Cationic Dynamics in the Crystalline Phases of $(CH_3NH_3)PbX_3$ (X: Cl, Br) as Studied by Proton Magnetic Resonance Techniques

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The temperature dependences of the ^{1}H spin-lattice relaxation time T_1, the linewidth parameter T_2^*, and the second moment M_2 of ^{1}H NMR absorption were measured for solid $(CH_3NH_3)PbX_3$ (X: Cl, Br). In the room-temperature cubic phases of both salts, and also in the high-temperature tetragonal phase of $(CH_3NH_3)PbBr_3$, the cations undergo rapid overall rotation or reorientation. In the lowest-temperature phase of both salts the orientation of the cations is fixed but rapid C_3 reorientation of the CH_3 and NH_3^+ groups of the cations about their C–N bond axes takes place. From the M_2 measurements, a precessional motion of the cations in the intermediate-temperature phase of both complexes is suggested. Above room temperature, ^{1}H T_1 of both salts can be explained by assuming spin-rotational relaxation operative due to the rapid rotation of the cations. An anomalous behavior of ^{1}H T_1, attributable to cross relaxation between ^{1}H and ^{81}Br nuclei, was detected for $(CH_3NH_3)PbBr_3$ when T_1 was measured at 42 MHz.

Introduction

The complexes $(CH_3NH_3)PbX_3$ (X: Cl, Br, I) are known to form cubic perovskite-type crystals at room temperature, in which the cations occupy sites having the symmetry m3m [1]. This means that the cations in these crystals should be dynamically disordered or behave as if they were spherical at room temperature. In fact, $(CH_3NH_3)PbX_3$ crystals undergo phase transitions mainly resulting from a change of the motional state of the cations when they are cooled [2]. Furthermore, an extremely rapid overall reorientation of the cations was found at high temperatures [2]. Poglitsch and Weber have concluded from their X-ray diffraction and complex permittivity measurements that $(CH_3NH_3)PbCl_3$ exhibits three phases belonging to the space groups Pm3m, P4/mmm, and $P222_1$, from high- to low-temperature, and that the cations are dynamically disordered in the Pm3m and P4/mmm phases [3]. In order to obtain detailed information about the cationic motion at these phase transitions, we have measured the ^{1}H NMR second moment M_2 and the ^{1}H spin-lattice relaxation time T_1 together with the ^{1}H NMR linewidth parameter T_2^* for $(CH_3NH_3)PbCl_3$ and $(CH_3NH_3)PbBr_3$ crystals.

Experimental

$(CH_3NH_3)PbX_3$ (X: Cl, Br) was prepared by adding conc. aqueous solution of $Pb(NO_3)_2$ or $Pb(CH_3COO)_2 \cdot 3\,H_2O$ to a slight excess of conc. hydrochloric or hydrobromic acid solution of $(CH_3NH_3)X$ at elevated temperature [1]. The samples were identified by taking X-ray powder patterns at room temperature [1].

^{1}H T_1 and ^{1}H T_2^* were determined by means of pulsed NMR spectrometers already described [4, 5]. A $180^\circ-\tau-90^\circ$ pulse sequence was employed for the determination of T_1 while T_2^* was determined from the free induction decay of the signals. The ^{1}H NMR absorption curves were recorded at 40 MHz on a JEOL JNM-MW-40 S cw spectrometer. The sample temperatures were determined with an estimated accuracy of ±1 and ±3 K for the pulsed and cw NMR experiments, respectively.

Results

Figure 1 shows for $(CH_3NH_3)PbCl_3$ the temperature dependences of T_1 observed at the Larmor frequencies of 20 and 42 MHz and of T_2^* determined mainly at 42 MHz.

Below room temperature, T_1 decreased with decreasing temperature down to 177 K. At this temperature

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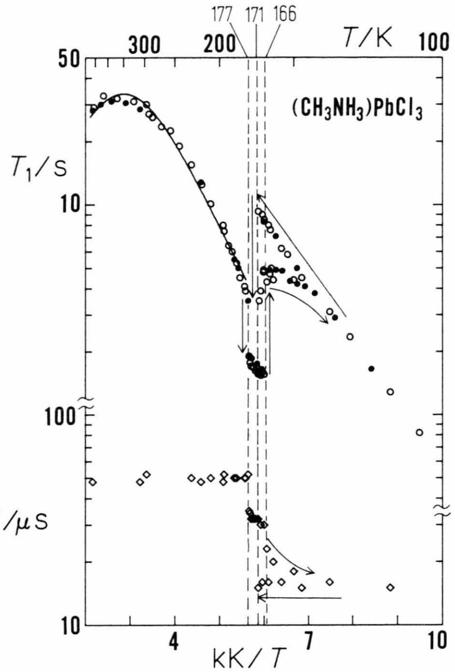

Fig. 1. Temperature dependences of the spin-lattice relaxation time T_1 (●: 42 MHz, ○: 20 MHz) and the linewidth parameter T_2^* (◇) of ${}^1H$ NMR in $(CH_3NH_3)PbCl_3$. Vertical broken lines indicate the phase transition temperatures determined by DTA. Arrows show the way of increasing or decreasing the sample temperature.

