Direct Observation of a Phason Gap in an Incommensurate Molecular Compound

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We report the results of an inelastic neutron scattering study of the lattice vibration spectra in the normal and incommensurate phases of $(ClC_6D_4)_2SO_2$. Because of unusually low soft mode damping, a finite value of the phason frequency at the satellite position is observed for the first time. The soft mode frequency saturation in the normal phase and this phason gap are consistent with the dynamical nature of the observed central peak. [S0031-9007(98)07373-6]

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Some crystals undergo a structural phase transition (SPT) from a high temperature normal (N) phase to a structurally incommensurate (IC) modulated phase at a certain transition temperature T_I. In the IC phase, at least one physical property is periodically modulated in such a way that the characteristic wave vector of the modulation $\mathbf{q}_s$ is irrational with the reciprocal lattice vectors of the N phase. As a consequence, the initial phase of the modulation wave is arbitrary, and the IC structure is continuously degenerated with respect to an arbitrary phase shift allowing the existence of special low energy excitations termed "phasons" [1,2]. The lattice dynamics of structural IC phases was the subject of many experimental studies; a review being given in Refs. [3] and [4]. In spite of the fact that the phason effects were clearly observed in the nuclear magnetic resonance (NMR) experiments (see Refs. [5,6]), the direct observation of phasons by inelastic neutron scattering remains rather scarce. For order-disorder SPT the reason is that the relaxational order parameter dynamics is, in the known cases, slower than the characteristic neutron scattering energy resolution [6,7]. Besides, for displacive SPT, in most cases the overdamped nature of the phason hinders its neutron observation in the vicinity of the satellite reflections, i.e., just in the region of the main interest. In some favorable cases, however, the damping is relatively small making possible this observation. Such an opportunity is provided by a molecular crystal: bis(4-chlorophenyl)sulfone (BCPS) also characterized by a broad temperature range IC phase.

Here we report results of the neutron scattering study of the order parameter dynamics in this compound. We shall argue that the central peak (CP) phenomenon, which is also of importance for many "ordinary" phase transitions (see, e.g., [8]), leads to a nontrivial effect in the phason scattering spectrum.

BCPS, $(ClC_6D_4)_2SO_2$, is a molecular compound crystallizing in the monoclinic I2/a structure in the N phase [9] which undergoes a second order displacive IC phase transition at $T_I = 150$ K [10]. The IC phase is known to persist down to the lowest temperatures. X-ray [11] and neutron [12] diffraction have shown that the wave vector of the incommensurate modulation, $\mathbf{q}_s \approx 0.78\mathbf{b}^*$ [13] varies smoothly with the temperature in the whole IC phase. One can note also that this IC wave vector always remains far from a high symmetry point of the Brillouin zone and that the misfit parameter is far from a simple rational pinning value. Besides, the existence of strong higher order satellites at a very low temperature [12] suggests that the static modulation is no longer sinusoidal far below T_I. Structural analyses made by x-ray [11,14] and ^{2}H-NMR experiments [15] have supported this assumption. Information on the dynamics came from light scattering [16,17] and from resonance techniques although with contradictory results [10,18,19].

The inelastic coherent neutron scattering experiments presented here were made on a cold neutron source triple-axis spectrometer 4F2 at the Laboratoire Léon Brillouin at Saclay (France). The fully deuterated sample was a $0.3 \times 0.7 \times 1.2 \approx 0.25$ cm^3 single crystal grown by the Bridgman technique. The mosaic spread was found, by neutron diffraction, to be about $35'$. The inelastic constant-Q spectra were recorded with a fixed incident wave vector $k_I = 1.20$ Å^{-1} (3 meV incident energy) with a frequency resolution of $\Delta\omega \approx 20$ GHz for accurate measurements close to the satellite position. A beryllium filter was used to avoid contamination of higher order harmonics in the incident neutron beam and no collimation was used during the experiments. The typical resolution in the reciprocal space was about 0.007 Å^{-1} near the (0 1.22 2) satellite position. A sample oriented in the $(\mathbf{b}^*, \mathbf{c}^*)$ plane of the reciprocal space was cooled in a Displex allowing a temperature control better than 0.1 K.

