The incommensurate phase of 4,4'-dichlorobiphenyl sulphone reinvestigated by $^{35}$Cl NQR

# The incommensurate phase of $4,4'$-dichlorobiphenyl sulphone reinvestigated by $^{35}$Cl NQR

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**Abstract.** In order to acquire new information about the normal–incommensurate (IC) phase transition and to check the existence of a lock-in transition in $4,4'$-dichlorobiphenyl sulphone ($4,4'$-DCBS), a comprehensive $^{35}$Cl nuclear quadrupole resonance (NQR) study is reported. Detailed NQR measurements of frequency, line width and spin relaxation time ($T_1$) were obtained in the temperature range 80–270 K. The results show that the IC phase is present from 150 K down to 80 K. The behaviour of the NQR spectrum in the transition region suggests that the IC modulation is dominated by the first-order term in the order parameter. The $t_1$ values at the peaks of the IC spectrum are quite different, suggesting strong anharmonic effects. No lock-in transition was detected at 115 K. Small changes in the temperature behaviour of the frequency and the $t_1$ of the low-frequency IC peak were observed from temperatures lower than 110 K. Neither impurities nor thermal hysteresis effects were detected.

## 1. Introduction

Biphenyl compounds show interesting structural and dynamical features. Members of this family, with resembling structures, exhibit quite different thermal behaviour. As a matter of fact, $4,4'$-dichlorobiphenyl sulphone (DCBS), a chlorosubstituted biphenyl, has been widely studied in recent years with several experimental techniques. Nevertheless, some controversy remains about the phase diagram of this compound.

At room temperature, DCBS crystallizes in a monoclinic structure with a space group $I2/a$ with four molecules per unit cell [1]. At 150 K this compound presents a structural phase transition to a low-ordered phase. By $^{35}$Cl nuclear quadrupole resonance (NQR) [2,3] and x-ray diffraction [4] experiments, this low-temperature phase was early characterized as incommensurate (IC). Raman scattering experiments [5] show the softening of a mode related to the twisting of the chlorophenyl rings. The existence of a lock-in transition at 115 K has been reported from $^{35}$Cl NQR [3,6] and calorimetric [7] experiments. Nevertheless, other studies performed with the same techniques show no evidence of this transition [8–10].

The aim of this work was to acquire information about the IC phase, and specially about the lock-in transition. $4,4'$-DCBS was reinvestigated by $^{35}$Cl NQR with an improved spectrometer. The temperature dependence of the NQR frequencies and spin-lattice relaxation times ($T_1$) were measured from 80 K to 270 K. Detailed measurements of $T_1$ for each peak in the IC phase were performed. In order to detect thermal hysteresis effects, experiments at different temperature scan rates were carried out on pure crystalline and packed powder samples.

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## 2. Experimental details

The specimen of 4, 4′-BCPS was obtained from Aldrich Chemical Co. It was divided into three samples, one of which was subjected to a recrystallization process and purified by the zone-melting method. The others were used without further purification. Of these, one was packed powder and the other powder recrystallized by single fusion. The sample containers were glass cylinders of length 2 cm and diameter 0.8 cm.

Measurements of NQR from the $^{35}$Cl frequency and $T_1$ as a function of temperature were performed between 80 K and room temperature. The spectrometer, based on the pulse method, has been described in [11]. Several improvements were made in the irradiation power and the data acquisition system. A sampling frequency between 200 kHz and 20 MHz was used. NQR spectra were obtained from the fast Fourier transform (FFT) of the digitized free induction decay (FID) after a pulse of length between 25 $\mu$s and 35 $\mu$s. Each peak present in the spectrum and at intermediate frequencies was irradiated with the maximum peak power of the 150 W transmitter. The instrumental width of the spectrometer response is approximately 12 kHz, with a pulse length of 25 $\mu$s. The NQR frequency determination was performed with the software PeakFit (Jandel Scientific), which can fit a set of typical spectroscopic functions to the experimentally obtained spectrum. Fitted NQR frequencies were obtained within 100 Hz. Measurements of $T_1$ were made by the standard two-pulse sequence ($\pi/2$–$\tau$–$\pi/2$), with separation times $\tau$ between pulses varying from 0.1 ms to $5T_1$. $T_1$ values were obtained from fitting the expression

