NMR studies of Heusler-type intermetallic compound Mn$_3$Si

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Abstract. In order to investigate the antiferromagnetic phase in Mn$_3$Si with $T_N = 23$ K microscopically, $^{55}$Mn NMR have been carried out in the temperature region between 2.2 and 17 K. The temperature dependences of spectrum and spin-lattice relaxation time $T_1$ of $^{55}$Mn NMR have been measured. In the antiferromagnetic state, two different spectra corresponding to Mn(I) and Mn(II) sites are found in the resonance frequencies of 143.5 and 6.3 MHz, respectively, at 4.2 K. From these results, the internal magnetic fields on $^{55}$Mn(I) and $^{55}$Mn(II) nuclei are obtained to be 13.6 and 0.6 T, respectively. According to NMR results, a helical structure in Mn spin states is well explained compared with the transverse sinusoidal structure.

1. Introduction

Itinerant Mn$_3$Si is an intermetallic compound with a cubic crystal structure of the Heusler-type [1]. Mn atoms are occupied on two different sites of Mn(I) and Mn(II). The Mn(I) and Mn(II) atoms are surrounded by the nearest neighbors of eight Mn(II) atoms, and four Mn(I) and four Si atoms, respectively. Mn$_3$Si becomes antiferromagnetic state below the Néel temperature of $T_N = 23$ K with a spin density wave (SDW) [2-4]. Due to their different nearest-neighbor configurations, Mn(I) and Mn(II) atoms have different magnetic moments [2-4]. This structure can be seen as a layered structure of (111) planes stacking along the [111] direction in a sequence of planes of Mn(I), Mn(II), and Si atoms, respectively.

From the study of unpolarized neutron diffraction [2], the spin structure in the SDW state has been found to be either a helical or a transversal sinusoidal structure. However, which structure is correct could not be determined. The magnetic moments of Mn(I) and Mn(II) obtained from the analysis of fundamental satellites by assuming the helical structure are 1.7 $\mu_B$ and 0.2 $\mu_B$, respectively, and for the transversal sinusoidal structure the maximum amplitudes of their magnetic moment are 2.4 $\mu_B$ and 0.28 $\mu_B$, respectively [2,4].

From inelastic neutron experiments in Mn$_3$Si [4], the 3Q harmonic satellites, whose amplitude of magnetic moment is about 2.5 % of the fundamental satellites 1Q, have been found at low temperatures. The 3Q harmonic satellites disappear at about 9 K, far below the $T_N$, with a first-order phase transition. The existence of the 3Q harmonics suppresses the amplitude of fundamental harmonics, and associated with this transition the intensity of 1Q increases above 10 K. From the existence of the 3Q harmonics the spin structure was suggested to be a sinusoidal SDW.
Figure 1. The resonance spectrum of $^{55}$Mn NMR in the antiferromagnetic state of Mn$_3$Si at 4.2 K. The spectrum at around 143.5 MHz corresponds to Mn(I) site. The solid line shows a Lorentzian-fitted line.

Figure 2. The resonance spectrum of $^{55}$Mn NMR in the antiferromagnetic state of Mn$_3$Si at 4.2 K. The spectrum at around 6.3 MHz corresponds to Mn(II) site. The solid line shows a Lorentzian-fitted line.

The specific heat with a single-crystal sample was measured in magnetic fields up to 6 T [4]. In addition to the large $\lambda$-type peaks at $T_N$ of 23 K, a very small hump was observed from 7 to 9 K with a maximum at about 8.5 K on the shoulder of the magnetic specific heat. This small peak just corresponds to the temperature region where the 3Q harmonics suddenly disappear. This peak is considered to be ascribed to the disappearance of the 3Q harmonics or the associated change of the amplitude of the 1Q harmonics. The specific heat measurement showed no magnetic dependence, which was consistent with that for polycrystalline samples up to 14 T [5]. Especially for the small hump observed in the single crystal, no change in peak shift and width has been observed. The lack of an observable change on the peak at 8 K due to application of strong magnetic fields indicates that 3Q harmonics continue to exist over very high magnetic fields and thus the same spin structure is conserved.

In order to investigate the physical properties of Mn$_3$Si microscopically, the $^{55}$Mn NMR have been carried out in antiferromagnetic phase in the temperature region between 2.2 and 17 K. The temperature dependences of spectrum and spin-lattice relaxation time $T_1$ of $^{55}$Mn NMR have been measured.

2. Experimental

Single-crystal samples of Mn$_3$Si, in which 99.9 % purity Mn and 99.999 % purity Si with normal stoichiometry were used as starting materials, were obtained by a bridgman method. Samples were fixed in the furnace and the furnace temperature was lowered. The powdered specimens prepared for NMR measurements were annealed in a sealed quartz tube with a vacuum state at 600 °C for one day. No secondary phase in the specimens was detected in the powder x-ray diffraction profile. A conventional pulse NMR spectrometer was utilized for the measurements of $^{55}$Mn NMR. The antiferromagnetic state in Mn$_3$Si was measured by a zero field NMR. Spin-lattice relaxation time $T_1$ was measured by means of the saturation recovery methods.

