrum can be reasonably assigned as follows:

$$\gamma_0 : \text{Fe}(0) \quad \gamma_1 : \text{Fe}(1) \text{ and } \text{Fe}(2, 90^\circ) \quad \gamma_2 : \text{Fe}(2, 180^\circ).$$

The value of QS for  $\gamma_2$  is not exactly twice that for  $\gamma_1$ . Probably the point charge approximation is incorrect in this case, or possibly the effect of nitrogen atoms situated at further sites cannot be neglected.

#### 4.2. Intensity analysis and models

The sign and magnitude of the interaction between nitrogen atoms in austenite can be deduced from the obtained fractional intensities. In an alloy of composition  $\text{Fe}_{1-x}\text{N}_x$  the fraction of octahedral sites occupied by nitrogen atoms is

$$p = x/(1 - x).$$

4.2.1. Case A. When nitrogen atoms are randomly distributed among the octahedral sites of the FCC lattice, the fraction of the previously classified iron atoms is

$$I_{\text{Fe}(0)} = \binom{6}{0} (1 - p)^6 = (1 - p)^6$$

$$I_{\text{Fe}(1)} = \binom{6}{1} p(1 - p)^5 = 6p(1 - p)^5$$

$$I_{\text{Fe}(2, 90^\circ)} = 12p^2(1 - p)^4$$

$$I_{\text{Fe}(2, 180^\circ)} = 3p^2(1 - p)^4$$

$$I_{\text{Fe}(3)} = \binom{6}{3} p^3(1 - p)^3 = 20p^3(1 - p)^3$$

and so on. Here, it is assumed that no interactions act between the neighbouring nitrogen atoms and, therefore, that the interaction energies between the first-nearest-neighbouring nitrogen atoms,  $J_1$ , and the second nearest,  $J_2$ , are both equal to zero.

4.2.2. Case B. When repulsive forces act between nitrogen atoms, nitrogen atoms tend to separate from each other. When strong repulsive forces act between both first- and second-nearest nitrogen atoms ( $J_1 \ll 0$ ,  $J_2 \ll 0$ ) then

$$I_{\text{Fe}(0)} = 1 - 6p \quad I_{\text{Fe}(1)} = 6p \quad I_{\text{Fe}(2)} = I_{\text{Fe}(3)} = I_{\text{Fe}(4)} = I_{\text{Fe}(5)} = I_{\text{Fe}(6)} = 0.$$

**Table 2.** The fractional intensities of the components obtained from experimental data compared with those of iron atom types calculated for various cases of atomic interactions  $J_1$  and  $J_2$  between nitrogen atoms.

	Experiment	Case A: $J_1 = 0$ $J_2 = 0$	Case B: $J_1 \ll 0$ $J_2 \ll 0$	Case C: $J_1 \ll 0$ $J_2 = 0$	Case D: $J_1 = -1.20 kT$ $J_2 = +0.05 kT$
$I_{\text{Fe}(0)}$	0.473	0.53	0.40	0.43	0.473
$I_{\text{Fe}(1)}$	0.496	0.35	0.60	0.54	0.461
$I_{\text{Fe}(2, 90^\circ)}$	—	0.079	0	0	0.035
$I_{\text{Fe}(2, 180^\circ)}$	0.031	0.020	0	0.030	0.031
$I_{\text{Fe}(3)}$	—	0.015	0	0	—

4.2.3. *Case C.* When a strong repulsive force acts between the first-nearest-neighbouring atoms and there is no interaction between the second ( $J_1 \ll 0$  and  $J_2 = 0$ )

$$I_{\text{Fe}(2, 180^\circ)} = 3p^2 \quad I_{\text{Fe}(2, 90^\circ)} = 0 \quad I_{\text{Fe}(1)} = 6p(1 - p) \quad I_{\text{Fe}(0)} = 1 - I_{\text{Fe}(2, 180^\circ)} - I_{\text{Fe}(1)}$$

The calculated fractional intensities for the composition of the present experiment ( $x = 0.09$  and  $p = 0.10$ ) are listed in table 2 together with the experimentally obtained values. The experimental value of  $\gamma_2$  is much larger compared with that calculated for case A, where nitrogen atoms are randomly distributed, or for case B, where they are repulsively distributed to avoid the first- and second-neighbouring pairing. The experimental values of both  $I_{\gamma_0}$  and  $I_{\gamma_1}$  lie between those of the two cases. When there is no interaction between the second-nearest nitrogen atoms (case C), the calculated intensities show better agreement with the experimental values. But there still exist discrepancies in the values of  $\gamma_0$  and  $\gamma_1$ . Further agreement can be expected in the case where the interaction between the first-nearest-neighbours ( $J_1$ ) becomes less repulsive and a weak attractive force is added between the second-nearest atoms.

4.2.4. *Case D.* If we assume that the nitrogen concentration is low enough, the intensity ratios of each configuration can be approximated by the equations:

$$I_{\text{Fe}(2, 90^\circ)} = 2 \times 6p^2 \exp(J_1/k_B T)$$

$$I_{\text{Fe}(2, 180^\circ)} = 3p^2 \exp(J_2/k_B T)$$

$$I_{\text{Fe}(1)} = 6p - 2I_{\text{Fe}(2, 90^\circ)} - 2I_{\text{Fe}(2, 180^\circ)}$$

