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Mössbauer Spectroscopy of Magnetic Ordered Phases in Heusler Compounds $Fe_{3-x}Mn_xSi$

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For $0.75 \leq x \leq 1.75$, the Heusler compound $Fe_{3-x}Mn_xSi$ undergoes two phase transitions: one ferromagnetic at T_C and another to a phase with antiferromagnetic properties at a lower temperature, T_A. It was recently discovered that for $x = 1.7$, another antiferromagnetic transition occurs at a temperature even lower than T_A, T_{A2}. In addition, the phase below T_{A2} is defined as the AF2 phase. In this study, Mössbauer spectroscopy measurements were performed for samples with $x = 1.5$, 1.68, and 1.7 down to ~10 K to explore the properties of these magnetically ordered phases. At high temperatures, a singlet peak was observed and no hyperfine field was detected. At low temperatures the peak became broader, reflecting the increase in the hyperfine field in the magnetically ordered phases. For $x = 1.7$ and 1.68, the hyperfine field increased smoothly with decreasing temperature from T_C through T_A and T_{A2} to low temperatures. T_C estimated via the temperature dependence of the hyperfine field agrees with the results of the magnetization measurements. These findings show that despite the small macroscopic magnetization below T_{A2}, an internal field exists, implying that the AF2 phase is an antiferromagnetic ordered phase.

KEYWORDS: Mössbauer spectroscopy, Heusler compound, antiferromagnetic transition

1. Introduction

The Heusler compound $Fe_{3-x}Mn_xSi$ has been studied for a long time and is known to show different magnetic transitions depending on the value of x [1–7]. For $x < 0.75$, $Fe_{3-x}Mn_xSi$ exhibits only a ferromagnetic transition at the Curie temperature, T_C. Below T_C, for $x \geq 0.75$, a phase transition from the ferromagnetic (F) phase to a phase with antiferromagnetic properties occurs [2]. Here, this phase and transition temperature will be referred to as the AF phase and T_A, respectively.

Heusler compounds are promising half-metal candidates; half-metals have 100% spin-polarized conduction electrons that are of significance in spintronics. The possibility that $Fe_{3-x}Mn_xSi$ may be a half-metal has invoked renewed attention [7–9]. However, Fe_2MnSi does not have a half-metallic ground state because the low-temperature phase contains antiferromagnetic components, as mentioned above. Additionally, in our recent study on $Fe_{1.3}Mn_{1.7}Si$, magnetization and specific heat measurements revealed that another transition occurs at a temperature below T_A [10, 11]; this phase and the transition temperature are referred to as the AF2 phase and T_{A2}, respectively. Based on the decline in magnetization just below T_{A2}, the AF2 phase is considered to be an antiferromagnetic phase with no ferromagnetic properties, unlike the AF phase. However, no evidence of magnetic order has been obtained thus far from microscopic measurements. Some results of magnetization and the magnetic phase diagram in the magnetic field for samples around $x = 1.7$ have also been reported, indicating that the existence of the three transitions are limited to a narrow x range near $x = 1.7$ [11, 12].

The formula of Heusler compounds is X_2YZ, and the crystal structure is $L2_1$, where four fcc sublattices that comprise each element penetrate one another. For example, see the figure in Ref.13. In $Fe_{3-x}Mn_xSi$, the Fe and Mn atoms prefer the X and Y sites, respectively. Although for $x = 1$, Mn atoms on the Y site should be surrounded by eight Fe atoms on the X sites, and in fact, exchanges of Mn and Fe occur for some parts [2]. For $x \geq 1.3$, Mn atoms completely occupy the Y site, and the Mn atoms on the Y sites are surrounded by the nearest-neighbor X atoms, which are mostly Fe atoms and excess Mn atoms. Moreover, the magnetic moment seems to be primarily carried by the regular Mn atom on the Y site.

Mössbauer spectroscopy is a powerful tool used to study local magnetic properties and chemical and crystallographic disorders. Studies on Mössbauer spectroscopy of $Fe_{3-x}Mn_xSi$ have been previously performed. For a small value of x, information on the local environment of the Fe atoms residing on the X and Y sites was obtained [14]. For $x = 1$ and 1.3, the spectra at various temperatures were measured, and T_C was reasonably estimated [15].

