Mössbauer study of $Mn_{1-x}Fe_xSi$ in external magnetic fields

Y. Nishihara, S. Waki, and S. Ogawa*
Electrotechnical Laboratory, Sakura, Ibaraki 305, Japan
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The Mössbauer effect and the magnetization of $Mn_{1-x}Fe_xSi$ were measured. With increasing FeSi dopant concentration, the weak itinerant-electron ferromagnetism of MnSi disappears around $x=0.15$. Mössbauer spectra in magnetic fields were analyzed by taking into account the effect of a ferromagnetic or induced magnetic moment. The external magnetic field induces a hyperfine magnetic field at ^{57}Fe in the nearly ferromagnetic samples ($x \gtrsim 0.15$).

I. INTRODUCTION

$3d$ transition-metal monosilicides MSi (M=Cr, Mn, Fe, and Co) with the cubic $B20$ structure are typical band magnets with weakly correlated electron systems, and they exhibit a wide variety of magnetic and electrical properties.[1] MnSi in a magnetic field larger than 6 kOe shows a magnetic behavior classified as weak itinerant-electron ferromagnetism.[2] The magnetic structure of MnSi has been determined to be helical below 30 K from neutron and nuclear-magnetic-resonance experiments.[3,4] When more than 10 mol % of paramagnetic FeSi or diamagnetic CoSi is doped in MnSi, the ferromagnetic moment of MnSi disappears.[1] Magnetic properties of the $Mn_{1-y}Co_ySi$ system were studied by Motoya *et al.*[5] These authors reported that samples with y smaller than 0.08 have magnetic order at low temperatures, and that doping of a small amount of CoSi produces two different Mn states in MnSi. Some of the Mn atoms have magnetic moments of nearly the same magnitude as those in pure MnSi, while the other Mn atoms which are near Co atoms lose their magnetic moments. From this result, Motoya *et al.* concluded that the disappearance of magnetic order by doping CoSi could be attributed to the increase in the number of nonmagnetic Mn. There is no report on magnetic properties of the $Mn_{1-x}Fe_xSi$ system.

We have measured the ^{57}Fe Mössbauer spectra in magnetic fields and the magnetization of $Mn_{1-x}Fe_xSi$. This paper gives the results and contains a discussion on the microscopic magnetic properties of this system.

II. EXPERIMENTAL RESULTS AND ANALYSIS

Alloys of $Mn_{1-x}Fe_xSi$ were prepared by induction melting. They were annealed at 900 °C for 2 d. All of the samples were confirmed by x-ray diffraction to have the cubic $B20$ structure.

Magnetization curves of $Mn_{1-x}Fe_xSi$ at 4.2 K are shown in Fig. 1. The magnetization M increases as the external magnetic field H_{ext} increases and saturates abruptly around 6 kOe in the sample with iron concentration less than 0.1. This behavior shows that the spin structure changes from conical to induced ferromagnetic structure as the external field increases. In the sample with iron concentration greater than 0.1 the linear part of the magnetization at low fields almost disappears and shows no abrupt saturation around 6 kOe. M^2-versus-H_{ext}/M plots for the samples with $x=0.1$ and 0.2 are also shown in Fig. 1. M^2 linearly increases with H_{ext}/M in the high-field region in both samples. From Fig. 1 we find that the magnetic state of the sample with $x=0.1$ is weakly ferromagnetic and that of $x=0.2$ is nearly ferromagnetic.

The Mössbauer spectrum of ^{57}Fe in $Mn_{1-x}Fe_xSi$ shows a quadrupole splitting above 30 K. With decreasing temperature the spectrum broadens owing to a superposition of a magnetic splitting. The temperature dependence of the hyperfine magnetic field H_w estimated from the broadening of the spectrum is shown in Fig. 2. Figure 2 shows that the Curie temperature decreases with increasing iron concentration, and that magnetic order disappears around $x=0.15$. The hyperfine field at ^{57}Fe has a strong temperature dependence.

