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The Nuclear Quadrupole Spin-Lattice Relaxation of ^{35}Cl in Methylammonium Hexachlorostannate(IV) and Hexachloroplatinate(IV)

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The ^{35}Cl nuclear quadrupole spin-lattice relaxation time, T_1, in $(CH_3NH_3)_2MCl_6$ (M=Sn and Pt) was measured from 4.2 to 434 K in order to clarify the dynamic aspect of the phase transitions at 156 and 125 K respectively. The relaxation process in both low-temperature phases is dominated by the rotational vibration of the octahedral $[MCl_6]^{2-}$ ions. Far above the transition point, T_{tr}, the T_1 decreases very rapidly with an increase in the temperature. This indicates that each octahedron reorients about its threefold axis, with the activation energies of 77±3 for $[SnCl_6]^{2-}$ ions and 95±10 kJ mol^{-1} for $[PtCl_6]^{2-}$ ions. At T_{tr}, the $\log(T_1/s)$ *vs.* kK/T curve shows a distinct minimum, as in some K_2PtCl_6-type compounds. This anomalous behavior can be explained in terms of a soft rotary mode of the $[MCl_6]^{2-}$ ions. The softening is estimated to be about 60%, according to Armstrong's approach.

Most hexahalogenometallates(IV) with cubic antifluorite structures of the K_2PtCl_6 type are known to undergo structural transitions to low-temperature phases of less symmetric structures. Recent studies of the nuclear quadrupole resonance (NQR) in these crystals have shown that their NQR frequencies and relaxation times near the transition points are greatly affected by the condensation of rotary lattice modes.[1]

On the other hand, methylammonium hexachlorometallates (IV) form rhombohedral R$\bar{3}$m crystals with a slightly deformed antifluorite structure.[2,3] Very recently, Kume *et al.* have, from ^{35}Cl NQR measurements, found phase transitions in $(CH_3NH_3)_2SnCl_6$ and $(CH_3NH_3)_2PtCl_6$ at 156 and 125 K respectively.[4] In interpreting the unusual behavior of the NQR frequency at the transition point, they suggested the existence of a soft mode involving the libration of the complex anions. On the other hand, the results of proton second moments and spin-lattice relaxation times showed that the methylammonium ion is reorienting as a whole about its three-fold symmetry axis in the low-temperature phase, giving rise to a deep minimum of T_1 at about 53 K for 60 MHz.[5] As the temperature increases toward the phase-transition point, the correlation times of the individual motions of CH_3 and NH_3 groups become very different. Consequently, another shallow minimum of T_1 appears on the high-temperature side of the deep minimum, but a few tens of degrees below T_{tr}. This second minimum may be ascribed to the dipole-dipole interaction between the CH_3 and NH_3 groups in the cation. Just at T_{tr}, however, the proton T_1 *vs.* $1/T$ curve showed no appreciable discontinuity, suggesting that the motion of the cation may play a rather indirect role in the phase transition.[5]

In general, spin-lattice relaxation times for quadrupolar nuclei are very sensitive to EFG (electric field gradient) fluctuations associated with the phase transition. The present study of the ^{35}Cl nuclear quadrupole relaxation has been undertaken in order to clarify the motion of the $[MCl_6]^{2-}$ anion in $(CH_3NH_3)_2MCl_6$(M=Sn, Pt), and also in order to ascertain whether or not it is responsible for the phase transition, as was suggested in previous papers.[4,5]

Experimental

The spin-lattice relaxation time of ^{35}Cl were measured with a Bruker pulsed NMR spectrometer (B-KR 322s 4—62 MHz). A boxcar integrator or a NIC 1074 signal averager was set up after the spectrometer in order to increase the SN ratio. The T_1 was determined by a 90°-t-90°-t'-180° pulse sequence and by fitting the echo amplitude to the $A(t)=A_0[1-\exp(-t/T_1)]$ equation for a fixed t'. In the temperature range studied, the recovery of the nuclear magnetization was well described by a single exponential function. The error of each T_1 value is within about 5%. The T_2 was measured by means of a 90°-t/2-180° spin echo pulse sequence and by fitting the echo amplitude to $A(t)=A_0\exp[-(t/T_2)^2]$. For both compounds, the T_2 values were temperature-independent at 550 μs, except above 330 K.

