

Investigation of the Fe_{1+x}Sb system

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X-ray diffraction, bulk magnetization, and ^{57}Fe Mössbauer spectroscopic measurements on Fe_{1+x}Sb system for various values of x ($0.14 \leq x \leq 0.35$) are reported. The x-ray data suggest that the ASTM (American Society for Testing and Materials) data file for Fe_{1+x}Sb should be modified. The lattice Néel temperatures obtained from magnetic susceptibility and Mössbauer spectroscopic measurements are in nice agreement with each other and decrease linearly with increase in x . The Néel temperatures for the ordering of interstitial Fe atoms are higher than 60 K and increase with x . The low-temperature Mössbauer spectra have been analyzed in terms of a Lorentzian distribution of the magnetic hyperfine field at lattice sites, a low-field site, and a relatively high-field interstitial site. Also included are comments on the low magnetic moment of Fe in Fe_{1+x}Sb .

I. INTRODUCTION

The nonstoichiometric iron antimonide Fe_{1+x}Sb , which has a NiAs-type crystal structure for $0.08 \leq x \leq 0.38$, has been investigated experimentally by a number of workers.¹⁻⁸ However, their findings are quite divergent.

The dependence of the lattice constants c and a on x was determined by Yamaguchi *et al.*¹ and their results are in excellent agreement with the data later quoted by Richter and Schmidt.⁴ But the d spacings and the intensities of the x-ray diffraction peaks corresponding to different (hkl) indices as listed in the American Society for Testing and Materials (ASTM) x-ray diffraction files⁹ are at variance with those recently reported by Lefevre *et al.*⁵

Yashiro *et al.*² carried out susceptibility measurements on a single crystal of $\text{Fe}_{1.14}\text{Sb}$, giving the lattice Néel temperature (T_{NL}) as 105 K and the interstitial Fe atom Néel temperature (T_{NI}) as 28 K. They also subjected their sample to neutron-diffraction studies below 105 K and concluded that the spin structure of Fe_{1+x}Sb is triangular and antiferromagnetic and that the interstitial Fe atoms do not order even at 10 K. Later, on the basis of their magnetization studies, Nösselt and Sondermann³ showed that the interstitial Fe atoms order at 10 K, whereas Picone and Clark⁸ concluded that these form magnetic clusters which freeze as typical micromagnets near 30 K.

Richter and Schmidt⁴ carried out ^{57}Fe Mössbauer spectroscopic studies on three samples with $x=0.13$, 0.22, and 0.30, and found their T_{NL} to be 211, 178, and 119 K,

respectively. They attributed their spectra for the ordered phase to the superposition of many sextets corresponding to the Fe atoms at different lattice sites, but did not resolve these into properly labeled subspectra. For the paramagnetic phase (317 K), they found quadrupole splitting (ΔE_Q) to be $0.272 \pm 0.008 \text{ mm s}^{-1}$ for all three samples; however, the isomer shift with respect to Fe (δ) was found to increase from 0.37 to 0.43 mm s^{-1} with x . Blaauw *et al.*⁶ analyzed their room-temperature spectra in terms of two doublets having the same δ (0.41 mm s^{-1}) but different ΔE_Q (0.22 and 0.49 mm s^{-1}). Picone and Clark⁷ found T_{NL} to change from 140 to 103 K as x varied from 0.29 to 0.325, while T_{NI} became 55 ± 5 K. Instead of resolving the low-temperature composite spectra into the possible components, these authors considered these to be the superposition of three sextets. Two of these with magnetic hyperfine field (B_{hf}) values of 12.0 and 9.9 T at 0 K were assigned to the lattice Fe atoms, whereas the third sextet with a B_{hf} of 16.0 T was attributed to the ordered interstitial Fe atoms. The room-temperature spectrum of $\text{Fe}_{1.30}\text{Sb}$ with $\delta=0.433 \pm 0.006 \text{ mm s}^{-1}$ and $\Delta E_Q=0.297 \pm 0.006 \text{ mm s}^{-1}$ was assigned to the lattice Fe atoms.

