Internal Magnetic Fields, Isomer Shifts, and Relative Abundances of the Various Fe Sites in FeSi Alloys

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The "Mössbauer" technique was used to measure the internal magnetic fields and isomer shifts of Fe^{57} atoms residing at various sites in the FeSi series. The relative abundances of the various sites present in a given alloy were obtained by measuring the relative intensities of the components in the resolved spectrum of the alloy. Alloys with Si content varying from 0 to ~27 at. % were studied. In the disordered region (<10 at. % Si) three different type sites were observed. These corresponded to Fe atoms having 8, 7, and 6 nearest-neighbor Fe atoms. The internal field decreased by 0.08 H_{Fe} for each Si nearest neighbor. In the ordered region the alloys try to go into a Fe_3Al type structure. Sites having 8 through 3 nearest-neighbor iron atoms were observed. For A-type sites (4 nearest-neighbor Fe atoms and 4 nearest-neighbor Si atoms at 25 at. % Si), the internal field decreased by 0.14 H_{Fe} for each Si nearest neighbor. Over the whole series the isomer shift indicated that there was progressively less electronic charge density at the origin as the number of nearest-neighbor Si atoms increased. A measure of the relative intensities of the various magnetic field components in the spectra of an alloy series is shown to give direct evidence on the type of ordering. No tendency to form intermediate compounds other than Fe_3Si was observed. An average internal magnetic field for each alloy could be obtained from the data. This average internal field does not vary in the same way as the magnetization on the FeSi series.

INTRODUCTION

THE ease with which internal fields in solids can be measured using "Mössbauer type" experiments has led to new attempts both experimentally[1-6] and theoretically[7,8] to understand the origin of the internal magnetic field existing at a nuclear site. For some materials the measured internal field follows the magnetization curves,[3,5] indicating that the internal magnetic field is proportional to the magnetic moment. Also, in the theoretical estimates of the effective field it is generally assumed that the polarization of the s electrons and thus the internal field is proportional to the magnetic moment. It was thought that the FeSi alloy series would be a good system in which to investigate this point and try to obtain more knowledge about the internal field for the following reasons. Both the magnetization[9] and the paramagnetic susceptibility[10] have been accurately measured for the FeSi alloy series. If we assume a localized magnetic moment picture is valid for this system, then since the magnetization depends on the magnetic moments in a linear manner and the paramagnetic susceptibility depends on the square of the moments, we can combine the results of these two sets of measurements and conclude that in the disordered region the magnetic moment is located on the Fe atoms and is constant and equal to that of pure iron. (In some cases, especially for alloys containing higher transition series elements, it is known that the paramagnetic susceptibility measurements cannot be interpreted as due to localized magnetic moments, however, in the case of the disordered FeSi alloys the susceptibility decreases in a manner which strictly follows simple dilution. Thus, it seems reasonable to assume that the behavior of these alloys is similar to pure iron in this respect and that the susceptibility does result from localized moments.) Also, the lattice constant of this series is essentially constant over the whole disordered range (it has decreased by only 0.3% at 10 at. % Si), so we can hope that the contribution to the internal field from the inner electrons remains constant for the disordered alloys. Thus, we might expect that if the changes in conduction electron density were negligible the internal field would remain constant as the silicon content is varied, or if a variation in the field is observed, we could consider it as arising from the conduction electrons.

EXPERIMENTAL SETUP

All measurements were made at room temperature. The source was either an Armco iron or a platinum foil with Co^{57} diffused into the front face. When using an Armco Fe absorber and correcting for its thickness we obtained the natural linewidth. The source or absorber was mounted on a vibrator normally used for the calibration of motion pickups. Most measurements were made with the source fixed and the absorber moving.

The disordered alloys (<10 at. % Si) were prepared in foil form, while the ordered alloys had to be used in powder form. The foils were rolled and then etched down to 1 to 2 mil. Both the powder and foils were

[1] S. S. Hanna, J. Heberle, C. Littlejohn, G. J. Perlow, R. S. Preston, and D. H. Vincent, Phys. Rev. Letters **4**, 177 (1960); S. S. Hanna, J. Heberle, G. J. Perlow, R. S. Preston, and D. H. Vincent, ibid. **4**, 513 (1960).

[2] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960).

[3] D. E. Nagle, H. Frauenfelder, R. D. Taylor, D. R. F. Cochran, and B. T. Matthias, Phys. Rev. Letters **5**, 364 (1960).

[4] A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, Phys. Rev. Letters **5**, 553 (1960).

[5] C. E. Johnson, M. S. Ridout, T. E. Cranshaw, and P. E. Madsen, Phys. Rev. Letters **6**, 450 (1961).

[6] P. A. Flinn and S. L. Ruby, Phys. Rev. **124**, 34 (1961).

[7] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

[8] D. A. Goodings and V. Heine, Phys. Rev. Letters **5**, 370 (1960).

[9] D. Parsons, W. Sucksmith, and J. E. Thompson, Phil. Mag. **3**, 1174 (1959); M. Fallot, Ann. Phys. (Paris) **6**, 305 (1936).