The soft branch, emanating from the lowest transverse acoustic branch, has been measured along the modulation direction showing a well-defined minimum at the satellite position, even at room temperature [20]. This result

agrees with lattice dynamics calculations [21]. The main characteristic of this molecular compound is the exceptional low damping of its soft mode (SM) in the high temperature (HT) phase. This allows one to observe an underdamped soft phonon down to a few K above the transition temperature (T_I + 10 K). The spectra in the inset in Fig. 1 show the SM side component plus a resolution limited CP (discussed below) growing from about $T = T_I + 50$ K = 200 K. The inelastic spectra have been fitted assuming a classical damped harmonic oscillator for the SM side component giving the frequencies reported in Fig. 1. From room temperature to 160 K, the SM inelastic structure factor (ISF) has been found constant, and we have expected that to be the case down to the transition temperature T_I. Close to T_I, we have assumed, furthermore, a **q**-independent damping for the soft branch $\Gamma(\mathbf{q}, T) \approx \Gamma(T)$ in the vicinity of $\mathbf{q}_s$ (as has been checked experimentally) allowing one to extract a damping from its dispersion at T_I + 1 K. As seen in Fig. 1, the squared SM frequency displays a linear behavior with the temperature (with a slope $a_{\mathrm{SM}} \approx 350$ GHz^2 K^{-1}), but reaches a finite value at the transition. The frequency gap is about $\omega_{\mathrm{SM}}(\mathbf{q}_s, T_I) = 78 \pm 4$ GHz with a damping $\Gamma_{\mathrm{SM}}(T_I) = 160 \pm 20$ GHz (the error bars correspond to extremal fitting values compatible with the above conditions).

In Fig. 2 are reported the constant-Q inelastic spectra in the low temperature (LT) phase close to $\mathbf{q}_s$. As can be seen from the spectra, the splitting of the HT side component SM line into two parts is clearly revealed. The highest frequency mode becomes stiffer when the temperature is lowered as expected for an amplitudon mode, and its frequency and damping extracted from the spectra follow, with good agreement, the same parameters gathered from Raman light scattering [17]. The second mode is observed to be temperature independent, at least in the accuracy of these neutron experiments. It is the phason because (i) it emerges from the soft mode along with the amplitudon, (ii) its intensity follows the Bose population factor while for an acoustic phonon one should observe additional temperature dependences following the Bragg-satellite peak intensity, and (iii) its frequency is not zero at the satellite position which is forbidden for an acoustic phonon. A direct measurement of a CP response has not been possible because of the presence of the Bragg satellite peak at $\mathbf{q}_s$.

Both LT modes have been fitted by a damped harmonic oscillator function with some constraints. Since the two new excitations are linear combinations of the SM coupled normal modes [2], their damping is supposed to be equal to the SM one $\Gamma_\phi(T) \approx \Gamma_A(T) \approx \Gamma_{\mathrm{SM}}(T)$, whereas their ISFs are expected to be $|F_{in,\phi}(\mathbf{Q}_\pm, T)|^2 = |F_{in,A}(\mathbf{Q}_\pm, T)|^2 = \frac{1}{2}|F_{in,\mathrm{SM}}(\mathbf{Q}_\pm, T)|^2$, where $\mathbf{Q}_\pm = \mathbf{G} \pm \mathbf{q}_s + \mathbf{k}$ in the neighborhood of $\mathbf{q}_s$ [22]. In our experiments, both conditions cannot be fulfilled simultaneously. During the fitting procedure we have imposed the first condition. We have also kept equal the phason and amplitudon ISF in the whole temperature range and, close only to T_I, their ISFs have been made equal to the half of the SM one (as it should be for the harmonic case). The set