No doubt, some of the discrepancies pointed out above have their origin in the difference in the method of the preparation of the systems studied by various workers, but there are still some basic issues which need to be settled properly. This paper, wherein we present the results of measurements carried out on Fe_{1+x}Sb over a complete

range of x values corresponding to NiAs structure, employing x-ray diffraction, bulk magnetization, and ^{57}Fe Mössbauer spectroscopy, is an effort directed toward better understanding of this system.

II. EXPERIMENTAL DETAILS

Appropriate amounts of 99.99% pure Fe and Sb powders were thoroughly mixed in an agate mortar and pellets of different samples were prepared under pressure. These pellets were sealed in separate silica tubes at a pressure less than 10^{-5} Torr and placed in a furnace at 500°C for two weeks to obtain properly homogenized solid solutions. Then each of these tubes was heated to 800°C for 24 hours and quenched by ice cold water. The samples so obtained were finely powdered for various studies. Obviously our method of preparing the samples is closer to that of Yamaguchi *et al.*¹ and is different from the one employed by Picone and Clark,^{7,8} who heated the samples to 1200°C and then cooled these in the furnace.

The x-ray diffraction traces (Fig. 1) have been recorded at 298 K on the Philips x-ray diffractometer (PW 1140/90) and have been used to derive the interplanar spacings. These, in turn, have been employed to determine the lattice constants c and a , and hence to completely identify the compounds formed (Table I). The presence of low-intensity peaks corresponding to the peaks for FeSb_2 , reported in Ref. 5, implies that some FeSb_2 is also formed in these samples.

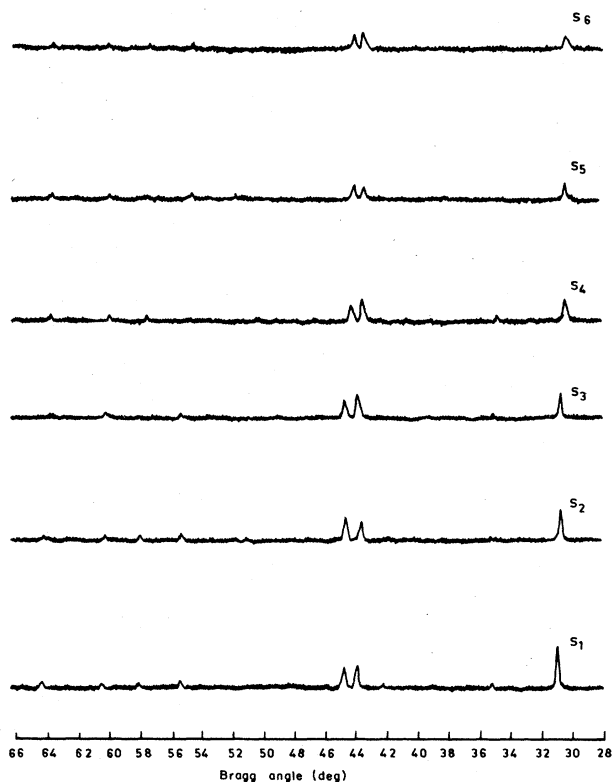


FIG. 1. The x-ray diffractometer traces for different Fe_{1+x}Sb samples. The numbers along the x axis are Bragg angles in degrees.

TABLE I. Lattice constants for different samples of Fe_{1+x}Sb .

Sample	x	c (nm)	a (nm)	c/a
S_1	0.14	0.513	0.407	1.260
S_2	0.20	0.514	0.408	1.260
S_3	0.23	0.515	0.409	1.259
S_4	0.26	0.516	0.411	1.255
S_5	0.32	0.517	0.412	1.255
S_6	0.35	0.518	0.413	1.254

The magnetic susceptibility (χ_g) of different samples has been measured as a function of temperature (T) down to 80 K using vibrating sample magnetometer (PAR 155) and the data have been used to determine lattice Néel temperatures.

