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Low-frequency single-molecule dynamics in incommensurate biphenyl

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An incoherent-neutron-scattering study of the incommensurate phase transition in biphenyl is reported. Experimental results show a departure from the Debye law in the low-energy part of the pseudodensity of states both on approaching the displacive transition and in the incommensurate phase. The analysis of the associated spectral autocorrelation function leads us to reexamine the interpretation of nuclear-magnetic-resonance results, nuclei having spin $I=\frac{1}{2}$ and above $\frac{1}{2}$, in order to estimate the real values for the gap in the phason branch.

I. INTRODUCTION

The analysis of local properties around structural phase transitions gives a complementary view of the collective excitations involved. Resonance methods [nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), electron paramagnetic resonance (EPR), etc.] are the most sensitive techniques for the study of such local critical dynamics, measuring the low- and very-low-energy part of the associated spectral autocorrelation function.[1,2] However, the analysis of the resulting complex spectral shape is sometimes ambiguous, as one only follows the temperature dependence of a very limited frequency range of this function. Theory[3,4] and experiment[5-7] have shown that incoherent neutron scattering (INS) can, in principle, give an alternative method for such a study. In addition, incoherent neutron scattering is the only technique that allows the observation of the spectral autocorrelation function as a whole. Here we extend this approach to the case of a displacive incommensurate system. For such a transition, the order parameter has, in the simplest case, a dimension $n=2$ and the twice degenerate soft phonon branch yields in the incommensurate phase to the phason and the amplitudon branches. A still open question is to understand how these collective excitations modify local properties such as the phonon density of states, Debye-Waller factor, and spectral autocorrelation function, and global properties such as the heat capacity. Within this general framework, for this study by INS, we retained the molecular crystal of biphenyl as it is certainly the most suitable compound: (i) the structural incommensurate transition is associated with large motional amplitudes of hydrogen atoms; (ii) the collective dynamics has been extensively studied. INS results in the high-temperature phase and in the incommensurate phase are presented. The effect of the collective characteristic excitations on the spectral autocorrelation function is discussed and compared with NMR data. Particular attention is devoted to the still controversial problem of the existence or not of the gapless phason.

Biphenyl ($C_{12}H_{10}$) is an aromatic molecule composed of two phenyl rings connected by single C-C bonds. In the high-temperature phase (phase I), the space group is monoclinic $P2_1/a$ with two molecules per unit cell. A structural instability at $T_\mathrm{I}=40$ K is driven by a soft mode principally related to an internal torsional motion of phenyl rings. The resulting incommensurate phase II has a four-dimensional order parameter ($n=4$).[8] It is characterized by four satellites localized at general points inside the Brillouin zone:

$$\pm\mathbf{q}_{s1}=\pm\left[(\delta_a\mathbf{a}^*-\delta_c\mathbf{c}^*)+\frac{1-\delta_b}{2}\mathbf{b}^*\right],$$

$$\pm\mathbf{q}_{s2}=\pm\left[-(\delta_a\mathbf{a}^*-\delta_c\mathbf{c}^*)+\frac{1-\delta_b}{2}\mathbf{b}^*\right],$$

where δ_a, δ_b, and δ_c evolve with temperature.

Coherent neutron scattering experiments at low temperatures under pressure have allowed the analysis of the collective excitations: a phason branch, an amplitudon branch, and a noncondensed doubly degenerate soft branch.[9] This result proves that this incommensurate phase has a single-q structure: the modulation propagates only along one of the directions, either $\mathbf{q}_{s1}$ or $\mathbf{q}_{s2}$. This structure has been also confirmed by Raman scattering,[10] EPR,[11] and deuteron NMR (Ref. 12) experiments. A proton NMR study concluded for the existence of a gapless phason in this phase.[13] A further transition between phases II and III at $T_\mathrm{II}=17$ K corresponds to a partial lock-in transition, the component along the $\mathbf{b}^*$ axis remaining incommensurate or close to a higher-order commensurate value with the modulation wave vector $\frac{6}{13}\mathbf{b}^*$.[8,14] Note that two different INS studies have been realized in biphenyl previously.[15,16] Due to the low energy resolution used, both failed in the observation of any INS signature for the first transition.

This paper is organized as follows. In Sec. II A, we recall the formalism of incoherent neutron scattering ap-

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plied to structural phase transitions. In Sec. II B, we present our experimental results, in Sec. II C the calculation of the contributions of critical collective excitations to the spectral autocorrelation function, and in Sec. II D the results of these calculations and their comparison with experimental data. In Sec. III, we reexamine the interpretation of experimental data obtained by magnetic resonance techniques, in Sec. III A for spin $I>\frac{1}{2}$ and in Sec. III B for spin $I=\frac{1}{2}$. In Sec. IV, we summarize the main conclusions.

II. INCOHERENT-NEUTRON-SCATTERING STUDY

A. The incoherent-neutron-scattering technique

The definition of the incoherent-neutron-scattering cross section is[17,18]

$$\left[\frac{d^2\sigma}{d\Omega\,d\omega}\right]_{\rm inc}=\sum_j \frac{\sigma^j_{\rm inc}}{4\pi}\frac{k_f}{k_i}S^j_{\rm inc}(\mathbf{Q},\omega)\ . \tag{1}$$

k_i and k_f are the incident and final neutron wave vector and, $\sigma^j_{\rm inc}$ and $S^j_{\rm inc}(\mathbf{Q},\omega)$ are, respectively, the incoherent cross section and the incoherent-scattering function for the nucleus j. This scattering function is essentially the sum of several contributions:

$$S^j_{\rm inc}(\mathbf{Q},\omega)=e^{-\langle(\mathbf{u}_j\cdot\mathbf{Q})^2\rangle}[S^{j,R}_{\rm inc}(\mathbf{Q},\omega)+S^{j,{\rm inel}}_{\rm inc}(\mathbf{Q},\omega)]\ , \tag{2}$$

with the following normalization conditions:

$$\int_{-\infty}^{+\infty}S^j_{\rm inc}(\mathbf{Q},\omega)d\omega=1 \quad\text{and}\quad \int_{-\infty}^{+\infty}S^{j,R}_{\rm inc}(\mathbf{Q},\omega)d\omega=1\ .$$

Here, $e^{-\langle(\mathbf{u}_j\cdot\mathbf{Q})^2\rangle}$ is the Debye-Waller factor for the nucleus j, $S^{j,R}_{\rm inc}(\mathbf{Q},\omega)$ includes all reorientational functions, when they exist, and, $S^{j,{\rm inel}}_{\rm inc}(\mathbf{Q},\omega)$ is the inelastic-incoherent-scattering function which in the one-phonon approximation is related to the scatterer-weighted phonon density of states $G(\omega)$:

$$S^{j,{\rm inel}}_{\rm inc}(\mathbf{Q},\omega)=\frac{3}{2M_j}\langle(\mathbf{e}^j_q\cdot\mathbf{Q})^2\rangle\frac{G(\omega)}{\omega}n(\omega)\ , \tag{3}$$

with M_j the mass of the nucleus j, $\mathbf{e}^j_q$ the polarization vector of the nucleus j for the mode q, $\langle(\mathbf{e}^j_q\cdot\mathbf{Q})^2\rangle$ the value of $(\mathbf{e}^j_q\cdot\mathbf{Q})^2$ averaged over all the modes q with frequency ω, and, $n(\omega)$ the Bose occupation factor. From formula (3) follows the definition of the spectral autocorrelation function $S(\omega)$:

