Fe substitution effect on the magnetic properties of SmMn$_{2-x}$Fe$_x$Ge$_2$ studied by NMR

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Abstract.
We have carried out $^{55}$Mn and $^{149}$Sm NMR measurements on SmMn$_{2-x}$Fe$_x$Ge$_2$ (0.05 ≤ x ≤ 0.6) at 4.2 K in order to elucidate the Fe substitution effect on the magnetic properties of SmMn$_{2-x}$Fe$_x$Ge$_2$. The NMR signals of Mn have been observed in the frequency range 180 - 210 MHz. The resonance frequency plotted against the Fe concentration shows an abrupt change between x = 0.3 and 0.4. This discontinuity suggests that the magnetic structure changes around x = 0.35 in the low temperature range where Sm and Mn sublattices order magnetically.

1. Introduction
The RMn$_2$Ge$_2$ (R = rare-earth) compounds crystallize in the ThCr$_2$Si$_2$-type structure (space group, I4/mmm), in which R, Mn and Ge atoms occupy the 2a, 4d and 4e sites, respectively. Those atomic sheets are stacked along the c-axis with the sequence -R-Ge-Mn-Ge- [1]. The magnetic properties of the compounds are known to be sensitive to the intralayer Mn-Mn distance $d_{\text{Mn-Mn}}$ [2, 3]. For the compound with $d_{\text{Mn-Mn}}$ smaller than ∼2.87 Å, antiferromagnetic ordering is observed, whereas ferromagnetic ordering is observed for that with $d_{\text{Mn-Mn}}$ larger than ∼2.87 Å [4, 6]. Among the RMn$_2$Ge$_2$ compounds, the magnetic properties of SmMn$_2$Ge$_2$, which has the critical Mn-Mn distance $d_{\text{Mn-Mn}}$ ∼2.87 Å, has attracted considerable attention in recent years. The compound has multiple magnetic transitions: transition from paramagnetic to antiferromagnetic states at $T_{N1}$ ∼385 K, ferromagnetic transition at $T_C$ ∼ 345 K, antiferromagnetic transition at $T_{N2}$ ∼150 K, re-entrant ferromagnetic transition of both Mn and Sm sublattices at $T_C$ ∼104 K [5, 6]. A complicated magnetic phase diagram for SmMn$_2$Ge$_2$ has been proposed from neutron scattering, ac susceptibility and NMR measurements [7, 8]: the Mn sublattice has a conical magnetic structure with ferromagnetic arrangement of Sm magnetic moment in the ab-plane below 100 K. The magnetic moments of Mn and Sm have been found to be 3.0μB and 0.65μB at 1.5 K, respectively. Similar magnetic structure has been observed in PrMn$_2$Ge$_2$ and NdMn$_2$Ge$_2$ with multiple magnetic phase transitions like SmMn$_2$Ge$_2$ [2]. The pseud-ternary compounds SmMn$_{2-x}$Fe$_x$Ge$_2$, where the Fe atom has no magnetic moment like other RFe$_2$Ge$_2$ compounds [5], have been studied by magnetization measurements [6]. Such replacement of Mn by Fe leads to a change in lattice parameter and causes much complicated magnetic phases in the compounds. In PrMn$_{2-x}$Fe$_x$Ge$_2$ [9, 10] and NdMn$_{2-x}$Fe$_x$Ge$_2$ [11]...
having the SmMn$_2$Ge$_2$-like magnetic transitions, complicated magnetic structures have also been observed by neutron diffraction, $^{57}$Fe Mössbauer effect, and magnetization measurements.

In this paper, we report the NMR results of $^{55}$Mn ($I = 5/2$, $\gamma/2\pi = 10.5$ MHz/T, $Q = 0.4b.$) and $^{149}$Sm ($I = 7/2$, $\gamma/2\pi = 1.45$ MHz/T, $Q = 0.05b.$) in SmMn$_{2-x}$Fe$_x$Ge$_2$ at 4.2 K and 1.4 K in order to study the local magnetic states of the compounds.

2. Experiment

Polycrystalline samples used in the present study were prepared by argon-arc melting an appropriate mix of constituents. The ingot was turned over and remelted several times in order to ensure homogeneity. The purity of the samples was checked by powder X-ray diffraction spectrometer. All of the samples were confirmed to have the ThCr$_2$Si$_2$-type structure. Spin-echo NMR measurements were carried out at 4.2 K and 1.4 K using a home-made coherent-type spectrometer.

