June, 1992] © *1992 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 65, 1707—1709 (1992)* 1707

Motions of Methylammonium Ions in $(CH_3NH_3)_3Sb_2I_9$ Crystals Studied by ^{1}H NMR

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(Received October 30, 1991)

Synopsis. The molecular motions and phase transitions at 147 and 111 K in solid tris(methylammonium) nonaiododiantimonate(III), $(CH_3NH_3)_3Sb_2I_9$, were investigated by measuring the temperature dependences of the proton spin-lattice relaxation times (T_1 and $T_{1\rho}$) in the static and rotating frames and the second moment (M_2) of ^{1}H NMR absorption above 90 K. In room-temperature phase I, it was revealed that the cations undergo a rapid overall rotation. The cations in low-temperature phases II and III were shown to have almost fixed orientations in the crystals, but performed a rapid C_3 reorientation about the C–N bond axis.

Methylammonium halogenoantimonates(III) and bismuthates(III) of the general formula $(CH_3NH_3)_3M_2X_9$ (M=Sb, Bi and X=Cl, Br, I) have been reported to form an interesting group of crystals in which the structure of the anions is strongly affected by the constituent halogen atoms.[1–4] The chlorine derivatives form one-dimensional double chains of MX_6 octahedra and undergo a single structural phase transition with changing temperature,[4] while the bromine analogs contain two-dimensional corrugated layers of MX_6 octahedra and show transitions to polar phases at low temperatures.[1] In iodine analogs, $(CH_3NH_3)_3Sb_2I_9$ and $(CH_3NH_3)_3Bi_2I_9$, simple double face-sharing octahedra are present in the crystalline lattice.[2,3] The common feature of these crystals is the presence of a plastic-like phase at high temperatures, in which the cations occupy sites of high symmetry. The dielectric response of this family resembles those expected for plastic crystals.

The iodine derivatives $(CH_3NH_3)_3Sb_2I_9$ (MAIA) and $(CH_3NH_3)_3Bi_2I_9$ (MAIB) are in the room-temperature isomorph and crystallize in the space group *P*6₃/*mmc*.[2,3] MAIA crystals have been reported to undergo two structural phase transitions at 147 K (T_{c1}) and 111 K (T_{c2}) upon cooling, the transition enthalpies of which are 1.9 and 0.2 kJ mol^{-1}, respectively.[2] A thermal hysteresis of ca. 2 K has been observed for both transitions, implying that the transitions are first-order.[2] The dielectric and pyroelectric properties seem to indicate antiferroelectric ordering below T_{c1}.[2]

The present investigation of the ^{1}H NMR second moment (M_2) and the ^{1}H NMR spin-lattice relaxation times (T_1 and $T_{1\rho}$) in MAIA was undertaken in order to obtain detailed information concerning cationic motions at the respective phases. Such measurements have so far been performed only for bromide crystals: $(CH_3NH_3)_3Bi_2Br_9$ (MABB)[5] and $(CH_3NH_3)_3Sb_2Br_9$ (MABA).[6]

Experimental

The title compound was obtained in a reaction of Sb_2O_3 and CH_3NH_2 in hot concentrated hydroiodic acid. Single crystals (ca. 5×5×1 mm^3) were grown by the slow evaporation of an acetonitrile solution at room temperature.[2] The pulverized crystals put in a glass ampoule for NMR measurements were dried in vacuo for 6 h at room temperature and then sealed off after adding a small amount of N_2 as a heat-exchange gas.

Pulsed NMR experiments were carried out with a laboratory-made NMR spectrometer (described elsewhere[7]). The proton spin-lattice relaxation time (T_1) was measured by a conventional 180°—τ—90° pulse sequence at a Larmor frequency of 42 MHz. The magnetization recovery curve for T_1 measurements was experimentally exponential over the entire temperature range studied. Measurements of the rotating-frame relaxation time ($T_{1\rho}$) at a Larmor frequency of 32 MHz were performed with a 90° pulse followed by a variable-duration pulse shifted in phase by 90° from the initial pulse; the spin-locking field (B_1) was 15 G (1 G$=10^{-4}$ T). The NMR second moment (M_2) was determined by a numerical integration of the recorded absorption lines using a JEOL JNM-MW-40S cw spectrometer operated at 40 MHz.

