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Distinguishing Different Stackings in Layered Materials via Luminescence Spectroscopy

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Despite its simple crystal structure, layered boron nitride features a surprisingly complex variety of phonon-assisted luminescence peaks. We present a combined experimental and theoretical study on ultraviolet-light emission in hexagonal and rhombohedral bulk boron nitride crystals. Emission spectra of high-quality samples are measured via cathodoluminescence spectroscopy, displaying characteristic differences between the two polytypes. These differences are explained using a fully first-principles computational technique that takes into account radiative emission from “indirect,” finite-momentum excitons via coupling to finite-momentum phonons. We show that the differences in peak positions, number of peaks, and relative intensities can be qualitatively and quantitatively explained, once a full integration over all relevant momenta of excitons and phonons is performed.

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The microscopic control of Van der Waals stacking configurations is emerging as an important tool for the engineering of the optoelectronic properties of layered materials. In graphite, for example, rhombohedral stacking may result in nontrivial topological properties [1], while the asymmetry of the interlayer coupling resulting from the same stacking motif leads to the emergence of ferroelectricity in transition metal dichalcogenides [2,3], as well as increased effective mobilities due to the change in interlayer coupling strength [4]. The local changes in stacking order in twisted boron nitride (BN) layers again give rise to ferroelectric domains [5]. Understanding the impact of single-layer stacking configurations on the electronic properties of Van der Waals materials is thus of paramount importance. Consequently, exploring BN polytypes serves as an exemplary platform for such investigations. Layered BN crystals are identified as strategic materials for the integration of graphene and 2D semiconductors in optoelectronic devices based on Van der Waals heterostructures [6–8]. To this end, largely scalable crystal growth methods able to produce high-quality samples are desirable. The highest-quality BN single crystals are mostly grown from a catalytic melt either at high pressure and high temperature [9–11] or, more recently, at intermediate or atmospheric pressure and high temperature [12–16]. The resulting crystals are limited in size or polycrystalline, which restricts their possible applications to optoelectronics. Up-scalable fabrication techniques at low pressure, such as chemical vapor deposition or molecular beam

epitaxy, allow instead for the controlled synthesis of BN thin films on large surfaces. However, they have encountered a limited success up to now due to the polymorphism of boron nitride. The layered bulk crystal can come, in principle, in six different polytypes [17], with the two most stable ones adopting the hexagonal (hBN) and rhombohedral (rBN) Bravais lattices. In hBN, two adjacent BN single layers differ by a π rotation, resulting in the so-called AA' stacking sequence, where boron and nitrogen atoms sit on top of each other [Fig. 1(a)]. Conversely, the unit cell of rBN crystals is composed of three BN monolayers, which are rigidly shifted along the same direction by the B-N planar interatomic distance: this stacking motif (ABC sequence) is shown in Fig. 1(b). While this stacking

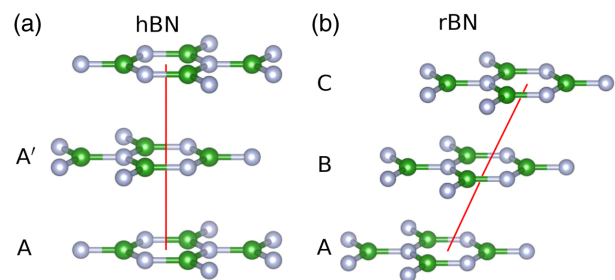


FIG. 1. Stacking sequences of sp_2 BN considered in this work: in (a) boron nitride with AA' stacking is shown, while in (b) the three shifted layers forming rBN unit cell are presented. Nitrogen and boron atoms are shown in grey and green, respectively.

65 difference entails an extremely high energy cost associated
 66 to the transformation from rBN to hBN [18], these two
 67 polytypes are difficult to distinguish experimentally from a
 68 crystallographic point of view. Even from a computational
 69 point of view, the calculated stability difference of the
 70 two polytypes is close to the limit of accuracy of modern
 71 *ab initio* methods [17,19,20]. In addition, the interaction
 72 with the substrate affects the abundance of stable rBN and
 73 hBN phases in synthetic products [21–24]. For these
 74 reasons, the stacking sequence is rarely characterized in
 75 recent reports about BN multilayer growth, so that possible
 76 differences in the respective optoelectronic properties of the
 77 two polytypes might have been overlooked.

