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Dynamical molecular disorder and diffuse scattering in an alkane/urea incommensurate inclusion compound

R. Lefort[1,a], B. Toudic[2], J. Etrillard[2], F. Guillaume[3], P. Bourges[4], R. Currat[5], and T. Breczewski[6]

[1] Laboratoire de Dynamique et Structure des Matériaux Moléculaires, EISA 8024, Cité Scientifique, 59655 Villeneuve d'Ascq Cedex, France
[2] Groupe Matière Condensée et Matériaux[b], Université de Rennes I, 35042 Rennes Cedex, France
[3] Laboratoire de Physico-Chimie Moléculaire[c], Université de Bordeaux I, 33405 Talence, France
[4] Laboratoire Léon Brillouin, CEA-CNRS, CE-Saclay, 91191 Gif-sur-Yvette, France
[5] Institut Laüe-Langevin, Avenue des Martyrs, BP 156, 38042 Grenoble Cedex 9, France
[6] Facultad de Ciencias, Universidad del Pais Vasco, Apdo 644, Bilbao, Spain

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Abstract. The diffraction pattern of n-alkane/urea inclusion compounds is known to contain a broad diffuse scattering related to the molecular form factor of the alkane species, indicating individual rotational and/or translational disorder of these molecules. Inelastic coherent neutron scattering reveals for the first time the entirely dynamical character of the alkane molecular disorder around room temperature. This observation fully agrees with a recent model of the coherent scattering cross section of totally uncorrelated motions. In the ordered phase this diffuse scattering remains, but elastic, and very low energy molecular vibrational modes are evidenced. These observations are discussed in relation with previous incoherent neutron scattering results.

PACS. 61.43.-j Disordered solids – 61.12.Ex Neutron scattering techniques (including small-angle scattering) – 61.44.Fw Incommensurate crystals

1 Introduction

Aperiodic composite crystals are systems in which two or more interlaced sublattices share crystallographic axes, with an irrational ratio of subcell parameters in at least one direction. For several years, they have raised considerable physical interest due to their intermediate complexity between incommensurate phases and quasicrystals. A typical example of such organic composites are urea inclusion compounds. In those supramolecular systems, urea molecules build up a network of hexagonal infinite and parallel channels with diameters (c.a. 5.25 Å) large enough to accommodate guest linear molecules such as n-alkanes [1]. The mean room temperature structure of the urea host subsystem is described by the hexagonal $P6_122$ space group [2], with cell parameters $a = b = 8.22$ Å and $c_{\text{host}} = 11.02$ Å. The a and b parameters are shared by both host and guest subsystems, but the misfit parameter $\alpha = c_{\text{host}}/c_{\text{guest}}$ can be irrational. In n-alkane/urea inclusion compounds, c_{guest} is close to the length of the free guest molecule in the all-trans conformation [1]. Thus an incommensurate intermodulation is expected due to the host/guest interactions, giving rise to additional satellite Bragg reflections. According to the theory of modulated composite structures [3], the complete diffraction pattern can be indexed within a four dimensional superspace. With the relation $\mathbf{Q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*_{\text{host}} + m\mathbf{c}^*_{\text{guest}}$, all diffraction maxima can be classified as follows: $m = 0$, main reflections from the host subsystem (urea); $l = 0$, main reflections of the guest subsystem (alkane); $l = m = 0$, common reflections from both subsytems; $l \neq 0$ and $m \neq 0$, satellite reflections. Such an aperiodic structural property has been experimentally demonstrated in the family of n-alkane/urea inclusion compounds [4–6], by the evidence of incommensurate satellite reflections in addition to the main Bragg sets from each sublattice.

The hexagonal form of urea inclusion compounds becomes unstable at lower temperatures ($T_{\text{C}} = 154$ K for $C_{19}D_{40}$/urea-d$_4$), and transforms into an orthorhombic arrangement *via* a doubling of the unit cell of both urea and alkane sublattices in the $(\mathbf{a}^*, \mathbf{b}^*)$ plane perpendicular to the incommensurate axis [1,3,6,14,20,21]. A translation-rotation model of the transition mechanism has been proposed [22], relating host lattice distortion to guest orientational ordering.

