Phase Transitions in Bis(4-chlorophenyl)sulfone as Studied by ^{35}Cl FT-NQR*

Hirokazu Nakayama, Taro Eguchi, and Michihiko Kishita

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan

Z. Naturforsch. **47 a,** 232–236 (1992); received July 10, 1991

The temperature dependence of ^{35}Cl NQR frequencies in bis(4-chlorophenyl)sulfone was measured in the temperature range of 4.2–297 K. Below 115 K four NQR lines due to four inequivalent chlorines exist in the commensurate phase, contrary to the single NQR line reported by Corbero et al. It follows that the commensurate-incommensurate transition is of the first-order, and the incommensurate-normal transition at 150 K is quasi-continuous. It is also suggested that the successive phase transitions are triggered by the small angle rotation of the molecules about their C_2-axes.

Key words: ^{35}Cl NQR, Bis(4-chlorophenyl)sulfone, ^{1}H NMR, Incommensurate phase, Phase transition.

Introduction

Bis(4-chlorophenyl)sulfone (BCPS) is composed of two chlorophenyl groups, each of which is connected to a sulfur through a single bond. Judging from the steric hindrance of the molecule, we can expect a low potential barrier for the twisting of two phenyl rings [1].

At room temperature BCPS forms monoclinic crystals (normal phase) with a space group of $I\,2/a$ [2–4], containing four molecules in a unit cell. The molecules are located on the two-fold axes and are all equivalent in the crystalline lattice. Recently, Corbero et al. [5–7] found successive phase transitions at 150 and 115 K by means of ^{35}Cl NQR measurements. This observation is, however, inconsistent with previous work based on both NQR [8, 9] and calorimetric data [10]. The latest AC-calorimetry measurement also confirmed the transition sequence [11]. Corbero et al., thus, concluded the intermediate phase to be incommensurate [5–7].

Furthermore, Kasano et al. observed the satellite reflections below 150 K by X-ray diffraction [12]. The satellite reflections appear at $\boldsymbol{q} = \boldsymbol{a}^* \pm (1/5 + \delta)\ \boldsymbol{b}^*$, where $\boldsymbol{a}^*$ and $\boldsymbol{b}^*$ represent the reciprocal lattice vectors in the normal phase and δ the misfit parameter. However, on cooling these satellites persist until 20 K, indicating no commensurate-incommensurate transition (so-called lock-in transition). In addition, using Raman scattering, Nakayama et al. [13, 14] detected a soft mode below 141 K which has the following relationship $\nu \propto (141 - T)^{0.39}$, but failed to find the lock-in transition.

In order to unravel the phase behavior of BCPS, which now seems to be confused, and to shed light on the mechanism of the phase transition, ^{35}Cl NQR frequencies were precisely determined from 4.2 K to room temperature. Proton spin-lattice relaxation times were measured to investigate the twisting of two phenyl rings and to reveal the correlation between the molecular motion and the transition sequence.

Experimental

BCPS (Wako Pure Chemical Industries, Ltd.) was purified by vacuum sublimation at about 100 °C. The powdered sample was sealed in a glass ampule (15 mm ∅) with He gas. ^{35}Cl NQR frequencies were measured by an FFT pulsed spectrometer based on a Matec gating modulator. In order to observe weak signals below 150 K, more than 4096 FID signals were accumulated before Fourier-transformation. The resonance frequencies were obtained within ± 1 kHz. The temperature of the sample was controlled within ± 0.1 K, otherwise the NQR lines were broadened because of the temperature gradient across the sample. Proton spin-lattice relaxation times were measured by

---

* Presented at the XIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, London, U.K., July 15–19, 1991.

Reprint requests to Dr. H. Nakayama, Institute of Chemistry, College of General Education, Osaka, University, Toyonaka, Osaka 560, Japan.

0932-0784 / 92 / 0100-0232 $ 01.30/0. – Please order a reprint rather than making your own copy.

