Mixed Acoustic Phonons and Phase Modes in an Aperiodic Composite Crystal

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Aperiodic crystals which are long range ordered materials present original dynamics features due to the lack of translational symmetry formally implying the nonvalidity of the Brillouin zone concept. This Letter reports the observation by neutron scattering of an overdamped acousticlike mode at a Bragg peak position in a *n*-alkane–urea inclusion crystal. This result implies the existence of a gap in the dispersion branch. The gap and anomalous damping of these collective modes are discussed in terms of specific dynamics and interaction in aperiodic materials.

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Aperiodic crystals show low lying excitations resulting from the infinite degeneracy of their ground state related to the possibility of describing these structures in a higher dimensional space [1,2]. Among the various types of incommensurate systems, one of the simplest is illustrated by uniaxial composite crystals. The hydrodynamics of these materials has been the object of several theoretical papers [3–8]. In displacively modulated crystals, a mean Brillouin zone can be determined and used in a perturbative approach of the dynamics [9], which is not the case in aperiodic composites and quasicrystals (QCs). In this Letter, we report the first experimental evidence of a gap and an anomalous damping in an acousticlike branch in a host-guest composite crystal.

n-alkane–urea composite crystals are incommensurate along the channels labeled the **c** axis (Fig. 1). A misfit parameter is defined by the ratio of the host ($c_h = 11.0$ Å at 300 K) and guest (c_g) periodicities: $\gamma = c_h/c_g$. The basal commensurate hexagonal plane is described by the **a** and **b** vectors shared by both host and guest subsystems. The room temperature superspace group is then in most cases of rank 4, $P6_122(00\gamma)$ [10–16] with the following Bragg peak vectors $\mathbf{Q}_{hklm}$:

$$\mathbf{Q}_{hklm} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}_\mathbf{h}^* + m\mathbf{c}_\mathbf{g}^*. \quad (1)$$

We distinguish the common reflections $(h\,k\,0\,0)$ in the $(\mathbf{a}^*, \mathbf{b}^*)$ plane generated by both sublattices from the main sublattice ones $(h\,k\,l\,0)$ and $(h\,k\,0\,m)$ for the host and the guest, respectively, as well as from satellite ones $(h\,k\,l\,m)$ with both nonzero l and m values. Figure 1 presents the predicted longitudinal acoustic branches along the channels in *n*-nonadecane–urea. Because of the existence of two length scales, we expect four dispersion branches, two polarized along the channels and two polarized in the $(\mathbf{a}^*, \mathbf{b}^*)$ plane. If the interaction between the sublattices could be neglected, one would get two zero energy modes at infinite wavelengths, each one corresponding to a rigid displacement of one sublattice with respect to its fixed counterpart. Two sound speeds (V_h and V_g, respectively, for host and guest sublattices) can then be defined. In real materials, this condition is not fulfilled since the crystal would not be stable without any interaction. This interaction intermodulates each sublattice and couples the sublattice acoustic modes to give rise to two new modes at infinite wavelengths [2]: (i) an actual unique acoustic mode for the composite V_- and (ii) a mode corresponding to the relative antitranslation (sliding mode) of both sublattices V_+ (left inset in Fig. 1). The slopes V_- and V_+ are functions of the individual linear densities and longitudinal

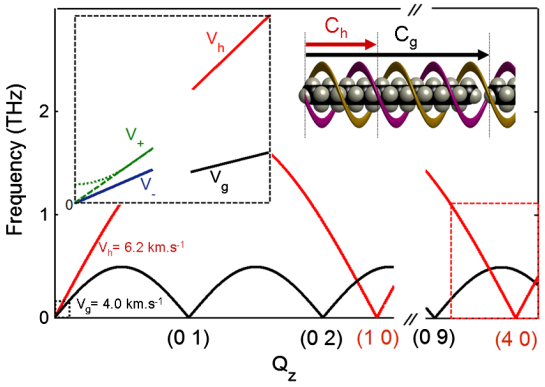

FIG. 1 (color online). Predicted dispersion curves of the longitudinal acoustic phonons propagating along the incommensurate direction $\mathbf{Q}_z$ of the aperiodic uniaxial host-guest crystal *n*-nonadecane–urea according to data discussed in the text [gray (red) refers to the host sublattice and black to the guest one]. The indices $(l\,0)$ and $(0\,m)$ define the host and guest reciprocal vectors. Close to the origin, the coupling between the two branches generates two modes, both may be gapless (left inset: blow up of the black dotted square). The gray (red) dotted rectangle refers to the $(\mathbf{Q}_z, \omega)$ range explored in the present experiment (see Fig. 4).

acoustic velocities of each sublattice and the intermodulation strength. Under certain circumstances, like a smooth intermodulation, the dispersion branch of the sliding mode may appear acousticlike since the relative shift of the lattices does not cost any potential energy due to incommensurability [2].

