Ionic Motion of Phenethylammonium Ion in [C₆H₅CH₂CH₂NH₃]₂PbX₄ (X = Cl, Br, I) as Studied by ¹H NMR
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The temperature dependences at 110 to 400 K of the ¹H spin-lattice relaxation time (T₁) of the phenethylammonium ion in phenethylammonium lead(II) halides, [C₆H₅CH₂CH₂NH₃]₂PbX₄ (X = Cl, Br, I), revealed that this ion shows reorientation of the NH₃ moiety around the three-fold axis and torsional motion of the alkyl chain (CH₃CH₂). Below room temperature, the chloride and the bromide yielded two minima of ¹H T₁ originating from NH₃ reorientation, whereas the iodide yielded only one minimum. These findings indicate that there are two kinds of NH₃ sites in the chloride and bromide but only one in the iodide. The T₁ minimum observed below room temperature gave similar activation energies of the NH₃ reorientation, Eₐ = 15.7, 15.1 and 15.5 kJ mol⁻¹ for the chloride, bromide and iodide, respectively, suggesting that the corresponding NH₃ groups are located at similar environments. Above room temperature, the T₁ minimum in the chloride and bromide gave larger Eₐ values of the NH₃ reorientation: Eₐ = 23.6 and 20.2 kJ mol⁻¹ for the chloride and bromide, respectively. These findings suggest that the NH₃ groups form stronger hydrogen bonding with halogen atoms (N–H⋯X). Furthermore, the amplitude of the CH₃CH₂ motion is discussed, using the two sites jump model. The activation energies for the CH₃CH₂ motion in these compounds are almost equal (Eₐ = 29.1, 30.0 and 28.2 kJ mol⁻¹ for the chloride, bromide and iodide, respectively), but that the torsional angles become larger in the order iodide< bromide< chloride.

Key words: NMR, Phenethylammonium lead(II) halides, Molecular motion, Disorder.

1. Introduction
It is known that phenethylammonium lead(II) halides, [C₆H₅CH₂CH₂NH₃]₂PbX₄ (X = Cl, Br, I) have a two-dimensional layered perovskite-type structure [1]. At about 200 K the iodide (hereafter abbreviated as Ph-PbI₄) is monoclinic, space group C2/m with the lattice parameters a = 3.2508 nm, b = 0.6131 nm, c = 0.6185 nm and β = 93.80°. The inorganic layer is built of corner-sharing PbI₆ octahedra and the organic layer of phenethylammonium ions (C₆H₅CH₂CH₂NH₃⁺), the phenyl groups facing each other. Each layer is stacking alternatively. The bromide and the chloride (hereafter abbreviated as Ph-PbBr₄ and Ph-PbCl₄, respectively) are isomorphous with the iodide [1]. These three halides are interesting because of their optical and electronic properties originating from the natural multi-quantum well structure [2, 3] and because of phenomena closely related to the dynamical behavior of the phenethylammonium ion, such as phase transitions and glass formation [4, 5].

In our previous work of ¹³C CP/MAS NMR on [C₆H₅CH₂CH₂NH₃]₂[CH₃NH₃⁺]ₙ–PbₙI₃n+¹ (n = 1, 2), we found that the phenyl groups undergo a 180° flip motion around the two-fold axis, of which the activation energy and the pre-exponential factor are 25 kJ mol⁻¹ and 8 x 10⁻¹⁰ s for the iodide with n = 1, and 26 kJ mol⁻¹ and 6 x 10⁻¹⁰ s for the iodide with n = 2 [6]. However, the thermal motion of the NH₃ and CH₃CH₂ groups have not yet been clarified.
In the present work, the lattice parameters of Ph-PbX₄ were determined using X-ray powder diffraction, the temperature dependence of the ¹H spin-lattice relaxation times (T₁) for [C₆H₅CH₂CH₂NH₃]₂PbX₄ (X = Cl, Br, I) were measured and the motional modes of phenethylammonium ion in Ph-PbX₄ are discussed.

2. Experimental
Sample Preparation
Ph-PbCl₄ was synthesized by the method used for preparing [C₆H₅NH₃]₂CuCl₄ [7]. PbCl₄ and phenethylamine (C₆H₃CH₂CH₂NH₃) were dissolved in

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concentrated hydrochloric acid in the molar ratio 1:6. The mixture was heated and completely dissolved. Thin white quadratic plates of Ph-PbCl$_4$ were grown by cooling the solution. The crystals were dried at ca. 60°C under reduced pressure. Crystals of Ph-PbBr$_4$ were obtained in the same way from concentrated hydrobromic acid. The samples of Ph-PbI$_4$ were obtained on described in [6]. The samples were sealed into glass ampoules with He heat exchange gas.

