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Structural modulation and low-frequency excitations in the incommensurate phases of biphenyl

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Abstract. The incommensurate phases IC II and IC III of biphenyl are investigated by means of ²H NMR. It is shown that the structural modulation appears along one direction, and can be described by a periodic twisting of the phenyl rings about the molecular axis. The temperature dependence of the maximum twist angle below the N–IC phase transition follows a power law with a critical exponent $\beta = 0.35 \pm 0.03$. A two-dimensional NMR exchange spectrum in the IC II phase of biphenyl is recorded. It clearly excludes a ‘floating’ of the modulation wave. The temperature and Larmor frequency dependences of the ²H NMR spin–lattice relaxation rates $1/T_1$ in the IC phases of biphenyl are measured. A distinct dependence of $1/T_1$ on the Larmor frequency is found and analysed on the basis of a relaxatory dynamics of the order parameter (OP). A reliable estimate of about 5 MHz for the characteristic frequencies of the OP dynamics is derived. In the IC III phase, the spectra as well as the spin–lattice relaxation rates indicate that the structure of biphenyl is not a truly incommensurate one.

1. Introduction

Several ionic and molecular crystals exhibit a transition from a high-temperature normal (N) phase to a structurally incommensurately (IC) modulated phase at a certain temperature T_i . In the IC phase the crystal structure is deformed with respect to the N phase with a periodicity given by an incommensurate wave vector q_i which cannot be expressed as a rational multiple of the reciprocal-lattice vectors of the N phase. The order parameter $Q(q_i)$ of the N–IC phase transition is complex, and is described by

$$Q = \rho e^{i\phi} = (P_1 + iP_2)e^{i\phi_0} \quad (1)$$

with $\phi_0 = \langle \phi \rangle$, reflecting the fact that two degrees of freedom have to be taken into account, namely the amplitude ρ and initial phase ϕ of the modulation wave. As a consequence of the incommensurability, the initial phase of the modulation wave is arbitrary or, in other words, the IC structure is continuously degenerate with respect to a phase shift. This leads to the occurrence of special low-frequency excitations in the IC phase termed phasons (Cowley and Bruce 1978, Levanyuk 1986). The normal modes of the order parameter (OP), however, are its longitudinal (δP_1) and transversal (δP_2) fluctuations for which the relation $\langle \delta P_1 \delta P_2 \rangle = 0$ holds according to the symmetry in the OP space. Although, due to their strong overdamping, the detection of these modes by usual Raman or neutron scattering methods is not possible in many cases, their existence is revealed unambiguously by the

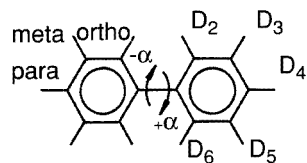


Figure 1. A schematic plot of the biphenyl molecule with the deuterium positions D_2 , D_3 , D_4 , D_5 and D_6 marked. The angle α indicates the twisting between the phenyl rings appearing in the IC phases (see the text).

large spin–lattice relaxation rates found in NMR or NQR experiments (Blinic *et al* 1986, Milia and Papavassiliou 1989, Walisch *et al* 1994).

Incommensurate phase transitions have been found in rather different systems, e.g. in members of the A_2BX_4 family such as Rb_2ZnCl_4 and K_2SeO_4 , in betaine calcium chloride dihydrate (BCCD), in thiourea, and in quartz (Cummins 1990). Here we are dealing with 2H NMR investigations of the incommensurate phases II and III of deuterated biphenyl ($C_{12}D_{10}$) which are stable in the temperature ranges between $T_{i1} = 38$ K and $T_{i2} = 20$ K, and below T_{i2} , respectively (Cailleau 1986). The normal phase I of biphenyl is monoclinic with space group $P2_1/a$ and $Z = 2$ (Charbonneau and Délugeard 1977). A schematic plot of the molecule is shown in figure 1. The structural modulation in the IC phases has been interpreted in terms of a periodic twisting of the phenyl rings relative to each other, in agreement with theoretical models (Plakida *et al* 1983, Cailleau 1986, Benkert *et al* 1987, Wasiutyński and Cailleau 1992). Elastic neutron scattering data revealed that the modulation in phase II is characterized by two different incommensurate wave vectors $\pm q_{i1}$ and $\pm q_{i2}$ (Cailleau 1986) corresponding to a four-component order parameter ($Q(q_{i1}), Q(q_{i2})$). In view of this result, the question has been discussed of whether the IC modulation in this phase is ‘stripe-like’ (i.e. neighbouring domains are one-dimensionally modulated either along q_{i1} or along q_{i2}), or ‘quilt-like’ (i.e. the whole crystal is modulated along both q_{i1} and q_{i2}). Theoretical calculations (Parlinski *et al* 1989, Wasiutyński and Cailleau 1992) as well as inelastic neutron scattering (INS) experiments (Launois *et al* 1989) provided arguments in favour of a ‘stripe-like’ modulation in the incommensurate phase II of biphenyl.

The transition from the IC II to the IC III phase has been found to be of first order (Cailleau 1986). Elastic neutron scattering experiments below T_{i2} revealed that the modulation wave in the IC III phase is characterized by only one wave vector $q_i = (1 - \delta)b^*/2$ with $\delta \approx 0.075$, but is not sinusoidal as in the IC II phase where the usual ‘plane-wave limit’ (PWL) is fulfilled. Instead, the modulation function shows a ‘squaring-up’ as predicted by theoretical models (Benkert *et al* 1987). It has been pointed out, however, that an alternative interpretation of the experimental data may be given in terms of a commensurately modulated structure. In that case, δ would be a rational fraction with a denominator equal to or larger than 13 (Cailleau 1986).

In Raman and inelastic neutron scattering experiments the soft mode of the N–IC phase transition in biphenyl has been identified down to about 50 K indicating a displacive-type transition (Wada *et al* 1981, Cailleau 1986). At lower temperatures above and below T_{i1} , however, the order parameter dynamics becomes strongly overdamped and can be observed only under high pressure (Launois *et al* 1989, Lemée-Cailleau *et al* 1992). The relaxatory character of the elementary excitations in the IC phase—at least for its lower-frequency parts—is also manifested in a large contribution to the 1H NMR spin–lattice relaxation rate (Liu and Conradi 1985) and by recent incoherent neutron scattering data (Etrillard *et al* 1995).