The sample temperature was controlled by the use of an Ohkura EC 61 temperature controller with a nitrogen gas-flow system. A copper vs. constantan thermocouple was used for determining the temperature with an estimated accuracy of ±1 and ±2 K for both pulsed and cw NMR experiments, respectively. All measurements were performed with increasing temperature. The sample was equilibrated for at least 20 min at a given temperature before each measurement.

Results and Discussion

The temperature dependence of ^{1}H M_2 observed between 96 and 305 K is shown in Fig. 1. An almost

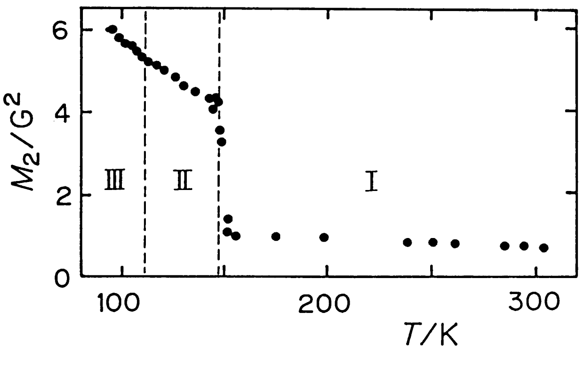

Fig. 1. Temperature dependence of the ^{1}H NMR second moment (M_2) observed in $(CH_3NH_3)_3Sb_2I_9$. The broken lines indicate the phase-transition temperatures reported in Ref. 2.

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linear decrease of M_2 from 6.0 to 4.3 G^2 was observed upon increasing the temperature from 96 K to just below T_{c1}. At T_{c1}, a sudden decrease of M_2 to 1.0 G^2 was detected. With further heating, M_2 remained almost constant and gave 0.7 G^2 at 300 K. Hereafter, we denote phases I, II, and III as the phases obtainable above T_{c1}, between T_{c1} and T_{c2}, and below T_{c2}, respectively.

The theoretical M_2 values were calculated for several motional modes of the methylammonium cation, and were reported to be 29, 19, and 8 G^2 for cations with rigid structure, with a reorientation of the CH_3 group about the C_3-axis, and with a reorientation of both the CH_3 and NH_3^+ groups, respectively.[8]

The M_2 values obtained in phase I are much smaller than that calculated for reorienting the CH_3 and NH_3^+ groups, indicating that the overall reorientation of the cations about their center of gravity occurs in this phase. By comparing the observed and theoretical values, one may see that both the CH_3 and NH_3^+ groups undergo C_3 reorientations, even in phase III. The decrease in M_2 from 6 to 4.3 G^2 observed in phases III and II can be interpreted as being a result of an additional motion, presumably attributable to a precession of the ions about some axis; the frequency of this motion is sufficiently high to narrow the resonance line. The III→II phase transition has no influence on the M_2 value, suggesting that no new cationic motion takes place at T_{c2}. In conformity with the result concerning dielectric and structural studies,[2] the present M_2 measurement implies that the I→II phase transition causes a freezing of the overall reorientation of methylammonium cations.