Figure 3 shows the Mössbauer spectra for $Mn_{0.995}(^{57}Fe)_{0.005}Si$ in external magnetic fields above 6 kOe at 4.2 K. The γ-ray direction is parallel to the exter-

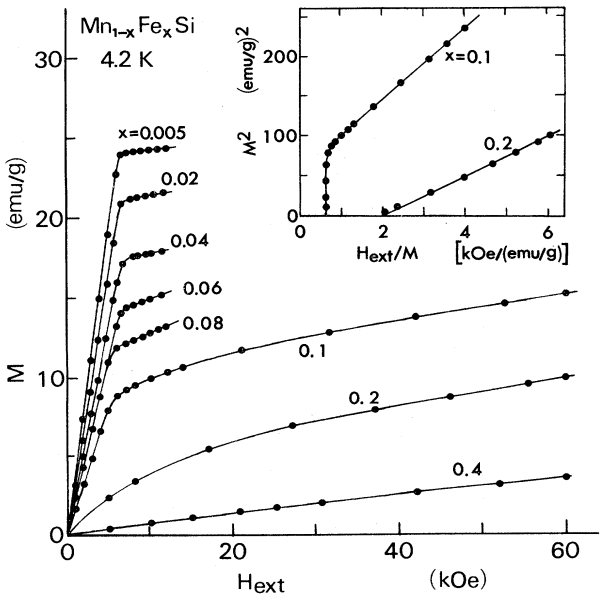

FIG. 1. Magnetization curves of $Mn_{1-x}Fe_xSi$ at 4.2 K.

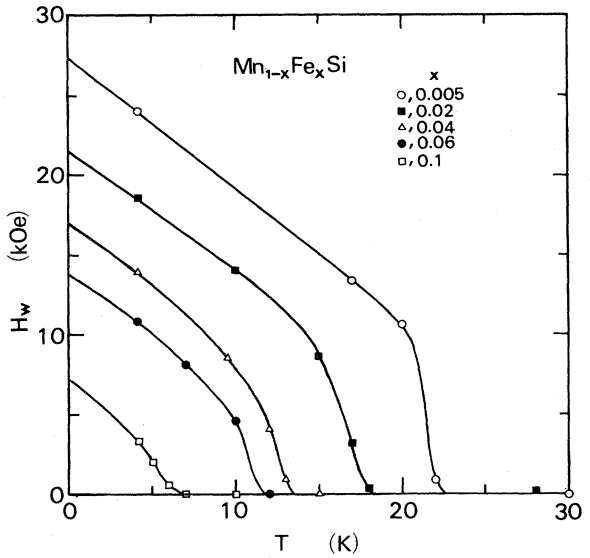

FIG. 2. Temperature dependence of the hyperfine field at ^{57}Fe in $Mn_{1-x}Fe_xSi$.

nal field. In terms of the external field, the effective internal field $\vec{H}_{eff}$ at ^{57}Fe can be expressed as

$$\vec{H}_{eff}=\vec{H}_{ext}+H(\theta)\,, \tag{1}$$

if the hyperfine coupling constant has the same trigonal symmetry as the electric field gradient (EFG) at Fe.[6] Here, $H(\theta)$ is the hyperfine field produced by the ferromagnetic or induced magnetic moment and θ is the angle between the principal axis of the EFG and the external field. With the use of the effective field given above and assuming that the γ-ray direction is parallel to the external field, we can compute Mössbauer spectra of a polycrystalline sample in magnetic fields. The summation is carried out over random orientations of the EFG axes.[7] We made a least-squares computer fitting of the observed spectrum to the computed spectrum. Solid curves in Fig. 3 were obtained from these fittings. An excellent fit was obtained when the sign of quadrupole splitting was positive. The fitting gives the hyperfine field $H(0°)=-36.5$ kOe when the ferromagnetic moment lies along the principal axis of the EFG and $H(90°)=-22.5$ kOe when the ferromagnetic moment is perpendicular to the principal axis. The hyperfine fields are nearly independent of external field. For paramagnetic $Mn_{0.8}Fe_{0.2}Si$, the quadrupole doublet is observed at zero external field. When the external field is applied, the spectrum broadens. However, a paramagnetic spectrum with an internal magnetic field equal to the external field was not fitted to the observed spectrum. The analysis with the effective field of Eq. (1) was also applied in this case. The anisotropy of the hyperfine field was smaller than that of $Mn_{0.995}Fe_{0.005}Si$. The hyperfine field $H(0°)$ is -11.3 kOe and $H(90°)$ is -8.8 kOe at the external field of 40 kOe. The hyperfine field increases with increasing external field in $Mn_{0.8}Fe_{0.2}Si$. The external field induces the hyperfine field in this sample. In paramagnetic FeSi, the spectrum