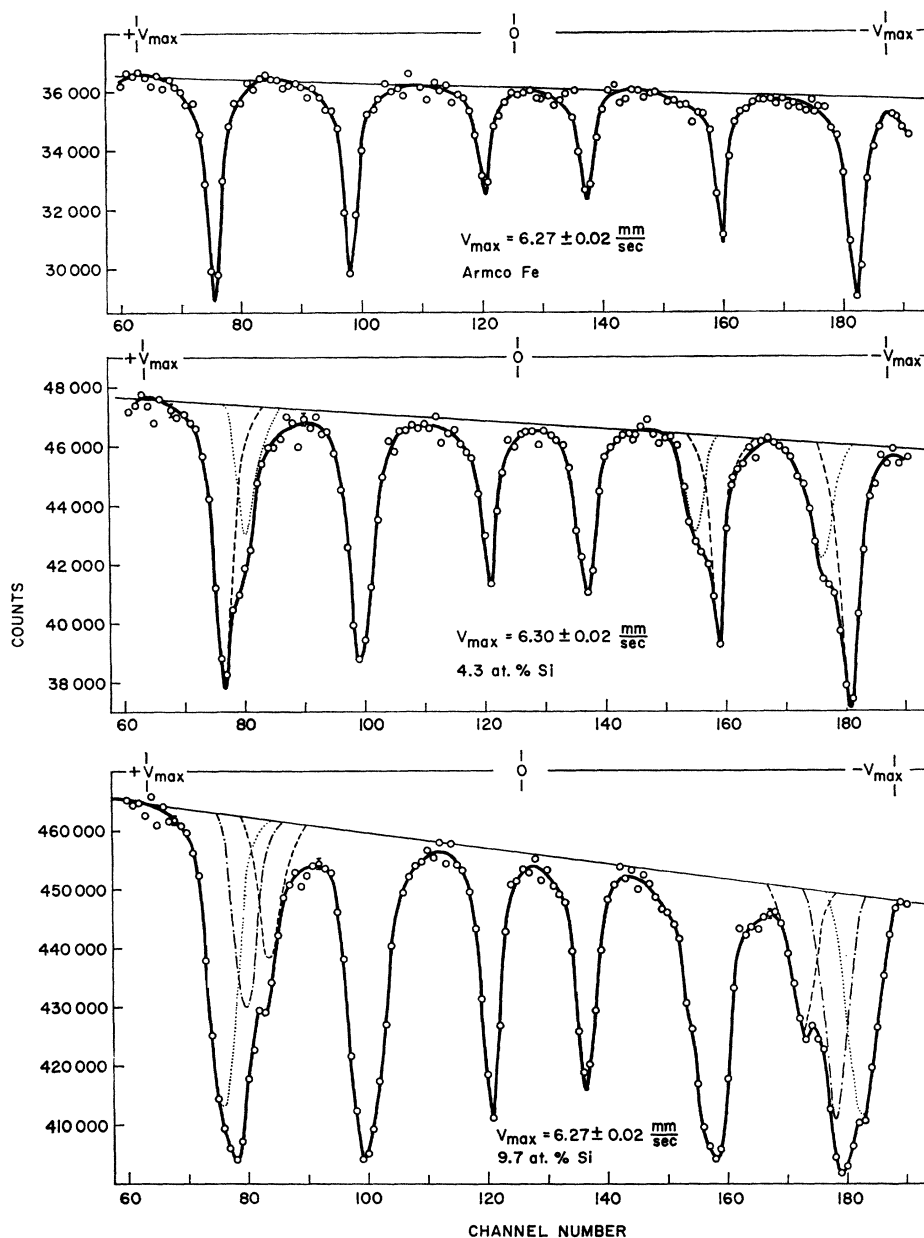[10] S. Arajs and D. S. Miller, J. Appl. Phys. **31**, 986 (1960).

FIG. 1. Typical spectra in the disordered alloy region. The outer dips are shown unfolded into their component fields.

annealed in vacuum at 900°C for about 2 h, then oven cooled to 400°C and left there for at least 2 h. This assured that those alloys that could order would be in the ordered state. The compositions and form of the alloys are given in Table I. All the samples contained from 0.002 to 0.005 weight percent carbon and about 0.002 weight percent oxygen. The chemical analysis is reliable to only about $\frac{1}{4}\%$.

The detector was a 40-mil-thick NaI(Tl) crystal which had a 5-mil Be window. It was mounted on an EMI 9536B phototube. The recording system was similar to many in the literature. The pulses from the photomultiplier tube were amplified and fed into a single-channel analyzer. The output of the single-channel

