

## 5. Phase Transition and Cation Dynamics in $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$ Crystal as Studied by $^1\text{H}$ and $^2\text{H}$ NMR

### 5.1 Introduction

In this chapter, phase transition and cation dynamics in  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$  (MABC) and the partially deuterated material  $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$  (MABCD) is discussed in according with ref. 1. Crystalline MABC undergoes a second order paraelectric-ferroelectric phase transition at  $T_{c1} = 307$  K, associated with the ordering of methylammonium cations [2]. No soft mode has been observed by Raman studies [3] around the phase transition. Moroz and Jakubas have reported the existence of another phase transition at  $T_{c2} = 170$  K from the pyroelectric measurement [4], whereas no evidence for its existence has so far been obtained by other methods. The X-ray structural investigation by Lefebvre *et al.* showed that the crystal structure is orthorhombic  $Pcab$  in the paraelectric phase and orthorhombic  $Pca2_1$  in the ferroelectric phase [5]. According to these authors the C-N axis orientation of three of the five methylammonium cations are disordered in the paraelectric phase and two are in the ferroelectric phase.

A critical slowing down of the cationic motion was observed by the dielectric dispersion measurement in the microwave region [6]. A phenomenological theory was presented by Iwata and Ishibashi to interpret the phase transition [7].  $^1\text{H}$  NMR studies were also performed by Medycki *et al.* [8] and Decressain *et al.* [9]. They investigated the motion of methylammonium cations by analyzing the second moment of line shape and relaxation times, but could detect no anomaly associated with the phase transition.

In order to clarify detailed nature of the paraelectric-ferroelectric phase transition and the critical dynamics of the methylammonium cations near the phase transition, we intend to measure the  $^1\text{H}$  spin-lattice relaxation time ( $T_1$ ) of MABC and partially deuterated material  $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$  (MABCD) and  $^2\text{H}$  NMR spectra of MABCD. The evidence of the lower phase transition expected at 170 K was also investigated.

## 5.2 Experimental

MABC crystals were prepared by slow evaporation of an aqueous solution containing the stoichiometric amount of methylammonium chloride and bismuth(III) chloride purchased from Wako Pure Chemical Industries, Ltd., after a small amount of hydrochloric acid was added for preventing hydrolysis. Large colorless crystals were obtained. Chemical analysis, found: C = 6.13, H = 3.15 and N = 7.03 (%); calcd. C = 6.20, H = 3.12 and N = 7.23. The deuterated specimen (MABCD) was obtained by evaporating *in vacuo* of a  $\text{D}_2\text{O}$  (Aldrich 99.9 %) solution of MABC containing deuterium chloride (Aldrich 99.5 % in  $\text{D}_2\text{O}$ ). The calculated deuteration ratio was *ca.* 96 %. The obtained powder crystals were put in a glass tube and dried *in vacuo* longer than 3 hours and then sealed with nitrogen gas for NMR measurements.

The  $^2\text{H}$  NMR measurement was carried out by a Bruker MSL-300 NMR system with the Larmor frequency of 46.07 MHz between 130 and 350 K. The quadrupole echo sequence was used for the spectrum measurement. The sample temperature was controlled by a VT-1000 temperature controller within 1 K and determined by a copper-constantan thermocouple within 2 K. The  $^1\text{H}$  NMR measurement was performed by a home-made apparatus with the Larmor frequency of 40.8 MHz and the spin-lattice

relaxation time was measured by the  $180^\circ$ - $\tau$ - $90^\circ$  pulse sequence between 85 and 370 K. The accuracy of the temperature measurement was  $\pm 0.2$  K and the uncertainty in relaxation time was estimated within 10 %.

### 5.3 Result and Discussion

#### 5.3.1 DSC and $^2\text{H}$ NMR spectra measurements

By DSC measurement of MABC a broad thermal anomaly whose peak is situated at 306.9 K was observed on heating. This value agrees well with previously reported  $T_{cl}$  of 307 K [2]. A similar anomaly was also observed for MABCD, whose peak temperature, 305.5 K, is very close to that in MABC. This fact suggests that the weak N-H...Cl hydrogen bond acts no important role for the phase transition.

