CHAPTER 3

MAGNETIC BEHAVIOUR IN $Fe_{3-x}Mn_xSi$ ALLOYS
3.1. INTRODUCTION

The properties of the quasi-binary alloy system $\text{Fe}_x \text{Mn}_y \text{Si}$ have been extensively studied and there is a considerable interest in understanding the unusual magnetic behaviour of the system. $\text{Fe}_3\text{Si}$ is a ferromagnet ($T_c = 810$ K) whereas $\text{Mn}_3\text{Si}$ is an antiferromagnet ($T_N = 25.8$ K) [1] and the state of magnetic order in $\text{Fe}_x \text{Mn}_y \text{Si}$ changes from ferromagnetic for $x < 0.75$ to a complex one for $x \geq 0.75$ due to the presence of mixed ferromagnetic and antiferromagnetic exchange interactions [2]. Single phase alloys in this system are formed in a wide concentration range $0 \leq x \leq 1.8$ with the end members $\text{Fe}_3\text{Si}$ and $\text{Mn}_3\text{Si}$ both existing as stable $\text{DO}_3$ ordered phases. The $\text{DO}_3$ structure is shown in Fig. 3.1 and consists of four interpenetrating sublattices labelled A, B, C, and D, shifted along the body diagonal and having origins at $(0,0,0)$, $(1/4,1/4,1/4)$, $(1/2,1/2,1/2)$ and $(3/4,3/4,3/4)$. In $\text{DO}_3$ ordered $\text{Fe}_3\text{Si}$, A, B, and C sites are occupied by Fe and the D sites are occupied by Si. A and C sites have identical first near neighbour environment (4 Fe atoms at B site and 4 Si atoms at D site) whereas the B site Fe atom have 8 iron neighbours belonging to the A and C sites. Table 3.1 shows the near neighbour (nn) configuration of $\text{Fe}_3\text{Si}$. Alloying of $\text{Fe}_3\text{Si}$ with other 3d metals led to a remarkable finding [2] that the metals to the left of Fe in the periodic table substitute preferentially at B sites whereas the ones to the right of Fe have a preference for A and C sites. This substitutional behaviour permits study of host-impurity interaction at high impurity concentrations because as seen from Table 3.1, impurity-impurity atoms come only as third
Fig. 3.1. $\text{DO}_3$ structure with A, B, C, and D sublattices having origins at $(0,0,0)$, $(1/4,1/4,1/4)$, $(1/2,1/2,1/2)$ and $(3/4,3/4,3/4)$ along the body diagonal.
Table 3.1. Near neighbour configurations of (AC), B and D sites in the DO₃ structure. The near neighbour distance in units of lattice constant a.

<table>
<thead>
<tr>
<th>Shell No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>4B</td>
<td>6AC</td>
<td>12AC</td>
<td>12B</td>
<td>12D</td>
<td>8A</td>
<td>6A</td>
<td>12B</td>
</tr>
<tr>
<td></td>
<td>4D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>8AC</td>
<td>6D</td>
<td>12B</td>
<td>24AC</td>
<td>8D</td>
<td>6B</td>
<td>24AC</td>
<td>24D</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>8AC</td>
<td>6B</td>
<td>12D</td>
<td>24AC</td>
<td>8B</td>
<td>6D</td>
<td>24AC</td>
<td>24B</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>nn distance $r/a_o$</td>
<td>0.433</td>
<td>0.5</td>
<td>0.707</td>
<td>0.829</td>
<td>0.866</td>
<td>1.0</td>
<td>1.09</td>
<td>1.118</td>
</tr>
</tbody>
</table>
neighbours. It was observed that in Fe$_3$Si based alloys the magnetic moments and hyperfine fields are sensitive only to the nearest neighbour **configurations** and a local environment model was found to explain the magnetic behaviour of these alloys [2].

Magnetisation and neutron diffraction studies on concentrated Fe$_{3-x}$Mn$_x$Si alloys [3] show that the average magnetic moment falls approximately linearly with Mn concentration for $x \leq 0.75$. Only Fe at B sites are substituted by Mn up to this concentration [3]. The magnetic moment of Fe at B sites (all 8 Fe neighbours at AC sites and no Mn nearest neighbours) stays nearly constant at about 2.2 $\mu_B$ whereas the AC site moment decreases linearly with Mn concentration to 0.4 $\mu_B$ as these sites have four B site near neighbours which have been substituted by Mn. Beyond $x = 0.75$, the AC sites also start getting occupied by Mn atoms and the B site moment also decreases rapidly due to the presence of Mn first neighbours. Since there are no more changes of the AC site environment the moment at this site stays constant at about 0.4 $\mu_B$.