3. Results and Discussion

Figure 1 shows zero-field $^{55}$Mn NMR spectra taken at 4.2 K for the compounds with $x = 0.05$, 0.1, 0.15, 0.3, 0.4, and 0.6. The resonance frequency of Mn in SmMn$_{1.95}$Fe$_{0.05}$Ge$_2$ is in good agreement with that of SmMn$_2$Ge$_2$ [7]. Sm spectrum has not been observable in the range 0.3 $\leq x$, because of rapid spin-spin relaxation time. The magnetic ordering temperature at which both Mn and Sm order magnetically decreases from $\sim$104 K to $\sim$25 K with increasing $x$ from 0 to 0.6 [6], which causes the short spin-spin relaxation time. No resolvable electric quadrupole splitting has been obtained for the spectra of all the samples, which is due to the inhomogeneous broadenings by alloying with Fe. For the $^{55}$Mn spectra of the compounds with $x = 0.1$ and 0.15, a weak shoulder is observed in the high frequency side. Probably, the shoulder would be associated to the Mn entering the Ge site. In Fe doped RMM$_2$Ge$_2$ compounds, 5 -10 % of Fe occupy the Ge site [5]. Similarly, a few percent of Mn would occupy the Ge site in SmMn$_{2-x}$Fe$_x$Ge$_2$. The full width at half maximum (FWHM) of the spectrum, which is shown in figure 2, increases gradually from 5 MHz to $\sim$15 MHz with increasing Fe concentration $x$. This may be due to the environmental effect around Mn.

Figure 3 shows the resonance frequencies of $^{149}$Sm and $^{55}$Mn in SmMn$_{2-x}$Fe$_x$Ge$_2$ plotted against Fe concentration $x$. The frequencies of $^{149}$Sm and $^{55}$Mn remain almost constant within the experimental errors in the range 0.05 $\leq x \leq 0.2$. For the non-S-state rare-earth ions like Sm$^{3+}$, the main contribution to the magnetic hyperfine field, $H_{hf}$, is the orbital field due to non-vanishing orbital moment of the 4f electrons [12, 13]. The observed $H_{hf}$ of $\sim$328 T is slightly smaller than the free ion value of 334 T, which might be attributed to the small magnetic moment of 0.65$\mu_B$ in SmMn$_2$Ge$_2$ compared with the free ion value of 0.7$\mu_B$ [8]. The $H_{hf}$ of Mn in SmMn$_{2-x}$Fe$_x$Ge$_2$ seems to be unaffected with the substitution of Mn by Fe up to $x = 0.2$.

For the compounds PrMn$_{2-x}$Fe$_x$Ge$_2$, $^{57}$Fe Mössbauer spectra have been analysed by taking into account the transferred hyperfine field arising from Mn atoms in the nearest neighbours (n.n) [5, 10]. The $H_{hf}$ at non-magnetic Fe is attributed only to the transferred field arising from the magnetic moments of Mn and Pr in the neighbouring sites around Fe. The $H_{hf}$ at Fe decreases with increasing Fe concentration in PrMn$_{2-x}$Fe$_x$Ge$_2$, and the hyperfine field analysis indicates Fe to be non-magnetic [10]. The analysis of $^{57}$Fe Mössbauer spectra for PrMn$_{2-x}$Fe$_x$Ge$_2$ has found the contribution to $H_{hf}$ from a single Mn in the n.n sites to be 1.2 T and 6.9 T from all other Mn atoms [5]. The probability that a Mn atom will have $z$ Fe atoms in the n.n sites around the Mn is given by a binomial expression, assuming random distribution for 4d sites in the ThCr$_2$Si$_2$ structure. For $x = 0.05$, the probability of finding one Fe in the n.n sites is 0.093. That is, almost the Mn atoms have 4 Mn atoms in the n.n sites. For $x = 0.3$, the probabilities of Mn with zero, one, two, three and four Fe atoms in n.n sites are 0.52, 0.37, 0.1, 0.01, and...
Figure 1. $^{55}$Mn zero-field NMR spectra taken at 4.2 K for SmMn$_{2-x}$Fe$_x$Ge$_2$ with $x$ = 0.05, 0.1, 0.15, 0.3, 0.4, and 0.6.

Figure 2. Full width at the half maximum of NMR spectrum of SmMn$_{2-x}$Fe$_x$Ge$_2$. The solid line is guide for eyes.

