Phenomenological theory of incommensurate phases in biphenyl

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The crystal of biphenyl can exist in the monoclinic normal phase I, incommensurate striplike phase II, and incommensurate phase III propagating along the twofold symmetry axis. The incommensurate phases II and III arise as a result of the condensation of modes of symmetry $T^{|k|}$ and $T^{|k,\pi|}$ for the wave vectors from a general point of the reciprocal space and a point on the twofold symmetry axis, respectively. We write the phenomenological free-energy expansion in terms of the basic functions of $\Gamma^{|k|}$ and describe both phases II and III. Hence, it follows that phase II proves to be a striplike phase and not a quillike one. The gain of symmetry in the phase transition from phase II to phase III is introduced into the free energy by imposing those relations between the basic functions of $\Gamma^{|k|}$ which follow from the projection of $\Gamma^{|k|}$ onto $T^{|k,\pi|}$. We show that in the local anharmonic approximation the free energies of phases II and III, written in terms of the first modulation harmonic, are equal up to infinite order of invariants. Moreover, the same free energies remain equal if one includes contributions following from the second, third, and fourth modulation harmonics. We argue that the phase transition between these phases is not of a usual lock-in type. One can, however, consider phase III as a lock-in phase with the modulation wave vector $k = \frac{\pi}{2}$. To find reasonable lock-in terms for this phase, higher-order anharmonic invariants should be introduced into the free-energy expansion.

I. INTRODUCTION

In recent years crystalline biphenyl ($C_{12}H_{10}$) has been extensively studied experimentally and theoretically. The fact that biphenyl exhibits two successive incommensurate phases, one of them persisting down to lowest temperatures, explains why the crystal has gained so much interest. In the high-temperature phase (phase I) the molecules are on average planar and form the monoclinic space group $P2_1/c$ ($Z = 2$). At $T_I = 40$ K a second-order phase transition to an incommensurate phase II takes place. Here the twist angle in each molecule varies sinusoidally throughout the whole crystal, and the wave vector has components along all three reciprocal-lattice vectors: $k_c = (0.05a^*, 0.13b^*, 0.46c^*)$. At $T_H = 17$ K a phase transition takes place which leads the crystal to another incommensurate phase called phase III. At $T_H$ the components of the wave vector in $a^*$ and $b^*$ directions disappear discontinuously but the component along the $c^*$ axis [$k = \pm (1 - \delta_c) c^* / 2$ and $\delta_c = 0.075$] remains.

These facts together with the observation of a coexistence of phase II and phase III around $T_H$ indicates that the phase transition II$\rightarrow$III is of the first order. From the experimental results it is not possible to decide whether phase III is really an incommensurate phase or a higher-order commensurate one with the wave vector $k_c = \frac{\pi}{2}$. No simple commensurate phase corresponding to the zone boundary point $Z$ with $k_c = \frac{\pi}{2}$ has been found down to 1.4 K.

Ishibashi has tentatively interpreted the existence of phase II by adding gradient terms which favor the incommensurate modulation along the $a^*$ direction. He has also described the phase transition to phase III by making the fourth-order term in the free-energy expansion $k$ dependent. However, in this phenomenological theory only a two-dimensional order parameter has been used, although in phase II the order parameter has four components. The phonon dispersion curves of biphenyl have been calculated and it was shown that the phase transition from phase I to phase II is induced by the soft mode of $T^{|k,\pi|}$ symmetry of a mixing between molecular torsions and acoustic phonons. Recently a microscopic model for this sequence of phases in biphenyl has been proposed. It turned out that the structural phase transitions in biphenyl are related to an interplay between competing intra- and intermolecular forces.

The lock-in phase transitions have been mainly studied for the one-dimensional incommensurate systems. Such a lock-in phase transition occurs between the incommensurate and commensurate phases. At the phase transition point the characteristic wave vector and the amplitude of the incommensurate modulation change discontinuously. Going from the incommensurate to the commensurate phase the system gains translational symmetry elements. This gain of symmetry is manifested in the free-energy expansion by the Umklapp terms, which lower additionally the free energy of the commensurate phase, making it stable in some finite temperature interval.

In the present paper we consider the phase transition between two strictly incommensurate phases II and III,
both one-dimensional but propagating in different directions. Then we show, contrary to the existing opinion, that the characteristic wave vector of the incommensurate modulation can vary in a continuous way across the phase transition point. Although in phase III new point symmetry elements appear, leading to additional lock-in terms of normal but not of Umklapp character, the free energy of phase III does not gain additional lock-in energy with respect to the free energy of phase II.

