Optoelectronic properties of hexagonal boron nitride

Guillaume Cassabois

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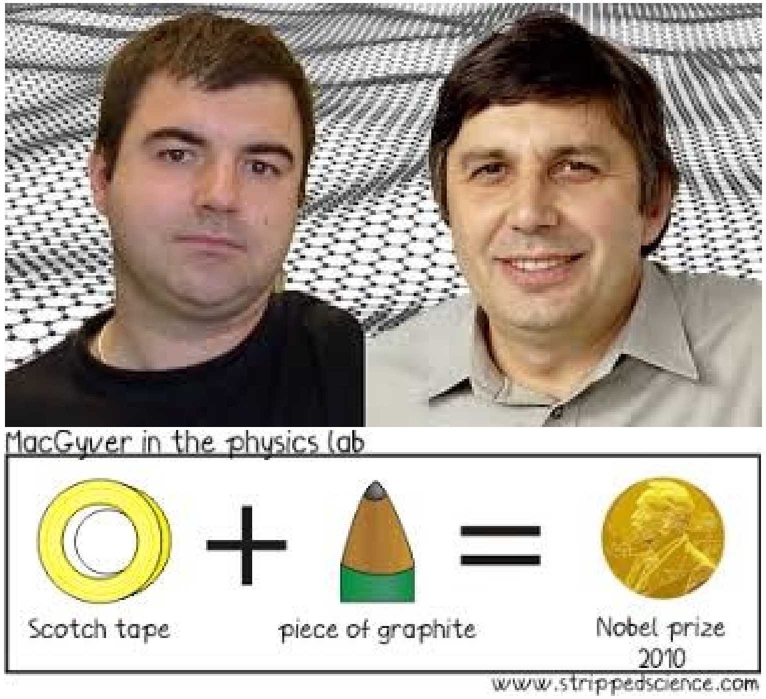
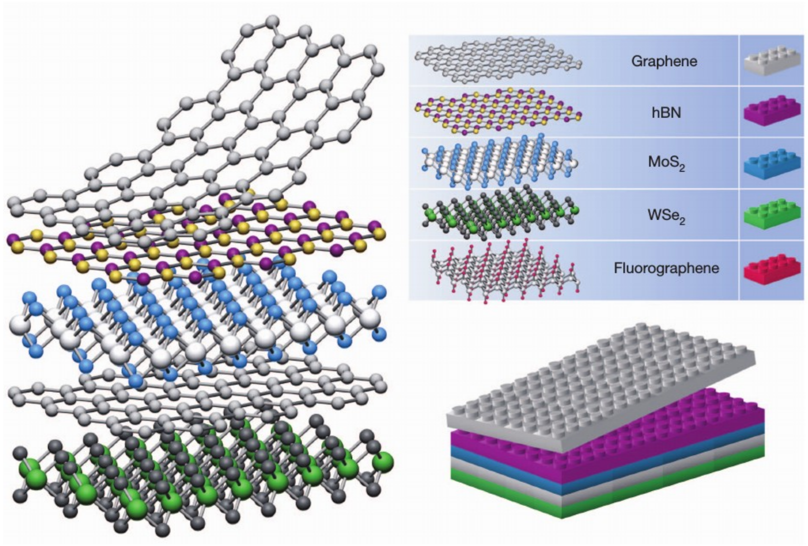
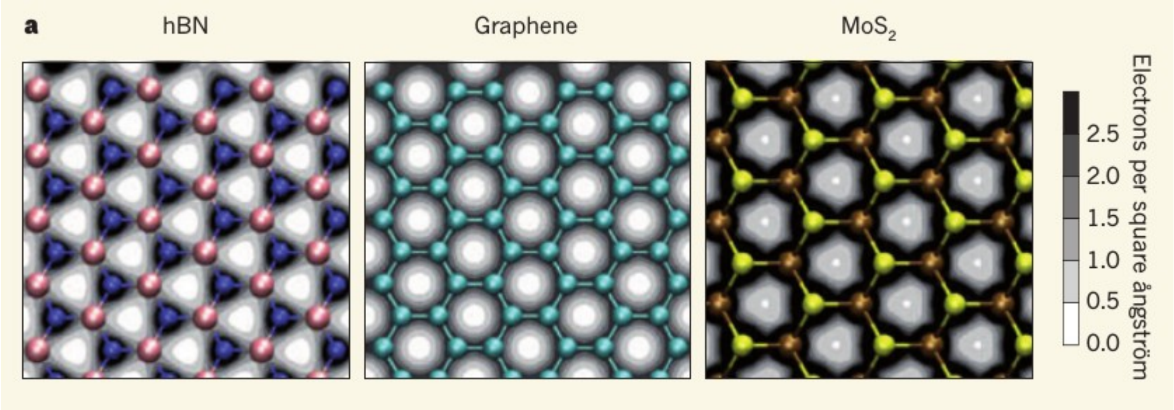
Beyond graphene



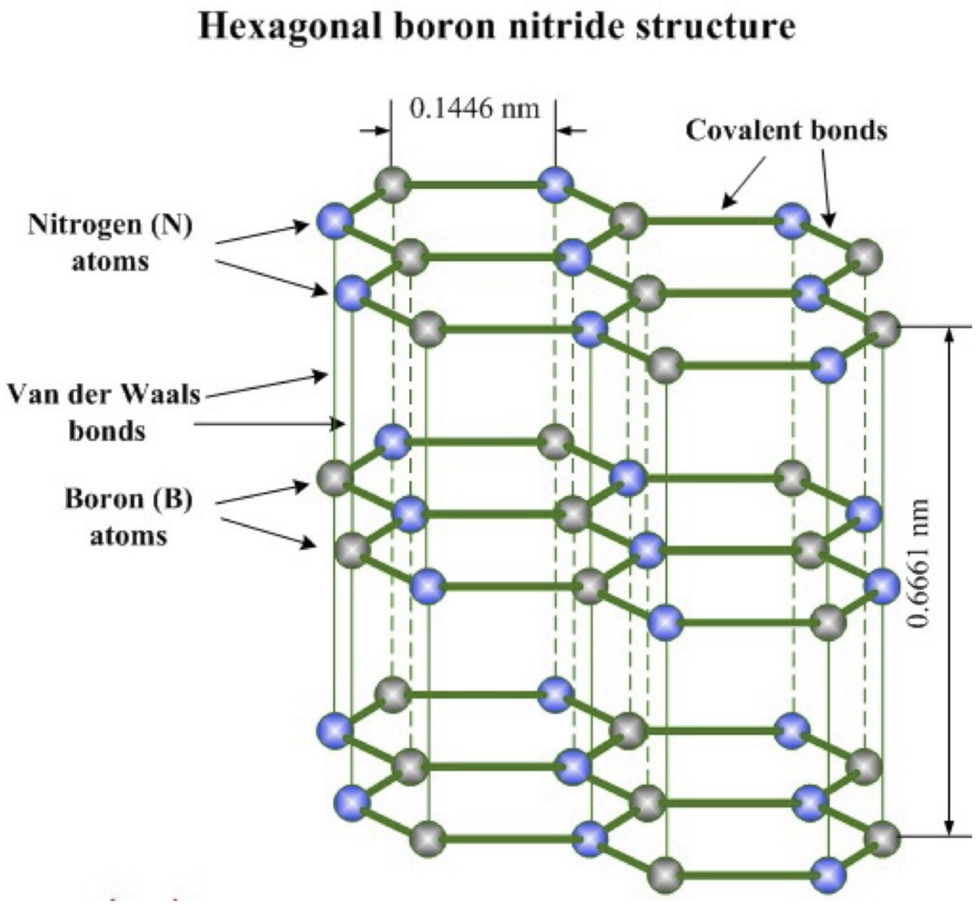
Van der Waals heterostructures



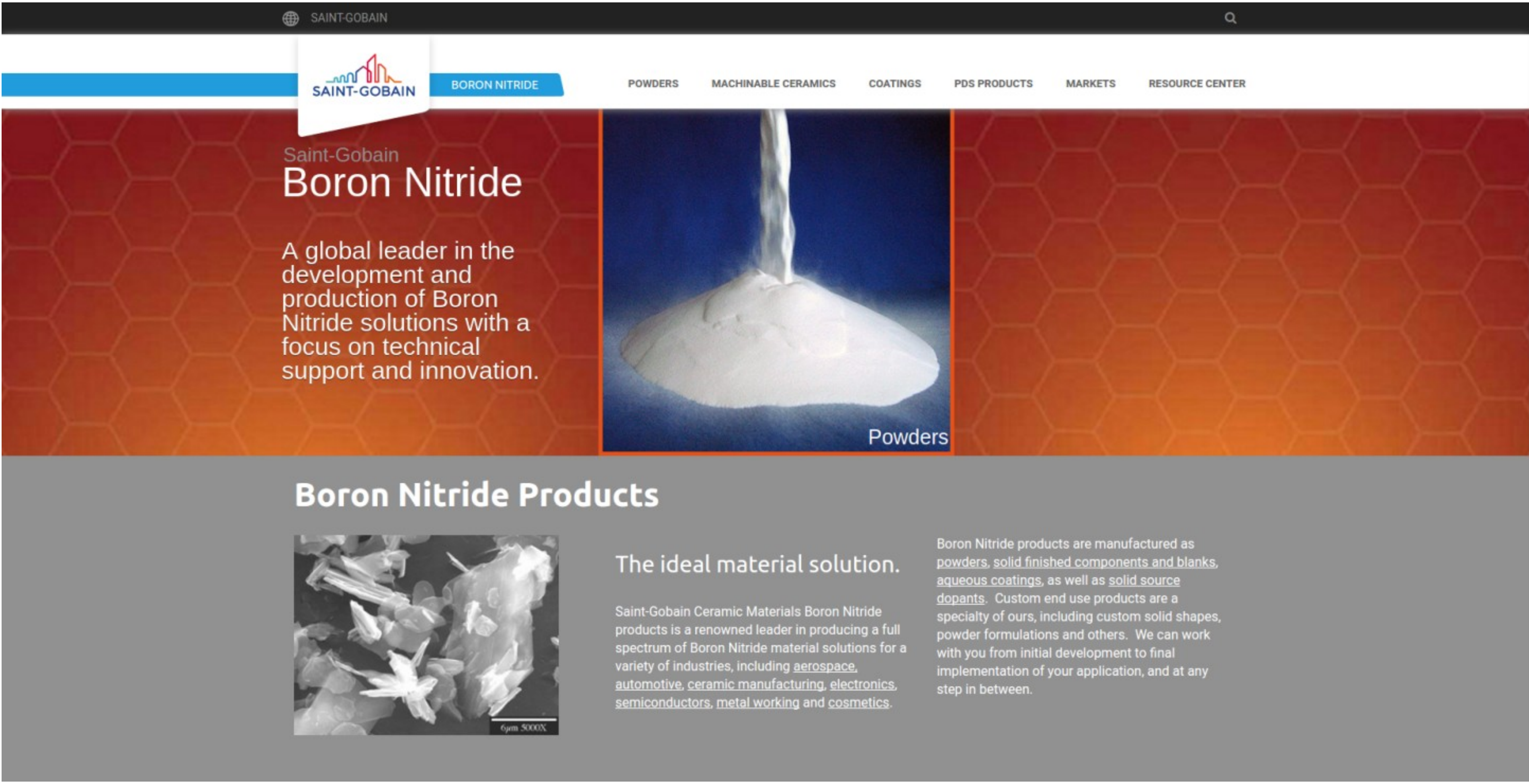
Geim, Nature **499**, 419 (2013)



“White graphite”



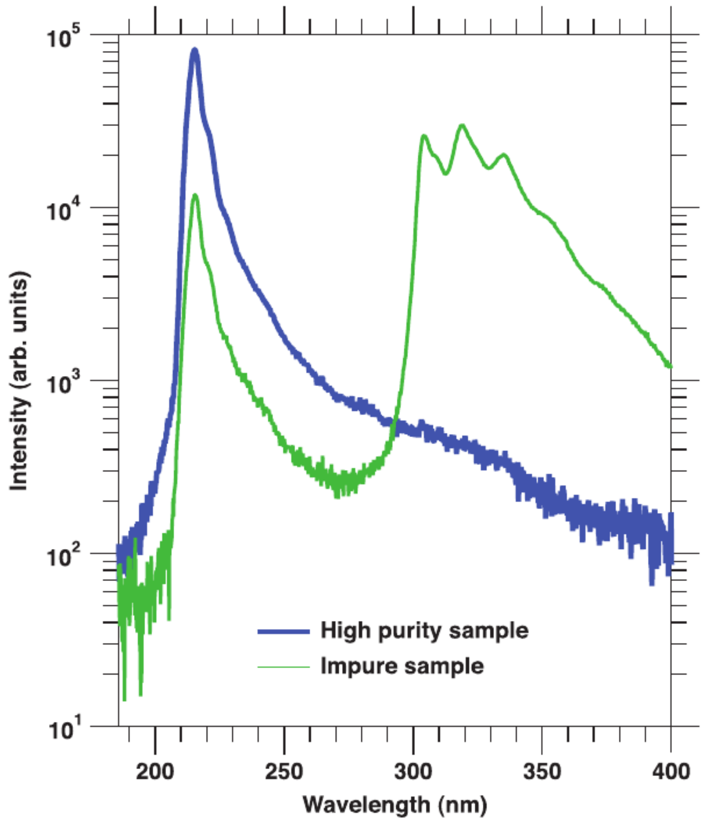
hBN in the industry



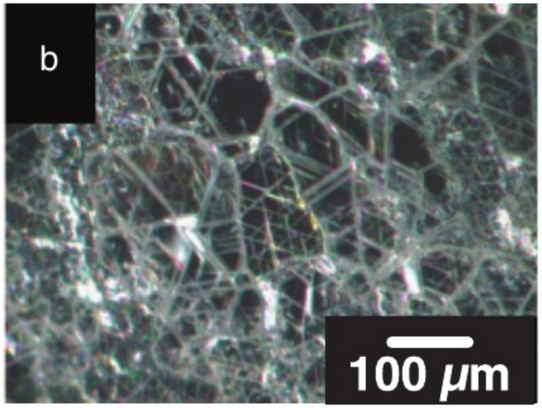
hBN in the industry

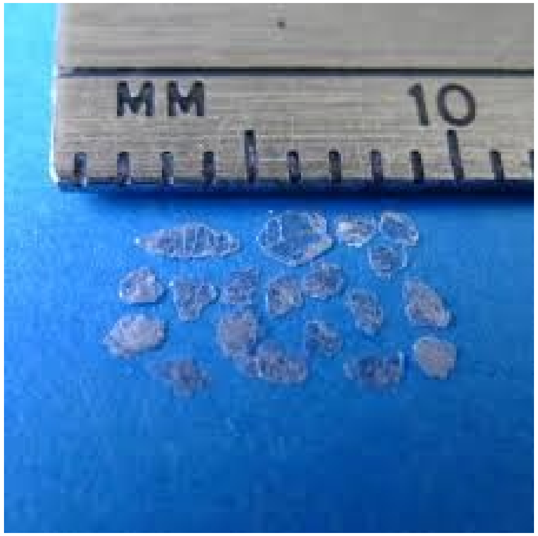
From the industry … back into the lab !

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



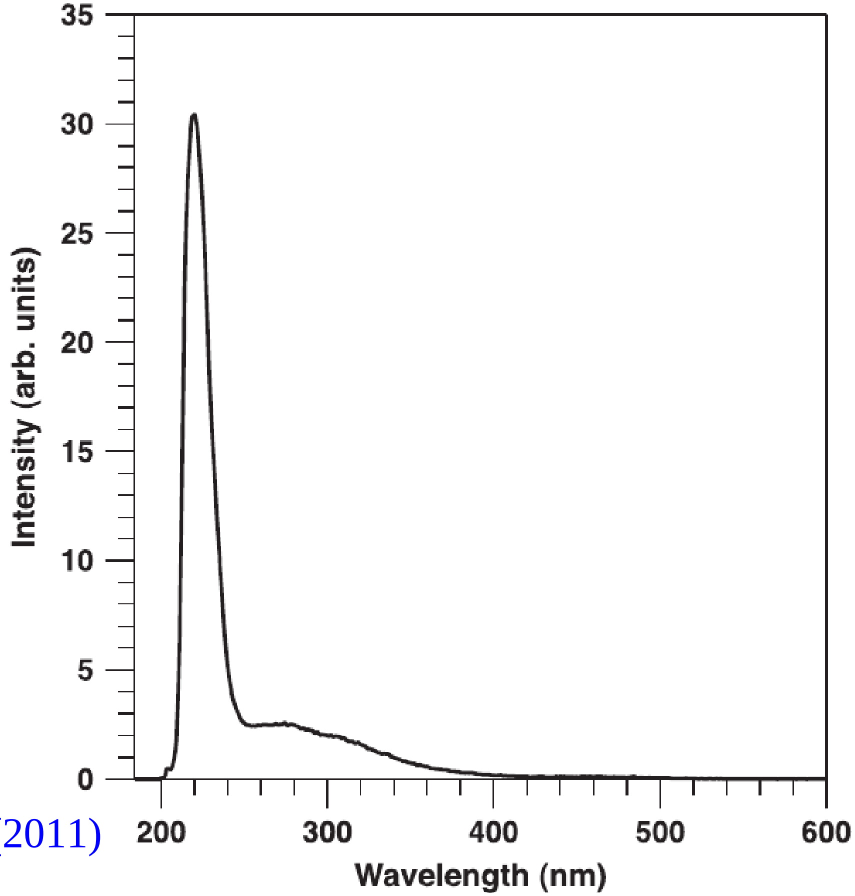
Watanabe, Int. J. Appl. Ceram. Technol. **8**, 977 (2011)





hBN for Deep-UV light emission

Field-emitter Deep-UV device

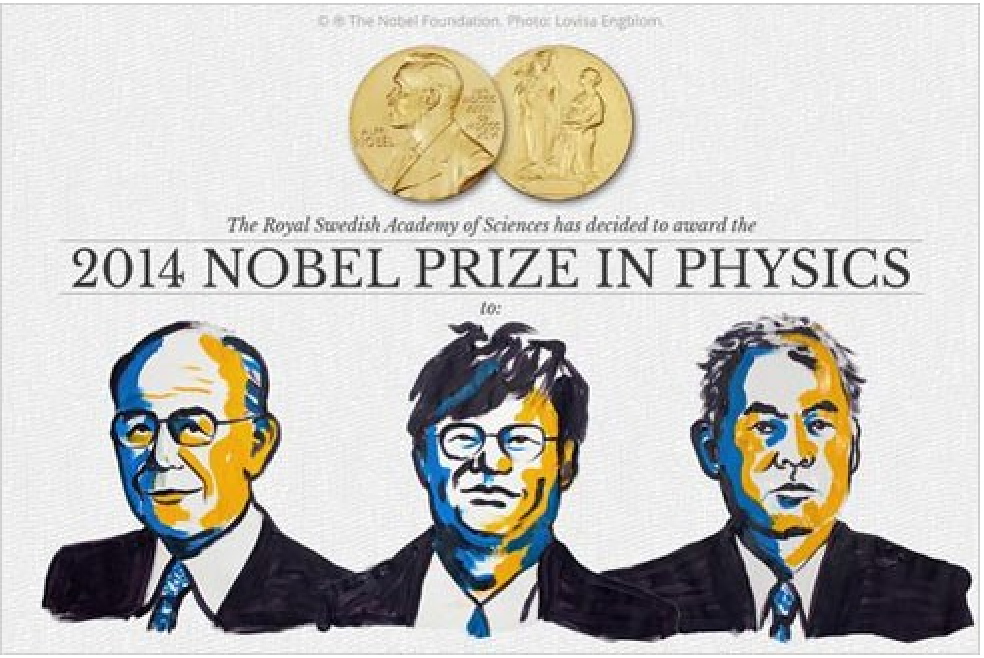


Watanabe, Int. J. Appl. Ceram. Technol. **8**, 977 (2011)

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

hBN: also a nitride semiconductor !

