Hexagonal boron nitride is an indirect bandgap semiconductor

G. Cassabois, P. Valvin and B. Gil*

Hexagonal boron nitride is a wide bandgap semiconductor with very high thermal and chemical stability that is used in devices operating under extreme conditions. The growth of high-purity crystals has recently revealed the potential of this material for deep ultraviolet emission, with intense emission around 215 nm. In the last few years, hexagonal boron nitride has been attracting even more attention with the emergence of two-dimensional atomic crystals and van der Waals heterostructures, initiated with the discovery of graphene. Despite this growing interest and a seemingly simple structure, the basic questions of the bandgap nature and value are still controversial. Here, we resolve this long-debated issue by demonstrating evidence for an indirect bandgap at 5.955 eV by means of optical spectroscopy. We demonstrate the existence of phonon-assisted optical transitions and we measure an exciton binding energy of about 130 meV by two-photon spectroscopy.

Hexagonal boron nitride (hBN) exhibits unique electronic properties, such as a wide bandgap, low dielectric constant, high thermal conductivity and chemical inertness. In contrast to other nitride semiconductors such as GaN and AlN, for which most stable crystalline phase is of the wurtzite type, the hexagonal structure of hBN makes it a prototype two-dimensional material, along with graphene and molybdenum disulphide. With a honeycomb structure based on sp² covalent bonds similar to graphene, bulk hBN, with its atomically smooth surface, first gained a great deal of attention as an exceptional substrate for graphene. Two-dimensional hBN, or ‘white graphene’, in the form of few-layer crystals or monolayers of hBN, has since emerged as a fundamental building block for van der Waals heterostructures.

In spite of this rising interest in hBN and the large number of studies devoted to this material, with its seemingly simple crystal structure, the very basic question of the nature of its bandgap remains controversial. There is a strong contrast between ab initio band structure calculations, which predict an indirect bandgap crystal1,8, and optical measurements, which indicate a direct bangap9–11. In 2004, Watanabe and colleagues demonstrated that hBN is a very promising material for light-emitting devices in the deep ultraviolet domain, with an intense luminescence peak at 5.76 eV, supporting the direct nature of the bandgap9. The use of high-purity hBN crystals has since allowed the demonstration of lasing at 215 nm by accelerated electron excitation9 and also the operation of field-emitter display-type devices in the deep ultraviolet12,13.

Here, we demonstrate that hBN has an indirect bandgap at 5.955 eV and that the optical properties of hBN are profoundly determined by phonon-assisted transitions. By means of two-photon spectroscopy, we reveal the existence of previously unobserved lines. The weakest one lies at the highest energy (5.955 eV), and it corresponds to the dim emission of the indirect exciton. Each emission line appearing at lower energy consists of a phonon replica, for which we identify the corresponding phonon mode. Finally, two-photon excitation spectroscopy allows us to measure, for the first time in an indirect bandgap semiconductor, the energy splitting between the 1s and 2p exciton states. We obtain an estimate of the exciton binding energy of 128 ± 15 meV, showing that excitons in hBN are of a Wannier type and that the single-particle bandgap is at an energy of 6.08 ± 0.015 eV in hBN.

Figure 1a presents a photoluminescence spectrum of hBN at low temperature, in the usual configuration of one-photon excitation at 6.3 eV. We observe the luminescence peak at 5.76 eV reported by Watanabe et al. in high-purity samples, attributed to the recombination of free excitons9. Spatially resolved cathodoluminescence measurements have confirmed this interpretation on the basis of the homogeneous spatial distribution of the emission intensity in hBN crystallites14,15 and in few-layer hBN flakes16,17. The presence of defects in hBN leads to two additional emission bands centred at 5.5 eV and 4 eV (refs 13,14,18–20). In contrast to the 5.76 eV emission line of the free exciton, these defect-related emission bands display strong localization near dislocations and boundaries in cathodoluminescence measurements14–17, with a striking spatial anticorrelation with the free exciton photoluminescence at 5.76 eV, as recently characterized with nanometric resolution in a transmission electron microscope17.