$$S(\omega)=\frac{G(\omega)}{\omega}n(\omega)\ . \tag{4}$$

Up to now the incoherent-neutron-scattering studies of structural phase transitions have concerned order-disorder transitions.[5-7] With the model of a relaxational motion of the atoms in a double-well potential, the local critical variable is described by a pseudospin variable taking two values (± 1). Therefore the order parameter corresponds to the time average of this critical variable. The associated phenomena (pretransitional effects and order-parameter evolution) only affect the reorientational scattering function $S^R_{\rm inc}(\mathbf{Q},\omega)$, i.e., the elastic incoherent structure factor (EISF) and the quasielastic-scattering function taking into account the collective critical fluctuations. At low energy transfer, the inelastic contribution $S^{\rm inel}_{\rm inc}(\mathbf{Q},\omega)$ results then only from the acoustic phonons which have there a negligible damping. If the phonon density of states $G(\omega)$ follows the Debye law $[G(\omega)\approx\omega^2]$, the inelastic-scattering function has the following expression:

$$S^{\rm inel}_{\rm inc}(\mathbf{Q},\omega)=B\langle(\mathbf{e}_q\cdot\mathbf{Q})^2\rangle\omega n(\omega)\ , \tag{5}$$

$$B\approx\frac{S^{\rm ac}(\omega)}{\omega n(\omega)}=\frac{1}{\omega n(\omega)}\int_{\rm BZ}n(\omega)\frac{\delta(\omega\pm\omega_q)}{\omega^2}d^3q\ , \tag{6}$$

where $S^{\rm ac}(\omega)$ is the spectral autocorrelation function of acoustic phonons and BZ indicates the Brillouin zone. The coefficient B in meV^{-2}, which is directly related to the sound velocity, is a constant independent of scattering angle and temperature.

The situation is quite opposite in the case of a displacive incommensurate transition. Here $S^R_{\rm inc}(\mathbf{Q},\omega)$ is $\mathbf{Q}$ independent and always equal to $\delta(\omega)$. Pretransitional phenomena associated with a softening of the phonon branch around peculiar points in reciprocal space affect only the phonon density of states and consequently the Debye-Waller factor. Whereas for an order-disorder phase transition the Debye-Waller factor related to single-site properties has a fixed value in the high-temperature phase, in the displacive case this parameter integrates also the contribution associated with the static susceptibility $\sum_q\chi(q,\omega_q)\approx\sum_q 1/\omega_q^2$.[19] This integral term is then expected to increase, but remaining finite at the transition. Inelastic incoherent neutron scattering somehow provides an energy analysis of this Debye-Waller function. At low frequencies, the function $S^{\rm inel}_{\rm inc}(\mathbf{Q},\omega)$ may be split into two contributions: one of the acoustic phonons and another one governed by critical excitations such as soft phonons and, in incommensurate phases, phasons and amplitudons:

$$\begin{aligned}S_{\rm inc}(\mathbf{Q},\omega)=e^{-\langle(\mathbf{u}\cdot\mathbf{Q})^2]}[\delta(\omega)+B\langle(\mathbf{e}_q\cdot\mathbf{Q})^2\rangle\omega n(\omega)\\ +\langle(\mathbf{e}_q\cdot\mathbf{Q})^2\rangle S^{\rm crit}(\omega)]\ ,\end{aligned} \tag{7}$$

where $S^{\rm crit}(\omega)$ is the spectral autocorrelation function of critical excitations.

B. Experimental results

The incoherent-neutron-scattering experiments were performed on a polycrystalline sample using the time-of-flight spectrometer MIBEMOL of the Laboratoire Léon Brillouin. It is located on a neutron guide viewing the cold source.[20] Measurements at very low temperatures were made in the standard cryostat of the spectrometer. The aluminum sample container was rectangular with a surface of $S=4\times1.5$ cm^2 and a thickness of $T=1$ mm. The incident wavelength was $\lambda_0=6.26$ Å. The corresponding elastic energy resolution is full width at half maximum (FWHM) $=120$ μeV. After the standard detector normalization procedure using a vanadium run, the empty-can contribution has been subtracted from the sample spectra. Because of the high transmission of 0.91, multiple-scattering corrections were neglected. Note that the density of states has been obtained by a method of extrapolation to $Q=0$:

$$\lim_{Q\to 0}\frac{S^{\rm inel}_{\rm inc}(\mathbf{Q},\omega)\omega}{n(\omega)\mathbf{Q}^2}\to G(\omega) .$$

This is justified by the fact that we used a hydrogenated sample, such that we mainly have measured the incoherent scattering arising from the self-correlation function which involves the motion of protons.

Far above $T_I=40$ K ($T=112$ and 79 K), $G(\omega)$ follows an apparent ω^2 law for small energy transfer (Fig. 1). On approaching the first transition, one observes a completely different spectral shape. The extra contribution below 1 meV is attributed to the overdamped soft phonon branch. Some remarks can be made to explain the intensity of the observed phenomenon.

(i) The order parameter has four components. Indeed, the soft phonon branch does not soften around a single point in reciprocal space but around four satellite points. It has weight 4 against 3 for the acoustic phonon branches.

(ii) Biphenyl is rather an anisotropic system with not very correlated directions. Because of the weak frequency dispersion around critical points, many modes remain at very low frequencies.

(iii) The vibration amplitude of hydrogenated atoms in *ortho* and *meta* positions is particularly affected by the torsional mode along the long molecular axis, associated with the structural instability.

In the incommensurate phase, the deviation from the ω^2 law persists and is explained by the contributions of characteristic excitations, phasons, amplitudons, and noncondensed soft modes (Fig. 2). Amplitudon and noncondensed soft mode branches are essentially similar to a low-temperature soft phonon branch and therefore contribute essentially to $G(\omega)$ near the transition. But the phason branch is temperature independent and is like a condensed soft phonon branch at $T_{\rm I}$. Whatever the temperature studied, its contribution remains constant.

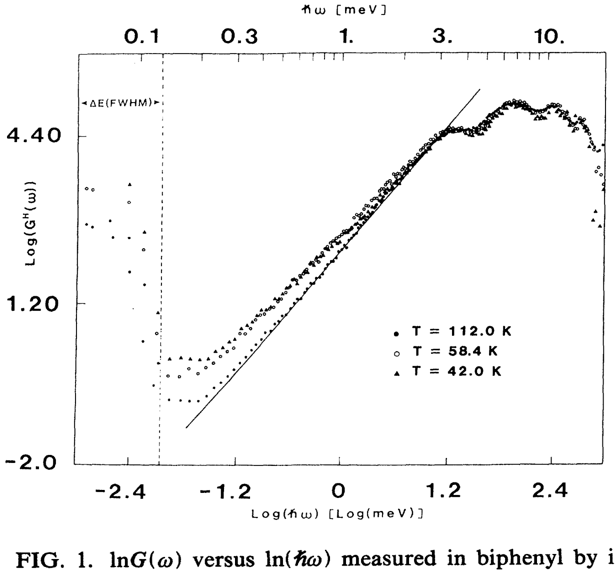

FIG. 1. ln$G(\omega)$ versus ln($\hbar\omega$) measured in biphenyl by incoherent inelastic neutron scattering, in phase I. The line corresponds to a Debye model (slope 2).

