Phonon symmetries in hexagonal boron nitride probed by incoherent light emission

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Abstract

Layered compounds are stacks of weakly bound two-dimensional atomic crystals, with a prototypal hexagonal structure in graphene, transition metal dichalcogenides and boron nitride. This crystalline anisotropy results in vibrational modes with specific symmetries depending on the in-plane or out-of-plane atomic displacements. We show that polarization-resolved photoluminescence measurements in hexagonal boron nitride reflect the phonon symmetries in this layered semiconductor. Experiments performed with a detection on the sample edge, perpendicular to the c-axis, reveal the strong polarization-dependence of the emission lines corresponding to the recombination assisted by the three acoustic phonon modes. We elucidate the dipole orientation of the fundamental indirect exciton. We demonstrate evidence of the so-far missing phonon replica due to the optical out-of-plane phonon mode.

Several experimental probes enable the determination of the phonon band structure in solid state physics, such as high-resolution electron energy loss spectroscopy, inelastic neutron or x-ray scattering, complemented by Raman spectroscopy. All these techniques consist in measuring the energy detuning between an incoming particle (electron, neutron or photon) and an outgoing one, the energy difference being accomodated by a specific phonon mode depending on the experimental configuration and the selection rules for the interaction process.

In contrast to these coherent scattering techniques, we use here incoherent light emission in order to investigate the impact of the phonon symmetries on the intrinsic optical response of hexagonal boron nitride (hBN) in the deep ultraviolet. Since hBN has an indirect bandgap [1, 2], radiative recombination must be assisted by phonon emission in order to fulfill momentum conservation. The emission spectrum of bulk hBN in the deep ultraviolet is thus composed of phonon replicas which are detuned by their corresponding phonon energy compared to the indirect exciton iX. In other words, although photoluminescence (PL) under non-resonant excitation is an incoherent emission process, the indirect exciton energy $E_{iX}$ is analogous to the incident particle energy $E_{in}$ in scattering techniques. Consequently, the polarization-dependence of the phonon-assisted recombination lines in PL spectroscopy can be traced back to the specific phonon symmetries in a layered semiconductor such as hBN.

Because of their pronounced structural anisotropy, layered compounds preferentially grow along their c-axis, perpendicular to the covalently bound layers which are held together by a weak Van der Waals coupling. As a matter of fact, the natural geometry in optical spectroscopy consists in exciting and collecting light from the top of the sample, with wave-vectors close to the c-axis direction. In opposition to this experimental configuration widely used in the optical studies in bulk hBN [3–9], we present measurements from the edge of the sample, enabling the collection of...
the PL signal emitted along a wave-vector orthogonal to the $c$-axis, as schematically depicted in figures 1 and 2(a). The additional implementation of a polarization-resolved detection in the deep ultraviolet (figure 1) allows us to perform a full characterization of the optical response as a function of the emitted wave-vector and polarization (figure 2).

Our sample was fabricated using the growth method developed at NIMS [4]. In our experimental setup (described in figure 1), the sample is held on the cold finger of a closed-cycle cryostat, with two positions which are either parallel or perpendicular to the cold finger for collecting along or perpendicular to the $c$-axis, respectively (figure 1, inset). Two-photon excitation spectroscopy is performed with an excitation beam tuned at 408 nm, provided by the second harmonic of a Ti:Sa oscillator [1]. For polarization-resolved measurements of the PL spectrum, we use optics based on MgF$_2$ components fabricated by Kogakugiken. A Rochon polarizer is placed in a fixed position in front of the spectrometer, together with a rotating half-wave plate which is achromatic in the spectral range 180–240 nm (more experimental details can be found in the supplementary data).