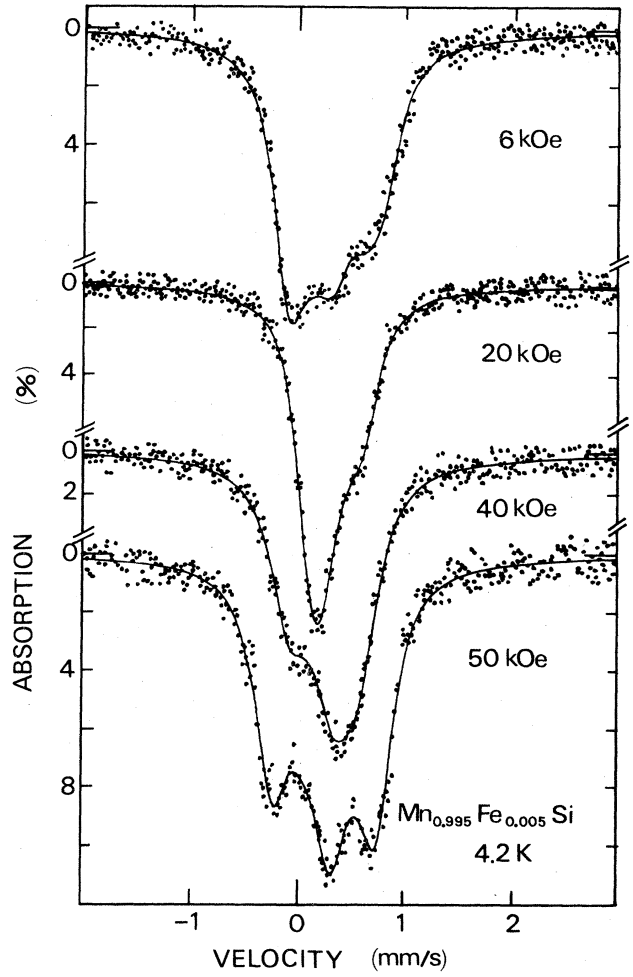

FIG. 3. Mössbauer spectra of $Mn_{0.995}Fe_{0.005}Si$ in external magnetic fields at 4.2 K.

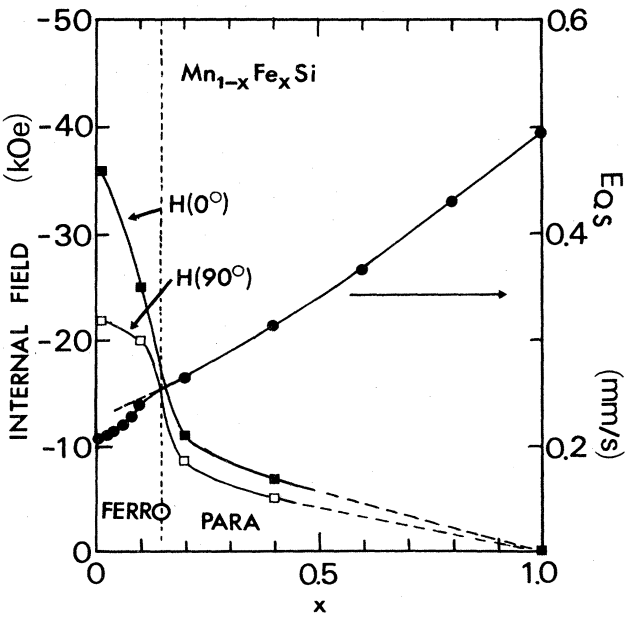

FIG. 4. Anisotropy of the hyperfine field and the quadrupole splitting in $Mn_{1-x}Fe_xSi$.

