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Phase Pinning by EPR Probe in Biphenyl Doped with Naphthalene

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Abstract. — The naphthalene Electronic Paramagnetic Resonance probe used to study the phase transitions in biphenyl does not account for the plane wave modulation of the incommensurate phase II. Its EPR spectra yields a phase distribution which looks like a “multi-soliton regime”. Moreover, the splitting between the edge singularities is not symmetrical in contradiction with a linear one. This behaviour is not exhibited by the phenanthrene EPR probe whose spectra account well enough for the plane wave modulation with a linear coupling to the order parameter. To analyse the defect behaviour of the probe, we first introduce a coupling between the probe and the modulation wave and determine the phase distribution within the phenomenological Landau theory. Furthermore, a calculation based on intermolecular interaction is performed in order to describe the microscopic origin of this distribution and is applied to naphthalene and phenanthrene molecular probes.

1. Introduction

In an incommensurate system, the phase correlation radius of the modulation is “infinite” even far from the phase transition, but the defects which couple to the modulation break this long range order [1] and can impose a phase value which minimize their energy. The experimental data concerning the influence of defects on the properties of incommensurate phase refer mostly to the multi-soliton regime [1–3].

Generally, the Electron Paramagnetic Resonance (EPR) probes introduced diluted in a diamagnetic material are chosen in such a way that they do not modify the crystalline cell: the relevant parameters are the charge and the ionic radius. Such a situation is encountered in Rb₂ZnCl₄ doped with Mn²⁺ which substitutes Zn²⁺ [4]. In another case, the paramagnetic ion fits the size of the substituted ion but needs a charge compensation as in ThBr₄ or ThCl₄ where Gd³⁺ substitutes Th⁴⁺ with a charge compensation on the Br⁻ or Cl⁻ site [5,6]. In all these cases, the defect is a non extensive one, and, in the incommensurate phase, these EPR probes account for the modulation.

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The theoretical study of EPR lines in an incommensurate phase is complicated. Nevertheless, Blinc [7] gave a simplified method to reconstruct the resonance spectra. At the transition, each high temperature line gives rise to a distribution that is the sum of local lines whose width and position depend on the local phase of the modulation:

$$\phi(r) = k \cdot r + \phi_0$$

(1)

where \( \phi \) takes all the values between 0 and \( 2\pi \) modulo \( 2\pi \). Therefore, \( I(H) \), the intensity of the incommensurate line for a magnetic field \( H \), is given by:

$$I(H) = \int_{-\pi}^{+\pi} P(\phi)f\left(\frac{H - H(\phi)}{\ell(\phi)}\right) d\phi$$

(2)

where the function

$$f\left(\frac{H - H(\phi)}{\ell(\phi)}\right)$$

(3)

describes the local line shape. It is an individual line resulting from an EPR probe which resonates for a magnetic field \( H(\phi) \). \( \ell(\phi) \) represents its width, and \( \phi \) is the local phase of the modulation. \( P(\phi) \) is the distribution of the phases \( \phi \) which accounts for the regime of the modulation: \( P(\phi) \) is constant in the plane wave regime and is given by the sine-Gordon equation in the multi-soliton regime [7]. In all cases the phase values between 0 and \( 2\pi \) are taken into account and the EPR spectra account for the phase distribution.

In the microscopic description, a local line position is defined by:

$$H(\phi) = H_0 + h_1 u(\phi) + h_2 u^2(\phi); \quad u(\phi) = A \cos(\phi + \phi_0).$$

(4)

It is as a function up to second order of the local amplitude \( u(\phi) = A \cos(\phi + \phi_0) \) of the order parameter. \( H_0 \) is the line position in the high temperature phase and \( A \) is the order parameter amplitude.

For a molecular crystal such as biphenyl, the EPR probes are molecules with large extensions which nearly modify half of a cell. Therefore, we expect them to act on the phase of the modulation as defects would. Figure 1a shows an EPR spectrum of phenanthrene-\( \text{H}_{10} \) in the incommensurate phase II of biphenyl. This spectrum exhibits the features of a plane wave modulation [8]. Figure 1b shows the EPR spectrum of naphthalene-\( \text{d}_{8} \) in the same conditions: this spectrum is typical of a multi-soliton regime [7] while the modulation is a plane wave one [9]. Hence, the two molecular probes do not exhibit the same behaviour, and the naphthalene one yields a defect character.

This paper devoted to this problem is outlined as follows. In Section 2, we recall the properties of the biphenyl crystal, the experimental method and the characteristics of the EPR probes in the normal phase. In Section 3, we present the experimental results for phenanthrene and naphthalene in the incommensurate phase II, and we discuss the particular behaviour of the naphthalene used as the EPR probe. In Section 4, we determine the phase distribution of the EPR probe and apply it to simulate the experimental spectra. In the last part, we describe the microscopic origin of the probe behaviour.

2. Characteristic Features of Biphenyl and EPR Probes

2.1. Biphenyl Properties. — The biphenyl molecular crystal with the chemical formula \( \text{C}_{12}\text{H}_{10} \) consisting of two phenyl rings connected by a single C-C bond, has been the object of extensive studies during these last few years. At room temperature, in the normal phase
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Fig. 1. — Typical lines in the incommensurate phase II of biphenyl: a) with the phenanthrene-$h_{10}$ probe; b) with the naphthalene-$d_{10}$ probe.

Fig. 2. — Crystal structure of biphenyl in the high temperature phase I: $a = 8.12$ Å, $b = 5.63$ Å, $c = 9.51$ Å, $\beta = 95.1^\circ$, from reference [12].

(named phase I), the crystal symmetry is $P2_1/a$ with two molecules in the unit cell (Fig. 2). When it is cooled from the high temperature phase, the crystal exhibits two structural phase transitions toward some incommensurate states at $T_1 = 40$ K and $T_{II} = 17$ K [9,10]. These transitions are characterized by a modulated twist of the two phenyl rings around the long molecular axis.
At $T_I = 40$ K, a second order phase transition occurs and the crystal becomes incommensurate. The order parameter has four components ($n = 4$) [9–11] and the wave vector star has four arms:

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

(5)

for this complicated phase (named phase II). It is worth noting that the high order satellites were not observed in this phase, which means that the modulation is a plane wave one [12,13]. After a first order phase transition which occurs at $T_{II} = 17$ K, the crystal remains (down to very low temperature) in a second incommensurate phase (namely phase III) whose modulation wave vector is:

$$\pm q_b = \frac{(1 - \delta_b)}{2} b^*$$

(6)

and exhibits some satellites up to the third order.

These phase transitions were extensively studied by electronic absorption and emission spectra in pure biphenyl-d$_{12}$ [14], neutron scattering [9,10,12,13], X-ray scattering [15,16] and Raman scattering [17,18]. Local investigations were also performed such as Nuclear Magnetic Resonance (NMR) [19,20] and Electronic Paramagnetic Resonance [21–24]. Nevertheless, the first investigations by EPR [21,22] were interpreted without any reference to the incommensurate characteristics of the states.

