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# $^{35}$Cl nuclear quadrupole resonance study in 4,4′-dichlorobiphenyl sulphone: A possible incommensurate system

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Pulsed nuclear quadrupole resonance (NQR) has been used to get information about the nature of the molecular dynamics in two crystalline phases of 4,4′-dichlorobiphenyl sulphone. This work includes detailed experimental measurements of the NQR frequency, spin-lattice relaxation time, and line intensity temperature behavior in the range of temperature where a possible normal-to-incommensurate phase transition occurs. The experimental results show the existence of strong precursor effects to the normal-incommensurate phase transition within the range 185–140 K.

## I. INTRODUCTION

The biphenyl ($C_{12}H_{10}$) group has attracted growing interest in recent years, since it exhibits several solid-solid phase transitions, which involve two incommensurate phases.[1,2] Although 4,4′-dichlorobiphenyl sulphone and biphenyl are similar molecular compounds, they show rather different phase diagrams. In previous papers[3,4] we reported a solid-solid continuous phase transition at 150 K and another, discontinuous one, at 115 K. In addition, some anomalous behaviors of the nuclear quadrupole resonance (NQR) parameters were observed near the continuous phase transition; such behavior was attributed to nonlinear anharmonic effects which produce fluctuations on the electric field gradient (EFG) at the $^{35}$Cl nuclei sites.

These results led us to propose that, from the NQR point of view, the crystal behaves as an incommensurate system for temperatures between 115 and 150 K, and as a commensurate one for $T > 115$ K.

This work reports the results of a comprehensive study of the temperature behavior of a $^{35}$Cl NQR frequency, $\nu_q(T)$, spin-lattice relaxation time $T_1(T)$, line intensity $I(T)$, and spin-spin relaxation time $T_2(T)$ in single crystal line and powder samples of 4,4′-dichlorobiphenyl sulphone.

## II. EXPERIMENT

The NQR measurements were performed in single crystals and high-purity polycrystalline Fluka 4,4′-dichlorobiphenyl sulphone samples. Single crystals were grown in a Bridgman apparatus. Optically acceptable single crystals without imperfections were obtained as cylinders of 1.2 cm diameter and 2 cm long.

The fast Fourier transform (FFT) pulsed spectrometer is a conventional instrument[5] equipped with a homemade temperature control which allows a temperature stability within 0.1 K in the range 80–350 K (the controller was calibrated with the NQR frequency data of $KClO_3$).[6] The $\nu_q$ values were obtained from the FFT spectrum with an error less than 1 kHz.

Measurements of $T_1$ were made by both repetitive pulses and the two-pulse sequences, with an interval between the pulses varying from 0.1 ms to $2T_1$ approximately; the two-pulse sequence was used to measure values of $T_1$ shorter than 50 ms. The data were fitted, with the least-squares method proposed by one of the authors,[7] obtaining $T_1$, with less than 10% error.

## III. CRYSTALLOGRAPHIC DATA

4,4′-dichlorobiphenyl sulphone crystallizes in a monoclinic structure $I2/a$ with four molecules per unit cell.[8] Figure 1 shows a schematic picture of the molecular structure and the arrangement of two molecules in the unit cell. Only two molecules are depicted, and one of them can be obtained from the other by a 5.01-Å translation along the molecule bisecting axes. The angle formed by the benzene ring with the Cl—S—Cl plane (dihedral angle) is the same for both rings (about 84°).

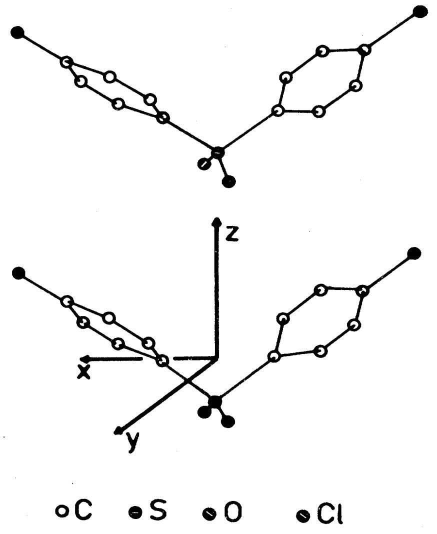

FIG. 1. Schematic 4,4′-dichlorobiphenyl sulphone molecular structure and unit-cell arrangement.