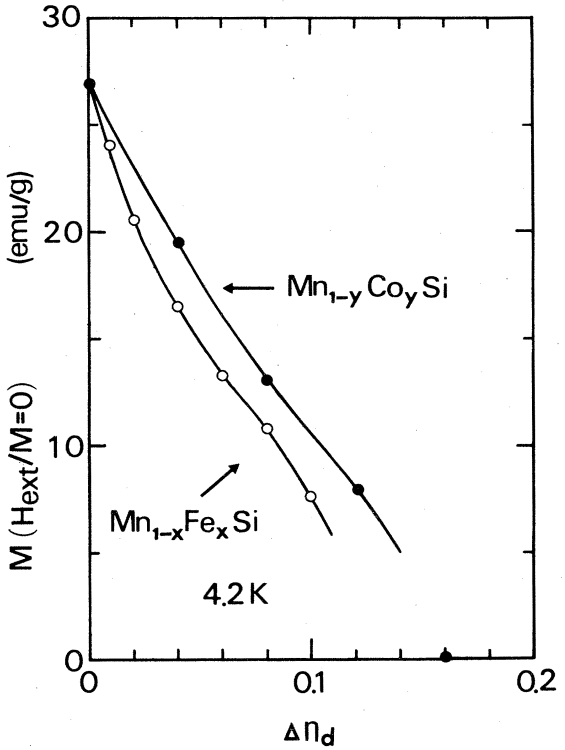

FIG. 5. Excess d-electron number Δn_d, and the dependence of magnetization extrapolated to $H_{\text{ext}}/M=0$ for $Mn_{1-x}Fe_xSi$ and $Mn_{1-y}Co_ySi$.

was fitted well to the paramagnetic spectrum with the internal field equal to the external field.

Figure 4 shows the hyperfine fields $H(0°)$ and $H(90°)$ determined from the spectra in external fields greater than 40 kOe. The anisotropy of the hyperfine field rapidly decreases with increasing iron concentration. When we divide the hyperfine field into two parts, that is, an isotropic part H_{iso} and an anisotropic part H_{aniso}, and assume that the anisotropic part depends on $3\cos^2\theta-1$ as well as the EFG, the hyperfine field $H(\theta)$ can be written as

$$H(\theta)=H_{\text{iso}}+H_{\text{aniso}}(3\cos^2\theta-1)\ . \tag{2}$$

The anisotropy of hyperfine field $R=H_{\text{aniso}}/H_{\text{iso}}$ is $+0.26$ for Fe in $Mn_{0.995}Fe_{0.005}Si$. According to the results of nuclear magnetic resonance,[8] the R value for Mn in MnSi is -0.135. Thus, the anisotropy of Fe is about 2 times as large as that of Mn and has a different sign. An-

TABLE I. Anisotropy $|H_{\text{aniso}}/H_{\text{iso}}|$ of the hyperfine magnetic field at ^{57}Fe.

Sample	$\lvert H_{\text{aniso}}/H_{\text{iso}}\rvert$	Reference
MnSi(Fe)	0.26	This work
CoS_2(Fe)	0.25	7
FeB	0.29	9
YFe_2	0.011	10
$ZrFe_2$	0.026	11
Fe_3Ge	0.044	12

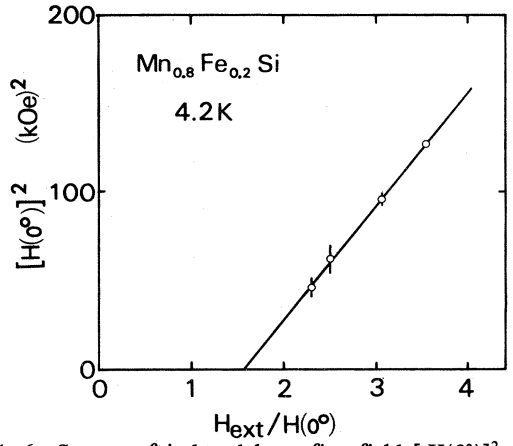

FIG. 6. Square of induced hyperfine field $[H(0°)]^2$ plotted against $H_{\text{ext}}/H(0°)$.

isotropies of the hyperfine field at ^{57}Fe were reported in CoS_2(^{57}Fe),[7] FeB,[9] YFe_2,[10] $ZrFe_2$,[11] Fe_3Ge,[12] etc. Magnitudes of the anisotropy R are summarized in Table I. The anisotropy of dipole field cannot explain these large anisotropies.[7,12] The anisotropy may result from a spatial distribution of d electrons depending on the direction of local magnetization. It should be noted that the large anisotropy of 0.25—0.29 is observed in typical itinerant-electron systems, such as MnSi, CoS_2, and FeB.