X-Ray Powder Diffraction Measurement

X-ray powder diffraction patterns were measured using a Rigaku RAD-B X-ray diffractometer at room temperature. The reflection data were collected over the reflection angle 10° < 2θ < 60°. The mean X-ray wave length was 0.15404 nm (the mean value of Cu Kα and Kβ). The lattice parameters were determined by simulation of the diffraction patterns using the RIETAN 94 program for Rietveld analysis [8].

$^1$H Spin-Lattice Relaxation Time ($T_1$) Measurement

The $^1$H NMR measurements were carried out with a Bruker Model CXP-100 pulsed spectrometer. The $^1$H spin-lattice relaxation times ($T_1$) were measured using the 90°-r-90° method at $^1$H Larmor frequencies of 12 and 22.5 MHz. The $^1$H magnetization of all materials recovered exponentially. A unique value of $T_1$ could be determined at each temperature. The experimental error was <5%. The temperature was controlled within 1 K by a flow of nitrogen gas, using a Bruker VT-1000 unit.

3. Results and Analysis

X-Ray Powder Diffraction

All the samples yielded diffraction patterns characteristic of a layered structure, i.e. intense reflections from the (0, 0, 2n) plane and else weak reflections. For Ph-PbI$_4$, the crystal lattice parameters were obtained by comparison of the experimental patterns with simulated ones on the basis of the monoclinic structure with space group C2/m reported by Calabrese et al. [1]. The lattice parameters thus obtained are in good agreement with the literature values [1]. For the other two compounds, the lattice parameters were determined by assuming the same crystal lattice as that of the iodide. The obtained lattice parameters are listed in Table 1. The lattice parameters of Ph-PbX$_4$ depend on the halogen atom in the PbX$_4^{2-}$-layer. As the ionic radius of the halogen atom increases, the crystal lattice of Ph-PbX$_4$ expands along the b- and the c-axis, whereas it contracts along the a-axis. The interlayer distance evaluated from a and β is 3.358 nm for Ph-PbCl$_4$, 3.336 nm for Ph-PbBr$_4$, and 3.244 nm for Ph-PbI$_4$. These values rise with increasing a. Nevertheless, the volume of the crystal lattice contracts as the ionic radius of the halogen atoms becomes larger.

$^1$H Spin-Lattice Relaxation

1. Ph-PbX$_4$

Figures 1–3 show that the $^1$H $T_1$ vs. 1/$T$ curves give three minima for Ph-PbCl$_4$ and Ph-PbBr$_4$, and two minima for Ph-PbI$_4$. The values of the $T_1$ minima and their temperatures are summarized in Table 2. When the Larmor frequency is changed from 12 MHz to 22.5 MHz, the $T_1$ minima become longer and their temperature becomes larger. These findings suggest that three kinds of motional modes exist in the phenethylammonium ion of Ph-PbCl$_4$ and Ph-PbBr$_4$, and two kinds in that of Ph-PbI$_4$. Hereafter, the motional modes corresponding to the $T_1$ minima are denoted with increasing temperature as mode I, mode I', and mode II for the chloride and bromide, and mode I and mode II for the iodide. Above 360 K,
1. Ionic Motion of Phenethylammonium Ion in \([\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_3]^2\text{PbX}_4\)

**Fig. 1.** Temperature dependence of the $^1\text{H}$ spin-lattice relaxation times ($T_1$) in Ph-PbCl$_4$. For $T_1$ observed at 12 MHz, the short-dashed, long-dashed and short-long-dashed lines represent the results of the least square's fittings for the component of mode I, mode I', and mode II, respectively. The total $T_1$ resulting from the three components, is represented by the solid line. For $T_1$ observed at 22.5 MHz, the solid line represents the results of the simulation.

**Fig. 2.** As Fig. 1, but for Ph-PbBr$_4$.

$^1\text{H}$ $T_1$ in Ph-PbCl$_4$ becomes shorter again, suggesting that a new motion in the phenethylammonium ion is excited above this temperature.

The profiles of the $T_1$ vs. $1/T$ curves of Ph-PbI$_4$ are different from those of Ph-PbCl$_4$ and Ph-PbBr$_4$. The minimum corresponding to mode I' disappears in Ph-PbI$_4$. The minimum value of $T_1$ for mode I in Ph-PbI$_4$ is half of those in Ph-PbCl$_4$ and Ph-PbBr$_4$, whereas that for mode II in Ph-PbI$_4$ is 8 times longer than that in Ph-PbCl$_4$ and 4 times longer than that in Ph-PbBr$_4$.