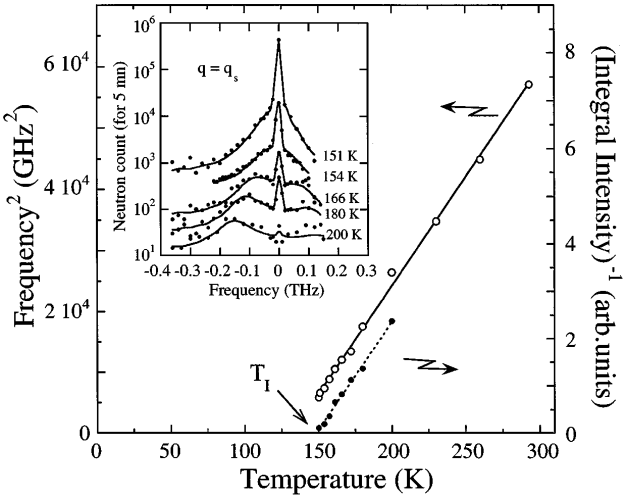

FIG. 1. (∘) Evolution of the squared SM side component frequency vs temperature at $\mathbf{q} = \mathbf{q}_s$ for $Q = (0\ 1.22\ 2)$. The straight line is a fit (see text). (•) Inverse of the total integral intensity (side plus central components) vs temperature in the region where both the SM and the CP are observed (dashed line is a guide to the eye). The inset shows the constant-Q spectra (on a semilogarithmic scale) at the satellite position emphasizing the side and central peak components. The incoherent elastic contribution has been subtracted from the spectra.

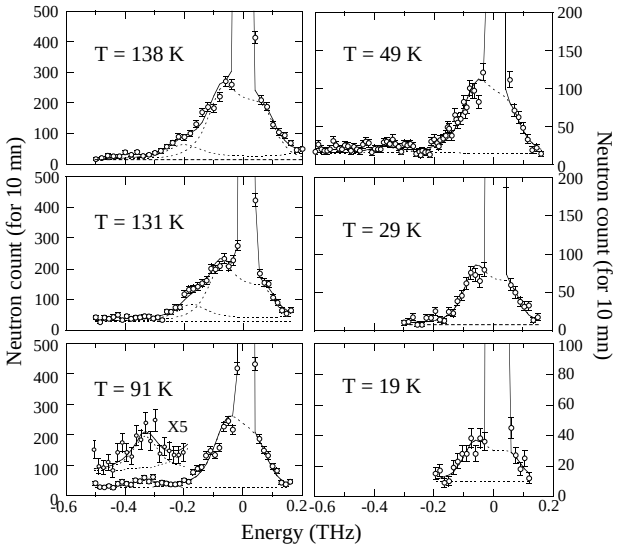

FIG. 2. Inelastic coherent neutron spectra in the LT phase close to $\mathbf{q}_s$ for different temperatures. The zero frequency component of the spectra is due to the Bragg satellite peak, the elastic incoherent scattering, and, presumably, to the central peak.

of parameters extracted from the fits according to the above conditions are reported in Fig. 3. The amplitudon frequency is observed to follow, with a good agreement, the light scattering one (dotted line in Fig. 3a), whereas the phason frequency is found to be constant with a mean value of $\overline{\omega}_\phi = 90 \pm 10$ GHz from T_I down to the lowest measured temperature (19 K). Another important point is that, within the error bars, we have a continuity of the frequencies through the transition with nearly the same gap for the phason in all of the LT phase as the one observed for the SM branch at T_I. One can note that high resolution light scattering experiments [17] concluded to a gap of the same order for the amplitudon at T_I, and very low temperature specific heat experiments [23] found a value for the phason gap compatible with our data. The phason width saturates gradually over 100 GHz (full width at half maximum) at a very low temperature, whereas the amplitudon damping behaves roughly like the one observed by light scattering.

