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PROTON AND CHLORINE SPIN-LATTICE RELAXATION IN α-NH_4HgCl_3

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The spin-lattice relaxation times of ^1H and ^{35}Cl as well as the ^{35}Cl NQR frequencies in α-NH_4HgCl_3 are reported. The proton T_1 data are explained in terms of C_3 reorientation and S_4 flip of NH_4^+ ions. The latter mode is also largely responsible for the ^{35}Cl quadrupole relaxation rate. A marked change in the proton T_1 at 55 K indicates a phase transition, ascribable to the ordering of the NH_4^+ ions.

In order to investigate torsional vibrations of chlorine atoms, we have measured temperature dependence of ^{35}Cl NQR frequencies in several complexes of mercury(II) chloride. Of these, an anomalous behavior in α-NH_4HgCl_3 suggested some interaction between chlorine atoms and ammonium ions. Because of this, it seemed worthwhile to study the relaxation processes of ^1H and ^{35}Cl nuclei by means of pulsed techniques.

A Dean-type oscillator with a PAR 122 lock-in amplifier was used to detect ^{35}Cl NQR absorptions. The relaxation times of ^1H and ^{35}Cl were measured with a Bruker B-KR 322s pulsed spectrometer. The spin-lattice relaxation times, T_1, were obtained from the 180°-τ-90° sequence for ^1H and 90°-τ-90° one for ^{35}Cl. The spin phase memory time, T_2, for ^{35}Cl was measured by the 90°-τ-180° sequence, and the inverse linewidth parameter, T_2*, was defined as the time for an amplitude of a free induction decay to fall to 1/e of its initial value.1) The temperature of measurement was varied from 4 to 320 K by use of liquid helium or liquid nitrogen, and controlled within ±0.3 K above 50 K. Polycrystalline NH_4HgCl_3 was prepared by melting an equimolar mixture of $HgCl_2$ and NH_4Cl at about 210 °C. The sample was identified as the α-form by an X-ray diffractometer.2)

The crystal has the tetragonal unit cell (P4/mmm, a=4.198 and c=7.935 Å, Z=1).3,4) The mercury(II) atom is surrounded by four Cl(1) and two Cl(2) atoms in a distorted octahedral arrangement. The octahedra form a sheet structure by sharing the edges of Cl(1) atoms. Between the sheets of $HgCl_3^-$, each ammonium ion is enclosed by eight Cl(2) atoms as shown in Fig. 1. Although the two-dimensional lattice

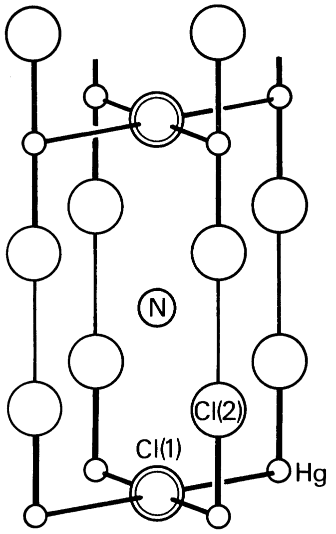

Fig. 1. The crystal structure of α-NH_4HgCl_3.

of "NH_4Cl" in this crystal structure is deformed tetragonally, the N-Cl distance (3.39 Å) is almost identical with that (3.36 Å) in cubic NH_4Cl. Of six chlorine atoms forming the octahedron, two Cl(2) atoms are much closer to the mercury atom than the four Cl(1) atoms; Hg-Cl(2)=2.34 and Hg-Cl(1)=2.97 Å. The former is bonded to only one mercury atom, whereas the latter to four mercury atoms. From these facts it is evident that Cl(2) is much more covalent than Cl(1).

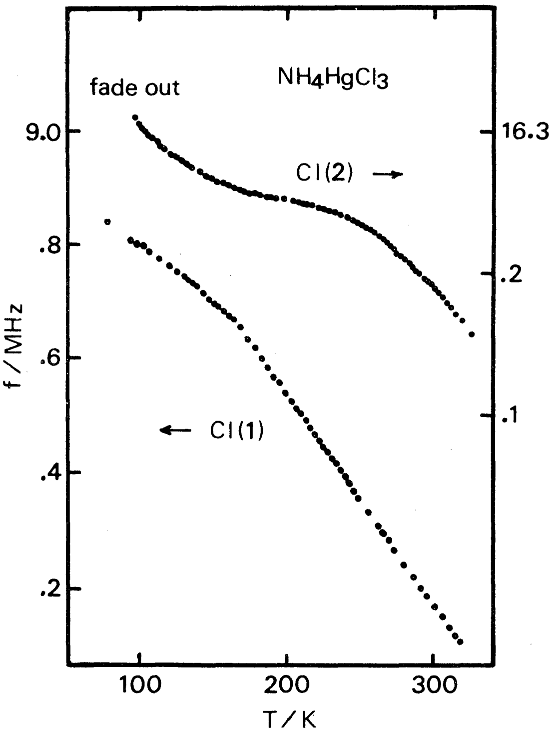

Fig. 2. Temperature dependence of the ^{35}Cl NQR frequencies in α-NH_4HgCl_3.