The paper is organized as follows: In Sec. II we derive the irreducible representations at a general point and along the high-symmetry line of the reciprocal space and study the relation between the basic functions of them. Section III contains the general form of the free energy, which includes all modulation harmonics. In Sec. IV the free energies of phases II and III are written in terms of the invariants of the first harmonic up to infinite order. The structure of the incommensurate modulation in phase II can be either two-dimensional quilllike or one-dimensional striplike with two orientational domains. We show that in the first-harmonic approximation the striplike phase is more stable than the quilllike one, but the free energies of the striplike phase II and phase III are in this approximation equal up to infinite order, in spite of additional lock-in terms entering the free energy of phase III. The next section is devoted to the influence of the higher-order modulation harmonics, and we have found that they modify the free energies of the striplike phase II and phase III by exactly the same amount. In Sec. VI we consider phase III as a higher-order commensurate phase \( \frac{1}{2} \) and estimate the contributions from the Umklapp terms in the free energy which would lock in the modulation at the wave vector \( \frac{1}{2} \). In Sec. VII, using the experimental temperature behavior of the soft mode, we show that phase III is more stable than the commensurate phase \( k = \frac{1}{2} \) down to zero temperature. Final conclusions close the paper.

II. IRREDUCIBLE REPRESENTATIONS

The space group of biphenyl above 40 K is \( P2_1/c \). Here we have retained the Kovalev\textsuperscript{15} coordinate system of axis and notation with the origin shifted by \((a/4, 0, c/4)\). The incommensurate modulation in phase III propagates along the \( c \) axis. We shall consider the irreducible representations at a general point \( k \) of the reciprocal space, and along the high-symmetry line of the twofold symmetry axis.

The irreducible representation at a general point \( k \) is four dimensional with four arms \( \{k_1, k_2, -k_1, -k_2\} \), where \( k = k_1, k_2, -k_1, -k_2 \), and \( -k = h_{23} k \). The matrix representations, \( \Gamma^{[k]} \{h_1 | \alpha_1 + t \} \), where \( h_1, \alpha_1 \), and \( t \) stand for the point symmetry element, and partial and lattice translations, respectively, as induced from the ray representation (given in Table I). By inspection of the criterion of reality\textsuperscript{16} one finds that the representation \( \Gamma^{[k]} \) is real. The four complex basic functions of \( \Gamma^{[k]} \) are denoted by \( \rho(k), \rho(-k), \rho(-k), \) and \( \rho(-k) \), respectively, and we have

\[
\rho^*(k) = \rho(-k) \quad \text{and} \quad \rho^*(k) = \rho(-k) .
\]

(2.1)

The two two-dimensional and real irreducible representations \( T^{(k,1)} \) and \( T^{(k,2)} \) related with the star \( k_3 = \mu b_2 \) of the space group \( P2_1/c \) are given in Table II. We denote their basic functions by \( \Phi_1(q), \Phi_1(-q) \) and \( \Phi_2(q), \Phi_2(-q) \). Their arguments \( q \) and \(-q\) correspond to the two arms \((0,0,q)\) and \((0,0,-q)\) of the star \( k_3 \), respectively.

To study the phase transition from phase II to phase III of biphenyl we should find, how the irreducible representation \( \Gamma^{[k]} \) subduces on the line \( k = (0,0,q) \) into the direct sum of \( T^{(k,1)} \) and \( T^{(k,2)} \). Using the unitary transformation

\[
\Gamma^{[k]} = U \Gamma^{[k]} U^+ ,
\]

(2.2)

where

\[
U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & \tau(k) & 0 & 0 \\ 0 & 0 & 1 & \tau(k) \\ 0 & -\tau(k) & 0 & 0 \\ 0 & 0 & 1 & -\tau(k) \end{pmatrix} ,
\]

(2.3)

\[
\tau(k) = \exp(2\pi i q \tau_z) ,
\]

(2.4)

the \( \Gamma^{[k]} \) from Table I can be brought at \( k = (0,0,q) \) into a direct sum

\[
\Gamma^{[k]} = T^{(k,1)} \oplus T^{(k,2)} .
\]

