

³⁵Cl NQR Study of 4,4'-Dichlorobenzophenone *

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Pulsed NQR has been used to get information about the two phase transitions (PT) in 4,4'-dichlorobenzophenone. The measurements of the NQR spectrum and spin-lattice relaxation suggest that the PT's correspond to a normal-incommensurate and to the lock-in of a commensurate structure at lower temperature. Strong hysteresis has been observed, which could be assigned to memory effects produced by defect migrations.

Introduction

During the last years, NQR and NMR techniques have been used as very sensitive probes to determine the existence of incommensurate systems [1, 2]. In molecular crystals the incommensurate phase is not only characterized by a lack of translational periodicity in the molecular arrangement, but also by conformational changes in the molecules due to modifications in the atomic arrangement within the molecules [3]. We suspected such phenomena to occur in molecular crystals of chlorinated biphenyl compounds [4]. As a matter of fact, we have demonstrated that 4,4'-dichlorobiphenyl sulphone (4,4'-DCBS) presents an incommensurate structure whose order parameter may be assigned to the dihedral angle between the benzene rings. The aim of our present work is to extend these studies to organic compounds with a similar molecular structure.

At higher temperatures the present compound (4,4'-dichlorobenzophenone; 4,4'-DCBP) crystallizes in the monoclinic space group C2/c, with $Z=2$ [13]. Figure 1 depicts the molecular arrangement. Coincidence is obtained by translation along the bisecting axis of the molecules. Several studies by Brillouin scattering, calorimetric [5] and Raman spectroscopy [6, 7] on this compound have previously been done. There exist two phase transitions (PT) [5] with a conformational

change in the molecule but without a noticeable change in the volume and space group of the primitive cell [6, 7]. Nothing is said in these papers about the nature of the observed PT's.

In this work we have studied the temperature dependence of the NQR frequencies, $\nu_Q(T)$, the spin-lattice relaxation time, $T_1(T)$, and the NQR line shapes in the temperature range around the PT's (150 to 220 K).

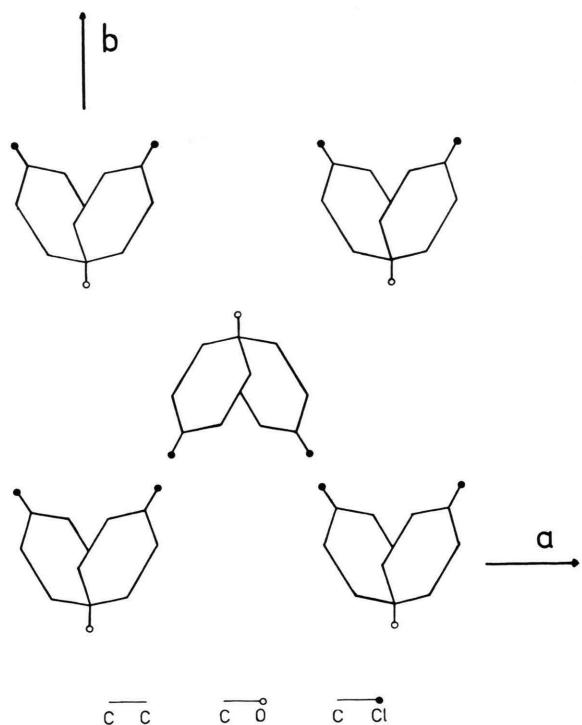


Fig. 1. Arrangement of the 4,4'-DCBP molecules in the higher temperature normal crystalline phase.

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Experimental

The sample was obtained from Aldrich Co. and sealed in a PTF container. A conventional high power pulsed spectrometer [8] was used. The temperature stability was within 0.1 K. The spectra were obtained through Fast Fourier Transformation (FFT) of the FID. The resonance frequencies were obtained from the FFT spectrum with an error of less than 1 kHz. Measurements of T_1 were performed by using the standard $90^\circ - \tau - 90^\circ$ two-pulse sequence with less than 5% error.