In the current study, we investigate the Mössbauer spectroscopy of $Fe_{3-x}Mn_xSi$ ($x = 1.5$, 1.68, and 1.7) to explore the properties of the magnetically ordered phases, the AF2, AF, and F phases.

2. Experimental

Polycrystalline samples of $Fe_{3-x}Mn_xSi$ with $x = 1.5$, 1.68, and 1.7 were prepared by arc-melting high-purity constituent elements in a high-purity argon atmosphere. The samples were melted and turned over several times to ensure homogeneity and then annealed at 600°C for 2 days. The crystal structures of the samples were examined using X-ray powder diffraction with Cu $K\alpha$ radiation. The results showed that the prepared samples were single-phase, and the crystal structure was $L2_1$. ^{57}Fe Mössbauer spectroscopic experiments were performed using a 1.85 GBq ^{57}Co(Rh) source by employing a conventional constant-acceleration method in the temperature range between 10 K and 300 K. The velocity scale was calibrated with α-Fe, which has a hyperfine field B_{hf} of 33.1 T. The Mössbauer parameters were refined using the NORMOS program [16, 17]. The Mössbauer measurements used powder samples which had been annealed after pulverizing to remove strain, as pulverizing affects the sharpness of the transitions and the behavior of the hysteresis in magnetization.

3. Results and Discussion

Mössbauer spectra were taken for $Fe_{3-x}Mn_xSi$ ($x = 1.5$, 1.68, and 1.7). The sample with $x = 1.5$ exhibited two transitions at T_A and T_C, and the samples with $x = 1.68$ and 1.7 exhibited three transitions at T_{A2}, T_A, and T_C. Their transition temperatures were determined from magnetization measurements: for $x = 1.5$, $T_A = 65$ K and $T_C = 140$ K; for $x = 1.68$, $T_{A2} = 54$ K, $T_A = 69$ K, and $T_C = 95$ K; for $x = 1.7$, $T_{A2} = 60$ K, $T_A = 69$ K, and $T_C = 85$ K. Figures 1 and 2 show Mössbauer spectra at various temperatures between 15 K and 300 K for $x = 1.7$ and $x = 1.68$, respectively. The results of the fit are represented by solid lines. All the spectra can be well-fitted by assuming one magnetic site. At high temperatures ($T > T_C$), the spectra show a singlet peak indicating the paramagnetic state. By decreasing temperature to low temperatures where the AF2 phase is realized, the spectra become broader and exhibit structure due to the development of the magnetic order. Table I shows the The Mössbauer parameters obtained by fitting with a sextet for the magnetic-ordered states at $T = 15$ and 60 K, such as the hyperfine field B_{hf}, quadrupole splitting QS, isomer shift IS, and line width W. The isomer shift and quadrupole splitting showed no significant changes with temperature.

The appearance of the spectra for $x = 1.5$ at 10 K, where the AF phase is realized and the AF2 phase does not exist, was the same as those previously reported [15] and appear to be not that different from the spectra for $x = 1.68$ and 1.7. For $x = 1.68$ and 1.7, the temperature dependence of the spectra

