

First One-Dimensional Stress-Strain Experiments inside an Aperiodic Inclusion Compound: Evidence of Depinning Effects

Lydie Bourgeois,^{1,*} Claude Ecolivet,¹ Bertrand Toudic,¹ Philippe Bourges,² and Tomaz Brezczewski³

¹*Groupe Matière Condensée et Matériaux-UMR CNRS 6626, Université de Rennes 1, 35042 Rennes, France*

²*Laboratoire Léon Brillouin, CEA-CNRS, CE Saclay, 91191 Gif-sur-Yvette, France*

³*Facultad de Ciencias, Universidad del País Vasco, Apartado 644, Bilbao, Spain*

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This Letter reports on the first observation of depinning under hydrostatic pressure of the guest and host sublattices inside the aperiodic nonadecane-urea inclusion compound. This leads to a unique way for a direct determination of the one-dimensional interguest interaction (1 N/m for nonadecane).

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Stress-strain experiments are the basic tool of material research when one tries to learn about the elastic properties of materials. When the material under investigation is not a bulky one, such as in the case of individual molecules or one-dimensional (1D) assemblies of molecules, applying a microscopically measurable stress may require sophisticated tools such as atomic force microscopy or optical tweezers where “handles” have to be grafted to molecule ends in order to test its elasticity. We present an original compression stress-strain experiment on a crystalline 1D molecular assembly confined inside the channels of a stiff aperiodic matrix. The feasibility of a selective stress-strain experiment inside a composite relies on the aperiodicity of such a structure, which theoretically enables an homogeneous displacement of one sublattice with respect to the other one without any restoring force. This property results from an infinitely degenerate ground state for an infinite aperiodic structure.

The stiffness of the aperiodic matrix is a necessary condition which may be fulfilled in the urea inclusion compounds. In that case, this matrix, playing the role of a compression cylinder, is built of urea molecules. They are known for their ability to form, via hydrogen bonds, solid 1D channels, almost cylindrical with an available diameter of 5.5 Å, which can accommodate linear guest molecules such as *n*-alkanes [1]. Inside these honeycomblike channels, these latter are confined in an ordered 1D dense packing with some 3D ordering despite some rotational and translational disorder [2]. Inside the host urea matrix, alkane molecules interact by Van der Waals forces between the terminal methyl groups. It has been found that, strikingly, the elastic properties of the crystalline composite formed by the host and guest sublattices are nearly independent of the alkane length [3], which is expected, in any chain model, to increment the guest sublattice longitudinal velocity in proportion to its square root. Consequently, the interalkane interactions have not yet been measured directly along the channels, and it was

also very rarely done in pure alkanes by a lack of suitable monocrystals.

In the present case, the aperiodicity of the composite results from the two independent periodicities of the sublattices: the alkane length and the pitch of the urea helices constituting the host structure independently of the guest length. Their ratio is called the misfit parameter. A convenient way to directly measure the lattice and sublattice strains is to apply hydrostatic pressure and to perform neutron diffraction. In composites, a major consequence of aperiodicity is the existence of four kinds of Bragg reflections located at different positions in the reciprocal space. We distinguish common reflections generated by both sublattices in the commensurate plane, and along the incommensurate direction, either main sublattice reflections labeled $(h k l 0)$ for the host and $(h k 0 m)$ for the guest, together with pure intermodulation satellites at combinatory positions [4]. By following the displacement in reciprocal space of a Bragg reflection of each sublattice versus pressure, it is possible to measure the different strains induced in the system and, in particular, inside the alkane sublattice.

The compound we have studied is the nonadecane-urea, which is a paradigm of such intergrowth crystals. The mean high symmetry structure of the urea host subsystem is described by the hexagonal $P6_122$ space group, with cell parameters $a = b = 8.22$ Å and $c_u = 11.02$ Å at room temperature and atmospheric pressure [5]. The a and b parameters are shared by both subsystems. The alkane parameter is 26.36 Å, giving the misfit parameter a value of 0.418, far away from any simple rational number.