In figures 2(a)–(c), we first display the polarization-resolved PL measurements at 8 K, in the novel configuration when collecting from the sample edge, with an emission wave-vector $k$ perpendicular to the $c$-axis. Above 5.7 eV, the PL spectrum displays five lines (at 5.76, 5.79, 5.86, 5.89, and 5.93 eV in figure 2(a)) which were recently identified as phonon replicas, with an energy spacing reflecting the splitting of the different phonon branches (LO, TO, LA, TA, ZA, respectively) in the middle of the Brillouin zone [1]. This original phenomenology arises from the electronic band structure in hBN, where the extrema of the conduction and valence bands lie in different high symmetry points, that are both away from the Brillouin zone center [10–12]. The consequences are twofold: it first implies that hBN is an indirect band-gap semiconductor, but also that the phonons assisting the radiative recombination are exceptionally in the middle of the Brillouin zone, and not in valleys close to the edge of the Brillouin zone as in diamond or silicon.

In figure 2(a), we further observe a striking variation of the PL spectrum as a function of the linear polarization of detection. In particular, the PL signal intensity of the ZA phonon replica varies by one order of magnitude when rotating the linear polarization of analysis. For the emission polarized along the $c$-axis (red line in figure 2(a)), the intensity of the ZA phonon replica is approximately one fifth of the LA phonon replica, whereas it decreases down to 1% in the opposite polarization, perpendicular to the $c$-axis (black line in figure 2(a)). In the latter geometry, the ZA line is indeed hardly observable, as for all polarization angles of analysis when collecting from the top of the sample (figure 2(d)). In that case, two-photon spectroscopy (see supplementary data) is a decisive tool for revealing the existence of such a weak line at 5.93 eV [1].

The strong polarization-dependence of the ZA phonon replica when collecting from the sample edge is a first fingerprint of the peculiar phonon symmetries in hBN. In layered compounds, the two types of transverse modes for a given phonon wave-vector perpendicular to the $c$-axis are separated into a mode with in-plane atomic displacements (which remains called transverse, and labeled TO and TA for the optical and acoustic branches, respectively), and an out-of-plane vibration mode (labeled ZO and ZA for the optical and acoustic branches, respectively).

Because of the structural anisotropy in layered compounds, the degeneracy of the in-plane and out-of-plane transverse modes is drastically lifted. The phonon band structure in hBN has been studied both
experimentally and theoretically [13–17]. While the ZA phonon branch displays a dispersion similar to LA and TA modes but with a smaller group velocity, the ZO band is down-shifted to approximately one-half of the Raman-active LO phonon energy [18–20]. This effect results in a significant overlap of the ZO branch with the LA and TA modes, with crossings both at the edge and in the middle of the Brillouin zone [20]. This latter aspect is of paramount importance for the energy position of the ZO phonon replica, which will be discussed at the end of this paper.

When inspecting the selection rules controlling radiative recombination assisted by phonon emission in hBN (supplementary information in [11]), the ZA and ZO phonon replicas are forbidden by symmetry for an emission wave-vector $k$ parallel to the $c$-axis (figure 2(d)), while they are allowed for a polarization along the $c$-axis, thus requiring an emission wave-vector $k$ perpendicular to the $c$-axis (figure 2(a)). Such a selection rule arises from the polarization of the ZA and ZO phonons along the $c$-axis, which stems from the out-of-plane atomic displacements specific to these phonon modes in layered compounds.

We thus conclude that the intensity increase of the ZA phonon replica when analyzing along the $c$-axis (figure 2(a)) is the signature of the out-of-plane mode symmetry, which is polarized perpendicular to the layer plane. Conversely, the selection rules impose a simultaneous decrease in intensity for the replicas due to the longitudinal and transverse phonon modes, which have an in-plane polarization. In figure 2(a), we observe the expected global reduction of the intensity of the four phonon replicas (LO, TO, LA and TA) when the linear polarization is parallel to the $c$-axis. This results in an anti-correlation of the polarization dependence of the LA and ZA phonon replicas, as
shown in figures 2(b) and (c), in agreement with the selection rules controlling the radiative recombination assisted by the emission of phonons of different symmetries. In figures 2(a) and (b), we note an incomplete extinction of longitudinal and transverse phonon replicas when analyzing along the c-axis, while the ZA phonon replica is maximally contrasted as a function of polarization angle figure 2(c). We interpret this phenomenon as due to orientation disorder at sample edges. A quantitative interpretation of the reduced contrast is presented in the supplementary data, together with additional optical measurements at the sample edges and x-ray diffraction experiments showing the crystal imperfections.