Results and Discussion

Figure 2 shows the temperature behaviour of v_Q and the NQR line shape observed in the process of cooling the sample from room temperature. We observed three well defined temperature regions related to different distributions of the electric field gradient (EFG) at the ^{35}Cl nuclei, as can be deduced from the NQR spectra:

i) At higher temperatures ($T > 186$ K) only one sharp resonance line is observed; consequently, all ^{35}Cl nuclei occupy equivalent sites in the crystal. The temperature dependence of the resonance frequency corresponds to that observed in normal molecular crystals under torsional oscillations [9].

ii) Complex spectra are observed between $T_1 = 186$ K and $T_C = 175$ K. The spectra evolve into two components with broad EFG distributions, each having two edge peaks and different thermal behaviour, as typically happens in incommensurate systems [11]. A typical spectrum obtained in the middle of this temperature regions ($T = 179$ K) is shown in Figure 3. We call α -region the higher frequency distribution and β -region the lower frequency one. In the α -region, we call a -peak the higher frequency edge peak and b -peak that found in the middle of the frequency distribution.

iii) Below T_C a single NQR line is observed again, having similar width and intensity to that measured in the high temperature region. $v_Q(T)$ shows a normal behaviour again, but the temperature coefficient of $v_Q(T)$ is different from that at the high temperature. The recovery of a spectrum similar to that at higher temperatures ($T > T_1$) could indicate that the PT's do not involve a net change in the position of the chlorine sites. This behaviour is closely similar to that observed in 4,4'-DCBP.

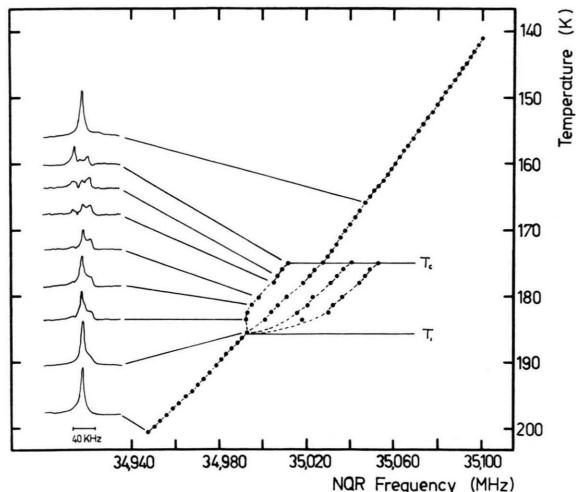


Fig. 2. Line-shape and temperature behaviour of NQR line-peaks on cooling 4,4'-DCBP from room temperature to 150 K.

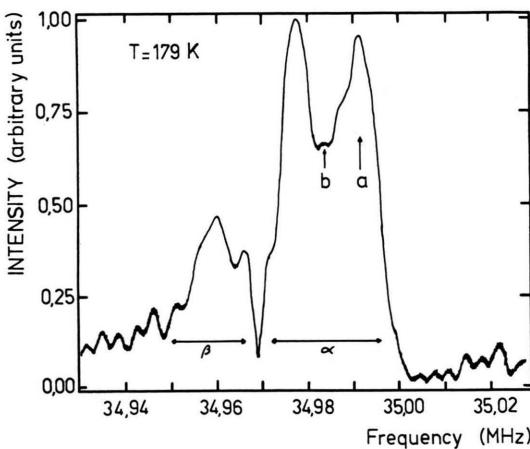


Fig. 3. NQR spectrum of 4,4'-DCBP at $T = 179$ K. Frequency regions α and β differentiate the EFG distribution at higher and lower frequencies, respectively. The a - and b -peaks in the α -region indicate the higher frequency edge singularity and that in the middle of the frequency distribution, respectively.

The data of $T_1(T)$ from the whole FID in Fig. 4 also evidence three well defined temperature regions. The temperature behaviour within each region is characteristic of a particular molecular dynamics:

- i) Above T_1 , the behaviour of $T_1(T)$ is normal and reflects a relaxation process mainly due to torsional oscillations [9].
- ii) At T_1 a dramatic drop of T_1 is observed, as expected for a PT driven by a soft mode; this might be

Table 1. $T_1(T)$ of the *a*-peak, $T_{1\phi}$, and *b*-peak, T_{1A} , for the α -region of the NQR spectrum at several temperatures with the compound in the intermediate (incommensurate) phase.

