Optoelectronic properties of hexagonal boron nitride

Guillaume Cassabois

Optoelectronic properties of hexagonal boron nitride

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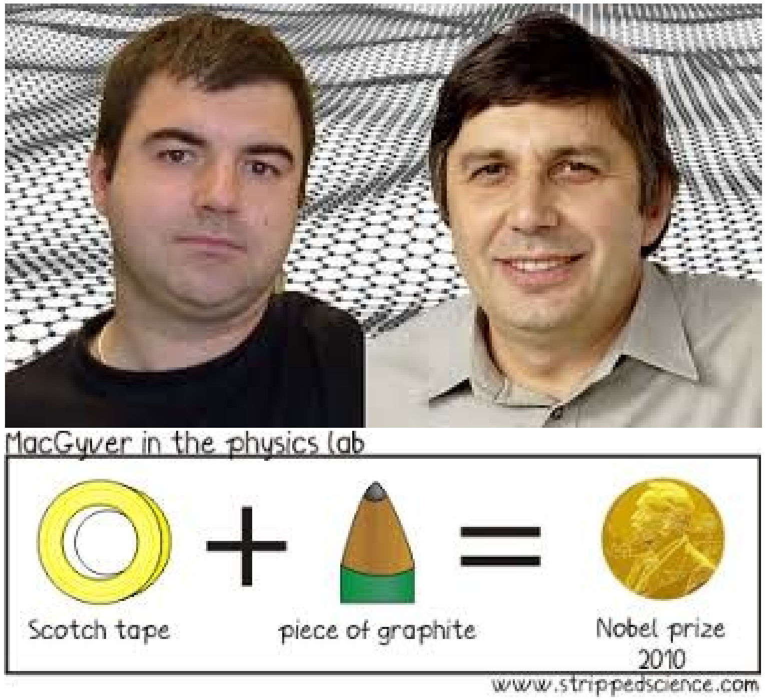
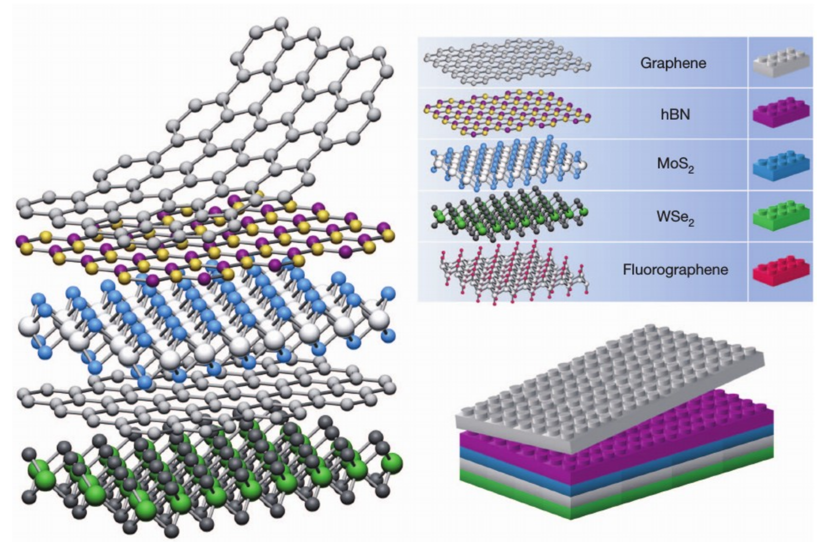
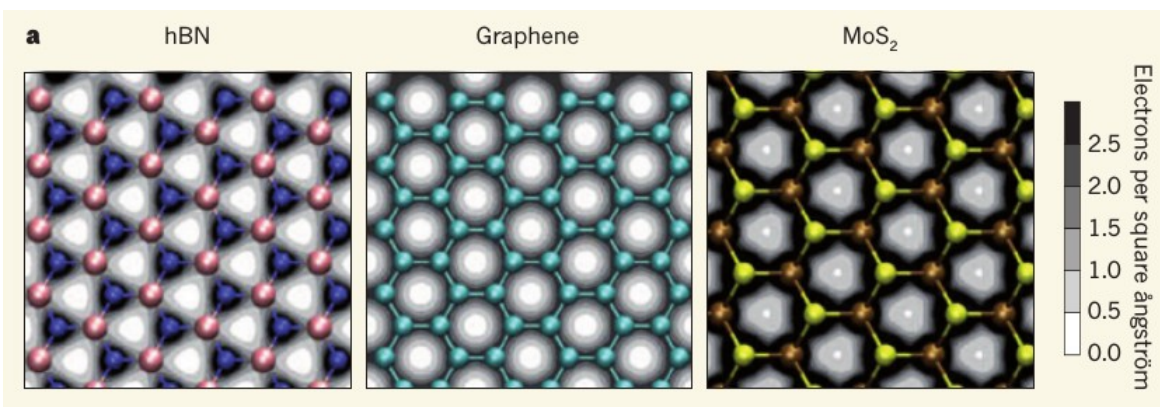
Beyond graphene



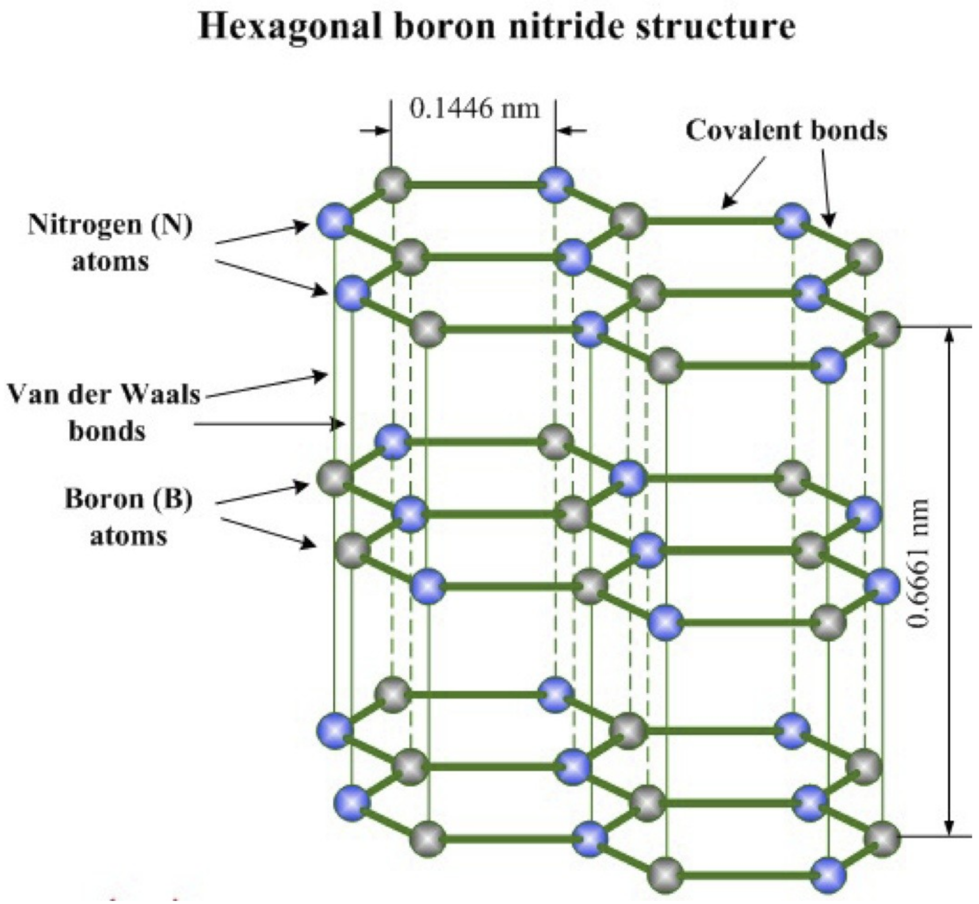
Van der Waals heterostructures



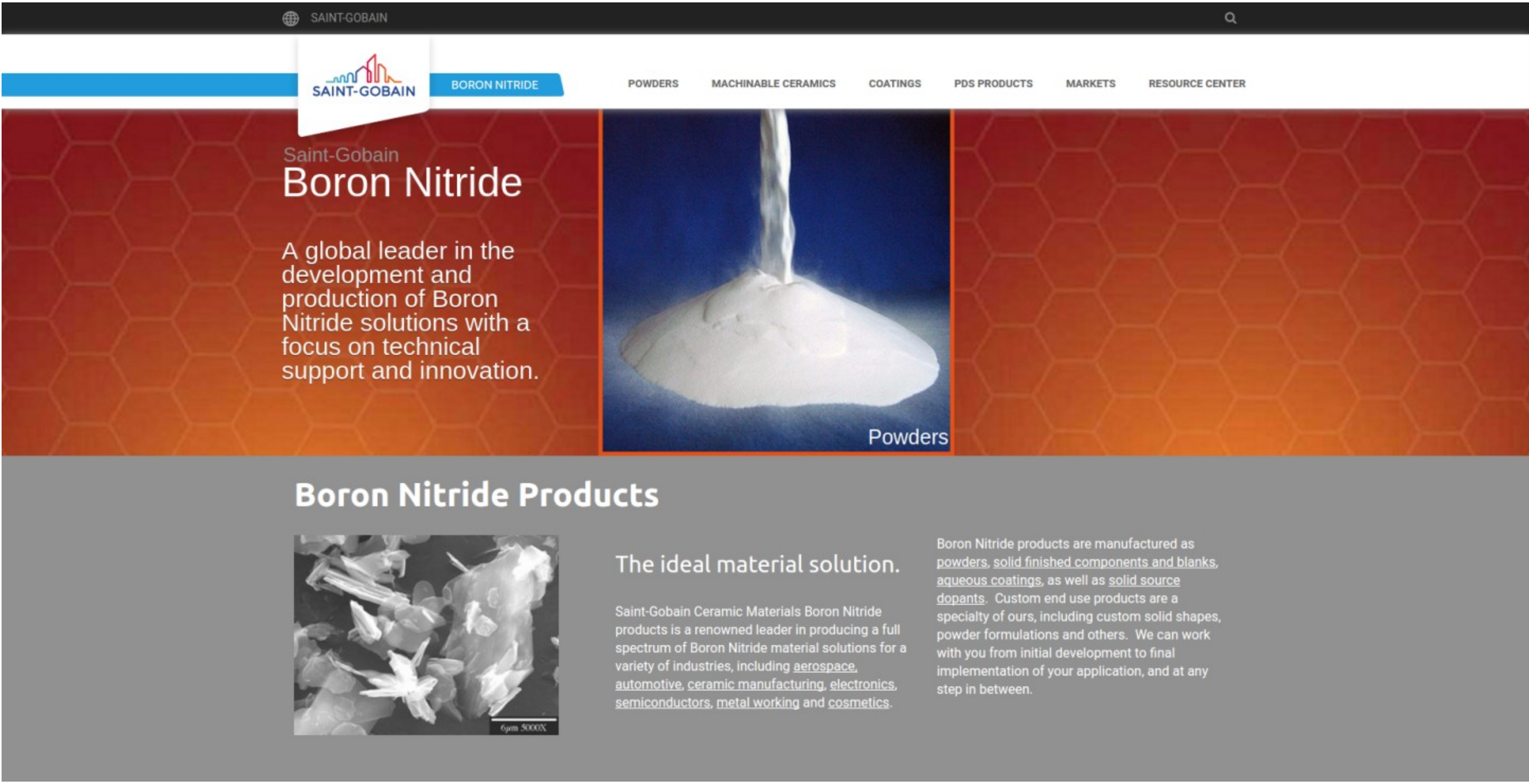
Geim, Nature **499**, 419 (2013)



“White graphite”



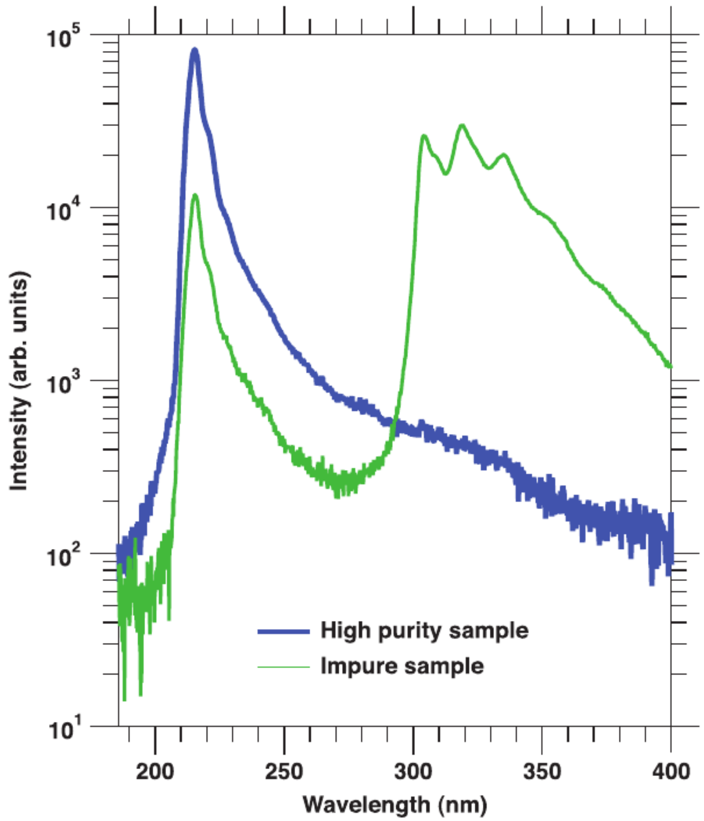
hBN in the industry



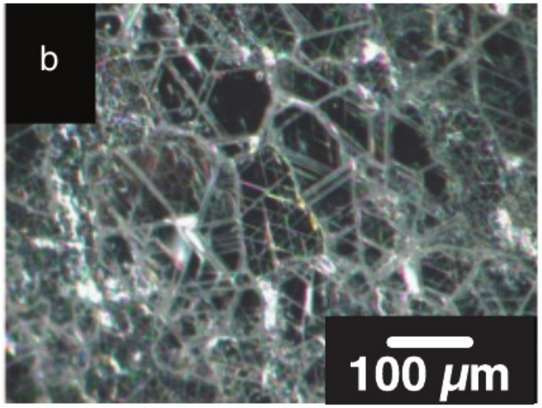
hBN in the industry

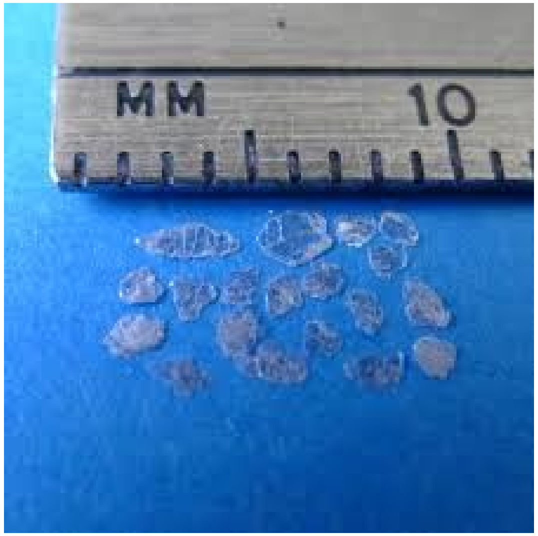
From the industry … back into the lab !

2004-breakthrough by Watanabe & Taniguchi
(Nat. Mat. **3**, 404, 2004)



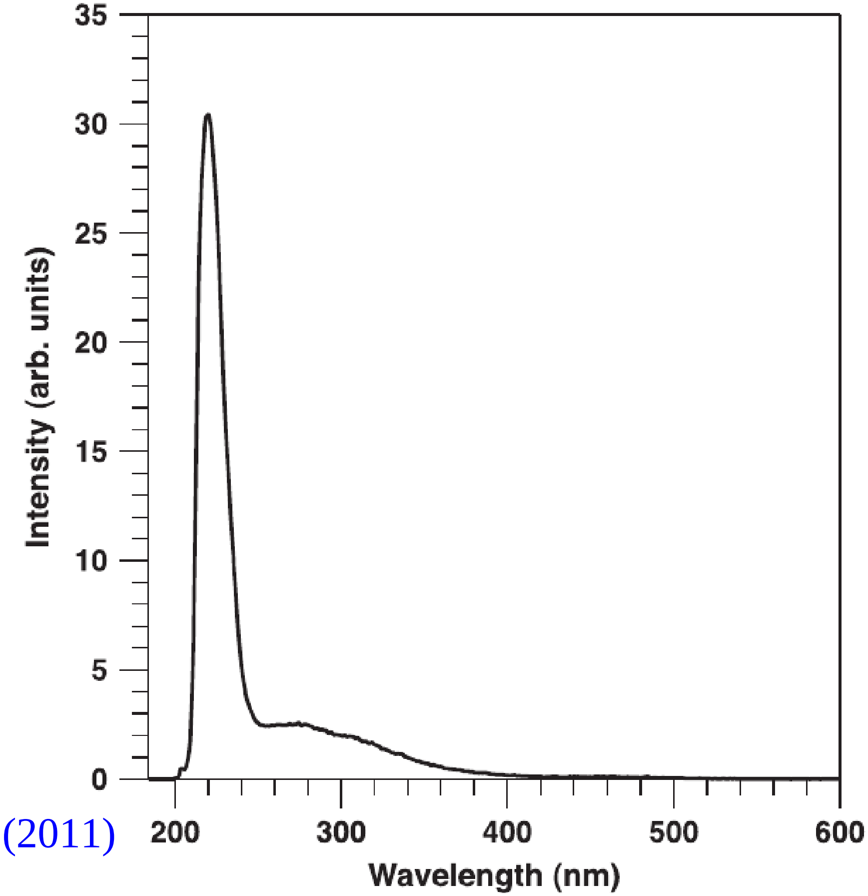
Watanabe, Int. J. Appl. Ceram. Technol. **8**, 977 (2011)





hBN for Deep-UV light emission

Field-emitter Deep-UV device

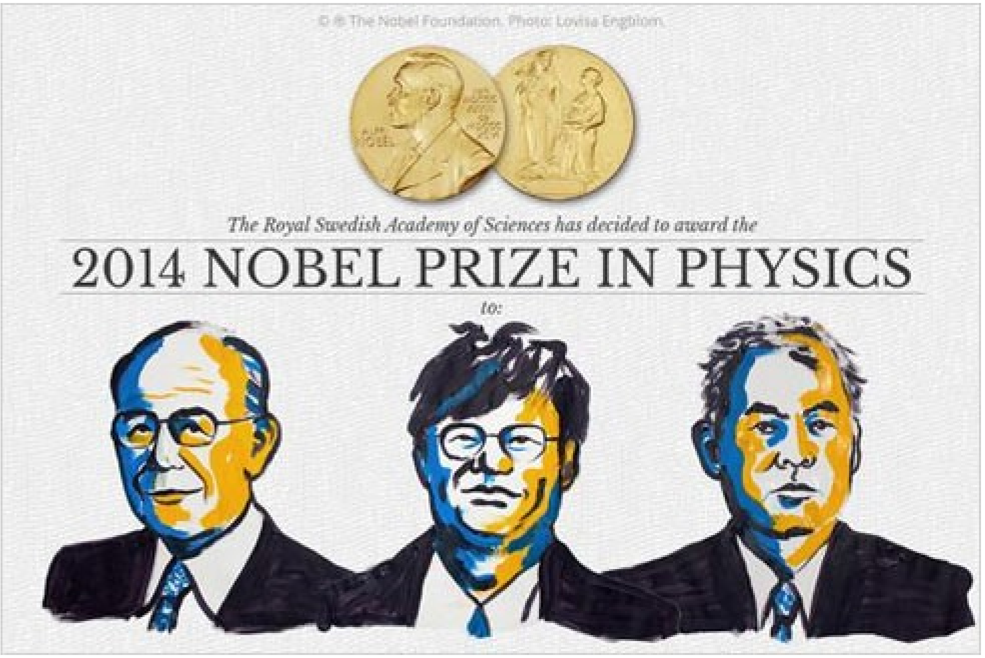


Watanabe, Int. J. Appl. Ceram. Technol. **8**, 977 (2011)

Watanabe, Nat. Phot. **3**, 591 (2009)

hBN: also a nitride semiconductor !

- Famous members of the family : GaN and AlN



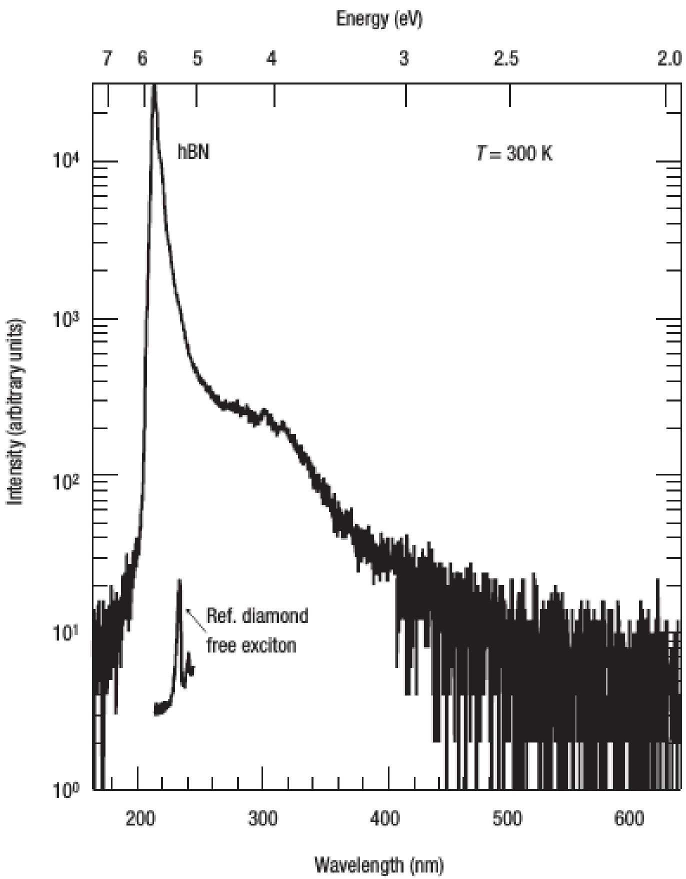
- hBN : a newcomer in the nitride industry for deep UV devices

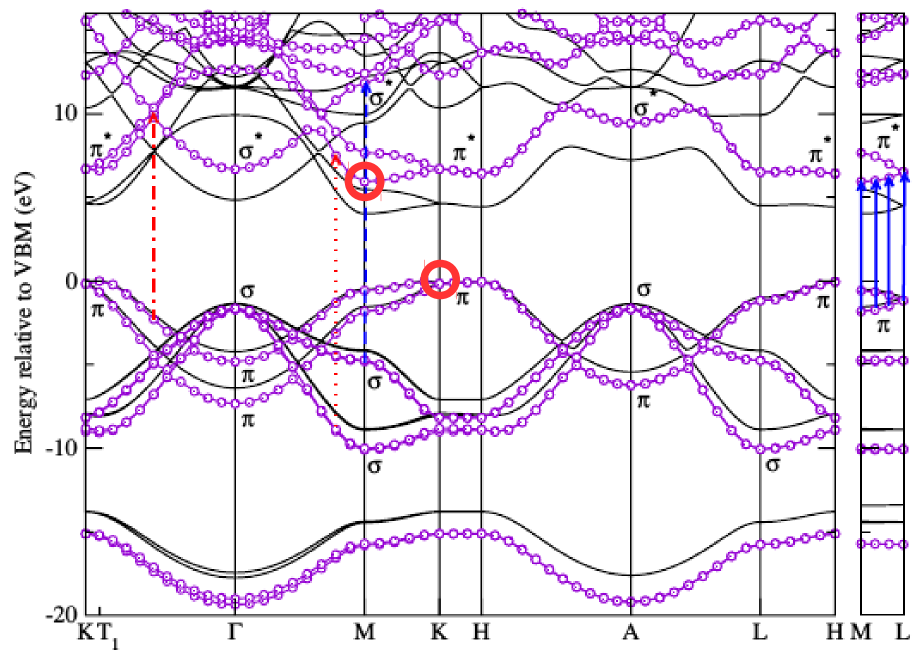
The (old) controversy of the bandgap nature

Direct
(optical spectroscopy)

OR ?

Indirect
(theoretical calculations)





- Conduction band min @ M
- Valence band max @ K

Watanabe, Nat. Mat. **3**, 404 (2004)

Arnaud, PRL **96**, 026402 (2006)

ONLY bulk hBN
TODAY

ONLY bulk hBN
TODAY

For monolayer hBN

Sergei NOVIKOV
(We-5i)

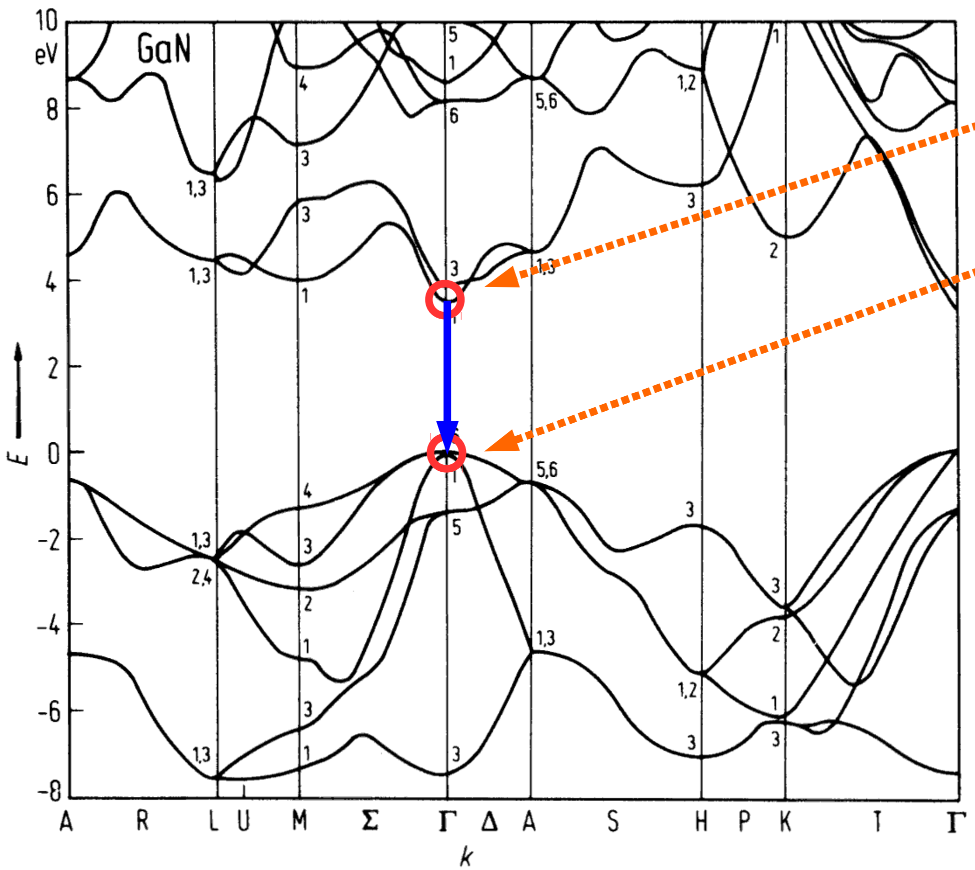
Christine ELIAS
(We-7o)

Outline

- Indirect vs direct bandgap semiconductors
- Two-photon spectroscopy
- Unconventional optical response
- Prospects

Direct bandgap

GaN : electronic bandstructure of wurtzite phase



- Conduction band min @ Γ
- Valence band max @ Γ
- Bandgap ~ 3.5 eV (UV)

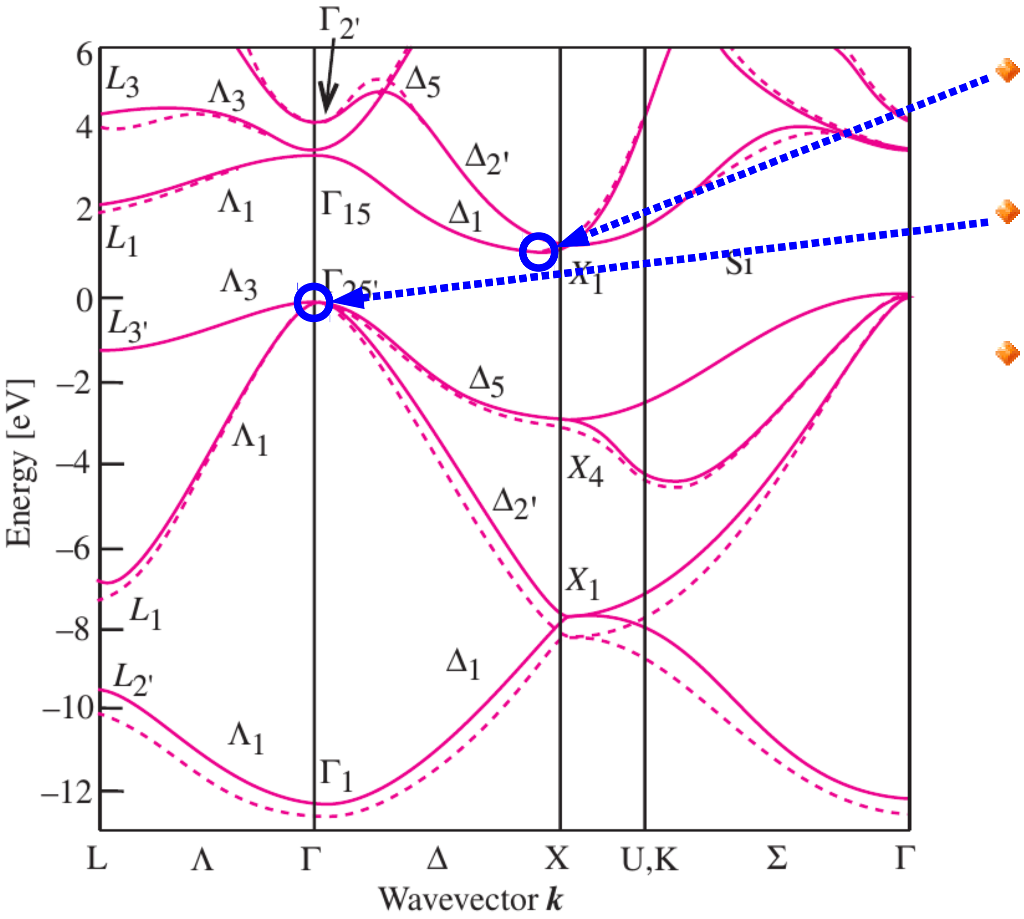
$$\lambda \sim 350nm \gg a \sim \mathring{A}$$

vertical transition in k-space

Direct recombination

Indirect bandgap : a well-known case

electronic bandstructure of SILICON



- Conduction band min @ X
- Valence band max @ Γ
- Bandgap ~ 1.12 eV (IR)

Momentum conservation

NOT FULFILLED

in direct recombination

Phonon-assisted recombination in silicon

- Phonon emission

⇒ momentum conservation

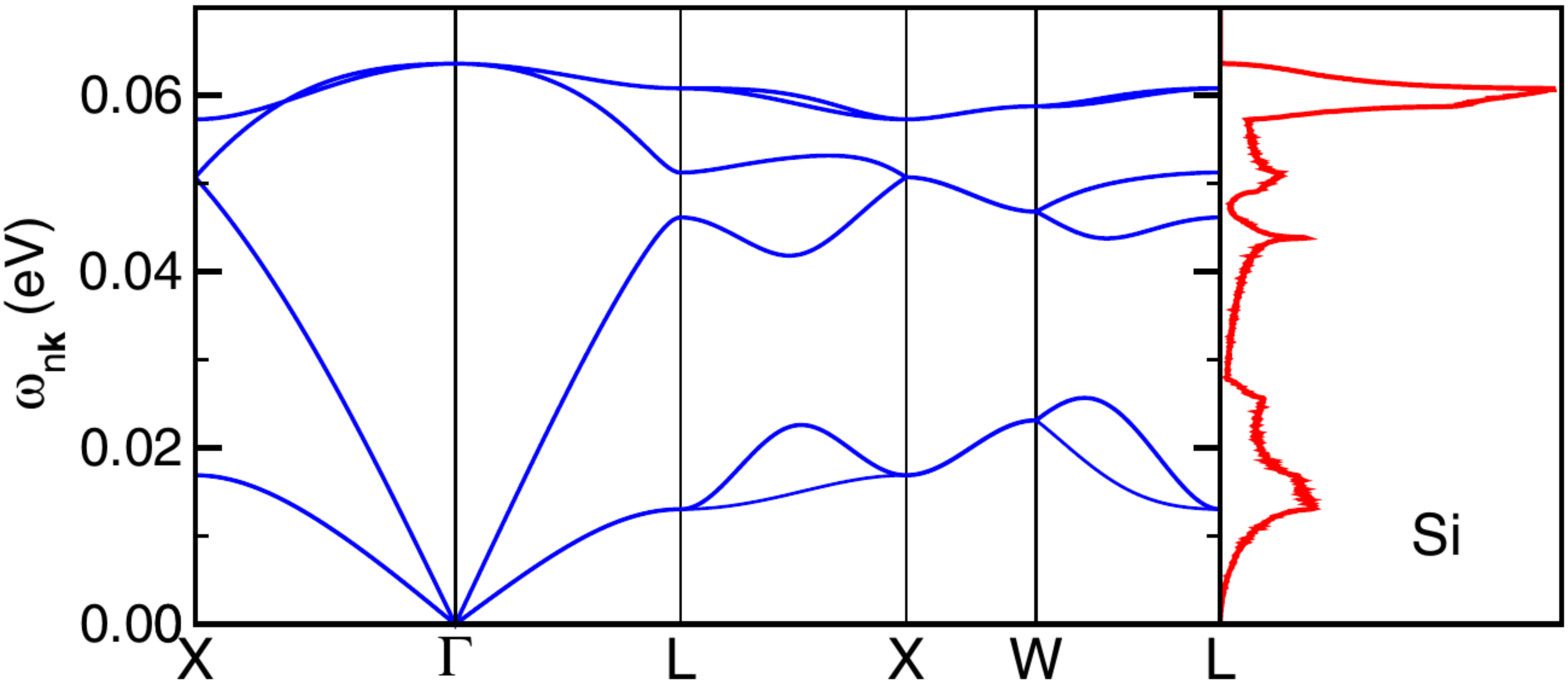
- Phonon wavevector

$$q = \Gamma X$$

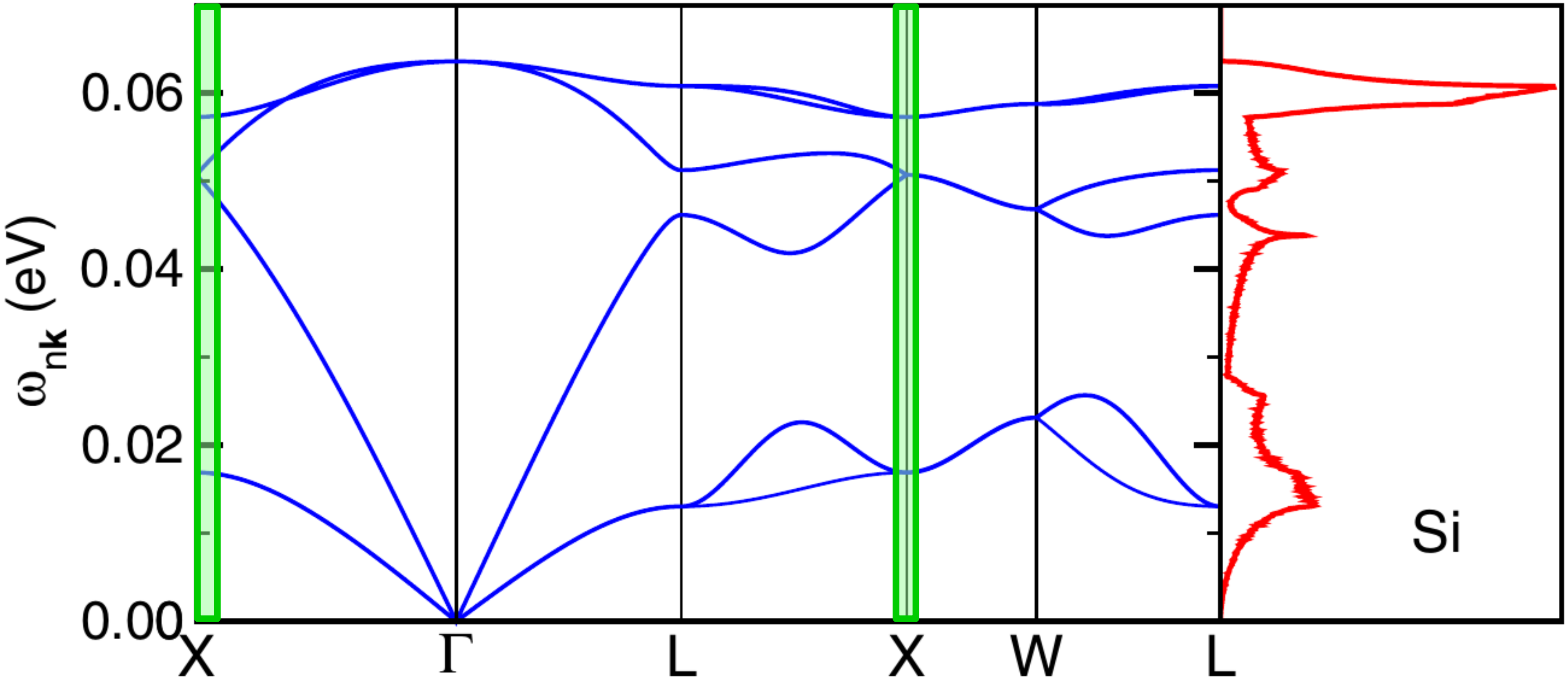
Since $k = 0$ at the zone center Γ ,

phonon-assisted recombination involves phonons from X valley

Phonon bandstructure in silicon



Phonon bandstructure in silicon



Usual (old) game in indirect bandgap materials :

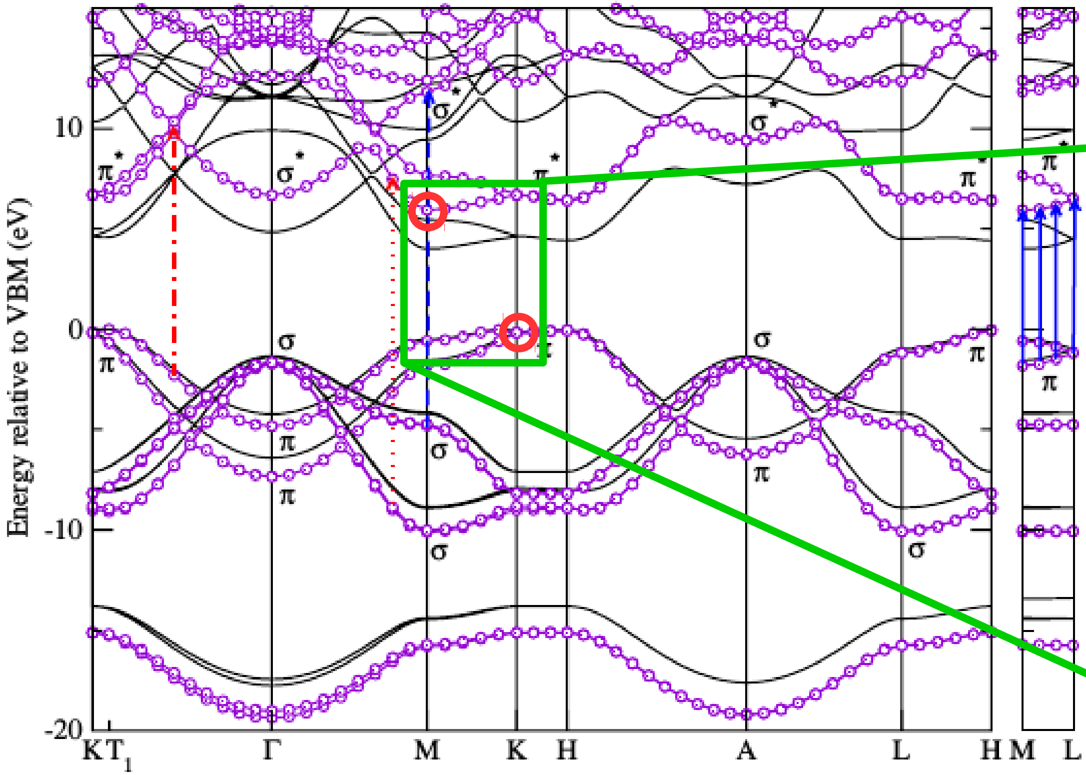
look for phonons in the same valley as the CB minimum !

