Phase Transitions in 4,4′-Dichlorobenzophenone as Studied by ^{35}Cl FT-NQR *

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The temperature dependence of ^{35}Cl NQR frequencies in 4,4′-dichlorobenzophenone was measured between 9.3 and 372 K by the pulse Fourier-transform method. Successive phase transitions were observed at 189 and 194 K. Concerning these phase transitions, the curious thermal hysteresis phenomenon found in a previous NQR experiment was not reproduced in the present study. It also follows that NQR indicates another phase transition around 220 K, although no thermal anomaly was detected there by DTA. Tentative explanations for these three phase transitions are presented in relation to the incommensurability between 189 and 220 K. In addition, a novel phase transition was found to occur at 331 K according to both DTA and ^{35}Cl NQR. A single NQR line observed at room temperature splits into two components above 331 K, suggesting that the symmetry above 331 K is lower than that at room temperature. This is the behavior of re-entrant phase transition, and it reveals the quasi-continuous nature.

Key words: ^{35}Cl NQR, 4,4′-dichlorobenzophenone, Phase transition, Incommensurate phase.

Introduction

We have been interested in phase transitions in the crystals of butterfly-like molecules which contain two phenyl groups, such as 4,4′-dichlorobiphenyl sulfone (bis(4-chlorophenyl)sulfone; BCPS) and 4,4′-dichlorobenzophenone (DCBP). Some of these compounds exhibit curious phase transitions which may be triggered by a coupling between the conformational change (internal rotation) of the phenyl groups and the translational displacement of the molecules in the crystalline lattice. In fact, our recent work [1] as well as other various experiments [2–4] suggested that BCPS shows an incommensurate phase.

In the case of DCBP two phase transitions have already been observed by DSC at 185 and 189 K [5], and the phase between these temperatures has been suggested to be incommensurate [6]. Especially, an unusual thermal hysteresis phenomenon of the NQR frequencies was reported to take place in the temperature range 170–194 K [6]. We were much interested in such a novel hysteresis and conducted both DTA and ^{35}Cl FT-NQR experiments on DCBP in order to obtain some clue to elucidate the mechanisms of the phase transitions. In the course of the experiments we found two new phase transitions at about 220 K and 331 K. This paper describes these experiments and a novel nature of the phase transitions.

Experimental

4,4′-dichlorobenzophenone (Wako Pure Chemical Industries, Ltd.) was purified by sublimation in vacuo at ca. 400 K and sealed into a glass ampule (15 mm ∅) for the NQR measurements, and into a DTA tube with a small amount of helium gas for heat exchange.

The pulsed NQR spectrometer is based on a Matec gating modulator (model 5100) and a home-made probe head. The temperature of the sample was determined by Au–Fe–Chromel thermocouples to within 0.1 K. In order to avoid the broadening of NQR lines due to the temperature gradient, we controlled the temperature fluctuation within 0.1 K and waited for longer than 30 minutes before measurements. We measured the signals below room temperature on heating up the specimen gradually from low temperatures (below 100 K) in order to avoid unexpected effects of supercooling associated with the complex thermal hysteresis around 200 K as reported previously [6].

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NQR frequencies were determined to within 0.1 kHz by Fourier transformation (FT) of the free induction decay (FID) signals which were accumulated to more than 1024. The resonance frequencies of these weak signals, especially in the vicinity of 200 K, were determined by measuring the FID's at two or more different excitation frequencies. ^{35}Cl spin-lattice relaxation times were measured by the $\pi/2-\tau-\pi/2$ pulse method to within 10% error.

DTA measurements were performed above 77 K by a home-built apparatus with Chromel-P-Constantan thermocouples.

