\textbf{Introduction}

Recently, we have studied the molecular dynamics of butylammonium cations (ba\textsuperscript{+}) in the three crystalline phases of \textit{n-C\textsubscript{4}H\textsubscript{9}NH\textsubscript{3}I} and its N-deuterated analog were studied in a wide range of temperatures between 77 K and 360 K. DTA experiments revealed a solid-solid phase transition between room and low temperature phases taking place at 268 K for the former salt and at 267 K for the latter. For rapidly cooled (\(\lesssim 2 \text{~K~min}^{-1}\)) samples, another phase transition possibly between substable low temperature phases was found at ca. 210 K for the former and ca. 205 K for the latter. The phase transition entropy observed at 268 K was 33 J K\textsuperscript{-1} mol\textsuperscript{-1}. This is much larger than the melting entropy (10 J K\textsuperscript{-1} mol\textsuperscript{-1}), suggesting that butylammonium ions obtain their motional freedom mostly at the phase transition. In the low temperature phase of \textit{n-C\textsubscript{4}H\textsubscript{9}NH\textsubscript{3}I}, the CH\textsubscript{3} groups perform \(180^\circ\) reorientation about their respective symmetry axes with the activation energy \(10.4\) and \(26.8\) kJ mol\textsuperscript{-1}, respectively. The rapidly cooled sample showed two \(T_1\) components attributable to the stable and substable low temperature phases indicating the coexistence of both phases. In the room temperature phase, the cations rotate rapidly about their long axes and partly conformational disorder of the alkyl chains takes place. The mechanism of the phase transitions is discussed.

\textbf{Experimental}

The salt bal has been synthesized by neutralizing an ethanol solution of butylamine with hydroiodic acid. The crystals obtained by evaporation were purified by recrystallizing them twice from absolute ethanol. Colorless thin plate crystals were obtained. A partially deuterated salt, \textit{n-C\textsubscript{4}H\textsubscript{9}ND\textsubscript{3}I} (bal-d\textsubscript{3}) was prepared by dissolving bal in heavy water and then evaporating the solvent. The above manipulation was done repeatedly in an airtight glass apparatus. Finally, the crystals obtained were purified by recrystallization from deuterated ethanol (C\textsubscript{3}H\textsubscript{5}OD). Because bal dissolved in water or ethanol is easily decomposed by making contact with air and also it is highly hygroscopic in the crystalline state, the preparative manipulation was performed, at all times, in an atmosphere of dry nitrogen.
The second moment $M_2$ of $^1$H NMR absorption at a resonance frequency of 40 MHz was determined at various temperatures between 77 and 420 K by means of a JEOL JNM-MW-40 S wide-line spectrometer. The measurements of the $^1$H spin-lattice relaxation time $T_1$ were carried out in the temperature range 100–300 K with a frequency-fixed (20 MHz) pulsed spectrometer [3] and a frequency-variable one [4]. A conventional $180^\circ - \tau - 90^\circ$ pulse sequence was used for the determination of $T_1$.

A homemade DTA apparatus [5] was employed for the observation of phase transitions. A Perkin-Elmer DSC-1B differential scanning calorimeter was used to determine enthalpy changes at the solid-solid phase transition and melting temperatures (hereafter denoted by $T_{tr}$ and $T_m$, respectively). The temperature of the sample was scanned at a rate of 5 K min$^{-1}$. The enthalpy changes of transition recorded at $T_{tr}$ and $T_m$ were calibrated by those of adamantane observed at 208.6 K [6] and of metallic indium, respectively.

Temperatures in the above physical measurements were mostly determined by use of a copper-constantan thermocouple and were estimated to be accurate within ± 1 K unless otherwise indicated.

**Results**

DTA curves recorded in a temperature range 77–460 K are shown in Figure 1.