There are two ways to consider an $n = 4$ order parameter:

- a superposition of two displacement fields, each one associated with the wave vectors $\pm q_{s1}$ and $\pm q_{s2}$ (2q modulated system);
- a bi-domain structure where, in each domain, the displacement is associated with the wave vectors $\pm q_{s1}$ or $\pm q_{s2}$ (1q modulated system).

Several neutron scattering [10,11] and the Raman scattering [25] studies showed the 1q bi-domain structure of the incommensurate phase II. A second class of studies, which gives more direct evidence of this behaviour, is concerned with local techniques: NMR [26] experiments performed on hydrogen nuclei and EPR studies [23,24] without any stress. The more direct proof of the bi-domain structure was performed by comparing an EPR study without and under stresses [27]. This experiment showed a change in the spectrum when stress was applied, demonstrating the disappearance of one domain.

2.2. EXPERIMENTAL METHOD. — In order to perform an EPR experiment on diamagnetic biphenyl we had to include some probes in the pure biphenyl in order to simulate conditions in the pioneer work [28]. The naphthalene (or phenanthrene) diluted molecules substitute the biphenyl one with a concentration equal to 0.5%. The biphenyl crystal was grown by lowering the melt through a temperature gradient (Bridgman method). The products, biphenyl, naphthalene and phenanthrene, were purchased from the Aldrich company and were purified before use.

The ground state in both naphthalene and phenanthrene is not paramagnetic. Therefore, the EPR experiments were performed in the lowest triplet state of these molecules [29]. The particular device to used to perform these experiments is described elsewhere [24,30]. EPR measurements were performed on an X-band spectrometer (9.5 GHz) equipped with a cryostat. The crystal was cooled down by helium gas flowing in a Dewar inside the cavity. The precise temperature of the sample may differ because of the temperature gradient of the flow.

2.3. PROPERTIES OF THE EPR PROBE. — In the normal phase, two systems of lines are observed [8,24] which correspond to the two inequivalent naphthalene (or phenanthrene)
Table I. — Orientation of the naphthalene [24] (Na) and phenanthrene [23] (Ph) spin Hamiltonian and of the biphenyl [31] (Bi) molecular axis (Θ_M, Φ_M) in the crystal frame a, b, c*.

<table>
<thead>
<tr>
<th></th>
<th>Θ_Na</th>
<th>Φ_Na</th>
<th>Θ_Bi</th>
<th>Φ_Bi</th>
<th>Θ_Ph</th>
<th>Φ_Ph</th>
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<tr>
<td>OX axis</td>
<td>18°</td>
<td>7°</td>
<td>17°</td>
<td>-5°</td>
<td>16°</td>
<td>0°</td>
</tr>
<tr>
<td>OY axis</td>
<td>95°</td>
<td>-63°</td>
<td>101°</td>
<td>-58°</td>
<td>98°</td>
<td>-63°</td>
</tr>
<tr>
<td>OZ axis</td>
<td>108°</td>
<td>38°</td>
<td>103°</td>
<td>35°</td>
<td>105°</td>
<td>29°</td>
</tr>
</tbody>
</table>

molecules in the cell. Three lines for each molecule are typical for a S = 1 spin: the Δ_ms = 2 transition in low field and the two Δ_ms = 1 transitions in high field. The anisotropy curves which describe the line positions versus the direction of the static magnetic field in the three crystallographic planes, give the spin Hamiltonian parameters defined by:

\[ \mathcal{H}_0 = \beta \mathcal{S} \mathcal{g} \mathcal{H} + \sum_{m=-2}^{m=2} B_2^m O_2^m \]  \hspace{1cm} (7)

and the orientation of the EPR probes in the biphenyl host crystal. In the molecular axis system the spin Hamiltonian parameters are:

\[ B_2^0 = 340 \times 10^{-4} \text{ cm}^{-1}; \quad B_2^2 = -150 \times 10^{-4} \text{ cm}^{-1} \]  \hspace{1cm} \text{for the naphthalene [24] probe}

\[ B_2^0 = 354 \times 10^{-4} \text{ cm}^{-1}; \quad B_2^2 = -484 \times 10^{-4} \text{ cm}^{-1} \]  \hspace{1cm} \text{for the phenanthrene one [8].}

The \( \mathcal{g} \) tensor is isotropic with the free electron value \( g = 2.0023 \). The molecular axes are given in Table I and can be compared with those of the biphenyl molecule in the pure crystal [31]. We can see that the molecular probes nearly take the same orientation as the biphenyl one. Nevertheless, it is worthy to note that these molecules differ in their sizes since the molecular widths are \( l = 2.0 \) Å, 2.8 Å, 3.0 Å in biphenyl, naphthalene, phenanthrene, respectively and the molecular lengths are \( L = 7.0 \) Å, 3.9 Å, 7.0 Å respectively (see Fig. 3).

We can see that the width of the phenanthrene and naphthalene molecule are higher than that of the biphenyl molecule, which must probably hinder the rotation of the probe around its long axis. Biphenyl and phenanthrene have the same length while naphthalene is shorter. This geometry may favour a rotation around an axis perpendicular to the long axis of the molecular probe.

3. Experimental Results in the Incommensurate Phase II

3.1. Phenanthrene-h_{10} Spectrum Particularities [8]. — The behaviour of the phenanthrene-h_{10} probe is a classical one [8]. If we consider one line of its EPR spectra shown in Figure 4, we can see that this high temperature line splits at the phase transition into two symmetrical singularities. This behaviour corresponds to a typical linear splitting described by the \( h_1 \) parameter (in Eq. (4)). Moreover, the singularity intensities are symmetrical, which means that the phase distribution \( P(\phi) \) is uniform as expected for a plane wave regime. The line splitting follows the law \( (T_1 - T)^{\beta} \) with \( \beta = 0.41 \), which corresponds to the order parameter
Fig. 3. — Size comparison of different aromatic molecules. The naphthalene molecule is shorter than the biphenyl one while the phenanthrene one is longer: a) biphenyl: $L_b = 7.0 \ \text{Å}, \ t_b = 2.0 \ \text{Å}$; b) phenanthrene: $L_n = 7.0 \ \text{Å}, \ t_n = 3.0 \ \text{Å}$; c) naphthalene: $L_p = 3.9 \ \text{Å}, \ t_n = 2.8 \ \text{Å}$.

behaviour for a universal class $n = 4, d = 3$ \[32\]. Finally, it was shown that this probe does not allow to differentiate the two domains. If we remember the plane wave character of the modulation in phase II of biphenyl, then it appears that the phenanthrene-h_{10} EPR probe behaviour accounts well enough for this modulation.

