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Neutron observation of phase and amplitude modes in an $n=4$ incommensurate system

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We report neutron-scattering measurements of phase and amplitude modes in the $n=4$ incommensurate phase II of biphenyl under hydrostatic pressure. Because of a strong lowering of the temperature range of existence of this phase with pressure, the damping of the modes is considerably reduced. It is therefore possible to measure the frequencies of three well-separated branches and their dispersion at different pressure values. These modes are clearly identified as phase and amplitude modes of a four-arm-star incommensurate structure and the results are discussed in the framework of the Landau theory.

In recent years, inelastic neutron scattering experiments have contributed to the knowledge of characteristic low-frequency excitations in displacive, incommensurate systems: phase and amplitude modes. Furthermore, theoretical works[1] have underlined that the damping of phase modes remains finite in the long-wavelength limit. Propagating phase mode and amplitude mode branches have been observed in two systems characterized by displacive transitions with low-damping soft modes—phase III of biphenyl[2-5] and $ThBr_4$ (Refs. 6 and 7)—while diffusive phase mode branches have been identified in K_2SeO_4.[8] In these three incommensurate systems, the star of the modulation wave vectors has two arms, corresponding to a two-component order parameter ($n=2$). The situation is much less clear for the dynamics of more complex incommensurate systems with $n=4$. No direct neutron observation of specific dynamics of such modulated structures has yet been reported. The incommensurate phase II of biphenyl appears to be a good candidate for such a study, since pressure effect allows a study at very low temperature where the damping is extremely reduced.

Biphenyl is an aromatic molecular compound ($C_{12}H_{10}$) which exhibits an unusual sequence of incommensurate phases at low temperature. The high-temperature-phase space group is $P2_1/a$ (phase I). The first structural phase transition occurs at $T_I=37$ K (Ref. 9) and is driven by a soft mode related to an internal torsion around the long molecular axis. Below T_I (phase II) this mode is frozen into a static incommensurate modulation wave characterized by four wave vectors ($n=4$) localized at a general point inside the Brillouin zone:

$$\pm\mathbf{q}_{s_I}=\pm\{(\delta_a\mathbf{a}^*-\delta_c\mathbf{c}^*)+[(1-\delta_b)/2]\mathbf{b}^*\}$$
$$\pm\mathbf{q}_{s_{II}}=\pm\{-(\delta_a\mathbf{a}^*-\delta_c\mathbf{c}^*)+[(1-\delta_b)/2]\mathbf{b}^*\}\ .$$

At $T_{II}=20$ K, a partial lock-in transition takes place, with an abrupt vanishing of δ_a and δ_c. Below T_{II} (phase III) the two modulation wave vectors lie along the twofold screw axis $\mathbf{b}^*$ ($n=2$). This incommensurate phase III exists at very low temperature, which has allowed the observation of propagating phase mode and amplitude mode branches.[2,3] But the same study in phase II encounters the following difficulties: (i) The number of low-frequency modes is larger than in phase III, (ii) the temperature range of existence of this phase is higher, so the modes are more damped. Hydrostatic pressure solves the latter difficulty. As discussed elsewhere,[4] pressure shifts the transition towards low temperatures (Fig. 1). T_I drops to absolute zero at about 1.85 kbar.

An inelastic neutron scattering experiment at low temperature ($T=3$ K), under pressure, has been performed at the reactor ORPHEE (Laboratoire Léon Brillouin, Saclay) on the triple-axis spectrometer 4F1 installed on a cold source. The incident neutron beam is monochromatized by means of a double pyrolytic-graphite monochromator. The equivalent horizontal collimations are 55'-30'-40'-40'. The single deuterated crystal has a size determined by the pressure cell: $10\times7\times4$ mm^3. The neutron measurements require long counting times for the following reasons: (i) the volume of the sample, and (ii) the absorption of half of the neutron flux by the high-

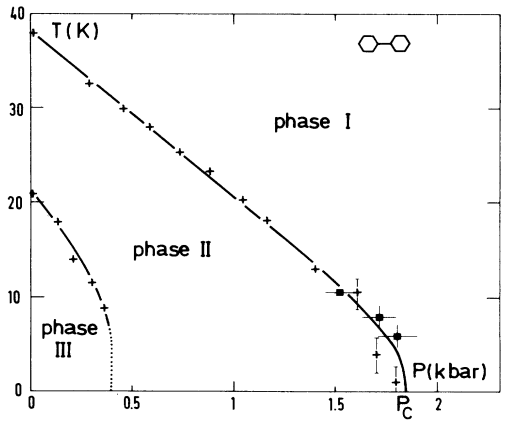

FIG. 1. Pressure-temperature phase diagram of deuterated biphenyl: + represents the data of Institut Laue-Langevin and ■ the data of Laboratoire Léon Brillouin.