Although a fair degree of understanding exists for the saturation moments and corresponding hyperfine fields at the different sites based on this local environment approach [4-6], the temperature dependent behaviour and the nature of magnetically ordered phases in the system in the compositions regions $x \geq 0.75$ is neither well studied nor understood. An extensive temperature dependent study of AC susceptibility (ACS), Ferromagnetic resonance (FMR), and hyperfine fields by Mössbauer spectro-
scopic measurements was carried out on the $\text{Fe}_3\text{Mn Si}$ system in the $0.75 \leq x \leq 1.2$ concentration region. These studies show interesting re-entrant spin glass behaviour and an attempt is also made to understand these properties in the light of existing models for re-entrant spin glasses [7-9].

3.2. EXPERIMENTAL

Four alloy samples of compositions $\text{Fe}_{3-x}\text{Mn Si}$ ($x = 0.75, 0.9, 1.0$ and $1.2$) were prepared by arc melting. Mössbauer effect studies in the temperature range $10 \text{ K} - 300 \text{ K}$ were performed on these samples in powder form. FMR studies in the temperature range $77 \text{ K} - 480 \text{ K}$ were carried out using cuboid shaped (dimensions $2\text{mm} \times 1\text{mm} \times 1\text{mm}$) alloy samples in the horizontal-parallel and vertical-parallel geometries. AC susceptibility measurements in the temperature range $10 \text{ K} - 400 \text{ K}$ were also carried out on the same samples at a frequency of $33 \text{ Hz}$ and $H = 0.5 \text{ Oe}$. Other details of experimental methods are given in chapter 2.

3.3. RESULTS

3.3.a. AC Susceptibility

Fig. 2a shows the measured temperature dependence of AC susceptibility for the four alloy samples. The data show very clearly a drop in AC susceptibility from the demagnetisation factor limited value at two temperatures $T_C$ and $T_{RE}$. This behaviour is usually considered as a canonical signature for re-entrant spin
a. Variation of AC susceptibility ($\chi$) with temperature ($T$) for Fe$_{3-x}$Mn$_x$Si$_{1-n}$ alloys. $T_{\text{DG}}$ denotes the reentrant spin glass temperature and $T_c$ is the ferromagnetic to paramagnetic transition temperature.

b. Variation of dc magnetisation ($M$) with temperature ($T$) for $x = 0.75$ and $x = 0.90$ alloy compositions. $T_c$ values are indicated.

Fig. 3.2
glass systems. The AC susceptibility measurements have been carried out in a low demagnetisation factor geometry (H parallel to surface of the sample and along its length). The calculated demagnetisation factor [10] for this geometry and sample dimensions is 0.1. The experimentally measured susceptibility is given by [11]

$$\chi_e = \frac{1}{1/\chi_i + D} \quad (3.1)$$

where $\chi_i$ is the internal susceptibility and D is the demagnetisation factor. For $\chi_i \gg D$ as in ferromagnetic region, $\chi_e$ reduces to the demagnetisation limited constant value of $\frac{1}{D}$. It was pointed out by Rakers and Beck [11] that in a low demagnetisation factor geometry, the susceptibility does not show demagnetisation limited behaviour in Au$_{82}$Fe$_{17.5}$ alloy and thus the transition at $T_c$ is not to a true ferromagnetic phase in the AuFe system. In our alloy system, the existence of demagnetisation limited behaviour even for low demagnetisation factor shows that the internal susceptibility is large as compared to $D = 10$ which is a substantially large value as compared to susceptibility of paramagnetic or superparamagnetic systems. The transition at $T_C$ therefore corresponds to formation of a ferromagnetic state. Evidence from specific heat measurements [12] show only a broad step like anomaly at the ferromagnetic transition and distinct cusp shape peaks are seen at $T_{RE}$ only. The change in magnetic entropy at $T_C$ is very small (2-3 J mole$^{-1}$ K$^{-1}$) as compared to the value $3R \ln 2 \approx 17.3$ J mole$^{-1}$ K$^{-1}$ expected for ordering of 3N magnetic spins with $S = 1/2$. This shows that all spins are not ordering
below the ferromagnetic transition at $T_c$ and this behaviour will be analysed in more detail later in terms of the unusual structure and site occupation by Fe and Mn atoms in the structure. From dc magnetisation measurements (Fig. 2b), $T_c$ value for $x = 0.75$ alloy composition was measured, and $T_c$ value for $x = 0.9$ alloy composition was confirmed. $T_c$ and $T_{RE}$ values are given in Table 3.2.