Figure 5.1 shows observed  $^2\text{H}$  NMR spectra of powdered MABCD at various temperatures. The line-shape of these spectra is governed mainly by the nuclear quadrupole interaction and characterized by three constants given by [10]

$$\Delta\nu_1 = \frac{3}{4}(1 - \eta) \frac{e^2 Qq}{h},$$

$$\Delta\nu_2 = \frac{3}{4}(1 + \eta) \frac{e^2 Qq}{h},$$

and

$$\Delta\nu_3 = \frac{3}{2} \frac{e^2 Qq}{h},$$

where  $e^2 Qq/h$  is the quadrupole coupling constant and  $\eta$  is the asymmetric parameter of

the electric field gradient (EFG) around the nuclei.

The  $e^2Qq/h$  and  $\eta$  were estimated by using above relation to be  $60 \pm 1$  kHz and  $0.1 \pm 0.05$ , respectively, from the spectrum observed at 122 K in the low-temperature phase. This  $e^2Qq/h$  value is about one third of 183.7 kHz [11] observed for  $\text{ND}_3^+$  group in methylammonium chloride and this reduction can be attributed to the averaging of the EFG by fast ammonium reorientation around the molecular  $C_3$  axis. The line-shape became gradually narrow with increasing temperature from about 130 K up to the phase transition temperature, 305.5 K. In the high-temperature phase, the spectrum was almost temperature independent and the estimated  $e^2Qq/h$  and  $\eta$  were  $38 \pm 1$  kHz and  $0.1 \pm 0.05$ , respectively. This spectral change is attributable to motions of the C-N bond axis. Furthermore, the small  $\eta$  value indicates that the motion has a pseudo three-fold or higher symmetry. The spectrum in the high-temperature phase can be explained by the model of a fast precessional motion of the C-N bond axis with the precession angle *ca.*  $30^\circ$  together with the  $\text{ND}_3^+$   $C_3$  reorientation. For these results, however, we cannot determine whether the motion is the continuous rotation or discrete jumps around the precession axis. All cations is expected to undergo similar motions to each other because the spectrum consists of only a single component in the high-temperature phase. This result is in consistent with the fact that the disorder was not observed for two of five cations in the X-ray study [5]. The recent calorimetric study [2] showed that the transition entropy is close to  $R \ln 4$  which is twice as the expected value from the disordering model predicted by X-ray study. This also indicates the higher disordering of the cations. The spectrum observed at 294 K showed a complicated line-shape as shown in Fig. 5. 1. This suggests that the rate of the motion at the intermediate

temperature region between 130 and 305 K is comparable to the line width, i.e.  $\sim 10$  kHz. Reference 12 reported that partially disordering of the cations occurs in a wide temperature range around 160 K. The cationic motion obtained from the analysis of the  $^2\text{H}$  spectra is expected to be closely related to the disordering. The line-shape consisting of two or more signals indicates the existence of nonequivalent methylammonium cations in the crystal. The X-ray structure investigation on MABC has also shown that the five kinds of cations in a unit cell are crystallographically nonequivalent [5].

### 5.3.2 $^1\text{H}$ NMR $T_1$ measurements

To investigate the critical phenomenon we measured the  $^1\text{H}$   $T_1$  of MABC and MABCD. The temperature dependences of  $T_1$  are shown in Fig. 5. 2. The  $T_1$  behavior is very close to the previously reported results [9]. Several  $T_1$  minima were observed in the low-temperature phase for both compounds, though the  $T_1$  values of the deuterated specimen was about twice as those in MABC because of the  $^1\text{H}$  dilution by deuteration. The minimum observed at the highest temperature for each specimen was attributed to the uncorrelated reorientation of  $\text{CH}_3$  and  $\text{NH}_3^+$  groups and the other minima at lower temperatures correspond to the correlated reorientation which is the uniaxial reorientation of cation as a whole [8, 9, 13]. The fact that the three or more minima were observed corresponds to the existence of nonequivalent cations as observed by the  $^2\text{H}$  NMR.