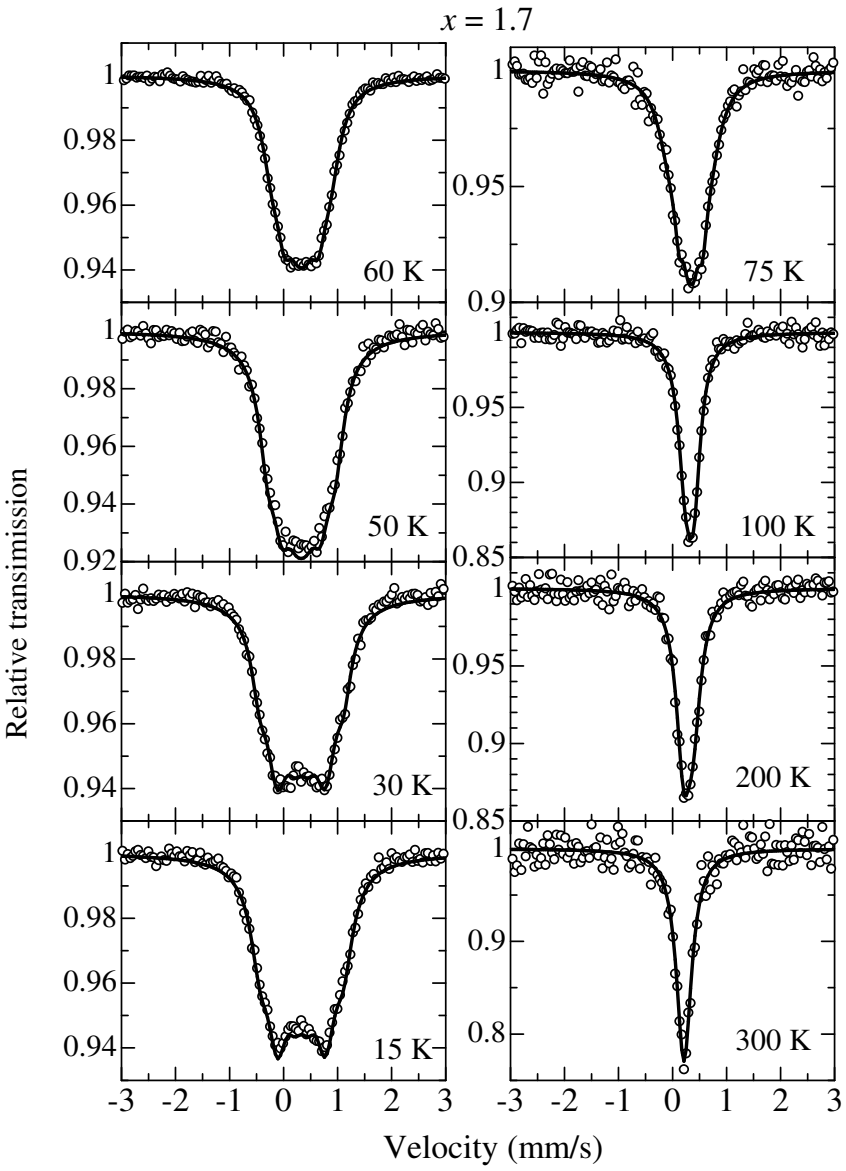

Fig. 1. Mössbauer spectra of $Fe_{1.3}Mn_{1.7}Si$ at different temperatures. Solid lines show the results of the fit.

appears to resemble that for $x = 1.3$ shown in Ref. 15. For $x = 1.5$, B_{hf} at 10 K obtained from the spectrum is $B_{hf} \sim 6$ T, which almost agrees with a previously reported result of $B_{hf} \sim 5.8$ T at 4.2 K [15].

Figure 3(a) shows the temperature dependence of B_{hf} for $x = 1.68$ and 1.7 obtained from the fits. As shown in Fig. 3(a), within the scatter in these measurements, B_{hf} for x =1.68 and 1.7 smoothly decreases with increasing temperature from 10 K to T_C. The estimated T_C values, indicated by the broken lines in the figure, are consistent with the values of T_C determined from magnetization. At the transitions at T_{A2} and T_A, B_{hf} does not exhibit significant changes, although a considerable change in the macroscopic magnetization at T_{A2} was observed. These findings are more clearly seen in Fig. 3(b), which shows the normalized hyperfine field, $B_{hf}/B_{hf}(0)$, as a function of temperature normalized by the Curie temperatures, T/T_C, for $x = 1.5$, 1.68, and 1.7. $B_{hf}(0)$ is B_{hf} at $T = 0$, as determined using

