Dynamic Behavior of Group 13 Elements in Bromocomplexes as Studied by NQR and NMR

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NMR, NQR, powder X-ray diffraction, DTA and AC conductivity were measured in $RMBr_4$ (R = Ag, Cu; M = Al, Ga) and RM_2Br_7 (R = Li, Ag; M = Al, Ga). In $RMBr_4$, the activation energy of Cu^+ diffusion was evaluated from ^{63}Cu NMR and was in good agreement with that from ^{81}Br NQR. In $CuAlBr_4$, the e^2Qq/h value of ^{63}Cu NMR and the η value of ^{27}Al NMR changed linearly with decreasing temperature, although the e^2Qq/h value of ^{27}Al NMR did not change so much. These temperature dependences are supposed to be due to Cu^+ diffusion and not to a variation of the lattice constants. In RM_2Br_7, the activation energy was obtained from the spin-lattice relaxation time T_1 of ^{81}Br NQR and is ascribed to a modulation of the cation diffusion. The line width of ^7Li NMR in $LiAl_2Br_7$ was about 5.9 kHz in the low-temperature phase and 0.4 kHz for the high-temperature phase. The ^{27}Al NMR spectrum was broadened by the quadrupole interaction and unchanged up to 400 K, suggesting that diffusion of Li^+ ions occurs in the high-temperature phase.

Key words: T_1 of ^{81}Br NQR; ^{27}Al NMR; ^7Li NMR; ^{63}Cu NMR; Cation Diffusion.

Introduction

In the system of alkali bromide-tribromide of Group 13 elements, not only 1:1 but also 1:2 complexes have been found [1, 2]. The 1:1 complex contains tetrahedral MBr_4^- anions and the 1:2 complex $M_2Br_7^-$ anions which consist of two tetrahedral MBr_4 sharing one corner. We have already reported the static and dynamic structures of compounds with the general formula $RBr-MBr_3$ (R = Li, Cu, Ag; M = Al, Ga) [3, 4] and the structure and bonding in $Al_2Br_7^-$ [5].

Since most of these complexes undergo phase transitions by cationic and anionic motions with increasing temperature, properties such as the electric conductivity will change abruptly at the phase transition temperature. The phase transition mechanism and the relation between the ionic motions and the conductivity are also very interesting. In the present study, we examined the anionic structure and ionic motions by measuring ^{81}Br NQR, ^7Li, ^{27}Al, and ^{63}Cu NMR, and the electric conductivity in order to clarify the conduction mechanism.

Experimental

$RMBr_4$ (R = Li, Cu, Ag; M = Al, Ga) were prepared by heating a mixture containing stoichiometric amounts of RBr (R = Li, Cu, Ag) and MBr_3 (M = Al, Ga) in an evacuated Pyrex tube at ca. 550 K. The complexes of RM_2Br_7 (R = Li, Ag; M = Al, Ga) were obtained by mixing MBr_3 (M = Al, Ga) with well-dried RBr (R = Li, Ag) in the stoichiometric ratio in a sealed tube. The samples were identified by a powder X-ray diffractometer (Rigaku Rad-B system) using Cu-K_α radiation.

The ^{81}Br NQR spectrum was observed with a Matec pulsed spectrometer and its spin-lattice relaxation time was determined by means of a conventional pulse technique. The ^7Li, ^{27}Al, and ^{63}Cu NMR spectra were observed using a Matec pulsed spectrometer at 6.3 T with the corresponding Larmor frequencies of 105.41 MHz, 70.68 MHz, and 71.89 MHz, respectively. The NMR spin-lattice relaxation time was determined with a $90°-\tau-90°$ pulse sequence. The electric conductivity was determined