In this work we present 2H NMR studies of static and dynamic properties of biphenyl in the incommensurate phases II and III. From the temperature dependence of the 2H NMR spectra, detailed information is derived on the nature of the structural modulation

of the crystal. The results obtained in both IC phases are compared and discussed in the light of a possible commensurability of the low-temperature phase. In order to investigate the dynamics of the modulation wave in biphenyl on a large timescale, two-dimensional exchange ^2H NMR spectra were recorded. The low-frequency excitations of the incommensurate phases were studied by means of the temperature and Larmor frequency dependence of the spin–lattice relaxation rate. The dependence of $1/T_1$ on the Larmor frequency provides a reliable estimate for the characteristic frequencies of these fluctuations. In particular, it is shown that longitudinal and transversal OP fluctuations—though they are decoupled due to the symmetry of the complex OP—are strongly interrelated as predicted by theoretical approaches beyond the quasi-harmonic theory (Bruce and Cowley 1978).

2. Experimental details

2.1. Samples

A single crystal of deuterated biphenyl, $\text{C}_{12}\text{D}_{10}$, was grown from the melt by the Bridgeman method. For orienting the crystal we took advantage of the fact that the plane perpendicular to the reciprocal-lattice vector c^* is an easy-cleavage plane. This plane could easily be identified with an optical goniometer. Subsequently, the crystal was fully oriented by means of x-rays. From the bulk crystal three pieces were cut and prepared as NMR samples. On a lathe they were formed into cylinders about 6 mm in length and 4.2 mm in diameter fitting exactly into standard 5 mm NMR tubes. The cylinder axes were chosen parallel to the a , b , and c^* crystal axes, respectively.

2.2. NMR measurements

Deuteron NMR spectra of the three sample crystals were recorded in an external magnetic field $B_0 = 11$ T with a home-built FT spectrometer operating, for deuterons, at a Larmor frequency of 72.1 MHz. Spectra were obtained by Fourier transformation of the free induction decay (FID) after (nominally) 90° pulses of $2.2 \mu\text{s}$ duration. Baseline distortions of the spectra resulting from the deadtime of the spectrometer (about $6 \mu\text{s}$) were eliminated by applying the numerical routine BCF (Heuer and Haeberlen 1989). A worm-and-gear goniometer in the NMR probehead allowed rotation of the sample about an axis perpendicular to the external magnetic field B_0 with an accuracy of a fraction of a degree.

The spectrometer was equipped with an Oxford Instruments gas-flow helium cryostat. The temperature was regulated with an ITC-4 temperature control unit from the same company. A stability within ± 0.1 K was attained.

Field cycling was applied for measuring the frequency dependence of the deuteron spin–lattice relaxation times T_1 in the IC phase II of biphenyl at 24.5 K. The sample was magnetized in the homogeneous field of a wide-bore 6.34 T magnet. Immediately after the preparation pulse, it was pushed, together with the NMR coil and a Lakeshore CGR-1500 temperature sensor, into the stray field below the centre of the magnet, and after the relaxation period it was pushed back into the homogeneous field for recording the NMR signal. A nonmagnetic commercial pneumatic unit, originally designed for the packing industry, served to move the sample. The sample attained a maximum speed of 1 m s^{-1} which was sufficient for our purposes since the relaxation times to be measured were of the order of 20 s and above. The precision of stopping at the desired position was about ± 0.5 mm. On preparing the experiments, the strength of the stray field was measured as a function of the sample position z below the centre of the magnet using a Hall probe.

From $z = 0$ to $z = 0.5$ m the field drops from 6.34 T down to 0.09 T. One might worry about the fact that the stray field to which the sample is exposed during the relaxation period varies over the sample volume. However, as we shall see in section 3.2, the field dependence of T_1 in biphenyl is sufficiently flat for rendering this variation unimportant. Instead, the most difficult problem in our field-cycling experiments concerned the sample temperature. Naturally, under stationary conditions there is an appreciable temperature difference between the positions at $z = 0$, where the sample is magnetized, and at a general position z , where in our case the relaxation takes place. For the maximum value of $z = 0.5$ m, this temperature difference amounts to 8 K which is clearly intolerable. Thus, in order to keep the sample during magnetization and relaxation at the same temperature, the controller was programmed in such a way that at an appropriate time before the sample displacement the set point temperature was switched to an appropriate new value which had been determined earlier for each value of z by trial and error. With this strategy, we were able to keep the temperature at 24.5 K within ± 0.8 K during all steps of the field-cycling experiments. In view of the rather weak temperature dependence of T_1 in the IC II phase of biphenyl (cf. section 3.2) this temperature stability was deemed acceptable.

Table 1. Quadrupole coupling constants, asymmetry parameters, and eigenvectors belonging to the largest principal values of the QC tensors of the deuterium positions in biphenyl determined from the orientation dependence of the ^2H NMR spectra at 300 K. Polar coordinates (in degrees) are given within the $\{a, b, c^*\}$ frame. The data in the right-hand columns are taken from elastic neutron scattering (ENS) measurements by Baudour and Sanquer (1983).

Deuterium position	Quadrupole coupling constant (kHz)	Asymmetry parameter	Polar coordinates of the C–D bond direction			
			^2H NMR data		ENS data	
			Θ	ϕ	Θ	ϕ
Para- (D_4, D_4')	181.6	0.09	17.7	−3.1	17.2	± 3.0
Ortho-/meta- (D_2, D_5)	175.6	0.03	108.0	128.4	109.1	128.5
Ortho-/meta- (D_2', D_5')	174.9	0.04	71.0	51.1	70.9	51.5
Ortho-/meta- (D_3, D_6)	176.6	0.04	51.3	113.2	51.6	112.1
Ortho-/meta- (D_3', D_6')	177.8	0.05	127.0	66.7	128.4	67.9

3. Results and discussion

3.1. ^2H NMR spectra

In the monoclinic normal phase of deuterated biphenyl, the ^2H NMR spectrum consists for a general crystal orientation of six pairs of lines which belong to the para- and to the meta-/ortho-positions at the phenyl rings of two crystallographically inequivalent molecules (cf. figure 1). This number is reduced by a factor of 2 for crystal orientations with the monoclinic b axis perpendicular to the external magnetic field B_0 . A series of spectra are shown in figure 2. From the orientation dependence of the spectra for crystal rotations about the crystallographic axes a , b , and $c^* = [a \times b]$ the complete quadrupole coupling (QC) tensors at the respective lattice sites have been determined at 290 K. The results are summarized in table 1.