The Mössbauer spectra of the sample powders containing 5 mg cm^{-2} of Fe were recorded in transmission geometry using ^{57}Co in a Rh matrix source and velocity drive in the constant acceleration mode, whose linearity and calibration were checked periodically. The measurements were made at a number of temperatures down to 6 K and these spectra for S_1 as typically representative are depicted in Fig. 2. The spectra of different samples at 6

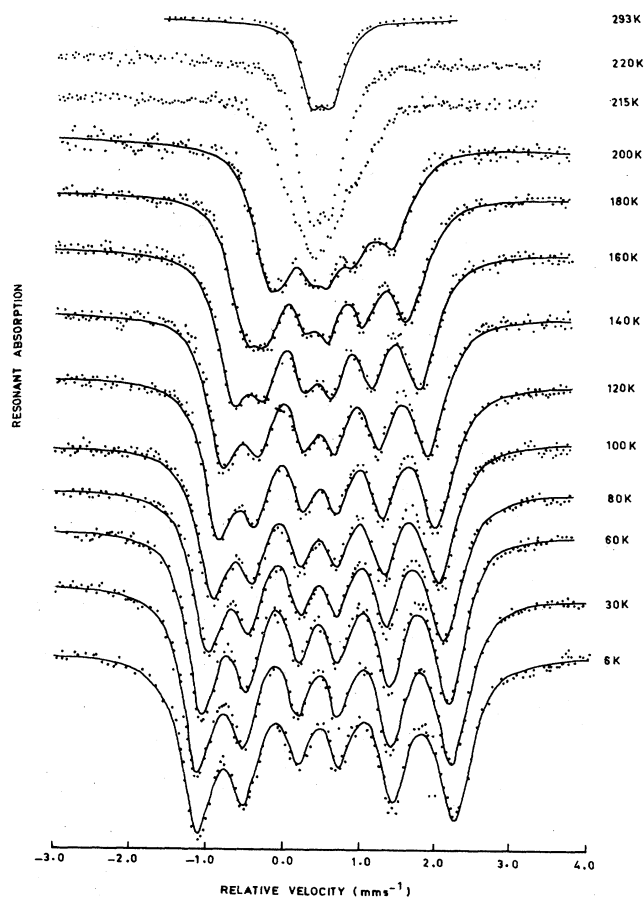


FIG. 2. Mössbauer spectra of S_1 at different temperatures ranging from 6 to 293 K.

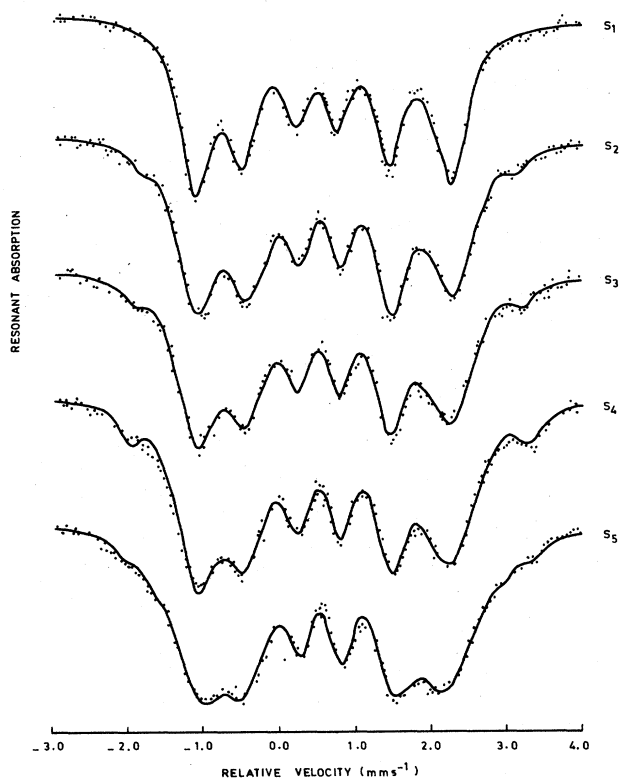


FIG. 3. Mössbauer spectra of different Fe_{1+x}Sb samples at 6 K.

K (except for S_6 whose spectra could not be recorded for T less than 60 K) are displayed in Fig. 3 to show their dependence on x .

