Effects of isotopic substitution on the phonons of van der Waals crystals: the case of hexagonal boron nitride

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Abstract. The recent availability of isotopically pure samples of hexagonal boron nitride (h-BN) has allowed the isotopic substitution effects to be studied in this highly interesting layered crystal. Here, we review the application of Raman scattering to investigate phonon anharmonic decay and its particularities in layered crystals, exemplified by h-BN. The modification of the phonon spectrum and anharmonic phonon decay paths in isotopically pure samples is specifically addressed. Detailed information about phonon lifetimes and decay channels is obtained for h-BN from a thorough analysis of temperature-dependent Raman scattering measurements in the light of density functional theory and perturbation theory calculations. The phonon lifetime is substantially increased in isotopically pure crystals, which may have important implications for the development of low-loss h-BN based phonon-polariton devices. On account of the low cation mass, isotopic substitution substantially alters the dominant phonon decay pathways and changes the strength of phonon anharmonic interactions.

Keywords: van der Waals crystals, phonon anharmonicity, isotopic substitution, Raman scattering

1. Introduction

Recent years have witnessed an impressive surge in research and technological applications of 2D materials. Graphene, the great variety of transition metal dichalcogenides and layered hexagonal boron nitride ($h$-BN) are paramount examples. $h$-BN is currently attracting much interest because of its unique properties: a layered honeycomb structure similar to graphene, wide bandgap ($\sim 6 \text{ eV}$), and good thermal properties. All these properties make $h$-BN an ideally suited material for dielectric layers in graphene-based stacked devices [1]. Additionally, $h$-BN displays an extreme optical anisotropy [2], which is being explored in hyperbolic phonon-polariton applications [3, 4].

Phonon excitations play a central role in determining the remarkable properties of $h$-BN. Namely, the existence of well-separated reststrahlen bands associated with infrared optical phonon modes polarized in the hexagonal plane and along the $c$ direction gives rise to type I and type II hyperbolic behavior, in which the in-plane and out-of-plane permittivities display opposite sign [3]. On the other hand, phonon lifetime is a key parameter to achieve low-loss phonon-polariton operation.

Traditionally, phonon lifetimes have been measured in frequency domain by means of high-resolution Raman scattering measurements [5]. The full width at half maximum of the Raman line is related to the phonon lifetime via energy-time uncertainty relation, and the analysis of its temperature dependence gives insight into the most likely phonon decay pathways. Early works [6] were based on oversimplified analytical ansatzs like the Klemens model [7], in which only decay into two acoustic phonons of opposite wavevector belonging to the same branch is considered. With the advent of widespread use of $ab$-$initio$ methods for the calculation of phonon dispersion [8], a much more detailed picture of the dominant anharmonic phonon decay pathways can be extracted from the analysis of Raman measurements [9, 10, 11].

Changes in atomic mass affect the phonon frequencies and their linewidths. Early Raman investigations on Ge isotopes [12] demonstrated that the phonon frequencies scale as the inverse square root of the mass, as expected from the harmonic approximation. Isotopic studies were extended to zinc-blende [13] and wurtzite [14] binary semiconductors. Isotope mass fluctuation in mixed composition crystals were shown to lead to additional frequency shifts and line broadenings [13]. All these studies were mainly performed on cubic semiconductors. Because of the strong structural anisotropy of layered van der Waals crystals, they present some particularities in their phonon dynamics [11] that affect the temperature dependence of their phonons. These were already revealed by infrared and Raman studies carried out on graphite [15]. The development of growth methods for producing high-quality $h$-BN single crystals with controled isotopic composition [16] has enabled us to explore isotopic effects on the technologically important $h$-BN layered crystal.

Here we present an overview of the experimental results on phonon anharmonic decay in isotopically pure $h$-BN samples that we have recently published [11, 17]. The
emphasize in this review is on a general description aimed at a non-specialist audience of the physical mechanisms that have a role in explaining the temperature dependence of the Raman peaks of isotopically contolled h-BN. An exhaustive discussion of the theoretical models used to accurately interpret the Raman data can be found in our previous works [11, 17].