pressure cell. Further, as most of measurements are performed at $T=3$ K, the scattered intensity is significant only for neutron energy loss. So the energy scans are made with constant scattered neutron wave vector k_F to escape the reduction of intensity by a k_F^3 resolution effect. k_F is most often chosen equal to 1.6 Å^{-1} without filter on incident beam. As second-order satellites are not measurable, second harmonic in incident beam does not spoil diffraction measurements. Inelastic spectra measured above and below P_c, given in Fig. 2, clearly show that there is no spurious effect induced. An improvement of the computer program driving the triple axis spectrometer allows us to now bring into the scattering plane the satellite wave vector $\mathbf{Q}_{S_1}=(2+\delta_a, 1+(1-\delta_b)/2, -\delta_c)$ and more generally $\mathbf{Q}=\mathbf{Q}_{S_1}+\mathbf{q}$, with wave vector $\mathbf{q}$ parallel to any main directions $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$.

The high-pressure system normally uses helium gas in the range 0–5 kbar, but at $T=3$ K, in the desired pressure range, helium is solid. Nevertheless one usually admits that pressure remains hydrostatic.[10] The determination of some points of the phase diagram (Fig. 1) is in good agreement with measurements made with the High Pressure Group at Institut Laue-Langevin, to within a precision of 100 bars.

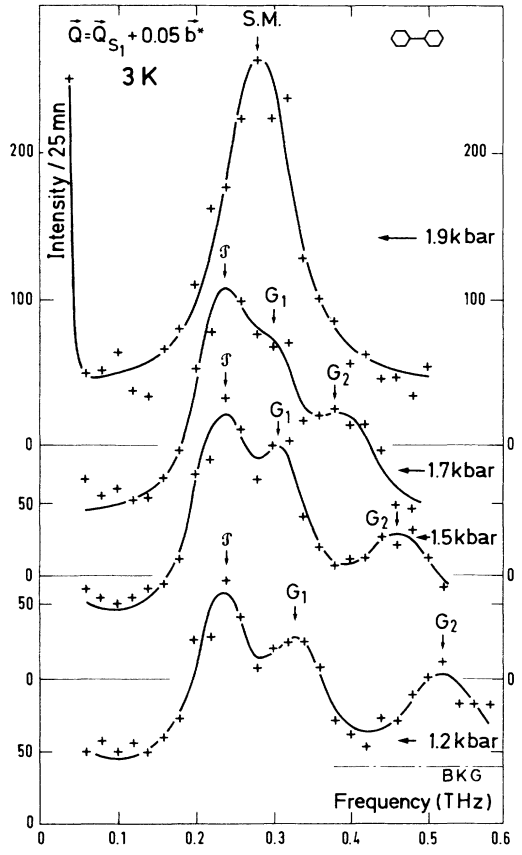

FIG. 2. Pressure behavior of neutron spectra measured at $\mathbf{Q}=\mathbf{Q}_{S_1}+0.05\mathbf{b}^*$ with $\mathbf{Q}_{S_1}=(2.07,1.45,-0.13)$. The soft mode (SM) splits into three modes: a phase mode $\mathcal{P}$ and two gap modes G_1, G_2. The lines are the result of the best fit with one or three damped harmonic oscillators.

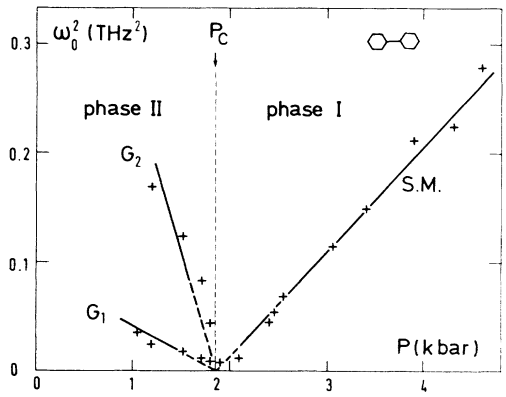

FIG. 3. Best-fit values of square quasiharmonic frequencies of the soft mode (SM) for $P>P_c$ and of amplitude modes G_1 and G_2 for $P<P_c$ at $\mathbf{Q}_{S_1}=(2.07,1.45,-0.13)$.