## IV. EXPERIMENTAL RESULTS

### A. Spin-lattice relaxation time

Measurements of the temperature dependence of the spin-lattice relaxation time $T_1$ were carried out between 80 and 340 K (see Fig. 2). The measurements were performed on polycrystalline and single-crystal samples.

The behavior of $T_1(T)$ above 230 K can be described as usual by molecular torsional oscillations.[9] Between 230 and 150 K, $T_1(T)$ is almost temperature independent, suggesting that an extra relaxation mechanism is present. This behavior could be due to precursor effects of the structural phase transition, which occurs at $T_I = 150$ K; and may be produced by fluctuations of the EFG in the Cl nuclei sites. Below 150 K a drop of the relaxation rate is observed. Such a behavior might indicate the onset of a transition to a possible incommensurate crystalline phase; $T_1(T)$ behaves as expected for any structural phase transition driven by a soft mode.[10] Between 145 and 110 K $T_1$ is anomalously short and almost temperature independent; this is a characteristic of an incommensurate phase whose fluctuations are dominated by phasons.[10] For temperatures below 110 K $T_1(T)$ sharply increases, presumably due to a change in the phason spectrum, which determines the lockin of a low temperature commensurate phase.

### B. NQR frequency

Measurements of NQR frequency $\nu_q$ were carried out in powder and single-crystal samples between 80 and 340 K. Similar temperature behaviors were obtained in the NQR spectrum for monocrystalline and polycrystalline samples; Fig. 3 shows the experimental data of the latter.

Above 150 K only one sharp resonance line is observed; but for temperatures between $115 < T < 150$ K the NQR spectrum is characterized by a broad line with two edge peaks (in Fig. 3 we plot the frequency of these edge peaks). This qualitative behavior is expected in an incommensurate phase.[11,12] For temperatures below 115 K the NQR spectrum shows only one peak which corresponds at the low-frequency edge peak of the incommensurate phase. Therefore we assume that this compound transforms to an incommensurate phase at 150 K and further down to a commensurate phase at 115 K.

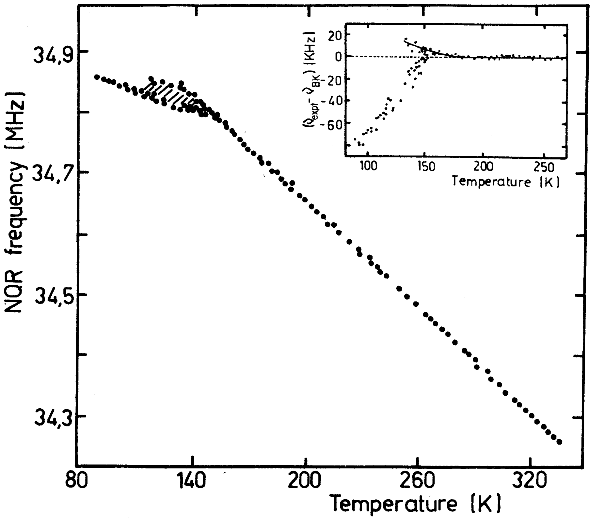

FIG. 3. 4,4′-dichlorobiphenyl sulphone NQR frequency vs temperature. In the upper right corner is plotted the temperature dependence of the difference between the experimental values of $\nu_q$ and the calculated ones by means of the Bayer-Kushida expression. Solid line represents the fit of the data through Eq. (18).