The powdered samples of methylammonium hexachlorostannate(IV) and its platinum analogue were the same as those used in the earlier NQR and proton NMR experiments.[4,5]

The sample temperature was measured with a copper *vs.* constantan thermocouple and was controlled with an estimated accuracy of ±0.5 K below and ±1 K above room temperature. Temperatures lower than 77 K were obtained by allowing the sample to warm from the temperature of liquid helium and measured with a gold-cobalt *vs.* copper thermocouple.

Results and Discussion

The nuclear quadrupole interaction Hamiltonian is given by

$$\mathscr{H}_Q = \Sigma_\mu Q_\mu V_\mu, \quad \mu = 0, \pm 1, \pm 2, \tag{1}$$

where the Q_μ's are the quadrupole operators and the V_μ's, the electric-field-gradient components. Each V_μ can be expanded as a power series in the relative displacements or fluctuations of the nuclei from their equilibrium positions. Thus, the time-independent terms are responsible for the NQR frequency, ν_Q, while the time-dependent ones are responsible for the spin-lattice relaxation.[6]

The compounds studied gave one NQR line in both the low- and high-temperature phases,[4] consistent with the crystal structure proposed by an X-ray diffraction study.[3] It was confirmed that the ν_Q-T curve exhibits a

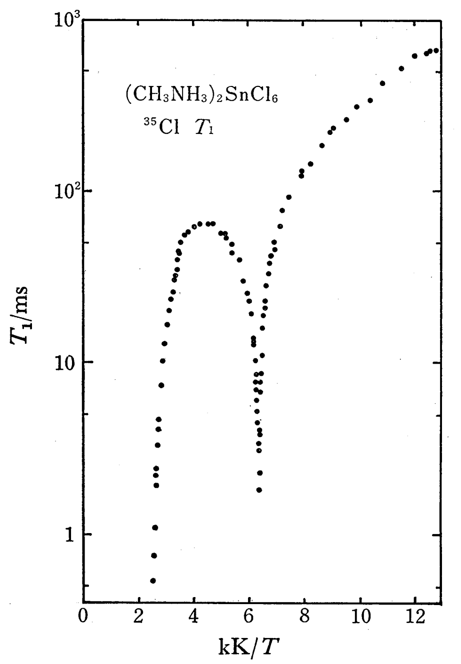

Fig. 1. A plot of the ^{35}Cl spin-lattice relaxation time in $(CH_3NH_3)_2SnCl_6$ as a function of $1/T$.

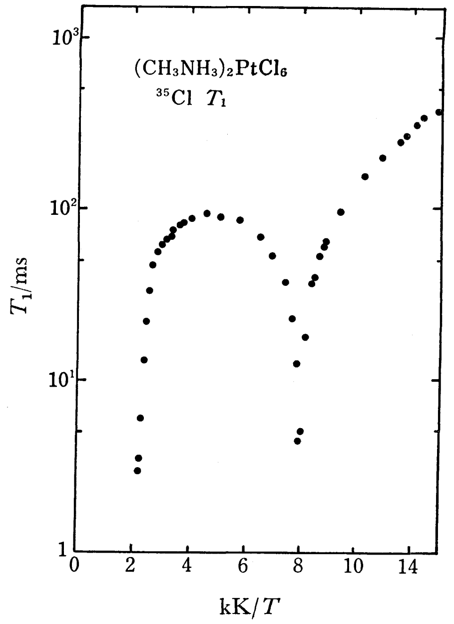

Fig. 2. A plot of the ^{35}Cl spin-lattice relaxation time in $(CH_3NH_3)_2PtCl_6$ as a function of $1/T$.

