Studies of $^{27}$Al NMR in SrAl$_4$

Haruo Niki$^1$, Nonoka Higa$^1$, Hiroko Kuroshima$^1$, Tatsuki Toji$^1$, Mach Morishima$^1$, Motofumi Minei$^1$, Mamoru Yogi$^1$, Ai Nakamura$^1$, Masato Hedo$^1$, Takao Nakama$^1$, Yoshichika Onuki$^1$, and Hisatomo Harima$^2$

$^1$ Faculty of Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan
niki@sci.u-ryukyu.ac.jp
$^2$ Faculty of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan

Abstract
A charge density wave (CDW) transition at $T_{CDW} = 243$ K and a structural phase (SP) transition at approximately 100 K occur in SrAl$_4$ with the BaAl$_4$-type body center tetragonal structure, which is the divalent and non-$4f$ electron reference compound of EuAl$_4$. To understand the behaviors of the CDW and SP transitions, the $^{27}$Al NMR measurements using a single crystal and a powder sample of SrAl$_4$ have been carried out. The line width below $T_{CDW}$ is modulated by an electrical quadruple interaction between $^{27}$Al nucleus and CDW charge modulation. The incommensurate CDW state below $T_{CDW}$ changes into a different structure below $T_{SP}$. The temperature dependences of Knight shifts of $^{27}$Al(I) and $^{27}$Al(II) show the different behaviors. The temperature variation of $^{27}$Al(I) Knight shift shows anomalies at the CDW and SP transition temperatures, revealing the shift to negative side below $T_{CDW}$, which is attributable to the core polarization of the $d$-electrons. However, $^{27}$Al(II) Knight shift keeps almost constant except for the small shift due to the SP transition. The $1/T_1T$ of $^{27}$Al(I) indicates the obvious changes due to the CDW and SP transitions, while that of $^{27}$Al(II) takes a constant value. The density of state at the Fermi level at Al(I) site below 60 K would be about 0.9 times less than that above $T_{CDW}$.

Keywords: NMR, Knight shift, spin-lattice relaxation time, charge density wave, structural phase transition, SrAl$_4$

1 Introduction
Strong electron correlations in rare-earth-based compounds induce various interesting physical phenomena such as heavy-electron behavior, multipole order, unconventional superconductivity, spin or valence quantum critical fluctuations, and non-Fermi liquid behavior [1–3]. Eu is a rare-earth element known to have two kinds of valence states: Eu$^{2+}$ ($4f^7$) and Eu$^{3+}$ ($4f^6$). The divalent Eu state is magnetic ($J = S = 7/2, L = 0$), where $J$ is the total angular momentum, $S$ is the spin angular momentum, and $L$ is the orbital angular momentum. Therefore, the
compounds with divalent Eu ions tend to order magnetically, following the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. On the other hand, the trivalent Eu state is non-magnetic ($J = 0$, $S = L = 3$).

The divalent Eu intermetallic compound EuX$_4$ (X = Al or Ga) crystallizes in the BaAl$_4$-type structure ($I4/mmm$) as shown in Fig. 1 [4–6]. Eu atoms occupy the corners and the center of the body-centered tetragonal lattice with local symmetry ($4/mmm$). X atoms have two crystallographically inequivalent sites, denoted X(I) and X(II), respectively, as indicated in Fig. 1. EuAl$_4$ and EuGa$_4$ order antiferromagnetically at $T_N \approx 16$ K with effective magnetic moments of 8.02 and 7.86 $\mu_B$, respectively, which are close to a divalent value of 7.94 $\mu_B$/Eu [4–6]. In the paramagnetic (PRM) phase, the magnetic susceptibilities of EuAl$_4$ and EuGa$_4$ follow the Curie-Weiss law with positive Curie-Weiss temperatures $\theta_P = +14$ and $+3$ K, respectively [4–6]. The antiferromagnetic (AFM) states in EuAl$_4$ and EuGa$_4$ are changed into the field induced ferromagnetic (FRM) states at critical fields $H_C$ of approximately 2 and 7 T, respectively [4–6]. The charge density wave (CDW) transition is occurred around 140 K at ambient pressure in EuAl$_4$ and around 160 K under about 2 GPa in EuGa$_4$ [6].