Splitting of the SM into two new excitations, namely, the phason and the amplitudon, has been reported by inelastic neutron scattering in several materials: potassium selenate (K_2SeO_4), thorium tetrabromide ($ThBr_4$) [3], biphenyl [3,24], and, more recently, in betaine calcium chloride dihydrate [25]. Among these compounds only $ThBr_4$ and biphenyl under pressure show well underdamped modes in both the HT and IC phases, but the occurrence of a phason gap in these crystals has not been conclusively established by the authors [24,26]. All of the other compounds present a highly overdamped phason at $\mathbf{q}_s$, ruling out the possibility of a *direct* observation of a phason gap. Thus, the observation of the SM side component frequency saturation with a related CP and, especially, the direct measurement of a gap in the phason branch constitute a very first direct experimental result.

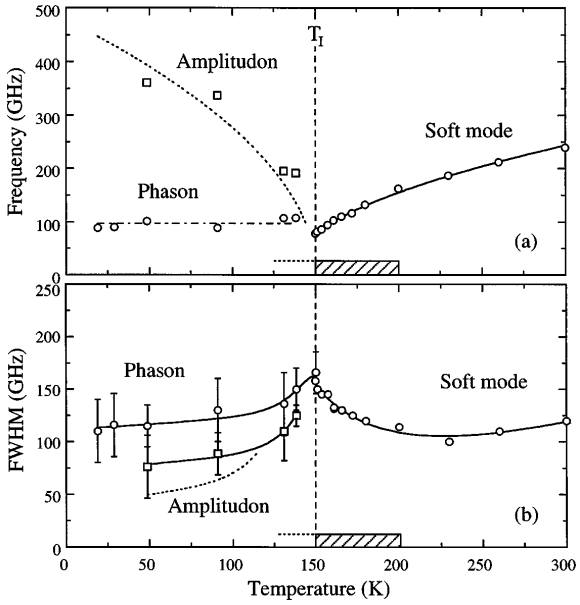

FIG. 3. (a) Frequencies of the amplitudon and phason at $\mathbf{q} \approx \mathbf{q}_s$ vs temperature. The dotted line is the fit of the amplitudon obtained from the Raman experiment (Ref. [17]) and the dashed area indicates the temperature range where both the SM side component and the central component are present in the spectra. Solid line: Same fit as in Fig. 1. Dash-dotted line: Guide to the eye. (b) Damping of the same modes. Solid lines are guides to the eye, the dotted line stands for the Raman experiment. Error bars stand for extremal values compatible with the fitting conditions (see text).

The existence of the CP phenomenon in the HT phase has been shown in several compounds presenting a structural phase transition, including IC ones. It is now well known that the CP is intimately connected to the saturation of the SM side component frequency in a displacive second order phase transition. Both theoretical and experimental studies have been made concerning the CP during the past years (see, e.g., [27]) but, presently, no unique and fully accepted description exists and several questions remain unresolved: has the CP an "intrinsic" (i.e., existing in ideally pure systems) or "extrinsic" (defect induced) origin and does the CP response include a dynamical part? It is now clear that a CP, together with a soft mode gap at T_I, exists even in highly purified and defect-free samples, for example, in $SrTiO_3$, where high quality samples are now commercially available, leading to the conclusion that the CP results in an intrinsic mechanism. But, it is also known that its strength and the soft mode gap are enhanced with the defect concentration, although it is less evident for the latter in neutron scattering experiments [28]. So, if the CP is defect related, it is on a wide range of concentration and the relation between the CP intensity and the defect concentration is not trivial.

