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Molecular Motions in Solid $CD_3NH_3PbBr_3$ as Studied by ^1H NMR

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Synopsis. The temperature dependence of the ^1H spin-lattice relaxation times (T_1) was measured through the successive phase transitions in solid $CD_3NH_3PbBr_3$. The T_1's in the lowest-temperature phase (phase-III) have a single minimum at 30 K, indicating that $CD_3NH_3^+$ undergoes a correlated C_3-reorientation (E_a=2.7 kJ mol^{-1}) about the C–N axis. This fact clearly supports the previous assignment of the relaxation mechanism near 65 K in phase-III of $CH_3NH_3PbBr_3$, where an uncorrelated C_3-reorientation of the cations is excited (E_a=7.5 kJ mol^{-1}).

Methylammonium lead(II) halides, $CH_3NH_3PbX_3$ (X=Cl, Br, I) undergo successive phase transitions in the solid state.[1-5] We have recently reported studies on the motions of $CH_3NH_3^+$ in all phases of these compounds using NMR and NQR.[5] In the lowest-temperature phase (phase-III: orthorhombic), a single minimum of the ^1H spin-lattice relaxation time (T_1) was observed in $CH_3NH_3PbCl_3$ and $CH_3NH_3PbI_3$; it was found to be due to the correlated C_3-reorientation of $CH_3NH_3^+$, in which the reorientational rate of a CH_3-group coincides with that of a NH_3-group in the cation. On the other hand, in phase-III of $CH_3NH_3PbBr_3$, a deep T_1 minimum appeared with a shallow dip on its high-temperature side (Fig. 1). Even though we assigned the relaxation mechanism for the shallow dip to the uncorrelated C_3-reorientation of $CH_3NH_3^+$ (dotted curve in Fig. 1), we cannot completely rule out other dipole-relaxation processes, such as small-angle flipping or precession of the cations. In order to unambiguously identify the relaxation mechanism in phase-III of $CH_3NH_3PbBr_3$ (H-compound), we measured the ^1H spin-lattice relaxation times in crystalline $CD_3NH_3PbBr_3$ (D-compound).

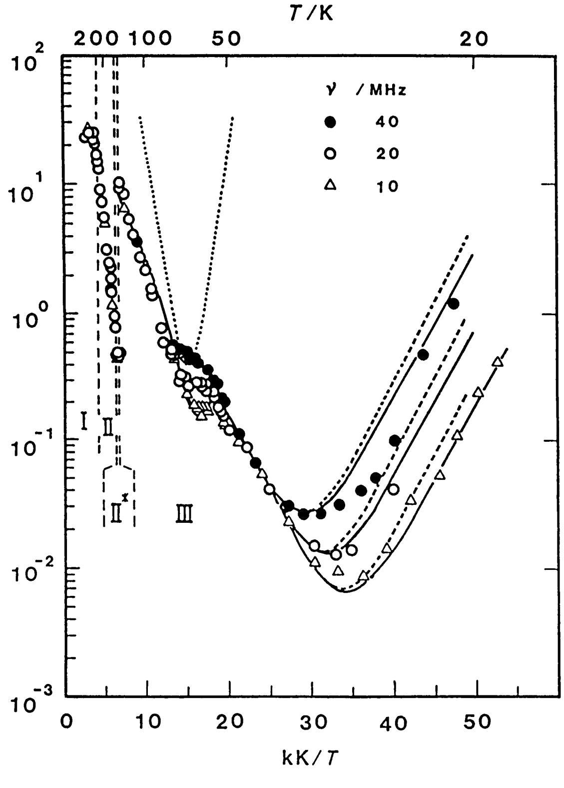

Fig. 1. Temperature dependence of the ^1H spin-lattice relaxation times in $CH_3NH_3PbBr_3$ crystals.[5] Use was made of the initial slope of the semilog plot of the magnetization recovery to determine T_1 (short component). The solid lines are the calculated T_1 curves (Eq. 3), which take account of the rotational tunneling (E_{01}=2.2 kJ mol^{-1}), the correlated C_3-reorientation (E_a=2.7 kJ mol^{-1}), and the uncorrelated reorientation of $CH_3NH_3^+$ (E_a=7.5 kJ mol^{-1}), the contribution of which is given by the dotted curve at 20.4 MHz. The broken lines are the results of a calculation adopted from Ref. 5.