analyzer was then put into coincidence with a sawtooth generator which was synchronized with the waveform which drove the vibrator. This output was fed into 256 channels of a multichannel analyzer and thus records the whole hyperfine spectrum. The sawtooth was triggered only once in each cycle. Each line thus appeared twice and provides a pattern which is reflected around the maximum velocity. The positions of the maximum velocity can be determined very accurately from the symmetry of the pattern. We used a parabolic waveform with a feedback system[11] to drive the vibrator. This motion gives a linear change in velocity so the
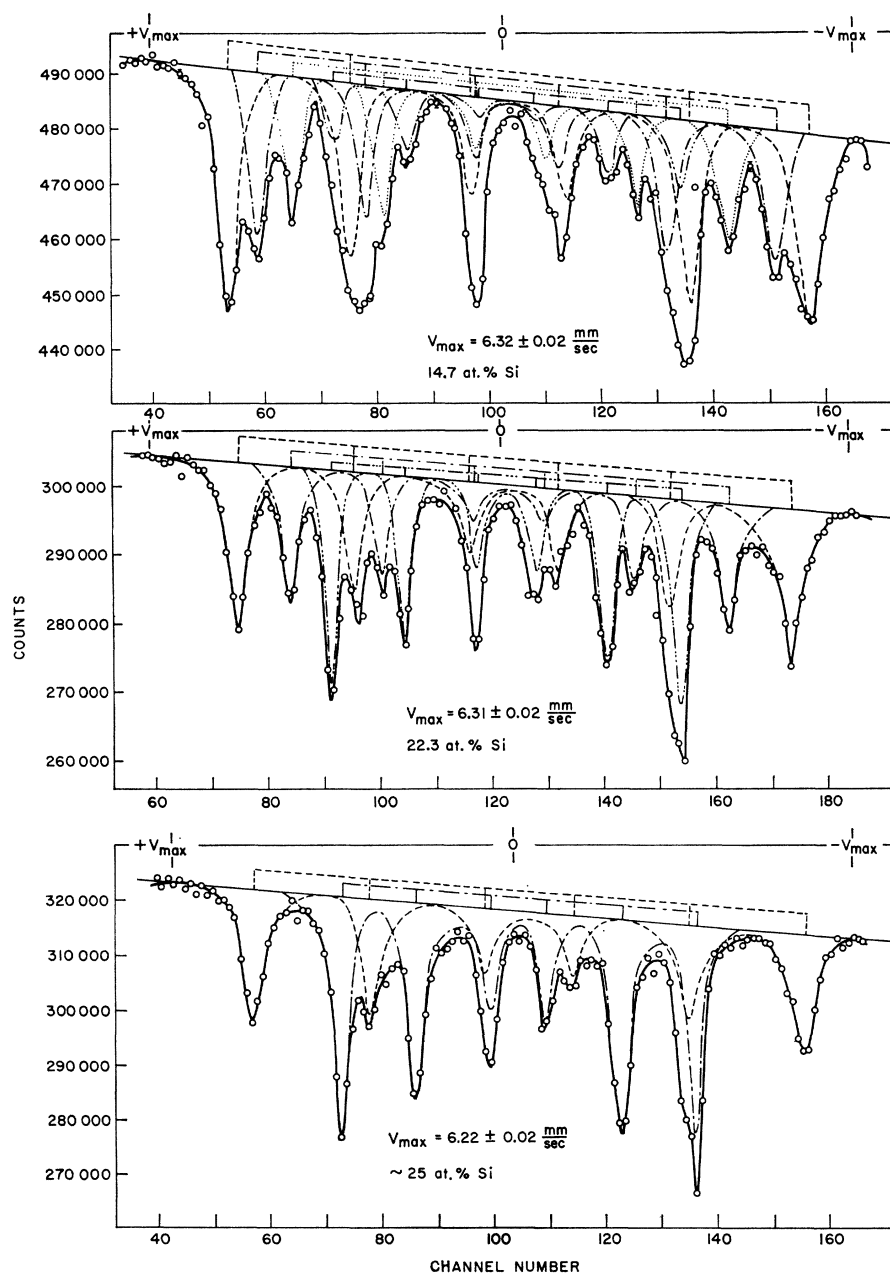
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[11] David Rubin, Rev. Sci. Instr. **33**, 1358 (1962).

FIG. 2. Some typical spectra of the ordered alloys. Each spectrum is shown unfolded into its various components.

In the top spectrum: $V_{max} = 6.32 \pm 0.02 \frac{mm}{sec}$, 14.7 at.% Si

In the middle spectrum: $V_{max} = 6.31 \pm 0.02 \frac{mm}{sec}$, 22.3 at.% Si

In the bottom spectrum: $V_{max} = 6.22 \pm 0.02 \frac{mm}{sec}$, ~25 at.% Si

TABLE I. Composition and form of the FeSi alloys.

Sample No.	At. % Si	Form
C92	0.8	1.1–1.5 mil foil
C94	4.3	1.3–1.5 mil foil
C46	9.7	1.8–2.0 mil foil
C53	14.7	No. 325 NBS mesh
C-15	17.3	No. 325 mesh
C-42	18.4	No. 325 mesh (contained 0.2 wt. % Hf)
CC-2	22.2–22.4	No. 325 mesh
C43	25.5	Nos. 325 and 200 mesh (contained 0.2 wt. % Hf)
CC-3	26.0–27.0	No. 325 mesh

data from the multichannel analyzer are in their final form.

In order to calibrate and check the apparatus, the spectrum of an Armco iron absorber was taken about every third run. Counting rates of about 500 cps into the multichannel analyzer were used.

EXPERIMENTAL RESULTS

Figures 1 and 2 show some typical spectra due to the hyperfine splitting of the ground and first excited state of Fe^{57} nuclei in the presence of their internal magnetic fields. Each curve contains only one complete spectrum,

TABLE II. Measured values of the internal magnetic fields and isomer shifts of the ordered alloys.

