

Phase and amplitude modes of the $n = 4$ incommensurate phase II of biphenyl: Neutron scattering experiments and theoretical results

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We report the only neutron scattering measurement of phase and amplitude modes in an incommensurate system with a four-component order parameter ($n = 4$): the phase II of biphenyl. Experiments have been performed at low temperature and under hydrostatic pressure, where phase II becomes the ground state of biphenyl. This allows a study at very low temperature, where the damping of the modes is extremely reduced. Three propagating excitations have been observed, one of which is twice degenerate. Comparison between their characteristics and that of the soft mode which drives the transition towards phase II proves unambiguously that they are the phase and amplitude modes of biphenyl phase II. We also develop theoretical calculations within the scope of the Ginzburg-Landau theory, including coupling between the order parameter and strains. Calculations lead to the exact assignment of the measured modes to the different possible excitations of phases and amplitudes according to a single- q or to a double- q structure of phase II. Moreover, comparison between theoretical and experimental results gives a strong argument in favor of the single- q structure.

I. INTRODUCTION

In the last few years, incommensurate systems have raised a great deal of experimental as well as theoretical interest (for a review on insulator incommensurate materials, see Ref. 1 and references therein). In particular, dynamics of these systems have been extensively investigated² with experimental techniques such as neutron and Raman scattering, NMR, and with microscopic or phenomenological theories. Indeed, the appearance of new periods in incommensurate phases induces the existence of new fluctuation modes of the atom positions. In this paper, we are interested in displacive incommensurate systems where the modulation wave is quasisinusoidal. For such systems, dynamical calculations can be performed within the scope of the phenomenological Ginzburg-Landau theory.³ For an incommensurate phase with a two-component order parameter ($n = 2$), one finds one phason, relative to the excitation of the phase of the incommensurate modulation and one amplitude mode (amplitudon), relative to the excitation of its amplitude. The amplitude mode has a soft-mode behavior, whereas at the infinite wavelength limit (that is $\mathbf{q} = \mathbf{q}_s$, where q_s is the reduced wave vector at the incommensurate satellite position) the phason frequency is zero.⁴ Furthermore, theoretical studies have demonstrated that its damping remains finite.⁵ Therefore, clear observation of phase modes, by inelastic neutron scattering, usually requires an incommensurate system where the damping is small so that the phason becomes underdamped away from satellite positions. Before our work (on which brief reports have already been given in Refs. 6 and 7) neutron measurements of phase and amplitude modes have only been performed in a few $n = 2$ incommensurate phases:

biphenyl phase III,^{8,9} ThBr₄,¹⁰ and K₂SeO₄.¹¹ No direct measurement of the excitations of a more complex incommensurate phase had been performed. It was therefore interesting to study a more complex system. Biphenyl, which incommensurate phase II has a four-component order parameter ($n = 4$), is a good candidate for such a study since pressure effect allows a study at very low temperature, where the damping of the modes is small.

This paper is organized as follows. In Sec. II we recall the main properties of the crystalline phases in biphenyl and its pressure behavior. In Sec. III we present the experimental conditions, in Sec. IV experimental results, and in Sec. V calculations. In Sec. VI experimental and theoretical results are compared. In Sec. VII we recall our main conclusions.

II. BIPHENYL INCOMMENSURATE PHASES

Biphenyl (C₁₂H₁₀) is an aromatic molecular compound. Each molecule consists of two phenyl rings connected by single C—C bonds. In the high-temperature phase of crystalline biphenyl, called phase I, the mean molecular conformation is planar. Transitions towards the low-temperature phases II and III (Fig. 1) are due to the occurrence of molecular twisting,⁹ where the two phenyl rings of a molecule are turned in opposite directions around the long molecular axis (Fig. 2).

The phase-I space group is monoclinic $P2_1/a(C_{2h}^5)$, the twofold screw axis \mathbf{b} being the direction in which the packing of the molecules is the most tightened (Fig. 3). Transition between phases I and II ($T_1 = 37$ K at atmospheric pressure¹²) is second order and driven by a soft mode,⁹ principally related to the torsional motion of the

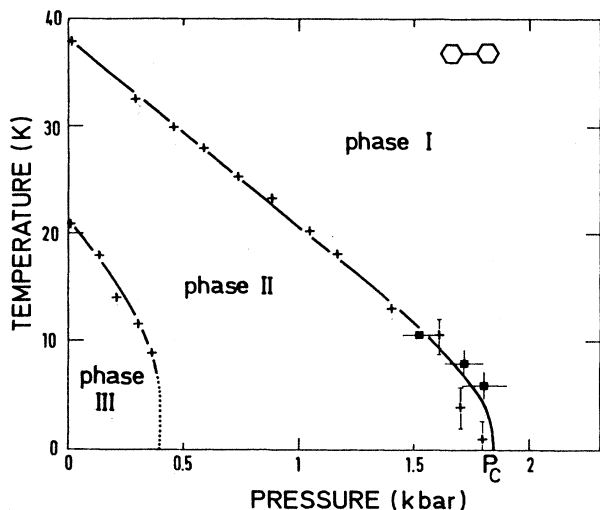


FIG. 1. Pressure-temperature phase diagram of deuterated biphenyl.

molecules.¹³

The incommensurate phase II is characterized by the appearance of four satellites localized at general points inside the phase-I Brillouin zone¹⁴ (Fig. 4):

$$\begin{aligned} \pm \mathbf{q}_{s_1} &= \pm \left[\delta_a \mathbf{a}^* + \frac{1-\delta_b}{2} \mathbf{b}^* - \delta_c \mathbf{c}^* \right], \\ \pm \mathbf{q}_{s_2} &= \pm \left[-\delta_a \mathbf{a}^* + \frac{1-\delta_b}{2} \mathbf{b}^* + \delta_c \mathbf{c}^* \right], \end{aligned} \quad (1)$$

where δ_a , δ_b , and δ_c are all nonrational numbers, with a clear temperature evolution.¹⁴ For a molecule the center of gravity of which is situated at the \mathbf{r} point, the torsional angle $\phi(\mathbf{r})$ is proportional to the sum of two sine functions of wave vectors \mathbf{q}_{s_1} and \mathbf{q}_{s_2} ,

$$\phi(\mathbf{r}) \propto A_1 \cos(\mathbf{q}_{s_1} \cdot \mathbf{r} + \Phi_1) + A_2 \cos(\mathbf{q}_{s_2} \cdot \mathbf{r} + \Phi_2). \quad (2)$$

The order parameter has four components ($n=4$) directly related to the modulation amplitudes and phases: A_1 , A_2 , Φ_1 , and Φ_2 . The sine approximation [Eq. (2)] has proved to be a good one: Second- and third-order satellites are hardly measurable in phase II.

The transition between phases II and III is a first-order

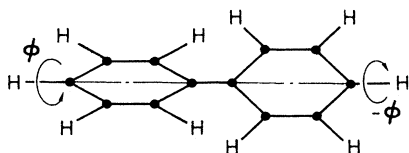


FIG. 2. Schematic drawing of the biphenyl molecule showing the twisting in phases II and III.

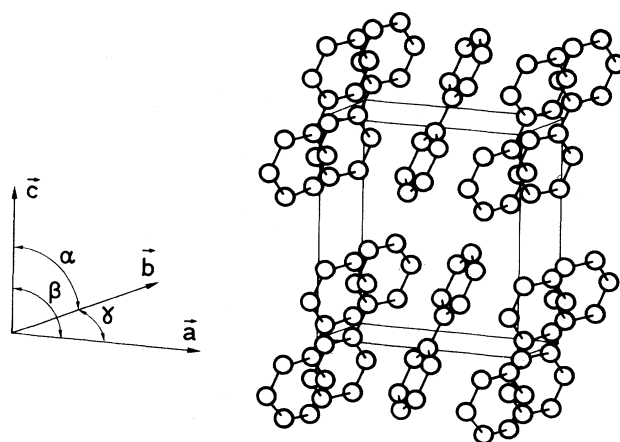


FIG. 3. Crystal structure of biphenyl in phase I ($P2_1/a, C_{2h}^5, \beta \neq 90^\circ$).

“partial lock-in” phase transition ($T_{II} \approx 20$ K at atmospheric pressure).^{9,15} Phase III exists till very low temperature, which has allowed the observation of propagating phase and amplitude mode branches.⁸ The absence of a simple lock-in phase is very peculiar, and it is at the origin of theoretical studies.¹⁶⁻¹⁸

In particular, from a microscopic approach, Heine, Price, and Benkert^{16,19} have shown, with their intermeshed rotation model, why the twisting of the molecules

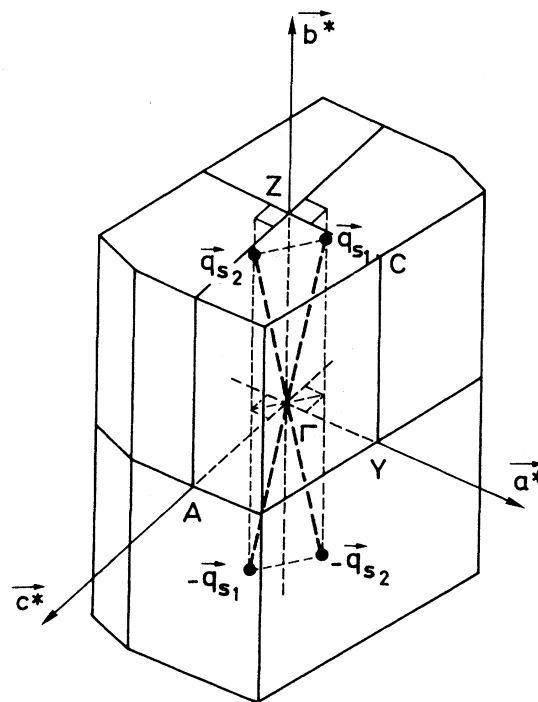


FIG. 4. Wave vectors of the incommensurate modulation of phase II in the phase-I first Brillouin zone.

produces frustration. So biphenyl is one of the rare displacive systems in which the nature of the frustration, responsible for the existence of the incommensurate phases, has been understood.

