NMR and Dilatometric Studies on $[N(CH_3)_4]_3M_2X_9$ $(M=Sb, Bi; X=Cl, Br)$

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Thermal expansion studies on $[N(CH_3)_4]_3Sb_2Cl_9$ and $[N(CH_3)_4]_3Sb_2Br_9$ are reported. The relaxation times ^1H T_1 were measured for $[N(CH_3)_4]_3Bi_2Cl_9$, $[N(CH_3)_4]_3Sb_2Br_9$, and $[N(CH_3)_4]_3Bi_2Br_9$ in the temperature range 100–290 K. To interpret the T_1 data on $[N(CH_3)_4]_3Bi_2Cl_9$ the method of T_1 calculation reported by Takeda *et al.* has been applied successfully. Two different, inequivalent types of $[N(CH_3)_4]_3^+$ cations for all tetramethylammonium crystals are found.

Key words: Tetramethylammonium crystals; Phase transitions; Thermal expansion; ^1H spin-lattice relaxation time.

1. Introduction

Alkylammonium halogenoantimonates(III) and bismuthates(III) of the type $[NH_{4-n}(CH_3)_n]_3M_2X_9$ (M = Sb, Bi, X = Cl, Br, I) have been the subject of many investigations. The dynamics of alkylammonium cations is found to be playing a dominant role in numerous structural [1–4], ferroelastic [5] and ferroelectric phase transitions (PT) [6, 7]. Dielectric [8], dilatometric [9], DSC [8] and NQR [2] studies on tetramethylammonium compounds in this family indicate the structural PTs of an order-disorder type: $[N(CH_3)_4]_3Sb_2Cl_9$ (TEMACA) at 223 K (2nd order) and 156 K (1st order), $[N(CH_3)_4]_3Sb_2Br_9$ (TEMABA) at 174 K and 112 K (both of 1st order), $[N(CH_3)_4]_3Bi_2Cl_9$ (TEMACB) at 155 K (1st order) and $[N(CH_3)_4]_3Bi_2Br_9$ (TEMABB) at 183 K (1st order). All above tetramethylammonium crystals have hexagonal $P6_3/mmc$ symmetry in the high temperature phase. The atomic positions are known only for two analogues: TEMACA [2] and TEMABA [10]. The earlier NMR studies on TEMACA by Medycki et al. [11] have revealed that two inequivalent tetramethylammonium cations undergo complex motions. On the other hand, the recent NMR studies on the same crystal reported by Jagadeesh et al. [12] have been interpreted as due to the isotropic tumbling of tetramethylammonium cations (TEMA). The TEMA dynamics is less hindered in the high temperature phase compared to the low temperature one (T_c = 223 K). The 156 K PT was not visible in the NMR studies. In order to obtain more information about the cationic motion for the remaining tetramethylammonium compounds; TEMACB, TEMABA and TEMABB, the ^1H spin lattice relaxation time has been measured. To clarify the nature of the PTs in TEMACA and TEMABA precise dilatometric studies have been performed.

2. Experimental

2.1. Samples

Single crystals of $[N(CH_3)_4]_3M_2X_9$ (X = Cl, Br) were grown by slow evaporation from aqueous solution, containing 3:2 mole fraction of $[N(CH_3)_4]OH$ and Sb_2O_3 or Bi_2O_3 with a great excess of HCl or HBr.

2.2. Thermal Expansion

The linear thermal expansion was measured by a thermomechanical analyzer Perkin-Elmer TMS-2. The studies were made in the heating and cooling mode at rates of 0.1–0.2 K/min. The anomalies were reproducible within 10% for each sample. The accuracy of the thermal expansion determination is about 2%. The samples had dimensions of 4 mm along the *a*-axis and 1.5–2 mm along the *c*-axis.

