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# PRE-MELTING STATE OF METHYLAMMONIUM NITRATE AND PERCHLORATE AS REVEALED BY $^1$H NMR STUDIES

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A new unusual crystalline phase of methylammonium nitrate and perchlorate, where methylammonium-ionic diffusion takes place, was found at various temperatures between 352 and 384 K, and above 451 K, respectively. The activation energy for the self-diffusion of the cation in both salts was determined as 29 kJ mol$^{-1}$.

Recently, we studied the $^1$H NMR of solid methylammonium iodide and found an unusual crystalline phase named ε above 414 K.1) This ε phase can be regarded as a pre-melting state, where methylammonium (MA) cations are fairly free to move. In other words, the cations perform translational diffusion as well as isotropic reorientation with high frequencies in the crystal, although they are considerably sizable ions. Ammonium ions, which are smaller than the present cation, are known to behave quite similarly in the highest-temperature crystalline phase of $NH_4NO_3$.2,3) This peculiar phase of the ionic crystal of $NH_4NO_3$ has been presumed to be a sort of the plastic phase which is well known to exist usually in molecular crystals.3,4)

Since methylammonium ions are more molecule-like than ammonium ions, it is expected that the appearance of the pre-melting state of (MA)I, which may be a kind of the plastic phase, is not strictly exceptional but rather common for some ionic crystals involving methylammonium cations. The present investigation on $(MA)NO_3$ and $(MA)ClO_4$ by $^1$H NMR and differential thermal analysis (DTA) has been undertaken in order to reveal an unusual phase such as the ε phase of (MA)I. Studies on the normal cationic motions of $(MA)NO_3$ observed below room temperature were already reported.5)

Methylammonium nitrate and perchlorate were prepared by neutralization of an aqueous solution of methylamine with nitric acid and perchloric acid, respectively. Colorless crystals obtained were recrystallized twice from ethanol and isopropyl alcohol for $(MA)NO_3$ and $(MA)ClO_4$, respectively.

The $^1$H spin-lattice relaxation time $T_1$ was determined at two different resonance frequencies of 16 and 20 MHz. The proton spin-spin relaxation time $T_2$ was measured at 16 MHz by use of Hahn's spin-echo method. The measurements of $T_1$ at 20 MHz and of DTA were carried out by means of the homemade apparatus described elsewhere.6,7) A broad-band pulsed NMR spectrometer constructed by us using a gating modulator and a receiver from Matec, Inc. was employed for the determination of $T_1$ and $T_2$ at 16 MHz.

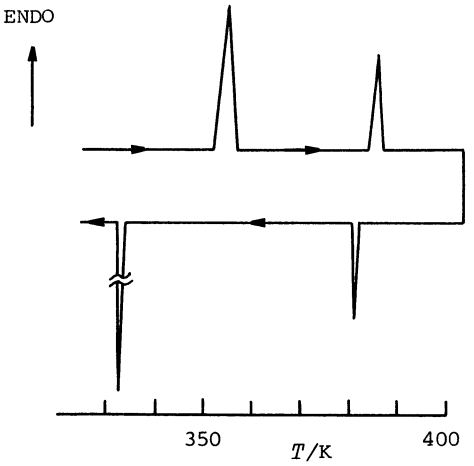

Fig. 1. DTA curves recorded for $CH_3NH_3NO_3$.

When $(MA)NO_3$ was heated from room temperature to 400 K, two endothermic anomalies at 352 and 384 K were recorded on the DTA curve as shown in Fig. 1. The beginning temperature of the latter anomaly agrees very well with the melting point of the nitrate salt.[8] With decreasing the temperature of the solid sample, exothermic anomaly appeared at ca. 335 K showing remarkable hysteresis. Accordingly one can conclude that $(MA)NO_3$ undergoes a first order solid state phase transition at 352 K. It is quite interesting that the heat anomaly of the solid state phase transition is larger than that of the melting.