At room temperature two chlorine NQR absorptions were observed. As Scaife has already reported, the higher frequency line (*ca.* 16 MHz) can be assigned to Cl(2) atoms, and the lower frequency one to Cl(1).[5] The temperature dependence of the two resonance frequencies is shown in Fig. 2. An anomalous temperature dependence of the higher frequency line cannot be explained in terms of the torsional vibration model presented by Bayer.[6] In addition, it fades out below about 95 K, whereas the lower frequency line is observed even at 77 K. Such remarkable broadening of the higher frequency line may be related to some motions of the NH_4^+ ions, because the Cl(2) atom is located closer to the ammonium ion than Cl(1) atom.

The proton spin-lattice relaxation times measured at 60 and 22 MHz are given in Fig. 3. The semi-logarithmic plot of T_1 *vs.* inverse temperature shows a single minimum, the position of which depends on the Larmor frequency. The high temperature side of the T_1 minimum gives an activation energy, E_a, of 8.2 kJ mol^{-1}, while the low temperature side yields 6.2 kJ mol^{-1}. The difference between these slopes suggests the presence of two or more reorientational modes of the ammonium ion with different activation energies.

Some workers have calculated the relaxation time, T_1, due to magnetic dipole-dipole interaction between protons in an ammonium ion, assuming its reorientation about the two- and the three-fold axes (denoted as C_2 and C_3, respectively).[7] In this crystal, however, the ammonium ion was assumed, like in NH_4Cl, to reorient about the C_2 axis by the 90° flip (S_4 flip) rather than by the 180° flip (C_2 reorientation). Moreover, the effects of cross-correlations were neglected, as the proton relaxation appeared exponential throughout the temperature range studied. Then, the proton T_1 can be expressed by[8,9]

$$1/T_1 = (3/80)\gamma^4\hbar^2 r^{-6}\,[3\Psi(\tau_3) + 4\Psi(\tau_4) + 2\Psi(\tau_4/2) + 8\Psi(\tau_{34}) + 7\Psi(\tau_{34}')] \qquad (1)$$

where $\Psi(\tau) = \tau/(1+\omega_0{}^2\tau^2) + 4\tau/(1+4\omega_0{}^2\tau^2)$, $\tau_3 = (3k_3)^{-1}$, $\tau_4 = (2k_4)^{-1}$, $\tau_{34}{}^{-1} = \tau_3{}^{-1} + \tau_4{}^{-1}$,

$\tau_{34}'^{-1} = \tau_3^{-1} + 2\tau_4^{-1}$, and k_3 and k_4 are the rates of the C_3 reorientation and the S_4 flip, respectively. Further, the usual Arrhenius relationship was assumed:

$$\tau_i = \tau_i^0 \exp(E_i/RT) \qquad (2)$$

where i is 3 or 4, and E_i is the activation energy for the i-th mode. Using r(H-H) =1.69 Å, the motional parameters were obtained as follows:

$$\tau_3^0 = 2.8 \times 10^{-13}\text{s},\ \tau_4^0 = 1.3 \times 10^{-14}\text{s, and } E_3 = 6.8 \text{ kJ mol}^{-1}.$$

In these calculations, E_4 was taken as 9.4 kJ mol^{-1} which was determined from the ^{35}Cl T_1 data given later. The resulting proton T_1 is illustrated by the solid line in Fig. 3. The activation energies for the C_3 reorientation and the S_4 flip of ammonium ions are considerably smaller than those in NH_4Cl, consistent with the less polar nature of the bonding of Cl(2) atoms. On the low temperature side of the T_1 minimum, the observed T_1 is significantly shorter than the calculated one, suggesting some effect of tunneling motion of the ammonium ions.

At 55 K, the proton T_1 increased suddenly, providing a strong evidence for the existence of a phase transition. This transition may be attributed to the ordering of the ammonium ions in analogy with NH_4Cl. The temperature, T_t, however, is much lower than that (242.8 K) in NH_4Cl, possibly owing to the lower dimensionality of the "NH_4Cl" lattice as well as the less polarity of Cl(2) in α-NH_4HgCl_3.