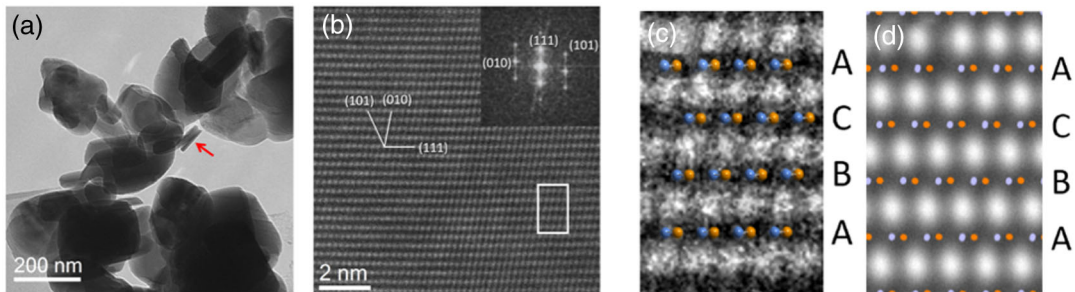
78 In this Letter, we present a spectroscopic investigation of
 79 rBN using cathodoluminescence (CL) spectroscopy. By
 80 comparing CL spectra obtained for rBN with analogous
 81 results for hBN [25,26], we demonstrate that the stacking
 82 sequence affects the emission fine structure of rBN and
 83 hBN crystals, making CL an ideal experimental probe to
 84 discriminate between the two polytypes. Our experimental
 85 observations are explained by *ab initio* calculations of
 86 luminescence spectra for the two polytypes, explicitly
 87 including exciton-phonon interactions.

88 The reference sample investigated here is the rBN
 89 powder fabricated by T. Sato [21], which is known as
 90 the international standard for the crystallographic diffrac-
 91 tion database [27]. To our knowledge, this is the highest-
 92 quality rBN single crystal available today. Figure 2(a)
 93 presents a transmission electron microscopy (TEM) image
 94 of the powder. It consists of cylindrical rBN crystallites
 95 with a typical 200 nm diameter and a 50 nm thickness. The
 96 ABC stacking sequence can be observed in the high-
 97 resolution image of the transverse section reported in
 98 Fig. 2(b). The distance between B and N in this projection
 99 is 0.072 nm, which cannot be resolved due to our 0.12 nm
 100 TEM limit resolution. Nevertheless, the positions of B and
 101 N atomic columns can be identified in Fig. 2(c) thanks to
 102 simulations performed in the conditions of the image
 103 acquisition in Fig. 2(d) (see Supplemental Material [28]

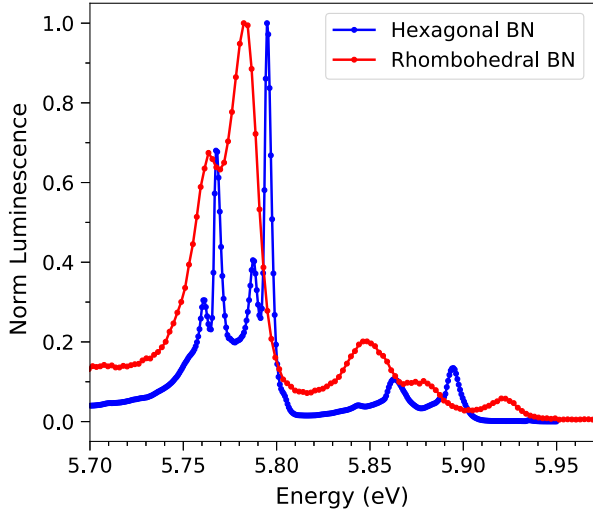
104 for details). The identification of the rBN structure is
 105 further confirmed by comparing its Raman spectrum
 106 with the one of hBN as presented in the Supplemental
 107 Material [28] section on Raman spectroscopy. In the
 108 following, the properties of the reference rBN sample
 109 (ABC stacking) will be compared with a reference hBN
 110 crystal grown by high pressure and high temperature [11].

