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The influence of carbon on nitrogen substitution in iron ε-phases

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Mössbauer spectroscopy of nitrided and carbonitrided iron powders and plates with total interstitial atom contents of between 24 and 33 at% has allowed the variation with composition of the hyperfine magnetic fields of metal atoms with 2 or 3 close interstitial atoms to be determined. Fe atoms with three non-metal nearest neighbours and paramagnetic behaviour have also been detected. Only when the content of non-metal atoms goes beyond 30 at%, do Fe atoms in ε-carbonitrides display higher magnetic fields than in the corresponding ε-nitrides. The lower number of electrons contributed to the iron 3d-orbitals by C atoms than by N atoms is considered the cause of the above phenomenon. The variation of other hyperfine parameters with composition is also discussed.

1. Introduction

In ε-iron nitrides and carbonitrides Fe atoms with different first-neighbour configurations of interstitial elements can be encountered. These phases have a wide field of homogeneity whose range varies appreciably with the temperature [1–4], see Fig. 1; whilst the maximum nitrogen content is very close to an Fe_2N composition in the 725 to 775 K range (i.e. 33 at%, $Fe_{2.03}N$) [2, 3], quantities as low as 15.8 at% ($Fe_{5.3}N$) have also been recorded in solids quenched from about 975 K [2, 4]. Also in the case of carbonitrides, their interstitial atom content has been seen to vary widely between $Fe_{4.38}(C_{0.26}N_{0.74})$ [5] and $Fe_{1.97}(C_{0.22}N_{0.78})$ [1]; in some cases C atoms can replace up to 55% of the N atoms [5].

Upon increasing the C and N content the lattice parameters of the hexagonal close-packed (h c p) unit cell vary, as indicated by the following equations [6], where $x_{(C+N)}$ is the (C + N) atomic fraction, and a and c are in nm,

$$a = (4.353 + 1.337x_{(C+N)}) \times 0.1 \pm 0.0007 \quad (1)$$

and

$$c = (4.233 + 0.578x_{(C+N)}) \times 0.1 \pm 0.0007. \quad (2)$$

The above equations can be considered valid for ε-nitrides and carbonitrides of iron in an interstitial atom content range of 18.6 to 33 at%, being slightly less approximate in the case of carbonitrides when $x_{(C+N)}$ exceeds 0.30 [7].

C and N atoms occupy the octahedral interstices in the metal h c p lattice. There are six holes of this type around each Fe atom in the h c p array, three in each of the two planes immediately above and below it.

Layers of these sites are positioned one on top of the other yielding a simple hexagonal lattice of interstices. They have a distance of closest approach in the metal lattice c direction. Such a distance is only $\sqrt{2/3}$ of the distance of closest approach in the hexagonal plane. Since interstitial atoms promote distortion of the metal lattice, they tend to position themselves as far apart as possible, thus never occupying first-neighbour interstices in the c direction at the same time. This leads to a possible simultaneous occupation of only three of the six holes surrounding each Fe-atom and thus to the Fe_2 (C, N) limiting composition; therefore, only Fe atoms with zero to three

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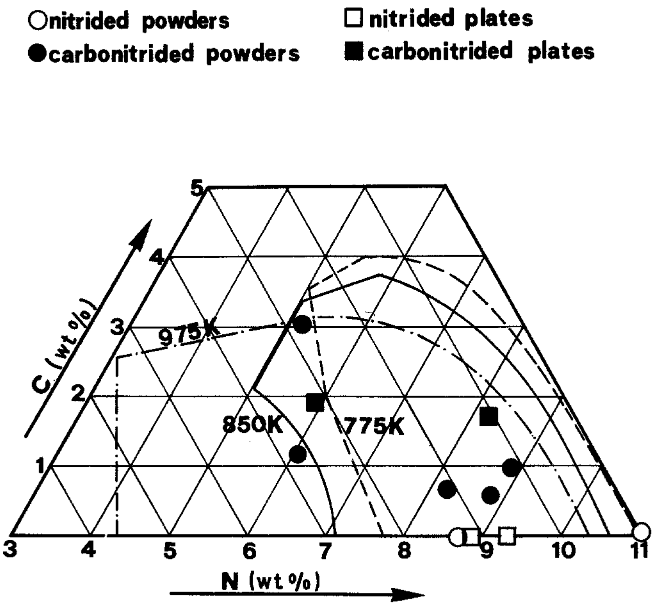

Figure 1 Boundaries of the ϵ-phase field in the metastable Fe–C–N system at various temperatures (from [1]); the different points represent the composition of prepared samples (Table II). Symbols refer to the same type of samples throughout the paper.

interstitial neighbours can be found in ϵ-type iron solids.

Shirane, Takei and Ruby [8] first suggested that different first-neighbour interstitial nitrogen configurations can cause different Mössbauer spectra of individual iron atoms in Fe_4N solids. This concept has been applied to the study of ϵ-iron nitrides close to the Fe_2N composition and to ζ-iron nitrides by Chababel, Janot and Motte [9]. Later Eickel and Pitsch [10], Mekata, Yoshimura and Takaki [11] and Foct [12] investigated ϵ-solids with lower nitrogen contents. They collectively identified three types of iron atoms with different electron distributions and ferromagnetic behaviour in addition to the type of iron atom with paramagnetic behaviour at room temperature identified in [9] and hereby indicated as Fe–Q. Table I lists all the results due to the above researchers. According to the different authors, different electronic distributions, as indicated by the isomer shifts pertaining to each type of atom, signal a different environment of first-neighbour interstitial N atoms: therefore, in Table I the notations Fe–0, Fe–I, Fe–II and Fe–III refer to iron atoms without close interstitial atoms and with 1, 2, or 3 interstitial N atoms, respectively. Although it is felt that the type of iron atom described in [11] for ζ-solids might be of the same type as the iron atom singled out in [9] (Fe–Q), it has been listed in a different column (Fe′–III), as there is a lack of correlated data between the two. Furthermore, both the above Fe atoms and the other one listed as Fe–III in Table I must have the same first-neighbour interstitial atom configuration, but their magnetic properties differ.

It must be noted that the existence of iron atoms with no close nitrogen atoms is not described by the above authors in ϵ-nitrides. De Cristofaro and Kaplow [13], by varying the N content between 17.1 and 25.5 at%, found that at the lowest N level and at 80 K, all Fe–0, Fe–I, Fe–II and Fe–III sets of Mössbauer peaks are present and a random arrangement of interstitial atoms exists. At higher N contents and at room temperature, spectra are composed of Fe–I, Fe–II and Fe–III sets of peaks, with average field intensities, H, being 284, 227 and 130 kOe, respectively (to convert to Si units: $1\,\text{kOe} \equiv 1/4\pi\ \text{MA}\,\text{m}^{-1}$).

Furthermore, results by the same authors show that the Fe–II room-temperature hyperfine magnetic field has a bell-shaped variation with N content, although the way it decreases for N-amounts greater than the maximum (24 to 25 at%) does not seem clearly established by existing data [9, 11]. Moreover, by ascertaining that the Curie temperature of low N solids drops below the ambient temperature, De Cristofaro and Kaplow suggested that this magnetic characteristic has a similar bell-shaped variation with the N content, falling to lower values at both sides of the peak value, which occurs at 567 K at a composition of about 24 at% [14].

