Phason dispersion in deuterated thiourea by inelastic neutron scattering

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The phason origin of the quasielastic diffuse scattering in the incommensurate phase of thiourea is demonstrated by inelastic neutron scattering on a deuterated crystal. The analysis of its frequency spectrum allows one to draw the dispersion of the phason relaxational frequency along the modulation direction. Results indicate that the lowest-frequency mode seen in submillimeter infrared spectra is an overdamped inhomogeneous phason mode corresponding to the antiphase motion of the nearest-neighbor nodes of the modulation profile.

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The vibrational order-parameter dynamics in displacive incommensurate dielectrics is discussed in terms of the so-called phason and amplitudon excitations.[1–5] The homogeneous amplitudon (representing ''breathing'' of the frozen modulation wave in amplitude) behaves much as an ordinary soft mode, and as a rule, it is best characterized in Raman scattering experiments. The phason excitation is more anomalous since the frequency of the homogeneous phason is usually zero or extremely small[12] in the whole incommesurate phase. For small wave vectors, the phason branch has ''acousticlike'' dispersion which, in principle, can be studied by inelastic neutron scattering (INS).[6–11] For certain special values of the wave vector, the phason mode acquires a noticeable dielectric strength through bilinear coupling to the zone center soft polar mode (homogeneous polarization). Such inhomogeneous phasons then contribute to the infrared and dielectric spectra.[13,14] In fact, they may cause quite spectacular effects, as, for example, in the case of the huge dielectric anomaly near the sevenfold phase of betaine calcium chloride dihydrate.[15] The interpretation of phason phenomena in dielectric and optical spectra is nevertheless very difficult without help from direct phason dispersion measurement by INS.

Thiourea is one of the most studied incommensurate dielectric crystals.[2] Its high temperature paraelectric phase ($T > T_i = 202$ K) and the low-temperature ferroelectric phase ($T < T_c = 169$ K) are both orthorhombic with 4 molecules per unit cell ($Pnma$ and $P2_1ma$, respectively). The intermediate- temperature interval ($T_c < T < T_i$) comprises incommensurate and commensurate phases with electric polarization directed along the a and modulated along the b axes. The modulation wave vector q_i displays a monotonous devil's-staircase-like temperature dependence with $\mathbf{q}_i(T_i) \approx 0.14\mathbf{b}^*$, $\mathbf{q}_i(T_c) = \mathbf{b}^*/9$. For the purpose of this paper, this whole interval can be considered as a single modulated phase. Deuterated thiourea $SC(ND_2)_2$ has essentially the same phase diagram, but with $T_c = 192$ K and $T_i = 218$ K.[2,17]

The order-parameter dynamics in thiourea was studied by infrared, Raman, and INS spectroscopic methods in all phases including the incommensurate one. While the amplitudon mode was remarkably well characterized,[16] almost nothing is known about the phason branch. The first INS measurements devoted to the search of the phason mode have indeed disclosed an additional low-frequency branch extrapolating to zero frequency at the first-order satellite,[18] but a more precise analysis[19] has later shown that it was the lowest-frequency transverse acoustic (TA) branch, polarized along the a direction, rather than the phason branch. Although the phason branch was clearly observed in several other incommensurate dielectrics,[6–8,10,11] we are not aware of any other subsequent attempt to measure the phason dispersion in thiourea.

Long-wavelength phasons are always overdamped[20] and give rise to quasielastic diffuse scattering (DS) located primarily around the first-order satellite reflections. Since the DS seen in the paraelectric phase of thiourea[19,21,22] was shown to be caused by the soft mode,[17] it is highly probable that the DS observed in the incommensurate phase[19] is also quasielastic and originates from the overdamped phason. The purpose of this study is to investigate this quasielastic DS in detail and, by its quantitative analysis, to obtain information on the phason dispersion.

