  Bull. Chem. Soc. Jpn., 54, 103—108 (1981)

Molecular Motion in Methylammonium Hexahalotellurates(IV) as Studied by Means of the Pulsed Nuclear Magnetic Resonance

Yoshihiro Furukawa,* Hideko Kiriyama,** and Ryuichi Ikeda†

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565

† *Department of Chemistry, Nagoya University, Chikusa-ku, Nagoya 464*

(Received February 8, 1980)

Molecular motion in solid $(CH_3NH_3)_2TeX_6$ (X=Cl, Br, and I) was studied by measuring the spin-lattice relaxation time, T_1, of ^1H and ^{35}Cl nuclei in several crystalline phases appearing below room temperature. A deep minimum of the proton T_1 was observed in the low-temperature phase of all the compounds, indicating that the methylammonium ion performs a rapid reorientation as a whole about its three-fold axis. The activation energies, E_a, for the motion of cations are determined to be 7.0, 3.7, and 2.7 kJ/mol for X=Cl, Br, and I respectively. In $(CH_3NH_3)_2TeI_6$, which has the lowest E_a value, the relaxation process associated with the tunneling of the cation is apparent at low temperatures. For all the complexes studied, a shallow T_1 minimum ascribable to the independent rotation of the CH_3 and NH_3 groups in the cation was observed on the high-temperature side of each deep T_1 minimum. The ^{35}Cl T_1 of $(CH_3NH_3)_2TeCl_6$ exhibited a distinct minimum at the lower phase-transition point at 139 K and a discontinuity at the higher one near 230 K. The hindered rotation of the $[TeCl_6]^{2-}$ octahedron occurs in the room-temperature phase, with an E_a value of 48 kJ/mol.

It has been reported that many methylammonium hexahalometallates(IV), $(MA)_2MX_6$ (MA=CH_3NH_3, M=Sn, Pt, Se, Pd, and Pb, and X=Cl, Br, and I), have a rhombohedrally distorted K_2PtCl_6-type structure with the space group $R\bar{3}m$ at room temperature[1] and undergo a structural phase transition at low temperatures.[2,3] Some of them have been studied by means of the halogen nuclear quadrupole resonance (NQR),[2-4] the ^1H nuclear magnetic resonance (NMR),[5] and single-crystal X-ray diffraction in high- and low-temperature phases.[6] It was found that these compounds all have one phase transition similar to one another in nature at temperatures between 103 and 163 K.[3]

On the other hand, methylammonium hexahalotellurates(IV), with crystal structures different from those of the above complexes, also show interesting phase transitions. Kume *et al.* have made halogen NQR and differential thermal analysis (DTA) experiments on $(MA)_2TeX_6$ and found a phase transition at 139 K and an anomaly in the NQR spectra near 230 K for $(MA)_2TeCl_6$, while its hexabromo and hexaiodo analogs gave phase transitions at 158 and 289 K, and at 119 K, respectively.[7] Kitahama and Kiriyama reported the results of their X-ray diffraction study of $(MA)_2TeCl_6$ at various temperatures.[8] According to them, the hexachlorotellurate(IV) has a hexagonal, layered, CdI_2-type structure at room temperature, with the space group $P\bar{3}$ (or $P\bar{3}m1$); the cell constants were $a=7.340$ and $c=7.066$ Å; and $Z=1$. The crystal can be supercooled down to about 105 K without any structural change at both 230 and 139 K. Around 105 K, the crystal is sluggishly transformed to the low-temperature phase (LTP), with an accompanying change in crystal symmetry from $P\bar{3}$ to $R\bar{3}m$. When the temperature is increased from LTP, no structural change was detected by the X-ray study at 139 K,[8] where a clear anomaly was observed by the NQR and DTA measurements.[7] On a further increase in the temperature, the crystal reverts to the room-temperature phase (RTP) near 230 K, even though the DTA study shows no anomaly around this temperature. On the other hand, at room temperature $(MA)_2TeBr_6$ and $(MA)_2TeI_6$ form cubic crystals, presumably belonging to the space group Fm3m.[7] In the present investigation, the proton T_1 and the ^{35}Cl NQR T_1 were measured to reveal the nature of the molecular motions in the tellurium complexes. The results thus obtained were compared with those in a similar series of complexes with the rhombohedral structure of the space group $R\bar{3}m$.

