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^{1}H NMR Studies on the Motion of Cations in the Three Solid Phases of Methylammonium Perchlorate Including Cationic Self-Diffusion in Its Highest-Temperature Solid Phase

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The temperature dependences of the second moment of ^{1}H NMR absorptions, the ^{1}H spin-lattice relaxation time, T_1, and the ^{1}H spin-spin relaxation time, T_2, of $CH_3NH_3ClO_4$ ($CH_3ND_3ClO_4$) were observed in the three solid phases existing over a wide range of temperature. In the phase I stable above 451 K, the onset of the isotropic reorientation as well as the self-diffusion of the cations with the activation energy of 36 kJ mol^{-1} was observed. In the phase II stable between 451 and 321 K, no remarkable change in the motional state of the cation was observed, but the dynamical orientational disorder of perchlorate anions was expected to occur. In the phase III stable below 321 K, the correlated reorientation defined as the C_3 reorientation of the cation having the rigid structure, was observed at lower temperatures for two nonequivalent cations in the crystal with small activation energies of 4.4 and 2.0 kJ mol^{-1}. The uncorrelated reorientation in which both CH_3 and NH_3^+ groups perform C_3 reorientation independently could be observed at a higher temperature with the activation energy of 6.4 kJ mol^{-1}. Nonexponential behavior appearing in the observation of T_1 below 40 K could be explained by the presence of a contribution to ^{1}H T_1 from the rotational tunneling of the cation.

Recently, we have found the presence of highly movable methylammonium $(MA)^+$ cations performing overall reorientation as well as self-diffusion in the highest-temperature solid phase of various simple $(MA)^+$ salts, such as (MA)I,[1,2] $(MA)NO_3$,[3,4] $(MA)ClO_4$,[3] and $(MA)_2SO_4$.[5] Furthermore, we also revealed the presence of such an unusual phase for $(CH_3)_3NHNO_3$[6] and $[C(NH_2)_3]ClO_4$[7] crystals. Very recently, Jurga and Spiess confirmed the existence of the unusual phase in $(MA)ClO_4$ crystals,[8] and also they found the appearance of a similar phase in $(CH_3)_2NH_2ClO_4$[9] and $(CH_3)_3NHClO_4$[10] crystals.

From our studies carried out up to date, it can be said that these highest-temperature solid phases of the above salts bear a strong resemblance to the plastic phase,[11] which is well-known to exist in molecular solids. Similarities are as follows. Both of the present and the plastic phases contain considerably freely moving constituents, i.e., molecule-like cations and such molecules, respectively. Additionally, an unusually large entropy change which is in some cases larger than that of melting, has been observed at the phase transition to the above phases with increasing temperature.[2,4,8,12]

Stammler et al.[13] carried out the experiments of differential thermal analysis (DTA) and powder X-ray diffraction and found three solid phases for $(MA)ClO_4$ above room temperature. The room-temperature phase (the phase III) obtainable below 321 K has a monoclinic unit lattice belonging to the space group $P2_1/n$.[14] With increasing temperature, this phase transforms at 321 K into the phase II, the crystal structure of which belongs to a tetragonal system.[14] The crystal of the highest-temperature phase (the phase I) existing above 451 K has a CsCl-type cubic structure.[14] The existence of the unusual solid phase in this salt was already reported as a letter.[3]

To obtain detailed information about dynamical properties of the cations in the above three phases, the present investigation of the temperature dependences of ^{1}H spin-lattice relaxation times (T_1) above 11 K, ^{1}H spin-spin relaxation times (T_2), and ^{1}H NMR second moments (M_2) has been undertaken for $(MA)ClO_4$ and $(CH_3ND_3)ClO_4$ [hereafter abbreviated as (MA-*d*)ClO_4]. Jurga and Spiess[8] reported ^{1}H NMR results obtained above 80 K for both salts. However, their data partly disagree with ours. Therefore, we again carried out sample preparations and ^{1}H T_1 measurements very carefully and confirmed our data presented here to be reasonable.

Experimental

$(MA)ClO_4$ was synthesized by neutralizing an aqueous solution of methylamine with perchloric acid by cooling the reaction vessel with an ice-bath. The resultant solution was placed in a desiccator, and crystals were separated after slowly evaporating water. The crystals obtained were purified by performing recrystallizations twice from isopropyl alcohol. A partially deuterated analog, (MA-*d*)ClO_4, was prepared from purified $(MA)ClO_4$ by successive crystallizations made three times from heavy water. These salts are so hygroscopic that the purified samples were dried over phosphorus pentaoxide in a vacuum desiccator for several weeks. After that, the samples, which had been put in glass ampoules for the measurements of NMR and DTA, were again dried by pumping out inner gas of the ampoules for ca. 8 h at ca. 90 °C before sealing them with a small amount of helium exchange gas.

DTA curves were recorded by using a homemade apparatus already described.[15] ^{1}H T_1, ^{1}H T_2, and M_2 of ^{1}H NMR absorptions were determined by use of apparatus already reported.[16,17] The T_1 measurements below 77 K were performed by employing a cryostat newly constructed by us. The cryostat could be used for the frequency variable pulsed spectrometer[17] for the measurements of NMR relaxation times between 4.2 and ca. 100 K. The sample temperature could be roughly controlled by adjusting the pressure of helium gas put in open space between the sample probe and a glass cylinder which was immersed in liquid helium. To obtain a given and constant temperature, electric power supplied into a heater wound on the probe was controlled by means of an Oxford model DTC2 temperature controller. When measurements were carried out with this cryostat, sample temperatures were determined by use of a gold (0.07% iron) vs. chromel thermocouple with an accuracy of ±0.2 K. For the other T_1 and T_2 measurements as well as DTA experiments, sample temperatures were measured with a copper vs. constantan thermocouple with an estimated error of ±1 K.

