Motions of Methylammonium Ions in $(CH_3NH_3)_2ZnBr_4$ Crystals Studied by ^1H NMR and Thermal Measurements

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Measurements of the ^1H spin-lattice relaxation time T_1, the linewidth parameter T_2^*, the second moment of ^1H NMR absorption, differential thermal analysis, and differential scanning calorimetry were performed on methylammonium tetrabromozincate(II) crystals from 58 to above 500 K. A solid-solid phase transition was located at 456 K. In the room temperature phase, 120° reorientational jumps of CH_3 and NH_3^+ groups in the cation about its C–N bond axis were detected. In the high-temperature phase, the cations undergo overall reorientation as well as translational self-diffusion. The activation energy for the cationic self-diffusion was evaluated to be 18 kJ mol^{-1}.

1. Introduction

In [1] we have studied the dynamics of cations in $(CH_3NH_3)_2ZnCl_4$ crystals by means of ^1H NMR and revealed the presence of two solid phases in the temperature range between 55 K and the melting temperature (552 K). In the high-temperature phase (HTP), stable above 477 K, it was found that the cations undergo overall reorientation as well as translational self-diffusion. This phase, containing highly movable cations, is analogous to the "ionic plastic phases" of methylammonium nitrate [2], iodide [3], perchlorate [4], and bromide [5]. From temperature dependence studies of ^1H spin-lattice relaxation times (T_1), in the room-temperature phase (RTP) two kinds of crystallographically nonequivalent cations [6, 7] were shown to be in characteristic motional states.

$(CH_3NH_3)_2ZnBr_4$ forms monoclinic crystals at room temperature belonging to the space group $P2_1/c$ with $a=13.19$, $b=8.14$, $c=11.65$ Å, $\beta=97.30°$ and $Z=4$ as determined by X-ray diffraction [8]. Although detailed crystal data for this complex are not available, the structure of $(CH_3NH_3)_2ZnBr_4$ at room temperature is expected to be isomorphous with that of $(CH_3NH_3)_2ZnCl_4$ in the RTP.

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In the present investigation, we have found a new solid phase corresponding to the HTP of $(CH_3NH_3)_2ZnCl_4$ using differential thermal analysis (DTA) and differential scanning calorimetry (DSC). To clarify the motions of methylammonium cations in the HTP and RTP of $(CH_3NH_3)_2ZnBr_4$, we have carried out measurements of the second moment (M_2) of ^1H NMR absorption, ^1H T_1, and the linewidth parameter (T_2^*) of ^1H NMR.

2. Experimental

$(CH_3NH_3)_2ZnBr_4$ was prepared by mixing CH_3NH_3Br and $ZnBr_2$, both dissolved in a 2 mol dm^{-3} hydrobromic acid. The crystals obtained were recrystallized from a methanol, hydrobromic acid (10:1) solvent. The purified crystals were identified by X-ray powder patterns and the usual elementary analysis. All diffraction lines could be explained by the reported crystal-structure data in RTP [8]. Anal. Calcd. for $(CH_3NH_3)_2ZnBr_4$: C, 5.35%; H, 2.69%; N, 6.24%; Zn, 14.56%. Found: C, 5.31%; H, 2.52%; N, 6.27%; Zn, 14.4%.

The crystals were dried in a vacuum desiccator over P_2O_5 and KOH, pulverized, put in glass ampoules for the NMR and DTA measurements in a dry bag, and

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dried under vacuum (ca. 10^{-3} Torr) at room temperature for 12 h and additionally at 60°C for 12 h. Finally, the ampoules were sealed after putting in a small amount of dry nitrogen gas.

DTA curves were recorded with an apparatus similar to that reported previously [9]. DSC was carried out with a Du Pont 9900 Thermal Analyzer. The wide-line ^{1}H NMR measurement was performed at 40 MHz by means of a JNM-MW-40S spectrometer from JEOL Co. Pulsed NMR spectrometers [1, 10] were used for the measurements of ^{1}H T_1 at the Larmor frequencies of 8.5, 18, 20 and 32 MHz and T_2* at 18 MHz. A $180°-\tau-90°$ pulse sequence was employed for the determination of T_1 while T_2* was determined from the shape of the free induction decay after a 90° pulse.