Experimental

The deuterated compound was prepared as follows. CD_3NH_2 gas was first obtained by adding an excess amount of NaOH to a saturated aqueous solution of CD_3NH_3Cl (Aldrich, more than 98% deuterated); it was then introduced into a concentrated aqueous solution of HBr with equimolar $Pb(CH_3COO)_2$. Samples were recrystallized by the method described in Ref. 5. Found: C, 2.52; H, 0.61; N, 2.93; D, 1.21%. Calcd for $CD_3NH_3PbBr_3$: C, 2.49; H, 0.623; N, 2.906; D, 1.245%. Transition temperatures determined by DTA (values in parentheses for H-compound): T_{c1}=235.2 K (236.9 K), T_{c2}=154.5 K (155.1 K), T_{c3}=152.2 K (149.5 K).

The proton spin-lattice relaxation times were measured at 20.4 MHz using a JEOL pulsed spectrometer (JNM-FSE-60SS) with a saturation—τ—$\pi/2$ pulse sequence.

Results and Discussion

Figure 2 shows the temperature dependence of the ^1H spin-lattice relaxation times between 18 K and room temperature in the D-compound. Nonexponential magnetization recoveries (●: short component, ▲: long component) were observed in the vicinity of the T_1 minimum. The relative weight of each component was determined to be approximately 1 : 1. This nonexponential behavior is mainly attributed to a cross correlation of dipolar interactions in a NH_3-group; we therefore just analyzed the short component of T_1 (Fig. 2).[6,7] Furthermore, since the T_1's in the higher-temperature phases (phase-I, -II, and -II*) of the D-compound are almost the same as those of the H-compound (see Fig. 1), we focus on the relaxation mechanisms in phase-III.

The log T_1 vs. $1/T$ curve exhibits only a single deep T_1^s minimum (6 ms) at 30 K in phase-III. Judging from the magnitude of the T_1^s minimum, it is suggested that the C_3-reorientation of a NH_3-group governs the spin-lattice relaxation for the entire temperature region of phase-III in the D-compound. This is consistent with

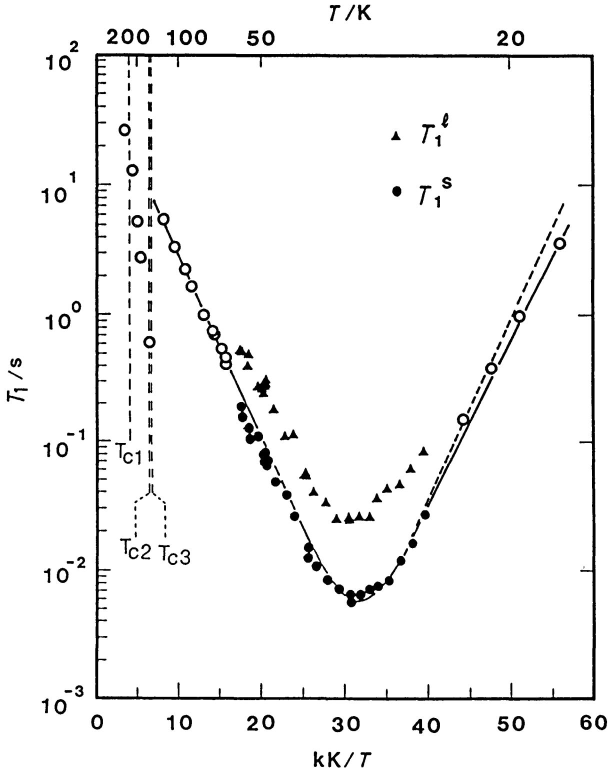

Fig. 2. Temperature dependence of the ^{1}H spin-lattice relaxation times at 20.4 MHz in $CD_3NH_3PbBr_3$ crystals. ○: single exponential, ●: short component, ▲: long component. The solid line is the calculated T_1 curve, which takes into account the rotational tunneling (E_{01}=2.2 kJ mol^{-1}) and the correlated C_3-reorientation of $CD_3NH_3^+$ (E_a=2.7 kJ mol^{-1}). Only the thermal process is assumed in the calculation of the broken line.

the orthorhombic structure of phase-III, in which the direction of the axes of the $CD_3NH_3^+$ ions can be considered to be fixed. If other dipolar mechanisms which conserve the average direction of the C–N axes, such as the precession of a whole cation, would begin to dominate the spin-lattice relaxation above 30 K, T_1 data would also indicate a shallow dip on the high-temperature side of the T_1 minimum, in contrast to the experimental result.

