Pressure dependence of the interlayer and intralayer E_{2g} Raman-active modes of hexagonal BN up to the wurtzite phase transition

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We present a Raman-scattering study of the interlayer and intralayer E_{2g} Raman-active modes of hexagonal boron nitride (h -BN) under hydrostatic pressure for pressures up to the transition to the wurtzite phase (10.5 GPa). Pressure coefficients and Grüneisen parameters are determined for both modes, and are compared to *ab initio* calculations based on density functional perturbation theory. The pressure coefficient of the low-energy interlayer mode is higher than that of the high-energy intralayer mode owing to the large compressibility of the h -BN crystal along the c direction. Both modes exhibit a sublinear phonon frequency increase with pressure, which is more marked in the case of the low-energy mode. The intensity of the low-energy mode increases with pressure, suggesting an enhancement of the mode polarizability as the honeycomb layers become closer. The Raman spectrum of the metastable wurtzite phase is observed at ambient pressure in the transitioned sample after decompression.

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I. INTRODUCTION

Hexagonal boron nitride (h -BN) is emerging as a key component in the burgeoning field of novel applications based on graphene and two-dimensional (2D) layered materials [1,2]. Since h -BN has a similar structure to graphene with a small lattice mismatch, a wide band gap [3], and large thermal conductivity [4], this material is an ideal substrate and dielectric layer in atomically thin stacked devices based on graphene [5,6]. Dielectric strengths up to 7.9 MV cm^{-1} have been reported on ultrathin h -BN layers [7]. Several other outstanding technological applications have been developed around the unique properties of h -BN, namely, subdiffractional nanophotonic devices based on phonon-polaritons [8] or high-efficiency solid-state neutron detectors based on ^{10}B -enriched h -BN crystals [9]. Recently, the broader importance of isotopical purification in h -BN has been recognized, and its impact on the physical properties of h -BN has been addressed [10]. A recent Raman-scattering study has shown that the large isotopic disorder present in natural h -BN is the predominant factor that limits the phonon lifetime, advocating ^{10}B as the best candidate to achieve the large phonon mean-free paths required for phonon-polariton devices [11]. Long phonon lifetimes of the infrared- (IR-) active E_{1u} phonons, which couple to IR light to produce phonon-polariton modes, have been determined in recent IR studies on h -BN [12].

Sequential large-area growth of graphene/ h -BN stacked layers was demonstrated by direct chemical vapor deposition (CVD) [13], opening new prospects for device fabrication. Strain plays an important role in ultrathin layers of graphene [14,15] and other 2D materials [16–18]. Given the large

mechanical strength of 2D materials and the versatility of strain engineering for controlling their optical and electrical properties [16–18], the graphene/ h -BN heterostructure has attracted much interest as a functional approach to transmit mechanical strain to encapsulated pristine graphene layers [19]. Raman scattering has long been established as a sensitive technique to probe strain in semiconductor structures [20] and has been widely used to characterize strained 2D layers in recent works [17,19,21]. Raman scattering has shown an enormous potential for characterization of the large family of 2D layered compounds [22]. The phonon shift rates and Grüneisen parameters have been determined in few-layer h -BN samples under tensile strain by means of Raman-scattering measurements [23]. For a precise calibration of the shifts in high-pressure data on bulk h -BN, fundamental studies of the high-pressure behavior of the Raman spectra of h -BN on high-quality crystals are required. Recently, the high-pressure behavior of the IR-active modes was studied by means of IR reflectance and absorption experiments [24], but Raman-scattering studies on high-quality h -BN are still lacking. High-pressure Raman-scattering experiments were reported on multiwalled h -BN nanotubes and the results were compared with Raman spectra of the intralayer E_{2g} mode obtained from low-quality pyrolytic h -BN bulk samples [25]. In the latter case, the spectra showed a substantial linewidth increase with pressure that precluded an accurate analysis. Nevertheless, the authors concluded that h -BN exhibits a phase transition to a wurtzitic phase at around 13 GPa, which, contrary to the case of multiwalled nanotubes, was reversible on decompression. This is in contradiction with more recent IR reflectivity experiments on high-quality h -BN crystals, which clearly showed that the high-pressure wurtzite phase

is metastable and is maintained on decompression down to ambient pressure [26].