111 We now turn to the discussion of the exciton-dominated
 112 luminescence spectra as studied by CL using the setup
 113 detailed in Supplemental Material [28]. A comparison
 114 between the experimental CL spectra of hBN and rBN
 115 at $T = 5$ K is shown in Fig. 3. The visible features are due
 116 to phonon-assisted excitonic recombinations as will be
 117 discussed below. The two spectra display several key
 118 differences, including a redshift of the rBN features with
 119 respect to the corresponding hBN ones (which amounts to
 120 15 meV for the highest peak), and, most importantly, the
 121 presence of two relevant structures at 5.847 and 5.919 eV
 122 only in rBN. The high accuracy of the experimental rBN
 123 spectrum is crucial to clearly resolve the fine structure of
 124 the intrinsic phonon-assisted peaks [17,42], enabling us to
 125 explain these points in conjunction with the theoretical
 126 modeling in the following. Experimentally, these reported
 127 differences are fully significant, as we obtained almost
 128 identical spectra from a rBN sample grown by chemical
 129 vapor deposition on 6H-SiC. A detailed comparison
 130 between the two samples is included in Supplemental
 131 Material [28], along with a discussion of the defect peaks
 132 appearing in the CL signal measured at frequencies lower
 133 than those shown in Fig. 3.

134 *Ab initio* calculations [43] indicate that rBN is an indirect
 135 band-gap insulator. The exciton dispersion resulting from
 136 the solution of the Bethe-Salpeter equation at finite
 137 momentum is indirect as well, its minimum being located
 138 near the point $\Omega = [\frac{1}{6}, \frac{1}{6}, 0]$ in the middle of the Γ K
 139 symmetry direction in the hexagonal Brillouin zone
 140 (hBZ). According to our calculation, the energy difference
 141 between the lowest-lying exciton (due to indirect electronic
 142 transition) and the optically accessible (i.e., direct and



F2:1 FIG. 2. (a) Bright field TEM image of the reference rBN powder. (b) High resolution TEM image in the $[10\bar{1}]$ zone axis of the
 F2:2 crystallite indicated by the red arrow in (a). The traces of (101), (001), and (111) rBN planes reported with white lines are identified with
 F2:3 the Fourier transform plotted in inset. (c) Magnified image of the white rectangle in (b) where the atomic positions of B and N (colored
 F2:4 spheres) are deduced from the simulation (d), which has been performed with the illumination conditions used experimentally.
 F2:5 Crystallographic notations refer here to the rhombohedral phase (see Supplemental Material [28] for details).



F3:1 FIG. 3. Comparison of experimental hBN (blue) and rBN (red)
 F3:2 CL spectra at $T = 5$ K.

143 dipole-allowed) Γ excitons is 230 meV (see Supplemental
 144 Material [28] for the exciton dispersion curve computed
 145 along this direction). This means that the excitonic radiative
 146 recombination in rBN requires the assistance of phonons
 147 with a wave vector around the Ω point, similarly to what
 148 happens in hBN.

149 The theoretical luminescence spectra have been computed
 150 using the expression [44,45]

$$I(E) \propto \sum_{\lambda} \sum_{\mathbf{Q}} \sum_{\nu} N[E_{\lambda}(\mathbf{Q})] \Gamma_{\lambda}^{\nu, \mathbf{Q}}(E), \quad (1)$$

152 where λ is an index running over exciton bands, \mathbf{Q} is the
 153 exciton momentum, and ν denotes the phonon branches.
 154 $N[E_{\lambda}(\mathbf{Q})] = e^{-[(E_{\lambda}(\mathbf{Q}) - \mu)/k_B T_{\text{exc}}]}$ is a Boltzmann distribution
 155 representing the exciton population from which light
 156 emission occurs, μ being the energy of the lowest-energy
 157 exciton in the system and T_{exc} the effective excitonic
 158 temperature. We fixed T_{exc} to 20 K, which is its exper-
 159 imental value obtained for low sample temperatures (below
 160 10 K, as in Fig. 3). (We have checked that our results are
 161 stable with respect to small changes of this parameter).

162 The probability $\Gamma_{\lambda}^{\nu, \mathbf{Q}}(E)$ describes photon emission by a
 163 finite-momentum exciton $|\lambda, \mathbf{Q}\rangle$, assisted by a phonon
 164 (ν, \mathbf{Q}) . This quantity has been computed using second-
 165 order time-dependent perturbation theory, similarly to
 166 Refs. [46,47], only considering phonon emission processes
 167 [48] (which dominate at small temperature):

$$\Gamma_{\lambda}^{\nu, \mathbf{Q}}(E) = |T_{\lambda}^{\nu, \mathbf{Q}}|^2 \frac{(1 + n_{\nu, \mathbf{Q}}) \delta[E - E_{\lambda}(\mathbf{Q}) + \hbar\omega_{\nu, \mathbf{Q}}]}{E_{\lambda}(\mathbf{Q}) - \hbar\omega_{\nu, \mathbf{Q}}}, \quad (2)$$