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[a] e-mail: `ronan.lefort@univ-lille1.fr`

[b] UMR CNRS 6626

[c] UMR CNRS 5803

In both phases, the perfect three-dimensional ordering of the guest molecules is never reached, even in the low temperature phase. This fact has been experimentally evidenced in the high symmetry phase by means of incoherent neutron scattering [7,8] and NMR [9–13] techniques, revealing important dynamical disorder of the included alkane chains, involving their orientational and translational degrees of freedom. This disorder gives rise to strong diffuse scattering well identified in the X-ray diffraction pattern [14]. Analytical calculations [15] and Monte-Carlo simulations [16] have been used to interpret this X-ray diffuse scattering in terms of positional and orientational disorder of the alkane molecules in urea channels. Up to now, only rigid-body models have been proposed, although some internal deformations of the guest chains might also contribute to the observed diffuse scattering [5]. In order to account for the X-ray patterns, only spatial disorder needs to be considered, and no information on the time scale of the involved phenomena can be obtained. A previous neutron scattering analysis of the diffuse scattering [14] could not resolve significant differences between the elastic profiles and those integrated over energy.

The aim of this paper is to report a new analysis of the diffuse scattering by means of coherent inelastic neutron scattering on a fully deuterated single crystal of n-alkane/urea inclusion compound. Within the n-alkane/urea family, the inclusion compound of n-nonadecane is certainly the best model system as many of its physico-chemical properties are known. Thus we shall, in the following, investigate by means of inelastic coherent neutron scattering the diffuse scattering in a single crystal of n-nonadecane/urea ($C_{19}D_{40}/\mathrm{Urea}-\mathrm{d}_4$) which misfit parameter is $\alpha = 0.418$ [4]. In the last section we show that the analysis of these results allows a description of the physical origins of the molecular disorder.

2 Broad diffuse scattering and molecular form factor in alkane/urea crystals

A perfectly three-dimensionally ordered alkane sublattice is not consistent with the superspace group $P6_122(00\rho)0\overline{1}\overline{1}$ of the high temperature hexagonal phase of the host sublattice [3], and orientational disorder of the guest molecules is therefore expected in order to recover in average the six-fold screw axis of the structure [3,6]. Diffuse scattering in n-alkane/urea inclusion compounds has been classified into two main types [14,15]. The first one (s-scattering) refers to sharp layers appearing perpendicular to $\mathbf{c}^*$ direction and extended in the $(\mathbf{a}^*, \mathbf{b}^*)$ plane. This diffuse scattering is associated to some one-dimensional character of the guest subsystem. The second one (d-scattering) refers to broader bands located at periodic positions corresponding to the repeat distance of the internal $-(\mathrm{CD}_2)-$ groups ($c_{\mathrm{int.}} = 2.54$ Å) of the n-alkane molecule [5]. Short-range correlated fluctuations of the orientations, and of the z-positions of the guest molecules could contribute to this d-diffuse scattering with intensity modulated by the n-alkane molecular form factor.

Let us investigate the d-scattering by considering first the diffraction pattern associated to a single n-nonadecane molecule in its all-trans conformation. According to previous work [15], we can calculate the molecular form factor obtained after averaging over all the orientations of the molecule about the channel axis:

$$F^a_m(\mathbf{Q}) = \sum_k \sum_m b_m i^k J_k\left(Q_\perp a^* \rho_m\right) \times \sum_{n=0}^{18} \mathrm{e}^{\mathrm{i}\left(nQ_\parallel d^* \frac{\mathrm{c_{int}}}{2}\right)} \mathrm{e}^{ki(n\pi+\Delta_\mathrm{m})} \quad (1)$$

where the scattering vector is: $\mathbf{Q} = Q_\perp \mathbf{a}^* + Q_\parallel \mathbf{d}^*$ and the summation on index m refers to the three atoms of a $-(CD_2)-$ group, that are located in the molecular frame by the polar coordinates $(\rho_m, n\pi + \Delta_m)$. In equation (1), the n-nonadecane molecule is approximated by a planar zig-zag arrangement of nineteen $-(CD_2)-$ groups. The calculated diffuse intensity is shown in Figure 1.