$$S(\tau) = S_0(1 - \alpha \exp(-\tau/T_1)) \tag{1}$$

which relates the amplitude at the irradiation frequency of the Fourier transform from the FID (after the second $\pi/2$ pulse) to the separation $\tau$. Each fit of $S(\tau)$ was performed with a minimum of 30 experimental data points and a maximum of 50.

The spectrometer temperature control provides temperature stability better than 0.1 K during the experiment. In order to detect possible hysteresis effects, as in other biphenyl compounds [12], measurements were made heating and slowly cooling the sample. In all cases the temperature scan rate was lower than 0.1 K min$^{-1}$. The sample thermal stabilization time was, for each temperature, approximately 1 h. In addition, experiments involving sudden cooling into the IC phase were performed.

## 3. Results

### 3.1. $^{35}$Cl NQR frequency

The temperature dependence of the NQR frequency is plotted in figure 1. Only one continuous phase transition at $T_1 = 150$ K is observed. There is no evidence of a lock-in transition, as was previously reported [3]. Figure 2 shows some typical NQR spectra at different temperatures through the phase transition.

It is observed that neither the way the temperature is changed (warming up or cooling down) nor the sample purity affects the spectral features or the phase diagrams. Only an improvement in the signal-to-noise ratio for the purest crystalline sample can be observed. This behaviour is quite different from that observed in 4, 4′-dichlorobenzophenone [12], another compound of the same family. All the measurements presented in this paper were performed in the purest sample going up in temperature. The characteristics of the two phases found are described below.
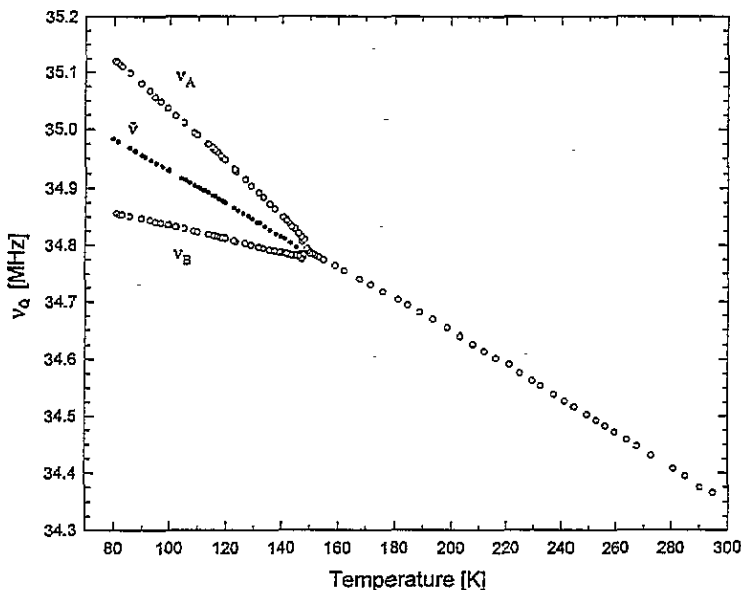
**Figure 1.** The temperature behaviour of the $^{35}$Cl NQR frequency in 4,4'-DCBS. $\nu_A$ and $\nu_B$ are the frequencies of the peaks in the IC phase spectrum. $\nu$ is the calculated average of $\nu_A$ and $\nu_B$.