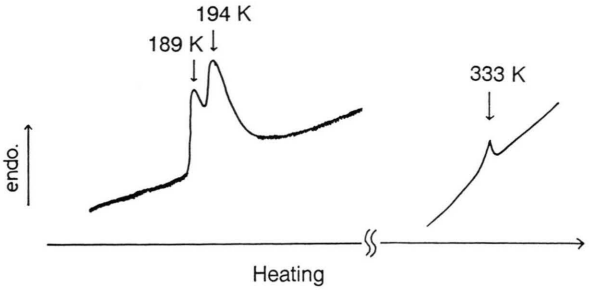

Fig. 1. Thermal anomalies in the temperature region of the phase transitions on heating 4,4′-dichlorobenzophenone. The phase transitions at 189 and 194 K can be supercooled by about 15 K. The peak area of the transition at 331–333 K was estimated to be about 5% of that for the melting (418 K). This anomaly did not appear throughout the transition region on cooling.

Results and Discussion

On cooling DCBP, two thermal anomalies were observed by DTA in the vicinity of 180 K, where the transition temperatures depended on the cooling rate. For example, rapid quenching of the sample with liquid nitrogen (faster than −10 K/min) brought both transition temperatures down to around 175 K. The sample cooled down below 175 K to pass the transitions prior to the measurements indicated in the heating run two anomalies at 189 and 194 K as shown in Figure 1. These transition temperatures are slightly different from those previously reported [5, 6]. They can be supercooled by about 15 K, indicating that they are of first order.

Figure 2 shows the temperature dependence of the ^{35}Cl NQR frequencies between 9.3 and 372 K. The typical values of the NQR frequencies are also listed in Table 1. Since the temperature gradient across the sample resulted in broadening of the NQR lines on cooling, the measurements were made only in the heating run on the sample pre-cooled down to 100 K. It can be seen that the frequency of the single resonance line below 189 K can be smoothly connected to the line above 220 K, except the transition region between 189 and 220 K where NQR lines show complex behavior. Figure 3 shows the details of the behavior of the NQR frequencies in this temperature region.

There is also a single resonance line at room temperature. This fact indicates that all chlorine nuclei are equivalent in the crystalline lattice, being consistent with the result of the X-ray structural analysis (C2/c, $Z=4$) [7]. Hence, it can be considered that the low temperature and the room temperature phases have the same symmetry. In other words, the room temperature phase is stable down to 9.3 K except in the

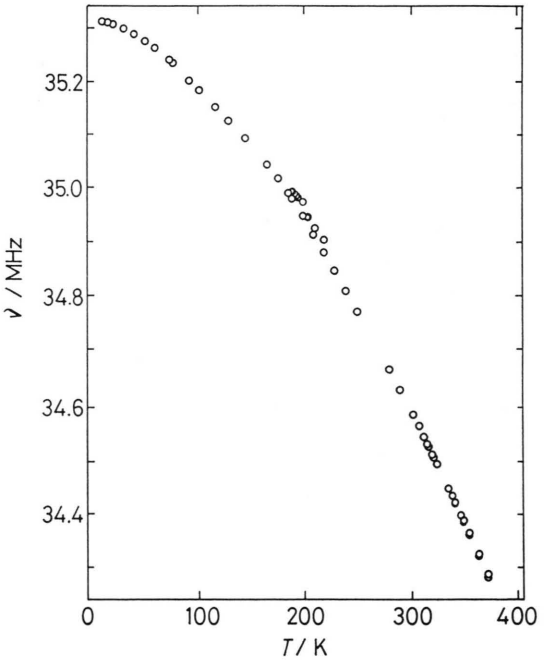

Fig. 2. Temperature dependence of ^{35}Cl NQR frequencies of 4,4′-dichlorobenzophenone in the whole temperature region observed (9.3–372 K).

temperature region between 189 and 220 K. Such a kind of phase behavior may be considered as a so-called "re-entrant" phenomenon [8].

Phase Transitions in the Temperature Region between 189 and 220 K

As shown in Fig. 3, the single resonance line in the lowest temperature phase splits abruptly into two at