Valence band maximum is <u>not</u> at zone center in hBN

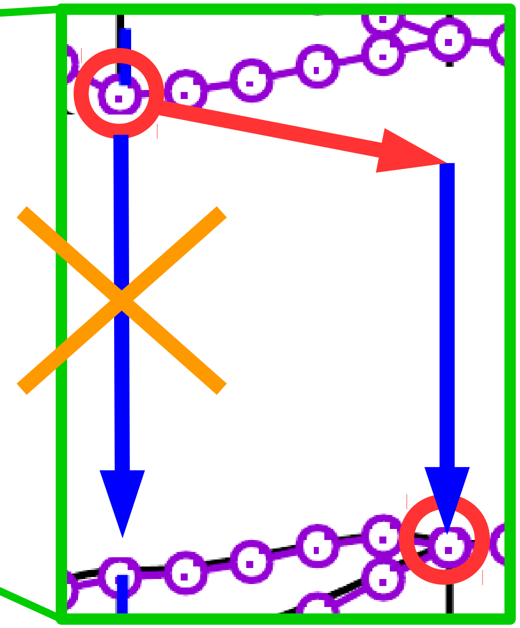
ab initio bandstructure calculations

- Conduction band min @ M
- Valence band max @ K

INDIRECT gap



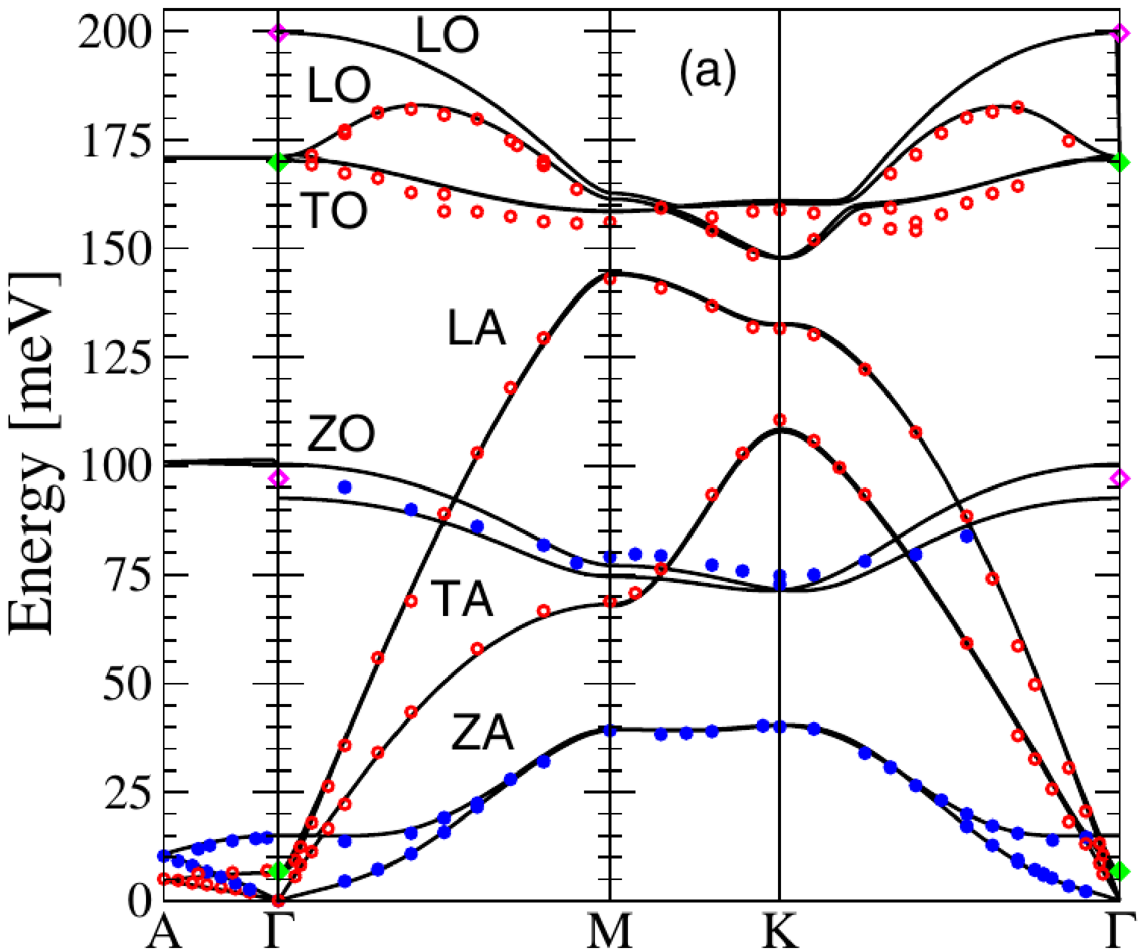
Arnaud, PRL **96**, 026402 (2006)



phonon-assisted recombination

Which phonons for emission in hBN ?

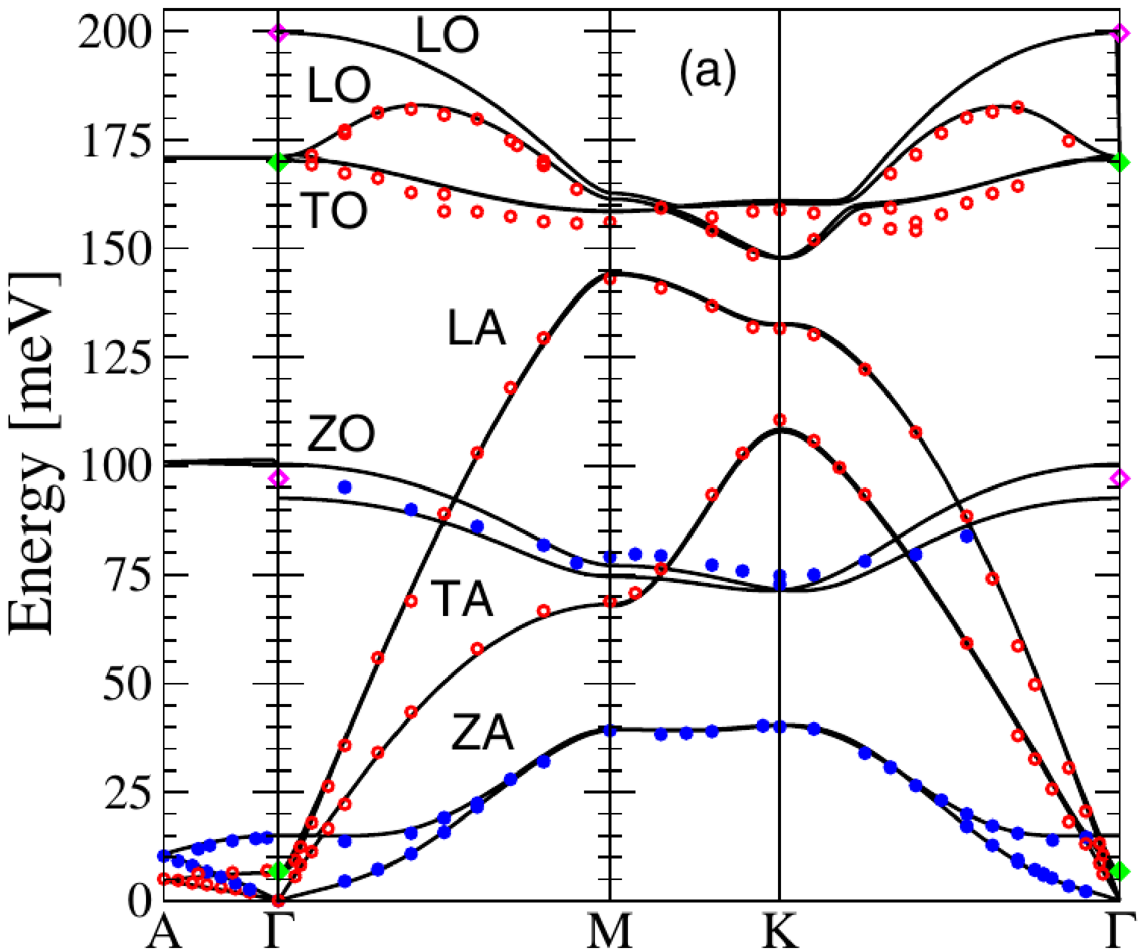
Phonon band-structure



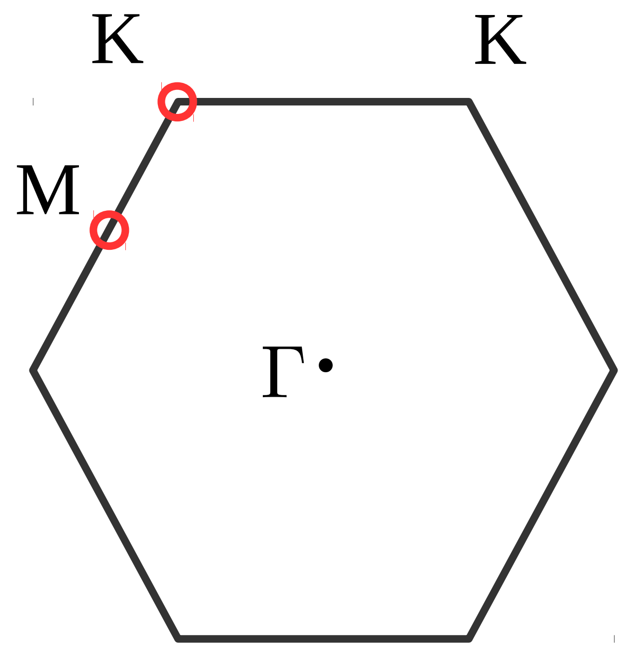
Serrano, PRL **98**, 095503 (2007)

Which phonons for emission in hBN ?

Phonon band-structure



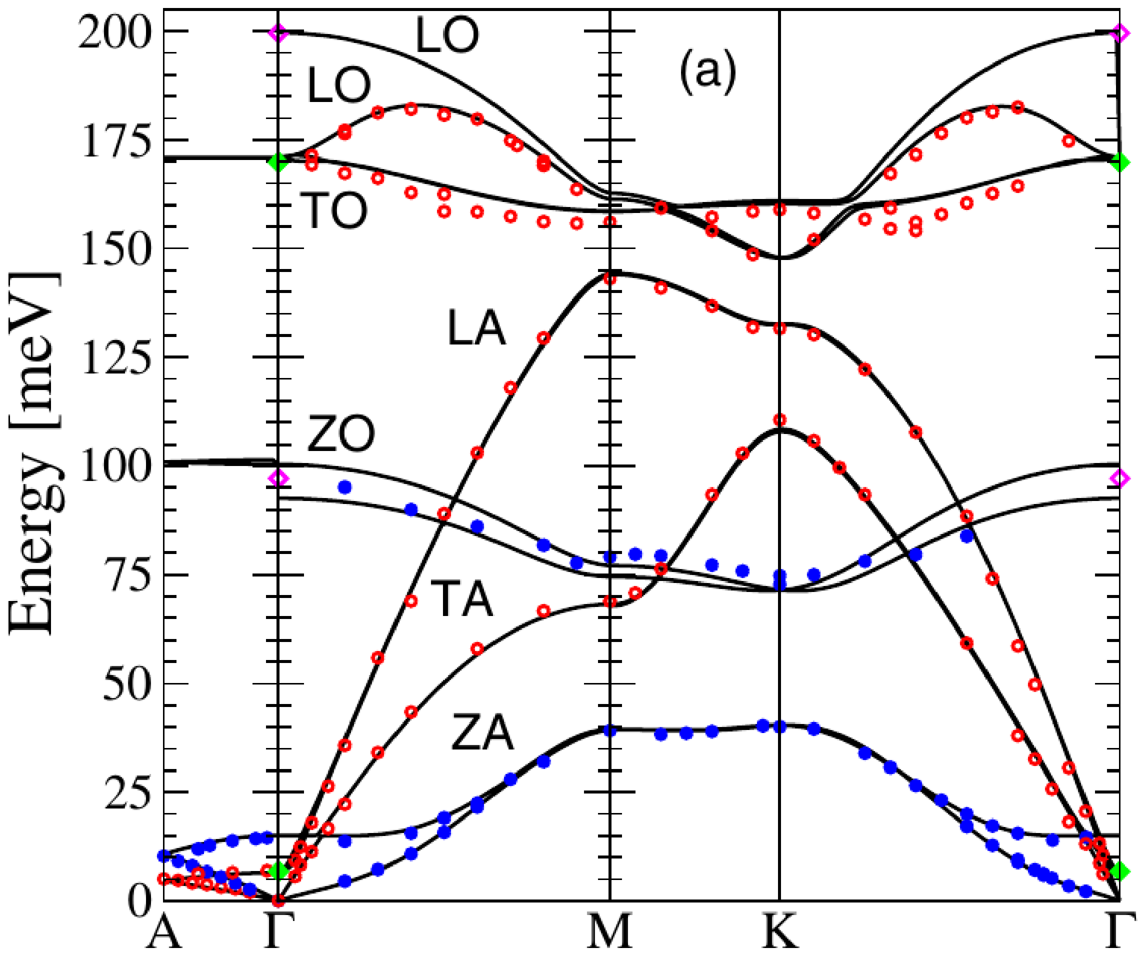
Serrano, PRL **98**, 095503 (2007)

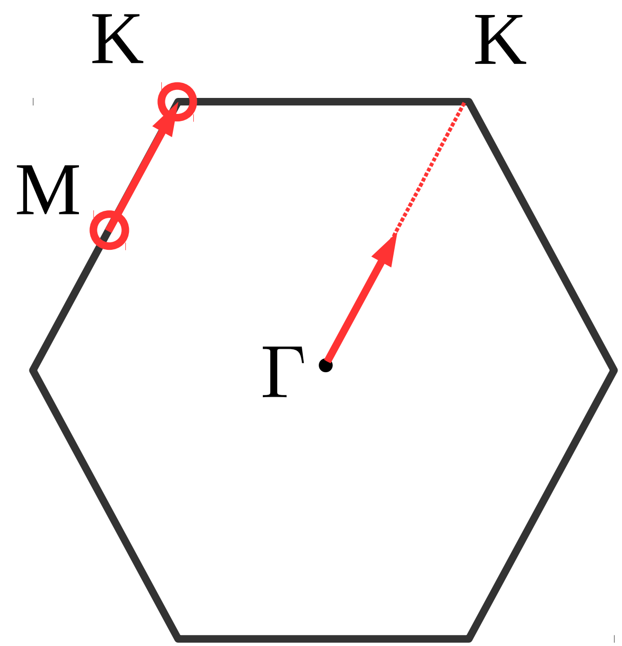


First Brillouin zone in hBN

Which phonons for emission in hBN ?

Phonon band-structure





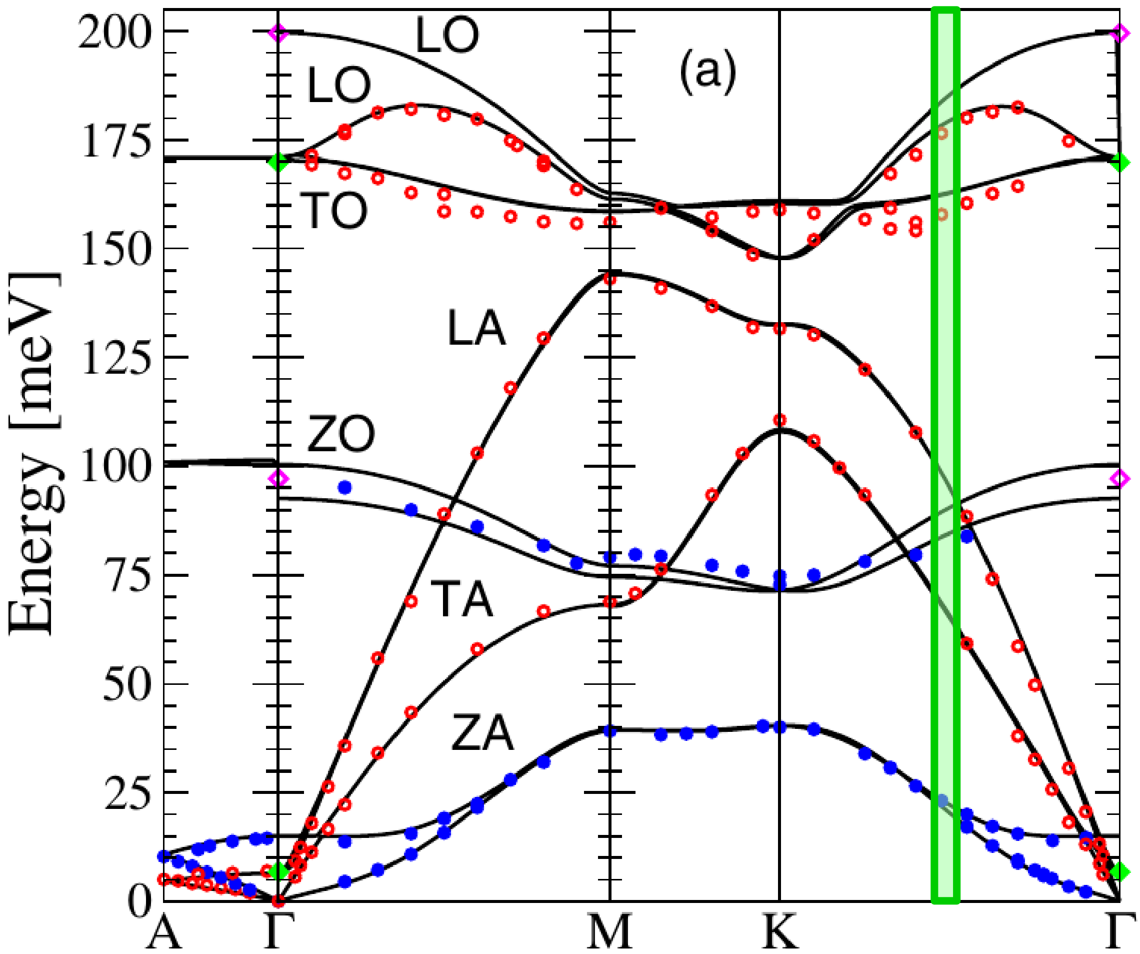
First Brillouin zone

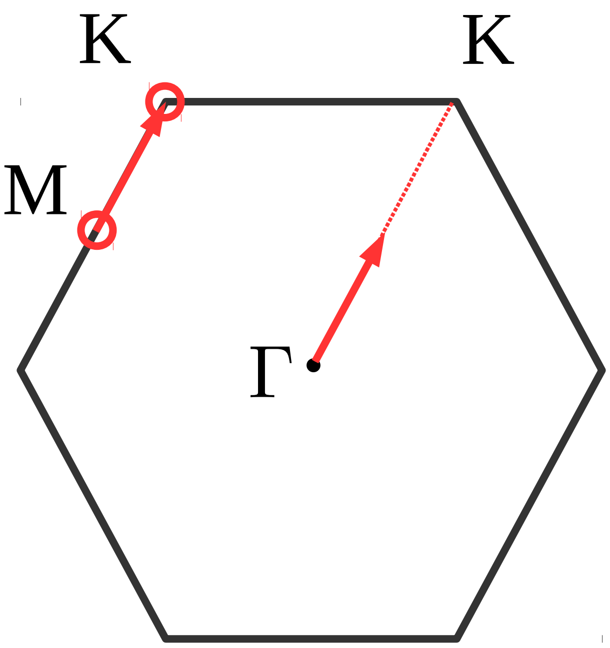
in hBN

Serrano, PRL **98**, 095503 (2007)

Which phonons for emission in hBN ?

Phonon band-structure





First Brillouin zone in hBN

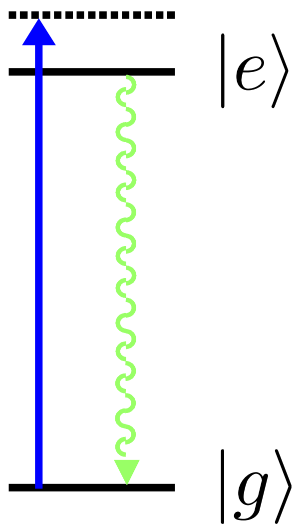
Serrano, PRL **98**, 095503 (2007)

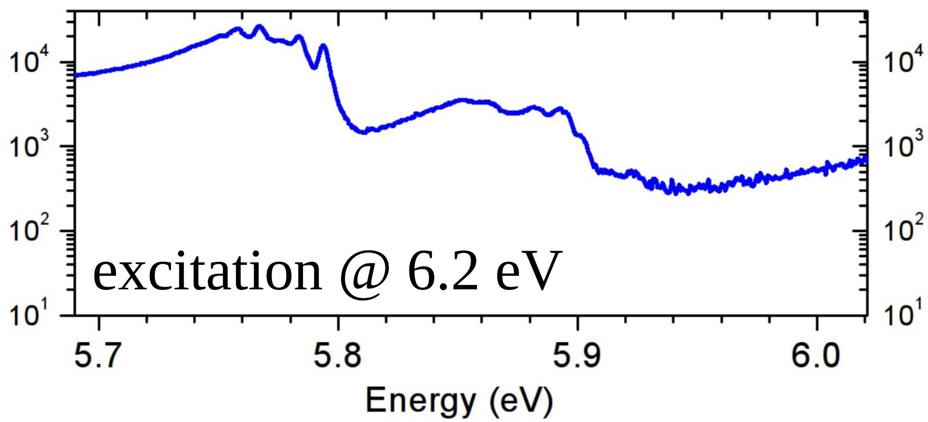
Outline

- Indirect vs direct bandgap semiconductors
- Two-photon spectroscopy
- Unconventional optical response
- Prospects

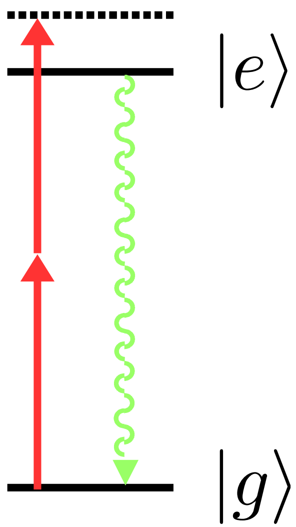
Two-photon spectroscopy

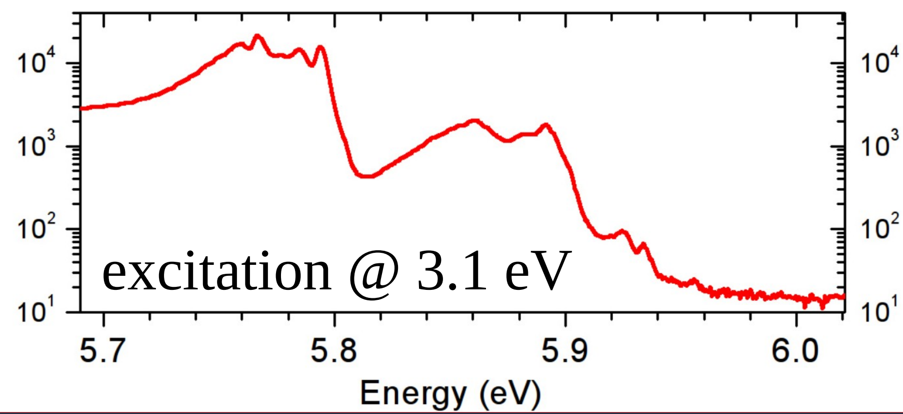
One-photon excitation





Two-photon excitation

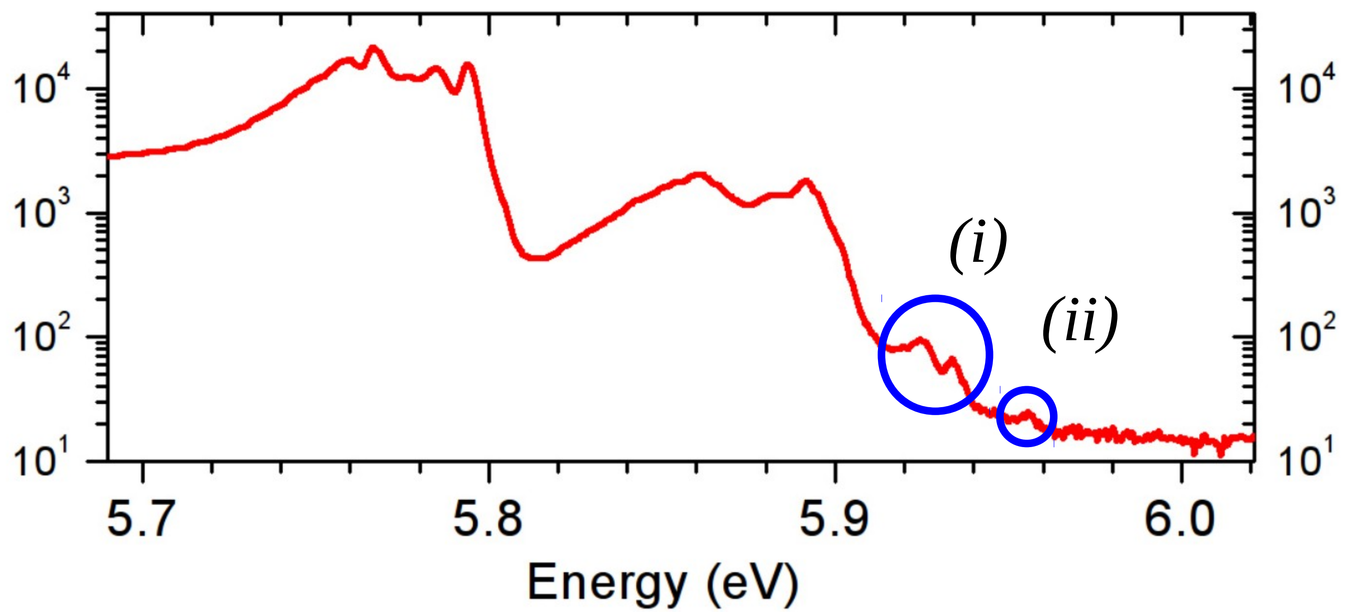




Suppression of laser background

Observation of previously undetected emission lines

Cassabois, Nature Photon. **10**, 262 (2016)

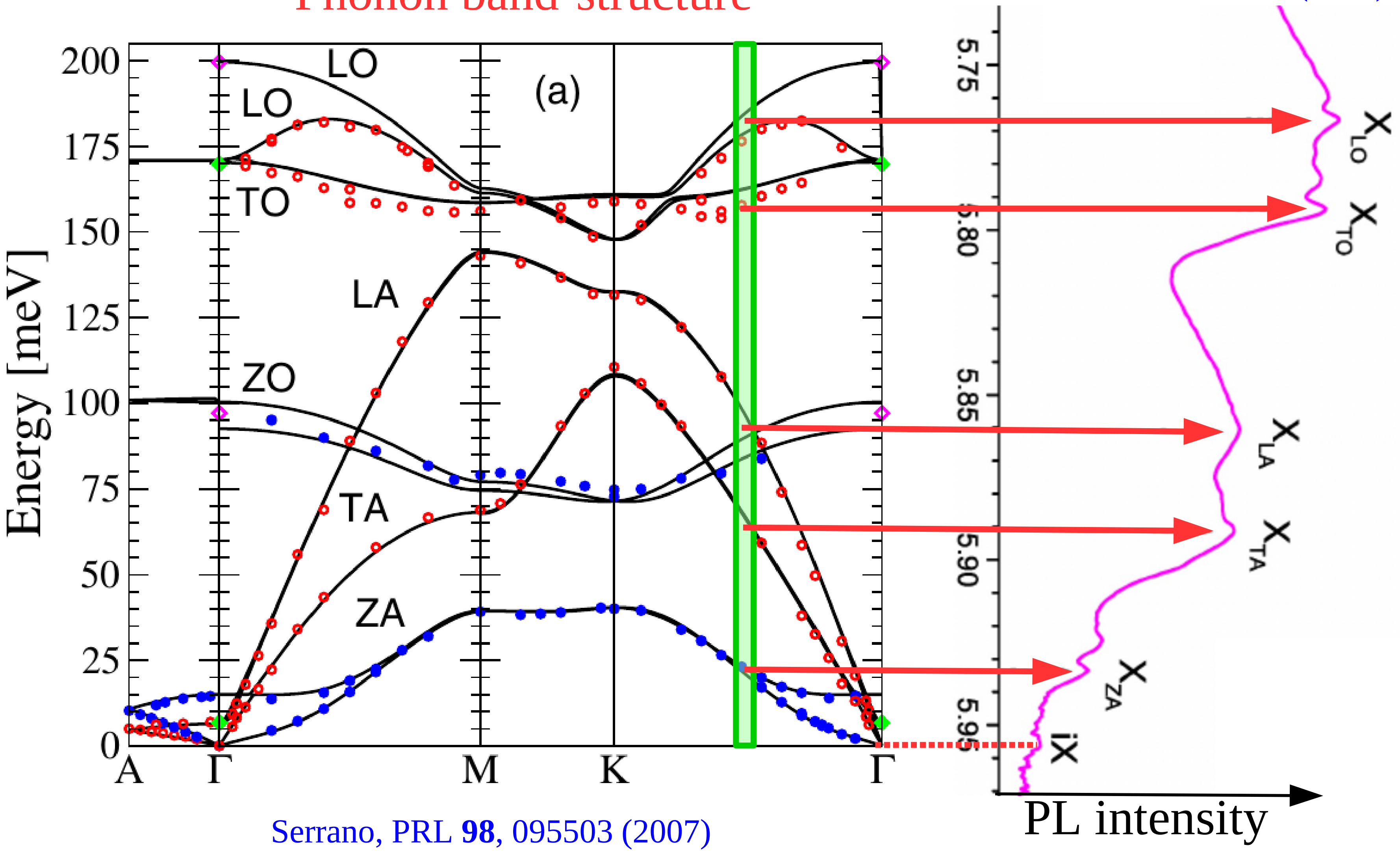


- *(i)*=doublet line @ 5.93 eV similar to emission lines at lower energy
- *(ii)*=weaker line @ 5.955 eV
- phonon-assisted recombination ?

Identification of phonon replicas

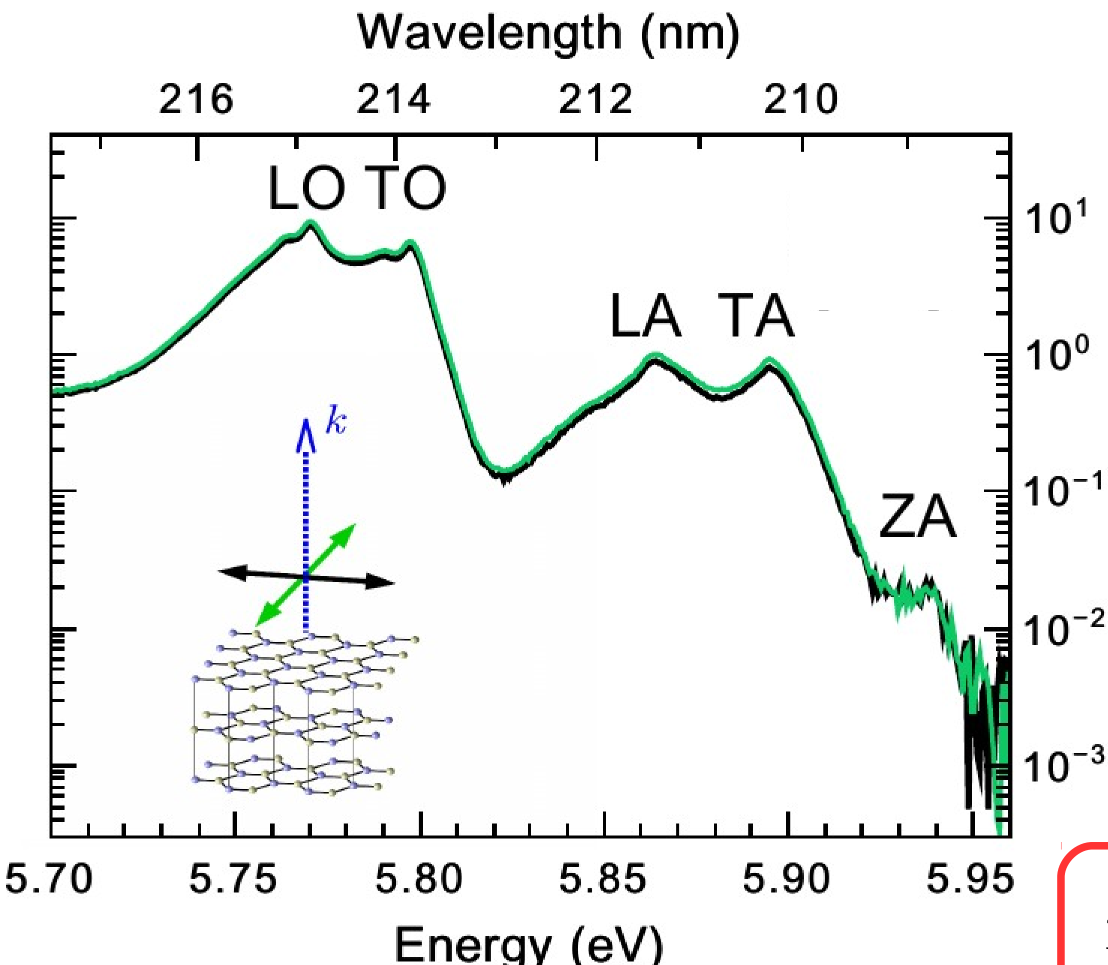
Phonon band-structure

Cassabois, Nature Photon. **10**, 262 (2016)



Serrano, PRL **98**, 095503 (2007)

Polarization-resolved measurements : along c-axis



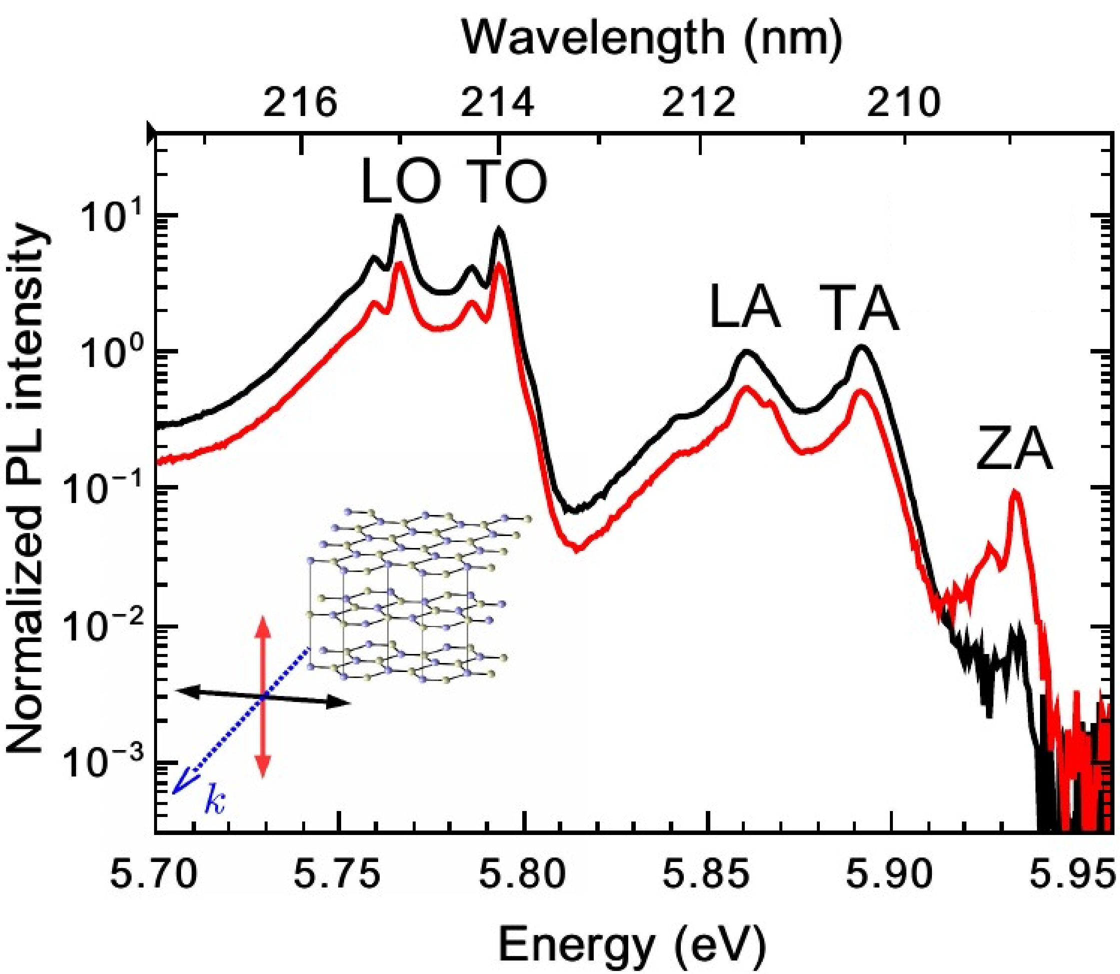
Vuong, 2D Mater. **4**, 011004 (2017)

- Intense optical phonon replicas (LO, TO)
- Weak acoustic phonon replicas (LA, TA, ZA)
- Selection rules for phonon-assisted recombination

ZA forbidden for $k \parallel c$

ZA = out-of-plane vibrations
LA, TA = in-plane vibrations

Polarization selection rules : edge detection



Vuong, 2D Mater. **4**, 011004 (2017)