In this work, we present a Raman-scattering study of state-of-the-art *h*-BN crystals at high pressures. Both the interlayer and intralayer E_{2g} modes are observed and analyzed up to the transition pressure to the wurtzitic phase. The elastic constants determined by Brillouin scattering [27] indicate that elastic anisotropy of *h*-BN is remarkably high, with an anisotropy ratio much higher than in other layered materials. The substantial differences between interlayer and intralayer interactions in the layered *h*-BN crystal give rise to widely differing frequencies for *in-plane* and *out-of-plane* phonon modes, which results in a large birefringence of the *h*-BN crystal, where, within the reststrahlen bands, the dielectric permittivities along orthogonal crystal axes are opposite in sign [8,28]. This makes the study of the two E_{2g} modes particularly interesting, as they are dictated by essentially different interatomic interaction mechanisms. The quality of the high-resolution spectra allowed us to accurately determine the pressure coefficients and Grüneisen parameters of these modes and to compare the experimental results with *ab initio* predictions based on density functional perturbation theory. The presence of the wurtzitic phase at ambient pressure after the high-pressure cycle is confirmed by the Raman measurements.

II. EXPERIMENT

The experiments were carried out on high-quality single-crystal *h*-BN grown using a nickel-chromium solvent at atmospheric pressure. A 50 wt.% Ni and 50 wt.% Cr mixture was loaded into a hot-pressed boron nitride ceramic boat which served as source material. During the crystal growth process, the N_2 and forming gases continuously flowed through the system with rates of 125 and 25 sccm, respectively. The forming gas was used to minimize oxygen and carbon impurities in the *h*-BN crystal. After a dwell time of 24 h at 1550 °C, the *h*-BN crystals were precipitated on the metal surface by cooling at a rate of 1 °C/h to 1500 °C, and then the system was quickly quenched to room temperature [29]. A sample of thickness about 100 μ m was cleaved from *h*-BN single-crystalline platelets.

High-pressure Raman-scattering measurements were performed up to 15 GPa at room temperature in a membrane diamond anvil cell (DAC) [30] equipped with type-IIa diamond anvils. Ne was used as the pressure transmitting medium (PTM). The pressure was determined using the ruby scale [31]. The Raman spectra were recorded in a backscattering configuration from the *c* face using the 514.5-nm line of an Ar^+ laser and a confocal microscope setup with a 50 $\times$ objective. The scattered light was analyzed using a Jobin-Yvon T64000 triple spectrometer equipped with a LN_2 -cooled charge-coupled device (CCD) detector. The spectral bandwidth of the experimental setup was ~ 2 cm^{-1} .

Density functional perturbation theory calculations (DFPT) were performed using the ABINIT code [32]. The calculations were carried out in the generalized gradient approximation (GGA). Nonlocal van der Waals interactions between layers [33] were taken into account by considering the density functional dispersion correction DFT-D3(BJ),

as proposed by Grimme *et al.* [34] and Becke and Johnson [35]. Following the recommendations in Ref. [33], Zhang and Wang's revPBE pseudopotential [36] was used. Contrary to plain GGA, which does not bind the hexagonal layers, the incorporation of nonlocal corrections to the functional yields a good description of the layered *h*-BN crystal [33].

III. RESULTS AND DISCUSSION

The optical phonons of *h*-BN at the Brillouin zone center can be classified according to the $E_{1u} + A_{2u} + 2E_{2g} + 2B_{1g}$ irreducible representations of the $P6_3/mmc$ space group. The *out-of-plane* A_{2u} mode and the doubly degenerate *in-plane* E_{1u} modes are infrared active whereas the doubly degenerate *in-plane* E_{2g} modes are Raman active. The *out-of-plane* B_{1g} modes are silent modes without optical activity.