- Famous members of the family : GaN and AlN



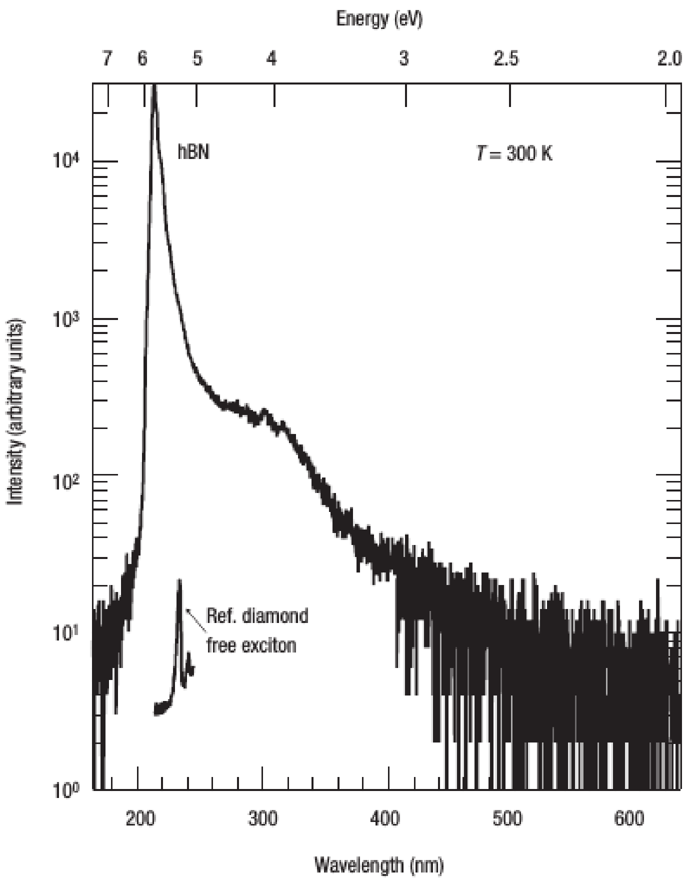
- hBN : a newcomer in the nitride industry for deep UV devices

The (old) controversy of the bandgap nature

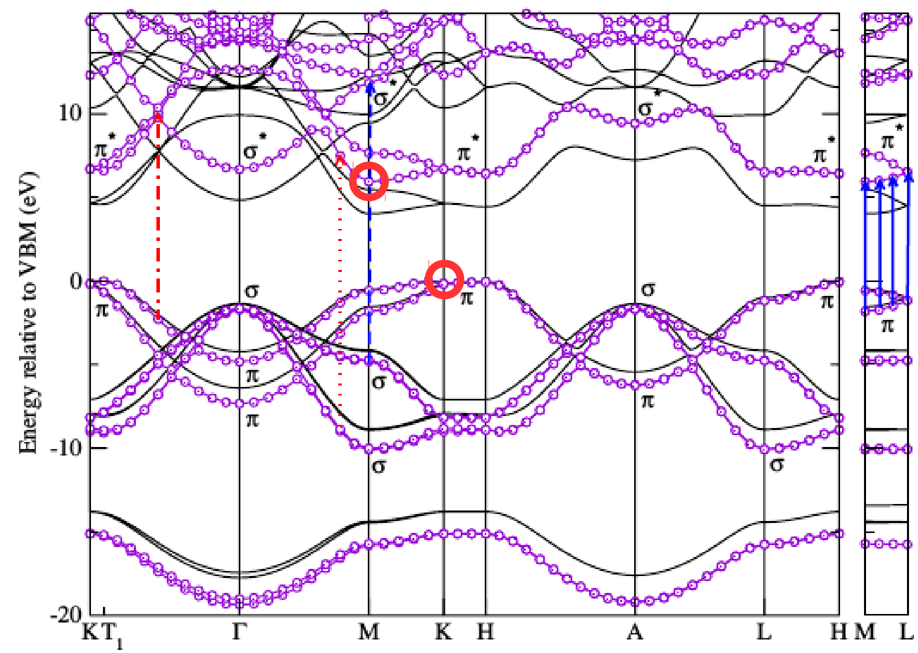
Direct
(optical spectroscopy)

OR ?

Indirect
(theoretical calculations)



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



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

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

ONLY bulk hBN
TODAY

ONLY bulk hBN
TODAY

For monolayer hBN

Sergei NOVIKOV
(We-5i)

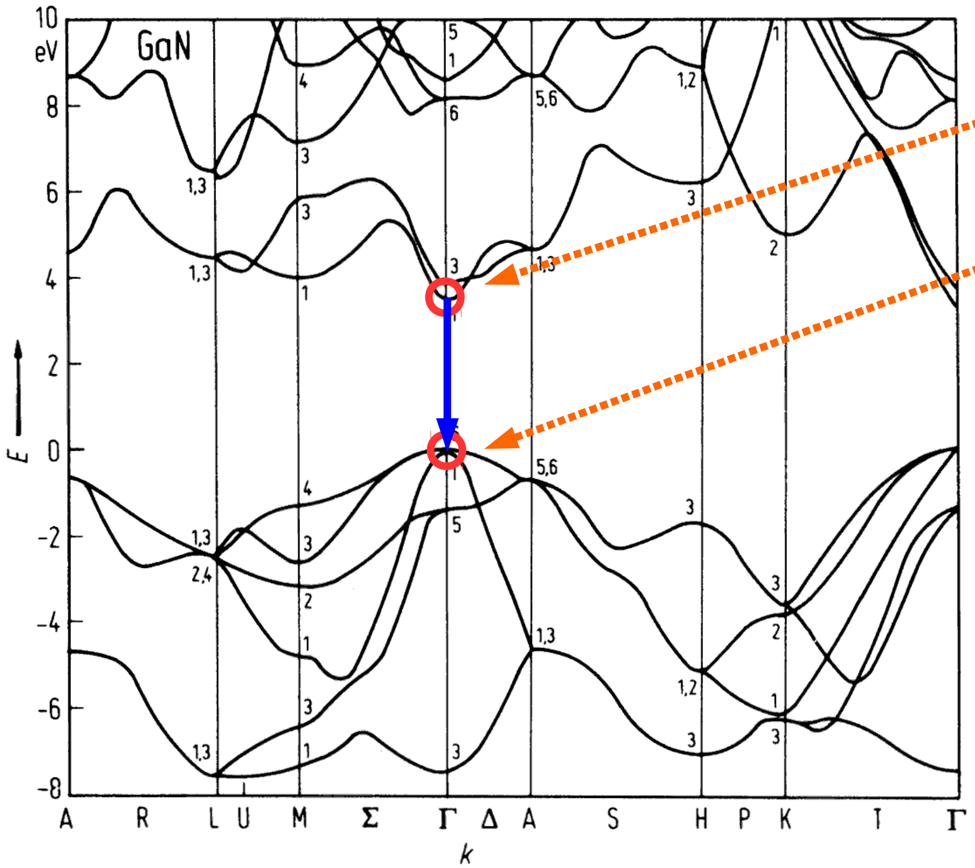
Christine ELIAS
(We-7o)

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)

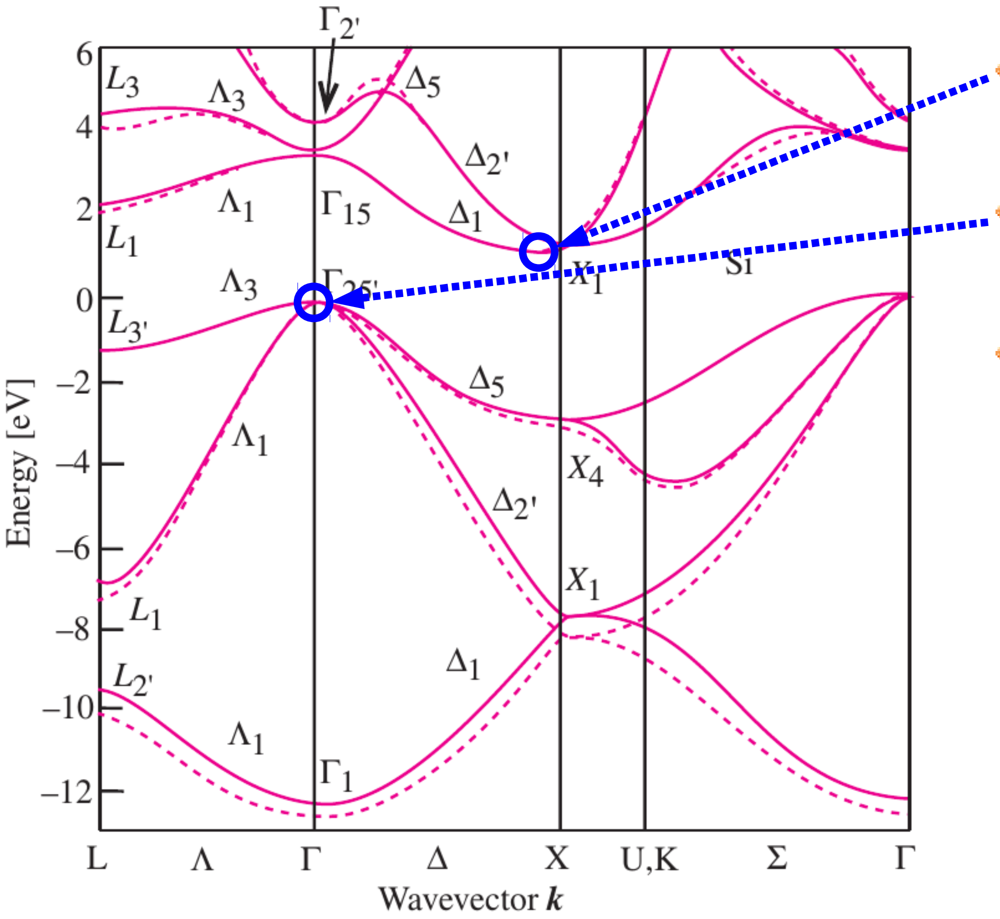
$$\lambda \sim 350nm \gg a \sim \mathring{A}$$

vertical transition in k-space

Direct recombination

Indirect bandgap : a well-known case

electronic bandstructure of SILICON



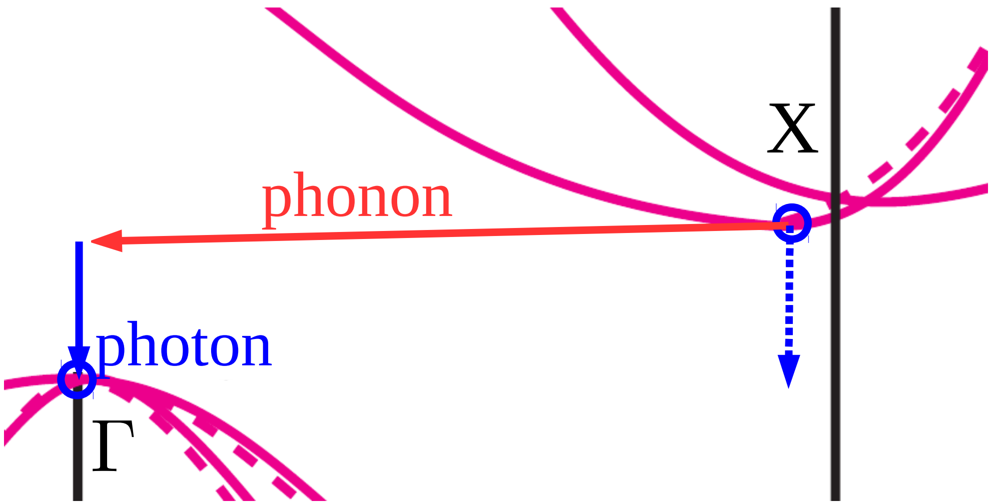
- Conduction band min @ X
- Valence band max @ Γ
- Bandgap ~ 1.12 eV (IR)