Neutron scattering experiments were performed at the Laboratoire Léon Brillouin at the Orphée reactor (Saclay, France). The data were collected on the triple axis spectrometer 4F1 installed on a cold neutron source. The incident wave vector was $k_i = 1.55$ Å⁻¹ with a refrigerated beryllium filter to remove higher order contaminations. Hydrostatic pressure up to 5.3 kbars was obtained in a

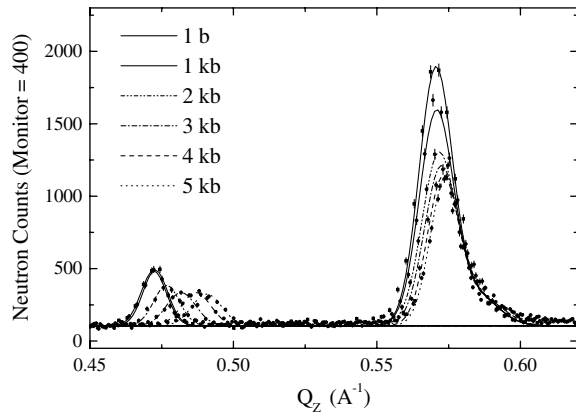


FIG. 1. Pressure evolution of two Bragg peaks related to the urea (1010) (right) and the alkane (1002) (left) sublattices. Q_z is the component of the diffraction wave vector along the incommensurate direction (in absolute units).

helium gas pressure cell at room temperature. The volume of the single crystal was $(2 \times 2 \times 12)$ mm³ and the retained scattering plane was $(\mathbf{a}^*, \mathbf{c}^*)$. Fully deuterated single crystals of *n*-nonadecane–urea were prepared by a slow evaporation of a mixed solution of urea and *n*-nonadecane in a mixture of ethanol and isopropanol.

The diffraction pattern has been followed versus pressure, revealing that the hexagonal high symmetry remains at all pressures with no asymmetric deformation of the host sublattice. Figure 1 shows on an absolute scale the evolution versus pressure of two Bragg peaks observed on the reciprocal line $(1, 0, l, m)$, which are (1010) and (1002). Obviously, these peaks, related, respectively, to the urea and the alkane sublattices, shift with a different pressure sensitivity. Within the experimental accuracy, the ratio of the integrated intensities of each sublattice remains constant, whereas some small broadening occurs in a narrow range around the pressure threshold (1 kbar) defined later on, probably in relation to some residual inhomogeneous deformation of the crystal. The high wave vector wing of the urea peak is contaminated by a small constant spurious scattering.

Although the absolute values of the lattice parameters are not so accurate on triple axis spectrometers, the relative variations of the parameters are very precise: ± 0.005 Å for urea and ± 0.01 Å for alkane. It is then possible to extract the evolution versus pressure of the different lattice and sublattice parameters variations: $\Delta a = \Delta b$, Δc_u , Δc_a . These variations rationalized to the atmospheric pressure value of these parameters define the strains induced along the \mathbf{a} direction (or any direction in the hexagonal commensurate plane) and along \mathbf{c} , the incommensurability direction. In the commensurate plane, the lattice parameter \mathbf{a} varies linearly versus pressure, as expected, whereas along \mathbf{c} a more complex behavior, impossible in regular crystals, is observed (Fig. 2).

At this point, it is important to compare the measured strains to the values computed from the elasticity

theory [6]:

$$e_1 = -\frac{c_{33} - c_{13}}{(c_{11} + c_{12})c_{33} - 2c_{13}^2}P,$$

$$e_3 = -\frac{(c_{11} + c_{12} - 2c_{13})}{(c_{11} + c_{12})c_{33} - 2c_{13}^2}P,$$

where e_1 and e_3 are the strain components and the C_{ij} are the elastic constants (in Voigt notation), which have been determined from Brillouin scattering [3]. Experimental data are expected in the sector defined by the dashed lines, which represent the upper and lower estimations for the elastic constants. It should be noticed that the elastic behavior is normal inside the commensurate plane as shown by the behavior of the strain e_1 related to the \mathbf{a} parameter variation, which only serves to validate and, somehow, calibrate the application of pressure to the whole system.

Original features appear along the incommensurate direction: (i) Below 1 kbar the measured strains are comparable within the experimental accuracy to the computed values of the elastic constants measured in standard conditions where the composite behaves as a regular crystal. Nevertheless, the measured strains fall at the lower edge of the computed values, such as for e_1 , and it could be so for two reasons: the first one could be a slight overestimation of the elastic constants, whereas the second one could be due to some inclusion of He atoms inside the crystal which would produce a smaller effective pressure inside the composite structure. However, the shortened lattice parameters and the close vicinity to the calculated strains indicate that if some He inclusion may occur it is certainly not a major concern here.

(ii) Above 1 kbar, one observes different strains for the two sublattices along the aperiodic direction, which appear as the individual responses of each sublattice. The variations observed which are an order of magnitude larger for the alkane sublattice than for the urea one are reversible and so indicate that the composite is neither destroyed nor altered under pressure. One can reasonably interpret the alkane behavior as due to the application of pressure at both ends of the urea channels by the He atoms on the alkane molecules. Then, on increasing pressure, we may imagine that a few He atoms with a Van der Waals diameter of ca. 2.8 Å can play the role of a piston inside each cylinder made of urea molecules by pushing the alkanes towards the inside of the crystal.