The parameters $h_1$ and $h_2$ in equation (4) originate from the modulated spin Hamiltonian parameters \[8, 23, 24, 27\]. Indeed, in the incommensurate phase the spin Hamiltonian reads:

\[
\begin{align*}
\mathcal{H}(\phi) &= \mathcal{H}_0 + \Delta \mathcal{H}(\phi) \\
\Delta \mathcal{H}(\phi) &= \sum_{m=-2}^{m=2} \Delta_1 B_2^m(\phi)O_2^m + \sum_{m=-2}^{m=2} \Delta_2 B_2^m(\phi)O_2^m
\end{align*}
\]

where $\mathcal{H}_0$ is the high temperature phase spin Hamiltonian and $\Delta \mathcal{H}(\phi)$ the modulated spin Hamiltonian developed up to second order of the displacement field experienced by the EPR probe. The main results obtained are the following:

- the comparison between the X band spectra \[8\] and those obtained in low field experiments \[21, 22\] have shown that the main parameters in the modulated spin Hamiltonian $\Delta \mathcal{H}(\phi)$ are $\Delta_{1,2}B_2^1(\phi), \Delta_{1,2}B_2^{-1}(\phi), \Delta_{1,2}B_2^{-2}(\phi)$;
- the EPR probe does not account for a twist displacement, but accounts for a rotation displacement;
Fig. 4. — Phase transition of biphenyl shown with the phenanthrene-h$_{10}$ molecular probe behaviour in the (b, c) plane.

- symmetry considerations [23] have shown that a large second order term in the X band spectra leads to a more important splitting than the one observed in zero field experiments [21, 22]. Thus, the splitting is essentially a first order function of the local displacement field, in agreement with the critical exponent value $\beta = 0.41$, i.e the local line position $H(\phi)$ in equation (4) must contain a predominant $h_1 \cos(\phi)$ term. Furthermore, the investigation of the incommensurate splitting as a function of the static magnetic field orientation [8] allows us to determine the spin Hamiltonian:

$$\Delta H(\phi) = \sum_{m=-2,-1,1} \Delta_1 B_2^m \cos(\phi - \phi_2^m) O_2^m$$

with the following numerical values at $T = 20$ K [8]:

$$\Delta_1 B_2^{-2} = 20 \times 10^{-4} \text{ cm}^{-1}, \quad \Delta_1 B_2^{-1} = 0 \times 10^{-4} \text{ cm}^{-1}, \quad \Delta_1 B_2^{1} = 13 \times 10^{-4} \text{ cm}^{-1}$$

$\phi_2^m = \phi$ in equation (10),

and with the temperature dependent amplitude $\Delta B_2^m(T) = A_2^m (T - T)^{0.41}$, in agreement with the experimental splitting.
This modulated spin Hamiltonian describes a rotation with an angle amplitude equal to 1.3° around an axis \( u \). This axis whose components in the molecular axis system are \( u_x = 0.00, u_y = 0.43, u_z = -0.90 \) is perpendicular to the long molecular axis which is parallel to the twist axis (see Fig. 3).

Moreover, the rotation amplitude of the molecular EPR probe is a linear function of the twist amplitude of the biphenyl molecule. In this case, the EPR probe cannot account for the biphenyl movement, but it does not act on the phase of the modulation which remains a plane wave one.

3.2. NAPHTHALENE-\( \text{d}_8 \) SPECTRUM PARTICULARITIES [23, 24, 27]. — Figure 5 shows the behaviour of the naphthalene-\( \text{d}_8 \) line as a function of temperature; the static magnetic field is in the (a, b) plane. This behaviour is similar for all the lines, for the two crystallographically different molecular probes in the cell and in all the planes. When the temperature is lowered from the high temperature phase, each line exhibits different changes at \( T_I = 40 \text{ K} \) and \( T_{II} = 17 \text{ K} \) due to the phase transitions which occur in the biphenyl crystal.

In phase II we observe three or four singularities which characterize an incommensurate spectrum [23]. The EPR experiments under stresses show that each spectrum is the superposition of two spectra [27]: one spectrum per domain. In the high temperature phase, there are two crystallographically equivalent sites. Therefore, in phase II a site is the image of another one by applying the symmetry plane lost at the phase transition. In this transformation,
the orientation of the biphenyl molecule (or the naphthalene one) is changed. Thus, in phase II we have two types of molecules with the same orientation but belonging to different domains transforming themselves by the symmetry plane. As the displacement fields on the two types of molecules are not exactly the same, it gives rise to two different incommensurate superposed lines. By applying stresses which break the symmetry, one domain becomes privileged and only one incommensurate line remains [27].

At the second phase transition, two singularities decrease while the two other increase in such a way that the total intensity is preserved [23]. During this phase transition the singularity positions remain nearly unchanged, and the intensity dissymmetry of the two remaining singularities in phase III is conserved. In the phase transition temperature range, the intermediate spectra can be simulated with a superposition of a spectrum of phase II and a spectrum of phase III; the proportion being temperature dependent [23]. This result accounts for the phase coexistence which is typical for a first order phase transition.

It has also been shown [24] by symmetry consideration and thanks to the modulated spin Hamiltonian that the naphthalene probe does not account for the twist in phase III but turns round an axis $u$ whose components in the molecular axes are $u_x = 0.00$, $u_y = 0.85$, $u_z = -0.52$ and with an amplitude equal to $2.5^\circ$. This movement is described by the modulated spin Hamiltonian of equation (10) with the numerical values at $T = 15$ K [24]:

$$\Delta_1 B_2^2 = -7 \times 10^{-4} \text{ cm}^{-1}, \Delta_1 B_2^{-1} = 0 \times 10^{-4} \text{ cm}^{-1}, \Delta_1 B_2^0 = -87 \times 10^{-4} \text{ cm}^{-1}$$

3.3. Discussion. — In phase II (Fig. 5), taking into account the domain effect on the spectra, each spectrum associated to one domain is characterized by two dissymmetrical edge singularities [23]. Such spectra could be analysed in one of several ways, well known for an incommensurate system:

- the more simple incommensurate spectrum is one with a linear splitting (i.e. $h_1 \neq 0$ and $h_2 = 0$ in Eq. (4)) where two singularities symmetrically grow on both sides of the high temperature line position and have the same intensity. This hypothesis is clearly in contradiction with the experimental results which show a dissymmetrical splitting [24]. Furthermore, it would be necessary to introduce a non uniform phase density to account for the singularity intensities while the modulation is a plane wave [12].

- a dissymmetrical splitting with symmetrical singularities is typical of a pure second order term in expression (4). It may be in agreement with the fact that the naphthalene molecular probe does not account for the twist [24], and consequently it may mean that the local amplitude of rotation is proportional to the square of the local twist. But, as in the first case, it is necessary to introduce a non uniform phase density to account for the dissymmetrical intensities, whose origin must to clarified.

