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NQR Study of Phase Transitions in $SbCl_3 \cdot (C_6H_5)_2NH_2^+Cl^-$ and $2SbCl_3 \cdot C_6H_5OCH_3$

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The temperature dependence of ^{35}Cl and $^{121,123}Sb$ NQR frequencies was measured in $SbCl_3 \cdot (C_6H_5)_2NH_2^+Cl^-$ between 77 and 300 K. A phase transition takes place at 108 K and ^{35}Cl NQR lines disappeared above about 275 K. Possible mechanisms of the phase transition and of the disappearance of ^{35}Cl NQR lines were suggested. The phase transition in $2SbCl_3 \cdot C_6H_5OCH_3$ was investigated by the NQR technique. The temperature dependence of the splitting of the $^{121}Sb(\nu_1)$ NQR lines in the low-temperature phase gave a critical exponent of $\beta = 1/2$ near the transition point T_c. A Zeeman-effect experiment revealed that the crystals in both low- and high-temperature phases were monoclinic.

In the course of the study regarding the bond character in $SbCl_3$ molecular complexes[1,2] we have observed the phase transition and the disappearance of ^{35}Cl NQR lines in $SbCl_3 \cdot (C_6H_5)_2NH_2^+Cl^-$. A possible mechanism for the phase transition could be inferred on the basis of the crystal structure.[3] Kyuntsel' and Rosenberg reported a phase transition at 141 K in $2SbCl_3 \cdot C_6H_5OCH_3$ and suggested that the change of the relative position of $SbCl_3$ and methoxybenzene molecules took part in the phase transition.[4] We carried out a Zeeman-effect experiment on this compound in order to obtain information regarding the crystal structure.

Experimental

The compounds were prepared by melting and mixing $SbCl_3$ with diphenylammonium chloride and methoxybenzene in a molar ratio of 1:1 and 2:1, respectively. A single crystal of $2SbCl_3 \cdot C_6H_5OCH_3$ was prepared by the Bridgman method. NQR lines were displayed on an oscilloscope using a supperregenerative oscillator with the frequency modulation or recorded on a pen-recorder using an oscillator with the Zeeman modulation and a lock-in amplifier.

Results and Discussion

The results of the NQR measurement are listed in Table 1. The values for $2SbCl_3 \cdot C_6H_5OCH_3$ at 77 K are comparable to those already reported.[5]

$SbCl_3 \cdot (C_6H_5)_2NH_2^+Cl^-$. Figure 1 shows the temperature dependence of ^{35}Cl and $^{123}Sb(\nu_1)$ NQR frequencies between 77 and 300 K. The frequency-temperature curves of ^{35}Cl NQR lines showed a discontinuity at 108 K. The $^{121,123}Sb$ NQR lines were not observed below 108 K. We intended to search for the Sb NQR lines at 77 K between 6 and 48 MHz.

Table 1. NQR Parameters for $SbCl_3 \cdot (C_6H_5)_2NH_2^+Cl^-$ and $2SbCl_3 \cdot C_6H_5OCH_3$

Compound	T/K	Assignment		ν/MHz	
$SbCl_3 \cdot (C_6H_5)_2NH_2^+Cl^-$	77	^{35}Cl		20.39, 18.03, 17.32	
	109	^{123}Sb	ν_1[a]	29.96	$e^2Qq/h(^{121}Sb) = 308.9$ MHz[b]
		^{121}Sb	ν_1	47.27	$\eta = 0.136$
	263	^{35}Cl		19.91, 17.85, 17.10	
		^{123}Sb	ν_1	28.06	$e^2Qq/h(^{121}Sb) = 294.4$ MHz[b]
		^{121}Sb	ν_1	44.85	$\eta = 0.119$
$2SbCl_3 \cdot C_6H_5OCH_3$	77	^{35}Cl		20.82, 20.50, 20.42,	
				20.19, 19.14, 19.12	
		^{121}Sb	ν_1	63.12	$e^2Qq/h(^{121}Sb) = 411.9$ MHz[c]
		^{121}Sb	ν_2[a]	123.09	$\eta = 0.141$
		^{121}Sb	ν_1	61.19	$e^2Qq/h(^{121}Sb) = 401.1$ MHz[c]
		^{121}Sb	ν_2	119.97	$\eta = 0.125$
	R.T.[d]	^{35}Cl		19.81, 19.72, 18.80	
	298	^{121}Sb	ν_1	59.41	$e^2Qq/h(^{121}Sb) = 389.1$ MHz[c]
		^{121}Sb	ν_2	116.38	$\eta = 0.130$