2. Phonons in layered compounds: the case of h-BN

The structure of h-BN consists of layers of flat B₃N₃ covalently bonded hexagons which are anchored together by weak van der Waals forces (see Fig. 1). The optical phonons at the Brillouin zone center belong to the $E_{1u} + A_{2u} + 2E_{2g} + 2B_{1g}$ representations of the $D_{6h}$ point group. The $E_{2g}$ modes are Raman active and the $E_{1u}$ and $A_{2u}$ are infrared active, whereas the $B_{1g}$ modes are optically inactive. Both $E_{2g}$ and $E_{1u}$ modes are in-plane polarized, whereas $A_{2u}$ and $B_{1g}$ modes are polarized along the $c$ axis. Here we shall be focusing on the $E_{2g}$ Raman active modes. On account of the high structural anisotropy, the two $E_{2g}$ Raman active modes exhibit vastly different frequencies. Whereas in the high-frequency mode ($E_{2g}^{\text{high}}$) the antiparallel motion of B and N atoms basically probe the strong in-plane covalent bonding, the low-frequency mode ($E_{2g}^{\text{low}}$) corresponds to an interlayer shear mode where all the B and N atoms in a given layer vibrate in phase and therefore its frequency is determined by the weak interlayer van der Waals forces (see Fig. 2 for a pictorial representation). These very low-frequency interlayer modes are
characteristic of layered compounds and are also encountered in graphite [18]. As will be discussed later on, the existence of such low-frequency modes has a strong impact on phonon dynamics [15, 11].

2.1. Phonon dispersion

The phonon dispersion of h-BN calculated for $^{10}$BN and $^{11}$BN using a density functional theory (DFT) approach [17] is shown in Fig. 2 as blue and red lines, respectively. The in-plane $E_{1u}$ and $E_{2g}$ optical modes in which B and N atoms vibrate against each other display the highest frequencies. They exhibit a substantial isotopical frequency shift over the whole Brillouin zone. The intermediate frequency range (from $\sim 600$ to $\sim 850$ cm$^{-1}$) corresponds to modes with atomic vibrations along the $c$ axis that lead to a buckling of the flat hexagonal layers. These modes display a smaller isotopic shift. Finally, at the low-frequency range one finds the low-energy $E_{2g}$ shear mode and $B_{1g}$ silent mode, which can be viewed, respectively, as the zone folding of transverse- and longitudinal-acoustic branches along the $A$ direction arising from the alternate layout of B and N atoms along the $c$ direction. These modes display essentially no shift with isotopic mass. The presence of low-frequency modes associated with interlayer interactions is characteristic of layered compounds and plays a relevant role in anharmonic interactions[15, 11]. As can be seen in Fig. 2 from the slope of the phonon dispersion, the group velocity of the low-frequency phonons propagating along in-plane directions is much smaller for phonons polarized along the $c$ direction (ZO$_1$ and ZA) than for the in-plane polarized phonons (TO$_1$, TA, LO$_1$, and LA) [19], and the ZO$_1$ and ZA branches are virtually dispersionless along the $M-K$ line. This yields a strong peak in the phonon density

Figure 2. Phonon dispersion and density of states for isotopically pure $^{10}$BN (blue lines) and $^{11}$BN (red lines). Arrows indicate the main phonon decay channels (see text). The atomic motions for the optical phonons are illustrated. Reproduced with permission from the American Physical Society.
of states (PDOS) that, as will be discussed next, has also a bearing on the phonon anharmonic decay.

2.2. Phonon anharmonic interactions

2.2.1. Phonon anharmonic decay  Anharmonic terms in the lattice Hamiltonian give rise to coupling of the harmonic eigenstates, which leads to phonon decay and finite phonon lifetime. Interacting phonons can be viewed as quasi-particles with a complex self-energy \( \Sigma(\omega) = \Delta(\omega) - i\Gamma(\omega) \), where \( 2\Gamma(\omega) \) yields the full width at half maximum (FWHM) of the phonon linewidth [5]. The imaginary part, which can be calculated from perturbation theory, contains contributions from downconversion and upconversion processes. In a cubic-anharmonicity downconversion process a phonon decays into two lower energy phonons, whereas an upconversion process involve the decay of a phonon into a higher energy phonon with the simultaneous annihilation of an existing phonon. Higher order quartic anharmonic processes involving the decay into three phonons may also contribute. Energy and crystal momentum conservation hold in all cases. In general, the decay frequencies cluster around a few dominating decay channels. These can be deduced by inspection of the PDOS, and they are depicted by the arrows in Figure 2 for the \( E_{3g}^{\text{high}} \) mode of h-BN. Orange arrows indicate downconversion to a pair of opposite wavevector ZO1 or ZA phonons at \( K \), whereas green arrows indicate an upconversion to a longitudinal optical optical branch with the annihilation of an acoustic phonon. The blue arrows represent a quartic-anharmonicity downconversion into a zone center \( A_{2u} \) phonon and a pair of opposite wavevector ZO1 or ZA phonons at \( M \). Since the ZO1 or ZA branches are virtually dispersionless along the \( M-K \) direction, any phonon along this line (shaded area) will fulfill energy conservation and therefore this quartic-anharmonic decay channel is expected to be important in h-BN.