At atmospheric pressure, phase II exists only above 20 K. Measurements of its phase and amplitude modes has been impossible because they are heavily damped. Fortunately, pressure shifts the transition towards low tem-

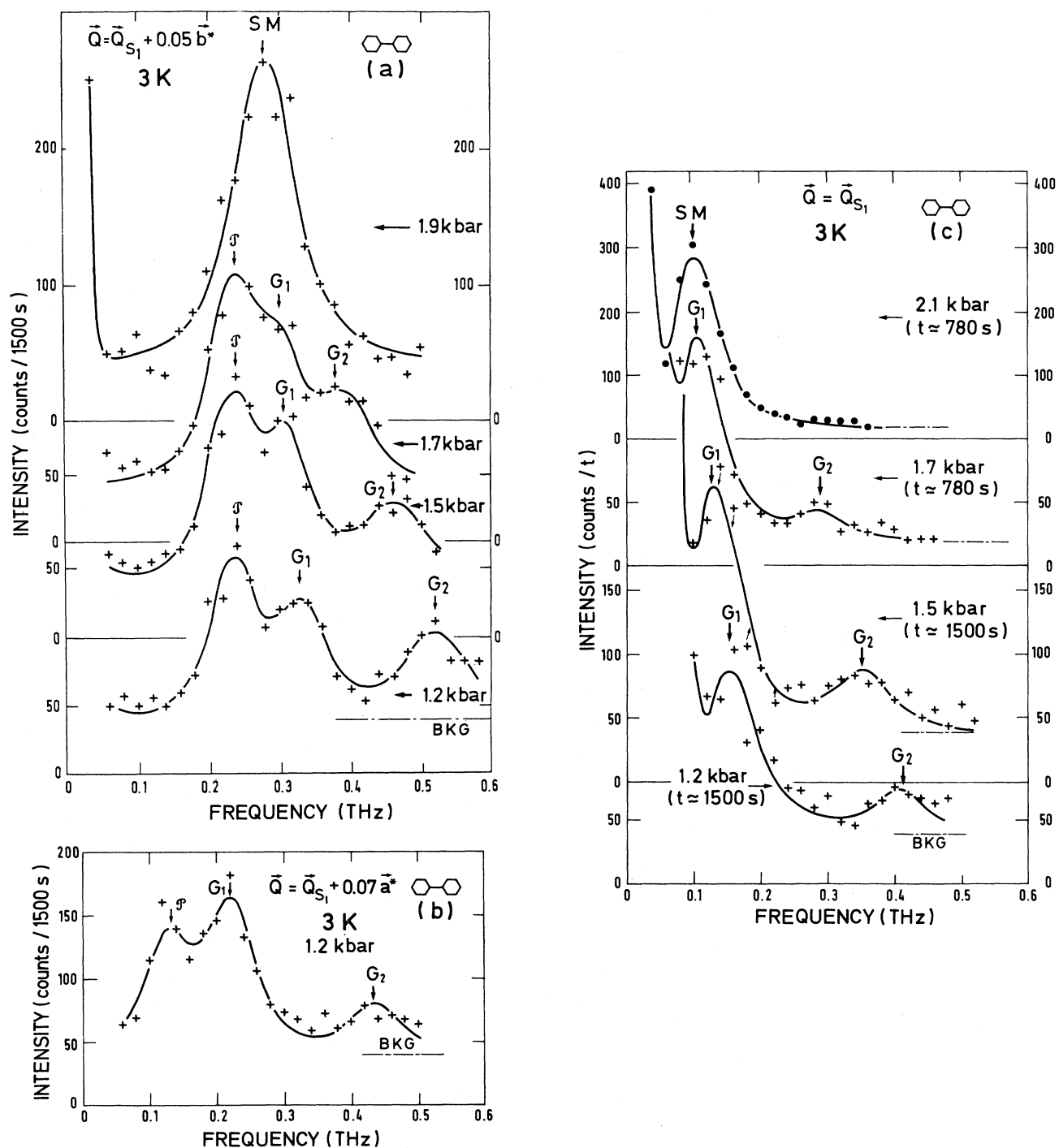


FIG. 5. The soft mode (SM) in phase I splits into three modes in phase II: a phase mode \mathcal{P} and two gap modes G_1 and G_2 . (a) Pressure behavior of neutron spectra measured at $\vec{Q} = \vec{Q}_{S_1} + 0.05\vec{b}^*$ with $\vec{Q}_{S_1} = (2.07, 1.45, -0.13)$ (Ref. 6). (b) Neutron spectrum measured at $\vec{Q} = \vec{Q}_{S_1} + 0.07\vec{a}^*$ and $P = 1.2$ kbar. (c) Pressure behavior of neutron spectra measured at $\vec{Q} = \vec{Q}_{S_1}$. Solid lines are the result of the fit of the data with one or three damped harmonic oscillators.

peratures^{9,14,20} (Fig. 1). T_I drops to absolute zero at a relatively weak pressure value: $P_c \simeq 1.85$ kbar. This offers the opportunity to study dynamics of the $n=4$ incommensurate phase II at very low temperature, where the damping is considerably reduced.

III. EXPERIMENTAL CONDITIONS

A. Crystal

Biphenyl-*d*10 ($C_{12}D_{10}$) of 99.4% nominal purity was obtained from Merck, Sharp, and Dohme Ltd. The single crystal was grown by the Bridgman technique (Groupe Physique Cristalline, Rennes). Its size adapted to the pressure cell was $10 \times 7 \times 4$ mm³.

B. Neutron experiments

Inelastic neutron scattering experiments have been done at the reactor Orphée (Laboratoire Léon Brillouin, Saclay) on the triple-axis spectrometer 4F1 installed on a cold source. They have been performed at constant temperature $T=3$ K ($P_c \simeq 1.85$ kbar) and at various pressures in phases I and II ($P=1.05$ – 4.6 kbar). At 3 K the scattered intensity is significant only for neutron energy loss ($\omega > 0$). So experiments have been made with constant scattered neutron wave vector k_F in order to avoid the reduction of intensity by a k_F^3 resolution effect. Horizontal collimations were $55'/30'/40'/40'$. For most of the measurements, the scattered wave vector k_F was chosen equal to 1.6 \AA^{-1} . The energy resolution full width at half maximum was equal to 0.04 THz (0.17 meV). Experiments were done without filter on the incident beam. One expects that it cannot induce any spurious effect due to phase and amplitude modes originating from second-order satellites since these satellites are hardly measurable. But acoustic modes could possibly spoil spectra [$\pm 2q_{s_i}$ ($i=1,2$) are situated near normal Bragg peaks]. Nevertheless, comparison of all the spectra obtained at different pressures in phases I and II, where the soft-mode frequency (phase I) and amplitude-like mode frequencies (phase II) shift continuously, have shown that actually there was not any spurious effect (see Refs. 6, 7, 21, and Fig. 5).

C. Pressure

High pressure was generated in an aluminum alloy (7049-AT6) cell with helium as pressure medium. The range of the pressure cell was 1–5000 bars. At 3 K in our pressure experiments helium is solid. It does not induce any problem in the pressure determination. (i) Pressure remains hydrostatic;²² (ii) the pressure value is not only determined via calculations²³ but also via the measurement of the (T,P) evolution of the strain gauges located on the pressure cell itself.^{24,21} Pressure is found with a precision of ± 80 bars. Temperature is controlled with an accuracy of ± 0.01 K.

IV. EXPERIMENTAL RESULTS

A. Data analysis

Most of our inelastic spectra have been obtained near the satellite position Q_{s_1} , with $Q_{s_1} = 2.07a^* + 1.45b^* - 0.13c^*$. The modes in phases I and II were fitted with damped harmonic oscillators for which

$$S(Q, \omega) \sim \frac{\omega \Gamma |F(Q)|^2}{\left[1 - \exp \left[-\frac{\hbar \omega}{k_B T} \right] \right] \{ [\omega^2 - \omega_0^2(Q)]^2 + \omega^2 \Gamma^2 \}} \quad (3)$$

$\omega_0(Q)$ is the quasi-harmonic frequency of the mode propagating with q wave vector originating from the satellite position: $Q = Q_{s_1} + q$. Γ is its damping constant and $F(Q)$ its inelastic structure factor. The fitting parameters are ω_0 , Γ , and $|F(Q)|^2$. At zero energy transfer, the intensity relative to elastic incoherent scattering or to the central peak phenomenon is fitted with a δ function. Let us emphasize that comparison between all the inelastic spectra obtained at different pressures in phases I and II and at different points of the reciprocal space around the satellite position Q_{s_1} shows that the background (BKG) is approximately flat and constant, $BKG \simeq 40$ counts in 25 min (Fig. 5). Note also that a constraint on the damping constants of the phase-II characteristic excitations was imposed in the fitting procedure. They were all taken to be equal. This constraint will be justified in the following.