Results

To confirm the phase transition temperatures (T_{tr}) reported,[13)] DTA curves were recorded for $(\mathrm{MA})\mathrm{ClO}_4$ and $(\mathrm{MA}\text{-}d)\mathrm{ClO}_4$ in the temperature range of 80—460 K. When $(\mathrm{MA})\mathrm{ClO}_4$ was heated, two endothermic anomalies appeared at 321 and 451 K. These temperatures agree well with the T_{tr} values determined by Stammler et al.[13)] from their DTA measurements and also by Jurga and Spiess from their DSC experiments.[8)] However, the higher T_{tr} of 452 K observed for $(\mathrm{MA}\text{-}d)\mathrm{ClO}_4$ by us was higher by as much 15 K as that reported by Jurga and Spiess,[8)] although the lower T_{tr} of 321 K obtained by us for the deuterated analog agreed well with their T_{tr} of 319.7 K reported.

The M_2 values of $(\mathrm{MA})\mathrm{ClO}_4$ observed at 77 K and at various temperatures between 260 and 460 K are shown in Fig. 1, where an M_2 value of $(\mathrm{MA}\text{-}d)\mathrm{ClO}_4$ determined at 77 K is also included. At 77 K, $(\mathrm{MA})\mathrm{ClO}_4$ and $(\mathrm{MA}\text{-}d)\mathrm{ClO}_4$ gave M_2 of $8._0$ and $7._0$ G^2, respectively. At 260 K, $(\mathrm{MA})\mathrm{ClO}_4$ still yielded a large M_2 of $7._5$ G^2. With further increasing temperature from 260 to 450 K, a gradual M_2 decrease to ca. 6 G^2 was observed. However, no discontinuous decrease in M_2 was detected at T_{tr} from the phase III to the phase II [hereafter, such T_{tr} as this will be abbreviated as T_{tr} (III →

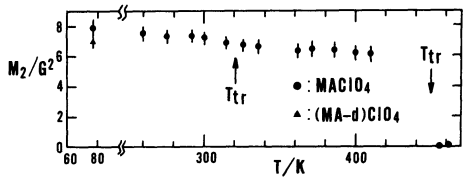

Fig. 1. $^1\mathrm{H}$ NMR second moments (M_2) observed for $\mathrm{CH_3NH_3ClO_4}$ at various temperatures. M_2 observed at 77 K for $\mathrm{CH_3ND_3ClO_4}$ is also included. Vertical lines written on observed values are error bars estimated. T_{tr} with arrows indicates phase transition temperature.