The QC tensors allow for a definite assignment of the ^2H NMR resonance lines to the corresponding deuteron positions. The results clearly demonstrate the inversion symmetry

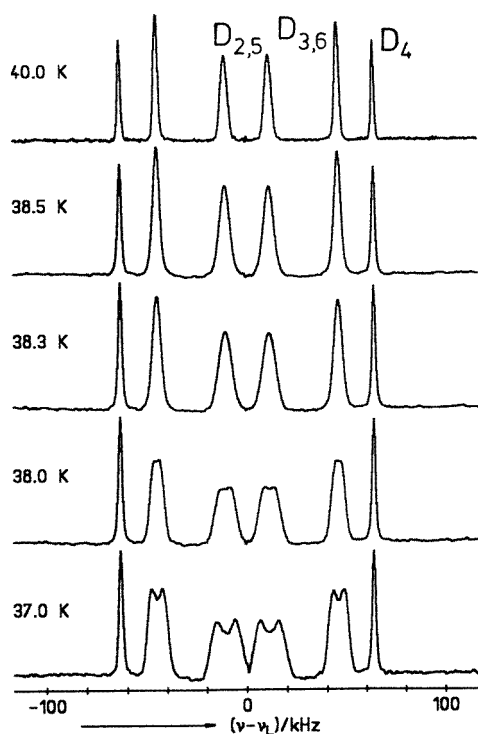


Figure 2. The series of ^2H NMR spectra of biphenyl obtained for the crystal orientation $b \perp B_0$, $\angle(c^*, B_0) = 97.4^\circ$ close above and below the N-IC II phase transition at $T_{i1} = 38$ K. As indicated in the spectra, the lines belong to the para- (D_4) or to the meta- and ortho-positions (D_2, D_5) and (D_3, D_6). The resonance lines from the deuterons (D_2, D_5) and from (D_3, D_6) coincide for each orientation of the crystal.

of the biphenyl molecules and the planarity of the phenyl rings as well with an accuracy better than $\pm 1^\circ$. This is in contrast to previous conclusions from x-ray data where the C-H bonds were assumed to be tilted with respect to the phenyl plane (Charbonneau and Délugeard 1977).

On passing from the normal phase I into the incommensurate phase II, the ^2H NMR resonance lines split into characteristic frequency distributions with two edge singularities (figure 2). This behaviour is typical for NMR spectra of crystals with a one-dimensional incommensurate modulation (Blinc 1981, Blinc *et al* 1986, Topic *et al* 1988). On the other hand, a two-dimensional modulation of the lattice with two different wave vectors $\pm q_{i1}$ and $\pm q_{i2}$ simultaneously would lead to completely different frequency distributions in the spectra with one central singularity and two shoulders at its edges (Blinc 1981, Blinc *et al* 1986). Thus, our ^2H NMR spectra provide a look-and-see proof for the one-dimensional 'stripe-like' modulation in the incommensurate phase II of biphenyl. This is in accordance with previous much less direct conclusions from theoretical calculations (Parlinski *et al* 1989, Wasiutyński and Cailleau 1992) and from experimental INS data (Launois *et al* 1989).

Moreover, our spectra reveal clearly that the ^2H NMR lines of the para-deuterons (the outermost pair of lines in figure 2) are obviously not affected by the N-IC phase transition. This clearly demonstrates that the phenyl rings become twisted about the $C_4-C_{4'}$ bond axis

in the IC phase since, of course, it is only such a kind of twisting that will not lead to a change in the C₄–D₄ bond direction and has therefore no influence on the corresponding ²H NMR lines. Again we find a nice agreement with theoretical models of the incommensurate modulation in biphenyl (Plakida *et al* 1983, Wasiutyński and Cailleau 1992).

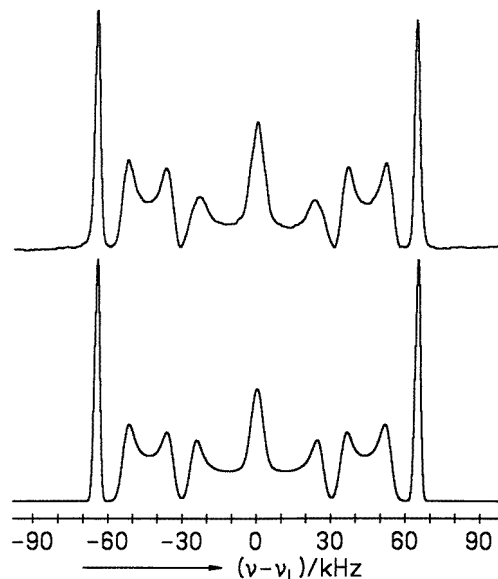


Figure 3. The ²H NMR spectrum of biphenyl obtained for the crystal orientation $\mathbf{b} \perp \mathbf{B}_0$, $\angle(\mathbf{c}^*, \mathbf{B}_0) = 97.4^\circ$ in the IC II phase at a temperature $T = 24.5$ K (top). The spectrum underneath shows the fit under the assumption of a sinusoidally modulated twisting of the phenyl rings with a maximum twist angle $\alpha_0 = 5.2^\circ$ (see the text).

In order to obtain more information about the structural modulation of the biphenyl molecules in the incommensurate phases, we turn our attention to the frequency distributions which stem from the deuterons at the meta- and ortho-positions. Generally, in order to analyse the NMR spectra of $I > 1/2$ nuclei in incommensurate crystals correctly, it is necessary to expand the quadrupole coupling tensors in terms of the static displacements of the surrounding atoms from their positions in the N phase. This results in a Fourier series for each tensor component (Perez-Mato *et al* 1987). In the present case, however, we take advantage of the facts that (i) the relevant structural modulation consists practically only of the phenyl ring twist $\alpha(\mathbf{r})$, i.e. of a single degree of freedom according to

$$\alpha(\mathbf{r}) = \alpha_0 \cos(\mathbf{q}_i \cdot \mathbf{r} + \phi_0) = \langle Q \rangle e^{i\mathbf{q}_i \cdot \mathbf{r}} + \text{CC} \quad (2)$$

and (ii) that the ²H quadrupole coupling tensor is determined predominantly by its local bond. Thus, the modulation of the quadrupole coupling tensors under consideration is equivalent to a modulated tilt of their principal directions with the eigenvalues remaining constant. It can be shown (Perez-Mato *et al* 1987) that this picture corresponds to the ‘local model’ for the tensor modulation introduced by Blinc and co-workers (Blinc 1981, Blinc *et al* 1986). Using these assumptions and the modulation function (2) of the plane-wave limit, the ²H NMR spectra of biphenyl obtained in the crystal orientation $\mathbf{b} \perp \mathbf{B}_0$, $\angle(\mathbf{c}^*, \mathbf{B}_0) = 97.4^\circ$ could be fitted with only one fitting parameter, the maximum twist angle α_0 . As can be inferred from figure 3, the fit is obviously good. (Here we note that we must