(2.5)

| Table I. The irreducible representation \( \Gamma^{[k]} \{h_1 | \alpha_1 + t \} \) at the general point \( k = (k_x,k_y,k_z) \) of the reciprocal space for the space group \( P2_1/c \). \( t = (t_x,t_y,t_z) = n_x a + n_y b + n_z c \) denotes the lattice vector. Here, \( \tau_x = a/2 \), \( \tau_y = b/2 \), and \( \tau_z = c/2 \) and \( \alpha = \exp(2\pi i (k_x t_x + k_y t_y + k_z t_z)) \), \( \delta = \exp(2\pi i (t_x a + t_y b + t_z c)) \), \( \alpha = \exp(2\pi i (k_x t_x - a - c)) \), \( \gamma = \exp(2\pi i (k_x t_x + a + c)) \). |
|---|---|---|---|
| \( \{h_1 | t + \alpha_1 \} \) | \( \{h_4 | t + \alpha_2 \} \) | \( \{h_{23} | t + \alpha_3 \} \) | \( \{h_{23} | t + \alpha_{23} \} \) |
| \( \alpha_1 = (0,0,0) \) | \( \alpha_4 = (t_x,0,t_z) \) | \( \alpha_3 = (0,0,0) \) | \( \alpha_5 = (t_x,0,t_z) \) |
| \( \alpha_1^* \) | \( \sigma^* \) | \( \alpha_4^* \) | \( \sigma^* \) |
| \( \beta_1^* \) | \( \delta^* \) | \( \alpha_4^* \) | \( \sigma \) |
| \( \alpha_2^* \) | \( \beta_1 \) | \( \alpha_4 \) | \( \sigma \) |
| \( \alpha_2^* \) | \( \sigma \) | \( \beta_1 \) | \( \sigma \) |
TABLE II. The irreducible representations $T^{(r,1)}[h_1 | a_1 + t]$ and $T^{(r,2)}[h_2 | a_2 + t]$ of the irreducible star $k_3 = (0,0,q)$ of the space group $P2_1/c$ ($G_3^2$). $t = (t_x, t_y, t_z) = n_a a + n_b b + n_c c$ denotes the lattice vector. Here, $x = a/2$, $y = b/2$, and $z = c/2$, and $a = \exp \left(2\pi i q x \right)$, $\mu = \exp \left(2\pi i q y \right)$.  

| $k = (0,0,q)$ | $h_1 | t + a_1$ | $h_2 | t + a_2$ | $h_22 | t + a_{22}$ | $h_225 | t + a_{225}$ | $h_225 | t + a_{225}$ | $h_225 | t + a_{225}$ |
|---------------|----------------|----------------|-------------------|-----------------|-------------------|-------------------|
| $a_1 = (0,0,0)$ | $\alpha^* \ 0$ | $\mu^* \ 0$ | $0 \ \alpha^* \ 0$ | $0 \ \mu^* \ 0$ | $0 \ \alpha^* \ 0$ | $0 \ \mu^* \ 0$ |
| $T^{(r,1)}$ | | | | | | |
| | | | | | | |
| $T^{(r,2)}$ | $a^* \ 0$ | $-\mu^* \ 0$ | $0 \ \alpha^* \ 0$ | $0 \ -\mu^* \ 0$ | $0 \ \alpha^* \ 0$ | $0 \ -\mu^* \ 0$ |

The transformation matrix $U$ relates the basic functions in the following way:

$$
\Phi_1(q) = \frac{1}{\sqrt{2}} \left[ \rho(k) + \tau^*(k) \rho(\bar{k}) \right],
$$

$$
\Phi_1(-q) = \frac{1}{\sqrt{2}} \left[ \rho(-k) + \tau^*(-k) \rho(-\bar{k}) \right],
$$

$$
\Phi_2(q) = \frac{1}{\sqrt{2}} \left[ \rho(k) - \tau^*(k) \rho(\bar{k}) \right],
$$

$$
\Phi_2(-q) = \frac{1}{\sqrt{2}} \left[ \rho(-k) - \tau^*(-k) \rho(-\bar{k}) \right],
$$

where $k, \bar{k} = (0,0,q)$. Since the soft mode in phase III of biphenyl belongs to the $T^{(r,1)}$ representation, the basic functions of the other representation $\Phi_2(q) = \Phi_2(-q) = 0$ should vanish along the line $k = (0,0,q)$, and then

$$
\rho(k) = \tau(k) \rho(k) \quad \text{and} \quad \rho(-k) = \tau(-k) \rho(-k).
$$

We remark that only this choice of the origin of the space group $P2_1/c$ which is quoted in Table I, has made it possible to write down such simple relationships between the basic functions.