From these strains, we can define the displacement of molecules of the guest and host sublattices located at the abscissa Z along the c direction, which will be noted U_a and U_u , respectively: $U_a(Z) = e_{3a(p)}Z$ and $U_u(Z) = e_{3u(p)}Z$. By considering the alkane displacements, it is possible, for the first time, to determine experimentally the elastic properties of the alkane sublattice. One can estimate the pushing force by multiplying the pressure by either the free area of the hexagonal channel which has a maximum diameter of 5.5 Å or by an average cross

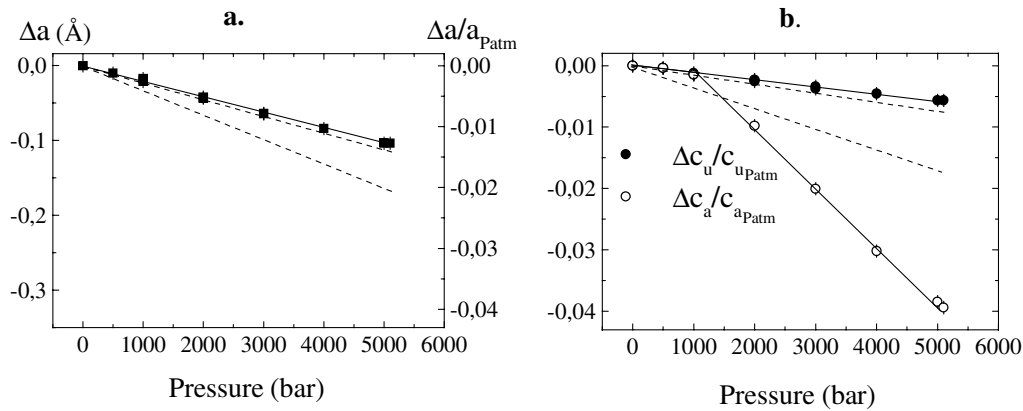


FIG. 2. (a) Evolution of the a parameter (left scale) and the related strain (right scale) versus pressure. (b) Evolution of the strains along c versus pressure (○) for the alkane and (●) the urea sublattices. The dashed lines indicate the extreme values computed from the elastic constants.

section of pure crystallized alkanes [7]. Both methods give about the same area, i.e., $19 \pm 1 \text{ \AA}^2$, and by assimilating the alkane cross section to a (rounded) square of 4.4 \AA , one can realize that He atoms cannot easily diffuse inside the crystal between alkanes and the urea channel walls. A pressure of 5 kbars corresponds then to a force of $95 \pm 5 \text{ pN}$ acting on the far ends of the alkane sublattice. This force is acting on the intramolecular and intermolecular degrees of freedom and may lead to a compression end-to-end of the molecules but also to some internal deformation. Clearly, “gauche” defects, buckling, or torsion of the chains may also occur. However, due to confinement in the channels, their amplitude can be severely restricted and, moreover, the continuous deformations of the chains involve intramolecular force constants which are known to be much larger than the intermolecular one.

The slope of the alkane deformation versus pressure would give a 1.3 \AA contraction of the alkane sublattice at 5 kbars in the case of a linear individual regime starting at atmospheric pressure. However, it has to be corrected from the influence of the conformational defects of the chain ends which also alter the chain length. Independent studies by NMR and Raman scattering [8] have detected an increase of the proportion of end chain gauche conformers under pressure, but NMR results have shown that the width of the rotational distribution of the methylenes remains about its atmospheric pressure value of 3° [9]. Therefore, no significant alkane torsion is observed. So, the relative intramolecular contribution to the lattice contraction in that pressure range is about 25%. Consequently, the alkane intermolecular force constant k is equal to $1 \pm 0.15 \text{ N/m}$. This value should be compared with the pure alkane case. However, direct determinations are scarce. Most of the data are coming from fits of thermodynamical properties of the liquid or critical state, which give values between 0.5 and 5 N/m [10,11]. In the solid state a value of 2 N/m can be deduced from Brillouin scattering on $\text{C}_{25}\text{H}_{52}$ [12]. By knowing the

intermolecular force constant, it is easy to derive the characteristic values of the acoustic wave dispersion of the alkane sublattice. The maximum circular frequency for the unperturbed longitudinal acoustic branch is equal to $2\sqrt{(k/M_a)}$, where M_a is the alkane mass. This maximum frequency corresponds to a discontinuity in the 1D density of states at 480 GHz (16 cm^{-1}) for the hydrogenated sample, which is in the same range (10 cm^{-1}) as a broad maximum of the density of states measured by incoherent inelastic neutron scattering [13].