Momentum conservation

NOT FULFILLED

in direct recombination

Phonon-assisted recombination in silicon



- Phonon emission

⇨ momentum conservation

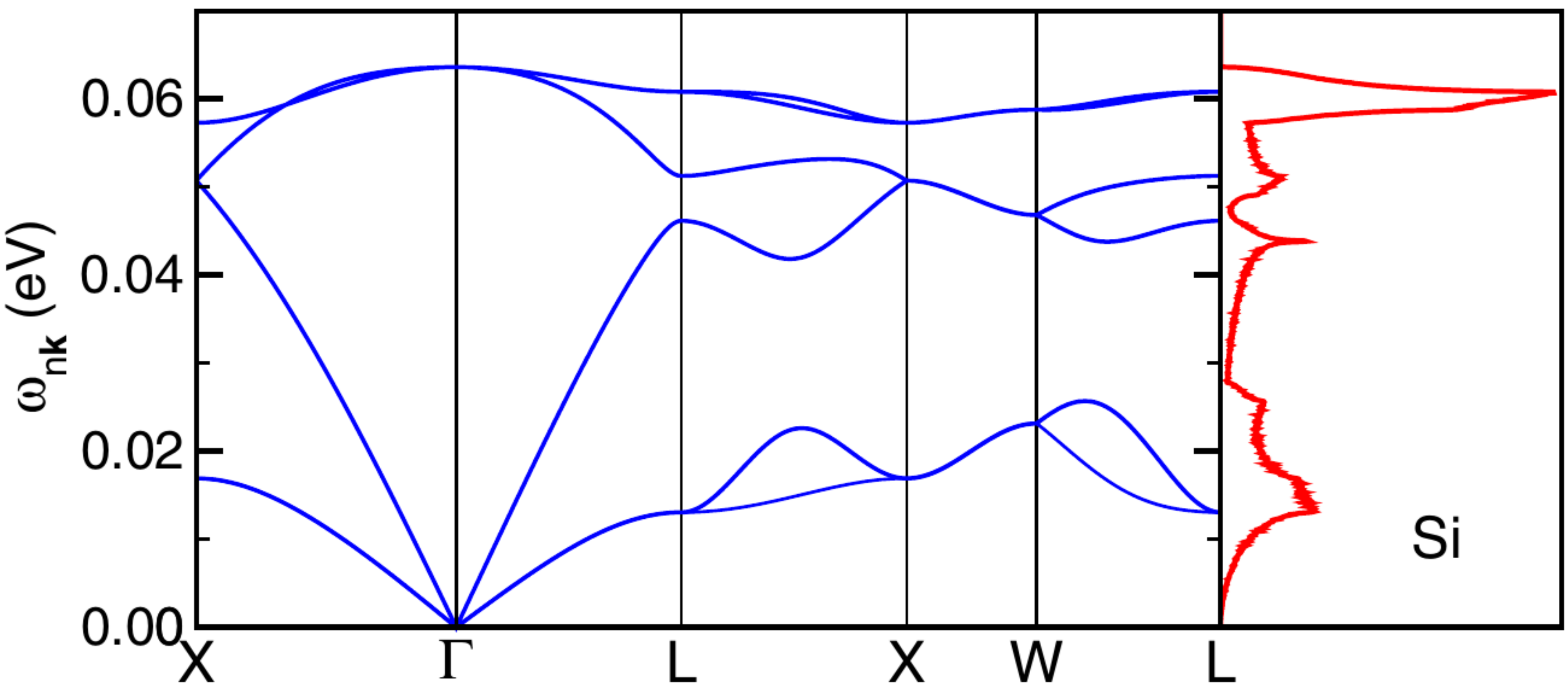
- Phonon wavevector

$$q = \Gamma X$$

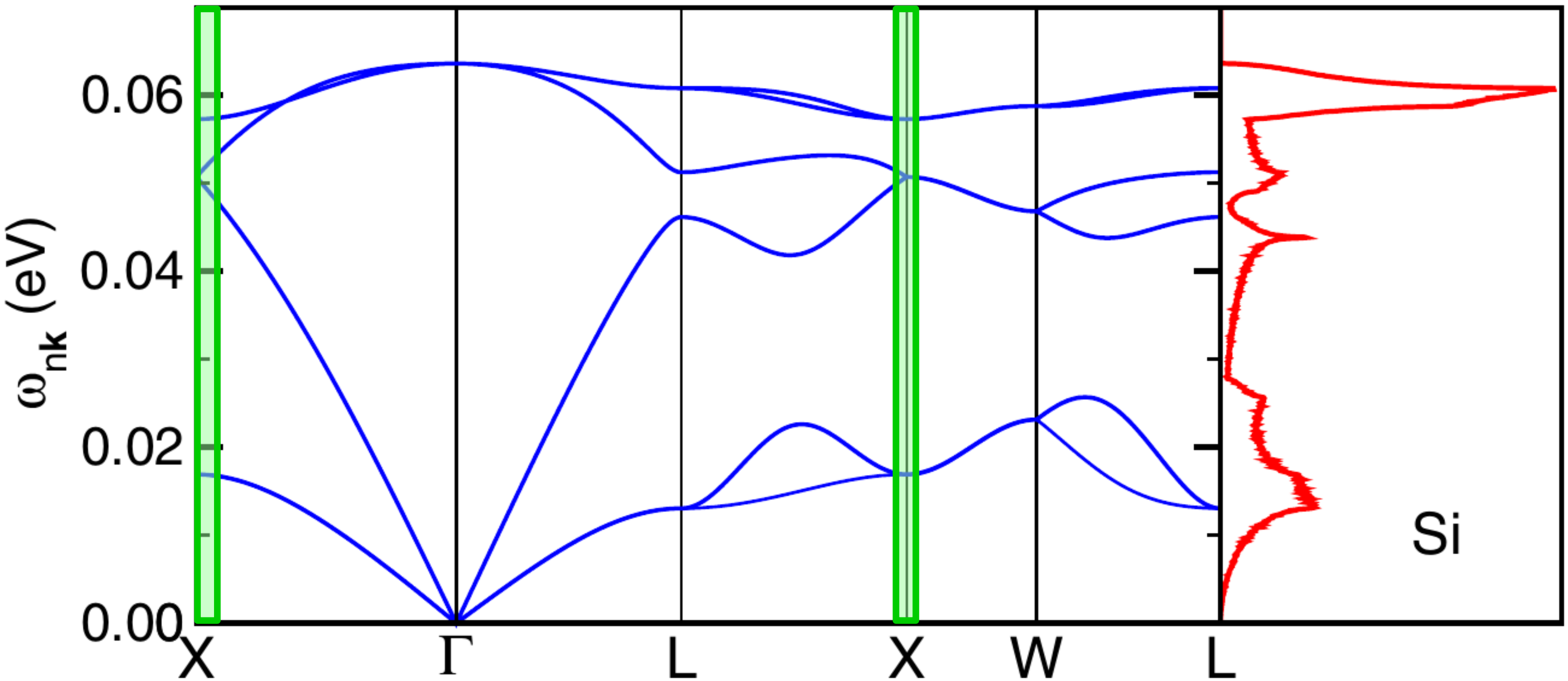
Since $k = 0$ at the zone center Γ,

phonon-assisted recombination involves phonons from X valley

Phonon bandstructure in silicon



Phonon bandstructure in silicon



Usual (old) game in indirect bandgap materials :

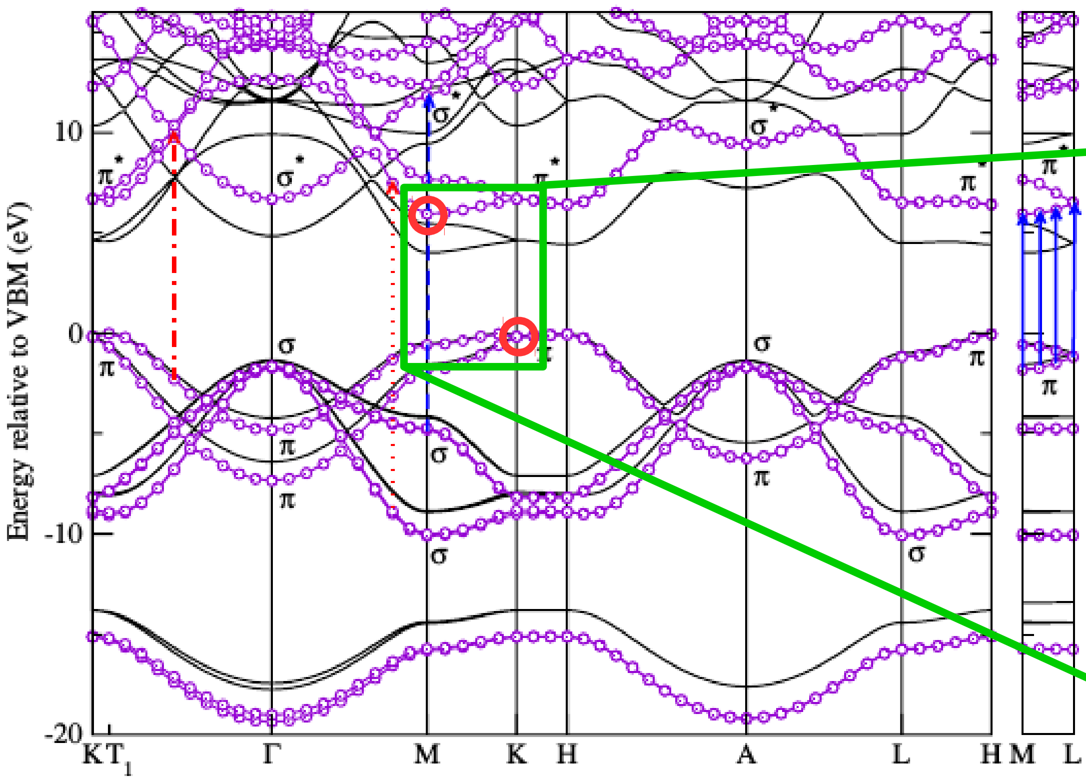
look for phonons in the same valley as the CB minimum !

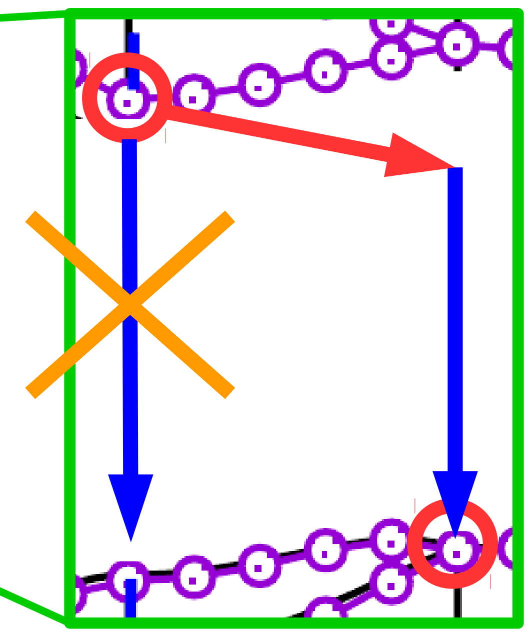
Valence band maximum is not at zone center in hBN

ab initio bandstructure calculations

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

INDIRECT gap



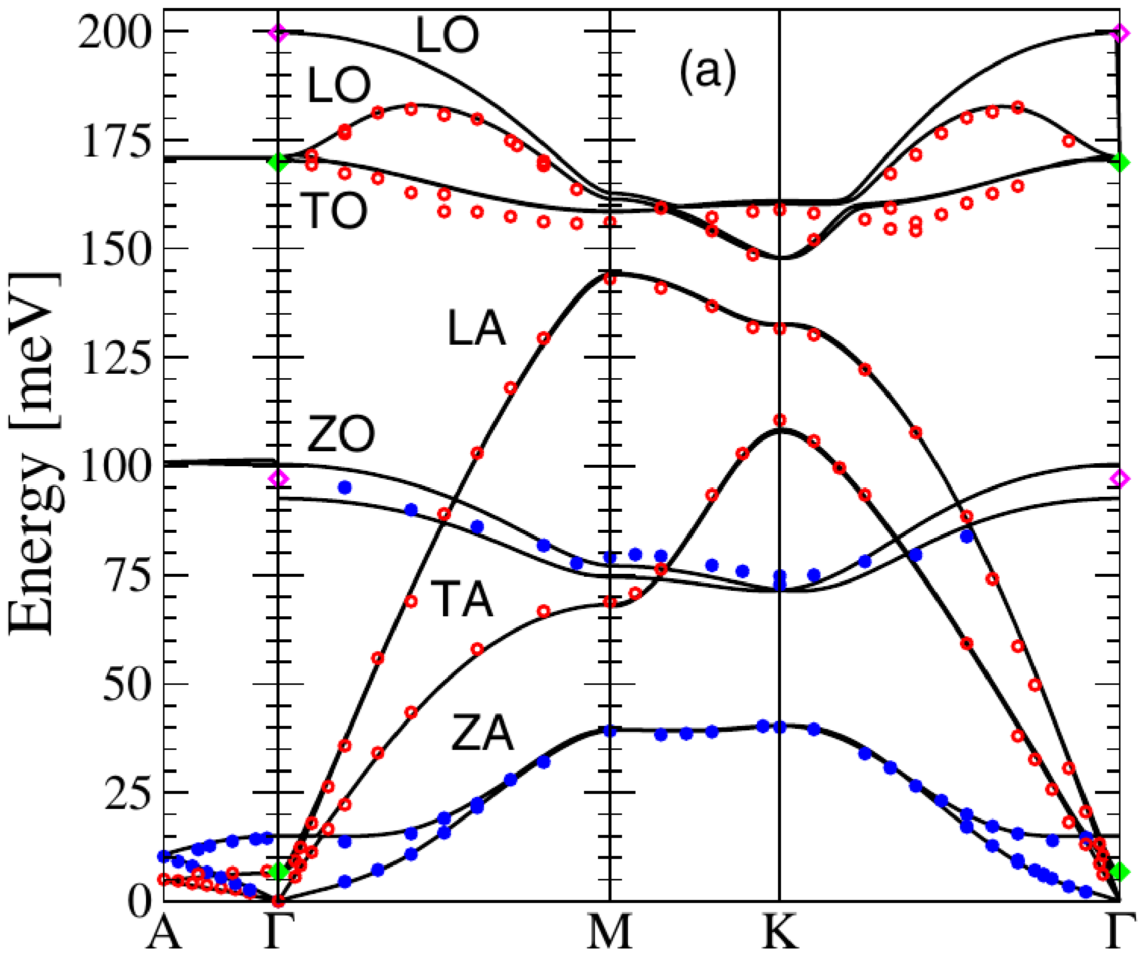


phonon-assisted recombination

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

Which phonons for emission in hBN ?

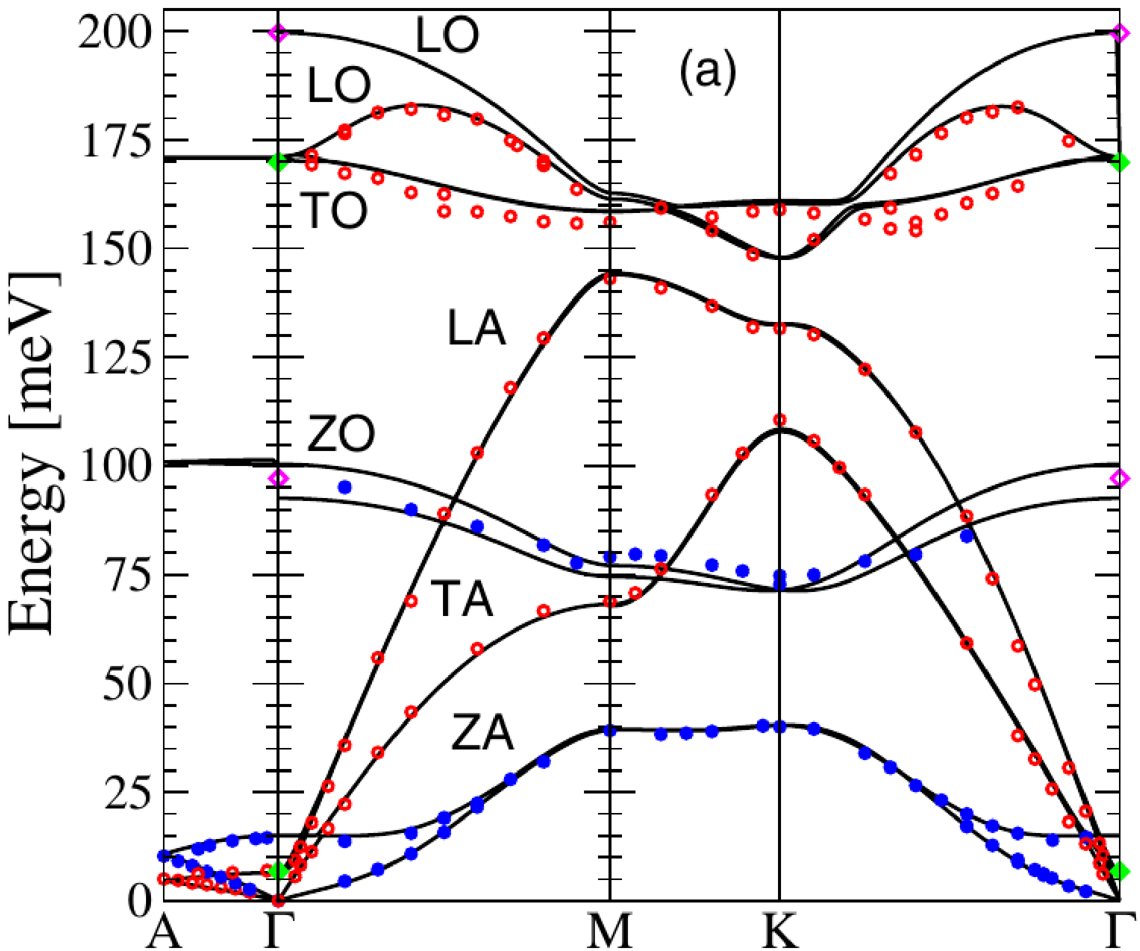
Phonon band-structure



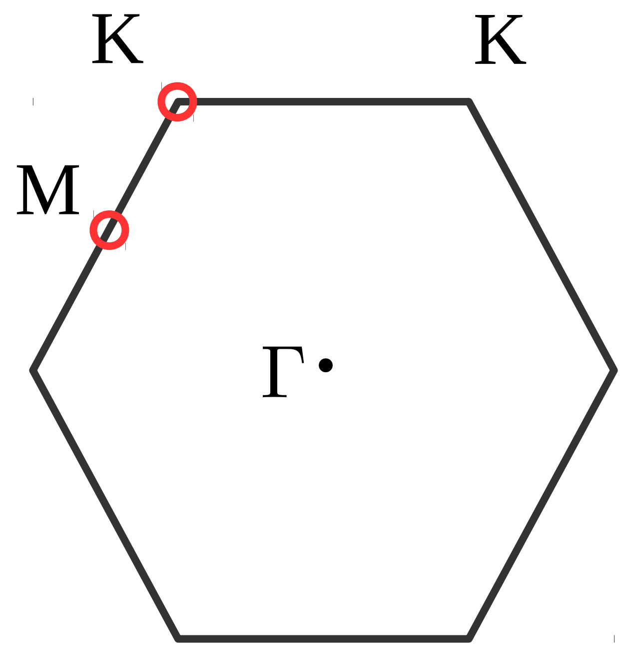
Serrano, PRL **98**, 095503 (2007)

Which phonons for emission in hBN ?

Phonon band-structure



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

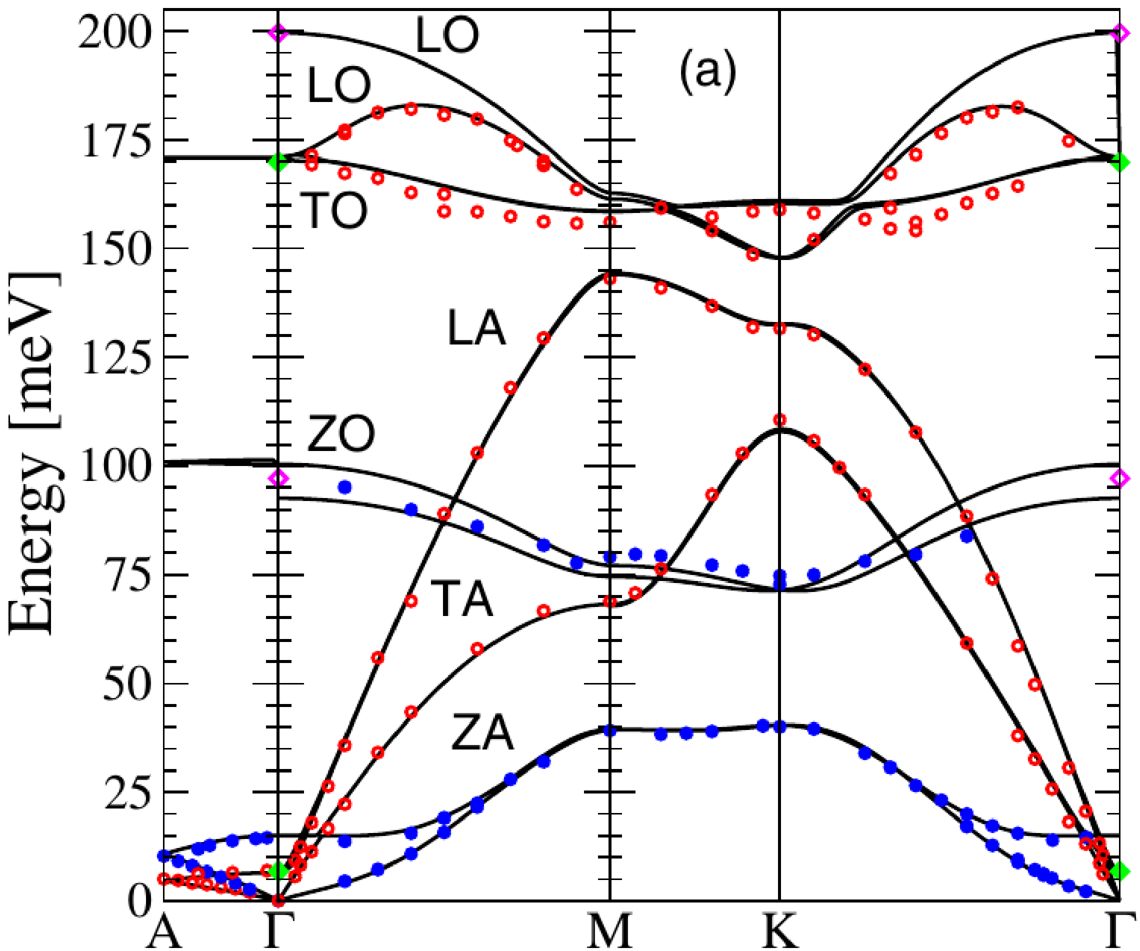


First Brillouin zone

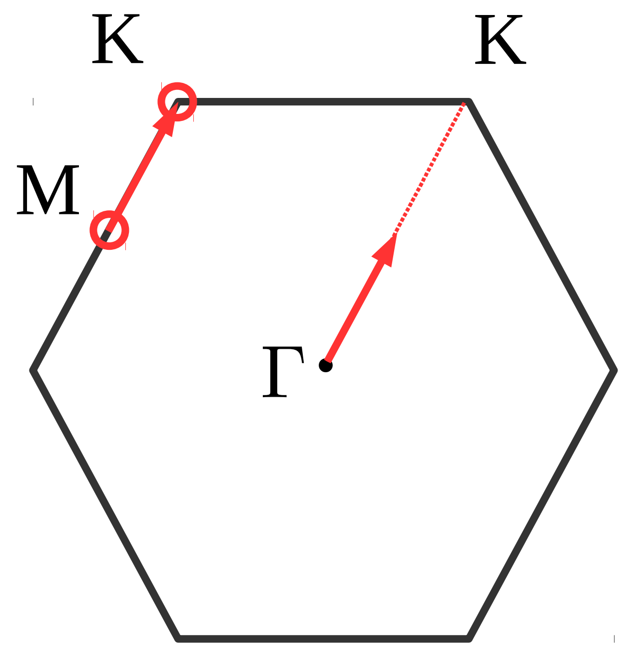
in hBN

Which phonons for emission in hBN ?