III. RESULTS AND DISCUSSION

A. X-ray data

The d spacings for different Bragg planes in the case of $\text{Fe}_{1.14}\text{Sb}$ are compared with the data from Refs. 5 and 9 in Table II. Obviously, the relative intensities obtained from the present work differ significantly from those given in Ref. 9, but are in excellent agreement with those listed in

Ref. 5. In a separate study,¹⁰ it has been found that the d spacings and relative intensities for the $(\text{Fe}_{1-y}\text{Ni}_y)_{1+x}\text{Sb}$ system having NiAs structure are also very close to those for Fe_{1+x}Sb given here. Therefore, it is recommended that the data on Fe_{1+x}Sb included in the ASTM x-ray diffraction files⁹ be replaced by the correct magnitudes presented in Table II.

B. Magnetic susceptibility

The T_{NL} values obtained through susceptibility measurements are found to decrease linearly from 210 K for S_1 to 85 K for S_5 (Fig. 4). The observed trend of T_{NL} indicates a decrease in the spontaneous magnetic field with an increase in the excess interstitial Fe atoms.

C. Mössbauer data

The temperature dependence of Mössbauer spectra has also been used to determine T_{NL} for different samples. These values are found to be very close to the ones obtained from the χ_g data and are also shown in Fig. 4. The T_{NL} data reported by Richter and Schmidt⁴ and Picone and Clark⁷ for some values of x are also included in Fig. 4. The relatively larger difference of the present data from those of Ref. 7 seems to be a consequence of the difference in the method of preparation of the two categories of samples.

In Fe_{1+x}Sb each lattice site Fe atom is surrounded by two lattice Fe atoms along the c axis and six interstitial sites, which are randomly occupied by the excess Fe atoms. Therefore, the lattice site Fe atoms may have 0, 1, 2, . . . , 6 interstitial Fe atoms as their second-nearest neighbors, giving rise to seven lattice sites with distinct Mössbauer parameters. If the contribution from the next-nearest-neighbor shell of interstitial atoms is also included then the expected number of different lattice sites increases manifold. Similarly, if attention is focused on the interstitial Fe atoms, these too are found to have randomly distributed interstitial Fe atoms as neighbors and hence there is a multitude of different interstitial Fe sites. Consequently, the Mössbauer spectra of a Fe_{1+x}Sb system are expected to be complex. Furthermore, a perusal of our low-temperature spectra (Figs. 2 and 3) shows that the peaks are reasonably broad and the spectra are quite asymmetric, which is indicative of intrinsic distribution of different Mössbauer parameters. However, since the

TABLE II. Observed d spacings and intensities of various x-ray diffraction peaks in $\text{Fe}_{1.14}\text{Sb}$ and those reported in Refs. 5 and 9 for Fe_{1+x}Sb , for different Bragg planes.

Plane indices (hkl)	Present data		Ref. 5		Ref. 9	
	d (nm)	I/I_0	d (nm)	I/I_0	d (nm)	I/I_0
101	0.2905	100	0.2910	100	0.294	70
002	0.2561	10	0.2556	8		
102	0.2074	55	0.2078	78	0.209	100
110	0.2038	65	0.2042	80		
201	0.1665	20	0.1667	19	0.169	70
112	0.1594	10	0.1600	10		
103	0.1538	15	0.1542	17	0.155	80
202	0.1453	15	0.1458	21		
121	0.1290	12	0.1296	14	0.131	100

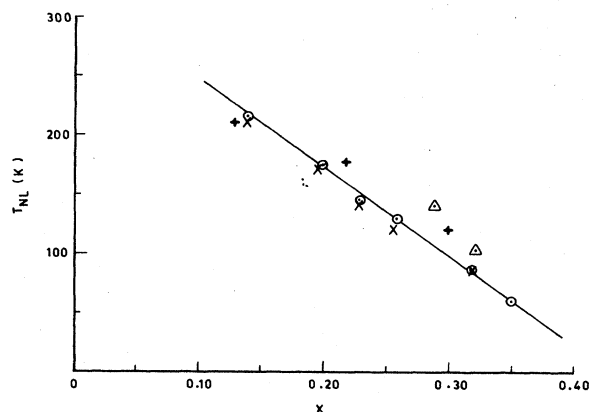


FIG. 4. Graph exhibiting dependence of lattice Néel temperature (T_{NL}) on the value of x in $Fe_{1+x}Sb$. The values obtained from the Mössbauer and susceptibility data are shown as \odot and \times . $+$ and \triangle show the results of Refs. 4 and 7, respectively.