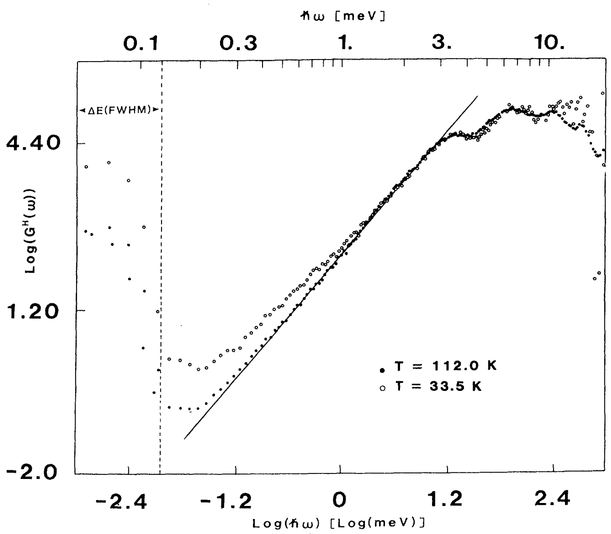

FIG. 2. ln$G(\omega)$ versus ln($\hbar\omega$) measured in biphenyl by incoherent inelastic neutron scattering, in phase II.

C. Calculation of the spectral autocorrelation function

In the displacive and incommensurate case, the critical dynamics is illustrated by a softening of a phonon branch. As for acoustic phonons [Eq. (6)], the spectral autocorrelation function $S(\omega)$ is again obtained by a summation over the Brillouin zone. However, these collective fluctuations are described by the model of a damped harmonic oscillator:

$$S(\omega)=\int_{\rm BZ} n(\omega)\omega\frac{\Gamma_q}{(\omega^2-\omega_q^2)^2+(\Gamma_q\omega)^2}d^3q . \qquad (8)$$

The calculation of $S(\omega)$ requires the knowledge of the dispersion and the damping of the critical modes. The parameters have been determined essentially by coherent-neutron-scattering experiments.[8,9]

Concerning the damping coefficient Γ_q, we have assumed that it is essentially constant around the satellite points ($\Gamma_q\approx\Gamma$). We have only taken into account its temperature variations.[8] For these quasiharmonic modes, we use the phrase "pseudo density of states" in order to differentiate the situation here from the usual case of acoustic phonons which are not damped. Around the satellite point, the dispersion of the soft phonon branch is described by the parabolic law

$$\omega_q^2=\omega_0^2+\alpha_x q_x^2+\alpha_y q_y^2+\alpha_z q_z^2 , \qquad (9)$$

with $\omega_0^2\approx A(T-T_{\rm I})$.

Biphenyl is a system with anisotropic dispersion. The dispersion coefficients α_x and α_z have the same order of magnitude ($\alpha_x\approx 4$ THz^2 Å^2 and $\alpha_z\approx 1$ THz^2 Å^2) and are clearly smaller than α_y ($\alpha_y\approx 22$ THz^2 Å^2).[9] In the vicinity of the $Z(0,\frac{1}{2},0)$ zone boundary point, the symmetrical and antisymmetrical torsional modes are degenerate with respect to the diad axis and merge with opposite but finite slopes. Such a behavior is labeled A.[8] The numerical calculations of the functions $G(\omega)$ and $S(\omega)$ have required knowledge of the dispersion of the collective mode branches in the Brillouin zone. We have assumed that the parabolic law [Eq. (8)] is valid throughout the Brillouin zone. As we focus our attention on the low-frequency part of the spectral autocorrelation function, this approximation is acceptable. The dispersion branches are calculated along several directions taking into account the satellite points $(\delta_a,(1-\delta_b)/2,\delta_c)$ and $(\delta_a,(1+\delta_b)/2,\delta_c)$. Whatever the temperature studied, the values are fixed: $\delta_a=0.06$, $\delta_b=0.05$, and $\delta_c=0.13$.

In the incommensurate phase, the theoretical frequencies of characteristic excitations at the satellite points are, for

$$\begin{aligned}&\text{the gapless phason } P\ ,\quad 0\ ,\\ &\text{the amplitudon } A\ ,\quad \omega_A^2\approx 2A(T_{\mathrm{I}}-T)\ .\end{aligned}\tag{10}$$

For the noncondensed soft mode D, no simple analytical temperature dependence is predicted but coherent-neutron-scattering results have revealed the behavior $\omega_D^2\approx 0.5A(T_{\mathrm{I}}-T)$.[9] The relative weight of these different critical branches is 4 for the soft phonon SM, 1 for the amplitudon A, 1 for the phason P, and 2 for the noncondensed soft mode D.

Before studying this real case, a simple calculation of $G(\omega)$ following the formulas (8) and (4) has been done considering an isotropic dispersion ($\alpha_x=\alpha_y=\alpha_z$) and a displacive transition with undamped and damped modes. Without the damping [Fig. 3(a)], the spectral autocorrelation function is of course zero below the frequency gap ω_0 of the branch, whereas an important contribution actually exists at much lower frequency than ω_0 when considering the damping [Fig. 3(b)]. This point will appear essential when looking for a quantitative value of this gap by resonance techniques as discussed further.

D. Calculations: Results and comparison with experimental data

In phase I, the displacive transition is second order and the soft phonon frequency is assumed to be zero at the satellite points. The intensity of the pseudo density of states increases if the temperature decreases (Fig. 4). Because of the damping, the resulting spectral autocorrelation function diverges at zero energy transfer. This result is similar to the one observed in an order-disorder transition;[6,7] the low-energy part of the spectral autocorrelation function is then found to behave as $\omega^{-1/2}$. In the incommensurate phase, phase II, the function $S(\omega)$ associated with the temperature-independent gapless phason branch has the same behavior as the one associated with the soft phonon branch at T_{I} but its weight is four times weaker (Fig. 5). One should keep in mind that the divergence of $S(\omega)$ at $\omega=0$ is directly related to the existence of a mode close to the satellite points $\mathbf{q}_s$, where the static susceptibility diverges, that is, the mean square amplitude of the collective fluctuation is infinite. The usual small-fluctuation limit, which simply defines the phason and the amplitudon, is certainly not valid there. Such problems do not affect the interpretation of the coherent- or incoherent-neutron-scattering data because the resolution of the spectrometer used is rather large (typically some 10 GHz). However, as discussed later, this aspect may be fundamental in the analysis of $S(\omega)$ by other local techniques sensitive to much lower values of the frequency, such as nuclear-magnetic-resonance techniques (frequency in and below the MHz range).

We determine the temperature dependence of the vibrational mean square displacement of the protons $\langle u^2\rangle$ by using the integral of the elastic peak and summing the detectors. At the transition and below, even if there are extra-low-frequency branches, $\langle u^2\rangle$ is not found to deviate significantly from a standard temperature dependence. Much more precise measurements should be done to observe such an expected effect, which would reflect the modification of the Debye-Waller factor in the pres-

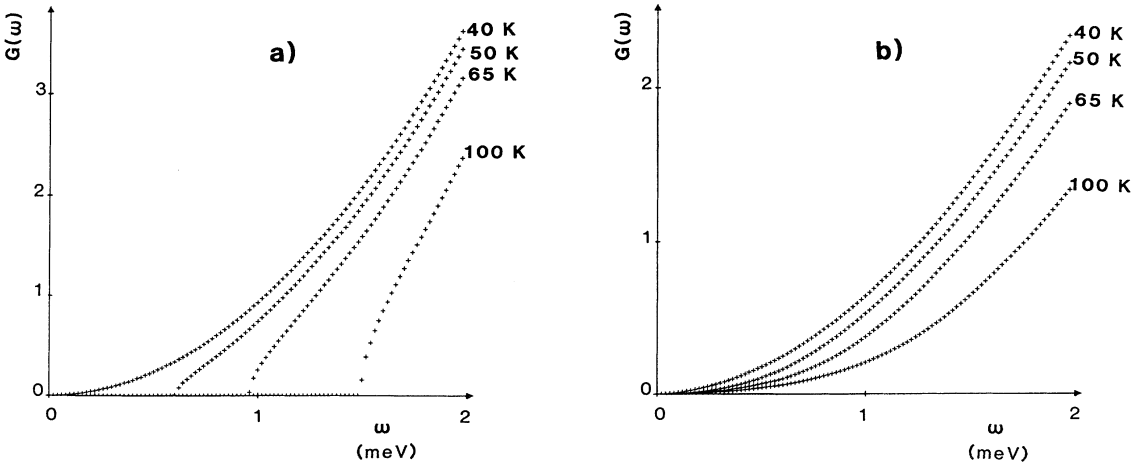

FIG. 3. Numerical calculations of the density of states in an isotropoic system (in arbitrary units) with (a) zero damping and (b) nonzero damping.