Before addressing the issue of the so-far missing ZO phonon replica, we aim at discussing the polarization-dependence of the dim emission of the indirect exciton iX, lying at 5.95 eV [1]. The corresponding line is even weaker than the ZA phonon replica because no phonon is emitted, thus violating the selection rule of momentum conservation in the recombination process. We have performed measurements with a much longer acquisition time (see supplementary data) in order to obtain polarization-dependent PL measurements around 5.95 eV, for an emission wave-vector k perpendicular to the c-axis. The experimental data are displayed in figure 3(a), where the increased signal-to-noise ratio compared to figure 3(a) allows us to resolve the iX line with an intensity more than four orders of magnitude smaller than the dominant LO phonon replica. While the intensity of the ZA phonon replica is maximal for a polarization parallel to the c-axis, the iX line appears to be counter-polarized with a maximum signal intensity perpendicular to the c-axis (figure 3(b)).

This anti-correlation as a function of polarization angle brings the evidence that the dipole of the fundamental indirect exciton is predominantly aligned in the layer plane. This phenomenon is the counterpart in the electronic properties, of the structural anisotropy previously discussed in the context of the vibrational ones with the phonon symmetries. Because of the in-plane covalent binding contrasting with the inter-layer Van der Waals coupling, the exciton is expected to be more strongly bound in the layer plane than along the c-axis [1], with an anisotropic wavefunction describing the electron–hole relative motion in the fundamental state. As far as the exciton dipole is concerned, this is to result in a predominant in-plane orientation, for which we bring the first experimental evidence in figure 3 from the challenging measurements of the polarization-dependence of the dim iX emission intensity.

We finally address the issue of the ZO phonon replica. Among the six types of phonons discussed above, five were previously identified in [1] from the energy spacing reflecting the splitting of the different phonon branches in the middle of the Brillouin zone, and also from the natural hierarchy in intensity between intense optical phonon replicas and weaker acoustic phonon ones. The present study highlights the impact of the phonon symmetries on the intrinsic optical response of hBN, with the striking polarization-dependence of the ZA phonon replica when collecting from the sample edge (figures 2(a)–(c)). This effect points out the requirement for a polarization analysis of the PL spectrum along the c-axis direction for the out-of-plane modes replicas. Furthermore, as discussed above, the phonon-assisted recombination in hBN involves phonons in the middle of the Brillouin zone so that the energy position of the ZO phonon replica is expected to lie in between the LA and TA replicas [20].

In figure 2(a), we indeed observe a deformation of the PL spectrum around 5.87 eV for a polarization detection parallel to the c-axis, while the spectrum remains unchanged in the spectral domain of the LO and TO phonon replicas, except for the global intensity reduction discussed above. The 10 meV detuning between the LA phonon replica and the new peak revealed in figure 2(a) exactly matches the LA–ZO splitting in the middle of the Brillouin zone [20], thus
In summary, we have analyzed the impact of the phonon symmetries on the optical emission spectrum in bulk hBN which consists of phonon-assisted recombination lines because of the indirect bandgap of this layered compound. Polarization-resolved PL experiments with a signal collection from the sample edge reveal with maximum contrast the phonon replicas due to the optical and acoustic out-of-plane modes. The comprehensive understanding of the six types of phonon replicas in hBN further points out the originality of the optical properties in this layered compound where the extrema of the conduction and valence bands lie in different high symmetry points which are both away from the zone center, thus leading to a very exotic phenomenology of the phonon-assisted emission. The expected crossover to a direct bandgap semiconductor in hBN monolayers opens fundamental questions on the phonon-assisted optical processes in few layers samples, and their sensitivity to the nature and to the symmetries of the implied phonons.

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