For $(MA)ClO_4$, two solid state phase transitions at 321 and 451 K were located by DTA in agreement with the DTA data reported by Stammler et al.[9]

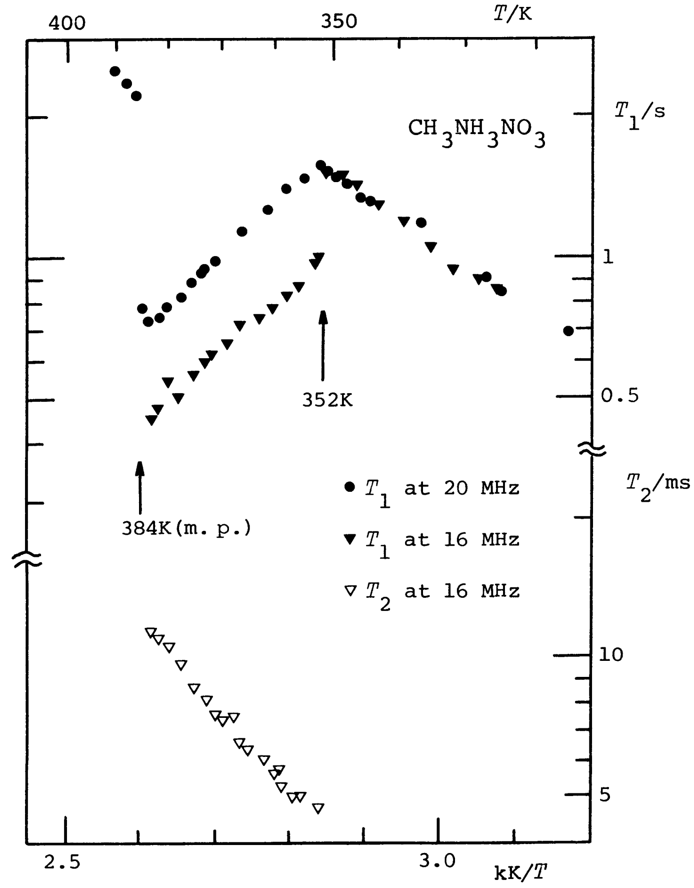

Fig. 2. Temperature dependences of the proton $T_1$ at 16 and 20 MHz, and of the proton $T_2$ at 16 MHz observed for $CH_3NH_3NO_3$.

Figure 2 shows the temperature dependence of the proton $T_1$ and $T_2$ observed for $(MA)NO_3$. The $T_1$ curves determined at both resonance frequencies showed an anomaly at 352 K in agreement with the transition temperature $T_{tr}$ obtained from our DTA experiments. At the same temperature, the $T_2$ value also changed discontinuously from several tens microseconds to 4 ms with increasing temperature.

As already reported,[5] the $T_1$ value of $(MA)NO_3$ observed below $T_{tr}$ is interpreted in terms of magnetic dipolar relaxation due to the reorientation of the cation about its $C_3$ axis. In the highest-temperature phase above $T_{tr}$, the $T_1$ curves having a negative temperature coefficient were obtained. This means that some new relaxation mechanism becomes important in the spin-lattice relaxation of $(MA)NO_3$. The $T_1$ values observed above $T_{tr}$

were dependent on the resonance frequency, indicating that the relaxation in the new phase is governed by magnetic dipolar relaxation mechanism.[10)] Moreover, the observed long $T_2$ values of the order of one millisecond indicate that not only the isotropic reorientation of the cations but also their self-diffusion takes place in this phase. Therefore, it can be presumed that the methylammonium cations of (MA)$NO_3$ perform isotropic reorientation with higher frequencies than $10^{10}$ Hz above $T_{tr}$ and the $T_1$ value is solely governed by the self-diffusion of the cations.

Since the diffusional correlation time $\tau_c$ in the highest-temperature solid phase of (MA)$NO_3$ is long enough as compared with the reciprocal of the angular resonance frequency $\omega_0$, it can be approximated that $T_1 \propto \tau_c$ and $T_2^{-1} \propto \tau_c$.[11)] If an Arrhenius-type relationship, $\tau_c = \tau_\infty \exp(E_a/RT)$, between $\tau_c$ and the activation energy $E_a$ of the self-diffusion is assumed, the temperature dependences of $T_1$ and $T_2$ yield the same $E_a$ value of 29 kJ $mol^{-1}$.