Experimental

The proton spin-lattice relaxation time, T_1, was measured at 20 and 60 MHz with a Bruker B-KR 322 s pulsed NMR spectrometer by employing the conventional 180°-t-90° pulse sequence. The recovery of nuclear magnetization after the 180° pulse was slightly non-exponential in the vicinity of the temperature of the T_1 minimum. In this case, T_1 value was evaluated from the initial part of the magnetization *vs.* t curve. The spin-locking pulse sequence was used for the determination of the rotating-frame spin-lattice relaxation time, $T_{1\rho}$, for $(MA)_2TeI_6$. The NQR T_1 of ^{35}Cl in $(MA)_2TeCl_6$ was determined by the use of a 180°-t-90°-t'-180° pulse sequence, while its resonance frequency was read directly on a Schomandl ND 100 M frequency synthesizer. A NIC 1074 signal averager was, if necessary, employed in order to increase the signal-to-noise ratio of the ^{35}Cl NQR echo.

The temperature above 77 K was controlled to within ±0.5 K by using an Ohkura EC 61 temperature controller and measured with a copper *vs.* constantan thermocouple. Temperatures below 77 K were obtained by allowing the sample to warm (*ca.* 0.2 K/min) from the temperature of liquid helium and measured with a gold-cobalt *vs.* copper thermocouple.

The samples used were prepared from tellurium dioxide, a methylamine solution, and the corresponding acid of hydrogen halide.[7]

Results and Discussion

Chlorine-35 NQR in $(MA)_2TeCl_6$. The temperature dependence of the ^{35}Cl NQR frequencies,

** Present address: Department of Chemistry, Faculty of Science, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657.

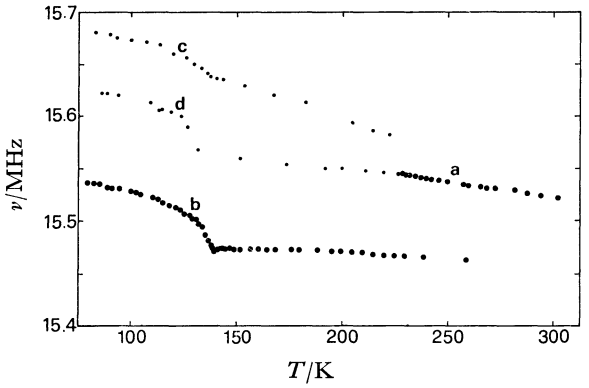

Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies in $(CH_3NH_3)_2TeCl_6$.

as measured by the pulse method, is shown in Fig. 1. The results are in good agreement with those of an earlier work.[7] At room temperature, only a single resonance line, **a**, is observed at 15.52 MHz. When the sample is cooled from room temperature, the **a** line fades out near 230 K. After further cooling down to about 100 K, another line, **b**, is detected, its frequency being 15.54 MHz at 80 K. When the sample is warmed from 80 K, the resonance frequency gradually decreases and gives rise to a small, cusp-shaped anomaly, as in the case of rhombohedral $(MA)_2SnCl_6$, in the vicinity of 139 K.[2,3] On further heating, the **b** line broadens and the **a** line again appears at about 230 K. The former line fades out at about 260 K, while the latter increases in its intensity.

Two additional resonance lines, **c** and **d**, are frequently observed together with the main line, **b**. These extra lines show a temperature dependence similar to that of the **b** line. The intensity of these lines, however, is very weak and varies from sample to sample with the thermal history. Especially, these extra lines are liable to be observed when the sample is cooled from the transition region where both main lines, **a** and **b**, are seen simultaneously in the heating run. Kitahama and Kiriyama observed heavy streaks in the X-ray photographs of LTP with the space group of $R\bar{3}m$, indicating the development of several crystal domains arising from stacking faults in the layered lattice, as well as weak reflections originating from the $P\bar{3}$ phase, which had not been transformed on cooling down to 92 K.[8] The strong NQR line **b** can be attributed to the $R\bar{3}m$ phase, while the weak extra lines may be attributed to some crystal domains associated with the stacking faults and to the unconverted $P\bar{3}$ phase. A similar unusual NQR feature was observed for polytypism found in some compounds with layered structures.[9]

The NQR relaxation time of chlorine-35 in $(MA)_2TeCl_6$ was measured above 80 K. In Fig. 2, the values of T_1 measured on the **a**, **b**, and **c** resonances are identified by different symbols. The T_1 of the **d** resonance could not be measured because of its poor signal intensity and also because of interference from the intense line **b**. The log T_1 *vs.* $1/T$ curve shows an anomalous minimum around the lower