Regarding ϵ-iron carbonitrides, no systematic

TABLE IA Hyperfine parameters relative to the spectrum of α-Fe of different Fe nuclei in iron nitrides, as ascertained by Mössbauer spectroscopy

Phase	T(K)	Magnetic components										Non-magnetic component		Reference
		Fe–0		Fe–I		Fe–II		Fe–III		Fe′–III		Fe–Q		
		δ (mm sec^{-1})	H (kOe)	δ (mm sec^{-1})	H (kOe)	δ (mm sec^{-1})	H (kOe)	δ (mm sec^{-1})	H (kOe)	δ (mm sec^{-1})	H (kOe)	δ (mm sec^{-1})	Δ (mm sec^{-1})	
α-Fe	295	0	330											[10]
γ'-Fe_4N	300	0.20	345			0.35	215							[8]
ϵ-$Fe_{4.4}N$	77			0.29	298	0.34	222							[12]
ϵ-$Fe_{3.2}N$	295			0.24	298	0.33	238							[10]
ϵ-$Fe_{2.5}N$	0					0.49	250*	0.49	150*					[11]
ϵ-$Fe_{2.09}N$	298											0.40	0.26	[9]
ζ-$Fe_{2.01}N$	298											0.42	0.27	[9]
ζ-$Fe_{2.01}N$	0									0.56	13*			[11]

TABLE IB Proposed electronic distributions for different Fe nuclei in iron nitrides

Component	Fe–0	Fe–I	Fe–II	Fe–III	Fe′–III	Fe–Q
Proposed distribution	$3d^7 4s^1$ [8]	$3d^{7.6} 4s^{0.9}$ [10]	$3d^8 4s^1$ [8] or $3d^{8.1} 4s^{0.9}$ [10]			$3d^9 4s^1$ [9] or $3d^{9.5} 4s^1$ [9]

*Extrapolated

study has been undertaken so far. Maksimov *et al.* [15] have determined for a $Fe_{2.67}(C_{0.39}N_{0.61})$ solid an hyperfine field of 250 kOe. Mössbauer spectra of these phases formed on C steel samples after N-implantation have been recently obtained [16, 17] and interpreted by means of different combinations of Fe–I, Fe–II, Fe–III, and Fe–Q individual sets of peaks for varying N-ion implanted doses. Unfortunately, no composition measurement could be performed and associated with Mössbauer data obtained.

From the above literature review, it was decided that the completion of the systematic study of ϵ-iron nitrides in the 25 to 33 at% range was very attractive, especially in ascertaining the variation of the Fe–II room-temperature hyperfine magnetic field intensities. Studies of ϵ-nitrides of this compositional range should also throw more light on the Fe–III hyperfine parameters about which data are very limited. A greater insight on the occurrence of Fe–Q type components should also be obtained. Furthermore, a systematic study of ϵ-carbonitrides in the same range of interstitial atom content has been undertaken to complete a series of studies on these phases, which was begun a few years ago [7, 18]. In fact the occurrence of ϵ-carbonitrided steel pieces has made the study of their properties very important [19, 6].

2. Experimental procedure

2.1. Sample preparation and analysis

Pure iron powders ($Fe \geqslant 99.99$ wt%) and Armco iron plates were heat-treated at various temperatures for different lengths of time in an ammonia or in ammonia and methyl alcohol flow to obtain nitrided and carbonitrided samples of varying compositions in the above proposed interstitial atom content range (Table II). One carbonitrided plate was treated in an alkali cyanate salt bath. Samples were quenched after the heat-treatment.

X-ray diffraction analysis of all samples was performed (radiation FeKα; $\lambda = 0.19373$ nm) either to determine their constitution (Table II) using the procedure already described elsewhere [6, 19] as a guide to the selection of Mössbauer spectra fitting components, or to obtain the individual values of the C and N contents in ϵ-phases as described below.

In fact, (0 0 2) (1 1 0), and (1 1 1) ϵ-phase reflection angles were measured to determine the individual a and c lattice parameters. These have been input into Equations 1 and 2 to determine the total interstitial atom content of each solid as an average of the $x_{(C+N)}$ values computed by the two equations. In the case of nitrided specimens $x_{(C+N)}$ values have been considered representative of the N content, as reported in Table II. For carbonitrided samples, C contents have been determined by oxygen combustion and CO_2 titration for powder specimens or by X-ray wavelength dispersion analysis in a microprobe connected to a scanning electron microscope in the case of heat-treated plates (see 18, 20]). C analysis results have been normalized according to X-ray phase determination results to compute the exact C content of the ϵ-phase when it was not the only phase present in the samples. In fact Fe_3C was formed in the samples with the highest C content; small amounts of Fe_3O_4 were evident from the X-ray diffraction spectra of some samples prepared at 975 K.

It must be noted that in the case of heat-treated plates a gradient in composition has to be expected in the top layers. Furthermore, in the case of the carbonitride samples an increase of C content at increasing distances from the surface has been found [20, 21]. Accordingly, X-ray diffraction analysis and C content microprobe determinations for these types of sample have been repeated at various depths as in [19] and [20] and results averaged. Finally, C wt% values and $x_{(C+N)}$ values have been combined in a computer program to derive the C and N individual weight and atomic percentages in ϵ-solids as reported in Table II. Points representing the C and N contents of each sample have been plotted in Fig. 1.

2.2. Mössbauer measurements

The Mössbauer spectra of samples kept at room temperature were recorded in transmission for powder samples and in back-scattering for plate specimens by means of a conventional spectrometer with a constant acceleration movement. A ^{57}Co source in a Rh matrix with 100 mCi nominal activity was used. Owing to the above mentioned gradients of composition in the top layers of surface nitrided and carbonitrided plates, it was decided to record the back-scattered conversion X-rays, which allow a greater penetration depth than conversion electrons. Counts in this case were detected by a gas flow proportional

TABLE II Preparation procedure, phase constitution and composition of ϵ-phases of nitrided and carbonitrided specimens.

Sample		Heat-treatment parameters			Sample constitution (wt %)	ϵ-phase composition		
Letter	Composition	Medium	Temp (K)	Time (h)		$x_{(C+N)}$	C (wt %)	N (wt %)
Nitrided iron powders								
F	$Fe_{2.66}N$	NH_3	775	200	ϵ	0.273	–	8.61
G	$Fe_{2.02}N$	NH_3	615	24	$\epsilon + \zeta$ (45 %)	0.331	–	11.05
Nitrided iron plates								
N	$Fe_{2.60}N$	NH_3	975	3	ϵ^*	0.277	–	8.79
H	$Fe_{2.47}N$	NH_3	775	200	ϵ	0.288	–	9.22
Carbonitrided iron powders								
C	$Fe_{3.16}(C_{0.18}N_{0.82})$	$NH_3 + CH_3OH$	925	4	ϵ	0.240	1.12	6.05
B	$Fe_{2.66}(C_{0.39}N_{0.61})$	$NH_3 + CH_3OH$	925	5	$\epsilon + Fe_3C$ (10 %)	0.273	2.93	5.23
A	$Fe_{2.55}(C_{0.08}N_{0.91})$	$NH_3 + CH_3OH$	975	7	ϵ	0.281	0.65	8.19
D	$Fe_{2.42}(C_{0.07}N_{0.93})$	$NH_3 + CH_3OH$	875	3	ϵ	0.292	0.53	8.77
E	$Fe_{2.25}(C_{0.11}N_{0.89})$	$NH_3 + CH_3OH$	775	5	ϵ	0.308	0.92	8.98
Carbonitrided iron plates								
M	$Fe_{2.82}(C_{0.27}N_{0.73})$	NH_3 + ($NH_3 + CH_3OH$)	975	3 + 3	$\epsilon + Fe_3C$ (5 %)*	0.260	1.87	5.94
Q	$Fe_{2.21}(C_{0.19}N_{0.81})$	alkali cyanates	845	12	ϵ	0.312	1.69	8.27

*Small amounts of magnetite were present counter employing a 90% Ar–10% methane mixture.