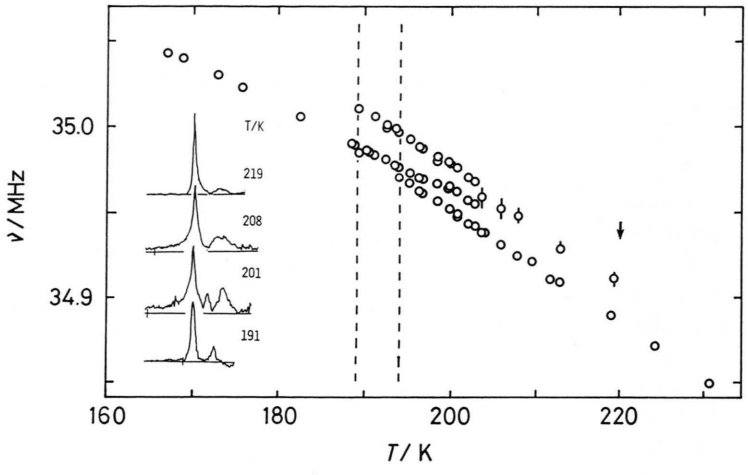

Fig. 3. Temperature dependence of ^{35}Cl NQR frequencies of DCBP in the phase-transition region of 160–230 K. Dashed lines indicate the transition temperatures, 189 and 194 K, determined by DTA, and the arrow indicates the temperature (ca. 220 K) where the high-frequency NQR signal broadens out. Typical resonance spectra are also shown in the insert.

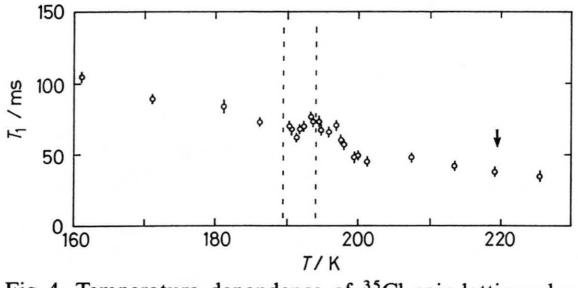

Fig. 4. Temperature dependence of ^{35}Cl spin-lattice relaxation time (T_1 : linear scale) of DCBP between 160 and 230 K.

Table 1. ^{35}Cl NQR frequencies in 4,4'-Dichlorobenzophenone

T/K	ν/MHz	T/K	ν/MHz
9.3	35.312_0	219[a]	34.912
			34.888
77.3	35.235_6	302	34.586_4
191[a]	35.004	372[b]	34.285_5
	34.983		34.281_4
201[a]	34.975		
	34.961		
	34.947		

[a] Line shapes at these temperatures are shown in Figure 3.
[b] Line shape is shown in Figure 5.

189 K, suggesting that this transition is of first order in consistency with our DTA results, although the intensity of the lower frequency line is stronger than that of the higher frequency line by a factor of 5 or more. We confirmed several times that at this transition point the NQR line does not undergo any "second-order like" splitting reported by Wolfenson et al. [6]. On further heating, the lower frequency line in the intermediate phase splits into two components at the second transition point, 194 K, whereas the higher frequency line persists above 194 K. In spite of the fact that the thermal anomaly at this phase transition is larger than that at 189 K, as can be seen in Fig. 1, the NQR data show only a small discontinuity at 194 K.

The two high frequency resonance lines collapse into a single line above 203 K, which then disappears (or fades out) above 220 K. This fact suggests that there must be another phase transition with negligible heat of transition around 220 K.

Furthermore, ^{35}Cl spin-lattice relaxation times (T_1) show a weak temperature dependence as shown in Fig. 4, where we cannot recognize, beyond the experimental error any significant effect such as critical slowing down at the transition temperatures.

Wolfenson et al. [6] stated on the basis of the line shape and the T_1 behavior in their NQR measurements that the phase in the temperature range of 189–194 K is incommensurate. However, our present work does not directly support this point of view, because the 189 K transition does not seem to correspond to a usual lock-in phase transition as mentioned above.

Generally, the normal (high temperature)-incommensurate phase-transition is of second-order, which takes place as a result of a small deviation of molecular or ionic arrangement from the lattice periodicity and is accompanied by a very small heat of transition. On the other hand, a usual lock-in (incommensurate-low temperature) phase transition is accompanied by a relatively large heat anomaly. For example, in BCPS

the small angle rotation of molecules about their C_2-axes transmits cooperatively and triggers the transition, as confirmed by an X-ray diffraction study [4].