When $\beta$C$_4$H$_9$NH$_3$I was cooled from room temperature with a slower cooling rate than 0.7 K min$^{-1}$, an exothermic anomaly was observed at 260 K. With increasing temperature, the sample which had been cooled down to 80 K with the slow cooling rate showed an endothermic peak at 269 K, indicating the occurrence of a first-order phase transition between room and low temperature phases.

When the sample was cooled rapidly (< 2 K min$^{-1}$), on the other hand, a new exothermic anomaly appeared additionally at 209 K. This anomaly was much smaller than that at 268 K. With increasing temperature, the sample which had been rapidly cooled down to 77 K yielded a heat anomaly around 210 K. This anomaly had an unusual shape as can be seen in Fig. 1 and in view of its shape one can conclude that three successive phase transitions occur around this temperature showing two endothermic peaks and an exothermic one. When the sample rapidly cooled to 245 ± 5 K was kept (annealed) at this temperature for ca. 1 h, this unusual anomaly disappeared completely, even though the sample temperature was scanned more rapidly than 2 K min$^{-1}$. Hereafter, we call the rapid temperature change employed above as “rapid-cooling”. Conversely, we use “slow cooling” for such cases where the temperature is changed with a rate slower than 0.7 K min$^{-1}$ or the temperature is changed at any rate after it was annealed for ca. 1 h at ca. 245 K.

The DTA curves of $\beta$C$_4$H$_9$NH$_3$I-d were very similar to those of $\beta$C$_4$H$_9$NH$_3$I. The slow and rapid cooling methods, respectively, gave a single exothermic peak at 259 K and two exothermic peaks at 259 and 205 K. With increasing temperature, the sample treated by the slow cooling showed an endothermic peak at 269 K while the sample treated by the rapid cooling showed an additional heat anomaly having a structure like that of $\beta$C$_4$H$_9$NH$_3$I around 205 K. It is interesting to note the low temperature anomaly (ca. 205 K)
Table 1. Changes in enthalpy $\Delta H$ and entropy $\Delta S$ at the solid-solid phase transition and melting temperatures of butylammonium iodide. The data for butylammonium bromide are also included for comparison. Data in parentheses are for the partially deuterated analogs ($n$-$C_4H_9ND_3X$).

<table>
<thead>
<tr>
<th>Salt</th>
<th>Transition</th>
<th>$T/K$</th>
<th>$\Delta H/kJ$ mol$^{-1}$</th>
<th>$\Delta S/$ K mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-$C_4H_9NH_3I$</td>
<td>solid to 210 (~ 205)</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>solid</td>
<td>268 (269)</td>
<td>8.8</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>melting</td>
<td>442 (448)</td>
<td>7.2</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>$n$-$C_4H_9NH_3Br$</td>
<td>solid to 200 (198)</td>
<td>1.5</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>solid</td>
<td>249 (249)</td>
<td>5.7</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>melting</td>
<td>478</td>
<td>8.3</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

always yielded the additional anomaly although we tried many runs using several kinds of cooling and annealing processes.

When bal and bal-d$_3$ were heated above room temperature, no heat anomaly was observed up to 442 and 448 K, respectively, where the samples melted with partial decomposition taking place. This was confirmed from the fact that by repeating the processes of melting and solidifying, $T_m$ gradually decreased and the sample changed its color to yellow or somewhat brown.

From the measurements of DSC, the enthalpy changes observed for the phase transition at 268 K and the melting are given in Table 1. The enthalpy change for the phase transition around 210 K could not be determined, the heat anomaly being too small.

The temperature variation of $^1H$ $M_2$ for bal was observed with increasing the temperature after the sample was cooled to 77 K by the slow cooling. The results are shown in Figure 2.

When bal was warmed from 77 K to ca. 270 K, $M_2$ decreased almost continuously from 27 to 11 G$^2$, however nearly constant values of 22 and 11.5 G$^2$ were obtained in two narrow temperature regions around 150 and 250 K, respectively. At ca. 270 K, a discontinuous decrease in $M_2$ was observed in agreement with the presence of the phase transition revealed by DTA. With increasing the temperature furthermore, $M_2$ decreased gradually and reached 2 G$^2$ at 420 K.