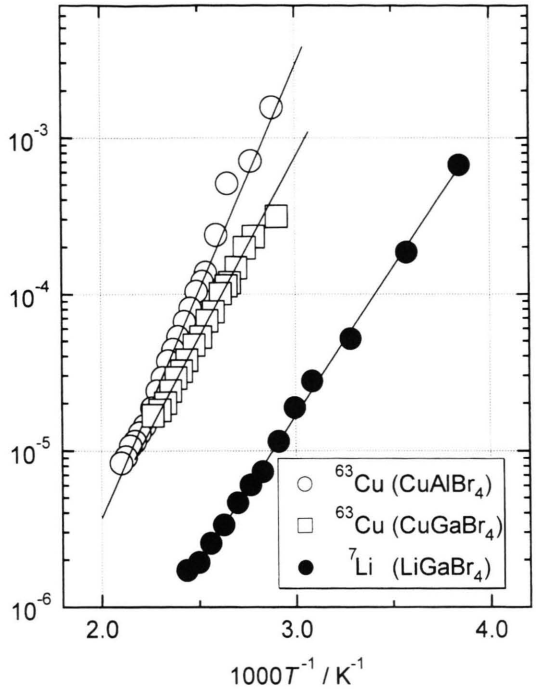

Fig. 1. Temperature dependence of the correlation times τ_c evaluated from ^{63}Cu and ^{7}Li NMR spectra in $CuMBr_4$ (M = Al, Ga) and $LiGaBr_4$.

with a complex impedance method at 10 different frequencies (100 Hz∼100 kHz, ANDO LCR meter AG-4311B).

Results and Discussion

$RMBr_4$ (R = Li, Cu, Ag; M = Al, Ga)

The crystal structures of $CuMBr_4$ were solved by the Rietveld analysis of powder X-ray diffraction patterns. They are isomorphous with $CuGaCl_4$ and belong to a tetragonal system. The space group was determined to be $P\bar{4}2c$ from the observed reflections. The Cu atom is tetrahedrally coordinated by four Br atoms, its site symmetry being $\bar{4}$ along *c*-axis. The Al atom is also tetrahedrally coordinated by four halogen atoms, and its site symmetry is 222.

^{63}Cu NMR measurements were carried out on the central transition ($m = -1/2 \leftrightarrow +1/2$) using a single crystal of $CuAlBr_4$. Since the nuclear spin of ^{63}Cu is 3/2 and the site of the Cu atom is not spherically symmetric, three peaks were observed, composed of one central peak and a pair of satellite peaks produced by the first-order quadrupole effect. With increasing temperature, the motional narrowing of the spectra began at 380 K and 330 K for $CuAlBr_4$ and $CuGaBr_4$, respectively.

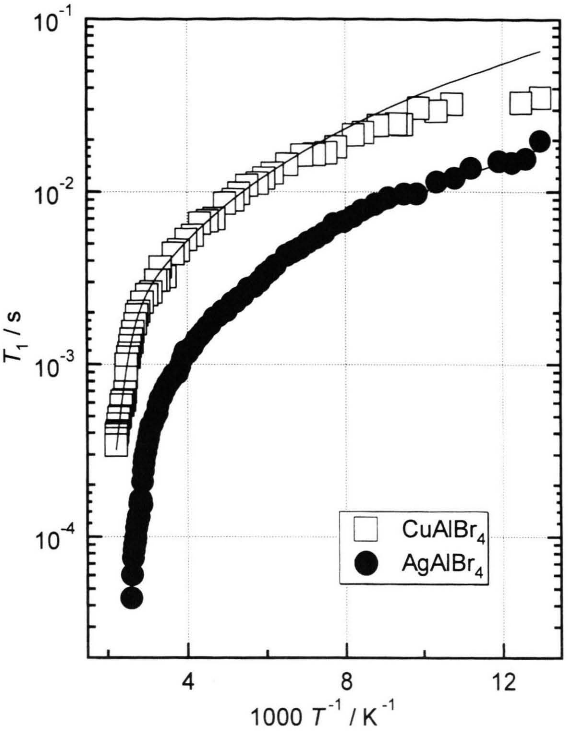

Fig. 2. Temperature dependence of ^{81}Br NQR spin-lattice relaxation times T_1 in $RAlBr_4$ (R = Cu, Ag).