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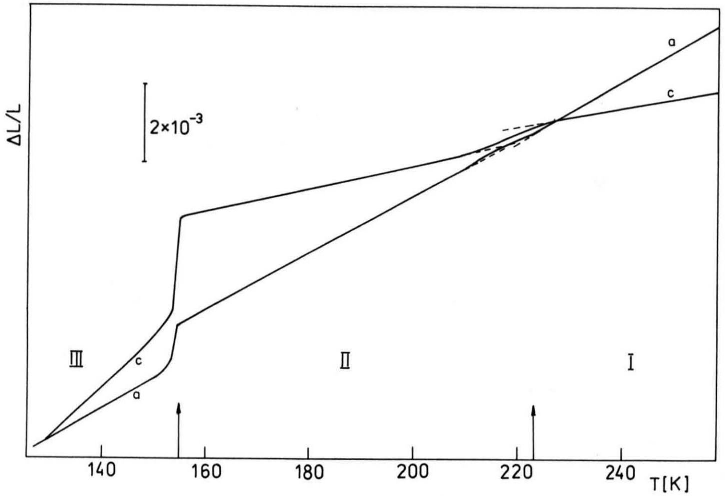
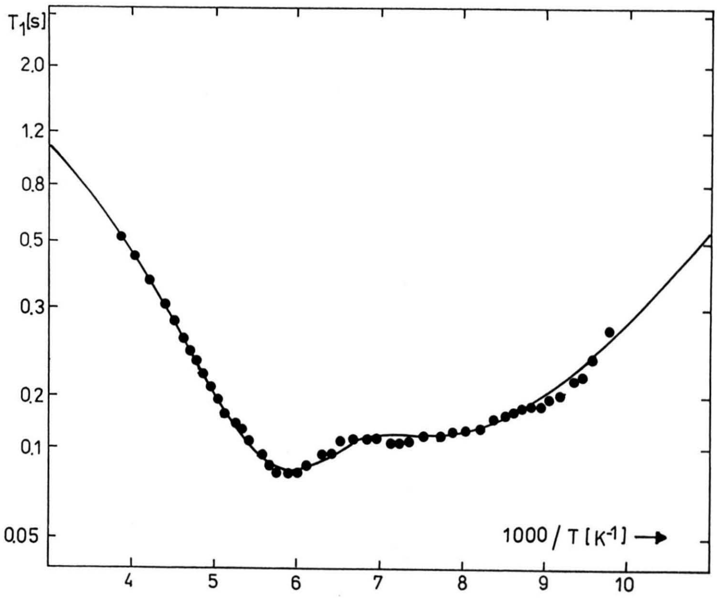


Fig. 1. Thermal expansion of $[N(CH_3)_4]_3Sb_2Cl_9$ (TEMACA) crystal along the *a*- and the *c*-axis.



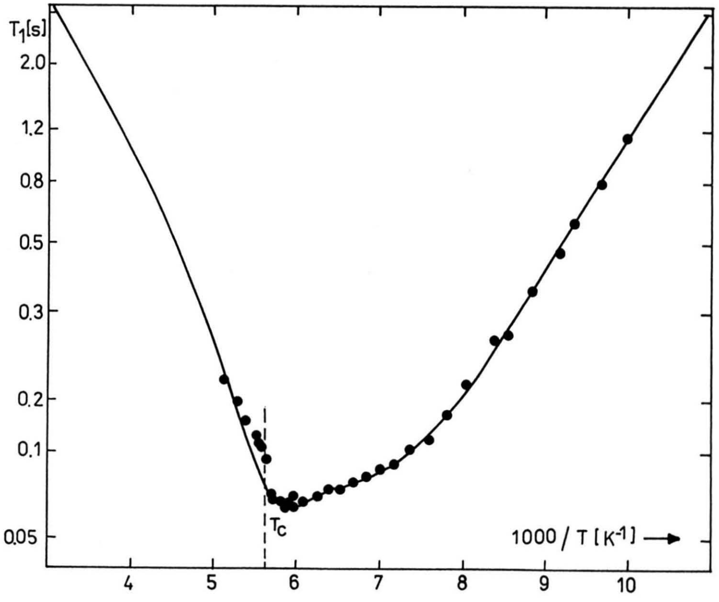


Fig. 4. Proton spin-lattice relaxation time (T_1) vs. temperature (T) in TEMABA. The solid line is the best fitted curve.

Fig. 5. Proton spin-lattice relaxation time (T_1) vs. temperature (T) in TEMABB. The solid line is the best fitted curve.

2.3. *NMR*

The ^1H relaxation time T_1 was measured with an SXP 4/100 Bruker pulse spectrometer at 90 MHz, within the temperature range 100–290 K. The crystals were powdered for the measurements. The relaxation time T_1 was measured with the magnetization recovery method $\pi-\tau-\pi/2$. The temperature was stabilized with a BS 100/700 temperature controller with an accuracy of 1 K.

