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Influence of an External Shear Stress on the Domain Structure in Incommensurate Phase II of Biphenyl

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Abstract. — The incommensurate phase II of biphenyl is a bi-domain one. The naphthalene paramagnetic molecular probes used in this experiment permit the differentiation of these two domains: each Electron Paramagnetic Resonance line of the high temperature phase of biphenyl gives rise to two incommensurate lines in the phase II. But by applying a relevant shear stress, one favours one domain; this behaviour is observed on the E.P.R. spectra which exhibit only one incommensurate line. These results complete the ones obtained about the domain structure of phase II of biphenyl.


1. Introduction

When the biphenyl molecular crystal with the chemical formula C_{12}H_{10} (Fig. 1) is cooled from the high temperature phase (phase I) it exhibits two structural phase transitions [1]: a second order one at T_I = 40 K and a first order one at T_{II} = 17 K. These phase transitions were extensively studied in the deuterated and hydrogenated compounds: electronic absorption and emission in pure biphenyl-d_{10} [2], neutron scattering [1,3–6], X-ray [7], Brillouin scattering [8,9],

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Fig. 1. — The high temperature structure of biphenyl $a = 8.12$ Å, $b = 5.63$ Å, $c = 9.51$ Å, $\beta = 95.1^\circ$.

Raman scattering [10], Nuclear Magnetic Resonance (N.M.R.) [11,12], Electron Paramagnetic Resonance [13–17]. While the biphenyl molecules are planar in the high temperature phase, these phase transitions are characterized by a twist of the two phenyl rings around their molecular axis. The amplitude of the twist is modulated through space with a wave vector $k$ in a general direction in the first incommensurate phase (phase II). The star of $k$ has four arms inside the phase I Brillouin zone:

$$\pm q_{s1} = (\delta_a a^* - \delta_c c^*) + \left(\frac{1 - \delta_b}{2}\right) b^*; \; \pm q_{s2} = - (\delta_a a^* - \delta_c c^*) + \left(\frac{1 - \delta_b}{2}\right) b^* \quad (1)$$

In the second incommensurate phase (phase III) the wave vector modulation is along the $b$ axis:

$$q_s = \left(\frac{1 - \delta_b}{2}\right) b^- \quad (2)$$

and the order parameter dimension changes from $n = 4$ in the first incommensurate phase to $n = 2$ in the second one. For a long time the main question was as follow: is the phase II a $2q$ mono-domain phase or is it a $1q$ bi-domain one? These two structures stand for two different incommensurate phases named quilt-like phase or stripe-like phase respectively. In the quilt-like phase (i.e. $2q$ mono-domain) the configuration of displacement fields would be a superposition of two modulation waves, with amplitudes $A_1$ and $A_2$, one propagating along $q_{s1}$ and the second along $q_{s2}$. In the stripe-like phase (i.e. $1q$ bi-domain) the modulation propagates along one direction only, either $q_{s1}$ or $q_{s2}$. Both directions are equivalent, being related by the application of the symmetry operations lost in the incommensurate phase and define the two structures: the two structures are characterized by $(A_1 \neq 0, A_2 = 0)$ for one domain and $(A_1 = 0, A_2 \neq 0)$ for the other one. Neutron scattering and Raman scattering results [3,4,10] have shown that the system is bi-domain. N.M.R spectra [12] are typical of a $1q$ structure and Electronic Paramagnetic Resonance (E.P.R.) [15,16] results also showed the two domain structures. Therefore, we conclude that the phase II of biphenyl has a $1q$ bi-domain structure. These results also agree with theoretical investigations [18–20].