Figure 1 shows the plots of the correlation time against the inverse temperature. The correlation time τ_c was evaluated from fitting the equation

$$\tau_c = \frac{1}{\alpha \delta\omega} \tan \frac{\pi(\delta\omega^2 - \delta\omega_A^2)}{2(\delta\omega_B^2 - \delta\omega^2)} \qquad (1)$$

to the observed linewidth by use of a non-linear least-square method $\delta\omega_A$, $\delta\omega$, $\delta\omega_B$ are the linewidth above, within, and below the transition region, respectively, and α is a numerical constant of about unity. The straight lines in Fig. 1 were drawn assuming an Arrhenius equation

$$\tau_c = \tau_0 \exp(E_a/RT). \qquad (2)$$

From the slopes of them, activation energies E_a of the cation diffusion were obtained to be 51 kJmol^{-1} and 44 kJmol^{-1} for $CuAlBr_4$ and $CuGaBr_4$, respectively. Cu diffusion was detected in all Cu salts, and there is

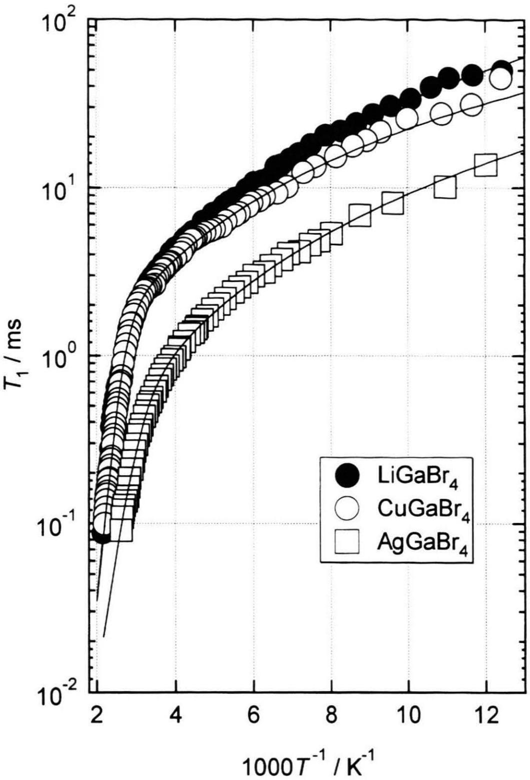

Fig. 3. Temperature dependence of ^{81}Br spin-lattice relaxation times T_1 in $RGaBr_4$ (R = Li, Cu, Ag).

a little difference in E_a value between the Al and Ga salts.

Figures 2 and 3 show the temperature dependence of the ^{81}Br NQR spin-lattice relaxation times T_1 in $RAlBr_4$ (R = Cu, Ag) and $RGaBr_4$ (R = Li, Cu, Ag). T_1 decreased gradually with increasing temperature up to ca. 300 K and then decreased exponentially. In the present compounds, there are two possible activation processes; one is the reorientation of the MBr_4^- anion and the other the diffusion of the cation. If these two activation processes, having different E_a values, simultaneously cause the exponential decrease in T_1, the activation energy obtained experimentally corresponds to the process with the larger contribution. Thus, the observed T_1 is expressed by [6]

$$(T_{1_{\rm obs}})^{-1} = (T_{1_{\rm Raman}})^{-1} + b\exp(E_a/RT), \qquad (3)$$

where $T_{1_{\rm Raman}}$ is the contribution of the Raman process which originates from the lattice vibration and governs the behavior at low temperatures. The activation energies of $CuMBr_4$ (M = Al, Ga) obtained from this equation are in good agreement with those from ^{63}Cu NMR. Therefore, the activation process detected from ^{81}Br NQR can also be assigned to the Cu^+ ion diffusion.