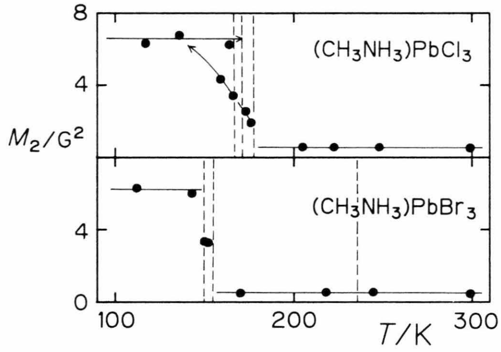

Fig. 2. Temperature dependence of the ${}^1H$ NMR second moment M_2 observed in $(CH_3NH_3)PbCl_3$ and $(CH_3NH_3)PbBr_3$. The broken lines indicate the phase transition temperature determined by DTA.

T_1 discontinuously shortened, indicating the cubic to tetragonal phase transition reported in [3]. On cooling further, log T_1 decreased approximately linearly with increasing T^{-1}. At 166 K, T_1 increased suddenly by a factor of ca. 5, indicating that another phase transition took place. The temperature of 166 K is by ca. 7 K lower than the one reported in [3] for the tetragonal to orthorhombic phase transition.

On decreasing the temperature furthermore, the magnetization recovery curves became slightly non-exponential between 166 and ca. 145 K. For this temperature range, only the T_1 values determined from the initial linear portion of the recovery curves are plotted in Fig. 1 because the longer T_1 component could not be determined. These repeatedly determined T_1 values were found to be almost temperature independent. Below ca. 145 K, the magnetization recovery became exponential again, and log T_1 decreased linearly with increasing T^{-1} down to 105 K.

When the temperature of $(CH_3NH_3)PbCl_3$ was raised from 105 K, T_1 increased monotonously to 171 K without any anomalous behavior. At 171 K, T_1 decreased discontinuously indicating the presence of a phase transition, and T_1 increased on further heating from this temperature, following the curve obtained on the cooling run. Accordingly, we found clear T_1 anomalies at 177 and 166 K on cooling and at 171 and 177 K on heating. From our differential thermal analysis experiments, we obtained three exothermic anomalies at 177, 171, and 166 K on decreasing the temperature, among which two lower-temperature anomalies changed their relative intensities when the experiments were repeatedly carried out. On the other hand, only two heat anomalies were detected at 171 and 177 K in every heating run from below 166 K. We denote the phase transition temperatures 177, 171, and 166 K as T_{c1}, T_{c2}, and T_{c3} and assume tentatively four phases I, II, III, and IV above T_{c1}, between T_{c1} and T_{c2}, between T_{c2} and T_{c3}, and below T_{c3}, respectively.

Above T_{c1}, T_2^* was ca. 50 μs, independent of temperature. On decreasing the temperature, T_2^* was shortened discontinuously at T_{c1} and T_{c3}. Below ca. 140 K, T_2^* took a constant value of ca. 15 μs. Thermal hysteresis as observed for the T_1 measurements was also detected in the measurements of T_2^*.

Figure 2 (above) shows the temperature dependence of ${}^1H$ M_2 for $(CH_3NH_3)PbCl_3$. In phase I and below 140 K in phase IV, M_2 took the temperature independent values 0.5 and 7 G^2, respectively. In the phases II and III, M_2 increased gradually from 2 to 4 G^2 with decreasing temperature. Figure 2 (below) shows the temperature variation of M_2 for $(CH_3NH_3)PbBr_3$. For this complex, three phase transitions are reported to occur at 236 (T_{c1}), 154 (T_{c2}), and 149 K (T_{c3}) [3, 6].