III. THE FREE ENERGY

To construct the free-energy expansion and to discuss the incommensurate phases one should know the invariants of this active irreducible representation that drive the crystal into the incommensurate phases. For biphenyl the most general approach relies on writing the free-energy expansion in terms of the basic functions of the irreducible representation $\Gamma^{[k]}$ from the general point of the reciprocal space. Using the projection operator technique and the matrix representation quoted in Table I, the invariants of $\Gamma^{[k]}$ belonging to different irreducible stars can be derived.

On the other hand the essential features of the incommensurate phases of biphenyl can be described by the low-frequency soft phonon branch $\omega^2(k)$, which has a minimum at the critical wave vector $k_c$. The free energy of biphenyl can be quite generally written in the form

$$
F = \frac{1}{2m} \left( \frac{1}{2m} \sum_{k_1, k_2} \cdots \sum_{k_m} G_m(k_1, k_2, \ldots, k_m) \right)
\times \rho(k_1) \rho(k_2) \cdots \rho(k_m)
\times \delta(k_1 + k_2 + \cdots + k_m - L \tau^*),
$$

where

$$
G_2(k, -k) = \omega^2(k).
$$

The factor $1/2^{2m}$ is introduced for convenience, and we assume below that all anharmonic interactions with $m > 2$, $G_m(k_1, k_2, \ldots, k_m) = G_m$, are constant, which means that they remain local in a direct space. The basic function of $\Gamma^{[k]}$ describes the harmonic $JK$ of the modulation wave. Here $j = 0, 1, 2, \ldots$ The wave vectors in the summations run over the first and higher-order harmonics, and all four arms $JK, -JK, J\bar{K}, -J\bar{K}$ of each harmonic. This expansion contains normal $L = 0$ and Umklapp $L \neq 0$ terms.

Generally, the basic functions are complex quantities, therefore, it is convenient to decouple them into the amplitudes $\eta(jk)$, $\eta(j\bar{K})$ and the phases $\epsilon(jk)$, $\epsilon(j\bar{K})$:

$$
\rho(jk) = \eta(jk) \exp \left( -i \epsilon(jk) \right),
$$

$$
\rho(j\bar{K}) = \eta(j\bar{K}) \exp \left( -i \epsilon(j\bar{K}) \right).
$$

From Eq. (2.1) it follows that $\eta(jk) = \eta(-jk)$, $\eta(j\bar{K}) = \eta(-j\bar{K})$ and $\epsilon(jk) = -\epsilon(j\bar{K})$, $\epsilon(j\bar{K}) = -\epsilon(jk)$. Along the high-symmetry line $k = (0,0,q)$, Eq. (2.7) the phases are related by $\epsilon(jk) = \epsilon(j\bar{K}) = \tau(k) \epsilon(k)$.

The incommensurate phases are described by the minimum of the free energy (3.1) together with relations (3.3) with respect to the wave vector, amplitudes and phases of the harmonics

$$
\frac{\partial F}{\partial k} = 0, \quad \frac{\partial F}{\partial \eta(jk)} = 0, \quad \frac{\partial F}{\partial \epsilon(jk)} = 0, \quad \text{etc}.
$$

IV. THE FIRST-HARMONIC APPROXIMATION

A. Phase II

The phase II of biphenyl seems to be well described by the first-harmonic approximation. It is strictly incommensurate with a sinusoidal modulation since in the neutron diffraction experiment no higher-order satellites have been detected. This phase can be either two-dimensional incommensurate, called quillike, or one-dimensional, called striplike. The analysis of the intensities of the dynamical phase and amplitude modes suggests that phase II of biphenyl is a striplike phase. Using Eqs. (3.1) and disregarding the higher-order harmonics and the Umklapp terms, and taking into account the transformation properties of the basic functions $\rho(k)$, $\rho(\bar{k})$. 
\[ \rho(-k), \rho(-\bar{k}), \] and \( \rho(-\bar{k}) \), the free energy at a general point of reciprocal space in the first harmonic approximation can be written as

\[ F_{II} = \sum_{n=1}^{\infty} \sum_{l=0}^{n} G_{2n} \frac{(2n)!}{2^n(n-l)!2^l(n-l)!} \times |\rho(k)|^{2l} |\rho(\bar{k})|^{2(n-l)}, \] (4.1)

where all anharmonic terms are included.