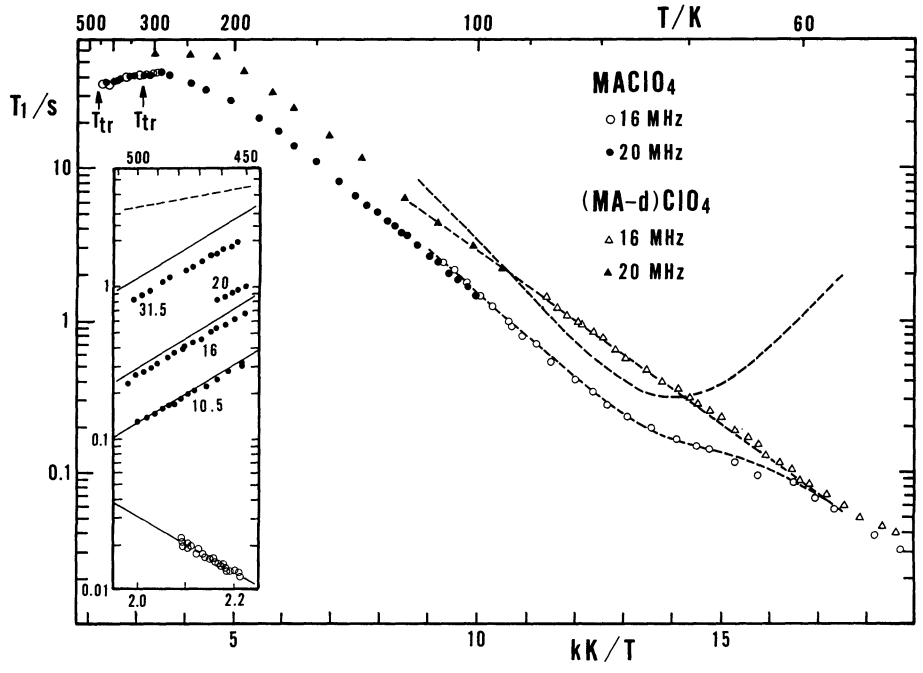

Fig. 2. Temperature dependences of $^1\mathrm{H}$ T_1 observed for $\mathrm{CH_3NH_3ClO_4}$ and $\mathrm{CH_3ND_3ClO_4}$ at 16 and 20 MHz. A log T_1 vs. T^{-1} curve written by a broken line, which has a shallow minimum, indicates the BPP curve for the uncorrelated reorientation of the $\mathrm{CH_3NH_3^+}$ cation, whereas a straight broken line is a hot-side fraction of the BPP curve corresponding to the correlated reorientation of the cation. The sum of the two curves is written by a broken line in agreement with the data of $\mathrm{CH_3NH_3ClO_4}$. Temperature dependences of $^1\mathrm{H}$ T_1 (●) observed at 10.5, 16, 20, and 31.5 MHz and $^1\mathrm{H}$ T_2 (○) determined at 31.5 MHz for $\mathrm{CH_3NH_3ClO_4}$ in its highest- temperature phase are shown as an inserted figure. Straight lines having negative temperature gradients denote $T_{1\mathrm{d}}$ derived at each Larmor frequency except 20 MHz, while the broken line indicates $T_{1\mathrm{i}}$. The straight line having a positive temperature coefficient is the best-fitted line to the T_2 data observed.

II)], although Jurga and Spiess reported a clear M_2 decrease of 2.6 G^2 around 300 K.[8] At the higher T_{tr} of 451 K, M_2 decreased discontinuously to an extremely small value less than 0.05 G^2.

Temperature dependences of ^1H T_1 determined for $(MA)ClO_4$ and $(MA\text{-}d)ClO_4$ in relatively high-temperature regions are shown in Fig. 2. ^1H T_1 values of $(MA)ClO_4$ determined in the temperature ranges of 53—107 and 296—505 K at the Larmor frequency of 16 MHz and of 100—462 K at 20 MHz are depicted. For $(MA\text{-}d)ClO_4$, ^1H T_1 measurements at 16 MHz were made between 53 and 87 K, while those at 20 MHz were carried out between 95 and 300 K.

The $\log T_1$ vs. T^{-1} plots of both salts determined at 16 MHz increased with increasing temperature, and the plots extrapolated to higher temperatures agree well with those of the corresponding salts observed at 20 MHz as can be seen in Fig. 2. The $\log T_1$ value of $(MA\text{-}d)ClO_4$ increased almost linearly with decreasing T^{-1} in the present temperature range, whereas $(MA)ClO_4$ yielded a shallow T_1 minimum around 75 K. Almost the same temperature-dependence curve of ^1H T_1 observed at 20 MHz was obtained for both salts between ca. 100 and ca. 200 K.

$(MA)ClO_4$ yielded a broad T_1 maximum around 300 K, above which temperature almost the same ^1H T_1 values were observed at a given temperature for the measurements made at both Larmor frequencies of 16 and 20 MHz and the observed ^1H T_1 decreased gradually with increasing temperature up to T_{tr}. No discontinuity in the ^1H T_1 curve was observed at T_{tr} of 321 K. However, ^1H T_1 changed discontinuously at T_{tr} of 451 K, where ^1H T_2 also increased discontinuously by about three orders of magnitude.

The temperature variations of ^1H T_1 values determined for $(MA)ClO_4$ in its phase I are inserted in Fig. 2 as an enlarged figure on the T^{-1} scale. In this phase, ^1H T_1 was observed at 10.5 and 31.5 MHz in addition to the above frequencies in the temperature range of T_{tr}—ca. 500 K. With increasing temperature in the phase I, each ^1H T_1 measured at four different Larmor frequencies decreased monotonously, whereas ^1H T_2 determined at 31.5 MHz between T_{tr} and ca. 480 K increased linearly with decreasing T^{-1}. The temperature gradient of the $\log T_1$ vs. T^{-1} plots observed in this phase became gentler when the Larmor frequency employed increased.

The temperature dependences of ^1H T_1 observed for $(MA)ClO_4$ and $(MA\text{-}d)ClO_4$ in the temperature ranges of 11—110 and 18—90 K are shown in Figs. 3 and 4, respectively. Above ca. 40 K, each ^1H T_1 value of $(MA)ClO_4$ observed at 16 and 30.5 MHz yielded a deep T_1 minimum of 17 ms at 46 K and of 34 ms at 50 K, respectively. Similarly, $(MA\text{-}d)ClO_4$ gave a T_1 minimum of 31 ms at 49 K and of 53 ms at 51 K for the measurements made at 16 and 30.5 MHz, respectively.

Below ca. 40 K, nonexponential behavior was observed for the ^1H spin-lattice relaxation of both salts. If one assumes the presence of two independent relaxation processes having different relaxation times, T_{1l} and T_{1s} ($T_{1l}>T_{1s}$), the ^1H magnetization $M_z(t)$ observed after each 90° pulse, where t is the time inter-