In order to microscopically investigate the magnetic properties of EuGa$_4$ and EuAl$_4$, the NMR measurements were carried out [7–9]. From the analysis of $^{153}$Eu NMR spectrum in the AFM state of EuGa$_4$ [7], the internal magnetic field at $^{153}$Eu nucleus was found to be 27.09 T at 4.2 K. Only $^{69,71}$Ga NMR spectra corresponding to the site II were found in the AFM and PRM phases of EuGa$_4$ [7, 8]. The Ga(II) NMR spectra in the PRM state of EuGa$_4$ indicate anisotropic configurations. The isotropic part $K_{iso}$ and anisotropic part $K_{aniso}$ of Knight shift were obtained. The $K_{iso}$ and $K_{aniso}$ shift to negative side with decreasing temperature due to the RKKY interaction. These temperature dependences follow the Curie-Weiss law with $\theta_P = +3$ K, which is consistent with the value obtained from the magnetic susceptibility $\chi$. From the $K - \chi$ plot, the values of the hyperfine fields $H_{hfiso}$ and $H_{hfaniso}$ are $-6.491$ and $-0.363$ kOe/$\mu_B$, respectively.
The $^{27}\text{Al}$ NMR spectra corresponding to the sites I and II were found in the PRM phase of EuAl$_4$ [9]. The $K_{\text{iso}}$ and $K_{\text{aniso}}$ obtained from the $^{27}\text{Al}$ NMR spectra shift to negative side with decreasing temperature due to the RKKY interaction. These temperature dependences follow the Curie-Weiss law with $\theta_P = +14$ K, which is consistent with the behavior of the magnetic susceptibility. From the $K - \chi$ plot, the hyperfine fields $H_{\text{hfiso}}$ and $H_{\text{hfaniso}}$ were found to be $-3.231$ and $-0.162$ kOe/\(\mu_B\) at Al(I) site, and $-1.823$ and $-0.264$ kOe/\(\mu_B\) at Al(II) site, respectively. The values of $1/T_1$ of $^{27}\text{Al}$ nuclei in both Al(I) and Al(II) sites are almost constant, since the random fluctuation of $f$-electron spins is fast in the PRM state.

To investigate fundamental physical properties of EuGa$_4$ and EuAl$_4$ in detail, the isostructural nonmagnetic SrGa$_4$ and SrAl$_4$ were prepared as reference materials [6]. SrAl$_4$ has the CDW transition at $T_{\text{CDW}} = 243$ K and the SP transition at $T_{\text{SP}} \approx 100$ K. The NMR measurement of $^{69\&71}\text{Ga}$ nuclei in SrGa$_4$ was carried out [10]. The Ga NMR spectra corresponding to Ga(I) and Ga(II) sites were obtained. The NMR spectra of $^{69\&71}\text{Ga}$ in the powder sample of SrGa$_4$ do not indicate a typical powder pattern caused by the nuclear quadrupole interaction (NQI) [11], but indicate the spectrum consisting of three well resolved resonance-lines, which represents that the nonuniform distribution of crystal orientation in the powder sample occurs because of the magnetic anisotropy. From the analysis of the Ga NMR spectrum, it was found that the $ab$-plane of the crystal is parallel to the external magnetic field, which would be attributed to the anisotropy of the magnetic susceptibility with the easy axis parallel to the $ab$-plane. The temperature change of Ga Knight shift of both sites is small because of the lack of the RKKY interaction of the divalent Eu. The values of $1/T_1$ of $^{69}\text{Ga(I)}$ is one order of magnitude less than that of $^{69}\text{Ga(II)}$, which would be the reason why the Ga(I) NMR spectra in EuGa$_4$ could not be detected.

Unfortunately, the physical phenomena about the CDW transitions in EuAl$_4$ could not be detected by the NMR measurement due to the strong effect of RKKY interaction [9]. Therefore, in order to investigate the physical properties of the CDW and SP transitions, the NMR measurements in SrAl$_4$ have been carried out. In this paper, we report on the measurement results of $^{27}\text{Al}$ NMR of SrAl$_4$.