B. Pressure effects on the soft mode

Transition between phases I and II is driven by a soft mode in phase I, principally related to the torsional motion of the molecules. Within the model of local potential and competing intramolecular and intermolecular interactions,^{25,20(a)} one easily predicts that the I-II transition remains displacive under pressure, which is the case.¹⁴ Moreover, we have measured a central peak at atmospheric pressure as well as under pressure.²¹ The intensity of the δ peak centered at zero energy transfer, which is roughly constant far away from the transition line, strongly increases when approaching the transition line. The fit of the spectra with a δ function is a good one: We have not measured any width for the central peak. Note also that there are indications of a possible finite value for the soft-mode frequency at the transition point ($\omega \leq 0.05$ THz), probably in connection with the central-peak phenomenon.²¹

Let us emphasize our results on the soft-mode dispersion (Fig. 6). With qualitative arguments they illustrate the increase of intermolecular interactions under pressure. The dispersion law can be fitted by the square root of a parabolic function. For $Q_{s_i} = q_{s_i} + \tau$, where τ is a normal Bragg peak position and for small $q = q_H a^* + q_k b^* + q_L c^*$,

$$\omega^2(\pm Q_{s_i} + q) = \omega^2(\pm Q_{s_i}) + g(q),$$

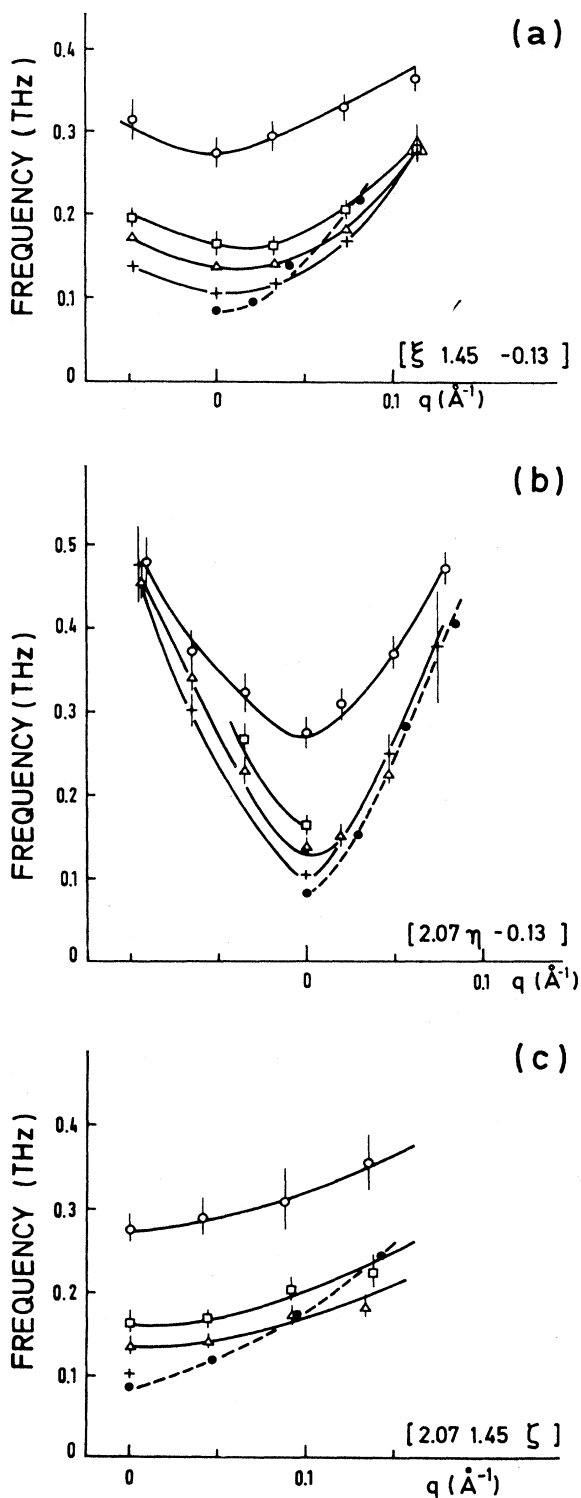


FIG. 6. Soft-mode dispersion curves at atmospheric pressure (solid lines) and different temperatures: +40.7, Δ 45, \square 50, \circ 70 K, and at $P=1.9$ kbar and $T=3$ K: \bullet (dashed lines); (a) along a^* , (b) along b^* , (c) along c^* . They originate at a satellite position. (See Ref. 7.)

where

$$g(\mathbf{q}) \approx \alpha q_H^2 + \beta q_K^2 + \gamma q_L^2. \quad (4)$$

At atmospheric pressure, the dispersion coefficients are roughly temperature independent; $\alpha \approx 4 \text{ THz}^2 \text{ \AA}^2$, $\beta \approx 21 \text{ THz}^2 \text{ \AA}^2$ and $\gamma \approx 1 \text{ THz}^2 \text{ \AA}^2$. At 3 K and 1.9 kbar, $\alpha \approx 6 \text{ THz}^2 \text{ \AA}^2$, $\beta \approx 22 \text{ THz}^2 \text{ \AA}^2$, and $\gamma \approx 2.5 \text{ THz}^2 \text{ \AA}^2$.⁷ Note that the dispersion is highest along b^* and smallest along c^* . This can be understood with the sterical hindrance model:^{16,19,26} The dispersion coefficients, which are related to intermolecular forces, are the highest in the direction in which the packing of the molecules is the closest (Fig. 3). Under pressure, dispersion practically does not change in b^* direction and strongly increases in a^* and c^* directions. Indeed, pressure increases dispersion coefficients most in the directions in which the packing of the molecules is the least tight.

Finally, note that the damping constant of the soft mode at 50 K (and at atmospheric pressure) is approximately equal to 0.25 THz (1 meV), whereas at 3 K (under pressure) it is approximately 0.05 THz (0.2 meV). As it will appear later (Fig. 7), the damping of the phase and amplitude modes is roughly the same as that of the soft mode. Therefore, the above data concerning the soft-mode damping clearly show why (although unresolved at atmospheric pressure) the phase and amplitude modes of phase II can be well resolved under pressure at low temperature.

C. Phase and amplitude modes in phase II

In Figs. 5(a) and 5(b), we report spectra measured near a satellite position. They show that the soft mode "SM" in phase-I splits into three well-resolved propagating modes called \mathcal{P} , G_1 , and G_2 in phase II. The frequency of the mode \mathcal{P} does not change with pressure, whereas that of G_1 increases a little when going away from the transition line and that of G_2 increases much more [Figs. 5(a) and 5(c)]. \mathcal{P} is a gapless phason (within the spectrometer resolution), whose dispersion along a^* and b^* is roughly constant within 1 and 1.8 kbar, G_1 and G_2 are amplitudonlike excitations. The "gapless" character of \mathcal{P}

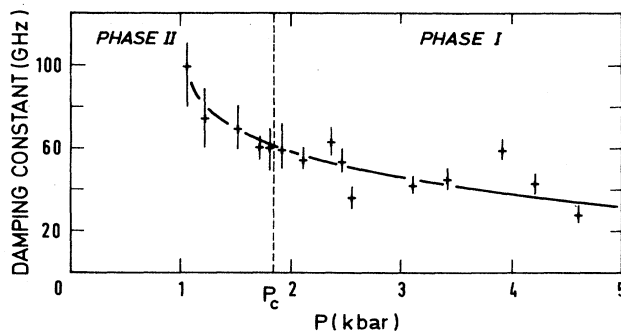


FIG. 7. Pressure dependence of the fitted damping constant of the soft mode in phase I and of the characteristic excitations of phase II. Solid line is a guide for eye.

is illustrated on Fig. 5(c). On inelastic spectra performed at a satellite position, one observes only the gap modes G_1 and G_2 , the phason \mathcal{P} contributing to the zero energy transfer peak. In the following, we discuss the dispersion, damping constant, frequency evolution versus pressure and inelastic structure factors of \mathcal{P} , G_1 , and G_2 .

1. Dispersion

Dispersion curves of \mathcal{P} , G_1 , and G_2 along \mathbf{a}^* and \mathbf{b}^* are compared to that of the soft mode (Fig. 8). \mathcal{P} , G_1 , and probably G_2 (the frequency of which is determined with less accuracy because of its weak intensity²¹) have the same dispersion as the soft mode. It proves that they proceed from the soft mode. So they are phase and amplitude modes of Biphenyl phase II.

Of course, dispersion changes with pressure (cf. Sec. IV B). But (i) this was shown comparing dispersion curves between $P_0=1$ bar and $P=1.9 \times 10^3 P_0$; (ii) dispersion changes the most in the \mathbf{c}^* direction. Therefore, for the \mathbf{a}^* and \mathbf{b}^* directions and between $P_1=1$ kbar and $P_2=2$ kbar $=2P_1$ only, dispersion can be roughly constant. Indeed, the same dispersion was measured for \mathcal{P} , G_1 , and G_2 between 1.05 and 1.8 kbar (for \mathcal{P} , see Fig. 8), which validates the comparison of their dispersion below P_c with the soft-mode one above P_c .