*3.1.1. High-temperature phase (HTP).* This ordered crystalline phase is present for temperatures above 150 K. The $^{35}$Cl NQR spectrum (figure 2) shows a single sharp Lorentzian line of central frequency $\nu_Q$. Following the Bayer–Kushida model [14] of the molecular torsional oscillations and assuming only one dominant mode, the temperature dependence of $\nu_Q$ between 170 K and 240 K can be fitted by [14]

$$\nu(T) = \nu_0 - \tfrac{3}{4}(\hbar\nu_0/I\omega)\coth[\hbar\omega/2k_B T] \qquad (2)$$

where $\omega = \omega_0(1 - \alpha T)$ is the torsional frequency of the mode, $I$ is the associated moment of inertia of the molecule and $\nu_0$ is the limiting static value of the NQR frequency. A least-squares fit of (2) to the experimental data yielded the following parameters:

$$\nu_0 = 35.17 \text{ MHz} \qquad I = 13\,300 \text{ amu Å}^2 \qquad \omega = 240 \text{ cm}^{-1} \qquad \alpha = 3 \times 10^{-4}.$$

Figure 3 shows the difference that exists between the experimental data of the HTP and the Bayer fit. There is a noticeable change of behaviour below 170 K, before the phase transition.

The temperature dependence of the half-height line width is plotted in figure 4. A progressive broadening can be observed below 170 K.

*3.1.2. Low-temperature phase (IC).* This phase starts at about 150 K and was observed down to liquid-air temperatures. It has been characterized as an incommensurate (IC) one [3, 4]. The NQR spectrum (figure 2) has a structure with two well defined maxima at the edges, which will be referred to here as peaks A and B. The temperature evolution of the NQR spectrum is plotted in figure 5. A continuous change in the spectral features can be observed in the whole temperature range. The whole spectra cannot be fitted as sums
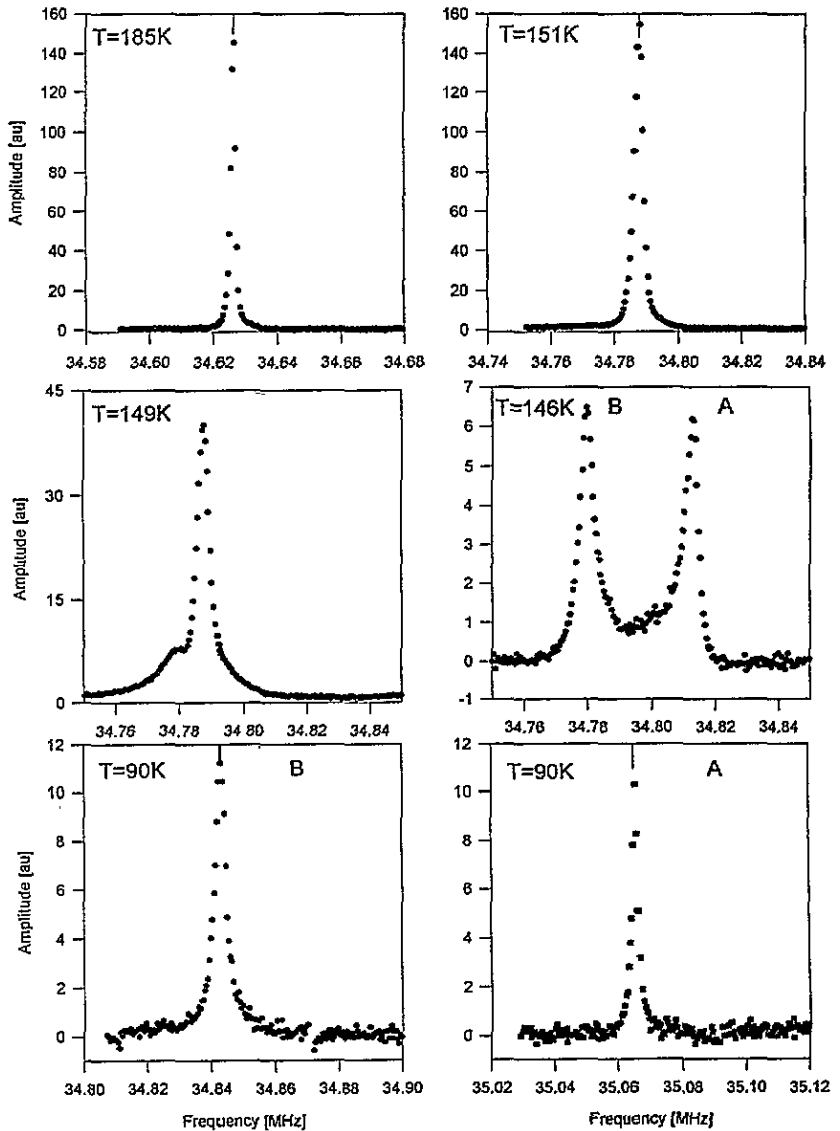
**Figure 2.** The temperature evolution of the NQR spectrum in the normal phase ($T > 150$ K) and the IC phase ($T < 150$ K). The small vertical line at the top of each spectrum shows the irradiation frequency.