3.3.b. Ferromagnetic Resonance

Fig. 3.3 shows the observed $dP/dH$ (Power absorption derivative) with $H$ for $x = 1.0$ alloy composition in the horizontal-parallel (||) geometry for a few selected temperatures. These are representative of vertical-parallel ($\parallel V$) geometry also and of alloys of other compositions in || and $\parallel V$ geometries. The equations representing the theoretical lineshape for $dP/dH$ has been presented by Kaul and Siruguri [13] and a least squares fit of the experimental data to this line shape gives a $g$ value of $2.07 \pm 0.02$ which is temperature independent and gives the accurate values of resonance field ($H_r$), linewidth ($AH$) and saturation magnetisation ($M_S$). The details of line shape analysis are given in chapter 1 (See Eqs. 1.38 and 1.39).

The temperature dependence of resonance field (in || geometry) and saturation magnetisation, $M_S$, are shown in Figs. 3.4 and 3.5 respectively. The observed temperature dependence of magnetisation is now used to distinguish between localised and itinerant electron models. The variation of spin wave stiffness coefficient with temperature is different for the two models [14] being given
Fig. 3.3. FMR power absorption derivative spectra at different temperatures for Fe$_2$MnSi alloy. The solid line indicates the fit to the experimental spectrum based on Eqs. 1.38 and 1.39.
Fig. 3.3. Continued.
Fig. 3.4. Variation of the FMR resonance field ($H_{res}$) with temperature ($T$) in Fe$_x$ Mn Si alloys.
Fig. 3.5. The dependence of saturation magnetisation \( (M_S) \) on temperature \( (T) \) for \( \text{Fe}_{3-x}\text{Mn}_x\text{Si} \) alloys. The solid line indicates the fit to the data using the spin wave relation [Eq. 3.4].
by

\[ D(T) = D(0)[1 - D_2 T^2] \]  \hspace{1cm} (3.2)  

and  

\[ D(T) = D(0)[1 - D_{5/2} T^{5/2}] \]  \hspace{1cm} (3.3)  

for the itinerant- and \textit{localised-electron} models respectively. The dependence of \textit{magnetisation} on temperature and spin wave stiffness coefficient is theoretically given by [15,16]

\[ M_S(T) = M_S(0) - g\mu_B Z(3/2, t_H) \left[ \frac{k_B T}{4\pi D(T)} \right]^{3/2} \]  \hspace{1cm} (3.4)  

where \( Z(3/2, t_H) \) denotes the Bose-Einstein integral function

\[ Z(s,t_H) = \sum_{n=1}^{\infty} n^{-s} \exp(-nt_H) \]  \hspace{1cm} (3.5)  

and

\[ t_H = T_g / T = \frac{g\mu_B H_{\text{eff}}}{k_B T} \]  \hspace{1cm} (3.6)  

The factor \( Z \) in Eq. 3.4 arises because there is an energy gap \( \Delta = g\mu_B H_{\text{eff}} \) in the spin wave spectrum in the presence of the effective field

\[ H_{\text{eff}} = H - 4\pi NM + H_k \]  \hspace{1cm} (3.7)  

where \( M \) is the magnetisation, \( N \) is the demagnetisation factor and \( H_k \) is the anisotropy field.

Fits to magnetisation data were carried out using Eq. 3.4 and for the two forms of \( D(T) \) given by Eqs. 3.2 and 3.3. The tern-
perature dependence of $D(T)$ for the \textit{localised-electron} model (Eq. 3.3) gave much better fits than those for itinerant-electron model. As a further check, a plot of \[
\frac{[M_S(0) - M_S(T)](D(T))^{3/2}}{Z(3/2, t_H)}
\] vs. $T^{3/2}$ with $D(T)$ from 3.3 gives a straight line passing through origin (Fig. 3.6) for all compositions.