Note also that the phason dispersion curve extrapolates to zero frequency at satellite position. Within the experimental resolution (~ 40 GHz), the phason is gap-

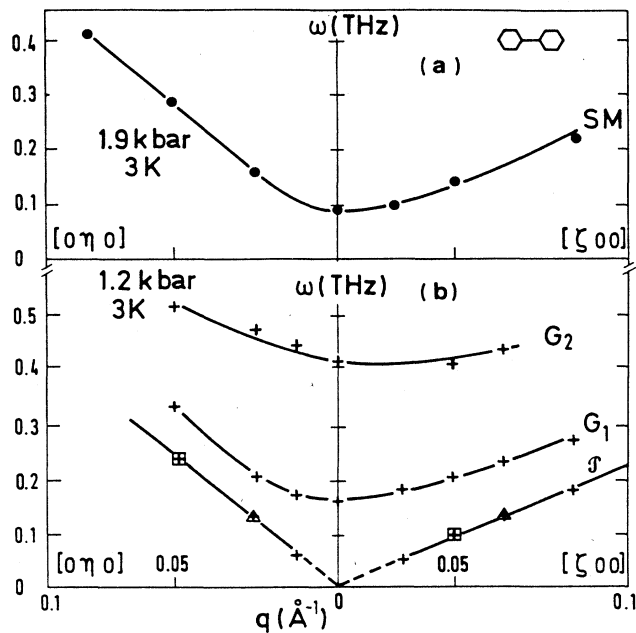


FIG. 8. Dispersion curves along \mathbf{a}^* and \mathbf{b}^* of (a) the soft mode at 1.9 kbar, (b) the phase and amplitude modes at 1.2 kbar (+), the phase mode at 1.05 kbar (Δ) and 1.7 kbar (\square). Dispersion curves originate at a satellite position.

less. Besides, this is in agreement with the Liu and Conradi NMR experiment, where they have observed a frequency dependence of spin-lattice relaxation, suggesting the existence of a gapless phason.²⁷

2. Damping

(a) Damping constants of the phase and amplitude modes are roughly equal. Indeed, we are allowed to take them equal in the fitting procedure because this agrees with the result of the fit without constraint on the spectra where the modes are clearly separated. (b) The phase and amplitude mode dampings as well as the soft-mode one are approximately constant around satellite positions. In particular, the phason is overdamped in the long-wavelength limit since its frequency goes towards zero, but its damping constant does not change. (c) The study of damping constants near the critical pressure P_c is difficult because when the soft mode (for example) is overdamped, its frequency and damping constant are strongly correlated in the fitting procedure. The fitting program trend is to increase both quantities. Nevertheless the damping is found, on the one hand, to be approximately constant around satellite positions and on the other hand, to present no discontinuity near P_c when going away from the satellite position where the mode gets underdamped. This holds for the phase-II excitations. So in the fitting procedure, we have imposed the continuity of damping constants near P_c . The fitted damping constants at a satellite position are plotted versus pressure in Fig. 7. In brief, the dampings of \mathcal{P} , G_1 , G_2 , and SM appear to be consistent with a continuous variation at the transition.

These results strongly support Golovko, Levanyuk, Zeyher, and Finger's theories about the damping of excitations in incommensurate phase.⁵

3. Soft-mode behaviors

The frequencies of G_1 and G_2 increase when going away from the transition pressure (Fig. 9). This soft-

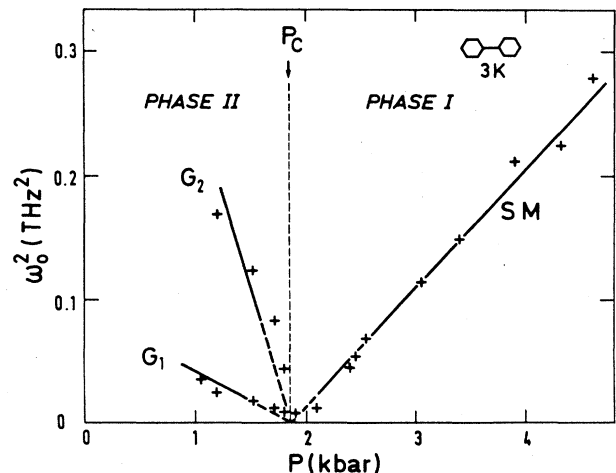


FIG. 9. Pressure dependence of the fitted square frequencies at a satellite position of SM, G_1 and G_2 (Ref. 6).

TABLE I. Examples of values of $|F_{G_1}/F_P|^2$.

P (kbar)	1.05	1.2	1.5	1.7
$\mathbf{q}=\mathbf{Q}-\mathbf{Q}_{s_1}$				
(0.05,0,0)		1.9	3	
(0.07,0,0)	2.8	2.4		
(0,0.025,0)		1		
(0,0.05,0)	1.7		1	1

mode behavior is an additional evidence for the amplitudonlike character of these modes. Moreover, the variation with pressure of the square frequencies of SM, G_1 , and G_2 is nearly linear, the slopes being about 0.1 THz²/kbar for SM, 0.05 THz²/kbar for G_1 , and 0.3 THz²/kbar for G_2 . This linear behavior supports the further utilization of the phenomenological Ginzburg-Landau theory to interpret the experiments. Very close to P_c , there is also an apparent deviation from the straight lines, at least for SM and G_1 , which could be related to the central-peak phenomenon ($\omega_{\text{pinning}} < 0.07$ THz).

In summary in the $n=4$ incommensurate phase II, only three characteristic excitations are observed: one phason (\mathcal{P}) and two amplitudonlike modes (G_1 and G_2).

4. Inelastic structure factors

Comparison between the inelastic structure factors of \mathcal{P} , G_1 , and G_2 shows that G_1 is probably twice degenerate. So the four degrees of freedom of the incommensurate phase II ($n=4$) could have been properly measured. Indeed, after fitting the intensities on the inelastic spectra, one obtains the square inelastic structure factor $|F_k(\mathbf{Q})|^2$ of the mode k [Eq. (3)]. The frequencies of \mathcal{P} and G_1 being relatively close to each other and G_2 being of weak intensity, determination of the inelastic structure factors of \mathcal{P} , G_1 , and G_2 is not very accurate. Nevertheless, one finds (Tables I and II) that on average

$$|F_{G_1}|^2/|F_P|^2 \simeq |F_{G_1}|^2/|F_{G_2}|^2 \simeq 2. \quad (5)$$

This indicates that G_1 is probably twice degenerate. To understand why there could be a degenerate mode and to which combination of phase or amplitude excitations the measured modes \mathcal{P} , G_1 , and G_2 could be exactly attributed, calculations have been performed within the framework of the Ginzburg-Landau theory.

TABLE II. Examples of values of $|F_{G_1}/F_{G_2}|^2$.

P (kbar)	1.2	1.5	1.7
$\mathbf{q}=\mathbf{Q}-\mathbf{Q}_{s_1}$			
(0,0,0)	1.5	1.5	2.7
(0.05,0,0)	2.8		
(0.07,0,0)	1.6		
(0,0.05,0)		1	1

V. CALCULATIONS (GINZBURG-LANDAU THEORY)

A. Free energy developed only in terms of the order parameter components

1. Statics

Biphenyl phase II being a four-ray star incommensurate system, its order parameter has at least four components. In fact, the Herring criterion²⁸ shows that it has only four components: $Q_1(\mathbf{q}_{s_1})$, $Q_1(-\mathbf{q}_{s_1})$, $Q_2(\mathbf{q}_{s_2})$, and $Q_2(-\mathbf{q}_{s_2})$. They are directly related to the phases and amplitudes of the sine modulations [Eq. (2)]:

$$\begin{aligned} Q_1(\mathbf{q}_{s_1}) &= \frac{A_1}{\sqrt{2}} e^{i\Phi_1} = Q_1(-\mathbf{q}_{s_1})^* , \\ Q_2(\mathbf{q}_{s_2}) &= \frac{A_2}{\sqrt{2}} e^{i\Phi_2} = Q_2(-\mathbf{q}_{s_2})^* , \end{aligned} \quad (6)$$

$$\left[\phi(\mathbf{r}) \propto \sum_{i=1,2; \epsilon=\pm 1} Q_i(\epsilon \mathbf{q}_{s_i}) e^{i(\epsilon \mathbf{q}_{s_i}) \cdot \mathbf{r}} \right].$$

From group-theory calculation, the form of the static free energy is^{29,21}

$$\begin{aligned} F(T, P) &= F_0(T, P) + a(P - P_c) \\ &\quad \times [|Q_1(\mathbf{q}_{s_1})|^2 + |Q_2(\mathbf{q}_{s_2})|^2] \\ &\quad + 4(u + v) [|Q_1(\mathbf{q}_{s_1})|^4 + |Q_2(\mathbf{q}_{s_2})|^4] \\ &\quad + 8u |Q_1(\mathbf{q}_{s_1})|^2 |Q_2(\mathbf{q}_{s_2})|^2 . \end{aligned} \quad (7)$$

For $P < P_c$ ($a > 0$), minimization of the free energy leads to the following solutions for the structure of biphenyl phase II.