3. Results and Discussion

Thermal Analysis and ^{1}H NMR Second Moments

DTA curves were recorded between 80–570 K. On heating the sample with a rate of ca. 2 K min^{-1}, a large endothermic heat anomaly, attributed to a solid-solid phase transition, appeared at 456 K. The entropy change ΔS_{tr} determined by DSC measurements was 19 JK^{-1} mol^{-1}. With further increase of the temperature, melting of the sample started at ca. 559 K together with decomposition heralded by a color change to brown. The obtained ΔS_{tr} value is almost the same as that of ΔS_{tr} (20 JK^{-1} mol^{-1}) determined for the transition from the RTP to the HTP in $(CH_3NH_3)_2ZnCl_4$ [1]. Since the structures of the RTP's of these complexes are very similar [8], one can expect the excitation of almost the same ionic motions in the HTP's of these complexes.

The temperature dependence of M_2 between 77 and 500 K is shown in Figure 1. An almost constant M_2 of (9.0 ± 0.5) G^2 was obtained below ca. 150 K. The agreement of this value with theoretical ones calculated for methylammonium halides [3, 11–13], indicates that the CH_3 and NH_3^+ groups in the cation reorient by 120° about their C–N bond axis (abbreviated C_3 reorientation) more frequently than with 10^5 Hz even around 77 K. Above ca. 150 K, M_2 decreased gradually to (5 ± 1) G^2 around 450 K, indicating the onset of a new cationic motion. With further heating, M_2 changed discontinuously to 0.5 G^2 above the phase transition temperature (T_{tr}) of 456 K. This small M_2 indicates that a rapid overall reorientation of the cation about its center of gravity occurs in this phase. With further increase of the temperature in the HTP, M_2 gradually decreased and became smaller than 0.2 G^2 at 500 K, implying the onset of cationic self-diffusion.

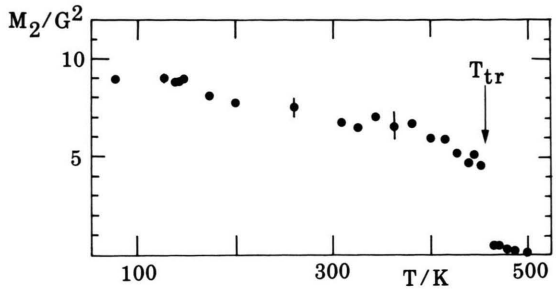

Fig. 1. ^{1}H NMR second moments (M_2) observed for $(CH_3NH_3)_2ZnBr_4$ at various temperatures. Error bars are shown for some data points. T_{tr} indicated by an arrow is the phase transition temperature determined by DTA.

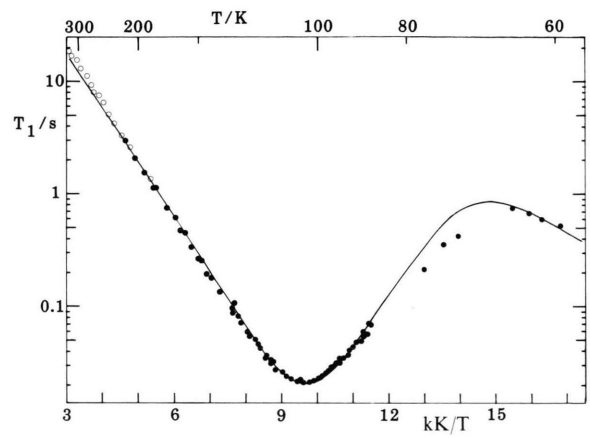

Fig. 2. Temperature dependence of ^{1}H T_1 observed at 20 (●) and 32 (○) MHz for $(CH_3NH_3)_2ZnBr_4$. The solid line indicates the sum of two independent BPP type T_1 curves attributable to two kinds of crystallographically nonequivalent cations.