Assuming the Arrhenius-type temperature dependence of the correlation time,

$$\tau_c=\tau_0 \exp(E_a/RT), \tag{1}$$

where E_a is the activation energy for the C_3-reorientation of $CD_3NH_3^+$, we calculated the T_1 curve (the broken line in Fig. 2) using the well-known BPP theory;[8] we obtained $\tau_0=1.6\times10^{-13}$ s and E_a=2.7 kJ mol^{-1}.

The calculated T_1 curve agrees fairly well with the experimental data above 25 K but slightly deviates from the data below 25 K. As in the case of the chloride or iodide compound,[5] we take account of not only the thermal process but also the effect of tunneling rotation. The actual correlation time can therefore be approximated by[9–14]

$$\tau_c^{-1}=\tau_0'^{-1}\exp(-E_{01}/RT)+\tau_0^{-1}\exp(-E_a/RT), \tag{2}$$

where E_{01} is the energy difference between the two lowest torsional states. By applying the same values of E_a and τ_0 as described above, we obtained the solid line shown in Fig. 2, where E_{01}=2.2 kJ mol^{-1} and $\tau_0'=6.5\times10^{-12}$ s.

We now re-examine the relaxation mechanisms in phase-III of the H-compound. According to the similarity in the T_1 curves, except for a shallow dip, it is reasonably supposed that the E_a values for the C_3-reorientation of the cation are equal for both compounds. Since E_a (2.7 kJ mol^{-1}) is much smaller than 8 kJ mol^{-1}, the height of the barrier for the internal rotation of $CH_3NH_3^+$,[15,16] the motions of NH_3 and CH_3 should be correlated with each other below 50 K. It is therefore unambiguous that the correlated C_3-reorientation of $CH_3NH_3^+$ is responsible for the deep T_1 minimum in the H-compound.

Upon heating at above 50 K, the thermal motion of the cation is so activated as to overcome the barrier for the internal rotation, i.e., the uncorrelated C_3-reorientation of $CH_3NH_3^+$ begins to take place, thus bringing about a shallow dip on T_1 near 65 K. (Of course, we cannot see this effect in the D-compound.)

In the presence of both correlated and uncorrelated reorientation, T_1 for a single cation can be written as[15–17]

$$T_1^{-1}=\sum_i K_i\{\tau_{ci}/(1+\omega_0^2\tau_{ci}^2)+4\tau_{ci}/(1+4\omega_0^2\tau_{ci}^2)\}, \tag{3}$$

where i=1,2, and $\tau_{c1}\ll\tau_{c2}$ is assumed. τ_{c1} represents the correlation time for the correlated C_3-reorientation and is written as Eq. 2; τ_{c2} corresponds to the relative correlation time of a CH_3- or NH_3-group.[15]

Now can we simulate the experimental data for the H-compound using Eq. 3. For the correlated C_3-reorientation (τ_{c1}), we used the same values for E_{a1} and E_{01} as those used for the D-compound, considering the analogous intermolecular interactions in both compounds. On the other hand, $\tau_{01}=5.9\times10^{-13}$ s and $\tau_{01}'=1.45\times10^{-12}$ s, which are slightly diffrent from those in the D-compound, were employed, reflecting the difference in the onset of the C_3-reorientation between $CH_3NH_3^+$ and $CD_3NH_3^+$. For an uncorrelated reorientation (τ_{c2}), the same values (E_{a2}=7.5 kJ mol^{-1} and $\tau_{02}=5.7\times10^{-15}$ s) as those in Ref. 5 were used in the calculation. Adopting $K_1=6.3\times10^9$ s^{-2} and $K_2=2.0\times10^8$ s^{-2}, we obtained the solid lines given in Fig. 1. It is obvious that the present calculations reproduce the experiments well, compared with the previous ones (indicated by the broken lines in Fig. 1), where E_a=2.4 kJ mol^{-1} for a correlated reorientation without the tunneling effect.

In our previous work,[5] it was rather difficult to distinguish between E_a for the correlated C_3-reorientation and E_{01} for the tunneling effect in $CH_3NH_3PbBr_3$ because of the presence of the shallow dip in T_1. Now, however, we can separate these contributions clearly, as described above. It is also worth noting that this E_a value (2.7 kJ mol^{-1}) is much smaller than that in the chloride (5.45 kJ mol^{-1}) or in the iodide (5.80 kJ mol^{-1}). In conclusion, the present work definitely permits a tentative interpretation[5] regarding such a small value of E_a in bromide; this is probably related to the strength of the N–H···X type hydrogen bonds, as well as the difference in the volume of the cavities formed by the X atoms in these PbX_3 complexes.

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