number of electrons is likely to exhibit only marginal local variation due to differences in the surrounding configuration, the variation in δ from one site to another has been ignored to simplify the fitting procedure. Thus, the spectra have been resolved into the components by assuming intrinsic distribution of B_{hf} and ΔE_Q only.

The analysis of the low-temperature spectra has been executed on a Digital Equipment Corporation (DEC-2050) computer keeping the above comments in mind. In order to subtract the contribution of $FeSb_2$ (whose presence has been indicated by the x-ray data) from the composite spectra, the Mössbauer parameters reported by Steger and Kostiner¹¹ at different temperatures have been employed to generate the corresponding subspectra. However, the intensity of the lines due to $FeSb_2$ has been kept as a free variable. For a particular sample the intensity is found to decrease with an increase in temperature, e.g., in some samples it fell from 8% at 6 K to 2% at 293 K. Such a sharp change in relative contribution from the $FeSb_2$ phase to the composite spectra is understandable because the Debye temperature for $FeSb_2$ has been es-

timated¹¹ as 380 K in comparison with 700 K for $Fe_{1+x}Sb$.⁷ The low value of Debye temperature of $FeSb_2$ also justifies the presence of very weak peaks in the x-ray diffraction traces recorded at room temperature.

The fitting of the Mössbauer spectra is found to be more acceptable if the interior distribution of B_{hf} is taken to be Lorentzian rather than Gaussian. However, the width of this Lorentzian distribution is different for different systems and increases with an increase in x . The proper fitting of the spectra has been obtained with Lorentzian distribution having the lion's share in intensity, a sextet with very low B_{hf} and zero ΔE_Q , and a sextet of relatively large B_{hf} and nonzero ΔE_Q . However, in the case of $Fe_{1.32}Sb$, two sextets with relatively large B_{hf} had to be included in the fitting. The linewidth (Γ) for the single sextets was always greater than the Γ of the sextets constituting the distribution of field, implying that even these sextets are also composed of distributions as mentioned earlier. The inclusion of a very low B_{hf} sextet in the analysis was necessary to ensure proper fitting of the central part of the spectra and is not surprising as Gonser *et al.*¹² had to go down to 0 T for a proper fitting of their low-temperature spectra of $Fe_{0.69}Ni_{0.28}Co_{0.03}$.

The Mössbauer parameters for $Fe_{1.14}Sb$ at different temperatures are given in Table III, whereas the parameters for various samples at 6 K constitute the content of Table IV. Here B_{hf} values for the lattice sites with Lorentzian distribution are those pertaining to the peak in the distribution and ΔE_Q values are the ones corresponding to the listed B_{hf} .

In the paramagnetic phase, the spectra for all the samples consist of a doublet as shown for S_1 in Fig. 2. The parameters extracted from the analysis of the spectra for different samples at 293 K are projected in Table V. The larger Γ for all these spectra, as compared to the calibration Γ (0.24 mm s^{-1}), implies distribution of δ and ΔE_Q for different lattice Fe atoms.

1. The isomer shift

For a particular sample, δ decreases with an increase in temperature, seen in Table III as typically representative.

TABLE III. Isomer shift (δ), quadrupole splitting (ΔE_Q), magnetic hyperfine field (B_{hf}), and relative percent intensity for different Fe sites in $Fe_{1.14}Sb$ sample, obtained from the analysis of Mössbauer spectra at different temperatures. The Lorentzian width for the interior distribution of B_{hf} is 1.27 T.