The measurements were carried out on the IN12 cold neutron three-axis spectrometer at the ILL high flux reactor. The instrument was operated with a fixed energy of analyzed neutrons ($k_f = 1.05$ Å^{-1}) and Soller collimators 43′, 60′, and 60′ in front of the sample, analyzer and detector, respectively. An optically transparent crystal with natural faces, wrapped in a thin aluminum foil was mounted on the cold finger of a standard closed-cycle cryostat with temperature stability better then 0.1 K. This 2.57 g crystal of $SC(ND_2)_2$ was grown by a slow evaporation and cooling method from deuterated methanol solution in the Institute of Physics ASCR in Prague. The comparison of the Raman-scattering intensities of the ND_2 and the residual NH_2 internal modes as well as the value of the phase transition temperature ($T_i = 218.5$ K) indicate that the level of deuteration in our sample was better than 98%, similarly as in the crystals used for previous INS investigations.[17,19]

In order to avoid the above-mentioned contribution of the low-frequency TA branch, the sample was oriented with the a axis vertical. This geometry allowed us to explore the $0KL$

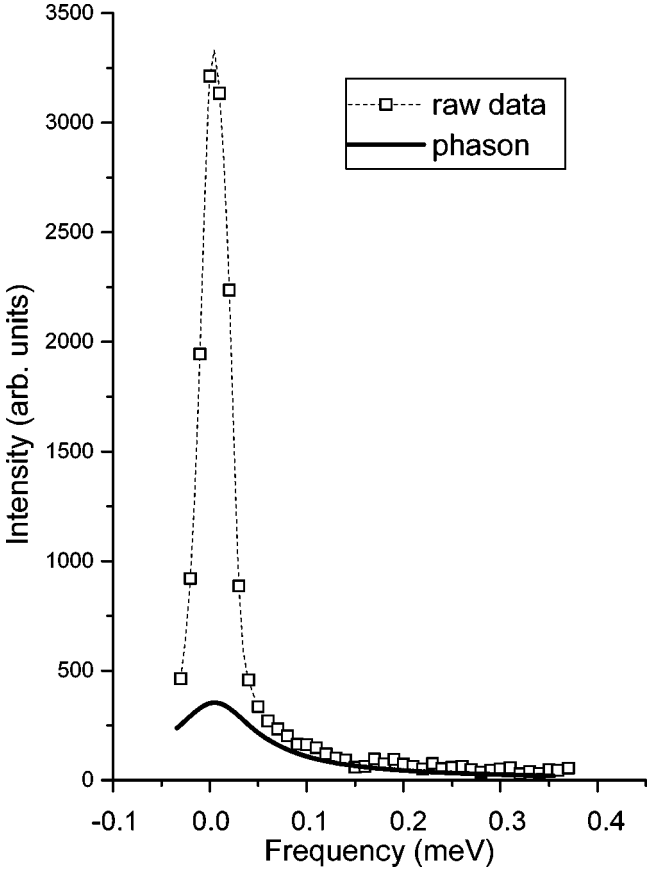

FIG. 1. Raw INS spectrum of $SC(ND_2)_2$ taken at $Q=(0,-0.16,1)$ at 195 K. The narrow, resolution limited central component comes from elastic incoherent scattering, the wide frequency tail reveals the quasielastic DS ascribed to the overdamped phason. The thick solid line represents the phason contribution as obtained from the fit to the background-corrected data (see Fig. 2), the thin line is only a guide for the eye.