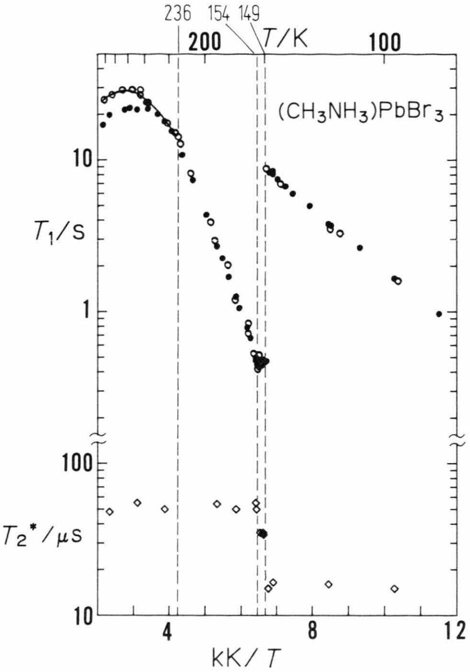

Fig. 3. Temperature dependence of ^1H T_1 and T_2^* observed in $(CH_3NH_3)PbBr_3$. ●: 42 MHz and ○: 20 MHz for T_1 and ◇ for T_2^*. Vertical broken lines indicate the phase transition temperatures.

Accordingly, four phases I, II, III, and IV can be defined as for the $(CH_3NH_3)PbCl_3$ crystal. In the phases I and II M_2 was temperature independent and took a value of 0.5 G^2. In the phases III and IV constant M_2 values of 3 and 7 G^2, respectively, were observed.

Figure 3 shows for $(CH_3NH_3)PbBr_3$ the temperature dependence of ^1H T_1 at 20 and 42 MHz, and of ^1H T_2^* at 42 MHz. Below room temperature, log T_1 decreased almost linearly with increasing T^{-1} both in the phases I and II, the temperature coefficient changing discontinuously at T_{c1}. With decreasing the temperature furthermore, T_1 increased discontinuously but slightly at T_{c2} and markedly at T_{c3}. In the range T_{c3} – ca. 120 K, the magnetization recovery became slightly nonexponential. In Fig. 3, only the longer values of T_1 are given because the shorter ones could not be determined. No frequency dependence of T_1 was detected below room temperature whereas T_1 at 42 MHz was shorter than that of 20 MHz above ca. 300 K.

A constant T_2^* value of ca. 50 μs was observed for the phases I and II. However, it shortened abruptly to 35 μs in III and again to ca. 15 μs in IV. The T_2^* values in each phase were temperature independent.

Discussion

^1H *NMR Second Moments*

In order to assign the observed temperature independent M_2 values to the motion of the cations, theoretical M_2 values were calculated for various models. In the calculations, all bond angles of the cation were assumed to be tetrahedral and the bond distances to be 1.04, 1.10, and 1.47 Å for the N–H, C–H, and C–N bonds, respectively. The M_2 values calculated were 29.8, 19.8, and 8.0 G^2 for the following motional states of the cations in rigid crystals, performing CH_3 C_3 reorientation, and performing C_3 reorientation of both CH_3 and NH_3^+ groups, respectively.

When the cation is placed at the body center of the cubic lattice with $a = 5.90$ Å [3] and performs overall rotation, M_2 can be estimated to be ca. 0.4 G^2. By comparing the observed values with the theoretical ones, one can conclude that the cations in phase I of both complexes as well as in phase II of $(CH_3NH_3)PbBr_3$ undergo overall rotation or reorientation about their center of mass. In IV of both complexes, the orientation of the C–N bond axis is fixed in the lattice whereas the CH_3 and NH_3^+ groups perform rapid C_3 reorientation. In the intermediate-temperature range between T_{c1} and T_{c3} of $(CH_3NH_3)PbCl_3$, M_2 gradually increased from 2 to 4 G^2 with decreasing temperature.

On III of $(CH_3NH_3)PbBr_3$, M_2 and T_2^* are temperature independent. This complex has a tetragonal structure in III belonging to the space group P4/mmm with $Z = 1$ [3]. In the structure, the cations occupy the lattice points with the site symmetry 4/mmm. Therefore, the cations in the C_4 symmetry axis of the crystal should undergo 180° flip motions in addition to rapid reorientation or rotation about the crystal C_4 axis.

When a CH_3 or an NH_3^+ group performs C_3 reorientation about the respective C_3 axis and simultaneously another reorientation about an axis with an n-fold symmetry ($n \geqq 3$), the M_2 reduction factor ϱ is given by [7]

$$\varrho = (1/16)(3\cos^2\chi - 1)^2, \qquad (1)$$

where χ is the angle between the C_3 axis of each group and the n-fold axis. Because the 180° flip motion is not significant for the reduction of M_2, a precessional motion of the C–N bond axis can be considered to explain the small M_2 value of 3.5 G^2 observed in III of $(CH_3NH_3)PbBr_3$. By assuming the occurrence of this motion, χ can be estimated as ca. 30°.

One possible orientation for the cations in the crystal giving $\chi \approx 30°$ is that the NH_3^+ hydrogens form nonequivalent H-bonds with three "bromide ions" in the unit cell located on the $\{102\}$ or $\{22\bar{6}\}$ plane, and the cations should be orientationally disordered in a dynamical sense in conformity with the site symmetry of the cations. Similar orientations of the cations are found in crystals having layered perovskite structure [8].