## 2 Experimental

High-quality single crystal of SrAl$_4$, which was composed of the BaAl$_4$-type tetragonal-structure as same as EuAl$_4$, was grown by the Al-self flux method. Details of the sample preparation are described elsewhere [4, 5]. A single crystal and a powdered sample of SrAl$_4$ were used for NMR measurements. The $^{27}\text{Al}$ NMR measurements were performed by a spin-echo method using a conventional phase-coherent pulsed spectrometer. A magnetic field of approximately 6.5 T for $^{27}\text{Al}$ NMR measurements was applied by a superconducting magnet with magnetic field homogeneity of $10^{-5}$. The NMR spectra were measured by sweeping the frequency and integrating the spin-echo signal intensity step by step.

## 3 Results and discussion

First of all, we need to describe the NMR theory to discuss about the NMR experimental results in SrAl$_4$. The nuclear spin Hamiltonian of Al nucleus (a nuclear spin $I = 5/2$) in SrAl$_4$ is given

765
Figure 2: $^{27}$Al NMR spectra for Al(I) and Al(II) sites in a powdered sample of SrAl$_4$ at 300 K. Open and solid arrows correspond to Al(I) and Al(II) sites, respectively. The first and second satellites on the lower frequency side for Al(I) and Al(II) sites overlap, respectively.

Figure 3: $^{27}$Al NMR spectra for Al(I) and Al(II) sites in a powdered sample of SrAl$_4$ at 4.2 K. Open and solid arrows correspond to Al(I) and Al(II) sites, respectively. The first and second satellites on the lower frequency side for Al(I) and Al(II) sites overlap, respectively.

by [11]

$$\mathcal{H} = -\gamma_n h I \cdot H_0 - \gamma_n h I \cdot H_{in} + \frac{h\nu_Q}{6} [3I_z^2 - I^2] = -\gamma_n h I \cdot H_0 [1 + K (\theta)] + \frac{h\nu_Q}{6} [3I_z^2 - I^2]. \quad (1)$$

The first term of the Hamiltonian represents the Zeeman interaction between the nuclear magnetic moment $\mu_n = \gamma_n h I$ and the external magnetic field $H_0$, where $\gamma_n$ is the nuclear gyromagnetic ratio and $I$ is the nuclear spin. The second term indicates the Zeeman interaction between the nuclear magnetic moment and the internal magnetic field $H_{in}$; this term corresponds to the Knight shift term. If the symmetry of the environment of a nuclear spin is lower than the cubic symmetry, the Knight shift depends on the direction of the applied field with respect to the crystalline axes. In the case of the tetragonal symmetry, the Knight shift is a function of $\theta$, where $\theta$ represents the angle between the external magnetic field and the $c$-axis [8–10].

The third term represents the nuclear quadrupole interaction between the electric field gradient EFG and the nuclear quadrupole moment $Q$. Here, $\nu_Q$ is the nuclear quadrupole frequency defined as $\nu_Q \equiv 3eQV_{zz}/2I(2I-1)h$. In SrAl$_4$, the EFG of the nuclear quadrupole interaction becomes axially symmetric because the crystal structure of SrAl$_4$ has the tetragonal symmetry. Therefore, the asymmetry parameter of the EFG, $\eta$, becomes zero and the EFG along the main principal axis, $V_{zz}$, is parallel to the $c$-axis.

The $^{27}$Al spectra in the powdered sample of SrAl$_4$ have been measured at temperatures between 4.2 and 300 K. From the analysis by eq. (1), the spectrum of $^{27}$Al NMR splits into five resonance-lines composed of a main resonance-line with four satellite-lines in all on both sides because of the nuclear quadrupole interaction by $I = 5/2$. As shown in Fig. 2, the well resolved spectra at 300 K, which are composed of the spectra of both Al(I) and Al(II) sites, are obtained. Each $^{27}$Al spectrum does not show a typical powder pattern caused by the NQR interaction [10], which indicates that the nonuniform distribution of crystal orientation in the
powder sample occurs because of the magnetic anisotropy [11]. It is found that the ab-plane of the crystal is parallel to the external magnetic field, which would be attributed to the anisotropy of the magnetic susceptibility with the easy axis parallel to the ab plane. This means \( H_0 \perp V_{zz} \) because of \( V_{zz} \parallel c \)-axis. Therefore, the values of \( \nu_Q \) of \( ^{27}\text{Al} \) for Al(I) and Al(II) at 300 K are found to be 924 and 426 kHz, respectively. The \( ^{27}\text{Al} \) spectra at 4.2 K in Fig. 3 show the complicated behavior compared with those at 300 K in Fig. 2 because of the CDW transition at \( T_{\text{CDW}} = 243 \) K and the SP transition at \( T_{\text{SP}} \approx 100 \) K. The theoretical values of \( \nu_Q \) of \( ^{27}\text{Al} \) in \( \text{SrAl}_4 \) are calculated based on the band calculation by a full potential linear augmented plane wave (FLAPW) method on the basis of a local density approximation (LDA) assuming with spin-orbit interaction [7–10]. The calculated values of \( \nu_Q \) of \( ^{27}\text{Al} \) in \( \text{SrAl}_4 \) are 925.9 kHz for Al(I) site and 421.1 kHz for Al(II) site. Therefore, the obtained \( \nu_Q \) values of 924 and 426 kHz from the NMR measurements can be assigned to the Al(I) and Al(II) sites, respectively.