Previous neutron studies of collective dynamics were reported in incommensurate composites such as mercury chains in AsF_6 [17,18], aperiodic layered crystals [19,20], and a self-hosting crystal [21]. In these cases, different sound velocities were reported depending on the nature of the originating Bragg peak. In urea inclusion compounds a few works were previously performed using Brillouin scattering. They came to contradictory results. A first study reported an underdamped supplementary mode in hexadecane-urea assigned to the sliding mode [22]. This observation was not reproduced in another study performed in several alkane-urea compounds which reveals a strong quasielastic scattering with a width in the 20 GHz range at 300 K for light beams polarized along the channel's direction [23]. Its origin at these very low Q values could be compatible with an overdamped sliding mode. The frequency of the longitudinal acoustic (LA) mode gives the sound velocity of the composite along the channels. Its value is associated with the whole composite crystal and found to be equal to 5.0 ± 0.1 km/s.

Neutron scattering experiments were performed at the Laboratoire Léon Brillouin at the Orphée reactor (Saclay, France) and at the Institut Laue-Langevin at Grenoble. Single crystals of fully deuterated n-nonadecane–urea ($\gamma = 0.418$ [13]) were prepared by a slow evaporation of a mixed solution of urea and n-nonadecane in a mixture of ethanol and isopropanol. Data were collected on the triple axis spectrometer 4F1 and IN14 installed on a cold neutron source at the LLB and at the ILL, respectively. The retained scattering planes were the commensurate ($\mathbf{a}^*$, $\mathbf{b}^*$) plane and the aperiodic ($\mathbf{a}^*$, $\mathbf{c}^*$) one. All acoustic modes are fitted with damped oscillator functions:

$$S(\mathbf{Q}, \omega) \sim \frac{\omega \mathbf{\Gamma}_q |F(\mathbf{Q})|^2}{(1 - e^{-\hbar\omega/k_B T})[(\omega^2 - \omega_q^2)^2 + \omega^2 \mathbf{\Gamma}_q^2]}, \quad (2)$$

where ω_q and Γ_q are, respectively, the frequency and the damping of the mode at the reduced normalized wave number q, whereas $F(Q)$ is the inelastic structure factor. This function was convoluted with the instrumental resolution function to fit the data. A constant value of $F(Q)$ is used for a given phonon branch within the studied q range.

Figure 2 presents the room temperature dispersion of the acoustic phonons at $\mathbf{Q} = \mathbf{Q}_{2000} + q\mathbf{a}^*$ propagating in the elastically isotropic commensurate plane. These modes show a classical behavior similar to the one observed in a fully periodic crystal, i.e., a linear dependence of the frequency dispersion function of the wave vector together with a damping which goes, as expected, quadratically to zero on the Bragg peak location. Because of anharmonic

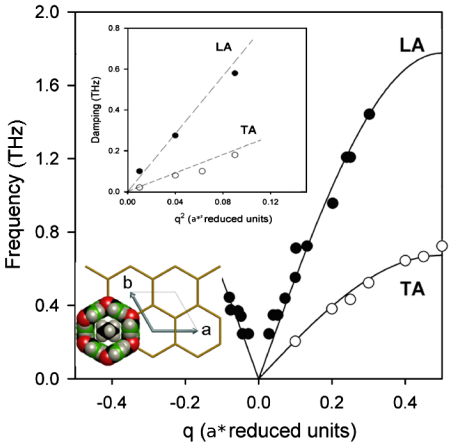

FIG. 2 (color online). Dispersion along $\mathbf{a}^*$ at 290 K of the LA and the polarized in-plane TA phonon branches, originating at (2 0 0 0) Bragg peak using the superspace high symmetry notation. Inset: Damping of the LA (filled circles) and TA (open symbols) modes. Incident wave vector was $k_i = 1.97$ Å^{-1}.

interactions, the damping of the LA modes is greater than the TA ones. The absolute values found for the slopes of the frequency dispersions of LA and TA modes in the commensurate plane are in agreement with the values extracted from Brillouin scattering [23]: $V_L = 3.6 \pm 0.1$ km/s, $V_T = 1.4 \pm 0.1$ km/s (polarized inside the plane). The second TA mode and a supplementary antitranslational mode [5] cannot be observed within this geometry.

