Magnetic Ordering in the Organic Conductor $(\text{DIETSe})_2\text{GaCl}_4$

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Abstract.

$^{77}\text{Se}$ NMR signals were observed in the metallic and insulating states of the quasi-one-dimensional organic compound $(\text{DIETSe})_2\text{GaCl}_4$. The $^{77}\text{Se}$ NMR spectra at low temperatures are broadened, indicating the presence of magnetic ordering. The shape of the spectra in the magnetically ordered state is characteristic of the spin density wave (SDW) ordering. The divergent behavior of the temperature dependence of the nuclear spin-lattice relaxation rate suggests that the SDW ordering occurs at about 7 K which is lower than the metal-insulator transition temperature of 12 K.

1. Introduction

Recently, a novel series of cation radical salts $(\text{DIETSe})_2MX_4$ ($M = \text{Fe, Ga}; X = \text{Cl, Br}$) were synthesized by the galvanostatic oxidation of a chlorobenzene solution containing tetraselenafulvalene (DIETSe) and the corresponding tetra-$n$-butylammonium tetrahalogenometallates as the supporting electrolyte [1]. Many exotic states, such as field induced superconductivity in $\gamma - (\text{BETS})_2\text{FeCl}_4$ [2], are realized on organic conductors with $\pi$-$d$ system. In the case of $(\text{DIETSe})_2\text{GaCl}_4$, in which the magnetic ion is absent, $\pi$-electrons contribute to the electrical conductivity and the magnetism. The temperature dependence of the resistivity in $(\text{DIETSe})_2\text{GaCl}_4$ shows a quasi-one-dimensional metallic behavior and then metal-insulator (MI) transition at 12 K [1]. The calculated Fermi surface is quasi-one-dimensional consistent with the resistivity measurement. Therefore, one can expect that the MI transition is attributed to the spin density wave (SDW) ordering. In this work, we studied $^{77}\text{Se}$ NMR to clarify the microscopic magnetism and the spin dynamics of $(\text{DIETSe})_2\text{GaCl}_4$.

$(\text{DIETSe})_2\text{GaCl}_4$ has the orthorhombic crystal structure with space group $Ibam$. The structure of DIETSe is shown in Fig. 1. The Se atoms occupy two crystallographic sites: one is near the sulfur site, and the other is near the iodine site. The nearest neighbor atoms of two Se sites are completely the same, and the atmospheres of two sites are quite similar. Because the $\pi$ electrons at the double bond centered by four Se atoms would contribute to the magnetic properties, $^{77}\text{Se}$ NMR can probe the dynamical and static properties in $(\text{DIETSe})_2\text{GaCl}_4$. 
Figure 1. Structure of DIETSe molecular. $^{77}$Se occupy two crystallographic sites. The double bond at the center of the molecular contributes to the magnetic and transport properties.

2. Experiments
The powder samples of $(\text{DIETSe})_2\text{GaCl}_4$ were prepared according to the previous reports [1, 3]. The $^{77}$Se (nuclear spin $I = 1/2$) NMR experiments were carried out for the powder sample by utilizing a coherent-type pulsed NMR spectrometer. The Knight shift was determined from the resonance center, gyromagnetic ratio of $^{77}$Se nuclear $\gamma = 8.129$ MHz/T together with the field calibration by the reference signal of $^2\text{D}$ nuclear in $\text{D}_2\text{O}$. The $^{77}$Se nuclear spin-lattice relaxation time $^{77}T_1$ was measured by an inversion recovery technique. The spin-echo signal $M(t)$ was measured as a function of long delay time $t$ after an inversion pulse, and $M(\infty)[\equiv M(t > 10T_1)]$ was recorded. All the recovery curves were measured at the resonance peak frequency. $^{77}T_1$ was estimated from the recovery curve fitted by the theoretical curve of $p(t) \equiv 1 - M(t)/M(\infty) = p(0)e^{-t/T_1}$ for the transition $I_z = -1/2 \leftrightarrow +1/2$, where $p(0)$ and $T_1$ are the fitting parameters.

Figure 2. (a) $^{77}$Se NMR spectra of $(\text{DIETSe})_2\text{GaCl}_4$ between 4.2 and 120 K. (b) Typical spectrum in the paramagnetic state. The dotted line indicates a theoretical line of the powder pattern with a presence of an uniaxial anisotropic Knight shift.