Temperature (K)	Lattice sites with Lorentzian distribution				Low- B_{hf} site with $\Delta E_Q = 0 \text{ mm s}^{-1}$		High- B_{hf} site		
	$\delta(Fe)$ (mm s^{-1})	ΔE_Q (mm s^{-1})	B_{hf} (T)	I (%)	B_{hf} (T)	I (%)	ΔE_Q (mm s^{-1})	B_{hf} (T)	I (%)
6	0.54	0.10	10.5	94.0	3.0	4.4	0.20	15.6	1.6
30	0.53	0.11	10.4	93.6	2.9	6.1	0.18	14.8	0.3
60	0.53	0.11	10.1	92.1	2.6	7.9			
80	0.52	0.11	9.8	90.8	2.4	9.2			
100	0.51	0.10	9.2	89.6	2.2	10.4			
120	0.50	0.11	8.8	89.0	2.1	11.0			
140	0.50	0.09	8.4	87.3	1.8	12.7			
160	0.48	0.11	7.6	86.9	1.4	13.1			
180	0.46	0.12	6.7	86.5	1.2	13.5			
200	0.46	0.14	5.2	84.4	1.0	15.6			

TABLE IV. Mössbauer parameters for different samples of Fe_{1+x}Sb at 6 K.

Sample	$\delta(\text{Fe})$ (mm s^{-1})	ΔE_Q (mm s^{-1})	Lattice sites with Lorentzian distribution having width Γ_L			Low- B_{hf} site with $\Delta E_Q=0 \text{ mm s}^{-1}$		High- B_{hf} site		
			B_{hf} (T)	Γ_L (T)	I (%)	B_{hf} (T)	I (%)	ΔE_Q (mm s^{-1})	B_{hf} (T)	I (%)
S_1	0.54	0.10	10.5	1.27	94.0	3.0	4.4	0.20	15.6	1.6
S_2	0.55	0.07	10.6	2.19	88.5	3.0	3.9	0.20	15.6	7.6
S_3	0.55	0.08	10.5	2.62	89.1	3.0	2.4	0.20	16.2	8.5
S_4	0.56	0.09	10.3	2.95	85.9	2.9	2.9	0.20	16.2	11.2
S_5	0.58	0.07	10.2	4.05	83.3	2.9	0.8	0.15	14.4	9.7
								0.20	16.9	6.2

On the other hand, at a particular temperature it increases almost linearly with x . In order to examine the latter aspect closely, best-fit straight lines have been obtained for the dependence of δ on x for different temperatures. The recorded δ values are then normalized with respect to the intercept for a particular temperature and the data have been used to get a plot between x and the normalized isomer shifts (δ_n) for various temperatures. The results for a number of temperatures are combined in Fig. 5 and it is found that the normalized data lie on a straight line defined by $\delta_n = 0.44x + 1.00$.

The present room-temperature value of δ for $\text{Fe}_{1.32}\text{Sb}$ (0.43 mm s^{-1}) matches well with the data quoted in the introduction for nearly the same value of x , in spite of the difference in the method of preparation adopted by various workers. This implies that δ is essentially independent of the heat treatments given to the material.

2. The magnetic hyperfine field

The sextet corresponding to higher B_{hf} ($\approx 16 \text{ T}$) is observed only at low temperatures and its intensity at a particular T (Table IV) increases with an increase in x ; for $x=0.32$, this is further resolved into two subcomponents. In view of these observations, this field is assigned to the ordered interstitial Fe atoms. Obviously, the present value of B_{hf} at the interstitial Fe atoms is in good agreement with the value derived by Picone and Clark.⁷ Since the spectra for interstitial sites have been resolved for temperatures below 60 K in all the samples, the ordering temperature for these sites (T_{NI}) should be higher than 60 K. Furthermore, the rate at which the intensity of these spectra decreases with an increase in T falls with an increase in x , e.g., in S_2 intensity falls from 7.6% at 6 K to 2.1% at 60 K, whereas in S_5 the sum of the interstitial-site intensities changes from 15.2% to 10.2% over the same

TABLE V. Mössbauer parameters (mm s^{-1}) for different samples of Fe_{1+x}Sb at 293 K. Γ is the linewidth of the doublet.