Temperature (K)	$T_{1\phi}$ (ms)	T_{1A} (ms)
184.3	54	53
181.8	43	53
180.2	44	49
178.6	57	67
176.5	52	76

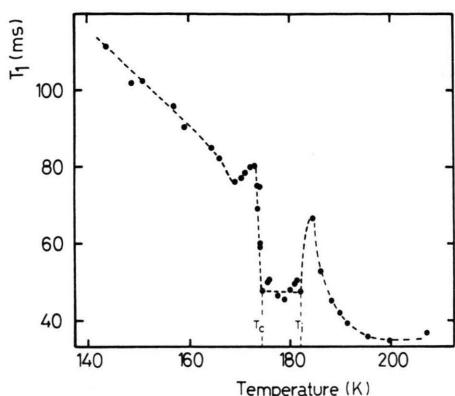


Fig. 4. Temperature dependence of T_1 in the temperature range from 220 to 150 K.

a consequence of the onset of the incommensurate phase. Between T_1 and T_C , the bulk signal T_1 is almost temperature independent. However, the individual T_1 's of the *a*- and *b*-peaks of the α -region in the spectrum show different thermal behaviours, as reported in Table 1. Figure 5 illustrates different evolutions of the recovering spectra at $T = 179$ K, after a saturating pulse sequence for several pulse interval times. T_1 for the *b*-peak ($T_{1\phi}$) remains temperature independent, indicating that relaxation is mainly produced by phase fluctuations of the incommensurate modulation wave [10]. On the other hand T_1 of the *a*-peak (T_{1A}) increases with decreasing temperature, suggesting the existence of an amplitude on contribution [1].

iii) On decreasing the temperature to below T_C , T_1 suddenly increases as a consequence of the lock-in of the low temperature commensurate phase.

Two thermal cycles were performed on the sample: i) cooling the compound from room temperature to 150 K (that is 25 K below T_C) and heating to room temperature. The $v_Q(T)$ data are shown in Figs. 6a (cooling) and 6b (heating) evidencing thermal hysteresis.

ii) Cooling the sample from room temperature to 176 K (that is, slightly above T_C) and then heating. Figures 6c and 6d illustrate a smaller hysteresis. By comparing the two heating processes in Figs. 6b and

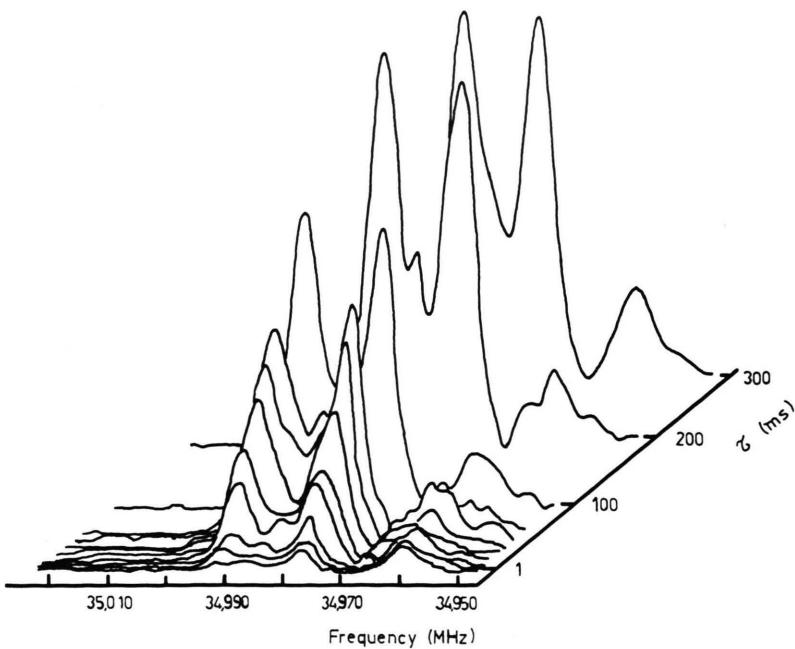


Fig. 5. Evolution of the NQR spectrum after a $90^\circ - \tau - 90^\circ$ pulse sequence as a function of τ at 179 K. The different τ -evolution of the *a* and *b*-peaks is shown.