In a previous study [16] we have shown the signature of the two domains on the E.P.R. spectra. To complete this study, we have investigated the influence of a shear stress on the
domain structure. In Section 2 we review the previous Electron Paramagnetic Resonance (E.P.R.) results in incommensurate phase II; this part is mainly devoted to the manifestation of the domain structure on the E.P.R. spectrum and the characteristic features of the E.P.R. probe. In Section 3 we review Landau theory of biphenyl and determine the stresses that break the symmetry and will favour one particular domain. Then we describe the experimental procedure and we present the experimental result. Some particular attention is devoted to the experimental set-up used to apply a stress inside the E.P.R. cavity, on a crystal that is studied in a photo-excited state. A comparison of the results under stress and without stress concludes this part.

2. Observation of Domain Structure in Incommensurate Phase II of Biphenyl

2.1. Experimental Procedure and Properties of the E.P.R. Probe [15, 16]

In order to perform an E.P.R. experiment on a molecular crystal, we include a paramagnetic probe in the pure biphenyl (as it was done in the pioneering work of Hutchison et al. [21]). Naphthalene-d₈ molecules were substituted for the biphenyl ones with a concentration equal to 0.5%. The products, biphenyl-h₁₀ and naphthalene-d₈, were purchased from Aldrich company and were purified before use. The biphenyl crystal was grown by lowering the melt through a temperature gradient (Bridgman method).

Although the ground state of naphthalene-d₈ is not paramagnetic, the excited triplet state is and it can be populated by photo-excitation. Some studies [22] have shown that the lowest triplet state responsible for the paramagnetism is also a phosphorescent state out of the exciton band of the biphenyl crystal, with a sufficiently long lifetime for E.P.R. measurement. In the single biphenyl crystal, this state is reached by irradiating the naphthalene-d₈ with a high pressure mercury arc lamp. The experimental set-up was as described previously [15, 16].

The E.P.R. experiments were performed on a X-band spectrometer equipped with a cryostat. The crystal was cooled down by helium gas flowing in the dewar within the cavity. The temperature is measured by a thermo-couple placed in the gas flow under the crystal. Although, an exact reading of the absolute temperature of the crystal could not be obtained with this system, the temperature could nevertheless be obtained by using the splitting between lines. Thus we obtain a temperature measurement at about ±0.1 K.

The features of the E.P.R. spectra of the probe are reported elsewhere [15, 16] and they can be summarized as follows. In the photo-excited state, the naphthalene has a $S = 1$ spin. For any direction of the static magnetic field, two systems of three peaks each are observed; they are associated with the two magnetic inequivalent naphthalene probes in the unit cell. Three lines for each molecule are typical for a $S = 1$ spin: the $\Delta_{ms} = 2$ transition in low field and the two $\Delta_{ms} = 1$ transitions in high field. When the magnetic field is in the symmetry plane (a, c), both molecules are magnetically equivalent giving rise to a spectrum with only three lines. The anisotropy curves which give the line positions as a function of the direction of the static magnetic field in the three crystallographic planes, enable us to define the spin Hamiltonian parameters in the high temperature phase (or normal phase):

$$\mathcal{H}_0 = \beta S \tilde{g} B_0 + B_2^0 O_0^2 + B_2^2 O_2^2$$

with $B_2^0 = 340 \times 10^{-4} \text{ cm}^{-1}$ and $B_2^2 = -150 \times 10^{-4} \text{ cm}^{-1}$  \hspace{1cm} (3)

The $\tilde{g}$ tensor is isotropic with the free electron value equal to 2.0023. This Hamiltonian has the symmetry of the naphthalene molecule and the directions of the axes are nearly the same as the ones of the biphenyl molecules [15, 16]: as a result the naphthalene molecular probe tends to align itself with the same orientation as the biphenyl one. The symmetry
of the spin Hamiltonian is the same as that of the molecular probe but not the same as that of the site: the crystalline field is weak, as expected for a molecular crystal, and the phase transition will be seen through the geometrical deformation and/or disorientation of the molecular probe [15,16]. For the present system, the E.P.R. probe is sensitive to the two phase transitions for all directions of the magnetic field.