Representative Raman spectra of the E_{2g} phonons are shown in Fig. 1 for pressures ranging from ambient pressure to near phase-transition pressure. The high-frequency mode (E_{2g}^{high}) [Fig. 1(a)] shifts to higher frequencies with increasing pressure, but maintains its line shape and intensity up to pressures close to the phase transition. The E_{2g}^{high} full width at half-maximum (FWHM) is ~ 8 cm^{-1} at 10.0 GPa, the same value that we find at 1.4 GPa, and consistent with the FWHM values reported on bulk high-quality *h*-BN crystals [37]. This is in stark contrast with the behavior reported in Ref. [25] on low-quality pyrolytic *h*-BN bulk samples, which showed a FWHM increase from 9.5 cm^{-1} at 1 GPa to 14 cm^{-1} at 10 GPa. Our results indicate that high-quality *h*-BN single crystals retain their crystallinity under high pressure and do not show signs of transition-related disorder up to pressures close to the phase transition. A slight increase of the background signal is observed for pressures above 5 GPa, concurring with the crystallization of the PTM at 4.8 GPa [38]. The background signal becomes stronger as the phase-transition pressure is approached.

The frequency of the low-frequency mode (E_{2g}^{low}), which involves the gliding motion of the honeycomb layers and thus it is primarily sensitive to the weak interlayer van der Waals interactions, also increases with pressure. The rate of increase is higher than for the E_{2g}^{high} mode due to the strong anisotropic character of the *h*-BN crystal and the much larger compressibility along the *c* direction. As the interlayer distance is rapidly reduced by the increasing pressure, Pauli repulsion increases and the frequency of the E_{2g}^{low} shear mode becomes higher. Unlike the intensity of the E_{2g}^{high} peak, which remained constant at all pressures, the E_{2g}^{low} mode intensity increases steadily with pressure. This suggests an enhancement of the mode polarizability under high pressure that could be associated with the augmented role of Pauli repulsion versus the weak van der Waals interactions. An increase of the line intensity of the E_{2g}^{low} mode of graphite was previously reported [39], and the possibility of a contribution from strongly pressure-dependent interband transition resonances was suggested. In the case of the *h*-BN crystal, such contributions can be ruled out on the grounds of its wide band gap, so that the intensity enhancement observed in Fig. 1(b) primarily originates from a stronger interlayer coupling under pressure.

FIG. 1. Raman spectra of the *h*-BN Raman-active modes of E_{2g} symmetry for pressures up to near phase-transition pressure, where Raman signal is rapidly quenched (dotted lines). (a) High-frequency interplanar shear mode. The atomic motions in these modes are illustrated as insets. A gradual increase of the background signal is observed for increasing pressure. AP stands for ambient pressure.

The pressure dependence of the E_{2g}^{high} and E_{2g}^{low} frequencies is shown in Fig. 2. The phonon frequencies depend on the interatomic distances, and they increase with pressure reflecting the reduction in lattice parameters. As the crystal is compressed, it becomes more difficult to compress, which translates into a sublinear variation of the lattice parameter with pressure. Assuming a linear variation of the bulk modulus with pressure, the nonlinear relation between lattice parameter and pressure can be described by a Murnaghan-type equation [39]

$$r/r_0 = [1 + (\beta'/\beta_0)P]^{-1/\beta'}, \quad (1)$$

where r is the lattice constant along a given crystal axis, $\beta_0^{-1} = -(d \ln r / dP)_{P=0}$ is the linear compressibility, and β' is the pressure derivative of β . In analogy with the derivation of the Murnaghan equation [Eq. (1)], where the modulus β is assumed to vary linearly with pressure, we consider here the

FIG. 2. Pressure dependence of the Raman-active E_{2g} mode frequencies up to the phase-transition pressure. Symbols correspond to Raman-scattering measurements whereas the solid line displays the results of the *ab initio* calculations. The dashed line is a fit to a Murnaghan-type expression [see Eq. (4)]. The dotted line, included as a guide to the eye, displays the extrapolated linear dependence using the experimental pressure coefficient at ambient pressure.