Spectral data were fed into a computer and interpreted by a calculation program based on the least squares method to fit a number of Lorentzian profiles. Since in most cases complex spectra were obtained, the fitting procedure was done assuming that the spectra were due to additions of individual spectra originated by Fe atoms with different environments, namely those already indicated as Fe–0, Fe–I, Fe–II, Fe–III and Fe–Q in Table I, coupled, where applicable, to iron atoms of the Fe_3C and Fe_3O_4 type.

The results of different computer runs for each spectrum were compared on the basis of both the resulting χ^2 distribution and the more reasonable spectral model foreseeable from composition and X-ray diffraction data.

The Mössbauer parameters obtained by the fitting procedure described above are reported in Table III. Values of the isomer shift, δ, with α-iron as a reference, the hyperfine magnetic field intensity, H, and the peak half-width of the outer lines, $\Gamma/2$, are listed for the magnetic components, whilst the quadrupole half-splitting, $\Delta/2$, was reported instead of H in the case of the non-magnetic component Fe–Q. The percentage area of the total spectrum pertaining to each component is also given in Table III, along with the χ^2 value obtained for each sample from the spectral data fitting calculation. It must be noted that for the sake of simplicity, only the normalized relative areas of the ϵ-components are reported in the table.

Individual Mössbauer spectra with the interpolating lines resulting from the selected fit are reported in Fig. 2 for nitrided powders and in Fig. 3 for nitrided plates. Spectra of the car-

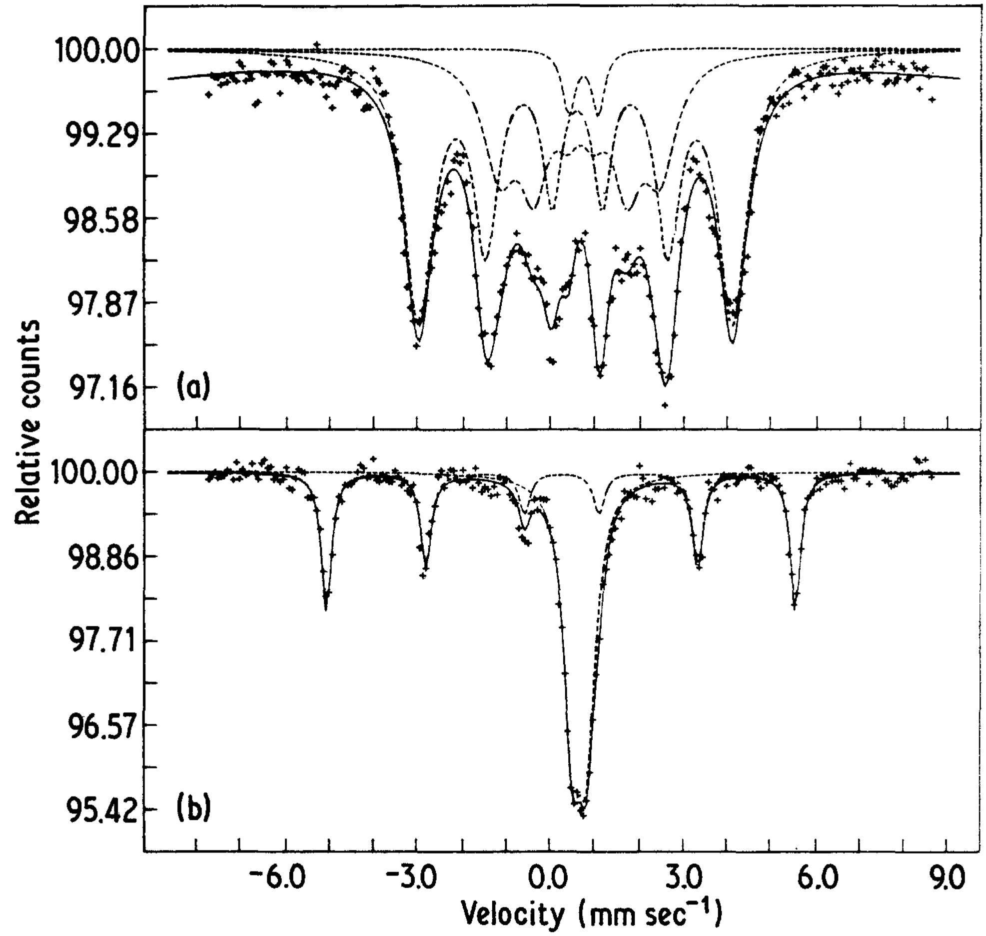

Figure 2 Mössbauer spectra with interpolating lines for nitrided powders showing (a) Sample F and (b) Sample G. Spectra of individual components are also shown as dashed lines. α-Fe was added to sample G for comparison purposes.

TABLE III The Mössbauer parameters of fitted spectra: H in kOe, δ, $\Delta/2$, and $\Gamma/2$ in mm sec^{-1}. Isomer shifts are referred to α-iron.

Sample		Magnetic components									Non-magnetic component			Area (%)				χ^2
Letter	Composition	Fe–I			Fe–II			Fe–III			Fe–Q			Fe–I	Fe–II	Fe–III	Fe–Q	
		δ	H	$\Gamma/2$	δ	H	$\Gamma/2$	δ	H	$\Gamma/2$	δ	$\Delta/2$	$\Gamma/2$					
Nitrided iron powders																		
F	$Fe_{2.66}N$				0.34	220	0.40	0.41	112	0.45	0.49	0.33	0.17		62	34	4	1.2
G	$Fe_{2.02}N$										0.40	0.18	0.26				100	1.0
Nitrided iron plates																		
N	$Fe_{2.60}N$				0.35	212	0.28	0.60	141	0.28	0.30	0.35	0.32		59	19	22	1.0
H	$Fe_{2.47}N$				0.32	211	0.40	0.40	110	0.31	0.31	0.43	0.40		59	35	6	0.6
Carbonitrided iron powders																		
C	$Fe_{3.16}(C_{0.18}N_{0.82})$	0.23	291	0.16	0.28	228	0.32	0.55	135	0.30				11	82	7		1.0
B	$Fe_{2.66}(C_{0.39}N_{0.61})$				0.29	229	0.29	0.42	139	0.33					65	35		1.1
A	$Fe_{2.55}(C_{0.08}N_{0.91})$				0.33	209	0.39	0.40	114	0.34	0.48	0.41	0.26		61	35	4	1.2
D	$Fe_{2.42}(C_{0.07}N_{0.93})$				0.30	199	0.39	0.38	100	0.58	0.40	0.32	0.33		42	46	12	1.4
E	$Fe_{2.25}(C_{0.11}N_{0.89})$				0.32	196	0.29	0.41	95	0.28	0.50	0.28	0.21		15	71	14	1.2
Carbonitrided iron plates																		
M	$Fe_{2.66}(C_{0.27}N_{0.73})$				0.31	228	0.27	0.57	136	0.28					76	24		1.0
Q	$Fe_{2.21}(C_{0.19}N_{0.81})$				0.34	201	0.32				0.41	0.14	0.21		11		89	1.0