^{1}H T_1 in the Room-Temperature Phase

The temperature dependence of ^{1}H T_1 between 58 and 330 K is shown in Figure 2. The log T_1 vs. T^{-1} plots for 20 MHz yielded a T_1 minimum of 21 ms at 105 K and a maximum around 68 K. The temperature variation of ^{1}H T_1 is similar to that in $(CH_3NH_3)_2ZnCl_4$ below room temperature, indicating the onset of the same kinds of cationic motions in

both complexes. From the foregoing discussion on M_2, the temperature dependence of ^1H T_1 in the RTP below 300 K can be explained in terms of the C_3 reorientation. It has been reported that there exist two kinds of crystallographically nonequivalent cations in the RTP of $(CH_3NH_3)_2ZnCl_4$, where the cations of one kind form N−H ... Cl type H-bonds with an H ... Cl distance much shorter than that formed by the other kind [6, 7]. Since the RTP's of $(CH_3NH_3)_2ZnCl_4$ and $(CH_3NH_3)_2ZnBr_4$ are expected to be isomorphous, it is thought that there are two kinds of cations in the RTP of $(CH_3NH_3)_2ZnBr_4$. Hereafter, we denote these cations as cation I and II and let the cation I be more tightly bound in the crystal than the cation II. The deep T_1 minimum at 105 K is assignable to the reorientation of the CH_3 and NH_3^+ groups in the cation I because the observed T_1 minimum of 21 ms is the same as that assigned to the same motion in $(CH_3NH_3)_2ZnCl_4$. Thus the ^1H T_1 decrease with decreasing temperature below 68 K is considered as arising from the same motion as described above for the cation II. This motion is regarded as "correlated reorientation" of II, which has been defined as the C_3 reorientation of the cation as a whole with keeping its rigid structure [14]. This is because the activation energy for the motion evaluated from the slope of the log T_1 vs. T^{-1} curve was ca. 4 kJ mol^{-1}, being much smaller than ca. 8 kJ mol^{-1} estimated for the barrier to the intracationic or internal rotation [4, 14, 15].

Here, we assume the correlation times for the motion of the CH_3 and NH_3^+ groups in I are the same for the simplicity. Then the ^1H T_1 data can be analyzed by the equation [16, 17]

$$\begin{aligned} T_1^{-1} = {} & (2/3)\,\gamma^2\,\Delta M_{2\mathrm{I}}\,[\tau_\mathrm{I}/(1+\omega_\mathrm{H}^2\,\tau_\mathrm{I}^2) \\ & +4\,\tau_\mathrm{I}/(1+4\,\omega_\mathrm{H}^2\,\tau_\mathrm{I}^2)] \\ & +(2/3)\,\gamma^2\,\Delta M_{2\mathrm{II}}\,[\tau_\mathrm{II}/(1+\omega_\mathrm{H}^2\,\tau_\mathrm{II}^2) \\ & +4\,\tau_\mathrm{II}/(1+4\,\omega_\mathrm{H}^2\,\tau_\mathrm{II}^2)], \end{aligned} \tag{1}$$

where γ, ω_H, ΔM_{2i}, and $\tau_i\,(i=\mathrm{I}, \mathrm{II})$ denote the gyromagnetic ratio of a proton, the ^1H angular Larmor frequency, the M_2 reduction due to the onset of the reorientation of the cation i, and the correlation time of the motion of the cation i, respectively. Since τ_II is considered to be much shorter than τ_I, in the temperature range studied it can be assumed that

$$\omega_\mathrm{H}\,\tau_\mathrm{II} \ll 1. \tag{2}$$

Table 1. Motional parameters of $CH_3NH_3^+$ ions: activation energies E_a, correlation times τ_0 at infinite temperature, and reductions of the ^1H NMR second moment ΔM_2 in methylammonium tetrabromozincate(II).