The imaginary part of the self energy is essentially proportional to the combined PDOS for phonon sums and differences, to the effective anharmonic coupling potentials, and to the Bose-Einstein occupation factors [9]. For the cubic-anharmonic decay, the imaginary part of the self-energy is

\[
\Gamma(\omega) = |V_3^+|^2 (1 + n_1 + n_2) \rho^+(\omega) + |V_3^-|^2 (n_2 - n_1) \rho^-(\omega),
\]

where \( \rho^+(\omega) \) and \( \rho^-(\omega) \) the two-phonon sum and difference density of states, and \( V_3^+ \) and \( V_3^- \) the effective third-order anharmonic potentials for decay into phonon sums and phonon differences, respectively. \( n_1 \) and \( n_2 \) are the Bose-Einstein factors for the phonons involved in the phonon sum or phonon difference. Similarly, the quartic anharmonic decay contribution can be approximated by

\[
\Gamma^{(4)}(\omega) \sim |V_4^+|^2 \left[ n(\omega_1^+) \right] \left[ n(\omega_2^+) \right] \left[ n(\omega_3^+) \right] \left[ n(\omega_4^+) \right] \rho^+(\omega - \omega_1^+)
\]

\[
+ |V_4^-|^2 \left[ n(\omega_1^-) \right] \left[ n(\omega_2^-) \right] \left[ n(\omega_3^-) \right] \left[ n(\omega_4^-) \right] \rho^-(\omega - \omega_1^-),
\]

where \( \omega_1 \) is the frequency of a zone-center mode and \( \omega_2, \omega_3 \) are the frequencies of opposite wave-vector phonon modes satisfying energy conservation.
Figure 3. Phonon occupation factor as a function of temperature and phonon energy. Phonon modes below $k_B T$ exhibit the highest temperature dependence. Note that the coupling potential (boxed labels) is negative for the lowest frequency $E_{2g}$ mode. Reproduced with permission from the American Physical Society.

Once the imaginary part of the self energy is known, the real part, which gives the associated frequency shift, can be readily obtained by a Kramers-Kronig transformation [9]. The line broadening determined by by Eqs.(1), (2) and (3) depends on temperature through the Bose-Einstein factors, and therefore, a fit to the temperature dependence of the Raman FWHM allows the effective anharmonic coupling potentials to be determined.

The Raman line shape of the anharmonic phonons is then calculated from the Lorentzian-like expression

$$I(\omega) \propto \frac{\Gamma(\omega)}{[\omega_0 + \Delta(\omega) - \omega]^2 + \Gamma(\omega)^2},$$

where $\omega_0$ is the bare phonon frequency. Note that, in the limit of slowly varying $\Gamma(\omega)$, the FWHM of the Raman line shape corresponds to two times the imaginary part of the phonon self-energy.

2.2.2. Phonon-phonon scattering in quartic anharmonicity In addition to the downconversion and upconversion processes discussed in the previous section, quartic anharmonicity also contains a contribution from a first-order loop diagram that represents the scattering with a pair of opposite wave-vector phonons [20, 11]. This yields a purely real contribution to the self energy, which under certain simplifying assumptions can also be expressed in terms of an effective phonon scattering constant,
the Bose-Einstein occupation factors, and the PDOS \cite{11} as

$$\Delta^s(T) \approx \tilde{V}^s \int_0^\infty d\omega [n(\omega, T) - n(\omega, T_0)]\rho(\omega),$$

(4)

where \( \tilde{V}^s \) is an effective phonon scattering constant. This results in an additional frequency shift of the phonon line that has to be added to the anharmonic decay shift. A fit to the temperature dependence of the phonon frequency measured in the Raman experiments allows the effective phonon scattering constant to be determined. The temperature dependence of Eq.(4) mainly arises from the Bose-Einstein occupation factors. As illustrated in Fig. 3, the thermal occupation factor show an appreciable increase with temperature only for low phonon energies \( \hbar\omega \lesssim k_B T \).