1. Quiltlike phase

The configuration of particles in the quiltlike phase would be a superposition of two modulation waves, one propagating along wave vector \( k \), the second along \( \bar{k} \). The amplitudes of both waves would be equal, \( \eta(k) = \eta(\bar{k}) \); their phases \( \epsilon(k) \) and \( \epsilon(\bar{k}) \), however, would not be related. Leaving in the free-energy expansion (4.1) terms up to fourth order invariants only, one finds from the extremum conditions (3.4) the free energy of the quiltlike phase as

\[ F_{Q} = -\frac{4}{9} \frac{\omega^4(k)}{G_4}. \] (4.2)

2. Stripedlike phase

In the stripedlike phase the incommensurate modulation propagates only along one of the directions, either \( k \) or \( \bar{k} \). Of course both directions are equivalent. The two orientation domains of the stripedlike phase are characterized by \( \eta(k) \neq 0, \eta(\bar{k}) = 0 \text{ or } \eta(k) = 0, \eta(\bar{k}) \neq 0 \), respectively.

Then the free energy of the sinusoidally modulated stripedlike phase, including contributions up to fourth order invariants only, is

\[ F_{S}^{(1)} = -\frac{2}{3} \frac{\omega^4(k)}{G_4}. \] (4.3)

From comparison of the free energies (4.2) and (4.3), it follows that the sinusoidal incommensurate stripedlike phase is always more stable than the corresponding quiltlike one, provided the anharmonic fourth-order term \( G_4 \) in the free energy is local.

The free energy (4.1) of the stripedlike phase written for all order invariants is

\[ F_{S} = \sum_{n=1}^{\infty} G_{2n} \frac{(2n)!}{2^{4n(n-1)/2}} \eta^2(k)^n. \] (4.4)

B. Phase III

In phase III the incommensurate modulation is one-dimensional and propagates along the \( z \) axis, the direction of the twofold symmetry axis. Only one orientational domain of this phase exists. The phase is described by the active two-dimensional irreducible representation \( T(\kappa,1) \). To account for the possible lock-in terms which should appear when going from phase II to phase III, the free energy ought to be written in terms of the basic functions of the irreducible representation \( T(\kappa) \) from a general point of the reciprocal space, where the four arms of the irreducible star, \( k, \bar{k}, -k, \) and \( -\bar{k} \) squeeze to \( (0,0,q), (0,0,q), (0,0,-q), \) and \( (0,0,-q) \), the two arms \( k = (0,0,q) \) and \( -k = (0,0,-q) \) of the star \( k_3 \), respectively. This condition produces many additional so-called lock-in terms in the free-energy expansion. Because phase III must be described by the \( T^{(k,1)} \) irreducible representation, the basic functions \( \rho(k) \) and \( \rho(-k) \) have to be replaced by \( \tau(q)p(q) \) and \( \tau(-q)p(-q) \), respectively, according to Eq. (2.7). Taking the above remarks into account, the general form of the free energy (3.1) at phase III and in the first harmonic approximation takes the following form:

\[ F_{Z} = \sum_{n=1}^{\infty} G_{2n} \frac{(2n)!}{2^{4n(n-1)/2}} \eta^2(q)^n [2[1+\cos(\pi q)]^n. \] (4.5)

Considering now contributions up to fourth-order invariants only, the free energy of phase III can be written as

\[ F_{Z}^{(1)} = -\frac{2}{3} \frac{\omega^4(q)}{G_4}, \] (4.6)

which is the same formula as for the free energy of the stripedlike phase II. In this approximation the free energies of both phases in question may differ, only owing to the different values of the soft-mode frequency \( \omega^4(q) \) belonging to different wave vectors.

C. Comparison of the free energies of stripedlike phase II and phase III

In order to compare the free energies of the stripedlike phase II and phase III, one should minimize the Eqs. (4.4) and (4.5) with respect to the amplitudes. Provided all corresponding coefficients are the same in both expansions, one finds after the substitution \( \eta^2(k) = \eta^2(q)2[1+\cos(\pi q)] \) the same free energies for both phases. Consequently, up to infinite order of invariants and in the first harmonic approximation the free energies of the stripedlike phase II and incommensurate phase III may differ, only owing to different values of the soft-mode frequency \( \omega^4(q) \) belonging to different wave vectors. That implies that the characteristic incommensurate wave vector can move in a continuous way from the general point of the reciprocal space to a point on the high-symmetry line. In these circumstances no lock-in transition will occur.