The center shift, within experimental error, has no concentration dependence. The value is (0.273 ± 0.003) mm/s relative to metallic iron. As shown in Fig. 4, the quadrupole splitting E_{QS} $(=e^2qQ/2)$ of $Mn_{1-x}Fe_xSi$ in the ferromagnetic state is smaller than that in the paramagnetic state. The quadrupole splitting in the Mössbauer spectrum arises from the EFG produced by distant charges modified by antishielding factors. The change in the quadrupole splitting by the substituting of Fe for Mn is

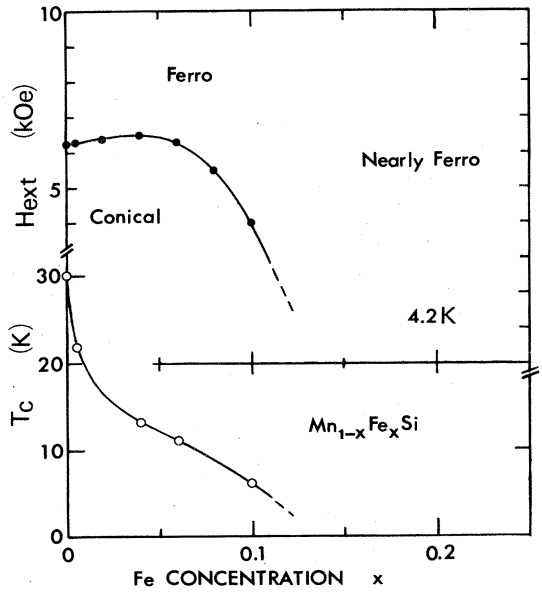

FIG. 7. Magnetic phase diagram of $Mn_{1-x}Fe_xSi$.

attributed to the change in shielding factors by electrons at the Fermi surface. Therefore, the result suggests that the density of states at the Fermi level is larger in the ferromagnetic state than in the paramagnetic state.

III. DISCUSSION

Figure 5 shows the magnetization extrapolated from the high-field region to zero for $Mn_{1-x}Fe_xSi$ and $Mn_{1-y}Co_ySi$.[5] The horizontal axis shows the excess number of d electrons Δn_d produced by the replacement of Fe or Co for Mn. Magnetizations decrease as the d-electron number increases. The ferromagnetic moment disappears around $\Delta n_d = 0.15$ in both systems. It seems that the effect of d-electron numbers plays a more important role than the effect of the number of nonmagnetic atoms.

The ferromagnetism disappears around $x=0.15$ in $Mn_{1-x}Fe_xSi$. In the nearly ferromagnetic sample with $x \gtrsim 0.15$, the hyperfine field is induced at Fe by the external magnetic field. Figure 6 shows the square of induced hyperfine field $[H(0°)]^2$ plotted against $H_{ext}/H(0°)$ for $Mn_{0.8}Fe_{0.2}Si$. The induced hyperfine field is nearly proportional to the bulk magnetization. The proportionality constant is nearly 80 kOe/μ_B. The Mössbauer spectra of $Mn_{0.8}Fe_{0.2}Si$ are fitted well to a powder pattern with one kind of hyperfine field. The linewidth obtained from this analysis slightly increases with increasing external magnetic field. The change in the hyperfine field estimated from this broadening is nearly 1 kOe. Therefore, it is concluded that the distribution of the magnetic moment of Fe is small in this system. A nuclear-magnetic-resonance study is desirable to obtain microscopic information about Mn atoms in this system.

The magnetic phase diagram of $Mn_{1-x}Fe_xSi$ is shown in Fig. 7. $Mn_{1-x}Fe_xSi$ shows weak ferromagnetism when $x < 0.15$. The magnetic structure is conical below about 6 kOe and ferromagnetic above 6 kOe. The paramagnetic samples with $x \sim 0.15$ show a nearly ferromagnetic behavior. The disappearance of ferromagnetism seems to be due to the increase in the d-electron number because of the replacement of Fe for Mn. This system is suitable for investigating magnetic properties ranging from weak ferromagnetic to paramagnetic states in one system. A study of spin-fluctuation effects on various physical quantities in this system is in progress.[13]

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*Present address: Institute for Solid State Physics, University of Tokyo, Roppongi, Tokyo 106, Japan.

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