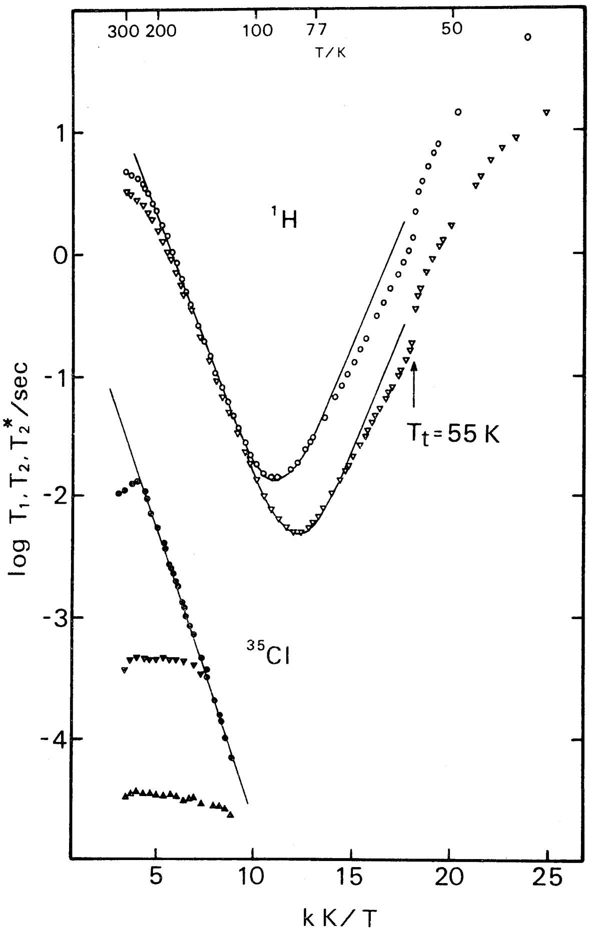

Fig. 3. Temperature dependence of the relaxation times in α-NH_4HgCl_3; proton T_1: 60 MHz(○), 22 MHz(▽), ^{35}Cl(2) : T_1(●), T_2(▼), T_2*(▲). The solid lines for protons show the calculated T_1 (see the text).

The data on the ^{35}Cl(2) relaxation, T_1, T_2 and T_2*, are also included in Fig. 3. The chlorine T_1 decreases with decrease of temperature until 100 K, below which its value appears to be close to that of T_2*; such an extremely fast relaxation rate may cause disappearence of the NQR signal described above. The temperature dependence of the chlorine T_1 cannot be explained on the basis of a torsional vibration model[1,6] nor a

Raman process,[10)] because the T_1 expected for either model should increase with decreasing temperature. It is noteworthy that the linear relation of log T_1 *vs.* $1/T$ gives an activation energy of 9.4 kJ mol^{-1}, which is comparable with that for the proton T_1 (8.2 kJ mol^{-1} from the high temperature side). The proximity of these values suggests that the motions of ammonium ions are responsible not only for the proton T_1 but also for the chlorine T_1.

According to Woessner and Gutowsky the T_1 for the quadrupolar nucleus can be expressed as

$$1/T_1 = (4\omega_Q{}^2/3)(q'/q)^2\{\tau_c/(1+\omega_Q{}^2\tau_c{}^2)\} \tag{3}$$

where q'/q is a fluctuation fraction of the electric field-gradient and τ_c is the correlation time of the ammonium ions which produce field-gradient fluctuations at the sites of chlorine nuclei. Of the two modes presented here, the S_4 mode changes the configuration of the ammonium ion, but the C_3 mode does not. Because the jumping process of the protons in the C_3 reorientation produces only a pulsed fluctuation, the C_3 mode is not so effective for the quadrupolar T_1 as the S_4 one. In fact, we have recently confirmed that C_2 or C_3 reorientation of ammonium ions or flip of water molecules of crystallization affects a chlorine T_1 very little in crystals of $K_2HgCl_4.H_2O$, $(NH_4)_2HgCl_4.H_2O$, $N_2H_5HgCl_3$ and $NaAuCl_4.2H_2O$. Hence, the fluctuation fraction in Eq.(3) was estimated to be 0.06 using $(2k_4)^{-1}$ from the proton T_1 data. The value of eq', which corresponds to 1 MHz, is in good agreement with the evaluated one in NH_4Cl.[11)]

Unfortunately, a free induction decay signal of $^{35}Cl(1)$ nuclei could not be observed on the pulsed spectrometer, because of the long dead times (~50 μs) at low frequencies of 8 to 9 MHz.

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