### C. Line intensity

Figure 4 shows the line intensity data versus $T$. For temperatures between 340 and 220 K the NQR line intensity $I(T)$ increases following the Curie law. But below 220 K, $I(T)$ decreases dramatically. This intensity loss could be associated to a homogeneous broadening of the

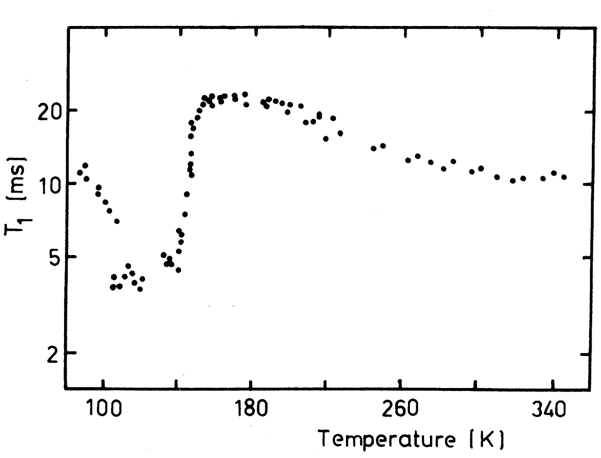

FIG. 2. Spin-lattice relaxation time vs temperature, for the whole data set.

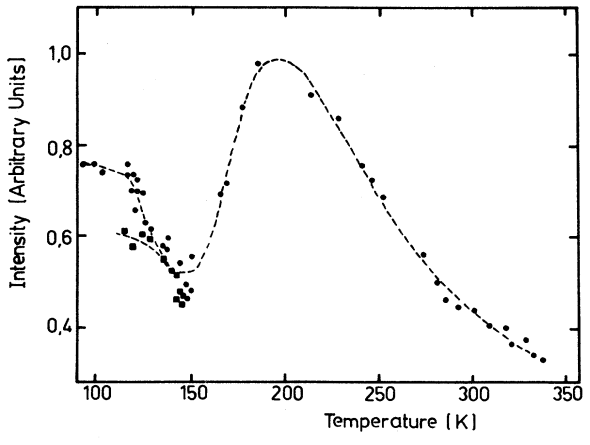

FIG. 4. Line intensity vs temperature: ■, high-frequency line in Fig. 3; ●, low-frequency line in the temperature range up to 145 K and the single line above that temperature.

resonance line, probably due to the fluctuations in the EFG, which were also observed on $T_1(T)$. Between 150 and 115 K the line intensity increases up to half its value above 220 K, approximately.

The temperature behavior observed for 4,4'-dichlorobiphenyl sulphone line intensity is qualitatively similar to that observed by others for $Rb_2ZnCl_2$,[10] which goes through a ferroelectric-incommensurate-commensurate phase transition.

### D. Spin-spin relaxation time

Measurements of $T_2(T)$ show no appreciable variation within the whole temperature range. Since $T_2$ is the static contribution to the NQR line width, its temperature behavior shows that the phase transition, which occurs at 150 K, does not involve a net change in the interatomic distances among the $^{35}$Cl nuclei.

## V. DATA ANALYSIS

For temperatures above 230 K the temperature behavior of NQR parameters are well described by the torsional oscillation model. The $T_1(T)$ data were fitted to the expression $1/T_1 = AT^{\lambda}$ (Ref. 9) and the $\nu_q$ data to the Bayer-Kushida expression.[9] The value of the parameters obtained in the fit are in agreement with those observed in other molecular compounds. The behavior of $I(T)$ for temperatures greater than 230 K can be accounted for by the torsional oscillations model for molecular dynamics as happened with $T_1$ and $\nu_q$.

Within the range 230–150 K, the bare temperature dependence for $T_1$ might indicate the presence of an extra relaxation mechanism. We attributed this behavior to correlated long-range fluctuations in the EFG in the $^{35}$Cl nuclear sites. The fluctuations in the EFG may be due to high-order anharmonicities in the vibrational potentials which increase as the temperature reaches its critical value ($T_I = 150$ K).