logarithmic pressure derivative of the phonon frequencies

$$\delta(P) = \frac{1}{\omega} \frac{d\omega}{dP}, \quad (2)$$

and assume a linear dependence on pressure of $\delta^{-1}(P)$ defined as

$$\frac{1}{\delta(P)} = \frac{1}{\delta_0} + \frac{1}{\delta'} P. \quad (3)$$

Then, substituting Eq. (3) into Eq. (2), the differential equation can be integrated to obtain a Murnaghan-type relation for the phonon frequencies [39]:

$$\omega(P) = \omega_0 [1 + (\delta_0/\delta')P]^{\delta'}. \quad (4)$$

Here, $\delta_0\omega_0$ is the pressure coefficient at ambient pressure and $1/\delta'$ is the pressure derivative of $\delta^{-1}(P)$. Equation (4) captures the effects on the phonon frequencies of the nonlinear variation of the lattice parameters with pressure. By fitting Eq. (4) to the experimental data, we find the parameters listed in Table I.

The pressure dependence given by Eq. (4) is plotted in Fig. 2 as a dashed line. Both modes exhibit a similar shift with pressure despite the vast difference in their frequencies. This behavior stems from the high anisotropy of the bonding forces, which results in the compressibility along the c axis being ~ 55 times higher than along the a axis [40]. Graphite, which possesses also a hexagonal layered structure,

TABLE I. Values of the parameters of Eq. (4) fitted to the experimental pressure dependence of the h -BN E_{2g} phonons. δ_0 is the normalized linear pressure coefficient at ambient pressure and δ' is the sublinearity parameter. The product $\omega_0\delta_0$ is equal to the pressure coefficient at ambient pressure α . The corresponding values reported on graphite in Ref. [39] (denoted by an asterisk) are also given for comparison.

Mode	h -BN				Graphite			
	ω_0 (cm^{-1})	δ_0 (GPa^{-1})	δ'	$\omega_0\delta_0$ ($\text{cm}^{-1} \text{GPa}^{-1}$)	ω_0 (cm^{-1})	δ_0 (GPa^{-1})	δ'	$\omega_0\delta_0$ ($\text{cm}^{-1} \text{GPa}^{-1}$)
E_{2g}^{low}	52.1(2)	0.151(4)	0.48(1)	7.9(2)	44(1)*	0.110(8)*	0.43(3)*	4.8(4)*
E_{2g}^{high}	1367.3(3)	$3.9(1) \times 10^{-3}$	$6.1(7) \times 10^{-2}$	5.3(2)	1579(1)*	$2.96(2) \times 10^{-3*}$	$8.0(5) \times 10^{-2*}$	4.7(1)*

displays E_{2g}^{high} pressure shifts very similar to those found here for h -BN, while for the E_{2g}^{low} mode the pressure shift is somewhat smaller [39]. Despite the fact that h -BN presents highly polar B-N bonds, the partly charged atomic centers have a negligible contribution to the interlayer binding [41] and the interlayer distance is practically the same in h -BN and graphite. However, for lateral shifts of the hexagonal layers, the electrostatic potential is significant and favors the AA' stacking in which every partially negatively charged N atom of one layer is located at a distance $c/2$ on top of a partially positively charged B atom of the adjacent layer. This atomic arrangement differs from the AB stacking of graphite, where only half of the carbon atoms in a layer are located at a distance $c/2$ on top of a carbon atom of the adjacent layer. The electrostatic component and the structural dissimilarity along the c axis of h -BN with respect to graphite would contribute to the fact that the frequency of the E_{2g}^{low} mode is higher in h -BN than in graphite. Under pressure, the sublinear behavior of the c lattice parameter [parameter β' in Eq. (1)] is significantly smaller in h -BN, and this results in a higher E_{2g}^{low} pressure coefficient (see Table I) and a noticeably higher absolute shift with pressure. On the other hand, both graphite and h -BN present extremely low compressibilities along *in-plane* directions, and their respective pressure coefficients for the E_{2g}^{high} modes are nearly the same.