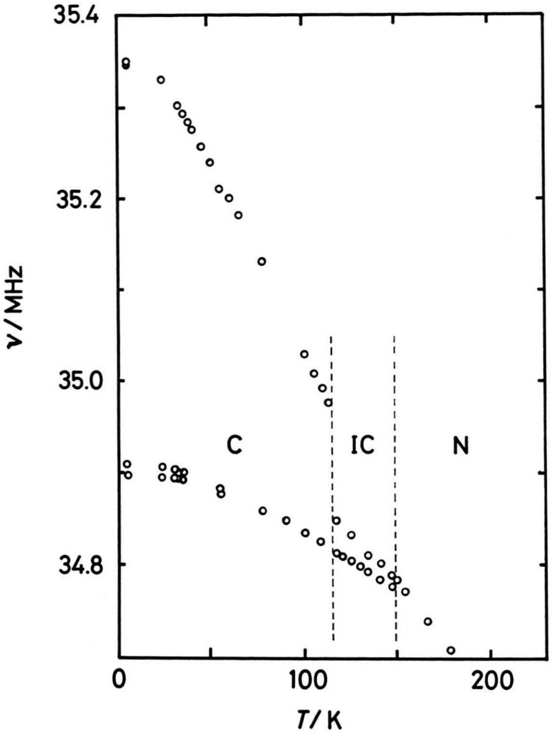

Fig. 1. Temperature dependence of the ^{35}Cl NQR frequencies in bis(4-chlorophenyl)sulfone. C: commensurate phase, IC: incommensurate phase, N: normal phase.

a saturation $-\tau-\pi/2$ pulse sequence at 20.4 MHz by using a JEOL pulsed spectrometer (JNM-FSE-60SS).

Results and Discussion

Figure 1 and Table 1 show the temperature dependence of the ^{35}Cl NQR frequencies in BCPS. Two phase transitions can be clearly recognized at 115 and 150 K. The transition temperatures are consistent with those determined from previous NQR [5–7] and heat capacity measurements [11]. The same resonance frequencies at 77 K were observed from samples which were either rapidly (−10 K/min.) or slowly cooled (−0.05 K/min.). We could not reproduce the thermal-hysteresis behavior previously suggested by both Raman measurements [13, 14] and X-ray diffraction [12].

Two doublets at 4.2 K (Fig. 2) arise from four inequivalent Cl atoms. The frequency difference between the two peaks of the lower-frequency doublet (Fig. 3) is found to be proportional to $T-T_c$, where T_c

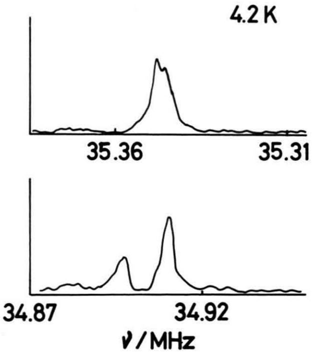

Fig. 2. ^{35}Cl NQR spectra in bis(4-chlorophenyl)sulfone at 4.2 K.

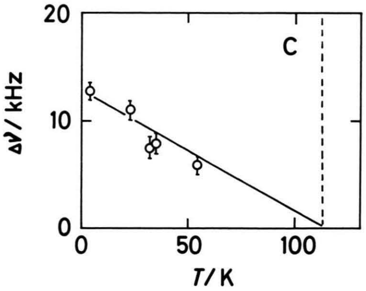

Fig. 3. Frequency difference between the two peaks of the lower-frequency doublet in the commensurate phase as a function of temperature. The solid line shows $\Delta\nu \propto (T-T_c)$.

Table 1. Temperature dependence of ^{35}Cl NQR frequencies in bis(4-chlorophenyl)sulfone.

T/K	ν/MHz		
	This work		Other works
4.2	35.349	34.908	
	35.346	34.896	
23.0	35.330	34.907	
		34.894	
55.0	35.210	34.883	
		34.877	
77.3	35.130	34.859	34.828 [a]
100.1	35.029	34.836	34.810 [b]
113.1	34.975	34.820	
117.3	34.835	34.814	
124.4	34.857	34.805	
134.3	34.811	34.793	
141.2	34.804	34.785	
150.0	34.786		
166.1	34.741		
296.8	34.353		34.330 [c]

[a] Ref. [8], [b] Ref. [9]; at 90 K, [c] Ref. [9]; at room temperature.