2. $^1\text{H}$ $T_1$ Analysis

In order to discuss the dynamical behavior of the phenethylammonium ion, we evaluate the activation energies and pre-exponential factors by data fitting using the BPP relaxation theory [9].

In systems with coexisting motional modes, the total $1/T_1$ is the sum of the $^1\text{H}$ spin-lattice relaxation rates corresponding to these motional modes, if correlation effects between these modes can be neglected and the modes take independently part in the different
Table 3. Activation parameters determined from $^1$H $T_1$ for Ph-PbX₄ (X = Cl, Br, I).

<table>
<thead>
<tr>
<th>X</th>
<th>Mode</th>
<th>Cᵢ/μrad² s⁻²</th>
<th>$τ_{0i}/$s</th>
<th>$E_{i}^{'/}$/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>I</td>
<td>1.24 x 10⁹</td>
<td>9.5 x 10⁻¹⁴</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>I'</td>
<td>1.28 x 10⁹</td>
<td>3.0 x 10⁻¹⁴</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.15 x 10⁹</td>
<td>10.0 x 10⁻¹⁴</td>
<td>29.1</td>
</tr>
<tr>
<td>Br</td>
<td>I</td>
<td>1.34 x 10⁹</td>
<td>6.1 x 10⁻¹⁴</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>I'</td>
<td>1.36 x 10⁹</td>
<td>8.6 x 10⁻¹⁴</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.12 x 10⁹</td>
<td>12.0 x 10⁻¹⁴</td>
<td>30.0</td>
</tr>
<tr>
<td>I</td>
<td>I</td>
<td>2.24 x 10⁹</td>
<td>9.2 x 10⁻¹⁴</td>
<td>15.5</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>0.7 x 10⁷</td>
<td>25.0 x 10⁻¹⁴</td>
<td>28.2</td>
</tr>
</tbody>
</table>

The experimental $T_1$ data and show that the relaxation behavior obeys the BPP relaxation theory very well.

### 4. Discussion

#### Motional Mode of Phenethylammonium Ion

The phenethylammonium ion consists of three functional groups, NH₃, CH₂CH₂, and C₆H₅. If the spin temperature is the same in the whole spin system, the experimental $1/T_1$ is given by [10, 11]

$$1/T_1 = \frac{1}{N} \left[ \frac{n_{(NH_3)}}{T_1^{(NH_3)}} + \frac{n_{(CH_2CH_2)}}{T_1^{(CH_2CH_2)}} + \frac{n_{(C_6H_5)}}{T_1^{(C_6H_5)}} \right], \quad (4)$$

where $n_{(NH_3)}$, $n_{(CH_2CH_2)}$, and $n_{(C_6H_5)}$ are the numbers of protons in NH₃, CH₂CH₂, and C₆H₅, respectively, and N is their total number.

Reorientation of the NH₃ group around the three-fold axis is undergone most easily. So, the total $T_1$ will be dominated by the relaxation time $T_1^{(NH_3)}$ at relatively low temperature. Therefore, the $T_1$ minima corresponding to the modes I and I' are considered to originate from the modulation of dipolar interaction owing to the NH₃ reorientation in the phenethylammonium ion. This is also supported by the comparison of the experimental $C_i$ values with the theoretical ones. For the NH₃ reorientation around the three-fold axis, the theoretical value of $C_{NH_3}$ in the phenethylammonium ion is represented by [10]

$$C_{NH_3} = \frac{9}{20} \frac{n_{(NH_3)}}{N} \gamma^4 \frac{h^2}{r^6} \quad (6)$$

where $\gamma$ is the gyromagnetic ratio of the proton and $r$ the interproton distance in the NH₃ group, whose typical value is 0.1706 nm [10]. The theoretical value of $C_{NH_3}$ is calculated to be $2.6 \times 10^9$ rad² s⁻². The experimental $C_i$ value for mode I in Ph-PbI₄ (2.24 x 10⁹ rad² s⁻²) is in good agreement with the theoretical one. On the other hand, for Ph-PbCl₄ and Ph-PbBr₄ the experimental $C_i$ values for the mode I and I' are about one half of the theoretical one ($\sim 1.3 \times 10^9$ rad² s⁻²) in both compounds. This suggests that in Ph-PbCl₄ and Ph-PbBr₄ there are two kinds of distinguishable NH₃ sites which are occupied by the NH₃ groups with equivalent population 0.5:0.5.