Layered crystals typically exhibit very low frequency optical modes associated with the weak van der Waals interlayer interactions. Therefore, unlike the case of common cubic semiconductors, phonon-phonon scattering plays a major role in the temperature dependence of phonons in layered compounds because of a strong coupling to the low frequency optical modes \cite{11}. In the case of \( h \)-BN, the anharmonic coupling to the lowest frequency mode is large and negative (see Fig. 3), which explains the large frequency downshift with temperature observed for the high-frequency \( E_{2g} \) mode of \( h \)-BN. Indeed, both in graphene \cite{15} and in \( h \)-BN \cite{11, 17} the large frequency redshift of the high frequency optical modes with increasing temperature is mostly due to this mechanism.

2.2.3. Lattice thermal expansion To zeroth order, the thermal lattice expansion gives a further contribution to the temperature-dependent frequency shift. In the quasi-harmonic approximation, the change in the lattice parameters arises from a temperature dependent term in the free energy associated to phonons (see Appendix A in Ref. \cite{17}). The large structural anisotropy of layered compounds results in a strongly anisotropic thermal expansion. Both graphite and \( h \)-BN display a negative thermal expansion.
coefficient in the covalently bonded basal plane and a positive thermal expansion coefficient, nearly one order of magnitude larger, along the c direction. Figure 4 shows the relative variation of the a and c lattice parameters of h-BN calculated by DFT in the quasiharmonic approximation. The results obtained using this approach are in excellent agreement with experimental determinations of the lattice parameters available in the literature. The thermal shift of the phonon frequencies can then be derived from DFT calculations on the thermally strained lattice. The decrease of the a lattice parameter implies a blue shift of the phonon modes that are in-plane polarized, which for the case of the \( E_{2g}^{\text{high}} \) mode is estimated to be \( \sim 7 \text{ cm}^{-1} \) at 600 K.

3. Effects of isotopic substitution

3.1. Mass scaling

The phonon frequencies are directly affected by the change of the average mass of the harmonic oscillators [virtual crystal approximation (VCA)]. This effect is particularly important in BN because, on account of the low cation mass, the substitution of the stable isotopes of boron (\(^{10}\)B and \(^{11}\)B) induces a large relative mass change. In the case of the \( E_{2g}^{\text{high}} \) mode, where B and N atoms vibrate against each other, the phonon frequency should scale as the inverse square root of the reduced mass, whereas the \( E_{2g}^{\text{low}} \) shear mode, which involves the gliding motion of the rigid hexagonal layers, is expected to scale as the inverse square of the unit cell mass. In crystals with a distribution of both isotopes, the VCA predicts a linear increase of the \( E_{2g}^{\text{high}} \) phonon frequency with the inverse square root of the average reduced mass from its value in \(^{10}\)BN (\( \sim 1360 \text{ cm}^{-1} \)) to its value in \(^{11}\)BN (\( \sim 1395 \text{ cm}^{-1} \)).

3.2. Mass disorder effects

The relaxation of wavevector conservation in the isotopically disordered crystals allows scattering to phonons of similar energies but different wavevectors, which leads to a renormalization of the phonon self-energy induced by isotopic disorder. The magnitude of this effect depends on the mass variance \( g = \sum_i C_i [1 - (M_i/\langle M \rangle)]^2 \), where \( M_i \) is the isotope mass, \( C_i \) its relative abundance, and \( \langle M \rangle \) is the average mass. In natural composition BN, where \( C_{^{10}} = 0.199 \) and \( C_{^{11}} = 0.801 \), the mass variance is quite large (\( g \sim 1.35 \)), nearly one order of magnitude higher than in GaAs. According to Tamura’s calculations [21], the scattering rate in a mass disordered lattice with a random distribution is proportional to the mass variance, to the PDOS weighted by the norm squared of the eigenvector projection onto other phonon branches, and to the squared phonon frequency. To the lowest order of perturbation theory, the scattering rate is given by