Table 3.2 gives the values of $D(0)$ and $D_{5/2}$ for alloys of different Mn concentrations. The validity of Eq. 3.3 in the present case implies that the \textit{localised-electron} model adequately describes $D(T)$. Moreover the ratio $D(0)/T_C$ of about 0.6 meV A$^2$K$^{-1}$ is obtained for all the compositions. This ratio is related to the mean square range of the exchange interaction [17]

\[
\frac{D(0)}{T_C} = \left[ \frac{k_B}{2(S+1)} \right] \langle r^2 \rangle
\]

and gives $\langle r \rangle \approx 0.9 a_0$ (where $a_0$ is lattice constant) and implies a range of the exchange interactions extending up to fifth nearest neighbours (Table 3.1)

The temperature variation of FMR linewidths is shown in Fig. 3.7. The linewidth first goes through a minimum at lower temperature followed by a maximum at higher temperature (Fig. 3.7). The linewidth increase below $T_c$ extends over a very large temperature region. This increase in linewidth is typical of re-entrant spin glass systems [13,18] and can be described by an empirical relation [19]
Table 3.2. Magnetic transition temperatures and spin wave parameters for Fe$_{3-x}$Mn$_x$Si. Numbers in brackets indicate errors.

<table>
<thead>
<tr>
<th>x at X</th>
<th>$T_C$ K</th>
<th>$T_{RE}$ K</th>
<th>$M_S(\emptyset)$ G</th>
<th>D(0) meVÅ$^2$</th>
<th>$D_{5/2}$ $10^{-7}$ K$^{-3/2}$</th>
<th>D(0)/$T_C$ meVÅ$^2$/K</th>
<th>$&lt;r^2&gt;$ Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>435(1)</td>
<td>32(1)</td>
<td>237(10)</td>
<td>225(10)</td>
<td>1.15(10)</td>
<td>0.52(2)</td>
<td>24.138</td>
</tr>
<tr>
<td>0.90</td>
<td>370(1)</td>
<td>35(1)</td>
<td>230(10)</td>
<td>160(10)</td>
<td>1.20(20)</td>
<td>0.43(3)</td>
<td>19.961</td>
</tr>
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<td>1.00</td>
<td>230(1)</td>
<td>58(1)</td>
<td>222(10)</td>
<td>150(10)</td>
<td>5.00(50)</td>
<td>0.65(5)</td>
<td>30.173</td>
</tr>
<tr>
<td>1.20</td>
<td>190(1)</td>
<td>72(1)</td>
<td>203(10)</td>
<td>115(10)</td>
<td>11.50(50)</td>
<td>0.61(3)</td>
<td>28.316</td>
</tr>
</tbody>
</table>
Fig. 3.6. Variation of \( \frac{[M_s(0) - M_s(T)](D(T))^{3/2}}{Z(3/2, t_H)} \) with \( T^{3/2} \) in \( \text{Fe}_{3-x}\text{Mn}_x\text{Si} \) alloys. The straight line passing through origin shows that the localised-electron model [Eq. 3.3 and 3.4] describes the temperature dependence of saturation magnetisation (\( M_s \)).
\[ \Delta H_{pp} = \Gamma_0 + \Gamma_1 (T/T_o) \exp(-T/T_o) \]  

(3.9)

where for a given Mn concentration and microwave frequency, \( r \), \( \Gamma_1 \) and \( T_o \) are constants. The observed temperature dependence of linewidth was fitted to Eq. 3.9 and the fits are also shown in Fig. 3.7. In re-entrant spin glass systems there is a region of constant linewidth below \( T_\alpha \) and the linewidth rises below about \( T \approx 2 T_{RE} \) and follows the empirical form given by Eq. 3.9 \[13\]. In the Fe\(_3\)Mn Si system however the increase in linewidth starts at a very high temperature (in fact just below \( T_\alpha \) for \( x = 1.0 \) and 1.2 compositions) and follows the form given by Eq. 3.9 in a very wide temperature range.