At. % Si	Internal field $H_{Fe}=1.0$					Isomer shift re Fe in Pt (mm/sec)			
	Type of Fe site					Type of Fe site			
	$D+A_8+A_7$	A_6	A_5	A_4		$D+A_8+A_7$	A_6	A_5	A_4
14.7	0.978	0.874	0.737	0.586		−0.30	−0.265	−0.16	−0.085
17.3	0.970	0.871	0.742	0.585		−0.26	−0.24	−0.155	−0.10
18.4	0.970	0.869	0.735	0.584		−0.28	−0.25	−0.145	−0.09
	$D+A_6$					$D+A_6$			
22.3	0.934		0.741	0.591		−0.25		−0.16	−0.11
	Pure D		Pure A			Pure D			Pure A
~25	0.940			0.612		−0.28			−0.11
	0.934			0.607		−0.28			−0.11
	D		A_4	A_3		D			A_4
26–27	0.911		0.600	0.449		−0.25			−0.115
	0.924		0.600	0.429		−0.29			−0.115
Average values	0.936	0.871	0.738	0.602	0.44	−0.28	−0.25	−0.155	−0.11
	±0.002	±0.004	±0.004	±0.004	±0.01	±0.005	±0.005	±0.005	±0.005

the reflected portion from which the position of the maximum velocities was obtained has been omitted. The data are tabulated in Tables II, IV, and V. The reproducibility of the results was excellent as seen in the tables and the errors quoted are estimated to contain both those due to statistics and any systematic errors. The isomer shift obtained for Armco iron with respect to Fe in Pt was −0.358±0.002 mm/sec.

The FeSi alloy series is disordered up to about 10 at. % Si (see reference 12) and above this goes into an ordered Fe₃Al type structure. This structure is a body-centered cubic lattice and is shown in Fig. 3. We discuss the results of the ordered region first, since from these results we can see the proper way to resolve the obtained spectra.

ORDERED REGION

Figure 2 shows three typical spectra obtained in the ordered region. Table II gives the measured internal

TABLE III. Calculated values of the probability of the various type sites to be occupied for the various alloys.

At. % Si	Number of nn Fe atoms		
	8	7	6
0.8	0.938	0.062	
4.3	0.704	0.253	0.040
9.7	0.442	0.380	0.143

	Type of site						
	D	A_8	A_7	A_6	A_5	A_4	A_3
14.7	0.414	0.017	0.096	0.206	0.196	0.013	
17.3	0.395	0.005	0.048	0.165	0.247	0.139	
18.4	0.387	0.003	0.033	0.138	0.258	0.180	
22.3	0.356	0.000	0.002	0.036	0.198	0.408	
25.0	0.333					0.667	
26.5	0.320					0.531	0.135

[12] G. Phragmin [J. Iron Steel Inst. (London) 116, 397 (1926)] states that the onset of order occurs at 13 at. % Si; F. W. Glaser and W. Ivanick [Trans. Am. Inst. Mining Met. Petrol. Engrs. 206, 1290 (1956)], observed some ordering occurring already for alloys of 9.5 at. % Si; M. C. Farquhar, H. Lipson, and A. R. Weill [J. Iron and Steel Inst. 152, 457 (1945)] first noticed ordering at 12.5 at. % Si.

magnetic fields and isomer shifts of the various runs. From the intensities of the various observed fields we can determine the manner in which the ordering is occurring. Table III gives the probabilities for an iron atom to occupy the different type sites, assuming that between 14 to 25 at. % Si the Si atoms have an equal probability of occupying any of the D-type Si sites shown in Fig. 3. Above 25 at. % Si we assume that the Si atoms go randomly into the D-type Fe sites. The notation used in the text to differentiate the various A sites is A_n, where n is the number of nearest-neighbor (nn) iron atoms. All D sites have eight nn iron atoms and all A-type sites have six next-nearest-neighbor (nnn) iron atoms for all compositions.

25 at. % Si. The most easily resolvable spectrum was that due to the 25 at. % alloy. Such an alloy has the correct ratio of Fe and Si atoms to give the Fe₃Si lattice as shown in Fig. 3. This structure has only two type sites; namely, ⅓ of the Fe atoms have eight nn iron atoms (D sites) and ⅔ have four nn Si atoms and four nn Fe atoms (A sites). The observed spectrum
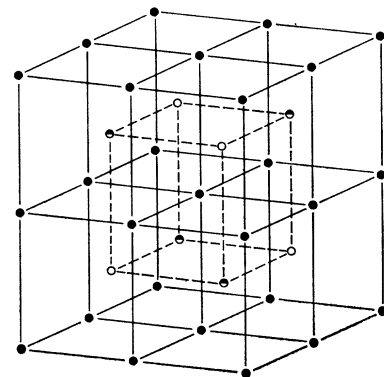

FIG. 3. Unit cell of the ordered Fe₃Si structure.

● Fe atoms on A sites
◒ Fe atoms on D sites
○ Si atoms on D sites

Table IV. Measured values of the internal magnetic fields and isomer shifts of the disordered alloys.