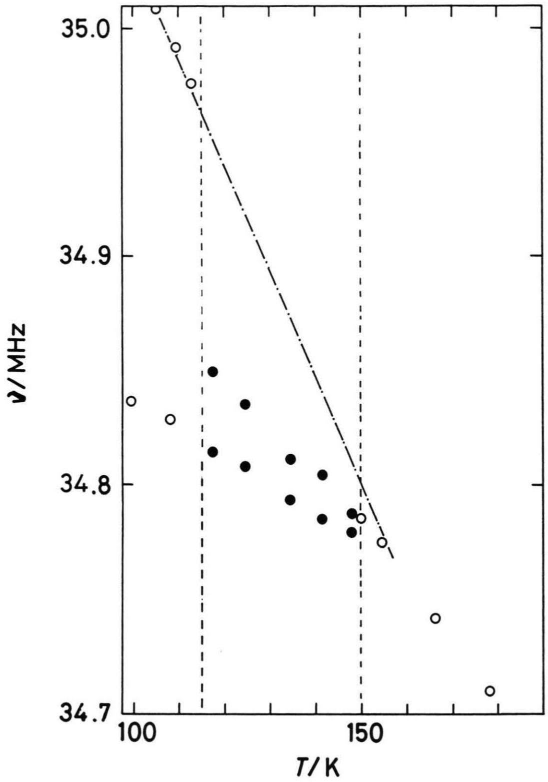

Fig. 4. Temperature dependence of the ^{35}Cl NQR frequencies in bis(4-chlorophenyl)sulfone in the vicinity of the incommensurate phase. Closed circles indicate the two edge peaks of the signals in the incommensurate phase. The dashed-dotted line represents the extrapolation of the higher-frequency signals of the commensurate phase.

is the lock-in transition temperature. The signals of the higher-frequency doublet overlap each other above 4.2 K, not because the phase transitions take place between 4.2 and 23 K but because the frequency difference between the two peaks is comparable to the linewidth. The lower-frequency doublet behaves in the same way above 55 K. The temperature coefficients of the resonance frequencies change continuously between 4.2 and 115 K. These facts suggest that there is no phase transitions between 4.2 and 115 K. The commensurate phase, therefore, persists down to 4.2 K. It is worth noting that in the commensurate phase four inequivalent Cl sites exist rather than the single site which has been claimed in previous papers [5–7]. The higher-frequency signal disappears above 115 K, indicating that the lock-in transition is of first-order. As shown in Fig. 3, the frequency difference between the two peaks of the lower-frequency doublet behaves just like an order parameter in spite of the first-order nature of this transition.

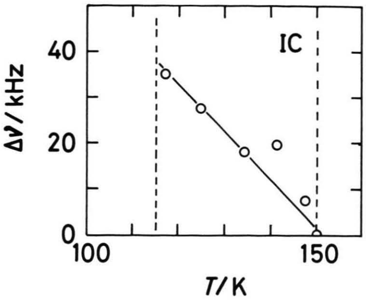

Fig. 5. Frequency differences between two edge peaks in the incommensurate phase of bis(4-chlorophenyl)sulfone as a function of temperature. The solid line shows $\Delta\nu \propto (T_I - T)$.

On further heating the incommensurate phase, the NQR spectra consist of broad lines with two edge peaks [15] (we plotted the frequencies of these peaks). The ^{35}Cl NQR frequencies in the vicinity of the incommensurate phase are shown in Figure 4. The higher-frequency peak smoothly continues to the data above 150 K (normal phase), although the temperature coefficients of the resonance frequencies are different in both phases. The lower-frequency peak, however, jumps by only 10 kHz at 150 K. The normal-incommensurate transition, thus, seems to be quasi-continuous.

In order to study the mechanism of the successive phase transitions we have investigated the spectra in the incommensurate phase from the phenomenological point of view [15]. Three characteristic features are noticeable in the frequency data.

i) The lower-frequency peak in the incommensurate phase continues to the resonance frequencies below the lock-in transition (115 K).

ii) The higher frequency peak in the incommensurate phase persists in the normal phase.

iii) The frequency difference between two edge peaks is almost proportional to $T_I - T$, where T_I is the normal-incommensurate transition temperature (150 K; see Figure 5).

