Ga NMR study of GdGa$_{2-x}$Al$_x$

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Abstract. $^{69}$Ga and $^{71}$Ga NMR signals in GdGa$_{2-x}$Al$_x$ ($x = 0.1, 0.25, 0.5, 0.75, 1$) have been observed at a low temperature in a zero magnetic field. Gd NMR signals were observed only for the samples with $x \leq 0.5$ in the frequency range less than 110MHz, but Ga NMR signals have been observed for all samples in the frequency range higher than Gd NMR frequencies. The features of the observed Ga NMR spectra of the samples with low Al concentration are quite different from those of highly Al concentrated samples. This difference is attributed to the change of the magnetic structure of these compounds. NMR parameters calculated from the Ga NMR results are reported, too. The magnetic structures of these compounds are discussed on the basis of the Ga NMR results.

1. Introduction
GdGa$_2$ crystallizes in the hexagonal AlB$_2$-type crystal structure (space group $P_6/mmm$) [1] and undergoes an antiferromagnetic phase transition at 23.6 K [2]. The powder neutron diffraction study on this compound shows that at the temperature of 2 K GdGa$_2$ exhibits an incommensurate magnetic structure with a propagation vector (0.39, 0.39, 0) [3]. Below Néel temperature the second magnetic transition occurs at $\sim 5$ K [2]. At this temperature the magnetic specific heat shows an anomaly [2] and the direction of the magnetic moment changes without the change of the propagation vector (0.39, 0.39, 0) [4]. Below Néel temperature the metamagnetic transitions are observed, which suggest the existence of the complex magnetic structures [2, 4].

The compounds GdGa$_{2-x}$Al$_x$ with Al substituted for Ga in GdGa$_2$ keep the AlB$_2$-type structure up to $x=1.5$. For the compounds with $x \leq 0.6$, the ratio of the lattice parameters $c$ and $a$ at a room temperature is about 0.97, and for $x \geq 0.75$, it is about 0.84. In the range between $x = 0.6$ and 0.75, two crystallographic forms coexist [5]. Thus, the lattice parameters of GdGa$_{2-x}$Al$_x$ compounds change abruptly at the Al concentration range $x = 0.6$ $\sim$ 0.75. It is also reported that the electric field gradient at Gd in GdGa$_{2-x}$Al$_x$ obtained by Mössbauer effect measurement changes its sign from positive to negative with the jump-like change in the lattice parameters around $x = 0.6$ [5]. The magnetic properties are as follows. Néel temperature is almost constant up to $x = 0.5$, but for the compounds with $x \geq 0.75$, increases with increasing $x$ [6,7]. The second transition is observed for the compounds with $x = 0.1$ and 0.25 and the transition temperature increases with increasing Al concentration [6]. For the compound with $x = 0.5$, this transition disappears. The compounds with $x \geq 0.75$ do not undergo this type of transition and exhibit a simple antiferromagnetic behavior. Below Néel temperature, the compounds with $x \leq 0.5$ show the complex metamagnetic transitions.
We have a plan to observe Ga NMR in GdGa$_{2-x}$Al$_x$ in a zero magnetic field, in order to clarify the magnetic structures of this system.

2. NMR measurement and results
GdGa$_{2-x}$Al$_x$ samples ($x = 0.1, 0.25, 0.5, 0.75$ and $1$) were prepared by the same method as reported previously [5]. A part of the obtained ingots was powdered and used for the measurement of NMR. NMR spectra were observed by a conventional spin echo technique at the low temperature of about 1.4 K in a zero magnetic field.

It is reported that the very broad Gd NMR spectra are observed in the frequency range from $10$ MHz to $110$ MHz for the compounds with $x \leq 0.5$ and that no Gd NMR signals are observed for the compounds of $x \geq 0.75$ [6]. The Gd NMR spectrum of GdGa$_{1.5}$Al$_{0.5}$ is a little different from the compounds with $x = 0.1$ and 0.25, that is, the clear peaks are not observed and the NMR signals are weak. We were able to observe Ga NMR signals for all prepared GdGa$_{2-x}$Al$_x$ samples in the frequency range higher than the observed Gd NMR frequency range. The nuclear spin-spin relaxation times were longer one order than ones of Gd NMR. The NMR signal of Al was not observed in this frequency range but may be hidden in the frequency range of Gd NMR or not observable due to the short relaxation time $T_2$. Figure 1 shows the Ga NMR spectra of GdGa$_{2-x}$Al$_x$, which are not corrected by the Boltzmann factor, the nuclear relaxation times and so on. There are two isotopes of Ga nuclei, $^{69}$Ga and $^{71}$Ga. Since the nuclear spin $I$ of each $^{69}$Ga and $^{71}$Ga is $3/2$, NMR lines of each isotope are split into three due to the quadrupole interaction, respectively. In the observed spectra, the quadrupole splittings are not clearly observed. Moreover, the spectra show the powder patterns like the case of Gd NMR. Because of the smaller quadrupole moments of Ga nuclei than Gd, we do not need to take account of the second-order perturbation of the interaction. Then, we consider that the line widths are caused only by the first-order perturbation. There are two types of spectra as shown in Figure 1. One is the spectrum with the lower resonance frequency and a relatively narrow line width, and another is with the higher resonance frequency and a broad line width. The resonance frequency decreases with increasing Al concentration and the line width increases. In the spectra of the samples with $x = 0.25$ and 0.5, two types of spectra seem to be mixed. The features of the spectra suggest that there are two types of the magnetic structures in GdGa$_{2-x}$Al$_x$ system at a low temperature.