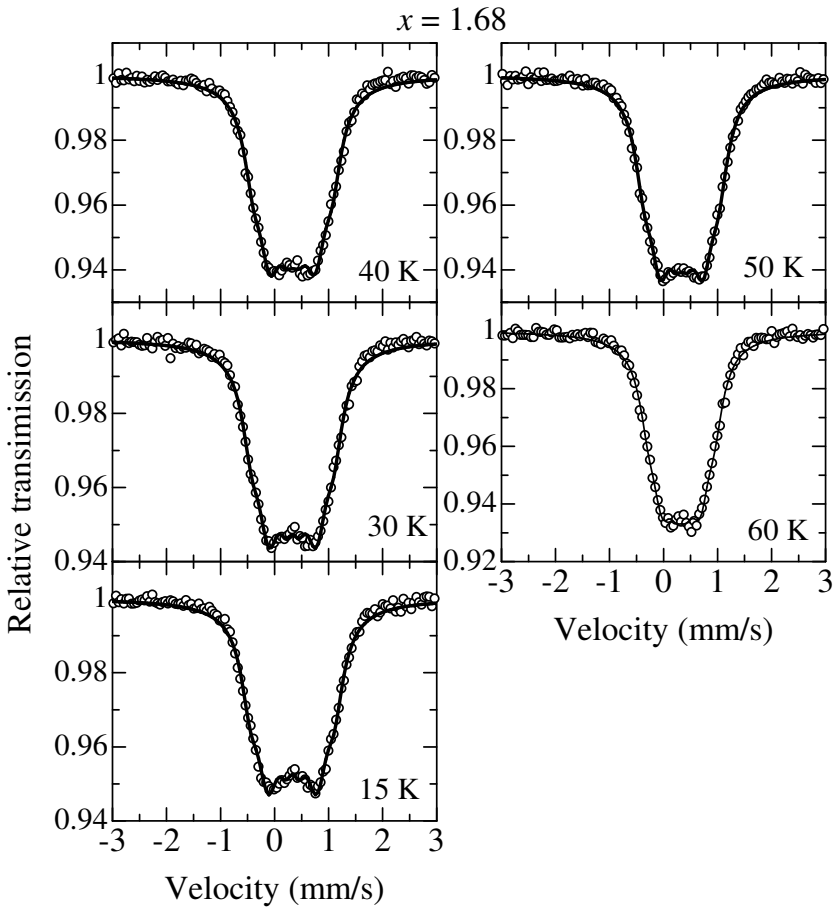

Fig. 2. Mössbauer Spectra of $Fe_{1.32}Mn_{1.68}Si$ at different temperatures. Solid lines show the results of the fit.

Table I. Hyperfine field B_{hf} (T), isomer shift IS, quadrupole splitting QS (mm/s), and line width W (mm/s) for $Fe_{3-x}Mn_xSi$ (x = 1.7 and 1.68) at T = 15 K and 60 K.

	T(K)	B_{hf} (T)	IS (mm/s)	QS (mm/s)	W (mm/s)
x = 1.7					
	15	4.78	0.33	0.008	0.45
	60	3.33	0.33	-0.002	0.42
x = 1.68					
	15	4.83	0.33	0.001	0.39
	60	3.78	0.33	0.004	0.42

data extrapolation. For comparison, the solid line shows the normalized spontaneous magnetization derived from the molecular field model with spin S = 2. For x = 1.5, although the measurements were performed only at three temperatures below 200 K, this result is consistent with T_C = 140 K obtained from magnetization measurements. The temperature dependence of B_{hf} appears to behave as if there is only one transition at T_C, regardless of the existence of multiple transitions: for x = 1.5, the transition occurs at T_A, and for x = 1.68 and 1.7, the transitions occur at T_{A2} and T_A.

These results clearly show that in the AF2 phase, an internal field is present at the Fe sites and that