In the close vicinity of  $T_{c1}$ , an anomalous  $T_1$  decrease was observed as shown in an enlarged scale in Fig. 5. 3, although no anomaly was observed around  $T_{c2} = 170\text{K}$ . The singular point of the  $T_1$  curve in MABCD was observed at ca. 306.5 K which temperature coincides with  $T_{c1} = 307$  K determined by DSC within the experimental

error. The observed  $T_1$  decrease which is more remarkable to the critical slowing down of the cationic motion associated with the order-disorder phase transition. We cannot assign this motion to be  $180^\circ$ -flip of the C-N axis, because this motion has in principle no effect on  $^1\text{H}$   $T_1$ . We expected that this motion has a close relation with the C-N axis motion derived from the  $^2\text{H}$  NMR spectrum analysis.

Around  $T_c$ , the total relaxation time  $T_1$  can be divided into two terms given by

$$T_1^{-1} = T_{1c}^{-1} + T_{1n}^{-1},$$

where  $T_{1c}^{-1}$  and  $T_{1n}^{-1}$  are the relaxation rate due to the critical fluctuation and the normal molecular motion, respectively. The experimental  $T_{1c}$  was obtained from the total  $T_1^{-1}$  by subtracting  $T_{1n}^{-1}$  due to axial rotation of the methylammonium ion around its C-N bond.

The proton relaxation which is governed by the averaging of the interproton dipole-dipole interaction due to a molecular motion is expressed as [14]

$$T_1^{-1} = \frac{3}{2} \gamma^4 h^2 I(I+1) \sum_k \left\{ J_{ik}^{(1)}(\omega_0) + J_{ik}^{(2)}(2\omega_0) \right\},$$

where  $\gamma$  is the gyromagnetic ratio,  $\omega_0$  is the Larmor frequency, and the spectral density of the motion  $J_{ik}^{(q)}$  is given by

$$J_{ik}^{(q)}(\omega) = \int_{-\infty}^{\infty} F_{ik}^{(q)}(t) F_{ik}^{(q)}(t + \tau) \exp(-i\omega\tau) d\tau,$$

where  $F_{ik}^{(q)}$  is the geometry factor depending on the relative positions of the two spins,  $i$  and  $k$ . For order-disorder phase transition this factor can be related to Ising type local variables  $p(t)$ , taking the values +1 and -1, according the orientation, 1 and 2, of a flipping dipole [15]. Then

$$F_{ik}^{(q)}(t) = \frac{1}{2}(1 + p(t))F_{ik1}^{(q)} + \frac{1}{2}(1 - p(t))F_{ik2}^{(q)}.$$

By using the mean field approximation and following the procedure in refs. 15 and 16, the relaxation time  $T_{1c}$  controlled by the critical fluctuation is expressed as

$$T_{1c} \propto |T - T_c|^{1/2},$$

in the close vicinity of the phase transition temperature  $T_c$ . Figure 5. 4 shows the plot of the  $T_{1c}$  against  $|T - T_c|$  in MABCD together with the straight line with slope 1/2, where the  $T_c$  of 306.5 K was regarded to the singular temperature of the  $T_1$  curve. This plot shows that the observed anomaly in  $T_1$  curve can be explained as the critical phenomenon at the phase transition.

#### 5.4 Conclusion

The  $^1\text{H}$  NMR  $T_1$  anomaly due to the critical slowing down associated with the paraelectric-ferroelectric phase transition was newly observed in MABC and MABCD crystals. The  $T_1$  anomaly could be explained by the classical mean field theory. The  $^2\text{H}$  NMR spectra showed that the methylammonium cations undergo the fast uniaxial reorientation and precessional motion, however it cannot be determined whether it is continuous motion or discrete jump around the precession axis. The line-shape change occurs in a wide temperature range of 130 to 305 K, which corresponds to that of the thermal anomaly attributed to the disordering of the cations reported in ref. 12. The observed cationic precessional motion is expected to be closely related to the disordering of the cations. The presence of several kinds of methylammonium cations having different rates of the precessional motion was shown in the low-temperature phase. This motion became frequent with increasing temperature and the cations became indistinguishable near the transition temperature, whereas two of the five different kinds of cations are expected to be still ordered as reported in the previous X-ray study [5].