Phonon band-structure



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

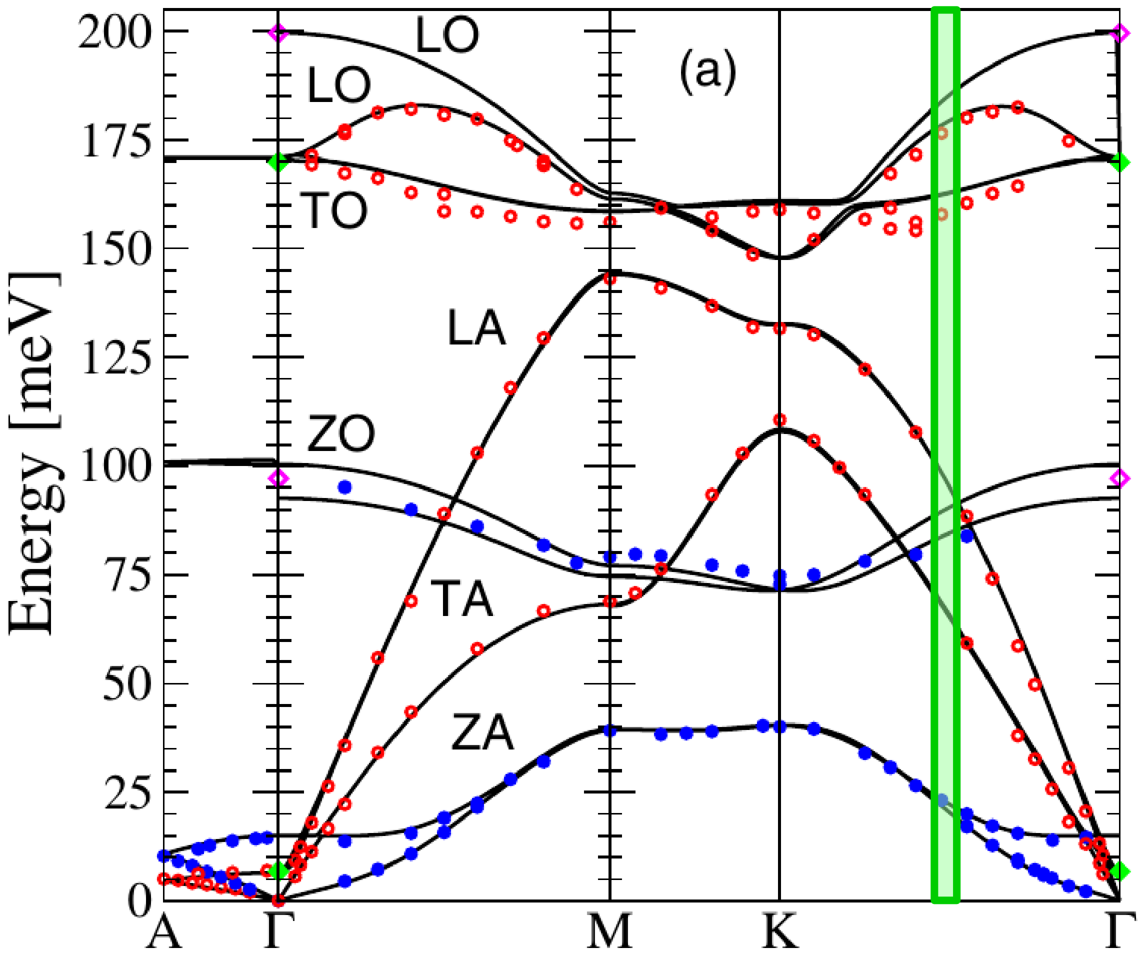


First Brillouin zone

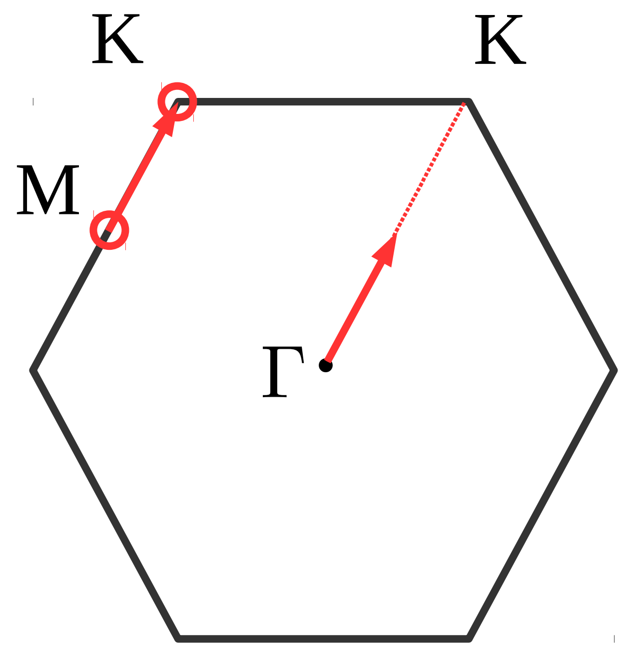
in hBN

Which phonons for emission in hBN ?

Phonon band-structure



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



First Brillouin zone

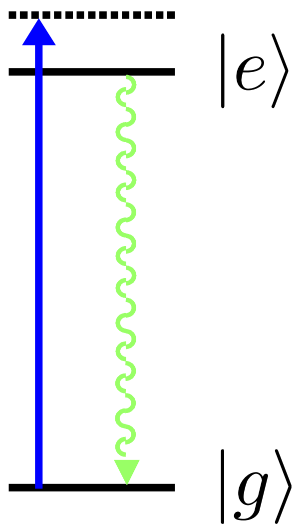
in hBN

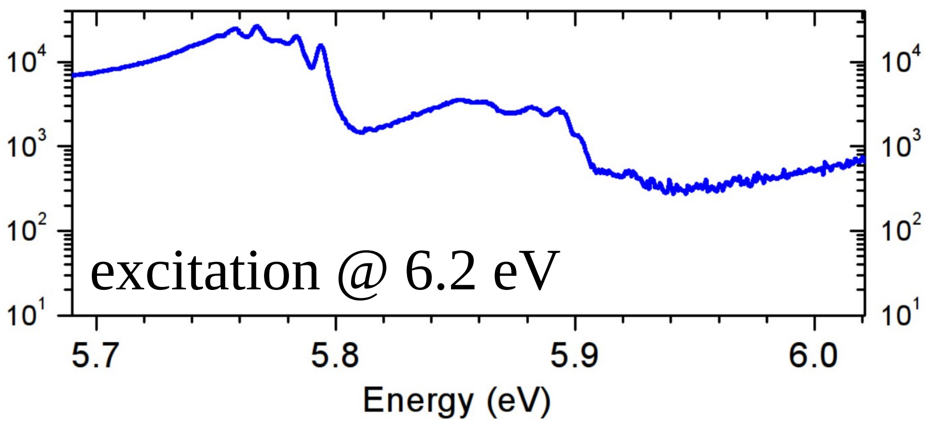
Outline

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

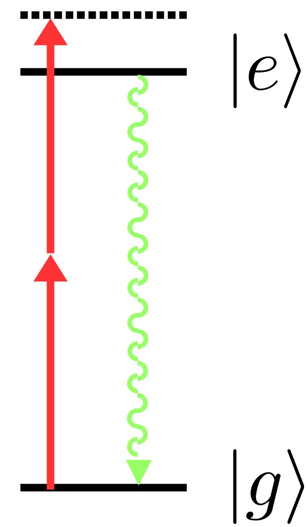
Two-photon spectroscopy

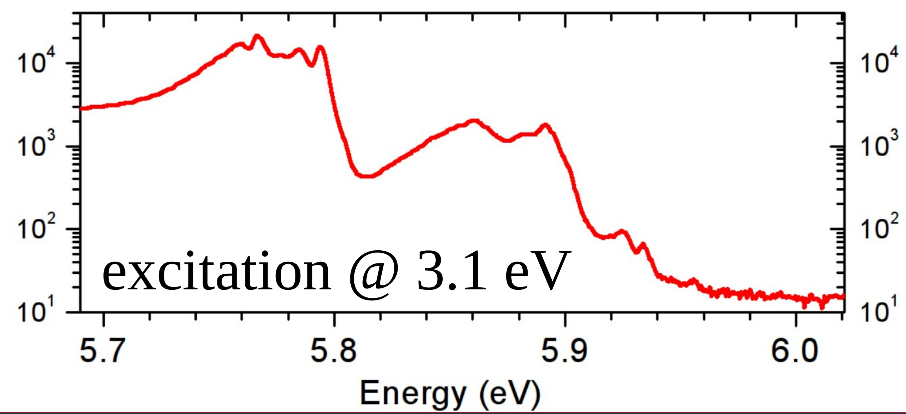
One-photon excitation





Two-photon excitation

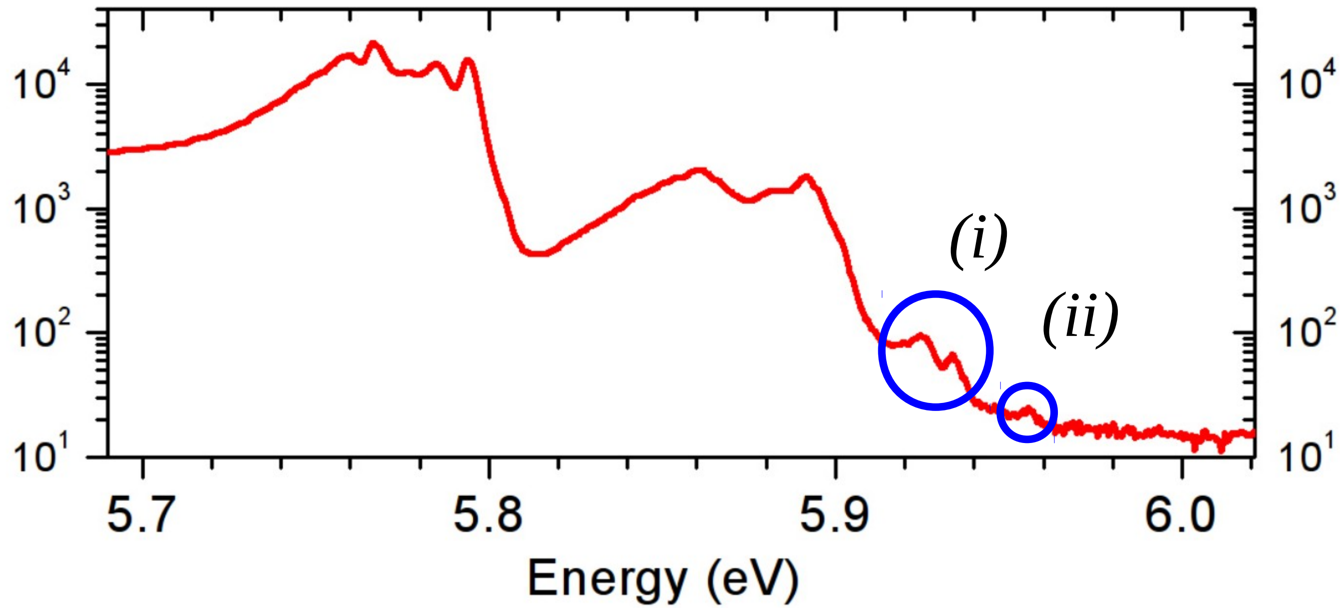




Suppression of laser background

Observation of previously undetected emission lines

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

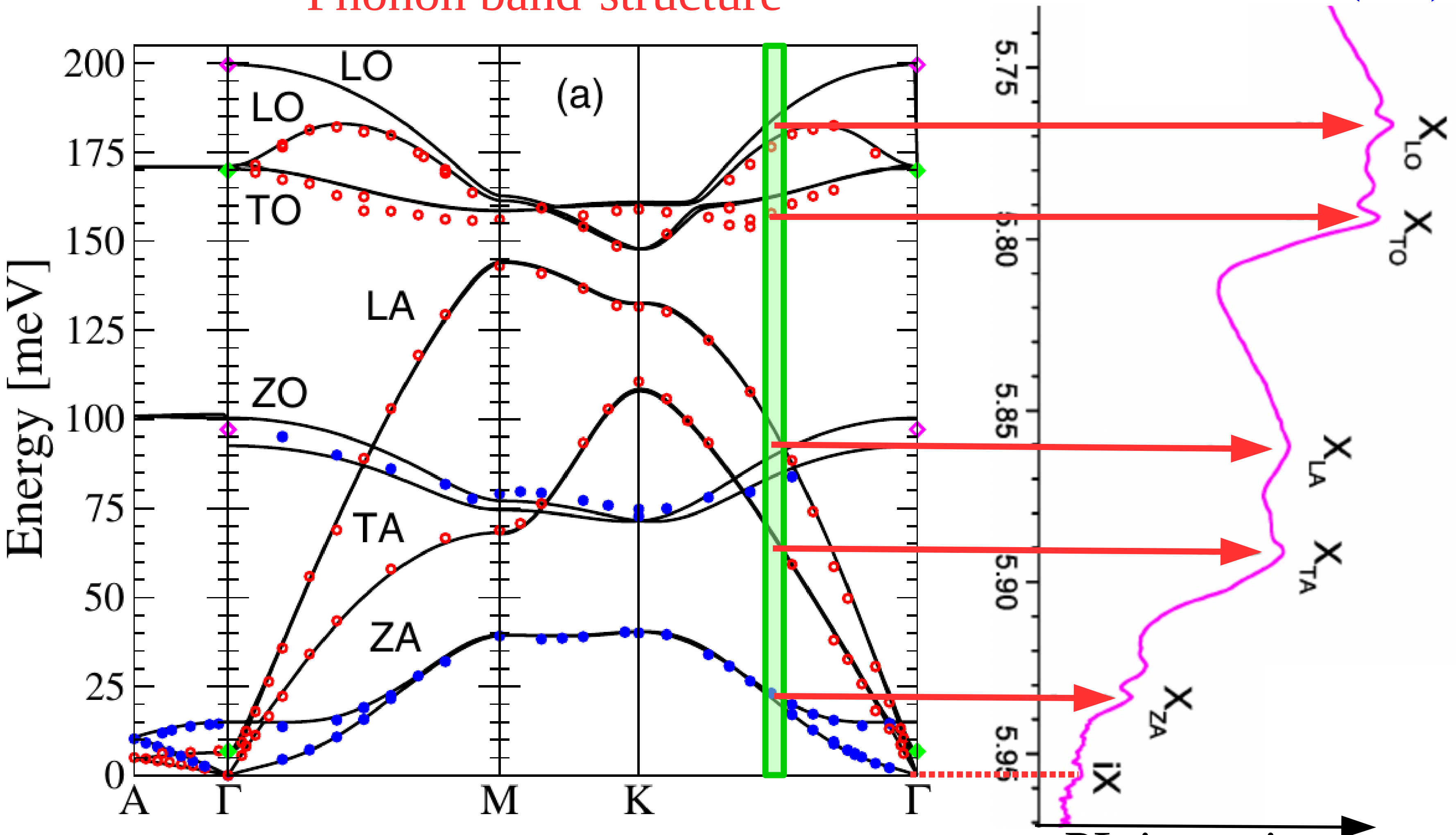


- *(i)*=doublet line @ 5.93 eV similar to emission lines at lower energy
- *(ii)*=weaker line @ 5.955 eV
- phonon-assisted recombination ?