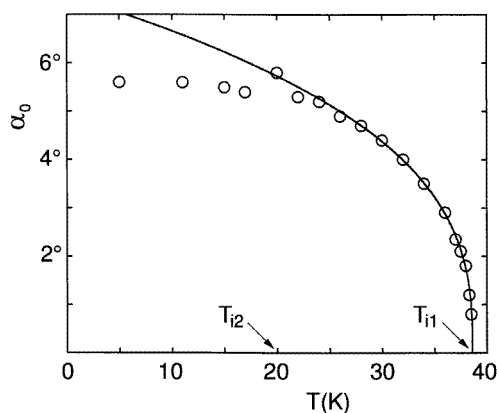


Figure 4. The temperature dependence of the maximum twist angle α_0 of the phenyl rings in the incommensurate phases of biphenyl obtained by a fit of the ^2H NMR spectra measured for the crystal orientation $\mathbf{b} \perp \mathbf{B}_0$, $\angle(\mathbf{c}^*, \mathbf{B}_0) = 97.4^\circ$ (cf. figures 2 and 3). The solid line corresponds to a power law proportional to $(1 - T/T_{i1})^\beta$ with a critical exponent $\beta = 0.35$.

take into account not only the modulation according to (2) but also a further deviation from the structure at 290 K, namely an additional tilt of the whole molecule about the twist axis which is observed already in the N phase on approaching T_{i1} from above. The corresponding tilt angle γ is about 2° .) The values of the maximum twist angle α_0 obtained from the fit of the ^2H NMR spectra are given as a function of the temperature in figure 4. In the lower part of the IC II phase, it attains a magnitude of about 5° , in nice agreement with previous theoretical calculations (Benkert *et al* 1987). According to (2), the angle α_0 represents the order parameter amplitude of the N–IC phase transition of biphenyl. It actually follows a power law proportional to $(1 - T/T_{i1})^\beta$ with a critical exponent $\beta = 0.35 \pm 0.03$. This value agrees with those found for several other one-dimensionally incommensurately modulated crystals such as Rb_2ZnCl_4 , Rb_2ZnBr_4 and BCCD (Walisch *et al* 1990, Holzer *et al* 1993). It is also in accordance with the theoretical predictions of the nonclassical 3d XY -model (LeGuillou and Zinn-Justin 1977). While it is true that critical exponents in general depend on the dimensionality of the OP, it has been pointed out by Cowley and Bruce (1978) that the 3d XY -model should describe the critical behaviour of second-order incommensurate phase transitions also for those cases where there is more than one critical wave vector involved. In any event, below T_i one has for each domain a single modulation wave and therefore a two-component order parameter, as in the one-dimensionally modulated IC systems mentioned above.

A closer inspection of the ^2H NMR spectra in figure 2 reveals that additional shoulders appear at the edge singularities which become even more pronounced on further cooling (see figure 5). It has been checked experimentally that this is not an effect of a misorientation of the crystal (Ermark 1992). Thus, it has to be concluded that the inversion symmetry of the biphenyl crystal is lost in the incommensurate phases also for the average (basic) structure. This means a disappearance of the inversion centre within the biphenyl molecules (even for those with $\alpha(\mathbf{r}) = 0$) corresponding to a space group Pa of the basic lattice. The deviation from the inversion symmetry, however, is only slight. This result agrees with the conclusions from elastic neutron scattering data for biphenyl at 20 K (Baudour and Sanquer 1983).

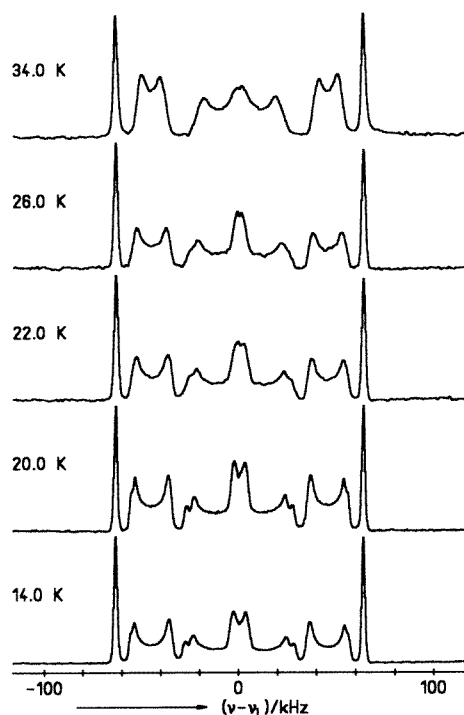


Figure 5. The series of ^2H NMR spectra of biphenyl obtained for the crystal orientation $b \perp B_0$, $\angle(c^*, B_0) = 97.4^\circ$ close to and below the IC II–IC III phase transition at $T_{i2} \approx 20$ K. Note that at lower temperatures the spectral intensities shift into the edge singularities, and that additional shoulders appear in the lineshapes.

The evolution of the ^2H NMR spectra in the IC III phase below 20 K is quite different from that in the IC II phase. First, as can be seen in figure 4, the maximum twist angle α_0 (i.e. the order parameter amplitude) increases no more on further cooling but reaches a constant value of about 5.5° . Second, the shape of the frequency distribution changes below T_{i2} (see figure 5): while the edge singularities grow and become narrower, the intensity inside the distribution shrinks markedly. As is intuitively clear, this behaviour can be explained by a ‘squaring-up’ of the modulation wave discussed in section 1 (Blic *et al* 1986). Alternatively, these results may be discussed in terms of a commensurate structure with a large multiplication of the lattice periodicity along the b direction below 20 K. A clear distinction between these two different cases, however, cannot be extracted from the experimental spectra. We shall come back to this question later on.

3.2. The dynamics in the incommensurate phases

In many papers dealing with NMR or NQR investigations of quadrupolar nuclei in incommensurate systems, the possible influence on the NMR or NQR spectra in the vicinity of the N–IC phase transitions of slow, large-scale phase fluctuations (so-called ‘floating’ or ‘diffusionlike motion’ of the modulation wave) has been discussed extensively (Blic *et al* 1984, 1986, Fajdiga *et al* 1992). In particular, it has been argued that a strong broadening of the spectra close to T_i would be expected. This would lead to an apparent smearing

out of the phase transition and, moreover, to an extra temperature dependence of the edge singularity distance below T_{i1} which destroys the power-law behaviour corresponding to a linear or quadratic coupling to the order parameter amplitude (Blinic *et al* 1986). The experimental data presented in these papers, however, were obtained from studies of $I = 3/2$ NMR central transitions where the resonance frequencies are related to the local quadrupole coupling tensor in a rather complicated way according to second-order perturbation theory (Abragam 1961) and where only a small frequency resolution can be achieved. The same holds, in principle, for NQR experiments. Contrarily, in the case of nuclear spins with $I = 1$ or in the case of NMR satellite transitions for $I = 3/2$, the frequencies are given by first-order perturbation theory which leads not only to a linear relation between NMR frequencies and QC tensor components but also to a much higher sensitivity of the spectra. In fact, in previous investigations of the IC systems Rb_2ZnCl_4 , Rb_2ZnBr_4 and BCCD by means of NMR satellite transitions a sharp transition from the N to the IC phase has been found as well as an exact power-law behaviour of the edge singularity distance even very close to T_i . Also, no significant broadening of the lineshapes in that temperature region has been observed (Walisch *et al* 1990, Holzer *et al* 1993). Therefore, for these systems a ‘floating’ of the modulation wave can be excluded at least on the timescale of about 10^{-4} s and below, which is given by the inverse of the smallest singularity distances observed. In view of the experimental ^2H NMR results presented in section 3.1, the same conclusion is to be drawn for the case of the incommensurate phases of biphenyl.