Performing a similar experiment perpendicular to this plane is not easy, due to the numerous systematic extinction rules. The host urea (0 0 6 0) Bragg peak is too weak for measuring phonons, and the same observation was also made around all the (0 0 0 m) guest Bragg peaks. Measurements were performed at $\mathbf{Q} = \mathbf{Q}_{1040} + q\mathbf{c}_h^*$, that is around a very strong urea Bragg peak. With the transfer vector $\mathbf{Q}$ at 21° from $\mathbf{c}^*$, a simultaneous measurement of the LA and the TA modes propagating along the aperiodic direction is done. The deuterated n-nonadecane–urea presents a hexagonal to orthorhombic phase transition at $T_{c1} = 150$ K [15]. The symmetry induced domains are known to dramatically split the Bragg peaks which are off the (0 0 $\mathbf{c}^*$) line [24]. Consequently, the reported measurements were obtained just above T_{c1}, at 160 K (Fig. 3). The obtained dispersion curves for the LA and TA branches are presented in Fig. 4(a). Usual behavior is obtained for the doubly degenerated TA propagating along the incommensurate direction both considering the damping which follows the hydrodynamics law in q^2 and the energy dispersion. The measured transverse sound velocity ($V_T = 2.0 \pm 0.1$ km/s) is in agreement with the one determined by Brillouin scattering (1.9 km/s). The striking result is the evidence of a totally new behavior for the longitudinal "acousticlike" excitation. Indeed, on the Bragg peak location it generates a well-resolved quasielastic scattering in the spectrum. This implies a gap in the

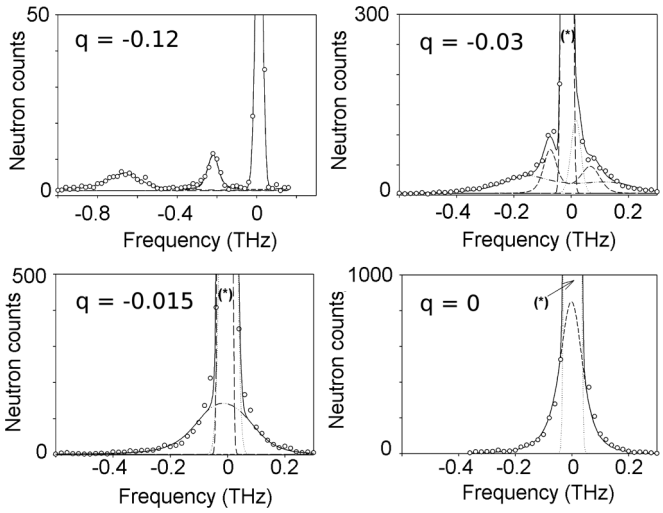

FIG. 3. Inelastic phonon excitations measured at $\mathbf{Q} = \mathbf{Q}_{1040} + q\mathbf{c}_\mathbf{h}^*$, at $T = 160$ K, i.e., in the high symmetry phase $P6_122(00\gamma)$. LA and TA modes are fitted with normalized damped oscillator functions convoluted with the spectrometer resolution. Constant incoherent neutron scattering is considered in this small Q range together with Bragg peak contamination (*), when needed.

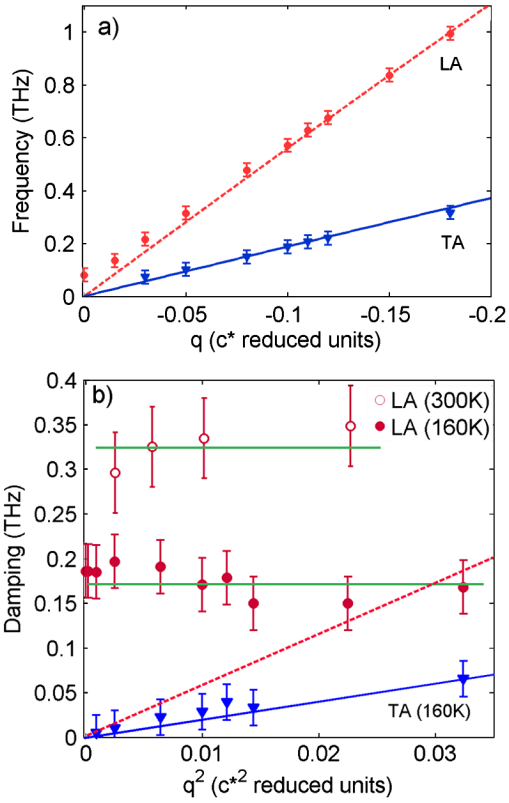

FIG. 4 (color online). Frequency at 160 K (a) and damping (b) of the LA (circles) and degenerate TA (triangles) modes propagating along the aperiodic $\mathbf{c}^*$ direction of n-nonadecane–urea. Dotted lines in (a) and (b) describe the usual LA behavior. Light gray (green) curves are guides for the eyes. Incident wave vector was $k_i = 1.5$ Å^{-1}.