168 with

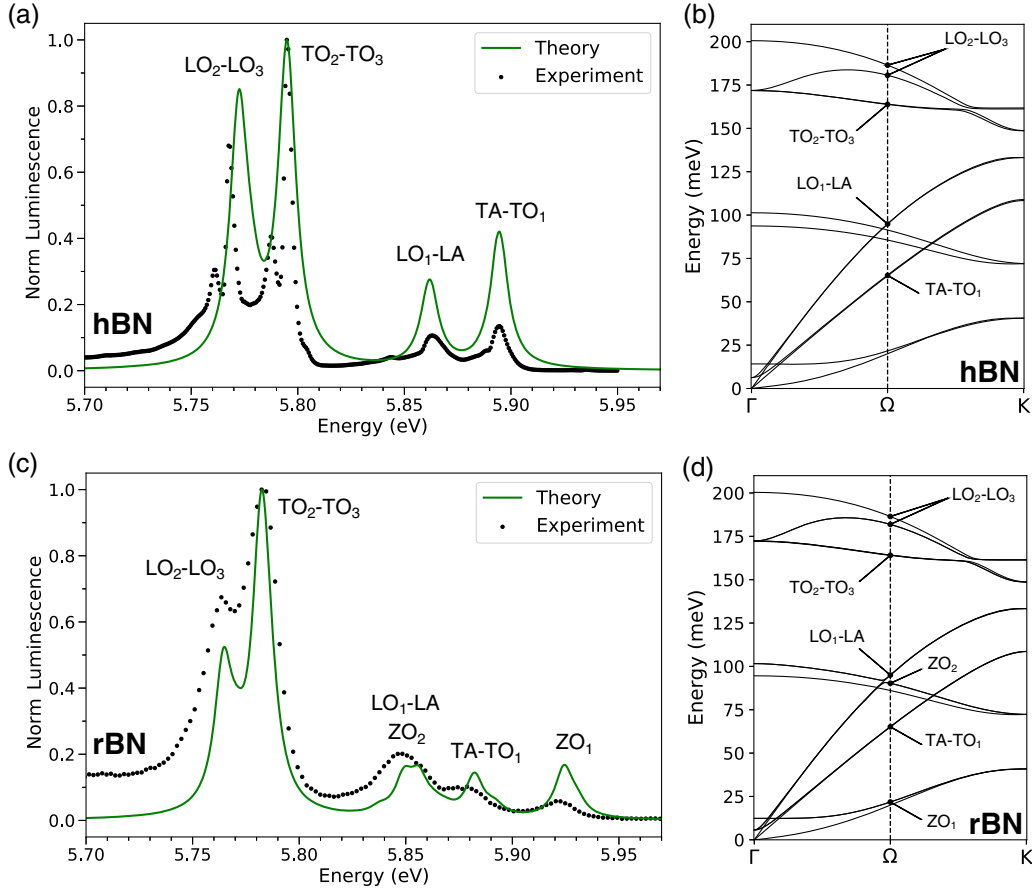
$$T_{\lambda}^{\nu, \mathbf{Q}} = \sum_{\lambda_2} \frac{D_{\lambda_2} G_{\lambda_2, \lambda}^{\nu}(\mathbf{Q}, -\mathbf{Q})}{E_{\lambda_2}(\Gamma) + \hbar\omega_{\nu, \mathbf{Q}} - E_{\lambda}(\mathbf{Q})}. \quad (3)$$

In Eqs. (2) and (3), the index λ_2 runs over the excitonic
 170 states at the Γ point with energy $E_{\lambda_2}(\Gamma)$. The quantity D_{λ_2}
 172 is the excitonic optical dipole strength averaged over in-plane
 173 polarization directions. $n_{\nu, \mathbf{Q}}$ corresponds to the Bose-
 174 Einstein phonon occupation factor, while E is the energy
 175 of the emitted photon; the Dirac delta guarantees energy
 176 conservation and has been numerically approximated with
 177 a Lorentzian function with FWHM equal to 5 meV in order
 178 to match the experimental peaks. Finally, the exciton-
 179 phonon coupling matrix element $G_{\lambda_2, \lambda}^{\nu}(\mathbf{Q}, -\mathbf{Q})$ describes
 180 the scattering amplitude for an exciton $|\lambda, \mathbf{Q}\rangle$ to states
 181 $|\lambda_2, \Gamma\rangle$ while assisted by phonon mode ν [45]:
 182