- Dissymmetrical singularity intensities can be attributed to the presence of first and second order terms in equation (4). Such a reconstruction with relation (2) is sketched in Figure 6. However, these parameters cannot account for the dissymmetrical splitting which would be due to a predominant second order term $h_2$ larger than the first order one. Moreover, the intensity dissymmetry obtained in this hypothesis is insufficient (see Fig. 6). When $h_2$ is weak compared with $h_1$, the spectrum exhibits a small dissymmetry which increases when the ratio $h_2/h_1$ increases; then when $h_2 \approx h_1$ the dissymmetry stops to increase but the intense singularity splits into two singularities when $h_2$ is still increasing. Therefore, we still must additionally introduce a phase distribution whose origin must also be clarified.

There are no other classical possibilities to account for the spectra: in all the cases a phase distribution is necessary while the modulation is sinusoidal [12,13] and some large second order terms are also necessary in the two last hypotheses. Symmetry considerations show [23,24] that a large second order term in X band spectra leads to a more important splitting than that
observed in zero field experiments. Thus, the splitting must essentially be a first order function of the local displacement field, i.e. the local line position \( H(\phi) \) must contain a predominant \( h_1 \cos(\phi) \) term. However, the splitting between edge singularities as a function of temperature follows a law \((T_1 - T)^\beta\) with \( \beta = 0.41 \) [23] which corresponds to an order parameter behaviour for a universal class \( n = 4, d = 3 \) [32]. This result suggests that the amplitude of the rotation linearly depends on the twist amplitude.

These remarks argue in favour of a first order splitting. But, in this case, it is not possible to have any dissymmetrical singularity intensities and any dissymmetrical singularity splitting. The single solution, to account simultaneously for the first order splitting and the dissymmetries, is to introduce a special phase distribution which forbids some displacement amplitudes in the relation \( u(\phi) = A \cos(\phi + \phi_0) \). We see that this requirement is equivalent to forbid some phase values.

One might think that the naphthalene molecular probes pin the phase of the modulation as a classical defect does. However, this hypothesis does not support the results of the phenanthrene which is a longer molecule than naphthalene and would have to act more seriously on the phase. According to this remark, naphthalene has a very particular behaviour.

The influence of defects on structural phase transition was extensively studied these last years [1–3]. A particular case concerns the incommensurate system. By their action on the modulation, the defects are classified into two classes: fixed defects and mobile defects.
A defect of the first class fixes the phase of the modulation at a preferential value which corresponds to a minimum value of its energy. Two limiting cases arise:

- high coupling: each defect imposes its phase on its site;
- low coupling: the defect concentration is so important that the modulation cannot adapt itself to each defect, and a phase distortion appears in the region of high defect density.

The defects of the second class originate the memory effect due to the diffusion of the interaction between punctual defects and the modulation wave. In this interaction the defects fit the local phase of the modulation by moving (displacement or orientation). Memory effects, due to the competition between the density defect wave and the locking potential, are observed in the vicinity of the locking transition. Although no locking transition exists in our case, we think the naphthalene probe could be considered as a mobile defect, because this molecule fits the modulation (rotation of the molecular probes). Nevertheless, our measurement system does not allow us to evidence any hysteresis phenomena. To account for this particular phase distribution, we consider two models of phase density in the following section.

4. Determination of the Phase Density \( P(\phi) \)

In a multi-soliton regime, the phase \( \phi(r) \) is no longer a linear function of the space variable \( r \). However, it is equivalent to a plane wave regime \( \phi(r) = k \cdot r \) but with a non uniform phase density \( P(\phi) \). If the probe exactly accounts for the modulation, it experiences all the phases with a phase distribution given by \( P(\phi) \). But in a more general case, where the probes behave as defects, one could imagine that the probes privilege some particular phases of the modulation in such a way that the phases experienced by the probe are distributed with a phase distribution \( P'(\phi) \) different of \( P(\phi) \). So even if the modulation is a plane wave one, the probe could account for an effective “multi-soliton” regime which would result from the interaction between the probe and the modulation. If we emphasize that in an EPR experiment we measure what happens exactly on the defect itself, then the observed phase distribution should be the \( P'(\phi) \) one defined above.

In the following section, we will show how a sinusoidal modulation leads to a non uniform phase distribution on the defects.

4.1. Distribution of the Phase Experienced by the Defects. — When the EPR probe behaves as a defect, its displacement field is no longer the modulation one. However, it should depend on it through the movement of the neighbouring molecules which approximately follow the modulation displacement field. A reasonable way to determine the phase distribution \( P'(\Phi) \) is to assume that the defect displacement field depends on the displacement field phases of the neighbouring biphenyl molecules. We transfer to the defect phase the displacement field anomalies, that means the defect phase distribution is no longer the one of the pure biphenyl. In the following model, we look at the crystal overall, while in the model developed in the next chapter we calculate the local field displacement of the molecular probe for a given value of the displacement field of the neighbouring biphenyl molecules. Then, the probe local phase is subjected to two kinds of energy:

- an elastic energy which always tends to bring back the wave to a plane wave one;
- a defect energy as a result of the molecular packing of the molecular probe.

The free energy of the system in a continuous model is [2]:

\[
F = \int \left[ \frac{1}{2} k \left( \frac{d\phi}{dx} \right)^2 + \sum_j (V_\eta(x - x_j)\eta(x) + V_\xi(x - x_j)\xi(x)) \right] \, dx \tag{11}
\]
where the first term in the integrand represents the elastic energy of the modulation and the second term the free energy of the defects linearly coupled to the two components $\eta$ and $\zeta$ of the local order parameter. The phase $\phi$ is defined by:

$$\eta = A \cos \phi \quad \text{and} \quad \zeta = A \sin \phi$$  \hspace{1em} (12)

where $A$ is the amplitude of the order parameter. $x_j$ represents the position of the $j$th defect along the modulation.