The position of the diffuse bands in the reciprocal space are defined by the intramolecular periodicity of the $-(CD_2)-$ groups and their widths along $\mathbf{c}^*$ axis correspond to the reciprocal distance of one molecular length. Additionally, the alkane molecule has a 2_1 helical conformation (zig-zag arrangement) giving rise to a kind of extinction for the odd order layers near $h = 0$ [14]. This pattern is very similar to the one observed experimentally. This similarity between observed diffuse scattering and molecular form factor suggests that the guest molecules in the crystal undergo very weakly correlated rotational and/or translational displacements from ideal Bravais positions. The d-diffuse scattering in single crystals of urea inclusion compounds becomes therefore a very powerful tool to probe the molecular disorder.

3 Coherent inelastic neutron scattering analysis of the d-scattering on a single crystal of $C_{19}D_{40}/CO(ND_2)_2$

The experiments were performed at the Laboratoire Léon Brillouin (CE-Saclay, France), on the cold-beam triple-axis spectrometer 4F2. The sample is a 13 mm × 3 mm × 4 mm fully deuterated single crystal of $\mathrm{C_{19}D_{40}/CO(ND_2)_2}$, grown by slowly cooling mixed solutions of $\mathrm{urea}-\mathrm{d}_4$ and $\mathrm{n}-\mathrm{d}_{40}$, nonadecane in deuterated ethanol and isopropanol solvents. The crystal was oriented within the $(\mathbf{a}^*, \mathbf{c}^*)$ diffusion plane, and incident wave vectors of 2.662 and 3.0 Å^{-1} were chosen for analysing respectively the first $d = 1$ and second $d = 2$ layers of diffuse scattering (see Fig. 1). A graphite filter was used to avoid contamination of higher order harmonics in the neutron beam ($k_i = 2.662$ Å^{-1}). Note that the choice of the incident wave vectors was imposed by the required large values of the vector transfer $\mathbf{Q}$. Additional collimations (from 10′ to 60′) were placed before and after the analyser, and the energy resolutions were respectively about 50 GHz ($k_i = 2.662$ Å^{-1}) and 100 GHz ($k_i = 3.0$ Å^{-1}) for the first and second d-bands. A Displex close-cycle