At. % Si	Internal field $H_{Fe}=1.0$ Number of nn iron atoms			Isomer shift re Fe in Pt (mm/sec) Number of nn iron atoms		
	8	7	6	8	7	6
0	1.00			−0.358±0.002		
0.8	1.00	0.910		−0.362	−0.279	
4.3	1.00	0.913		−0.356	−0.281	
	1.00	0.919		−0.352	−0.322	
9.7		0.922	0.834	−0.357	−0.320	−0.257
		0.920	0.835	−0.343	−0.326	−0.287
Average values	1.00±0.002	0.917±0.005	0.834±0.005	−0.357±0.002	−0.32±0.005	−0.27±0.01

was resolved into two distinct fields in the following manner. Starting with the two outermost dips we filled in and subtracted a spectrum of the same characteristics as that obtained from pure iron (see Fig. 1). Thus, we unfolded the higher field spectrum from the total curve. The result of this unfolding was then a spectrum whose shape and intensities corresponded to that of a single weaker magnetic field. The two separated fields are indicated in the ∼25 at. % spectrum in Fig. 2. Not only did the spectrum unfold cleanly into two separate fields, but the widths of both of these fields were essentially unbroadened, i.e., they were the same as that of the field in pure Armco iron. The values of the two fields and their isomer shifts are given in Table II. The higher field observed is clearly that due to atoms on the D sites with eight nn iron atoms. Its value is $(0.936\pm0.002)H_{Fe}$. The lower field is that due to the atoms at A sites with four nn Fe atoms and four nn Si atoms. Its value is $(0.602\pm0.004)H_{Fe}$. The relative number of atoms at the two sites was determined by measuring the areas of the best resolved dips for each field with a planimeter. The ratio of intensity of the lower field with respect to the higher field with 1.8±0.2 which agrees with the expected value. Both fields had positive isomer shifts with respect to pure iron. The A sites were more positive than the D sites.

26–27 at. % Si. When the 26–27 at. % alloy was unfolded in the manner described above, another field became evident. Its shape and intensity indicated that it corresponded to A-type sites wlith three nn iron atoms. The value of this third field was $(0.44\pm0.01)H_{Fe}$. The ratio of intensities of the A_3 to the A_4 dips was 0.31±0.05 which agrees with a calculated intensity ratio of 0.25 for a 26.5 at. % Si alloy.

22.3 at. % Si. This alloy showed three easily resolvable fields. See Fig. 2. As seen in Table III, the highest field would be expected to contain 91% D-site iron atoms and 9% A_6-site irons. The latter small fraction would clearly not be resolvable here. However as seen in Fig. 2 there is some suggestion in the spectra that the higher field has a low-energy tail due to the A_6 sites. The value of the highest field is $0.934H_{Fe}$, agreeing well with being essentially pure D-type sites. The intensities of the other two fields agree well with being assigned to A_6- and A_4-type sites. (See Table V.) The

field values and isomer shifts of these sites are listed in Table II.

18.4 at. % Si. This alloy had four resolvable fields. Again the same type unfolding operation described above was used. Namely, to first subtract out the spectrum associated with the outermost dips and then proceed inward. Here again the highest field was probably not pure but as seen in Table III would be composed of about 8% A_7-site atoms. The fourth field that appeared agreed well in intensity with the expected value for an A_6-type site. The values of fields and isomer shifts observed for A_5- and A_4-type sites are the same as obtained previously and all are listed in Table II.

14.7 and 17.3 at. % Si. For these alloys we again observed four different magnetic fields. These are the same four fields as seen in the 18.4 at. % Si alloy. The 14.7 spectrum is shown in Fig. 2. The 17.3 and 18.4 at. % spectra are very similar in appearance to the 14.7 spectrum, except that the relative intensities of the four fields are different for the three compositions. The measured intensities agree reasonably well with the calculated values. They are tabulated in Table V. The field values and their isomer shifts for each run are tabulated in Table II.

DISORDERED REGION

In this region the Si atoms are assumed to go into each atomic site with equal probability. The probabilities for an Fe atom to have 8, 7, or 6 nearest-neighbor iron atoms are listed for each alloy in Table III.

Figure 1 shows two of the spectra obtained in this region. The 0.8 and 4.3 at. % alloys contained two resolvable fields. From the outer dips of these spectra we found that the peak positions were the same as for pure Fe. However, in these alloys there was a definite tail at the lower velocity side of the dips. By reflecting the high-velocity side about the peak position we could subtract out the higher field from the total curve and obtain a second lower field. This unfolding of the outer dip is shown for the 4.3 at. % alloy in Fig. 1. For both alloys the resulting second field was the same in value and had the same isomer shift. These values are

TABLE V. Comparison of measured and calculated relative intensities of the various sites.
(The intensity of the highest field is arbitrarily taken equal to 1.0.)

At. % Si	Relative intensities					
Disordered	Number of nn Fe's					
	8	7	6			
0.8	1.0	0.06±0.01				meas.
	1.0	0.06				calc.
4.3	1.0	0.40±0.04				meas.
	1.0	0.36				calc.
9.7	1.0	0.60±0.1	0.35±0.06			meas.
	1.0	0.86	0.32			calc.
Ordered	Sites					
	$D+A_8+A_7$	A_6	A_5	A_4		
14.7	1.0	0.45±0.09	0.40±0.06	0.19±0.06		meas.
	1.0	0.39	0.37	0.13		calc.
17.3	1.0	0.48±0.1	0.60 ±0.1	0.27±0.1		meas.
	1.0	0.37	0.55	0.31		calc.
18.4	1.0	0.45±0.15	0.55±0.05	0.36±0.1		meas.
	1.0	0.33	0.61	0.42		calc.
	$D+A_6$					
22.3	1.0		0.53±0.1	1.04±0.1		meas.
	1.0		0.50	1.04		calc.
	Pure D			Pure A		
~25	1.0			1.8 ±0.2		meas.
	1.0			2.0		calc.
				A_4	A_3	
26–27				1.0	0.31±0.05	meas.
				1.0	0.25	calc. (26.5)

tabulated in Table IV. As expected, the two alloys had different relative intensities of the two fields. These intensities agreed well with the calculated probabilities, as seen in Table V.