0.0005, respectively. About 48% of Mn atoms have one or more Fe atoms in the n.n sites. This leads to reduction in the hyperfine field of Mn, assuming the transferred hyperfine field has the same sign as that of core polarization field which is the main contribution to the hyperfine field of Mn.

If the behaviour of the $H_{hf}$ at Mn in the SmMn$_{2-x}$Fe$_x$Ge$_2$ is expressed by a simple dilution with non-magnetic Fe atom, the $H_{hf}$ would decrease gradually with increasing $x$. The resonance frequency, however, is almost constant within the errors in the range $x = 0.05 - 0.2$, and increases discontinuously between $x = 0.3$ and 0.4. Thus, the nearest neighbour contribution to the $H_{hf}$ at Fe obtained by $^{57}$Fe Mössbauer effect seems to be rather large for the hyperfine field at Mn, even though taking into account the difference in the hyperfine coupling constant between Fe and Mn. The FWHM shown in figure 2 may reflect the transferred hyperfine field arising from neighbouring Mn, and is $\sim 15$ MHz, corresponding to $\sim 1.4$ T, for $x = 0.4 - 0.6$. The neighbouring contribution to the $H_{hf}$ at Mn would be of the order of 1.4 T.

The behaviour of $H_{hf}$ observed for the present measurements has also been observed for La$_{1-x}$Y$_x$Mn$_2$Si$_2$ [14]. The discontinuous change in $H_{hf}$ has been attributed to the change in the magnetic structure. For $0 \leq x \leq 0.4$ in PrMn$_{2-x}$Fe$_x$Ge$_2$ in the low temperature range, where Pr orders ferromagnetically, Mn sublattice has a conical magnetic structure with ferromagnetic component along the c-axis ($F_{mc}$ structure) and Pr sublattice has a ferromagnetic structure along the c-axis ($F_R$ structure), and in the range $0.4 \leq x \leq 0.75$, the canted ferromagnetic structure of Mn with ferromagnetic arrangement of Pr ($F_{mc} + F_R$) [9, 10]. The notation of magnetic structure is according to Venturini et al. [4]. Thus, $F_{mc} + F_R$ and $F_{mc} + F_R$ magnetic structures have been proposed for PrMn$_{2-x}$Fe$_x$Ge$_2$ with ferromagnetic phase in the Mn-rich
composition range [9, 10]. Furthermore, it has been proposed that the magnetic transition from \( F_{mi} + F_R \) to \( F_{mc} + F_R \) has occurred around \( x = 0.4 \) with increasing \( x \) in the low temperature range [10]. In the case of \( \text{SmMn}_{2-x}\text{Fe}_x\text{Ge}_2 \), similarly, the discontinuous change in the \( H_{hf} \) obtained by \(^{55}\text{Mn} \) NMR may be attributed to the change in the magnetic structure from \( F_{mi} + F_R \) to \( F_{mc} + F_R \). The discontinuity which occurs for \( x \) between 0.3 and 0.4 corresponds to \( d_{\text{Mn-Mn}} \sim 2.853 \text{ Å} \) as shown in figure 3 (c).

In summary, we have done \(^{55}\text{Mn} \) and \(^{149}\text{Sm} \) NMR measurements on the pseud-ternary compounds \( \text{SmMn}_{2-x}\text{Fe}_x\text{Ge}_2 \). The \( H_{hf} \) at Mn shows a discontinuous increase with increasing the Fe concentration, which suggests that the magnetic structure of Mn changes at a critical value of Fe atoms in the n.n sites around Mn in addition to the change in the intraylayer Mn-Mn distance. The energy band calculation would be necessary to understand the magnetic properties of \( R\text{Mn}_{2-x}\text{Fe}_x\text{Ge}_2 \).

**Figure 3.** Resonance frequencies of (a) \(^{149}\text{Sm} \) and (b) \(^{55}\text{Mn} \) plotted against \( x \) in \( \text{SmMn}_{2-x}\text{Fe}_x\text{Ge}_2 \). (c) Resonance frequency plotted against \( d_{\text{Mn-Mn}} \) in \( \text{SmMn}_{2-x}\text{Fe}_x\text{Ge}_2 \). The \( d_{\text{Mn-Mn}} \) of \( x = 0.3 \) is estimated by interpolating the data in reference [6]. The solid and dashed lines are guides for eyes.

4. References

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