Figure 3 shows the temperature dependences of $^1H$ $T_1$ at 20 MHz observed for bal. Dots indicate $T_1$ values measured with increasing temperature after
Fig. 4. Time dependence of $^1$H magnetization recovery at 248 K. Measurements were made immediately (a), 2 h (b), and 8 h (c) after setting the temperature.

The slowly cooled sample yielded, on the warming run, two deep $T_1$ minima of 51 and 37 ms at 127 and 260 K, respectively, in the low temperature phase. With increasing the temperature $T_1$ increased discontinuously by two orders of magnitude at 268 K which agreed well with $T_m$ determined by DTA, and increased again monotonously above this temperature.

When bal was slowly cooled from room temperature, nonexponential $^1$H magnetization recovery curves were observed between 240 and 260 K. At a given temperature in this range, the shape of free induction decay (FID) signals was observed to change gradually over a period of several ten minutes, indicating that the room temperature phase is transformed gradually into the low temperature phase.

To examine the transformation rate of the room temperature phase more in detail, $^1$H magnetization recovery was measured at 248 K every 1 h by the $180^\circ - \tau - 90^\circ$ pulse sequence. Each measurement was completed within 15 min to avoid complexity arising from a considerable change of the FID signals during our measuring time. The results obtained just after setting the temperature and after 2 and 8 h from that are shown in Figure 4. Two $T_1$ components, 43 ± 3 and 190 ± 20 ms could be directly obtained by dividing the recovery curves into two parts. The intensity ratios of the divided FID signals giving rise to the long $T_1$ component and the short one were 1:1 immediately after fixing the temperature, 1:4 after 2 h, and almost zero after 8 h.

The sample bal treated by rapid cooling yielded nonexponential $^1$H magnetization recovery curves at various temperatures between 145 and 260 K. Therefore, the $T_1$ values were determined in this temperature range by assuming the presence of two magnetization components having different $T_1$ values. The roughly estimated ratio of the intensities of these two components was 1:1. Below ca. 130 K, the magnetization showed normal exponential decay curves giving a unique $T_1$. In the narrow temperature range 130–145 K, the magnetization recovery curves were apparently not due to a single relaxation mechanism. However, it was difficult in the present experiment to determine two $T_1$ values separately from the recovery curve, because the two magnetization components were too close to each other.

The $T_1$ values of bal-d$_3$ determined on both slow and rapid cooling are shown in Figure 5.

When bal-d$_3$ had been rapidly cooled and then was warmed, nonexponential $^1$H magnetization recovery curves yielding two different $T_1$ values were
Table 2. Calculated values of $^1\text{H}$ NMR second moment $M_2$ for various motional states of butylammonium cations in $n$-C$_4$H$_9$NH$_3$I.

<table>
<thead>
<tr>
<th>Contribution</th>
<th>rigid lattice</th>
<th>CH$_3$ rot.</th>
<th>(CH$_3$+NH$_3^+$) rot.</th>
<th>(CH$_3$+NH$_3^+$) rot. + Chain 180° flip</th>
<th>(CH$_3$+NH$_3^+$) rot. + Chain) rot.</th>
</tr>
</thead>
<tbody>
<tr>
<td>intra-ionic</td>
<td>21.9</td>
<td>17.3</td>
<td>11.1</td>
<td>7.94</td>
<td>2.78</td>
</tr>
<tr>
<td>inter-ionic</td>
<td>~ 4.4</td>
<td>~ 3.5</td>
<td>~ 2.8</td>
<td>~ 1.7</td>
<td>~ 1.3</td>
</tr>
<tr>
<td>total</td>
<td>26.3</td>
<td>20.8</td>
<td>13.9</td>
<td>9.6</td>
<td>4.1</td>
</tr>
</tbody>
</table>

observed between 140 and 260 K in the low temperature phase just as in bal. This indicates that some substable phase, probably the same as that of bal is mixed with the low temperature stable phase of bal-d$_3$. Below 136 K and above $T_u$, the sample treated by rapid cooling gave the normal exponential recovery curves. A $T_1$ minimum of 39 ms was located at 130 K, although the short $T_1$ component showed another $T_1$ minimum of 60 ms at ca. 180 K.