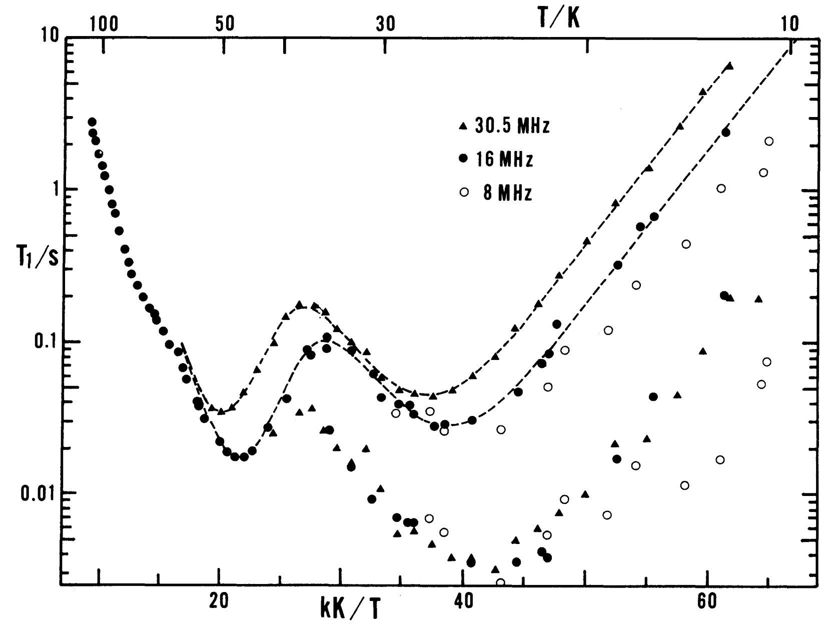

Fig. 3. Temperature dependences of ^1H T_1 observed for $CH_3NH_3ClO_4$ at 8, 16, and 30.5 MHz. Below ca. 40 K, long(T_{1l}) and short (T_{1s}) components of T_1 for each Larmor frequency were obtained from nonexponential free induction decay curves observed. The sum of two independent BPP type T_1 curves corresponding to two kinds of crystallographically nonequivalent cations is written with broken lines for each frequency.

val between 180 and 90° pulses, can be given by

$$M_0 - M_z(t) = A_s\exp(-t/T_{1s}) + A_\ell\exp(-t/T_{1\ell}). \qquad (1)$$

Here, M_0 denotes the M_z value under the thermal equilibrium of the spin system, i.e., $M_0 = M_z(\infty) = -M_z(0)$. To evaluate T_{1s} and $T_{1\ell}$, the $M_z(t)$ values observed at various intervals were fitted to Eq. 1 by use of the least-squares method under the condition of $A_s + A_\ell = 2M_0$. As an example, $M_z(t)$ values observed for (MA)ClO$_4$ at 19 K with the best-fitted $M_z(t)$ recovery curve are shown in Fig. 5.

For (MA-*d*)ClO$_4$, it became difficult to obtain two T_1 values accurately around 40 K, because T_{1s} and $T_{1\ell}$ values come close to each other with increasing temperature. Accordingly, averaged T_1 values, T_{1av}, were evaluated from

$$T_{1av} = (t_{half})/\ln 2, \qquad (2)$$

where (t_{half}) denotes the time interval t when a half-recovery value of the ^{1}H magnetization is reached. T_{1av} values derived from this method agree with the $T_{1\ell}$ values roughly estimated by using Eq. 1. Since these T_{1av} values were very near to the $T_{1\ell}$ curve extrapolated from the low-temperature side, T_{1av} was assumed to have the same origin of ^{1}H relaxation as $T_{1\ell}$ and plotted in Fig. 4.

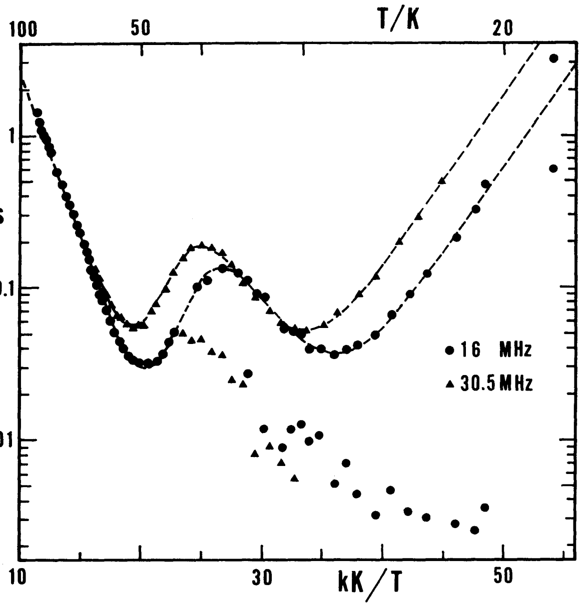

Fig. 4. Temperature dependences of ^{1}H T_1 observed for CH$_3$ND$_3$ClO$_4$ at 16 and 30.5 MHz. Below ca. 40 K, ^{1}H T_1 observed at each frequency showed nonexponential behavior and, $T_{1\ell}$ and T_{1s} could be determined as in the case of CH$_3$NH$_3$ClO$_4$ shown in Fig. 3. The sum of two different BPP curves arising from the two nonequivalent cations is indicated by broken lines calculated at each Larmor frequency. Around the high-temperature minima appeared, ^{1}H T_1 observed at both frequencies showed somewhat nonexponential behavior. However, it was difficult to obtain short T_1 component values accurately. Therefore, these values are omitted from the figure.

The T_1 curves of both salts thus obtained were connected smoothly to the respective T_1 curve observed in a higher-temperature region than 40 K. Each $T_{1\ell}$ curve of (MA)ClO$_4$ obtained from the measurements at 16 and 30.5 MHz exhibited a minimum of 28 ms at 26 K and 44 ms at 27 K, respectively. Similarly, (MA-*d*)ClO$_4$ yielded a $T_{1\ell}$ minimum of 36 ms at 28 K and 52 ms at 30 K for the measurements at 16 and 30.5 MHz, respectively. On the other hand, T_{1s} values measured at these two frequencies at a given temperature were approximately equal to each other in the temperature range where the nonexponential recovery curves could be observed for each analog. A minimum of 3.2 ms for the T_{1s} curve of (MA)ClO$_4$ could be located at 23 K, whereas no clear minimum could be found for (MA-*d*)ClO$_4$ down to 20 K.