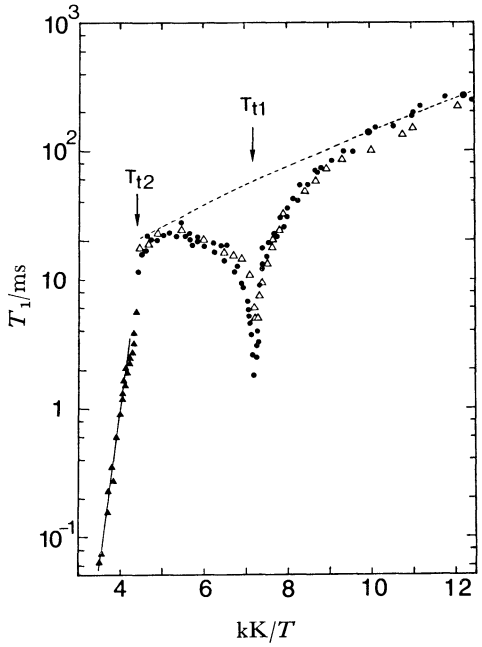

Fig. 2. Temperature dependence of ^{35}Cl NQR spin-lattice relaxation times in $(CH_3NH_3)_2TeCl_6$.
▲: **a**, ●: **b**, △: **c**.

transition temperature (T_{t1}=139 K) and a discontinuous change near 230 K (T_{t2}), where the crystal structure sluggishly changes from $R\bar{3}m$ to $P\bar{3}$ in the heating run.

One can expect the following three processes to interpret the observed relaxation: the usual lattice vibration at low temperatures, the hindered rotation of the $[TeCl_6]^{2-}$ octahedron at high temperatures, and the phase transition around 139 K. The relaxation rate due to the lattice vibration is given by:

$$(T_1)_{vib}^{-1} = aT^2 + b, \quad (1)$$

where a and b are constants.[10] The temperature dependence predicted from this relation is shown in Fig. 2 by the dotted line, which was fitted on the experimental values at 82 and 100.5 K. On the other hand, the T_1 in RTP decreases exponentially with a decrease in the inverse temperature, indicating the occurrence of a hindered rotation of the complex anion. The relaxation due to such hindered rotation is given by $T_1 = C\tau_c$.[11] The correlation time, τ_c, for the rotation is assumed to have this form:

$$\tau_c = \tau_0 \exp(E_a/RT). \quad (2)$$

The constant, C, is 2/3 for the rotation around the C_3-axes of the octahedral anion, which lie on the crystal C_3-axis.[4] The straight line in Fig. 2 is calculated by taking E_a=48 kJ/mol, and $\tau_0 = 1.3 \times 10^{-13}$ s.

The last relaxation process is characterized by the distinct T_1 minimum at T_{t1}. This phenomenon is very similar to those of the halogen NQR T_1 of cubic A_2PtBr_6 ($A=K^+$ and NH_4^+)[12,13] and of rhombohedral $(MA)_2MCl_6$ (M=Sn and Pt).[4] For the former compounds, the T_1 anomaly is interpreted in terms of a softening of the zone-center rotary-lattice mode of the octahedron, which causes a transition from the cubic to the tetragonal phase. A very similar type

of anomalous T_1 change at the transition point was observed in the latter compounds. This anomaly was also explained in terms of a softening of the rotary mode of the complex ion,[4] although no distinct structural change was disclosed on the phase transition.[6] Accordingly, it may be that the T_1 anomaly in the present tellurium complex ion also originates from a softening of the rotary mode of the complex. Quite similary to $(MA)_2SnCl_6$, no structural change was detected at the transition point of the present compound; that is, both LTP and MTP (the middle-temperature phase between T_{t1} and T_{t2}) belong to the same space group, $R\bar{3}m$.[8] One may, therefore, presume that, in the crystals of rhombohedral $(MA)_2MCl_6$, the rotation angle of the octahedral anion at the phase transition is too small to be detected by means of X-ray diffraction.