Recently, it has been argued on the basis of ^{35}Cl NQR spin-echo measurements for the IC phase of Rb_2ZnCl_4 that in this system a ‘diffusionlike motion’ of the modulation wave in a temperature range of several K below T_i would occur with diffusion constants of the order of 10^{-16} $\text{m}^2 \text{s}^{-1}$ (Papavassiliou *et al* 1995). According to the modulation wavelength in the IC phase of Rb_2ZnCl_4 this would mean that within one second the modulation wave should propagate through the crystal with a mean displacement that corresponds to a mean phase shift of several times 2π . (In such a case, one might question whether the system were actually in an IC phase since the time average of the order parameter $Q = \rho \exp(i\phi)$ would be zero.) In any case, it is of basic importance to study the dynamical behaviour of the incommensurate modulation at very long timescales. For answering the question of whether the modulation wave in the IC II phase of biphenyl is ‘floating’ or not, the method of choice is a two-dimensional ^2H exchange NMR experiment (see, e.g., Schmidt *et al* 1988). We performed an experiment of this type at a temperature of about 33 K, i.e. at 5 K below the N–IC phase transition, using the same crystal orientation as given in the caption of figure 2. Since the relevant spin–lattice relaxation times are of the order of 30 s and above, a mixing time of 20 s could be chosen. Here we focus on the frequency distribution of one resonance line which stems from the ortho-/meta-deuteron positions (cf. figure 2). The corresponding exchange NMR spectrum is shown in figure 6 as a contour plot drawn down to a very small level of intensity. It is obvious that no off-diagonal intensities can be found in the frequency area of interest between 35 kHz and 65 kHz. This is an unambiguous proof for the fact that a ‘floating’ of the modulation wave does not occur in the incommensurate phases of biphenyl. Therefore, at least for biphenyl, the usual description of the dynamics in incommensurate phases in terms of lattice excitations (Bruce and Cowley 1978) need not be extended by taking into account ‘diffusionlike motions’ but comprises only more or less typical fluctuations of the order parameter about its thermal average although, as will be shown later, they may be very slow compared with usual lattice vibrations. In addition, the two-dimensional exchange NMR spectrum also demonstrates the absence of spin diffusion between the relevant spectral intensities at least on a timescale of 20 s.

In view of these conclusions, it is obvious that NMR spin–lattice relaxation experiments

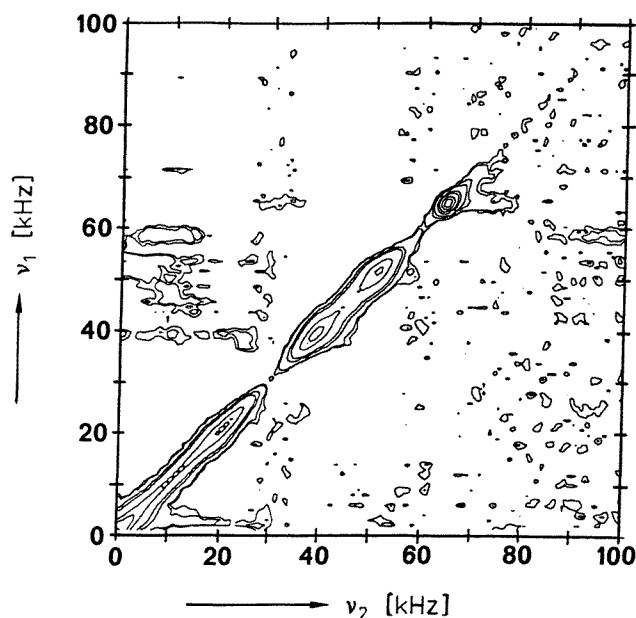


Figure 6. The two-dimensional ^2H NMR exchange spectrum of biphenyl obtained for the crystal orientation $\mathbf{b} \perp \mathbf{B}_0$, $\angle(\mathbf{c}^*, \mathbf{B}_0) = 97.4^\circ$ in the IC II phase at a temperature of 33 K. The mixing time was 20 s. The frequency distributions belonging to the ortho-/meta-positions appear between 0 kHz and 25 kHz (D_2 , D_5) and between 35 kHz and 55 kHz (D_3 , D_6). Only one quadrant of the full 2D spectrum is shown. The levels of intensity plotted here are 5, 10, 50, 100, 400, 700, 1500, and 2500. Note the absence of any cross-peak intensity.

should be an appropriate tool for investigating the characteristic low-frequency dynamics in the IC phases of biphenyl. The results of our measurements of T_1 are shown in figure 6. On approaching T_{i1} from above, $1/T_1$ increases by a factor of about 10 due to the contribution of order parameter fluctuations. Thus, background relaxation rates can be neglected in the following. The same conclusion has been drawn in corresponding studies of other incommensurate crystals (Blinic *et al* 1986, Walisch *et al* 1994, Häcker *et al* 1995). Above T_{i1} the temperature dependence of $1/T_1$ follows a power law proportional to $(T/T_{i1} - 1)^{-\zeta}$ with a critical exponent $\zeta = 0.9$. This value agrees reasonably well with previous ^1H NMR measurements where a value of $\zeta = 1.05$ has been reported (Liu and Conradi 1985). On the other hand, it is rather different from the result $\zeta = 0.625$ which has been found at the incommensurate phase transition of Rb_2ZnCl_4 and BCCD (Holzer *et al* 1993).