Discussion

Second Moments of ^{1}H NMR Absorptions. According to the theoretical calculation of M_2 by use of Van Vleck's method,[18] (MA)$^+$ cations which rotate about the respective C-N bond axes give rise to ^{1}H M_2 of 8.9 G^2.[19,20] The fact that M_2 of 8.0 G^2 was observed for (MA)ClO$_4$ at 77 K indicates that the cations perform this motion with higher frequencies than 10^5 Hz even at 77 K.

A drastic decrease in M_2 to a value less than 0.05 G^2 at T_{tr} of 451 K clearly indicates the onset of the diffusional jumps as well as the isotropic rotation of the cations in the phase I. This is because M_2 observed in

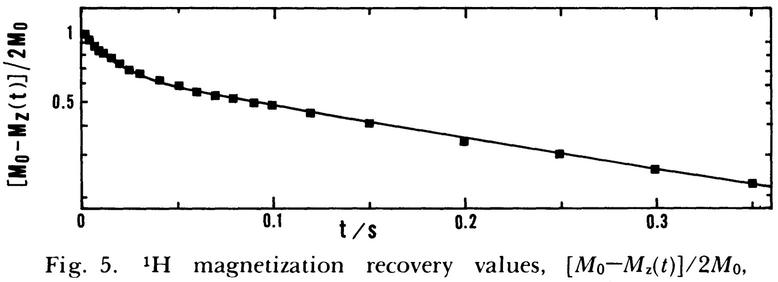

Fig. 5. ^{1}H magnetization recovery values, $[M_0 - M_z(t)]/2M_0$, observed for CH$_3$NH$_3$ClO$_4$ at 19 K by changing the interval time, t, between 180° and 90° pulses. M_0 denotes the thermal equilibrium value of the magnetization value. The solid line is the best fitted curve obtained by the least-squares method.

this phase is much smaller than the theoretical value of 0.8 G^2 calculated for the isotropically rotating cations in crystals using the crystal structure[13] of the phase I. A similar M_2 reduction has been already observed in some $(MA)^+$ salts.[1-6] For (MA)I[2] and $(MA)NO_3$[4] crystals, ^1H NMR and also electrical conductivity data obtained could be explained in terms of the above motional state of the cations.

Room-Temperature Phase (Phase III). (MA-*d*)ClO_4 yielded two deep minima of T_1 (including T_{1l}) below 100 K. These T_1 minima are attributable to magnetic dipolar relaxation because their frequency dependence is well explained by the BPP theory.[21] Since M_2 of 7.0 G^2 observed for this salt at 77 K is close to the theoretical value of 6.1 G^2 calculated for the cation reorienting about its C_3 axis,[19] these T_1 minima can be assigned to this motion. $(MA)ClO_4$ also showed two T_1 (including T_{1l}) minima at about the same temperatures as those of (MA-*d*)ClO_4. These results indicate the existence of two kinds of crystallographically nonequivalent $(MA)^+$ ions in the phase III crystal, in agreement with the results of X-ray diffraction analysis carried out by Zanazzi.[14] The fact that each of the T_1 and T_{1l} minimum temperatures is approximately the same for both salts implies that the CH_3 and NH_3^+ groups in a cation have the correlation time of the C_3 reorientations very close to each other.

From the reason described below, this C_3 reorientation is attributable to the "correlated reorientation" of the cation, which has already been defined as the C_3 reorientation of the cation as a whole with keeping its rigid structure.[22] This motional mode is expected to exist for the cation in crystals where the C_3 rotation of the whole cation has a lower hindering barrier than the intracationic or internal C_3 rotation. The correlated reorientation of the $(MA)^+$ cation has been found in $(MA)_2MX_6$ (M=Sn, Te, Pt; X=Cl or Br) complexes, from the study of ^1H T_1 at lower temperatures.[22,23]

When the correlated reorientation of the cation takes place at a lower temperature, the "uncorrelated reorientation," which has been also defined before as the independent reorientation of the CH_3 and NH_3^+ groups in the identical cation,[22] is expected to occur with increasing temperature. In fact, a shallow T_1 minimum assignable to the uncorrelated reorientation was observed for the foregoing $(MA)_2MX_6$-type complexes.[22,23]

As shown in Fig. 2, $(MA)ClO_4$ gave a shallow T_1 minimum at ca. 75 K, whereas no such minimum was observed for (MA-*d*)ClO_4 in the same temperature range. The appearance of the shallow T_1 minimum is responsible for the averaging of magnetic-dipole interactions between protons belonging to the different groups in a cation, which reorient independently. Accordingly, the shallow minimum observed for $(MA)ClO_4$ can be assigned to the uncorrelated reorientation of the cation.