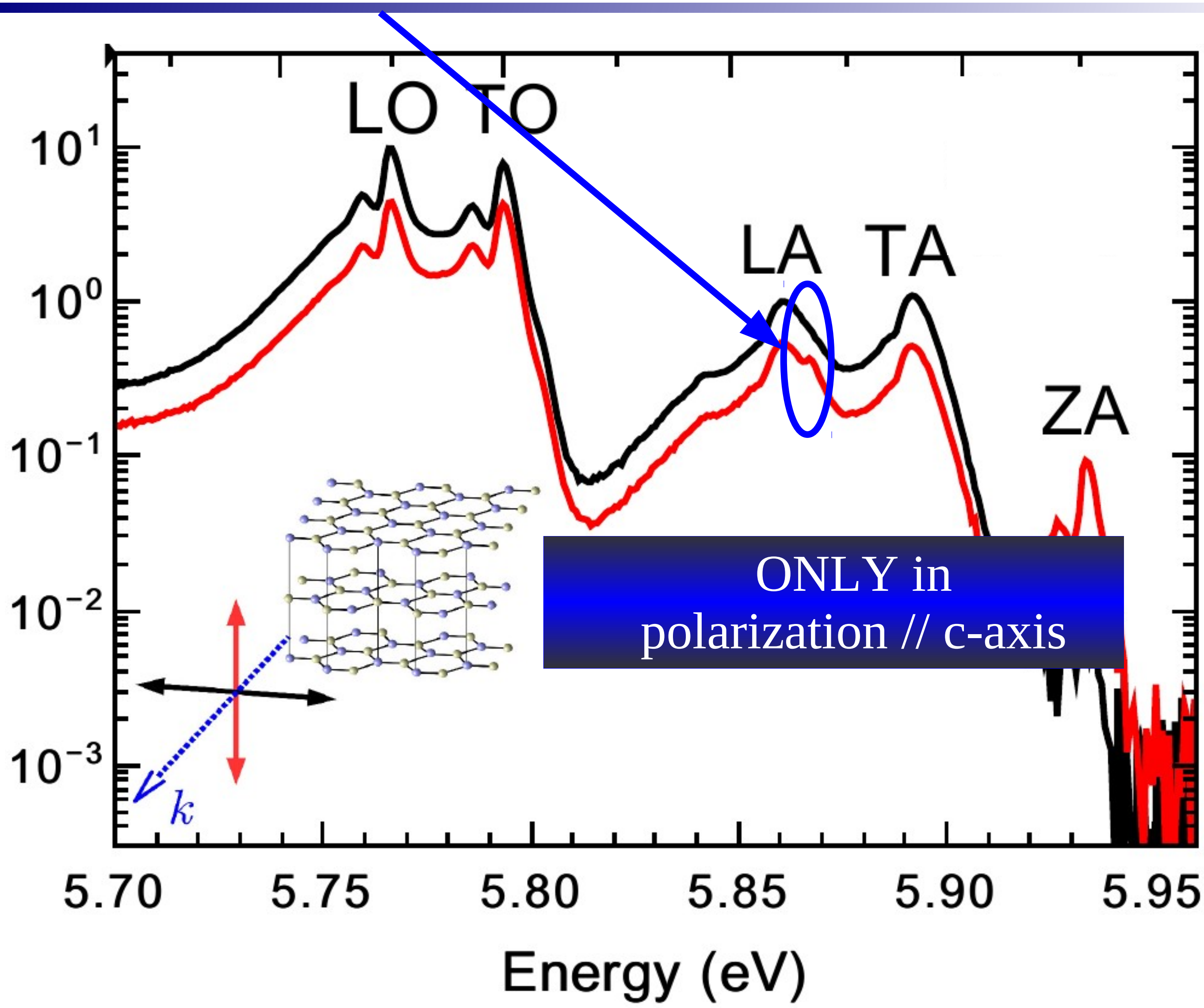
- Detection from sample edge

  $k \perp c$

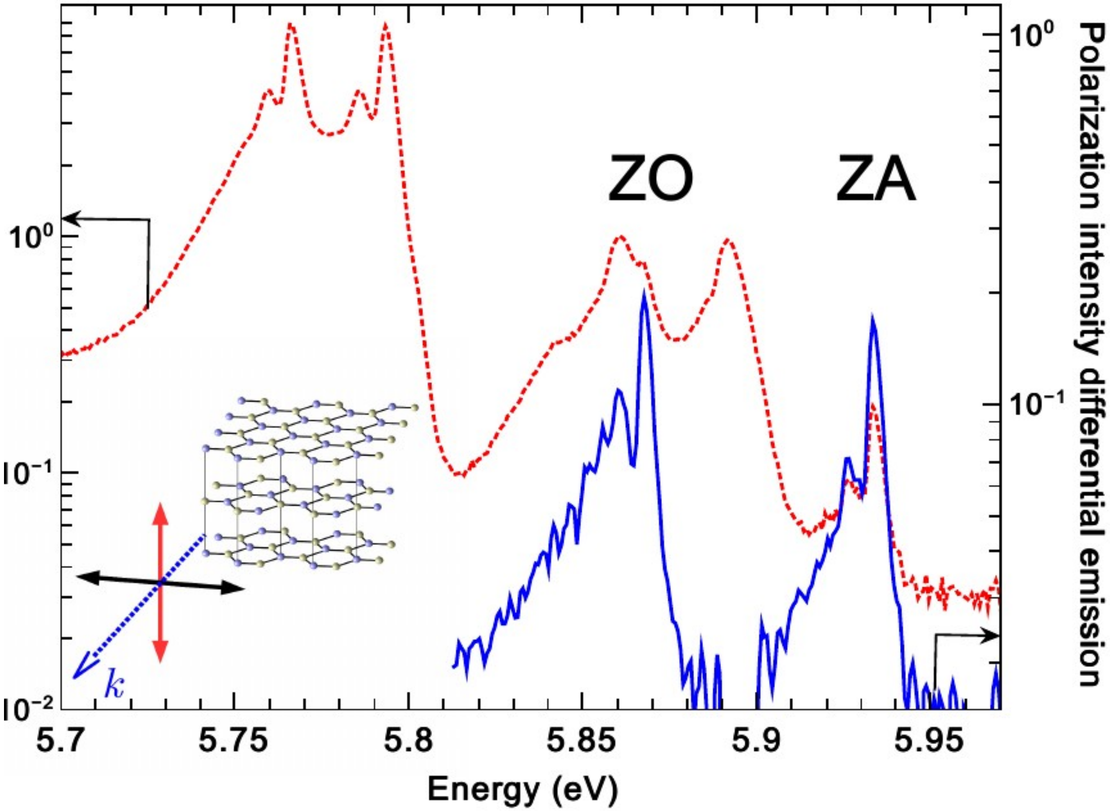
- Strong polarization dependence
- Anti-correlation between ZA and (LA, TA, LO, TO)
- ZA = out-of-plane vibrations

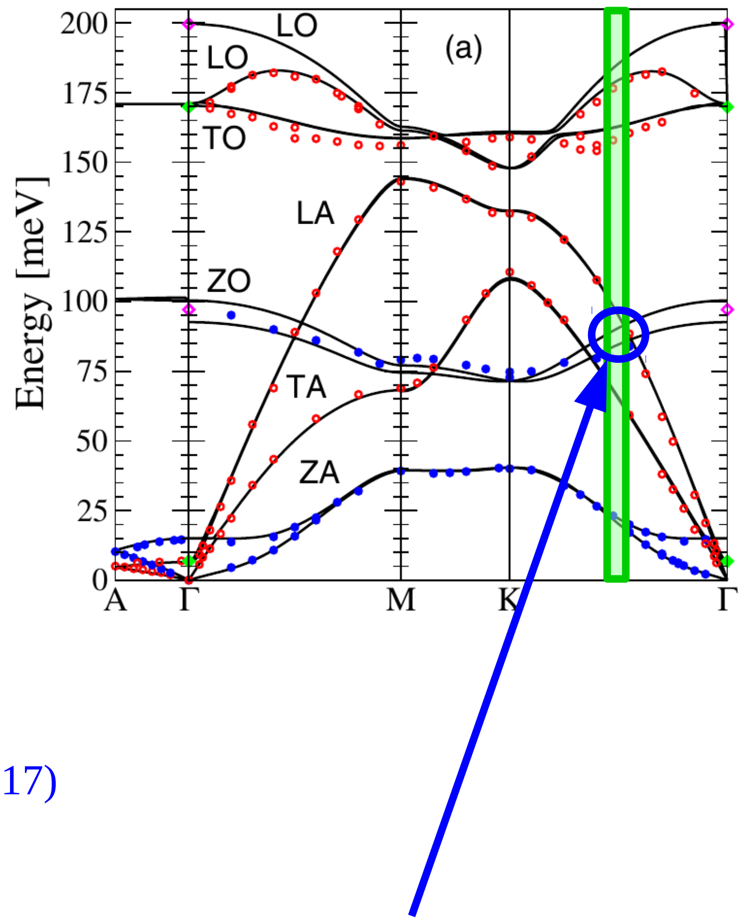
  allowed for $k \perp c$

Another previously undetected emission line...



ZO phonon replica

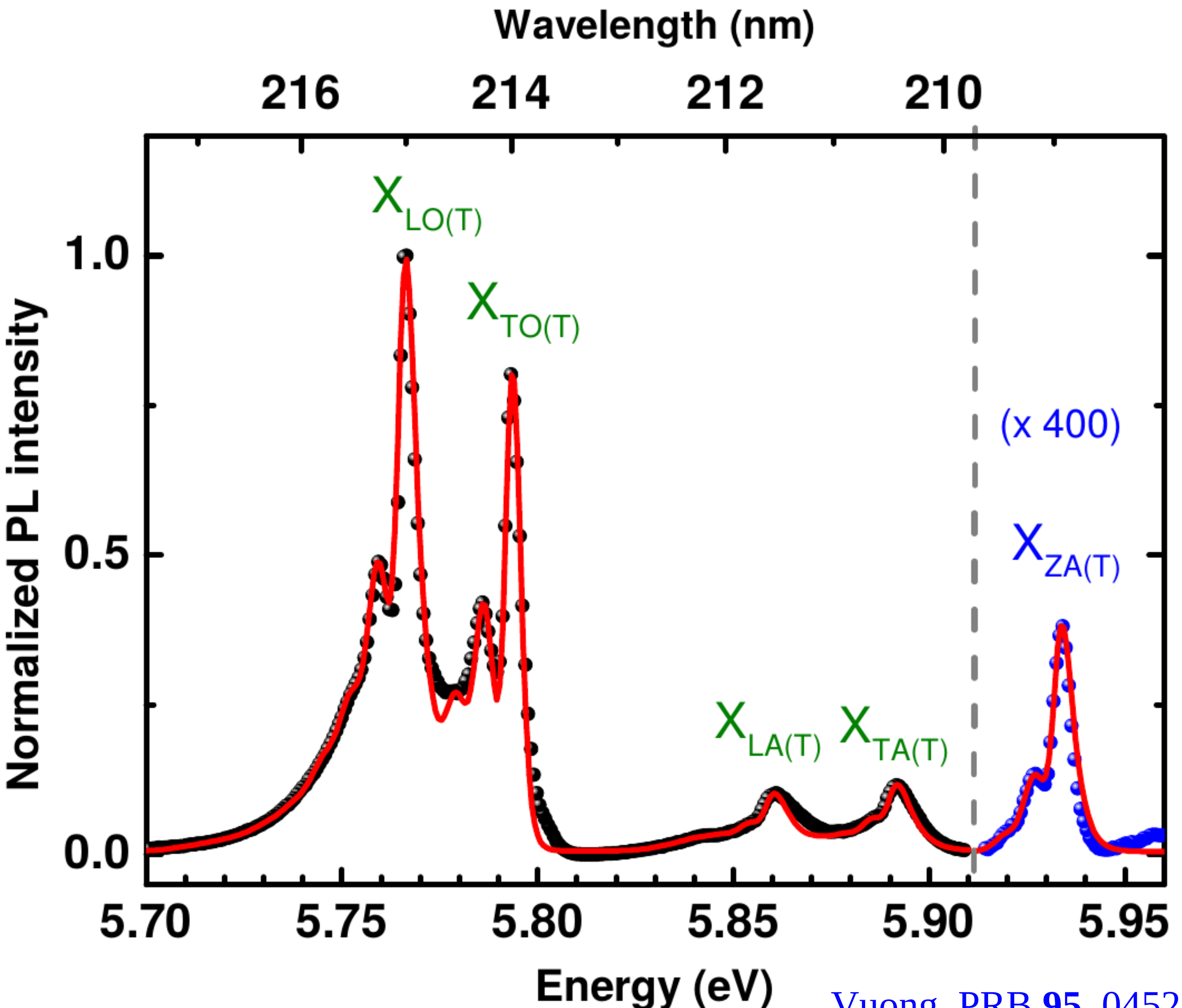




Vuong, 2D Mater. **4**, 011004 (2017)

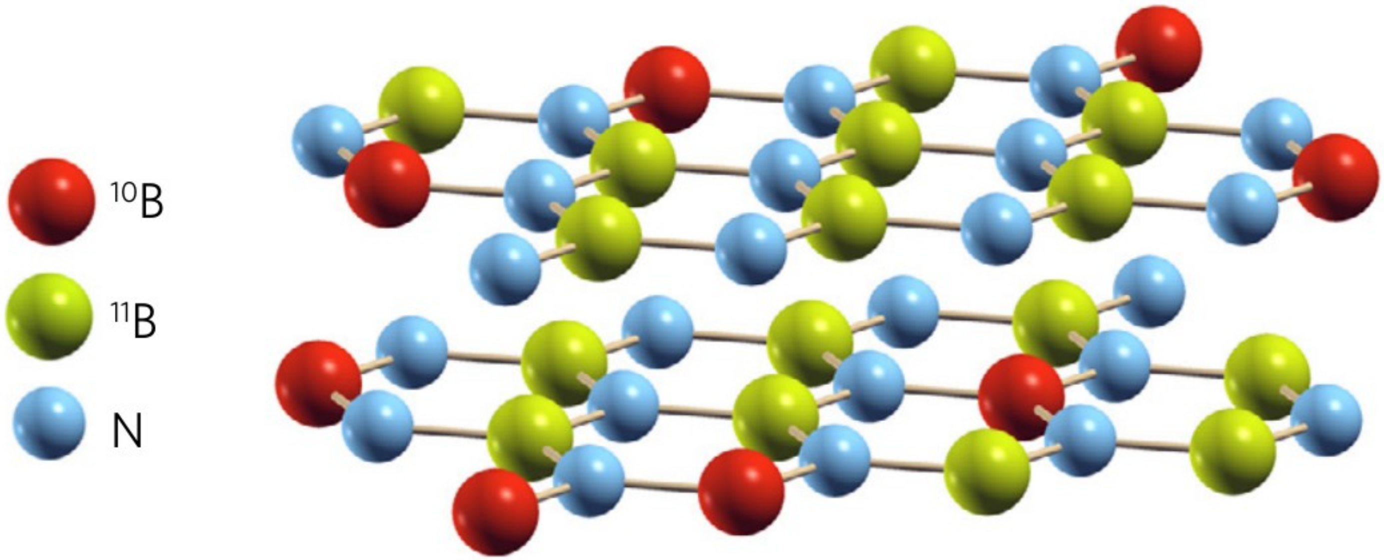
- observation of missing sixth replica
- ZO branch in between LA and TA in middle of Brillouin zone

Phonon group velocity



Vuong, PRB **95**, 045207 (2017)

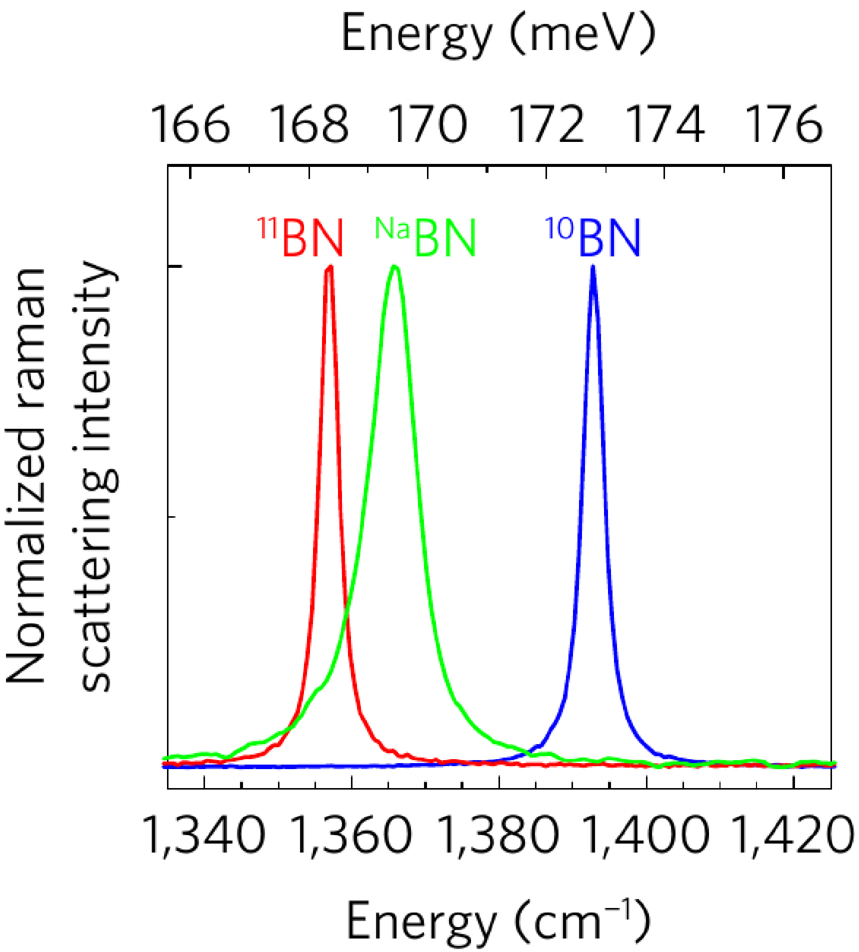
Two boron isotopes : ^{10}B and ^{11}B



- Boron isotopes : 20 at% ^{10}B and 80 at% ^{11}B
- Nitrogen isotopes : 99.6 at% ^{14}N

Vuong, Nature Mat. **17**, 152 (2018)

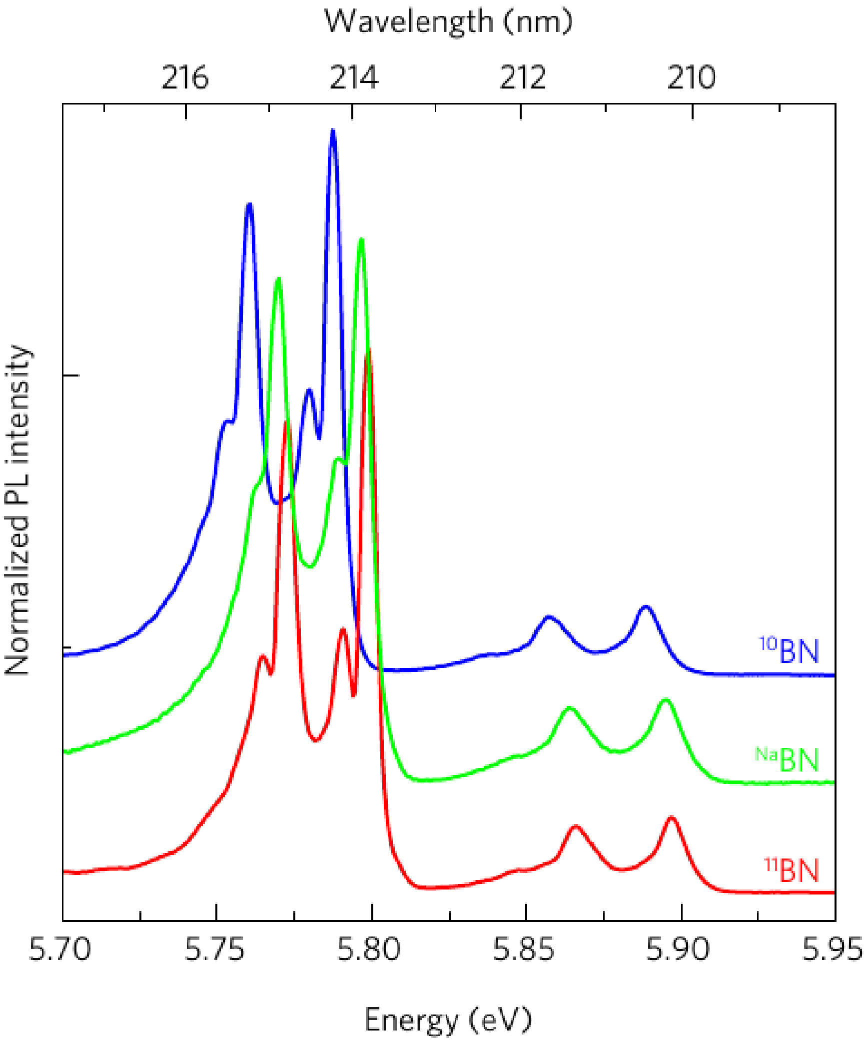
Raman spectroscopy



Vuong, Nature Mat. **17**, 152 (2018)

- Raman-active E_{2g} mode of high energy
- $\omega \sim \sqrt{\frac{k}{m}}$
- Narrower lines in ^{10}BN and ^{11}BN
- Broadening due to isotopic mass disorder in ^{Na}BN

Isotopic purification



Vuong, Nature Mat. **17**, 152 (2018)

- Global red-shift from ^{11}BN to ^{10}BN
- PL spectrum composed of phonon replicas
- $h\nu = E_{gap} - E_{phonon}$

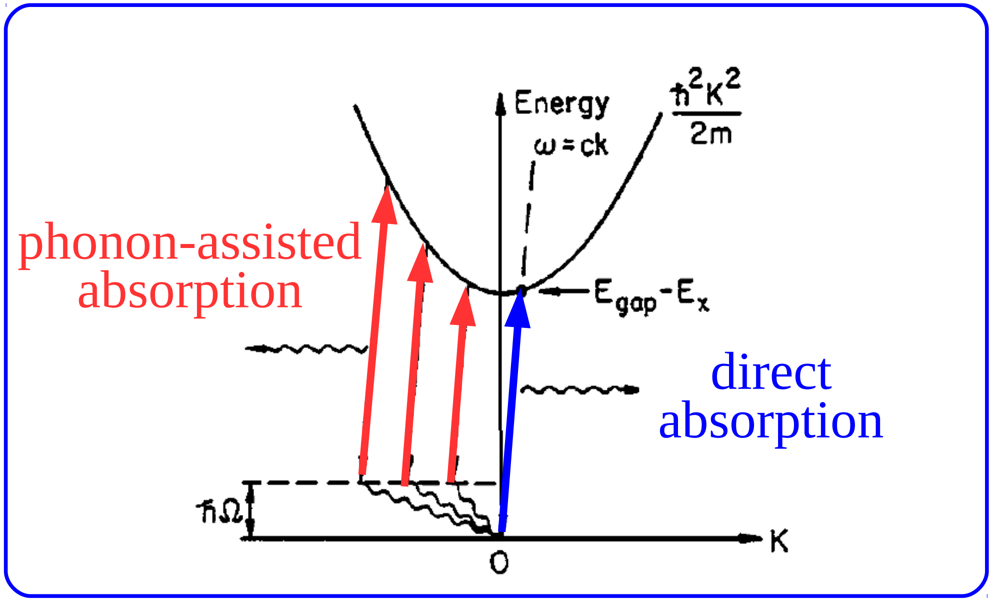
$$\delta E_{gap} \propto \frac{-1}{\sqrt{m}}$$

$$\propto \frac{1}{\sqrt{m}}$$

Outline

- Indirect vs direct bandgap semiconductors
- Two-photon spectroscopy
- Unconventional optical response
- Prospects

Phonon-assisted absorption



- direct absorption : within the light-cone

  > narrow line

- indirect absorption : maps the full exciton dispersion

  > typical 3D JDOS given by

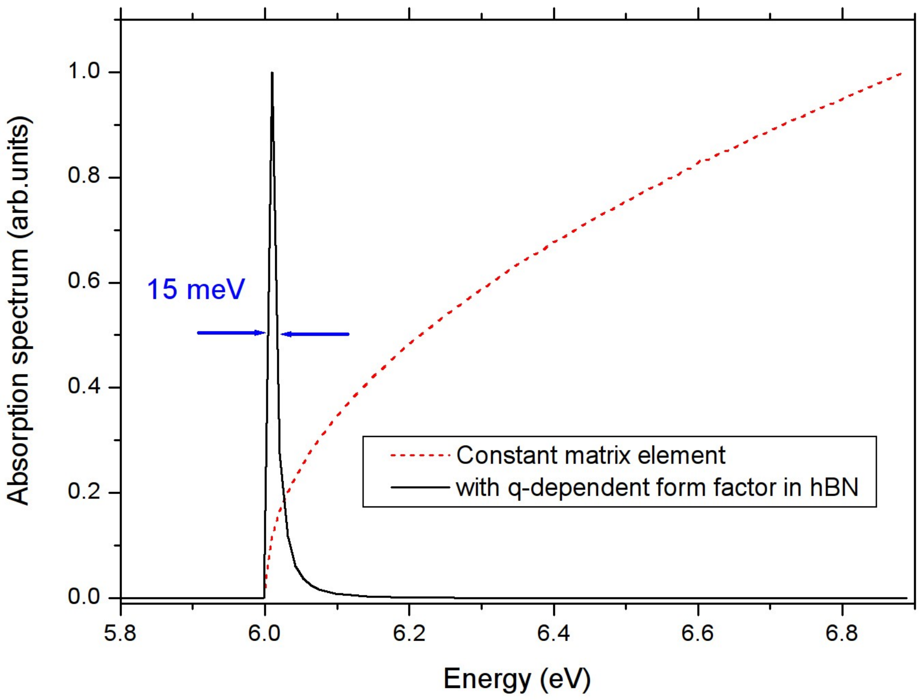
$$\sqrt{E - E_0}$$

Elliott, Phys. Rev. **108**, 1384 (1957)

Absorption profile in hBN

Two ingredients :

- joint density of states
- q-dependent exciton-phonon matrix element : cut-off for

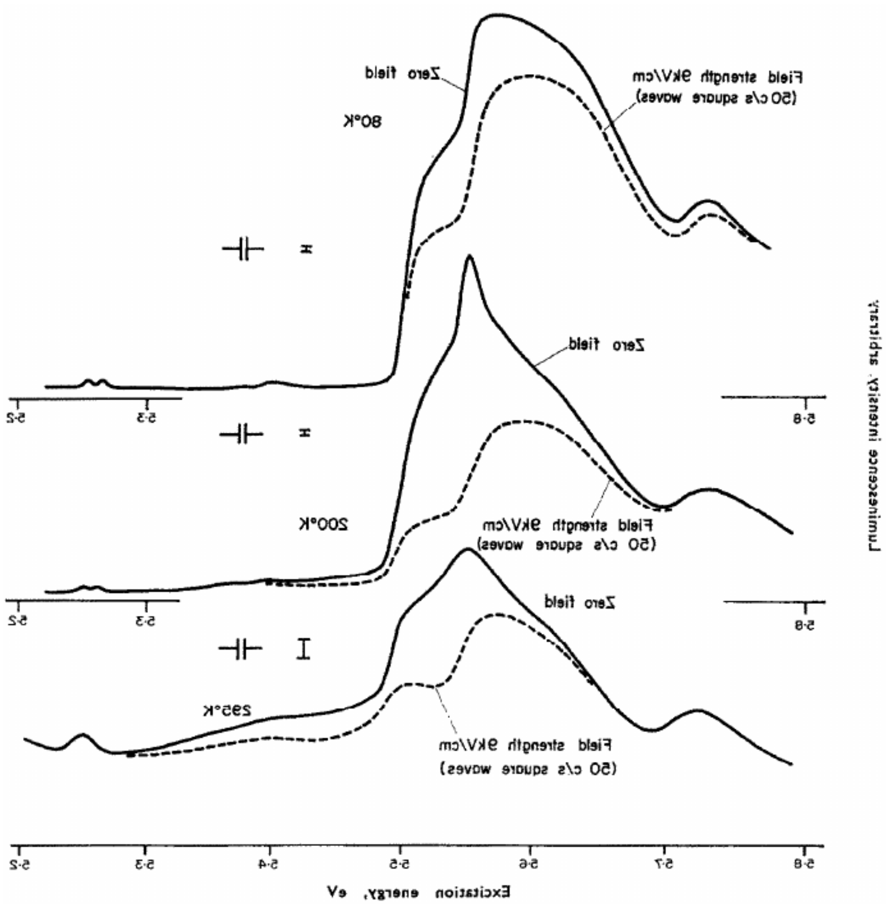


$$q \gg 1/a_B$$

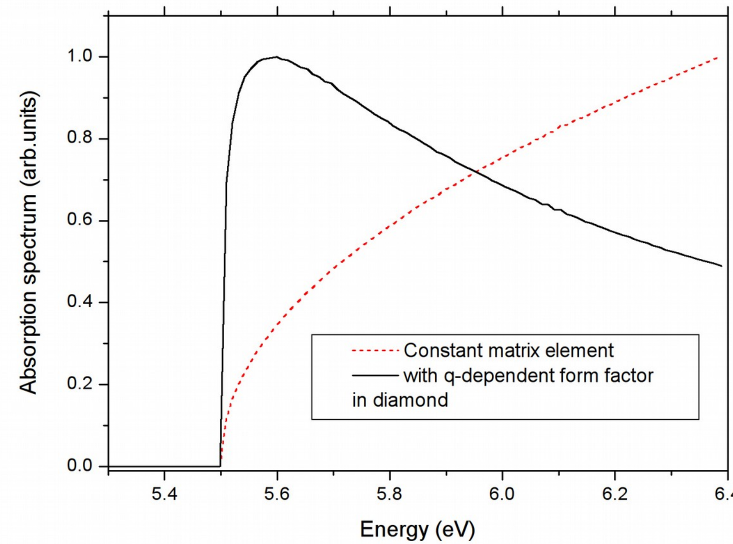
with a_B the exciton Bohr radius

Understanding the spectrum of indirect absorption

Diamond : Valence band @ zone center



Dean, J. Phys. Chem. Solids, **25**, 1369 (1964)



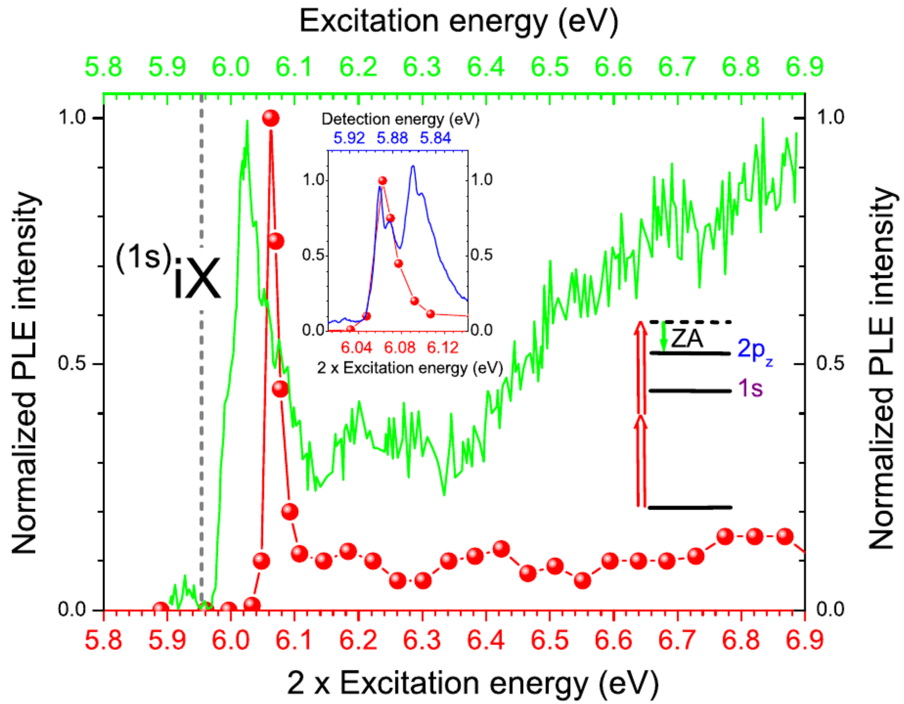
- $\sqrt{E - E_0}$ within the approximation of
  Elliott, Phys. Rev. **108**, 1384 (1957)

- q-dependence of exciton-phonon form factor

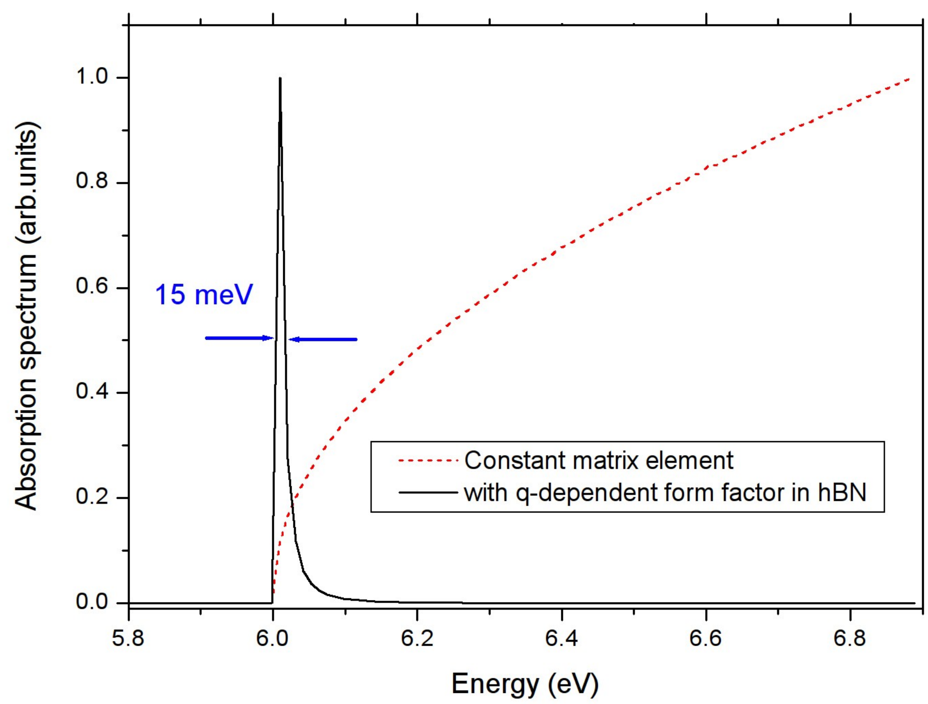
Understanding the spectrum of indirect absorption in hBN

hBN : Conduction *AND* Valence bands away from zone center

- a unique configuration for indirect bandgap materials
- observation of narrow lines for indirect bandgap material



Cassabois, Nature Photon. **10**, 262 (2016)



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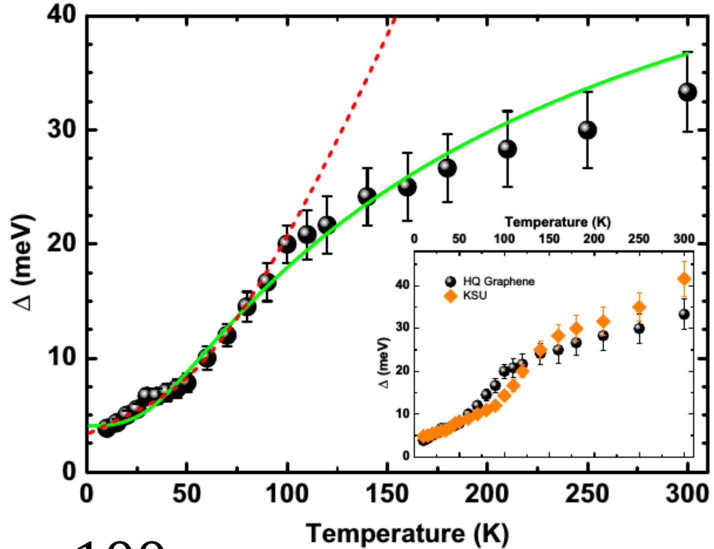
Strong exciton-phonon coupling in hBN, but why ?

- Thermally-assisted broadening

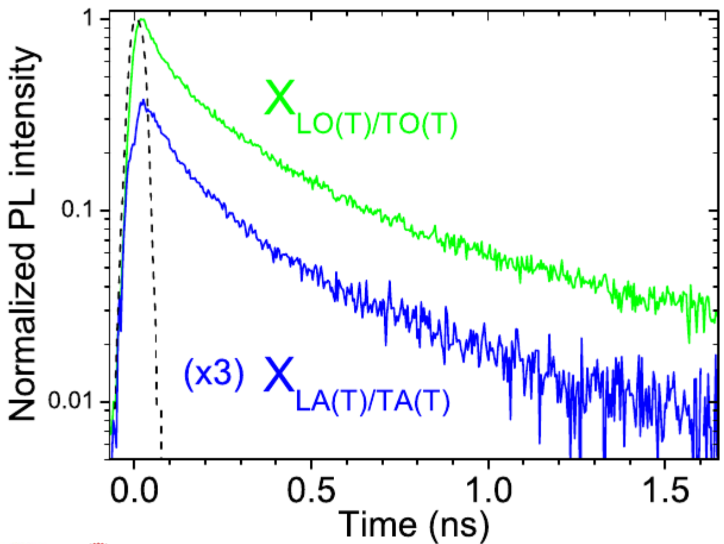
Phys. Rev. B **95**, 201202(R) (2017)

Gaussian profile

+ width increasing as $\sqrt{T}$



- Phonon-assisted recombination time ~ 100 ps



Phys. Rev. B **93**, 035207 (2017)

Fast enough to :

- bypass non-radiative recombination

- get high internal quantum efficiency

First *ab initio* calculations of phonon-assisted emission

PHYSICAL REVIEW B **99**, 081109(R) (2019)

Rapid Communications

Theory of phonon-assisted luminescence in solids: Application to hexagonal boron nitride

E. Cannuccia,[1,2] B. Monserrat,[3] and C. Attaccalite[1,4,5]

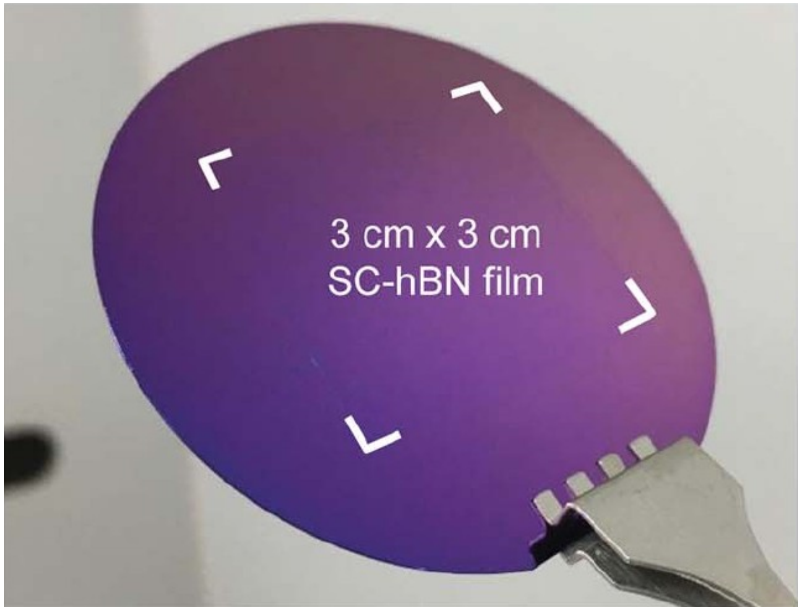
PHYSICAL REVIEW LETTERS **122,** 187401 (2019)

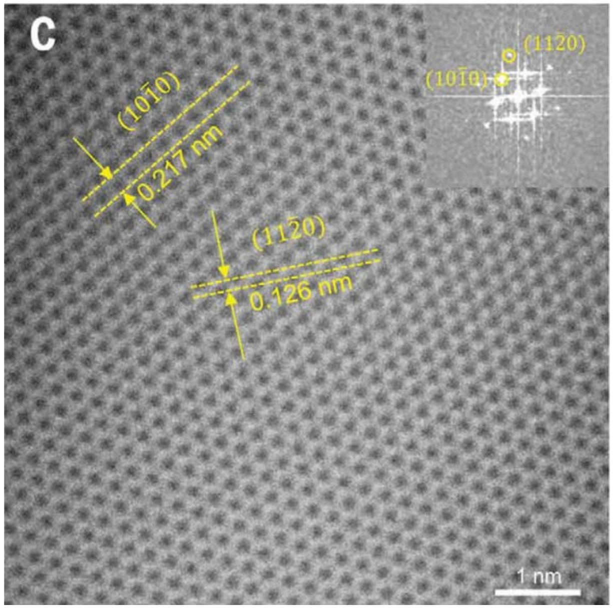
Exciton-Phonon Coupling in the Ultraviolet Absorption and Emission Spectra of Bulk Hexagonal Boron Nitride

Fulvio Paleari,[1,*] Henrique P. C. Miranda,[1,2] Alejandro Molina-Sánchez,[3] and Ludger Wirtz[1]

Epitaxy of high-quality hBN

Wafer-scale <u>single crystal</u> of monolayer hBN (KIST, Korea)



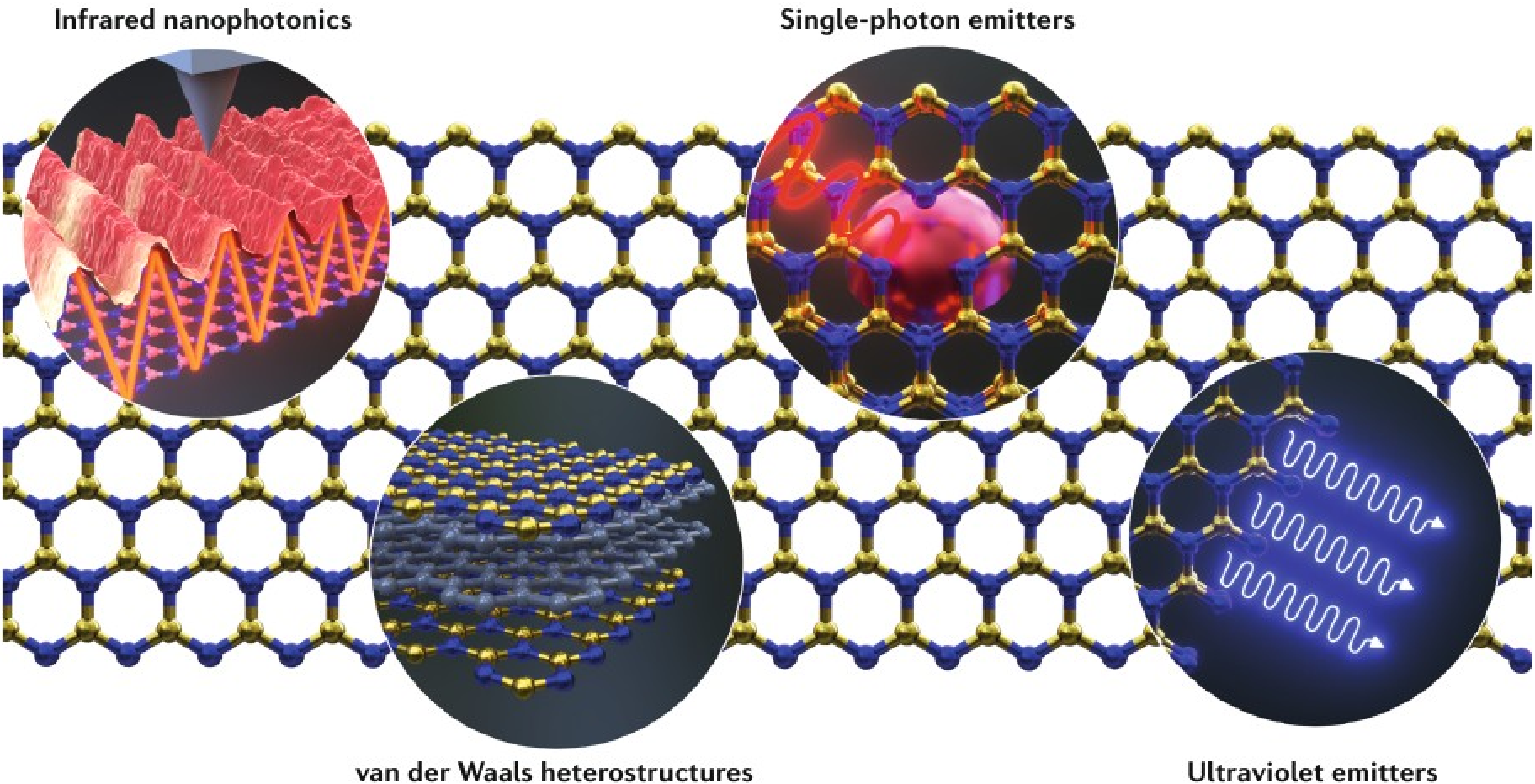


Lee, Science **362**, 817–821 (2018)

NEXT STEPS : Thick epilayers
+ DOPING !