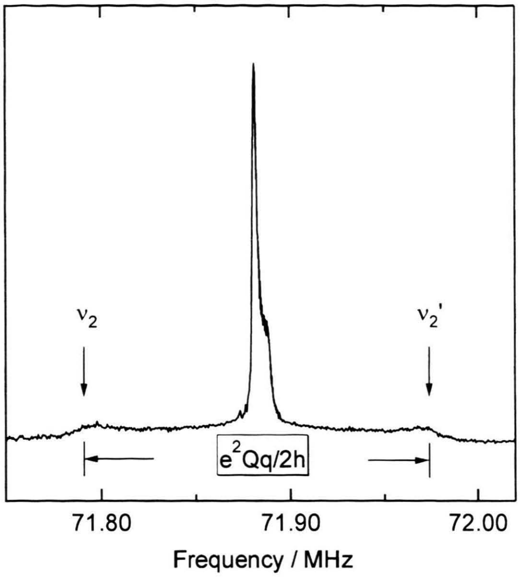

Fig. 4. ^{63}Cu NMR spectrum in $CuAlBr_4$ at 289 K. Arrows indicate the satellite transitions ($m = \pm 1/2 \leftrightarrow \pm 3/2$).

Figure 4 shows the ^{63}Cu NMR in a powder sample of $CuAlBr_4$. Since e^2Qq/h is 350 kHz and η is zero for the Cu^+ ion, one central peak and two pairs of shoulders are expected according to the first-order quadrupole interaction. The shoulders of the outer pair were so weak that only the inner pair could be detected. The central peak was asymmetrical, and its line width was ca. 9 kHz. The ^{63}Cu NMR spectrum is broadened by the chemical shift anisotropy, the magnetic dipole interaction, and the second-order quadrupole interaction. Since the efg of the Cu site is cylindrical, the linewidth due to the second-order quadrupole effect was evaluated to be 0.22 kHz at 299 K and amounting to only 2.4% of the observed linewidth. Thus, the central transition of ^{63}Cu NMR of $CuAlBr_4$ is a convolution of the chemical shift anisotropy and the magnetic dipole interaction.

Figure 5 shows the observed central peak of the ^{63}Cu NMR spectrum for a powder sample and the results of the simulation for the chemical shift anisotropy and the magnetic dipole interaction. The magnetic dipole interaction is averaged out at ca. 450 K but the chemical shift anisotropy does not change even at 525 K, whereas the rate of the Cu^+ ion

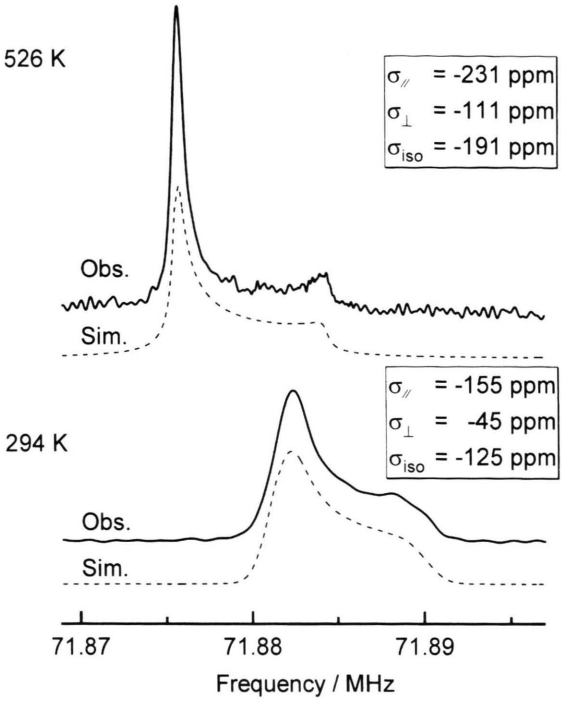

Fig. 5. Temperature dependence of ^{63}Cu NMR spectra ($m = -1/2 \leftrightarrow +1/2$) in CuAlBr$_4$. The solid and dashed lines are the observed and simulated spectra, respectively.