The ^{35}Cl spectrum of BCPS has the following feature characteristic of incommensurate phase transition [1]: (i) The line in the incommensurate phase consists of doublets with equal intensities and with steep edges. (ii) The lower-frequency line continues smoothly through the lock-in transition. (iii) The higher-frequency line persists in the normal, the highest temperature, phase. (iv) The frequency difference between the two lines is nearly proportional to $T_I - T$, where T_I is the normal-incommensurate transition temperature. We presented a model for the transition in which the successive molecular rotational displacement is represented by a simple one-dimensional plane wave, and applying Landau's phenomenological theory we were able to interpret the above four features in a qualitative manner.

In the case of DCBP, however, the present DTA results show that the transitions at 189 and 194 K are both of typical first-order, and so these transitions do not correspond to "usual" lock-in and normal-to-incommensurate transitions as in BCPS.

Therefore, the above mechanism does not at the first sight apply to the curious transitions in DCBP. However it can interpret both the present DTA and NQR results if we take into account the 220 K transition and make the following assumptions; (i) An incommensurate transition with a very small heat of transition occurs somewhere above 220 K where the higher NQR line broadens; (ii) The 189 K transition is a lock-in transition with a large heat of transition; and (iii) The incommensurate phase undergoes a transition to another incommensurate phase at 194 K at which the phase of the plane wave is reversed for some reason. This model can account for the DTA and NQR data without any conflict with the general feature of the incommensurate transition.

The remaining problems are as follows. According to the lineshape, is it possible to consider small islands which acquire the incommensurate structure? Can a phase reversal of the incommensurate plane wave occur? Does the phase reversal bring about the interchange of two resonance frequencies? Can we apply a model for the multiple-q modulated incommensurate phase transitions [9] to our NQR results? These points require further development of the theories for incommensurate transitions as well as rigorous structural studies below about 220 K.

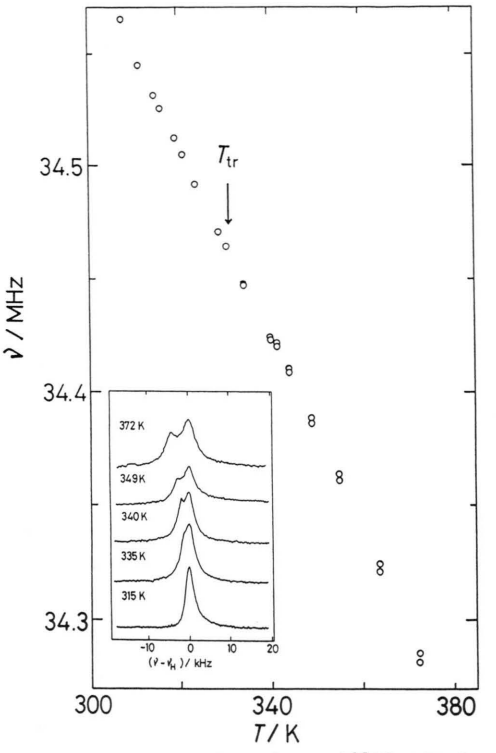

Fig. 5. Temperature dependence of ^{35}Cl NQR frequencies of DCBP between 300 and 372 K. The line shapes are also inserted.

Phase Transition above Room Temperature

On heating the sample from room temperature, DTA exhibited a small thermal anomaly at $T_{tr} = 331 - 333$ K, as shown in Fig. 1, and a very large melting peak at 418 K. The peak area of the transition at 331 K was estimatd to be about 0.5 percent of that for the melting and is still very small compared with those of the transitions at 189 and 194 K. The shape of the anomaly suggests that the transition is of second-order. The anomaly did not appear throughout the transition region on cooling, but the specimen precooled down to 200 K showed the anomaly at 331 K on heating. These facts together with the NQR results given below suggest that the transition at 331 K is a quasi-continuous first order transition [10].