Looking for a dynamical CP can be made independently from its microscopic origin. A simple phenomenological model developed earlier to describe the CP in strontium titanate gives a coherent description of the observations in the HT phase [8]. In a Landau-type phenomenological treatment, this model expresses the existence of a linear (in the first approximation) coupling between the order parameter associated to the SM and a variable with a Debye-type relaxation behavior [29]. As a consequence, the total SM spectral response function is composed of two contributions, well separated under some conditions generally fulfilled [8], namely, a side component SM and a Lorentzian-shaped CP (not resolved by neutron scattering). For $\mathbf{q} = \mathbf{q}_s$, the SM renormalized frequency becomes $\omega_\infty^2(0,T) = a_{\mathrm{SM}}(T - T_I) + \delta^2$ which describes quite well our data (straight line in Fig. 1) with the temperature-independent coupling parameter $\delta = \omega_\infty(0,T_I) = \omega_{\mathrm{SM}}(q_s,T_I)$. The fact that the total SM intensity is proportional to $(T_I - T)^{-1}$ (see Fig. 1) supports the assumption that the CP is of a dynamic nature in BCPS (solid circles and dashed line in Fig. 1).

Let us recall that the phason in an IC phase displays basically the same properties as those of an ordinary soft

mode at the transition temperature. In the CP situation the total dynamical response at the transition has side components at a finite frequency together with a critical central peak. It is then natural to expect that the same situation may take place for the phason because of the continuity of the parameters through the IC transition. Therefore, one can easily extend the model to determine the spectrum of the amplitudon and phason in the IC phase. One has now to assume the real and imaginary part of the complex order parameter $\eta = (\eta_1, \eta_2)$ that, in the IC phase, can be associated, respectively, with the longitudinal (amplitude) and transverse (phase) fluctuations linearly coupled to some relaxational variable $\xi = (\xi_1, \xi_2)$ with the same symmetry properties. The Landau free energy can then be written as

$$\phi = \phi_o + \frac{A}{2}(\eta_1^2 + \eta_2^2) + \frac{B}{4}(\eta_1^2 + \eta_2^2)^2 + \frac{D}{2}(\nabla\eta_1^2 + \nabla\eta_2^2) + \frac{1}{2}(\xi_1^2 + \xi_2^2) + \delta(\eta_1\xi_1 + \eta_2\xi_2) + \ldots, \quad (1)$$

where the last term expresses a linear coupling between the order parameter and the relaxational variable. δ is the coupling parameter (same as in the N phase). Of course, the nature of the latter variables cannot be specified and nothing can be said about the temperature dependence of the involved constants. Computing in a straightforward way the resulting dynamical equations, the model leads to a side component phason with an associated CP and a side component amplitudon with its own CP. At $\mathbf{q} = \mathbf{q}_s$, the frequencies actually measured are then expressed as $\omega_{\infty\phi}^2(0) = \delta^2$, giving also in the IC phase a temperature-independent coupling parameter, and $\omega_{\infty A}^2(0, T) = -2a_{\mathrm{SM}}(T - T_I) + \delta^2$, where the subscripts "$\infty$" have the same meaning as in the N phase and "ϕ" and "A" stand for phason and amplitudon, respectively. As the frequencies are continuous through the transition, the parameter δ remains unchanged between the two phases: $\delta = \omega_{\mathrm{SM}}(\mathbf{q}_s, T_I) = \overline{\omega}_\phi \approx 80$ GHz (Fig. 3). The low frequency spectra in both phases are in agreement with the above picture. However, the model discussed above predicts equality of both the phason and the amplitudon width, which is not the case in our experiments.

Let us emphasize that the observed phason gap in our neutron experiments is seen at high frequencies and from this point of view differs from the very low frequency dynamics probed by NMR which did not reveal any gap [18]. Following our description, these NMR results could be interpreted as due to the dynamic CP part.

In conclusion, we have observed a soft mode frequency saturation at the N-IC transition related to the growth of a CP in the spectra when lowering the temperature in the N phase. In agreement with the continuity of this second order displacive transition a similar frequency saturation is found in the phason branch in the whole IC phase. Within the neutron accuracy, this gap has been observed to be temperature independent. We argue that one could reasonably assume that both the SM frequency saturation and the phason gap are of the same microscopic nature, including a dynamical CP in both phases in the spectral responses.