On the other hand no evidence of the phase transition at 170 K could be crystallographically quite similar to each other and this may be the reason why the detection of the transition is difficult.



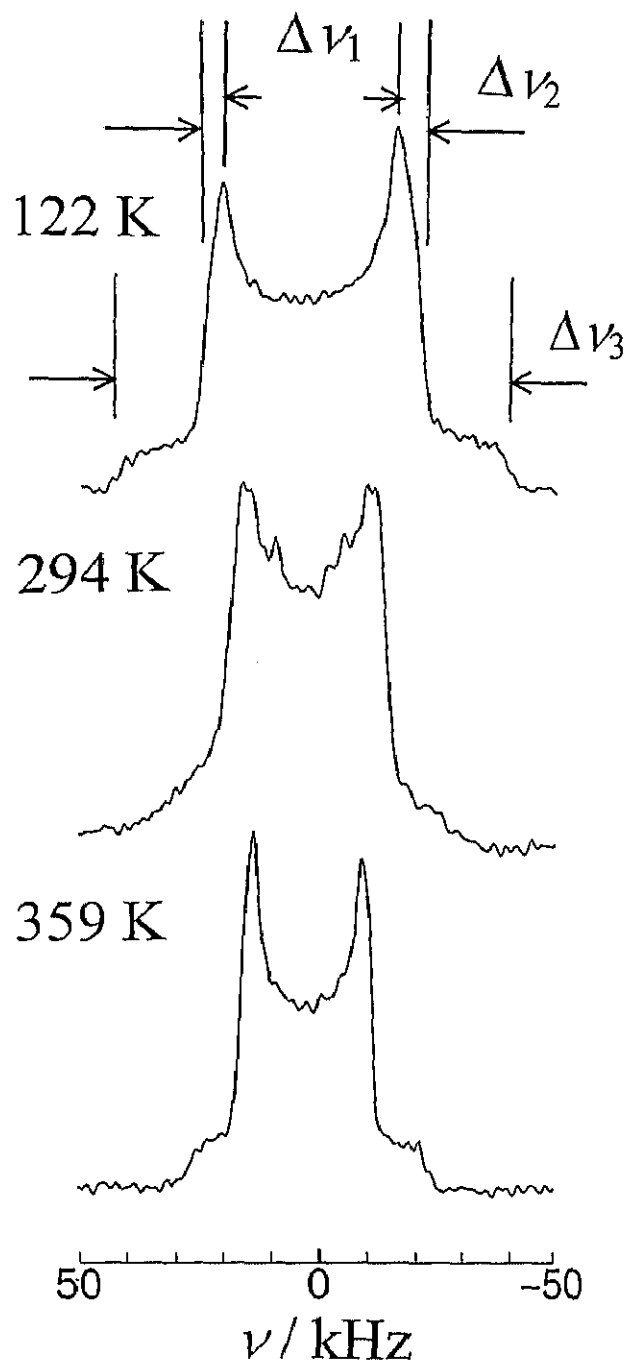


Fig. 5.1 Typical  $^2\text{H}$  NMR spectra of  $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$  above and below the phase transition temperature of 305.5 K.