The ^1H T_1 curve around this minimum can be expressed as[24]

$$T_1^{-1}=(2/3)\gamma^2[\Delta M_{2c}g(\tau_c)+\Delta M_{2u}g(\tau_u)], \tag{3}$$

where

$$g(\tau)=\frac{\tau}{1+\omega^2\tau^2}+\frac{4\tau}{1+4\omega^2\tau^2}. \tag{4}$$

Here, γ, ω, and τ are the gyromagnetic ratio of a proton, the angular Larmor frequency, and the correlation time of a motion involved in the averaging of ^1H-^1H dipolar interactions, respectively. ΔM_{2c} is an M_2 reduction through the onset of the correlated reorientation of the cation from the rigid lattice M_2 value. ΔM_{2u} denotes the difference between the M_2 values for the cations performing the correlated reorientations and those having independently reorienting CH_3 and NH_3^+ groups. τ_c and τ_u indicate the correlation time for the correlated reorientation of the cation and for the uncorrelated reorientation which is the relative intracationic reorientation of the two groups, respectively. Each of these correlation times can be related to the activation energy, E_a, for the corresponding motion using the Arrhenius relationship given by

$$\tau=\tau_0\exp(E_a/RT), \tag{5}$$

where τ_0 is the correlation time at the limit of infinite temperature.

A fitting calculation of the ^1H T_1 values of $(MA)ClO_4$ observed between 57 and 110 K was carried out using the program SALS[25] at the Computation Center of Nagoya University. The best-fitted T_1 curve and the values of the unknown parameters determined from the calculation are given in Fig. 2 and Table 1, respectively. M_{2u} of 0.5 G^2 obtained agrees well with that of 0.4 G^2 calculated from the theoretical T_1 minimum for the same motion in the $(MA)_2MX_6$-type

Table 1. Activation Energy, E_a, the Correlation Time, τ_0, at the Limit of Infinite Temperature, and the Motional Mode of Methylammonium Ions in the Phases I and III of Methylammonium Perchlorates

Compound	Phase	E_a/kJ mol^{-1}	τ_0X10^{13}/s	Motional Mode (data obtained from)
$CH_3NH_3ClO_4$	III	2.0±0.2	5±3	Correlated C_3 reorient. (T_{1l})
	III	4.4±0.1	0.8±0.1	Correlated C_3 reorient. (T_1)
	III	6.4±0.3	1.3±0.6	Uncorrelated C_3 reorient.(T_1)
	I	37±3	—	Self-diffusion (T_1)
	I	35±3	—	Self-diffusion (T_2)
$CH_3ND_3ClO_4$	III	2.2±0.2	5±3	Correlated C_3 reorient. (T_{1l})
	III	4.4±0.1	1.3±0.1	Correlated C_3 reorient. (T_1)

complexes.[22] This means that two kinds of nonequivalent $(MA)^+$ cations existing in the crystal yielded their T_1 minima attributable to the uncorrelated reorientation at approximately the same temperature. This is expected from the foregoing discussion made on this reorientation which is hindered mostly by the intracationic potential barrier. E_a of 6.4 kJ mol^{-1} evaluated for this cationic motion in the present salt is lower than that of ca. 8 kJ mol^{-1} already reported for the same motion in $(MA)_2MX_6$-type complexes.[22] The present small E_a can be explained if the T_1 curve observed is broadened due to the presence of two different T_1 curves overlapping each other, which arise from the two nonequivalent cations, each of which gives the T_1 minimum at a little different temperature.

Next, we try to explain the ^{1}H T_1 and ^{1}H T_1 minima observed for both salts below 50 K by the BPP theory.[21] This theory predicts that the ratios of the T_1 minima observed at two different Larmor frequencies should be equal to the ratio of these frequencies. The ratios observed for the high-temperature T_1 minima, $T_{1\min}$(30.5 MHz)/$T_{1\min}$(16 MHz) were 1.9 and 1.8 for $(MA)ClO_4$ and $(MA\text{-}d)ClO_4$, respectively, in good agreement with the theoretical value of 1.91. On the other hand, the low-temperature T_1 minima yielded the ratios of 1.6 and 1.4 in the same order as above, which were much smaller than the theoretical value. Moreover, the squared ratios of T_1 observed at 30.5 MHz to that of 16 MHz at the same temperature on the low-temperature side of the minima were 2.5 and 2.6 for $(MA)ClO_4$ and $(MA\text{-}d)ClO_4$, respectively. These values were also much smaller than the theoretical value of 3.6 $[(30.5/16)^2]$ predicted from the BPP theory.[21]

These facts and the foregoing nonexponential T_1 behavior observed below 40 K cannot be explained by the usual mechanism, i.e., the averaging of magnetic dipolar interactions due to the cationic motions, and suggest the existence of some contribution to ^{1}H T_1 from the rotational tunneling of the cation in $(MA)ClO_4$ crystals.[26–28] Another fact that T_{1s} of $(MA)ClO_4$ has a minimum at 23 K, suggests that the tunneling frequency is of the order of 10^7 Hz around this temperature.[28]

Here, we roughly evaluate E_a values for the correlated reorientation of the $(MA)^+$ cation. Assuming that the T_1 and $T_{1\ell}$ curves observed at 16 MHz can be expressed by the superposition of two independent BPP curves, we have

$$T_1^{-1}=(1/2)[Cg(\tau_c)+C'g(\tau_c')], \tag{6}$$

where C and C' are the motional constants of the correlated reorientation of the two kinds of cations with the correlation times τ_c and τ_c', respectively. Equations 5 and 6 were fitted to the observed values by the least-squares method. The unknown parameters determined and the best-fitted T_1 curves are shown in Table 1 and Figs. [4, 5], respectively. The activation energies for the correlated reorientation of the cation in both salts were much smaller than the corresponding value of the uncorrelated reorientation. This supports our expectation that the whole-cation reorientation is less hindered than the intracationic reorientation of the CH_3 and NH_3^+ groups.