V. THE FREE ENERGIES OF THE PHASES II AND III INCLUDING HIGHER-ORDER HARMONICS

A. Stripedlike phase II

We show below that also the higher-order harmonics cannot provide lock-in energies for the phase transition between the stripedlike phase II and phase III. For that we have written the free-energy expansion at the general point of the reciprocal lattice, retaining only the leading terms needed to describe the first-, second-, third-, and fourth-order harmonics. Up to second-order harmonics one gets
amplitudes, Eqs. (5.2)–(5.5), into the free-energy expansion (5.1) and find the contributions coming from the second- and third-order harmonics as

\[ F_\Sigma^{(2)} = -\frac{1}{8}\left(\frac{G_3}{G_4}\right)^2 \frac{\omega_4^2(k)}{\omega_2^2(2k)-2\omega_2^2(k)}, \]

\[ F_\Sigma^{(3)} = \frac{1}{27G_4} \frac{|\omega_6^2(k)|}{\omega_2^2(3k)-2\omega_2^2(k)}, \]

respectively.

### B. Phase III

In phase III, as mentioned above, the one-dimensional incommensurate modulation propagates along the \( z \) axis. Taking into account the relations between the basic functions, counting the corresponding number of terms in the summations, and using Eq. (3.3), one can write the free energy, Eq. (3.1), for phase III as

\[ F_Z = \frac{1}{4}[\omega^2(q)\eta^2(q)[1+c(q)] + \omega_2^2(2q)\eta^2(2q)[1+c(2q)] + \cdots]

\[ -\frac{1}{4}G_3\eta^2(q)\eta(2q)c(q)[1+c(q)] + \frac{1}{3}G_4\eta^2(q)[1+c(q)]^2 + \frac{1}{2}G_4\eta^2(2q)[1+c(2q)] + \cdots, \]

where

\[ c(q) = \cos(\pi q). \]

The phase factor \( c(q) \) follows from the relation between the basic functions, Eq. (2.7). Comparing Eqs. (5.1) and (5.7) one notices that larger numerical values of the coefficients occur in the free energy of phase III. The differences in the values of the coefficients are introduced by the lock-in terms. In (5.7), we have included terms up to second-order harmonics. From the extremum condition, Eq. (3.4), the first-, second-, and third-order harmonics can be estimated as

\[ \eta_Z^2(q) = \frac{4}{3} \frac{1}{1+c(q)} \frac{\omega^2(q)}{G_4}, \]

\[ \eta_Z(2q) = -\frac{1}{2c(q)} \frac{G_3}{G_4} \frac{\omega_2^2(q)}{\omega_2^2(2q)-2\omega_2^2(q)}, \]

\[ \eta_Z(3q) = \frac{[1+c(q)][1-2c(2q)]\omega^2(q)\eta_Z^2(q)}{[1+c(3q)][2\omega^2(3q)-2\omega_2^2(3q)]}, \]

### C. Comparison of the free energies

The higher-order harmonics lower the free energy. Substituting (5.9)–(5.11) into the free energy of phase III (5.7), the contributions coming from the second- and third-order harmonics can be found. Additionally we add the contribution from the fourth-order harmonic. They are

\[ F_Z^{(1)} = F_S^{(1)}, \quad F_Z^{(2)} = F_S^{(2)}, \quad F_Z^{(3)} = F_S^{(3)}, \quad F_Z^{(4)} = F_S^{(4)}, \]

exactly the same as those for the stripelike phase, with the obvious modification that now the \( \omega^2(jq) \)'s belong to the soft mode along the \((0,0,q)\) direction. The free-energy contributions are independent of the phase factor \( c(q) \).

We conclude that within the local-anharmonic approximation the higher-order harmonics lead to the same contributions in the free energy in both cases: A difference in the free energies \( F_S \) and \( F_Z \) may arise only from different values of the soft-mode \( \omega^2(k) \) or \( \omega^2(q) \), respectively. Therefore, in this phase transition the characteristic wave vector of the modulation of the stripelike phase can in a continuous way reach the high-symmetry line. It is worthwhile to mention that all the discussed lock-in terms have arisen from the normal invariants \((L=0)\) only.

