February, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***60***, *463—466 (1987)*

# Cationic Motions and Phase Transitions in $[(CH_3)_4N]GaBr_4$ Crystals as Studied by $^1H$ NMR and Differential Thermal Analysis Techniques

Setsuko SATO and Daiyu NAKAMURA*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

(Received August 6, 1986)

Two phase transitions were located for solid $[(CH_3)_4N]GaBr_4$ at 404 and 138 K. The temperature dependences of $^1H$ NMR spin-lattice relaxation times were determined mainly at 20 MHz. A shallow $^1H$ $T_1$ minimum appearing at ca. 400 K and a deep one below ca. 250 K were observed. The latter minimum could be explained by the occurrence of the overall reorientation of the cation as a whole with an activation energy of 14.5 kJ mol$^{-1}$. The shallow $^1H$ $T_1$ minimum may come from temperature dependent quadrupolar relaxation of bromine nuclei through the dipolar relaxation of the second kind.

Dynamical behavior of tetramethylammonium, (tetMA)$^+$, cations in various crystalline salts has been extensively studied mainly using $^1H$ NMR techniques,[1-13] because of several motional modes of the cation expected to be activated with increasing temperature. The motions of the cation which contribute to $^1H$ spin-lattice relaxation time, $T_1$, around room temperature were shown in various solids to be random reorientation of the $CH_3$ groups about each C-N bond axis by 120°, i.e., the $CH_3$ $C_3$ reorientation, and the overall reorientation of the cations about the center of gravity.

In some crystals such as (tetMA)X (X=Cl, Br, I),[3] the above two kinds of motional modes are activated successively at well-separated temperatures. However, it is shown from our NMR studies on $(tetMA)_2MX_6$[10,11] and $(tetMA)_2CdX_4$[12] type complexes and some clathrate hydrates of (tetMA)OH[13] that the above reorientational processes of the cation do not necessarily take place step by step distinctly with changing temperature. The present investigation of the motion of (tetMA)$^+$ cations in $(tetMA)GaBr_4$ crystals has been undertaken to find an example of crystals in which the cation performs a different type of motions from those already clarified.

## Experimental

At first, we carried out synthetic experiments to obtain $(tetMA)_2Ga_2Br_6$ according to the method described in literature[14] except adding bromine. The synthetic procedure was as follows. Granular gallium was dissolved in hydrobromic acid involving bromine in a temperature range of 70—80 °C. When (tetMA)Br was added to the resulting solution, a white precipitate was obtained from the hot solution. When the solution was cooled to room temperature, the precipitate completely dissolved. The precipitate obtained at higher temperatures was $(tetMA)GaBr_4$ in contrast to the product reported in the literature.[14] The existence of $[GaX_4]^-$ (X=Cl, Br) had been reported elsewhere.[15,16] Purification was made by successive recrystallizations from a warm hydrobromic acid solution and finally from a $CH_3NO_2$ solution. Anal. Calcd for $[(CH_3)_4N]GaBr_4$: C, 10.4; H, 2.6%. Found: C, 10.4; H, 2.6%. The sample prepared was further identified by taking far IR spectra. The $\tilde{\nu}_3$ band of $[GaBr_4]^-$ was observed at 273 cm$^{-1}$ with a shoulder at 280 cm$^{-1}$ as already reported for the same complex.[16]

$^1H$ $T_1$ was measured at various temperatures by use of pulsed NMR spectrometers already reported[10,17] at the Larmor frequencies of 20 and 10.5 (partly) MHz. The conventional inversion method to observe free induction decay signals was employed to determine $T_1$ values. Differential thermal analysis (DTA) experiments were carried out with a homemade apparatus already described.[18] Temperatures in the above two kinds of experiments were determined employing a copper vs. constantan thermocouple and could be estimated to be accurate within ±1 K. The 2nd moments of $^1H$ NMR absorptions were determined by means of a JEOL-MW-40S spectrometer at several temperatures measured with an accuracy of ±3 K.