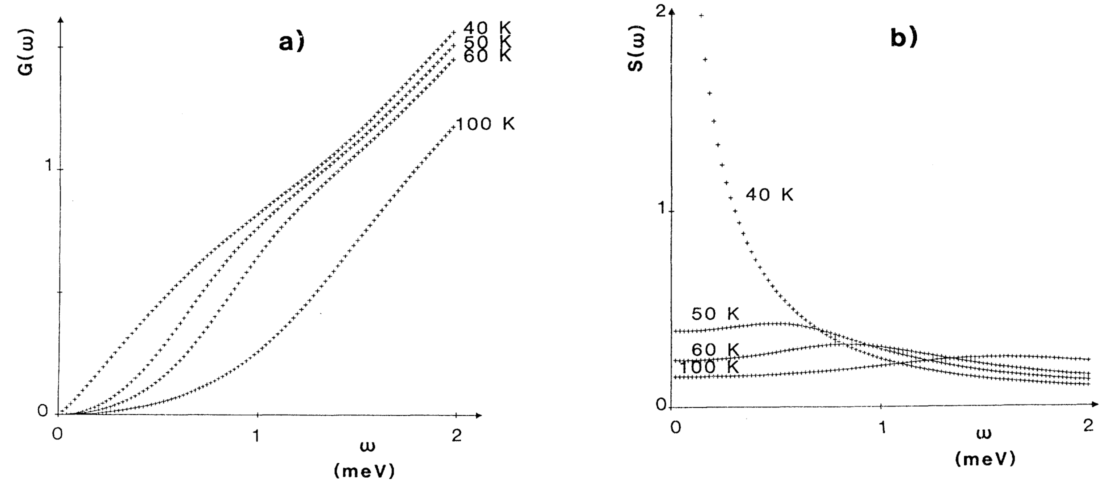

FIG. 4. Numerical calculations of pseudodensities of states (a) and spectral autocorrelation functions (b) of soft phonons of biphenyl in phase I. The ordinate axes are in arbitrary units.

ence of these branches whose static susceptibility diverges.

For $T \geq 150$ K, $\langle u^2 \rangle$ is approximately represented by a linear temperature relation,

$$\langle u^2(T) \rangle = 4.5 \times 10^{-4} T \ , \qquad (11)$$

where $\langle u^2 \rangle$ is given in Å^2 and T in K. For $T \leq 50$ K, $\langle u^2 \rangle$ becomes practically constant,

$$\langle u^2 \rangle = 0.052 \text{ Å}^2 \ . \qquad (12)$$

The incoherent-neutron-scattering function for a polycrystalline sample which has been used to fit the data has the following expression:

$$S_{\text{inc}}(\mathbf{Q},\omega) = Ae^{-\langle u^2 \rangle \cdot Q^2} R(\omega) \otimes [\delta(\omega) + B'Q^2 \omega n(\omega) + CQ^2 \tilde{S}^{\text{crit}}(\omega)] \ . \qquad (13)$$

For $T \geq T_{\text{I}}$, $\tilde{S}^{\text{crit}}(\omega) = S^{\text{SM}}(\omega)$. For $T < T_{\text{I}}$,

$$\tilde{S}^{\text{crit}}(\omega) = S^P(\omega) + S^A(\omega) + S^D(\omega) \ .$$

The functions $S^{(i)}(\omega)$(i = SM, P, A, or D) include the relative weight of the branches. $R(\omega)$ is the normalized resolution function of the spectrometer. The coefficient B', in meV^{-1}, is the acoustic phonon contribution ($B' = B/A$). It will be fixed at all temperatures following the procedure discussed below. The fitting parameters are

(i) the amplitude factor A in meV^{-1} which depends on the normalization of the spectra, and

(ii) the parameter C which is independent of temperature and is expressed in meV^2.

To determine the contribution B from the acoustic phonons, we have used the incoherent-neutron-scattering results concerning p-terphenyl[16] and p-quaterphenyl.[21]

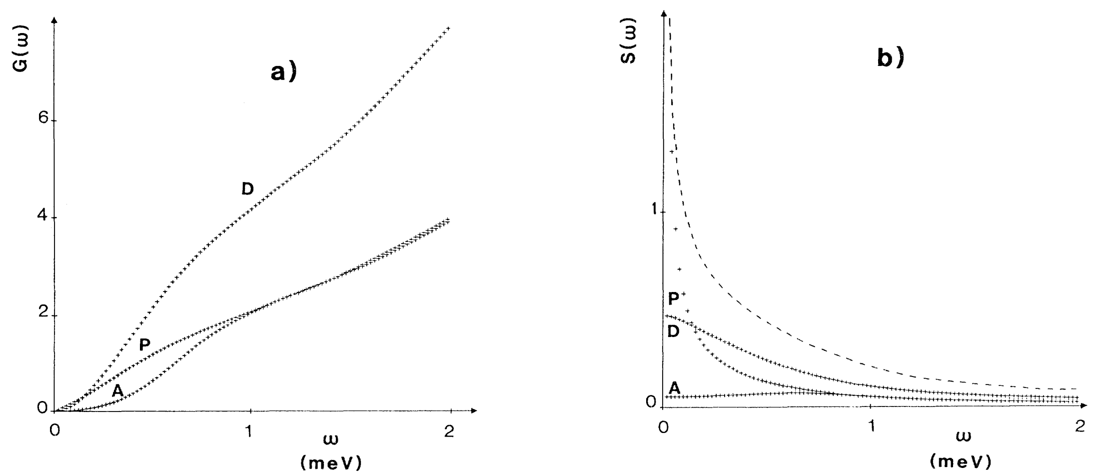

FIG. 5. Numerical calculations of pseudo densities of states (a) and spectral autocorrelation functions (b) of gapless phasons, amplitudons, and noncondensed soft modes of biphenyl in phase II. The dotted line represents the total spectral autocorrelation function. The ordinate axes are in arbitrary units.