3. Analysis and discussion
The observed spectra will be analyzed in comparison with the simulated ones. Assuming the random distribution of the electric field gradient axis with respect to the hyperfine field $H_N$, we simulated the powder pattern of the spectrum. In the simulation, we fixed the ratios of $\gamma$-values, the quadrupole moments $eQ$ and the natural abundance of two isotopes $^{69}$Ga and $^{71}$Ga ($I = 3/2$), and used the first-order perturbation treatment of the quadrupole interaction. Assuming a gaussian distribution of each resonance frequency with a width $\Delta f$, we made a convolution of the calculated powder pattern and a gaussian distribution to get the spectrum [8]. The NMR parameters to be determined are $\nu_0 = \gamma H_N/2\pi$, the quadrupole frequency $\nu_0 = e^2Qq/h$ and $\Delta f$ for $^{71}$Ga nuclei, where $eq$ is the electric field gradient. Figure 2 shows the simulated spectrum for each GdGa$_{2-x}$Al$_x$, which is corrected by the NMR sensitivity [8]. We omit the weak spectra from the figure for $x = 0.25$ and 0.5. The best fit parameters for $^{71}$Ga nuclei are listed in Table 1. The agreement between the simulated and the experimental spectra may be satisfactory. The hyperfine fields change abruptly at $x = 0.5$. The electric field gradients increase with increasing Al concentration. Except $x = 0.5$, the tendency of the change of the hyperfine fields is coincident to the change of the nearest distance between Ga and Gd at a room temperature. The distribution parameters $\Delta f$ of the resonance frequency increase with
increasing Al concentration. This may mean that the random occupation of Al in the lattice sites causes the wider distribution of the hyperfine fields or the electric field gradients.

The sample with $x = 0.5$ has the crystal structure with high $c/a$ ratio at a room temperature, but the main feature of Ga NMR spectrum is the same as that of the samples with low $c/a$ ratio crystal structure. In the spectrum of the sample with $x = 0.25$, a small amount of the spectrum is mixed which is observed for the high Al concentrated samples. Moreover, the sample with $x = 0.75$ includes $\sim 3\%$ of high $c/a$ ratio form at a room temperature [5], but no Ga NMR signal due to this structure is observed. This means that the Al substitution induces the magnetic structure of the high Al concentrated compounds. We may be able to say that the complex magnetic structures of the low Al concentrated compounds are caused by the peculiar crystal structures.

4. Summary
We have observed $^{69}$Ga and $^{71}$Ga NMR signals in GdGa$_{2-x}$Al$_x$ ($x = 0.1, 0.25, 0.5, 0.75$ and $1$) at a low temperature in a zero magnetic field. The observed spectra are analyzed by simulating the powder pattern. The magnetic properties of the compound with $x = 0.5$ in a low temperature phase are same as those of the compounds with $x \geq 0.75$ with a small amount of the magnetic structure of the low Al concentrated compounds. The magnetic properties of the compound with $x = 0.25$ are complex including a small amount of the magnetic structure of the high Al concentrated compounds.

Figure 1. Observed $^{69}$Ga and $^{71}$Ga NMR spectra in GdGa$_{2-x}$Al$_x$ in a zero magnetic field.

Figure 2. Simulated $^{69}$Ga and $^{71}$Ga NMR spectra for GdGa$_{2-x}$Al$_x$. Only the main spectra are shown for $x = 0.25$ and $x = 0.5$. Used NMR parameters are listed in Table 1.
Table 1. Best fit $^{71}$Ga NMR parameters of GdGa$_{2-x}$Al$_x$ and the hyperfine field $H_N$ and the electric field gradient $eq$ calculated from these NMR parameters

| $x$   | $\nu_0$(MHz) | $\nu_Q$(MHz) | $\Delta f$(MHz) | $H_N$(T) | $eq(10^{21}V/m^2)$ |
|-------|---------------|---------------|-----------------|---------|-----------------|
| 0.1   | 150.3         | 8             | 1               | 11.6    | 3.0             |
| 0.25  | 148.0         | 9             | 2.2             | 11.4    | 3.3             |
| 0.5   | 166.5         | 16            | 1.8             | 12.8    | 5.6             |
| 0.75  | 162.0         | 19.3          | 3               | 12.5    | 7.0             |
| 1.0   | 160.0         | 22            | 4.5             | 12.3    | 8.2             |

References

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