a) ν_1 and ν_2 are frequencies corresponding to the transitions $\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$, respectively. b) The values of e^2Qq/h and η were derived from the frequency ratio of $\nu_1(^{121}Sb)/\nu_1(^{123}Sb)$. c) The values of e^2Qq/h and η were derived from the frequency ratio of ν_1/ν_2 for ^{121}Sb. d) R.T. signifies room temperature.

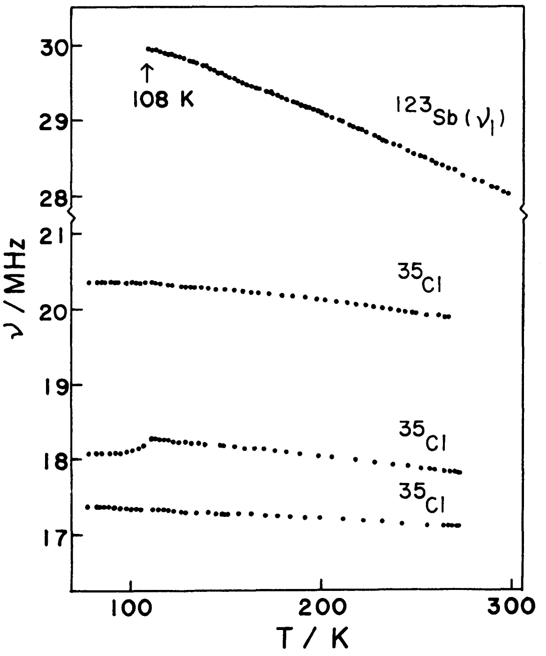

Fig. 1. Temperature dependence of $^{123}Sb(\nu_1)$ and ^{35}Cl NQR frequencies in $SbCl_3\cdot(C_6H_5)NH_2^+Cl^-$.

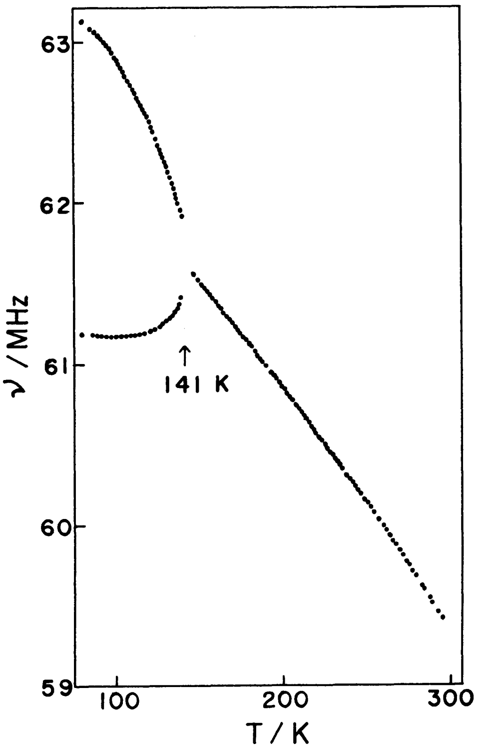

Fig. 2. Temperature dependence of $^{121}Sb(\nu_1)$ NQR frequencies in $2SbCl_3\cdot C_6H_5OCH_3$.

One weak NQR line was recorded at 20.52 MHz and this line could not be assigned because the NQR line due to the corresponding isotope was not observed. One ^{35}Cl NQR line shows a greater frequency shift than the other two lines in the low-temperature phase. An assignment of the ^{35}Cl NQR lines to each chlorine atom in a crystal can be made on the basis of the relation between the Sb–Cl bond length and the ^{35}Cl NQR frequency,[2] *i.e.*, the NQR frequency generally decreases with an increasing bond length. Accordingly, this line is assigned to the chlorine atom in a position *trans* to the chloride ion situated at a distance of 3.130 Å from the Sb atom.[3] This chloride ion also forms a $N\text{–}H\cdots Cl^-$ hydrogen bond with the diphenylammonium cation.[3] We consider that in the low-temperature phase the N–H bond length becomes short and this results in the weakning of the $H\cdots Cl^-$ interaction and the approach of the chloride ion to the Sb atom. Therefore, below the transition point the coordination state about the Sb atom changes and then the Sb NQR frequencies change greatly. In addition, a ^{35}Cl NQR line due to a chlorine atom in the Sb–Cl bond *trans* to this chloride ion shows a decreased frequency since the Sb–Cl bond is weakened by the *trans* influence. This could be seen in some other $SbCl_3$ complexes.[1,2]