The higher field had no observable isomer shift. For the 4.3 at. % alloy the isomer shift was also measured by using as a source, Co^{57} in Armco Fe. Since this gives a peak near zero velocity, we could then operate at low velocities (maximum velocity ~0.5 mm/sec) and thus obtain a very accurate determination of the dip position relative to that of pure iron. This method of measurement gave the result that in the 4.3 at. % alloy the higher field had no isomer shift to less than ±0.002 mm/sec. The atoms with seven nn iron atoms have a positive isomer shift whose values are listed in Table IV.

The 9.7 at. % alloy was more difficult to resolve. We have done so by assuming that the iron atoms with eight nn irons have a field and isomer shift of the same value as pure Fe, as was observed in the 0.8 and 4.3 at. % alloys. By making this assumption the outer dips then unfolded into three fields whose values and isomer shifts are listed in Table IV. The unfolded outer dips are shown for this spectrum in Fig. 1. The field obtained for the sites with seven nn iron atoms was in excellent agreement with the value obtained for the lower Si content alloys. The intensities of the three components are listed in Table V and agree well with those calculated assuming a random distribution for the Si atoms.

With one exception, the widths of the spectra due to the internal fields (when corrected for the thicknesses of the alloys) for the alloys seemed to be about the same as

for pure iron. The exception was for some of the highest fields in the ordered alloys. However, these would be expected to be broadened since, as discussed above, these fields often had various components in them.

DISCUSSION OF RESULTS

Disordered Region. The internal fields and isomer shifts for all runs are listed in Table IV. In this region three different fields were observed. The intensities of the three different fields are given for each alloy in Table V. They agree well in all cases with the calculated intensities indicating that in this region these alloys are indeed disordered. Thus, we can conclude that the different fields correspond to iron atoms at sites with 8, 7, or 6 nn iron atoms. In Table IV we see that the observed magnetic field value for a given type atom was not dependent on the percentage of Si atoms present in the alloy but only on the nearest neighbors, indicating that essentially only nearest neighbors are important to a given atom in this disordered region. In Fig. 4 the relative internal magnetic field values are shown as a function of the number of nearest-neighbor iron atoms. The three values are seen to lie on a straight line indicating that for the internal field the effects of neighboring silicon atoms are not cooperative but independent of each other.

The isomer shifts are seen to become more positive with number of nearest-neighbor Si atoms. They are shown plotted as a function of nearest-neighbor iron atoms in Fig. 5. We found that for the iron atoms with eight nn iron atoms there was no isomer shift with
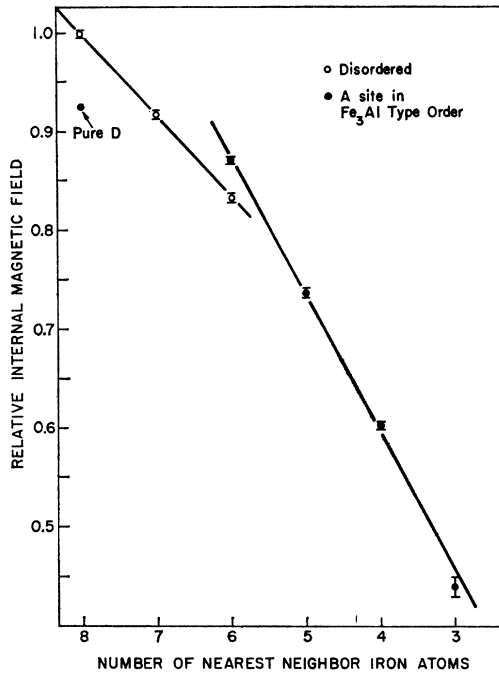
FIG. 4. The variation of the relative internal magnetic fields ($H_{Fe}=1.0$) with number of nn iron atoms. The A-type sites all have 6 nnn iron atoms. The pure D site has 8 nn Fe atoms and 6 nnn Si atoms.

respect to pure iron to within ±0.002 mm/sec. If we interpret this shift or lack of shift in terms of conduction electrons only, we can get an estimate of what this value corresponds to by considering the work of Walker, Wertheim, and Jaccarino.[13] They showed that the isomer shifts of various valence states of Fe can be interpreted quite well in terms of calculations of Watson[14] on the charge density at the origin for various $3d$ configurations. From their graph we see that adding one conduction electron to a $(3d)^7$ configuration corresponds to an isomer shift of about 1.4 mm/sec. We observed that the isomer shift for the disordered alloys is less than 1/700 this value. Considering the 4.3 at. % alloy this means that the change in the number of conduction electrons at a Fe nucleus which are contributed by a Si atom in this alloy is less than 1/30 of an electron. It is likely that the average conduction electron density is changing but that each Fe atom polarizes the conduction electrons around it and effectively screens itself such that the charge density at the iron nucleus remains constant to this accuracy.