The contribution to $T_I$ from this extra relaxation mechanism could be calculated from the usual spin-lattice relaxation expression for a quadrupolar system with spin $I = \frac{3}{2}$:

$$\frac{1}{T_1} = \frac{e^2Q^2}{6\hbar^2}\left|J_1(\omega_Q)+J_2(\omega_Q)\right| , \tag{1}$$

where $J_1$ and $J_2$ are the spectral densities of the correlation functions of $V_{\pm 1}$ and $V_{\pm 2}$, respectively [see Eq. (2)], which in turn are the lattice contribution to the EFG components. In the assumption that the frequency of the EFG fluctuations is $1/\tau_c$ the correlation functions are

$$\langle V_{\pm 1,2}(t)V^{*}_{\pm 1,2}(t+\tau)\rangle = \langle V_{\pm 1,2}(0)V^{*}_{\pm 1,2}(0)\rangle e^{-|\tau|/\tau_c} . \tag{2}$$

Then the contribution to $T_1$ from the EFG is given by

$$\left[\frac{1}{T_1}\right]_f = \frac{e^2Q^2}{12\hbar^2}\left[4\langle V_{\pm 1}(0)V^{*}_{\pm 1}(0)\rangle + \langle V_{\pm 2}(0)V^{*}_{\pm 2}(0)\rangle\right]\frac{\tau_c}{1+\omega_Q^2\tau_c^2} \tag{3}$$

with two limiting cases

$$\omega_Q\tau_c \ll 1 => (1/T_1)_f = A\tau_c , \tag{4}$$

$$\omega_Q\tau_c \gg 1 => (1/T_1)_f = B\tau_c^{-1} , \tag{5}$$

where $A$ and $B$ are temperature-independent constants.

Therefore the influence of the EFG fluctuations on the $T_1$ temperature rate must be accounted by the temperature dependence of $\tau_c$.

If the contribution of the lattice vibration is also considered, the total relaxation rate $1/T_1$ is

$$\frac{1}{T_1} = \left[\frac{1}{T_1}\right]_{\mathrm{lv}} + \left[\frac{1}{T_1}\right]_f . \tag{6}$$

The experimental data can be fitted by assuming that the EFG fluctuations corresponds to an Arrhenius thermally activated process

$$\tau_c = \tau_0 e^{E_a/kT} , \tag{7}$$

$$\frac{1}{T_1} = Ae^{B/T} , \tag{8}$$

where $E_a$ is the activation energy ($E_a = 0.87$ kcal/mol). Therefore the frequency of the fluctuations corresponds to the high-frequency limit [Eq. (5)].

The behavior of the single crystal is quantitatively similar to the powder sample, suggesting that the mechanisms which produce the EFG fluctuations is intrinsic in nature.

The temperature dependence of $\nu_q$ cannot be described by the Bayer-Kushida model for temperatures between 150 and 220 K. The divergence of the experimental data of $\nu_q(T)$ from the Bayer-Kushida formula ($\nu_{q\,\mathrm{expt}} - \nu_{q\,\mathrm{BK}}$) is plotted in the upper right corner of Fig. 3. This effect could be explained by a similar argument as for $T_1(T)$. Equation (9) represents the resonance frequency for a nuclei with $I = \frac{3}{2}$ belonging to a site surrounded by an axially symmetric electric charge distribution (hereafter the chemical bond)[9]

$$\nu_q = \frac{e^2\bar{q}Q}{4h} , \tag{9}$$

where $e$ is the electron charge, $\bar{q}$ is the mean value of the higher component of the EFG Cl, $Q$ is the quadrupole moment, and $h$ the Planck constant. The mean value of $q$ is taken over the molecular vibrations,[9] then in the small oscillation limit

$$\bar{q} = q_0(1 - \tfrac{3}{2}\langle\theta^2\rangle) , \tag{10}$$

where $q_0$ is the $q$ value for a static molecule and $\langle\theta^2\rangle$ is the mean-square amplitude of oscillation. Fluctuations of the EFG yield changes in $\langle\theta^2\rangle$. As Woessner and Gutowsky[13] we represent the electric charge distribution oscillations by a quantum-mechanical oscillator, i.e., $\theta_r(t) = D_r(t)\cos(wt)$. Fluctuations on the $\theta_r(t)$ decrease the correlation of the oscillation amplitude; this loss of correlation can be represented by

$$\langle\theta_r^2\rangle = \tfrac{1}{2}\langle D_r(t)D_r(t+\tau)\rangle , \tag{11}$$

where $D_r$ is the $r$th level oscillation amplitude; i.e., $D_r=(2r+1)h/\nu_e$, $\nu_e$ is the frequency of the torsional oscillation.