Photonics with hBN

Nature Reviews Materials **4**, 552 (2019)



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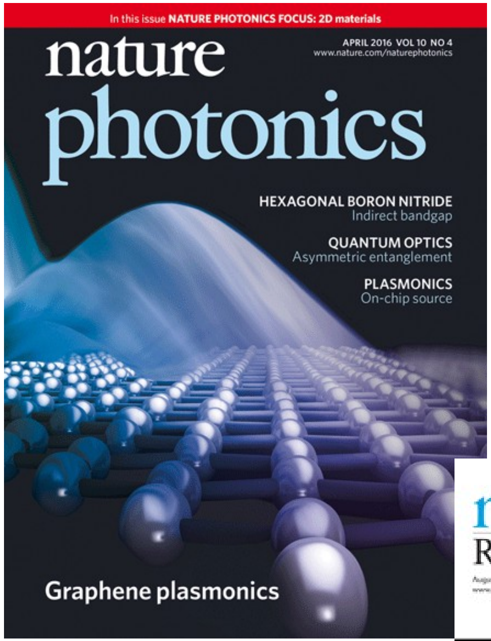
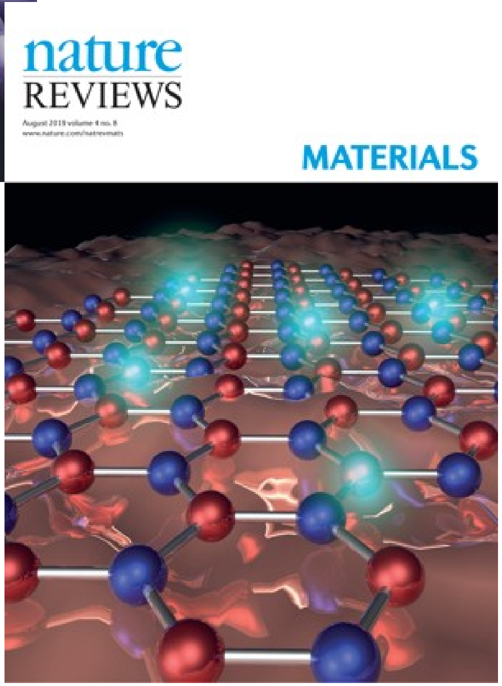
K. Watanabe
T. Taniguchi

Barcelona, Spain
L. Artus
R. Cusco

KSU, USA
J. Edgar

Nottingham, UK
S. Novikov





Optoelectronic properties of hexagonal boron nitride

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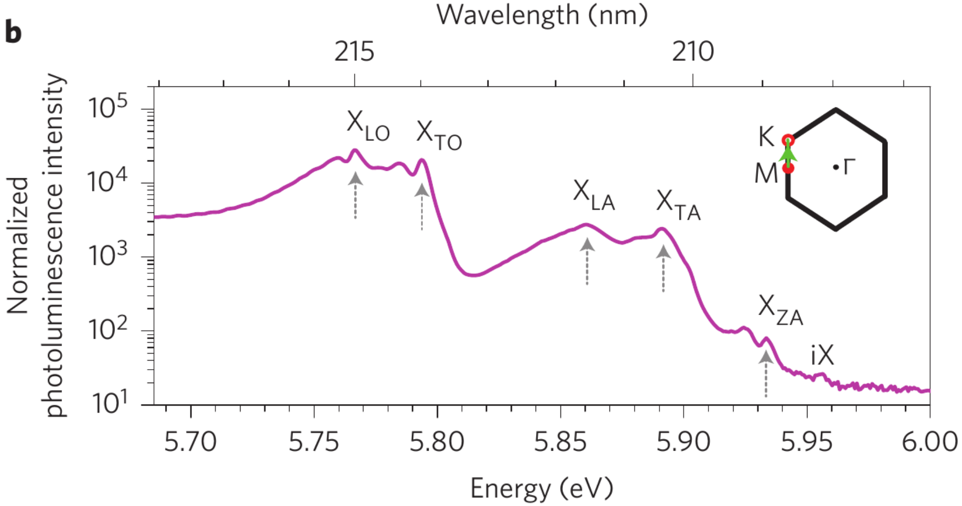
Laboratoire Charles Coulomb

CNRS / Université de Montpellier

Montpellier, France

Bulk hBN: an indirect bandgap material

- Optical spectroscopy



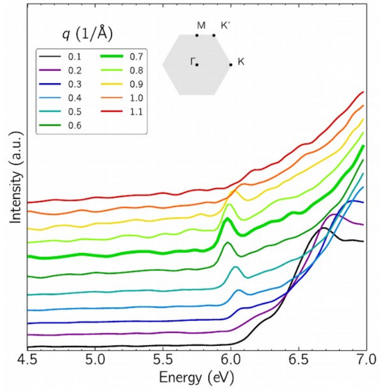
- Phonon-assisted emission

  Cassabois, Nature Photon. **10**, 262 (2016)

- Isotopic purification — Vuong, Nature Mat. **17**, 152 (2018)
- Polarization selection rules — Vuong, 2D Mater. **4**, 011004 (2017)
- Phonon group velocity — Vuong, PRB **95**, 045207 (2017)

- EELS

  Schuster, PRB **97**, 041201 (2018)

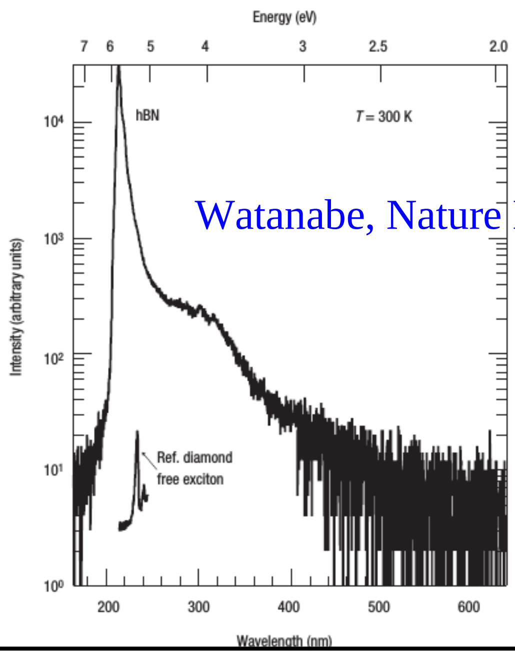


Deep UV opto-electronics

hBN = perfect candidate for deep UV

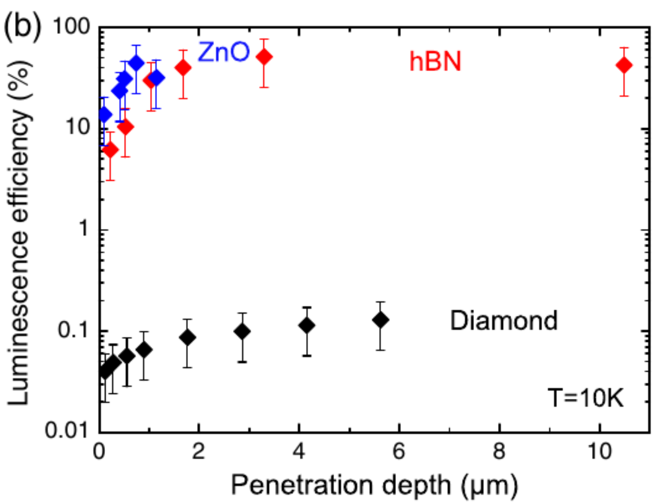
- High extraction efficiency
  (as usual for indirect semiconductors)

- High internal quantum efficiency
  VERY UNUSUAL



Watanabe, Nature Mat. **3**, 404 (2004)

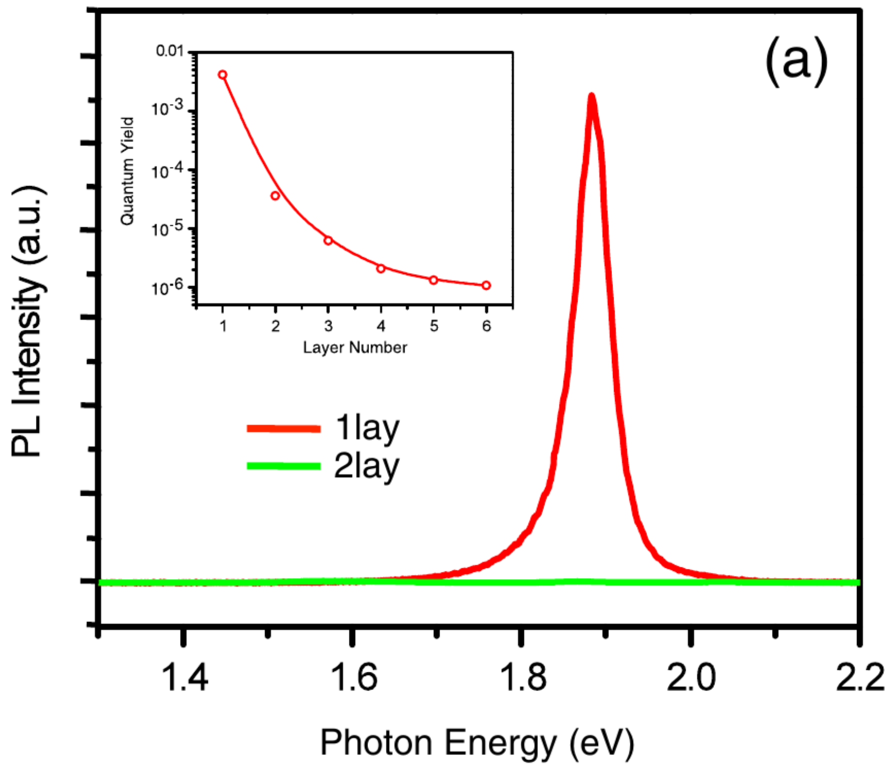
Schue, PRL **122**, 067401 (2019)



Monolayer hBN :
a direct bandgap semiconductor

Direct bandgap emission in monolayer

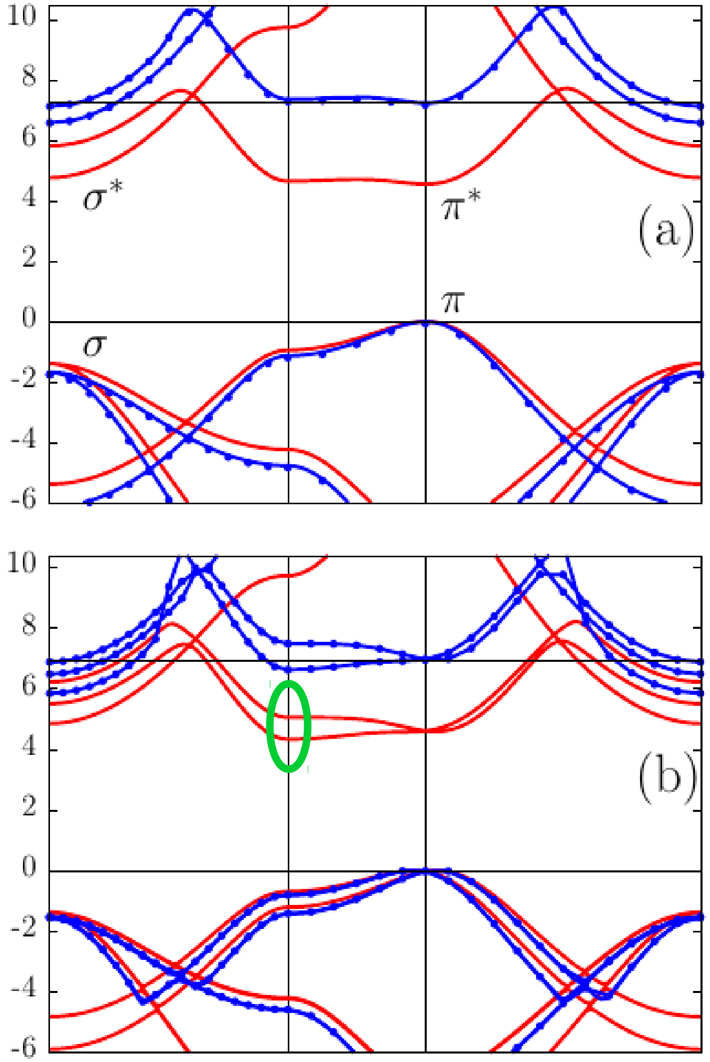
- The textbook example of MoS_2



Phys. Rev. Lett. **105**, 136805 (2010)

- Same effect is predicted in hBN !!

Electronic bandstructure vs layer number



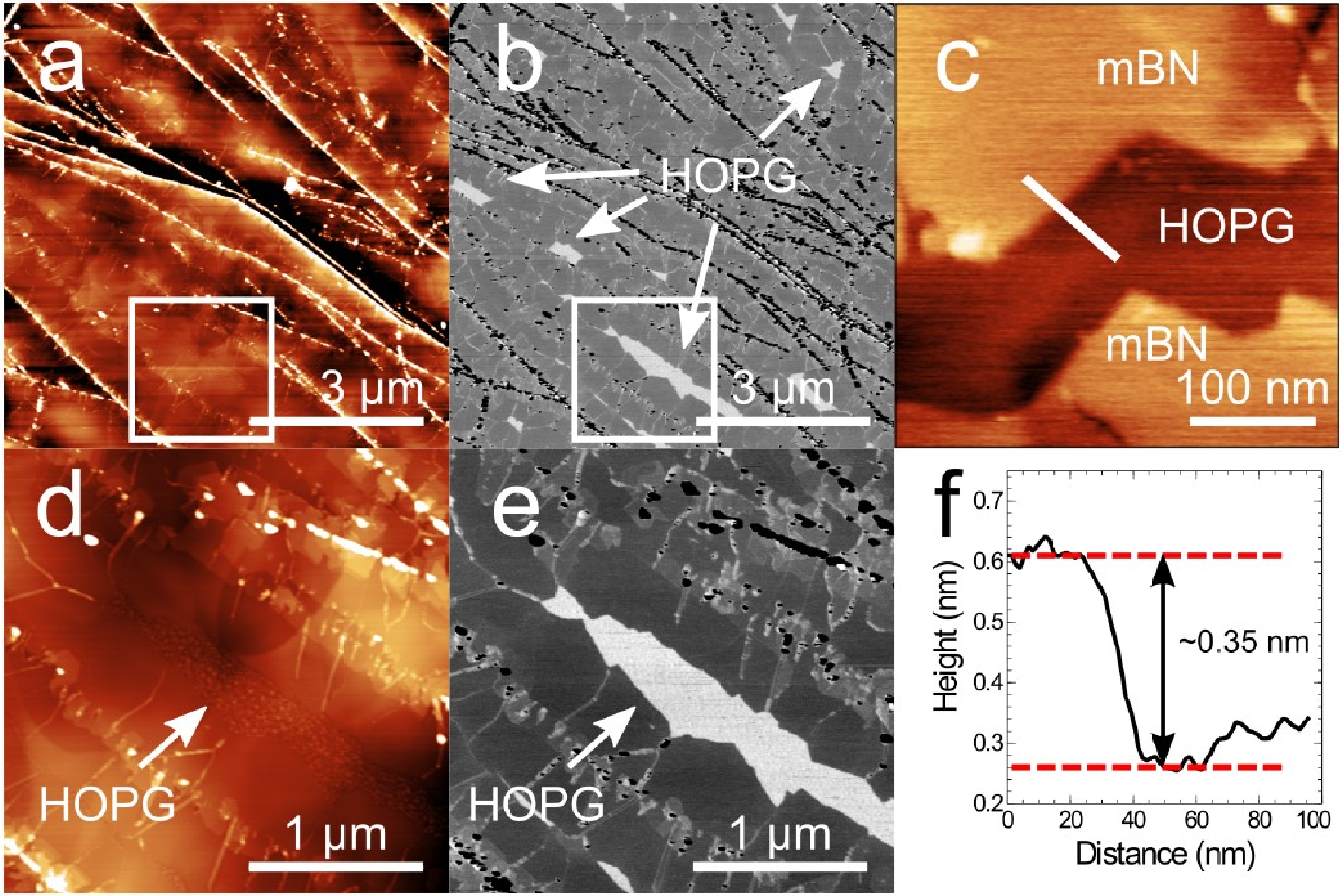
1 layer : direct bandgap

2 layers : indirect bandgap
to bulk

2D Materials **5**, 045017 (2018)

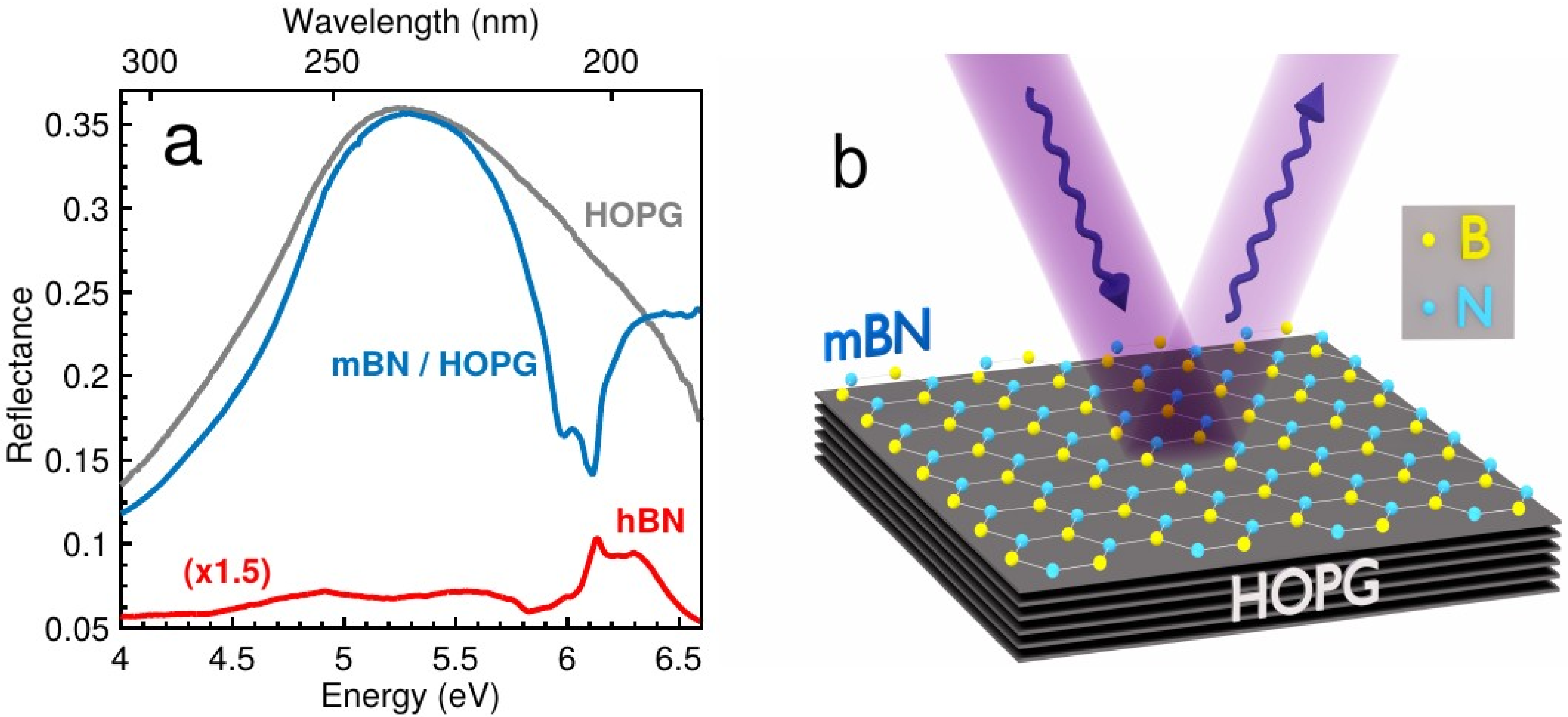
AFM in epitaxial monolayer hBN

High-temperature MBE S. Novikov (Nottingham)



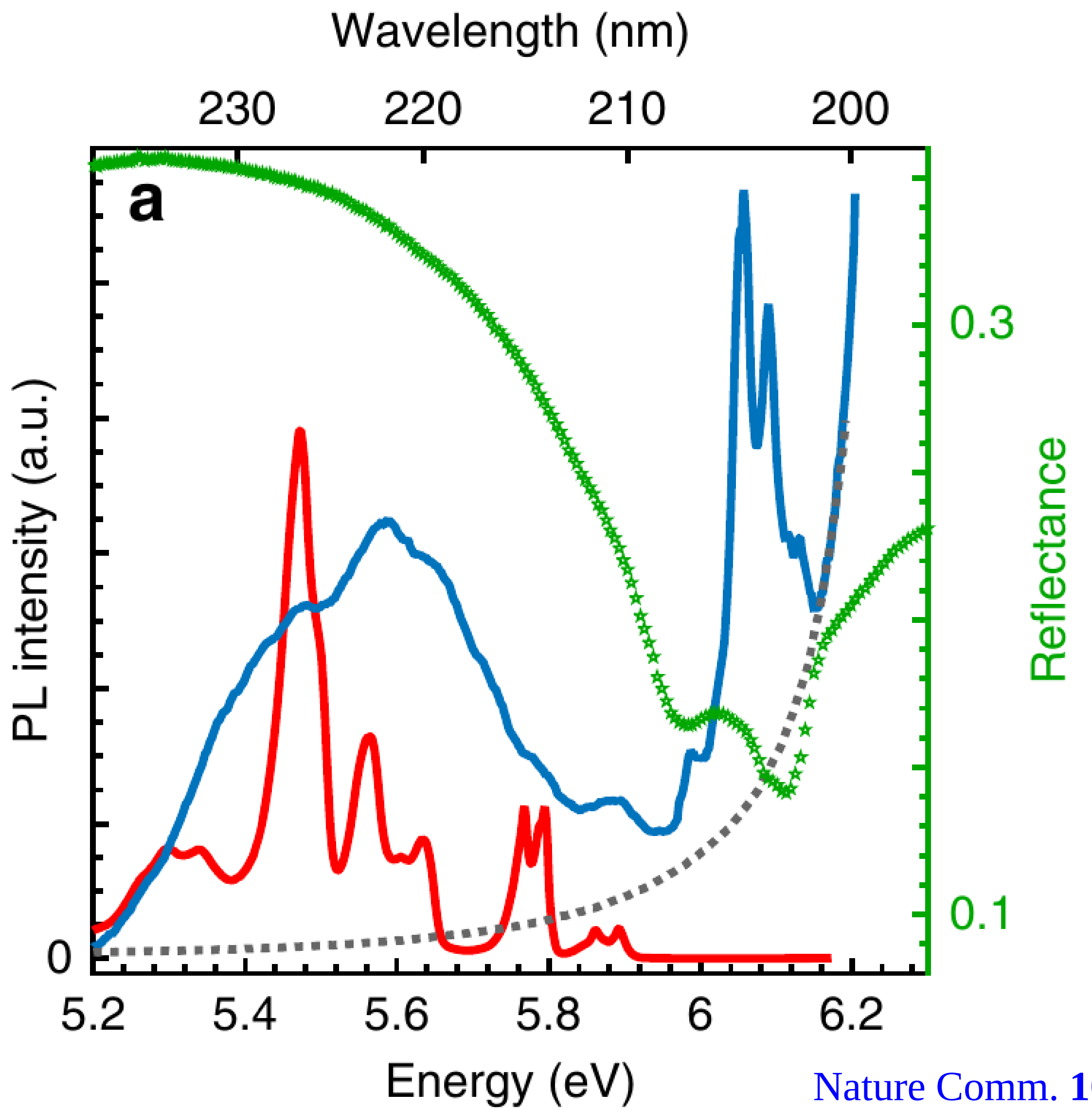
Nature Comm. **10**, 2639 (2019)

Reflectance in epitaxial monolayer hBN



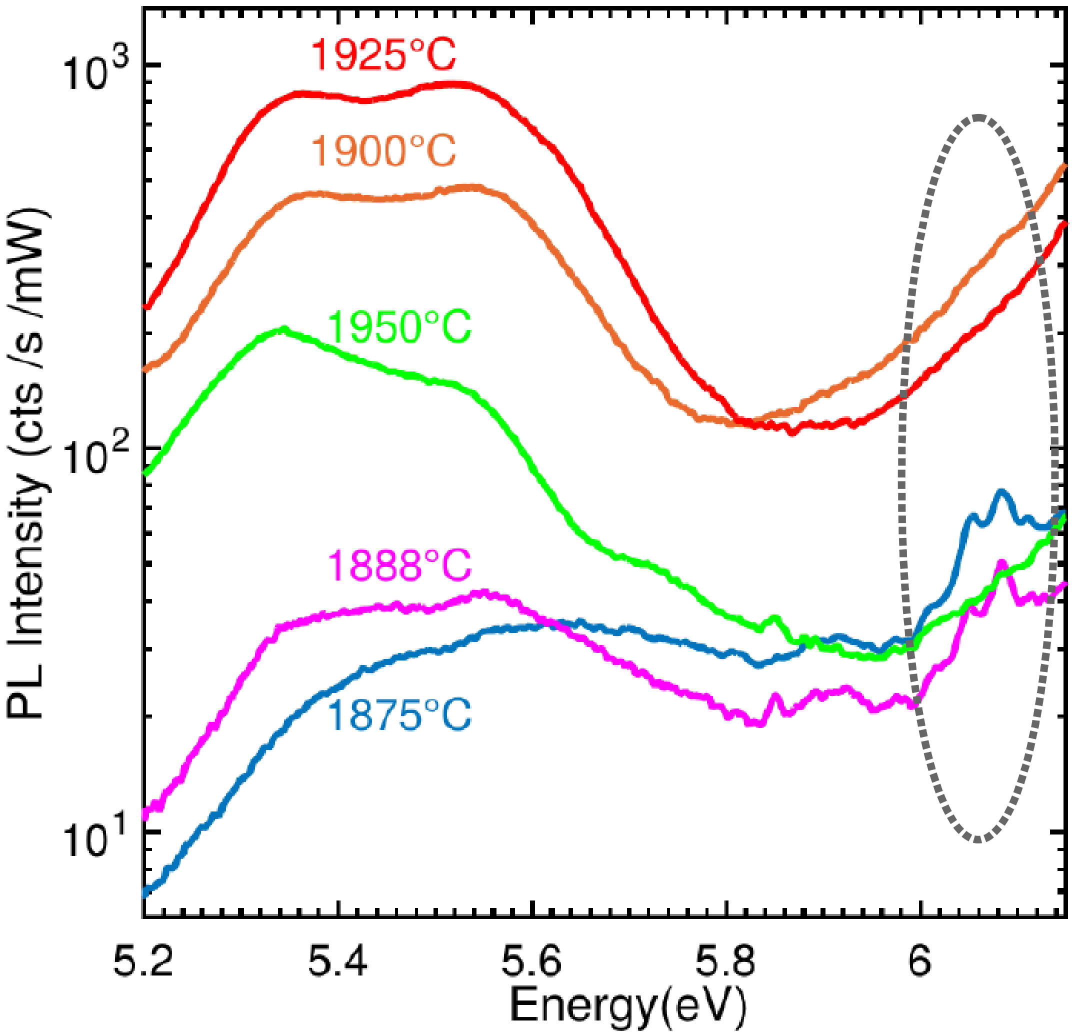
Nature Comm. **10**, 2639 (2019)

Photoluminescence in epitaxial monolayer hBN



Nature Comm. **10**, 2639 (2019)

Thickness dependence

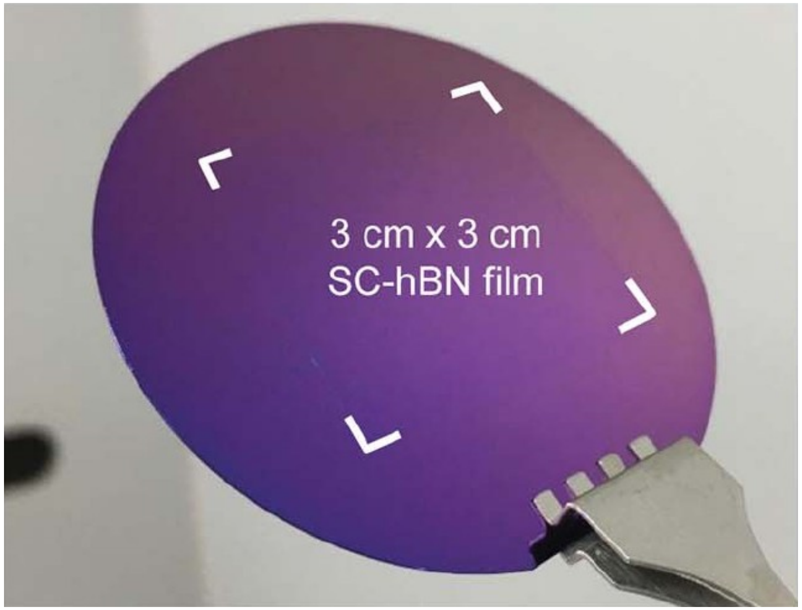


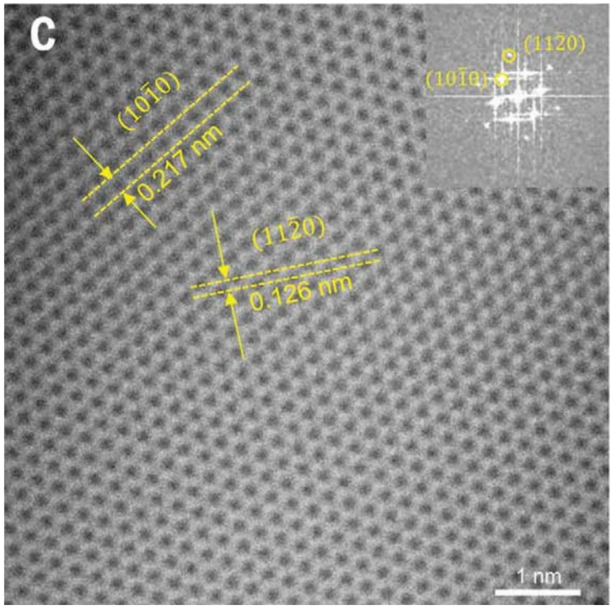
- BN coverage increases with boron-cell temperature
- Simultaneous suppression of monolayer emission

Nature Comm. **10**, 2639 (2019)

Recent breakthrough in CVD

Wafer-scale single crystal of monolayer hBN (KIST, Korea)

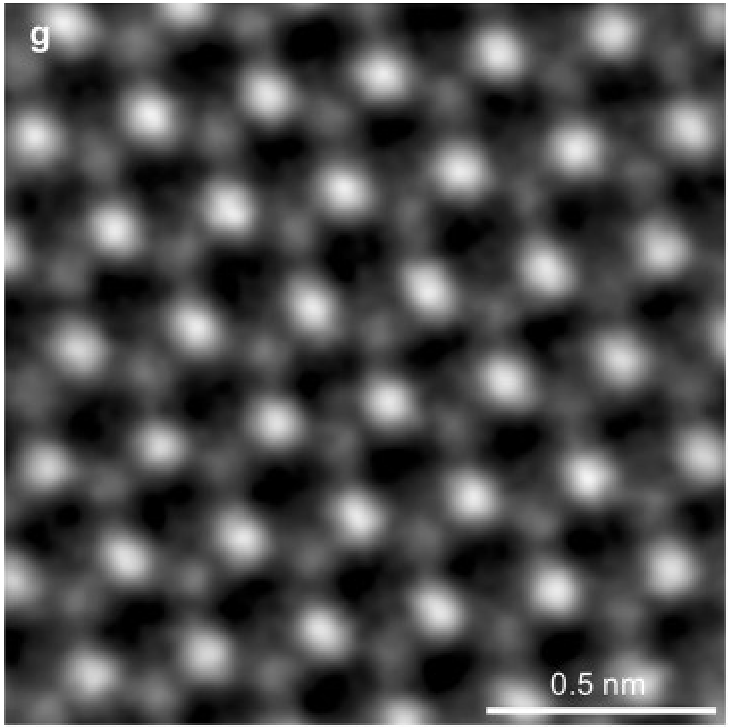




Lee, Science **362**, 817–821 (2018)

Another recent breakthrough in CVD

Wafer-scale single crystal of monolayer hBN (Peking Univ., China)



Wang, Nature **570**, 91 (2019)

Deep UV Emission in Hexagonal Boron Nitride: from Bulk to Monolayer

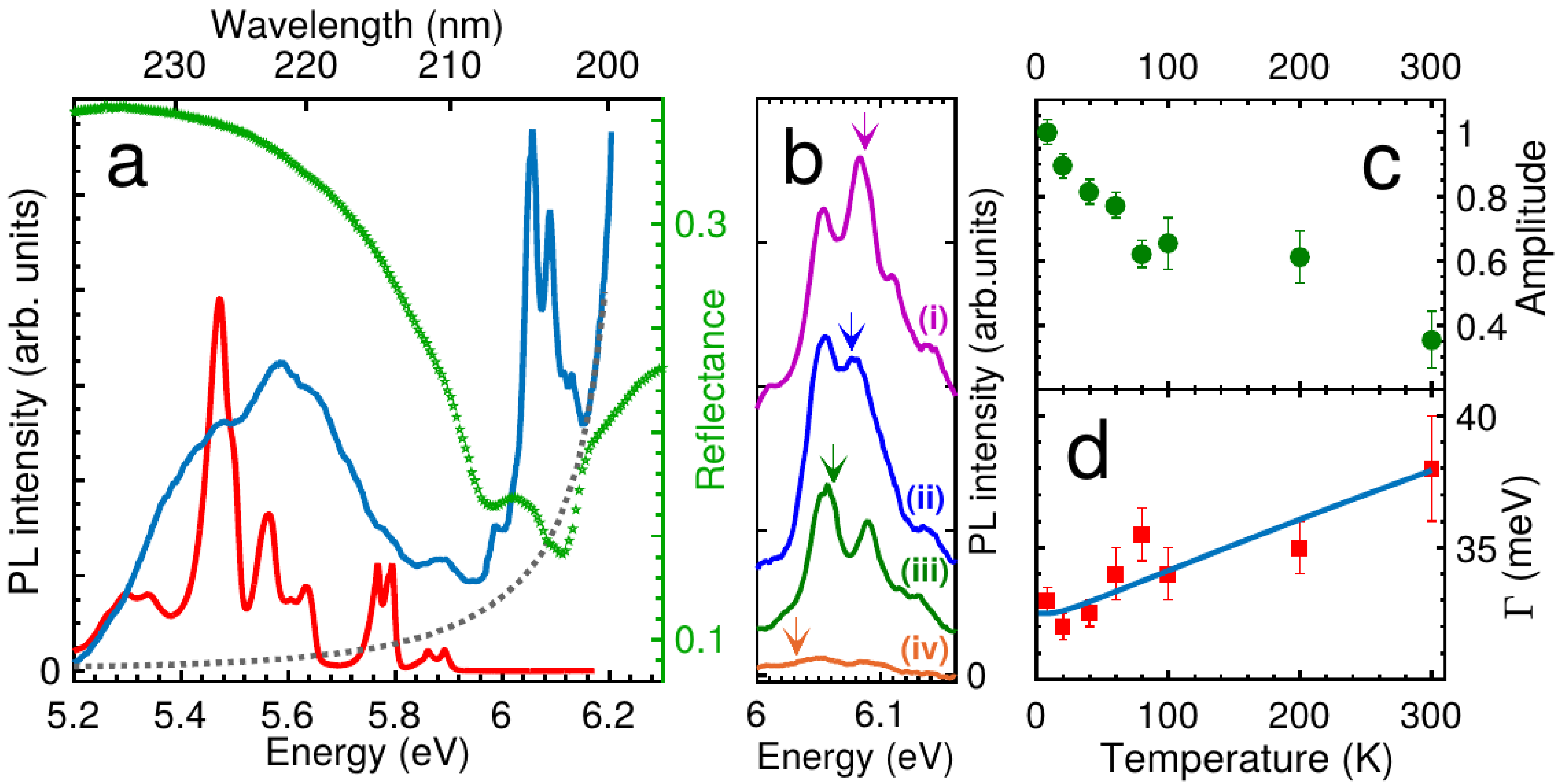
G. Cassabois

Laboratoire Charles Coulomb

CNRS / Université de Montpellier

Montpellier, France

Direct bandgap crossover in epitaxial monolayer hBN

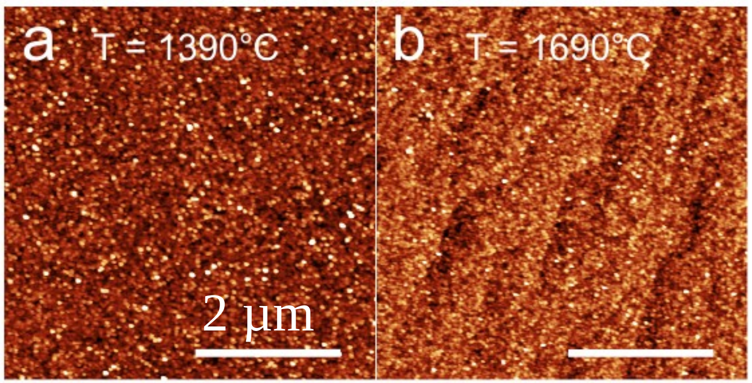


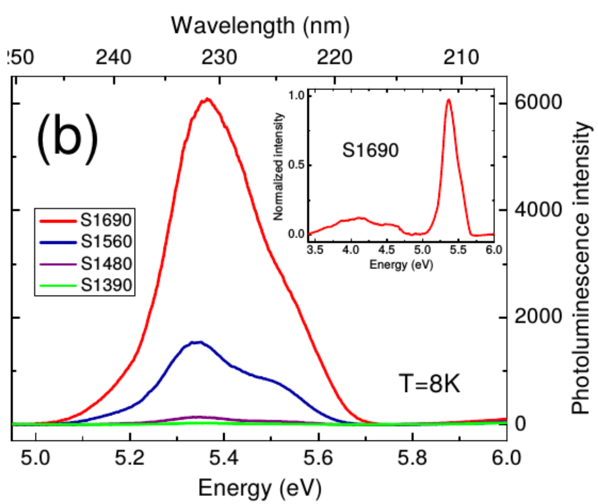
Nature Comm. **10**, 2639 (2019)