$$G_{\lambda_2, \lambda}^{\nu}(\mathbf{Q}, -\mathbf{Q}) = \sum_{vc'k} A_{\lambda_2}^{*\Gamma}(v\mathbf{k}, c\mathbf{k}) A_{\lambda}^{\mathbf{Q}}(v\mathbf{k}, c'\mathbf{k} + \mathbf{Q}) g_{cc'}^{\nu}(\mathbf{k} + \mathbf{Q}; -\mathbf{Q}) - \sum_{vv'ck} A_{\lambda_2}^{*\Gamma}(v\mathbf{k}, c\mathbf{k}) A_{\lambda}^{\mathbf{Q}}(v'\mathbf{k} - \mathbf{Q}, c\mathbf{k}) g_{v'v}^{\nu}(\mathbf{k}; -\mathbf{Q}), \quad (4)$$

where $A_{\lambda}^{\mathbf{Q}}(v\mathbf{k}_h, c\mathbf{k}_c)$ is the envelope function for exciton
 183 $|\lambda, \mathbf{Q}\rangle$, with v, v' (c, c') running over the valence (con-
 185 duction) states and \mathbf{k} being the electronic wave vector in the
 186 hBZ. The electron-phonon coupling matrix element
 187 $g_{n,n'}^{\nu}(\mathbf{k}, \mathbf{Q})$ represents the scattering between single-particle
 188 states $|n', \mathbf{k}\rangle$ and $|n, \mathbf{k} + \mathbf{Q}\rangle$ [49]. Importantly, within our
 189 numerical methodology, $G_{\lambda_2, \lambda}^{\nu}(\mathbf{Q}, -\mathbf{Q})$ is computed using
 190 the same single-particle Kohn-Sham states both for elec-
 191 tron-phonon and excitonic quantities, thus overcoming
 192 phase mismatch problems as described in Ref. [47]. The
 193 \mathbf{Q} integration appearing in Eq. (1) has been performed in
 194 local neighborhoods of the symmetry-equivalent Ω points
 195 corresponding to the excitonic dispersion minima in the
 196 hBZ. The computational details [50] needed to reproduce
 197 the theoretical results are provided in the Supplemental
 198 Material [28].
 199

In Fig. 4, we present the comparison between exper-
 200 imental CL spectra (black dots) and theoretical Bethe-
 201 Salpeter equation results (continuous green lines) for hBN
 202 [Fig. 4(a)] and rBN (Fig. 4(c)). Figures 4(b) and 4(d) show
 203 the calculated in-plane phonon dispersion along the ΓK
 204 direction for hBN and rBN, respectively. We find very good
 205 agreement between experimental and theoretical data. The
 206 relative energy shift between the two spectra is reproduced
 207 theoretically. As the phonon energies in the two systems
 208 differ only for a few meV, the 15 meV shift closely matches
 209 the underlying difference between the lowest-lying, finite-
 210 momentum exciton levels (which is around 12 meV). In
 211 turn, this difference can be traced back to the combined
 212 effects of rBN having both a smaller quasiparticle band gap
 213 (by 166 meV) and exciton binding energy (by 150 meV)
 214



F4:1 FIG. 4. Experimental (black dots) and theoretical (green lines) luminescence spectra for hBN (a) and rBN (c). In both (a) and (c),
 F4:2 theoretical spectra are blueshifted by 1.04 eV to match the position of the highest intensity peak in the experimental spectrum (in order to
 F4:3 compensate for the systematic theoretical undercorrection of the *GW* quasiparticle band gap in BN). Phonon dispersions in hBN (b) and
 F4:4 rBN (d) along the Γ -K direction: phonon branches contributing to the luminescence spectra are highlighted at the Ω point, in the middle
 F4:5 of the Γ -K direction. See the main text for the phonon mode labeling. Almost-degenerate phonon branches are paired with a hyphen.