A fluctuation in the oscillation amplitude might produce a transition of the quantum-mechanical oscillator from the $r$th to $r'$th level. Therefore $D_r(t+\tau)$ will be a weighted sum over all values of $D_r$:

$$D_r^2(t+\tau)=\sum_{r'=0}^{\infty}\frac{n_{r'}}{n_r}D_{r'}^2(t), \quad \text{where } \sum_{r'} n_{r'}=n_r \ , \tag{12}$$

where $n_r$ and $n_{r'}$ are the populations of the $r$th and $r'$th level, respectively. Equations (11) and (12) yield to an expression for the square average of $\theta_r$, evaluated for one period, i.e., for $t=1/\nu_e$

$$\langle\theta_r^2\rangle_{\text{av}}=\tfrac{1}{2}D_r^2\exp\left[-\frac{1}{\nu_e\tau_r}\right]\times\left[\frac{\nu_e^3\tau_r^3}{1+\nu_e^2\tau_r^2}\sinh\left[\frac{1}{\nu_e\tau_r}\right]\right] , \tag{13}$$

where $\tau_r$ is the average lifetime of the molecule in the $r$th level. We will not attempt an explanation of the interactions causing he EFG fluctuations. We instead introduce an average lifetime $\tau_a$ for the molecule in a molecular state by the expression (see Ref. 13)

$$\frac{1}{\tau_r}=[r+(r+1)\exp(-x)]\frac{\exp(x)-1}{2\tau_a} , \tag{14}$$

where $x=h\nu_e/kT$. Therefore using Eqs. (13) and (14) it is possible to write

$$\langle\theta^2\rangle=\tfrac{1}{2}D_r^2\exp[-(\alpha+\beta)r] , \tag{15}$$

where $\alpha=[\exp(x)-1]/2\nu_e\tau_a$; $\beta=\alpha\exp(x)$.

And adding over all oscillation levels, we obtain

$$\langle\theta^2\rangle=\frac{1}{2}\frac{h}{I\nu_e}\exp(-\beta)[1-\exp(-x)]\times\frac{1+\exp(-\alpha-\beta-x)}{1-\exp(-\alpha-\beta-x)} . \tag{16}$$

In the high-temperature limit ($x \ll 1$) Eq. (16) can be reduced to

$$\langle\theta^2\rangle=\langle\theta^2\rangle_{\text{BK}}\left[1-\frac{1}{2\nu_e\tau_a}[1-\exp(-x)]\right] , \tag{17}$$

where $\langle\theta^2\rangle_{\text{BK}}$ is the mean angular amplitude calculated in the Bayer-Kushida model.[9] The final expression of $\nu_q(T)$ in this limit can be written as

$$\nu_q=\nu_0\left[1-\tfrac{3}{2}\langle\theta^2\rangle_{\text{BK}}\left[1-\frac{1}{2\nu_e\tau_a}[1-\exp(-x)]\right]\right] . \tag{18}$$

The temperature dependence of $\tau_a$ contains the whole physical significance of the influences of the EFG fluctuation on the $\nu_q$ temperature behavior (if $\tau_a\to\infty$, that is, absence of EFG fluctuations, then $\nu_q$ converges to the Bayer-Kushida model), if we assume again the temperature behavior of $\tau_a$ as representing EFG fluctuations due to a thermally activated mechanism [Eq. (7)] we obtain an activation energy in agreement with that obtained from $T_1(T)$ data.