When bal-d$_3$ was slowly cooled and warmed, somewhat nonexponential $^1\text{H}$ magnetization recovery curves indicating the existence of two $T_1$ components were observed at all temperatures studied in the low temperature phase. This was always true although the sample was treated by several kinds of annealing processes. These $T_1$ results are consistent with those of the above DTA experiment: it was not easy to cause the anomaly around 205 K to disappear by annealing whereas the correspondingly anomaly of bal always disappeared by annealing. The foregoing observations of $T_1$ and DTA suggest that another solid phase of slowly cooled bal-d$_3$, possibly the same substable phase obtained for rapidly cooled bal-d$_3$ is always mixed with the low temperature phase. This behavior of the substable phase of bal-d$_3$ forms a contrast with that of bal. Slowly cooled bal-d$_3$ yielded a $T_1$ minimum of 38 ms at 130 K. With increasing temperature, $T_1$ increased monotonously up to ca. 210 K, above which $T_1$ decreased. At $T_u$, $T_1$ increased discontinuously and in the high temperature phase $T_1$ again gradually increased with temperature.

Discussion

The theoretical values of $^1\text{H}$ $M_2$ for five motional states of the ba$^+$ cations in bal can be calculated by use of Van Vleck’s formula [7] and are given in Table 2. In the calculation of $M_2$, the intraionic contributions were assumed to be the same as those calculated for a few motional states of the cation in our previous study of baBr [1]. At room temperature, bal forms tetragonal crystals belonging to the space group P4/nmm with $a = 5.18$ Å, $c = 15.30$ Å and $Z = 2$ [2]. Since no data are available for the structure of the low temperature phase, the intercotic contribution to $M_2$ was estimated by assuming the same crystal structure as that of the room temperature phase.

According to the BPP theory, $^1\text{H}$ $T_1$ due to homonuclear magnetic dipolar interaction can be written as

$$T_1^{-1} = C \left[ \frac{\tau}{(1 + \omega^2 \tau^2)} + 4 \tau/(1 + 4\omega^2 \tau^2) \right].$$

(1)

Here, $C$, $\tau$, and $\omega$ denote the motional constant, the correlation time of a motion responsible for the relaxation in question, and the angular resonance frequency, respectively. Assuming an Arrhenius relationship between $\tau$ and the activation energy $E_a$ of the motional process, one has

$$\tau = \tau_0 \exp \left( \frac{E_a}{RT} \right).$$

(2)

When two kinds of motions contribute to $T_1$ without any correlations between them, the resulting relaxation rate $T_1(r)^{-1}$ can be written approximately by the sum of two relaxation rates $T_1(a)^{-1}$ and $T_1(b)^{-1}$:

$$T_1(r)^{-1} = T_1(a)^{-1} + T_1(b)^{-1}.$$  

(3)

The Low Temperature Phase

The $M_2$ value observed at 77 K was 27 G$^2$ in good agreement with that calculated for bal by assuming a rigid lattice. This indicates that all molecular motions of the cation given in Table 2 are frozen below 77 K.

The nearly constant $M_2$ value (22 G$^2$) obtained around 150 K can be explained by the cation having a reorienting CH$_3$ group about its C$_3$ axis. The other plateau value (11.5 G$^2$) observed just below $T_u$, however, is somewhat smaller than the value calculated for rotating CH$_3$ and NH$_3^+$ groups about their respective C$_3$ axis. This suggests that some new motion other than those given above also contributes to the decrease of $M_2$ to 11.5 G$^2$. 