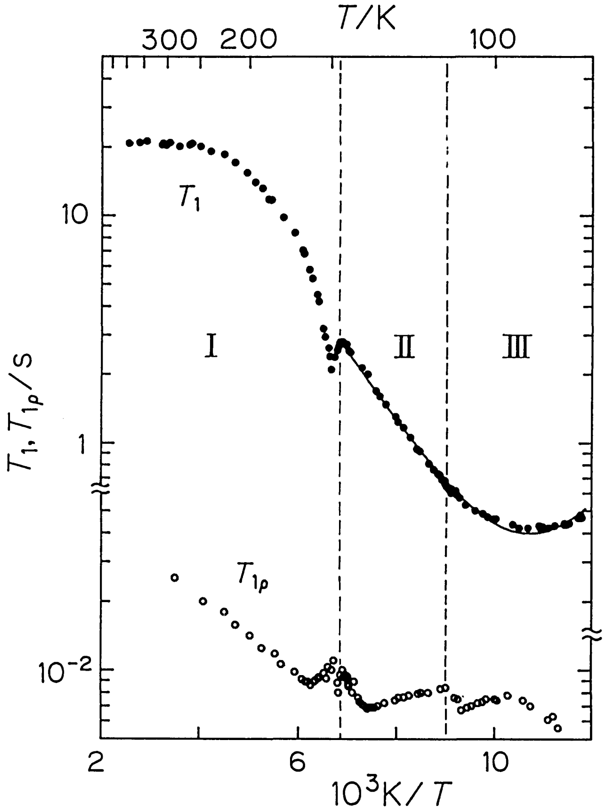

Fig. 2. Temperature dependences of ^{1}H T_1 (●) and $T_1\rho$ (○) observed in $(CH_3NH_3)_3Sb_2I_9$. The B_1 field employed for the $T_1\rho$ measurements was 15 G. The solid curve below 140 K was calculated using BPP theory. The broken lines indicate the phase-transition temperatures reported in Ref. 2.

The experimental ^{1}H T_1 and $T_{1\rho}$ data are given in Fig. 2, where $\log T_1$ and $\log T_{1\rho}$ are plotted against the inverse temperature. The T_{c1} transition was clearly found as being anomalies in both T_1 and $T_{1\rho}$, while the T_{c2} transition had little affect on both values. The latter result indicates that the low-temperature phase transition is accompanied by no marked change in the cationic motion. At 92 K in phase III, a T_1 minimum of 420 ms was observed. We performed a fitting calculation of the T_1 data observed beow 140 K to the Bloembergen–Purcell–Pound equation regarding magnetic dipolar relaxation.[9] The activation energy (E_a) was obtained as 5.8 kJ mol^{-1} with $\tau_0=1.2\times10^{-12}$ s, where the motional correlation time τ_c is expressed by an Arrhenius-type equation given by $\tau_c=\tau_0\exp(E_a/RT)$. Two kinds of modes are possible for the C_3 reorientation of $CH_3NH_3^+$ ions. The first is a correlated reorientation of the CH_3 and NH_3^+ groups in the cation, that is, the reorientation of the cation as a whole; the other is an uncorrelated reorientation of the CH_3 and NH_3^+ groups. Since the correlated reorientation is thought to be activated at temperatures much lower than 80 K, the shallow T_1 minimum observed at 92 K is assigned to the uncorrelated reorientation of the CH_3 and NH_3^+ groups, where the correlation time is specified for the relative reorientation of the two groups. This assignment is supported by the facts that the minimum value is almost the same as the theoretical value for this motion and that the E_a value is characteristic for this type of motion,[10] even though T_1 measurements should be extended to lower temperatures in order to observe a deeper T_1 minimim assignable to a correlated reorientation. The T_1 decrease below room temperature in phase I was assigned to an overall reorientation of the methylammonium cations. The E_a value of this motion, however, could not be determined, since no linear part in a $\log T_1$ vs. $1/T$ plot was observed. On the other hand, an E_a value of 5 kJ mol^{-1}, deduced from the $T_{1\rho}$ data in phase I, could be assigned to this overall reorientation, since ^{1}H $T_{1\rho}$ in this phase is determined by a cross interaction between the protons and halogen nuclei, which is controlled by strong modulation due to the overall reorientation.[5] The gradual change of the T_1 values observed in the high-temperature region (above 260 K) indicates that some new relaxation mechanism becomes important.

One of us (P.K.) thanks the Japan Society for the Promotion of Science for a grant which enabled him to stay six months at Nagoya University. We are thankful to Professor Ryuichi Ikeda, University of Tsukuba, for kind discussions concerning the experimental results.

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