Identification of phonon replicas

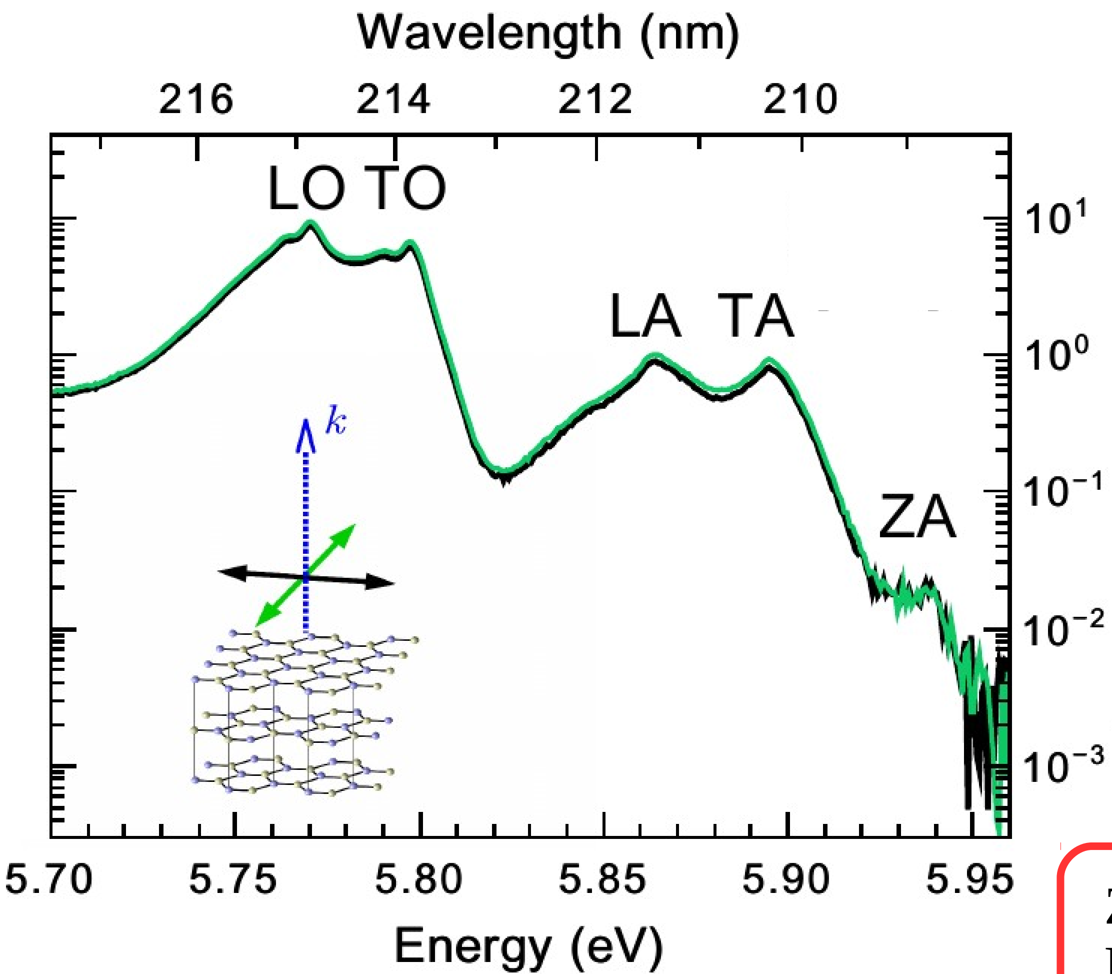
Phonon band-structure

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



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

Polarization-resolved measurements : along c-axis



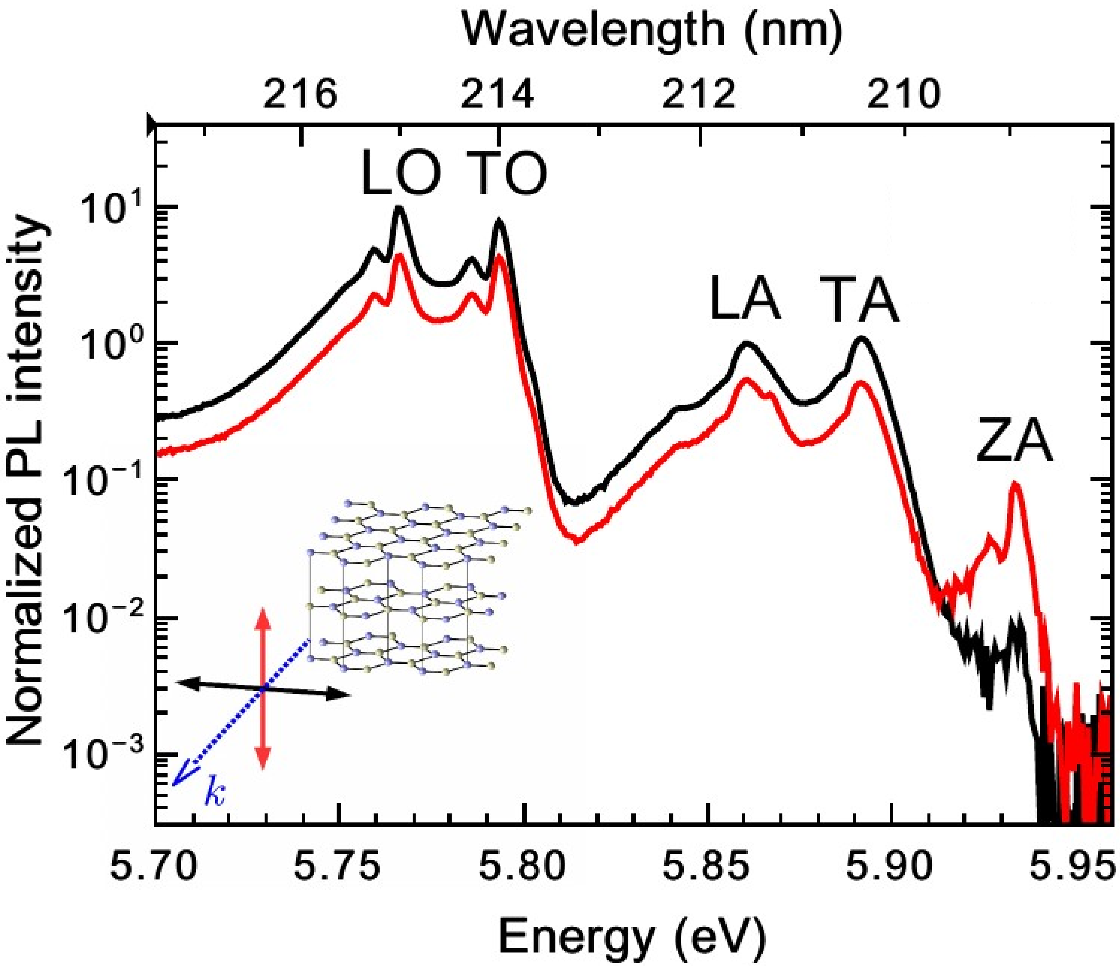
Vuong, 2D Mater. **4**, 011004 (2017)

- 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

  $k \perp c$

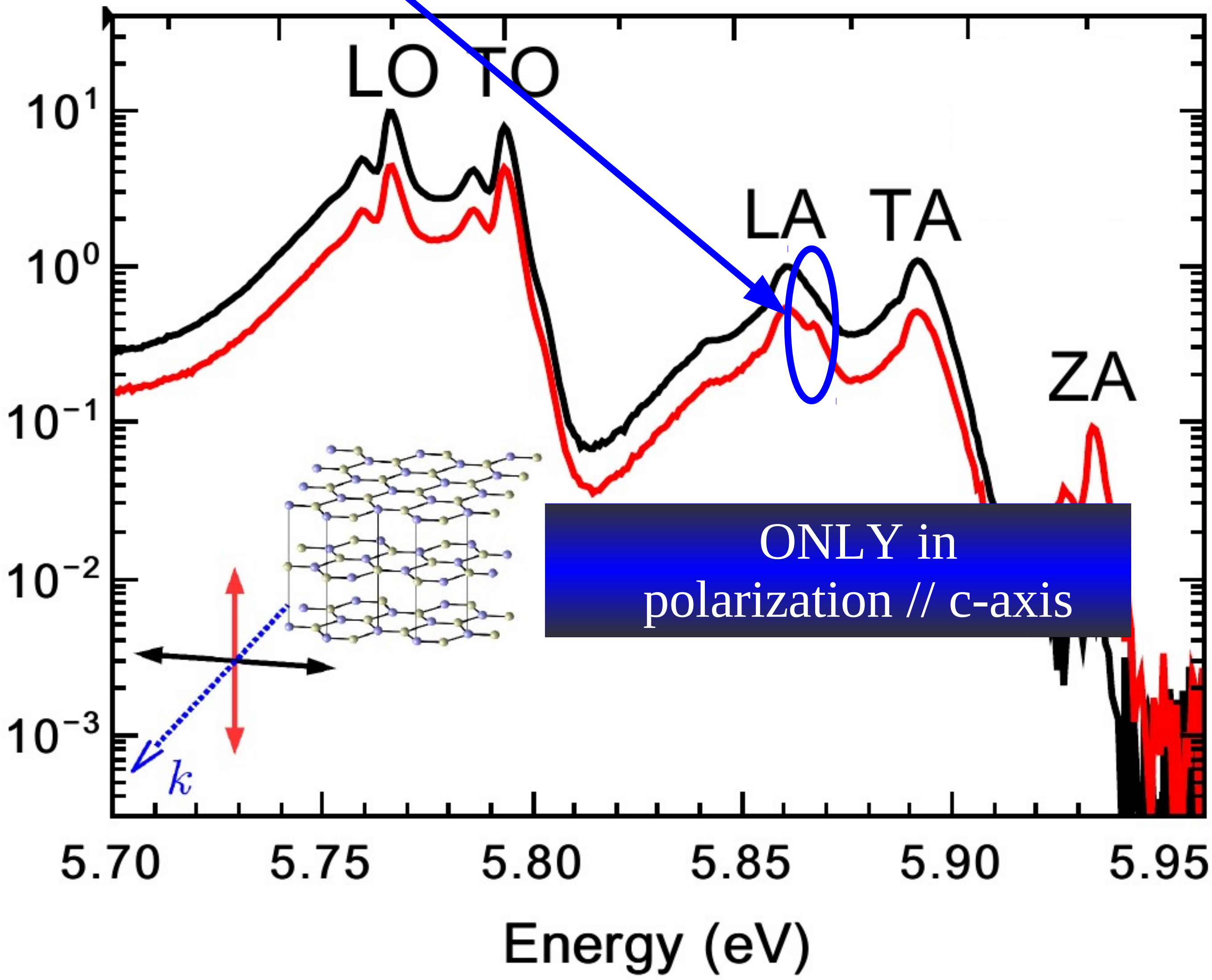
- Strong polarization dependence

- Anti-correlation between ZA and (LA, TA, LO, TO)

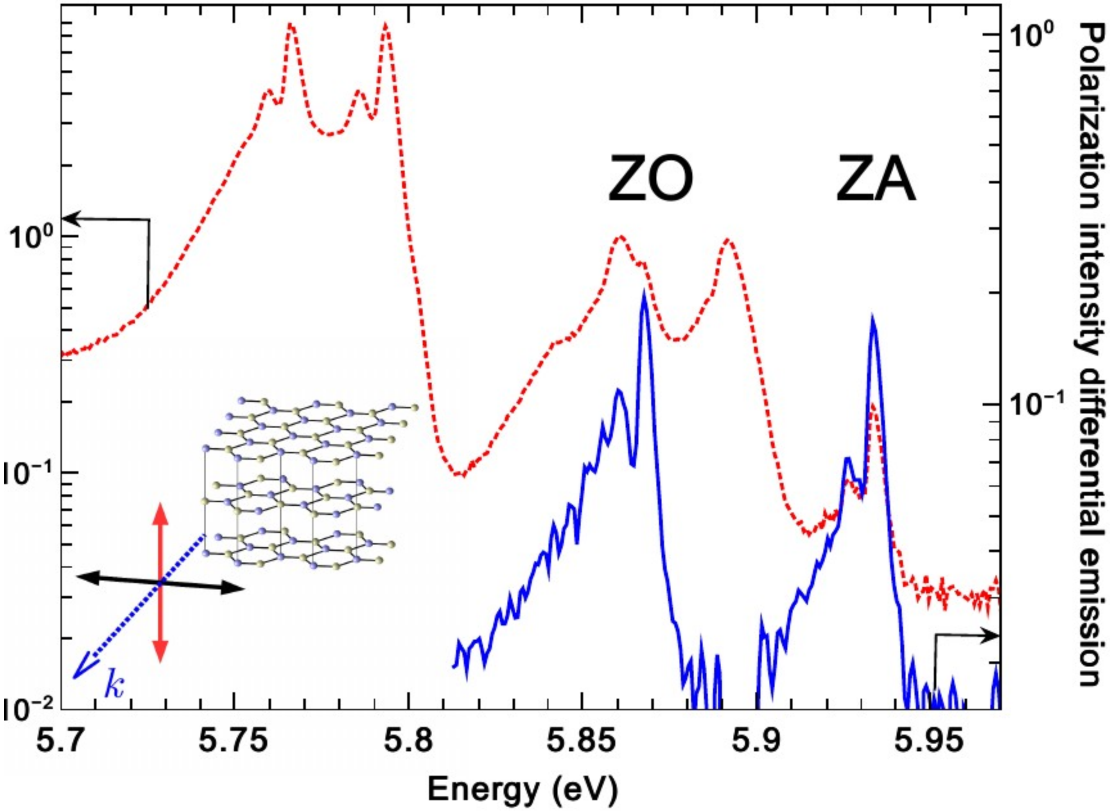
- ZA = out-of-plane vibrations

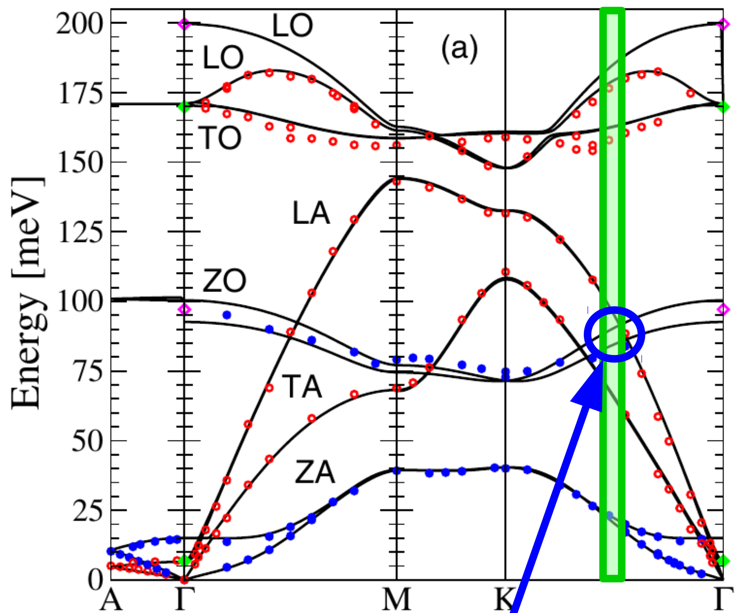
  allowed for $k \perp c$

Another previously undetected emission line...



ZO phonon replica

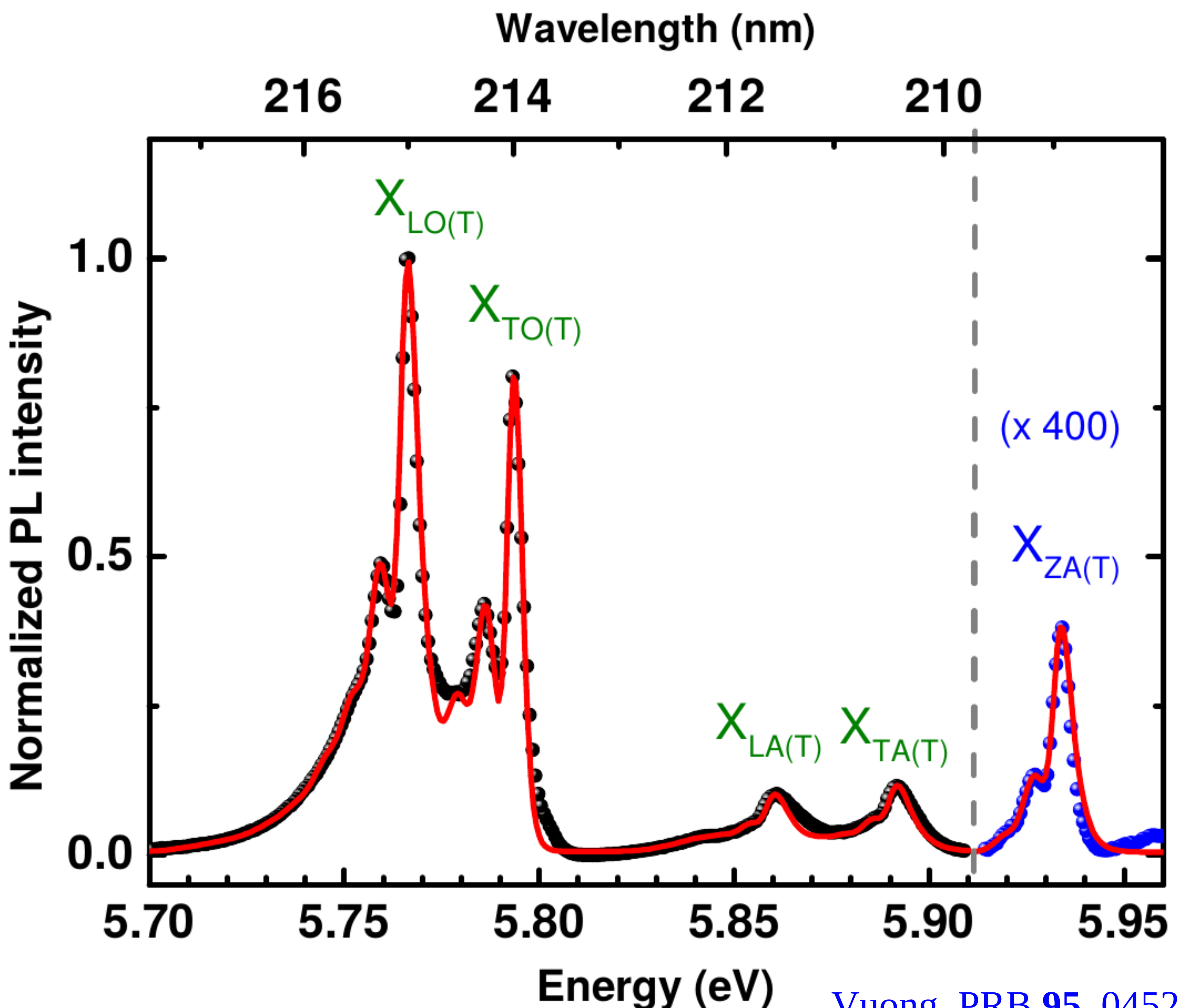




Vuong, 2D Mater. **4**, 011004 (2017)