The single ^{35}Cl NQR line splits into two components above 331 K as shown in Fig. 5, suggesting the lowering of the site symmetry of the ^{35}Cl nuclei in the DCBP molecule. The frequency difference ($\Delta\nu$) between the two lines in the highest temperature phase is plotted in Figure 6. $\Delta\nu$ can be expressed as

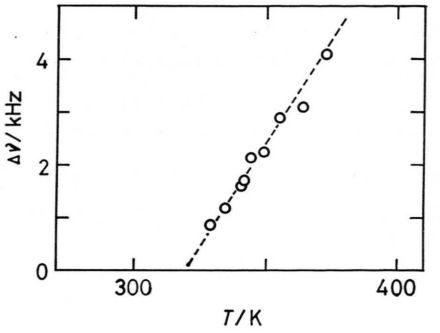

Fig. 6. Frequency difference between the two NQR lines against temperature in the highest temperature phase of DCBP. The broken line represents $\Delta\nu \propto (T - T_0)$, where $T_0 = 320$ K.

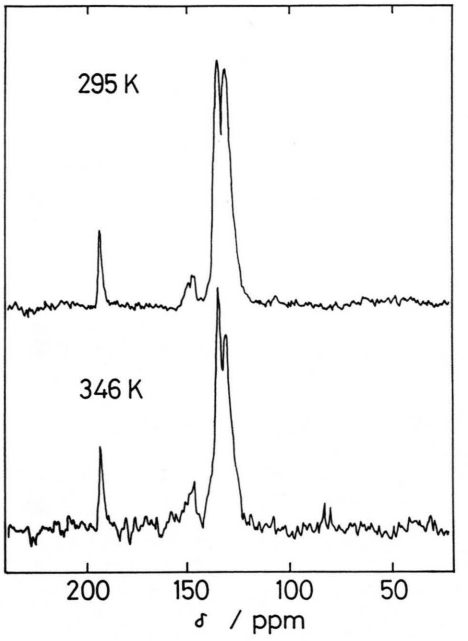

Fig. 7. ^{13}C CP/MAS NMR spectra of 4,4′-dichlorobenzophenone.

$\Delta\nu \propto (T - T_0)$, where $T_0 = 320$ K. The fact that T_0 is lower than T_{tr} determined by DTA suggests that the transition is of first order but has a quasi-continuous nature. The amount of the frequency difference between two lines is only 4 kHz even at 372 K. Such a small difference indicates that the structure of the high temperature phase must be very similar to that of the room temperature phase. This behavior of the NQR spectrum resembles that in malononitrile crystal [11]. Symmetry lowering in the middle temperature phase (triclinic) has been reported by a ^{14}N NQR study concerning the re-entrant phase transitions of malononitrile, and one can recognize that both the low- and the high-temperature phases assume almost the same monoclinic structure.

In the case of malononitrile the re-entrant phenomenon was thought to take place as a result of an anharmonic coupling between the order parameter and the anisotropic thermal expansion of the crystal lattice [8]; that is, the alignment of the molecules with a large dipole moment 3.75 D induces some anisotropic strain in the crystal lattice and leads to re-entrant phase transitions. Since DCBP has also a large dipole moment (2.7 D) [12] a coupling between the molecular alignment and an anisotropic expansion of the unit cell might be associated with such a curious phase transition.

In order to obtain evidence for any change in the molecular structure between the highest temperature phase and the room temperature phase of DCBP, we measured the ^{13}C CP/MAS NMR spectrum as shown in Figure 7. We did not, however, find any significant change in the spectrum. This fact indicates that the variation of the molecular structure through the 331 K transition is minimal.

Furthermore, we tried to determine the crystal structure of the highest temperature phase by X-ray diffraction but failed on account of the gradual sublimation of the single crystal sample of DCBP.

Concluding Remarks

We found a curious sequence of phase-transition in 4,4′-dichlorobenzophenone, which we attributed to incommensurate phase transitions and a novel re-entrant phenomenon. We found that the DCBP molecule has C_2 symmetry and stays at the high symmetry site in the crystalline lattice where all chlorine atoms are equivalent below 189 K and between 220 and 331 K. It is probable that the intermediate phases in the temperature range of 189–220 K are both incommensurate on the assumption that a phase reversal of the incommensurate plane-wave occurs at 194 K. A symmetry lowering takes place above 331 K, at which a large dipole moment of the DCBP molecule may induce an anisotropic thermal expansion leading to a re-entrant like phase transition.

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