Figure 1a also shows that the 5.76 eV emission line is a multiplet with fine structures extending over 40 meV, accompanied by a similar satellite band at 5.86 eV of lower intensity15,16,21. This satellite band shows the same delocalized emission over the hBN crystals as the 5.76 eV one, characteristic of free exciton recombination17. The different free-exciton levels observed in Fig. 1a (usually called S lines in the literature) have been tentatively attributed to dark and bright excitons with a degeneracy lifted by a Jahn–Teller effect21. Still, all theoretical calculations predict an indirect bandgap for hBN4–8. Moreover, our two-photon excitation scheme allows us to detect two previously unreported lines, namely a weak doublet around 5.93 eV and an even dimmer line at 5.955 eV (Fig. 1b), thanks to the detuning of the laser at about half the detection energy, and the subsequent suppression of the laser stray light present in one-photon spectroscopy (Fig. 1a). In the following, we will provide a comprehensive understanding of the optoelectronic properties of hBN in the deep ultraviolet, which display all the features of an indirect bandgap semiconductor.

Ab initio calculations predict an indirect bandgap for hBN with extrema of the band structure located around the M and K points of the Brillouin zone for the conduction and valence bands,
Excitonic effects modify the single-particle picture of band structure calculations, whatever the direct or indirect nature of the optical transition\(^{22}\). As in other indirect semiconductors\(^{23}\), the hBN indirect exciton (iX) corresponding to the electron–hole pair built around the M and K points of the Brillouin zone is thus not coupled to light in the dipolar approximation, and phonon scattering is required to fulfil momentum conservation during photon emission or absorption\(^{24}\).

The first evidence for recombination assisted by phonon emission in hBN arises from the observation of a thermal distribution of excitons in the high-energy tail of the different emission lines. Figure 1b presents the photoluminescence spectrum of hBN as a function of temperature for two-photon excitation at 3.03 eV. Thanks to our background-free excitation scheme, we see that, for both the 5.76 and 5.86 eV emission lines, the photoluminescence signal intensity falls exponentially on their high-energy side, with the slope decreasing on raising the temperature. On the contrary, on their low-energy side, these emission bands remain unchanged with temperature, except for some residual contamination by the intense redshifted neighbouring lines. To quantitatively analyse the exponential decrease in the photoluminescence signal at high energy, we fitted our data with Boltzmann distributions of the effective temperature \(T_e\). As shown, for instance, at 75 K in Fig. 1b, we obtain excellent agreement, with systematically the same effective temperature for the 5.76 and 5.86 eV emission lines. The effective temperature \(T_e\) is also plotted as a function of lattice temperature \(T_l\) in Fig. 1c and, for temperatures larger than 25 K, we observe a thermalization of the excitonic system with the surrounding crystal.

Such a phenomenology is typical of semiconductor materials. Hot excitons are initially created with a large kinetic energy after electrical or optical excitation. During carrier relaxation their energy distribution converges to a thermal Boltzmann law via exciton–exciton collisions and phonon-assisted scattering processes. However, in photoluminescence experiments, the exciton thermalization cannot be observed in the so-called zero-phonon line because only excitons with wavevector close to zero can contribute to the photoluminescence signal by direct emission of photons. The population of free excitons with large wavevectors can only be monitored by studying phonon replicas, because phonon emission ensures momentum conservation in their radiative recombination. This universal effect has been observed in many different semiconductors\(^{25–28}\). In the specific context of exciton condensation, the transition from a Boltzmann to a Bose–Einstein distribution is investigated by a careful study of the high-energy tail of phonon replicas\(^{29}\). As only phonon-assisted processes can give an accurate replica of the energy distribution of excitons, we first conclude that the observation of a thermal distribution of excitons in hBN is a first piece of evidence for the nature of the 5.76 and 5.86 eV emission lines being phonon replicas.

As far as the thermalization process is concerned, the strong structural anisotropy of hBN translates into an effective temperature \(T_e\) of the Boltzmann law larger than the lattice temperature \(T_l\), as can be seen in Fig. 1c, where the linear regression (dashed curve) has a slope of 1.85. Although striking at first sight, this effect simply arises when taking into account the \(k\)-dependence of the phonon energy in the phonon-assisted recombination process (Supplementary Section A). Although usually negligible in other semiconductors, leading to \(T_e \sim T_l\) (ref. 29), this correction is important in hBN because of the flatness of both the phonon and electron dispersions along the \(z\) axis\(^{27,30}\). In fact, the corresponding large effective mass (schematically shown in Fig. 1d) leads to a huge increase in the density of exciton states, so the phonon replicas mostly monitor exciton thermalization along the \(z\) axis. Such a situation is strongly analogous to the case of quantum well superlattices, where two-dimensional excitons thermalize and efficiently redistribute over the whole superlattice mini-zone\(^{31}\).