### 3.3.3. Mössbauer Spectroscopy

The temperature dependence of Mössbauer absorption spectra for \( x = 0.75 \) composition is shown in Fig. 3.8. The hyperfine magnetic field distribution derived from the spectra using Le Cäer's method (Chapter 2) are also shown. The assignment of the higher fields in the region 300 kOe to Fe atoms at B sites (8 AC near neighbours) and the lower fields (200 kOe and lower) to AC sites (B and D site neighbours) has been established quite uniquely by several experiments and analysis procedures, not only for Fe\(_3\)Si based systems [4-5, 20] but for other DO\(_3\) ordered A-B alloys as well [21-23]. The magnetic moment for the B site atom (both Fe and Mn) is about \( 2 \mu_B \) for Mn concentration upto 0.75 whereas the AC site moment falls from 1.5 \( \mu_B \) to 0.4 \( \mu_B \) with Mn concentration due to substitution of Mn neighbours in their nn environment.
Fig. 3.7. Variation of FMR linewidth ($\Delta H$) with temperature in $\text{Fe}_x \text{Mn}_y \text{Si}$ alloys. $T_c$ is the temperature at which linewidth goes to a minimum. $T_c$ values from AC susceptibility measurements are indicated. The solid line through the data points in low temperature region is the fit to the data using Eq. 3.9.
For low Mn concentration, the Mn atoms go to occupy only the B site exclusively but at $x = 0.75$ although all B sites have not been filled, some Mn atoms start filling the AC sites as well [24]. This gives a wide variety of environments and the field distributions in Fig. 3.8 clearly depicts this situation. The field distributions below 200 kOe peaked at different field values arise due to Fe (AC) sites with different numbers of Mn neighbours, the lower field values corresponding to higher number of Mn neighbours. The correlation between hyperfine field (at 80 K), Fe(AC) moment and number of Mn . (n = 0 - 4 as there are always 4 Si D neighbours to this site) neighbours is shown in Fig. 3.9. The observed linear correlation gives us a good deal of confidence in our assignment of peaks in the field distribution to the number and type of B site near neighbours around Fe (AC) sites. The fields originating from B site Fe atoms also have a distribution at 300 kOe which arises predominantly from variations in Mn occupation in third neighbour shell (Table 3.1) and also from Mn first neighbours substituting at AC sites. The field changes are not easily resolvable in the distributions. However they approximately correspond to Fe atoms with (8Fe, 0Mn), (7Fe,1Mn) etc. configurations.

The temperature dependence of hyperfine field for each of these configurations is shown in Fig. 3.10. The decrease in hyperfine field with temperature is faster for the higher Mn configurations. This behaviour is further analysed for the $x = 0.9$ alloy sample for which data were recorded in a wider temperature range of 10 K - 300 K.
Fig. 3.8. Mössbauer spectra and their hyperfine field distributions (calculated using model-independent Le Cäer program) at different temperatures for Fe$_2$Mn$_{0.75}$Si alloy.
Fig. 3.8. Continued.
Fig. 3.9. Correlation between Fe hyperfine field and magnetic moment ($\mu_{Fe}$) for AC site Fe atoms. The number of tin nn atoms for these sites is indicated by n.
Fig. 3.10. Temperature dependence of hyperfine field ($H_{hf}$) for Fe(AC) atoms having different number of Mn near neighbours (n) for $\text{Fe}_{2.25}\text{Mn}_{0.75}\text{Si}$ alloy.
Fig. 3.11 shows the temperature dependence of Mössbauer spectra for \( x = 0.9 \) composition in the temperature range 10 K - 300 K. The assignment of peaks in the field distributions to various \( H_n \) neighbours of AC site Fe atoms is done as discussed earlier for \( x = 0.75 \) composition. Fig. 3.12 shows the temperature dependence of hyperfine field for each of the Fe(A,C) sites with different \( H_n \) first neighbours. The temperature dependence is clearly more pronounced for the configurations with higher number of Mn near neighbours. This behaviour can be attributed to the weaker Fe-Mn exchange interaction relative to Fe-Fe exchange. Neutron scattering studies at lower Mn concentration [25] give \( J_{Fe-Fe} = 25.4 \text{ meV}, J_{Fe-Mn} = 8.2 \text{ meV} \) and a very small or negative value for \( J_{Mn-Mn} \). The faster decrease in hyperfine field for the Fe configuration with higher number of Mn neighbours is then due to a smaller exchange interaction with its neighbours. Jaccarino et. al [26] proposed a phenomenological model to take into account the exchange coupling at a solute site in the host matrix. He gave a modified Brillouin function to express the temperature dependence of reduced hyperfine field at the solute atom in terms of the reduced magnetisation \( M(T)/M(0) \) of the host, and an exchange coupling parameter, \( \zeta \).