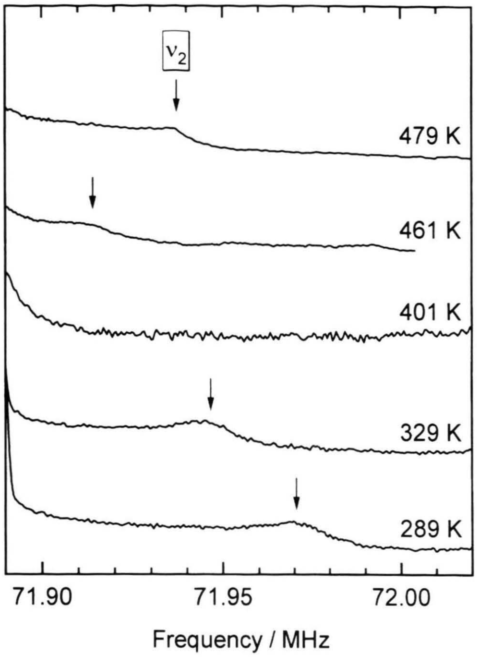

Fig. 6. Temperature dependence of the satellite shoulders of the ^{63}Cu NMR spectrum for a powder sample of CuAlBr$_4$. Arrows indicate shoulders of the satellite transitions ($m = \pm 1/2 \leftrightarrow \pm 3/2$).

diffusion is fast enough to average out the chemical shift anisotropy. If Cu$^+$ ions diffuse randomly in the crystal, the chemical shift anisotropy must be averaged out, suggesting that the surrounding sites occupied by Cu$^+$ ions in their diffusion process are similar to those of normal sites.

Figure 6 shows the temperature dependence of the satellite shoulders of the ^{63}Cu NMR spectrum for a powder sample of CuAlBr$_4$. The arrows indicate the satellite shoulders. With increasing temperature, the shoulder approaches the central peak below 420 K and goes away again above 420 K.

The nuclear quadrupole coupling constant e^2Qq/h for ^{63}Cu was evaluated from the frequency separation between the satellite shoulders by use of the equation

$$\Delta\nu_2 = \nu_2 - \nu_2' = \frac{1}{2}e^2Qq/h, \tag{4}$$

where ν_2 is the frequency of the shoulder.

Figure 7 shows the temperature dependence of ^{27}Al NMR spectra for a powder sample. The nuclear spin of ^{27}Al is 5/2, and the symmetry of the Al site is 222 and not cylindrical. Therefore a central peak and several pairs of shoulders should be observed. The arrows of ν_1 and ν_2 point to the satellite shoulders. The assignment of each shoulder was confirmed by the measurement of the angular dependence of single crystal ^{27}Al NMR spectra. The principal axis system of the efg for the Al site is similar to the crystal axis system. e^2Qq/h and the asymmetry parameter η of ^{27}Al were evaluated from the separation of the shoulders (ν_1 and ν_2) and the central transition (ν_0), $\delta\nu_1$ and $\delta\nu_2$ by use of the equations

$$\begin{aligned} \delta\nu_1 &= \nu_0 - \nu_1 = \frac{3}{40}(1-\eta)e^2Qq/h, \\ \delta\nu_2 &= \nu_0 - \nu_2 = \frac{1}{20}(1-\eta)e^2Qq/h. \end{aligned} \tag{5}$$

Since e^2Qq/h of ^{63}Cu is zero at around 420 K, the Cu site seems to have a spherically symmetric efg, and the sign of e^2Qq/h changes at this temperature. However, from consideration of the temperature dependence of both lattice constants and the chemical shift anisotropy, the Cu site is expected to have a non-spherical efg. On the other hand, e^2Qq/h of ^{27}Al did not change much although the η value decreased linearly with increasing temperature. The behavior