dispersion of this LA branch since for a damped oscillator of intrinsic frequency ω_0 and width Γ_0 the quasielastic width tends towards ω_0^2/Γ_0 when approaching the overdamped regime. The inelastic structure factor $F(Q)$ is determined far away from the Bragg peak and its value is then constrained to a constant value leading to a gap of 80 GHz at the Bragg peak position. The damping of this branch also presents a very unusual behavior since it does not go to zero at low q values, violating the hydrodynamics rules in q^2 expected for infinite wavelength, close to $\mathbf{Q}_z = 0$. Its value at 160 K is almost constant around 180 GHz, in total disagreement with the expected dependence shown by the dotted line in Fig. 4(b). Moreover, the room temperature damping is 330 GHz, indicating a rather linear temperature dependence. Despite the energy gap at the Bragg peak position, it is nevertheless possible to extract an equivalent "sound speed" for the LA mode propagating along the incommensurate direction in the host sublattice. From this neutron scattering measurement, the speed associated with the acousticlike branch of urea is found to be $V_h = 6.2 \pm 0.1$ km/s, which is very similar to the maximum sound velocity in tetragonal urea [25].

Previously, the longitudinal sound velocity of the nonadecane sublattice along the same direction was derived from a selective stress-strain measurement $V_g = c_a\sqrt{k/M_a} = 4.0$ km/s [26]. These experimental speed values are used in Fig. 1, considering independent sublattices. It should be noticed that the host Bragg peak (1 0 4 0) is nearly halfway from the neighboring guest (1 0 0 m) Bragg peaks, corresponding to $m = 9$ and $m = 10$, respectively. Because of the large energy separation, no evidence of the alkane pseudoacoustic phonon is expected around the strong urea (1 0 4 0) Bragg peak. At variance to $\mathbf{Q}_z = 0$, the dispersion branches intersect in the upper part of the alkane branch (Fig. 1). According to theories, a gap should occur when the frequencies $\omega_h(\mathbf{Q}_z)$ and $\omega_g(\mathbf{Q}_z)$ are equal [8]. However, no flattening of the dispersion branch is observed around this value of $q = -0.1$ in the c_h^* reduced unit.

In aperiodic composites, the acoustic mode and the phase mode possess their pure character only in the hydrodynamics limit around $\mathbf{Q}_z = q\mathbf{c}_\mathbf{h}^* = 0$ [7]. There, the coupling by the interaction of the two LA modes along the aperiodic direction may induce a gap in the low frequency spectrum (inset of Fig. 1). In n-alkane–urea, Brillouin scattering experiments [23] reveal a broadened composite acoustic mode with an unusual width and an overdamped mode with a half-width of ca. 20 GHz, similar to the one reported here away from $\mathbf{Q}_z = 0$. There, the coupling is likely of different nature due to the different locations of the host and guest Bragg peaks at the origin of the dispersion curves of the acoustic modes. Around the $\mathbf{Q} = \mathbf{Q}_{1040}$ Bragg peak, there is a large energy separation between host and guest LA modes. The observed gap, at the lowest

frequencies, could be the consequence of a strong interaction between both sublattices when the intermodulation function becomes nonanalytic [8]. This nonanalyticity induces a large variety of gaps in the dispersion curves occurring in nearly all wave vector regions. In *n*-alkane–urea compounds, this strong interaction is indeed observed with depinning and lock-in phenomena [26,27] and could account for both the reported observations close to $\mathbf{Q} = \mathbf{Q}_{1040}$ and $\mathbf{Q}_z = 0$.

Similar observations to the ones done in this Letter were never performed before in any type of aperiodic crystals, although all these materials enter the superspace crystallographic description. In QCs, it has been shown that strong Bragg peaks can act as the pseudo-Brillouin zone center [28]. In their vicinity, well-defined LA and TA modes are observed in icosahedral QCs. The width of the LA mode was found to be limited by the instrumental resolution for $q < 0.3$ Å^{-1} [29,30]. Phason modes are there diffuse modes with a very large time scale of tens of seconds and thus decoupled from the phonons [31]. In inorganic aperiodic composites $Hg_{(3-\delta)}AsF_6$, different longitudinal acoustic modes at various sublattice Bragg reflections were observed, with a normal behavior for the dispersion and the damping [17,18,22]. In self-hosting, similar magnitude of the speed $V_h = V_g$ are reported, the same species belonging to the different sublattices, and again no anomalous behavior was observed [21]. In layered incommensurate compounds, high T_c superconducting cuprates, two propagating acousticlike branches around the Bragg peaks are reported associated to a composite crystal with two weakly interacting sublattices [19,20]. Theoretical modelizations including actual interaction energy terms are necessary to go further on in order to describe the complex observation in the acoustic phonon spectrum beyond the hydrodynamics limit.

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