3. Results and Discussion

3.1. *Thermal Expansion*

Figure 1 shows the thermal expansion of $[N(CH_3)_4]_3Sb_2Cl_9$ along the *a*- and *c*-axis on heating. It can be seen that the weak thermal anomaly at about 220 K corroborates the continuous character of the PT at 223 K found in the dielectric measurements [8]. A clear sharp anomaly observed in the vicinity of 155 K corresponds to the 1st order PT visible as well in DSC and dielectric studies [8]. Above $T_{c\,(II-III)}$, within the phases I and II TEMACA expands linearly with thermal expansion coefficients: $\bar{\alpha}_c = 3 \times 10^{-5}\ K^{-1}$, $\bar{\alpha}_a = 7.5 \times 10^{-5}\ K^{-1}$ (the mean value of α is defined as $(\Delta L_1 - \Delta L_2)/L_{0\,(300\,K)}(T_1 - T_2)$.

The thermal dilatation, $(\Delta L/L)$, along the *a*- and the *c*-axis for $[N(CH_3)_4]_3Sb_2Br_9$ in the temperature range 80–170 K (on heating) is shown in Figure 2. A distinct anomaly at 177 K, seen as contraction along the *a*-axis and dilation along the *c*-axis with decreasing temperature, corresponds to the PT found by DSC and dielectric techniques [8]. It is also known from these studies that TEMABA undergoes one low temperature PT at 114 K. Our dilatometric measurements for the lowest temperature range revealed the complex picture of dilation both along the *a*- and the *c*-axis (see Figure 2). Starting from higher temperatures, it is clearly seen that the strong anomaly of thermal expansion around 115 K is preceeded by a rather week anomaly at about 119 K. The last anomaly possesses a distinct jump of $(\Delta L/L)$ along the *a*-axis and a change of the sign of the temperature expansion coefficient, α, for the *c*-axis.

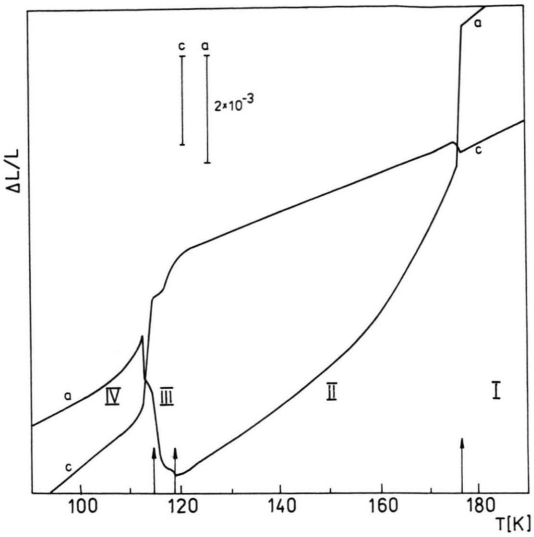


Fig. 2. Thermal expansion of $[N(CH_3)_4]_3Sb_2Br_9$ (TEMABA) crystal along the *a*- and the *c*-axis.

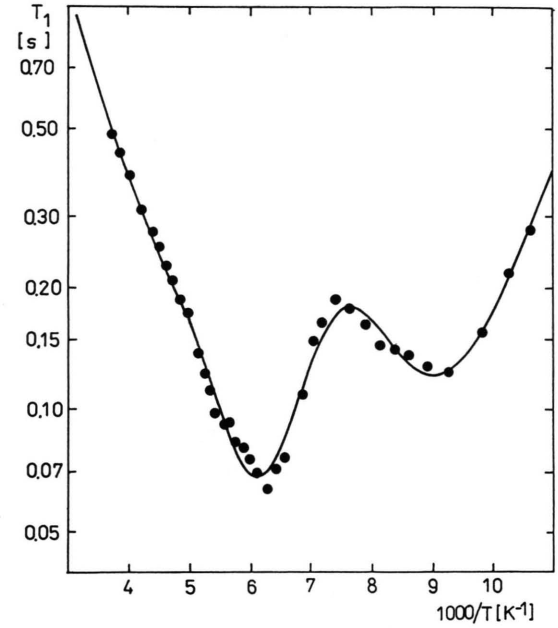


Fig. 3. Proton spin-lattice relaxation time (T_1) vs. temperature (T) in TEMACB. Circles: experimental points. Solid line: the best fitted curve according to (1).