To understand the physical properties of \( \text{SrAl}_4 \) in detail, the single crystal of \( \text{SrAl}_4 \) has been used for the \( ^{27}\text{Al} \) NMR measurements. The single crystal is set to be \( H_0 \perp c \)-axis. As shown in Fig. 4, the well resolved sharp spectra at 300 K, which are composed of the spectra of Al(I) and Al(II) sites, are obtained. However, the \( ^{27}\text{Al} \) spectra at 4.2 K in Fig. 5 show the complicated behavior compared with those at 300 K in Fig. 4 because of the CDW and SP transitions. The values of \( \nu_Q \) of \( ^{27}\text{Al} \) for Al(I) and Al(II) sites in \( \text{SrAl}_4 \) at 300 K are obtained to be 925 and 427 kHz, respectively. These values are well consistent with those obtained by the powdered sample and theoretical calculation as mentioned above.

The temperature dependence of the first satellite on the lower frequency side of \( ^{27}\text{Al} \) NMR spectra for Al(II) site of the single crystal of \( \text{SrAl}_4 \) have been measured at the temperatures between 120 and 300 K, as shown in Fig. 6. The single satellite resonance-line splits into a double-horned shape below \( T_{\text{CDW}} \) [12, 13]. The line width of the satellite resonance-line
Figure 6: Temperature dependence of the first satellite line on the lower frequency side of $^{27}$Al NMR spectrum for Al(II) site in a single crystal of SrAl$_4$. The dashed line is a guide for eyes.

below $T_{CDW}$ is modulated by an electrical quadruple interaction between $^{27}$Al nuclei and the incommensurate CDW charge modulation. The temperature dependence of the splitting width of the double-horned spectrum is shown in Fig. 7. The value of the splitting width corresponds to the CDW amplitude. The CDW intensity develops rapidly below $T_{CDW}$ and it is getting to be constant around 140 K. However, below about 140 K, a new resonance-line appears in the vicinity of the center of the double-horned spectrum. This phenomenon would be the precursory phenomenon for the SP transition around 100 K. The first satellite spectrum for Al(II) site at 4.2 K in Fig. 5 has the same structure compared with that at 120 K in Fig. 6. Therefore, the state of the CDW below $T_{SP}$ would change into a different structure from the simple incommensurate CDW above $T_{SP}$.

The temperature dependences of the Knight shifts of $^{27}$Al NMR for Al(I) and Al(II) sites of the single crystal of SrAl$_4$ have been obtained from the spectra analysis by using eq. (1), as shown in Fig. 8. The value of $^{27}$Al(I) Knight shift is almost constant above $T_{CDW}$, decreases monotonously below $T_{CDW}$, and has a step-like anomaly at $T_{SP}$. Then, it keeps constant until
Figure 8: Temperature dependence of $^{27}$Al Knight shifts for Al(I) and Al(II) sites in SrAl$_4$. The dashed line is a guide for eyes.

Figure 9: Temperature dependence of $1/T_1T$ for Al(I) and Al(II) sites of $^{27}$Al NMR in SrAl$_4$. The dashed lines are guides for eyes.