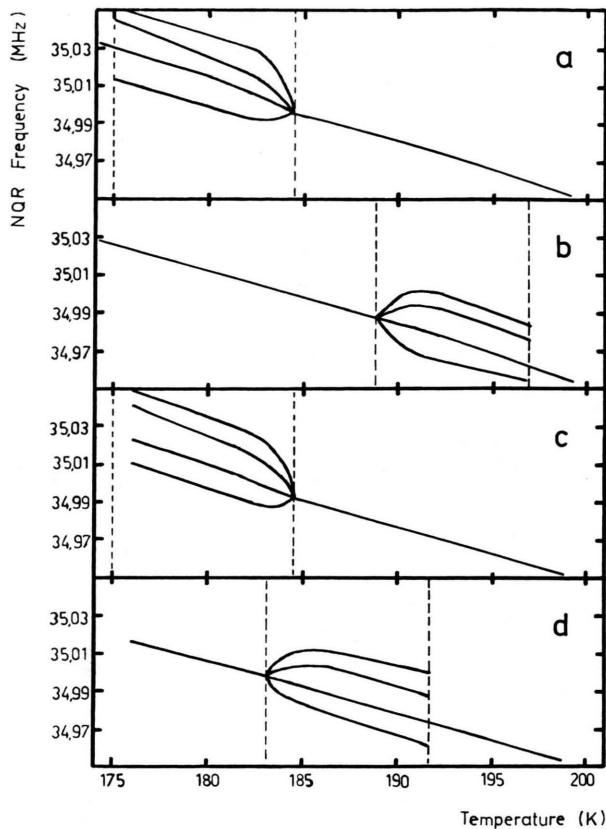


Fig. 6. Temperature behaviour of the NQR peak frequencies for: a) cooling the sample from room temperature to 150 K; b) heating to room temperature; c) cooling the sample to 176 K (1 K above T_c) after performing the thermal cycles a) and b); d) heating to room temperature. The memory effects are obvious, see text.

6d it is clear that the respective temperature ranges of the intermediate phase are strongly different, evidencing the occurrence of memory effects [12]. Meanwhile, in the two cooling processes the intermediate phases occur in the same temperature range (Figs. 6a and 6c). This suggests that heating the crystal to room temperature causes the memory effects to vanish.

Conclusions

Like the previously investigated compound of the chlorinated biphenyl series [4], 4,4'-DCBP has an incommensurate phase, as revealed by:

a) The line shape of the NQR spectra (see Figs. 1 and 2) shows an EFG distribution which is characteristic of the incommensurate systems [1, 2].

b) The $T_1(T)$ dependence (see Fig. 3) shows a commensurate to incommensurate PT at $T_l = 186$ K with a sudden decrease of T_1 correlated with the line shape changes; and a lock-in PT at $T_c = 175$ K, where the linewidth of the high temperature line is recovered while a sudden increase in T_1 occurs.

The temperature of the PT's on heating is well correlated with those previously determined by Raman spectroscopy [6, 7], Brillouin scattering and calorimetric analysis [5]. Our data also suggest that the phase transitions do not involve large changes in the static contribution to the EFG at the ^{35}Cl sites, but the normal and commensurate phases do differ in the temperature change of $v_Q(T)$ and consequently in their respective molecular dynamics.

On the basis of the conclusions of Kirin *et al.* [7] on PT's involving only changes in the molecular conformation, the continuity in $v_Q(T)$ that we observed between the normal and commensurate phases, and also because of the analogy existing between this compound and a previously studied 4,4'-DCBS [4], we propose that the order parameter of the normal-incommensurate PT is the departure of the dihedral angle, between the two benzene planes, from the value of the high temperature normal structure. A plausible conclusion is that the incommensurate phase involves a molecular conformational change consisting in a partial rotation of the two benzene rings (along the C–Cl axis), each molecule taking a different dihedral angle following an incommensurate modulation.

Thermal hysteresis was also observed in Raman spectroscopy, calorimetric and Brillouin scattering experiments, but the reported effects are less marked than those we observed. Such a difference may be due to the different cooling and heating rates (5 K/min in the calorimetric experiment while 1 K/hour in our experiment). A slower cooling rate could allow the intermediate phase to stabilize through the mobility of defects. This would modify the thermal characteristics of the sample, just as it happens for instance with the permittivity in the ferroelectric $(\text{NH}_4)_2\text{BeF}_4$ [14].

Finally, taking into account the similarities in the hydrostatic pressure [7] and temperature [6] dependences of the Raman experiments and the agreement of the last one with the present results, we expect that under hydrostatic pressure a normal to incommensurate PT could also be obtained in these previously reported experiments [5–7].

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