Table 3. Activation energy $E_a$ for each mode of reorientation, the motional constant $C$, and pre-exponential factor $\tau_0$ determined from NMR $T_1$ for $n$-C$_4$H$_9$NH$_3$I, $n$-C$_4$H$_9$ND$_3$I, and $n$-C$_4$H$_9$NH$_3$Br (for comparison).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$C \times 10^{-9}$</th>
<th>$\tau_0 \times 10^{13}$/s</th>
<th>Mode of reorientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-C$_4$H$_9$NH$_3$I</td>
<td>10.4 ± 1</td>
<td>1.6(1.95)</td>
<td>2.3</td>
<td>CH$_3$</td>
</tr>
<tr>
<td></td>
<td>26.8 ± 1</td>
<td>2.6(2.59)</td>
<td>2.2</td>
<td>NH$_3$</td>
</tr>
<tr>
<td>$n$-C$_4$H$_9$ND$_3$I</td>
<td>10.5 ± 1</td>
<td>2.2(2.60)</td>
<td>2.2</td>
<td>CH$_3$ alkyl chain</td>
</tr>
<tr>
<td></td>
<td>12 ± 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$-C$_4$H$_9$NH$_3$Br</td>
<td>11.0</td>
<td>2.2(1.95)</td>
<td>4.2</td>
<td>CH$_3$</td>
</tr>
</tbody>
</table>

* The values in parentheses are theoretical ones.

As a possible motion which accounts for the additional decrease of $M_2$, a 180° flip motion or free rotation of the cation as a whole about its long axis can be considered. However, the $M_2$ values calculated for these motions are much smaller than the observed value. Accordingly, a large amplitude libration or a hindered rotation of the cation as a whole is thought to be excited just below $T_{1r}$ together with the CH$_3$ and NH$_3$ reorientations.

In the low temperature phase of slowly cooled bal, the $T_1$ minimum at 127 K is attributable to the random reorientation of CH$_3$ groups about their respective C$_3$ axis. This assignment is reasonable in view of the above analysis of $M_2$. The other deep $T_1$ minimum at 260 K just below $T_{1r}$ can be assigned to the C$_3$ reorientation of the NH$_3$ group by taking the foregoing discussion into account. This assignment is strongly confirmed by the fact that bal-d$_3$ never gives such a deep minimum.

Since the log $T_1$ versus $T^{-1}$ curve obtained in the stable low temperature phase of bal can be approximately expressed by the superposition of the above two relaxation processes, a least squares fitting calculation of the $T_1$ curve according to (1)–(3) was carried out. The best fitted values of the parameters $E_a$, $C$, and $\tau_0$ are given in Table 3. The calculated $T_1$ curve is also shown in Fig. 3 by the solid line. The theoretical values of $C$ given in Table 3 were calculated by employing the same interprotonic distances in the CH$_3$ and NH$_3$ groups as those used in the preceding calculation of $M_2$ [1].

The $E_a$ value obtained for the C$_3$ reorientation of CH$_3$ groups in bal is nearly the same as that of baBr [1]. This indicates that the intraionic potential barrier hindering the CH$_3$ reorientation is mainly responsible for $E_a$, like in the case of baBr. On the other hand, $E_a$ for the NH$_3$ reorientation in bal is somewhat greater than that estimated for baBr. This may be due to greater steric hindrance of the iodide anions.

Immediately below $T_{1r}$, $T_1$ of slowly cooled bal-d$_3$ decreases with increasing temperature, indicating that a new relaxation process begins to contribute appreciably to $T_1$. This agrees well with the additional $M_2$ decrease found for the plateau near $T_{1r}$. Therefore, we assign this decrease in $T_1$ to the large amplitude libration or the hindered rotation of the cation. To estimate $E_a$ for this motional process roughly, we carried out $T_1$ measurements. The log $T_1$ versus $T^{-1}$ curve obtained at 12.6 MHz affords an $E_a$ which is given in Table 3 along with the motional parameters for the CH$_3$ reorientation in slowly cooled bal-d$_3$.