In the IC phase, we must distinguish between longitudinal (δP_1) and transversal (δP_2) OP fluctuations which are no longer identical as in the N phase. These excitations are sometimes termed ‘amplitudon’ or ‘phason’ fluctuations. (As much as possible, we avoid these somewhat misleading terms; instead we use the definition of the OP normal coordinates P_1 and P_2 given by Bruce and Cowley (1978).) Thus, we must deal with two different types δP_1 and δP_2 of order parameter fluctuation which are responsible for the spin–lattice relaxation. (Here we note that, in this special case of an IC modulation with two critical wave vectors \mathbf{q}_{i1} and \mathbf{q}_{i2} , an additional relaxation contribution might be present arising from the fluctuations of the modulation which is suppressed in each particular domain. In the following we will neglect this contribution as rationalized at the end of this section.)

Usually, the assignment of the relevant contributions to experimental NMR relaxation data is a difficult task since, in general, $1/T_1$ is a linear combination of the corresponding spectral densities $J_1(\omega)$ and $J_2(\omega)$ evaluated at $\omega = \omega_L$ and $\omega = 2\omega_L$ (Walisch *et al* 1994). These spectral densities are defined as

$$J_\beta(\mu\omega_L) = \int_{-\infty}^{+\infty} \langle \delta P_\beta(0) \delta P_\beta(t) \rangle e^{-i\mu\omega_L t} dt. \quad (3)$$

This can be rewritten, using the fluctuation-dissipation theorem, as

$$J_\beta(\mu\omega_L) \propto k_B T \sum_{\mathbf{k}} \frac{\chi''_\beta(\mathbf{k}, \mu\omega_L)}{\mu\omega_L} \quad (4)$$

where $\chi''_\beta(\mathbf{k}, \omega)$ is the imaginary part of the corresponding dynamic susceptibility depending on the frequency and on the reduced wave vector $\mathbf{k} = \mathbf{q} - \mathbf{q}_i$. For $I = 3/2$ NMR satellite transitions and the analogous case $I = 1$, the assignment of $1/T_1$ to the spectral densities J_1 and J_2 can be obtained only by comparing carefully the modulation functions of the relaxation transition probabilities with that of the NMR resonance frequency (Walisch *et al* 1994). Fortunately, in the present case of ^2H NMR measurements on biphenyl the validity of the ‘local model’ for the QC tensor modulation can safely be assumed (cf. section 3.1). It has been shown that, under this condition, the relevant modulation functions are comparatively simple (Zumer and Blinc 1981, Blinc *et al* 1986, Perez-Mato *et al* 1987, Walisch *et al* 1994). In particular, it turns out in this case that the spin–lattice relaxation rate measured at the edge singularities is proportional to J_1 whereas the one measured at the centre of the frequency distribution is proportional to J_2 . While the latter should exhibit only a slight temperature dependence according to (4) due to a constant ‘phason’ susceptibility over the whole IC phase, the former is expected to decrease critically on lowering the temperature below T_{i1} as a consequence of the hardening of the longitudinal OP fluctuations (Zumer and Blinc 1981, Walisch *et al* 1994).

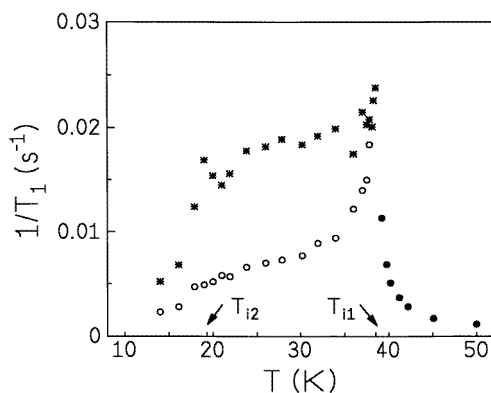


Figure 7. The temperature dependence of the spin–lattice relaxation rate measured for the ortho-/meta-positions (D_2 , D_5) of biphenyl in the crystal orientation $\mathbf{b} \perp \mathbf{B}_0$, $\angle(\mathbf{c}^*, \mathbf{B}_0) = 97.4^\circ$. The data obtained for the N phase are marked by full circles; the ones obtained in the IC phases are marked by open circles (edge singularities) and by stars (centres of the frequency distributions).

In figure 7 we have plotted for $T \leq T_{i1}$ the spin–lattice relaxation rates obtained for the edges (\circ) and for the centre ($*$) of the frequency distribution of the ^2H NMR lines belonging to the ortho-/meta-deuteron positions. Thus, these data should reflect the temperature

dependence of J_1 (\circ) and J_2 (*). In particular, as can be seen, the δP_2 - ('phason'-) induced relaxation rate is roughly proportional to T in the IC II phase, as it should be (Zumer and Blinc 1981, Walisch *et al* 1994). On the other hand, the spectral density J_1 is found to decrease rapidly below T_{i1} , also in agreement with the above arguments. This behaviour, in turn, confirms the assignment of the relaxation rates according to the 'local model'.

On passing the transition from the IC II to the IC III phase, the temperature dependence of the spin-lattice relaxation rates changes markedly (see figure 7): the values measured for $1/T_1$ at the edge singularities as well as those obtained for the centre of the frequency distribution show a sharp decrease below T_{i2} giving evidence that the character of the 'phason' fluctuations changes on passing the phase transition. Such a decrease has also been found for the ^1H NMR spin-lattice relaxation rate (Liu and Conradi 1985). This is a somewhat surprising result since, for a transition from one IC phase to another one with essentially the same nature of its structural modulation, the basic features of the order parameter dynamics should be retained. On the other hand, a very similar behaviour of $1/T_1$ is observed in several incommensurate crystals at the transition to a subsequent commensurate phase (Zumer and Blinc 1981, Walisch *et al* 1994, Häcker *et al* 1995). In this case, the 'phason branch' is transformed to a particular optical branch of the commensurate structure (Bruce and Cowley 1978) which is of lower efficiency for spin-lattice relaxation. Therefore, the experimental values of T_1 presented here can be considered as an indication that the crystal structure of biphenyl in fact becomes commensurately modulated below about 20 K. Alternatively, one may also speculate that biphenyl for $T < 20$ K is neither in a commensurate, nor in an incommensurate phase, but in a frozen-in nonequilibrium state which exhibits features both of the truly incommensurate phase II (continuous frequency distributions in the ^2H NMR spectra) and of a truly commensurate state (harder lattice dynamics, temperature-independent modulation wave vector).