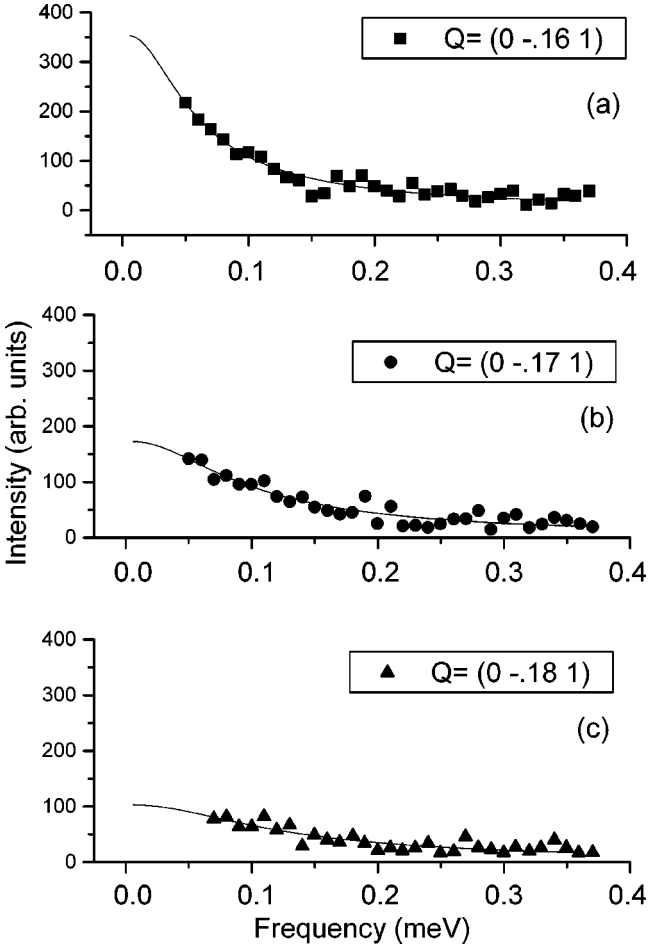

FIG. 2. Measured quasielastic DS intensity (background subtracted, see the text) fitted using Eq. (3). (a), (b), and (c) shows data taken at $Q=(0,-0.16,1)$, $(0,-0.17,1)$ and $(0,-0.18,1)$, respectively.

scattering plane, where the structure factor of the *a*-polarized TA branch vanishes. Typical momentum resolution widths measured on $0\pm q_i/b^*1$ satellites were $0.1a^*$, $0.01b^*$, $0.01c^*$. The energy resolution, as given by the energy profile of elastic incoherent scattering, was 32 μeV. This rather tight resolution was necessary in order to separate the quasielastic DS from the intense elastic incoherent background caused by the residual hydrogen in the sample. The experiment was performed at 195 K, i.e., just a few degrees above T_c, in order to be sure that the amplitudon contribution to the quasielastic DS could be neglected. The modulation wave vector $\mathbf{q}_i=0.118\mathbf{b}^*$ at this temperature, determined from the position of the pair of the third-order satellites $(0\pm 3q_i/b^*\ 1)$, confirms that the chosen temperature was above the stability region of the $b^*/9$ commensurate phase.

A typical energy scan in 001 Brillouin zone (Fig. 1) shows the narrow, resolution limited elastic incoherent line and a wider profile reminding an overdamped phonon. The investigated frequencies ($\nu<40$ μeV) are much lower than the damping constant of the phason, which should be roughly the same as that of amplitudon[16] or that of the zone center infrared active soft mode[24] ($\Gamma\approx 10\ \mathrm{cm}^{-1}\approx 1.2$ meV). The response function of an overdamped phason at $kT\gg h\nu$ should then be well described by

$$S(\mathbf{q},\nu)\propto \frac{kT}{\Gamma_\mathbf{q}}\,\frac{1}{\nu^2+\gamma_\mathbf{q}^2},\qquad \gamma_\mathbf{q}\equiv\frac{\nu_\mathbf{q}^2}{\Gamma_\mathbf{q}}, \tag{1}$$

where $\gamma_\mathbf{q}$, $\nu_\mathbf{q}$, and $\Gamma_\mathbf{q}\approx\Gamma$ are the relaxational frequency, vibrational frequency, and damping parameter of the phase mode at a wave vector $\mathbf{q}=(q_x,q_y,q_z)$. For wave vectors close to the satellite position (i.e., in the region contributing to the quasielastic DS), the dispersion of the relaxation frequency $\gamma_\mathbf{q}$ follows a parabolic law,[2,10]

$$\gamma_\mathbf{q}=\gamma_{\min}+D_x q_x^2+D_y(q_y-q_{i,y})^2+D_z q_z^2. \tag{2}$$