The 5.76 and 5.86 eV emission lines having now been identified as phonon replicas, we now turn to the determination of the indirect exciton iX energy. In the optical response of indirect semiconductors there is a mirror symmetry between the two processes of absorption and emission assisted by phonon emission\(^{32,33}\); compared with the bandgap energy, photon emission is redshifted by the phonon energy, while photon absorption is blueshifted by the same value (see energy level schemes in Fig. 2a). We will show now that the emission line of smallest intensity, observed at 5.955 eV in Fig. 1b, corresponds to the indirect exciton iX. To check the mirror image between emission and absorption around 5.955 eV, in Fig. 2a we plot the normalized photoluminescence spectrum (red diamonds) and the normalized photoluminescence excitation (PLE) spectrum (blue open squares) in a spectral window centred at 5.955 eV. It is essential to compare the photoluminescence spectrum of free excitons with the PLE one detected at the corresponding emission energy, as is the case in ref. 32 (Supplementary Section C), but not in previous studies reporting PLE spectroscopy for detection windows centred at defect-related lines\(^{31,19,20,33}\). In Fig. 2a we observe that the signal intensity is on the order of the noise around 5.955 eV in both cases, and that it

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**Figure 1** Monitoring exciton thermalization in phonon replicas.

**a** Photoluminescence spectrum of hBN at 10 K for one-photon excitation at 6.3 eV. **b** Photoluminescence spectrum of hBN for two-photon excitation at 3.03 eV as a function of temperature (the spectra are shifted for clarity). Dotted lines indicate a Boltzmann law with an effective temperature of \(T_e = 145\) K superimposed on a constant baseline. **c** Effective temperature \(T_e\) (symbols) as a function of lattice temperature \(T_l\). Error bars indicate the standard deviations for least-squares fitting of the photoluminescence spectra with a Boltzmann law and the dashed curve is a linear regression with a slope of 1.85. **d** Schematic representation of the anisotropic energy dispersion of the indirect exciton iX around the MK point of reciprocal space. The colourmap corresponds to a thermal distribution of indirect excitons, with the density decreasing from red to blue.
increases to its maximum value by a blueshift (redshift) of 60 meV in the PLE signal. Moreover, the lines have a half-width at half-maximum (HWHM) on the order of 25 meV in both emission and absorption spectra (see Supplementary Section C for an interpretation of the line profile in hBN). Although the rise in the PLE signal around 6.01 eV is not as steep as in the photoluminescence spectrum around 5.9 eV (due to a poorer spectral resolution in the one-photon excitation spectrum), we highlight that the energy detunings $\delta_0 = 26 \pm 1$ meV and $\delta_1 = 31 \pm 1$ meV (Fig. 2c) discussed in the literature$^{27}$ simply reflect the TO–LO energy splitting and the TA–LA one in the middle of the Brillouin zone.

We thus demonstrate that hBN does have an indirect bandgap, in agreement with theoretical calculations$^{4-8}$. Furthermore, our estimation of 5.955 eV is fully consistent with electron energy loss spectroscopy in hBN, where electronic momentum transfer allows the excitation of indirect bandgap material, in contrast to optical spectroscopy. The bandgap of bulk hBN was found to be 5.9 ± 0.2 eV (ref. 36), and in multilayered boron nitride nanotubes in which quantum confinement is negligible, a value of 5.8 ± 0.2 eV (ref. 37) was obtained.

With a view to further elucidate the fundamental optoelectronic properties of hBN, we performed two-photon excitation spectroscopy to determine the exciton binding energy. Two-photon spectroscopy is a powerful technique with which to access information on the bound states of exciton relative motion$^{25}$, which has recently regained attention in carbon nanotubes$^{8,39}$ and transition-metal dichalcogenide monolayers$^{40,41}$. In the case of direct bandgap materials, the optical selection rules for two-photon absorption impose the excitation of $p$-exciton states, thus providing an estimate of the $1s$–$2p$ energy splitting. The case for indirect bandgap compounds is less documented, with evidence for phonon-assisted two-photon absorption only in germanium$^{42}$, to the best of our knowledge.