MBE

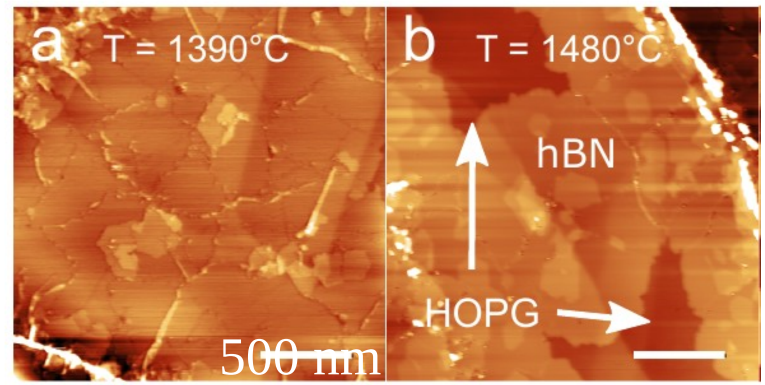
S. Novikov (Nottingham)

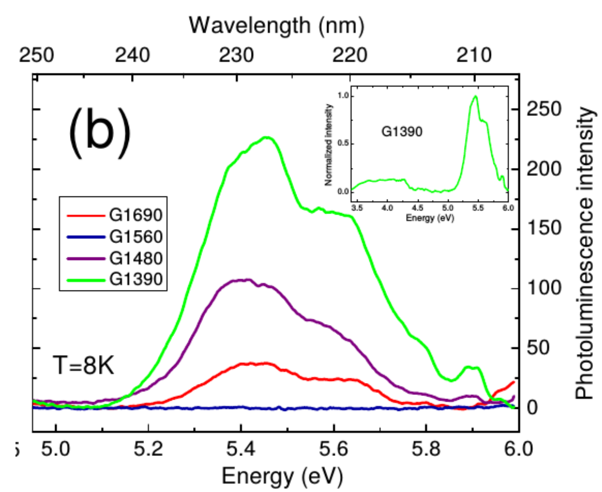
hBN on sapphire





hBN on graphite

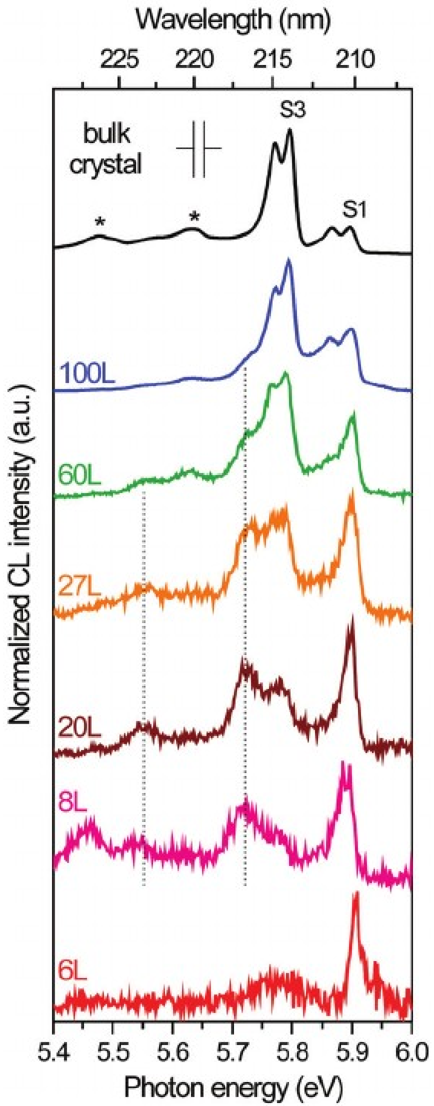




Vuong, 2D Mater. **4**, 021023 (2017)

Few-layer hBN crystals

- Cathodoluminescence down to 6 monolayers
  - Exfoliated flakes
  - Modification of phonon replica intensity
  - Dominant emission at 5.9 eV (TA phonon)

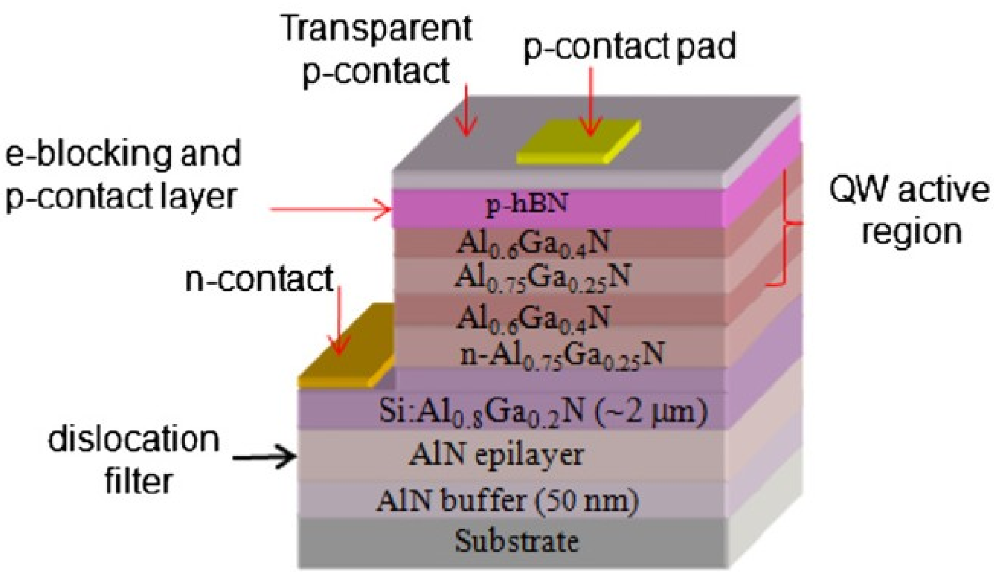


Schué, Nanoscale, 10.1039/C6NR01253A

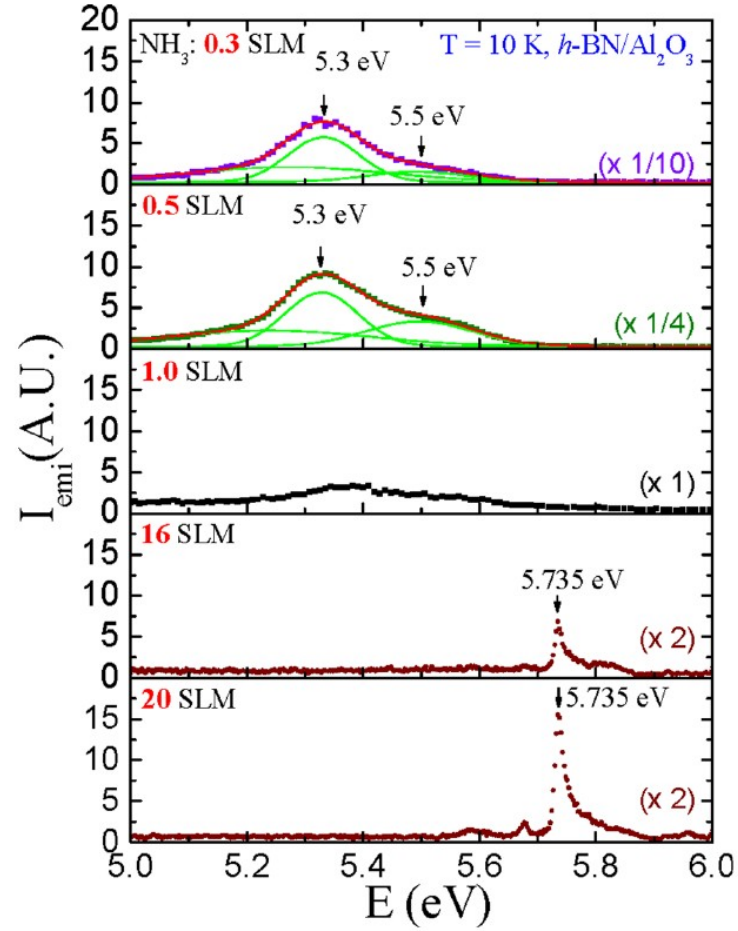
MOCVD

Pioneering work at Texas Tech (H.X. Jiang)

Deep-UV LED device



Jiang, Semicond. Sci. Technol. **29**, 084003 (2014)

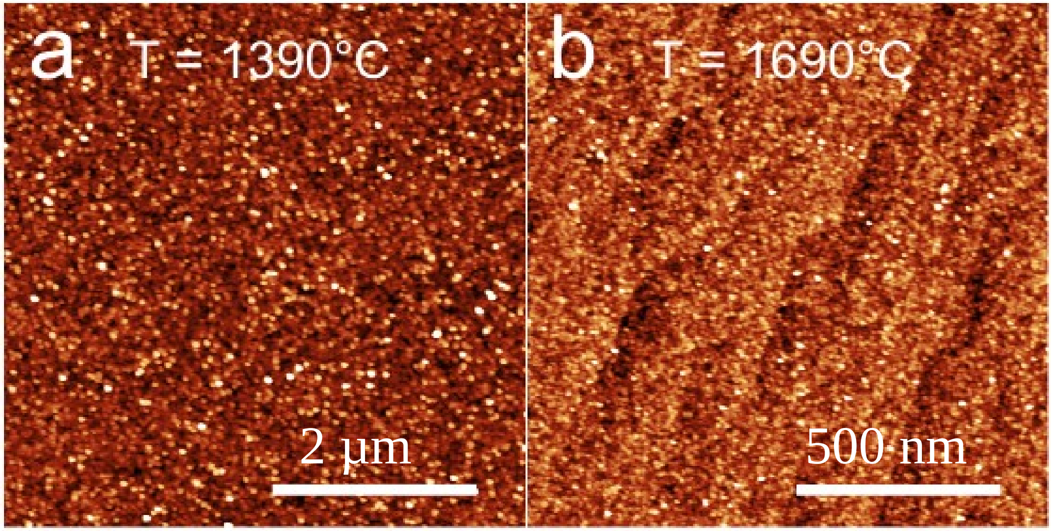


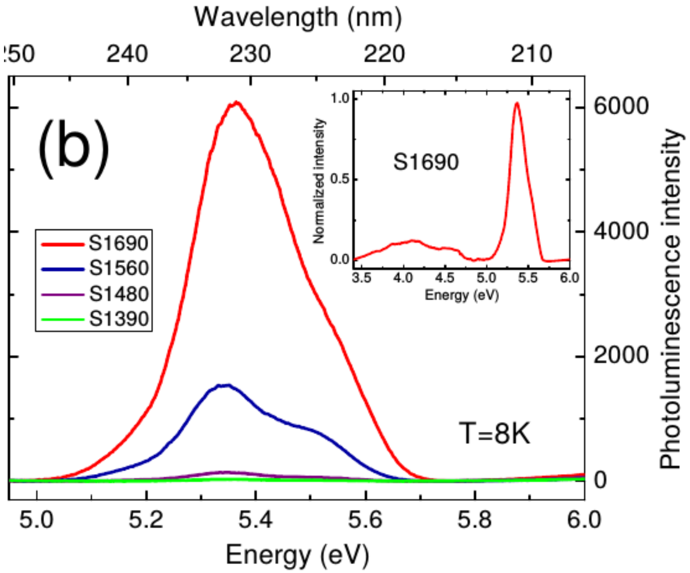
Du, APL **108**, 052106 (2016)

MBE

S. Novikov (Nottingham)

hBN on sapphire

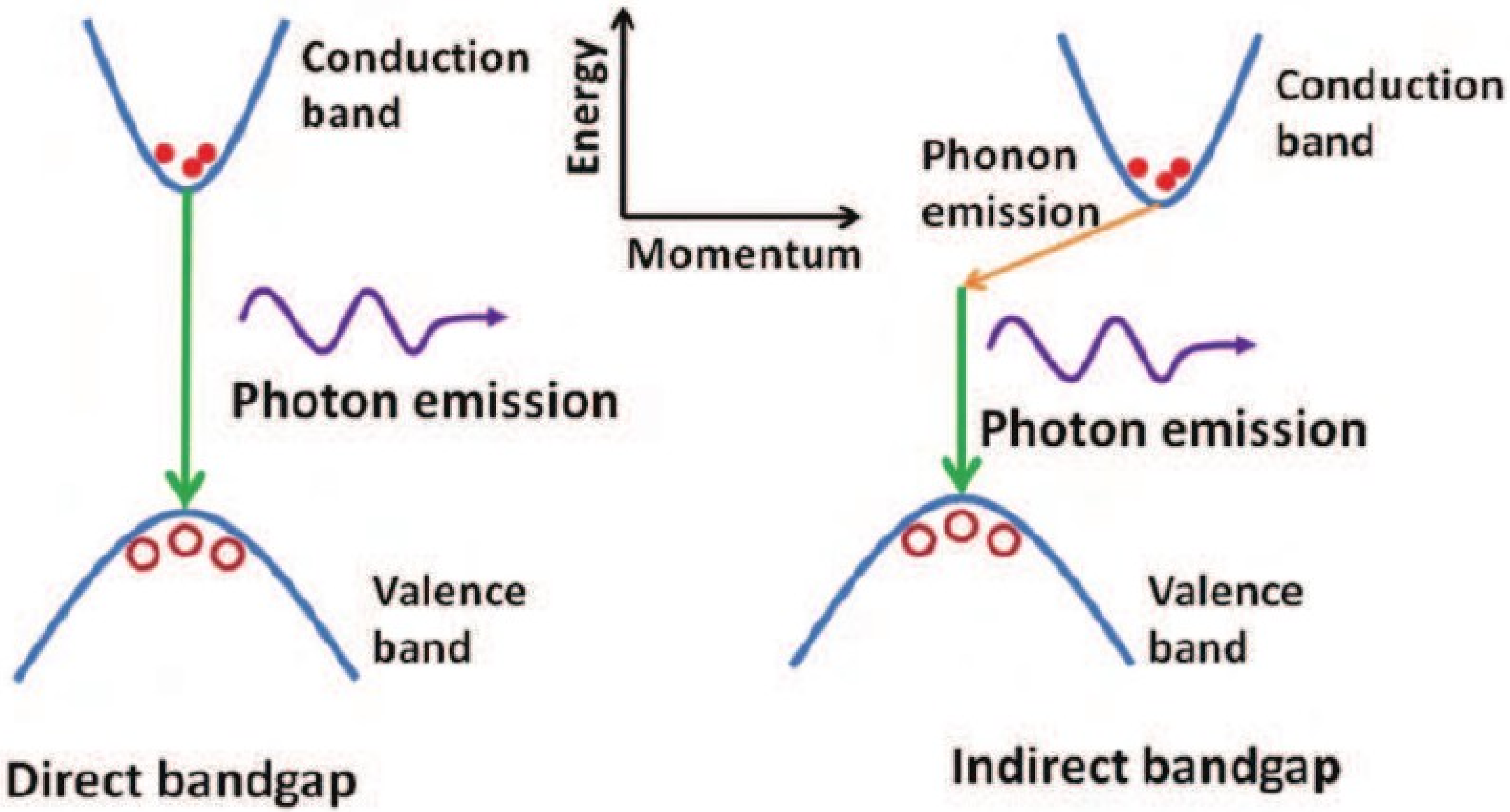




Vuong, 2D Mater. **4**, 021023 (2017)

Direct versus indirect recombination

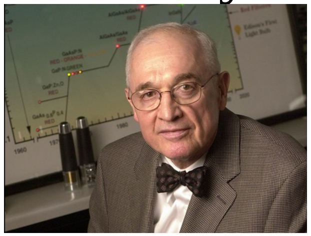
Direct | Indirect



Back in the early times of LED research

- In the 1920s : the amazing contribution of Losev (Leningrad) with the first LED based on SiC

- In the 1960s : the Holonyak work on GaAsP



at that time, the best strategy was not clear :

direct or indirect semiconductors ?

EQE=IE*IQE*EE

external quantum efficiency

injection efficiency

internal quantum efficiency

extraction efficiency

LEDs based on a bulk active region

	Direct bandgap	Indirect bandgap
internal quantum efficiency	**HIGH**	**LOW** **(phonon-assisted emission)**
extraction efficiency	**LOW** **(re-absorption)**	**HIGH**

LEDs based on a bulk active region

	Direct bandgap	Indirect bandgap
internal quantum efficiency	**HIGH**	**LOW** **(phonon-assisted emission)**
extraction efficiency	~~**LOW** **(re-absorption)**~~	**HIGH**

In the 1980s, came the revolution of quantum wells

High IQE in hBN

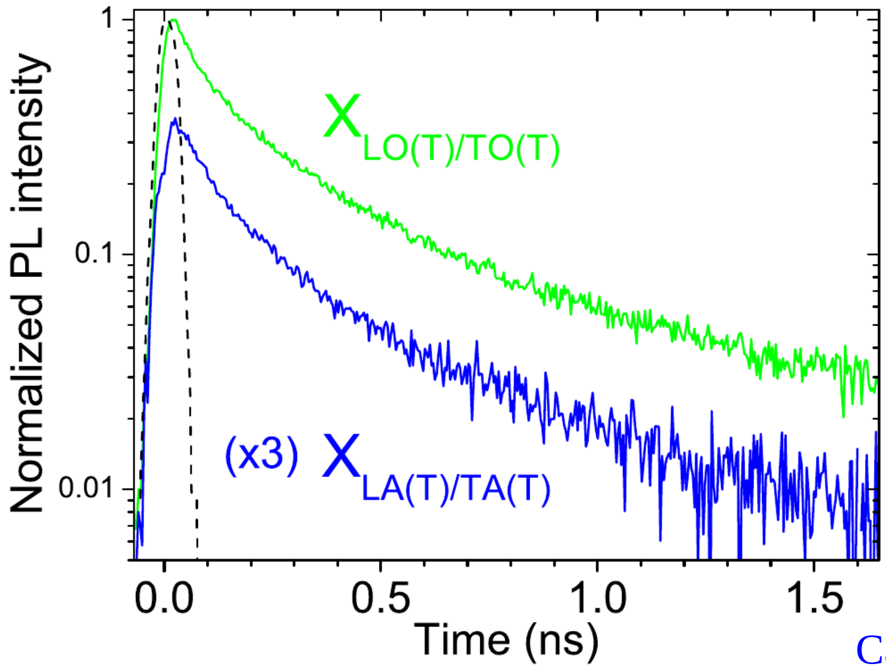
- $$IQE = \frac{\gamma_{rad}}{\gamma_{rad} + \gamma_{nrad}}$$

  - Direct semiconductors : $\gamma_{rad} \gg \gamma_{nrad}$
  - Indirect semiconductors : $\gamma_{rad} \ll \gamma_{nrad}$
  - In hBN : $\gamma_{rad} \gtrsim \gamma_{nrad}$

Phonon-assisted recombination fast enough to bypass non-radiative processes

Recombination dynamics

- time-resolved PL measurements at the energy of the optical and acoustic phonon replicas



200 ps lifetime

Cassabois, PRB **93**, 035207 (2016)

- identical decays reflecting the dynamics of the *iX* indirect exciton reservoir

Progress of Theoretical Physics, Vol. 20, No. 1, July 1958

Theory of Line-Shapes of the Exciton Absorption Bands

Yutaka TOYOZAWA

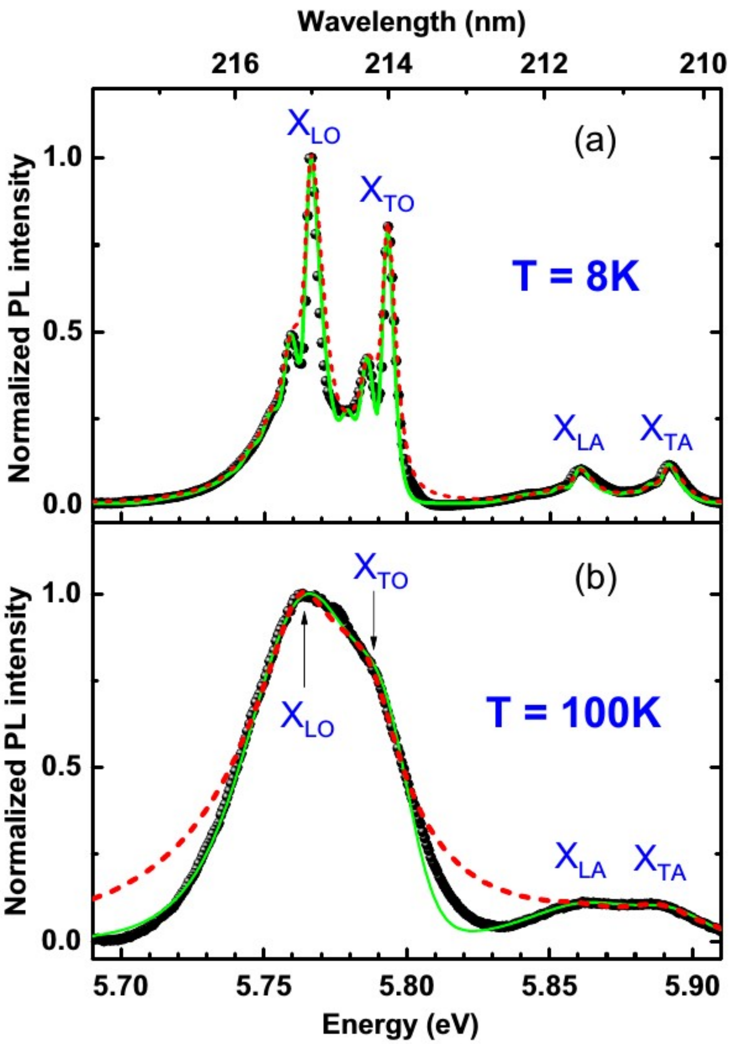
Research Institute for Fundamental Physics, Kyoto University, Kyoto

(Received April 12, 1958)

A general theory of line-shapes of the exciton absorption bands is developed with the help of generating function method. When the exciton-lattice coupling is weak, and the exciton effective mass is small, the absorption band is of a Lorentzian shape, provided that the temperature T is not too high. The half-value width H is given by the level broadening of the optically produced $\boldsymbol{K}=0$ exciton due to lattice scattering, so that it is proportional to T except at low temperatures. If the coupling is strong, or the exciton effective mass is large, or the temperature is very high, the absorption band is expected to be of a Gaussian shape, and H is proportional to $\sqrt{T}$. The mutual influence of adjacent absorption bands is also discussed; it causes the asymmetry and repulsion of the components as temperature rises.

Strong coupling	Weak coupling
Gaussian profile + width increasing as $\sqrt{T}$	Lorentzian profile + width increasing as T

Gaussian lineshape

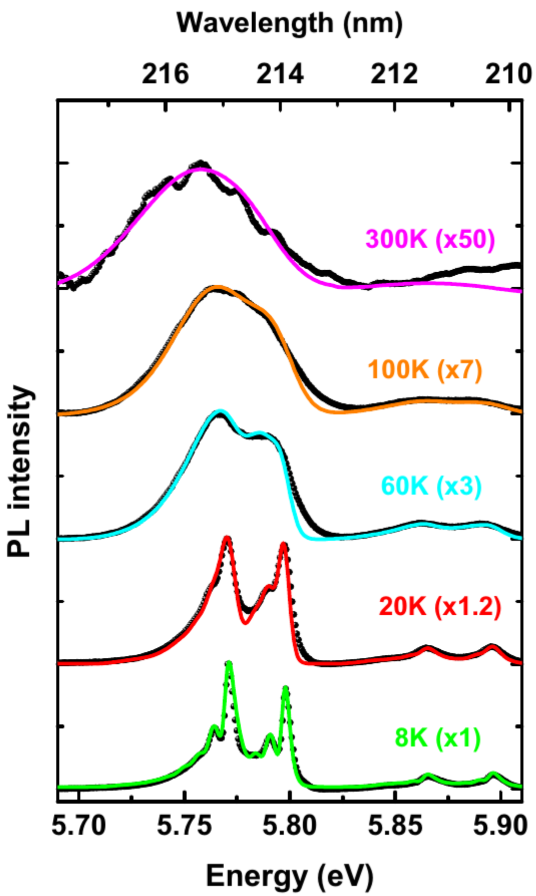


Gaussian profile

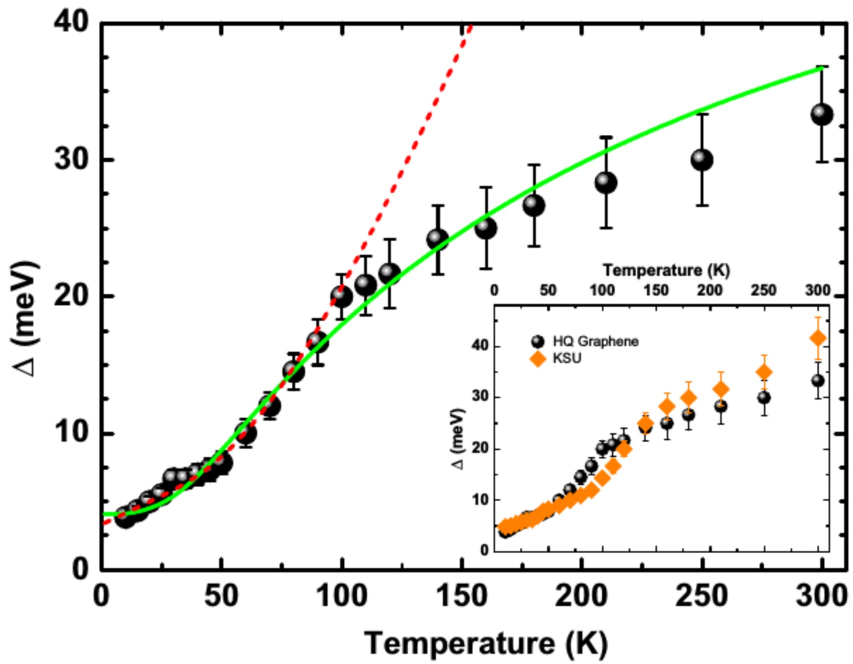
- at low temperature
- AND at high temperature

Vuong, PRB **95**, 201202(R) (2017)

Thermal broadening

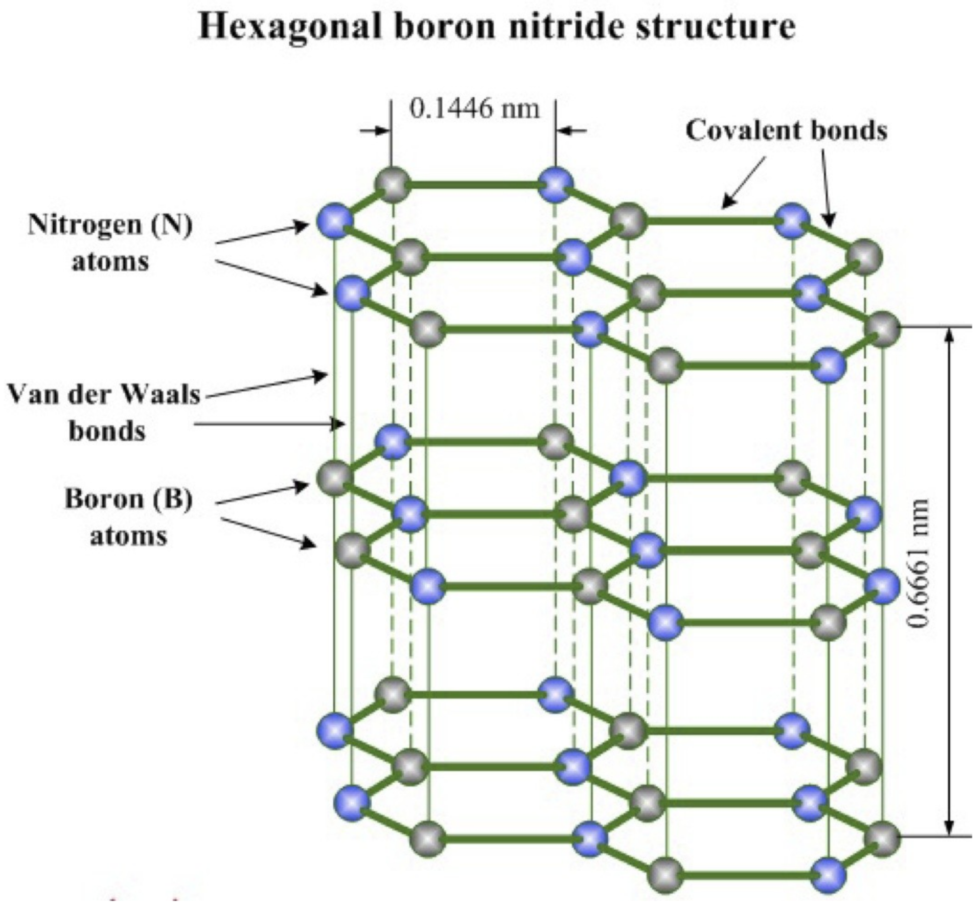


width increasing as $\sqrt{T}$

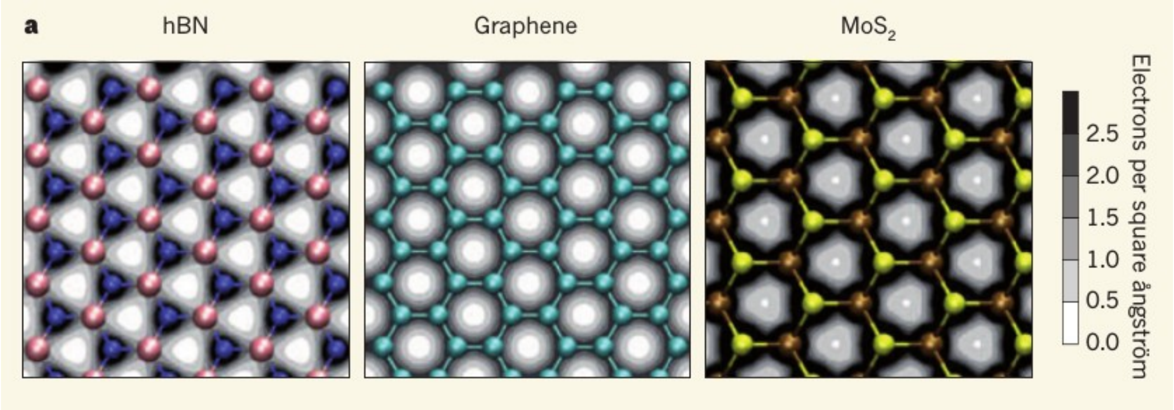


Vuong, PRB **95**, 201202(R) (2017)

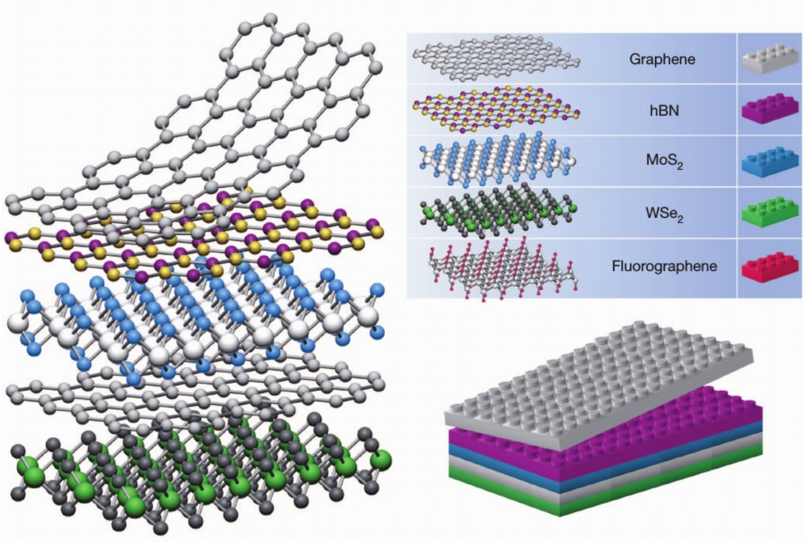
“White graphite”



Beyond graphene

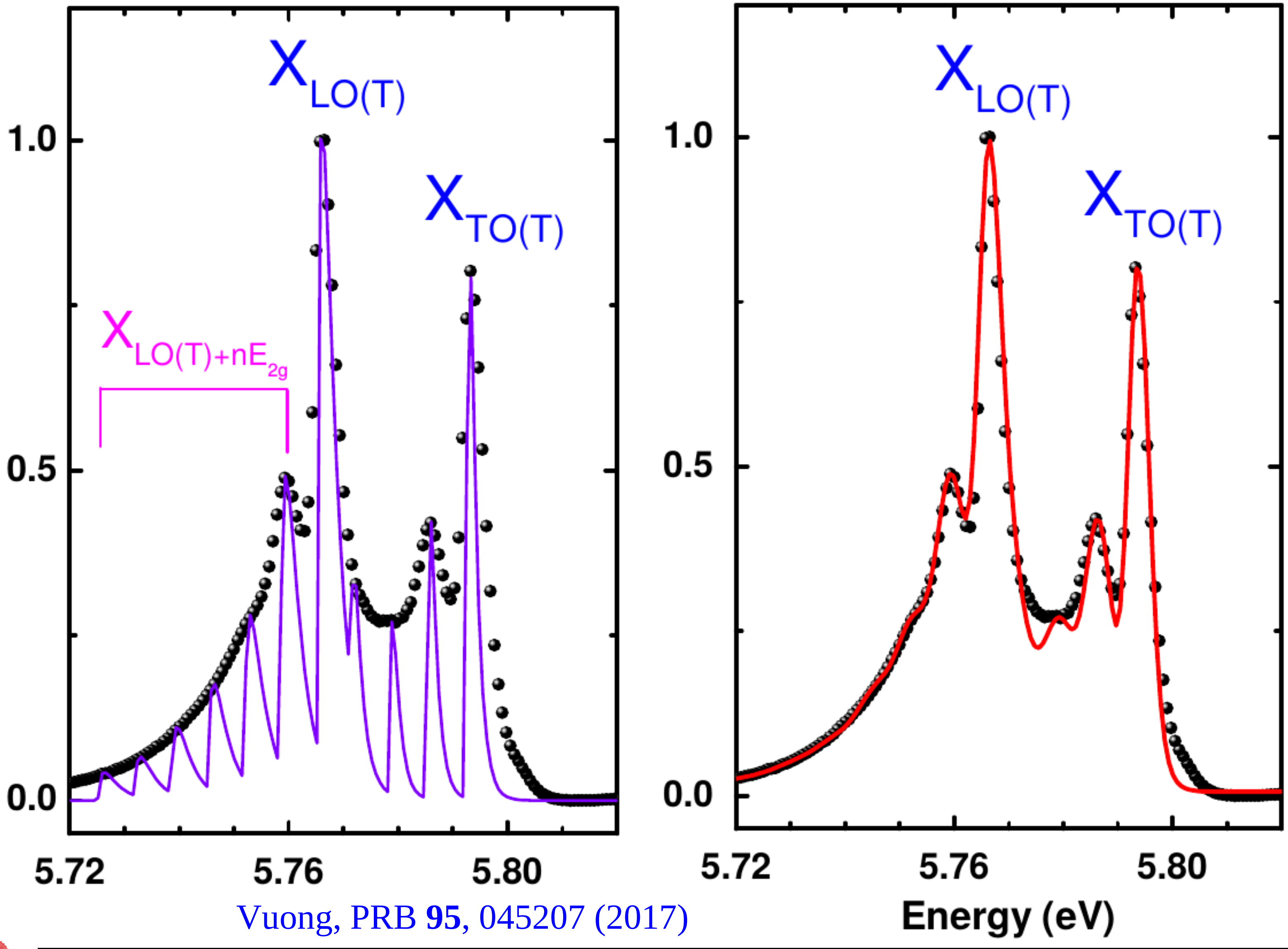


Van der Waals heterostructures



Geim, Nature **499**, 419 (2013)