We also observed that the internal field for the iron atoms having eight nn iron atoms is the same as that in pure iron to within ±0.003H_{Fe}. Thus, for the iron atoms with eight nn irons atoms, neither the charge

[13] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters 6, 98 (1961).

[14] R. E. Watson, Solid State and Molecular Theory Group Report No. 12, Massachusetts Institute of Technology, 1959 (unpublished).

density nor the spin density (as determined from the internal field) changes by adding silicon. Since it is most likely that adding Si to Fe does change the number of conduction electrons, this would indicate that the observed changes in the internal field for the other sites are not due to the conduction electrons.

Watson's[14] calculation showed that for a fixed number of $4s$ electrons, the $3s$ electrons are mainly responsible for the charge-density variation and the main effect is that due to shielding of the $3s$ electrons by the $3d$ electrons. A positive isomer shift as we observed corresponds to having less charge density at the nucleus. Thus, the observed positive increase in isomer shift and decrease in internal field for atoms with increasing number of nearest-neighbor Si atoms would suggest a picture of each neighboring Si atom contributing some d-like electrons to the iron atom thus decreasing the magnetic moment of the iron atom. This increased number of d electrons causes more shielding of the $3s$ electrons and thus decreases the charge density at the nucleus. This picture, however, is in direct contradiction to the interpretation of the magnetization and susceptibility measurements given in the introduction where the conclusion was that the Fe moment and thus the number d electrons did not change as Si was added in the disordered region.

Ordered Region. Table II lists the internal magnetic fields and isomer shifts of these alloys. In Table V is tabulated a comparison of the measured and calculated intensities for each type site in the various alloys. We see that the intensities agree reasonably well with the
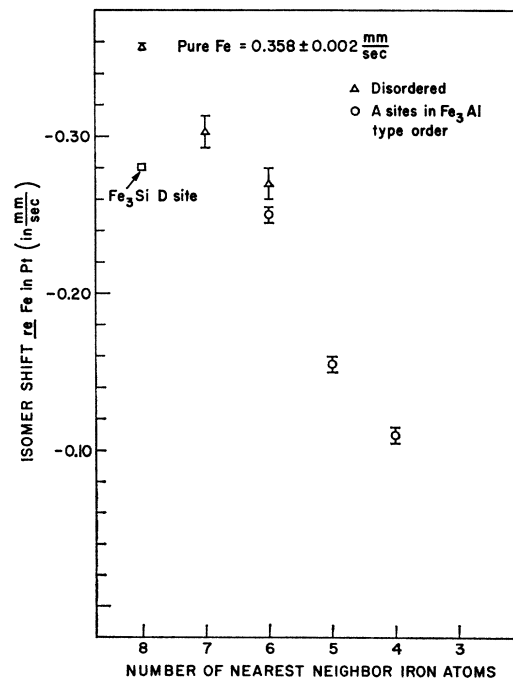

FIG. 5. The variation in the isomer shifts (relative to Fe in Pt) with number of nn iron atoms.

type ordering described above. In particular, we see that the 18.4 at. % alloy definitely has many Fe atoms at sites having six nn iron atoms. This is very near the composition of the possible compound, $Fe_{13}Si_3$. If this intermediate compound were formed, we would observe
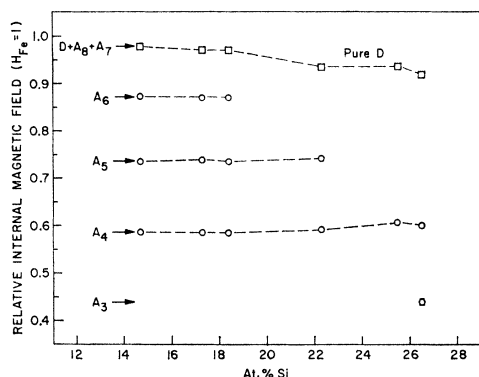

FIG. 6. The relative internal magnetic fields of the ordered alloys as a function of at. % Si. The field values do not depend on the % Si present.

no A_6-type iron atoms. Clearly this is not the case, so there seems to be no tendency for this type ordering, at least for the heat treatment these alloys received.

Figure 6 shows the internal field as a function of the at. % Si. Notice that all the A_n type fields are independent of the Si content. This indicates that for these type sites the nearest neighbors predominantly determine the magnitude of the internal field. For these sites this is not unexpected since the next nearest neighbors for A sites are always the same, namely, six iron atoms. The average values of the internal magnetic fields for the A_n type sites are shown plotted as a function of nearest-neighbor irons in Fig. 4. We see that these values are linear indicating that each nearest-neighbor Si atom acts independently.

From Table III we see that the highest field in the ordered region often has many components. For a 25 at. % alloy this higher field is made up entirely of nn iron atoms and six nnn Si atoms. The decrease in field from H_{Fe} to $0.936\pm0.002H_{Fe}$ observed for these D sites is probably a measure of the effect of the six nnn Si atoms. Between the onset of ordering (~10 at. % Si) and 25 at. % Si we would expect values intermediate to H_{Fe} and $0.936H_{Fe}$. This is what was observed.