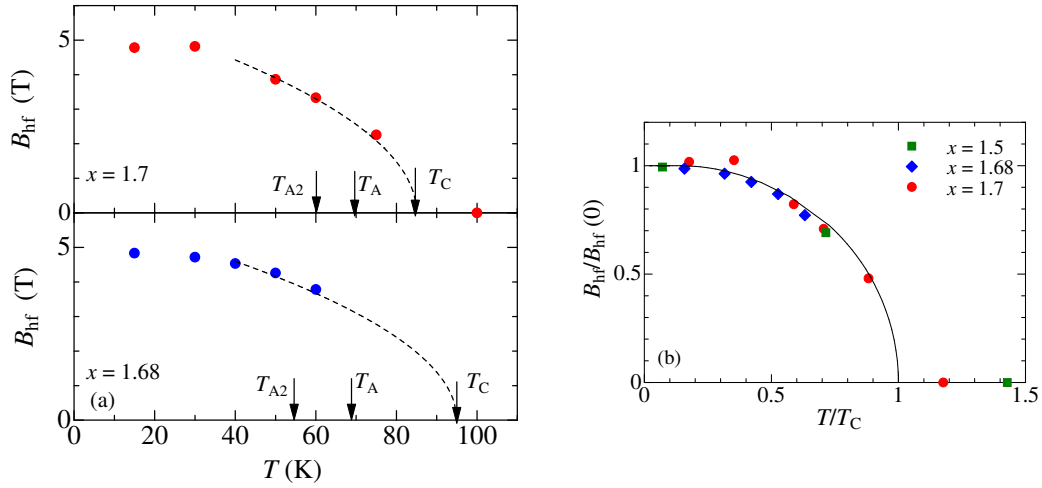

Fig. 3. (a) Temperature dependence of the hyperfine field B_{hf} in $Fe_{3-x}Mn_xSi$ (x = 1.68 and 1.7). The transition temperatures, T_{A2}, T_A, and T_C (see the text), are indicated by arrows; the transitions were determined from magnetization. The broken lines serve as a visual reference. (b) B_{hf} normalized by $B_{hf}(0)$ (B_{hf} at T = 0) is shown as a function of T/T_C for $Fe_{3-x}Mn_xSi$ (x = 1.5, 1.68, and 1.7). The solid line is derived from the molecular field model with spin S = 2.

the AF2 phase is a magnetically ordered phase. Although the AF2 phase was discovered recently and no microscopic studies have been conducted, the AF2 phase is considered to be an antiferromagnetic phase, because the macroscopic magnetization is almost zero but the internal field is present [10, 11]. The magnitude of the hyperfine field decreases with increasing x, which agrees with the tendency for the lower x previously reported [15].

As previously stated in $Fe_{3-x}Mn_xSi$ ($x > 1.3$), all Fe atoms are considered to occupy the X sites, while all Y sites are considered to be occupied by Mn. Therefore, all Fe atoms are reasonably assumed to occupy one equivalent site, and the nearest neighbors of the Fe atoms are four Mn atoms on the Y sites and four Si atoms on the Z sites.

The magnetic structure of the AF phase was investigated in Fe_2MnSi via neutron diffraction and numerical calculations, and a commensurate antiferromagnetic structure with canted moments was suggested [3, 6]. The magnetic moment is mainly carried by the Mn atoms on the Y site, just as it is often carried by the Y site atoms in Heusler compounds. Currently, the magnetic structure of the AF2 phase is not known. However, previous studies have suggested that for $2 < x < 2.8$, a commensurate antiferromagnetic structure in the antiferromagnetic phase might be realized [18, 19]. Considering this, it is possible to develop a commensurate antiferromagnetic alignment associated with the AF phase during the AF2 phase. It should be noted that in the end material, Mn_3Si, a complex incommensurate SDW (spin density wave) state is realized [18]. The relatively simple structures of the AF and AF2 phases are consistent with the assumption of a single magnetic site. Furthermore, this result is consistent with the inference obtained from the temperature dependence of B_{hf} that the local magnetic environment of Fe does not significantly change around T_{A2}.

However, it is unclear at this stage what the definite magnetic structures of the AF and AF2 phases are, as well as what role the Fe and excess Mn atoms on the X site and the Mn atoms on the Y site play in the magnetic orders. If the effects of the next nearest neighbors should be considered or if a change to a complex magnetic structure occurs, it would be more appropriate to assume multiple non-equivalent magnetic sites. Therefore, further studies are needed to clarify the magnetic structures of the AF and AF2 phases.

4. Conclusions

Mössbauer spectroscopy was investigated in $Fe_{3-x}Mn_xSi$ (x = 1.5, 1.68, and 1.7), focusing on the magnetically ordered phases, namely, the F, AF, and AF2 phases. The spectra become broader and show a structure reflecting the magnetic orders at low temperatures. Overall, the hyperfine field increases smoothly with decreasing temperature from T_C through T_A and T_{A2}. T_C estimated via the temperature dependence of the hyperfine field agrees with T_C determined from macroscopic magnetization measurements. The hyperfine field does not exhibit notable anomalies at T_{A2}, although the macroscopic magnetization decreases to almost zero, just below T_{A2}. These results demonstrate that the AF2 phase is indeed a magnetically ordered phase and is antiferromagnetic.

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