50 K, and decreases below 50 K. However, the value of $^{27}$Al(II) Knight shift keeps almost constant from room temperature to $T_{SP}$. Then, it increases until about 50 K corresponding to the change of the magnetic susceptibility due to the SP transition, and it becomes constant below about 50 K. The shift to the negative side of the Knight shift at the Al(I) site below $T_{CDW}$ is attributable to the core polarization of the $d$-electrons. On the other hand, the constant value of $^{27}$Al(II) Knight shift would be mainly contributed by the $s$-electrons. Weak temperature hysteresis of Knight shift for only Al(I) site can be detected in the vicinity of $T_{SP}$.

Spin-lattice relaxation time $T_1$ of $^{27}$Al for the powdered sample of SrAl$_4$ has been measured from 4.2 to 300 K. The nuclear longitudinal magnetization recovery $f(t) = 1 - (M(t)/M_0)$ can be generally expressed by a single exponential type [11]. However, as the structure is tetragonal symmetry, nuclear magnetic relaxation is affected by nuclear quadrupole interaction because of Al nuclear spin of $5/2$. Therefore, it can be expected that the nuclear magnetization recovery in the case of the transition $+1/2 \leftrightarrow -1/2$ can be explained by using the following equation [14]:

$$f(t, T_1) = y \left\{ \frac{1}{35} \exp \left( -\frac{t}{T_1} \right) + \frac{8}{45} \exp \left( -\frac{6t}{T_1} \right) + \frac{50}{63} \exp \left( -\frac{15t}{T_1} \right) \right\}, \quad (2)$$

where $y$ is an arbitrary constant. However, the recovery equation is slightly modified because $T_1$ is distributed. The recovery curve can be well explained by $g(t, T_1) = c f(t, T_{1S}) + (1-c) f(t, T_{1L})$, consisting of two components of short $T_{1S}$ and long $T_{1L}$. The values of $c$ are about 0.95 for Al(I) site and about 0.05 for Al(II) site. This means that the main contribution to $T_1$ is the short $T_{1S}$ part for Al(I) and the long $T_{1L}$ part for Al(II). The reason why $T_1$ is distributed in this material is not clear. The value of the $1/T_1T$ of $^{27}$Al(I), as shown in Fig. 9, takes an almost constant value above $T_{CDW}$, then decreases monotonously below $T_{CDW}$, and keeps constant below 60 K. However, the value of $1/T_1T$ of $^{27}$Al(II) takes a constant value between 4.2 and 300 K. As mentioned above, the main contribution to conduction electrons in this material would be $d$-electrons at Al(I) site and $s$-electrons at Al(II) site, respectively. Therefore, the $1/T_1T$ of $^{27}$Al(I) would change against temperature and the $1/T_1T$ of $^{27}$Al(II) would keep
constant against temperature. The density of state at the Fermi level at Al(I) site below 60 K would be about 0.9 times less than that above $T_{\text{CDW}}$ as the density of state at the Fermi level is proportional to the square root of $1/T$. Weak temperature hysteresis in the vicinity of $T_{\text{SP}}$ is observed in the temperature dependence of $1/T$ for Al(I) site as well as in that of Knight shift.

In summary, to understand the behaviors of the CDW and SP transitions, the $^{27}$Al NMR measurements using the powder sample and single crystal of SrAl$_4$ have been carried out. The line width below $T_{\text{CDW}}$ is modulated by an electrical quadruple interaction between $^{27}$Al nucleus and CDW charge modulation. The incommensurate CDW state below $T_{\text{CDW}}$ changes into a different structure below $T_{\text{SP}}$. The temperature dependences of Knight shifts of the $^{27}$Al(I) and $^{27}$Al(II) show the different behaviors. The temperature variation of $^{27}$Al(I) Knight shift shows anomalies at the CDW and SP transition temperatures, revealing the shift to negative side below $T_{\text{CDW}}$, which is attributable to the core polarization of the $d$-electrons. However, $^{27}$Al(II) Knight shift keeps almost constant except for the small shift due to the SP transition. The $1/T$ for $^{27}$Al(I) indicates the obvious changes due to the CDW and SP transitions, while that of $^{27}$Al(II) takes a constant value. The density of state at the Fermi level at Al(I) site below 60 K would be about 0.9 times less than that above $T_{\text{CDW}}$.

References