\[
\frac{H_{hf}(T)}{H_{hf}(\Theta)} = B_J \left( \frac{3J}{J+1} \zeta \frac{M(T)/M(\Theta)}{T/T_C} \right) \tag{3.10}
\]

where

\[
B_J(x) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} x - \frac{1}{2J} \coth \frac{x}{2J} \tag{3.11}
\]

For \( \zeta = 1 \), the reduced hyperfine field follows the same tempera-
Fig. 3.11. Mössbauer spectra and their hyperfine field distributions (calculated using model-independent Le Cäer program) at different temperatures for Fe$_{2+1}$Mn$_9$Si alloy.
Fig. 3.11. Continued.
Fig. 3.11. Continued.
ture dependence as the host magnetisation whereas for $\xi < 1$, the reduced hyperfine field decreases faster than the host magnetisation. This model gave a very good description of hyperfine field at impurity Fe atoms in nickel and manganese hosts [27]. The difference in temperature dependence of hyperfine field at Fe(A,C) site for different number of Mn near neighbours can be described by an extension of this model, if we choose different values of the coupling parameter, $\xi$, for the different configurations. Fig. 3.12 shows the fits to the hyperfine field data using Eq. 3.10. The reduced hyperfine field for the configuration with 8 Fe near neighbours was used to represent the reduced magnetisation.

For the Fe(AC) configurations with no manganese neighbours we get $\xi = 1$, whereas for configuration with more Mn neighbours $\xi$ decreases and we get $\xi = 0.4$ for the configuration with the largest number of Mn neighbours ($n = 4$). This provides a good evidence that Mn near neighbours to Fe sites decrease the effective exchange interaction at these sites. The small entropy change at $T_m$ mentioned earlier is also consistent with this because there is a large thermal disorder at these sites and only a partial ordering of spins even much below $T_C$.

The average hyperfine field $H_{av}$ and the isomer shift correlation parameters $A$ and $B$ defined by [23]

$$\delta(H_{hf}) = A\bar{H}_{hf} + B$$

(3.12)
Fig. 3.12. Temperature dependence of hyperfine field ($H_{hf}$) for Fe(AC) atoms having different number of Mn near neighbours ($n$), and Fe(B) atoms with 8 Fe and 6 Fe near neighbours for Fe$_2$Mn$_{x}$Si alloy. The solid line indicates the fit to the data using Eq. 3.10.
are shown in Fig. 3.13 for the x = 0.9 alloy composition. This correlation was introduced in the field distribution fits carried out using the Le Cäer program. This enables us to determine a unique isomer shift value for each configuration and to follow its temperature dependence. Fig. 3.14 shows the temperature dependence of isomer shift for the n = 0 to 5 (number of Mn first neighbours to Fe(AC) sites) configurations. These plots show a pronounced increase below the re-entrant temperature. The physical origin of the isomer shift increase is because of either a loss of 3d charge or 3d spin at the neighbouring solute site [28]. But since we are observing a temperature dependent effect, the loss of 3d spin rather than 3d charge seems to be the likely cause for the isomer shift increase. Thus although the average hyperfine field does not show a change in behaviour at T_{pr} (Fig. 3.13) the individual isomer shifts at the sites do show an effect related to the change in the near neighbour Mn moment. A slight increase in hyperfine field for individual Fe(AC) configurations having 2-4 Mn near neighbours can also be observed at low temperatures.