Intermediate Phase (Phase II). When the temperature was raised above 300 K, ^{1}H T_1 decreased monotonously in the phases III and II without showing any detectable anomaly at T_{tr}(III→II). Since no frequency dependence of ^{1}H T_1 was observed in this temperature range, this T_1 decrease cannot be attributed to magnetic dipolar relaxation. From the preceding discussion, it is apparent that the cations in $(MA)ClO_4$ crystals are considerably free. This suggests that the cations perform a rapid rotation around the C–N bond axis. Such a rapid axial rotation of the cations may give rise to spin-rotation relaxation which is known to yield frequency-independent T_1 decrease with increasing temperature even in solids.[29,30]

Jurga and Spiess have reported a clear M_2 decrease around T_{tr}(III→II) and assigned it to the onset of the precession of the cations about an axis inclined at an angle of 18° to each C–N bond axis.[8] However, neither T_1 minimum nor frequency-dependent T_1 corresponding to this M_2 decrease could be detected in the present study and also in their T_1 measurements.

If the above motional model of the cation proposed by Jurga and Spiess is considered, ^{1}H T_1 arising from this motion can be calculated by substituting the parameters (E_a, τ_0, and ΔM_2) of this motion given in their paper[8] into Eq. 5 and the following BPP equation[21]

$$T_1^{-1} = (\tfrac{2}{3})\gamma^2\Delta M_2 g(\tau). \tag{7}$$

Therefore, the T_1 values roughly evaluated at the Larmor frequency of 20 MHz were ca. 16 and 1.2 s at 350 and 440 K, respectively. These results indicate that ^{1}H T_1 in the phase II should decrease more rapidly than the observed values with increasing temperature. Furthermore, these T_1 values should show frequency dependency due to magnetic dipolar relaxation caused by the precessional motion in contrast to the present experimental fact.

In our M_2 measurements, no marked change in M_2 was found around room temperature although a gradual decrease in M_2 with increasing temperature was found over a wide range of temperature. This M_2 decrease can be interpreted in terms of a gradual increase of the amplitude of lattice vibrations.[31,32] The activation of lattice vibrations usually gives no remarkable effect on T_1 which is consistent with our T_1 data observed in the phase II.

Jurge and Spiess[8] reported a large entropy change ΔS_{tr} (20.9 J K^{-1} mol^{-1}) of transition at T_{tr}(III→II) of 321 K for $(MA)ClO_4$, indicating that the ions forming the crystal obtain motional freedom considerably at T_{tr}(III→II). This ΔS_{tr} is larger than that (16.9 J K^{-1}

mol^{-1}) obtained at T_{tr}(II→I). However, the fact that no marked discontinuity in either ^{1}H T_1 or M_2 was observed at T_{tr}(III→II) indicates that the cationic motion is little affected through this transition. Accordingly, the large ΔS_{tr} observed at T_{tr}(III→II) suggests that a sudden increase in the motional freedom of ClO_4^- anions takes place at 321 K. That is, the onset of anionic rotation around each chlorine atom is expected to occur in the phase II. This expectation is consistent with the ^{1}H spin-lattice dipolar relaxation time, T_{1D}, data reported by Jurga and Spiess.8) They observed a discontinuous decrease in T_{1D} at T_{tr}(III→II), and also a monotonous decrease of T_{1D} in the phase II with increasing temperature. These facts observed by them can be explained in terms of the averaging of the dipolar interactions between ^{1}H and ^{17}O nuclei caused by the anionic rotation.33)

The ΔS_{tr} value of 16.9 J K^{-1} mol^{-1} at T_{tr}(II→I)8) can be compared with those of (MA)I2) and (MA)$NO_3$4) at the highest-temperature solid-solid phase transition. These salts perform the same kind of phase transitions as (MA)ClO_4 at high temperatures and transform into highly disordered crystals with a CsCl-type cubic structure. ΔS_{tr} of 15 J K^{-1} mol^{-1} observed for (MA)I at T_{tr} to the ε phase2) is comparable to that of (MA)ClO_4, whereas (MA)NO_3 gives a larger ΔS_{tr} of 28 J K^{-1} mol^{-1} at the corresponding T_{tr}.4) This ΔS_{tr} of the nitrate can be assigned to an increase in the motional freedom of both cations and anions at the phase transition. We have previously shown for the iodide, however, that only the cationic motion is responsible for the transition entropy observed.2) Accordingly, the phase transition at 451 K occurring in (MA)ClO_4 crystals can be characterized mainly by the change in the motional state of the cation. This is consistent with our previous expectation that the dynamical orientational disorder of the anions will take place at the low-temperature T_{tr}.