Figure 3 presents (red circles) the two-photon excitation spectrum in hBN for detection at 5.86 eV as a function of twice the excitation energy. The data are compared to the one-photon
obtain an energy splitting of 85 ± 1 meV between the 1s spectrum as being assisted by a ZA phonon. Given the estimated value up to 7 eV. From a comparison of the one-photon and two-photon excitation spectrum and photoluminescence spectrum for the same 115 meV range, but for increasing and decreasing energy, respectively. In contrast to two-photon absorption, from which we have derived an exciton binding energy of about 130 meV, thus revealing that the indirect excitons in hBN are of the Wannier type, in contrast to theoretical calculations predicting Frenkel excitons.

Under the assumption of the Rydberg series usually observed for Wannier excitons, such a splitting would lead to an exciton binding energy of 113 meV in an isotropic material. However, because of the strong anisotropy of hBN, one has to correct this value in the framework of the theory developed for anisotropic excitons in semiconductors. Depending on the value of the so-called anisotropy factor \( \gamma \) given by the ratio, for the in- and out-of-plane cases, of the dielectric constant times the effective mass, one finds a 1s–2p splitting ranging from 0.75 (for \( \gamma = 1 \)) to 0.6 (for \( \gamma = 0.1 \)) in units of the excitonic Rydberg, therefore giving an upper bound of 142 meV for the exciton binding energy in the limit of strong anisotropy (\( \gamma = 0.1 \)). The mean value of 128 ± 15 meV is larger than the exciton binding energy in diamond (70 meV) or AlN (52 meV) but still far from a Frenkel exciton.

Eventually, we estimate the single-particle bandgap of hBN at 6.08 ± 0.015 eV. This value indeed corresponds to the onset of the large absorption band in the one-photon PLE spectrum (Fig. 3). As a consequence, the \( X_{115} \) and \( X_{110} \) virtual states at 6.12 and 6.14 eV, respectively, are resonant with the continuum, thus preventing their observation in the one-photon PLE spectrum. It also explains a posteriori why the two-photon PLE spectrum displays only the ZA phonon mode, because the next expected one, corresponding to the TA mode, lies at 6.1 eV, that is, already above the continuum onset.

In conclusion, we have resolved the long-debated issue of the bandgap nature of hBN by demonstrating that the bandgap is indirect with a value of 5.955 eV. We have shown that the emission spectrum of hBN in the deep ultraviolet is profoundly structured by phonon-assisted recombination, and we have identified the various phonon modes in the replicas. We have performed phonon-assisted two-photon absorption, from which we have derived an exciton binding energy of about 130 meV, thus revealing that the indirect excitons in hBN are of the Wannier type and that the single-particle bandgap in hBN is about 6.08 eV. We highlight the need for theoretical calculations explaining the efficient exciton–phonon interaction in hBN. We hope our results will stimulate experiments addressing these questions, with the exciting possibility to study either the three-dimensional case in high-purity crystals or the two-dimensional one in hBN monolayers, where a transition to a direct bandgap is further expected, as in transition-metal dichalcogenide compounds.

**Methods**

Methods and any associated references are available in the online version of the paper.

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Author contributions
All authors conceived and designed the experiments, which were carried out by G.C. and B.G. The data were analysed by all authors. The interpretation and writing of the manuscript were performed by G.C. and B.G.

Additional information
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Competing financial interests
The authors declare no competing financial interests.
Methods
Sample and experimental setup. The sample was a commercial hBN crystal from HQ Graphene (http://www.hqgraphene.com/). In the experimental setup, the sample was held on the cold finger of a closed-circle cryostat for temperature-dependent measurements from 10 K to room temperature. Optical excitation was performed at normal incidence. In the standard configuration of one-photon excitation, the excitation beam was provided by the fourth harmonic of a continuous-wave mode-locked Ti:sapphire oscillator with a repetition rate of 82 MHz, and in the case of two-photon excitation by the second harmonic of the Ti:sapphire oscillator. The spot diameter was on the order of 200 µm, with a power of 20 µW in one-photon excitation and 2.5 mW in two-photon excitation spectroscopy, except for Fig. 2c, where the power was decreased by a factor of 10. An achromatic optical system coupled the emitted signal to the detection system, and was composed of an f = 500 mm Czerny–Turner monochromator, equipped with a 300 grooves/mm grating blazed at 250 nm and a back-illuminated charge-coupled device camera (Andor Newton 920), with a quantum efficiency of 50% at 210 nm, operating over integration times of 1 min. For two-photon spectroscopy, we used a band-pass filter around 200 nm with low transmission at 400 nm in front of the spectrometer for complete laser stray light rejection.