## Results and Discussion

Since many kinds of crystals involving (tetMA)$^+$ cations are known to exhibit structural phase transition in their solid phase,[3-7,9-13] we carried out the experiments of DTA. When the sample at room temperature was cooled to 80 K, no heat anomaly could be detected as shown in Fig. 1. However, a broad and small endothermic anomaly was recorded at ca. 138 K with increasing temperature fairly rapidly (≈3.4 K min$^{-1}$). When the sample was heated from room temperature, an endothermic anomaly showing marked thermal hysteresis appeared at 404 K. Accordingly, it can be concluded that $(tetMA)GaBr_4$ crystals undergo a first order phase transition at 404 K and an unusual small phase transition at ca. 138 K.

The temperature dependences of $^1H$ $T_1$ observed at 20 MHz in a temperature range of 96—440 K and at 10.5 MHz between 246 and 435 K are shown in Fig. 2.

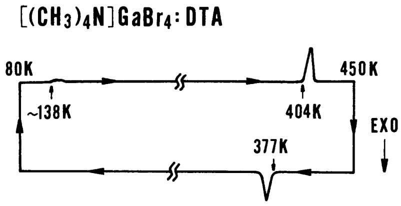

Fig. 1. Differential thermal analysis curves recorded for $[(CH_3)_4N]GaBr_4$.

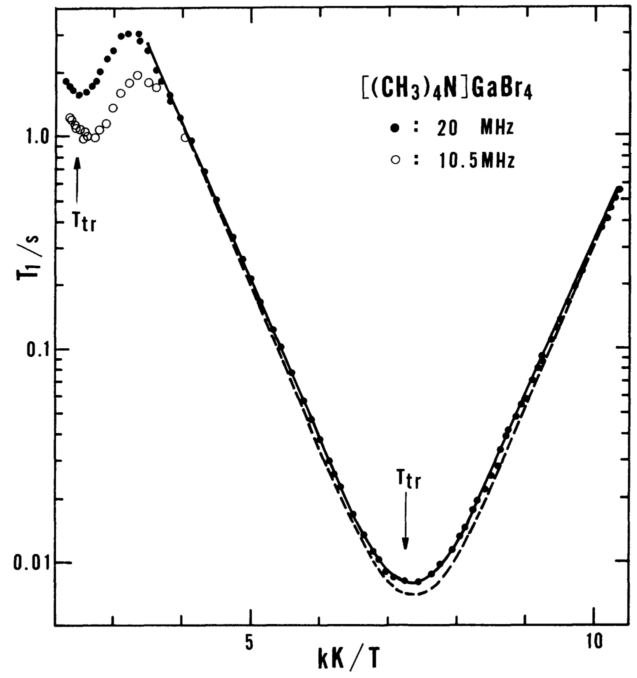

Fig. 2. Temperature dependence of $^1$H $T_1$ observed for $[(CH_3)_4N]GaBr_4$ at 20 (●) and 10.5 (○) MHz. Solid and broken lines indicate the calculated curves using the BPP theory and the Takeda et al. method, respectively. $T_{tr}$ indicates the phase transition temperatures determined from differential thermal analysis.

Below ca. 250 K, $^1$H $T_1$ values determined formed a deep V-shaped curve, the minimum value of which was 8 ms obtained at ca. 135 K. On the other hand, $^1$H $T_1$ values observed above ca. 250 K deviated from the V-shaped curve with increasing temperature and yielded a maximum around 310 K, above which temperature a very shallow $T_1$ minimum was obtained at ca. 400 K when observation was made at the Larmor frequency of 20 MHz. In this paper we mainly discuss about the $T_1$ curve having the deep minimum.

To assign the deep $T_1$ minimum to the motional mode of the cation, we determined the $^1$H NMR 2nd moment, $M_2$, at several temperatures. The results are as follows: 24 G$^2$ at 77 K, 0.4 G$^2$ at 135, 167, and 215 K, $0.3_6$ G$^2$ at 298 K, and $0.3_4$ G$^2$ at 425 K. The rigid lattice $M_2$ value of an isolated (tetMA)$^+$ cation was calculated in a previous report[10] as 26.72 G$^2$ by use of the geometrical data reported by Andrew and Canepa.[1] For the present complex, the $M_2$ value observed at 77 K is very near to and only slightly smaller than the rigid lattice value. This suggests that the motions of the cation in (tetMA)$GaBr_4$ crystals are almost frozen at 77 K. On the other hand, very sharp $^1$H NMR absorption lines were recorded above 135 K, indicating that the cations perform isotropic reorientation in the crystal. Accordingly, the deep $T_1$ minimum can be attributed to the isotropic reorientation, i.e., the $C_2$ and $C_3$ reorientations of the whole cation with or without the $CH_3$ $C_3$ reorientation of the four $CH_3$ groups.