2.2. DOMAIN STRUCTURE. — In incommensurate phase, where the translational lattice periodicity is lost, there is an essentially infinite number of non-equivalent paramagnetic sites which contribute to the magnetic resonance spectrum. A quasi-continuous distribution of local E.P.R. line is expected for the paramagnetic absorption. This absorption is marked by discontinuities (named singularities) at its extremities [23]. In our experiments we use the derivative of the absorption. A typical E.P.R. spectrum, obtained in an X band experiment [16] is sketched in Figure 2. Near 40 K the normal phase line splits into two singularities. Then two other singularities appear and remain down to 20 K. Between 20 K and 15 K a second phase transition arises and the spectrum becomes more simple with only two singularities in the low temperature phase (below 15 K). In a previous paper [16] it was established, by using symmetry considerations, that the four singularity spectra are due to the superposition of two types of domains. Therefore, E.P.R. spectra account for the two phase transitions at \( T_1 = 40 \) K and \( T_1 = 17 \) K.

In phase II (between 40 K and 20 K) the E.P.R. probe exhibits peculiar behaviour [15,16]:
- First, the analysis of the spin Hamiltonian parameters shows that the E.P.R. probe rotates around a direction that is perpendicular to its long axis. The rotations of the molecules in the two domains have the same amplitude (i.e. the maximum value of the modulated rotation angle), but their axes are not equivalent (they do not correspond to each other by a symmetry operation lost at the phase transition). This behaviour makes the two domains geometrically inequivalent, and thus they can be observed separately.
- Secondly, even though the modulation is a plane wave one, the naphthalene probe molecule
exhibits a "soliton regime" [24, 25], as is sketched in Figure 2, where we can see that the splitting near the high temperature phase line and the edge singularities are not symmetrical. This behaviour persists in phase III but the harmonics of the modulation (up to the third order) could be observed [1].

To understand why the different domains can be observed separately, it must be noted that the naphthalene molecules have two possible orientations in the high temperature phase. Let us call the two chains a and b, and assume that the two molecular probes in the unit cell move according to two different displacement fields (for example the displacement field $U_a$ in site a and the displacement field $U_b$ in site b in the first domain). Such effects are certainly due to the particular behaviour of the E.P.R. probes which favours some phases of the modulation. By virtue of the application of the symmetry operation lost at the phase transition, we obtain the second domain from the first one. This symmetry operation is specific to the exchange of sites a and b. Thus the displacement field $U_a$ in site a of domain 1 lies in site b of domain 2, the same goes for the displacement field $U_b$ which lies in site a of domain 2 (Fig. 3). In the high temperature phase, the "a" sites of the two domains are equivalent, thus a single line is observed. By contrast, in phase II two different displacement fields $U_a$ and $U_b$ are experienced at these sites, which lead to two different splittings around the same high temperature line position. This result explains the appearance of four singularities in phase II.

An experiment under uniaxial stress can favour one domain over the other and lead to a simpler E.P.R. spectrum.

3. Influence of an External Stress

3.1. Landau Theory [26]. — In this part, using Landau theory, we analyze the role of strain and determine the relationship between it and specific types of domans.

Given the coupling between the strains and the order parameter components, the Ginzburg-Landau free energy reads [5]:

$$F(T) = F_0(T) + a(T - T_1)(|Q_{q_1}|^2 + |Q_{q_2}|^2) + 4(u - v)(|Q_{q_1}|^4 + |Q_{q_2}|^4)$$
\[8u|Q_{qs_1}|^2|Q_{qs_2}|^2 + 2(g_1e_1 + g_2e_2 + g_3e_3 + g_5e_5)(|Q_{qs_1}|^2 + |Q_{qs_2}|^2)
+ 2(g_4e_4 + g_6e_6)(|Q_{qs_1}|^2 - |Q_{qs_2}|^2) + \frac{1}{2} \sum_{i,j=1}^{6} C_{ij} e_i e_j \]

(4)

where \(|Q_{qs_1}|\) and \(|Q_{qs_2}|\) are the amplitudes of the four-dimensional order parameter and \(e_i (i = 1, 2, 3, 4, 5, 6)\) the strain components in the abbreviated notation \((e_i = e_{\alpha} \text{ for } i = 1, 2, 3; e_4 = 2e_{23}, e_5 = 2e_{13}, e_6 = 2e_{12} \text{ with } e_{\alpha\beta} = \frac{1}{2} \left( \frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) \alpha, \beta = 1, 2, 3)\).