Case I, $A_1 = A_2 = [a(P_c - P)/4(2u + v)]^{1/2}$, this solution being stable for $v > 0$ and $2u + v > 0$. It corresponds to a double- q incommensurate structure where the two modulations of wave vector \mathbf{q}_{s_1} and \mathbf{q}_{s_2} coexist spatially with the same amplitude. The point symmetry group of phase I is preserved.

Case II,

$$A_1 = \left[\frac{a(P_c - P)}{4(u + v)} \right]^{1/2} \neq 0 \text{ and } A_2 = 0$$

or $A_1 = 0$ and $A_2 \neq 0$, this solution being stable for $v < 0$ and $u + v > 0$. It describes a single- q incommensurate structure with two types of domains. One domain (associated with $A_1 \neq 0$) is relative to the static modulation of wave vector \mathbf{q}_{s_1} and the other to the modulation of wave vector \mathbf{q}_{s_2} . The point group of phase I is no longer preserved. At the microscopic level, the symmetry operations C_6^2 and σ^y disappear (notations from Ref. 30). These symmetry operations now relate the two types of domains.

Case III occurs in the limit case where $v = 0$ ($u > 0$) and corresponds to a very peculiar solution: $A_1^2 + A_2^2 = [a(P_c - P)/4u]$. The incommensurate system may take any orientation in the space (A_1, A_2).

2. Dynamics

The method used to calculate the dynamics of phase I and of incommensurate phase II is introduced by Axe.³ Taking into account all the excitation $Q_i(-\mathbf{q}_i - \mathbf{q})$ of the order-parameter component $Q_i(-\mathbf{q}_i)$,

$$Q_i(\epsilon \mathbf{q}_{s_i} + \mathbf{q}) \propto \exp -i[\omega(\epsilon \mathbf{q}_{s_i} + \mathbf{q})]t,$$

$$\delta\phi(\mathbf{r}, t) \propto \sum_{i=1,2; \epsilon=\pm 1} Q_i(\epsilon \mathbf{q}_{s_i} + \mathbf{q}) e^{i(\epsilon \mathbf{q}_{s_i} + \mathbf{q})\mathbf{r}},$$

one finds the excess free energy,

$$\begin{aligned} \delta F_{\mathbf{q}_{s_1,2} + \mathbf{q}} = & [a(P - P_c) + g(\mathbf{q})][|Q_1(\mathbf{q}_{s_1} + \mathbf{q})|^2 + |Q_2(\mathbf{q}_{s_2} + \mathbf{q})|^2] \\ & + 8(u + v)\{2[|Q_1(\mathbf{q}_{s_1})|^2|Q_1(\mathbf{q}_{s_1} + \mathbf{q})|^2 + |Q_2(\mathbf{q}_{s_2})|^2|Q_2(\mathbf{q}_{s_2} + \mathbf{q})|^2] \\ & + [Q_1(\mathbf{q}_{s_1})^2 Q_1(-\mathbf{q}_{s_1} + \mathbf{q}) Q_1(-\mathbf{q}_{s_1} - \mathbf{q}) + Q_2(\mathbf{q}_{s_2})^2 Q_2(-\mathbf{q}_{s_2} + \mathbf{q}) Q_2(-\mathbf{q}_{s_2} - \mathbf{q})]\} \\ & + 8u \left\{ |Q_1(\mathbf{q}_{s_1})|^2 |Q_2(\mathbf{q}_{s_2} + \mathbf{q})|^2 + |Q_2(\mathbf{q}_{s_2})|^2 |Q_1(\mathbf{q}_{s_1} + \mathbf{q})|^2 \right. \\ & + Q_1(\mathbf{q}_{s_1}) Q_2(\mathbf{q}_{s_2}) \sum_{\epsilon=\pm 1} Q_1(-\mathbf{q}_{s_1} - \epsilon \mathbf{q}) Q_2(-\mathbf{q}_{s_2} + \epsilon \mathbf{q}) \\ & \left. + \sum_{\epsilon=\pm 1} Q_1(\epsilon \mathbf{q}_{s_1}) Q_2(-\epsilon \mathbf{q}_{s_2}) Q_1[-\epsilon(\mathbf{q}_{s_1} + \mathbf{q})] Q_2[\epsilon(\mathbf{q}_{s_2} + \mathbf{q})] \right\}. \end{aligned} \quad (8)$$

The direct space origin is chosen so that the static values of the phases Φ_1 and Φ_2 are zero, which is not a restrictive condition since they are not correlated by any umklapp term. Within the scope of the Ginzburg-Landau low-temperature approximation, in Eq. (8) $Q_i(\pm \mathbf{q}_{s_i})$ is replaced by its static value. Then one looks for harmonic solutions of the Lagrange equations of motion

$$\frac{d}{dt} \left[\frac{\partial L}{\partial \dot{Q}_i(-\mathbf{q}_{s_i} - \mathbf{q})} \right] - \frac{\partial L}{\partial Q_i(-\mathbf{q}_{s_i} - \mathbf{q})} = 0, \quad (9)$$

where

$$L = \sum_{i=1,2} \dot{Q}_i(-\mathbf{q}_{s_i} - \mathbf{q}) \dot{Q}_i(\mathbf{q}_{s_i} + \mathbf{q}) - \delta F_{\mathbf{q}_{s_1,2} + \mathbf{q}}.$$

One gets two equations relating $Q_1(\pm \mathbf{q}_{s_1} + \mathbf{q})$ and $Q_2(\pm \mathbf{q}_{s_2} + \mathbf{q})$. Replacing \mathbf{q}_{s_i} by $(-\mathbf{q}_{s_i})$ in them, one finds two new equations. Hence the matrix equation

$$\omega^2 \mathbf{Q} = \underline{D} \mathbf{Q} \quad (10)$$

with

$$\mathbf{Q} = \begin{pmatrix} Q_1(\mathbf{q}_{s_1} + \mathbf{q}) \\ Q_1(-\mathbf{q}_{s_1} + \mathbf{q}) \\ Q_2(\mathbf{q}_{s_2} + \mathbf{q}) \\ Q_2(-\mathbf{q}_{s_2} + \mathbf{q}) \end{pmatrix},$$

where \underline{D} is the dynamical matrix. Its eigenvalues are the square frequencies of the phase-II characteristic excitations and its eigenvectors, the normal modes, lead to the exact excitation of phases and amplitudes to which these modes correspond and to their inelastic structure factors.

In the following, the results of our calculations in phase I and in phase II in cases I, II, and III are presented; in cases I and II, eigenvectors have also been reported by Poulet and Pick²⁹ and square frequencies at satellite

positions by Cowley.³¹

Phase I. For P greater than P_c , the dynamical matrix is given by

$$\underline{D} = \begin{pmatrix} \alpha & 0 & 0 & 0 \\ 0 & \alpha & 0 & 0 \\ 0 & 0 & \alpha & 0 \\ 0 & 0 & 0 & \alpha \end{pmatrix},$$

where $\alpha = a(P - P_c) + g(\mathbf{q})$. The soft mode corresponds to the fourfold degenerate normal mode, its square frequency is $\omega_{SM}^2(\pm \mathbf{Q}_{s_i} + \mathbf{q}) = a(P - P_c) + g(\mathbf{q})$, $i=1,2$ [cf. Eq. (4)].

Phase II. Case I: double- q structure [Figs. 10(a) and 11(a)]. The dynamical matrix is given by

$$\underline{D} = \begin{pmatrix} \beta & \alpha & \gamma & \gamma \\ \alpha & \beta & \gamma & \gamma \\ \gamma & \gamma & \beta & \alpha \\ \gamma & \gamma & \alpha & \beta \end{pmatrix},$$

where

$$\alpha = \frac{u+v}{2u+v} a(P_c - P), \quad \beta = \alpha + g(\mathbf{q})$$

and

$$\gamma = \frac{u}{2u+v} a(P_c - P).$$

It has three different eigenfrequencies, relative to three modes called M_{ph} , A_+ , and A_- .

$$\omega_{M_{ph}}^2(\pm \mathbf{Q}_{s_i} + \mathbf{q}) = g(\mathbf{q}),$$

$$\omega_{A_+}^2(\pm \mathbf{Q}_{s_i} + \mathbf{q}) = 2a(P_c - P) + g(\mathbf{q}),$$

and

$$\omega_{A_-}^2(\pm \mathbf{Q}_{s_i} + \mathbf{q}) = \frac{2v}{2u+v} a(P_c - P) + g(\mathbf{q}), \quad i=1,2.$$