The features described above resemble those observed in the temperature dependence of the ^{81}Br NQR frequencies in Cs_2CdBr_4 and Cs_2HgBr_4 [16, 17]. As a result, we analyze our present data in an analogous way.

According to the phenomenological theory [15] the resonance frequency of a Cl atom in the incommensurate phase can be expressed as

$$\nu = \nu_0 + a_1 u + \tfrac{1}{2} a_2 u^2 + \ldots, \tag{1}$$

where ν_0 is the resonance frequency in the normal phase, u the displacement of an atom from the original position in the normal phase, and a_1 and a_2 are appropriate constants.

For simplicity, we adopt the "one dimensional plane wave model", so that the displacement can be given by

$$u(\mathrm{x}) = A \cos(k_\mathrm{I} x + p_0), \tag{2}$$

where k_I is the wave vector of the incommensurate modulation. Putting (2) into (1) we obtain the frequency distribution as

$$f(\nu) = \{(2\pi \nu_2^*)^2 \, V(1-V)\}^{-0.5}, \tag{3}$$

$$V = (\nu - \nu_0)/(\nu_2^*/2), \tag{4}$$

where $\nu_2^* = a_2 A^2$ for the quadratic case, i.e., the quadratic term of (1) is dominant. The edge peaks appear at $\nu = \nu_0$ and $\nu = \nu_0 + a_2 A^2/2$. This means that one edge in the incommensurate phase continues to the frequencies above T_I.

Landau's phenomenological theory [15] also gives

$$A \propto (T_\mathrm{I} - T)^{0.5}. \tag{5}$$

This leads to

$$\Delta\nu = a_2 A^2/2 = a_2 (T_\mathrm{I} - T)/2, \tag{6}$$

i.e., the splitting is proportional to $T_\mathrm{I} - T$. The above theory can, therefore, explain our experimental results qualitatively.

In order to obtain such a conclusion the quadratic term must be dominant in (1). This demands that the site symmetry of the Cl atom in the normal phase is such that ν is a symmetric function of the order parameter. This will give a clue to obtain information about the mode of the modulation wave ($\boldsymbol{q} = (1/5 + \delta)\, \boldsymbol{b}^*$).

Corbero et al. [5–7] suggested that the phase transition accompanied the twisting of the phenyl rings about the Cl–S bond, which results in a change of the dihedral angle between two planes of the phenyl rings. This mode results in fluctuations of the dipolar interactions between protons. Proton spin-lattice relaxation times (T_1's) are, however, longer than 1000 s and almost constant over the whole temperature range measured (Figure 6). As a result, very small amounts of paramagnetic impurities probably govern the relaxation. In BCPS crystals, the molecules seem to be rigid on the NMR time scale, which suggests that there is a high activation barrier for the twisting of the phenyl ring about the Cl–S axis.

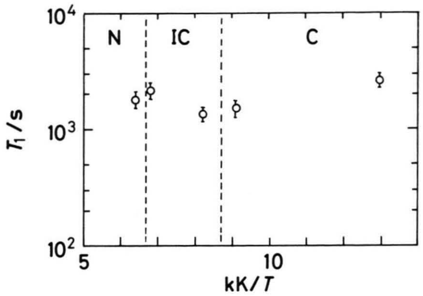

Fig. 6. Temperature dependence of ^{1}H spin-lattice relaxation times in bis(4-chlorophenyl)sulfone.

A more probable mode is the small angle rotation about C_2-axes of the molecules. In this case, the order parameter corresponds to the rotation angle, which is modulated by the plane wave with the wave vector, $\boldsymbol{k} = (1/5 + \delta)\, \boldsymbol{b}^*$ [12].