As can be seen in Fig. 2, the dependence of the E_{2g}^{high} frequency with pressure is fairly linear for $P \lesssim 4$ GPa, whereas at higher pressures it shows a sublinear bowing that is well reproduced by the *ab initio* calculations. The GGA approach used in these calculations provides an improved description of the strong intralayer valence bonds in relation to previous studies based on the local density approximation [37,42–44], and yields frequency values that are in excellent agreement with the experimental results. In the case of graphite, it has been argued that the sublinear pressure dependence of the E_{2g}^{high} frequency is largely due to the reduced *in-plane* force on the sp^2 bonds resulting from the large c -axis compression under pressure, which introduces sublinearity in the pressure dependence of the biaxial *in-plane* force [45]. Since the c -axis linear compressibility of h -BN ($\beta_0 = 37.7$ GPa, $\beta' = 6.3$) is comparable to that of graphite ($\beta_0 = 35.7$ GPa, $\beta' = 10.8$), the same effect is expected in h -BN. In fact, the frequency sublinearity parameters δ' obtained for h -BN from the fit to the experimental data are very close to the values reported on graphite (see Table I).

The sublinear behavior of the E_{2g}^{low} frequency is far more pronounced. At 10 GPa, the departure from the linear trend is $\sim 12\%$ for the E_{2g}^{low} frequency, whereas it is only $\sim 3\%$ for the E_{2g}^{high} mode. This marked sublinear behavior is a direct consequence of the large compression of the interlayer distance, which slows down as the pressure increases. The interlayer distance decreases much more rapidly than the *in-plane* lattice constant. Since the E_{2g}^{low} mode is an interlayer shear mode, this mode is primarily affected by the interlayer distance and should be highly responsive to pressure. However, the sensitivity of the weak interlayer van der Waals interactions to the decrease in interlayer separation is expected to be lower than the sensitivity of the force constant of the boron-nitrogen covalent bond on the interatomic distance, and thus the pressure coefficient found for the interlayer shear mode in the low-pressure linear range is only moderately higher than that of the *in-plane* E_{2g}^{high} mode.

In Table II, we give the ambient-pressure frequencies of the E_{2g}^{low} and E_{2g}^{high} modes and their respective pressure coefficients and Grüneisen parameters. The Grüneisen parameters $\gamma_G = B_0\delta_0$ were calculated using the bulk modulus determined by Solozhenko *et al.* [40] from x-ray scattering measurements using synchrotron radiation. These results are compared with DFPT calculations in the GGA approach using the DFT-D3(BJ) correction to take into account van der Waals interactions. Previous *ab initio* results obtained in the local density approximation (LDA) are also given for comparison.

The E_{2g}^{high} frequency calculated within the GGA + vdW approach agrees quite well with the experimental value. As expected, the GGA gives a superior account of the valence bonds in the hexagonal layers compared to the LDA, which clearly overestimates the E_{2g}^{high} frequency. The experimental E_{2g}^{low} frequency is, however, somewhat lower than the GGA + vdW prediction, even if we take into account the temperature effect on the frequency measured at room temperature, which would amount to a downshift of $\sim 2 \text{ cm}^{-1}$ relative to the $T = 0 \text{ K}$ value provided by the *ab initio* calculations [46]. This suggests that the DFT-D3(BJ) density functional dispersion correction may be overestimating the interlayer van der Waals forces. Indeed, the equilibrium interlayer distance predicted by these calculations is $\sim 6\%$ shorter than the c parameter measured in x-ray experiments, and the calculated bulk modulus is somewhat higher than the value reported in Ref. [40]. Considerable dispersion of the experimental values of the bulk modulus exists in the literature [40,47,48]. This has been attributed to the different degree of

TABLE II. Ambient-pressure frequencies (ω), pressure coefficients (α), and Grüneisen parameters (γ_G) for the Raman-active modes of *h*-BN, calculated using density functional perturbation theory in the local density approximation (LDA) (Ref. [44]) and in the generalized gradient approximation (GGA) with the van der Waals density functional correction DFT-D3(BJ), compared with the experimental values. The isothermal bulk modulus (B_0) reported in Ref. [40] as well as the values predicted by the calculations are also given.