According to the BPP theory,[19] $T_1$ due to magnetic dipolar relaxation mechanism can be written as

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

Here, $\omega$, $C$, and $\tau$ represent the angular Larmor frequency employed, the motional constant, and the correlation time for the motion, respectively. By assuming the Arrhenius relation for the correlation time, one has

$$\tau = \tau_0 \exp(E_a/RT), \tag{2}$$

where $\tau_0$ is the correlation time at the limit of infinite temperature and $E_a$ is the activation energy for the motion.

$^1$H $T_1$ values observed below ca. 250 K were fitted to Eqs. 1 and 2 using $E_a$ and the $T_1$ minimum values determined experimentally. The values of $E_a$ and the $T_1$ minimum were 14.5 kJ mol$^{-1}$ and 8 ms, respectively. The calculated BPP curve agrees very well with the observed data, suggesting that the motion of the cation can be described by a single motional mode, possibly the isotropic overall reorientation of the cation as a whole. However, we cannot say whether or not the $CH_3$ $C_3$ reorientation is involved in the cationic motional process giving rise to the deep $T_1$ minimum. The present type of motional process activated for (tetMA)$^+$ cations is a unique example in various crystalline salts containing the cation ever studied.

To confirm the adequacy of the above interpretation of the deep $T_1$ minimum obtained, we calculated quantitatively the $T_1$ curve based on the more general method developed by Takeda et al.,[20] which has been successfully employed for the analysis of the $T_1$ data obtained for some (tetMA)$^+$ salts of cadmium(II) complexes[12] and also clathrate hydrates of (tetMA)OH.[13]

In this calculation, each $^1$H-$^1$H vector involved in the $CH_3$ $C_3$ reorientation, the cationic reorientation about its $C_3$ axes, and that about its $C_2$ axes was assumed to jump at the rates of $\omega_{CH_3}$, $\omega_3$, and $\omega_2$, respectively, which gave transition matrices for intramethyl and intermethyl $^1$H-$^1$H vectors. The transition matrices constructed at a given temperature were diagonalized numerically, where $\omega_{CH_3}$, $\omega_3$, and $\omega_2$ were given as reciprocals of $\tau$ values expressed by Eq. 2 with $E_a$ and $\tau_0$ taken as adjustable parameters. For $\omega_3$ and $\omega_2$, the same $E_a$ but the different $\tau_0$ values were assumed. To obtain good agreement between the observed values and the calculated curve, the $E_a$ value of $14._8$ kJ mol$^{-1}$ was employed, which is slightly different from the foregoing value obtained from the BPP analysis. The bond lengths of C-H and C-N were assumed to be 1.09 and 1.50 Å, respectively, according to Albert et al.,[3] while the all bond angles of the cation to be tetrahedral. The present geometry is thought to be more suitable to check the adequacy of the above discussion than that of Andrew and Canepa[1] because the present complex will form loosely packed crystals in contrast to those of (tetMA)X (X=Cl, Br, I) studied by Albert et al.[3] The calculated curve with the values of $E_a=14._8$ kJ mol$^{-1}$ and $\tau_0=1._3\times10^{-13}$ s for the all reorientations of the CH$_3$ $C_3$ and the whole cationic $C_2$ and $C_3$ is shown in Fig. 2. The calculated curve explains still fairly well the observed values although the $T_1$ minimum calculated is slightly smaller than the observed one.