Generally, the symmetry in the commensurate phase falls into a subgroup of the symmetry in the normal phase. An analogous situation is observed in the relationship between the space group of the high-temperature phase and that of the low-temperature phase in the case of the second-order phase transition. As shown in Fig. 1, the temperature coefficients of the resonance frequencies of the high-frequency signal remain constant above 30 K in the commensurate phase. The extrapolation of these frequencies above the lock-in transition crosses the frequencies of the lower-frequency signal at about 150 K, which is just at the normal-incommensurate transition temperature (see Figure 4). This may support the idea that the space group of the commensurate phase belongs to the subgroup of the symmetry in the normal phase.

At the lock-in transition the wave vector, $\boldsymbol{k}$, of the incommensurate modulation becomes commensurate. According to X-ray diffraction [12], the probable soft-phonon mode to obtain the commensurate structure is characterized by the wave vector, $\boldsymbol{b}^*/5$, the lattice constant along the b-axis being five times larger than that in the normal phase. However, only four resonances are observed in the commensurate phase, which could be accounted for in two different ways. Firstly, four chlorine sites become inequivalent, without changing the size of the unit cell, but this seems unlikely since there are more than thirty phonon modes observed at 4.2 K [13–14]. Secondly, the more plausible mode results from the lattice constant along *b*-axis becoming four (or two) times larger than that found in the normal phase instead of five times. Thirty two (or sixteen) chlorine atoms are classified into four inequivalent groups.

To sum up, four inequivalent Cl sites exist in the commensurate phase of BCPS. The lock-in transition at 115 K is first-order. The normal-incommensurate transition occurs quasi-continuously at 150 K. The transition sequence can be triggered by the small angle rotation of the molecules about their C_2-axes.

Acknowledgements

The authors wish to express their thanks to Dr. K. Saito of the Tokyo Metropolitan University for his stimulating discussions. They are also grateful to Professor B. T. Heaton of the University of Liverpool for his critical reading of the manuscript.

[1] B. Rerat and R. Rerat, J. Chim. Phys. **77,** 167 (1980).
[2] J. G. Sime and S. C. Abrahams, Acta Crystallogr. **13,** 1 (1960).
[3] R. G. Treuting and S. C. Abrahams, Acta Crystallogr. **14,** 190 (1961).
[4] G. E. Bacon and N. A. Curry, Acta Crystallogr. **13,** 10 (1960).
[5] J. Corbero, D. J. Pusiol, A. E. Wolfenson, and A. H. Brunetti, Phys. Status Solidi a, **91,** K97 (1985).
[6] J. M. Corbero, A. E. Wolfenson, D. J. Pusiol, and A. H. Brunetti, Phys. Lett., **114 A,** 105 (1986).
[7] D. J. Pusiol, A. E. Wolfenson, and A. H. Brunetti, Phys. Rev. B **40,** 2523 (1989).
[8] P. J. Bray and R. G. Barnes, J. Chem. Phys. **27,** 551 (1957).
[9] G. Chakrapani, V. V. S. Sarma, and C. R. K. Murty, J. Phys. Soc. Japan **34,** 994 (1973).
[10] N. V. Novoselova, L. Ya. Tsvetkova, I. B. Rabinovich, E. M. Moseeva, and L. A. Faminskaya, Russ. J. Phys. Chem. **59,** 350 (1985).
[11] K. Saito, H. Kamio, K. Kikuchi, and I. Ikemoto, Thermochimica Acta **163,** 241 (1990).
[12] H. Kasano, T. Koshiba, H. Kasatani, and H. Terauchi, J. Phys. Soc. Japan **59,** 408 (1990).
[13] H. Nakayama, H. Kano, T. Sakata, and K. Ishii, presented at Molecular Structure Symposium, Tokyo 1988, Abstract 3C06 (in Japanese).
[14] H. Nakayama, T. Sakata, H. Kano, and K. Ishii, presented at the 58th Annual Meeting of the Chemical Society of Japan, Kyoto 1989, Abstract 1IC12 (in Japanese).
[15] R. Blinc, Phys. Rep. **79,** 331 (1981).
[16] H. Nakayama, N. Nakamura, and H. Chihara, J. Phys. Soc. Japan **56,** 2927 (1987).
[17] S. Plesko, R. Kind, and H. Arend, Phys. Status Solidi a **61,** 87 (1980).