Due to the well known rapid falloff of the quasielastic DS intensity in the polar *a* direction[19,21] and in view of our rather wide momentum resolution in the corresponding direction (about $0.1a^*$, given by the natural vertical divergence of the spectrometer), we are actually integrating the quasielastic DS intensity over this ''hard direction.'' On the other hand, the scans were carefully chosen in order to keep the resolution function in the energy and in the other two spatial directions

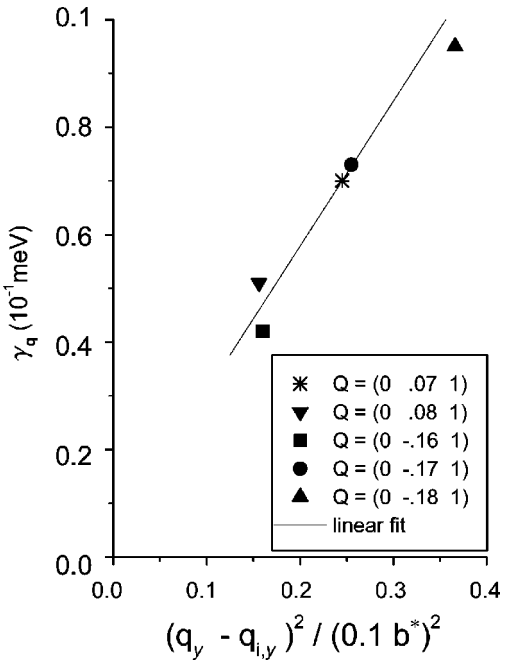

FIG. 3. Dispersion of the phason relaxational frequency $\gamma_{\mathbf{q}}$ for $\mathbf{q} \| \mathbf{q}_i$. Full symbols are obtained by fitting the data to Eq. (2). The line is a fit of the dispersion using Eq. (2).

sufficiently narrow in comparison with the width of the investigated quasielastic DS signal. (Apparent widths of the quasielastic DS were about $0.1a^*$, $0.1b^*$, $0.05c^*$, 0.15 meV.) Assuming a parabolic dispersion along the a^* axis as in Eq. (2), the a^*-integrated intensity obtained from Eq. (1) for scans taken at a nominal wave vector $\mathbf{q}$ with $q_x = 0$ reads

$$I(\mathbf{q},\nu) \propto \frac{i\pi kT}{2\nu\Gamma\sqrt{D_x}} \frac{\sqrt{\gamma_{\mathbf{q}} - i\nu} - \sqrt{\gamma_{\mathbf{q}} + i\nu}}{\nu^2 + \gamma_{\mathbf{q}}^2}. \qquad (3)$$

Before comparing the data with this somewhat unusual but quite simple expression, we have subtracted the inelastic background obtained by smoothing a spectrum taken at $Q = (0, -0.2, 0.85)$, where the quasielastic DS intensity is negligible. The resulting data were fitted by the expression in Eq. (3) with $\gamma_{\mathbf{q}}$ and an overall normalization factor as the only fitting parameters. The overall agreement was rather good (Fig. 2). The normalization factor was roughly the same for all wave vectors, suggesting that the phason structure factor variation can be neglected. On the other hand, $\gamma_{\mathbf{q}}$ shows a fast variation with wave vector, as expected (Fig. 3).

In view of Eq. (2), a linear fit of the $\gamma_{\mathbf{q}}$ vs q_y^2 plot shown in Fig. 3 should provide directly both the phason relaxation frequency gap $\gamma_{\min}$ and the dispersion parameter D_y. In reality, the phason gap seems to be much smaller than our energy resolution (anything between 0 and 10 μeV would be consistent with our data) and its further investigation is beyond the scope of this study. In any case the $\gamma_{\min}$ of thiourea is much lower than that of (4-chlorophenyl) sulfone, which is the only incommensurate dielectric crystal in which the phason gap could be determined by INS measurements[12] (with $\gamma_{\min} = 0.15$ meV–0.3 meV).