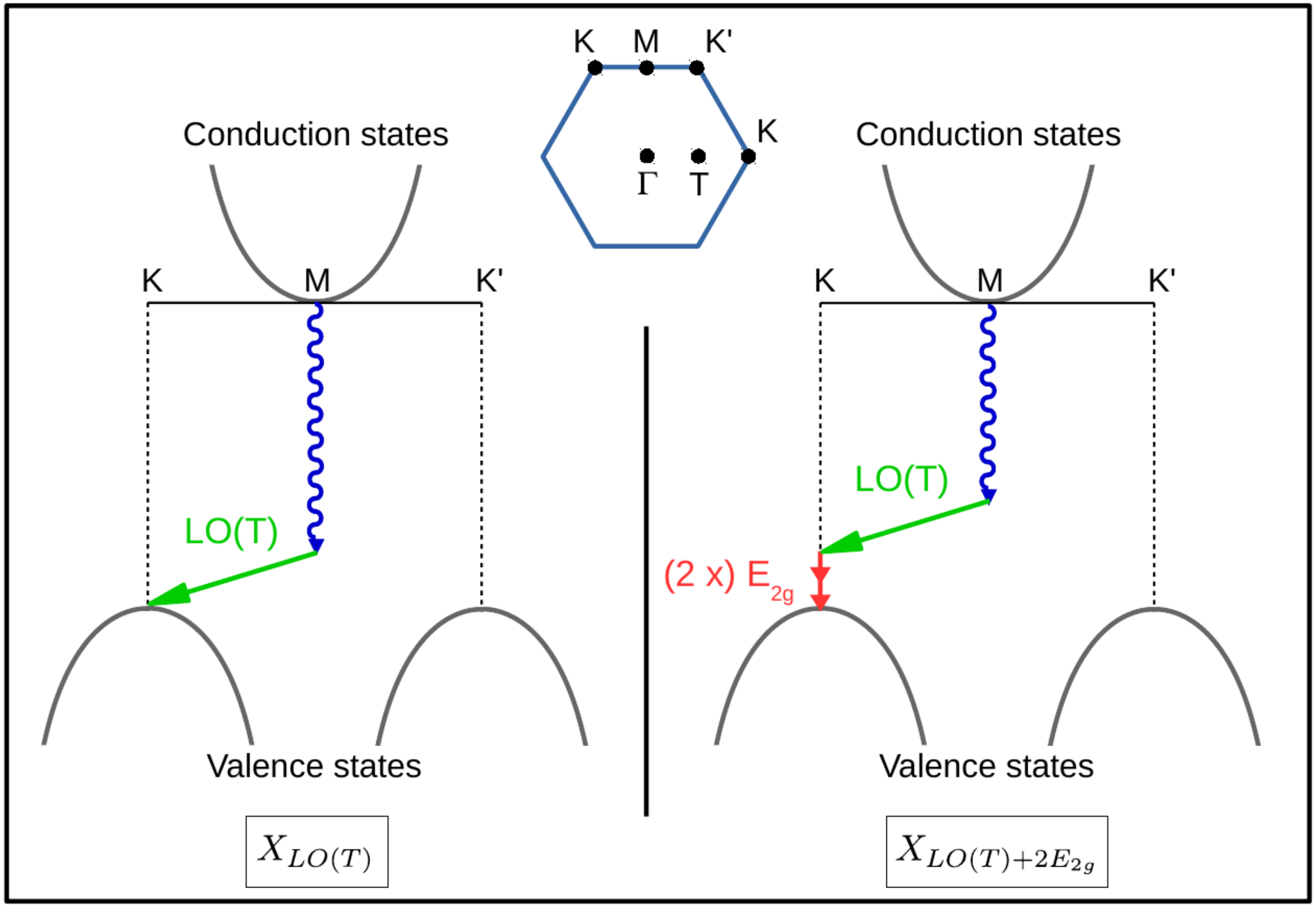
Raman overtones



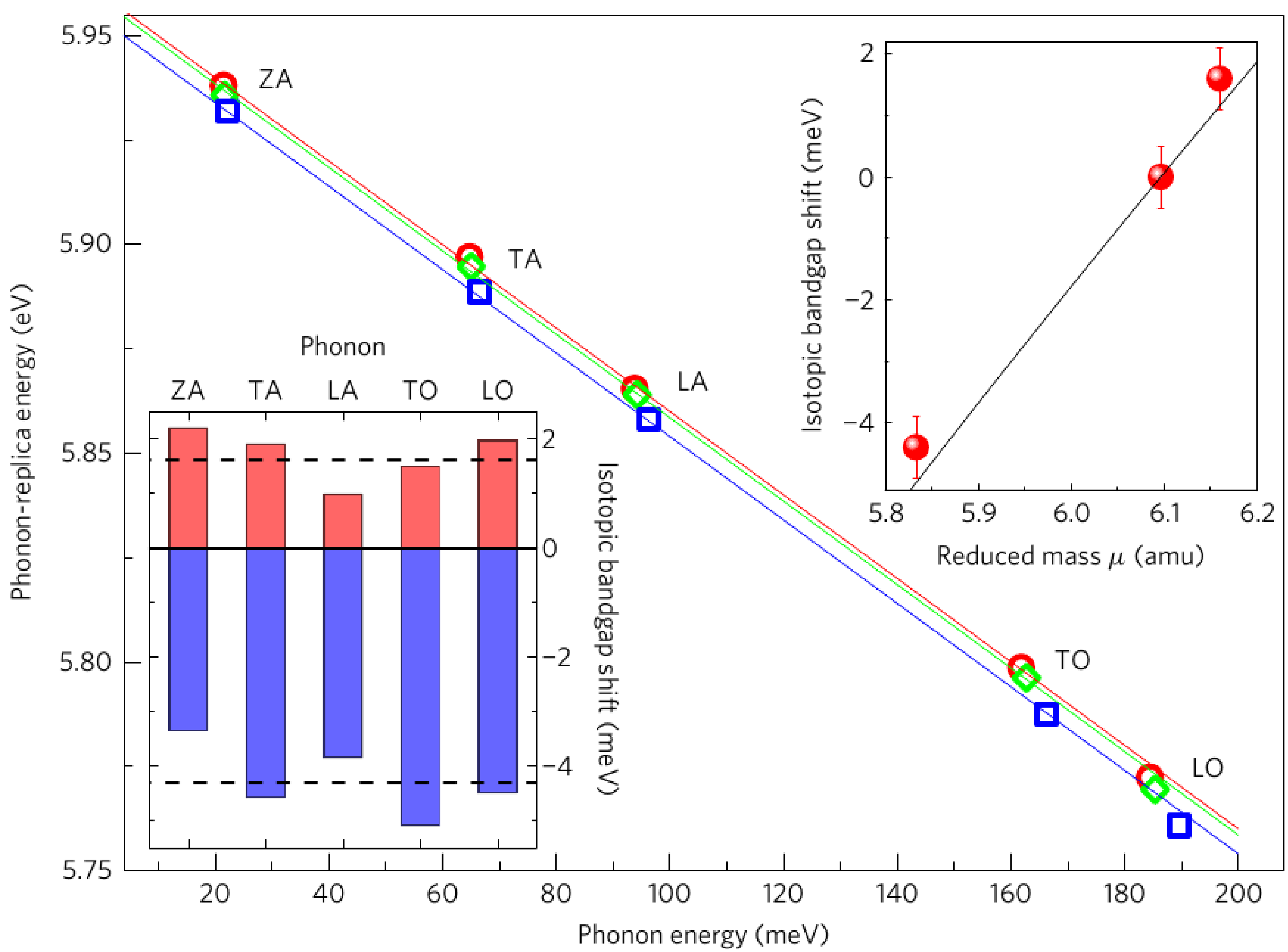
Vuong, PRB **95**, 045207 (2017)

High-order phonon-assisted processes

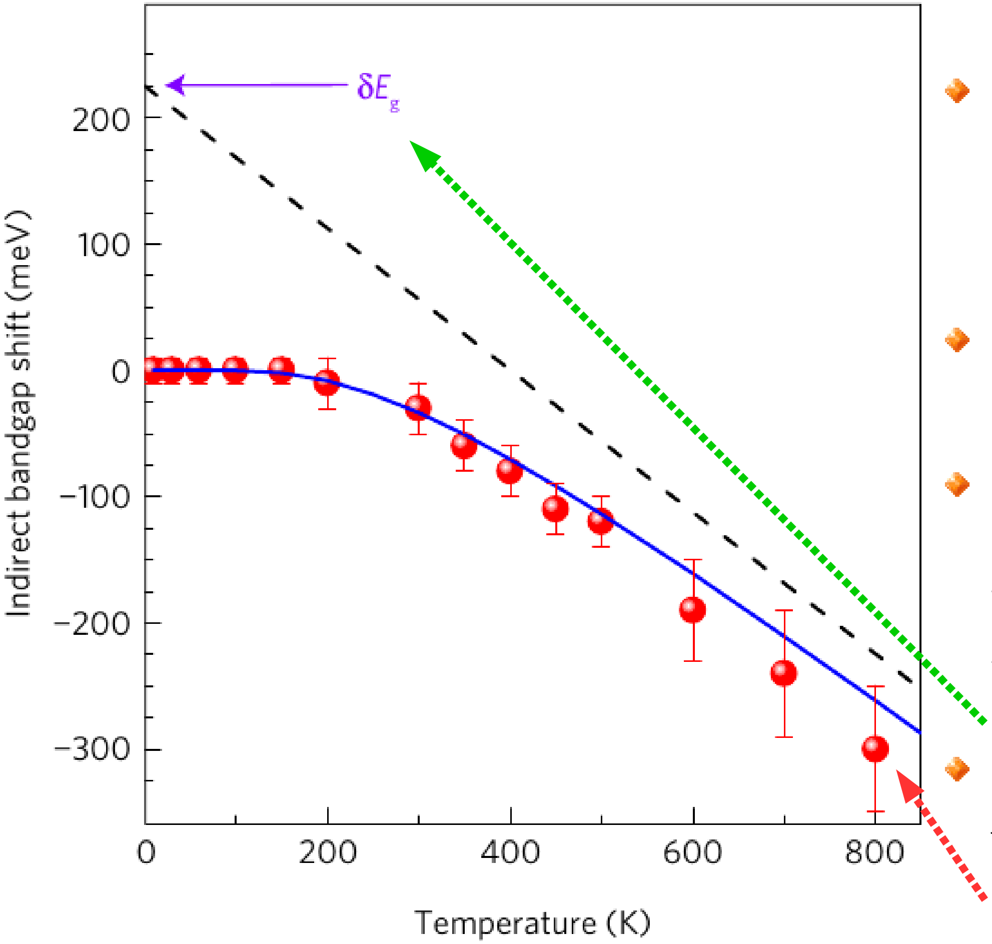
- low-energy Raman-active mode @ zone center
- no momentum change



Isotopic tuning of phonon replicas

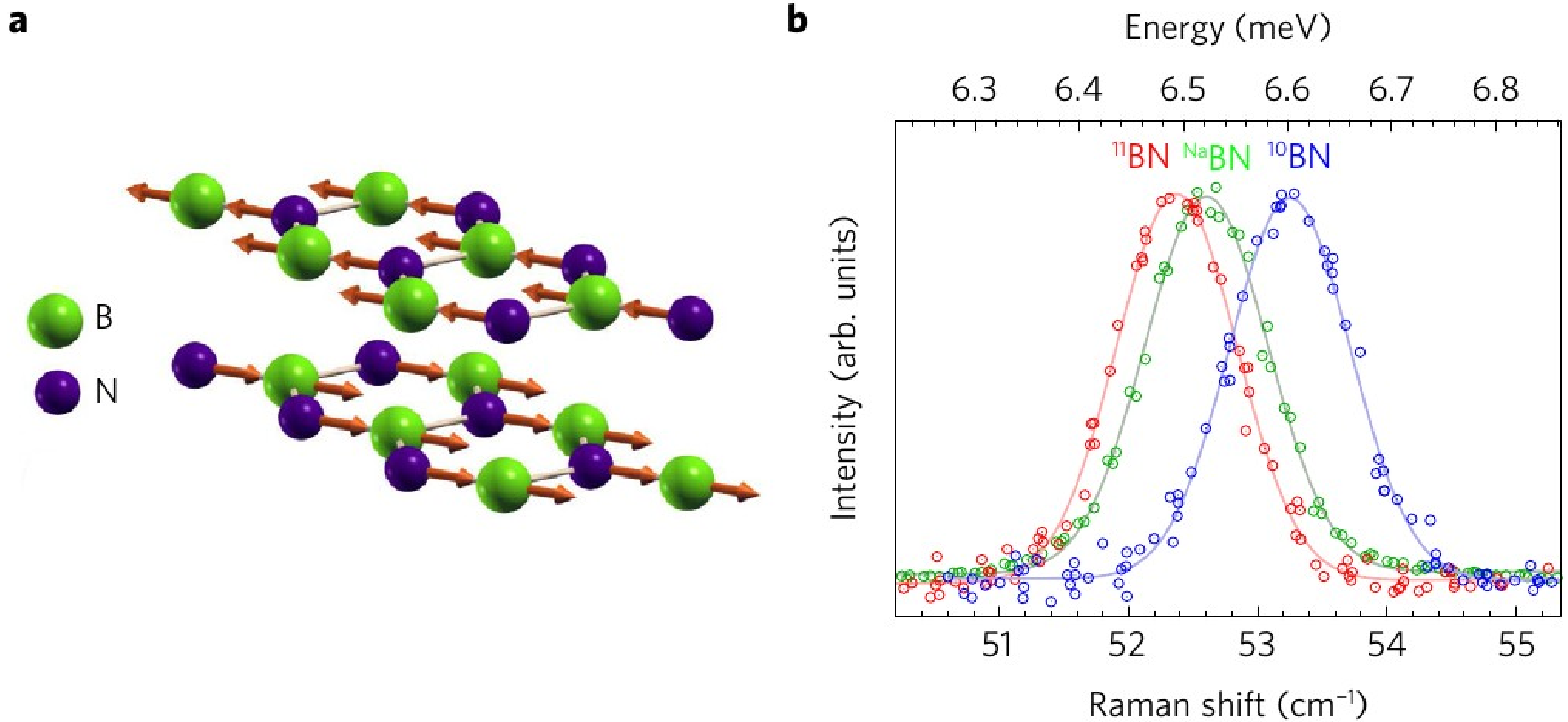


Bandgap renormalization



- Isotope-dependent bandgap renormalization δE_{gap}
- 6 meV change from ^{10}BN to ^{11}BN
- δE_{gap} in ^{Na}BN = single fitting parameter in isotopic tuning of phonon replicas
- 225 meV-value in fair agreement with temperature-dependent data from JAP **115**, 53503 (2014)

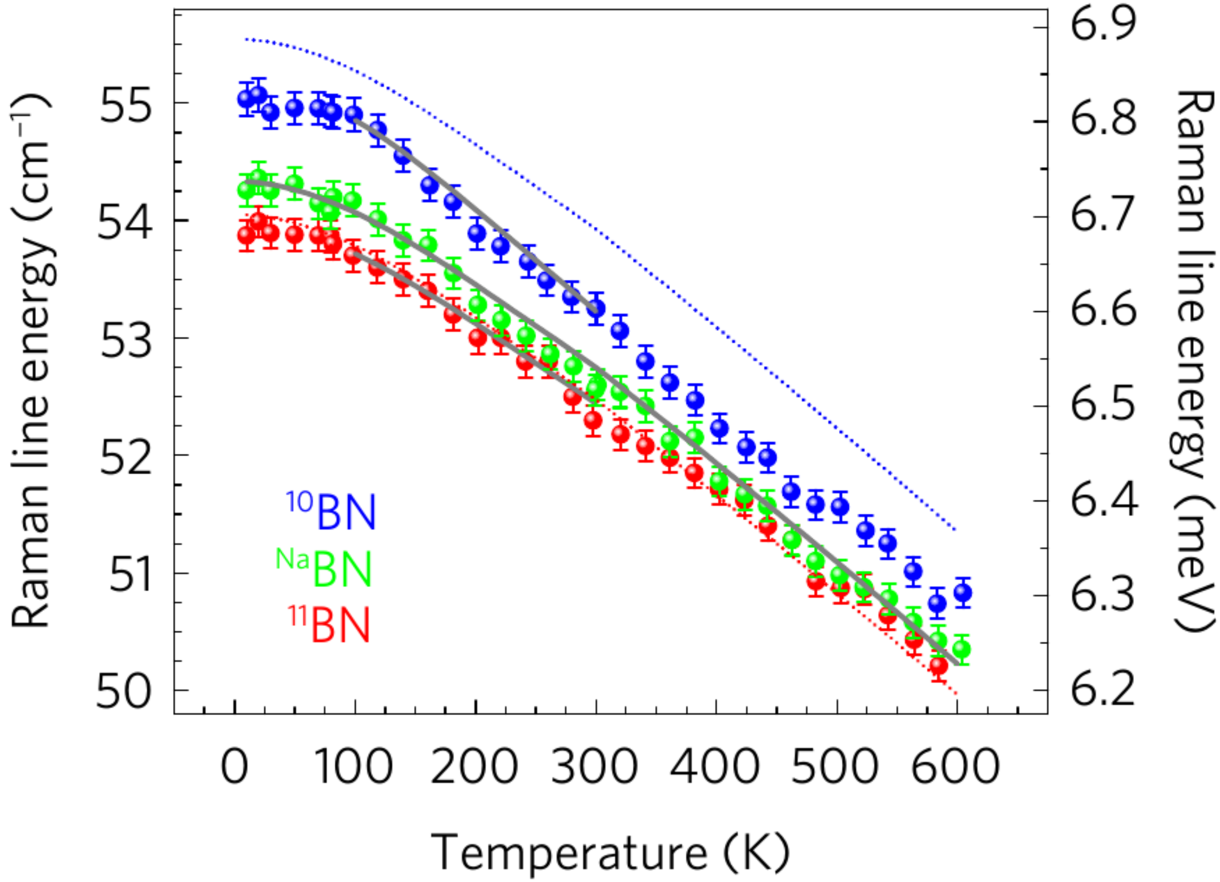
Interlayer shear mode



- Raman-active E_{2g} mode of low energy
- High-resolution Raman spectra around 50 cm^{-1} !

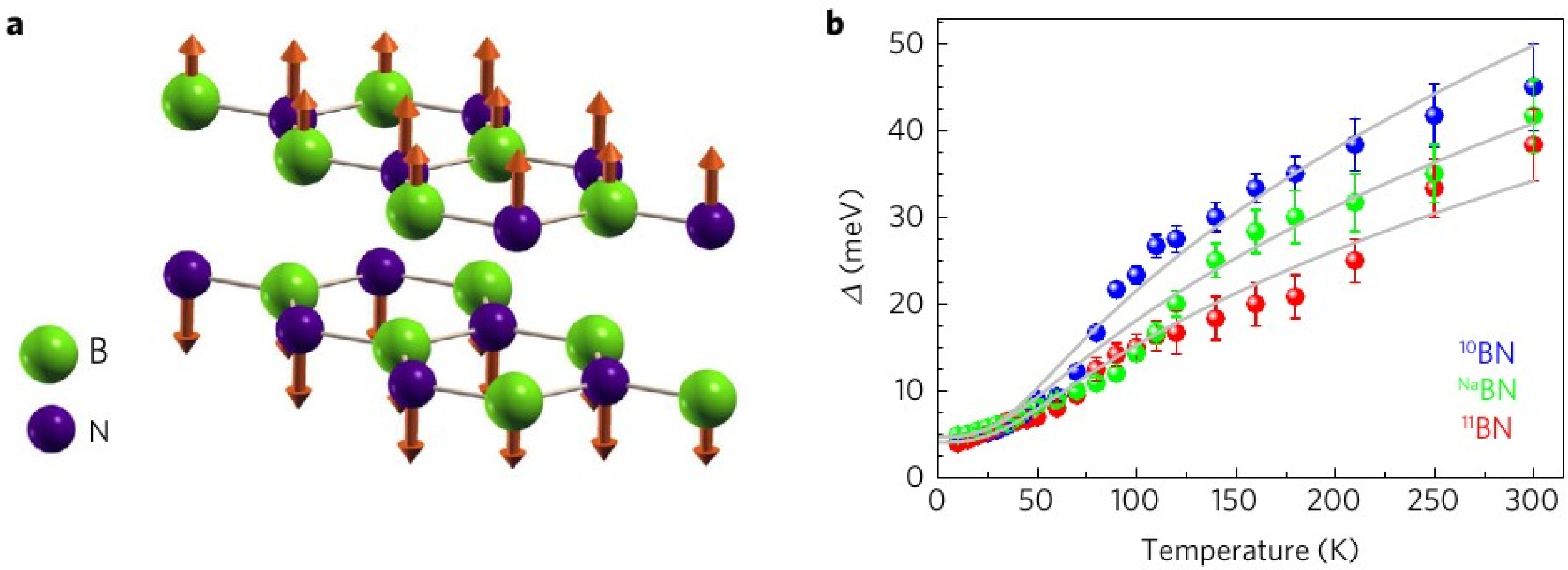
The lower the B mass, the higher the phonon energy : again, BUT…

Isotope-dependent thermal shift



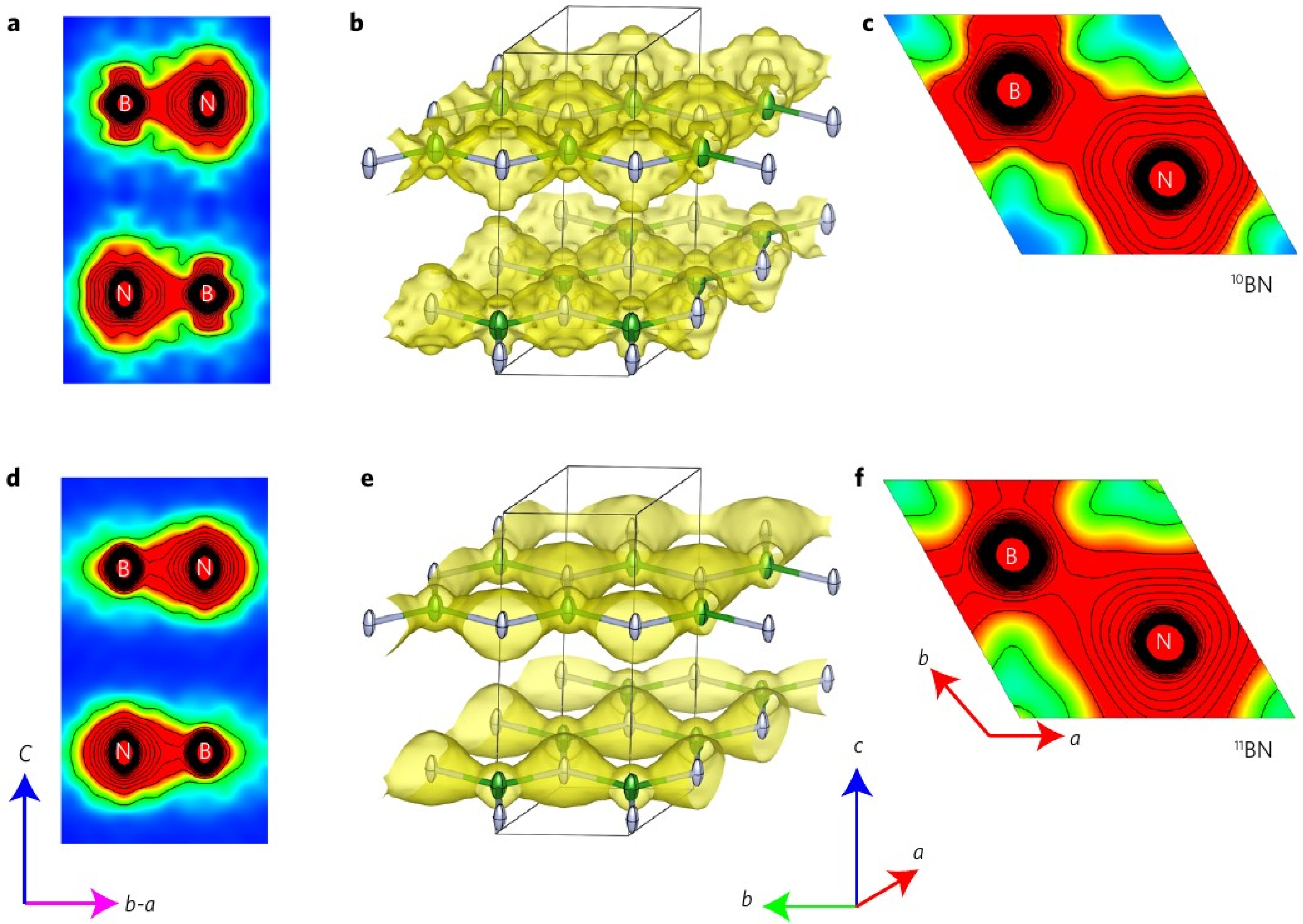
- **Isotope-dependent** temperature dependence !
- $E \propto 1/c^p$ with *c* the interlayer distance ; p depends on isotope

Interlayer breathing mode

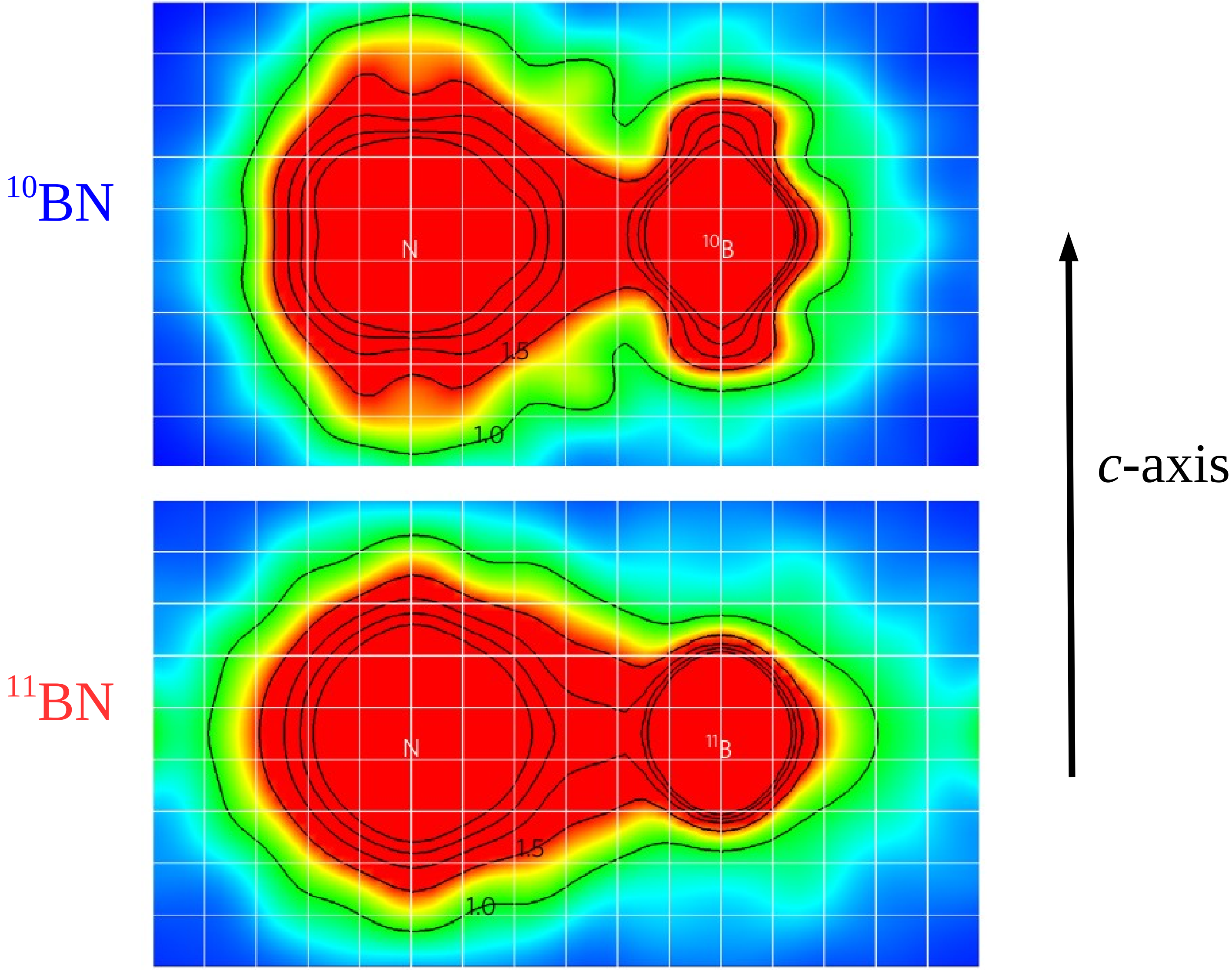


- IR and Raman inactive phonon : silent B_{1g} mode
- Silent but driving the PL thermal broadening
  (PRB **95**, 201202 (2017))
- **Isotope-dependent** phonon broadening

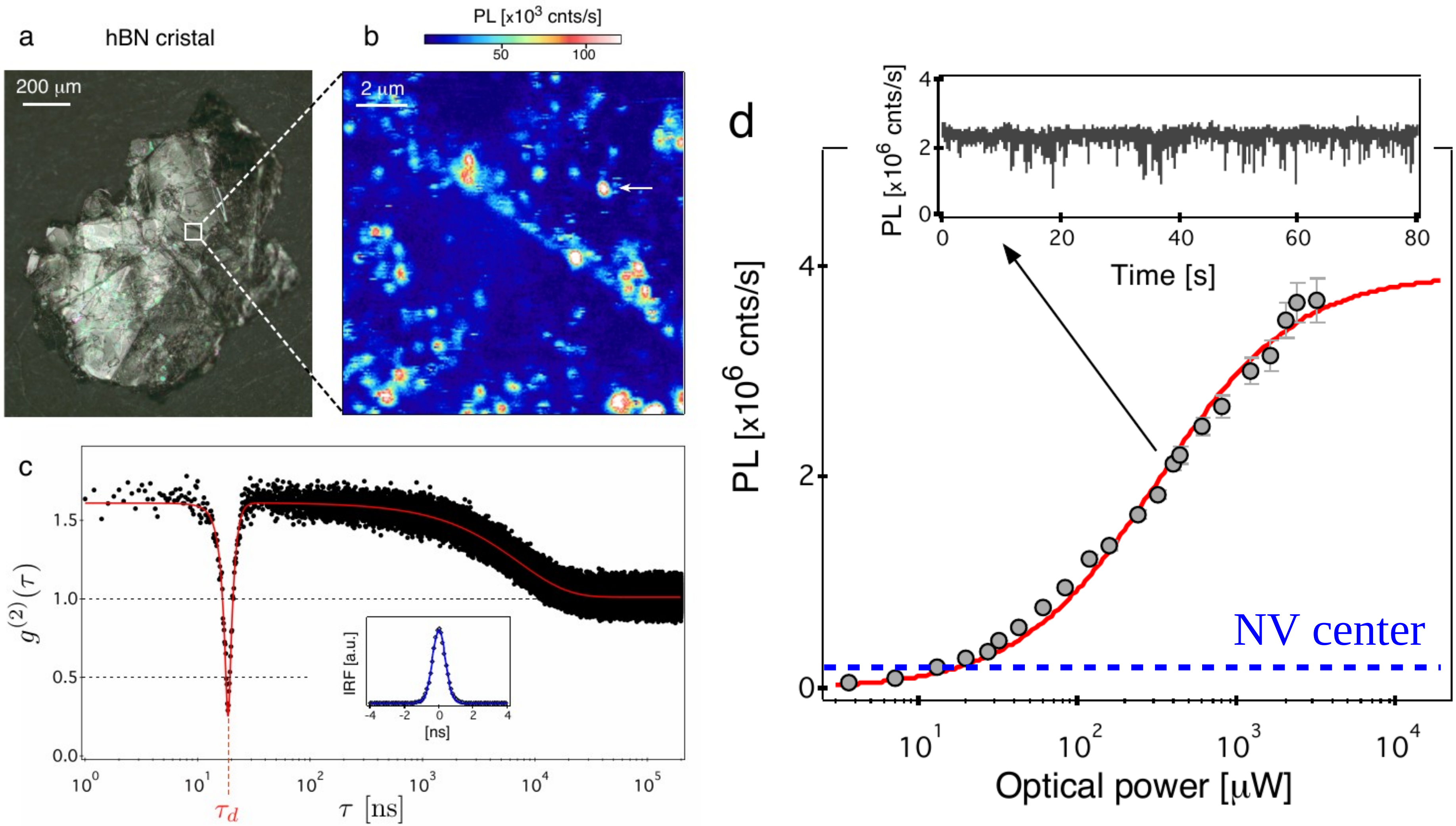
X-ray diffraction experiments



Isotope-dependent electronic distribution



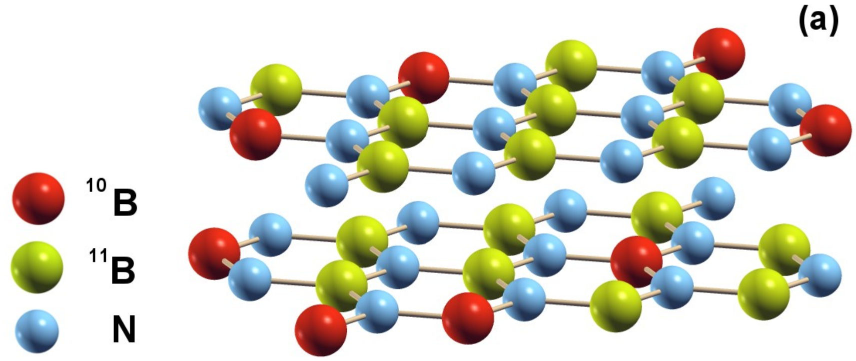
Point defects in hBN as bright single-photon sources



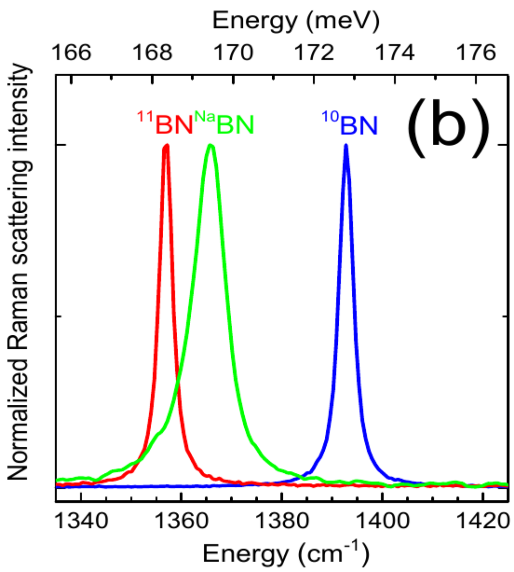
Phys. Rev. B **94**, 121405(R) (2016)

Isotopic purification

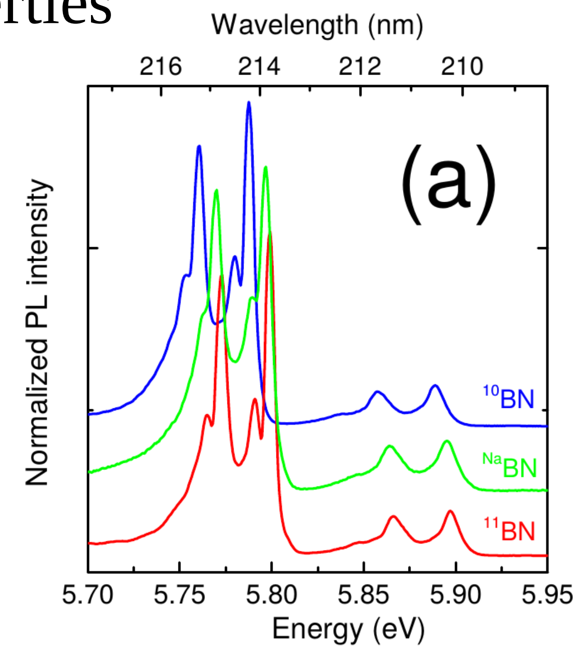
- Isotopic mixture



- Impact on vibrational and electronic properties



submitted for publication



Applications

Powder

« white graphite »

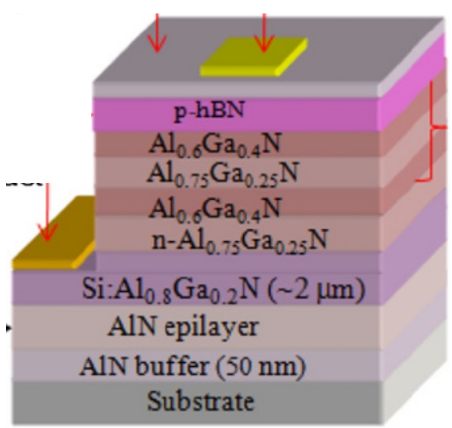
- many industrial applications
- solid lubricant, thermal coating, additive in plastics, cosmetics...

Polycrystals

Watanabe, Nature Mater. 3, 404 (2004)

- deep-UV light emission
- graphene substrate
- Van der Waals heterostructures

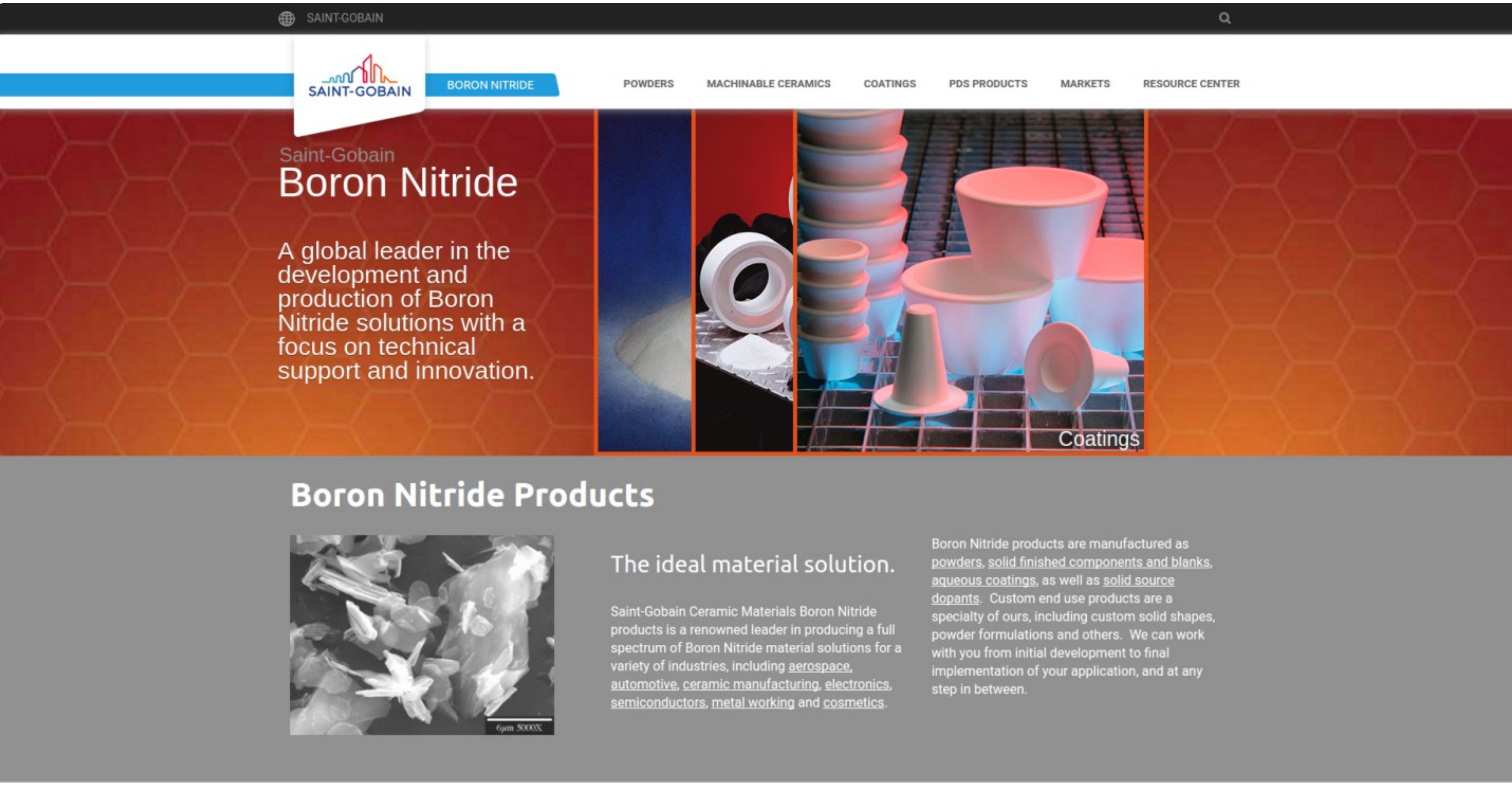
Epilayers



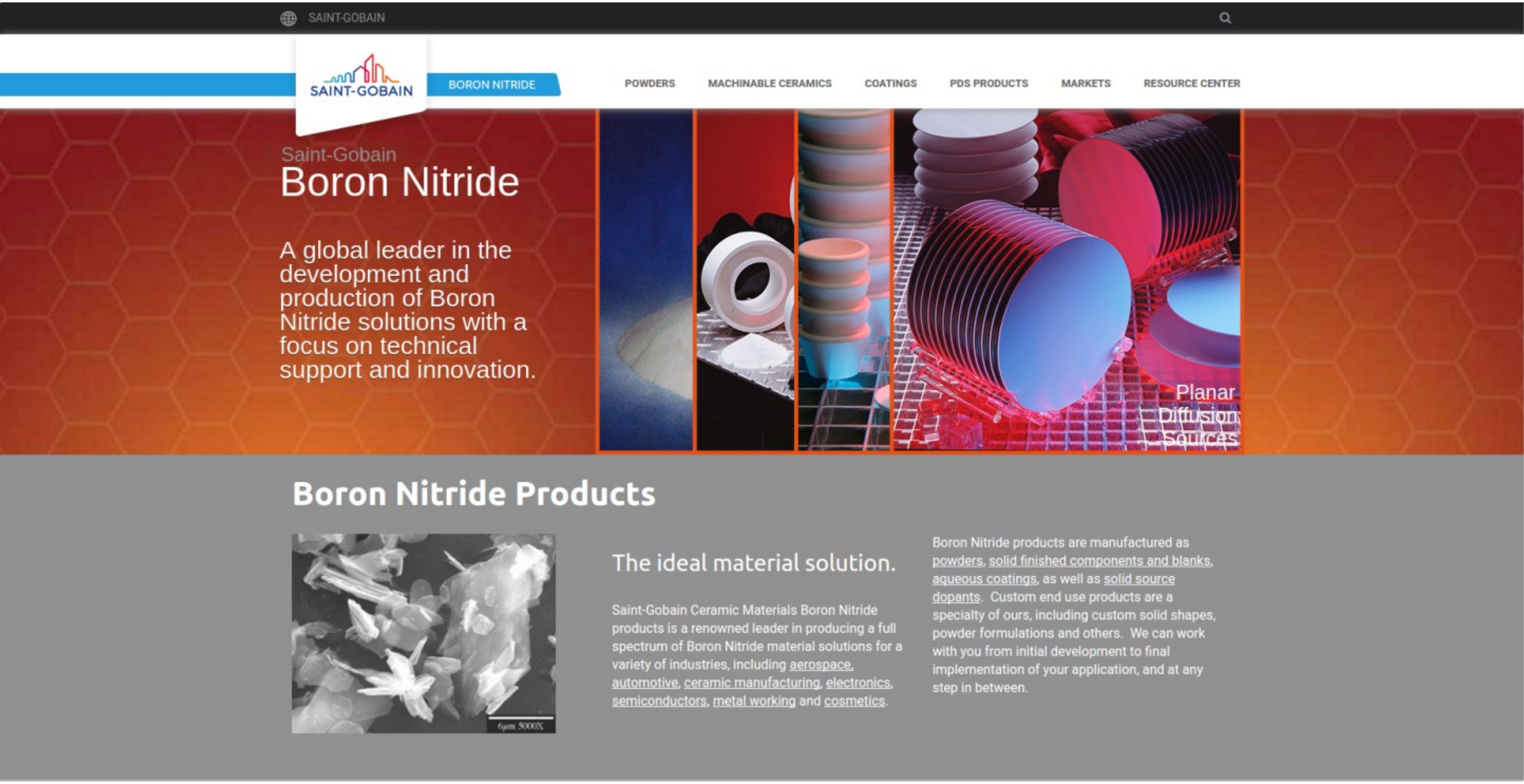
Jiang, Semicond. Sci. Technol. 29, 084003 (2014)