of two independent Lorentzian functions. Nevertheless, it is possible to fit satisfactorily each maximum separately (for the whole temperature range) with a Lorentzian, due to the sharpness and frequency separation of the peaks. The values of $\nu_Q$ and line width obtained in this way are shown in figures 1 and 4 respectively. Because of the effective irradiating width used in the experiments (less than 10 kHz) and the frequency separation between peaks, it was not possible to excite the whole spectra. In those cases, each peak and the intermediate regions of the spectrum were irradiated separately. The NQR signal between the main peaks becomes progressively smaller as the sample is cooled. No appreciable
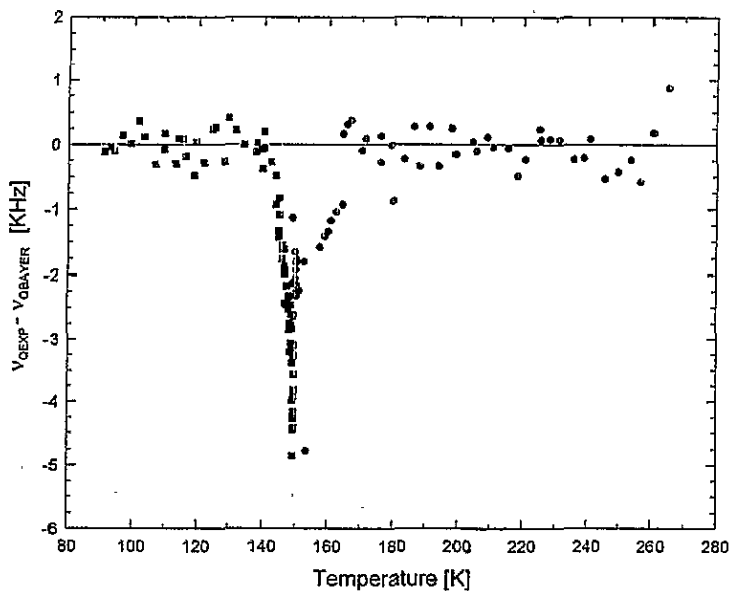
**Figure 3.** The difference between the experimental data and the Bayer fit: circles, HTP data; squares, IC-phase data (fit of the average between $\nu_A$ and $\nu_B$).
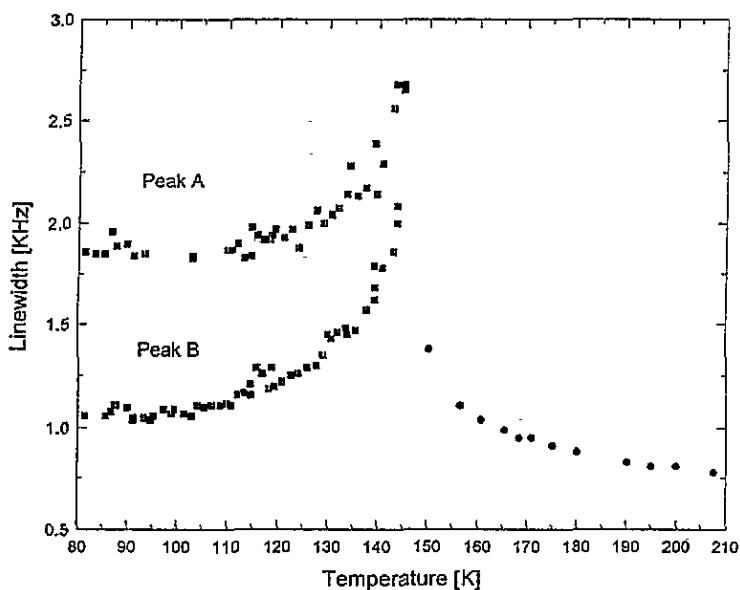