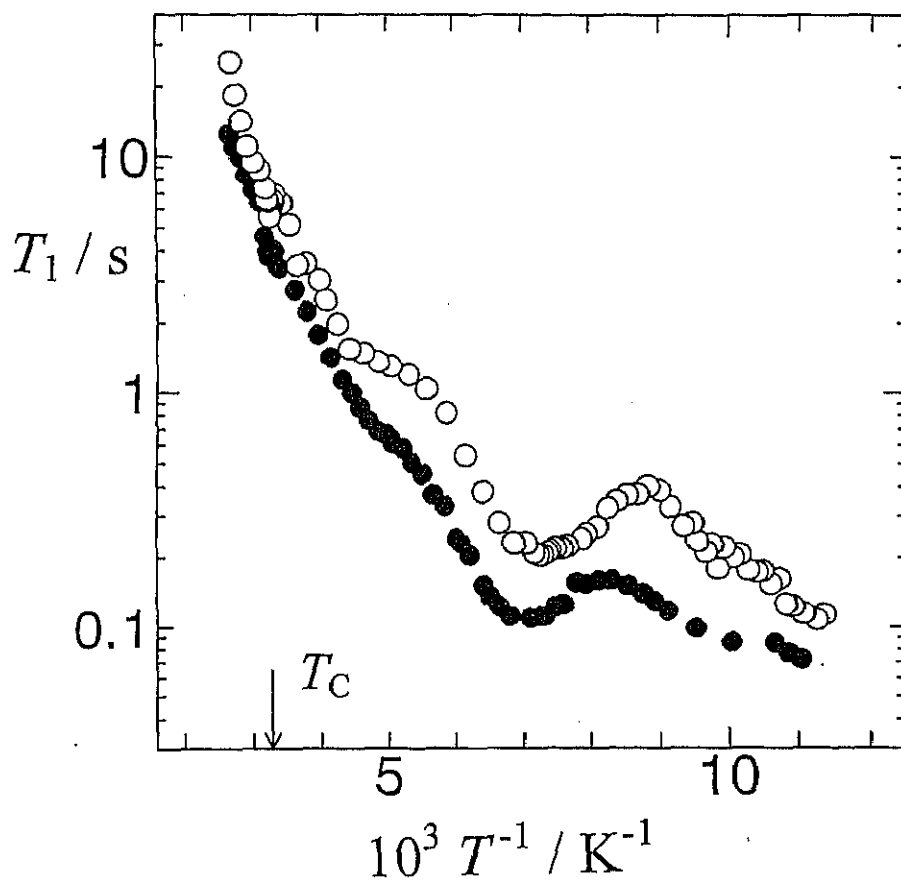


Fig. 5. 2 Temperature dependence of  $^1\text{H}$  NMR  $T_1$  of  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$  (closed circle) and  $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$  (open circle). The phase transition temperature  $T_c$  determined by DSC of 305.5 K of  $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$  is shown by arrow.