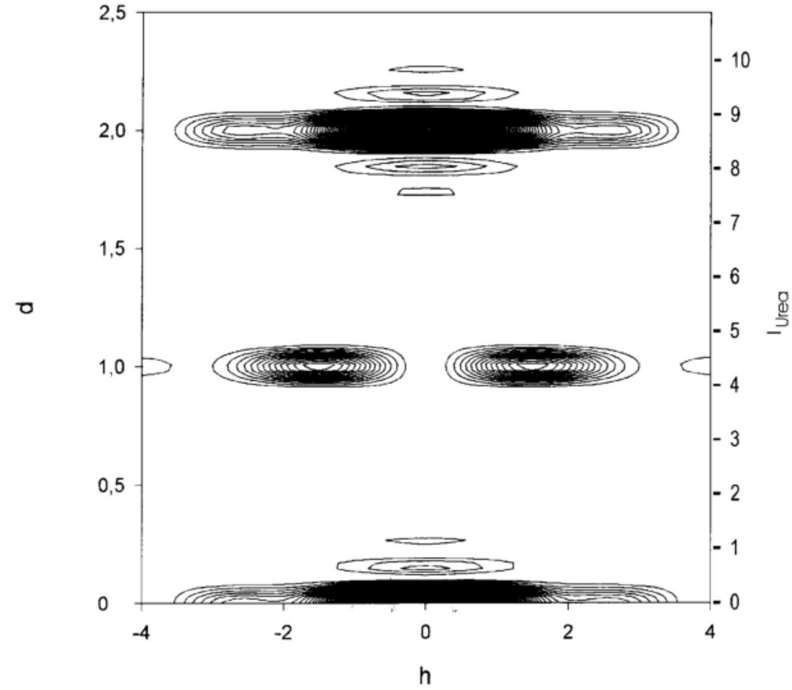

Fig. 1. Calculated single deuterated $C_{19}D_{40}$ molecule neutron diffraction pattern. The index d refers to the reciprocal parameter $c^*_{\text{int.}} = 2.47$ Å^{-1} of the internal $-(CD_2)-$ groups. The index l_{urea} corresponds to the hexagonal urea cell parameter along the channels. The index h corresponds to the hexagonal cell parameter.

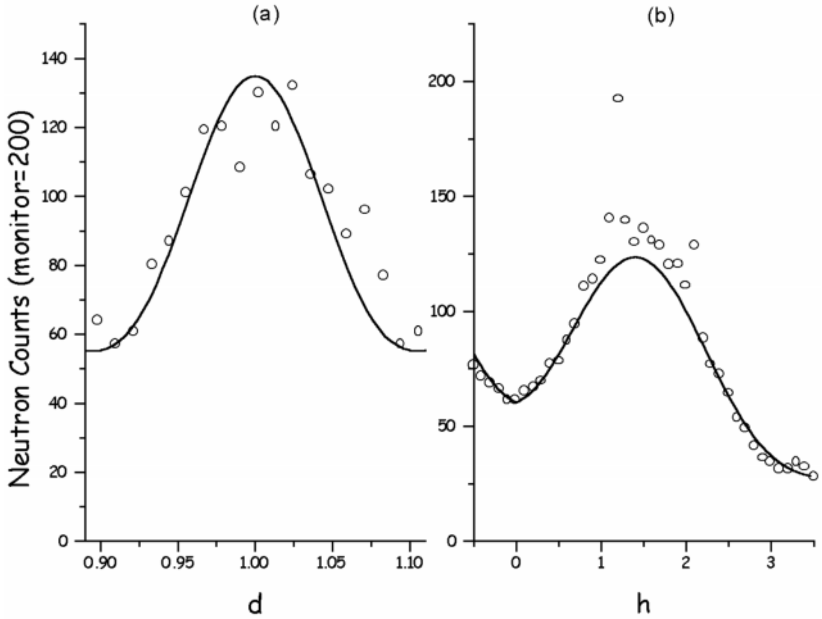

Fig. 2. Elastic scans through the first d-layer at room temperature ($k_i = 2.662$ Å^{-1}). The calculated molecular form factor is represented by the solid lines. (a): Scan along $\mathbf{c}^*$ with $h = 1.8$; (b): Scan along $\mathbf{a}^*$ with $d = 1$. The sharp peaks appearing around $h = 1$ and $h = 2$ are the Al (1 1 1) and Al (2 0 0) Debye-Sherrer lines.

refrigerator was used to cool the sample. All points in a given spectrum were classically recorded counting the number of scattered neutrons during the time needed for the same arbitrary number (monitor) of incident neutrons to be counted upstream of the sample.

Figures 2 and 3 display several elastic scans $S(\mathbf{Q}, \omega = 0)$ across the first and second d-layers respectively. The observed intensity is in good agreement with the calculated molecular form factor. The elastic incoherent scattering contribution was taken into account in the calculations. It is worth to notice that the finite energy resolution of the triple-axis spectrometer actually leads to a partial integration of the dynamical response $S(\mathbf{Q}, \omega)$ instead of rendering the true $S(\mathbf{Q}, \omega = 0)$. Triple axis allows the energy analysis of this diffuse scattering in contrast with X-ray diffraction measurements which gives the fully