small, but distinct cusp-shaped reduction in a narrow temperature range about the T_{tr}. This cusp may be due to certain fluctuations enhanced as the transition point is approached, probably caused by soft librational modes of the octahedron, in analogy with K_2PtBr_6.[1]

The ^{35}Cl spin-lattice relaxation times in $(CH_3NH_3)_2SnCl_6$ are shown in Fig. 1 as a function of the inverse temperature. A distinct minimum was found at T_{tr}, in contrast to the proton spin-lattice relaxation time, which does not show such an anomaly.[5] The temperature dependences of the ^{35}Cl T_1, as well as of the NQR frequency, of $(CH_3NH_3)_2PtCl_6$ are very similar to those of $(CH_3NH_3)_2SnCl_6$ (Fig. 2). This indicates that the relaxation process and the mechanism of the phase transition can be interpreted from the same standpoint for both compounds.

Low-temperature Region. Armstrong *et al.* have extensively studied the lattice dynamics and phase transitions in cubic antifluorite-type crystals, R_2MX_6, and in cubic perovskite-type $CsPbCl_3$ by means of NQR spectroscopy.[1] They have derived theoretical equations for the quadrupole relaxation time and have pointed out that the most dominant relaxation process for the X nuclei is the anharmonic Raman process, with a rotary lattice mode of the $[MX_6]^{2-}$ octahedron. On the other hand, the internal vibration is less important than the former process, and so its contribution is negligible. According to them,

$$T_1^{-1} = CT^2/\bar{\omega}^5, \qquad (2)$$

where C is a constant depending on the crystal structure, and $\bar{\omega}$, the zone-averaged rotary mode frequency. Then, T_1^{-1} would be proportional to T^2 in a stable lattice such as Cs_2PtCl_6.[1] The C coefficient is much too complicated to estimate for the rhombohedral lattice, although it was estimated for the cubic K_2PtCl_6-type structure.[1]

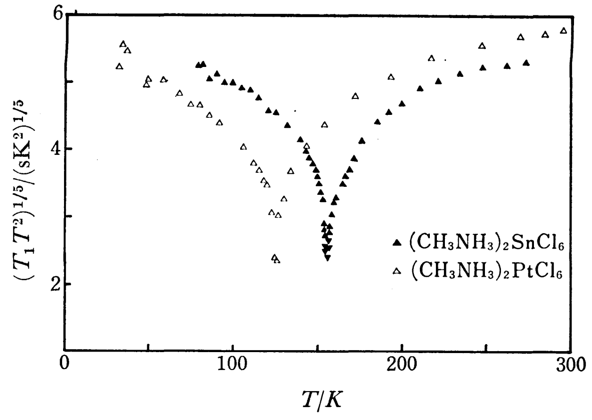

Fig. 3. Temperature dependences of $(T_1\ T^2)^{1/5}$ in $(CH_3NH_3)_2SnCl_6$ and in $(CH_3NH_3)_2PtCl_6$.

In Fig. 3 the $(T_1T^2)^{1/5}$ value is plotted against the temperature in order to see whether or not Eq. 2 holds even in the vicinity of T_{tr}.[1] Far below or above T_{tr}, the $(T_1T^2)^{1/5}$ is nearly constant, indicating that $T_1^{-1} \propto T^2$. The T_1 measurement was further extended to the region from 77 to 4.2 K only on the platinate complex, as Fig. 4 shows. The T_1^{-1} data in this temperature region show no T^2 dependence, because the high-temperature approximation breaks down in Eq. 2. In such a case, the T_1^{-1} is expressed by:

$$T_1^{-1} = C' \sinh^{-2} (\hbar\bar{\omega}/2kT). \qquad (3)$$

The temperature dependence of T_1 (Eq. 3) is shown in Fig. 4 by a full line with parameters of $C'=2.69\ s^{-1}$ and $\hbar\bar{\omega}/k=137$ K. The agreement between the calculated and observed values below 80 K indicates that the relaxation of the ^{35}Cl nuclei is associated with the harmonic rotational vibration of the octahedron in this temperature region.