The ^{35}Cl NQR lines disappeared above about 275 K, but the Sb NQR lines were observed at room temperature. From the results of a ^1H NMR measurement, the second moment decreased from 9 G^2 at 270 K to 5 G^2 at 300 K. In addition, the thermal parameters of the carbon atoms in the diphenylammonium cation have large values according to an X-ray crystal-structure analysis.[3] These facts show that some motions of the cation take place at room temperature. We consider that these cation motions and/or the reorientation of the $SbCl_3$ molecule as is seen in $SbCl_3\cdot C_8H_{10}$[2] cause the disappearance of the ^{35}Cl NQR lines. We could not observe the thermal anomaly around the transition point by a differential thermal analysis.

$2SbCl_3\cdot C_6H_5OCH_3$. Figure 2 shows the temperature dependence of $^{121}Sb(\nu_1)$ NQR frequencies between 77 and 300 K. Below the transition point, the resonance line splits into two lines with equal intensity. The frequency difference Δ in the low-temperature phase serves as a measure of the order parameter.[6,7] It could be seen from the plot of Δ^2 as a function of temperature that Δ^2 was a linear function between 123 and 138 K. Then, the transition point T_c was obtained by a best-fit procedure and it gave $T_c=141.3\pm0.8$ K. Using this value, it was also possible to fit Δ to the function[6]

$$\Delta = D\varepsilon^{\beta}, \qquad (1)$$

where $\varepsilon=|T_c-T|/T_c$ and β is the critical exponent. The values of D and β were obtained by the best fit of a log-log plot and it gave $D=3.2\pm0.2$ MHz and $\beta=0.50\pm0.01$ between $\varepsilon=2.1\times10^{-2}$ and $\varepsilon=1.2\times10^{-1}$. In

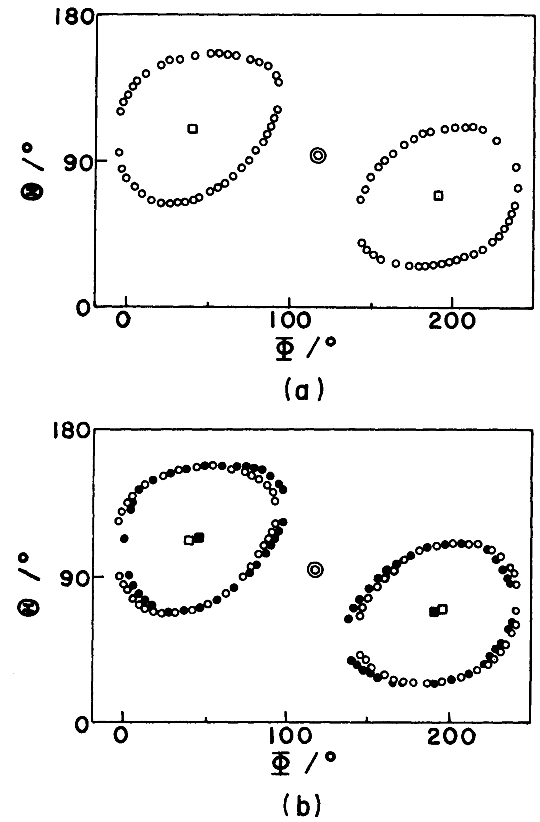

Fig. 3. Zero-splitting loci for $^{121}Sb(\nu_1)$ NQR lines in $2SbCl_3\cdot C_6H_5OCH_3$.
(a) Zero-splitting loci at room temperature.
(b) Zero-splitting loci at liquid-nitrogen temperature, ● for the 63-MHz line and ○ for the 61-MHz line. ■ and □: principal z-axes of EFG tensors; ◎: two-fold axis.