In the above calculation, we assumed that the CH$_3$ $C_3$ and the overall cationic reorientations are activated simultaneously with the same $E_a$ value. However, it is possible to assume alternatively that the overall reorientation of the cations occurs from lower temperatures with $E_a$ similar to the above value whereas the CH$_3$ $C_3$ reorientation is activated at higher temperatures with a larger $E_a$ value. In other words, we regarded the cation itself as in a rigid state with no CH$_3$ $C_3$ reorientation in the present temperature region. Even in this case, the same calculated $T_1$ curve could be obtained by taking very large $E_a$ for the CH$_3$ $C_3$ process such as 50 kJ mol$^{-1}$.

When the cation keeping the four CH$_3$ groups in rigid performs overall reorientation rapidly, $^1$H-$^1$H dipole interactions in the cation are completely averaged out. This means that any $M_2$ reduction does not occur even if the CH$_3$ $C_3$ reorientation is activated at a temperature higher than the $T_1$ minimum temperature at ca. 135 K. Therefore, we can say for this complex that the CH$_3$ $C_3$ reorientation occurs rapidly enough at the $T_1$ minimum temperature with the same $E_a$ of $14._8$ kJ mol$^{-1}$ as that of the overall reorientation or at a higher temperature than ca. 135 K, and we cannot determine which is the true situation for this complex.

The present $E_a$ value for the overall reorientation of the cation is very small indicating that the cation experiences a weak crystal field. Previously, we observed the small-angle reorientation of each CH$_3$ group of the cation in a lower temperature region of some hexahalometallates(IV) forming high symmetric crystals.[10,11] In these crystals, the cation also undergoes weak crystal field. For the present complex, however, we did not detect the small-angle reorientation of the CH$_3$ groups.

Since no structural data of the (tetMA)GaBr$_4$ crystal were available, we took X-ray powder patterns at room temperature by means of a Model VD-1A X-ray diffractometer from Shimadzu Seisakusho Co. However, the patterns shown in Fig. 3 could not be explained in terms of a cubic or a tetragonal crystal system indicating that (tetMA)GaBr$_4$ forms a crystal structure of lower symmetry. From the appearance of a shoulder for the IR $\tilde{\nu}_3$ band of [GaBr$_4$]$^-$ in solid (tetMA)GaBr$_4$,[16] it can be said that the complex anion is located on a site having lower symmetry than cubic. Accordingly, it is highly probable that the cation is also located on a lower symmetry site. This may be the reason why the small-angle reorientation was not observed in the present complex.

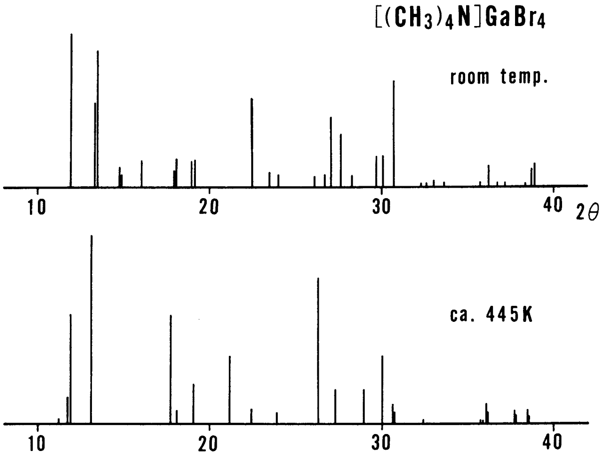

Fig. 3. X-Ray powder patterns taken at room temperature and at ca. 445 K for [(CH$_3$)$_4$N]GaBr$_4$.

In the higher temperature region above room temperature, (tetMA)GaBr$_4$ yielded a first order phase transition at 404 K. To know something about the crystal structure of the high temperature phase, we took X-ray powder patterns at ca. 445 K and obtained simpler patterns than those recorded at room temperature as shown in Fig. 3. The strong diffraction lines can be approximately interpreted in terms of a cubic structure with a lattice constant of ca. 15 Å. Since those strong lines have very weak side lines unexplainable by the cubic system, however, the crystal structure might belong to a less symmetric system, possibly a monoclinic one which is very close to the cubic system. It is very interesting that the phase transition did not give any detectable influence on the temperature dependence of $^1$H $T_1$. This suggests that the motional state of the cation is not directly altered above and below the phase transition.