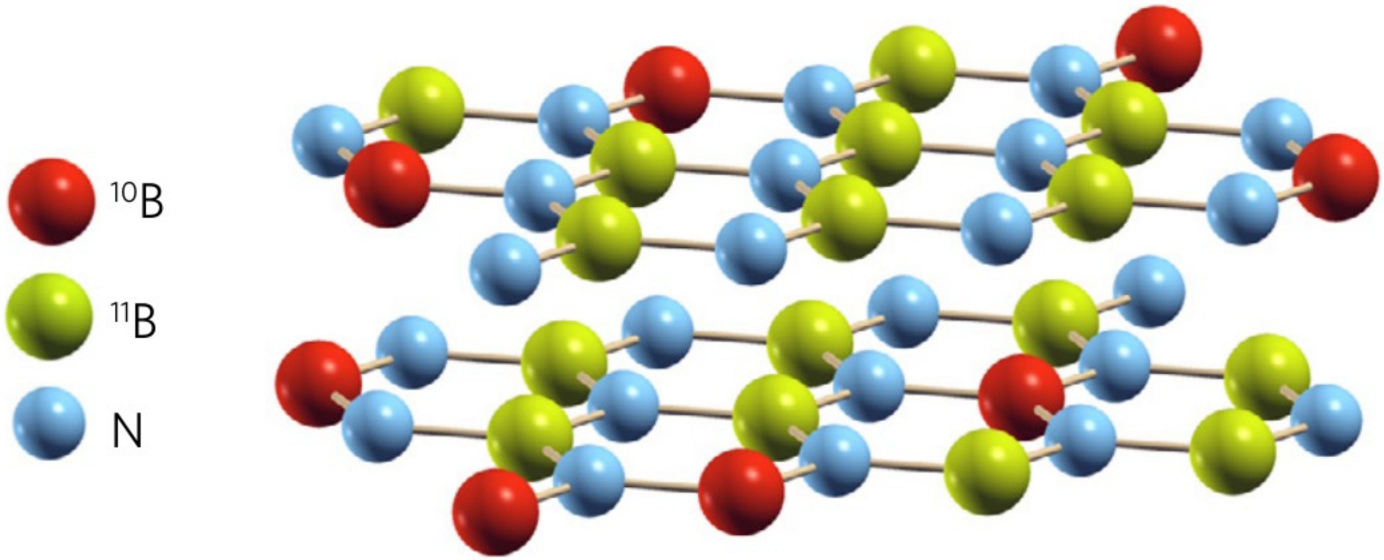
- observation of missing sixth replica
- ZO branch in between LA and TA in middle of Brillouin zone

Phonon group velocity



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

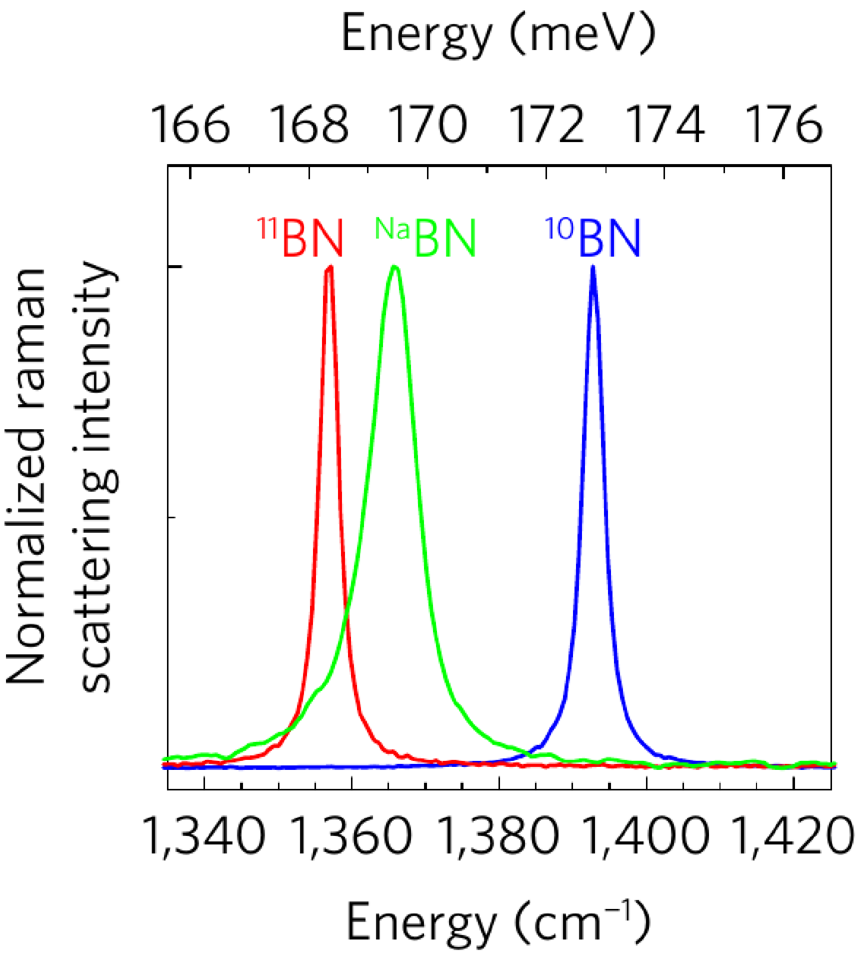
Two boron isotopes : ^{10}B and ^{11}B



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

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

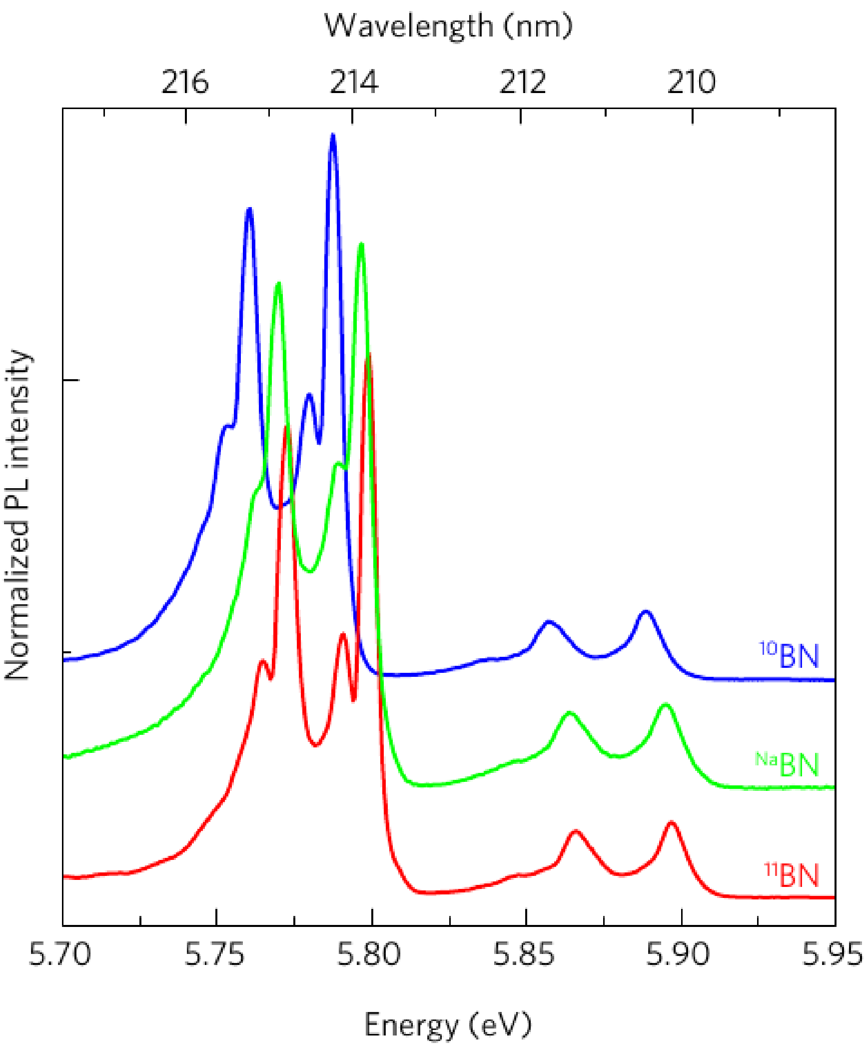
Raman spectroscopy



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

- Raman-active E_{2g} mode of high energy
- $\omega \sim \sqrt{\dfrac{k}{m}}$
- 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
- $h\nu = E_{gap} - E_{phonon}$

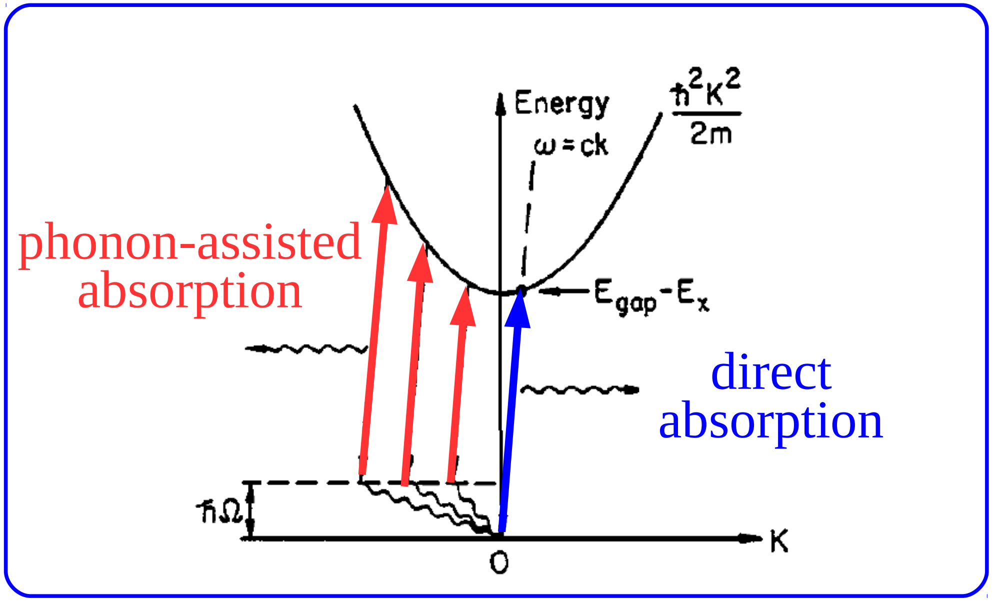
$$\delta E_{gap} \propto \frac{-1}{\sqrt{m}}$$

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

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

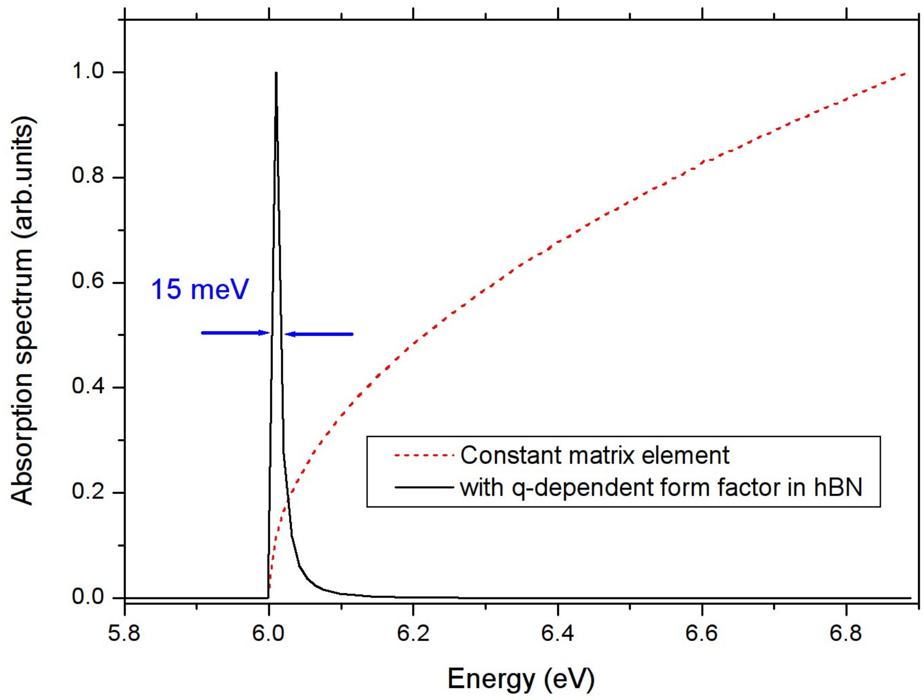
$$\sqrt{E - E_0}$$

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

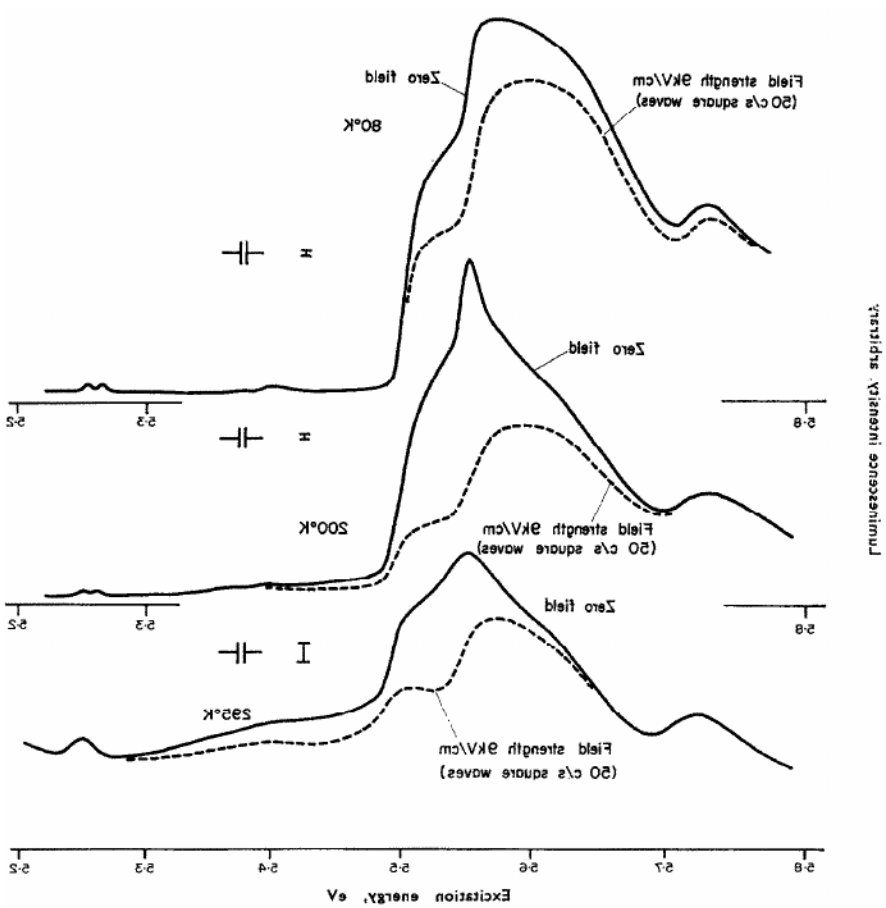


$$q \gg 1/a_B$$

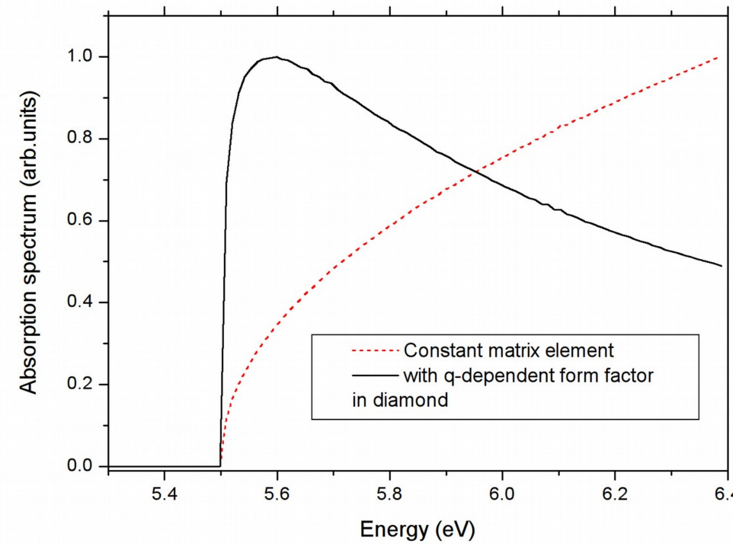
with a_B the exciton Bohr radius

Understanding the spectrum of indirect absorption

Diamond : Valence band @ zone center



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



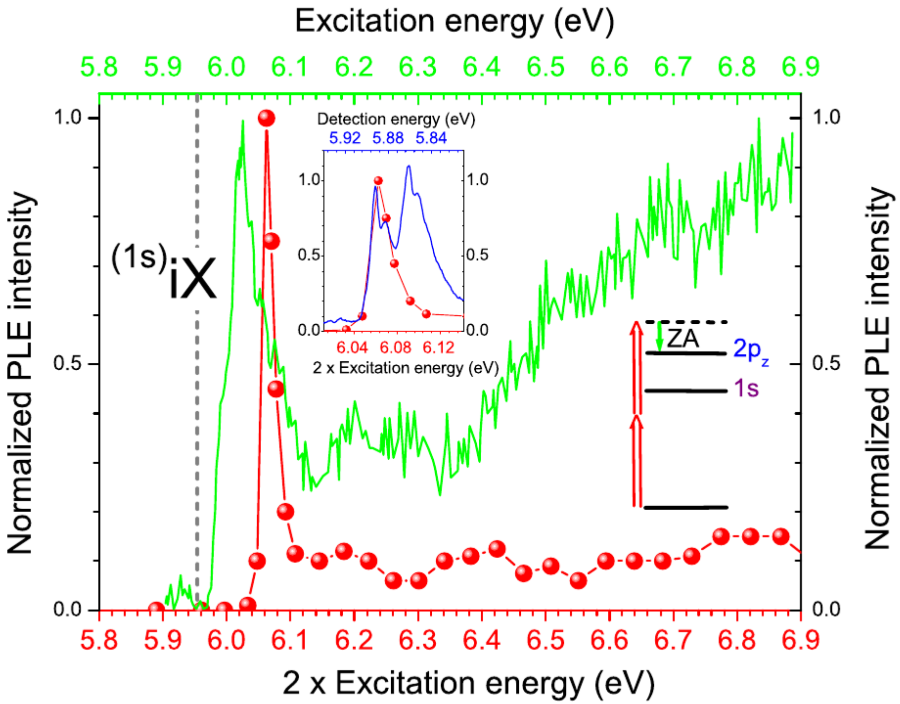
- $\sqrt{E - E_0}$ within the approximation of
  Elliott, Phys. Rev. **108**, 1384 (1957)
- q-dependence of exciton-phonon form factor