E_a/kJ mol^{-1}	$\tau_0 \times 10^{14}$/s	ΔM_2/G^2	Motion
Room-temperature phase			
9.5±0.2	7.9±0.7	9.0±0.2	CH_3 and NH_3^+ reorientation
3.5±0.5			CH_3 and NH_3^+ reorientation
High-temperature phase			
18±4			Cationic self-diffusion

Using this relation, (1) can be rewritten as

$$\begin{aligned} T_1^{-1} = {} & (2/3)\,\gamma^2\,\Delta M_{2\mathrm{I}}\,[\tau_\mathrm{I}/(1+\omega_\mathrm{H}^2\,\tau_\mathrm{I}^2) \\ & +4\,\tau_\mathrm{I}/(1+4\,\omega_\mathrm{H}^2\,\tau_\mathrm{I}^2)] + (10/3)\,\gamma^2\,\Delta M_{2\mathrm{II}}\,\tau_\mathrm{II}. \end{aligned} \tag{3}$$

We assume an Arrhenius relationship between τ_i and the activation energy $E_{ai}\,(i=\mathrm{I}, \mathrm{II})$ for the motion under consideration:

$$\tau_i = \tau_{0i} \exp\,(E_{ai}/RT). \tag{4}$$

The ^1H T_1 data observed were fitted to (3) and (4) using the least-squares method. The obtained motional parameters, E_{ai}, τ_{0i}, and ΔM_{2i} are listed in Table 1, and the best fitted T_1 curve using these parameters is given by a solid line in Figure 2. The activation energies of 9.5 and 3.2 kJ mol^{-1} for the cation I and II, respectively, evaluated from this fitting are somewhat smaller than the corresponding values of 10.7 and 3.8 kJ mol^{-1} obtained for $(CH_3NH_3)_2ZnCl_4$, indicating that the cations are more loosely bound in $(CH_3NH_3)_2ZnBr_4$ than in $(CH_3NH_3)_2ZnCl_4$. These small values indicate that the H-bonds of N−H ... Br type in the present complex are fairly weak. In particular, the cation II is expected to be quite free to move in crystals permitting the correlated reorientation.

The temperature dependence of ^1H T_1 determined at 8.8, 18 and 32 MHz, and of ^1H T_2^* at 18 MHz is shown in Figure 3. In the high temperature region of the RTP, a frequency dependent T_1 decrease with increasing temperature was observed. Taking into account the M_2 decrease observed in the same temperature range, this T_1 decrease is attributable to a cationic motion other than the C_3 reorientation. However, the frequency dependent T_1 change could not be explained in terms of superimposed two BPP type relaxation mechanisms in which one arises from the new

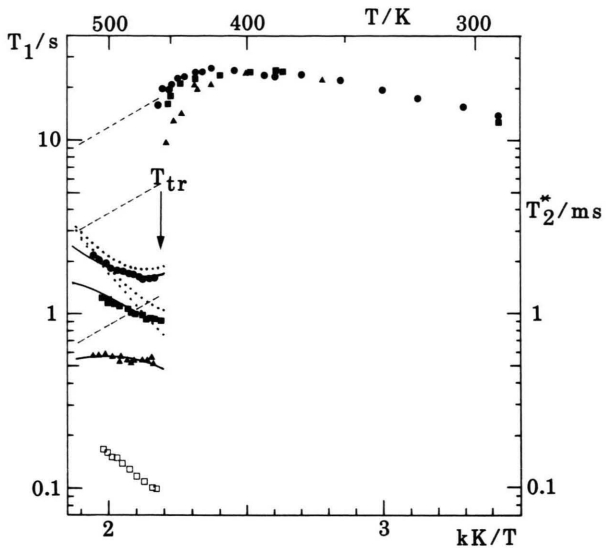

Fig. 3. Temperature dependences of ^{1}H T_1 at 8.5 (▲), 18 (■), and 32 (●) MHz, and of ^{1}H T_2^* at 18 (□) MHz. The separated two T_1 components $T_1(a)$ and $T_1(b)$ given in the text are shown by broken and dotted lines, respectively. Solid lines indicate best fitted theoretical curves.

cationic motion while the other is due to the C_3 reorientation of the cation giving the frequency independent T_1. We have to consider the presence of some other relaxation mechanisms in the high temperature range. Possible mechanisms are the spin-rotation interaction originating from the uniaxial rotation of the cation and the magnetic dipolar interaction between the ^{1}H and bromine (^{79}Br, ^{81}Br) nuclei.