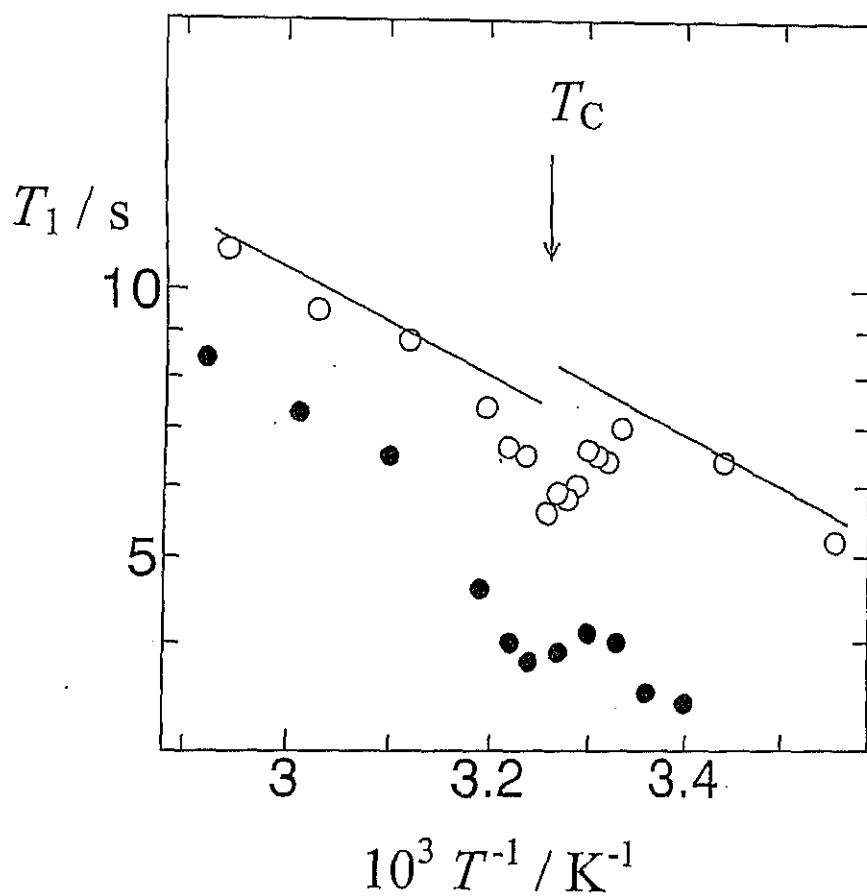


Fig. 5. 3 Temperature dependence of the  $^1\text{H}$  NMR  $T_1$  of  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$  (closed circle) and  $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$  (open circle) in the close proximity of the transition temperature. The solid lines indicate the contribution from the normal molecular motion attributed to the uniaxial reorientation of methylammonium cations. The shown  $T_c$  of 306.5 K indicates the singular point of the  $T_1$  curve of  $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$ .

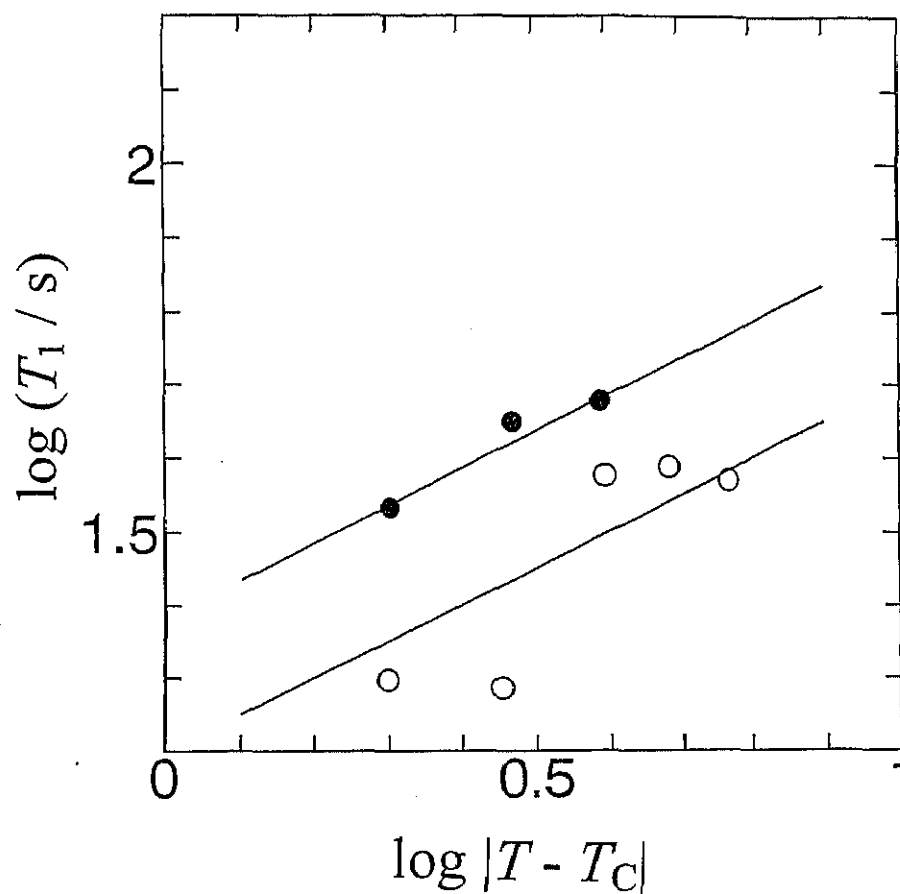


Fig. 5. 4 The logarithm of the relaxation time  $T_1$  attributed to the critical fluctuation around  $T_c$  plotted against  $\log |T - T_c|$  above (closed circle) and below (open circle) the transition temperature. Straight lines with slope 1/2 are the theoretical values.

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