The principal axes \(x_1, x_2, x_3\) of the strain tensor are defined with the \(x_2\) axis along \(b\) vector, the other axis are in the \((a, c)\) plane.

The \(Q_{qs}\) are the order parameter components; the \(e_i\) are the strain components that become non-zero at the phase transition (in phase I they are all equal to zero) \([5]\).

The last term in the free energy represents the elastic energy having the symmetry of the high temperature phase. Consequently this term could split into two parts, the first containing the strain components \(e_1, e_2, e_3, e_5\) and the second, the strain components \(e_4, e_6\).

By making the following changes of variable: \(Q_{qs_i} = \frac{A_i}{\sqrt{2}} e^{i\phi_i}, i = 1, 2\) and \(A_1 = \rho \cos \theta, A_2 = \rho \sin \theta\) the free energy can be rewritten:

\[F(T) = F_0(T) + \frac{g}{2} \rho^2 + \left[ u + \frac{v}{4} (3 + \cos 4\theta) \right] \rho^4
+ (g_1e_1 + g_2e_2 + g_3e_3 + g_5e_5) \rho^2 + (g_4e_4 + g_6e_6) \rho^2 \cos 2\theta + \frac{1}{2} \sum_{i,j} C_{ij} e_i e_j \]

(5)

Minimizing this free energy leads to the following results:

- in the \(2q\) structure, and without any external stress, the amplitudes \(A_1\) and \(A_2\) of the two modulations are equal, and the spontaneous strains \(e_4\) and \(e_6\) are equal to zero; the average symmetry is monoclinic as in phase I.

- in the case of a \(1q\) structure with domains, \(A_2 = 0\) or \(A_1 = 0\) corresponding to \(\theta = 0\) or \(\theta = \pi/2\), \(e_4\) and \(e_6\) are non zero (they are proportional to \((A_1^2 - A_2^2)\)) ; the average symmetry is now triclinic.

Since the \(1q\) structure has been suggested or demonstrated by previous results \([3, 4, 10, 12, 16, 18-20]\), it will be the only case considered below. Under an external stress, the equilibrium equations are:

\[\frac{\partial F}{\partial e_i} = \sigma_i, \quad i = 1, 2, 3, 4, 5, 6\]
\[\frac{\partial F}{\partial \rho} = 0\]
\[\frac{\partial F}{\partial \theta} = 0 \]

(6)

where the \(\sigma_i\) are the stress components.

These equations give \(e_i = \Gamma'_i + \Gamma_i \rho^2\) for \(i = 1, 2, 3, 5\) in which \(\Gamma'_i\) and \(\Gamma_i\) are functions independent of \(\theta\) and \(e_4 = \gamma'_4 + \gamma_4 \rho^2 \cos 2\theta, e_6 = \gamma'_6 + \gamma_6 \rho^2 \cos 2\theta\). The order parameter amplitude is written as follows:

\[\rho^2 = \frac{a' + 2(g_4 \gamma'_4 + g_6 \gamma'_6) \cos 2\theta}{(4u' + v(3 + \cos 4\theta) + 4(g_4 \gamma_4 + g_6 \gamma_6) \cos^2 2\theta)} \]

(7)
with
\[
\gamma'_4 = \frac{C_{66}\sigma_4 - C_{48}\sigma_6}{C_{66}C_{44} - C_{46}^2}, \quad \gamma'_6 = \frac{C_{44}\sigma_6 - C_{46}\sigma_4}{C_{66}C_{44} - C_{46}^2}
\]
\[
\gamma_4 = \frac{C_{48}\sigma_6 - C_{66}\sigma_4}{C_{66}C_{44} - C_{46}^2}, \quad \gamma_6 = \frac{C_{66}\sigma_4 - C_{66}\sigma_6}{C_{66}C_{44} - C_{46}^2}
\]