	ω (cm ⁻¹)		α (cm ⁻¹ GPa ⁻¹)		γ_G		B_0 (GPa)
	E_{2g}^{low}	E_{2g}^{high}	E_{2g}^{low}	E_{2g}^{high}	E_{2g}^{low}	E_{2g}^{high}	
LDA ^a	50.8	1377	9.10	4.13	4.83	0.08	26.6
GGA + wdW	59.5	1367	6.50	5.31	4.49	0.16	41.1
Expt.	52.1(2)	1367.3(3)	7.9(2)	5.3(2)	5.5(2)	0.14(1)	36.7(5) ^b

^aReference [44].

^bReference [40].

three-dimensional ordering (P_3) in the stacking sequence among different samples [47], which modifies substantially the effective interlayer interaction. While in more disordered samples ($P_3 \leq 0.9$) lower values of B_0 are found, a sample with $P_3 = 1$ was found to have the same equation of state as the highly ordered sample reported in Refs. [40,47]. Since the *ab initio* calculations are performed on a perfectly ordered crystal, we compare our theoretical values of the bulk modulus with the experimental determination of Solozhenko *et al.* [40]. The GGA + wdW approach yields a bulk modulus value that is in better agreement with experiment than the LDA approach (see Table II). As pressure increases, the interlayer distance rapidly decreases because of the high compressibility along the *c* direction and, consequently, the role of Pauli repulsion in the interlayer interactions is enhanced. The shorter interlayer distance predicted by DFT implies a more pronounced stiffening of the *c* axis and therefore an overestimation of the E_{2g}^{low} nonlinearity with pressure. Both the compressibility along the *c* direction and the pressure coefficient of the E_{2g}^{low} mode are smaller at higher pressures, which explains that the bowing of the frequency vs pressure curve is larger for the interlayer E_{2g}^{low} mode than for the intralayer E_{2g}^{high} mode. Overall, there is good agreement between the experimental and GGA + wdW theoretical values for the pressure coefficients and Grüneisen parameters of both E_{2g} modes. The experimental values for the pressure coefficient and the Grüneisen parameter of the E_{2g}^{high} mode are on the same order of those of the *in-plane* E_{1u} IR-active modes [24].

When the pressure is increased above 10 GPa, the intensity of the E_{2g}^{high} peaks drastically reduces while maintaining its FWHM, and it completely vanishes for $P > 10.5$ GPa. The intensity of the E_{2g}^{low} mode exhibits a parallel behavior (see Fig. 1). This indicates that the phase transition to a metastable wurtzite phase [26] occurs at around this pressure, and that a fraction of *h*-BN domains with good crystallinity coexist with the transitioned phase until the phase transition is completed at ~ 10.5 GPa, when the *h*-BN peak is fully quenched. The phase transition induces a change in the visual aspect of the sample surface, which becomes texturized. Then, the elastic contribution to scattering is enhanced and, as a consequence, the background signal increases significantly. Previous IR studies [24] indicated a somewhat higher transition pressure, around 13 GPa. The variation in the transition pressure obtained from these studies could be related to the different experimental techniques used and to the presence of non-

hydrostatic tensions in the KBr PTM employed for the IR measurements. Since the Raman-scattering cross section of the *w*-BN is much lower than that of the *h*-BN, no signal from the wurtzite phase can be detected inside the DAC. However, after decompression, the Raman spectrum of the wurtzite phase can be observed in the transitioned sample in the open DAC, as can be seen in Fig. 3.

The Raman spectrum of Fig. 3 is consistent with the Raman spectrum of a millimeter-sized *w*-BN bulk crystal obtained by a high-pressure, high-temperature transformation recently reported [49]. The *w*-BN frequencies calculated by Ohba *et al.* [43] using LDA *ab initio* methods are indicated on Fig. 3 with dashed lines. Taking into account that LDA tends to overbind and give phonon frequencies that are too high [50], the broad peaks observed in the Raman spectrum at 964 and 1028 cm⁻¹ can be assigned to the E_{2g}^{high} and A_1 transverse-optic (TO) modes of *w*-BN, respectively. The observation of the A_1

FIG. 3. Raman spectra (after background subtraction) of the transitioned sample in the open DAC at ambient pressure. The Raman peaks of the wurtzite phase are indicated by the green arrows. The E_{2g} spectrum of the pristine *h*-BN sample prior to the pressure cycle is displayed as a red line for comparison. The strong Raman signal marked with an asterisk is due to the diamond anvil. The phonon frequencies of the *w*-BN modes calculated in Ref. [43] are indicated by the dashed lines.