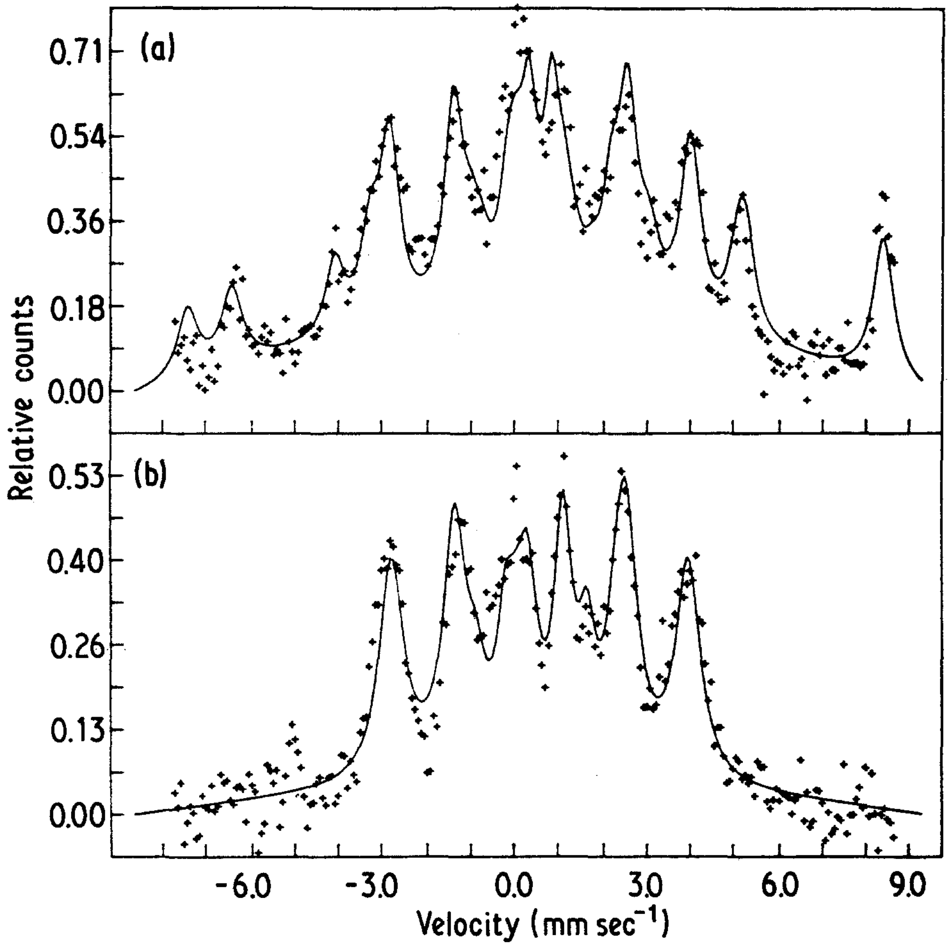

Figure 3 Mössbauer spectra with interpolating lines for (a) Sample N and (b) Sample H (nitrided plates).

bonitrided powders and plates are shown in Figs 4 and 5, respectively.

2.3. Analysis of results

The evolution of Mössbauer spectra with the increase of the interstitial atom content is essentially the same for nitrided and carbonitrided samples. As $x_{(C+N)}$ is raised above 0.25 the sextet due to Fe–I nuclei disappears, and the one due to the Fe–III atoms tends to become more evident; when $x_{(C+N)}$ approaches 0.3 spectral analysis is more troublesome and individual components are difficult to isolate (see, for instance, Fig. 4). When the atomic fraction is between 0.31 and the maximum of 0.33, the spectrum shows only a quadrupole split doublet characteristic of a ferromagnetic substance above its Curie point (see spectra of Samples Q, Fig. 5, and G, Fig. 2).

It is worth noting that in ε-nitrides and carbonitrides with a high interstitial atom content the occurrence of such a doublet can be detected in Mössbauer spectra well before $x_{(C+N)}$ reaches 0.33. In fact, for $x_{(C+N)} > 0.27$, the occurrence of such a spectral component cannot be mistaken and its contribution increases as the interstitial occupancy increases.

In Sample G, ε-Fe_2N and ζ-Fe_2N are simultaneously present. In this respect, Chabanel, Janot and Motte [9] attributed essentially the same isomer shifts and quadrupole splittings to iron atoms of the ε-phase close to maximum composition and of the ζ-phase. Our results, indeed, confirm the presence in room temperature spectra of only one non-magnetic component with Mössbauer parameters similar to the reported ones [9]. On the other hand, a further test carried out at 77 K on Sample G showed no significant difference with respect to the room-temperature spectra. This is in accord with the magnetic studies of Mekata, Yoshimura, and Takaki [11], who

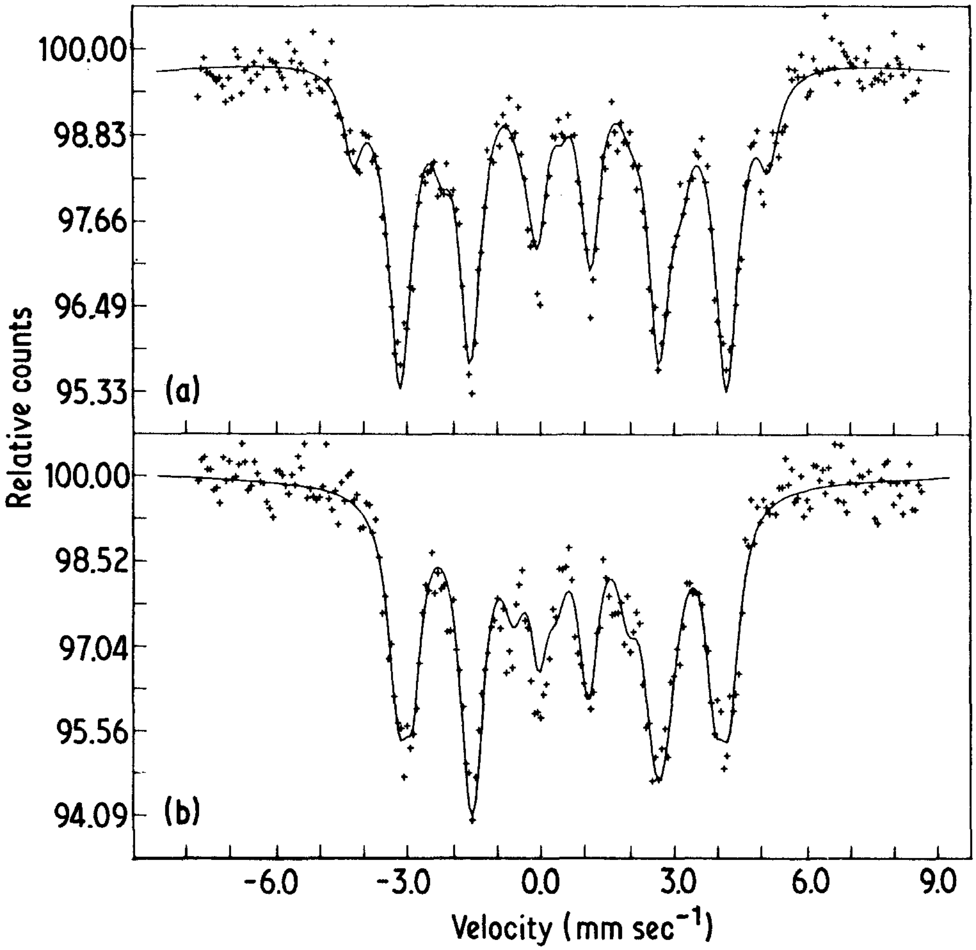

Figure 4 Mössbauer spectra with interpolating lines for carbonitrided powders showing (a) Sample C (b) Sample B (c) Sample A (d) Sample D and (e) Sample E.

found that the Curie temperatures of the ϵ-phases at maximum N content and of the ζ-phase are much lower than those proposed by Bridelle [9] and by Chabanel, Janot and Motte [14], i.e., 103 and 83 K, respectively.