For these two compounds, which present an order-disorder transition, the low-energy purely inelastic contribution only stems from acoustic phonons. We have calculated the densities of states for acoustic phonons of biphenyl (B), of p-terphenyl (P), and of p-quaterphenyl (Q). We have used the values for the elastic constants measured by Brillouin scattering[22] and applied the Every method[23] to define the sound velocity V in the crystal studied. The calculation of the density of states $G(\omega)$ has been done by slicing the Brillouin zone into elementary constant spaces $dv=\sin\theta\, d\theta\, d\varphi\, q^2 dq$ (spherical coordinates) and summing the number of modes with a frequency between ω and $\omega+d\omega$, with $\omega=Vq$. The following relation between the constants B is found: $B_B\approx 0.7B_P\approx 0.5B_Q$. Taking into account the normalization of the spectra, we have established an average value $B'_B\approx 1.8\times 10^{-4}$ meV^{-1} for biphenyl and fixed it for the refinement. The analytical treatment of the INS data has required another simplification of the system. We have considered a system with a semianisotropic dispersion ($\alpha_x=\alpha_z\neq\alpha_y$), in the reduced Brillouin zone. The satellite points (with the coordinates q_1,q_2,q_3, in reduced units) are assumed to obey the relation $q_1=q_3=\frac{1}{2}(\delta_a+\delta_c)$. The dispersion of the critical modes has been described by means of the coefficients $\alpha_x=\alpha_z=\alpha=1$ THz^2 and $\alpha_y=\beta=28$ Thz^2. The A behavior of the dispersion branch along the $\mathbf{b}^*$ direction has been taken into account with $q_2\pm 0.05$. The spectral autocorrelation function can not be analytically calculated if one considers the real coordinates of the satellite points in the directions $\mathbf{a}^*$ and $\mathbf{c}^*$. For this reason, we have defined the fictitious satellite point

$$q_L=(q_1^2+q_3^2)^{1/2}=2^{1/2}q_1\approx 0.15\ .$$

In the reciprocal space (a^*,c^*), the dispersion of the critical modes is schematically given by the relations: for $q\leq q_L$, $\omega_q^2=\omega_0^2+\beta(q_y-q_2)^2$ and, for $q\geq q_L$, $\omega_q^2=\omega_s^2+\alpha q^2+\beta(q_y-q_2)^2$, $\omega_s^2=\omega_0^2-\alpha q_L^2$. We have assumed that the parabolic law was valid throughout the Brillouin zone. These calculations are detailed in the Appendix.

The incoherent-neutron-scattering spectra have been obtained by summing ten detectors ($\phi_{\min}=102.15°$ and $\phi_{\max}=135.55°$) with an average scattering angle $\phi=119.7°$, i.e., an elastic momentum transfer Q_0 of 1.74 Å^{-1}. Far above the first transition ($T\geq 79$ K in Fig. 6), the soft phonons are strongly damped, and the associated spectral autocorrelation function is very large and practically energy independent. Using the formulas (4) and (8), the resulting pseudo density of states follows an apparent ω^2 law. The parameter C in the formula (13) has been found at 6.9×10^{-4} meV^2. Near the transition, the spectral autocorrelation function gives a quasielastic component whose intensity increases (Fig. 6). Our model accounts for this increase of the integral [Eq. (8)] essentially

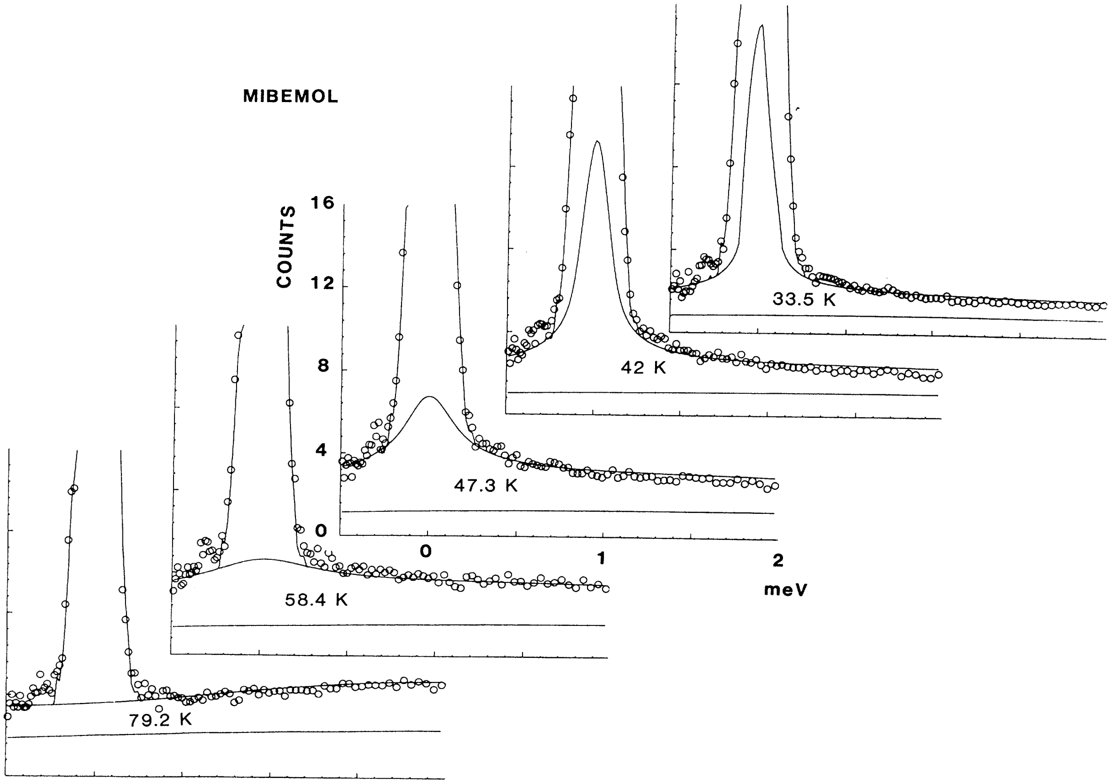

FIG. 6. Incoherent-neutron-scattering spectra obtained with MIBEMOL at $Q_0=1.74$ Å^{-1} from a powder sample of biphenyl. Full lines are the results of a fit using the formula (13).

as $\sum_q 1/\omega_q^2$, so the fitting value C should be constant. However, it was experimentally found to slightly decrease down to 5.8×10^{-4} meV^2 at $T_{\rm I}$. This may come from the simplified calculation which introduces extra modes ($q \leq q_L$) which are not negligible close to the transition. In the incommensurate phase, phase II, this value of C yields a good description of the experimental data (Fig. 6). At 33 K, the resulting function $S_{\rm inc}(\mathbf{Q},\omega)$ contains the sum of the contributions from the phason, amplitudon, and noncondensed soft modes. The very-low-energy part of the experimental data is expected to behave essentially as $S^p(\omega)\approx\omega^{-1/2}$ in the whole incommensurate phase as at $T_{\rm I}$, but with a weight of $\frac{1}{4}$ with respect to the critical contribution $S^{\rm SM}(\omega)$. Far below $T_{\rm I}$, at low energy transfer, the main weight in the associated spectral autocorrelation function results from the phason contribution (Fig. 5). Restricted by the instrumental resolution of MIBEMOL (30 GHz), we cannot conclude if the phason branch has a gap ω_P or not. However, this information may also be found by other local techniques, e.g., nuclear magnetic resonance, which measure the same kind of spectral autocorrelation function but in a much lower frequency range.

III. REEXAMINATION OF NUCLEAR-MAGNETIC-RESONANCE RESULTS

Independent information on the numerical values of the phason gaps can be obtained by spin-lattice relaxation rates measured by nuclear-magnetic-resonance techniques. The spin-lattice relaxation rate corresponds to a single point of the spectral autocorrelation function at the Larmor resonance frequency ω_L (MHz):

$$T_1^{-1}\approx S(\omega_L)\ . \tag{14}$$

General calculations of this function were done several years ago for incommensurate systems.[24–26] The results are summarized below.