215 with respect to hBN around the Ω points in momentum
 216 space. In both hBN and rBN, the spectra are dominated by
 217 the two peaks in the low-energy part of the spectrum. These
 218 are phonon-assisted satellites due to longitudinal optical
 219 phonons—denoted as LO_2 - LO_3 modes in the phonon
 220 dispersion—and transverse optical ones (the almost-
 221 degenerate pair [56] TO_2 - TO_3). For hBN, these assign-
 222 ments are in good agreement with the results obtained
 223 in Refs. [46,57], using a finite-difference approach.
 224 Furthermore, the experimental intensity ratio between these
 225 peaks is well-reproduced by *ab initio* calculations, with the
 226 LO peak being less intense than the TO one. The additional
 227 overtones appearing in the measurements in this energy
 228 region are due to higher-order scattering processes [58] and
 229 are thus not captured by our theoretical approach, which is
 230 restricted to first-order exciton-phonon interaction. The
 231 phonon branches involved in the emission process are
 232 explicitly labeled in Figs. 4(b) and 4(d) for the Ω point
 233 only [59]. Luminescence spectra of hBN and rBN are
 234 qualitatively different at higher energies, as confirmed by
 235 *ab initio* results. In the case of hBN, we observe only two

236 main peaks: the first (at about 5.86 eV) corresponds to a
 237 replica of the LO_1 -LA phonons, while the higher intensity
 238 structure at 5.89 eV is mainly due to TO phonons, with a
 239 small contribution from the almost-degenerate transverse
 240 acoustic mode (TA - TO_1). *Ab initio* results reproduce with
 241 great accuracy both the splitting between these peaks and
 242 their intensity ratio (the LO_1 -LA peak being less pro-
 243 nounced than the TO_1 -TA one), while they tend to
 244 overestimate their relative strengths, with respect to the
 245 dominant, low-energy satellites. [The agreement may be
 246 further improved with a more complete \mathbf{Q} -point integration
 247 in Eq. (1).] We also note that, in agreement with the group
 248 theory analysis discussed in Ref. [57], no contributions
 249 from the out-of-plane phonon modes appear in the lumi-
 250 nescence spectra. This selection rule, which is strictly
 251 respected by Eq. (4), can be slightly broken in a real
 252 experiment, leading to the appearance of a very small signal
 253 corresponding to this mode (usually 100 times smaller than
 254 the other peaks [60]).

255 In the case of rBN, the high-energy portion of the CL
 256 spectrum shows three large peaks, respectively at about

257 5.847, 5.878, and 5.919 eV, instead of the two peaks
 258 appearing in hBN. They are also recovered in the *ab initio*
 259 results. The first structure is a combination of phonon-
 260 assisted replicas due to the almost-degenerate LA-LO₁
 261 branches, albeit with a relevant contribution from optical
 262 out-of-plane modes (denoted as ZO₂; see Supplemental
 263 Material [28] for a mode-resolved spectrum). Conversely,
 264 the peak at 5.878 eV is associated to the TA-TO₁ phonons
 265 in analogy with the hBN case. We emphasize that *ab initio*
 266 results correctly reproduce the intensity ratio among these
 267 peaks. Finally, the highest-energy structure at 5.919 eV
 268 turns out to be due to the out-of-plane optical mode ZO₁.
 269 This is forbidden for the centrosymmetric hBN lumines-
 270 cence while it is allowed in the rBN case because of the
 271 lowered symmetry of the crystal lattice.

272 In conclusion, we have demonstrated that cathodolumi-
 273 nescence is a viable tool to characterize fundamentally
 274 similar BN polytypes, which are hardly distinguishable
 275 otherwise. We have explained both experimentally and
 276 theoretically how the radiative emission spectrum is
 277 affected by the interaction between electronic excitations
 278 and lattice vibrations in rhombohedral and hexagonal boron
 279 nitride, two prototypical polytypes of low-dimensional
 280 layered materials with indirect band gap. Using a first-
 281 principles methodology that accounts for exciton-phonon
 282 interactions beyond the state of the art, we are able to
 283 provide a comprehensive and accurate description of the
 284 finite-momentum exciton states and phonon modes
 285 involved, thus showing the discriminating role of out-of-
 286 plane lattice vibrations assisting excitonic radiative recom-
 287 bination for rBN but not for hBN. We believe that our
 288 analysis and methodology could be useful for the growth
 289 and characterization of indirect-gap layered materials,
 290 which find widespread application as basic building blocks
 291 in novel 2D optoelectronic devices.

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lowest-energy phonon mode to be a pair of acoustic (ZA) 468
and optical (ZO_1) out-of-plane modes, with only the latter 469
being responsible for the signal in Fig. 4(c). In the 470
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