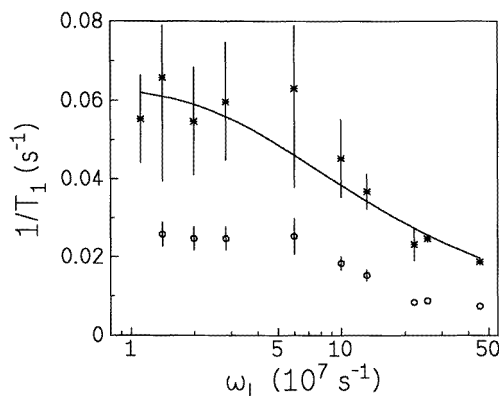


Figure 8. The dependence on the Larmor frequency of the spin-lattice relaxation rate measured for the ortho-/meta-positions (D_2 , D_5) of biphenyl in the crystal orientation $b \perp B_0$, $\angle(c^*, B_0) = 97.4^\circ$ in the IC II phase at 24.5 K. The data were obtained at the edge singularities where $1/T_1 \propto J_1$ (\circ), and at the centres of the frequency distributions where $1/T_1 \propto J_2$ (*). The fit curve corresponds to equation (10) (see the text).

In the ^1H NMR spin-lattice relaxation study of the IC phases of biphenyl cited above, a distinct dependence of $1/T_1$ on the Larmor frequency employed in the experiment has been reported. It is well known from the theory of NMR spin-lattice relaxation (Abragam 1961) that in any case such a result gives evidence for the fact that the characteristic

frequencies of the fluctuations responsible for $1/T_1$ —at least partially—are of the order of the Larmor frequencies or below. Thus, the data for T_1 obtained by Liu and Conradi (1985) demonstrate that the frequency scale of the order parameter dynamics in the incommensurate phase II of biphenyl is obviously in the MHz region or even below. The contributions from longitudinal and transversal OP fluctuations to the ^1H spin–lattice relaxation, however, could not be separated due to the insufficient frequency resolution in the ^1H NMR spectra. In contrast to that, in our case of ^2H NMR such a separation is actually possible, as has been demonstrated above. Therefore, in order to study the order parameter dynamics in the IC phases in more detail, it is of particular interest to investigate the Larmor frequency dependence of the two contributions proportional to J_1 and J_2 . For this purpose, ^2H NMR relaxation measurements were performed using the field-cycling technique for adjusting the Larmor frequency. We chose the same crystal orientation as that for recording the spectra in figure 2. The spin–lattice relaxation rates measured at the edge singularities (\circ) and at the centre of the frequency distribution ($*$) are shown in figure 8. According to the above discussion, they are proportional to the spectral densities J_1 (\circ) and J_2 ($*$), respectively. A distinct dependence of $1/T_1$ on the Larmor frequency for both contributions is found. For a quantitative analysis of the experimental results, we must introduce in (4) a special dynamical model. In view of the strong overdamping of the OP fluctuations in biphenyl discussed in section 1, we assume a relaxatory dynamics in the following. Consequently, we start from

$$\chi_\beta(\mathbf{k}, \omega) = \frac{\chi_\beta(\mathbf{k}, 0)}{1 - i\omega\tau_\beta(\mathbf{k})} \quad (5)$$

and apply the Lyddane–Sachs–Teller relation

$$\chi_\beta(\mathbf{k}, \omega)/\tau_\beta(\mathbf{k}) = \text{constant}(\mathbf{k}) \quad (6)$$

where the $\tau_\beta^{-1}(\mathbf{k})$ are the characteristic frequencies of the relaxators with wave vectors \mathbf{k} . Inserting (5) and (6) into (4), we obtain

$$J_\beta(\mu\omega_L) \propto k_B T \chi_\beta^2(0, 0) \sum_{\mathbf{k}} \frac{1}{1 + (\mu\omega_L \tau_\beta(\mathbf{k}))^2}. \quad (7)$$

Obviously, the frequency dependence of this expression will depend strongly (i) on the ratio of the Larmor frequency and the characteristic frequencies $\tau_\beta^{-1}(\mathbf{k})$, and (ii) on the shape of the dispersion curve $\tau_\beta^{-1} = \tau_\beta^{-1}(\mathbf{k})$. Assuming for simplicity an isotropic dispersion according to

$$\tau_\beta(\mathbf{k}) = \tau_\beta(0)/(1 + \xi^2 \mathbf{k}^2) \quad (8)$$

for the (relevant) small wave vectors \mathbf{k} and replacing the sum in (7) by an integral, one finds (Holzer *et al* 1995)

$$J_\beta(\mu\omega_L) \propto k_B T \frac{\chi_\beta^2(0, 0)}{\xi^3} \left(\frac{\mu a + i}{2\mu a \sqrt{1 - i\mu a}} \arctan \left(\frac{\xi \Lambda}{\sqrt{1 - i\mu a}} \right) + \text{cc} \right) \quad (9)$$

where $a = \omega_L \tau_\beta(0)$ gives a measure for the frequency scale of the OP fluctuations and Λ is a cut-off wave vector which is of the order of the radius of the first Brillouin zone. It is reasonable to assume that the variation over \mathbf{k} of the characteristic frequencies $\tau_\beta^{-1}(\mathbf{k})$ is large, leading to a large argument in the arctan function, and to

$$J_\beta(\mu\omega_L) \propto J_\beta(0) \frac{\sqrt{2}}{\mu a} \sqrt{\sqrt{1 + \mu^2 a^2} - 1} \quad (10)$$

(Holzer *et al* 1995). For large Larmor frequencies $\omega_L \gg \tau_\beta^{-1}(0)$, equation (10) yields a square-root dependence of $1/T_1$ as $1/T_1 \propto J_\beta(\mu\omega_L) \propto \sqrt{1/\omega_L}$. This kind of Larmor frequency dependence has also been derived on the basis of an oscillatory dynamics (Zumer and Blinc 1981).

In view of equations (9) and (10), we may expect from our experimental data the answer to two questions about the characteristic excitations in the incommensurate phase II of biphenyl: on the one hand, a successful fit of the data in figure 8 according to equation (9) should confirm our dynamical model used in equations (5)–(8). On the other hand, the fit itself will provide the value of $\tau_\beta(0)$ and, from that, the time constant of the order parameter dynamics below T_{i1} .

The fit curve for the spin–lattice relaxation rates proportional to J_2 according to equation (10) is given in figure 8. As can be seen immediately, a good agreement is found. In particular, at higher values of the Larmor frequency the behaviour of $1/T_1$ obviously follows the square-root dependence predicted by (10) while for $\omega_L < 5 \times 10^7 \text{ s}^{-1}$ the spin–lattice relaxation rate becomes essentially independent of ω_L . Here we note that, contrary to our results, a dependence of the ^1H NMR spin–lattice relaxation rate on the Larmor frequency was observed even in the kHz region (Liu and Conradi 1985). It was described by a power law with a small exponent of about 1/3 which could not be rationalized.