**Figure 4.** The temperature behaviour of the line width (obtained from Lorentzian fittings) in the normal and IC phases.

signal was observed below 140 K between the peaks. Conversely, the height of the peaks increases continuously as is shown in figure 5.

The temperature dependence of the experimentally obtained frequencies in the IC phase
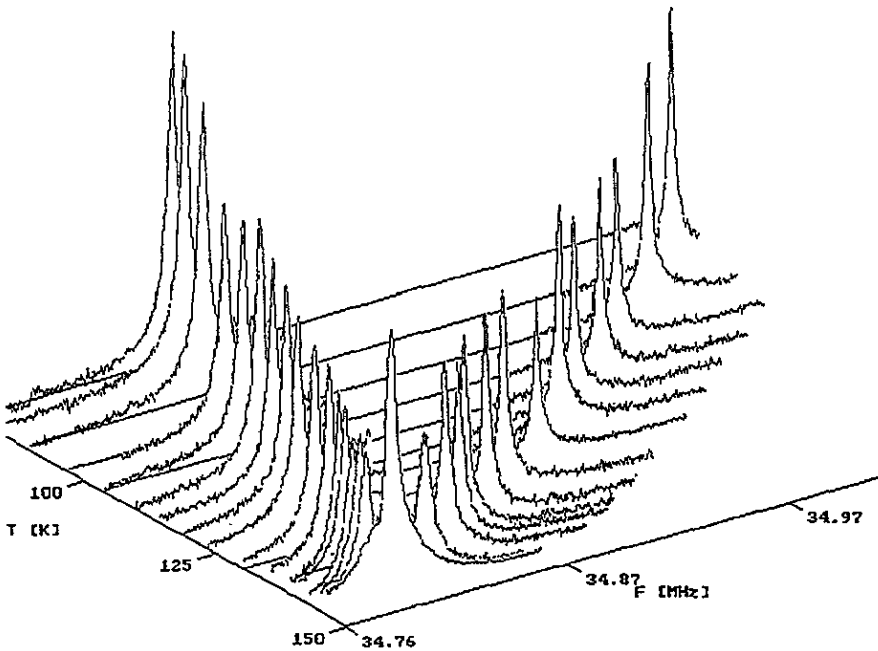
**Figure 5.** The temperature evolution of the $4 - 4'$-DBCS NQR spectra in the IC phase.

has been studied following the Blinc model [13]. The modulation of the incommensurate parameter $u$, assuming the one-dimensional plane-wave model, can be written as follows:

$$u = \cos(\varphi(x)) \tag{3}$$

where the phase $\varphi(x)$ of the spatial modulation is

$$\varphi(x) = \varphi_0 + q_s x \tag{4}$$

and $q_s$ is the incommensurate wavevector. On the other hand, the NQR frequency at the lattice site of coordinate $x$ can be expanded in powers of $u$ as

$$\nu_Q = \nu_0 + \nu_1 \cos(\varphi) + (\nu_2/2)\cos^2(\varphi) + \cdots. \tag{5}$$