3. Results and Discussions
The NMR spectra at 7.4847 T are shown in Fig. 2 (a). We measured Fourier transform spectra above 30 K and frequency-swept spectra below 20 K. At the paramagnetic state, the $^{77}$Se NMR spectrum of $(\text{DIETSe})_2\text{GaCl}_4$ shows a typical powder pattern with an uniaxial anisotropic shift. The magnified spectrum at 15 K is shown in Fig. 2(b). Although there are two crystallographic sites in $(\text{DIETSe})_2\text{GaCl}_4$, the local circumstances of the two sites are very similar, implying the presence of similar hyperfine fields. Therefore, the asymmetric spectrum of $(\text{DIETSe})_2\text{GaCl}_4$ is not mainly due to the two different sites but due to the anisotropic Knight shift. Similar
asymmetric NMR signals were observed for other organic conductors including the selenium [4, 5]. The dotted line in Fig. 2(b) is a theoretical powder pattern with an uniaxial anisotropic shift $K_{\text{aniso}} = 0.04 \%$. Isotropic Knight shift was estimated to $K_{\text{iso}} = -0.01 \%$. We cannot divide $K_{\text{iso}}$ into the chemical shift and the paramagnetism contributed Knight shift because the insulating DIETSe salts with the homogeneous structure have not been obtained yet. Between 7 and 120 K, $K_{\text{aniso}}$ seems to change slightly while $K_{\text{iso}}$ does not change.

![Figure 3. (a) $^{77}$Se NMR spectrum of (DIETSe)$_2$GaCl$_4$ at 2 K under $H = 4.6501$ T. Solid line indicates the theoretical line under the internal field distributed as shown in Fig.(b). (b) Internal field at the Se sites.](image)

At the low temperatures below 7 K, the spectrum shows broadening, indicating a magnetic ordering. We measured the NMR spectrum at lower temperature of 2 K and lower field of 4.6501 T to clarify details of the magnetic ordering. The spectrum is shown in Fig. 3(a). In the commensurate magnetic ordering case, the powder pattern spectrum shows a characteristic rectangular shape. The spectrum of (DIETSe)$_2$GaCl$_4$ in the magnetically ordered phase is typical powder pattern of the SDW state, in which the intensity of the center part of the spectrum is enhanced markedly. In the SDW state, the internal magnetic field $H_{\text{int}}$ is given as

$$H_{\text{int}}(R_j) = (H_{\text{int}})^{\max} \cos(Q \cdot R_j),$$

(1)

where $(H_{\text{int}})^{\max}$ is the maximum amplitude of the internal field and $R_j$ and $Q$ are the position vector of the Se site and the wave vector of the SDW, respectively [6]. In the case of external field much larger than $H_{\text{int}}$, the powder NMR shape function $f(x)$ for fixed frequency $\omega_0$ is written as

$$f(x) = \frac{1}{\pi} \ln \left| \frac{1 + (1 - x^2)^{\frac{3}{2}}}{x} \right|,$$

(2)

where $x = (\gamma_N - \omega_0)/\gamma_N (H_{\text{int}})^{\max}$, $-1 \leq x \leq 1$ and $\gamma_N$ is the nuclear gyromagnetic ratio [6]. The solid line in Fig. 3(a) is a theoretical line expressed by Eq. (2) with $(H_{\text{int}})^{\max} = 0.23$ T. The internal field distribution corresponding to the solid line in Fig. 3(a) is shown in Fig. 3(b), where $x$ denotes $Q \cdot R_j$. In the incommensurate SDW, $R_j$ is incommensurate to $Q$, giving a equivalent distribution for $x$. In the case of (DIETSe)$_2$GaCl$_4$, SDW ordering in the $\pi$-electron system causes the distribution of the internal field at Se sites as shown in Fig. 3(b).

The nuclear spin-lattice relaxation rate $1/T_1$ of $^{77}$Se in (DIETSe)$_2$GaCl$_4$ under $H = 4.6501$ T is shown in Fig. 4. Between 12 and 120 K, $1/T_1$ decreases monotonically with decreasing temperature. Then $1/T_1$ increases, shows divergent behavior and takes a maximum at about 7 K, indicating the magnetic long-range ordering. Under the higher external field of 7.4847 T,
the maximum temperature does not change. Therefore, taking into consideration of the fact that the MI transition occurs at 12 K [1], in (DIETSe)$_2$GaCl$_4$, the resistivity and $1/T_1$ increases even below about 12 K due to short-range ordering effects of SDW and the temperature of 7 K, where $1/T_1$ shows maximum, is regarded as the SDW transition temperature. Abnormally large temperature range of the short-range ordering might be the intrinsic property of the quasi-one-dimensional system. In the present stage, we cannot conclude whether $1/T_1$ at the paramagnetic state is attributed to the quasi-one-dimensional spin dynamics, or not. To discuss the details of the spin dynamics, we need NMR experiments for a single crystal and estimate the Korringa term of $1/T_1 T$ with the Knight shift.

4. Summary
We studied $^{77}$Se NMR in the quasi-one-dimensional conductor (DIETSe)$_2$GaCl$_4$. The broadened $^{77}$Se NMR spectra at low temperatures indicate the presence of magnetic ordering and the line shape of the spectrum is characterized as that of the SDW state. Maximum behavior of $1/T_1$ suggests that the SDW ordering occurs at about 7 K, which is lower than the MI transition temperature of 12 K. The large range of the temperatures of short-range ordering might be due to the low dimensional characteristics.

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