The quasiharmonic frequencies of the different observed modes are obtained from a fit of the data to a damped harmonic-oscillator function,[11]

$$S(\mathbf{Q},\omega)\sim\frac{\omega\Gamma|F(\mathbf{Q})|^2}{[1-\exp(-\hbar\omega/k_BT)]\{[\omega^2-\omega_0^2(\mathbf{Q})]^2+\omega^2\Gamma^2\}}$$

convoluted with the instrumental resolution function. $\omega_0(\mathbf{Q})$ is the quasiharmonic frequency of the mode propagating with $\mathbf{q}$ wave vector originating from the satellite position $\mathbf{Q}_s$: $\mathbf{Q}=\mathbf{Q}_s+\mathbf{q}$. Γ is its damping constant and $F(\mathbf{Q})$ the appropriate inelastic structure factor.

We have been able to measure neutron inelastic scattering at the exact position of the satellite and its neighborhood. All the measurements were performed at $T=3$ K with different pressures. At high pressure (phase I) one

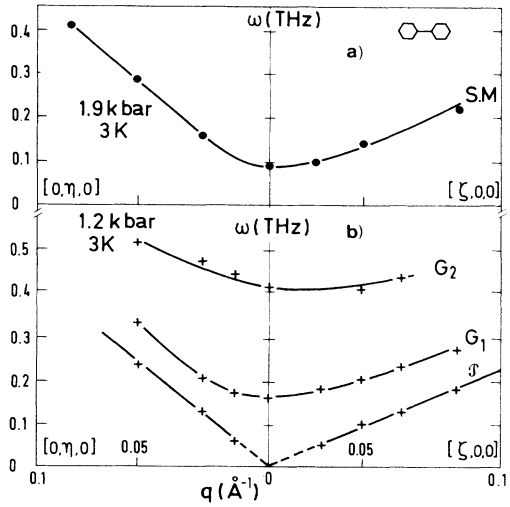

FIG. 4. Dispersion curves along $\mathbf{a}^*$ and $\mathbf{b}^*$ of (a) the soft mode at $P=1.9$ kbar, and of (b) the phase and amplitude modes $P=1.2$ kbar, originating at $\mathbf{Q}_{S_1}=(2.07,1.45,-0.13)$. Please note that the scale in Å^{-1} is the same in both directions.

TABLE I. Examples of values of the ratio $|F_{G_1}/F_{\mathcal{P}}|^2$.

$Q-Q_s$ / P (kbar)	$0.025\mathbf{b}^*$	$0.05\mathbf{b}^*$	$0.025\mathbf{a}^*$	$0.05\mathbf{a}^*$	$0.07\mathbf{a}^*$
1.2	1 ± 0.2	1 ± 0.2	2.1 ± 0.3	2 ± 0.3	2.5 ± 0.4
1.7	2 ± 0.3	1 ± 0.2	3 ± 0.5	3 ± 0.5	1 ± 0.2

measures the soft mode (SM) whose frequency decreases when pressure is decreased towards the critical value $P_c \simeq 1.85$ kbar. Figure 2 shows the spectra taken at $\mathbf{Q}=\mathbf{Q}_{S_1}+0.05\mathbf{b}^*$. At $P=1.9$ kbar, i.e., just above P_c, one sees clearly one underdamped mode (SM) related to the soft phonon branch. As pressure is lowered below P_c, this mode splits into three modes $\mathcal{P}, G_1, G_2$, which become more resolved as the pressure decreases. As seen In Fig. 2 the frequency of the mode $\mathcal{P}$ does not change with decreasing pressure, while the frequencies of the modes G_1 and G_2 increase slightly for the former and much more for the latter. The spectra, not represented, taken at $\mathbf{Q}_{S_1}$ exhibits one SM if $P > P_c$ and two modes G_1 and G_2 if $P < P_c$: This means that the energy mode $\mathcal{P}$ vanishes at $\mathbf{Q}_s$, within the precision of the triple axis spectrometer. The data at $\mathbf{Q}_{S_1}$ are fitted by one or two damped harmonic oscillators and the square quasiharmonic frequencies are reported in Fig. 3. The variation with pressure of these square frequencies is nearly linear. The slope for the soft mode is about 0.1 THz^2/kbar; it is nearly 0.3 THz^2/kbar for G_2 and approximately 0.05 THz^2/kbar for G_1. The deviation from the straight lines near P_c can possibly be due to the occurrence of the central peak as already seen in other systems.[8] As for the damping constant of the modes, it increases regularly when pressure decreases.