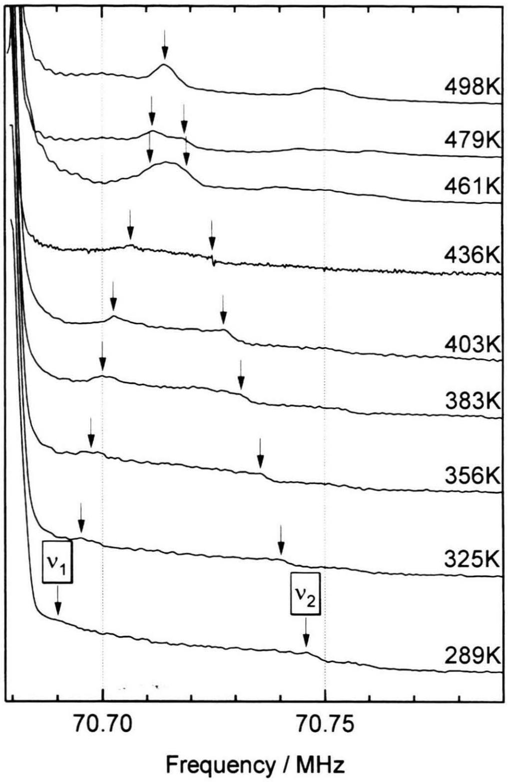

Fig. 7. Temperature dependence of ^{27}Al NMR spectra in $CuAlBr_4$. Arrows indicate shoulders of the satellite transitions ($m = \pm 1/2 \leftrightarrow \pm 3/2$).

of these parameters differs much from that of ^{63}Cu nuclei.

The coordinates of interstitial tetrahedral sites are (0, 1/2, 1/4), (1/2, 1/2, 1/4), and (0, 0, 0). The former two sites have the same symmetry as the Al site, and the temperature dependence of e^2Qq/h and η of the Al site are much different from those of normal Cu sites. On the other hand, the symmetry of (0, 0, 0) is $\bar{4}$, which is identical to that of the normal Cu site, and its environment is expected to be similar to that of the Cu site. Thus the Cu^+ ion may diffuse via interstitial sites.

RM_2Br_7 (*R* = *Li*, *Ag*; *M* = *Al*, *Ga*)

By the DTA measurements on $LiAl_2Br_7$, a thermal anomaly was detected at 330 K on heating and 322 K on cooling. The thermal hysteresis indicates that this transition is of first order. AgM_2Br_7 (M = Al, Ga) did not show any phase transition from 77 K to the melting point.

Table 1. ^{81}Br NQR frequencies of $LiAl_2Br_7$ and AgM_2Br_7 (M = Al, Ga).

	— Frequency/MHz —	
Compound	77 K	297 K
$LiAl_2Br_7$	81.21, 82.64, 85.43, 87.21	78.80, 80.68, 82.81
$AgAl_2Br_7$	78.192, 81.778, 84.441, 84.561, 84.894, 87.304, 93.443	77.580, 79.842, 83.175, 82.395, 82.063, 85.483, 91.122
$AgGa_2Br_7$	104.142, 111.507, 113.904, 114.828, 116.284, 120.205, 136.452	101.470, 109.793, 110.521, 110.723, 113.116, 118.823, 133.032

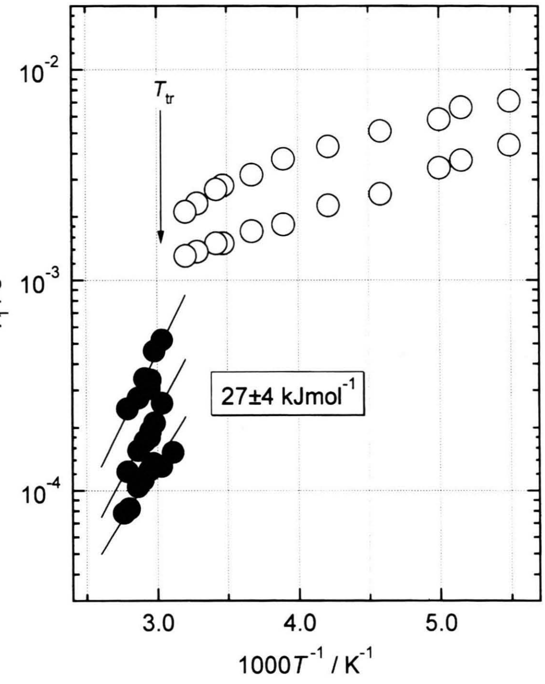

Fig. 8. Temperature dependence of ^{81}Br NMR spin-lattice relaxation times T_1 in $LiAl_2Br_7$. The open and solid circles belong to the low- and high-temperature phases, respectively.