\[
\tau^{-1}(j|q; \omega) = \frac{\pi}{2N} \omega_j^2(q) \sum_{j', q'} \delta[\omega - \omega_j^{(q)}(q)] \times \sum_{\kappa} g_{\kappa} |e^{\kappa}(\kappa|j'q') \cdot e(\kappa|jq)|^2. \quad (5)
\]
Here N is the number of unit cells and \( e(\kappa|1/jq) \) is the orthonormal eigenvector of the sublattice \( \kappa \) of the phonon with wave vector \( q \) in the \( j \) branch. The evaluation of the eigenvector projection must be explicitly performed in the case of layered compounds because of the strong anisotropy between *in-plane* and *out-of-plane* vibrations. The fact that the scattering rate is proportional to the squared phonon frequency, makes the isotopic disorder scattering relevant for the \( E_{2g}^{\text{high}} \) mode, but entirely negligible in the case of the \( E_{2g}^{\text{low}} \) mode. The phonon frequency shift associated with the line broadening induced by mass disorder can be evaluated by a Kramers-Kronig transformation.

### 3.3. Anharmonic interactions

The isotopic substitution affects the phonon energies over the whole Brillouin zone and hence the possible pathways for anharmonic phonon decay. Figure 2 displays the shifts in phonon bands and PDOS between isotopically pure \(^{10}\text{BN}\) and \(^{11}\text{BN}\) crystals, obtained from DFT calculations. Since the isotopic frequency shifts are more pronounced for the high-frequency optical bands, this affects the energy match of certain decay channels. Most notably, the cubic anharmonic decay of the \( E_{2g}^{\text{high}} \) phonon into a pair of zone edge acoustic phonons (orange arrows in Fig. 2) achieves a nearly perfect energy match in \(^{10}\text{BN}\), and this strongly enhances the role of this decay pathway in relation to the dominant decay channels identified in \(^{11}\text{BN}\) and natural composition crystals [17].

### 4. Raman scattering experiments on isotopically engineered h-BN

With the development of the growth of high quality h-BN single crystals from high purity elemental boron-10 or boron-11, it has been possible to experimentally investigate isotopic effects on a layered compound. The experiments discussed here were performed on nominally pure \(^{10}\text{BN}\), \(^{11}\text{BN}\), and natural composition samples that were grown from mixed powders in a furnace with a continuous flow of \( \text{N}_2 \) and forming gas. Single crystal growth of millimeter-sized isotopically pure h-BN is described in detail in Ref. [16]. The Raman measurements were carried out using a Jobin-Yvon T64000 triple spectrometer with a spectral bandwidth of \( \sim 0.7 \text{ cm}^{-1} \). The intrinsic phonon linewidths were corrected for instrumental broadening. For further details on the experimental conditions, see Ref. [17].

#### 4.1. Temperature dependence of the Raman spectra

Figure 5 displays representative Raman spectra of the \( E_{2g}^{\text{high}} \) mode recorded at 80, 320, and 600 K on isotopically pure h-BN samples compared to spectra of natural composition samples. The isotopically pure samples exhibit narrow (FWHM \( \sim 2.7 \text{ cm}^{-1} \) at 80 K), symmetric Lorentzian line shapes and a substantial frequency shift of \( \sim 35 \text{ cm}^{-1} \) from the heavier to the lighter isotope. This is in excellent agreement with the DFT calculations shown in Fig. 2. As temperature increases, the Raman peaks maintain their symmetrical Lorentzian shape but broaden significantly as a result of the intensification
of phonon-phonon interactions leading to anharmonic decay. Given the natural isotopic composition (80% \textsuperscript{11}B), the phonon frequency in the natural composition sample is close to that of the isotopically pure \textsuperscript{11}BN sample. However, it does not follow the expected scaling with the inverse square root of the effective mass. The $E_{2g}^{\text{high}}$ frequency measured in the natural composition sample is higher by $\sim 2$ cm$^{-1}$ than the VCA prediction. This is in excellent agreement with the real part of the isotopic-disorder-induced phonon self-energy $\Delta_{\text{iso}}$ calculated using a DFT and perturbation theory approach [17].