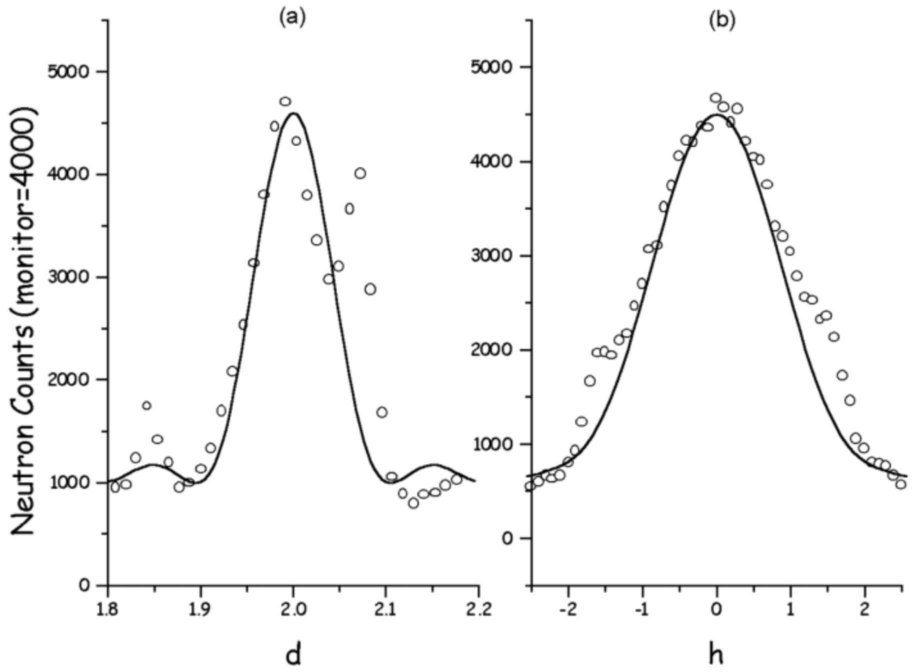

Fig. 3. Elastic scans through the second d-layer at room temperature ($k_i = 3$ Å^{-1}). The calculated molecular form factor is represented by the solid lines. (a): Scan along $\mathbf{c}^*$ with $h = 0$. The sharp peaks at $d = 1.84$ and $d = 2.07$ are the (0 0 8) and (0 0 9) multiple diffraction peaks of the urea sublattice; (b): Scan along $\mathbf{a}^*$ with $d = 2$. The symmetric shoulders are assigned to the Al (3 1 1) Debye-Scherrer lines.

integrated scattering function $S(\mathbf{Q})$. Below is presented the energy dependence of the scattering response on the two first $d = 1$ and $d = 2$ layers of d-diffuse scattering, at two temperatures.

Figure 4 reports the spectra at 99 K and 250 K obtained for fixed momentum transfer $\mathbf{Q}_1 = 1.5\mathbf{a}^* + 4.34\mathbf{c}^*$ and $\mathbf{Q}_2 = 0.3\mathbf{a}^* + 8.68\mathbf{c}^*$ on respectively the first and second layers of d-diffuse scattering. Inspection of the spectra recorded at 99 K (Figs. 4b and d) show that two inelastic modes are observed at energies of ca. 250 GHz and 600 GHz. These modes still appear at 250 K but are significantly damped (Fig. 4a and c). The origin of these inelastic contributions will be discussed in the next section. At low temperature, coherent elastic scattering is important whereas at high temperature, the only remaining elastic contribution is due to incoherent scattering. This is proved by independent measurements at reciprocal space positions where the molecular form factor is negligible (see Fig. 1). Since no additional elastic component is present, the whole coherent diffuse scattering is of inelastic character far above the transition temperature ($T_c + 100$ K).

4 Discussion

We have shown in the previous section that the diffuse scattering is totally inelastic around room temperature. This is in agreement with a model of molecules undergoing completely uncorrelated individual motions [17,18]. This is an original feature peculiar to the coherent cross section of a disordered system, where the elastic scattering is thoroughly rejected into the diffraction pattern –(h, k, l, m) Bragg peaks–, provided the three-dimensional order remains preserved on the average over the whole crystal. It comes out that each dynamical process causes an inelastic response only weighted by the molecular form factor, in agreement with the observed dependence on the vector transfer $\mathbf{Q}$ (see Figs. 2 and 3).