If the soft phonon frequency is far above the Larmor frequency, the spin-lattice relaxation rate is also independent of the measured frequency:

$$T_{\rm SM}^{-1}\approx\frac{\Gamma T}{\omega_0},\quad \omega_0\gg\omega_L\ . \tag{15}$$

In an incommensurate phase, one considers separately the different critical excitations. For the amplitudon, far below the transition, one obtains the same kind of result as for a soft phonon:

$$T_A^{-1}\approx\frac{\Gamma T}{\omega_A},\quad \omega_A\gg\omega_L\ . \tag{16}$$

The same behavior is also found for the phason branch with an important gap ω_P compared to the Larmor frequency:

$$T_P^{-1}\approx\frac{\Gamma T}{\omega_P},\quad \omega_P\gg\omega_L\ . \tag{17}$$

If the phason is gapless or has a small gap,

$$T_P^{-1}\approx\frac{\Gamma^{1/2}T}{\omega_L^{1/2}},\quad \Gamma\gg\omega_L \text{ and } \omega_p\ll(\Gamma\omega_L)^{1/2}\ . \tag{18}$$

A. Spin $I>\frac{1}{2}$ NMR and NQR

In the literature, the analysis of the experimental data obtained by quadrupolar NMR (nuclei having spin above $\frac{1}{2}$) and nuclear quadrupolar resonance always predicted very large phason gaps (typically 50–100 GHz).[27–31] This result is extracted from the ratio of the spin-lattice relaxation rates at different parts of the resonance distribution spectrum. In the "local approximation" and assuming fluctuations of small amplitudes, the theory used shows that there are nuclei at peculiar resonance frequencies where the spin-lattice relaxation rate is only governed by the phason (T_P^{-1}) and by the amplitudon (T_A^{-1}), respectively. Actually, the experimentally observed evolution of the spin-lattice relaxation rate inside the incommensurate resonance spectrum is generally found to be quite different. Indeed, the rate T_A^{-1} attributed to the amplitudon process is much bigger than it should be according to what we know about the equivalent high-temperature soft mode process. Consequently, as the gap of the phason ω_P, in this theory, is directly related to the known gap ω_A of the amplitudon ($\omega_P/\omega_A=T_P/T_A$), all the gaps extracted are strongly overestimated. Let us first simply remark that the so-called amplitudon spin-lattice relaxation rate T_A is experimentally found to be much lower than its value calculated when the soft mode spin-lattice relaxation rate $T_{\rm SM}$ is known. Already, inserting the calculated value T_A instead of the experimental one in the ratio T_P/T_A would yield values for the phason gaps which are at least one order of magnitude lower than found. This makes these values more consistent with the ones found by neutron scattering, which also gives an upper value as determined by its best energy resolution (typically of some 10 GHz). In biphenyl, as discussed above, the problem is actually even more complex because of the existence of a noncondensed soft branch in phase II. Apart from its weight (2), this branch is similar to the usual amplitudon branch and so gives the same frequency spectrum,

$$T_D^{-1}\approx\frac{2\Gamma T}{\omega_D},\quad \omega_D\gg\omega_L\ . \tag{19}$$

These qualitative features are essentially found in our real quantitative calculations of $S(\omega)$ for biphenyl discussed above [Fig. 5(b)]. One clearly sees that, at very low frequencies, the contributions of the amplitudon and the noncondensed soft mode branches are indeed frequency independent. Already, at first glance, one clearly sees that the contribution to $S(\omega)$ of the noncondensed soft branch is much more dominant than the one related to the usual amplitudon. A second important result that is immediately obvious when looking at these calculations is that the low-frequency part of the spectral autocorrelation function is strongly dominated by the contribution of the phason branch. Assuming that the phason is gapless, this central part behaves as $\omega_L^{-1/2}$, i.e., diverges at $\omega_L=0$. As seen before, this comes from the phason modes, at the satellite positions, whose static susceptibility (mean square amplitude) diverges. One fundamental question is then if the assumption found in the literature when describing quadrupolar NMR and NQR data, called the small-fluctuation limit, is valid. Such a limit defines phasons and amplitudons as associated with small fluctuations of the phase and the amplitude of the static incommensurate modulation, implying that peculiar nuclei could be relaxed separately by these excitations, as mentioned above. Nonvalidity of this hypothesis should cancel this restriction, suggesting that the spectral autocorrelation function $S^P(\omega)$ of the phason (gapless or with a small gap) may be effective throughout the resonance spectrum [Fig. 5(b)] such as the spin-lattice relaxation rate should have the same frequency dependence. Values for such frequency dependence of spin-lattice relaxation rates for quadrupolar nuclei which could confirm this result[32] are very rare in the literature. The problem of the nonvalidity of the small-fluctuation limit has been discussed outside the framework of a mean-field theory by Bruce and Cowley. In this large-phase-fluctuation case, they introduced symmetric and antisymmetric modes instead of amplitudons and phasons, respectively, and found a divergent static susceptibility for both excitations.[33] A completely different reason for the low-frequency dependence of the spin-lattice relaxation rate in the resonance line has been mentioned by Dolinsek, Apih, and Blinc.[34] They made the hypothesis that the magnetic dipolar coupling between nuclei transfers the polarization from phason-relaxed to amplitudon-relaxed nuclei in a cross-polarization process. Such a hypothesis requests severe resonance conditions which are usually not fulfilled and so this explanation cannot be valid in all cases. Other possible effects, such as resolution broadening resulting from a random distribution of the electric-field-gradient (EFG) tensor in the sample due to defects, may also yield an averaging of the measured spin-lattice relaxation rate over a rather large frequency range. The limitation of the "local approximation" for the EFG modulation may also not be fulfilled. Nuclei can be out of phase in their displacements and the influence region for a given EFG modulation should not be reduced to one nucleus.[35,36] At the moment, it is not obvious that one may extract more information on the value of the phason gap from NMR for spin $I>\frac{1}{2}$ than for spin $I=\frac{1}{2}$, i.e., from the T_1^{-1} frequency dependence, as discussed below.

B. Spin $I=\frac{1}{2}$ NMR

The phason gaps in incommensurate systems are often extracted from the frequency dependence [Eq.(18)] of the spin-lattice relaxation rate T_1^{-1}, measured by dipolar NMR (nuclei having spin $I=\frac{1}{2}$). In biphenyl[13] and bis(4-chlorophenyl)sulfone,[37] the authors concluded for the existence of a gapless phason branch. They made a wrong use of this theoretical law as the real conditions are $\Gamma \gg \omega_L$ and $\omega_P \ll (\Gamma\omega_L)^{1/2}$. As in the molecular compounds, the damping is usually very large (some 100 GHz),[8,38] it may very much affect the pseudodensity of states (Fig. 3). So, the $\omega_L^{-1/2}$ law may be observed down to much lower frequencies than the gap ω_P. Then no direct determination of this gap can be done. To get an estimation of this gap in biphenyl at 35 K, we performed quantitative calculations of the spectral autocorrelation function associated with the phason contribution considering the damping (200 GHz) and different values of the gap (Fig. 7). We examined the $\omega_L^{-1/2}$ law for a gapless phason branch but also for a 100 MHz phason gap. A gap of about 0.5 GHz induces an $\omega_L^{-1/2}$ variation down to a resonance frequency of about 0.5 MHz. In other words, there may be three orders of magnitude between the effective value of the gap and the frequency value for which the $\omega_L^{-1/2}$ law is not followed. Comparison of our calculated T_1^{-1} frequency dependence with experimental results[13] (from 58 MHz to 10 KHz) agrees with a gap for the phason of about 100 MHz.