The NQR spectrum can be obtained by using expression (5) to calculate the spectral density. Several maxima will appear in the NQR spectrum, arising from singularities in the spectral density. How many maxima will appear and their temperature behaviour will depend on the relative magnitude of $\nu_1$ and $\nu_2$ [13]. The observed splitting (figure 1) suggests that the linear term $\nu_1$ dominates over the quadratic one in (5). None of these peaks has the same temperature dependence as in the HTP. In fact, the presence of only two maxima is a clear indication that at least $|\nu_1| > |\nu_2|$.

The frequency separation between peaks A and B, $\Delta \nu = \nu_A - \nu_B$, can be considered as the order parameter of this phase transition [13], in either the linear case or the quadratic case. The temperature dependence of $\Delta \nu$ in the critical region is exponential:

$$\Delta \nu = A(T_I - T)^\beta. \tag{6}$$

Figure 6 shows the measured $\Delta \nu$ against the reduced temperature $\epsilon = T_I - T$. Fitting the data with expression (6) the following values of the parameters are obtained:

$$A = 21 \pm 2 \text{ kHz} \qquad \beta = 0.45 \pm 0.05 \qquad T_I = 150.5 \pm 0.3 \text{ K}.$$

The best fit to $\Delta \nu$ data using these values is also shown in figure 6. It can be observed that the linear zone, corresponding to the critical behaviour, is restricted at about 3 K below $T_I$. The critical exponent is classical, suggesting that mean-field models can be used to explain this phase transition.
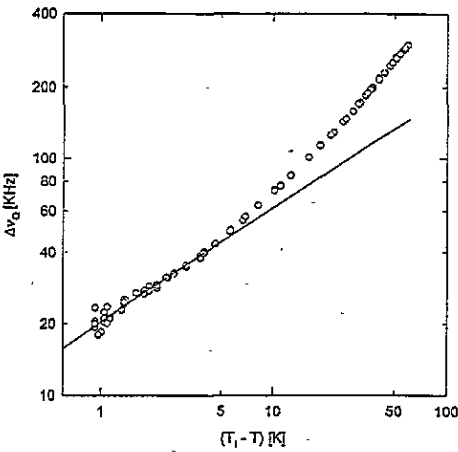


**Figure 6.** The frequency difference between the two peaks of the spectrum in the IC phase as a function of temperature: solid line, the fit of the experimental data to $\Delta \nu = A(T_I - T)^\beta$ in the temperature range 146 K$< T < 150$ K.
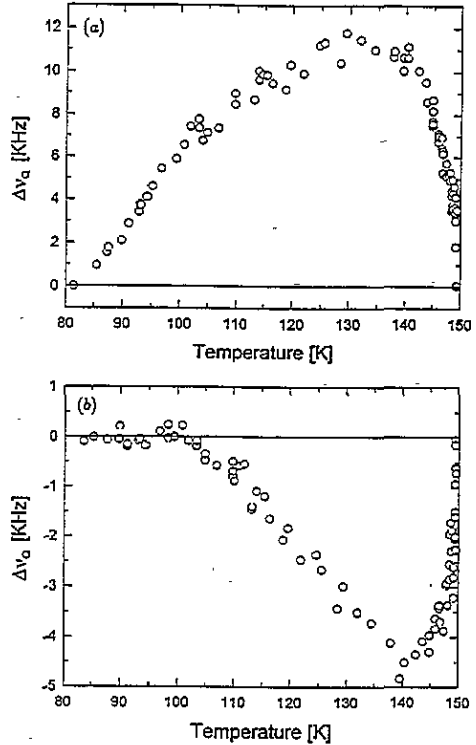
**Figure 7.** Differences between the experimental frequencies of the peaks in the IC phase and straight lines joining the first and last data.