High-Temperature Phase (Phase I). The discontinuous decrease of M_2 to a value less than 0.05 G^2 and the sudden increase of T_2 to 14 ms as well, occurring at T_{tr}(II→I), indicate the onset of the isotropic reorientation and the self-diffusion of the cations in the phase I. The log T_1 vs. T^{-1} plots of the phase I, as determined at four different Larmor frequencies shown in Fig. 2, increase almost linearly with increasing T^{-1} and the gradients against T^{-1} become gentler with increasing frequency. The T_1 behavior similar to this was also reported for the cubic phase of (MA)$NO_3$4) and (MA)I.2) According to the analysis of the T_1 data of these salts, the present T_1 values could also be expressed by the superposition of the two components, T_{1d} and T_{1i}, as written by

$$T_1^{-1} = T_{1d}^{-1} + T_{1i}^{-1}. \tag{8}$$

Here, T_{1d} and T_{1i} denote ^{1}H T_1 proportional to ω^2 and independent of ω, respectively. As the most probable origin of T_{1i}, the spin-rotation interaction due to the isotropic rotation of the cation can be considered. On the other hand, T_{1d} is assignable to the self-diffusion of the cations in agreement with the vanishingly small M_2 determined in this phase.

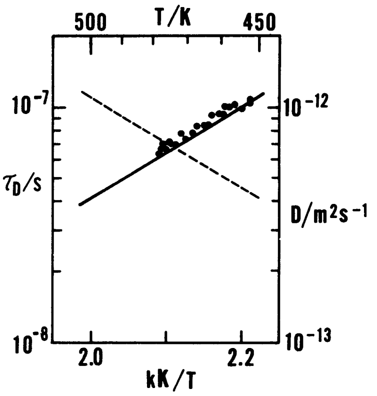

Fig. 6. The correlation times of the self-diffusion estimated from the ^{1}H T_2 values are shown by dots. The solid line indicates the calculated one from the T_{1d} values derived. The broken line indicates the temperature variations of the diffusion constant, D, calculated from T_{1d} values.

If the monovacancy mechanism proposed by Torrey34) and Sholl35) is applicable for the self-diffusion of the cations in the present crystal, we have4)

$$T_{1d}^{-1} = (36/5)\gamma^4\hbar^2 a_0^{-6}\omega^{-2}\tau_D^{-1}(S_0 - S_1/Z). \tag{9}$$

Here, a_0, τ_D, and Z are the lattice constant of the phase I, the correlation time of the self-diffusion, and the number of the nearest neighbors in the simple cubic sublattice formed by the cations, respectively. The numerical values of S_0 and S_1 are given in Sholl's paper.35) When we derived Eq. 9, we used the condition of $\omega\tau_D \gg 1$. By introducing ^{1}H T_1 values observed to Eq. 9 and using $Z=6$, we could estimate τ_D at various temperatures.

The diffusion constant D of the cations in the crystal can be expressed as36)

$$D = \langle r^2 \rangle / 6\tau_D, \tag{10}$$

where $\langle r^2 \rangle$ is the mean-square jump distance of the cations, which is taken as a_0^2 in the monovacancy mechanism. The values of τ_D and D calculated using the above equations are shown in Fig. 6.

τ_D can be also calculated independently from the ^{1}H T_2 data determined using the relation written by4)

$$T_2^{-1} = (27/20)\gamma^4\hbar^2 a_0^{-6}\tau_D g(0). \tag{11}$$

Substituting $g(0)=17.98$35) into Eq. 11, we obtained τ_D as shown by dots in Fig. 6. The τ_D values derived from the T_2 values agree well with the line calculated from T_{1d}.

For (MA)$^+$ cations in the highest-temperature solid phase of (MA)ClO_4, the D value of the order of 10^{-13} m^2 s^{-1} was obtained. The same order of D for the diffusion of the same cation was also obtained in the highest-temperature solid phase of (MA)NO_3.4) It is known that many plastic crystals which are formed by neutral molecules have analogous D values of ca. 10^{-13} $m^2 s^{-1}$ observed near their melting temperatures (T_m) although they are distributed over a wide range of temperature.[36] τ_D values obtained in the phase I are very similar to those of $(MA)NO_3$ and also of the plastic crystals. By extrapolation to higher temperatures, τ_D of $(MA)ClO_4$ at T_m can be obtained from the $\log \tau_D$ vs. T^{-1} curve as ca. 3×10^{-8} s. This is close to the value of 9.8×10^{-8} s evaluated for $(MA)NO_3$[4] and also to those τ_C values of the plastic crystals forming a bcc lattice, which are ca. 1×10^{-7} s on the average.[36] These facts suggest that the highest-temperature solid phase of the ionic crystals of $(MA)ClO_4$ and $(MA)NO_3$ has solid state properties similar in many respects to those of the plastic crystals.

The activation energies for the self-diffusion of the cations calculated from the T_{1d} and T_2 data employing Eq. 5 are given in Table 1. The E_a values obtained from both relaxation values agree well with each other within experimental errors. These E_a values of $(MA)ClO_4$ are very close to that (35 $kJ\,mol^{-1}$) of (MA)I for the same motion,[2] whereas they are much higher than 28 $kJ\,mol^{-1}$ obtained for $(MA)NO_3$.[4] Since these phases of the three salts containing diffusive $(MA)^+$ cations have the isomorphous CsCl-type cubic structure, the E_a values obtained can be compared by considering the differences in the shape and the size of the anions. The bulky and nearly spherical ClO_4^- anions and also bulky I^- anions seem to provide higher barriers for the translational jumps of the cations than the planar NO_3^- anions.[37]

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