Besides the lines due to iron nitrides and carbonitrides, sextets due to the presence of Fe_3O_4 are evident in spectra of Samples N and M (Figs 3 and 5). The presence of the unresolved sextet of Fe_3C (considered on the basis of X-ray diffraction measurements) was ascertained in Samples B and M.

3. Discussion

3.1. Variation of hyperfine parameters with the composition of ϵ-solids.

The above reported results clearly confirm that in ϵ-iron nitrides and carbonitrides room-temperature Mössbauer spectra are due to the contributions of four types of Fe nuclei, i.e., Fe–I, Fe–II, and Fe–III, which are ferromagnetic and Fe–Q which is paramagnetic.

Many of the room-temperature hyperfine parameters of the above nuclei vary widely with the compositon, thus justifying the scattering of the data attributed to them by different authors upon analysing samples of different composition.

Fig. 6 shows the variation of the room-temperature hyperfine magnetic field intensity, H, at Fe–II and Fe–III nuclei against the interstitial atom fraction, $x_{(C+N)}$. In Fig. 6, values of room-temperature fields at Fe–II nuclei, as determined by De Cristofaro and Kaplow [13] and by Foct, Dubois and Le Caer [22], have also been inserted, along with data of Fe–II and Fe–III atoms, derived from results by Mekata, Yoshimura and Takaki [11].

The variation of Fe–II room-temperature

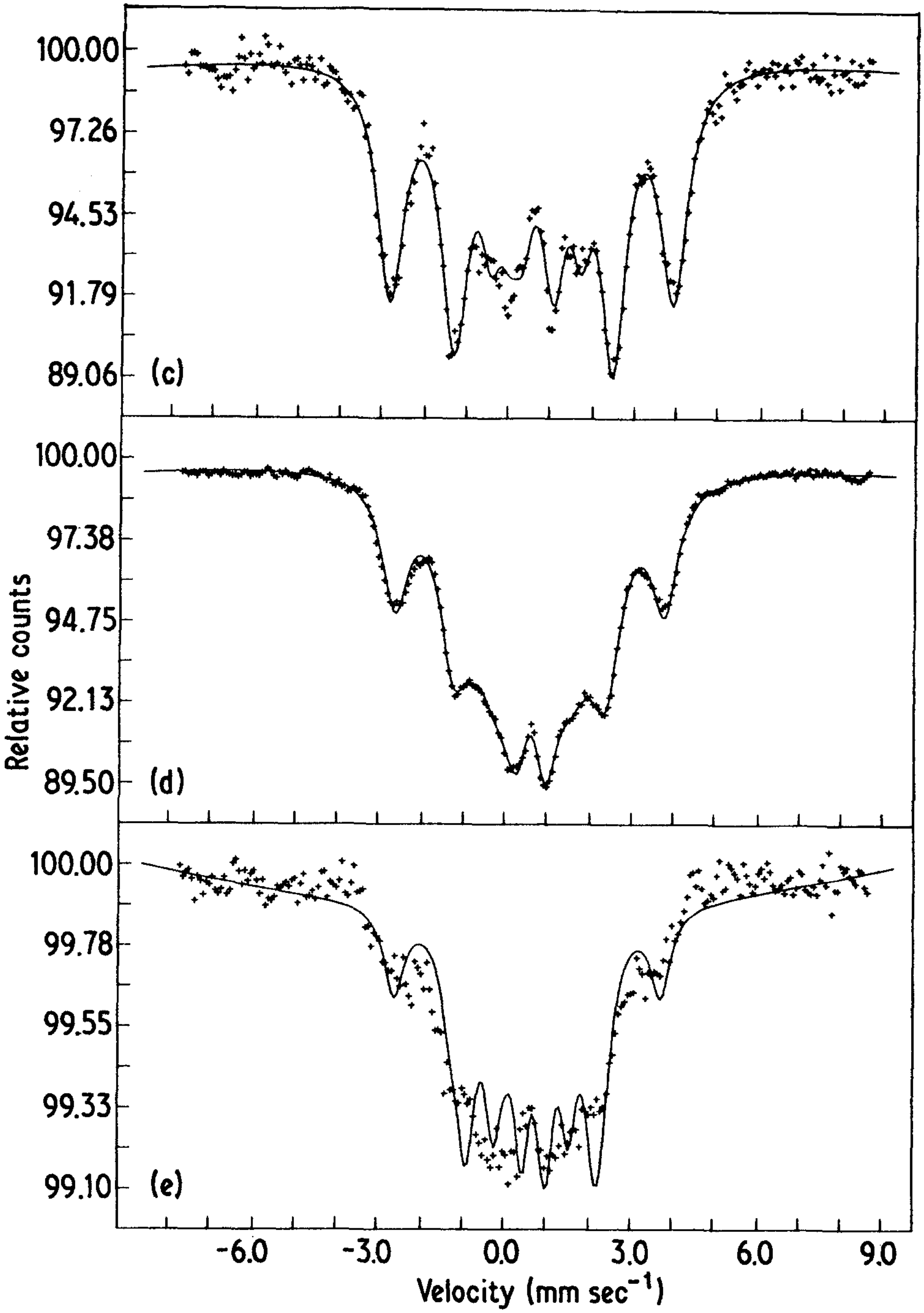

Figure 4 Continued.

fields is definitely established by the scatterband of ϵ-nitride results. As already discussed elsewhere [13], $H_{(\text{Fe—II})}$ reaches a maximum value of 225 to 230 kOe in the 0.24 to 0.27 $x_{(\text{N})}$ range and then drops to lower and lower values on both sides of the maximum. By considering that at 17.1 [13] and at 32.2 at % N [9] the Fe—II fields are already zero, the extreme compositions at which the Curie point reaches room temperature must correspond to about $x_{(\text{N})} = 0.175$ and $x_{(\text{N})} = 0.305$. The Fe—II band in Fig. 6 has been drawn accordingly.