When the temperature of (MA)$ClO_4$ was decreased from room temperature, the $T_1$ values observed at 20 MHz decreased monotonously down to 77 K as shown in Fig. 3. This decrease of the $T_1$ values is attributable to the slowing down of the random jumps of the cation about its $C_3$ axis. From the slope of the $T_1$ curves, the activation energy $E_a$ for the $C_3$ reorientation of the cation was

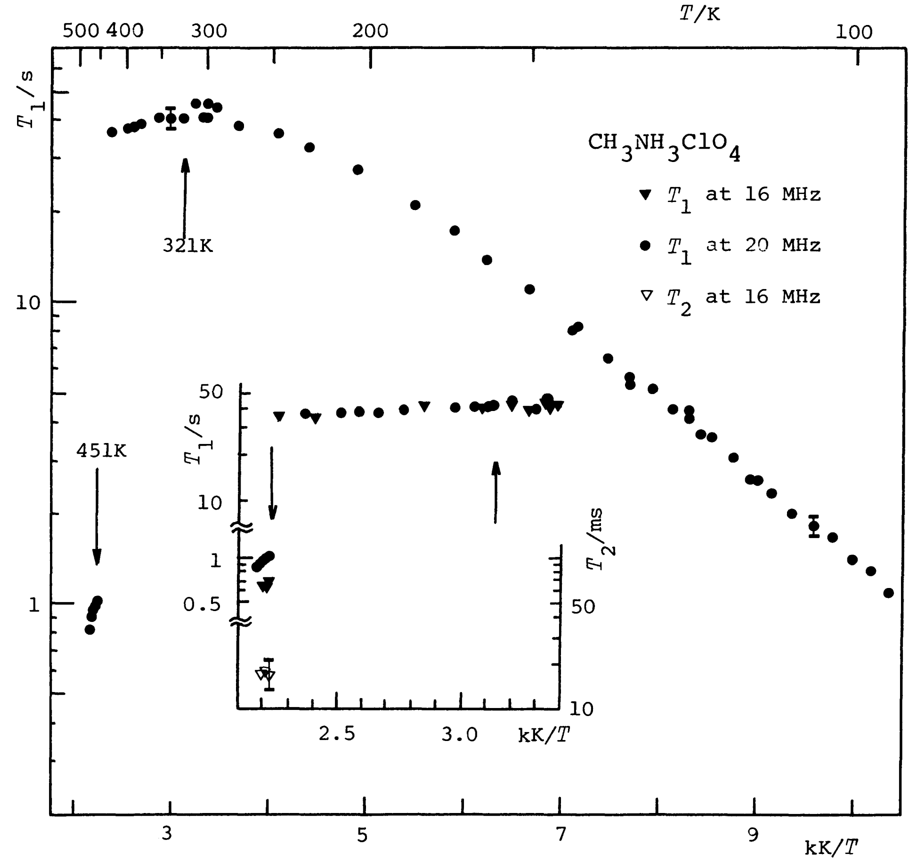

Fig. 3. Temperature dependences of the proton $T_1$ at 16 and 20 MHz, and of the proton $T_2$ at 16 MHz observed for $CH_3NH_3ClO_4$.

evaluated as 5.0 kJ mol$^{-1}$. This low value of $E_a$ suggests that the correlated reorientation of the cation,[12] which is the reorientation of the whole cation about its $C_3$ axis with keeping its rigid structure, is mainly responsible for the $T_1$ value observed below room temperature.

Around room temperature, $T_1$ showed a very broad maximum without any detectable anomaly at the lower $T_{tr}$ of 321 K observed by DTA. Above about this temperature, the $T_1$ value slightly decreased with increasing temperature up to the higher $T_{tr}$ of 451 K. Since the measurements of $T_1$ at two different resonance frequencies gave the same value at any temperature observed between ca. 300 K and 451 K, it is considered that no new magnetic dipolar relaxation mechanism is operative in this spin system.

At the higher-temperature $T_{tr}$ of (MA)ClO$_4$, the $T_1$ value decreased discontinuously from ca. 35 s to 1 s (at 20 MHz) or 0.7 s (at 16 MHz) with increasing temperature, while the $T_2$ value increased abruptly from several tens microseconds to 16 ms. The $T_1$ and $T_2$ values obtained in this highest-temperature phase of (MA)ClO$_4$ can be explained by the self-diffusion of the cations based on the same reasoning employed in the foregoing discussion on (MA)NO$_3$. The slope of the observed $T_1$ curve yielded the same activation energy of 29 kJ mol$^{-1}$ as that of the iodide and nitrate salts.

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