The CH₂CH₂ and C₆H₅ groups less mobile than the NH₃ group. In fact, we found previously that above room temperature the C₆H₅ group of the phenethylammonium ion in Ph-PbI₄ undergoes a 180° flip motion with a time scale of $10^{-6} \sim 10^{-5}$ s [6]. The time scale for this motion is too slow to contribute to the $1/T_1$ efficiently. Therefore, $T_1^{(CH_2CH_2)}$ will contribute more efficiently than $T_1^{(C_6H_5)}$ to the total $T_1$ and brings about the minimum corresponding to the mode II. $T_1^{(C_6H_5)}$ will be responsible for the decrease of $T_1$ above 360 K. In order to discuss the motional mode of the CH₂CH₂ group in more detail, we propose the model shown in Figure 4. Although the CH₂CH₂ group can rotate independently around the $C_1 - C_2$ and $C_2 - C_3$ bonds, torsional motion around each bond with small flip angles is considered to be the most probable motion of the CH₂CH₂ group because the NH₃ and C₆H₅ groups restrict the motion of CH₂CH₂ group. The torsional angles about the $C_2 - C_3$ and $C_1 - C_2$ bonds shall be named $\phi_a$.
Fig. 4. Model for the motion of the CH$_2$CH$_2$ group in the phenethylammonium ion. (a) The most stable conformation. The alkyl chain holds the trans-conformation and is lying in a mirror plane. (b) Rotation of the alkyl chain around the C$_\alpha$–C$_\beta$ bond. For clockwise rotation the angle $\phi_a$ is positive, and for counterclockwise negative. (c) Rotation of the alkyl chain around the C$_1$–C$_\beta$ bond. For clockwise rotation the angle $\phi_b$ is positive, and for counterclockwise negative. The CH$_2$CH$_2$ group undergoes torsional motion rotating the C$_2$–C$_\beta$ and C$_1$–C$_2$ bond simultaneously with small flip angles of $\phi_a$ and $\phi_b$, respectively.

The CH$_2$CH$_2$ group jumps between these conformations, the motion of the CH$_2$CH$_2$ group can be treated by a two sites jump model between one conformation (A site) and its symmetrical one (B site). Assuming equivalent population at the A and B sites, the corresponding relaxation constant $C_{CH2}$ is expressed by

$$C_{CH2} = \frac{3}{20} \frac{n_{(CH2CH2)}}{N} \gamma^4 h^2 \sum_{i,j} \left[ R_{ijA}^{-6} + R_{ijB}^{-6} - R_{ijA}^{-3} R_{ijB}^{-3} (3 \cos^2 \theta_{ij} - 1) \right],$$

where $R_{ijA}$ and $R_{ijB}$ are the interatomic distances in the conformation A and B, respectively, and $\theta_{ij}$ is the angle between the $R_{ijA}$ and $R_{ijB}$ vectors. Assuming the molecular structure of the phenethylammonium ion determined in the C$_6$H$_5$CH$_2$CH$_2$NH$_3$Cl crystal [15], (7) makes it possible to seek a pair of the flip angles $\phi_a$ and $\phi_b$ which satisfies the experimental value of $C_{CH2}$. Figure 5 shows the pairs of the flip angles $\phi_a$ and $\phi_b$ determined for each compound. The size of the ellipses represents the amplitude of the fluctuation of the CH$_2$CH$_2$ group. The remarkable aspect in Fig. 5 is the relative magnitude of the flip angles among the three compounds. The flip angles are within $\pm 15^\circ$ for $\phi_a$ and $\pm 10^\circ$ for $\phi_b$ in Ph-PbCl$_4$, whereas they are within $\pm 3^\circ$ for
Local Structure of Phenethylammonium Ion

The local structure around the NH$_3$ group, especially about the NH$_3$ site, was examined through the activation energy ($E_a$) of the NH$_3$ reorientation. In systems possessing the hydrogen bonding N–H...X, the strength of the hydrogen bonding is the dominant factor for the $E_a$ values of the NH$_3$ reorientation. For example, in hydrogen bonding systems such as CH$_3$NH$_2$X [10, 16, 17] and (CH$_3$NH$_3$)$_2$TeX$_2$ [18] (X = Cl, Br, I) the strength of the hydrogen bonding has been studied through the $E_a$ values of the NH$_3$ reorientation in CH$_3$NH$_3^+$, which becomes stronger in the order I < Br < Cl. If the NH$_3$ group forms hydrogen bonding in Ph-PbX$_4$, the $E_a$ value of NH$_3$ reorientation should increase in the order I < Br < Cl. The experimental values of $E_a$ for mode I in the three compounds are of the order 15.5 ± 0.5 kJ mol$^{-1}$. On the other hand, the $E_a$ values for mode I', i.e., 20.2 kJ mol$^{-1}$ for Ph-PbBr$_4$ and 23.6 kJ mol$^{-1}$ for Ph-PbCl$_4$, are larger than for mode I. Furthermore, $E_a$ of model I' of Ph-PbCl$_4$ is larger than that of Ph-PbBr$_4$. These findings reveal that the NH$_3$ group corresponding to mode I has a similar environment in the three compounds and is scarce affected by hydrogen bonding, whereas the NH$_3$ group corresponding to mode I' is affected by the hydrogen bond N–H...X.