ϵ-iron-carbonitrides results fall in the same scatterband as ϵ-nitrides as long as $x_{(\text{C+N})}$ stays below 0.295. At higher interstitial atom content

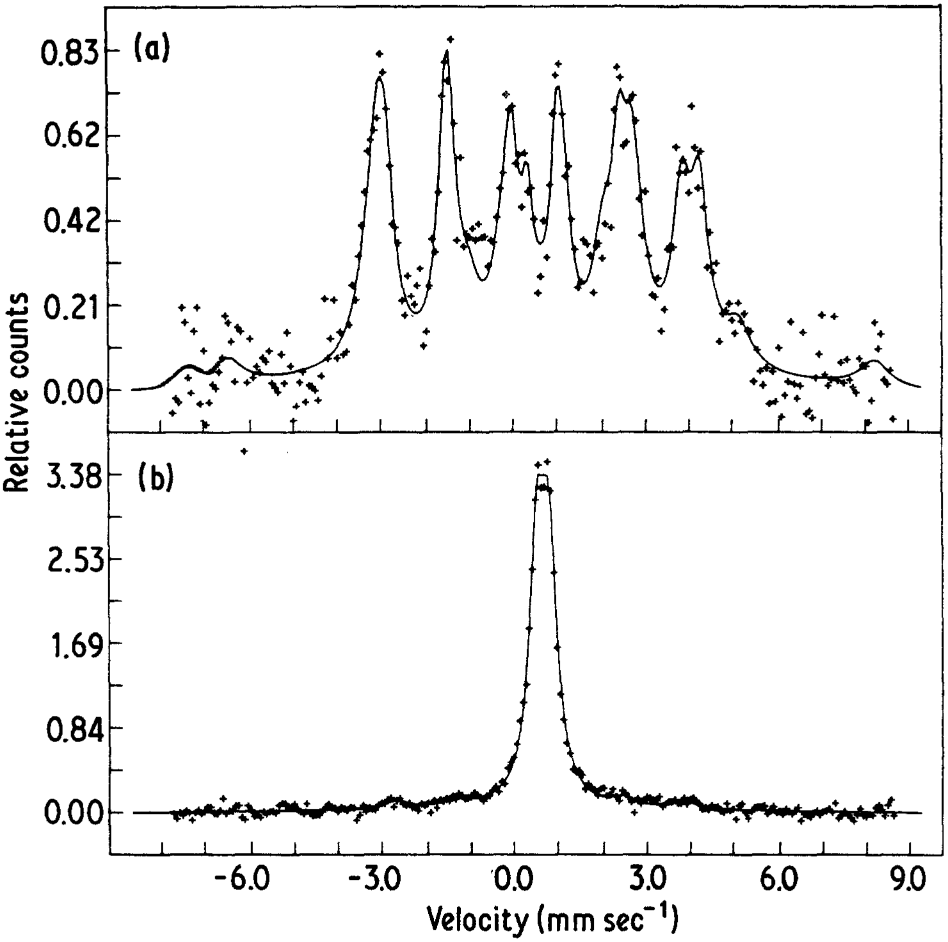

Figure 5 Mössbauer spectra with interpolating lines for carbonitrided plates (a) Sample M and (b) Sample Q.

however, data from Samples E and Q indicate that $H_{(\text{Fe—II})}$ for carbonitrides is decidedly higher than for nitrides.

The above described behaviour of the Fe–II type of nuclei has been taken as a clue in drawing the scatterband pertaining to Fe–III atoms. In fact, lacking detailed data up to $x_{(\text{N})} = 0.255$ from De Cristofaro and Kaplow [13], the results of ϵ-carbonitrides of the present investigation in the 24 to 27 (C + N) at % range are taken as representative of those of the corresponding nitrides. This would indicate a maximum Fe–III field of 135 to 140 kOe which is very close to the 130 kOe average value already found [13]. Above $x_{(\text{N})} = 0.27$ a drop in H values also can be seen for Fe–III. In this range the scatterband has a negative slope slightly lower than that of Fe–II so that for $x_{(\text{N})}$ values greater than 0.30 the two bands coalesce. Also in this case, at high interstitial atom contents, the presence of C yields a higher field than when it is absent, whereas for $x_{(\text{C+N})} < 0.295$ carbonitride data are comparable to those of the corresponding nitrides.

The close resemblance of the variations of the Fe–II and Fe–III room-temperature hyperfine fields of ϵ-iron nitrides and carbonitrides for $x_{(\text{C+N})} \geqslant 0.24$ is a proof that, whatever the iron–interstitial atom degree of co-ordination, the ferromagnetic characteristics of iron atoms are equally affected by the composition. A corresponding behaviour should be expected for Fe–I type atoms in their field of existence; for $x_{(\text{C+N})} < 0.24$, Fe–I room-temperature fields should yield values progressively lower than the maximum of approximately 295 kOe that can be obtained by averaging results of this study and of that by Eickel and Pitsch [10]. The single value found in the literature for this range of compositions, 225 kOe [22], confirms the above hypothesis.

The fact that the variation of room-tempera-

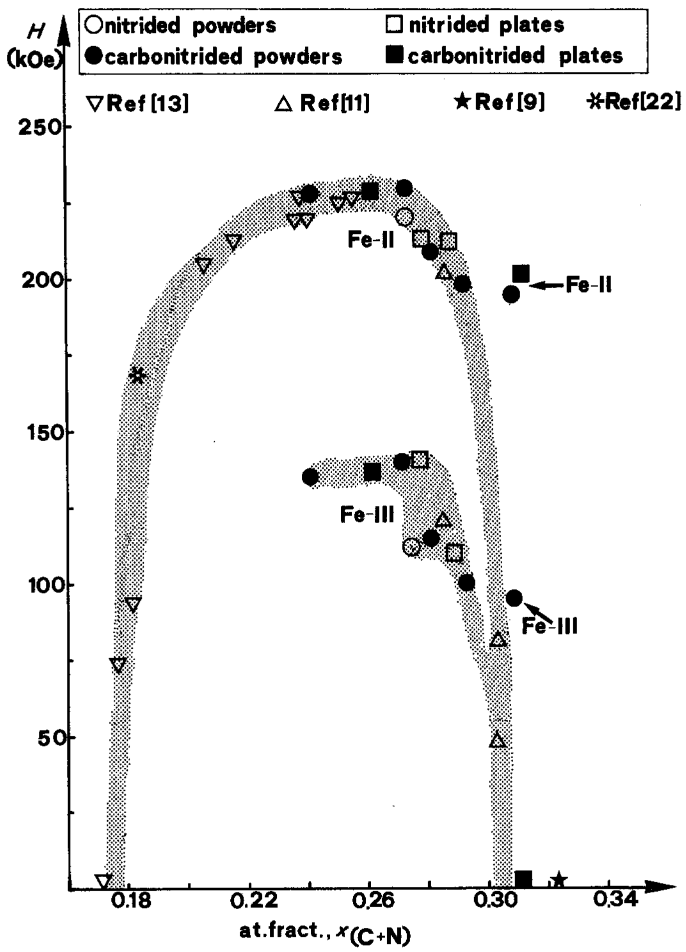

Figure 6 Room-temperature hyperfine magnetic fields of Fe–II and Fe–III as a function of interstitial atom content. The scatterbands refer to ϵ-nitrides results.

ture hyperfine fields with composition in ϵ-solid solutions is strongly related to the corresponding variation of the Curie temperature has already been pointed out [13]. The present work shows that, in effect, a C for N substitution does not play any role in the magnetic properties of ϵ-phases as long as their interstitial content does not go beyond about 30 at%. This seems to be in contrast with the Curie point measurements performed by Bridelle [14] on ϵ-iron nitrides and carbonitrides. His conclusions seem to indicate a constant rise of about 100 K in the Curie temperature upon substituting carbon for nitrogen. Yet, a closer examination of Bridelle's data leads to different considerations. In fact, neglecting the sudden rise in Curie temperture for a carbonitride with a (C + N) atomic content of 23.9% (no individual values of the C and N contents are ever given by the author), the difference between the ϵ-nitride and ϵ-carbonitride Curie points, in the whole field of $x_{(C+N)}$ from about 0.24 to 0.28, is of no more than 20 K and goes to larger values only at higher interstitial contents. With some difference in the limiting composition, a similar conclusion has already been drawn from the present results.