Table 1 summarizes the ^{81}Br NQR frequencies for $LiAl_2Br_7$ and AgM_2Br_7 (M = Al, Ga) which contain the $M_2Br_7^-$ (M = Al, Ga) anion consisting of two MBr_4 tetrahedra by sharing one corner. The low-temperature phase of $LiAl_2Br_7$ has four ^{81}Br NQR signals and the high-temperature phase has three signals. In the high-temperature phase, the intensity ratio of the three signals is 1:4:2 from the higher frequency to the

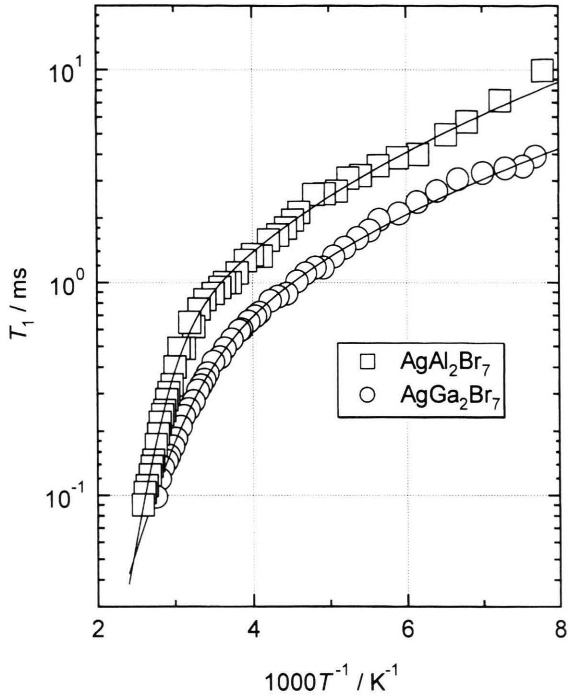

Fig. 9. Temperature dependence of ^{81}Br NQR spin-lattice relaxation times T_1 in AgM_2Br_7 (M = Al, Ga).

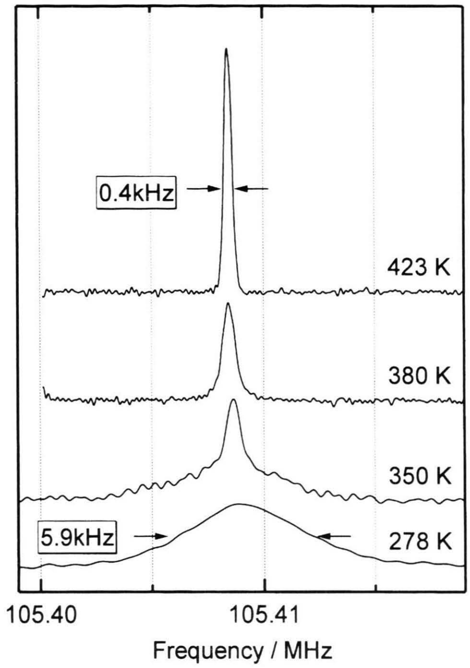

Fig. 10. Temperature dependence of ^{7}Li NMR spectra ($m = -1/2 \leftrightarrow +1/2$) in $LiAl_2Br_7$.

lower. This suggests two informations about the anion structure: (i) The $Al_2Br_7{}^-$ anion of $LiAl_2Br_7$ has two mirror planes; one of them is perpendicular to the Al-Br-Al plane and the other is parallel to the Al-Br-Al plane. (ii) The higher frequency signal corresponds to the bridging Br^- ion, the middle one is the terminal Br^- out of the mirror plane, and the lowest one is the terminal Br^- on the mirror plane.

Figure 8 shows the temperature dependence of spin-lattice relaxation times T_1 for these three signals in $LiAl_2Br_7$. Their T_1 varied discontinuously at the phase transition. T_1 of all signals varied gradually in the low-temperature phase and decreased exponentially in the high-temperature phase. If the reorientation of the $AlBr_3$ group in the $Al_2Br_7{}^-$ anion produces an exponential decrease in T_1, the temperature dependence in T_1 for the bridging Br can not be similar to those of the others. Therefore, the exponential decrease of T_1 is due to the modulation effect caused by the diffusion of Li^+, and its E_a was evaluated to be 27 ± 4 kJmol^{-1}.