- growth by MOCVD + MBE
- deep-UV light emission
- UV opto-electronics (transparent p-contact, mechanical release layer)

hBN in the industry

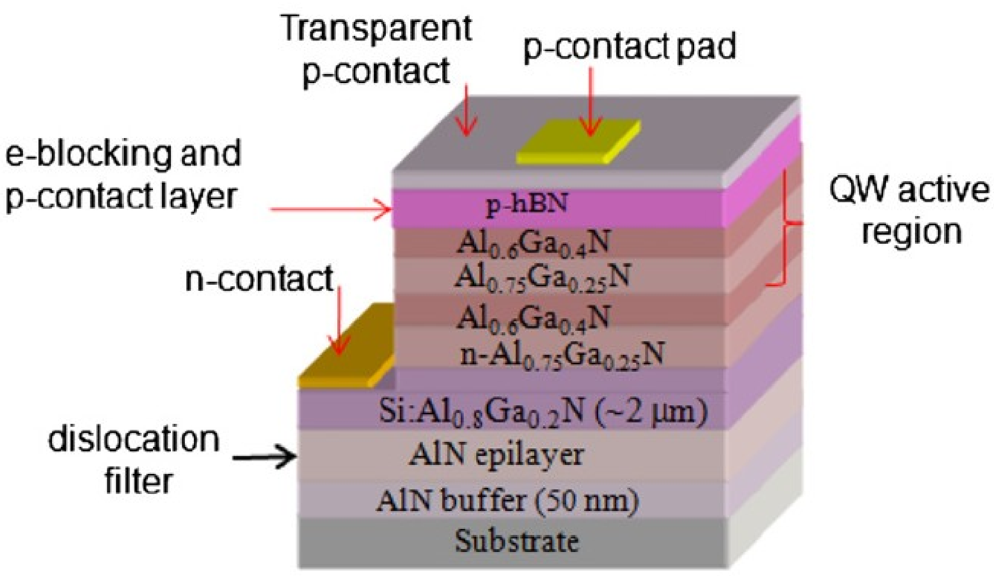


hBN in the industry

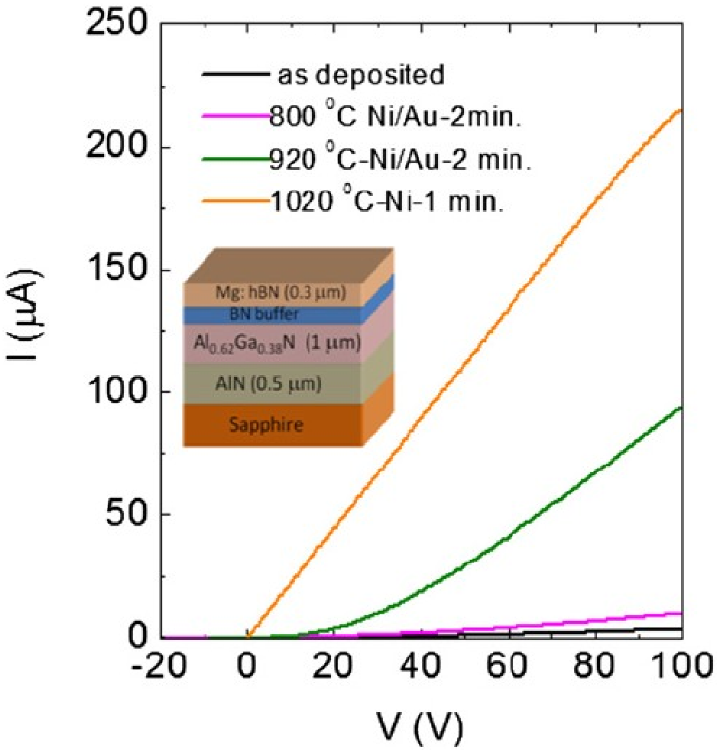


Highly conductive p-type hBN layer

Deep-UV LED device

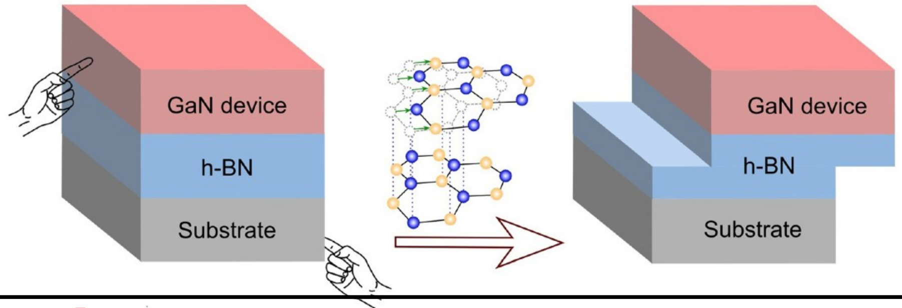


p-BN:Mg /n-AlGaN structure

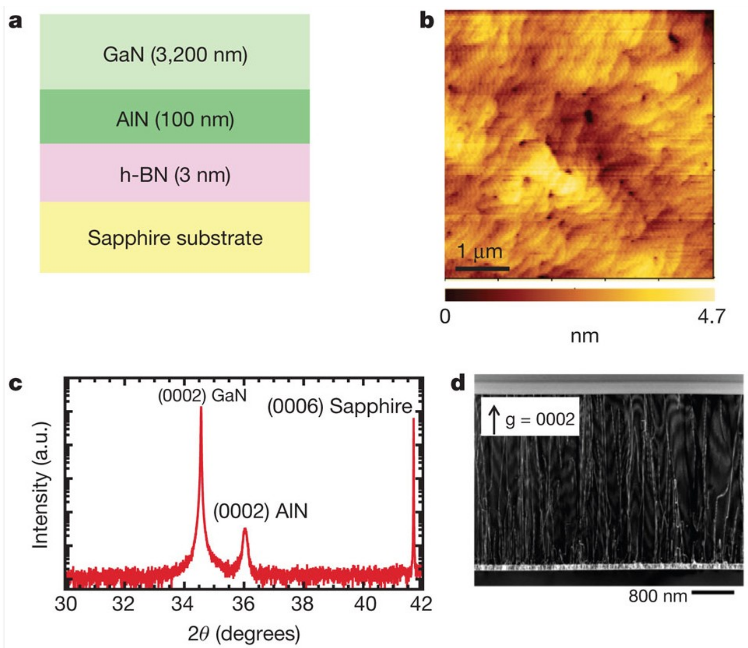


Jiang, Semicond. Sci. Technol. 29, 084003 (2014)

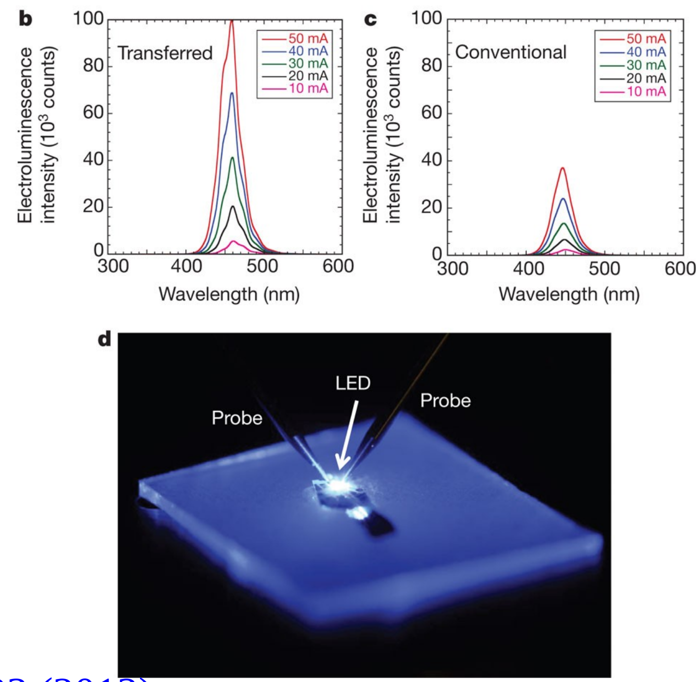
hBN as release layer for mechanical transfer



Growth of AlN on hBN



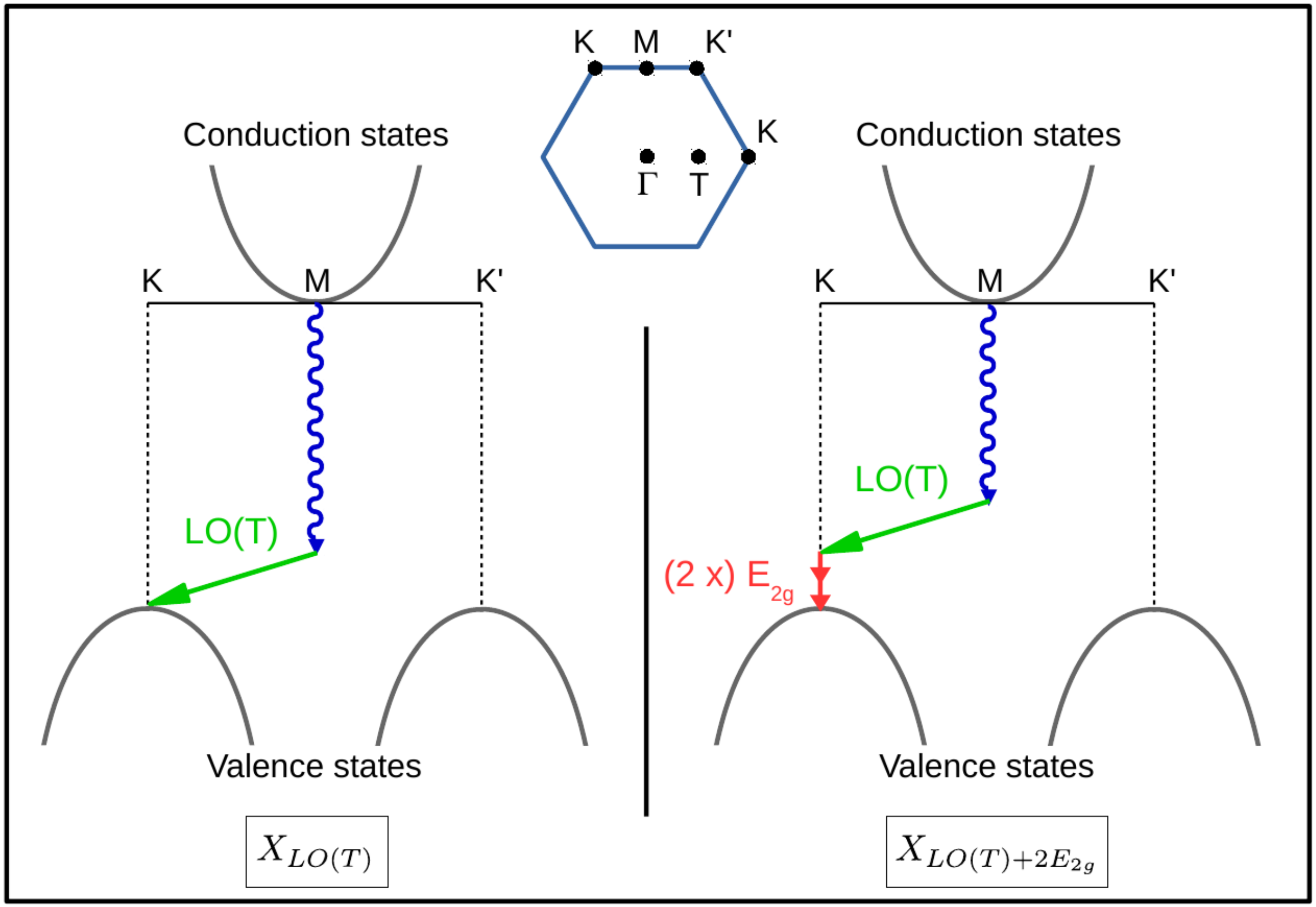
Multi-quantum well LED



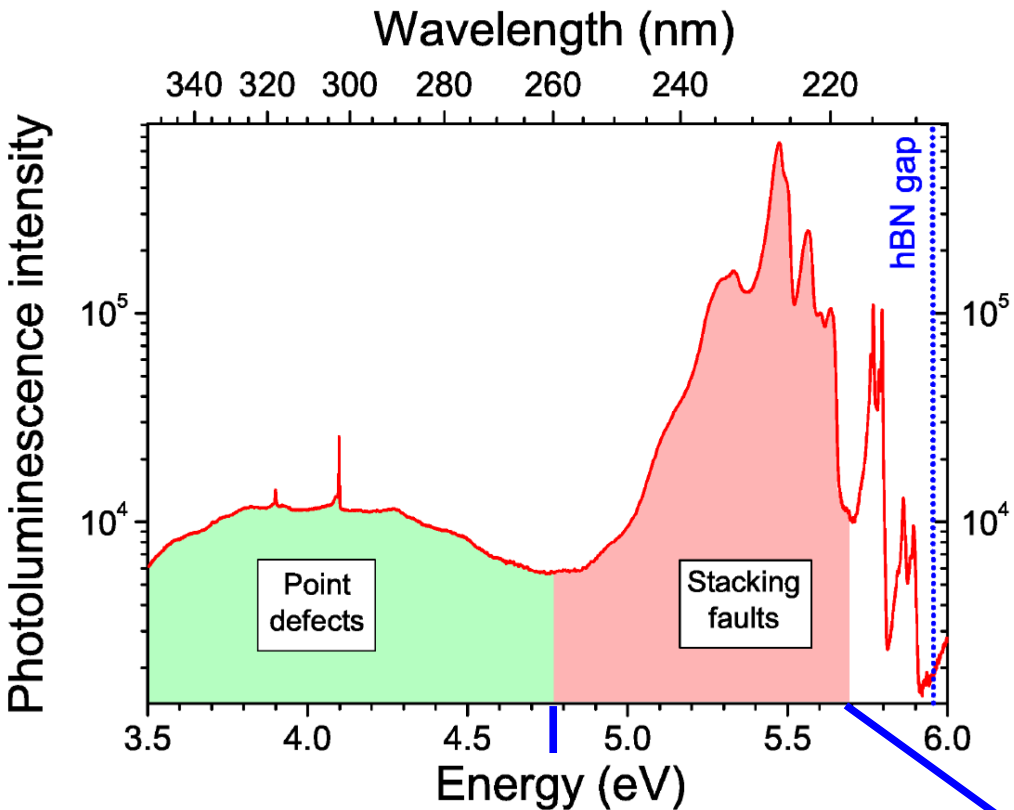
Kobayashi, Nature 484, 223 (2012)

High-order phonon-assisted processes

- low-energy Raman-active mode @ zone center
- no momentum change



Optical properties



Phonon replicas above 5.7 eV

Indirect bandgap
Nature Photonics **10**, 262 (2016)

Phonons & anharmonicity
PRB **94**, 155435 (2016)

Single-photon source
PRB **94**, 121405(R) (2016)

Intervalley scattering
PRB **10**, 262 (2016)

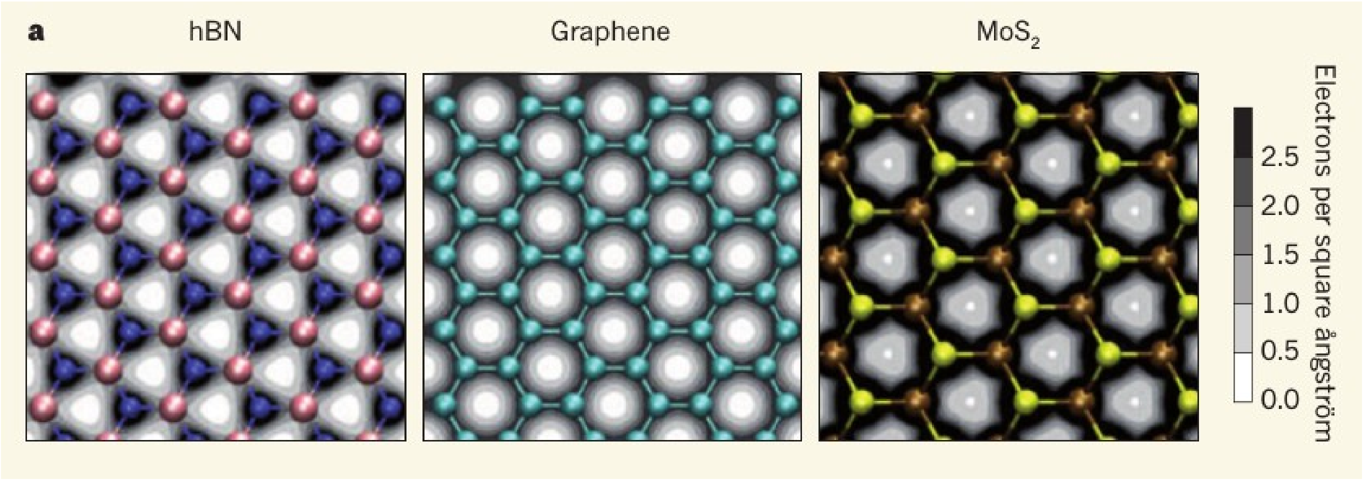
poster 1.160 by P. Vuong

Phonon-photon mapping
PRL **117**, 097402 (2016)

Direct vs indirect bandgaps

- 2D crystals

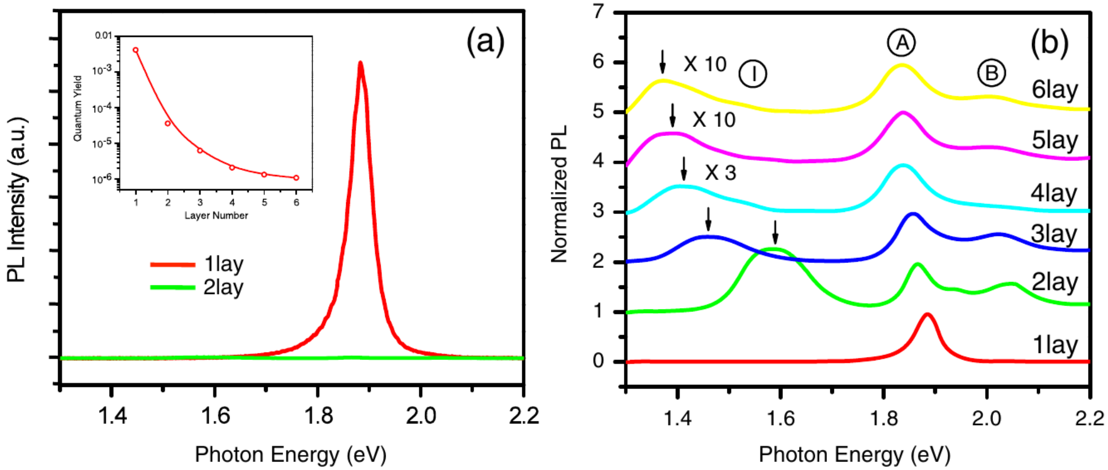
Geim, Nature 499, 419 (2013)



- Monolayer = direct bandgap

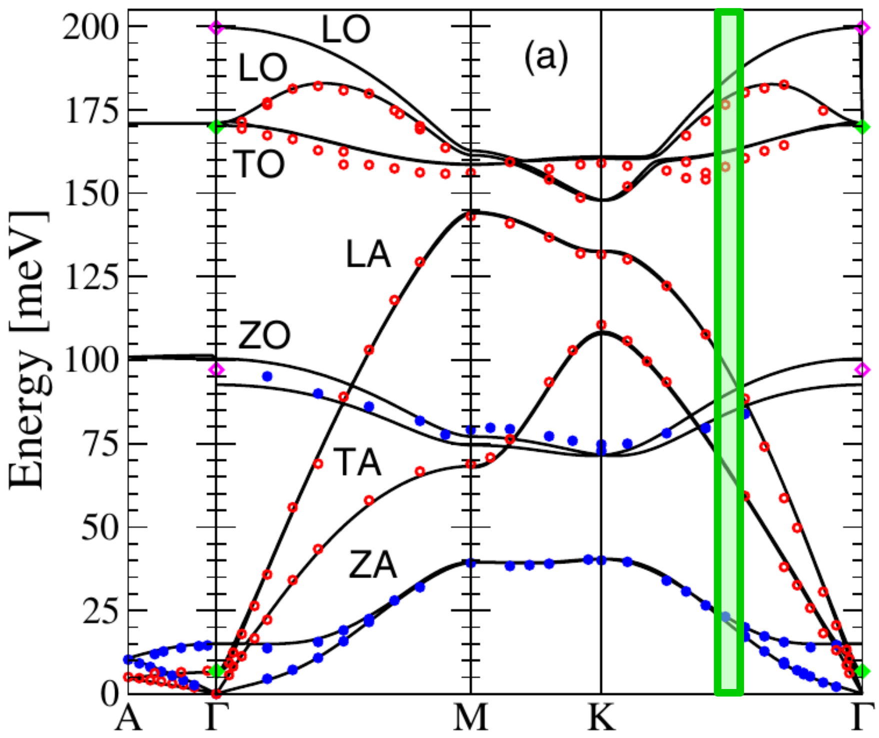
Mak, PRL 105, 136805 (2010)

MoS$_2$

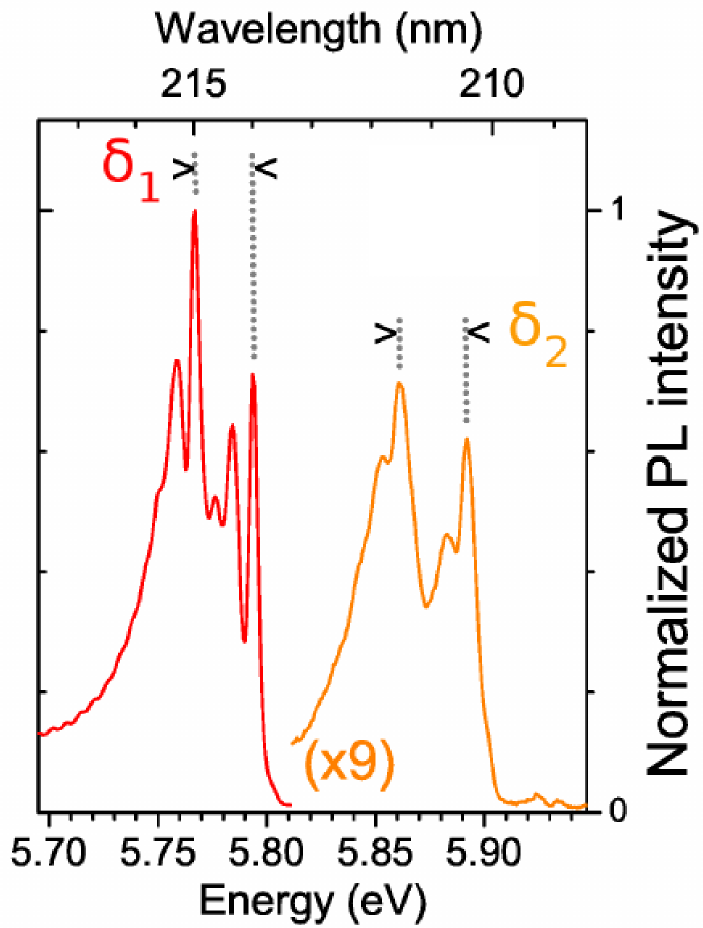


Phonon group velocity & multiplet visibility

Phonon band-structure



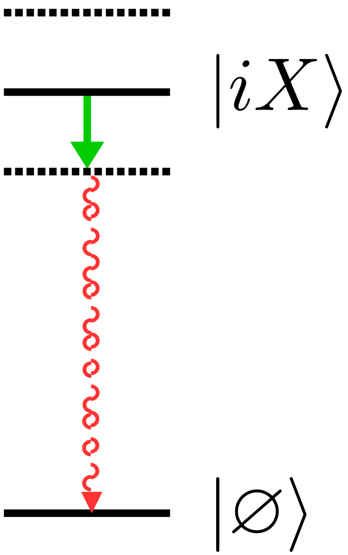
Serrano, PRL 98, 095503 (2007)

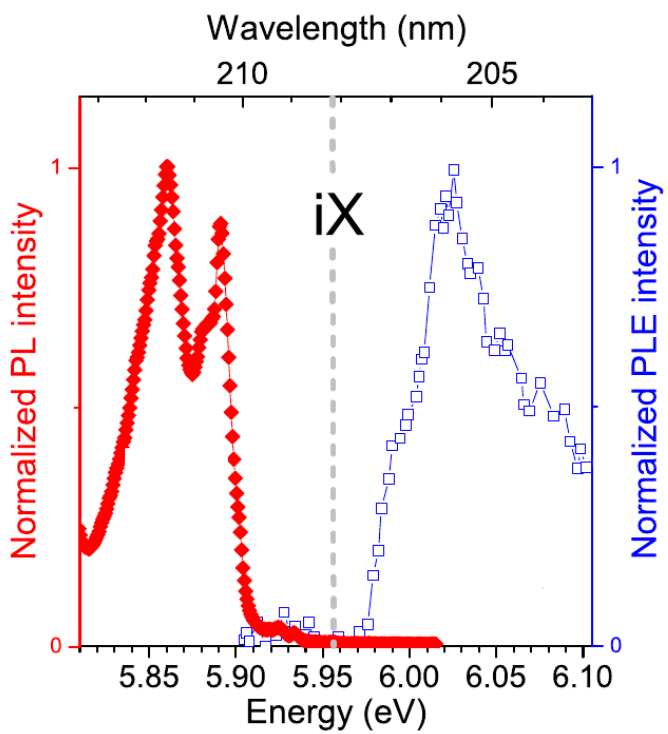


Mirror symmetry between emission and absorption

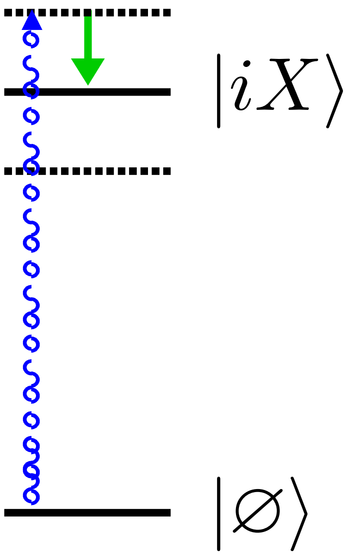
- Phonon-assisted recombination = red-shifted by phonon energy
- Phonon-assisted absorption = blue-shifted by phonon energy

Phonon-assisted recombination



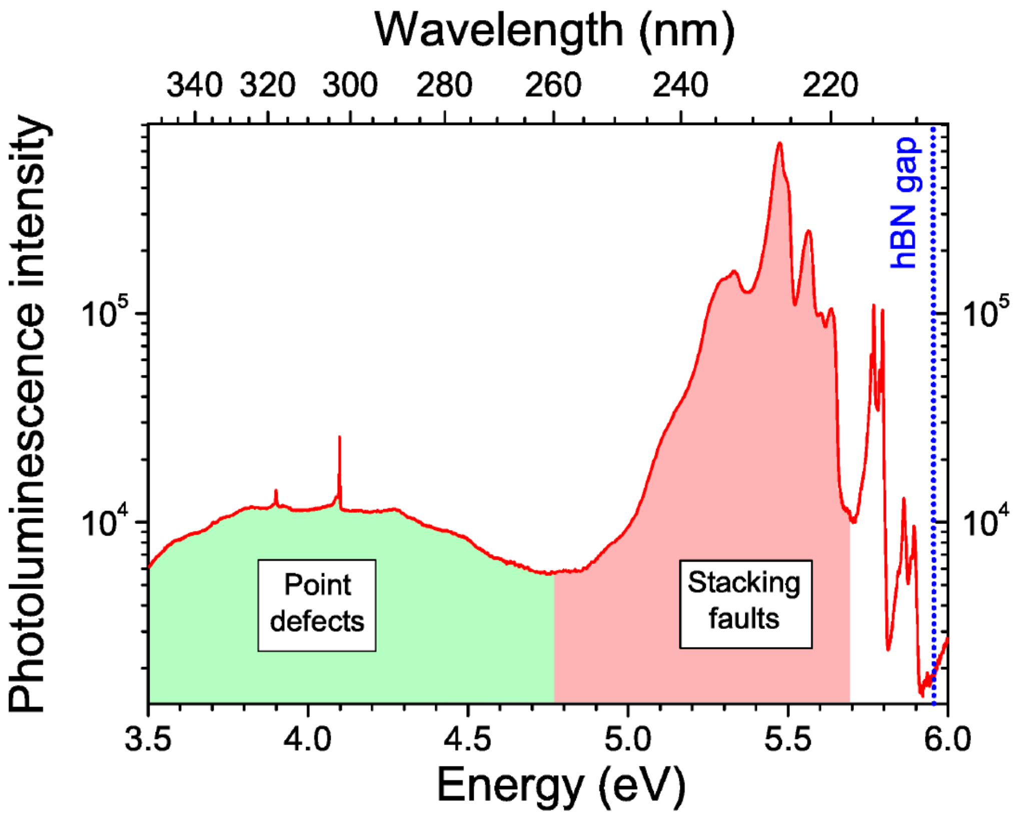


Phonon-assisted absorption



PLE from Museur, pss RRL 5, 214 (2011)

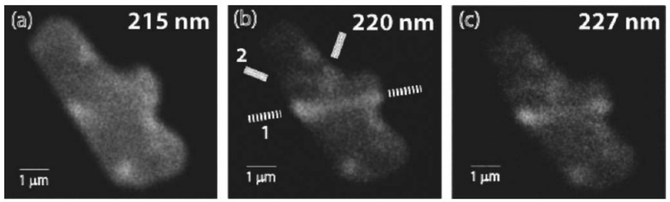
Outline



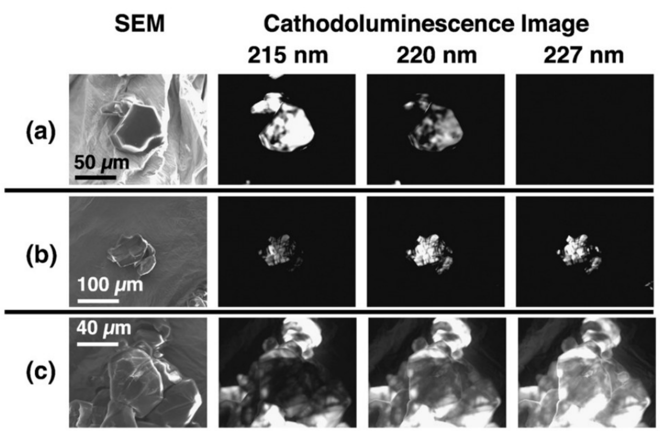
- Phonon replicas (at the band edge)
- Intervalley scattering (stacking faults)
- Phonon-photon mapping (point defects)

Spatially-resolved cathodoluminescence

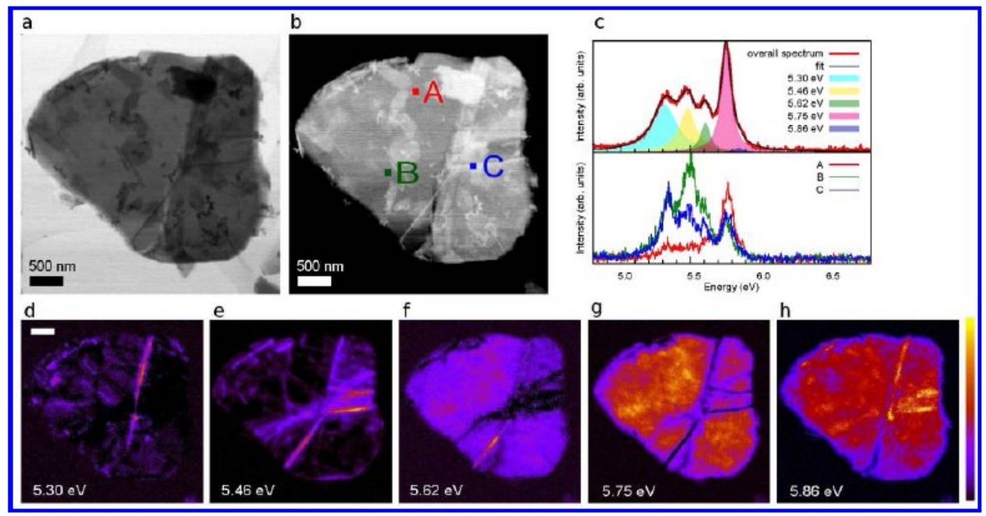
localization at defects of luminescence below 5.7 eV



Jaffrenou, JAP 102, 116102 (2007)

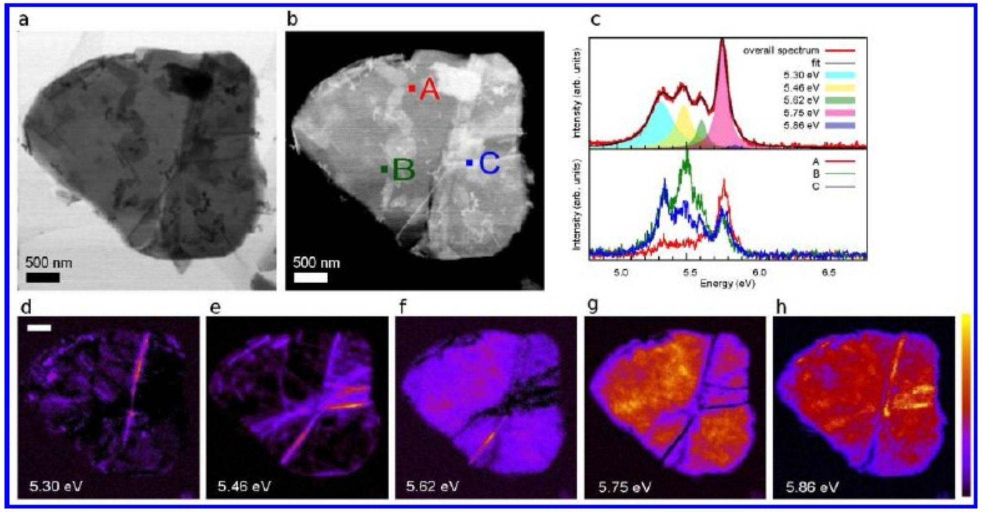


Watanabe, Diam. Rel. Mat. 20 849 (2011)

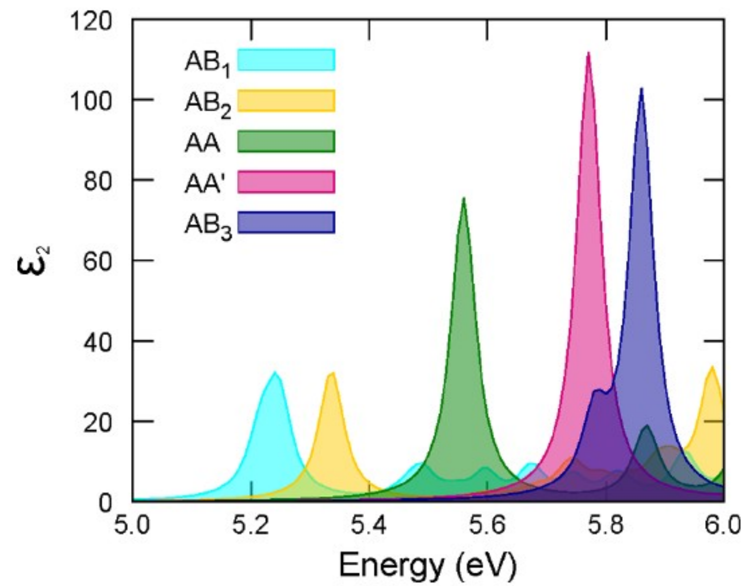


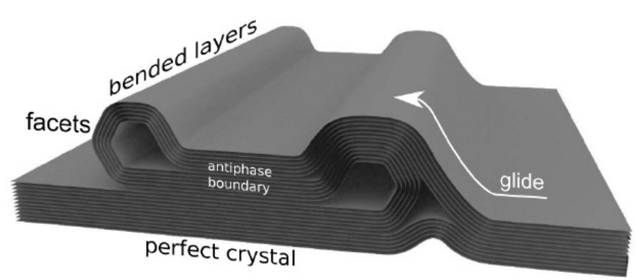
Bourrelier, ACS Photonics 1, 857 (2014)

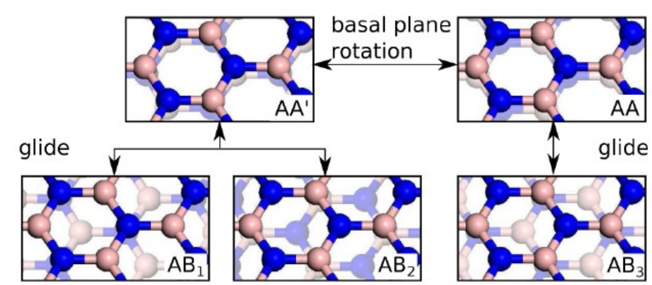
Defect-related emission band



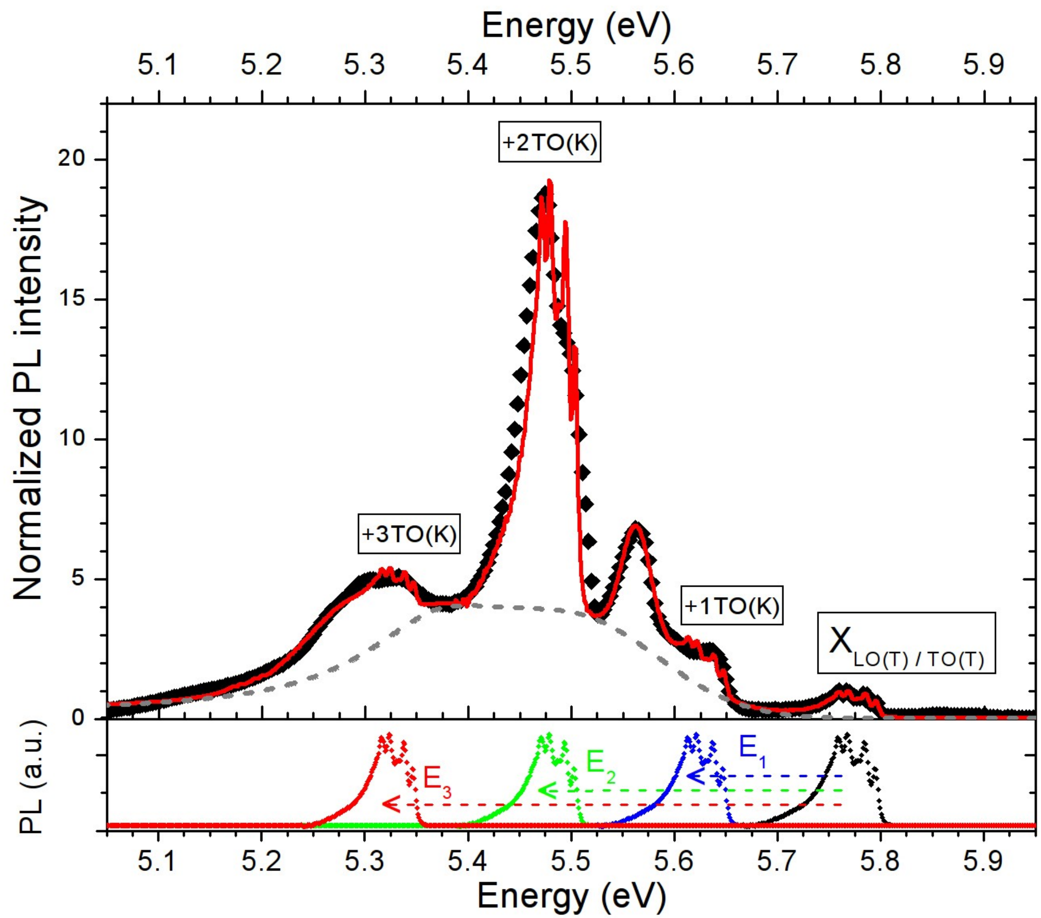
Bourrelier, ACS Photonics 1, 857 (2014)