The analysis of isomer shifts of Mössbauer spectra ferromagnetic components as a function of the composition of ϵ-phases can be carried out with the help of Fig. 7. δ values of Fe–II atoms are essentially constant at a 0.32 mm sec^{-1} level (standard deviation, σ, equal to 0.022 mm sec^{-1}). On the other hand, isomer shift values for Fe–III atoms, if an inordinately large one is neglected (Sample N), are constant at a high level up to $x_{(C+N)} \simeq 0.27$ and then decrease to a lower level as the composition goes beyond this value.

The half-width of the outer lines for Fe–II and Fe–III do not seem really to be influenced by the composition. The mean values for the

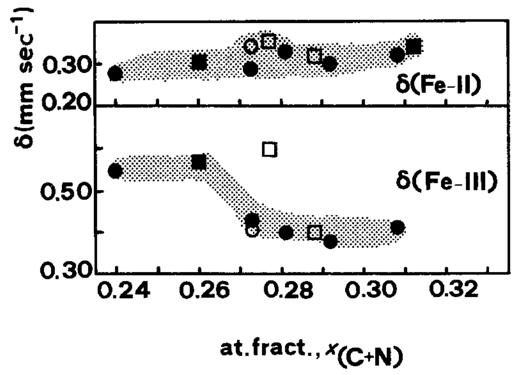

Figure 7 Variation of the isomer shift, δ, for Fe–II and Fe–III type atoms against the interstitial atom content.

half-width are large, 0.33 and 0.35 mm sec^{-1}, respectively, with a greater dispersion for Fe–III. This is a signal of a multiplicity of second-order neighbour interstitial configurations.

Also, δ and $\Gamma/2$ values of Fe–Q atoms do not seem to be influenced by the interstitial atom content. Their scatter is wide: $\delta = 0.41 \pm 0.14$ mm sec^{-1}; $\Gamma/2 = 0.27 \pm 0.14$ mm sec^{-1} (mean values $\pm\, 2\sigma$). Instead, $\Delta/2$ values decrease with the interstitial atom content (Fig. 8); this can be ascribed to a progressively more regular electronic charge distribution at Fe–Q nuclei. These nuclei become predominant in the structure as the sum of C and N atoms increases. The limiting value of 0.14 mm sec^{-1} corresponds to that measured for an Fe_2N compound by Chabanel *et al.* [9].

No clear influence of the C for N substitution on values of δ, $\Delta/2$, and $\Gamma/2$ has been recorded for any component. In fact, for values pertaining to ϵ-iron nitrides or carbonitrides, no particular subset of values can be referred specifically to one phase or the other.

3.2. Ordering in ϵ-solids

Although four types of Fe atoms contribute to the formation of the above Mössbauer spectra, only three types of Fe atoms can be singled out in the ϵ-phase investigated with regard to the first-neighbour interstitial site occupancy, namely atoms with 1, 2 or 3 close occupied holes. Therefore, Fe–III and Fe–Q atoms must indeed be of the same type regarding the interstitial atom configuration, their differing magnetic behaviour being caused by different electronic configurations (see below). The Fe′–III type of atoms (Table I) [11] should be the low-temperature magnetic counterpart of the room-temperature Fe–Q type atoms.

The computer separation of spectra into individual components clearly signals that a strong tendency to ordering exists as the (C + N) atomic content goes beyond 25%. In fact, no Fe–I type atoms have been detected above such a limiting composition, whereas, given the hypothesis of random occupancy, some of these should be observed.

The sum of the areas under the Fe–III and Fe–Q components of the spectra (iron atoms with 3 interstitial atoms as first-neighbours) has been plotted in Fig. 9, and shows a regular behaviour. In fact, the data points cluster around a straight line showing an increase of the fraction of (Fe–III + Fe–Q) atoms at increasing interstitial atoms content, as can be expected from composition considerations.

In Fig. 9 the points representing the areas pertaining to iron atoms with a paramagnetic behaviour, Fe–Q, have also been plotted. It is evident that there is a slow increase of the number of Fe–Q atoms in the 0.27 to 0.31 range followed by a sudden jump to reach the total of iron atoms with 3 close interstitials atoms at $x_{(C+N)}$ equal to about 0.31. It can be considered that at this composition the Curie point has fallen to temperatures lower than the ambient one [14].

If the above considerations of the effect of C for N substitution on the Curie temperature of ϵ-solids are taken into account, such a jump should occur at a somewhat lower value of the interstitial atom content when carbon is absent.

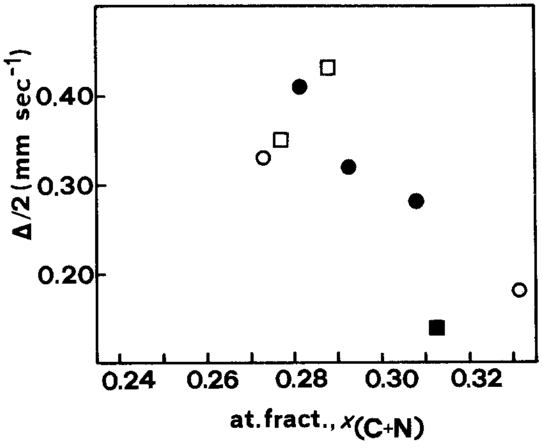

Figure 8 The quadrupole half-splitting, $\Delta/2$, for Fe–Q type atoms against the interstitial atoms content.

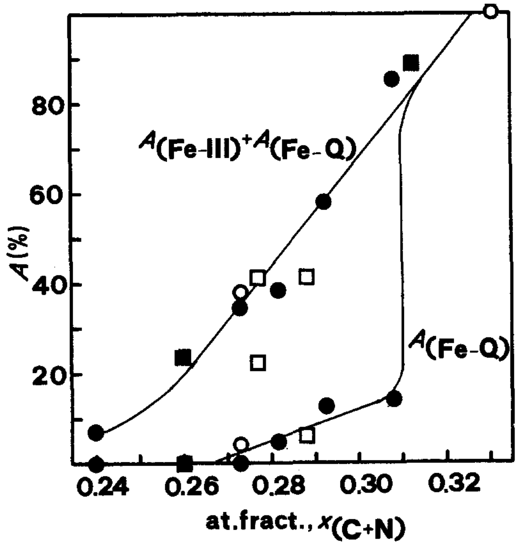

Figure 9 Sum of the relative areas, A, of Fe–III and Fe–Q components of Mössbauer spectra as a function of the composition of ϵ-phases. The variation of $A_{(Fe-Q)}$ is also reported.

Isomer shift values for Fe–III nuclei signal that they are characterized by a higher electronic density than Fe–II type nuclei [23]. The hypothesis that interstitial atoms can contribute electrons to the incompletely filled 3d band of the metal atoms has long been formulated for ϵ- and γ'-iron nitrides [24, 25]. The nitrogen was regarded either as a positive ion or as forming a covalent bond by interaction of its p electrons with the unpaired d electrons of the nearest iron atoms.