In contrast with the isotopically pure samples, the Raman peaks in the natural composition sample are considerably broader (FWHM $\sim 7$ cm$^{-1}$ at 80 K) and asymmetric with a low-frequency tail. The asymmetry in the line shape is brought about by a steep edge of the imaginary part of the isotopic-disorder-induced phonon self-energy at the $E_{2g}^{\text{high}}$ frequency, which stems from the ridge structure in the PDOS (see encircled area in Fig. 2) [17].

**Figure 5.** Raman spectra of \textsuperscript{10}BN, natural-composition BN, and \textsuperscript{11}BN single crystals recorded at 80 K, 320 K, and 600 K in backscattering configuration from a $c$ face. Solid lines correspond to line-shape model fits to the data. Reproduced with permission from the American Physical Society.
In all cases, the Raman peaks show a similar red shift and broadening with increasing temperature. Figure 6 displays the temperature dependence of the FWHM, which exhibits a superlinear increase with temperature. This trend is a clear indication of a substantial contribution of quartic anharmonicity terms involving the decay into three phonons. As pointed out in Section 3.3, a cubic anharmonicity channel is particularly enhanced in $^{10}$BN. By fitting the line shape model outlined in Section 2 and described in more detail in Ref. [17], semi-empirical cubic and quartic effective anharmonic coupling potentials can be determined in this sample. The excellent quality of the line shape fits can be observed in Fig. 5. The same cubic anharmonic potentials are assumed for the $^{11}$BN and $^{nat}$BN crystals. In these cases, the FWHM exhibits low sensitivity to the cubic anharmonic potentials due to the predominance of the quartic anharmonicity, which makes unreliable the evaluation of the cubic anharmonicity contribution. In both isotopically pure samples, the background impurity contribution to the FWHM is very low ($\sim 1.3$ cm$^{-1}$). The much higher FWHM measured in the natural composition sample is mainly due to the isotopic disorder, but a higher background impurity contribution is also found in this sample [17].

Once the effective anharmonic potentials are determined from the FWHM fits, the frequency shift with temperature can be evaluated from a Kramers-Kronig transformation of the imaginary self-energy, taking due account of the separate thermal
expansion and phonon-phonon scattering contributions. Figure 7 plots the temperature dependence of the $E_{2g}^{\text{high}}$ frequency measured on the three isotopically controlled samples (symbols). While all samples exhibit a large red shift with temperature, the frequency shift due to the thermal expansion of the lattice is large and positive. The isotopic disorder introduces an additional frequency shift of $\sim 2 \text{ cm}^{-1}$ in the natural composition sample. The anharmonic decay interactions tend to decrease the frequency but they have only a minor effect and cannot reverse the lattice expansion trend. This highlights the importance of quartic anharmonicity phonon-phonon scattering mechanisms in layered compounds, as discussed in Section 2.2.2. By including an additional effective potential describing this specific scattering mechanism, an excellent fit to the experimental data is obtained (solid lines).

4.2. Phonon lifetime

A straightforward estimate of the phonon lifetime can be derived from the FWHM of the Raman peak using the energy-time uncertainty relation $\Gamma_R = \hbar (\tau_1^{-1} + \tau_0^{-1})$. 

\textbf{Figure 7.} Temperature dependence of the $E_{2g}^{\text{high}}$ phonon frequency experimentally determined from Raman measurements (symbols) and model fits to the data (lines). The separate contributions of lattice thermal expansion and phonon anharmonic decay are plotted. The phonon-phonon scattering has a prominent role in determining the redshift of the Raman peak with temperature. Isotopic disorder increases the Raman shift by $\sim 2 \text{ cm}^{-1}$ in natural $h$-BN.
The intrinsic phonon lifetime $\tau_i$, which is limited by anharmonic decay and mass-disorder effects, depends on temperature through its dependence on the Bose-Einstein occupation factors. Therefore, fitting the model defined by Eqs. (1), (2) and (3) to the temperature dependence of the phonon linewidth allows one to separate the intrinsic phonon lifetime ($\tau_i$) and the contribution to phonon finite lifetime arising from scattering with background impurities ($\tau_b$).