[1] A. W. Overhauser, Phys. Rev. B **3**, 3173 (1971).
[2] A. D. Bruce and R. A. Cowley, J. Phys. C **11**, 3609 (1978).
[3] See *Incommensurate Phases in Dielectrics*, edited by R. Blinc and A. P. Levanyuk (North-Holland, Amsterdam, 1986), Vols. 1 and 2.
[4] See H. Z. Cummins, Phys. Rep. **185**, 211 (1990), and references therein.
[5] R. Blinc, D. C. Ailion, J. Dolinšek, and S. Žumer, Phys. Rev. Lett. **54**, 79 (1985).
[6] P. Mischo, F. Decker, U. Häcker, K.-P. Holzer, J. Petersson, and D. Michel, Phys. Rev. Lett. **78**, 2152 (1997).
[7] D. Durand *et al.*, Phys. Rev. B **39**, 2453 (1989).
[8] S. M. Shapiro, J. D. Axe, G. Shirane, and T. Riste, Phys. Rev. B **6**, 4332 (1972).
[9] J. G. Sime, Acta Crystallogr. **13**, 1 (1960).
[10] D. J. Pusiol, A. E. Wolfenson, and A. H. Brunetti, Phys. Rev. B **40**, 2523 (1989).
[11] H. Kasano *et al.*, J. Phys. Soc. Jpn. **59**, 408 (1990).
[12] J. Etrillard *et al.*, Solid State Commun. **87**, 47 (1993).
[13] An alternative to this notation on the boundary of the first Brillouin zone is $\mathbf{q}_s \approx \mathbf{a}^* + 0.22\mathbf{b}^*$.
[14] F. J. Zuñiga, J. M. Perez-Mato, and T. Breczewski, Acta Crystallogr. Sect. B **49**, 1060 (1993).
[15] C. Meinel *et al.*, Phys. Rev. B **56**, 13 774 (1997).
[16] K. Ishii *et al.*, J. Phys. Soc. Jpn. **61**, 2317 (1992).
[17] C. Ecolivet, M. Sougoti, Y. Délugeard, and S. Beaufils, J. Phys. I (France) **4**, 1451 (1994).
[18] R. de Souza, M. Engelsberg, and D. J. Pusiol, Phys. Rev. Lett. **66**, 1505 (1991).
[19] R. Blinc *et al.*, Phys. Rev. B **51**, 1354 (1995).
[20] J. Ollivier, Ph.D. thesis, University of Rennes, 1997.
[21] K. Saïto, K. Kikuchi, and I. Ikemoto, Solid State Commun. **81**, 241 (1992); A. Criado, J. Phys. Soc. Jpn. **64**, 2471 (1995).
[22] R. Currat, L. Bernard, and P. Delamoy, in Ref. [3], Vol. 2.
[23] J. Etrillard *et al.*, Phys. Rev. Lett. **76**, 2334 (1996).
[24] P. Launois *et al.*, Phys. Rev. B **40**, 5042 (1989).
[25] J. Hlinka *et al.*, J. Phys. Condens. Matter **9**, 1461 (1997).
[26] L. Bernard *et al.*, J. Phys. C **16**, 433 (1983).
[27] R. A. Cowley, Philos. Trans. R. Soc. London A **354**, 2799 (1996).
[28] J. B. Hastings, S. M. Shapiro, and B. C. Frazer, Phys. Rev. Lett. **40**, 237 (1978); K. Hirota, J. P. Hill, S. M. Shapiro, and G. Shirane, Phys. Rev. B **52**, 13 195 (1995).
[29] V. L. Ginzburg, A. P. Levanyuk, and A. A. Sobyanin, Phys. Rep. **57**, 151 (1980).