The term $\nu_0$ in (5) can easily be obtained in the linear case by the average between $\nu_A$ and $\nu_B$. The average values are shown in figure 1 (filled circles). Their temperature dependence can be fitted by the Bayer–Kushida model [14] considering only one dominant mode for temperatures lower than 145 K. From this fit the following values of the parameters are obtained:

$$\nu_0 = 35.12 \text{ MHz} \qquad I = 14\,700 \text{ amu } \overset{\circ}{\text{A}}{}^2 \qquad \omega = 250 \text{ cm}^{-1} \qquad \alpha = 4 \times 10^{-4} \text{ K}^{-1}.$$

These parameters are quite similar to those obtained in the HTP. This could suggest that the dynamics of the torsional modes is weakly affected outside the transition region

(145 K > $T$ > 80 K). Figure 3 shows the difference between the experimental data and the Bayer fit.

There is no evidence of the presence of another phase transition below 150 K, although a small change in the B-maximum temperature dependence is observed near 110 K in figure 7. This figure shows the NQR frequency difference of each peak with respect to a straight line joining the first and last experimental point (at 90 K and 150 K, respectively). Peak A has a behaviour similar to that observed in other molecular crystals. On the other hand, peak B shows a behaviour that could indicate an almost linear temperature dependence of the NQR frequency below 110 K.

The observed spectral characteristics below 150 K are different from NQR results previously reported [3, 6]. As a matter of fact, Nakayama *et al* [6] observed two NQR lines in the IC phase just down to 115 K. They claimed that, at this temperature, a first-order transition to a commensurate (C) phase occurs, where two lines can be observed. While the low-frequency peak smoothly changes from one phase to another, the high-frequency peak shows a discontinuity of about 100 kHz. The NQR frequencies reported in the present work for temperatures lower than 115 K agree with the measurement of Nakayama *et al*. Nevertheless, no discontinuities were observed down to liquid-air temperatures (figure 1). In this case, the so-called phase C of Nakayama *et al* could really be the IC one, and the intermediate one (115–150 K) a disordered state, probably strongly dependent on sample preparation or cooling rate during the experiments.

In order to decide whether fast cooling could lead the system to an intermediate state, the sample temperature was changed from 170 K to 140 K at a mean rate of 1 K min$^{-1}$. The NQR spectrum was observed while the sample returned to equilibrium. No differences were found either in the frequencies of the peaks or in the spectral features with respect to the ones observed at very slow cooling rates. A sudden cooling from room temperature to 140 K showed the same results.

Etrillard *et al* [8], using NQR and differential thermal analysis (DTA), observed only the transition at 150 K to the IC phase. Neither NQR nor DTA measurements performed by these authors showed any evidence of changes at 115 K. The $^{35}$Cl NQR spectra reported show a wide structure, where no sharp peaks can be distinguished, but maxima inside a continuous EFG distribution. Two lateral maxima are observed, with the same frequencies reported here, and a third intermediate one, in disagreement with the previous NQR works [3, 6]. All these frequencies vary smoothly down to liquid-air temperatures. The authors explain the observed spectral temperature behaviour assuming the presence of comparable linear and quadratic terms in the $\nu_Q$ expansion (5) with $|\nu_1| < |\nu_2|$.