Figure 8 plots the $E_{2g}^{\text{high}}$ phonon lifetimes derived from the Raman spectra for the isotopically controlled samples. Phonon lifetimes are above 2 ps at 80 K in the isotopically pure samples (red diamonds). This is $\sim 2.7$ times higher than in natural composition samples, and reflects the suppression of mass-disorder scattering and the superior crystalline quality of the samples. It is interesting to note that the intrinsic phonon lifetime ($\tau_i$) reaches values of $\sim 4.2$ ps at 80 K in the pure samples. This suggests that phonon-polariton propagation length, which is essentially limited by the phonon lifetime and is a crucial parameter in phonon-polariton applications, will be further increased as the growth of samples with reduced background impurity concentration is developed. The values of intrinsic phonon lifetime obtained from the Raman measurements are however a factor of 2 lower than prior DFT theoretical estimates, and therefore the gain in polariton propagation length achievable in pure samples may
not be as high as previously anticipated [4].

Phonon polaritons in h-BN arise from coupling to the $E_{1u}$ polar mode; the Raman-active $E_{2g}$ mode is not polar and therefore does not couple to the light field. Then, a comparison between the $E_{2g}$ phonon lifetime and the phonon-polariton lifetime is not strictly valid. Nevertheless, one would expect a parallel increase in lifetime for the $E_{1u}$ and $E_{2g}$ modes due to the suppression of isotopic disorder. Phonon-polariton lifetimes of $\sim 0.8$ ps have been reported in h-BN flakes on lossy Si/SiO$_2$ substrates [22, 23]. These are on the same order as the $E_{2g}$ phonon lifetime for natural composition h-BN (see Fig. 8). However, phonon-polaritons are strongly influenced by the dispersive substrate, and for free-standing h-BN flakes, phonon-polariton lifetimes have been predicted to be in the 2–5 ps range [22, 23]. This range of phonon-polariton lifetimes implies that the lifetime of the $E_{1u}$ phonon is actually larger than the value of $E_{2g}$ phonon lifetime determined by Raman measurements, as previously reported for graphite [15]. Therefore, high-resolution infrared measurements that can accurately determine the $E_{1u}$ phonon lifetime would be necessary in order to establish the actual lifetime of the polar phonon mode that gives rise to phonon-polariton modes in h-BN.

5. Conclusions

h-BN is a paradigm of a 2D layered crystal held together by van der Waals forces with a primary role in the development of novel phonon-polariton applications that take advantage of its optical hyperbolic nature. The anisotropic character of phonons in layered h-BN is at the heart of the remarkable optical properties of this material. The change of phonon properties in isotopically engineered samples opens opportunities for a new generation of tailored applications, ranging from extended propagation length in ultra-low loss phonon-polariton devices and hyperlensing to high-efficiency thermal neutron detection in $^{10}$BN. Isotopic substitution may also have a fundamental bearing on van der Waals interactions in layered compounds.

Raman scattering is a powerful probe into the changes induced by isotopic substitution to the phonon spectrum. The development of growth methods to obtain high quality h-BN single crystals has allowed the experimental study of isotopic effects on that highly anisotropic layered compound by means of high-resolution Raman spectroscopy. The mechanisms for anharmonic phonon decay of the high-frequency $E_{2g}$ phonon have been investigated and the main decay channels have been identified based on DFT calculations of the phonon dispersion. A substantial contribution of quartic anharmonicity decay is found in natural composition h-BN. The isotopic shifts of the phonon bands strongly enhance the relative significance of cubic anharmonicity in $^{10}$BN crystals. Due attention has to be given to the anomalous in-plane negative thermal expansion effects on the phonons of this highly anisotropic crystal, which would result in a blue shift of the high-frequency $E_{2g}$ phonon. However, this is overcompensated by a phonon-phonon scattering mechanism in quartic anharmonicity that is particularly strong in layered compounds on account of the existence of the characteristic low-lying
optical modes associated with the weak interlayer van der Waals interactions.

The suppression of isotopic disorder scattering in isopolitically pure samples results in a significant increase of phonon lifetime. This opens an avenue for improving performance in phonon-polariton applications that rely on phonon-polariton propagation length, which is presently limited by the their relatively small group velocity. The intrinsic phonon lifetime limited by anharmonic decay in isopolitically pure samples is a factor of two higher than the full lifetime determined by the Raman measurements at 80 K, which suggests a possible pathway to enhance phonon-polariton propagation lengths by developing growth strategies to reduce the point-defect and impurity density in the crystals.

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