Here,  $k_B$  is Boltzmann's constant. Using the relations

$$I_{\gamma_1} = I_{\text{Fe}(1)} + I_{\text{Fe}(2, 90^\circ)}$$

$$I_{\gamma_2} = I_{\text{Fe}(2, 180^\circ)}$$

and substituting the measured values of  $I_{\gamma_0}$  and  $I_{\gamma_1}$  into the relations, the interaction energies  $J_1$  and  $J_2$  between nitrogen atoms are obtained to be

$$J_1/k_B T = -1.20 \pm 0.10$$

$$J_2/k_B T = +0.05 \pm 0.03.$$

The ratios of Fe(1) and Fe(2, 90°) are also derived to be  $I_{\text{Fe}(1)} = 0.461$  and  $I_{\text{Fe}(2, 90^\circ)} =$

0.035, respectively. The results are listed in the last column of table 2 as case D. Since it can be presumed that the distribution of nitrogen atoms is in equilibrium after a long time ( $>1$  Ms) at room temperature, by putting  $T = 300$  K, the following pairwise interaction energies are obtained

$$J_1/k_B = -360 \pm 30 \text{ K}$$

$$J_2/k_B = +15 \pm 10 \text{ K}.$$

The results indicate that the repulsive force between the first-nearest nitrogen atoms is very strong and a weak attractive force works between the second-nearest-neighbours.

As mentioned before, the octahedral interstitial sites in a FCC lattice also form a FCC lattice (see figure 1). In the present case, the points of this lattice are occupied with a nitrogen atom or a vacancy. Considering the composition of the specimen, the nitrogen atoms are the minority component on this lattice. Based on the theoretical investigation of the ground state structures of FCC ordered binary alloys, a  $\text{Cu}_3\text{Au}$  type structure is expected to form when the composition of the minority atom is less than  $\frac{1}{4}$ , and when the first- and second-neighbour interactions between the same kinds of atoms are repulsive and attractive, respectively [18]. Together with the iron atoms at the original lattice sites, this would lead to the  $\text{Fe}_4\text{N}$  structure [6]. Since  $J_1 < 0$  and  $J_2 > 0$  in the present work, it can be concluded that the  $\text{Fe}_4\text{N}$  type short-range order is stable in the austenite phase. If  $J_1$  and  $J_2$  are both negative, the stable ground state structure should be the  $\text{Fe}_8\text{C}$  type superstructure [12, 13] in the composition range of nitrogen less than  $\frac{1}{8}$ .

When we calculated the Mössbauer spectra, we made two assumptions. One is that the value of  $is$  is equal for the Fe(1) and Fe(2,  $90^\circ$ ) components, and the other is that the recoilless fraction is equal for each component. In order to check the validity of these assumptions we have calculated the next three sets of spectra with the same intensities  $I_i$ . First is the set in which the value of  $is$  of the Fe(2,  $90^\circ$ ) component was assumed to be twice as large as that of Fe(1). Second is the set in which the recoilless fractions for Fe(1), Fe(2,  $90^\circ$ ) and Fe(2,  $180^\circ$ ) were different. We used the values of recoilless fractions (0.77 and 0.81) estimated from the Debye temperatures, 397 K and 443 K for Fe(0) and Fe(1) components, respectively, in Fe–Ni–C austenite determined by the measurement of the second-order Doppler shift [19]. We used these values as a trial since we have no information for the case of an Fe–N system. In the third set, both the  $is$  and recoilless fraction were changed. The curve fittings were done for the three cases and the results were compared with the original one. Possible isomer shift changes and recoilless fraction changes will affect the intensities by 1% for  $I_0$  and  $I_1$ , and at most by 0.3% for  $I_2$ , and, therefore, the values of  $J_1$  and  $J_2$  could be changed.

Finally, the effect of the iron atoms surrounded by more than three nitrogen atoms should be considered. An iron atom can be surrounded by three nitrogen atoms in two ways as shown in figure 5. In the first type (figure 5(e)), nitrogen atoms are situated in a plane, and in the second (figure 5(f)), they are placed three-dimensionally. For the former type:

$$QS = 0.75e^2 |q| Q(1 + \eta^2/3)^{1/2}$$

and for the latter  $QS = 0$ . However, a spectrum component corresponding to the former type was not observed within the experimental accuracy, and a component for the latter could not be distinguished from that for Fe(0).

De Cristofaro and Kaplow concluded from the intensity ratio of  $\gamma_0$  and  $\gamma_1$  that nitrogen atoms are randomly distributed [8]. However, their result seems to be less reliable, since they have only observed  $\gamma_0$  and  $\gamma_1$  and failed to detect the  $\gamma_2$  component because of statistical accuracy.

Bauer and co-workers reported for the Fe–C system the existence of two single peak components with different  $I$  values [12, 13]. The origin of the first component is attributed to the Fe atoms with no first- and second-nearest C atoms, while that for the second component is attributed to those with no first-nearest C atoms but several second-nearest atoms. However, in the present work for Fe–N austenite, the second single peak component was not distinct.

From the previous measurements of activity as mentioned in section 1, it has been concluded that the interaction between nitrogen atoms in austenite is repulsive. The activity measurement gives only an overall effect of the interaction between nitrogen atoms in the solid solution, and is therefore in reasonable agreement with the present Mössbauer data, which show that the magnitude of the repulsive force interacting between the first-nearest-neighbouring nitrogen atoms exceeds that of the attractive force between the second-nearest atoms.

## 5. Conclusion

The interaction between nitrogen atoms in Fe–N FCC austenite was investigated by Mössbauer spectroscopy taking the effect of thickness explicitly into account. Comparing the experimentally obtained fractions of Fe–N pairs and N–Fe–N linear configurations with those calculated by assuming the random distribution of nitrogen atoms, it is concluded that the interaction is strongly repulsive ( $-360$  K) between the first-nearest-neighbouring atoms and weakly attractive between the second-nearest.

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