If we assume $V_\eta$ and $V_\zeta$ to be delta-functions (assumption of local defect), i.e. $V_\eta(x) = V_\eta^0 \delta(x)$ and $V_\zeta(x) = V_\zeta^0 \delta(x)$, then the free energy becomes:

$$F = \int \frac{1}{2} k \left( \frac{d\phi}{dx} \right)^2 \; dx + \sum_j \left( V_\eta^0 \cos \phi_j + V_\zeta^0 \sin \phi_j \right)$$  \hspace{1em} (13)

where $\phi_j = \phi(x_j)$. We minimize the free energy in two steps:

- Firstly, we fix the phase $\phi_j$ on the defect and we minimize the first term, the solution reads [33]:

$$\phi(x) = \frac{x_{j+1} - x}{x_{j+1} - x_j} \phi_j + \frac{x - x_j}{x_{j+1} - x_j} \phi_{j+1} \quad \text{for} \quad x_j < x < x_{j+1}$$  \hspace{1em} (14)

so that the phase $\phi$ varies linearly between the $j$th and the $(j+1)$th defects;

- Secondly we insert this result in the free energy and we minimize it in relation with the variables $\phi_j$, then the free energy reads:

$$F = \sum_j \frac{1}{2} k \left( \frac{\phi_{j+1} - \phi_j}{x_{j+1} - x_j} \right)^2 (x_{j+1} - x_j) + A \sum_j \left( V_\eta^0 \cos \phi_j + V_\zeta^0 \sin \phi_j \right)$$  \hspace{1em} (15)

and after minimization, we obtain:

$$\left( \frac{\phi_j - \phi_{j-1}}{x_j - x_{j-1}} \right) - \left( \frac{\phi_{j+1} - \phi_j}{x_{j+1} - x_j} \right) = \frac{A}{k} (-V_\eta^0 \sin \phi_j + V_\zeta^0 \cos \phi_j).$$  \hspace{1em} (16)

If we change the phase origin, this equation can be written as:

$$\left( \frac{\phi_{j+1} - \phi_j}{x_{j+1} - x_j} \right) - \left( \frac{\phi_j - \phi_{j-1}}{x_j - x_{j-1}} \right) = \frac{A}{k} V_0 \sin \phi.$$  \hspace{1em} (17)

After the first term of equation (17) is divided by the factor $(x_j - x_{j-1})$, we recognize in the continuous limit the second derivative of the phase $\phi$. Now we replace, in the second member of equation (17), the additional factor $1/(x_j - x_{j-1})$ by $1/l_d$ where $l_d$ represents the average distance between two consecutive defects. It is then obvious that this factor is the concentration $c_d$ of defects in the crystal. Therefore, making the continuous approximation, equation (16) writes:

$$\frac{d^2\phi}{dx^2} = K \sin \phi \quad \text{with} \quad K = \frac{Ac_dV_0}{k}$$  \hspace{1em} (18)

where $\phi(x)$ now represents the continuous spatial variations of the defect phase. We recognize the equation which describes the soliton regime [7]. It is now possible to find the phase distribution by integrating equation (18), since we have the relation $P(\phi) \propto dx/d\phi$. First integration gives:

$$\left( \frac{d\phi}{dx} \right)^2 - \left( \left( \frac{d\phi}{dx} \right)_0 \right)^2 = 2K(\cos \phi - \cos \phi_0)$$  \hspace{1em} (19)
or
\[ \left( \frac{d\phi}{dx} \right)^2 = 2K \cos \phi - (2K \cos \phi_0 - K_0) \text{ with } K_0 = \left( \frac{d\phi}{dx} \right)_0^2 \] (20)

Equation (18) is the same as the one describing the pendulum motion, two cases which depend on the initial conditions can be considered:

- The first corresponds to the usual multi-soliton regime and is analogous to the turning pendulum. It occurs when:
  \[ 2K \cos \phi_0 - K_0 < -2K. \] (21)
In this case all the phases between 0.2 \( \pi \) modulo 2\( \pi \) are realized and the phase density is given by:
\[ P(\phi) \propto \frac{dx}{d\phi} \propto \frac{1}{\sqrt{K_0 - 2K \cos \phi_0 + 2K \cos \phi}} \propto \frac{1}{\sqrt{\delta + 2K \cos \phi}}. \] (22)
- The second corresponds to the oscillating pendulum and occurs when:
  \[ -2K < 2K \cos \phi_0 - K_0 < 2K. \] (23)
In this case, some phases are forbidden because \( 2K \cos \phi - (2K \cos \phi_0 - K_0) \) must be a positive quantity. Thus, the phase density can be written as:
\[ P(\phi) \propto \frac{1}{\sqrt{2K(\cos \phi - \cos \phi_1)}} \text{ for } \phi \in ] - \phi_1, \phi_1[ \] (24a)
and
\[ P(\phi) = 0 \text{ for } \phi \notin ] - \phi_1, \phi_1[ \] (24b)
where \( \phi_1 \) is defined by \( \cos(\phi_1) = \frac{2K \cos(\phi_0) - K_0}{2K} \) and is named “cut phase”.

Although the phase density diverges at \( \pm \phi_1 \), the integral \( \int_{-\phi_1}^{\phi_1} \frac{d\phi}{\sqrt{2K(\cos \phi - \cos \phi_1)}} \) converges toward an elliptic function in such a way that we can normalize the distribution. We will see in the next section how this distribution accounts for the experimental results.

4.2. Comparison with the Experimental Results. — The second phase distribution is more suitable to account for the experimental results of naphthalene. Indeed, we recall that the intensity of the line as a function of the magnetic field \( H \) is given by equation (2). Therefore, if we introduce the previous phase density, we obtain:
\[ I(H) = \int_{-\phi_1}^{+\phi_1} f \left( \frac{(H - H(\phi))}{\ell(\phi)} \right) \frac{d\phi}{\sqrt{2K(\cos \phi - \cos \phi_1)}} \] (25)
with
\[ H(\phi) = H_0 + h_1 \cos \phi \]
for a first order splitting.

The singularities of such a system are situated at :
\[
\begin{align*}
H_0 + h_1 & \quad \text{which corresponds to an extremum of } H(\phi) \\
\text{and} & \\
H_0 + h_1 \cos \phi_1 & \quad \text{because the phase distribution diverges at } \pm \phi_1.
\end{align*}
\] (26)
Table II. — *Experimental results: A and B chain properties* [23].

<table>
<thead>
<tr>
<th>Chain</th>
<th>Parameters</th>
<th>Distribution P(φ)</th>
<th>Rotation parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔB₁ = -87 × 10⁻⁴ cm⁻¹</td>
<td>Cut phase = 100°</td>
<td>Rotation axis:</td>
</tr>
<tr>
<td></td>
<td>ΔB₂⁻¹ = 0</td>
<td>δ = 0.001</td>
<td>ux = 0.00</td>
</tr>
<tr>
<td></td>
<td>ΔB₂ = -6 × 10⁻⁴ cm⁻¹</td>
<td></td>
<td>uy = 0.85</td>
</tr>
<tr>
<td>Chain B</td>
<td></td>
<td></td>
<td>uz = -0.52</td>
</tr>
<tr>
<td></td>
<td>ΔB₁ = 37 × 10⁻⁴ cm⁻¹</td>
<td>Cut phase = 140°</td>
<td>Rotation axis:</td>
</tr>
<tr>
<td></td>
<td>ΔB₂⁻¹ = 0</td>
<td>δ = 0.001</td>
<td>ux = 0.00</td>
</tr>
<tr>
<td></td>
<td>ΔB₂ = -12 × 10⁻⁴ cm⁻¹</td>
<td></td>
<td>uy = 0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>uz = -0.93</td>
</tr>
</tbody>
</table>

Moreover, the second singularity will be very intense because it is associated with the cut phase. Let us remark that if φ₁ ≈ π/2, then the intense singularity will appear near H₀, the high temperature line position in agreement with the experimental results.