(8)

The \( \gamma'_i \) being dependent on external stress parameters, the amplitude \( \rho \) of the order parameter varies from one domain to another. The free energy is now given by:

\[
F(T) = \overline{F}_0 + \overline{\alpha}\rho^2 + \rho^4 \left( \overline{\alpha} + \frac{u}{4}(3 + \cos 4\theta) \right) + (g_4\gamma_4 + g_6\gamma_6)\rho^4 \cos^2 2\theta
\]

\[
+ (g_4\gamma'_4 + g_6\gamma'_6)\rho^2 + \cos 2\theta + K_0(\sigma) + K_2(\sigma)\rho^2 \cos 2\theta + K_4\rho^4 \cos^2 2\theta
\]

(9)

with the definition:

\[
\frac{1}{2} \sum_{ij} C_{ij} e_i e_j = K_0(\sigma) + K_2(\sigma)\rho^2 \cos 2\theta + K_4\rho^4 \cos^2 2\theta
\]

\( K_0 \) and \( K_2 \) can be seen to depend upon the external stresses.

Therefore a relevant stress, i.e. one containing at least \( \sigma_4 \) or \( \sigma_6 \), can differentiate the two domains. It is worth noting that the \( \sigma_i \) with \( i = 1, 2, 3, 5 \) does not break the symmetry nor does it modify the equilibrium state. They only renormalize the various coefficients in the free energy whereas \( \sigma_4 \) and \( \sigma_6 \) break the high temperature phase symmetry and will favour one of the two domains.

3.2. EXPERIMENTAL PROCEDURE TO APPLY THE SHEAR STRESS INSIDE THE E.P.R. CAVITY. — Let us recall that the sample is set at the bottom of a quartz switch (used as a wave guide) with an altuglass cap. To perform experiments under stress inside the E.P.R. cavity, we use the contraction properties of the cap. The altuglass cap is replaced by another one built with Teflon, since the contraction of the latter is more significant than of the former when the temperature is lowered. The \( \sigma_4 = \sigma_{23} \) and \( \sigma_6 = \sigma_{21} \) are shear stresses which are generated by the contraction of the cylindrical cap as described as follows: the crystal, inside the cap, is a parallelepiped; the \( (a, b) \) face is horizontal and the \( (110) \) face is parallel to the cap axis. The contraction is transmitted to the two opposites faces \( (110) \) of the crystal through two semi-cylindrical altuglass holds, whose curved faces are in contact with the interior face of the Teflon cap and the plane faces are in contact with the \( (110) \) faces of the crystal. Thus, by applying a compressional and uniaxial stress perpendicular to the \( (110) \) face, we obtain a shear stress \( \sigma_6 = \sigma_{21} \) with a maximum value. This device does not permit us to monitor the stress intensity and makes the experiment difficult; the opposite faces on which the stress is applied must be flat. But given that the E.P.R. experiment is performed in an optically excited state (obtained by irradiating the sample inside the cavity through a quartz cap), this is the only possibility.

3.3. EXPERIMENTAL RESULTS. — In Figure 4 we present a particular E.P.R. line measured at different temperatures: under stresses in Figures 4a and 4b, and without any external stress in Figures 4c and 4d.