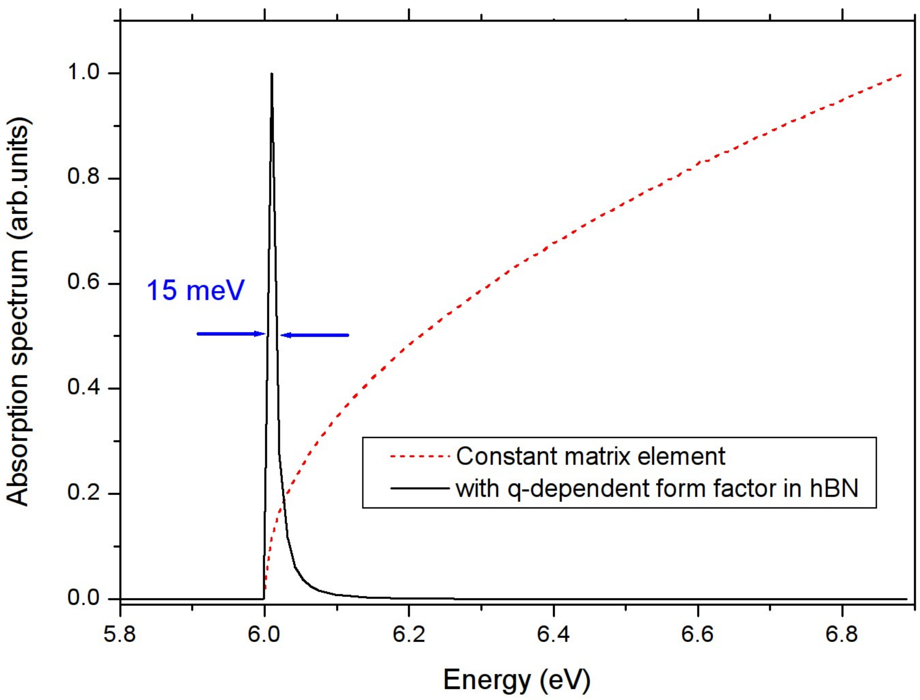
Understanding the spectrum of indirect absorption in hBN

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)

Outline

- Indirect vs direct bandgap semiconductors
- Two-photon spectroscopy
- Unconventional optical response
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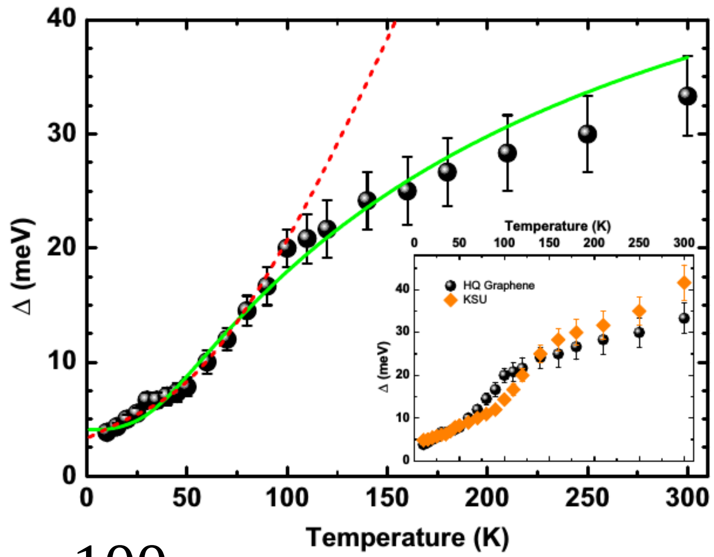
Strong exciton-phonon coupling in hBN, but why ?

- Thermally-assisted broadening

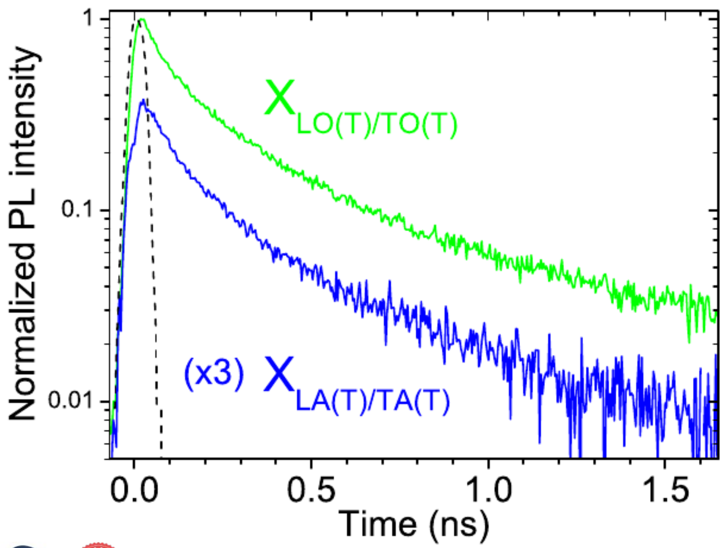
Phys. Rev. B **95**, 201202(R) (2017)

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]

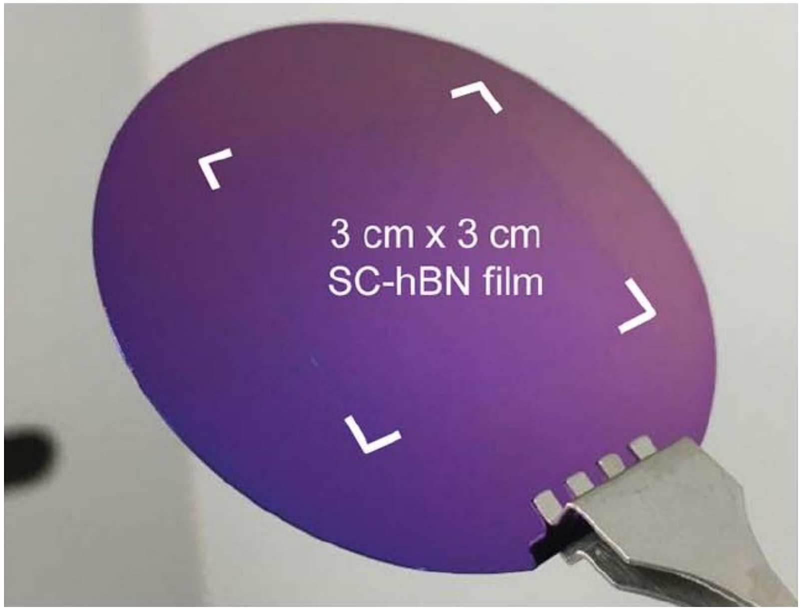
PHYSICAL REVIEW LETTERS **122**, 187401 (2019)

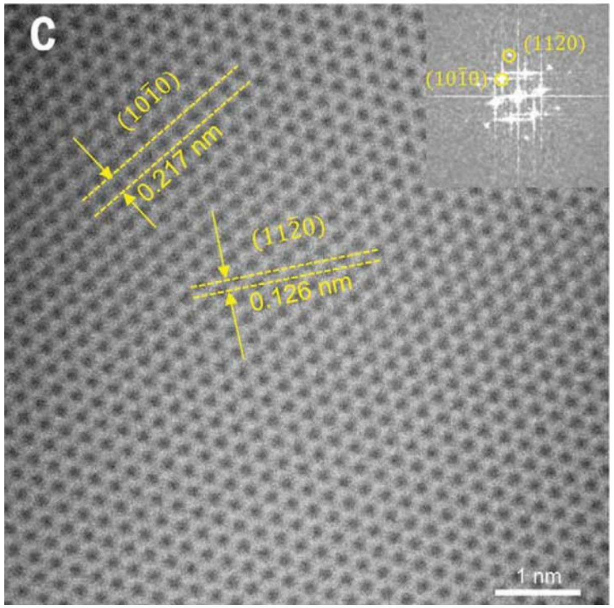
Exciton-Phonon Coupling in the Ultraviolet Absorption and Emission Spectra of Bulk Hexagonal Boron Nitride

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

Epitaxy of high-quality hBN

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



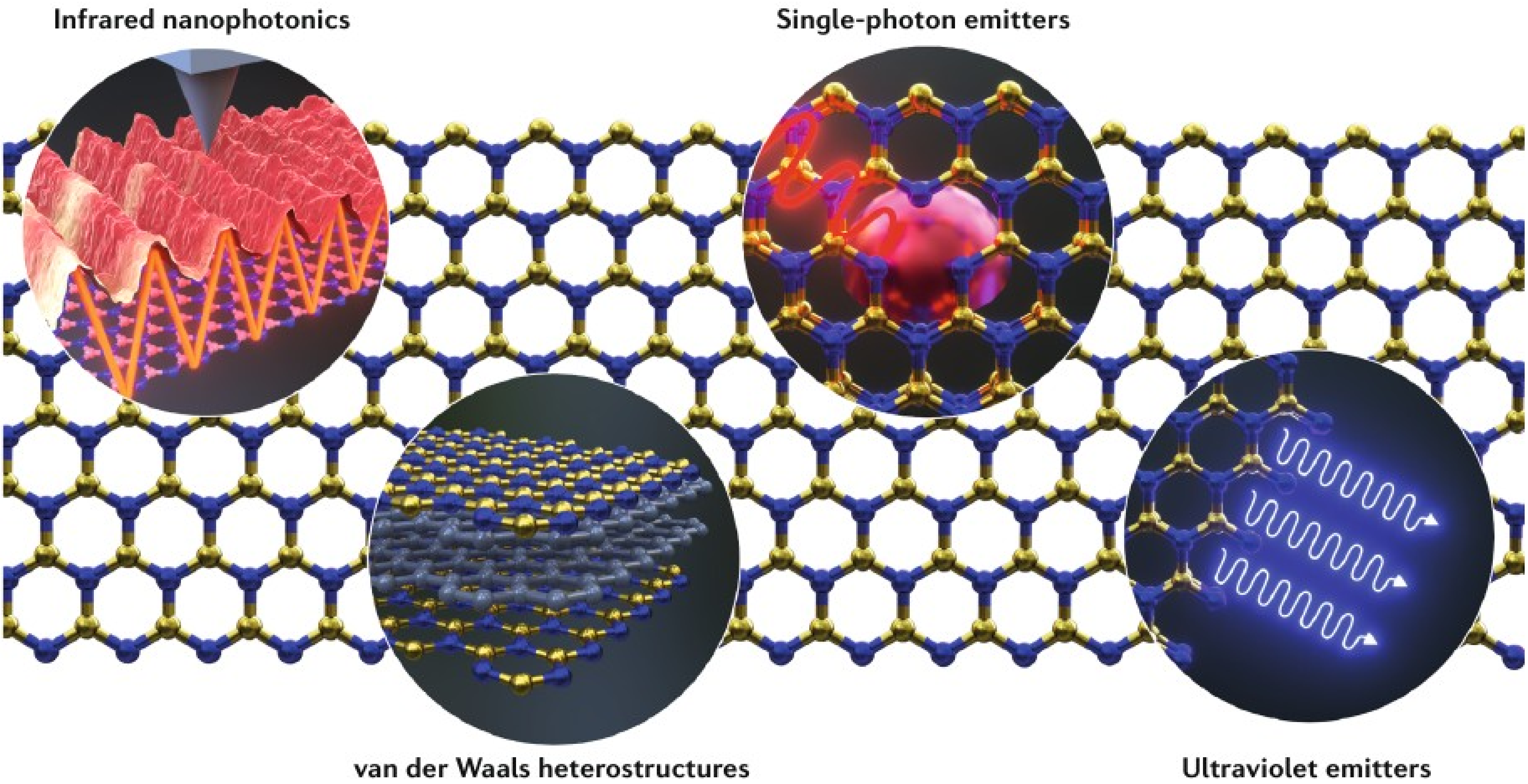


Lee, Science **362**, 817–821 (2018)

NEXT STEPS : Thick epilayers
+ DOPING !

Photonics with hBN

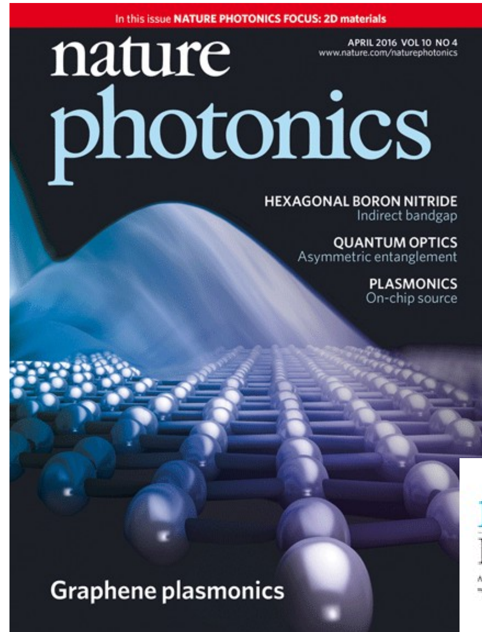
Nature Reviews Materials **4**, 552 (2019)

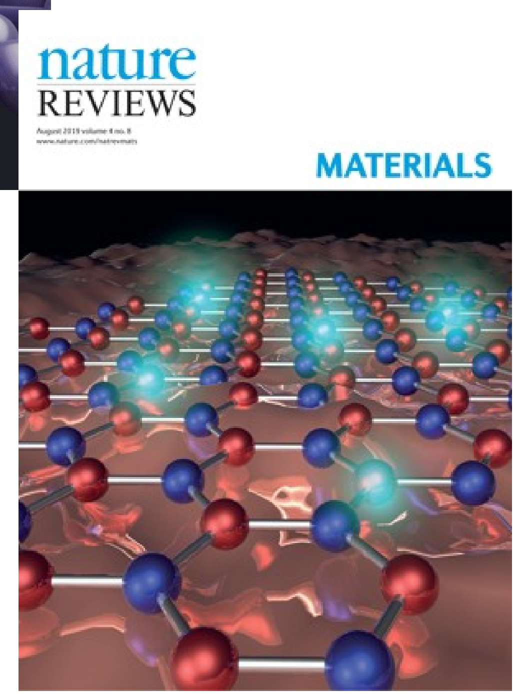


Acknowledgements

L2C, Montpellier, France
C. Elias
P. Vuong
T. Pelini
P. Valvin
L. Martinez
V. Jacques
B. Gil

LPS, Orsay, France
A. Zobelli
C2N, Saclay, France
A. Ouerghi
NIMS, Ibaraki, Japan
K. Watanabe
T. Taniguchi
Barcelona, Spain
L. Artus
R. Cusco





KSU, USA
J. Edgar
Nottingham, UK
S. Novikov

Optoelectronic properties of hexagonal boron nitride

G. Cassabois

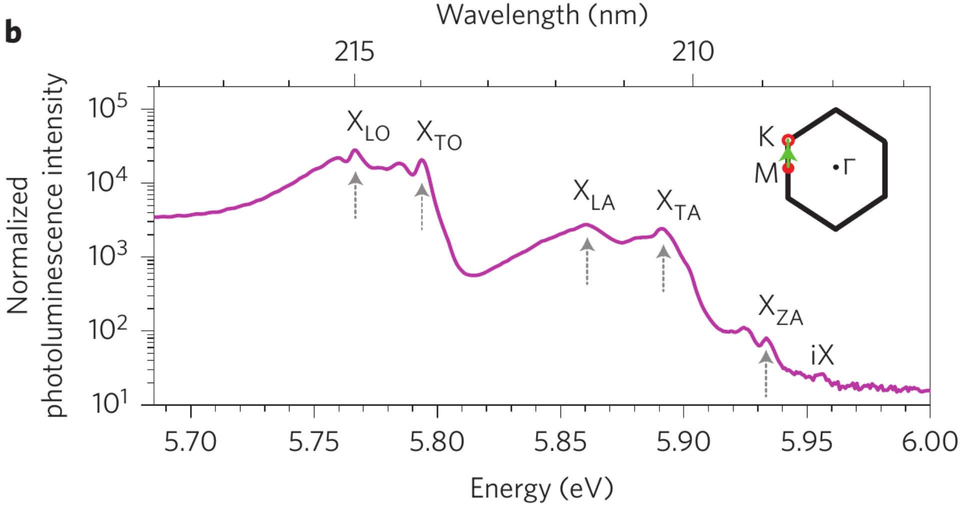
Laboratoire Charles Coulomb

CNRS / Université de Montpellier

Montpellier, France

Bulk hBN: an indirect bandgap material

- Optical spectroscopy



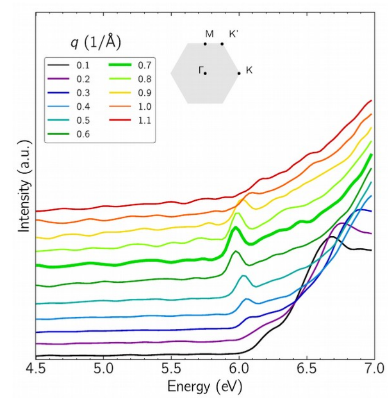
- Phonon-assisted emission

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)