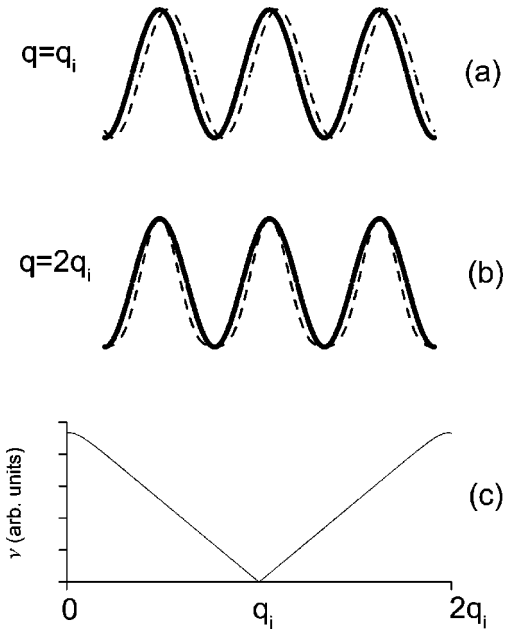

FIG. 4. Schematic representation of the homogeneous (a) and inhomogeneous (b) phason associated with the zone center ($\mathbf{q} = \mathbf{q}_i$) and the zone boundary ($\mathbf{q} = 2\mathbf{q}_i$) of the first Brillouin zone corresponding to the modulation period $2\pi/q_i$ (c). Full line in (a) and (b) represents the equilibrium polarization wave, dashed lines show instantaneous configurations induced by the represented phason fluctuations.

The slope of the $\gamma_{\mathbf{q}}$ vs q_y^2 plot yields $D_y \approx 27 \pm 5$ meV$(b^*)^{-2} = 50 \pm 10$ meV Å^2. This value is clearly smaller than the corresponding values for the systems with well dispersive phasons such as $ThBr_4$ (210 meV Å^2, Ref. 8) and K_2SeO_4 (120 meV Å^2, Ref. 7); but it is higher than values for betaine calcium chloride dihydrate (BCCD) (20 meV Å^2, Ref. 10) and for the order-disorder incommensurate system $NaNO_2$ (0.05 meV Å^2, Ref. 23). The present experimental arrangement did not allow us to extend the investigated wave vector range much further because of the intensity limitation on $|q_y - q_{i,y}| > 0.06b^*$ side and due to the resolution limits on the $|q_y - q_{i,y}| < 0.03\ b^*$ side. Nevertheless, we assume that the parabolic approximation is reasonably good at least within the pseudo-Brillouin zone defined with respect to the modulation period $2\pi/q_i$.

The mode corresponding to the boundary ($\mathbf{q} = 2\mathbf{q}_i$) of this ''incommensurate'' Brillouin zone should have the ($E \| a$) infrared activity.[13,14] The relaxational frequency extrapolated using Eq. (2) to $\mathbf{q} = 2\mathbf{q}_i$ ($\gamma_{2q_i} \approx 3$ cm^{-1}) indeed corresponds to the lower-frequency mode observed in the submillimeter infrared spectra[24] at $\nu^2/\Gamma \approx 2$ cm^{-1} (previously tentatively assigned as inhomogeneous amplitudon[24]).

Thus, the present INS measurements allow one to provide the correct interpretation of this previously found[24] low-frequency dielectric mode as inhomogeneous phason: it corresponds to the antiphase motion of the nearest-neighbor nodes of the modulation function,[14] as shown in Fig. 4. Most probably, this inhomogeneous phason can be further identified with the so-called ''REL2'' relaxational mode found by

fitting of the compiled available dielectric data for $SC(NH_2)_2$ in the early work of Ref. 25.

In conclusion, the present study has elucidated the phason origin of the DS in the incommensurate phase of thiourea. Dispersion of the phason relaxation frequency is smaller than in the prototype K_2SeO_4 crystal but higher than in the BCCD one, where all the phason modes with $\mathbf{q} \| q_i$ are overdamped. The experimentally established slope of this dispersion allows one to assign the lowest-frequency infrared active mode seen in the previous dielectric measurements in the submillimeter range as the inhomogeneous phason. Further details of our analysis, extension of the measurements to the entire Brillouin zone, and a more advanced modeling will be published elsewhere.

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