It has been already shown that the molecular dynamics of the included alkane chains involves either translations of the center of mass along the channel axis or whole-body rotations around this axis [7,8]. The $h = k = 0$ line (meridian) represents the reciprocal image of the radial projection of the structure on the $\mathbf{c}^*$ axis, and reflects translational processes only. Our measurements show a strong diffuse scattering intensity of the $d = 2$ layer around the meridian. The response measured at that point is therefore due to molecular motions polarised along the channel axis. Thus the alkane sublattice is at least translationally disordered. The measurements presented in this paper on the $d = 1$ layer correspond to a vector transfer $\mathbf{Q}_1$ with comparable components along $\mathbf{a}^*$ and $\mathbf{c}^*$, and then might simultaneously probe molecular translations along the channels and molecular processes polarised perpendicular to the channel axis (like rotations).

As shown in Section 3, damped harmonic oscillators describe the inelastic spectra for both $d = 1$ and $d = 2$ layers at low temperature. These inelastic peaks have been fitted also at room temperature by means of damped oscillator functions of nominal energy of about 300 and

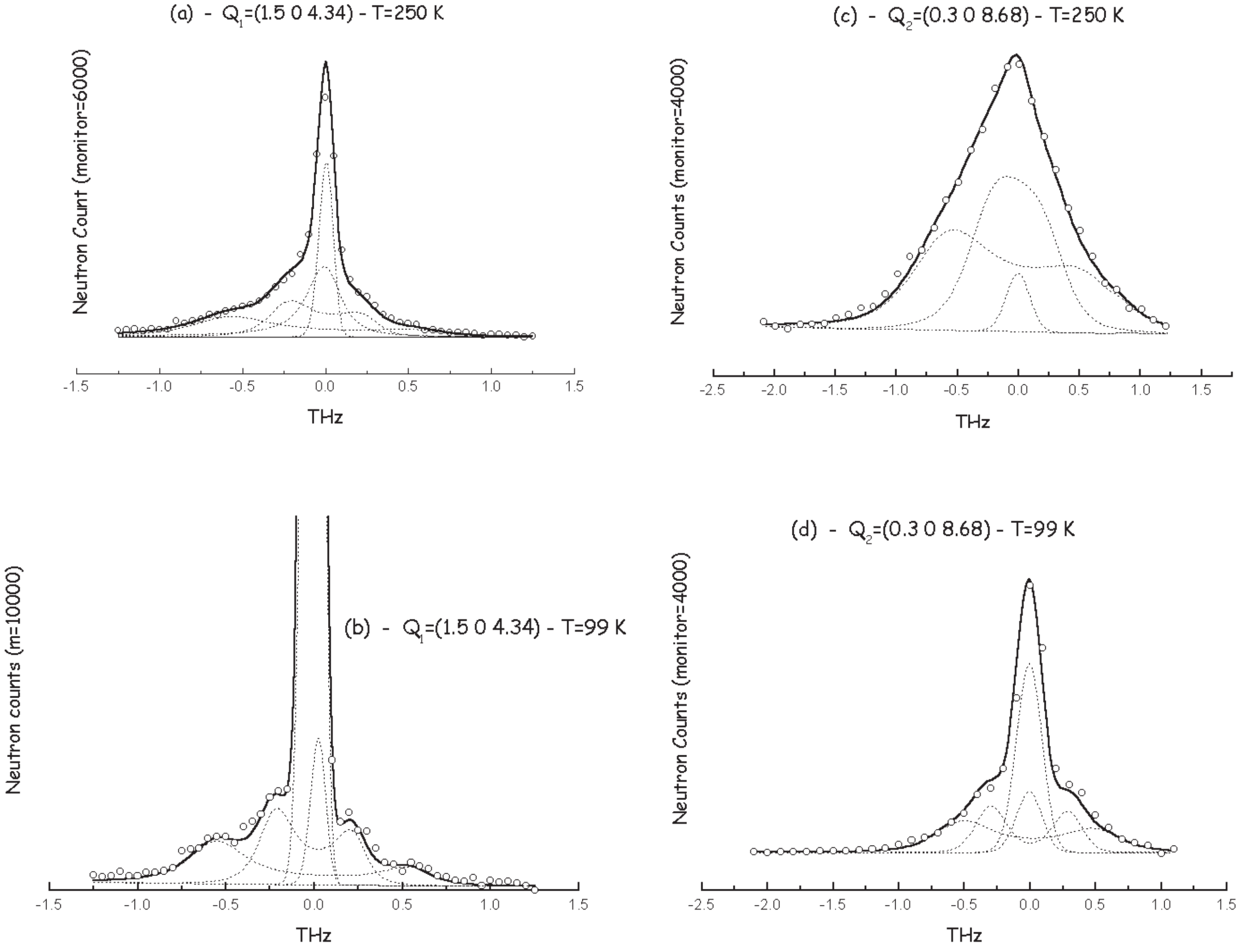

Fig. 4. Q constant scans on a single crystal of $C_{19}D_{40}$/urea$-d_4$. (a, b): ($k_i = 2.662$ Å^{-1}), $h = 1.5$; $l = 4.34$ (first d diffuse layer) at (a): 250 K, (b): 99 K. (c, d) ($k_i = 3$ Å^{-1}), $h = 0.3$; $h = 8.68$ (second d diffuse layer), at (c): 250 K, (d): 99 K.