Next, we discuss the anomalies observed in the a-distance and the interlayer distance of Ph-PbX$_4$, both of which become larger in the order I < Br < Cl in spite of a decrease in the ionic radius of the halogen atoms. This may be interpreted by the dynamical behavior of the phenethylammonium ion located between the inorganic layers. Both the large amplitude motion of the CH$_2$CH$_2$ group and the disorder of the NH$_3$ group bring about a larger free volume around the alkyl chain in the phenethylammonium ions and at the interface between the organic and inorganic layers. The increase in free volume of the organic layers extends the crystal lattice. The free volume of the phenethylammonium ion, expected from our results, is larger in the following order; Ph-PbI$_4$ < Ph-PbBr$_4$ < Ph-PbCl$_4$. On the other hand, the average volume of a phenethylammonium ion, as derived from the lattice parameters and the ionic radii of Pb$^{2+}$ and X$^-$ [19, 20], is estimated to be 0.94 x 10$^{-4}$ m$^3$ mol$^{-1}$ for Pb-PbCl$_4$, 1.07 x 10$^{-4}$ m$^3$ mol$^{-1}$ for Ph-PbBr$_4$ and 1.08 x 10$^{-4}$ m$^3$ mol$^{-1}$ for Ph-PbI$_4$. The average volume is larger in the reverse order of the free volume expected from the dynamical behavior of the phenethylammonium ion. The difference these the trends seems to come from the evaluation of the average volume without taking account of the shape and the local structure of the phenethylammonium ion. Actually, the free volume of the phenethylammonium ion reflects the local motion and the structure of the organic ion rather than the average volume. The phenyl groups as well as the NH$_3$ and CH$_2$CH$_2$ groups may play an important role in extending the organic layers. The distances between the phenyl groups facing each other in those systems, and the free volume around them, will relate more directly to the lattice extension along the a-axis than the distances between the NH$_3$ and CH$_2$CH$_2$ groups. Thus, information about the motion of the phenyl groups will advance the discussion.

5. Conclusion

The molecular motion of the phenethylammonium ion located between the inorganic PbX$_4^{2-}$ layers in [C$_6$H$_5$CH$_2$CH$_2$NH$_3$]$_2$PbX$_4$ (X = Cl, Br, I) has been investigated by means of the temperature dependence of the $^3$H spin-lattice relaxation time ($T_1$). The motional modes of the phenethylammonium ion were assigned on the basis of the analysis of the relaxation constant determining the minimum values of $T_1$. The activation energy ($E_a$) and the pre-exponential factor ($\tau_0$) for each motional mode were determined from data fitting using the BPP theory. On the basis of the $E_a$ values, the local structure of the phenethylammonium ion was discussed. The following aspects were elucidated:

(1) The two NH$_3$ groups in Ph-PbCl$_4$ and Ph-PbBr$_4$ occupy two different sites; one is little affected by hydrogen bonding and the other is strongly affected by the bond N–H...X.

(2) The CH$_2$CH$_2$ group undergoes a two-sites jump motion between the sites causing torsion of the C$_1$–C$_a$ and C$_a$–C$_b$ bonds, and the magnitude of the flip angles becomes larger in the order Ph-PbI$_4$ < Ph-PbBr$_4$ < Ph-PbCl$_4$. 

$E_a$ and ± 2° for $\phi_a$ in Ph-PbI$_4$. This finding reveals that the amplitude of the CH$_3$CH$_2$ motion is larger in the order I < Br < Cl for the series of Ph-PbX$_4$, although the corresponding activation energy $E_a$ changes little among three compounds.
(3) The $a$-values of the Ph-PbX$_4$ crystals increase in the order Ph-PbI$_4$ < Ph-PbBr$_4$ < Ph-PbCl$_4$, which is the reverse order of the ionic radii of the halogen atoms. The motion of the phenethylammonium ion is considered to be one of the reasons for the anomalous lattice expansion along the $a$-axis.