Table II also gives the observed values of the isomer shifts. These are plotted in Fig. 7 as a function of at. % Si. The isomer shifts are a smaller number of channels than the internal field shifts and, therefore, cannot be determined as accurately. This is evident in Fig. 7 where we see that the shifts fluctuate somewhat for the various alloys. The average values with the rms errors obtained by averaging all the values for each type site are given in Table II and plotted as a function of nearest-neighbor iron atoms in Fig. 5. We see that the isomer shift becomes more positive as the number of

Si nearest neighbors increases. The isomer shift of the D site atoms for the ~25 at. % alloy as compared to pure Fe is probably again a measure of the effect of 6 nnn Si atoms.

The same type behavior as was observed here for the ~25 at. % alloy has also been seen in polarized neutron scattering experiments.[15] There two distinct magnetic moments have been observed for Fe_3Al. The moments were 0.97 ± 0.05 and 0.66 ± 0.05 that of the magnetic moment in pure iron. We have also run the FeAl alloy series and find the results are similar to the FeSi series. This will be described more fully in a later article. The two fields for the ~25 at. % Al alloys were $0.91H_{Fe}$ and $0.66H_{Fe}$ to $\frac{1}{2}\%$ accuracy.

These neutron scattering results support an interpretation of the results for the ordered region which agrees with that mentioned earlier. Namely, that each Si atom contributes or shares some d-like electrons with the neighboring iron atoms. These added d electrons then decrease the moment and also the internal field of the Fe atom. They also shield the $3s$ electrons from the Fe nucleus giving rise to the observed isomer shift. In the disordered region we observed a decrease in internal field of $0.08H_{Fe}$ per nearest-neighbor Si atom. In the ordered region the A-type Fe atoms undergo a decrease of $0.14H_{Fe}$ per nearest-neighbor Si atom.

It is of interest to calculate an average internal magnetic field from the observed field values. This average internal magnetic field is obtained by taking the weighted sum of the fields at the different sites, i.e., $\bar{H}_{int}=\sum_n p_n H_n$; where the p_n's are the fraction of Fe atoms in the nth site and the H_n's are the measured field values for the various sites. The p_n values used are the calculated values given in Table III. The H_n values are the measured averages listed in Tables II
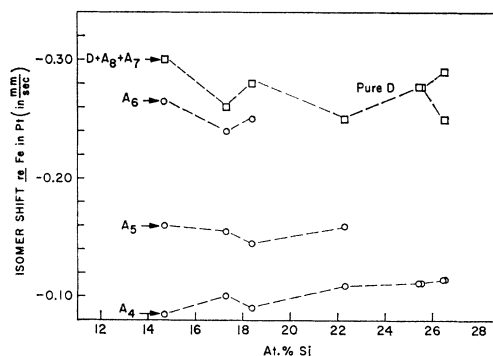

FIG. 7. The isomer shifts for the ordered alloys as a function of at. % Si.

and IV. Since the magnetization measurements are interpreted as an average moment, assuming a localized moment model is valid they correspond to the quantity $\bar{\sigma}=\sum_n p_n \sigma_n$, where the σ_n's are the moments at the

[15] R. Nathans, M. T. Pigott, and C. G. Shull, J. Phys. Chem. Solids 6, 38 (1958).
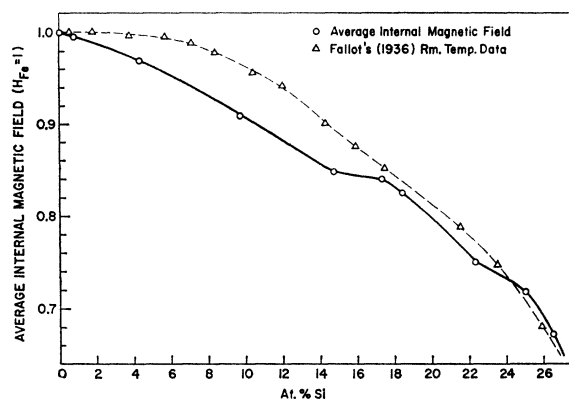
FIG. 8. The average internal magnetic field of the alloys as a function of at. % Si. Fallot's room temperature values of the magnetization per iron atom relative to pure iron are shown for comparison.

different type sites. Thus, if H_n is proportional to σ_n, the magnetization and the average internal magnetic field should exhibit the same behavior. Figure 8 shows the average internal field calculated from these results and also the room-temperature saturation magnetization values per iron atom of Fallot.[9] The values of Parson et al[9] lie slightly above Fallot's values. The $\bar{H}_{int}$ values are estimated to be accurate to about 1%. We see that the average internal field and the magnet-

ization measurements are quite different below 14 at. % Si. Above this they are in better agreement.

CONCLUSIONS

The room temperature average internal magnetic field values do not have the same behavior as the magnetization curve as Si is added to Fe. It seems that the Si atoms contribute d-like electrons to neighboring iron atoms, each Si atom acting quite independently of other nearby Si atoms. The FeSi system is disordered below 9.7 at. % Si; by 14.3 at. % Si it is ordering into the Fe$_3$Al-type structure. There was no tendency to form other intermediate compounds, e.g., Fe$_{13}$Si$_3$, for the annealed samples prepared for this work.

ACKNOWLEDGMENTS