3. Results and Discussion

$^{55}$Mn NMR in Mn$_3$Si has measured in the temperature range between 2.2 and 17 K. Figures 1 and 2 show the resonance spectra of $^{55}$Mn NMR corresponding for Mn(I) and Mn(II) sites, respectively, in the antiferromagnetic state of Mn$_3$Si at 4.2 K, whose spectra have been obtained by frequency-sweep. The resonance spectra have been found around 143.5 MHz for Mn(I) and
Figure 3. Temperature dependence of the resonance frequencies of $^{55}$Mn NMR in the antiferromagnetic state of Mn$_3$Si. Open circles and triangles correspond to Mn(I) and Mn(II) site, respectively.

Figure 4. Temperature dependence of the line width of $^{55}$Mn NMR in the antiferromagnetic state of Mn$_3$Si. Open circles and triangles correspond to Mn(I) and Mn(II) site, respectively.

6.3 MHz for Mn(II) at 4.2 K. These hyperfine fields are obtained to be 13.6 T for Mn(I) and 0.6 T for Mn(II) at 4.2 K. The resonance line of $^{55}$Mn(I) shows a sharp width of about 0.80 MHz (half width of half maximum), whereas the resonance line of $^{55}$Mn(II) shows a broad width of about 1.55 MHz.

Figure 3 shows the temperature dependence of resonance frequencies at the center positions of the spectra of $^{55}$Mn NMR for both Mn(I) and Mn(II) sites in Mn$_3$Si between 2.2 and 17 K. These temperature variations of both Mn sites indicate the similar behavior. The resonance frequencies for both Mn sites represent almost maximum values from 2.2 to 5 K and decrease rapidly with increasing temperature above 5 K, which corresponds to the temperature changes of magnetic moments for both Mn sites [4].

Figure 4 shows the temperature dependence of the line width of $^{55}$Mn NMR for both Mn(I) and Mn(II) sites in Mn$_3$Si between 2.2 and 17 K. The line width of the resonance spectra of $^{55}$Mn NMR for Mn(I) site shows about 0.8 MHz below about 10 K and increase rapidly with increasing temperature above about 10 K. On the other hand, the line width of $^{55}$Mn NMR for Mn(II) site represents about 1.55 MHz below about 4.2 K and decreases with increasing temperature above about 4.2 K. In the antiferromagnetic state, the line width of NMR generally increases enormously larger as approaching $T_N$, since the fluctuations by magnetic moments become extremely larger. Therefore, the line width for Mn(I) site increases rapidly above 10 K, whereas the line width of Mn(II) site decreases above 10 K. The line width of Mn(II) would increase more than 18 K. Unfortunately, it has been difficult to measure the line width of Mn(II) site above 18 K because of the lower limit of frequency of an NMR apparatus used at that time and poor signal to noise ratios of the resonance signal for Mn(II) site above 18 K.

According to neutron diffraction studies [2,4], the transverse sinusoidal structure for SDW is more preferable than the helical structure due to the existence of 3Q. In this case, many NMR spectra would appear corresponding to the magnitudes of magnetic moments at Mn(I) and M(II) sites whose moments vary largely due to sinusoidal SDW. On the other hand, in the case of the helical structure, the magnitude of magnetic moment at each Mn site is the same.
Figure 5. Temperature dependence of $1/T_1 T$ of $^{55}$Mn NMR in the antiferromagnetic state of Mn$_3$Si. Open circles and triangles correspond to Mn(I) and Mn(II) site, respectively.

Therefore, only one spectrum should be found for each corresponding Mn site. Other spectra except for the above mentioned two spectra at 143.5 and 6.3 MHz have been searched for in the frequency range between 3 and 230 MHz. However, no spectrum except for them has been found in this frequency region. From the NMR point of view, a helical structure in Mn spin states is well explained compared with the transverse sinusoidal structure.

As shown in Fig. 4, the line width for Mn(II) site increases with decreasing temperature below 10 K and becomes about two times larger than that for Mn(I) site at 4.2 K. This behavior may be ascribed to $3Q$ harmonics that appear below 10 K.

Spin-lattice relaxation time $T_1$ has been measured from 2.2 to 17 K in the antiferromagnetic state ($T_N = 23$ K). The nuclear longitudinal magnetization recovery $f(t) = 1 - (M(t)/M_0)$ cannot be expressed by a single exponential type at low temperature region for Mn(I) site and all temperature region for Mn(II) site in the antiferromagnetic state. The deviation from the single exponential type of the nuclear longitudinal magnetization recovery would be caused by magnetic origins like impurities. Therefore, the recovery $f(t)$ is analyzed by means of the stretched exponential relaxation (SER) type, whose function shows $f(t) = a \exp[-(t/T_1)^p]$.

The values of power $p$ represent about 1.0 for Mn(I) site and about 0.8 for Mn(II) from 16 to 8 K, and monotonously decrease for both sites with decreasing temperature below 8 K, and then become about 0.8 for Mn(I) site and about 0.5 for Mn(II) site at 2.2 K.

The temperature dependence of $1/T_1 T$ from 2.2 to 17 K is shown in Fig. 5. $1/T_1 T$ for Mn(I) site is extremely larger than that for Mn(II) site because Mn moments for Mn(I) sites are strongly larger than those for Mn(II) sites. Above 10 K, as the fluctuations of magnetic moments of both Mn sites becomes stronger with increasing temperature, $1/T_1 T$ becomes larger. Below 10 K, $1/T_1 T$ becomes constant because magnetic moments line up and the contribution of conduction electrons to $T_1$ mechanism would become a main part.

Further investigations of $^{55}$Mn NMR, including the line width for Mn(II) site, will be needed.

References
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