Sample	$\delta(\text{Fe})$	ΔE_Q	Γ
S_1	0.40	0.27	0.33
S_2	0.41	0.29	0.40
S_3	0.41	0.29	0.38
S_4	0.42	0.28	0.37
S_5	0.43	0.28	0.40
S_6	0.43	0.29	0.40

temperature range. This implies that T_{NI} increases with x .

The B_{hf} pertaining to a maximum fraction of Fe atoms has a Lorentzian distribution. At a particular temperature the width (Γ_L) of this distribution increases with x (Table IV). Following Picone and Clark,⁷ [$B_{\text{hf}}(T)/B_{\text{hf}}(0 \text{ K})$] correspond to the peak in the distribution and have been plotted as a function of T/T_{NL} for different samples (Fig. 6).

In order to compare the above results with the molecular-field theory of magnetism, the fields at the lattice and the interstitial Fe atoms have been calculated¹³ by assuming these to belong to two sublattices. Since the spins at lattice and interstitial sites have been shown² to be $\frac{1}{2}$ and 0, respectively, the reduced magnetizations of the lattice and interstitial substructures are found to be

$$\sigma_L = B_{1/2} \left[\frac{(g\mu_B)^2}{4kT} \gamma_{LL} \frac{N}{1+x} \right]$$

and

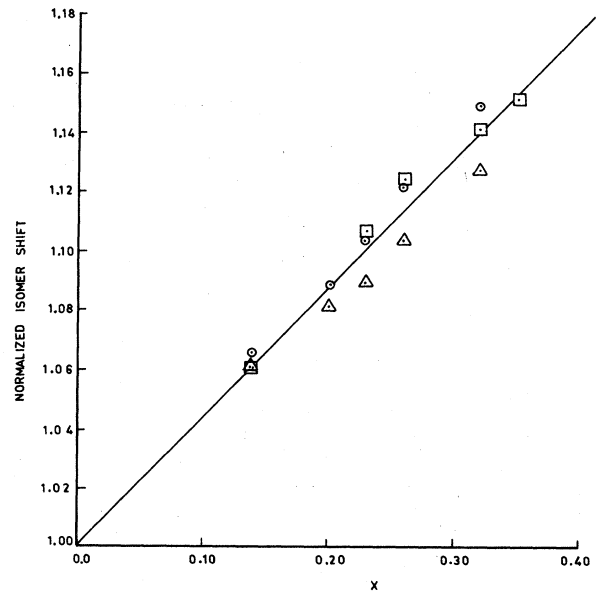


FIG. 5. Isomer shifts normalized with respect to the values corresponding to $x=0$ as a function of x at temperatures 6 K (\odot), 30 K (\triangle), and 293 K (\square).

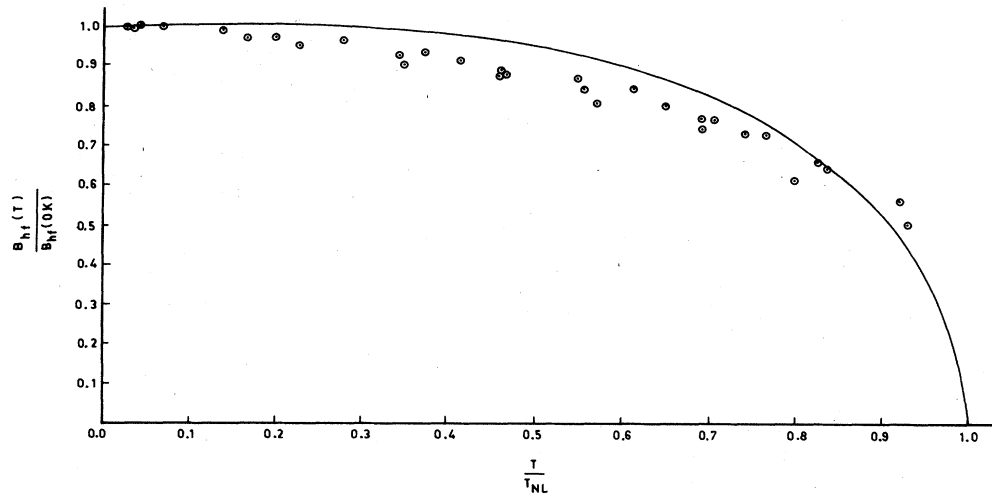


FIG. 6. Reduced magnetic hyperfine field for the lattice sites with Lorentzian distribution [$B_{\text{hf}}(T)/B_{\text{hf}}(0\text{ K})$] as a function of reduced temperature (T/T_{NL}) for Fe_{1+x}Sb . Also shown is the Brillouin curve for $S = \frac{1}{2}$.