Phase-transition Region. The anomalous behavior

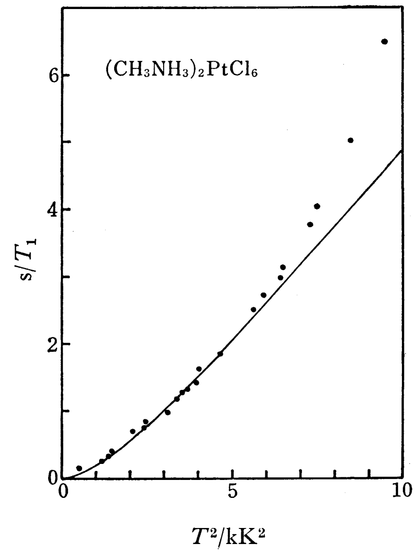

Fig. 4. The ^{35}Cl spin-lattice relaxation rate as a function of T^2 in $(CH_3NH_3)_2PtCl_6$. The full line was calculated by Eq. 3.

of T_1 around T_{tr} is very similar to that of R_2MX_6, which has the antifluorite structure.$^{1)}$ This deep, distinct T_1 minimum in $(CH_3NH_3)_2MCl_6$ suggests that the phase transition is ascribable to a softening of a rotary lattice mode of the octahedron. If this is the case, then, according to Eq. 2, the temperature dependence of $(T_1T^2)^{1/5}$ reflects the variation in the average rotary mode frequency. The value of $(T_1T^2)^{1/5}$ was reduced by about 60% as the T_{tr} was approached from above for both compounds (Fig. 3). Referring to Armstrong *et al.*, this reduction denotes a 60% apparent softening of a rotary mode frequency, which is comparable to the 40 and 58% softening of zone-center phonons in K_2PtBr_6 and $(NH_4)_2PtBr_6$ respectively obtained from the Br T_1 measurements.$^{1)}$

Such softening of some rotary mode of the $[SnCl_6]^{2-}$ or $[PtCl_6]^{2-}$ octahedron suggests the possibility of a lowering of the crystal symmetry in the low-temperature phase, as is found in cubic R_2MX_6. An X-ray study was, therefore, performed on the tin complex in our laboratory.$^{3)}$ It revealed that the space group ($R\bar{3}m$) and crystal structure are unchanged on passing through T_{tr}. Moreover, the X-ray results suggested that a $k=0$ acoustic mode softens to make a bulk deformation without any structural change. This mode, however, could not explain the T_1 anomaly occuring at T_{tr}.$^{1)}$ It is, therefore, conceivable that the tilting of the octahedra is too small to be detected by X-ray diffraction.

High-temperature Region. At high temperatures (above 300 K), a rapid decrease in T_1 occurs exponentially with a decrease in $1/T$, showing that another relaxation mechanism is dominant. This process is attributable to the hindered rotation of the $[MCl_6]^{2-}$ octahedron, probably around its three-fold axis, which coincides with the triad axis of the rhombohedral cell. The relaxation time is given as

$$T_1 = C\cdot\tau_0 \exp(E_a/RT) \qquad (4)$$

where C is a constant, equal to 2/3 for the C_3 rotation of octahedra.$^{7)}$ By fitting the data in Figs. 1 and 2 to Eq. 4, the activation energies (E_a) of the hindered rotation were determined to be 77 ± 3 for the $[SnCl_6]^{2-}$ ion and 95 ± 10 k J mol^{-1} for the $[PtCl_6]^{2-}$ ion. These values are comparable to 78.7 and 76.6 k J mol^{-1} for the C_4 rotation in cubic K_2PtCl_6 and K_2IrCl_6 respectively.$^{1,8)}$

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