650 GHz which damping reaches factors of about 500 and 700 GHz respectively. The occurrence of the two vibrational modes at similar energies on the $d = 2$ layer insures that their polarisation is principally longitudinal with respect to $\mathbf{c}^*$. These features match the phonon density of states obtained by incoherent neutron scattering on semi-oriented single crystals of nonadecane/urea inclusion compound [7,8]. This is shown in Figure 5 where two maxima at ~ 250 GHz and ~ 650 GHz on the incoherent quasielastic spectra are observed only when the scattering vector $\mathbf{Q}$ is parallel to the channel axis $\mathbf{c}$ of the inclusion compound. Moreover, molecular dynamics simulations performed on this system [24] have demonstrated that only centre of mass translational vibrations of the guest molecules along the channels were contributing to these inelastic features, *i.e.* no intramolecular contribution of the n-nonadecane molecules could be expected within this frequency range.

The results obtained by means of coherent neutron scattering give the localisation in the reciprocal space for these inelastic responses, showing that these vibrational modes merge only from the broad diffuse scattering. These vibrational modes are not dispersive and reflect dynamical molecular disorder. These very low frequency modes are polarized along the aperiodic direction of this crystal and a possible relation with the incommensurate feature of this compound has to be further investigated.

According to previous experimental analysis [7–11], and to molecular dynamics simulations [19], an additional quasielastic component was introduced for the fit of the first d-layer, where the scattering geometry allows to probe rotational diffusion of the alkane chains on the ps time scale. The guest molecules reorientational dynamics has already been analysed by means of incoherent neutron scattering and nuclear magnetic resonance spectroscopy