^1H T_1 *below Room Temperature*

The temperature dependence of ^1H T_1 due to magnetic dipolar interactions is given by [9]

$$T_1^{-1} = C\{\tau/(1+\omega^2\tau^2)+4\,\tau/(1+4\,\omega^2\tau^2)\}. \quad (2)$$

Here C, ω, and τ are the motional constant determined through the dipolar interactions modulated by the cationic motion of interest, the ^1H NMR angular frequency, and the correlation time of the motion, respectively. The Arrhenius relationship is assumed for τ as

$$\tau = \tau_0 \exp(E_a/RT). \quad (3)$$

As can be seen in Figs. 1 and 3, no T_1 minimum could be detected in any phases. Therefore, the E_a value was estimated only from the gradient of the linear portion of the log T_1 vs. T^{-1} curves for the motional modes assumed from the foregoing second moment discussion. The E_a values estimated are listed in Table 1. Here, the E_a values for the motion in phase I of both complexes were corrected, as described below in detail, by taking into acount some contribution from a spin-rotational relaxation at high temperatures.

Table 1. Activation energy E_a/kJ mol^{-1} of the reorientations of $CH_3NH_3^+$ ions in $(CH_3NH_3)PbX_3$ (X: Cl, Br).

Motion	X=Cl		X=Br	
	E_a	Phase	E_a	Phase
Overall rotation	8.3	I	7.6	I
			12	II
Precession	~6	II, III	~6	III
C_3-rotation	5.6	IV	3.8	IV

From the ^1H NMR results obtained, we can conclude that the cations in I of both complexes are dynamically disordered or perform overall rotation with the E_a values given in Table 1. These E_a values are somewhat larger than 6.1 kJ mol^{-1} reported for the same motion of the cations in the cubic phase of $(CH_3NH_3)_2TeI_6$ [10]. This may be due to the difference of H-bonding strength because the ionicity of iodine in $(CH_3NH_3)_2TeI_6$ is expected to be smaller than that of chlorine and bromine in the present complexes.

In II of $(CH_3NH_3)PbBr_3$, the cations still perform rapid overall reorientation. Because the structure of this phase is not cubic, the cationic reorientation should be performed over nonequivalent potential barriers. In II and III of $(CH_3NH_3)PbCl_3$ and in III of $(CH_3NH_3)PbBr_3$, the cations are thought to perform precessional reorientation. Since the gradient of the log T_1 vs. T^{-1} curves observed for the above temperature regions of the respective complexes is negative, the correlation time of the motion assigned should be shorter than 10^{-9} s.

On the cooling run for the measurements of T_1 in IV of both complexes, nonexponential magnetization recovery was observed in a limited temperature range. This can be explained by assuming the existence of at least two different types of crystal domains. However, a detailed discussion may be fruitless at present because precise structural data are not available.

^1H T_1 *Above Room Temperature*

^1H T_1 of $(CH_3NH_3)PbCl_3$ is frequency independent above room temperature even in the temperature region where T_1 rises with increasing T^{-1}. Therefore, we assumed that T_1 in this temperature region is mainly governed by spin-rotation interaction of the cation performing rapid overall rotation [11]. When spin-rotation interaction contributes to the observed T_1, one has

$$T_1^{-1} = T_{1d}^{-1} + T_{1SR}^{-1}. \quad (4)$$

Here, T_{1d} and T_{1SR} indicate the magnetic-dipolar and spin-rotation relaxation times, respectively. T_{1SR} can be written as

$$T_{1SR}^{-1} = C_{SR}\,\tau^{-1}, \quad (5)$$

where C_{SR} is a constant. By fitting (4) to the observed T_1 values in I of $(CH_3NH_3)PbCl_3$, E_a for the overall rotation of the cation was estimated as given in Table 1.

For $(CH_3NH_3)PbBr_3$, the ^1H T_1 values observed at 20 MHz were larger than those at 42 MHz above room temperature, where the high temperature approximation for T_1 should be satisfied. To explain this anomaly, cross relaxation is considered to be operative between the ^1H and ^{81}Br nuclei. This is because the ^{81}Br NQR frequency at 295 K reported for this compound is 58.84 MHz [12] and, therefore, the ^1H NMR frequency of 42 MHz and the Zeeman-perturbed transition frequencies of the ^{81}Br nuclei partly coincide. When ^1H T_1 was observed at 20 MHz, on the other hand, no level crossing between proton and bromine nuclei is expected to exist. By fitting the values observed at 20 MHz to (4), E_a for the overall reorientation of the cations in the crystal can be estimated to be 7.6 kJ mol^{-1}.

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