In γ'-nitride and N-austenite the occurrence in the Mössbauer spectra of a sextet due to face-centred iron atoms with an isomer shift of 0.3 mm sec^{-1} suggested again to Gielen and Kaplow [26] that these iron atoms are in a $3d^8 4s^1$ state due to covalent bonding with the neighbouring nitrogen atoms.

X-ray and electron diffraction experiments [27–29], while not discounting the covalent bonding hypothesis, would signal an increased density of electrons on non-metal atoms in γ'- and ϵ-nitrides so that their scattering factors would be augmented with respect to the neutral atoms.

In any case the formation of covalent-type bonding between the iron atoms and their close interstitial atoms in nitrides and carbonitride by interaction of hybrid sp orbitals with the unfilled Fe 3d orbitals which have an energy level considerably lower than the Fermi energy, would cause a higher screening of the iron s electrons, thus justifying positive isomer shifts of the Mössbauer components of iron nuclei.

It can be thus explained why Mössbauer spectra interpretations have always confirmed the acceptability of the donor model for the interstitial N atoms [8–10], so that in an Fe_3N ϵ-solid the contribution of 3 electrons per N atom would yield a $3d^{8.1} 4s^{0.9}$ configuration for Fe–II atoms [10].

The Fe atom electron density can increase either as a consequence of an increase of the number of donor atoms per metal atom (what happens when $x_{(C+N)}$ is raised) or by a rise in the number of electrons contributed by each interstitial atom to the bond with the metal, or by both of these phenomena.

Whilst the increase of $x_{(C+N)}$ from the lowest values up to 0.25 can account for the small increase in isomer shift on passing from Fe–I atoms to Fe–II atoms (from 0.27 to 0.32 mm sec^{-1} on average), both the phenomena must be called upon to explain the larger difference of δ values between Fe–II and Fe–III (0.32 as opposed to 0.41 mm sec^{-1}, if the average of values for $x_{(C+N)} > 0.27$ is considered). Chabanel, Janot and Motte [9] indeed hypothesized a transfer of 2 or 2.5 electronic configuration of the $3d^9 4s^1$ type can be at the 0.40–0.42 mm sec^{-1} level (see Table I).

The H values for Fe–III compared to those of Fe–II (135 as opposed to 230 kOe at maximum) would point to a 1.1 μ_B magnetic moment at 0 K for the former atoms, if the 1.9 μ_B value calculated for the latter ones [10] is taken into account. Thus, it seems reasonable that an electronic configuration of the $3d^9 4s^1$ type can be attributed to Fe–III atoms.

An additional transfer of 1 electron per N atom to the iron 3d unfilled orbitals does not cause a great change of isomer shift; the scatterband of values for Fe–Q atoms is large and the mean value (0.41 mm sec^{-1}) tends to lose a definite meaning. The fact that these Fe–Q atoms in effect yield a non-magnetic component in room-temperature Mössbauer spectra can be interpreted as a sign of a greater occupancy in their 3d band and therefore of magnetic moments (at 0 K) decidedly lower than those pertaining to Fe–III atoms. It is thus logical to conclude that Fe–Q atoms have an electronic configuration of the $3d^{9.5} 4s^1$ type. This proposed occupancy of the iron 3d orbitals is in agreement with results of studies by Fatseas [30], who on the other hand indicates a somewhat lower occupancy of 4s orbitals.

C atoms, which cannot contribute as many electrons as N atoms, cause the sudden increase of the fraction of Fe–Q atoms which occur at a higher interstitial atom content of the ε-phases and thus yield an increase of the Curie temperature of ε-carbonitrides in respect to ε-nitrides in the Fe–III → Fe–Q transition region. Also the higher Curie temperature recorded in ζ-iron carbonitrides [13, 14] in respect to ζ-iron nitrides can be explained on such a basis.

Finally, three types of ordering transitions which take place with an increase in the number of interstitial atoms can be identified in ε-type iron solid solutions obtained at 775 to 975 K. Up to a very low intersitial atom content (17.1 at % for nitrides) no ordering exists at all; Fe–0 atoms are present [13]. At higher values of the interstitial element atomic fraction, a certain degree of ordering is signalled by the disappearance of Fe–0 atoms. Then, above 25 at % (C + N) an ordered occupancy of the interstitial sites is seen with the exclusion of Fe–I type of atoms. Finally, in a region where $x_{(C+N)}$ is between 0.30 and 0.31, depending on the carbon content, an "electronic order" takes place with the disappearance of Fe–III atoms. Only when the fraction of Fe–II atoms becomes really small does a symmetry transition occur in the phase structure with the formation of ζ-solid solutions. C atoms, which tend to stabilize Fe–III and Fe–II atoms owing to their inability to contribute 5 electrons to the metal 3d orbitals, slightly enlarge the field of the ε-phase at the expense of that of the ζ-phase.

4. Conclusions

The room-temperature study of hyperfine properties of iron ε-nitrides and carbonitrides with an interstitial atom fraction, $x_{(C+N)}$, of between 24 and 33.1 at % has established the fact that 3 types of Fe atoms can be identified on the basis of the first-neighbour octahedral site occupancy, namely Fe atoms with 1, 2 or 3 close interstitial atoms. Fe atoms with three close non-metal atoms are further differentiated on the basis of their hyperfine magnetic properties; in fact, increasing fractions of these atoms with a paramagnetic behaviour (named Fe–Q) have been detected by Mössbauer spectroscopy when the interstitial atom fraction increases beyond 0.27. These seem to progressively replace the ferromagnetic atoms (Fe–III).

In the above range of homogeneity the room-temperature hyperfine fields of Fe–II (atoms with 2 close interstitials) and Fe–III atoms in ε-nitrides decrease continuously to reach a zero value when $x_{(C+N)}$ is 0.305. The carbon to nitrogen substitution does not have any significant effect on the fields as long as the atomic fraction stays below 0.295. As a consequence of this behaviour, it can be assumed that the Curie temperature also does not differ between ε-nitrides and carbonitrides. The scatterband of Fe–II H values is very narrow; together with the determination of other individual Mössbauer spectra components, it can constitute a valuable tool in determining the total interstitial atom contents of very thin ε-nitride and carbonitride layers (such as those obtained by ion-implantation on steels), to which X-ray diffraction analysis is not applicable. At (C + N) contents larger than about 30 at %, Fe–II and Fe–III fields in ε-carbonitrides are higher than those of the nitrides of corresponding composition. The above is explained by the hypothesis that Fe–III and Fe–Q atoms differ in the number of electrons, 2 and 2.5, respectively, contributed to their unfilled 3d orbitals by neighbouring non-metal atoms.

Since C atoms can share 4 electrons each at maximum, they tend to control the number of Fe–Q atoms when $x_{(C+N)}$ increases, thus causing the Curie temperature of carbonitrides to be higher than that of nitrides when the interstitial atom content is very large.

Three types of ordering transitions in ε-phases quenched from between about 775 to 975 K have been detected; from a random to a quasi-ordered occupancy of possible interstitial sites around 17.5 at % non-metals (Fe atoms with no close interstitial neighbours are no longer present) and then to an ordered occupancy as $x_{(C+N)}$ goes beyond 0.25 (atoms with only one non-metal neighbour disappear). At $x_{(C+N)}$ values around 0.30, Fe–III atoms are eliminated (only Fe–II and Fe–Q atoms remain). Only the last transition is influenced by the C content.

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