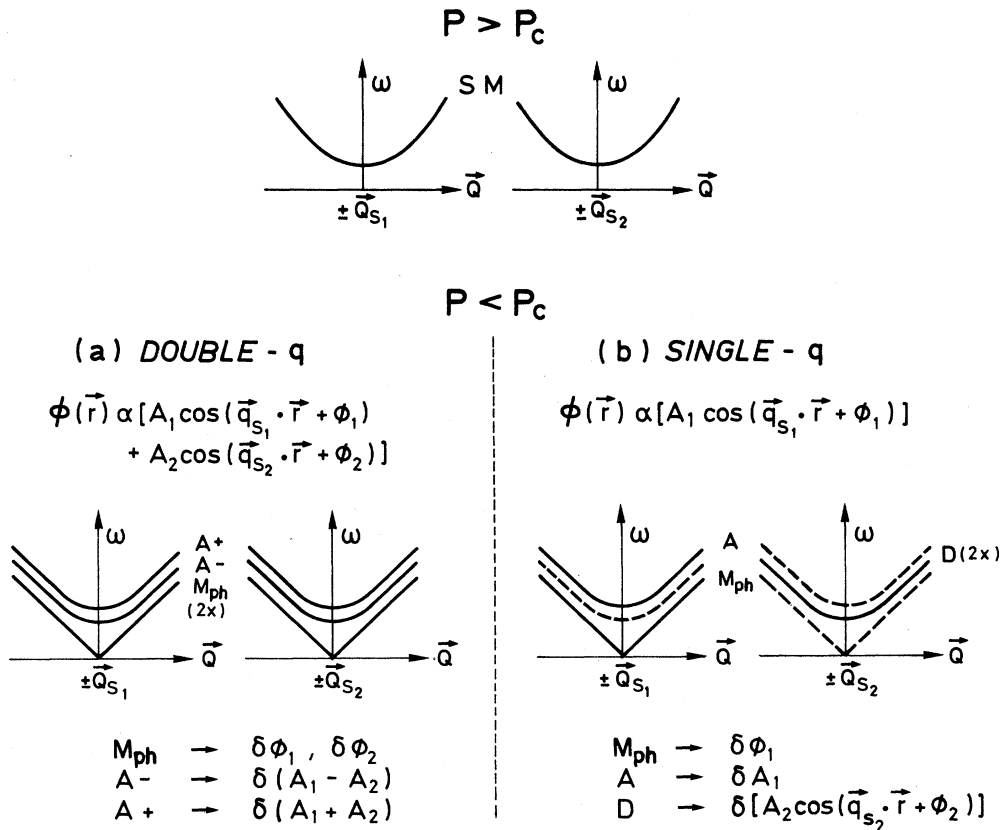


FIG. 10. For $P > P_c$ calculated dispersion curve of the soft mode in phase I, around satellites ($\pm Q_{S_1}$) and ($\pm Q_{S_2}$), in an arbitrary direction ($\pm Q_{S_i} = \pm q_{S_i} + \tau$, τ being a basic vector of the normal lattice). For $P < P_c$ dispersion curves for the phase-II characteristic excitations (a) double- q structure; (b) single- q structure; in solid lines for a domain $A_1 \neq 0$, and in dotted lines for a domain $A_2 \neq 0$ (see the text).

The corresponding eigenvectors are $(\mu, -\mu, \nu, -\nu)$ with $(\mu^2 + \nu^2)^{1/2} = 1/\sqrt{2}$ for M_{ph} , $\frac{1}{2}(1, 1, 1, 1)$ for A_+ and $\frac{1}{2}(1, 1, -1, -1)$ for A_- . M_{ph} is twice degenerate, it corresponds to the excitations $\delta\phi_1$ and $\delta\phi_2$ of the phases ϕ_1 and ϕ_2 . The two remaining modes A_+ and A_- relate to the excitation of the amplitudes A_1 and A_2 , respectively, in phase [$\delta(A_1 + A_2)$] and in antiphase [$\delta(A_1 - A_2)$]. An inelastic neutron scattering measurement performed at $Q = \tau \pm q_{S_i} + q$, where τ is a normal Bragg peak position, projects out the displacement component proportional to $Q_i(\pm q_{S_i} + q)$.^{10(b)} So the inelastic structure factors [Eq. (3)] of M_{ph} , A_+ , and A_- satisfy the following relations:

$$|F_{M_{ph}}(\mathbf{Q})|^2 / |F_{A_+}(\mathbf{Q})|^2 = |F_{M_{ph}}(\mathbf{Q})|^2 / |F_{A_-}(\mathbf{Q})|^2 = 2. \tag{11}$$

Case II: single- q structure [Figs. 10(b) and 11(b)]. First, let us assume that all the crystal is formed of only one domain, where the static modulation has the wave vector q_{S_1} ($A_1 \neq 0$, $A_2 = 0$). The dynamical matrix is given by

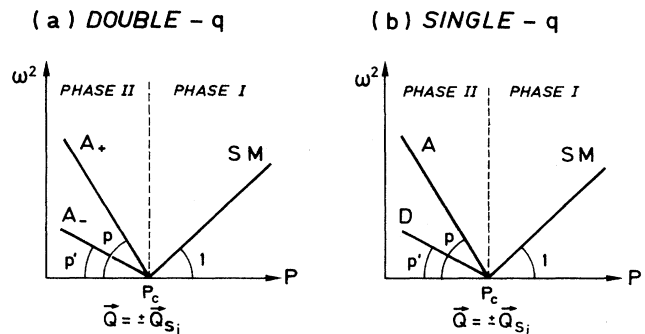


FIG. 11. Calculated pressure dependence of the square frequencies at a satellite position of the gap modes in phase II normalized to the soft-mode square frequency evolution. For calculation not including coupling between order parameter and strains (a) $p = 2$, $p' = 2v / (2u + v)$; (b) $p = 2$, $p' = -v / (u + v)$. For calculation including the coupling (a) $p = 2(2u + v) / (2u + v + t)$, $p' = 2v / (2u + v + t)$; (b) $p = 4(u + v) / [2(u + v) + r + t]$, $p' = (-2v - 2r) / [2(u + v) + r + t]$ (see the text).

$$\underline{D} = \begin{pmatrix} \beta & \alpha & 0 & 0 \\ \alpha & \beta & 0 & 0 \\ 0 & 0 & \gamma & 0 \\ 0 & 0 & 0 & \gamma \end{pmatrix},$$

where

$$\alpha = a(P_c - P), \beta = \alpha + g(\mathbf{q}),$$

$$\gamma = \frac{-v}{u+v} a(P_c - P) + g(\mathbf{q}).$$

It has three different eigenfrequencies, relative to three modes called M_{ph} , A , and D . Eigenfrequencies are

$$\omega_{M_{\text{ph}}}^2(\pm\mathbf{Q}_{s_1} + \mathbf{q}) = g(\mathbf{q}),$$

$$\omega_A^2(\pm\mathbf{Q}_{s_1} + \mathbf{q}) = 2a(P_c - P) + g(\mathbf{q}),$$

$$\omega_D^2(\pm\mathbf{Q}_{s_2} + \mathbf{q}) = \frac{-v}{u+v} a(P_c - P) + g(\mathbf{q}).$$

The corresponding eigenvectors are $1/\sqrt{2}(1, -1, 0, 0)$ for M_{ph} , $1/\sqrt{2}(1, 1, 0, 0)$ for A , and $(0, 0, \mu, \nu)$ with $(\mu^2 + \nu^2)^{1/2} = 1$ for D . Contrary to case I, where satellite positions \mathbf{Q}_{s_1} and \mathbf{Q}_{s_2} are equivalent, in case II, for a domain where $A_1 \neq 0$, the modes M_{ph} and A originate from satellites $\pm\mathbf{Q}_{s_1}$ and the mode D from satellites $\pm\mathbf{Q}_{s_2}$ [Fig. 10(b), solid lines]. M_{ph} and A are the phase and amplitude modes relative to the excitations $\delta\Phi_1$ and δA_1 of the phase and amplitude of the nonzero static modulation of wave vector \mathbf{q}_{s_1} . They are the "usual" phase and amplitude modes of $n=2$ incommensurate systems. Yet, the order parameter has not only two but four components. There is also a twice-degenerate mode D which relates to the excitation of the zero amplitude modulation of wave vector \mathbf{q}_{s_2} . It is an amplitudonlike mode [Fig. 11(b)]. Schematic drawings are shown in Fig. 12 to explain the meaning of this rather peculiar mode D and why it is twice degenerate. In Fig. 12(a) are represented the effect of the phase and amplitude excitations on the torsional angle $\phi(\mathbf{r})$ for the nonzero static modulation of wave vector \mathbf{q}_{s_1} . M_{ph} is gapless; a global change in the phase costs no energy since the period of the modulation ($\lambda_1 = 2\pi/|\mathbf{q}_{s_1}|$) is incommensurate with any linear combination of the lattice constants. In Fig. 12(b) are represented two excitations of the modulation of wave vector \mathbf{q}_{s_2} around its mean zero value. They differ by their phases. Obviously, the modulation period ($\lambda_2 = 2\pi/|\mathbf{q}_{s_2}|$) being incommensurate with all linear combinations of the lattice constants, these two excitations cost the same energy. Actually, the mode D in phase II has the same meaning as soft modes in high-temperature phases.