Proton T_1 *in* $(MA)_2TeCl_6$. The temperature variation of the proton T_1 in $(MA)_2TeCl_6$ gives two different results, depending on the direction of the change in the temperature. Figure 3 shows the results for T_1 as the temperature increases from 4.2 or 77 K. No drastic change was recognized in the log T_1 *vs.* $1/T$ curves at either phase transition point, T_{t1} or T_{t2}, indicating that the motion of the MA^+ ion is almost unaffected by these transitions. By analogy with $(MA)_2SnCl_6$,[5] the deep minimum near $kK/T \approx 15$ is assignable to the reorientation of the MA^+ ion as a whole about its C_3-axis, while the small depression near $kK/T \approx 10$ is assignable to the independent reorientation of the CH_3 and NH_3 groups in the cation. In this system, the spin-lattice relaxation rate for the MA^+ ion is written by:

$$T_1^{-1} = A[\tau_1/(1+\omega_0^2\tau_1^2)+4\tau_1/(1+4\omega_0^2\tau_1^2)] + B[\tau_2/(1+\omega_0^2\tau_2^2)+4\tau_2/(1+4\omega_0^2\tau_2^2)], \quad (3)$$

where $\tau_1 \ll \tau_2$.[5,14] The motional constants, A and B, stand for the contributions to T_1^{-1} from the dipolar interaction modulated *via* the C_3 rotation of the MA^+ ion as a whole, and *via* the independent rotation of the CH_3 and NH_3 groups on the coordinates of the MA^+ ion, respectively. These constants can be determined theoretically from the dimensions of the MA^+ ion[5,14] or experimentally from the T_1 minimum values. The τ_1 symbol is the correlation time for the rotation of the cation as a whole, while τ_2 symbolizes the uncorrelated rotation of the two groups. The preexponential factor, τ_0, and the activation energy, E_a, in the usual Arrhenius relation are determined experimentally.

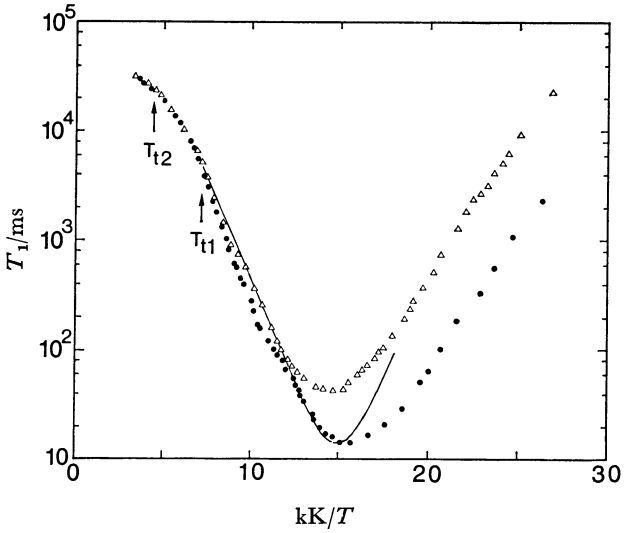

Fig. 3. The spin-lattice relaxation times of protons in $(CH_3NH_3)_2TeCl_6$ measured on heating run from 4.2 or 77 K.
●: 20 MHz, △: 60 MHz.

The experimental points in LTP, however, cannot be fitted to Eq. 3 because the deep T_1 minimum is broad and asymmetric, although all the MA^+ ions are crystallographically equivalent.[8] One possible explanation is that the correlation time is widely distributed because of the stacking faults previously described. The rather long T_1 minimum compared with the theoretical value is consistent with such breadth of the T_1 minimum. Therefore, the activation parameters are evaluated separately from the slopes on the low- and high-temperature sides of the T_1 minimum (Table 1). The T_1 curve simulated by the use of these activation parameters is represented in Fig. 3 by a solid line. The activation energy for the reorientation of the MA^+ ion reflects the intermolecular potential barrier, which is determined partly by the NH···Cl hydrogen bonding and partly by the MA^+···Cl van der Waals force. The E_a values in the Pt, Sn, and Te chloro complexes are 3.6, 4.2, and 6.0 (averaged value) kJ/mol respectively.[5] This order is the same as that of the chlorine ionicity, i, in these complexes, as deduced from ^{35}Cl NQR frequencies, which give $i=0.43$, 0.66, and 0.67 in that order.[3] This suggests that the former interaction is more effective on the motion of MA^+ ions than the latter one in the present system. The small value of E_a indicates that, in these compounds, the NH···Cl hydrogen bonds are quite weak as compared with that in CH_3NH_3Cl.[15]

When the crystal is cooled down from room temperature, the T_1 behavior is very different from that of the heating process described above. It has been reported that the crystal structure remains unchanged until 105 K on cooling[8] and that the DTA curve shows no heat anomaly in the temperature range of 260—230 K.[7] As can be seen from Fig. 4, the T_1 value at 20 MHz is clearly shortened by about one quarter in the narrow temperature range of 230—222 K. This T_1 anomaly indicates that the motional state of the MA^+ ion abruptly changes at T_{t2}. The T_1 curve between $kK/T=4.5$—7.5 shows the presence of a new relaxation process superimposed on the rapid reorientations of the CH_3 and NH_3 groups. The long T_1 value of about 4 s observed in this temperature range suggests that the predictable additional motion is, for example, a small-angle tilting of the C_3 axis of the MA^+ ion from its original orientation. This suggestion is supported by the fact that the ^{35}Cl NQR line (**a** in Fig. 1) fades out at 230 K, because such a tilting motion introduces a large fluctuation of the electric-field gradient (EFG) at the chlorine site.[7]