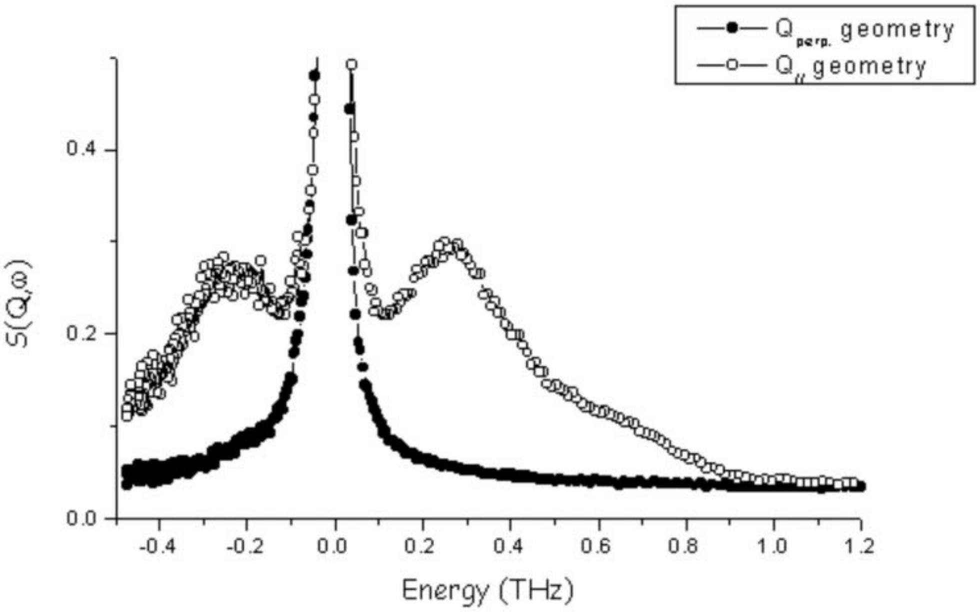

Fig. 5. Incoherent inelastic neutron scattering spectra recorded at $T = 140$ K using semi-oriented single crystals of $C_{19}D_{40}/CO(ND_2)_2$ on the time-of-flight spectrometer IN6 (ILL, see Ref. [7,8]). The two spectra were recorded with different experimental geometries: the scattering vector **Q** either parallel (open circles) or perpendicular (solid circles) to the channel axis of the inclusion compound.

and was found in the range of 10^{-11} s [7–9]. The separation between the different contributions to the coherent quasielastic spectra appears quite complicated. For the same reason, since these excitations are at rather low frequencies, they might all have a non-negligible contribution to the total diffuse scattering (integrated over energy), as reported by X-ray scattering.

In the low symmetry phase, these vibrational modes are still present at very similar frequencies at much lower temperature, the totally inelastic character of the d-diffuse scattering being lost. The elastic contributions measured at low temperatures on both diffuse layers suggest that the n-alkane molecules adopt some uncorrelated frozen disordering at least for the positions along the channels.

5 Conclusion

The analysis by inelastic coherent neutron scattering of the so-called d-diffuse scattering in n-nonadecane/urea inclusion compound has shown the entirely dynamical character of the molecular disorder of the guest sublattice at room temperature. The energy analysis of the $d = 2$ diffuse band gives direct information on the translational dynamical disorder of the alkane molecule, whereas the $d = 1$ diffuse band might reveal both rotational and translational dynamical disorder of the molecule. The translational disorder appears to result partially at all temperatures from uncorrelated center-of-mass vibrations of the alkane that seem not to be affected by the phase transition. The rotational disorder is measured through a diffusive contribution that slows down when temperature is decreased, and becomes unresolved in the orthorhombic phase. This unresolved contribution to the $d = 1$ diffuse band remains down to lowest temperatures, bringing to conclusion that no fully three-dimensional order is ever reached, even in the low symmetry phase. In the same manner, the $d = 2$ diffuse band also remains, indicating molecular translational disorder in this phase. Dynamic features of the disorder only appear then through inelastic low-frequency modes emerging from the d-bands.

The work reported here presents experimental data in full agreement with recent theoretical analysis of the coherent neutron scattering process of molecules on a lattice undergoing uncorrelated motions. It proposes a new link between previous studies that had up to now opposite point of views, coping with the problem of molecular disorder either *via* its spatial (X-ray diffraction) or time (incoherent neutron scattering) dimensions. The specificity of coherent inelastic neutron scattering is to investigate the dynamical collective properties of the disordered system. The temperature and **Q** dependences of the inelastic diffuse scattering functions should therefore bring out some new insights on how ordering correlations can occur within the guest sublattice in alkane/urea composites, by analyzing the transition from a self-to pair-correlation function.

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