The observed drop in the $I(T)$ rate, for temperatures below 220 K, might be explained by assuming intrinsic EFG fluctuations. This behavior is just a manifestation of the homogeneous line-broadening caused by anharmonic effects in the vicinity of the normal-to-incommensurate (N-I) structural phase transition, which is driven by a soft mode.

As was stated by Zumer and Blinc,[14] $T_1$ should decrease for temperatures between 150 and 145 K, as expected for any structural phase transition driven by a soft mode. The dominating relaxation mechanism will be the so-called Raman indirect processes.[15] Therefore the new contribution to $T_1(T)$ will be described by[14]

$$T_{1\text{sm}}=K_1(T-T_I)^{-1/2} . \tag{19}$$

From the data fit to Eq. (19), we obtained the following parameters:

$$T_1=150 \text{ K} \quad \text{and} \quad K_1=0.025 \text{ ms K}^{-1/2} ,$$

but the best fit of the data was obtained by

$$T_{1\text{sm}}=0.0038(T-150.5)^{-1.6} . \tag{20}$$

This type of behavior could be explained by assuming collective atomic motions near the phase transition.[16]

The NQR spectrum outlines the microscopic environment of the resonant nuclei. In a commensurate system the number of NQR lines is determined by the chemically nonequivalent nuclear sites in the unit cell. In an incommensurate system, when the translational periodicity is lost, every nucleus is nonequivalent; therefore there is a continuous frequency distribution which reflects the spatial variation of the order parameters.

When the phase behavior of the incommensurate modulation is one dimensional and linear in the crystal, the NQR spectrum is characterized by a broad line with two edge singularities (this is known as the "wave-plane limit"[10]). The frequency values for the two edge singularities are

$$\nu_1=\nu_0+\tfrac{1}{2}a_2A^2 \quad \text{and} \quad \nu_2=\nu_0 , \tag{21}$$

where $\nu_0$ is the resonance frequency of the high-temperature phase (commensurate) and the amplitude $A$ of the order parameter is proportional to $(T-T_1)^{1/2}$ as obtained from the standard Landau theory.[17] That is confirmed by the linear temperature behavior of $\Delta\nu=\nu_1-\nu_2$ that we obtained.

For temperatures between 145 and 110 K, $T_1(T)$ is anomalously short and nearly temperature independent. This behavior is expected for systems whose fluctuation spectrum is dominated by phasons.[14] For temperatures close to the discontinuous incommensurate-commensurate phase transition (at 115 K) the $T_1(T)$ rate increases due to a change in the phason spectrum.[14] This fact is correlated with that obtained by Zeyen[18] by using neutron diffraction in a biphenyl molecular crystal.

The $T_1(T)$ behavior dominated by phasons suggests that the occurrence of "narrow solitons" in this compound might be excluded, with the possible exception of a narrow temperature zone in the neighborhood of the incommensurate-commensurate phase transition. In the "phase soliton" approximation the incommensurate phase could be described as commensurate regions separated by narrow domain walls or "discommensurations" where the phase and amplitude of the order parameter change steeply.

Above 115 K, close to the incommensurate-commensurate phase transition, small commensurate regions appear in the crystal and their resonance frequency coincides with the low-frequency edge singularity.

The $T_1(T)$ temperature behavior for temperatures below 115 K is qualitatively described by the Zumer-Blinc model[14] related to the relaxation process concerned with a commensurate phase. Although 4,4′-dichlorobiphenyl sulphone and biphenyl have a similar molecular structure, they show quite different phase diagrams, since the commensurate phase has not yet been observed in the biphenyl.[1,18]