The dispersion of these excitations in both phases are studied. We report the dispersion of the soft mode along directions parallel to $\mathbf{a}^*$ and $\mathbf{b}^*$ at $P=1.9$ kbar in Fig. 4(a) and that of incommensurate phase modes at $P=1.2$ kbar in Fig. 4(b). Far from the satellite $\mathbf{Q}_{S_1}$ taken as the origin, one can see that the slopes of the three modes of phase II are nearly the same as the slope of the soft mode in phase I: 18 $\mathrm{THz}^2\text{Å}^2$ along $\mathbf{b}^*$ and 5 $\mathrm{THz}^2\text{Å}^2$ along $\mathbf{a}^*$.

In order to identify the three observed modes $\mathcal{P}$, G_1, G_2, we consider the dynamics of the $n=4$ incommensurate phase II of biphenyl in the scope of the classical Landau theory.[12-14] One minimizes the static free energy given by Cowley[13] and valid for biphenyl phase II:[14(b)]

$$F=F_0+a(P-P_c)(|Q_1|^2+|Q_2|^2)$$
$$+4(u+v)(|Q_1|^4+|Q_2|^4)+8u|Q_1|^2|Q_2|^2 ,$$

where $Q_i(\mathbf{q}_{si})=(A_i/\sqrt{2})e^{i\phi_i}$ with $i=$I or II, and Q_i^* are the four components of the order parameter. The $n=4$ phase II can correspond either to a monodomain structure (case I) where the two modulations of wave vectors $\mathbf{q}_{s_I}$ and $\mathbf{q}_{s_{II}}$ $[A_I\cos(\mathbf{q}_{s_I}\cdot\mathbf{r}+\phi_I)$ and $A_{II}\cos(\mathbf{q}_{s_{II}}\cdot\mathbf{r}+\phi_{II})]$ have the same amplitude ($A_I=A_{II}$), or to a two-domain structure (case II) where only one of the modulations exists in each domain ($A_I\neq0$ and $A_{II}=0$, or $A_I=0$ and $A_{II}\neq0$). In both cases, in an inelastic neutron scattering experiment, one should observe the splitting of the soft mode branch into three modes, one of which is degenerate. One of them is a gapless phason: Unambiguously, the observed mode $\mathcal{P}$ corresponds to this phason branch.[15] The two other modes present gaps whose frequencies vary with pressure. In the frame of the Landau theory, one of them is expected to vary twice as rapidly with pressure as the soft mode. It is associated with fluctuations of (A_I+A_{II}) in case I or with fluctuations of the nonzero modulation wave amplitude (A_I or A_{II}) in case II. As the measured pressure dependence of the frequency of the mode G_2 is much more pronounced than that of the soft-mode frequency, the mode G_2 is clearly identified with this amplitude mode. The main difference between case I and case II lies in the meaning of the mode G_1. In case I G_1 is associated to fluctuations of (A_I-A_{II}) and the degenerate branch is the phason branch. In case II G_1 corresponds to the excitation of the zero amplitude modulation with wave-vector $\mathbf{q}_{s_{II}}$ and then is the degenerate mode. It is visible at at $\mathbf{q}_{s_I}$ because of the existence of domains in the system. Our main argument in favor of case II concerns the inelastic structure factor of the modes with $F_{\mathrm{SM}}(\mathbf{Q})$, $F_{\mathcal{P}}(\mathbf{Q})$, and $F_{G_1}(\mathbf{Q})$ being the inelastic structure factors near a satellite position of, respectively, the soft mode, the phase mode, and the mode G_1. A straightforward calculation gives for case I $|F_{\mathcal{P}}|^2=\frac{1}{2}|F_{\mathrm{SM}}|^2$ and $|F_{G_1}|^2=\frac{1}{4}|F_{\mathrm{SM}}|^2$. In case II, with the simple hypothesis that the two types of domains are equally present, $|F_{\mathcal{P}}|^2=\frac{1}{4}|F_{\mathrm{SM}}|^2$ and $|F_{G_1}|^2=\frac{1}{2}|F_{\mathrm{SM}}|^2$. While the inelastic structure factors determined from the experimental data must be used cautiously since we have no quantitative information on the volume of the different domains in the crystal, the measured ratio $|F_{G_1}|^2/|F_{\mathcal{P}}|^2$ systematically lies between 1 and 3 (see Table I). So, this supports case II, a two-domain structure. This agrees with theoretical predictions of Benkert and Heine.[16]

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