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NQR Study of the Phase Transition in $2SbCl_3$·o-Xylene

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Temperature dependence of ^{121}Sb NQR frequencies for $2SbCl_3$·o-xylene showed that a phase transition takes place at about 139 K, whereas the DTA experiment showed no thermal anomaly around the transition temperature.

The formation of the 2:1 complexes between $SbCl_3$ and o-, m-, and p-xylene was reported as the results of phase diagram studies.[1] We studied the bond characters between $SbCl_3$ and xylene in $2SbCl_3$·p-xylene[2] and $2SbCl_3$·m-xylene[3] by means of nuclear quadrupole resonance(NQR). For $2SbCl_3$·o-xylene, we obtained the different NQR results from the reported ones,[4] i.e., six NQR lines were observed at 77 K in contrast to one resonance line reported before and from the temperature dependence of NQR frequencies a phase transition was found as stated below.

$2SbCl_3$·o-xylene was obtained by mixing $SbCl_3$ with o-xylene in the 2:1 molar ratio. The melting point of this complex was 35 °C(33.5 °C according to Ref. 1). NQR spectra were displayed on a pen-recorder by using a superregenerative oscillator and a lock-in amplifier and were also detected by a Matec pulsed NQR spectrometer(Model 5100 + 525 + 625). The temperature dependence of NQR frequencies was measured for the sample immersed into a bath of petroleum ether cooled by liquid nitrogen. The differential thermal analysis(DTA) was performed between 98 and 210 K using a homemade apparatus.

NQR parameters for $2SbCl_3$·o-xylene are listed in Table 1. The quadrupole coupling constant e^2Qq/h and the asymmetry parameter η were derived from the ratio of NQR frequencies at about 280 K. Since resonance lines except for ν_1(ν_1 stands for the resonance line due to the transition m=±1/2 - m=±3/2) for ^{121}Sb and ^{123}Sb were too weak at 77 K to determine the frequency accurately, we could not assign a pair of ^{121}Sb and ^{123}Sb NQR lines to each equivalent atom in the crystal. The one ^{121}Sb NQR line was observed for $2SbCl_3$·p-xylene,[2] which indicates that the asymmetric unit in the crystal corresponds to one $SbCl_3$ molecule and a half p-xylene molecule with the inversion center.[5] Although no X-ray analysis is available for $2SbCl_3$·o-xylene, the unit which consists of two $SbCl_3$ molecules and one o-xylene molecule without the inversion center is basically asymmetric one and then two Sb atoms in this unit have a different coordination environment and, therefore, two units like this exist in the crystal at room temperature considering the number of the NQR lines. The temperature dependence of $^{121}Sb(\nu_1)$ NQR frequencies is shown in

Fig. 1. Six NQR lines were observed at 77 K with the intensity ratios of 2:1:1:2:3:3 in order of decreasing frequency. On raising the temperature, the number of the six resonance lines reduced to four at about 139 K with the intensity ratios of 1:1:1:1. This means that the structural phase transition takes place at about 139 K and the symmetry of the crystal structure becomes the higher one above the transition temperature. No thermal anomaly appeared on the DTA curves around the transition temperature in the heating process. We tried to observe the free induction decay(FID) of ^{121}Sb NQR below the transition temperature by using a pulsed NQR spectrometer. On raising the temperature the FID's of four higher-frequency lines were able to be observed up to ca. 90 K and for the rest up to ca. 115 K. The disappearance of the FID signal may be caused through the non-secular part of the time constant T_2^* by the shortening of the spin-lattice relaxation time T_1.[6] We are planning to measure the temperature dependence of T_1's in order to clarify this point. We consider that the only one line, which was relatively strong, of the six NQR lines observed at 77 K was reported as the early NQR results.[4]

Table 1. NQR Parameters for $2SbCl_3 \cdot$o-Xylene

Temperature		Frequency/MHz		
77 K	$^{121}Sb(\nu_1)$	62.27, 62.10, 60.14		
		59.38, 58.92, 58.59		
	$^{123}Sb(\nu_1)$	40.13, 39.34, 37.96		
		36.12, 35.81[b]		
ca. 280 K	$^{121}Sb(\nu_1)$	60.12	e^2Qq/h/MHz	η
	$^{123}Sb(\nu_1)$	38.35	391.98	0.146
	$^{121}Sb(\nu_1)$	58.13		
	$^{123}Sb(\nu_1)$	36.93	379.52	0.140
	$^{121}Sb(\nu_1)$	57.83		
	$^{123}Sb(\nu_1)$	35.17	385.25	0.027
	$^{121}Sb(\nu_1)$	57.12		
	$^{123}Sb(\nu_1)$	35.51	378.90	0.067

a) The experimental errors are within ±0.02 MHz.
b) Doublet.

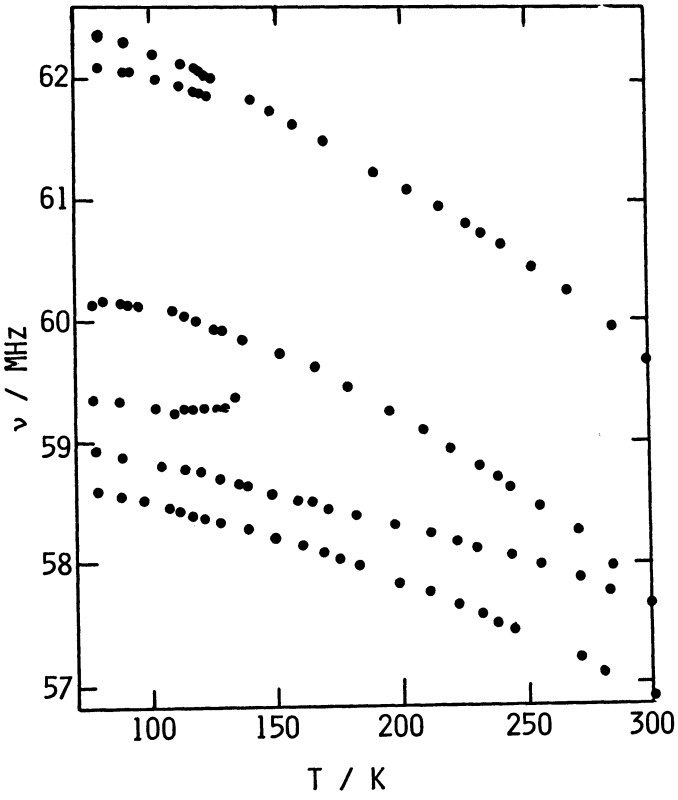

Fig. 1. Temperature dependence of $^{121}Sb(\nu_1)$ NQR frequencies.

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