Calculations of inelastic structure factors [Eq. (3)] give (i) that the square structure factors of M_{ph} and A at $\mathbf{Q}_1 = \pm\mathbf{Q}_{s_1} + \mathbf{q}$ are equal to half the soft-mode one at the same point and (ii) that the square structure factor of the mode D at $\mathbf{Q}_2 = \pm\mathbf{Q}_{s_2} + \mathbf{q}$ is equal to the soft-mode one at

the same point

$$\begin{aligned} |F_{M_{\text{ph}}}(\pm\mathbf{Q}_{s_1} + \mathbf{q})|^2 &= |F_A(\pm\mathbf{Q}_{s_1} + \mathbf{q})|^2 \\ &= \frac{1}{2} |F_{\text{SM}}(\pm\mathbf{Q}_{s_1} + \mathbf{q})|^2, \\ |F_D(\pm\mathbf{Q}_{s_2} + \mathbf{q})|^2 &= |F_{\text{SM}}(\pm\mathbf{Q}_{s_2} + \mathbf{q})|^2. \end{aligned} \quad (12)$$

Now, let us consider a more realistic case. The two types of domains ($A_1=0$ or $A_2=0$) are present in the crystal. Around each satellite position $\pm\mathbf{Q}_{s_1}$ and $\pm\mathbf{Q}_{s_2}$ the three modes M_{ph} , A , and D should now be observed [Fig. 10(b)]. For example, around satellites $\pm\mathbf{Q}_{s_1}$, M_{ph} and A are relative to the excitation of the phase Φ_1 and of the amplitude A_1 in domains in which A_1 is nonzero, and D is relative to the excitation of the modulation of wave vector \mathbf{q}_{s_1} in domains in which its static amplitude A_1 is equal to zero. From this argument and Eq. (12), the inelastic structure factors at $\mathbf{Q} = \pm\mathbf{Q}_{s_i} + \mathbf{q}$, $i=1,2$ are found to obey the relations

$$|F_D(\mathbf{Q})|^2 = 2|F_{M_{\text{ph}}}(\mathbf{Q})|^2 = 2|F_A(\mathbf{Q})|^2. \quad (13)$$

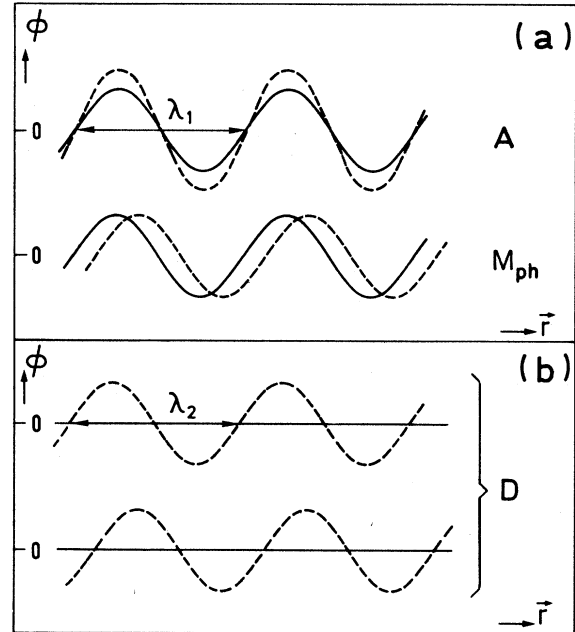


FIG. 12. $\phi_{\text{static}}(\mathbf{r}) \propto A_1 \cos(\mathbf{q}_{s_1} \cdot \mathbf{r} + \Phi_1) + A_2 \cos(\mathbf{q}_{s_2} \cdot \mathbf{r} + \Phi_2)$ with $A_2=0$. (a) Solid lines indicate equilibrium values of the torsional angle $\phi(\mathbf{r})$ in the direction of the propagation wave vector \mathbf{q}_{s_1} . Dotted lines indicate the values of this angle as the result of the amplitude excitation A and of the phase excitation M_{ph} in the infinite wavelength limit. (b) Straight solid lines illustrate that the static torsional angle is zero in the direction of the propagation wave vector \mathbf{q}_{s_2} . Both dashed lines correspond to the values of the torsional angle for two excitations of wave vector \mathbf{q}_{s_2} , which only differ by their phases, hence the twice-degenerate mode D .

These equations are obtained under the assumption that the two types of domains are equally present in the crystal, which seems reasonable due to the large size of the sample. Note also that satellite reflections being Bragg peaks within the experimental resolution, domains are large enough to enable us to neglect their static, and *a fortiori* dynamic, interferences.³²

Remark. In cases I and II, if the soft-mode dispersion curve $g(\mathbf{q})$ is not assumed to be a symmetrical function in \mathbf{q} [$g(-\mathbf{q}) \neq g(\mathbf{q})$], this induces²¹ that (i) the degenerate mode (M_{ph} in case I and D in case II) is now degenerate only at the satellite positions, its splitting increasing with \mathbf{q} (ii) the dispersion curves of the phase-II characteristic excitations are no longer all equal to the soft-mode one, and (iii) the ratios between inelastic structure factors change with \mathbf{q} . However, the measured $g(\mathbf{q})$ being found roughly symmetrical, the above effects have been neglected.

Case III. In the peculiar case III, there are only two different eigenfrequencies for the dynamical matrix,²¹

$$\omega^2(\pm\mathbf{Q}_{s_i} + \mathbf{q}) = g(\mathbf{q})$$

and

$$\omega^2(\pm\mathbf{Q}_{s_i} + \mathbf{q}) = 2a(P_c - P) + g(\mathbf{q}).$$

The gapless mode is threefold degenerate and relative to the excitation of the three degrees of freedom: Φ_1 , Φ_2 , and $(A_1^2 - A_2^2)^{1/2}$ on which the free energy does not depend. The gap mode is related to the excitation of the amplitudes A_1 and A_2 along the radius of the circle defined by $A_1^2 + A_2^2 = [a(P_c - P)/4u]$. Since case III has only one gap mode, it is not allowed for biphenyl phase II. Therefore, it will not be discussed further.

In summary, in cases I and II one calculates three modes (Figs. 10 and 11): one gapless phason and two gap modes. They have the same dispersion law as the soft mode. But, for the double- q structure, the phason is twice degenerate, whereas for the single- q structure, the degeneracy affects one of the gap modes.

B. Free energy including coupling between the order parameter and strains

Ratios between the measured slopes of the square-frequency evolution versus pressure of the phase-II gap

$$\begin{aligned} F_c(T, P) = & F_{c0}(T, P) + a(P - P_c)[|\mathcal{Q}_1(\mathbf{q}_{s_1})|^2 + |\mathcal{Q}_2(\mathbf{q}_{s_2})|^2] \\ & + 4(u + v)[|\mathcal{Q}_1(\mathbf{q}_{s_1})|^4 + |\mathcal{Q}_2(\mathbf{q}_{s_2})|^4] + 8u|\mathcal{Q}_1(\mathbf{q}_{s_1})|^2|\mathcal{Q}_2(\mathbf{q}_{s_2})|^2 \\ & + 2(g_1e_1 + g_2e_2 + g_3e_3 + g_5e_5)[|\mathcal{Q}_1(\mathbf{q}_{s_1})|^2 + |\mathcal{Q}_2(\mathbf{q}_{s_2})|^2] \\ & + 2(g_4e_4 + g_6e_6)[|\mathcal{Q}_1(\mathbf{q}_{s_1})|^2 - |\mathcal{Q}_2(\mathbf{q}_{s_2})|^2] + \frac{1}{2} \sum_{i,j} C_{ij}e_i e_j. \end{aligned} \quad (15)$$

Minimization of this free energy shows the following. (i) In case I (double- q structure, $A_1 = A_2$) e_4 and e_6 are equal to zero. The average symmetry is monoclinic as in phase I (the point symmetry group is preserved). (ii) In case II (single- q structure, domains $A_2 = 0$ or $A_1 = 0$) e_4 and e_6 are nonzero [they are proportional to $(A_1^2 - A_2^2)$].

modes G_1 and G_2 and of the phase-I soft mode (SM) are

$$\frac{\omega_{G_2}^2}{\omega_{\text{SM}}^2} = 3, \quad \frac{\omega_{G_1}^2}{\omega_{\text{SM}}^2} = 0.5. \quad (14)$$

But the above calculations indicate that $\omega_{A_+}^2/\omega_{\text{SM}}^2 = 2$ in case I and $\omega_A^2/\omega_{\text{SM}}^2 = 2$ in case II. The measured mode G_2 being the one which frequency is determined less accurately, the value of 2 for the ratio between its square frequency and the soft-mode one could be regarded as acceptable. Nevertheless, it is in the extreme limit of the error bar. So, in order to get a better fit of the measured pressure dependence of the amplitudonlike mode frequencies,³³ we have performed calculations including coupling between the order parameter and strains. Moreover, calculation of the static equilibrium values of these strains points out an interesting difference in the average symmetries of case I and II.³⁴

1. Statics

For

$$\begin{aligned} e'_1 &= \frac{\partial u_x}{\partial x}, \quad e'_2 = \frac{\partial u_y}{\partial y}, \quad e'_3 = \frac{\partial u_z}{\partial z}, \\ e'_4 &= \frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y}, \quad e'_5 = \frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x}, \\ e'_6 &= \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}, \end{aligned}$$

where \mathbf{u} is the $q=0$ displacement of centers of gravity of the molecules, one defines e_i as the difference between the strain component e'_i and the value that it would have if there was no phase transition. So, in the phase I, the components e_i are all equal to zero and in phase II, they give the effect of the coupling to the order parameter on the phase-I unit cell (i.e., on $a, b, c, \alpha, \beta, \gamma$). Group theory enables us to find the form of the free energy including coupling between e_i , $i=1-6$, and the order-parameter components. The static free energy has the following form:³⁵

The angles α and γ (Fig. 3) are no longer equal to 90° . So the average symmetry is now triclinic (the point symmetry group is not preserved).