The main features of the spectra without any stress can be summarized as follows. At the first phase transition (from phase I to phase II) the E.P.R. line splits in two singularities. As the temperature is lowered the spectrum evolves rapidly, showing a succession of three singularities, seen in Figure 4c. However we remark that the low field singularity (marked by
Fig. 4. — Behaviour of line in the (a, b) plane: under stresses a) and b), without stress c) and d). a) The spectra in phase II exhibit only two singularities. b) During the second transition, the spectra move from a two singularities system to another one. The singularity (indicated by an arrow) remained in phase III, appears in this range of temperature. c) The spectra exhibit early in phase II four singularities. Indeed, the low field singularity is broaden. The singularity (indicated by an arrow) remained in phase III is already present. d) In phase III the spectra exhibit two singularities as in (b). We note a change in the splitting between (b) and (d).

the symbol $\uparrow$) is broaden because it is itself the superposition of two singularities, as can be observed in Figure 2 where four singularities are clearly separated. During the second phase transition (shown in Fig. 4d) two singularities disappear: the one near 3950G and the other partially overlapping with the low field singularity (and marked by the symbol $\uparrow$).

Indeed, this line narrows proving the phase transition. Phase III is characterized by a spectrum with two singularities. Finally we remark that the high field singularity (indicated
by an arrow in Fig. 4d) that persists in phase III is the one which appears first in phase II (see arrow in Fig. 4c).

Under an applied stress the spectra (Fig. 4a and 4b) are simplified. In phase II (Fig. 4a), as in phase III (Fig. 4b), they exhibit only two singularities. Four singularities appear in the temperature range where the two phases coexist. The two singularities that appear last are the ones that persist in phase III, and, in particular, the high field singularity indicated by an arrow in Figure 4b. During the phase transition from phase II to phase III we move from a two singularity system to another one and the splitting between singularities shows a gap in the two phases. We can also remark that the splitting between singularities is smaller with stress than without.

Although we observe the two transitions in the stressed sample, it is not possible to determine the effect of the stress on the phase transition temperature for two reasons:

- With our experimental device we do not have access to the absolute temperature.

- According to equation (7), the splitting between the singularities is not comparable between the two experiments (more important in the sample without stress than in the stressed one). So the sample itself cannot be used to recalibrate the temperature between the two types of experiments.

In the stressed sample experiment (Figs. 4a and 4b) the spectrum is that which is generally observed during the first order phase transition: single spectrum in phase II and in phase III, and a superposition of two spectra in the vicinity of the phase transition \( T_{II} = 17 \) K. We do not observe any persistence of one phase in the other. So we think that the high field singularity, which is present in the two phases when the sample is not stressed, cannot be attributed to the persistence of one phase in the other.

The two domains can be differentiated because the rotations of the molecules in each of them are not equivalent (their rotation axes do not correspond to each other by the symmetry operation which is lost at the phase transition [15, 16]). Moreover the naphthalene molecular probe does not account for the plane wave modulation. This particular behaviour of the naphthalene molecules can also suggest a possible location of the guest molecule within the domain boundaries. This last suggestion is supported by the behaviour of the hydrogenated or deuterated phenanthrene probes [24, 27]: the incommensurate distributions associated with the two domains are confused (sample without stress), and account for a plane wave modulation. Certainly the sizes of the molecular probes play an important role.

4. Conclusion

In previous papers [15, 16] we have developed the study of the incommensurate phase of biphenyl by E.P.R. in a photo-excited state of a naphthalene probe. Analyzing the experimental results, we conclude that a superposition of two incommensurate distributions arises from each domain.

In this paper we have determined, using Landau theory, the relevant stress allowing the differentiation between domains. Moreover, we have designed a particular device to apply a shear stress on the sample inside the cavity. It is important to emphasize that the application of a stress to such a molecular system is difficult. Indeed, several samples were broken during the experiment because of strains. Moreover, even when this experiment is correctly performed, by heating the crystal from the low temperature phase, some strains remain and broke the crystal. The experimental spectra obtained under stresses, are typical of a single modulated displacement field. They demonstrate that we have successfully favoured one domain over the other in phase II and confirm the previous result [16]. In particular they clearly show the
existence of two displacement fields associated with the two chains of the naphthalene probe. However, with this particular device we cannot analyze the E.P.R. spectra in all the planes nor can we determine the spin Hamiltonian parameters either.

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