The ratios of the higher-order-harmonic contributions of the free energy to the first-order-harmonic contribution are

\[ \frac{F_Z^{(2)}}{F_Z^{(1)}} = \frac{\eta_Z(2q)}{\eta_Z(q)} \left( \frac{\omega_2^2(2q)-2\omega_2^2(q)}{\omega_2^2(q)} \right)^2, \]

\[ \frac{F_Z^{(3)}}{F_Z^{(1)}} = \frac{2}{9} \frac{|\omega_2^2(q)|}{\omega_2^2(3q)-2\omega_2^2(q)}, \]

\[ \frac{F_Z^{(4)}}{F_Z^{(1)}} = \frac{4c^2(q)}{1+c(q)} \frac{|\omega^2(q)|}{\omega_2^2(4q)-2\omega_2^2(q)} \left( \frac{\eta_Z(2q)}{\eta_Z(q)} \right)^2. \]

In phase III the first- and second-order satellites have been experimentally observed\(^1\) and their ratio can be estimated to be \([\eta_Z(2q)/\eta_Z(q)]^2 = 0.02\). Taking \( q = 0.4575 \) and the following experimental values\(^1\) from the soft-phonon branch at 13 K, \( \omega^2(q) = -0.036 \), \( \omega^2(2q) = 0.0529 \), \( \omega^2(3q) = 0.56 \), and \( \omega^2(4q) = 0.64 \) (THz)\(^2\), one finds that the contributions of second-, and third-, and fourth-order harmonics to the free energy are \( F_Z^{(2)}/F_Z^{(1)} \approx 0.4\%),
The intensity of the $j$th order satellite in the diffraction pat-tern is proportional to the square of the $j$th order amplitude of the modulation. According to our approach to the modulation in a one-orientational domain of stripe-like phase is described by two basic functions $\rho(k)$ and

$$
\rho(-k),
$$
while for phase III four basic functions $\rho(q), \rho(q), \rho(-q),$ and $\rho(-q),$ equal in pairs, were used. Taking that into account, the ratio of intensities of satellites of the order $j$ in the stripe-like phase II and phase III is

$$
\frac{I_{Z,j}^{(j)}}{I_{Z,j}^{(1)}} = \left[ \frac{2\eta_j(q_j)}{\eta_5(q_j)} \right]^2 \left[ 1 + \cos(\pi q_j) \right].
$$

(5.16)

Inserting into it Eqs. (5.2)—(5.4) and (5.9)—(5.11) one finds that the ratio of the intensities $I_{Z,j}^{(j)}/I_{Z,j}^{(1)} = 1$ for $j = 1, 2, 3, 4$. That result tells us that at the phase transition from phase II to phase III no discontinuity in satellite intensities should be expected.

VI. PHASE III AS A LOCK-IN PHASE

The neutron diffraction experiment shows that the phase transition from phase II to phase III is accompanied by a discontinuity in the intensity of the first-order satellite and by the abrupt appearance of second- and third-order satellites. As pointed already out by Calleau et al., phase III might be the lock-in phase. The experimental critical wave vector is close to $\frac{5}{13}$ and remains constant up to the lowest temperature.

If one uses the conventional truncation of the free energy (3.2) at the fourth-order invariant, then the largest Umklapp terms which may produce the lock-in phase are

$$
\Delta F_{6,13}^{(4)} = \frac{1}{8} G \left[ -A_1 \eta(2q) \eta(3q) \eta(3q) \eta(4q) + A_2 \eta(q) \eta(4q) + A_3 \eta(3q) \eta(4q) \right] \times \cos(13\epsilon(q)) \delta(q - \frac{5}{13}).
$$

(6.1)

The coefficients $A_1 = 1.033$, $A_2 = 10.962$, and $A_3 = -2.848$ originate from combinations of the phase factor $c(q)$, Eq. (5.8), where we have used $q = \frac{5}{13}$. Similarly to the contribution of higher-order harmonics to the free energy, Eqs. (5.13)—(5.15), one can estimate the relative magnitude of Umklapp terms of the lock-in phase $\frac{5}{13}$. Then, one finds

$$
\frac{\Delta F_{6,13}}{F_{Z}} = \left(0.2 \times 10^{-6}\right) \cos(13\epsilon(q)) \delta(q - \frac{5}{13}).
$$

(6.2)

which is a very small quantity in comparison, for example, with the third-order harmonic contribution to the free energy (5.14). We remind that the lock-in terms contain in this case the unobserved fourth-order harmonics.