Proton T_1 *in* $(MA)_2TeBr_6$. The temperature

dependence of the proton T_1 at 20 MHz is shown in Fig. 5. The two phase transitions found in the NQR and DTA experiments[7] are marked by discontinuity in the log T_1 *vs.* $1/T$ curve. It is interesting to note that a shallow T_1 minimum near 100 K is clearly observed, because the deep T_1 minimum appears at 44 K, lower by 20 K than that of $(MA)_2TeCl_6$. The T_1 curve in LTP is apparently asymmetric and broad. At the present stage, however, the proton relaxation below 70 K is ascribable to the reorientation of the whole MA^+ ion. The relaxational parameters thus obtained are listed in Table 1. The observed asymmetric T_1 minimum is probably due to the tunneling-assisted relaxation, because of the low rotational barrier of the C_3 reorientation of the cation.[16] As the crystal structures of both LTP and MTP are yet unknown, we cannot, though, rule out the possibility that the presence of two or more nonequivalent MA^+ ions causes the asymmetry of the T_1 curve.

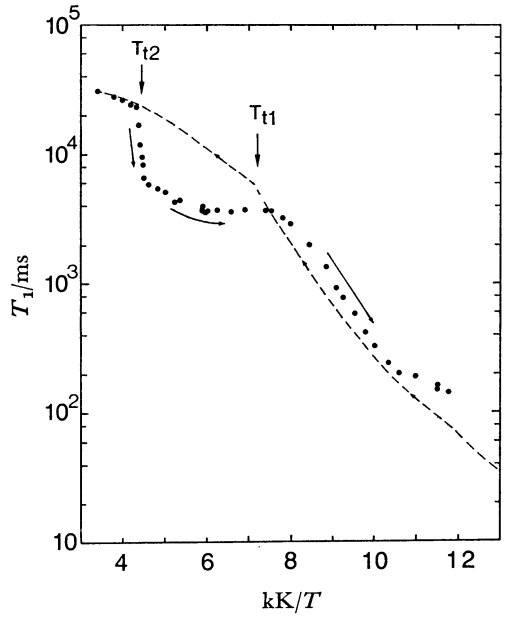

Fig. 4. The spin-lattice relaxation times of protons in $(CH_3NH_3)_2TeCl_6$ measured at 20 MHz on cooling run from room temperature. The broken line shows the data at 20 MHz on heating run.

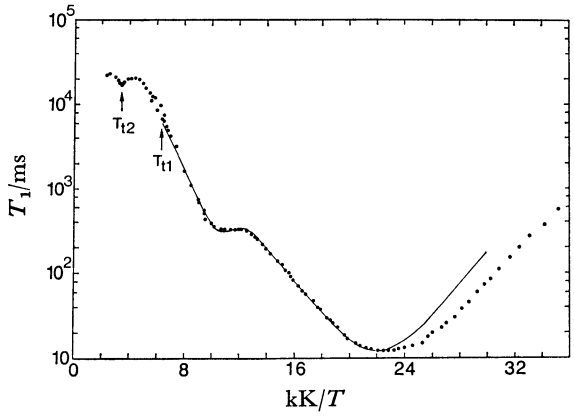

Fig. 5. Temperature dependence of the proton T_1 at 20 MHz in $(CH_3NH_3)_2TeBr_6$.

By using Eq. 3 and assuming that $\omega_0\tau_1 \ll 1$, the data between kK/T=6 and 18 were analyzed for the motion specified by τ_2, yielding a T_1 minimum of 430 ms at kK/T=10.6 and an activation energy of 9.0 kJ/mol. This process can be assigned to the intergroup dipolar interaction in the cation.[5] The theoretical T_1 minimum due to the independent reorientation is evaluated to be 460 ms, which is in good agreement with the observed value. The E_a value of 9 kJ/mol is reasonable as the internal rotation barrier in the MA^+ ion.[5]