At various temperatures below 130 K, rapidly cooled bal yields a $T_1$ which can be approximated as being single and nearly the same as that on slow cooling. This indicates that both the stable and substable low temperature phases of bal exhibit almost the same $T_1$ attributable to CH$_3$ reorientation and that the local environments of the CH$_3$ groups are very similar in the two phases.

Above 130 K, rapidly cooled bal gave two quite different log $T_1$ versus $T^{-1}$ curves attributable to the two phases. The substable phase yielded a broad $T_1$ minimum of 32 ms at ca. 150 K. The depth of this minimum is almost the same as the $T_1$ minimum of the stable phase observed at 260 K, which is attributed to NH$_3$ reorientation. Accordingly, the broad $T_1$ minimum of the substable phase can be assigned to NH$_3$ reorientation, indicating that NH$_3$ groups reorient more easily in the substable phase than in the stable phase, as is to be expected [9, 10]. The broadening of the $T_1$ curve is thought to be originated partly from the low activation energy of the NH$_3$ reorientation as well as partly from the distributing correlation times of the NH$_3$ reorientation [11]. Such distribution in $\tau$ is mostly related to a disordered arrangement of molecules in crystals, which is often found in substable phases similar to the present system [12].

The assignment of the broad $T_1$ minimum to the NH$_3$ reorientation is confirmed by the following: We measured $^3$H NMR absorptions of rapidly
cooled bal at 155 K, where the NH$_3^+$ groups should be fixed in the stable phase but reorient rapidly in the substable phase. Because rapidly cooled bal contains both stable and substable phases, the resonance absorption of the substable phase was obtained by estimating difference spectra from the spectra of slowly and rapidly cooled samples observed at the same temperature by adjusting their integrated intensity ratio to 1:2. This is because the abundance ratio of two phases in the rapidly cooled sample is approximately 1:1. The $M_2$ value of the substable phase calculated based on the difference spectra derived above was ca. 13 G$^2$. This agrees well with the theoretical value of 13.9 G$^2$ for the cation having reorienting CH$_3$ and NH$_3^+$ groups.

In rapidly cooled bal-d$_3$, two $T_1$ components are also observed similarly in bal, which are attributable to the stable and substable low temperature phases. The substable phase yields a shallow $T_1$ minimum at ca. 180 K in addition to the deep one due to the CH$_3$ reorientation. The additional minimum can be interpreted as arising from the relaxation process of the large amplitude libration or the hindered rotation of the cation chains. This is because the same motional process detected above 210 K for slowly cooled bal-d$_3$, namely for the stable low temperature phase, is considered to be activated at lower temperatures in the loosely packed substable phase.

No anomaly in the $T_1$ curves of the substable phase of rapidly cooled bal and bal-d$_3$ could be found near 210 K although the DTA curves showed a thermal anomaly. This suggests that the phase transition occurring between the substable phases gives no appreciable effect on the motion of the cation.

The Room Temperature Phase

The value of $^1$H $M_2$ observed for bal at ca. 300 K is (3.4 ± 1.0) G$^2$, which agrees very well with the one calculated for the model of chain rotation together with CH$_3$ and NH$_3^+$ reorientations. Here, the chain rotation means random rotational jumps of the ba$^+$ cation about its long axis keeping its trans zigzag conformation. With increasing temperature, $M_2$ decreases gradually suggesting that some other motions of ba$^+$ chains such as motions of the alkyl chain and local translational motion of the cation as a whole are additionally excited. The log $T_1$ versus $T^{-1}$ curve of this phase is slightly convex for both bal and bal-d$_3$. This also indicates the existence of more than one motional mode involved in the relaxation process, in agreement with the above $M_2$ results.