It is very probable that the above anomaly at 119 K is related with an additional structural PT in TEMABA and exhibits features between the 1st and the 2nd order type. Precise calorimetric studies for this temperature range are needed to confirm such sequence of the PTs. The spontaneous changes of lenghts along the *a*- and *c*-axes close to PT points for TEMACA and TEMABA are listed in Table 1. The pressure coefficients of the transition temperature, dT_c/dp, can be estimated from the Clausius-Clapeyron relation: $dT_c/dp = \Delta V/\Delta S$, where ΔV is the change in molar volume at T_c and ΔS is the entropy change taken from [8].

Summarizing the dilatometric studies on tetramethylammonium crystals of $[N(CH_3)_4]_3M_2X_9$ one can state:

1. Structural 1st order PTs existing in all tetramethylammonium crystals of $[N(CH_3)_4]_3M_2X_9$ type, between 150–185 K, (TEMACA 155 K, TEMACB 152 K, TEMABA 177 K and TEMABB 183 K) reveal a considerable similarity with respect to the thermal expansion properties. It suggests a similar mechanism of these PTs.
2. TEMABA appeared to be an exception in this family showing a complex sequence of the PTs the lowest temperature range. It is interesting to notice that the PT at 115 K has a negative pressure coefficient (see Table 1). The origin of this transformation is unclear, and additional studies are needed.

3.2. *NMR Results*

The temperature dependence of ${}^{1}H$ T_1 for TEMACB is shown in Figure 3. The chlorine analogue exhibits two considerably well-separated T_1 minima, 120 ms and 65 ms at 110 and 152 K, respectively. The structural phase transition at 155 K detected by NQR [2] and dilatometric [9] methods is not visible in temperature T_1 measurements at 90 MHz.

It is known from crystallographic studies performed on TEMABA [10] and very recently on TEMACA [2] that these crystals are isomorphous at room temperature. Tetramethylammonium cations occupy two different positions in the unit cell, which suggests some difference in their motional state. Generally, in the unit cell there are four crystallographically equivalent cation positions of a type we denote as A-type and two crystallographically equivalent cation positions of an other type we denote as B-type. For simplicity we shall use the designations A cation and B type cation.

Table 1. Spontaneous changes of length along the *a*- and *c*-axis and volume, and the pressure coefficients (dT_c/dp) at the transition temperatures of $[N(CH_3)_4]_3Sb_2Cl_9$ and $[N(CH_3)_4]_3Sb_2Br_9$.

T_c/K	Axis	$\Delta L/L$ $\times 10^{-3}$	$\Delta V/V$ $\times 10^{-3}$	ΔS $\mathrm{J\,mol^{-1}\,K^{-1}}$	dT/dp $\times 10^{-2}$ $\mathrm{kMPa^{-1}}$
TEMACA					
155	*a* *c*	+1.42 +2.33	+4.79	10.5	+10.8
TEMABA					
177	*a* *c*	+3.22 −0.36	+5.22	11.0	+25.0
115	*a* *c*	−2.60 +3.70	−0.80	6.3	− 6.7

Table 2. Activation energies E_a and correlation times τ_0 for ${}^{1}H-{}^{1}H$ vector jump rates of the $[N(CH_3)_4]^+$ cation of $[N(CH_3)_4]_3M_2X_9$ (M = Sb, Bi, X = Cl, Br).

Jump rate	E_a/kcal mol^{-1}	τ_0/s
	TEMACB	
${}^{A}\tau_{CH_3}^{-1}$	4.0	$2.0 \cdot 10^{-14}$
${}^{A}\tau_2^{-1}$	2.2	$8.2 \cdot 10^{-11}$
${}^{A}\tau_3^{-1}$	2.4	$4.0 \cdot 10^{-11}$
${}^{B}\tau_{CH_3}^{-1}$	3.6	$1.2 \cdot 10^{-14}$
${}^{B}\tau_2^{-1}$	3.5	$3.2 \cdot 10^{-15}$
${}^{B}\tau_3^{-1}$	1.9	$2.0 \cdot 10^{-12}$
	TEMABA	
${}^{A}\tau_{CH_3}^{-1}$	1.2	$3.9 \cdot 10^{-10}$
${}^{A}\tau_2^{-1}, {}^{A}\tau_3^{-1}$	3.7	$2.9 \cdot 10^{-13}$
${}^{B}\tau_{CH_3}^{-1}$,	1.8	$2.5 \cdot 10^{-12}$
${}^{B}\tau_2^{-1}, {}^{B}\tau_3^{-1}$	1.2	$2.3 \cdot 10^{-10}$
	TEMABB	
${}^{A}\tau_{CH_3}^{-1}$	1.5	$1.4 \cdot 10^{-10}$
${}^{A}\tau_2^{-1}, {}^{A}\tau_3^{-1}$	6.9	$3.0 \cdot 10^{-17}$
${}^{B}\tau_{CH_3}^{-1}$,	2.3	$1.2 \cdot 10^{-10}$
${}^{B}\tau_2^{-1}, {}^{B}\tau_3^{-1}$	2.2	$6.8 \cdot 10^{-12}$