### 3.2. Spin-lattice relaxation time

The $^{35}$Cl spin-lattice relaxation-time data are shown in figure 8. For the HTP, the obtained $T_1$ values agree with [3] and [8]. Below 170 K, there is a dramatic drop in $T_1$, associated with the line broadening (figure 4) and the change in behaviour of $\nu_Q$ (figure 3). In the IC phase, $T_1$ was measured by saturating each peak separately. In the intermediate region of the spectrum it was not possible to obtain reliable measurements. As is shown in figure 8, the values of $T_1$ for each peak and their thermal dependence are very different. This is not the expected behaviour for an IC phase, according to the usual quasiharmonic approach [13]. Relaxation in the environment of both EFG extremes is dominated by modulation fluctuations of 'amplitudon' type. The relaxation time should be the same for both peaks, and almost temperature independent. Instead, the relaxation time for peak A, $T_1^A$, shows a linear dependence up to 140 K, of the type associated with the molecular torsional oscillation
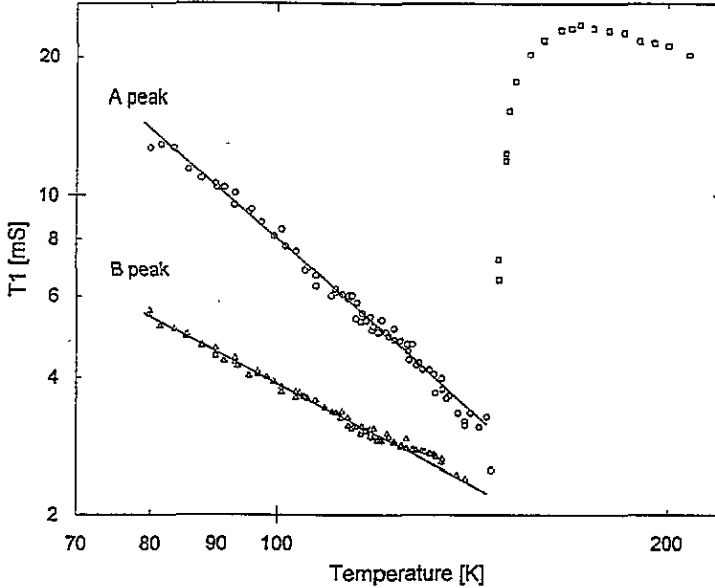
**Figure 8.** The temperature behaviour of $t_1$ in normal and IC phases: solid lines, fit of $t_1 = AT^{-\lambda}$ for each peak in the IC phase. The line for peak B was extrapolated for temperatures greater than 110 K.

model [14]:

$$T_1 = AT^{-\lambda}. \tag{7}$$

The resulting fitting parameters for $T_1^A$ are

$$A = 8 \times 10^5 \qquad \lambda = 2.49.$$

The $T_1^B$ values show a linear dependence only for temperatures lower than 110 K. The resulting fitting parameters of expression (7) for $T_1^B$ are

$$A = 3700 \qquad \lambda = 1.49.$$

As is shown in figure 8, there is a smooth change of behaviour from 110 K to the phase transition temperature. The values of $T_1$ are lower than the extrapolated fit in the temperature range 110–125 K, and greater than the fit in the range 125–150 K. This behaviour suggests the presence of a thermally activated process at abuot 110 K, probably associated with the observed change in the thermal dependence of $\nu_B$ (figure 8).

## 4. Conclusions

The present NQR study of DCBS shows the existence of a continuous phase transition at 150 K from a crystalline ordered phase to an IC phase, with a classical critical exponent. The spectral features and the thermal dependence of $\nu_Q$ suggest a one-dimensional linear modulation in the IC phase. Below 150 K no lock-in transition is observed and the IC phase

persists down to liquid air temperature. Neither impurity effects nor hysteresis are observed in the phase diagram of DCBS. Substantially different scan temperature rates cannot lead the sample to any metastable state. Unfortunately, it was not possible to determine what kind of process in the sample preparation could lead the crystal to an intermediate state, as was detected in [3] and [6].

Small changes in the temperature behaviour of $T_1^B$ and $\nu_B$ were detected at about 100 K and 125 K. These effects could be associated with recent results obtained by elastic neutron scattreing [15]: the appearance of comparable second- and third-order satellites at 120 K and 100 K, respectively.

The difference between $T_1$ values for each peak in the IC phase suggests the presence of a mixing between the amplitudon and phason contributions to the relaxation along the measured NQR spectrum. This could indicate strong anharmonic effects in the dynamics of the IC phase of DCBS.

## Acknowledgments

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