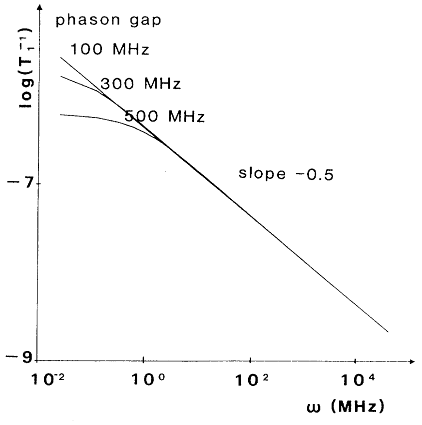

FIG. 7. Analytical calculation of the logarithm to base 10 of the spin-lattice relaxation T_1^{-1} of the phason branch, in biphenyl, at $T=35$ K. The ordinate axes are in arbitrary units.

IV. CONCLUSION

We have analyzed the problem of collective characteristic excitations in incommensurate structures by a local approach. Incoherent-neutron-scattering experiments have allowed the measurement of the whole spectral autocorrelation function near the displacive incommensurate transition of biphenyl. In the high-temperature phase, on approaching T_I, the soft phonon branch gives an extra contribution which is illustrated by a very narrow quasielastic line. In the incommensurate phase, for a gapless phason branch, the low-frequency part of this function is described by the $\omega_L^{-1/2}$ law. Such a frequency behavior has usually been applied for dipolar NMR down to very low frequencies (kHz), to conclude that the phason gap is below these values. We show why this conclusion is inaccurate. Only a maximum value for the phason gap can be given based on the value of the damping of the modes. Taking into account the damping in biphenyl, we found a value of the gap around 100 MHz. We have studied the origin of the divergence of the spectral autocorrelation function at very low frequencies. The contribution from the phason branch is very much predominant and it comes from modes very close to the satellite points, whose mean square amplitude diverges (gapless phason) or at least becomes very large (small phason gap). This brings us to the point that in resonance spectra, at peculiar frequencies, the amplitudon is never efficient to relax nuclei. So no information on the real value of the phason gap should be extract from any spin-relaxation rate. The nonvalidity of the limit of small fluctuations was mentioned a long time ago by Bruce and Cowley,[33] who demonstrated that the static susceptibilities for the symmetric and antisymmetric modes diverge. Both excitations could be efficient in any resonance process. Further investigations should be done now in order to know if such a situation is really present in resonance spectroscopy. Finally, the existence of a central peak[2] in the collective spectral function may also complicate the interpretation of NMR results.

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APPENDIX

In this Appendix, we present an analytical expression of the spectral autocorrelation function. To be able to calculate such a function, we have assumed an isotropic dispersion of the collective modes in the reciprocal plane (q_x,q_z). The frequency is described by the parabolic law, $\omega_q^2=\omega_0^2+\alpha_x q_x^2+\alpha_y q_y^2+\alpha_z q_z^2$, $\alpha=\alpha_x=\alpha_z$, and $\beta=\alpha_y$, when $0\le q\le q_m$ and $0\le q_y\le q_{ym}$.

The spectral autocorrelation function becomes

$$S^{\text{anis}}(\omega)=\frac{2\pi}{i}n(\omega)\int_0^{q_m}\int_0^{q_{ym}}\left[\frac{1}{\omega^2-\omega_0^2-\alpha q^2-\beta q_y^2-i\Gamma\omega}-\frac{1}{\omega^2-\omega_0^2-\alpha q^2-\beta q_y^2+i\Gamma\omega}\right]q\,dq\,dq_y\ .$$

Changing the variables, we determine the intermediate function $K(u,v)$:

$$K(u,v)=\frac{2}{i}\int_0^u\int_0^v\left[\frac{1}{1-v^2-u^2-ia^2}-\frac{1}{1-v^2-u^2+ia^2}\right]v\,dv\,du\ ,$$

$$K(u,v)=\frac{1}{i}\int_0^u[\ln(1-v^2-u^2+ia^2)-\ln(1-v^2-u^2-ia^2)]du\ ,$$

with $u=\beta^{1/2}q_y/|\omega^2-\omega_0^2|^{1/2}$ and $v=\alpha^{1/2}q/|\omega^2-\omega_0^2|^{1/2}$. To calculate $K(u,v)$, we use the complex notation

$$K(u,v)=2u\arctan\frac{a^2}{1-u^2-v^2}-2x\left[\delta\pi+\arctan\frac{2X}{1-X^2-Y^2}\right]+y\ln\frac{X^2+(Y+1)^2}{X^2+(Y-1)^2}\ ,$$

where $\delta=0$ if $\arctan(\cdots)\ge 0$, $\delta=1$ if $\arctan(\cdots)<0$, and

$$x=[(1-v^2)^2+a^4]^{1/4}\cos\frac{\theta}{2}\ ,\quad y=[(1-v^2)^2+a^4]^{1/4}\sin\frac{\theta}{2}\ ,$$

$$X=\frac{u}{[(1-v^2)^2+a^4]^{1/4}}\sin\frac{\theta}{2}\ ,\quad Y=\frac{u}{[(1-v^2)^2+a^4]^{1/4}}\cos\frac{\theta}{2}\ ,$$

$$\cos\frac{\theta}{2}=\frac{1}{2^{1/2}}\frac{\{(1-v^2)+[a^4+(1-v^2)^2]^{1/2}\}^{1/2}}{[a^4+(1-v^2)]^{1/4}}\ ,\quad \sin\frac{\theta}{2}=\frac{1}{2^{1/2}}\frac{\{-(1-v^2)+[a^4+(1-v^2)^2]^{1/2}\}^{1/2}}{[a^4+(1-v^2)]^{1/4}}\ ,$$

with $u_m=\beta^{1/2}q_{ym}/|\omega^2-\omega_0^2|^{1/2}$ and $v_m=\alpha^{1/2}q_m/\,|\omega^2-\omega_0^2|^{1/2}$.

Finally, we obtain

$$S^{\text{anis}}(\omega)=\frac{\pi}{\alpha\beta^{1/2}}n(\omega)|\omega^2-\omega_0^2|^{1/2}[K_{(\ldots)}(u_m,v_m)-K_{(\ldots)}(u_m,0)]\ ,$$

$$\begin{aligned}K_{\omega>\omega_0}(u,v)={}&2u\arctan\frac{a^2}{1-u^2-v^2}\quad[\text{zero for } v=0\ (q=0)]\\&-2\left\{\frac{[(1-v^2)^2+a^4]^{1/2}+(1-v^2)}{2}\right\}^{1/2}\left\{\delta\pi+\arctan\frac{2^{1/2}u\{[(1-v^2)^2+a^4]^{1/2}-(1-v^2)\}^{1/2}}{[(1-v^2)^2+a^4]^{1/2}-u^2}\right\}\\&+\left\{\frac{[(1-v_2)^2+a^4]^{1/2}-(1-v^2)}{2}\right\}^{1/2}\ln\frac{u^2+[(1-v^2)^2+a^4]^{1/2}+2^{1/2}u\{[(1-v^2)^2+a^4]^{1/2}+(1-v^2)\}^{1/2}}{u^2+[(1-v^2)^2+a^4]^{1/2}-2^{1/2}u\{[(1-v^2)^2+a^4]^{1/2}+(1-v^2)\}^{1/2}}\ ,\end{aligned}$$

$$K_{\omega<\omega_0}(u,v)=-2u\arctan\frac{a^2}{u^2+v^2+1}\quad(\text{zero for } v=0)$$
$$-2\left\{\frac{[(1+v^2)^2+a^4]^{1/2}-(1+v^2)}{2}\right\}^{1/2}\left\{\delta\pi+\arctan\frac{2^{1/2}u\{[(1+v^2)^2+a^4]^{1/2}+(1+v^2)\}^{1/2}}{[(1+v^2)^2+a^4]^{1/2}-u^2}\right\}$$
$$+\left\{\frac{[(1+v^2)^2+a^4]^{1/2}+(1+v^2)}{2}\right\}^{1/2}\ln\frac{u^2+[(1+v^2)^2+a^4]^{1/2}+2^{1/2}u\{[(1+v^2)^2+a^4]^{1/2}-(1+v^2)\}^{1/2}}{u^2+[(1+v^2)^2+a^4]^{1/2}-2^{1/2}u\{[(1+v^2)^2+a^4]^{1/2}-(1+v^2)\}^{1/2}}\ .$$