Proton T_1 *and* $T_{1\rho}$ *in* $(MA)_2TeI_6$. The experimental relaxation times for $(MA)_2TeI_6$ are given in Fig. 6, where the log T_1 and log $T_{1\rho}$ are plotted against the inverse temperature, and in Fig. 7, where the log T_1 below 70 K is shown against the temperature. The occurrence of a phase transition was confirmed at 119 K by the discontinuity in both the T_1 and $T_{1\rho}$ curves. There are three temperature regions, characterized by different relaxation processes, for T_1: the linear region of the T_1 curve in RTP, the shallow T_1 minimum in the kK/T=10 to 15 region, and the two T_1 minima at very low temperatures. In the series of $(MA)_2MX_6$ (X=Cl and Br), each complex shows a single deep T_1 minimum attributed to the C_3 reorientation of the whole MA^+ ion. The T_1 behavior of $(MA)_2TeI_6$, however, is rather different from that of the foregoing complexes. This is because the T_1 curve in the low temperature rigion yields two T_1 minima, the values of which

Table 1. Motional parameters for $(MA)_2TeX_6$

Compound	A or B[a]/s^{-2}	E_a[b]/kJ mol^{-1}	τ_0/s	Motion
$(MA)_2TeCl_6$	6.2×10^9	7.0 (5.0)	1×10^{-14}	C_3-rotation of MA^+ ion
	—	—	—	independent rot. of CH_3 and NH_3 groups
	—	48	1.3×10^{-13}	hindered rot. of $[TeCl_6]^{-2}$ ion
$(MA)_2TeBr_6$	7.1×10^9	3.7 (3.3)	4×10^{-13}	C_3-rotation of MA^+ ion
	2.1×10^8	9.0	5×10^{-14}	independent rot. of CH_3 and NH_3 groups
$(MA)_2TeI_6$	—	2.7	—	C_3-rotation of MA^+ ion
	2.0×10^8	5.0	3×10^{-12}	independent rot. of CH_3 and NH_3 groups
	—	6.1	—	overall rot. of MA^+ ion

a) The calculated values are $A=10\times10^9$ and $B=1.9\times10^8$ s^{-2} for r(C-H)=1.10, r(N-H)=1.04, r(C-N)=1.47 Å, and all the tetrahedral angles.[4] b) The value in parentheses is estimated from the slope on the low-temperature side of the T_1 minimum.

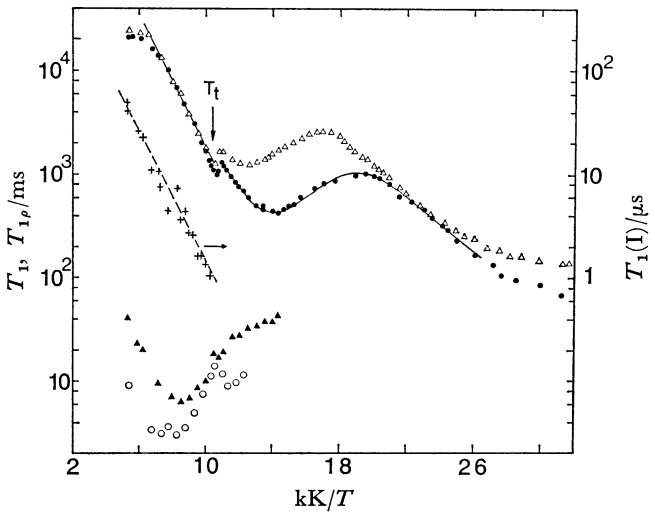

Fig. 6. The spin-lattice relaxation times of protons in $(CH_3NH_3)_2TeI_6$ against kK/T.
●: T_1 at 20 MHz, △: T_1 at 60 MHz, ○: $T_{1\rho}$ at 5 G, ▲: $T_{1\rho}$ at 10 G, and +: T_1(I) calculated from Eq. 5.

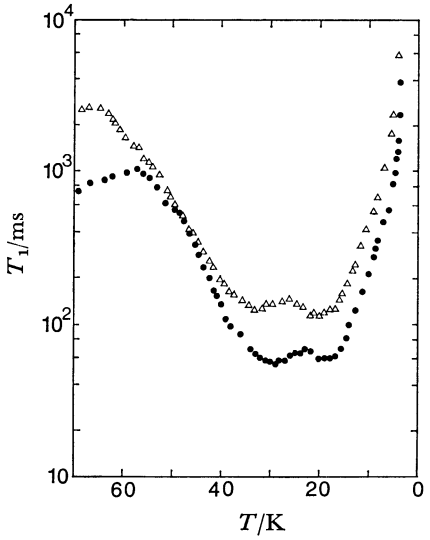

Fig. 7. The spin-lattice relaxation times of protons in $(CH_3NH_3)_2TeI_6$ against T below 70 K.
●: 20 MHz and △: 60 MHz.