$$\sigma_I = 0,$$

where γ_{LL} is the molecular-field constant and N is the number of Fe atoms per unit volume.

Within the framework of this model, B_{hf} is proportional to σ so that B_{hf} at the lattice site should vary as $B_{1/2}$. Accordingly, this has also been included in Fig. 6. The deviation between the experimental data and the theoretical curve is reasonably significant, though not as marked as reported in Ref. 7. The agreement is improved if the Brillouin function pertaining to higher spin (say $7/2$) is considered. But such a large value of spin is untenable. Rather, this departure implies nonvalidity of the molecular-field theory for this system. The situation becomes more serious when the prediction about the interstitial Fe atoms is considered because according to this model $\sigma_I = 0$ and hence $(B_{\text{hf}})_I = 0$, in contrast with the experimental value of 16 T at 6 K. However, since the molecular-field theory has met with some success in the interpretation of the data for intermetallic compounds and alloys, we are inclined to conjecture that the failure in the present case is not only due to the nonlocalized nature of the spins but also due to the presence of a strong short-range order.

In view of the discussion presented by Van der Woude and Sawatzky,¹⁴ we believe¹³ that B_{hf} at the lattice sites obtains contributions from the terms corresponding to spin polarization of core as well as conduction s electrons, the orbital magnetization, the short-range nonlocal field, dipolar field from the central atom, and the zero-point spin-wave deviation. However, in the case of interstitial Fe atoms, the contribution from the polarization of core and $4s$ conduction electrons due to the central atom is zero and the contribution from the short-range overlap and supertransferred hyperfine fields is large.

The above qualitative explanation of the experimental data on B_{hf} leads us to a very important question: why is

the magnetic moment of Fe so small² ($=0.86\mu_B$) in Fe_{1+x}Sb ? The detailed analysis of this problem looks impossible at this stage due to a number of reasons. Firstly, various microscopic parameters needed for the development of proper theory are not known. Secondly, the theory of inhomogeneous magnetic structures, which are expected to occur in a triangular antiferromagnetic structure with randomly distributed interstitial atoms, is not developed. Thirdly, Fe_{1+x}Sb contains frustrated interactions similar to the ones present in the spin glasses and so far the understanding of frustrated systems has been gained only in very simple systems with nearest-neighbor interactions. In contrast, Fe_{1+x}Sb is a reasonably complicated system with significant interactions up to the third shell of neighbors and if all these interactions are taken into account, the number of neighbors to be considered becomes 20. In view of these difficulties, only a modest attempt has been made to analyze the problem.

If FeSb were assumed to have an ideal NiAs structure then all the Fe atoms would be in octahedral sites of the hexagonal close-packing lattice of Sb atoms and the distances between the Fe atoms would be such that the d electrons would remain localized. But the FeSb structure becomes stable when some extra Fe atoms get randomly distributed in the bipyramidal interstitial sites. The occupation of the interstitial sites by Fe atoms leads to more overlap and hybridization of the $3d$ and $4s$ orbitals of Fe atoms with the $5p$ orbitals of Sb. This in turn, makes the d electrons delocalized. Furthermore, Goodenough¹⁵ has also argued that stabilization energy in such systems comes from the delocalization of d bands and the interstitial sites provide paths for d -electron conduction. Therefore, the magnetic moment on the iron sites has to be understood in the context of a narrow d band, which is disordered due to random placement of the interstitial Fe atoms. Consequently, the itinerancy and disorder are responsible for the small magnetic moment of the iron atoms.

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