To obtain information for the characterization of the shallow $T_1$ minimum, we observed $^1$H $T_1$ by a different Larmor frequency of 10.5 MHz as shown in Fig. 2. $^1$H $T_1$ observed at both frequencies showed a clear frequency dependence in a temperature region of the shallow $T_1$ minimum. However, the ratios of $T_1$ values determined at the two frequencies measured at a given temperature were not $\omega^2$ but nearly $\omega$. This indicates that the relaxation mechanism yielding the shallow minimum cannot be attributed to the simple BPP type. Also the 2nd moment at 425 K was almost the same as that at room temperature, this is, no drastic decrease of the 2nd moment was found. The facts indicate that this $T_1$ minimum cannot be explained through a simple dipolar relaxation mechanism such as the self-diffusion of the cations. In a previous paper,[12] a $^1$H $T_1$ decrease with increasing temperature observed at higher temperatures for (tetMA)$_2$CdBr$_4$ and (tetMA)$_2$CdI$_4$ was attributed to the $^1$H relaxation through magnetic interactions between $^1$H and halogen nuclei, where the quadrupolar relaxation of bromine and iodine nuclei, respectively, is very fast because of a fluctuating electric field gradient possibly by the molecular or anionic reorientation. This relaxation mechanism named as dipolar relaxation of the second kind[21)] may be the main origin for the present shallow $T_1$ minimum. The appearance of the $T_1$ minimum suggests that $[GaBr_4]^-$ reorients more rapidly than $[CdBr_4]^{2-}$ in almost the same high temperature region.

## References

1) E. R. Andrew and P. C. Canepa, *J. Magn. Reson.*, **7**, 429 (1972).

2) M. Mahajan and B. D. Nageswara Rao, *J. Phys. C*, **7**, 995 (1974).

3) S. Albert, H. S. Gutowsky, and J. A. Ripmeester, *J. Chem. Phys.*, **56**, 3672 (1972).

4) A. A. V. Gibson and R. E. Raab, *J. Chem. Phys.*, **57**, 4688 (1972).

5) H. Rager and A. Weiss, *Z. Phys. Chem.*, **NF93**, 299 (1974).

6) T. Tsuneyoshi, N. Nakamura, and H. Chihara, *J. Magn. Reson.*, **27**, 191 (1977).

7) H. Rager and A. Weiss, *Ber. Bunsenges. Phys. Chem.*, **80**, 138 (1976).

8) H. Rager and A. Weiss, *Ber. Bunsenges. Phys. Chem.*, **82**, 535 (1978).

9) T. Tsang and D. B. Utton, *J. Chem. Phys.*, **64**, 3780 (1976).

10) L. S. Prabhumirashi, R. Ikeda, and D. Nakamura, *Ber. Bunsenges. Phys. Chem.*, **85**, 1142 (1981).

11) S. Sato, R. Ikeda, and D. Nakamura, *Ber. Bunsenges. Phys. Chem.*, **86**, 936 (1982).

12) S. Sato, R. Ikeda, and D. Nakamura, *Bull. Chem. Soc. Jpn.*, **59**, 1981 (1986).

13) S. Sato, R. Ikeda, and D. Nakamura, *J. Chem. Soc., Faraday Trans. 2*, **82**, 2053 (1986).

14) C. A. Evans and M. J. Taylor, *Chem. Commun.*, **1969**, 1201.

15) D. F. C. Morris, B. D. Andrews, and E. L. Short, *J. Inorg. Nuclear Chem.*, **28**, 2436 (1966).

16) M. J. Taylor, *J. Chem. Soc. A*, **1968**, 1780.

17) S. Gima, Y. Furukawa, R. Ikeda, and D. Nakamura, *J. Mol. Struct.*, **111**, 189 (1983).

18) Y. Kume, R. Ikeda, and D. Nakamura, *J. Magn. Reson.*, **33**, 331 (1979).

19) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).

20) S. Takeda, G. Soda, and H. Chihara, *Mol. Phys.*, **47**, 501 (1982).

21) M. O. Norris, J. H. Strange, J. G. Powles, M. Rhodes, K. Marsden, and K. Krynicki, *J. Phys. C*, **1**, 422 (1968).