For $\omega=\omega_0$,

$$S^{\text{anis}}(\omega_0)=\frac{\pi}{\alpha\beta^{1/2}}n(\omega_0)[K_{\omega=\omega_0}(q_{ym},q_m)-K_{\omega=\omega_0}(q_{ym},0)]\ ,$$

$$K_{\omega=\omega_0}(q_y,q)=-\beta^{1/2}q_y\arctan\frac{\Gamma\omega_0}{\alpha q^2+\beta q_y^2}\quad(\text{zero for } q=0)$$
$$-\left\{\frac{(\alpha^2q^4+\Gamma^2\omega_0^2)^{1/2}-\alpha q^2}{2}\right\}^{1/2}\left\{\arctan\frac{2^{1/2}\beta^{1/2}q_y[(\alpha^2q^4+\Gamma^2\omega_0^2)^{1/2}+\alpha q^2]^{1/2}}{[\alpha^2q^4+\Gamma^2\omega_0^2]^{1/2}-\beta q_y^2}\right\}$$
$$+\left\{\frac{(\alpha^2q^4+\Gamma^2\omega_0^2)^{1/2}+\alpha q^2}{2}\right\}^{1/2}\ln\frac{\beta q_y^2+[\alpha^2q^4+\Gamma^2\omega_0^2]^{1/2}+2^{1/2}\beta^{1/2}q_y[(\alpha^2q^4+\Gamma^2\omega_0^2)^{1/2}-\alpha q^2]^{1/2}}{\beta q_y^2+[\alpha^2q^4+\Gamma^2\omega_0^2]^{1/2}-2^{1/2}\beta^{1/2}q_y[(\alpha^2q^4+\Gamma^2\omega_0^2)^{1/2}-\alpha q^2]^{1/2}}\ .$$

We improve this analytical description for a system possessing satellite points q_s with the coordinates (q_1,q_2,q_3). But the components q_1 and q_2 must obey the relation $q_1=q_3$ and give a new integral which cannot be analytically calculated. It was essential to find another model that can be used to fit the incoherent-neutron-scattering data of biphenyl. Therefore we schematically describe the dispersion of modes in the plane (q_x,q_z).

For $q\le q_L$, $\omega_q^2=\omega_0^2+\beta(q_y-q_2)^2$,

For $q\ge q_L$, $\omega_q^2=\omega_s^2+\alpha q^2+\beta(q_y-q_2)^2$,

$q_L=(q_1^2+q_3^2)^{1/2}=2^{1/2}q_1$, $\omega_s^2=\omega_0^2-\alpha q_L^2$.

The spectral autocorrelation function is written

$$4\pi\int_0^{q_L}\int_{-q_2}^{q_{ym}-q_2}\frac{n(\omega)\omega\Gamma q\,dq\,dq_y}{(\omega^2-\omega_0^2-\beta q_y^2)^2+(\Gamma\omega)^2}+4\pi\int_{q_L}^{q_m}\int_{-q_2}^{q_{ym}-q_2}\frac{n(\omega)\omega\Gamma q\,dq\,dq_y}{(\omega^2-\omega_s^2-\alpha q^2-\beta q_y^2)^2+(\Gamma\omega)^2}$$
$$=2\pi q_L^2[S'(\omega)_{q_{ym}-q_2}+S'(\omega)_{q_2}]+S^{\text{anis}}(\omega)_{q_m,q_{ym}-q_2}+S^{\text{anis}}(\omega)_{q_m,q_2}-S^{\text{anis}}(\omega)_{q_L,q_{ym}-q_2}-S^{\text{anis}}(\omega)_{q_L,q_2}\ ,$$

$$S'(\omega)=\frac{n(\omega)}{\beta^{1/2}}\frac{1}{|\omega^2-\omega_0^2|^{1/2}}\frac{1}{2}\frac{1}{(1+a^4)^{1/2}}I_{(\cdots)}\ ,$$

$$a=\frac{(\Gamma\omega)^{1/2}}{|\omega^2-\omega_0^2|^{1/2}}\quad\text{and}\quad u=\frac{\beta^{1/2}q}{|\omega^2-\omega_0^2|^{1/2}}\ .$$

$$I_{\omega>\omega_0}=\left[\frac{1+(1+a^4)^{1/2}}{2}\right]^{1/2}\left[\delta\pi+\arctan\frac{2^{1/2}u_m[(1+a^4)^{1/2}-1]^{1/2}}{(1+a^4)^{1/2}-u_m^2}\right]$$
$$+\left[\frac{-1+(1+a^4)^{1/2}}{2}\right]^{1/2}\frac{1}{2}\ln\frac{u_m^2+(1+a^4)^{1/2}+2^{1/2}u_m[(1+a^4)^{1/2}+1]^{1/2}}{u_m^2+(1+a^4)^{1/2}-2^{1/2}u_m[(1+a^4)^{1/2}+1]^{1/2}}\ .$$

$\delta=1$ if $\arctan(\cdots)<0$, $\delta=0$ if $\arctan(\cdots)\ge 0$,

$$I_{\omega<\omega_0}=\left[\frac{-1+(1+a^4)^{1/2}}{2}\right]^{1/2}\left[\delta\pi+\arctan\frac{2^{1/2}u_m[(1+a^4)^{1/2}+1]^{1/2}}{(1+a^4)^{1/2}-u_m^2}\right]$$
$$+\left[\frac{1+(1+a^4)^{1/2}}{2}\right]^{1/2}\frac{1}{2}\ln\frac{u_m^2+(1+a^4)^{1/2}+2^{1/2}u_m[(1+a^4)^{1/2}-1]^{1/2}}{u_m^2+(1+a^4)^{1/2}-2^{1/2}u_m[(1+a^4)^{1/2}-1]^{1/2}}\ .$$

For $\omega=\omega_0$,

$$S_q'(\omega_0)=\frac{n(\omega_0)}{2\alpha_x^{1/2}}\frac{1}{(2\Gamma\omega_0)^{1/2}}\left[\delta\pi+\arctan\frac{2^{1/2}\alpha_x^{1/2}q_m(\Gamma\omega_0)^{1/2}}{\Gamma\omega_0-\alpha q_m^2}+\frac{1}{2}\ln\frac{\alpha q_m^2+\Gamma\omega_0+2^{1/2}\alpha_x^{1/2}q_m(\Gamma\omega_0)^{1/2}}{\alpha q_m^2+\Gamma\omega_0-2^{1/2}\alpha_x^{1/2}q_m(\Gamma\omega_0)^{1/2}}\right]\ .$$

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