We are able now to simulate the spectra with a modulated spin Hamiltonian containing only first order terms, this procedure was described elsewhere [23] where it was also demonstrated that this modulated Hamiltonian has the form:

\[
\Delta \mathcal{H}(\phi) = (\Delta B₂⁻²O₂⁻² + \Delta B⁻¹₂O⁻¹₂ + \Delta B₁²O₁²) \cos(\phi).
\] (27)

We recall that we must define two spin Hamiltonians, one for each chain [23], and we precise that the phase density used in this simulation is not exactly the previous one but a similar one where a parameter δ has been added to monitor the intensity of the singularities:

\[
P(\phi) = \frac{1}{\sqrt{\delta + \cos \phi \cos \phi_1}}.
\] (28)

We think the parameter δ accounts for the competition between the lattice modulation and the defect modulation wave which would have to appear in a more realistic model. We have verified that this phase density gives the correct splitting for any direction of the magnetic field, in particular, a splitting toward high or low field in agreement with the experimental result. It was necessary to verify this point to confirm the coherence of the model with the experimental results. The spin Hamiltonian parameters allow us to determine the movement of the probe [23]. All the results are shown in Table II and some simulated spectra are shown in Figures 7 and 8.

In the last section, we show the origin of this particular phase distribution for naphthalene.

5. **Origin of the Phase Distribution**

The purpose of this section is to deduce the behaviour of the molecular probe from the interactions between the molecules in the crystal. When the overlap of electron clouds is small,
the intermolecular energy may be separated into three terms: the interaction energy of the static molecular multipole moments, the dispersion energy and the repulsive energy due to the clouds overlap [34]. When there is a centre of symmetry, the first contribution is mainly a quadrupole one. The repulsive energy takes into account the interactions between individual atoms of the two molecules,

\[ U = V_1 (H-H) + V_2 (C-H) + V_3 (C-C) \]  

(29)

where the three potentials on the right-hand side apply to intermolecular hydrogen-hydrogen, hydrogen-carbon and carbon-carbon contacts, respectively.

The dispersion, quadrupole-quadrupole and hydrogen-hydrogen repulsion energies have been calculated for the equilibrium structure of crystalline naphthalene for several displaced structures which are small rotations of the molecules about their symmetry axes [34]. The authors show that the dispersion and quadrupole interaction are not minimized at the equilibrium structure while the hydrogen-hydrogen repulsions have a strong minimum. Consequently, the attractive dispersion and quadrupole interaction determine the crystal cohesion while the hydrogen-hydrogen repulsion determines the orientations of the molecules. Although this work [34] was performed for naphthalene, it is reasonable to use this result for molecules belonging

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**Fig. 7** — Reconstruction of naphthalene-d₈ incommensurate spectra of phase II, in the (a, b) plane, with a phase distribution containing a cut phase (experimental: dashed line, theoretical: solid line).

**Fig. 8** — Reconstruction of naphthalene-d₈ incommensurate spectra of phase II, in the (a, c) plane, with a phase distribution containing a cut phase (experimental: dashed line, theoretical: solid line).
Fig. 9. — This figure shows the biphenyl molecules (solid line) in the plane of the probe (dashed line) taken into account to calculate the total potential energy of the probe molecule. The equivalent molecule in the plane just above and just below are also taken into account in this calculation.

to the same family, such as biphenyl or phenanthrene. Besides, we point out that this conclusion has been used by some authors for several aromatic molecules [35–37].

Our approach to the problem of the molecular EPR probe behaviour in the incommensurate phase of biphenyl is based on the assumption that it is the intermolecular repulsive interactions which are of primary importance [34]. The orientation of the molecular probe is assumed to be given by the minimum of the total repulsive energy of the molecular probe in the field of the neighbouring biphenyl molecules. Only the first and second neighbours are taken into account since the other molecules have no contact with the probe (see Fig. 9). The total repulsive energy is a sum over pairs of atoms H-H (it is assumed that the hydrogen contacts give the largest contribution to the repulsion energy [34]).

The potential function for H-H repulsion is represented by an exponential

$$V(r) = A \exp(-cr)$$  \hspace{1cm} (30)

where $r$ is the distance between the two atoms, $c$ a constant which characterizes the hardness of the potential and $A$ is an arbitrary constant. The constant $c$ is found to be 2.1 Å$^{-1}$ for naphthalene, 1.4 Å$^{-1}$ for phenanthrene and 2 Å$^{-1}$ for biphenyl.

Figures 10a, b and c show the total potential energy of one molecule (biphenyl, phenanthrene and naphthalene respectively) in the high temperature phase as a function of its orientation. The molecule is rotated about one of its molecular axes ($x$, $y$ or $z$) and the angle is zero at the equilibrium position. We can notice a particular behaviour of naphthalene when this molecule
Fig. 10. — Total potential energy of biphenyl (a), phenanthrene (b) and naphthalene (c) as a function of the rotation angle about a molecular axis. Circle: rotation about the $x$ axis (molecular long axis). Square: rotation about the $y$ axis (molecular short axis). Triangle: rotation about the $z$ axis

is rotated about its $z$ axis. Indeed, the curve is very dissymmetrical in this case while it is parabolic in all the other cases (rotation about $x$ or $y$ axis for naphthalene and rotation about $x$, $y$ or $z$ axis for phenanthrene and biphenyl). It is worth noting that phenanthrene never exhibits such a dissymmetrical potential energy when we modify the interaction potential, while naphthalene exhibits very dissymmetrical potential energy for some suitable interaction coefficient. It is a great difference between the two probes which singularize the naphthalene probe. The effect of this dissymmetry of naphthalene will be described below.

Before performing the calculations in the low temperature phase, we verified the model in the high temperature phase. Indeed, this model must at least account for the equilibrium position of the biphenyl, naphthalene and phenanthrene molecules in the high temperature phase. This point is satisfactorily verified when we compare Tables I and III which give the experimental and calculated orientations of the molecular axes, respectively. Afterwards, the calculations
are performed with a given incommensurate modulation corresponding to the observed ones in phases II and III. The principle of this calculation is the following: we apply a torsion to the first and second biphenyl neighbours (Fig. 9) of an EPR probe (naphthalene or phenanthrene) and we calculate the new equilibrium position of the probe induced by this torsion. We point out that the torsion angles of the biphenyl molecule are defined in accordance with one of the three wave vectors $q_3$, $q_{32}$, $q_5$ defined in relations (5, 6). The new equilibrium orientation of the probe is described by the rotation which is needed to obtain this new orientation from the initial one (high temperature orientation). This allows for a direct comparison with the experimental results mentioned in Sections 3.1, 3.2 and Table II. The rotation is calculated for a set of values of the modulation phase on the probe site in order to obtain the distribution of the probe displacement as a function of the phase. The calculations were performed for naphthalene and phenanthrene probes.