In the higher concentration region x > 0.9, the individual hyperfine field configurations become difficult to resolve and we have therefore fitted the spectra to only two sets of Gaussian distributions peaked at two different values. Initial estimates of the hyperfine field values were obtained from model independent LeCäer fits. The Mössbauer spectra and field distributions are shown in Fig. 3.15 and Fig. 3.16 for x = 1.0 and 1.2 compositions. For x = 1.0, the Gaussian field distribution peaked at the
Fig. 3.13. Variation of mean hyperfine field ($H_{hf}$) and isomer shift parameters (A and B defined in Eq. 3.12) with temperature (T) for Fe$_2$Mn$_{28}$Si alloy.
Fig. 3.14. Temperature dependence of isomer shift ($\delta_n$) for Fe(AC) atoms having different number of Mn near neighbours ($n$) for Fe$_2$Mn$_0$ gSi.
Fig. 3.15. Mössbauer spectra and their hyperfine field distributions (fitted to two Gaussians) at different temperatures for Fe$_2$MnSi alloy.
Fig. 3.15. Continued.
Fig. 3.16. Mössbauer spectra and their hyperfine field distributions (fitted to two Gaussians) at different temperatures for Fe_{18}Mn_{12}Si alloy.
Fig. 3.16. Continued.
Fig. 3.16. Continued.
higher value corresponds to \( n = 2 \) and the lower field value corresponds to \( n = 3 \) configurations. The fraction of these two configurations (as obtained from area under the two distributions) is consistent with the probability for substitution of the B sites by Mn atoms [24]. Similarly for \( x = 1.2 \) composition the higher field peak (lower fraction) corresponds to \( n = 3 \) configuration whereas the lower field peak (higher fraction) corresponds to \( n = 4 \) configuration. The temperature dependence of hyperfine fields and fraction of the peaks as shown in Figs. 3.17 and 3.18 respectively for \( x = 1.0 \) and 1.2 compositions.

3.4. DISCUSSION

The experimental findings of AC susceptibility, FMR and Mössbauer studies on the \( \text{Fe}_x \text{Mn}_s \text{Si} \) alloys \( (0.75 \leq x \leq 1.2) \) together with earlier experimental results can be summarised as follows:

(i) The transition at \( T_C \) is from a paramagnetic to ferromagnetic state.

(ii) The temperature dependence of hyperfine field at the Fe sites with different Mn neighbours is strongly dependent on the first near neighbour Mn atoms. The exchange interaction between Fe and Mn is ferromagnetic but much weaker as compared to Fe-Fe exchange.

(iii) The FMR linewidth begins to increase just below \( T_C \) and shows a behaviour characteristic of re-entrant spin glass systems.
Fig. 3.17  a. Temperature dependence of hyperfine field $\tilde{H}_L$ (lower field) and $\tilde{H}_H$ (higher field) for Fe$_2$MnSi alloy.  
b. Variation of area under low field peak (LFS) and high field peak (HFS) for Fe$_2$MnSi.
Fig. 3.18 a. Temperature dependence of hyperfine field $H_{hf}^L$ (lower field) and $H_{hf}^H$ (higher field) for Fe$_{1.8}$Mn$_{1.2}$Si alloy.

b. Variation of area under low field peak (LFS) and high field peak (HFS) for Fe$_{1.8}$Mn$_{1.2}$Si.
(iv) The system is described by localised exchange interactions up to fifth neighbour shells.

(v) There is a lower transition temperature $T_{RE}$ (which depends on Mn concentration) and there are pronounced changes in hyperfine interactions (magnetic hyperfine field and isomer shift behaviour) below this temperature.

(vi) The exchange interactions between second neighbour manganese sites is weak and negative as measured from neutron inelastic scattering measurements [25] at low temperatures and gives rise to an antiferromagnetic ordering of moments at Mn sites as observed from neutron diffraction [29,30] determination of magnetic structure.

3.4. a. Effect of Preferential Substitution of Mn on Exchange Interactions

Based on these findings a simple model is proposed to describe the magnetic properties of the Fe$_{3-x}$Mn$_x$Si alloy system. The $D0_3$ structure (Fig. 3.1) and the preferential occupation of B sites by Mn atoms in this structure gives rise to the following distinct magnetic behaviour of Fe and Mn moments occupying these sites (see Table 3.1)

(i) Fe at (A,C) sites with a moment of 0.4 $\mu_B$ having a first near neighbour environment of predominantly B site Mn moments ($\mu = 2 \mu_B$) and D site Si atoms ($\mu = 0$). These Fe moments have a weak local ferromagnetic first neighbour exchange with Mn neighbours which depends on the number of Mn neighbours and becomes weaker with more Mn neighbours.
(ii) A very small number of Fe atoms at B sites are with a magnetic moment of $2 \mu_B$ and a first neighbour exchange with its Fe(AC) neighbours which is ferromagnetic. For Mn concentrations ($x \geq 1$) however these B sites are almost fully occupied by Mn and we need not consider the B site Fe atoms.