are much greater than that expected for the classical C_3 reorientation. The second moment, evaluated from the solid-echo envelope,[17] was 9.5 ± 1.5 G^2 even at 4.2 K. This value is much smaller than the theoretical one of 29.8 G^2 for the MA^+ ion in its stationary state, but close to that for the rapidly reorienting MA^+ ion about its C_3-axis.[5] Additionally, the linear portion of the high-temperature side of the deep T_1 minima gives a very low E_a value of 2.7 kJ/mol. All of these results suggest the existence of tunneling-assisted relaxation in the present system.[18] Considering the transitions among tunneling sublevels in the torsional states of the CH_3 or NH_3 groups, Haupt proposed the following expression of the relaxation rate:[19]

$$T_1^{-1} = AJ(\omega_t \pm n\omega_0) = \frac{A\tau}{1+(\omega_t \pm n\omega_0)^2\tau^2}, \quad (4)$$

where A is a constant, ω_t is the tunnel-splitting frequency, and $n=1$ or 2. If $\omega_t \gg \omega_0$, the relaxation rate due to the intramolecular dipolar coupling associated with $J(\omega_t \pm n\omega_0)$ becomes frequency-independent, while the rate due to the intermolecular one is of the usual BPP type.[20] Therefore, two T_1 minima should be observed, one at $\omega_t\tau=1$ and the other at $\omega_0\tau=0.62$. The T_1 minima in Fig. 7 are frequency-dependent, but to a lesser extent than would be expected from the BPP theory; that is, the ratio, $(T_{1\,min})^{60\,MHz}/(T_{1\,min})^{20\,MHz}$, which is equal to 3 in the classical dipolar relaxation, is less than 2 in the present case. Although this T_1 behavior can be explained qualitatively in terms of $J(\omega_t \pm n\omega_0)$, it is difficult to deduce the tunneling frequency because two spin systems (CH_3 and NH_3) complicate the problem and because it has not been established that all the MA^+ ions are equivalent in LTP. It is desirable to measure the T_1 and $T_{1\rho}$ of selectively deuterated CH_3ND_3 or CD_3NH_3 salts as well as to determine the crystal structure of LTP.

The activation energy, E_a, for the MA reorientation changes greatly with X in $(MA)_2TeX_6$, as Table 1 shows. The order of the E_a values is the same as that of the electronegativity of halogens in the complex ions. Quite a similar inclination of the E_a value was discussed above for $(MA)_2MCl_6$ with M=Pt, Sn, and Te. Therefore, the differences in the potential barrier among the present tellurium compounds may be determined mostly by the electrostatic interaction between NH_3 groups and halogens in complex ions.

By fitting the experimental points between 110 and 42 K to Eq. 3 ($\omega_0\tau_1 \ll 1$), the shallow T_1 minimum for the motion specified by τ_2 is determined to be 490 ms at 20 MHz. This value is comparable to those of the other MA-compounds and also to the calculated one for the uncorrelated rotation of the MA^+ ion.[5] The E_a value of 5.0 kJ/mol, however, is significantly smaller than those (8—9 kJ/mol) of the others. The difference in E_a seems to be large in contrast with our estimate of a nearly constant energy.[5] Therefore, it may be acceptable to consider that some other relaxation processes, for example, a tunneling or 180° flip of the MA^+ ion, exist in this temperature range in addition to that of the foregoing two motional modes. It may be also plausible to anticipate that the geometry of the MA^+ ion in the present complex is not the same as that in the earlier complexes because of the difference in interionic interactions or packing of the ions in the crystal.

In RTP, the log T_1 value decreases linearly with $1/T$ from room temperature to T_t; the slope of the decrease gives the E_a value of 6.1 kJ/mol. Since the crystal structure is cubic and the proton second moment is only 0.5 G^2 in this phase, this relaxation process is ascribable to the overall reorientation of the dumbbell-like cation.