To analyze the observed T_1 dependence on temperature for TEMACB we used exactly the same model as presented in our previous paper [11] for TEMACA crystal. The total relaxation rate can be described by the formula

$$T_1^{-1} = 4/6\,[T_{1A}^{-1}] + 2/6\,[T_{1B}^{-1}], \qquad (1)$$

where T_{1A}^{-1} and T_{1B}^{-1} denote the relaxation rates for protons of the cations A and B, respectively. Using the method of Takeda et al. [13] (see also [11]) we fitted our results. The best fitted T_1 curve is presented in Figure 3 by the solid line. The values of the fitted parameters are given in Table 2, where $\tau_{CH_3}^{-1}$ denotes the jump rates of the ${}^{1}H-{}^{1}H$ vectors resulting from the reorientation of the CH_3 groups about their symmetry axes (C_3'), τ_3^{-1} denotes the jump rates of the ${}^{1}H-{}^{1}H$ vectors resulting from the reorientation of the whole cation about its four equivalent C–N bond axes (C_3), and τ_2^{-1} denotes the jump rates of the $^1H-^1H$ vectors resulting from the reorientation about three equivalent two-fold symmetry axes (C_2). When we look on the molecular parameters obtained for both chlorine crystals (for TEMACA see Table 1 in [11]), we can conclude that the molecular dynamics of the tetramethylammonium cations in both crystals are similar. For these crystals it is characteristic that the temperature T_1 curves exhibit two well shaped minima. Different values of T_1 minima give information about the proportion of both types of cations. It is worthy to notice the subtle differences in the behaviour of the A and B type cations. In TEMACA crystal, for A cation the τ_2 and τ_3 correlation times and the respective activation energies of this motion are very similar, which indicates isotropic character of motion of this cation. On the contrary, the dynamic parameters of the B type cation suggest anisotropicity of its motion. In TEMACB the situation is opposite. Here we must stress that TEMACA, in contrary to TEMABA, has at 223 K an additional phase transition. Therefore a quite different dynamic state of the cation should be expected.

The temperature dependences of log T_1 for the bromine crystals TEMABA and TEMABB are presented in Figs. 4 and 5. The bromine analogue, in contrast to the chlorine one, revealed only one broad T_1 minimum (TEMABA, 80 ms at 171 K and TEMABB, 63 ms at 168 K) with a shoulder on the low temperature side. This picture confirms an essential differences in the motional behaviour of the tetramethylammonium cations in bromine crystals in comparison to the chlorine ones, especially in the low temperature region. It should be also stressed that TEMABB reveals a distinct jump in $T_1(T)$ at about 178 K, corresponding to the PT visible by DSC, dilatometric and NQR techniques (183 K) [9, 2].

The above fitting procedure used for the experimental data of the bromine analogues did not allow to obtain satisfactory results. The main reason we consider to be unresolved T_1 minima in these crystals. Therefore it is impossible to determine the mutual proportion of both cation types as it was shown in crystallographical studies. In this paper we have presented results obtained with substantially changed conditions for the fitting procedure. The fit is possible when we take the equivalent cation relation 3:3 (instead 2:4). The obtained activation energies and correlation times are the same as in the cases of C_2 and C_3 motion for both types of cations. Generally, this means that the number of motions is reduced from three to two in which the tetramethylammonium cation undergoes isotropic tumbling (with $\tau_2 = \tau_3$), and CH_3 groups of this cation are undergoing three-fold reorientations as it is given in [14]. The calculated parameters for bromine crystals are presented in Table 2. In both crystals the correlation times are longer than in case of the chlorine analogues besides the correlation times of the tumbling of A cation. The parameters of the tumbling of the A cation of TEMABB are presumably not precisely determined due to the jump of T_1 at the 183 K PT temperature. The activation energie determined from the slope of the measured points above this phase transition is 2.9 kcal/mol. Here we must mention that the formulas obtained by Albert et al. [14] and B. Jagadeesh et al. [12], in which we used a variety of proportions of both cation types to fit the observed relaxation times, did not give us satisfied results.

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