A qualitative analysis of the temperature dependence of $\nu_q$ in the commensurate phase ($T<115$ K) was made by using a model proposed by one of the authors,[19] which makes it possible to isolate the contribution to $\nu_q(T)$ due to the external vibrational modes of the molecule from the internal-mode contribution, when two or more crystalline phases are monitored through their $\nu_q$ temperature dependence. Therefore it is possible to access the solid-state contribution to the $\nu_q(T)$ of both phases by analyzing the temperature dependence of the NQR frequency difference, $\Delta\nu_q(T)$. In this model a good approximation to the change with temperature of $\Delta\nu_q(T)$ is given by[19]

$$\Delta\nu_q=\Delta\nu_s+AT+BT^2\ , \tag{22}$$

where $\Delta\nu_s$ accounts for the different contributions to the electric field gradient of neighbor molecules; this term is derived solely from the difference in the crystalline structure of the solid in the two phases. Coefficients $A$ and $B$ account for the different molecular motions in each phase and are related to solid-state interaction of each phase: $A$ is proportional to $1/\nu_{ec}^{02}-1/\nu_{en}^{02}$, where $\nu_e^0$ is the effective torsional frequency at $T=0$ K, belonging to $C$ and $N$ phases, respectively. $B$ is proportional to the same difference, but each term is weighted with the respective $g$ factor ($g$ being the temperature coefficient of the corresponding torsional effective frequency).

The data of $\Delta\nu_q(T)$ were fitted by Eq. (22), and the obtained parameters are

$$\Delta\nu_s=0.251\ \text{kHz}\ ,$$

$$A=-2.23\times10^{-3}\ \text{kHz/K}\ ,$$

$$B=3.93\times10^{-3}\ \text{kHz/K}^2\ .$$

From this analysis we might conclude the following.

(a) The small value of $\Delta\nu_{sq}$ indicates that there are not notable changes in the molecular arrangement on going through the normal to the commensurate phase. This fact is in agreement with the $T_2(T)$ results discussed above.

(b) From the values of the coefficients $A$ and $B$ we can deduce the following inequalities relating to the molecular dynamics of both phases:

$$\nu_{en}^0>\nu_{ec}^0\ , \tag{23a}$$

$$g_N<g_c\ . \tag{23b}$$

The effective torsional oscillations have a lower frequency in the $C$ phase than in the $N$ phase. Furthermore, (23b) shows that the anharmonicities in the intermolecular potential are higher in the $C$ phase than in the $N$ phase. These results could be correlated with the assumption that the $C$ phase possesses a less compact crystalline structure than the $N$ phase.

## VI. CONCLUDING REMARKS

From a bulk view of the experimental NQR data reported in this paper, we can conclude that the 4,4′-dichlorobiphenyl sulphone presents a normal (commensurate) crystalline phase at temperatures above 150 K. The crystal undergoes a continuous structural phase transition, at 150 K, to an incommensurate phase. Further down, at 115 K, it goes through a lockin phase transition.

The molecular dynamics of the compound in the high-temperature zone ($T>150$ K) is well described by the standard rigid molecule model. For temperatures between 230 and 150 K, the crystal evidences the onset of instabilities which produce fluctuations in the EFG at the $^{35}$Cl nuclei sites. This kind of intrinsic fluctuations was detected in a wide temperature range (more or less 60 K). In addition, the $T_1(T)$ has been shown to be the most sensible NQR parameter to detect EFG fluctuations. These effects on the NQR parameters have been interpreted as precursor effects which appear in the proximity of the N-I structural phase transition.

About the incommensurate phase, we might conclude that the incommensurate ordering of the C—Cl bonds and, consequently, the values of the mean EFG at the $^{35}$Cl nuclei sites, is well correlated to a "plane-wave" model description. $T_2(T)$ and molecular structure data, as well as $\nu_q(T)$, suggest that the strongest candidate to be the order parameter is the dihedral angle between the two benzene ring planes. We propose that the phase transition involves a rotation of the benzene rings around the Cl—S bond, that is, a change in the dihedral angles which does not alter the interatomic distances between Cl nuclei. As observed from our measurements, this fact is in agreement with the low activation energy involved in this process, the small variation of the EFG at the nuclei sites, and the flatness of the $T_2(T)$ behavior.

## ACKNOWLEDGMENTS

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