This force constant gives for the first time information on the peculiar dynamics of composites, which has been extensively modeled but very rarely observed. The aperiodicity along the channel direction strongly suggests a comparison with a double chain model generalizing the double Frenkel-Kontorova with intermodulation between chains and incommensurate periods [14]. Such theoretical studies indicate that a wide hierarchy of gaps is expected in the phonon branches along the chains; now, more realistic models can be built knowing this force constant. Moreover, under certain conditions of analyticity of the atomic function describing the intermodulation, one could observe a phase mode characterized by an antitranlation of both sublattices with a zero frequency for infinite wavelengths. This mode is equivalent to the phason in modulated structures or in quasicrystals. At variance to these structures, this dynamics has never been unambiguously detected even if some experiments seem to be not far from it (see Ref. [15] and references therein). In our static measurements, the atomic displacements have a common part (U_u), which corresponds to a common translation, and a differential one ($U_a - U_u$), which describes the sliding of a sublattice with respect to the other one. The nonlinear behavior of this sliding displacement suggests that, at low pressures, sublattices are pinned together and cannot freely slide as expected. Above a pressure threshold (1 kbar), the barriers, which locally precluded the sliding motion, are overcome and the sliding can occur. In our experiments, by applying

pressure inside the channels, we have been able to move statically one sublattice with respect to the other one. Therefore, one can deduce the static susceptibility of the sliding mode as

$$\chi_s(0) = Z \frac{\partial[e_{3a}(p) - e_{3u}(p)]}{\partial p}.$$

Its behavior is nonlinear, with, at low pressures, a low value within the experimental noise but much smaller than the elastic susceptibility deduced from U_u , whereas above the 1 kbar threshold, the value for the sliding susceptibility is nearly 8 times the elastic one, corresponding to the ratio $(e_{3a} - e_{3u})/e_{3u}$ in that range. This nonlinear effect is reminiscent of the behavior of 1D charge-density wave (CDW) systems which also exhibit depinning effects above some threshold of the electric field [16]. In these systems, the pinning of the CDW has been assigned to impurities, defects, and/or properties of the modulation potential. In the present experiment, the detection of motion occurs at the microscopic level by diffraction, whereas in CDW, motions were detected macroscopically by measuring the intensity flowing through the sample. Consequently, a microscopic origin of the pinning is more likely in $C_{19}H_{40}$ -urea. Recent numerical studies on double-chains models mimicking inclusion composites have proposed that analytic intermodulation can exist only for very weak host-guest interactions [17]. In that case, two phonon branches have a linear dispersion for small wave vectors with slopes V_+ and V_- , which are functions of the individual densities ρ_1 , ρ_2 , and velocities of longitudinal acoustic waves V_1 , V_2 of each sublattice [14]:

$$V_{\pm}^2 = \frac{V_1^2 + V_2^2}{2} \left(1 \pm \frac{V_1^2 - V_2^2 \rho_1 - \rho_2}{V_1^2 + V_2^2 \rho_1 + \rho_2} \right).$$

Having in one hand, V_+ (4.95 km/s) the sound velocity of the composite [3], and in the other hand, $V_1 = c_a \sqrt{(k/M_a)} = 3.96$ km/s ($C_{19}H_{40}$) characteristic of the alkane sublattice through a simple chain model, it is possible to predict the sliding mode velocity $V_- = 4.29$ km/s and the acoustic one $V_2 = 5.2$ km/s of the urea sublattice. One should notice the close values of V_+ and V_2 which reflect the weakness of the interalkane interactions and explain the very small influence of the alkane length on the composite sound velocity.

In conclusion, for the first time, we have observed selective compressions in a crystal due to its aperiodic nature. This gives a direct way of measuring the elastic properties of the guest sublattice in urea inclusion compounds by diffraction experiments under hydrostatic pressure. This experiment, where He atoms are the piston and urea channels of the cylinders is, to our knowledge, the only example of a "molecular press." The interalkane force constant (1 N/m) gives an essential clue to understand and predict experimental and more realistic numerical results.

This experiment shows also that the relative motion of a sublattice are pinned at low pressures and that a depinning occurs under the effect of pressure such as CDW under the effect of an electric field above some threshold. The pinning found at lower pressures implies the existence of a gap for the sliding mode. For light scattering and considering the damping, this would generate a quasielastic response which has been already reported [18]. The knowledge of the interalkane force constant will facilitate the definition of better experimental conditions for the sliding mode observation.

The continuous control of the interguest distance gives a unique tool for tuning and studying 1D properties of these compounds. In this way, we can also expect to transform an aperiodic composite into a periodic one by modification of the misfit parameter under pressure.

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*Present address: Laboratoire Léon Brillouin, CEA-CNRS, CE Saclay, 91191 Gif-sur-Yvette, France.

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