Figure 9 shows the temperature dependence of ^{81}Br NQR spin-lattice relaxation times T_1 in AgM_2Br_7 (M = Al, Ga). T_1 decreased gradually up to ca. 300 K and then exponentially. For each AgM_2Br_7, T_1 of all seven signals varied in the same way and the E_a values are equal. For the same reason the exponential decrease in T_1 for $LiAl_2Br_7$ is due to the modulation effect caused by the diffusion of Ag^+ ions. Then, the temperature dependence of T_1 is expressed by (3) and the activation energy of the Ag^+ ion diffusion was evaluated to be 42 kJmol^{-1} and 26 kJmol^{-1} for $AgAl_2Br_7$ and $AgGa_2Br_7$, respectively. The exponential decreases in T_1 for seven ^{81}Br NQR signals in $AgAl_2Br_7$ or $AgGa_2Br_7$ began at slightly different temperatures from each other. This can be explained by the difference of b in (3). Furthermore, since the exponential decreases of all T_1 for each AgM_2Br_7 (M = Al, Ga) are produced by the same motion, τ_c must have the same motion. Thus, it was found that the diffusion of Ag^+ ions produces a partial fluctuation of the efg, and these fluctuations at the seven Br atoms differ little.

Figure 10 shows the temperature dependence of ^{7}Li NMR spectra in $LiAl_2Br_7$. These spectra correspond to the central transition ($m = -1/2 \leftrightarrow +1/2$). The spectrum changes significantly at the phase transition point. The linewidth of the spectrum in the low-temperature phase is about 5.9 kHz and narrowed to about 0.5 kHz in the high-temperature phase. The linewidth of the NMR spectrum in the rigid lattice was calculated from the second moment assuming Li-Br = 2.7 Å, using the procedure of van Vleck [7, 8]. The calculated linewidth is 5.6 kHz and is consistent with the measured linewidth for the low-temperature phase. Therefore, the ^{7}Li NMR spectra are broadened by the contribution of the magnetic dipole interaction in the low-temperature phase, and the change at the phase transition point indicates that some molecular motions average this dipole interaction.

On the other hand, the ^{27}Al NMR spectrum in $LiAl_2Br_7$ is broadened by the quadrupole interaction and unchanged up to 400 K as shown in Figure 11. The behavior of the ^{7}Li and ^{27}Al NMR spectra suggests that translational diffusion of Li^+ ions occurs in the high-temperature phase, and that the reorientation of the $AlBr_3$-group is too slow to be observed by NMR.

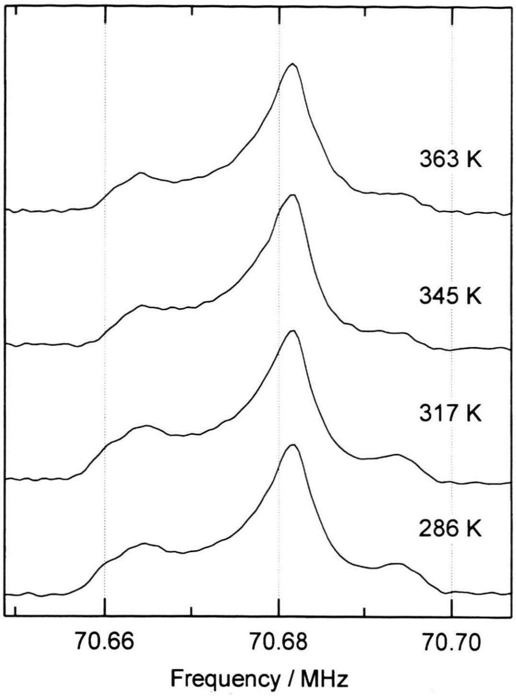

Fig. 11. Temperature dependence of ^{27}Al NMR spectra ($m = -1/2 \leftrightarrow +1/2$) in $LiAl_2Br_7$.

Acknowledgement

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