NMR Study of $^{55}\text{Mn}$ and $^{59}\text{Co}$ in MnCoGe


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NMR spectra of $^{55}\text{Mn}$ and $^{59}\text{Co}$ in MnCoGe with two different structures have been measured in zero field at 4.2 K. In MnCoGe with an orthorhombic structure the peak frequencies of $^{59}\text{Co}$ and $^{55}\text{Mn}$ resonances are observed at 180 MHz and 350 MHz, respectively. In MnCoGe with a hexagonal structure these are observed at 143 MHz and 287 MHz. The Mn magnetic moments of MnCoGe with the orthorhombic structure is found to be larger than that of MnCoGe with the hexagonal structure.

Key words: ferromagnet, MnCoGe, NMR

1. Introduction

The intermetallic compound MnCoGe has an orthorhombic TiNiSi-type structure at room temperature and transforms to a hexagonal ordered Ni2In-type structure at high temperature 1)-3). These structures can be considered to be derived from the hexagonal Ni3As-type structure partly by filling up the trigonal bipyramidal holes of this structure, and partly by an orthorhombic distortion of the hexagonal unit cell similar to that occurring in the Ni3As$\rightarrow$MnP transition. If the sample of MnCoGe is quenched into water from high temperature, the structural phase transition does not appear and the hexagonal form is preserved at low temperature 4). According to the results of magnetic and neutron diffraction studies, it was found that MnCoGe exhibits collinear ferromagnetic properties in both phases over the whole temperature range of magnetic ordering 4)-6). Furthermore, it was also found that in the case of the orthorhombic phase the magnetic moments at 4.2 K of the Mn and Co atoms were found to be 2.9 $\mu_B$ and 0.9 $\mu_B$, respectively, while in the hexagonal phase the magnetic moments are localized on the Mn atoms only. The magnetic moment of the Co atoms is zero within the limit of experimental error.

The purpose of present study is to measure the NMR spectrum to obtain more information on the magnetic moments for MnCoGe.

2. Experimental

Polycrystalline sample with TiNiSi-type structure slowly cooled, MnCoGe (sc), has been prepared by the following procedures. A mixture of appropriate amounts of Mn (99.9%), Co (99.9%) and Ge (99.999%) powders was sealed in an evacuated silica tube, annealed at 850°C for 7 days and cooled slowly to room temperature in 7 days. The reaction product was pulverized, mixed and annealed by the same condition. We needed the same heat treatment once more to get the homogenized sample of MnCoGe(sc). To prepare sample with Ni2In-type structure quenched, MnCoGe(q), a mixture of appropriate amounts of Mn, Co and Ge powders was sealed in an evacuated silica tube, gradually heated up to 850°C, annealed at 850°C for 5 days and then quenched. The reaction product was crushed, annealed at 850°C for 2 days and at 950°C for 3 days, followed by quenching. The reaction product was again crushed, melted at 1300°C for 10 min, then cooled down to 1000°C and then quenched.

Figure 1 shows the powder X-ray diffraction lines of MnCoGe(sc) and MnCoGe(q) indexed with the orthorhombic and hexagonal structure, respectively and no extra line due to impurity phases was observed. The lattice parameters of MnCoGe(sc) are found to be $a$=5.986 Å, $b$=3.824 Å and $c$=7.073 Å. On the other hand, the lattice parameters of MnCoGe(q) are $a$=4.070 Å and $c$=5.292 Å.

High field magnetization at 4.2 K was measured by using a vibrating sample magnetometer in high fields up to 200 kOe. Nuclear magnetic resonance spectra of $^{55}\text{Mn}$ and $^{59}\text{Co}$
nuclei in MnCoGe(sc) and MnCoGe(q) at 4.2 K have been measured using a spin-echo NMR technique.

3. Experimental Results and Discussion

Figure 2 shows the magnetization curves at 4.2 K for MnCoGe(sc) and MnCoGe(q). The magnetic moments of MnCoGe(sc) and MnCoGe(q) are found to be 3.86 \( \mu_B \) and 2.76 \( \mu_B \) per formula unit, respectively. These values are in good agreement with those reported in Ref. 4.

Figure 3 shows the spin-echo spectra at 4.2 K in zero field for MnCoGe(sc), where the spectra are raw data. We find the strong two resonance lines with their peak frequencies of 350 MHz and 180 MHz. Those peaks in the spectrum are considered to come from \(^{59}\text{Co}\) and \(^{55}\text{Mn}\) nuclei, since the natural abundance of \(^{73}\text{Ge}\) is small (7.7%). Further, since the magnetic moment of Mn atom is larger than that of Co atom for MnCoGe(sc), the resonance lines with the peaks of 180 MHz and 350 MHz are attributable to \(^{59}\text{Co}\) and \(^{55}\text{Mn}\) nuclei, respectively. We find the weak resonance lines on the low-frequency sides of the main two lines in Fig. 3. These may be due to the disorder between the Mn and Co atoms in MnCoGe(sc). As mentioned above, MnCoGe(sc) crystallizes in the orthorhombic TiNiSi-type...
structure at low temperature, where there are two different metal atom sites: a tetrahedral site and a pyramidal site. According to the result of the neutron diffraction measurement for MnCoGe(sc), the Mn atoms occupy preferentially the pyramidal site.

The spin-echo spectrum at 4.2 K in zero field for MnCoGe(q) is shown in Fig. 4. We find the strong two resonance lines with the peak frequencies of 143 MHz and 287 MHz. Those are considered to come from $^{59}$Co and $^{55}$Mn nuclei, respectively. The half width from $^{55}$Mn nuclei is wide compared with that from $^{59}$Co nuclei for both compounds. The weak resonance line on the low-frequency sides of the spectrum with the peak of 143 MHz in Fig. 4 may be due to $^{59}$Co nuclei on 2(a) site. MnCoGe(q) crystallizes in the hexagonal Ni$_2$In-type structure over the whole temperature range, where there are two different metal sites of 2(a) and 2(d). Szytula et al. investigated the atomic distribution for the compounds with the Ni$_2$In-type crystal structure by neutron diffraction study; a random distribution of metals among both sites was detected to be (0.93Mn+0.07Co on 2a site, 0.93Co+0.07Mn on 2d site).

It is thought that a linear relation exists between nuclear hyperfine field and magnetic moment of atoms in intermetallic compounds. This relation has been confirmed on a set of many alloys and intermetallic compounds. Assuming that the results of the neutron diffraction measurements for MnCoGe(q) is correct and linear relation exists between nuclear hyperfine field and magnetic moment of atoms for MnCoGe, the magnetic moments of the Mn and Co atoms for MnCoGe(q) can be deduced to be 2.4 $\mu_B$ and 0.7 $\mu_B$, with the use of the above date, respectively. The sum of these values is somewhat larger than the magnetic moment 2.8 $\mu_B$ per formula unit deduced from the magnetic measurement.

This experimental results indicate that for orthorhombic and hexagonal phases of MnCoGe the lowering of the magnetic moment in hexagonal phase is not due to the disappearance of the magnetic moments on the Co sites, but mainly the reduction of the magnetic moments on the Mn sites. The shortest Mn-Mn distance in the hexagonal structure has the value of 2.7 Å and the shortest Mn-Mn distance in the orthorhombic structure is 3.1 Å. This will lead the narrowing of the Mn d-band, which may explain the larger magnetic moment on the Mn sites in the orthorhombic phase.

References