This important difference between cases I and II will be discussed when comparing experimental and theoretical results. Note also two of the stability conditions which

will be used when studying the phase-II dynamics. If one defines

$$r = - \sum_{i,k=4,6} g_i S_{ik} g_k$$

and

$$t = - \sum_{i,k=1,2,3,5} g_i S_{ik} g_k,$$

where (S_{ij}) is the inverse matrix of the elastic constant matrix (C_{ij}) , (C_{ij}) eigenvalues being positive, one finds in case I as well as in case II that

$$r < 0 \text{ and } t < 0. \quad (16)$$

2. Dynamics

To calculate in detail the phase-II dynamics taking into account coupling between order parameter and strains, one should look for the eigenvectors and eigenvalues of the 10×10 dynamical matrix.³⁶ In ThBr₄ Bernard, Currat, Delamoye *et al.*^{10(a)} have shown a change in the amplitudon dispersion due to its coupling with an acoustic branch. In quartz, Walker and Gooding³⁷ have studied coupling between phase and acoustic modes. In this paper, we are not interested in the above-mentioned effects since we have measured the same dispersion for the characteristic excitations in phase II and for the soft mode in phase I. We are looking for the pressure dependence of the amplitudonlike mode frequencies. Not too close to P_c , they are relatively high and acoustic vibrations can no longer follow the order parameter fluctuations. In this case, the gap-mode frequencies at satellite positions are simply the second derivative of the free energy F_c with respect to the normal modes found by performing calculations without coupling.³⁸

Phase I. In phase I coupling to strains does not change the pressure dependence of the soft-mode frequency. It is, for example, calculated as the second derivative of the free energy F_c with respect to the amplitude variable A_1 and taken at static values of the parameters $Q_i(\pm \mathbf{q}_i)$, $i = 1, 2$ and e_i , $i = 1-6$,

$$\omega_{SM}^2(\pm \mathbf{Q}_{s_i}) = \left. \frac{\partial^2 F}{\partial A_1^2} \right|_{\text{static}} = a(P - P_c).$$

Phase II. Case I, double- q structure. Calculation of

$$\omega_{A_+}^2(\pm \mathbf{Q}_{s_i}) = \left. \frac{\partial^2 F}{\partial \left[\frac{A_1 + A_2}{\sqrt{2}} \right]^2} \right|_{\text{static}}$$

and

$$\omega_{A_-}^2(\pm \mathbf{Q}_{s_i}) = \left. \frac{\partial^2 F}{\partial \left[\frac{A_1 - A_2}{\sqrt{2}} \right]^2} \right|_{\text{static}}$$

gives

$$\omega_{A_+}^2(\pm \mathbf{Q}_{s_i}) = \frac{2(2u + v)}{2u + v + t} a(P_c - P) \quad (17a)$$

and

$$\omega_{A_-}^2(\pm \mathbf{Q}_{s_i}) = \frac{2v}{2u + v + t} a(P_c - P). \quad (17b)$$

Case II, single- q structure. For a domain $A_1 \neq 0$, for example, calculation of

$$\omega_{A_1}^2(\pm \mathbf{Q}_{s_1}) = \left. \frac{\partial^2 F}{\partial A_1^2} \right|_{\text{static}}$$

and

$$\omega_{D_2}^2(\pm \mathbf{Q}_{s_2}) = \left. \frac{\partial^2 F}{\partial A_2^2} \right|_{\text{static}}$$

gives

$$\omega_{A_1}^2(\pm \mathbf{Q}_{s_i}) = \frac{4(u + v)}{2(u + v) + r + t} a(P_c - P) \quad (18a)$$

and

$$\omega_{D_2}^2(\pm \mathbf{Q}_{s_i}) = \frac{-2v - 2r}{2(u + v) + r + t} a(P_c - P). \quad (18b)$$

Therefore, in case I as well as in case II, the slope of the pressure dependence of the gap-mode square frequency which was found to be equal to twice the soft-mode one is now found greater than two since r and t are negative in Eqs. (17a) and (18a). So these calculations including coupling between strains and the order parameter will allow a better fit of the evolution of the amplitudonlike mode square frequencies versus pressure (Figs. 9 and 11).

VI. DISCUSSION

First, let us consider only the experimental results on the mode frequencies, ignoring their inelastic structure factors. In case I as well as in case II, three modes have been measured, in agreement with calculations: a gapless phason and two amplitudonlike excitations, which have the same dispersion as the soft mode. Concerning the evolution versus pressure of the gap-mode frequencies, in cases I and II, theory allows a good fit of the data and distinguishes between G_1 and G_2 , getting their exact assignment to the different possible excitations of phases and amplitudes. Indeed, only the square frequency of G_2 varies more than twice as fast as the soft-mode square frequency. So, if phase II has a double- q structure (case I), G_2 is the calculated mode A_+ and if it has a single- q structure (case II), it is the mode A . Then G_1 corresponds to A_- in case I or to D in case II. And \mathcal{P} is obviously the calculated phason. Theoretical values of the slopes relative to the pressure dependence of the gap-mode frequencies [Eqs. (17) and (18)] fit the measured slopes [Eq. (14)] (i) in case I, for

$$t = -2v \text{ and } u = 5v/2 \quad (19)$$

and (ii) in case II, for

$$2v = t - r \text{ and } u = -r - 2t. \quad (20)$$

In summary, considering only the experimental results on the mode frequencies, theory and experiments are in good

agreement in case I as well as in case II.

Experimental inelastic structure factors are not determined with a good accuracy. Nevertheless, these results are used to discriminate between a double- q or a single- q structure for biphenyl phase II. Indeed, in inelastic neutron scattering measurements, the only difference between these two types of structures lies in the mode degeneracy. For the double- q structure, it is the phason \mathcal{P} which is degenerate and for the single- q structure, it is the mode G_1 . Comparison between the ratios of inelastic structure factors of \mathcal{P} , G_1 , and G_2 [Tables I and II, Eq. (5)] and the calculated ratios [Eqs. (11) and (13)] shows that our results are strongly in favor of case II. Phase II would have a single- q structure. So, in a domain where $A_1 \neq 0$,

$$\phi_{\text{static}}(\mathbf{r}) \propto A_1 \cos(\mathbf{q}_{s_1} \cdot \mathbf{r} + \Phi_1),$$

\mathcal{P} and G_2 are relative to the excitations of the phase Φ_1 and of the amplitude A_1 and the twice degenerate mode G_1 is relative to the excitation of the modulation of wave vector \mathbf{q}_{s_2} (Fig. 12).

Benkert and Heine have calculated a single- q structure in biphenyl phase II.¹⁹ But this result is based on the assumption that fourth-order terms in intermolecular interactions are negligible with respect to the fourth-order intramolecular one. If so, the free-energy coefficients u and v satisfy $u = -2v$. In Eq. (20), it implies $t = -2r$, which is impossible because r and t are both negative. So, within the scope of our calculations, fourth-order intermolecular terms are not found negligible with respect to the intramolecular ones.

Although the experimental argument for the single- q structure is supported by several inelastic structure factors measured at each pressure at different points of the reciprocal space, the proof is still only indirect. We have tried to get a more direct answer from elastic measurements performed on a triple-axis spectrometer. On the one hand, if the structure of phase II is triclinic, the angle γ must be very close to 90° since no significant difference between its value and 90° has been measured. On the other hand, we have measured no combinations of satellite positions \mathbf{q}_{s_1} and \mathbf{q}_{s_2} , which, on the contrary, would have been a proof of a double- q structure. Nevertheless, this does not allow us to definitely exclude this structure since second-order satellites are hardly measurable. In fact, determination of the structure of biphenyl phase II has not yet been done. This would be very interesting since it is a rather complex case ($n=4$), and it could give an unambiguous answer. Nonetheless, note that another indirect proof of the single- q structure of phase II, at atmospheric pressure, has recently been obtained by simulation³⁹ of experimental RPE spectra.⁴⁰ Finally, Raman

experiments under pressure are in progress and agree with neutron results.⁴¹ There are strong arguments in favor of a single- q structure for phase II at atmospheric pressure³⁹ and at 3 K, between 1.05 and 1.8 kbar (our results). Raman selection rules will possibly allow one to distinguish between the single- q and double- q structures. Then short time needed in Raman experiments could permit exploration of a large area of phase II in the (P, T) diagram (although for not too high temperatures); one could look for an area in the (P, T) space where phase II should have a double- q structure. Very recently, this type of crossover has been observed in quartz at atmospheric pressure.⁴²

VII. CONCLUSION

By using inelastic neutron scattering, at $T=3$ K, we have studied the dynamics of the incommensurate phase II of biphenyl under pressure, the order parameter of which has four components ($n=4$). In this paper, we have reported the only direct observation, by inelastic neutron scattering, of the phase and amplitude modes of such a complex incommensurate system. Three well-resolved modes have been measured: one gapless phason and two amplitudonlike modes, one of which is twice degenerate. They have been unambiguously identified as the characteristic excitations of incommensurate phase II. Moreover, within the framework of the Ginzburg-Landau theory, calculations have allowed us to determine to which specific combinations of phase and amplitude excitations they correspond. We have also given strong arguments in favor of a single- q structure of biphenyl phase II at $T=3$ K.

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