The change of entropy observed at the phase transition to the room temperature phase is 33 J K$^{-1}$ mol$^{-1}$. This transition entropy is very large and comparable to those reported for phase transitions to plastic crystals [13]. Such a large transition entropy has been found also in baBr [1]. On the other hand, the entropy of melting is 16 J K$^{-1}$ mol$^{-1}$ which is fairly small in spite of the presence of many allowable conformations in the cation chain. Even ionic crystals having no conformational freedom of the ions such as NaSCN, KSCN, and KN$_3$ give melting entropies of 30–40 J K$^{-1}$ mol$^{-1}$ [14]. Evidently the cations in baBr crystals obtain most of their motional freedom at the phase transition to the room temperature phase. This means that the cations in the room temperature phase are thought to be in a highly dynamically disordered state. With increasing temperature, various motional modes of the cation will be activated successively. This is an explanation of the gradual decrease of $M_2$ with increasing temperature in the room temperature phase.

Mechanism of Phase Transitions

When bal was slowly cooled and kept at 248 K, it was found from the $T_1$ measurements that the transition to the low temperature phase, which had started at 260 K required several hours before it was completed. The reproducibility of the starting temperature of the transition was quite good although we checked it by repeating the slow cooling runs of DTA several times.

On these $T_1$ experiments, we observed two FID components giving rise to long and short $T_1$ values which are hereafter called $L - T_1$ and $S - T_1$, respectively. The population of protons having $L - T_1$ slowly decreased with time going by at a fixed temperature, whereas that having $S - T_1$ conversely increased. Since the $S - T_1$ value (43 ms at 248 K) is independent of time and is identical with the $T_1$ value of the stable low temperature phase determined at the same temperature, $S - T_1$ is definitely identified as arising from the stable low temperature phase. However, $L - T_1$ is much shorter than the extrapolated value (2 s) from the $T_1$ curve of the room temperature phase, although it is also time
independent. This suggests that the cations in the crystal, whose protons yield $L - T_1$, are in a transient state different from both states of the room and low temperature phases.

The crystal structure of the low temperature phase is unknown. However, it can be anticipated to have a lower crystal symmetry than tetragonal because the axial symmetry of the rotating $ba^+$ chains existing in the room temperature phase is never retained in this phase involving non-rotating cations. Moreover, we can expect that the non-rotating cations are more compactly packed between the layers of iodide ions than the rotating cations of the room temperature phase. In fact, $n$-$C_{10}H_{21}NH_3Cl$, being an analogous compound to bal, was reported to transform into a new crystalline phase with a disordered structure above room temperature [15, 16], while, below the transition temperature, it forms monoclinic crystals in which the arrangement of the alkyl chains is completely ordered. The cations are compactly packed between the layers of the anions and their long axes are tilted with respect to the normals of the layers. We can expect that the structure of bal in the low temperature phase is similar to that of $n$-$C_{10}H_{21}NH_3Cl$.

From the foregoing discussion, the following mechanism can be proposed for the phase transition. When bal is slowly cooled from room temperature, the phase transition to the low temperature phase seems to take place in two steps. At first, the room temperature phase is transformed, within a shorter time than several minutes, into an intermediate state having $L - T_1$. In this stage, the cations have lost most of their freedom of motion and, together with the anions, fulfill already approximately the symmetry of the low temperature phase.

From the $T_1$ measurements, the relaxation time from the intermediate towards the stable low temperature phase is estimated to be some ten minutes just below $T_g$ and about 4.5 h at 248 K.

When bal is cooled rapidly, the intermediate state may be partly frozen at lower temperatures without changing into the stable low temperature phase because of the long relaxation time of the state. However, this frozen intermediate state is transformed into a substable phase at 209 K which is the additional $T_g$ located on the rapid cooling run of DTA. When this substable phase yielding shorter $T_1$ values is warmed, it is transformed into another substable phase at ca. 210 K. The new substable phase seems to be different from the intermediate state in two respects: First, the latter gave a different $T_1$ value from that of the former when $T_1$ measurements were made at 248 K. Secondly, the time required for the latter to be transformed into the stable phase is much shorter than the time for the former, which is not shorter than 10 h.

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This paper is dedicated to Professor Dr. Alarich Weiss of Technische Hochschule Darmstadt in commemoration of his sixtieth birthday.