There is, however, a possibility to enhance the lock-in energy. Namely, one should couple only harmonics of these orders which are visible. For that, the anharmonic part of the free energy must not be of the fourth order, but higher. In the simplest case one can leave in the free energy (3.1) the second-order harmonic invariant and the 2nth order anharmonic invariant, where $n \geq 3$, with a local coefficient $G_{2n}$. Physically that means that biphrenyl molecules face at large displacements a much steeper potential than served by the fourth-order anharmonicity. Then, the lock-in energies of the corresponding orders are

$$
\Delta F_{6,13}^{(6)} \sim G_6 \eta(2q) \eta(3q) \cos[13\epsilon(q)] \delta(q - \frac{5}{13}),
$$

$$
\Delta F_{6,13}^{(2n)} \sim G_{2n} \eta(q) \eta(3q) \eta(2q) \cos[13\epsilon(q)] \delta(q - \frac{5}{13}).
$$

(6.3)

for $n = 4, 5, 6$. For $n = 5, 6$, when one couples only first- and second-order harmonics, one can make the lock-in energy of the same order as the free energy of incommensurate modulation. In light of these arguments, phase III should be treated as a commensurate phase $\frac{5}{13}$, which arises as a result of lock-in phase transition from the stripe-like phase II.

VII. NONEXISTING PHASE $\frac{5}{13}$

The phase $q = \frac{5}{13}$ would be completely described by the first-order harmonic and its free energy, as inferred from Eq. (5.1), can be written in the form

$$
F_{1/2} = \frac{1}{2} \omega^2(q) \eta^2(q) + \frac{1}{8} G_4 \eta^4(q)
$$

$$
- \frac{1}{8} G_4 \eta^4(q) \cos[4\epsilon(q)] \delta(q - \frac{1}{8} e^*)
$$

(7.1)

where the fourth-order Umklapp terms have been added. At the minimum, the free energy reaches the magnitude

$$
F_{1/2} = -\frac{\omega(\frac{5}{12})}{4G_4}.
$$

(7.2)

The experimentally established temperature dependence of the soft mode at the critical wave vector $q = 0.4575$ is

$$
\omega^2(q, T) = \beta(T - T_c),
$$

(7.3)

where $\beta = 0.00133$ (THz)$^2$/K and $T_c = 37$ K. The phonon frequency at $q = \frac{5}{13}$,

$$
\omega^2(q, T) = \omega^2(q, T) + 0.062$ (THz)$^2$,
$$

(7.4)

is higher by a constant not depending on temperature. Comparing the free energies of phase III, Eq. (5.3), and lock-in phase $\frac{5}{13}$, Eq. (7.2), one finds that the incommensurate phase III has lower free energy until absolute zero temperature and therefore it remains stable until that temperature. The lock-in phase $\frac{5}{13}$ would become more stable only below $-210$ K.

VIII. CONCLUSIONS

We have proposed a phenomenological model for the sequence of phases in biphrenyl, based on the expansion of the free energy in terms of the basic functions of the irreducible representation at a general point of reciprocal space. The main results within this general approach are summarized as follows: Within the local anharmonic approximation the stripe-like phase turns out to be more stable than the quiltlike one. In the first harmonic approximation the free energies at the general point in re-
ciprocial space and on the high-symmetry line have proved to be the same up to infinite-order invariants. Inclusion of higher-order harmonics up to the fourth order does not change this result. This implies that within the local anharmonic approximation there is no driving force for the usual lock-in phase transition from the incommensurate phase II to the lock-in phase III. The contributions to the free energy of the Umklapp terms which lock in the stripelike phase to phase III at \( q = \frac{\pi}{3} \)
along the high-symmetry direction explain qualitatively the lock-in character of the phase transition, but to describe it quantitatively, higher-order anharmonic terms which stiffen the local potential are necessary. Comparing the free energies on the high-symmetry line and at \( k = \frac{1}{2} \) we find that the incommensurate phase III is stable down to zero temperature. This is in contrast to the results, which state that phase III is metastable and the commensurate phase \( \frac{1}{2} \)
is the ground state of biphenyl at atmospheric pressure.

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