^{1}H T_1 in the High-Temperature Phase

At the transition point from RTP to HTP determined by DTA, ^{1}H T_1 decreased suddenly by one order of magnitude, and ^{1}H T_2^* increased from ca. 20 to 100 μs. In the HTP, both T_1 and T_2^* increased with temperature. The ^{1}H T_2^* increase is attributable to the onset of cationic self-diffusion corresponding to the M_2 decrease with increasing temperature in this phase.

From the experimental results of M_2 and T_2^*, the fluctuation of the magnetic dipolar interaction between protons made by the cationic self-diffusion is considered as a dominant relaxation mechanism. In fact, the T_1 behavior in the corresponding phase of $(CH_3NH_3)_2ZnCl_4$ could be explained by this mechanism [1]. However, the present ^{1}H T_1 data are unexplainable by only this relaxation mechanism, being strikingly different from those of $(CH_3NH_3)_2ZnCl_4$, where long T_1 values of ca. 10 s decreasing with increasing temperature were observed at 32 MHz. Therefore, some other mechanisms being less effective in $(CH_3NH_3)_2ZnCl_4$ should be operative in the present complex.

We assume that the observed T_1 can be written as

$$T_1^{-1} = T_1(a)^{-1} + T_1(b)^{-1}, \tag{5}$$

where $T_1(a)$ and $T_1(b)$ are the relaxation times due to the cationic self-diffusion and another spin-lattice relaxation mechanism, respectively.

Since the observed T_2^* values were shorter than 1 ms, the condition of $\omega_H \tau_H \gg 1$ is reasonably assumed over the whole temperature range in this phase, where τ_H is the diffusion correlation time of the cation. Then $T_1(a)$ can be written as [16, 18]

$$T_1(a)^{-1} = C(a)/\omega_H^2 \tau_H, \tag{6}$$

where $C(a)$ is the motional parameter dependent on the self-diffusion mechanism and the crystal structure.

Comparing (5) and (6) with the T_1 data, it is found that $T_1(b)$ should depend on the ω_H employed. For the frequency dependence of $T_1(b)$ we assume the following BPP type equation

$$T_1(b)^{-1} = C(b)\,\tau_b/(1+\omega_H^2 \tau_b^2). \tag{7}$$

Here, τ_b is the correlation time associated with the relaxation process in question and $C(b)$ is an adjustable motional parameter.

Assuming an Arrhenius relationship for the two correlation times τ_H and τ_b, the ^{1}H data were fitted to (5)–(7) by the least-squares method. The best fitted T_1 curves using the values of the adjustable parameters given in Table 1 are shown in Fig. 3 by solid lines. The agreement of the T_1 data with the calculated curves indicates that (7) is an adequate approximation for the dependence of $T_1(b)$ on ω_H. The E_a value of 18 kJ mol^{-1} obtained for the self-diffusion of the $CH_3NH_3^+$ cation according to (5)–(7) is smaller than that of 26 kJ mol^{-1} for the same motion in the HTP of $(CH_3NH_3)_2ZnCl_4$. This implies that larger $[ZnBr_4]^{2-}$ anions enable the cations to translate through the crystal lattice more easily. The activation energy for τ_b, 38 kJ mol^{-1}, is larger than that for cationic diffusion. This, and the fact that the calculated τ_b is much shorter than τ_H, indicates that the correlation time τ_b is not assignable to any cationic motion but to an anionic motion. It is highly possible that the reorientational motion of the $[ZnBr_4]^{2-}$ anions becomes an

effective relaxation mechanism on ^1H T_1 through the modulation of the magnetic dipolar interaction between proton and bromine nuclei. This is because this anionic motion is expected to occur quite frequently at high temperatures, resulting in shorter relaxation times of bromine nuclei than T_1 (*a*) through the averaging of the electric quadrupole interactions. The existence of this mechanism has been reported for several complex compounds [19–22].

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