The observed values of the proton $T_{1\rho}$, on the other hand, behave unusually in RTP. Contrary to the $T_{1\rho}$ expression based on the BPP theory, the $T_{1\rho}$ minimum at the r.f. strength, H_1, of 5 G appeared at a higher temperature than that of the $T_{1\rho}$ at 10 G. Furthermore, on the high-temperature side of both

$T_{1\rho}$ minima, the $T_{1\rho} \propto H_1^2$ relation holds for the six observed $T_{1\rho}$ values in the H_1 range of 2.5—15 G. Such anomalous behavior suggests an intermolecular dipolar relaxation of the second kind between the protons and iodine nuclei.[21] The overall rotation of the MA^+ ion may result in a large fluctuation of the EFG at the site of iodine, in contrast to its C_3 reorientation, which affects the EFG only slightly. This fluctuation shortens the iodine spin-lattice relaxation time $T_1(I)$. Thus, the dipole interaction between the protons and iodine nuclei affects the proton $T_{1\rho}$ through the cross relaxation. This type of relaxation is expressed as follows:[22]

$$T_{1\rho}^{-1} = M_2(\text{H-I})\gamma_H^2 T_1(I)/[1+\omega_1^2 T_1(I)^2], \quad (5)$$

where M_2(H–I) is the proton second moment due to the H–I dipole interaction and where $\omega_1=\gamma_H H_1$. The value of M_2(H–I) was estimated to be 0.078 G^2 from the $T_{1\rho}$ minimum. Then, the $T_1(I)$ value was obtained by substituting the known parameters into Eq. 5. The results are also included in Fig. 6. It may be noted that the $T_1(I)$ of 50 μs at room temperature shortens with decreasing temperature, while retaining the same slope as that of the proton T_1 above T_t. This finding is strong evidence for the idea that the proton $T_{1\rho}$ is governed by the proton–iodine interaction modulated *via* the overall reorientation of the MA^+ ion. On a lowering of the temperature, the $T_1(I)^{-1}$ becomes large beyond the order of the usual NQR linewidth. This is a reason why the NQR signal fades out below 156 K.[7]

The authors are grateful to Professor Emeritus Ryôiti Kiriyama of Osaka University and Professor Daiyu Nakamura of Nagoya University for their continued interest and encouragement.

References

1) R. W. G. Wyckoff, *Am. J. Sci.*, **16**, 349 (1928).
2) Y. Kume, R. Ikeda, and D. Nakamura, *J. Magn. Reson.*, **20**, 276 (1975).
3) Y. Kume, R. Ikeda, and D. Nakamura, *J. Magn. Reson.*, **33**, 331 (1979).
4) Y. Furukawa, H. Kiriyama, and R. Ikeda, *Bull. Chem. Soc. Jpn.*, **50**, 1927 (1977).
5) R. Ikeda, Y. Kume, D. Nakamura, Y. Furukawa, and H. Kiriyama, *J. Magn. Reson.*, **24**, 9 (1976).
6) K. Kitahama, H. Kiriyama, and Y. Baba, *Bull. Chem. Soc. Jpn.*, **52**, 324 (1979).
7) Y. Kume, R. Ikeda, and D. Nakamura, *J. Phys. Chem.*, **82**, 1926 (1978).
8) K. Kitahama and H. Kiriyama, *Acta Crystallogr., Sect. A*, **34**, S302 (1978).
9) D. Brinkmann and W. Freudenreich, *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.*, **143**, S67 (1976).
10) J. van Kranendonk, *Physica.*, **20**, 781 (1954).
11) M. Goldman, "Spin Temperature and Nuclear Magnetic Resonance in Solids," Oxford Univ. Press, England (1970), Chap. 3.
12) H. M. Van Driel, M. Wiszniewska, B. M. Moores, and R. L. Armstrong, *Phys. Rev. B*, **6**, 1596 (1972).
13) M. Wiszniewska and R. L. Armstrong, *Can. J. Phys.*, **51**, 781 (1973).
14) D. E. Woessner, *J. Chem. Phys.*, **42**, 1855 (1965).
15) S. Albert and J. A. Ripmeester, *J. Chem. Phys.*, **58**, 541 (1973).
16) P. S. Allen and S. Clough, *Phys. Rev. Lett.*, **22**, 1351 (1969).
17) J. G. Powles and J. H. Strange, *Proc. Phys. Soc.*, **82**, 6 (1963).
18) P. S. Allen, *J. Chem. Phys.*, **48**, 3031 (1968).
19) J. Haupt, *Z. Naturforsch., Teil A*, **26**, 1578 (1971).
20) W. Güttler and J. U. Von Schültz, *Chem. Phys. Lett.*, **20**, 133 (1973).
21) R. Blinc, J. Pirš, and S. Žumer, *Phys. Rev. B*, **8**, 15 (1973).
22) N. Bloembergen and P. P. Sorokin, *Phys. Rev.*, **110**, 865 (1958).