The incommensurate structure of biphenyl was used for all calculations. The C-H and C-C bond length were taken as 0.9 Å and 1.4 Å, respectively, except the C-C bond between the two phenyl rings of biphenyl which is taken as 1.5 Å [38]. The calculations were performed for a torsion amplitude of 5 degrees which corresponds to the observed value for a temperature of 20 K [38].

In reference [36], the authors have found a repulsive energy of phenanthrene in biphenyl as a function of the rotation angle about the $x$-axis which exhibits a double minimum. This result seems to disagree with ours results shown in Figure 10b. In fact, we must point out that these authors have placed the repulsive centre out of the position of the hydrogen nuclei in order to obtain such a double minimum. We think that this approach is not really justified, because this artefact was used in order to interpret the multiplet structure in the electronic spectra of phenanthrene in biphenyl at a time in which the incommensurate structure of biphenyl was not known.

5.1. RESULTS FOR NAPHTHALENE. — Figures 11a and 11b show the axes and the angle of the calculated rotations, respectively, as a function of the modulation phase.

In Figure 11a, the axis of rotation is characterized by its angle with the $x$ and $z$ axes of the molecule. We can see that the axis of rotation is always perpendicular to the $x$ axis, while its angle with the $z$ axis varies with the modulation phase between 20 and 60 degrees. It should be emphasized that a rotation of the EPR probe about an axis perpendicular to its long axis ($z$ axis) was the first important and surprising experimental result [24]. However, the calculations predict a phase dependence of the rotation axis which is not reported in the experimental results. It should be noted that to find the phase dependence of the rotation axis from EPR spectra would be very difficult. Indeed, in the work [23] we demonstrate that
Fig. 11. — Axis and angle of rotation for the naphthalene molecule as a function of the modulation phase. a) Axis of rotation (modulation of phase II which gives the great splitting circle: angle between the rotation axis and the z axis of naphthalene molecule; square: angle between the rotation axis and the z axis of naphthalene molecule; b) Angle of rotation: circle: for the modulation $q_a = +0.07$, $q_b = +0.45$, $q_c = -0.13$ of phase II; triangle: for the modulation $q_a = -0.07$, $q_b = +0.45$, $q_c = +0.13$ of phase II; square: for the modulation $q_a = 0.00$, $q_b = +0.45$, $q_c = 0.00$ of phase III. The arrows on the right show the angle which correspond to a singularity in the EPR spectrum. The arrows in the centre clearly show the dissymmetrical splitting.
the parameters $\Delta B_{2}^{-1}$ and $\Delta B_{2}^{1}$ of equation (27) are related to the direction of the rotation axis. Therefore, a modulated rotation axis should entail a phase dependence of the parameters $\Delta B_{2}^{-1}$ and $\Delta B_{2}^{1}$ which should be added to the existing phase dependence of equation (27). If we drop out this point, it appears that our mechanical model gives results in good agreement with the experiments.

Figure 11b plots the rotation angle as a function of the modulation phase for the two modulations of phase II and the one of phase III. It is clear that the amplitude of the rotation is more important for one side than for the other one (see vertical arrows in Fig. 11b). This result is obviously the origin of the dissymmetrical splitting observed in the EPR spectra (Fig. 5). We can understand the origin of this effect if we remember the form of the potential energy (Fig. 10c) when the molecule is rotated about its z-axis. The large dissymmetry of the potential energy makes the naphthalene rotation towards one side more easy than the other.

We notice that the different modulations of phase II and III do not produce the same displacement field distribution. Indeed, the value of the maximum angle of rotation is not the same for the two modulations of the phase II, but, the angle distribution for the modulation of the phase III is the same as the modulation of phase II which gives the largest splitting. When we know that the extrema of these curves give the position of the singularities of the EPR spectra (see horizontal arrows in Fig. 11b), we understand why we obtain in phase II a superposition of two different spectra with the following characteristics: the singularities corresponding to the negative angle are confused and the two other singularities corresponding to the positive angle are well separated. Thus, a spectrum with at least three well resolved singularities must be observed. It is worth noting that this behaviour gives the possibility to differentiate the two domains of phase II [23, 27]. Moreover, the spectrum of phase III must be the same as that of phase II which gives the largest splitting, which is exactly what we observe by EPR. We emphasize that it is the great success of the mechanical model to be able to account for such specific behaviours of naphthalene.

If we compare the angle variation around the two extrema, we notice that this variation is slower for the extremum near the zero position (high temperature position) than for the other one. When we know that a slow variation of the angle entails an intense singularity in the EPR spectrum, we can deduce that the singularity near the zero position will be more intense than the one far from the zero position. This is another result of the mechanical model which is in good agreement with experiments.

The phase origin of the modulation is chosen in such a way that $\phi = 0$ corresponds to a maximum torsion of the molecule 1 in Figure 9. Therefore, if we investigate the phase dependence of the rotation angle, we notice that the maximum of the rotation occurs when the torsion amplitude is a maximum for the first neighbours (molecules 1, 2, 3 and 4 in Fig. 9). It is interesting to note that the torsion of biphenyl is not produced by the first neighbours but rather by the second neighbours (molecules 5 and 6) [39]. Thus, the rotation of the probe and the torsion of the biphenyl do not have the same origin. Actually, it is relatively easy to see, thanks to the Heine model [39], that molecules 5 and 6 (Fig. 9) should have two opposite rotation effects which cancel on a rigid probe.

Figure 12 plots the amplitude of the splitting (difference between maximum and minimum angle) as a function of the amplitude of the torsion. We observe that the dependence is linear with a good approximation. This result confirms the first order character of the EPR spectra deduced from the study of the temperature dependence of the splitting of the EPR lines.

5.2. RESULTS FOR PHENANTHRENE. — Compared with naphthalene, phenanthrene exhibits a simple behaviour. Figures 13a and 13b show the axes and the angle of rotation, respectively, of the phenanthrene molecule as a function of the modulation phase.
Fig. 12. — Amplitude of the rotation of naphthalene molecule (difference between maximum angle and minimum angle) as a function of the torsion amplitude.

From Figure 13a, we can see that the angle between the rotation axis and the \( x \) axis varies between 50 and 80 degrees while the angle between the rotation axis and the \( z \) axis remains around 45 degrees. The EPR spectra were interpreted with a phase independent rotation axis perpendicular to the \( x \) axis, making an angle of 25° with the \( z \) axis (see Sect. 3.1). The results of the calculations do not fit exactly to the experimental results, maybe because we did not try to determine the phase dependence of the rotation axis. Nevertheless, they show that the phenanthrene molecules rotate around an axis very different from that of the \( x \) axis.