The fit curve corresponding to (10) of the data in figure 8 provides the parameter $\tau_2(0) \approx 3 \times 10^{-8} \text{ s}$ which corresponds to a relaxation frequency $1/2\pi\tau_2(0) \approx 5 \text{ MHz}$. Since the transversal OP fluctuations are directly related to the soft phase fluctuations, this time constant represents the timescale of the phason dynamics in the incommensurate phase II of biphenyl. Therefore, the value of 5 MHz can be considered as the ‘relaxatory phason gap’ of biphenyl which, of course, is not identical with the ‘phason gap’ ω_{ϕ_0} used, e.g., in the oscillatory model by Zumer and Blinc. Considering the relaxatory dynamics as the limit of the oscillatory one for a large damping constant Γ_ϕ , both quantities are related by $\tau_\phi(0) = \Gamma_\phi/\omega_{\phi_0}^2$. Since we are dealing here with relaxatory fluctuations, however, the value of ω_{ϕ_0} is not of physical importance and the relevant timescale is given by $\tau_\phi(0)$. Similar statements concerning the ‘phason gap’ in incommensurate systems were already made by Walisch *et al* (1994) and by Etrillard *et al* (1995).

As can be inferred from figure 8, the data pertinent to the spectral density J_1 exhibit a similar behaviour to those pertinent to J_2 : while at lower frequencies they are nearly constant, for frequencies larger than about $\omega_L = 5 \times 10^7 \text{ s}^{-1}$ a marked decrease of $1/T_1$ is observed. Thus, the characteristic time constants $\tau_\beta(0)$ of longitudinal and transversal OP fluctuations are practically the same. This means that both kinds of fluctuation are strongly interrelated to each other via the soft phase fluctuations as has been predicted theoretically (Bruce and Cowley 1978). In conclusion, the longitudinal (δP_1) OP fluctuations obviously cannot be identified with fluctuations of the OP amplitude ($\delta\rho$) alone but are influenced by the soft phase fluctuations. In view of this result one may even conjecture that the quasi-harmonic approximation is not valid as argued already by Bruce and Cowley (1978). We refrain from a more detailed discussion of the frequency dependence found for the spectral density J_1 since suitable theoretical approaches to this problem are still lacking.

In the above considerations, the discussion has been restricted to the $1/T_1$ contributions from the δP_1 and δP_2 fluctuations which describe the excitations of a two-component order parameter corresponding to a one-dimensional modulation. In the IC phase II of biphenyl, however, there exists a second soft mode which represents, for a given domain with the modulation, say, along q_{i1} , the ‘suppressed’ modulation along q_{i2} which is formed in neighbouring domains. Since the corresponding order parameter $\hat{Q} = Q(q_{i2})$ has a zero expectation value, its ‘longitudinal’ and ‘transversal’ fluctuations are degenerate (Launois

et al 1989). As a result of the formation of the modulation along q_{i1} in the domain under consideration, it should be expected that these fluctuations are restrained and harden on cooling below T_{i1} . Therefore, we assume them to be of low efficiency for the spin–lattice relaxation (except very close to T_{i1}). Note that the corresponding relaxation contribution should be constant over the whole frequency distribution in the spectrum. Moreover, its Larmor frequency dependence (if it exists at all) should differ considerably from that of the spectral density J_2 which is related to the soft dynamics of the modulation wave present in the specific domain. Thus, the $\tilde{Q}(q_{i2})$ fluctuations can be neglected at least for the analysis of J_2 . Of course we concede that these arguments are only indirect.

4. Summary and conclusions

In this work we presented an extensive ^2H NMR study of the incommensurate phases of biphenyl. We took advantage of the unique assignment of the resonance lines to the different deuterium positions which was derived from the corresponding QC tensors. In the high-temperature phase, the results clearly demonstrated the inversion symmetry of the biphenyl molecules as well as the planarity of the phenyl rings correcting previous conclusions from x-ray data (Charbonneau and Délugeard 1977).

The structural modulation in the incommensurate phases has been examined via ^2H NMR spectra. It was ascertained that the IC phases of biphenyl are ‘stripe-like’ modulated. The modulation itself can be well described by a single degree of freedom which is given by a twist of the phenyl rings about the molecular axis. The maximum twist angle α_0 attains a magnitude of about 5° , which is in nice agreement with previous theoretical calculations (Benkert *et al* 1987). Its temperature dependence below T_{i1} follows a power law with a critical exponent $\beta = 0.35 \pm 0.03$. This value agrees with those found for other one-dimensionally incommensurately modulated crystals (Walisch *et al* 1990, Holzer *et al* 1993).

Moreover, it was concluded that the inversion symmetry of the biphenyl crystal is lost in the incommensurate phases. This corresponds to a space group Pa of the average structure. The deviation from the inversion symmetry, however, is only slight.

As regards the dynamics of the modulation wave, a two-dimensional ^2H NMR exchange spectrum revealed unambiguously that a ‘floating’ of the modulation wave does not occur in the incommensurate phases of biphenyl. From a general point of view, the concept of a ‘floating’ or ‘diffusionlike’ motion appears to be questionable: first, large-scale fluctuations of the initial phase of the modulation wave of the order of several times 2π would mean that the expectation value of the order parameter $Q = \rho e^{i\phi}$ is zero and that the modulation itself would just be a dynamical phenomenon. Second, we point out that the effect of the phase fluctuations is already reflected by the nonclassical critical behaviour of the order parameter amplitude below T_{i1} which has been found here for biphenyl, as well as previously for other incommensurate systems (Walisch *et al* 1990, Holzer *et al* 1993).

The ^2H NMR spin–lattice relaxation rates in the IC phases of biphenyl were measured at the edge singularities and at the centres of the frequency distributions and were analysed on the basis of the ‘local model’ introduced by Blinc *et al* (Zumer and Blinc 1981, Blinc *et al* 1986). Their temperature dependences confirm the assignments to the spectral densities J_1 and J_2 of longitudinal and transversal OP fluctuations. Below the IC II–IC III phase transition, all relaxation rates decrease drastically reflecting a hardening of the OP dynamics. This result as well as the particular behaviour of the modulation wave in the IC III phase provide arguments in favour of a commensurate rather than an incommensurate modulation of the crystal structure below about 20 K.

Field-cycling experiments at 24.5 K revealed a distinct dependence on the Larmor

frequency of the spin–lattice relaxation rate proportional to J_2 as well as of that proportional to J_1 . A quantitative evaluation of the experimental results was presented on the basis of a relaxatory dynamics of the order parameter. The analysis of the relaxation rates yielded the characteristic frequency $1/2\pi\tau_2(0) = 5$ MHz of the OP dynamics. This time constant represents the timescale of the phason dynamics in the incommensurate phase II of biphenyl.

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