(iii) Mn atoms of magnetic moment ($\approx 2 \mu_n$) at the B sites which have an antiferromagnetic exchange with the other B site Mn atoms and these Mn-Mn sites are third neighbours. Around $x = 0.75$ composition and beyond, the AC sites are also occupied by Mn and this gives rise to first neighbour Mn-Mn exchange also.

(iv) A small number (less than number at B site) of Mn atoms of magnetic moment about 0.4 $\mu_B$ at AC sites which have predominantly Mn and Si near neighbours at B and D sites.

A schematic representation of the various configurations is shown in Fig. 3.19. Since Fe atoms at (A,C) sites and Mn atoms at B sites are the majority atoms in the system we consider the magnetic behaviour of the system by a consideration of these sites. The behaviour of Mn (AC) and Fe(B) sites are also consistent with this behaviour.

3.4. b. Spin Canting and Magnetic Structure

Saslow and Parker studied analytically [31] a Heisenberg spin system on square and simple cubic lattice when antiferromagnetic bonds are substituted for ferromagnetic host nearest nei-
Fig. 3.19

a. Schematic representation of Fe and Mn atomic moments on AC and B sites and their exchange interactions with neighbours.

b. Canting of Hm spins at low temperatures.

c. Frustration at Fe(AC) site due to antiferronagnetic ordering on B sublattice.
ghbcur exchange bonds. The same situation applies to Mn(B) sites
where the ferromagnetic Mn-Fe bonds are substituted by antiferro-
magnetic Mn-Mn bonds. Saslow and Parker's results show that for
such a system there is a spin canting at low temperatures but at
higher temperatures there is ordinary ferromagnetic behaviour. In
our system the other site viz. the Fe(AC) site has always a
ferromagnetic exchange with Fe or Mn neighbours and it is only
the Mn(B) site which shows a canting at low temperatures.
Fig. 19b depicts the magnetic structure in the canted state. This
canted spin structure is also physically understandable in terms
of the frustration that sets in at the Fe(A,C) site. For an anti-
ferromagnetic ordering at Mn(B) sublattice, the ferromagnetic Fe-
Mn exchange interaction, gives a conflicting Fe(A,C) ordering due
to the two Mn(B) neighbouring spins (Fig. 19c). The canting of Mn
spins as shown in Fig. 19b gives a stable ground state for the
system. The neutron diffraction data of Yoon and Booth [3,29] are
also consistent with this Mn spin canting as they observed an
antiferromagnetic component on the B sublattice perpendicular to
the magnetisation direction. Yoon and Booth observed additional
superlattice lines from spins in other planes but no superlattice
reflection from (1/2,1/2,1/2) planes which are also expected for
antiferromagnetic spin structures in (111) planes.

We therefore associate the lower transition temperature to
a spin canting of the Mn moments and the magnetic phase diagram
is shown in Fig. 3.20. It has also been predicted in all models
for re-entrant spin glasses [7-9] that a replica symmetry break-
ing state (marked by onset of irreversibility) is obtained at low
Fig. 3.20. Magnetic phase diagram for Fe$_{3-x}$ Mn Si alloy system.
temperatures below the canted state. A careful external field dependent study is required to confirm this for our system but the hyperfine fields do show an increase at low temperatures (Fig. 3.12) and suggest a re-entrant phase formation.

3.5. CONCLUSIONS

In conclusion we find that a combined AC susceptibility, FMR, and Mossbauer effect study of the complex Fe$_{x}$ Mn$_{1-x}$ Si magnet alloy system shows that there is a strong effect of near neighbour environment on the exchange interactions and corresponding magnetic behaviour of the system. AC susceptibility and magnetization studies show magnetic transitions clearly at two temperatures ($T_c$ and $T_{RR}$) whereas FMR studies show a spin glass type increase in linewidth just below ferromagnetic $T_m$. Mossbauer hyperfine magnetic field and isomer shift variations from site to site depending on Mn neighbours suggest the importance of near neighbour effects. A magnetic structure consisting of canted Mn spins due to antiferromagnetic Mn-Mn exchange interactions is suggested.
REFERENCES