Figure 13b shows the rotation angle as a function of the modulation phase for the two modulations of phase II and the one of phase III. The three curves are almost superposed, which means these three modulations are not distinguishable. Thus, the EPR spectra must appear as a single incommensurate line in phase II and no change must occur in the line shape at the second phase transition (between phase II and III). The splitting is symmetric and the amplitude of the rotation about 2 degrees is clearly smaller than for naphthalene, which can be explained by the sizes of the molecules. We note that the \( \phi \) dependence of the rotation angle looks like a cosine function, which means that the distribution of the displacement field is classical and corresponds to a uniform phase distribution. All these results are in agreement with the observation of a simple 1q EPR spectrum.

5.3. DISCUSSION. — It clearly appears that the model of repulsive interaction between hydrogen accounts very well for all the behaviours of the naphthalene and phenanthrene probes. We emphasize that it is a remarkable success of this mechanical model to account for the non trivial behaviour of naphthalene probe: superposition of two incommensurate spectra in phase II, conservation of one of the two spectra at the second phase transition, dissymmetry of the splitting and dissymmetry of the singularity intensities. We have related this specific behaviour to the dissymmetrical shape of the potential energy. Indeed, if we modify the potential interaction for naphthalene in such a way as to render the potential energy symmetric,
Fig. 13. — Axis and angle of rotation for the phenanthrene molecule as a function of the modulation phase. a) Axis of rotation. Full circle: angle between the rotation axis and the x axis of naphthalene molecule (This direction varies with the local phase). Empty circle: angle between the rotation axis and the z axis of naphthalene molecule. (This direction is almost constant with the phase). b) Angle of rotation. Circle: for the modulation $q_a = +0.07$, $q_b = +0.45$, $q_c = -0.13$ of phase II. Triangle: for the modulation $q_a = -0.07$, $q_b = +0.45$, $q_c = +0.13$ of phase II. Square: for the modulation $q_a = 0.00$, $q_b = +0.45$, $q_c = 0.00$ of phase III. The arrows on the right show the angle which correspond to a singularity in the EPR spectrum.
Fig. 14. — This figure shows: i) the real phase dependence of the rotation angle corresponding to a uniform phase distribution (dashed line); ii) the fictive cosine phase dependence of the rotation axis corresponding to an non uniform phase distribution with forbidden values of the phase (solid line).

Fig. 15. — Phase distribution between 0 and 180 degrees (the function is even): a) calculated from the microscopic model; b) calculated from the phenomenological model (Eq. (28)).

then the splitting becomes symmetric. Therefore, the dissymmetry of the spectra is explained by the fact that the distribution of the field displacement of the probe is dissymmetrical.

It is possible to relate the microscopic mechanical model to the phenomenological model described in the previous section. In the simple case of the phenanthrene probe, the microscopic parameter (the rotation angle \( \alpha \) of the EPR probe) is related to the modulation phase by a simple cosine function: \( \alpha = A \cos(\phi) \), and a uniform distribution of the phase \( \phi \) (\( P(\phi) = \text{constant} \)) applies. \( A \) is the amplitude of the order parameter which is temperature dependent and
it occurs in a classical critical behaviour [32]. The situation is different with the naphthalene probe because the rotation angle $\alpha$ is no longer a cosine function of the phase $\phi$ but some function $f$: $\alpha = Af(\phi)$, associated with an uniform distribution of the phase $\phi$. The order parameter amplitude $A$ appears as a multiplicative factor to ensure that the angle splitting has a critical temperature behaviour as observed. This situation is equivalent to the following one where we write $\alpha = A \cos(\phi)$, but, it is now associated with a new phase distribution $P'(\phi)$ (it is what we do when we simulate the spectra with the relations (2, 4) and in Eq. (12) of the phenomenological model). In Figure 14, the phase dependence angles corresponding to both situations are plotted. The dotted line which is a cosine function with a flattened negative part is similar to the calculated phase dependence angle plotted in Figure 11b. It is obvious that the fictive phase distribution $P'(\phi)$ associated with the solid line ($\alpha = A \cos \phi$) is zero between $\phi_1$ and $\phi_1'$ (see Fig. 14), because for this $\phi$ value range, $\alpha = A \cos \phi$ is out of the real rotation angle range. These phases are called forbidden phases. Moreover, $P'(\phi)$ seriously diverges at $\phi_1$ since it corresponds to a very flat extremum of the angle. We can rebuild the $P'(\phi)$ phase distribution as follows. For a given range of rotation angle $[\alpha, \alpha + \Delta \alpha]$, corresponds two ranges of $\phi$ values $[\phi, \phi + \Delta \phi]$ and $[\phi', \phi' + \Delta \phi']$, associated to $A \cos \phi$ and $Af(\phi)$ respectively, where the ranges $\Delta \phi$ and $\Delta \phi'$ are generally different. If we assume that the real phase distribution is uniform (i.e. $P(\phi) = \text{constant} = P$) then the range $\Delta \phi'$ corresponds to a number of probes $\Delta n = P \Delta \phi'$, but the same number of probes must also be associated with the fictive phase $\phi$, thus we have $\Delta n = P'(\phi) \Delta \phi$. These relations entail $P'(\phi) \propto \Delta \phi'/\Delta \phi$. Figure 15 shows two phase distributions: one given by the microscopic model and the other calculated from equation (28). We can note a very good agreement between these two distributions.

6. Conclusion

First, to demonstrate the particular behaviour of the naphthalene EPR probe, we compared the EPR results obtained in incommensurate biphenyl with naphthalene and phenanthrene EPR probe. It has been shown that the splitting of the line is a linear function of the local order parameter in spite of the dissymmetries. Furthermore, it has been demonstrated that a special phase distribution of a multi-soliton regime type with forbidden phases is necessary in order to simulate the EPR lines.

Secondly, we have shown how we can obtain a special phase distribution while the phase distribution of the modulation is uniform. Such a distribution is obtained within the Landau theory by assuming a linear coupling between the defects and the modulation and using the solution of the sine-Gordon equation corresponding to the oscillating pendulum. Lastly, a microscopic mechanical model has been performed. In this model, it is assumed that the hydrogen-hydrogen repulsion is of primary importance in order to determine the equilibrium orientation of the molecules. It has been shown that the torsion of the neighbouring biphenyl molecules entails a rotation of the probe molecule due to its rigidity. All the experimental features of the EPR probes have been interpreted with this model. The axes of rotation of molecular probes are well accounted for. The special phase distribution for the naphthalene originates in the dissymmetrical forces undergone by these molecules, which entails a dissymmetrical displacement field around the high temperature equilibrium position. The two modulations do not have the same effect on the naphthalene probe which makes it possible to differentiate the domains. Finally, the splitting obeys the classical critical behaviour. For phenanthrene molecular probe, the microscopic model predicts a classical behaviour.
References