(TO) modes suggests angular deviations in the nanometric *w*-BN domains and/or light propagation in the basal plane favored by grain boundaries. The intensity of the A_1 (TO) signal is comparable to that of the E_2 mode, with some small fluctuations across the sample. The weak feature detected at 1302 cm^{-1} is probably due to the A_1 longitudinal-optic (LO) mode, taking into consideration that LDA is known to underestimate the LO-TO splitting [51]. An additional Raman peak is detected at 1365 cm^{-1} , which corresponds to the E_{2g}^{high} mode of *h*-BN, as can be seen by direct comparison with the Raman spectrum of a pristine *h*-BN sample. The Raman-scattering cross section of the hexagonal phase is exceptionally large in comparison with the cubic and wurtzite phases [52]. This allows the detection of the E_{2g}^{high} signal, which indicates that a small fraction of *h*-BN exists in the transited sample. The presence of this residual *h*-BN phase was not detected in previous IR measurements performed at ambient pressure in cold-pressed transited BN samples [26]. Given the sharpness of the phase transition observed in the upstroke, and considering that the maximum pressure achieved was 15 GPa, we interpret that *h*-BN was fully transformed in the upstroke and therefore the *h*-BN residual phase recovered in ambient conditions corresponds to back-transformed sample.

IV. CONCLUSIONS

We have carried out a detailed study of both E_{2g} Raman-active modes of *h*-BN under high pressure. This study reveals the fundamental differences in the lattice dynamics of these modes arising from the high anisotropy of the *h*-BN crystal. The E_{2g}^{low} shear mode is primarily governed by the weak van der Waals interlayer forces and, given the large compressibility of the *h*-BN crystal along the *c* direction, exhibits a pressure coefficient that is higher than that of the *in-plane*, covalently bonded E_{2g}^{high} mode. The large compression of the interlayer distance with pressure introduces a sublinearity in the pressure dependence of the E_{2g} phonon frequencies. This behavior is parallel to that observed in graphite. The sublinearity in the E_{2g}^{high} frequency is small and primarily determined by the sublinear decrease of the *c* lattice parameter with pressure. On the other hand, the frequency of the E_{2g}^{low} mode shows a marked sublinear behavior at higher pressure as the interlayer Pauli repulsion increases with decreasing interlayer

distance. *h*-BN exhibits a higher E_{2g}^{low} pressure coefficient and a larger absolute frequency shift with pressure than graphite, as a consequence of the smaller sublinear decrease of the interlayer distance with pressure. In both *h*-BN and graphite, the different interlayer coupling regime at higher pressures is reflected in an enhancement of the E_{2g}^{low} mode polarizability, which leads to a steady increase of the Raman intensity with pressure. In contrast, the E_{2g}^{high} intensity remains unchanged up to the phase-transition pressure.

We have shown that a phase transition to a wurtzitic phase takes place at high pressure and is essentially completed at ~ 10.5 GPa, as attested by the full quenching of the E_{2g}^{high} Raman peak of the hexagonal phase. Contrary to the suggestions made in previous Raman studies, there is no significant crystallinity loss with increasing pressure, and the phase transition is not reversible but the metastable wurtzitic phase remains stable down to ambient pressure, with only a residual recovery of the hexagonal phase.

The phonon frequency dependence measured in the Raman experiments is well reproduced by *ab initio* GGA calculations that take into account the nonlocal van der Waals interactions between layers through a density functional dispersion correction. This approach significantly improves the accuracy of the E_{2g}^{high} frequency over previous LDA calculations, but it yields E_{2g}^{low} frequencies that are somewhat too high at low pressures, suggesting that the dispersion correction introduced may be overestimating the van der Waals interactions. These results should stimulate further theoretical investigations based on self-consistent van der Waals–density-functional methods that can improve the description of the layered crystals. Being a shear mode governed by van der Waals forces, the E_{2g}^{low} phonon of *h*-BN is an ideal test bench for the theoretical approaches to nonlocal interactions.

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