addition, the average frequency of the two split lines in the low-temperature phase was not continuously connected with the extraporation of the high-temperature curve. These experimental results confirm that β=0.5. This value is consistent with what the usual molecular field theory predicts.[6,7]

Figure 3 shows the zero-splitting loci at room temperature and liquid-nitrogen temperature. The single crystal for the Zeeman experiment was not broken by repeated heating and cooling cycles through the transition point. The measured points were fitted to the equation of a quadratic cone by the least-squares method in order to obtain the direction of the principal axes of the electric field gradient (EFG) tensor and the asymmetry parameter η. The obtained values of η were 0.142±0.007 for the 63-MHz line and 0.130±0.003 for the 61-MHz line at liquid-nitrogen temperature and 0.138±0.005 for the line at room temperature, respectively. The polar coordinates (Φ, Θ) for the principal z-axes of the EFG tensors in both phases are listed in Table 2 with respect to an orthogonal-axis system fixed to a crystal. The four zero-splitting loci which showed a Laue symmetry $2/m$ were obtained for each line in both phases. Only a pair of cones related to each other by the two-fold axis are represented in Fig. 3. The polar coordinates for the two-fold axis were obtained from the symmetry among the zero-splitting loci, *i.e.*, (117.7, 95.1) for the high-temperature phase and (117.6, 95.3) for the low-temperature phase. The Laue symmetry shows that the crystal in each phase belongs to a monoclinic system considering .a number of ^{35}Cl and $^{121,123}Sb$ NQR lines. It is also apparent that two $SbCl_3$ molecules represented by the chemical formula are crystallographically equivalent in the high-temperature phase. We consider that the crystal in the high-temperature phase has two types of symmetry elements, *i.e.*, a two-fold screw axis and a center of symmetry by which two $SbCl_3$ molecules are related to each other and that the crystal loses its center of symmetry in the low-temperature phase. A phenomenon like this has been actually observed in $NH_4H\ (ClCH_2COO)_2$.[8] In addition, we suggest that the loss of the center of symmetry arises from the displacement of a methoxybenzene molecule. This suggestion could be derived from the results of an observation of the ^{35}Cl NQR lines.

Table 2. Polar coordinates of the principal z-axes of EFG tensors

Temperature	Resonance line	$(\Phi, \Theta)/°$ a)	
ca. 300 K		(39.0, 112.1)	(192.6, 70.2)
ca. 77 K	63-MHz	(42.1, 113.8)	(189.0, 69.4)
	61-MHz	(36.9, 111.8)	(194.3, 70.3)

a) The standard deviations of the directions of the magnetic field for zero-splitting from the leat-squares method are 0.2° at room temperature and 0.5° at liquid-nitrogen temperature.

In the 2:1 $SbCl_3$ molecular complexes with aromatic compounds, the lowest NQR line is generally assigned to the chlorine atom in the Sb–Cl bond perpendicular to the aromatic ring and the other chlorine atoms in the Sb–Cl bonds parallel to the ring give the higher NQR lines.[2] On the basis of the NQR frequencies for $2SbCl_3\cdot C_6H_5OCH_3$ at room temperature, two resonance lines around 19 MHz were assigned to the chlorine atoms in the parallel Sb–Cl bonds and the line around 18 MHz to the one in the perpendicular Sb–Cl bond. Although each resonance line splits into two lines and, therefore, six resonance lines are observed in the low-temperature phase, we could distinguish three pairs of lines and also assigned them to individual lines in the high-temperature phase on the basis of the intensity ratio of the resonance lines for a single crystal. The magnitudes of the splittings at 77 K are 400 and 310 KHz for the chlorine atoms in the parallel Sb–Cl bonds and 20 KHz for the one in the perpendicular Sb–Cl bond. The change of the crystal field which arises from the displacement of the methoxybenzene molecule must largely affect the chlorine atoms in the parallel Sb–Cl bonds near the ring. This is consistent with a suggestion by Kyuntsel' and Rosenberg.[4] For a more detailed discussion, a crystal-structure analysis is necessary. A differential thermal analysis shows that there is a small shift of the base line at the transition point and it is considered that a discontinuous change in the specific heat takes place.

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