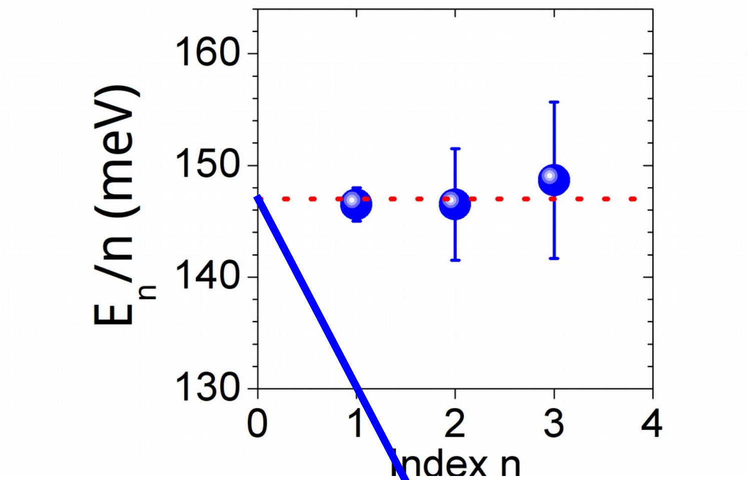


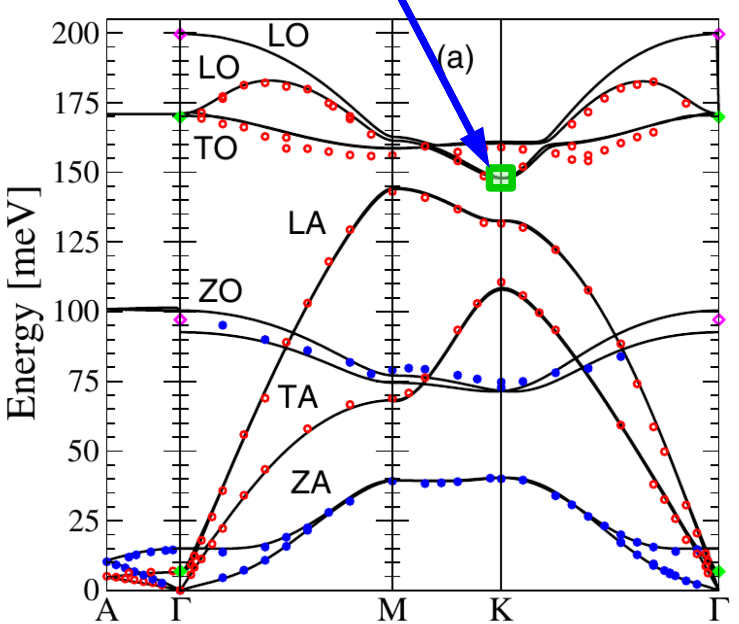




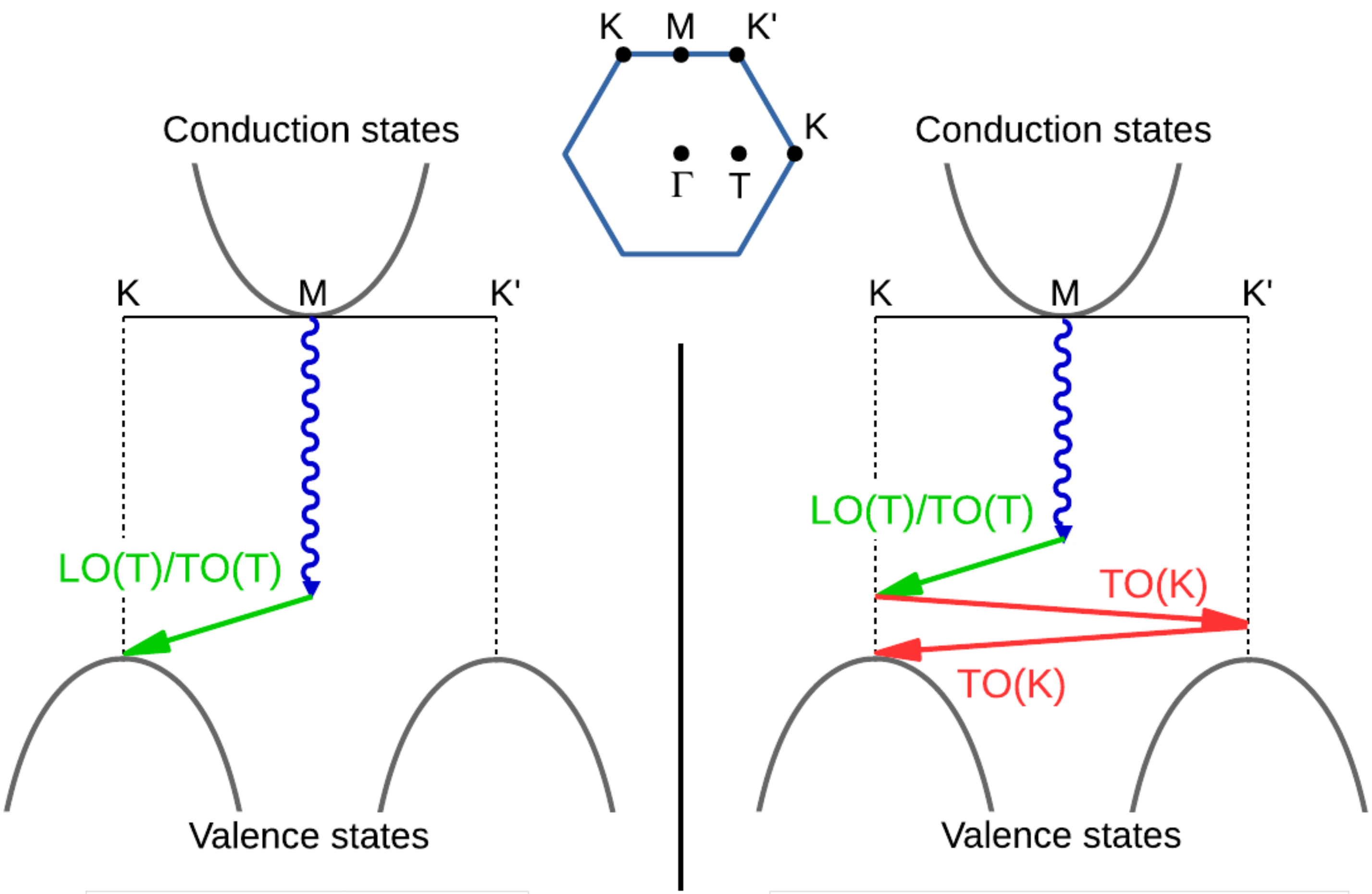
Phonon replicas...again







Intervalley scattering



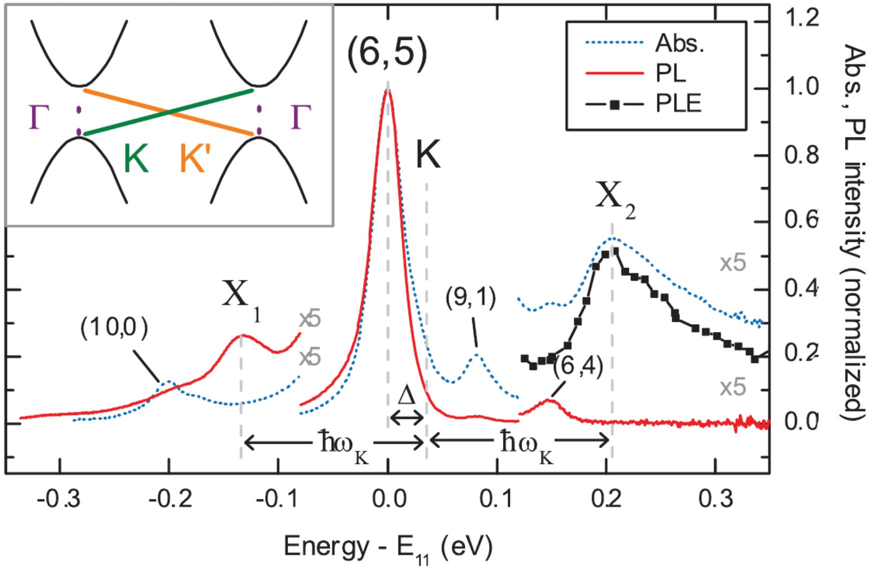
$X_{LO(T)/TO(T)}\ (5.76eV)$

$\widetilde{X}_{LO(T)/TO(T)+2TO(K)}\ (5.47eV)$

TO(K)-assisted intervalley scattering

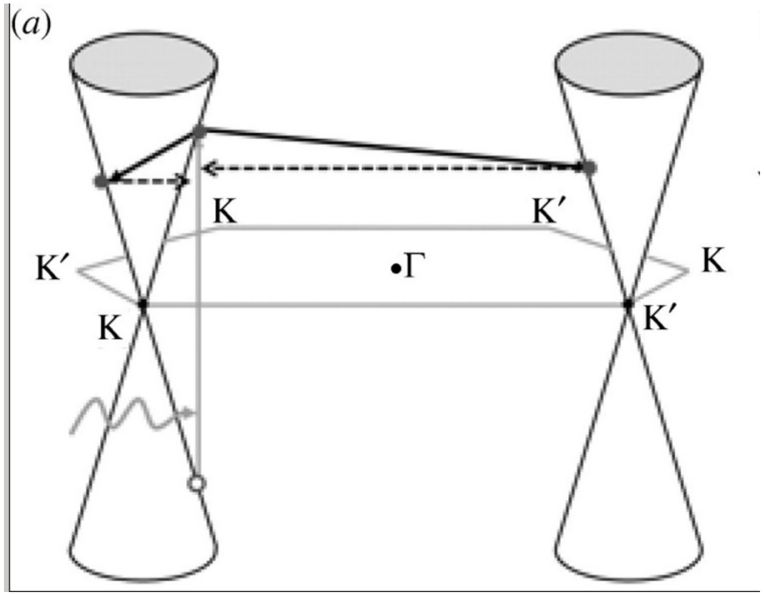
same TO(K) phonon found in two similar systems

Carbon nanotubes
(emission of valley-dark exciton)



Torrens, PRL 101, 157401 (2008)

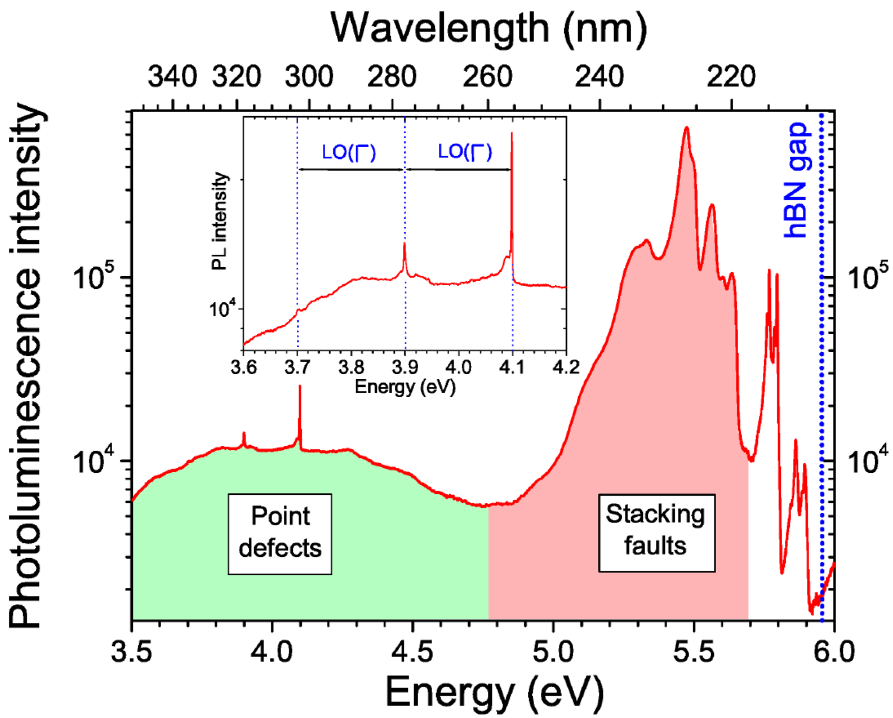
Graphene
(Raman D band)



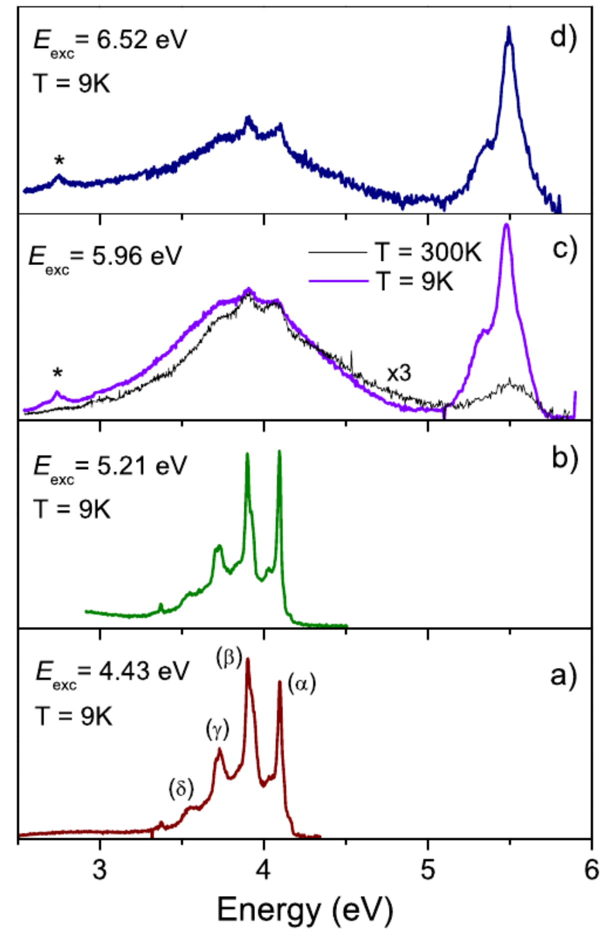
Thomsen, PRL 85, 5214 (2000)

Excitation spectroscopy

above bandgap excitation

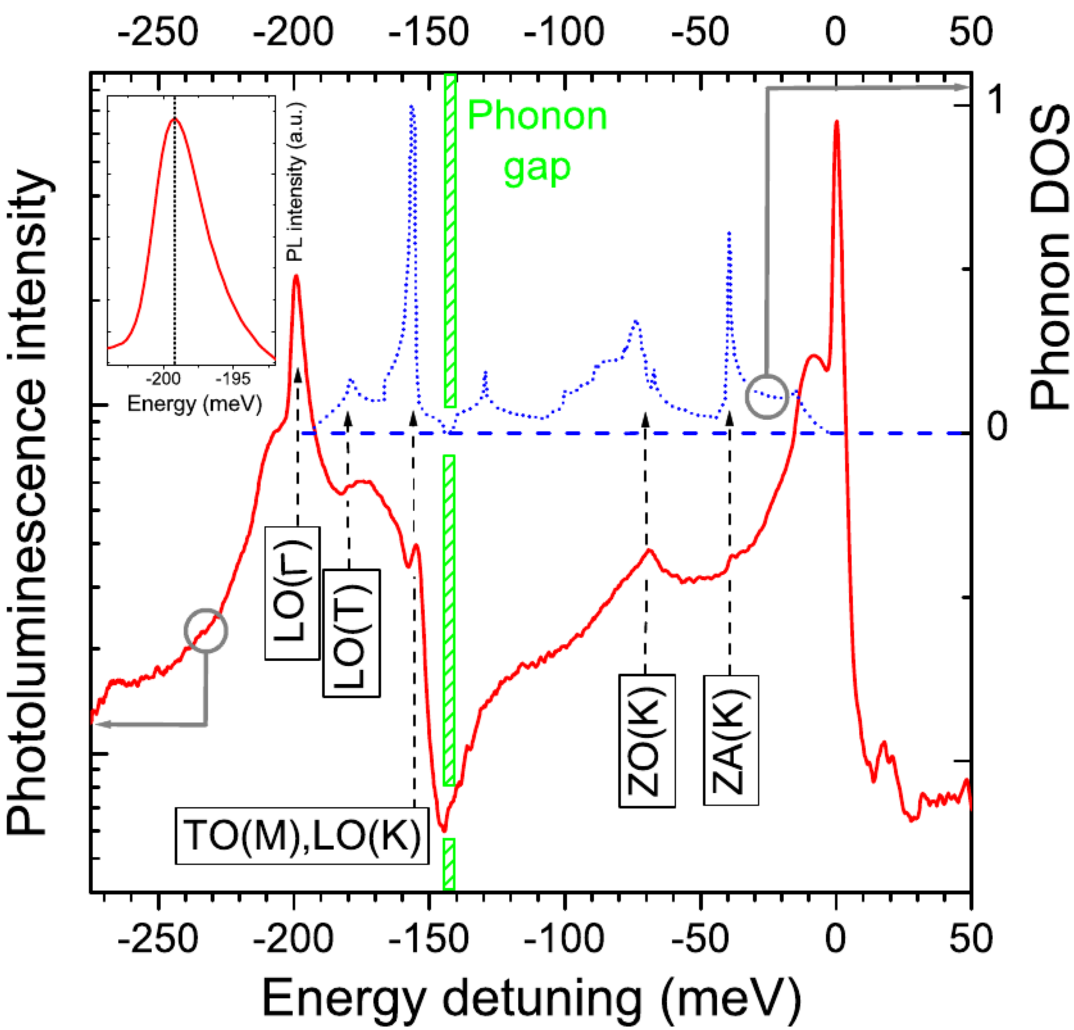


below bandgap excitation



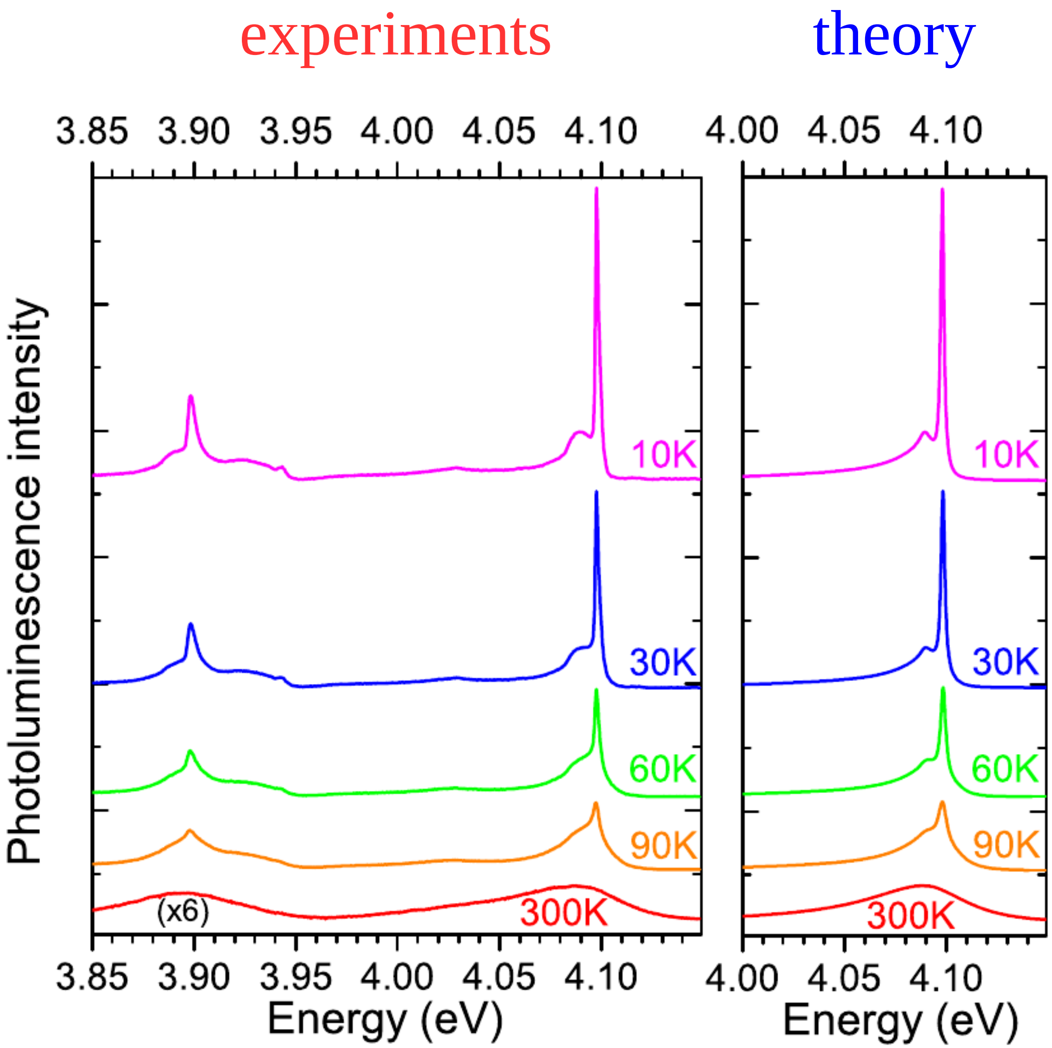
Museur, PRB 78, 155204 (2008)

PL spectrum vs phonon DOS



- excitation @ 4.6 eV
- no PL signal @ phonon gap
- observation of phonon DOS extrema in PL spectrum
- one-phonon processes dominant at 10K

Acoustic phonon sidebands



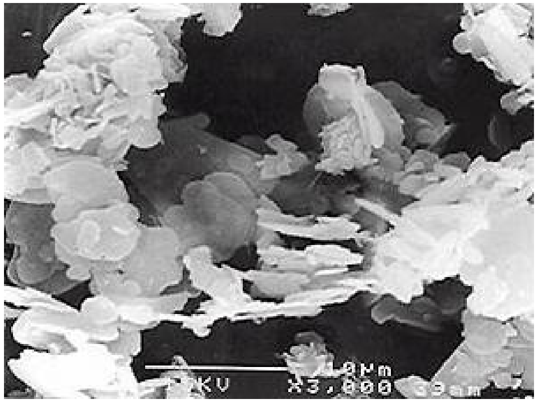
- non-perturbative calculations of LA phonon sidebands
- excellent agreement from 10K to room temperature
- deformation potential
  D ~ 11 eV
- defect size ~ 2 Å

White graphite

an old story ...

a versatile material displaying :
- chemical inertness
- low dieletric constant
- thermal stability

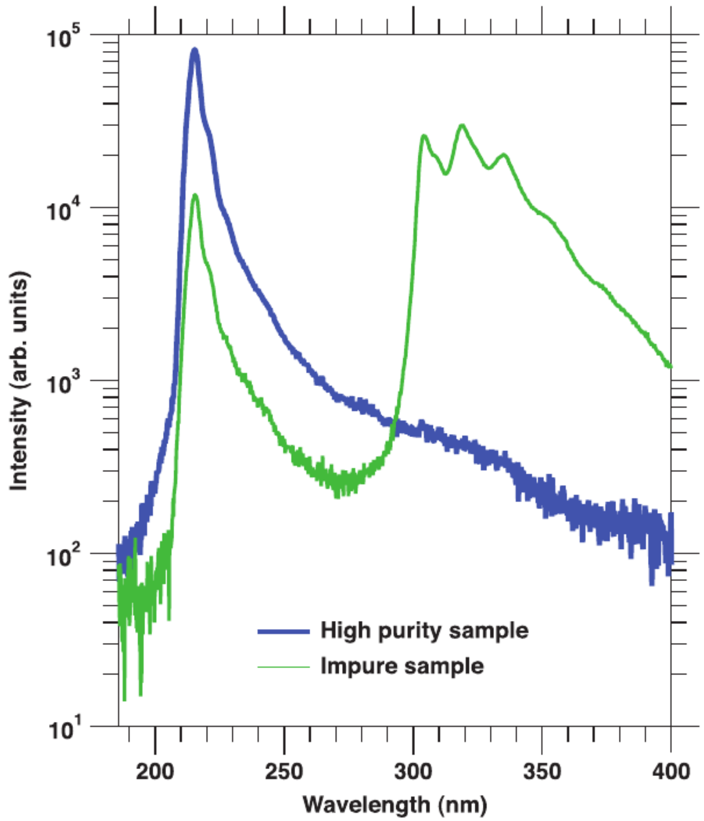
widely used as :
- solid lubricant
- thermal coating
- additive in plastics, ceramics
- cosmetic powder



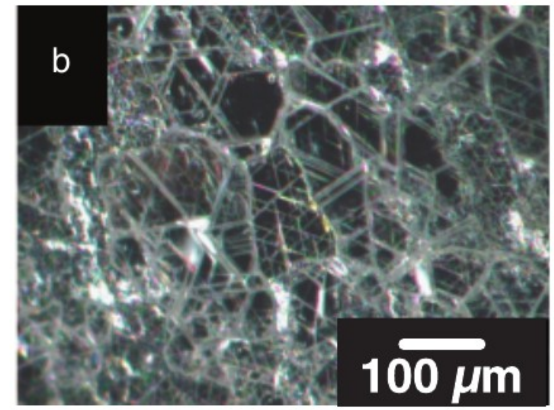
High-quality monocrystals

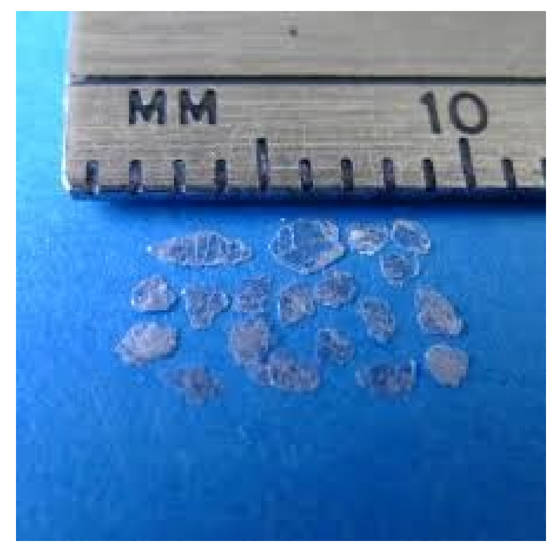
2004-breakthrough by Watanabe & Taniguchi

(N



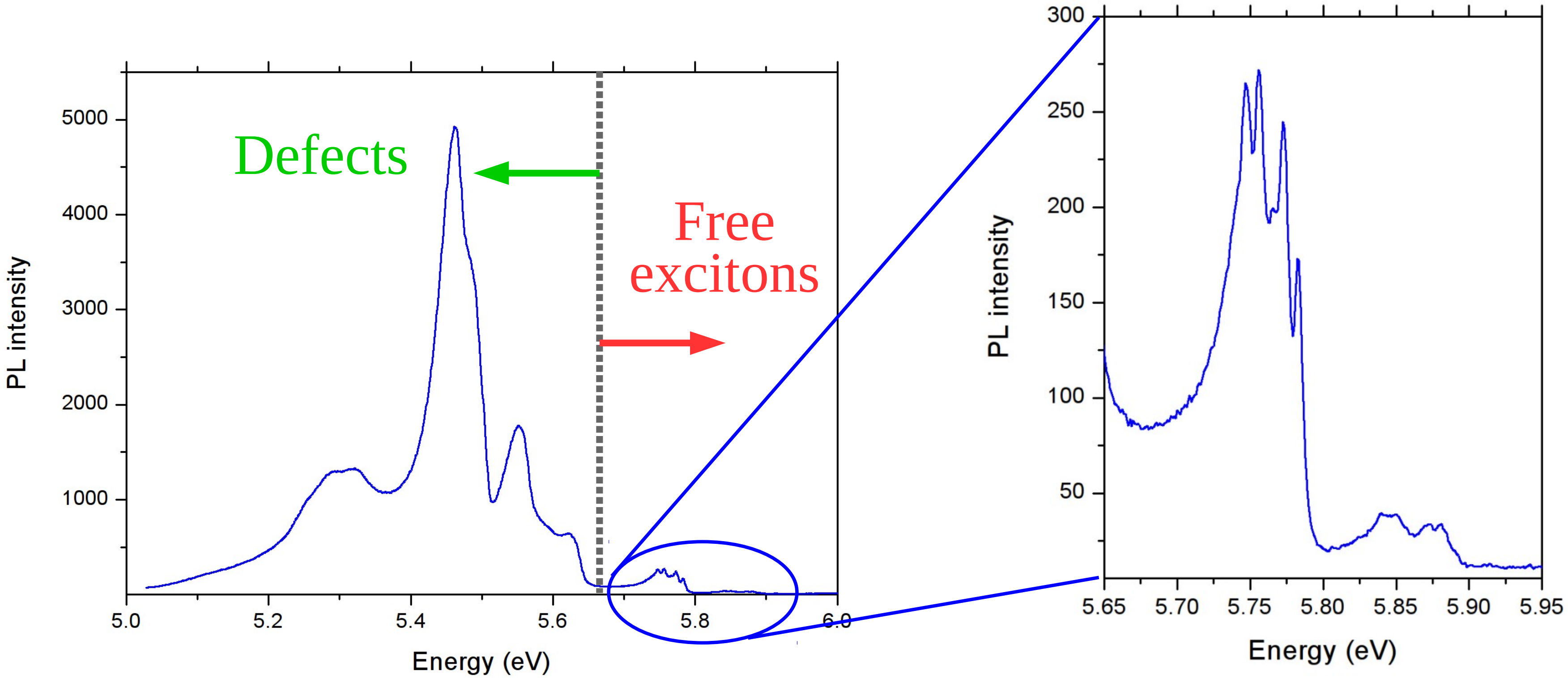
Watanabe, Int. J. Appl. Ceram. Technol. 8, 977 (2011)



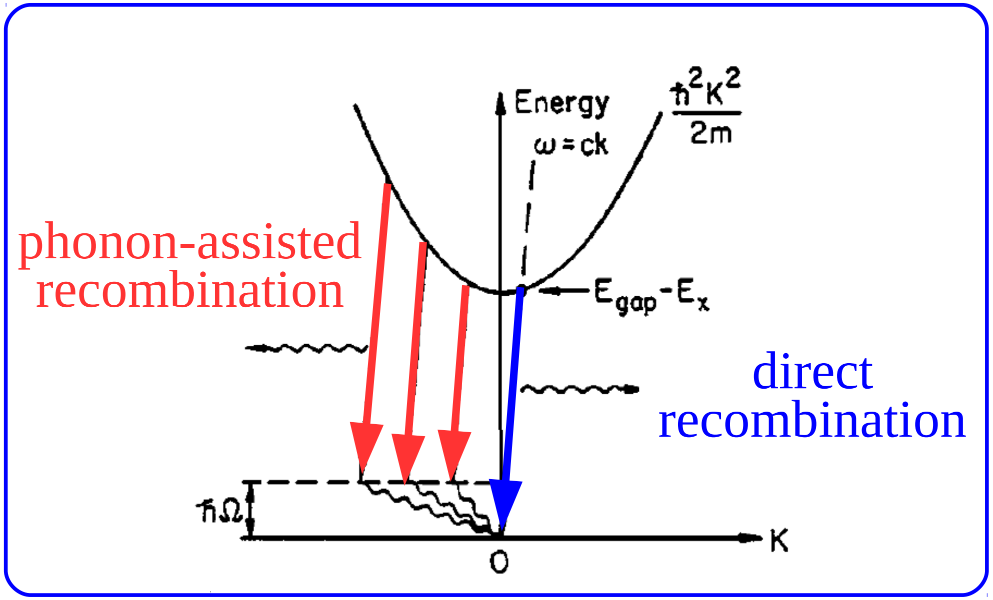


Photoluminescence spectrum

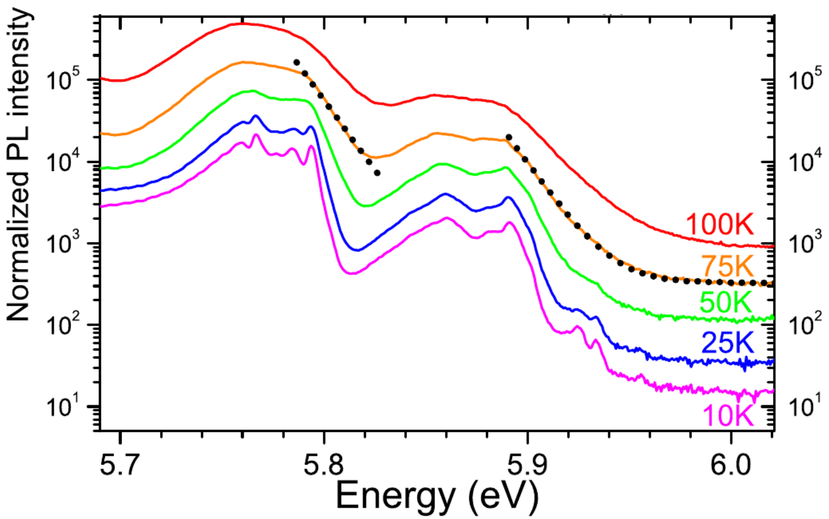
- hBN sample from HQ Graphene (www.hqgraphene.com)
- PL spectroscopy at 10K under laser excitation @ 6.3 eV

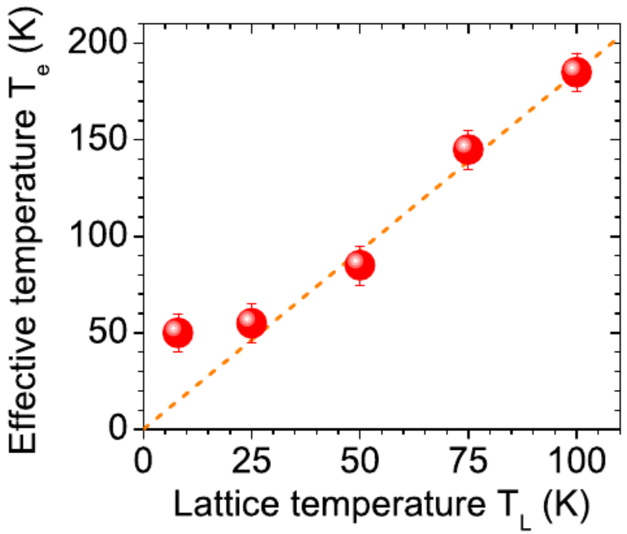


Monitoring the thermalization of high-K excitons



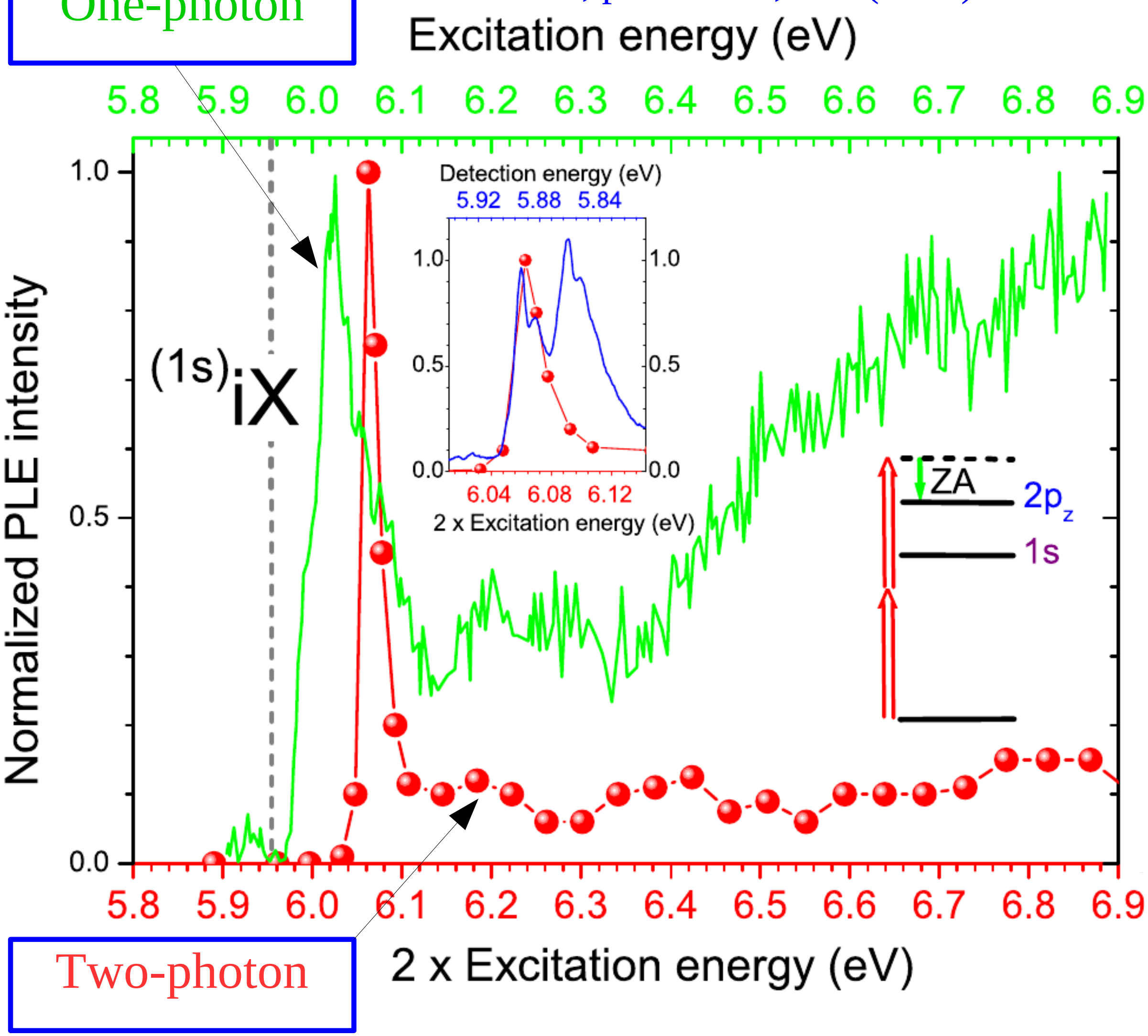
- direct recombination probes excitons at K~0
- thermal distribution of high-K excitons only monitored in phonon replicas





Two-photon excitation spectroscopy

from Museur, pss RRL 5, 214 (2011)



- Different PLE spectra for one- and two-photon excitations

one-photon

$$\left| \sum_{|int_1>} < v|P|int_1 >< int_1|Q|c > \right|^2$$

two-photon

$$\left| \sum_{|int_1>,|int_2>} < v|P|int_1 >< int_1|P|int_2 >< int_2|Q|c > \right|^2$$

- Sharp resonance in two-photon PLE
= ZA phonon-assisted absorption of $2p_z$-state

Exciton binding energy

- 1s-2p$_z$ splitting = 85 meV

Wannier excitons in hBN !!

- For isotropic material, 1s-2p splitting = $\frac{3}{4}$ exciton binding energy
- Strong anisotropy of hBN reduces this value

depending on anisotropy factor γ

Gil, pss B 249, 455458 (2012)

- Exciton binding energy = 130±15 meV
- Single-particle gap (or band-to-band energy) = 6.08 eV