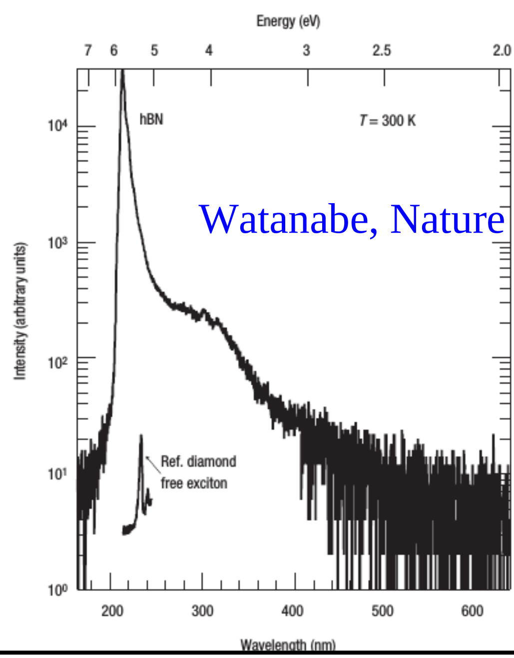


Deep UV opto-electronics

hBN = perfect candidate for deep UV

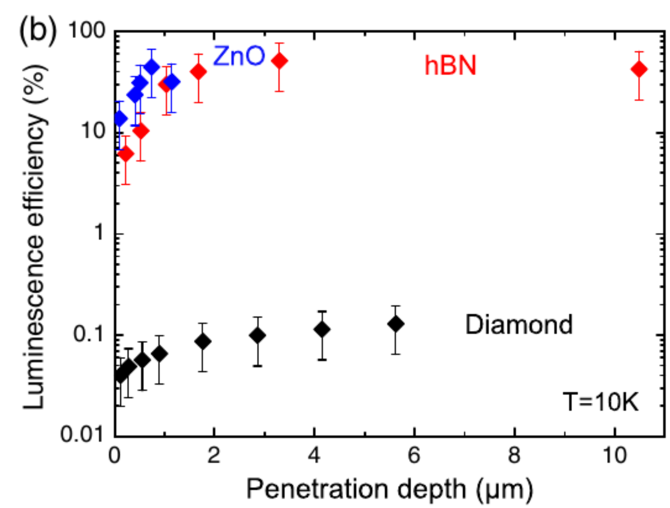
- High extraction efficiency
  (as usual for indirect semiconductors)

- High internal quantum efficiency
  VERY UNUSUAL



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

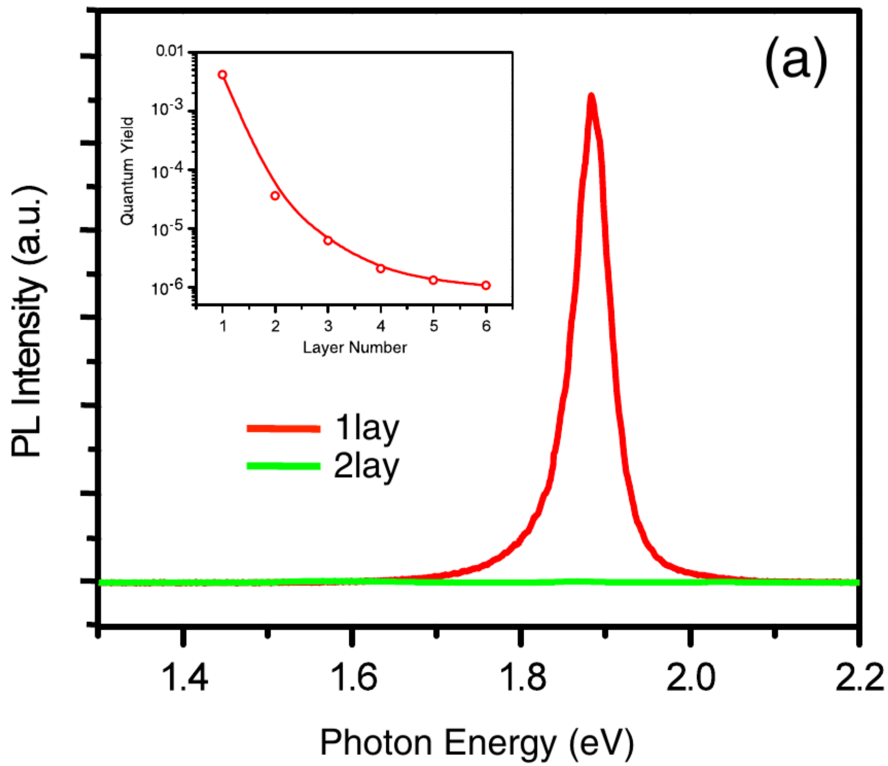
Schue, PRL **122**, 067401 (2019)



Monolayer hBN :
a direct bandgap semiconductor

Direct bandgap emission in monolayer

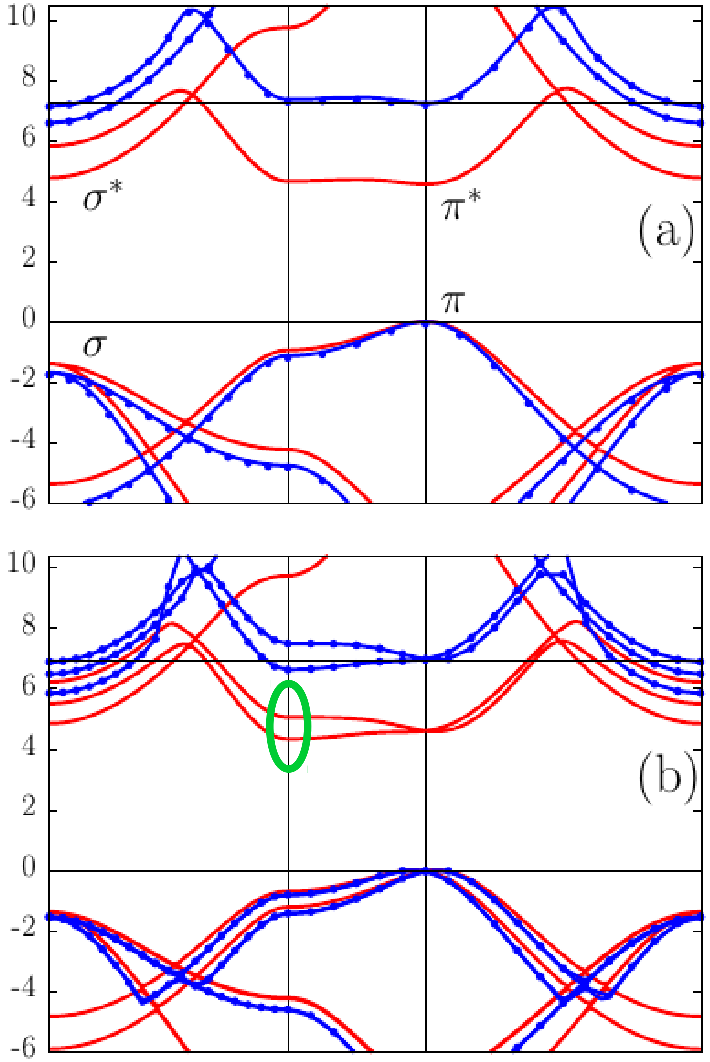
- The textbook example of MoS_2



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

- Same effect is predicted in hBN !!

Electronic bandstructure vs layer number



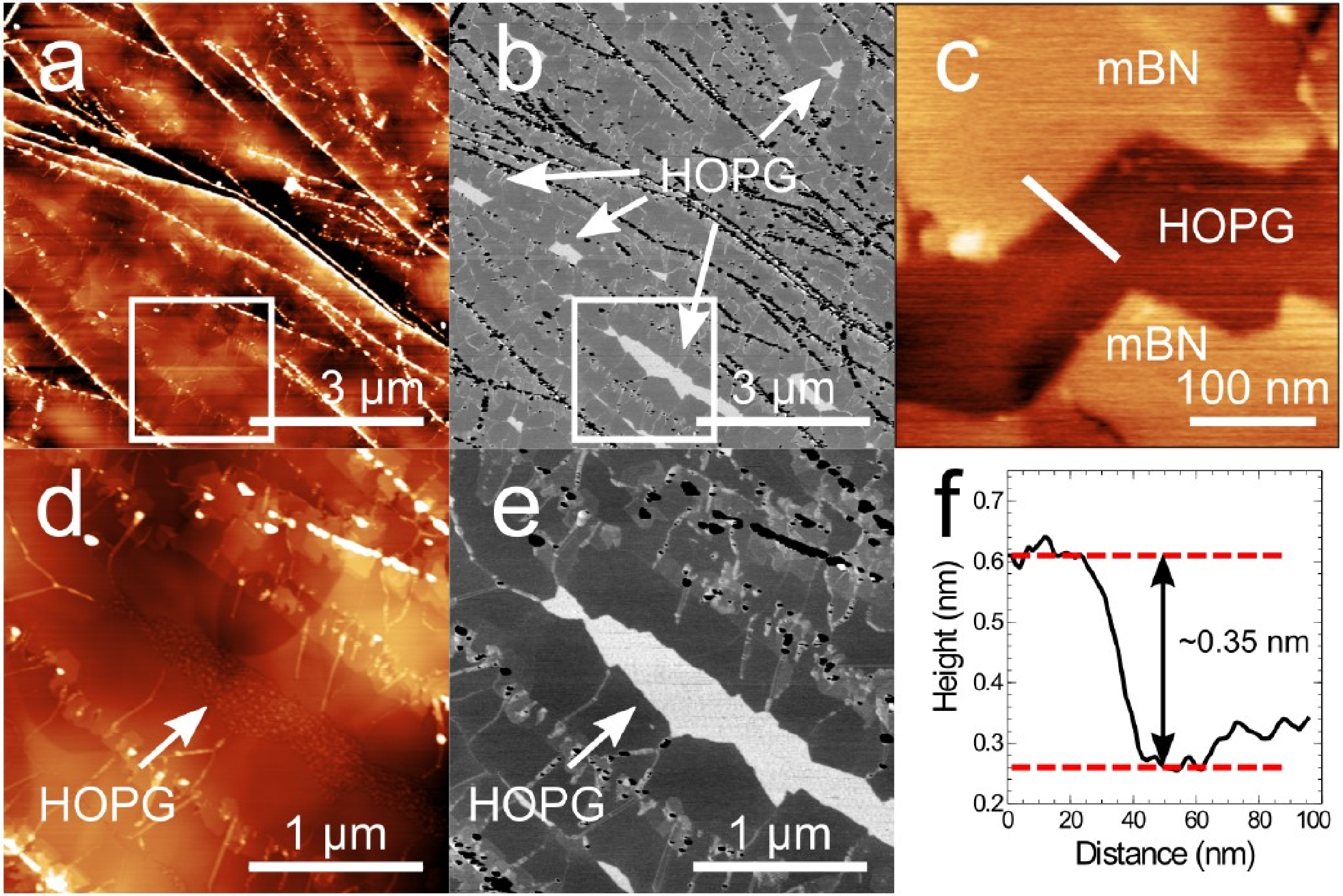
1 layer : direct bandgap

2 layers : indirect bandgap to bulk

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

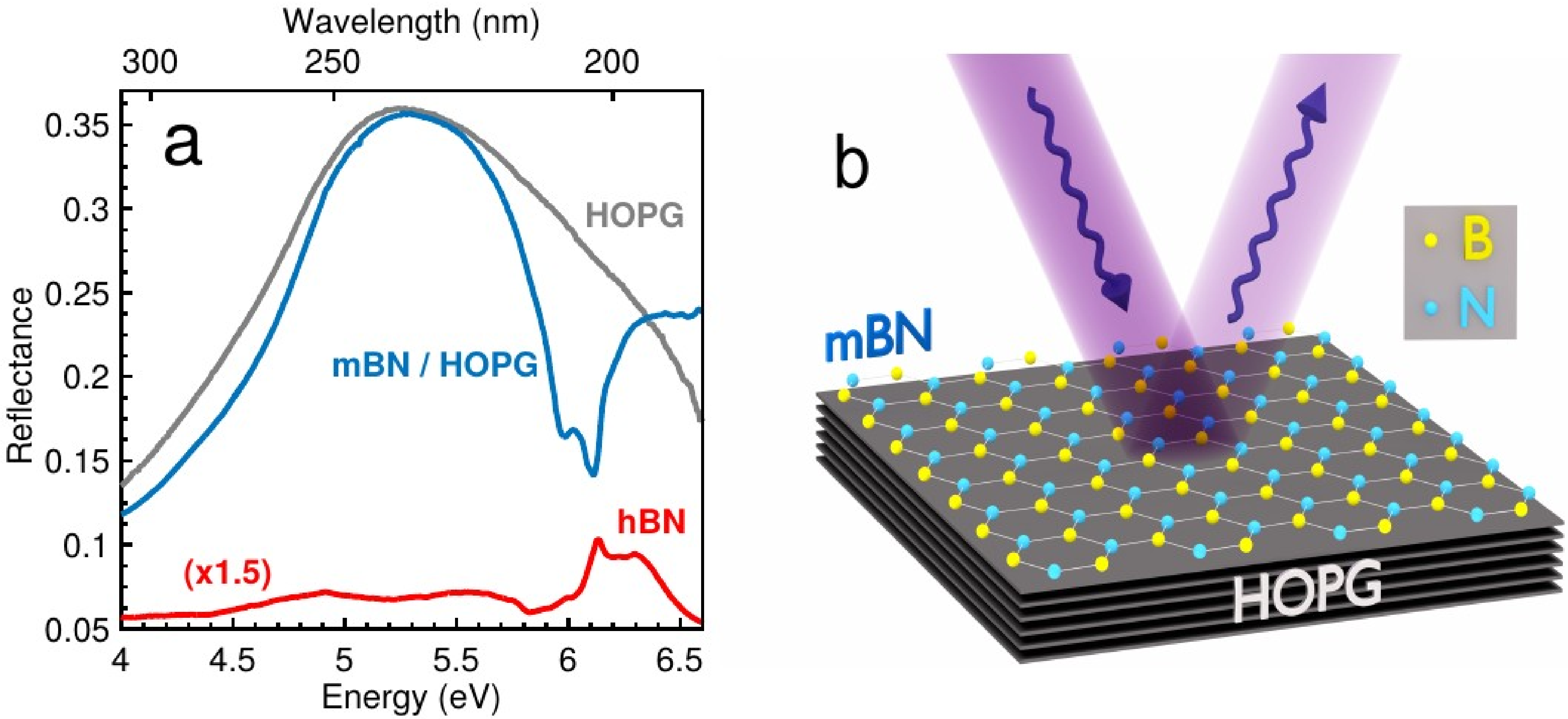
AFM in epitaxial monolayer hBN

High-temperature MBE S. Novikov (Nottingham)



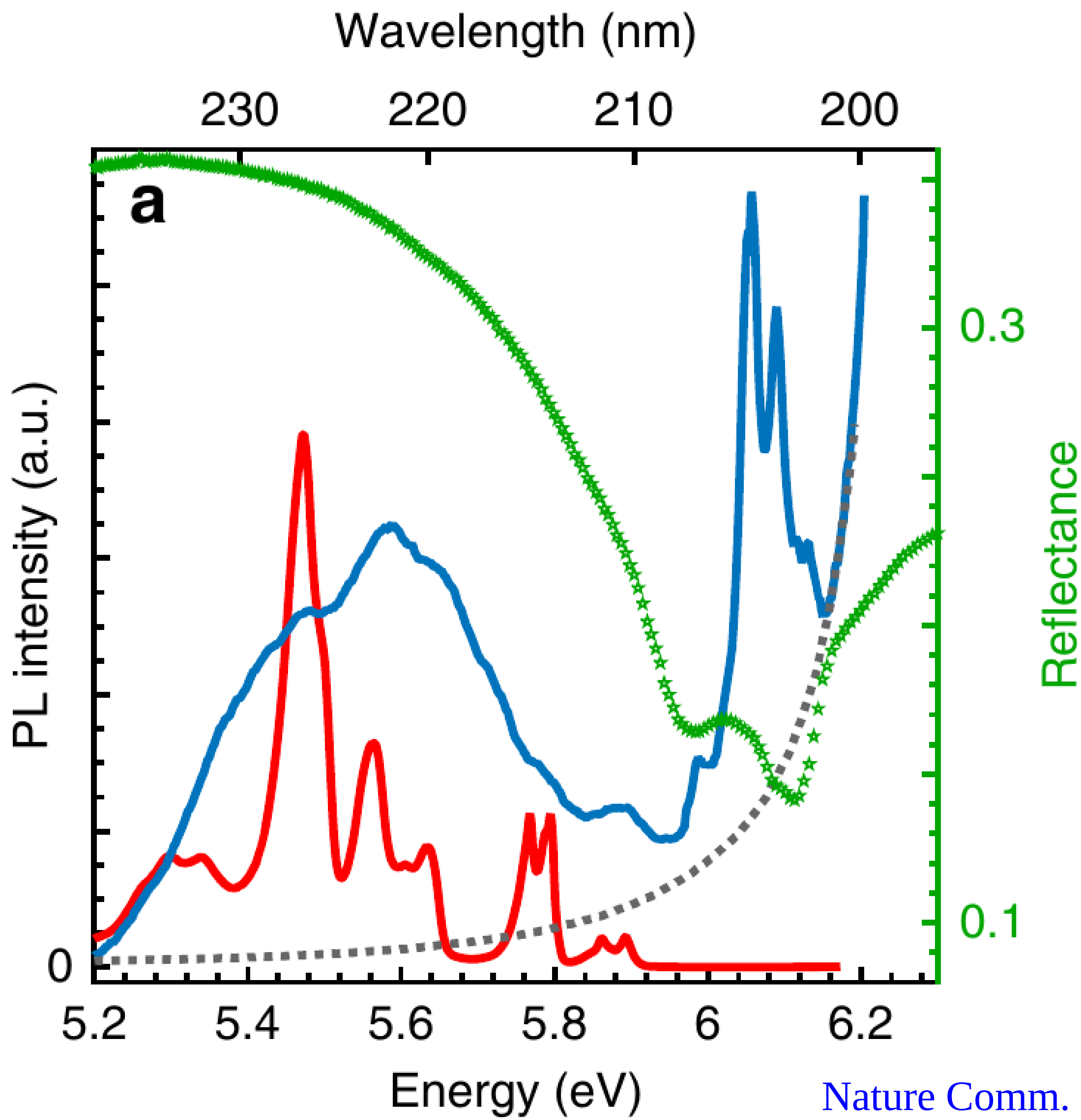
Nature Comm. **10**, 2639 (2019)

Reflectance in epitaxial monolayer hBN



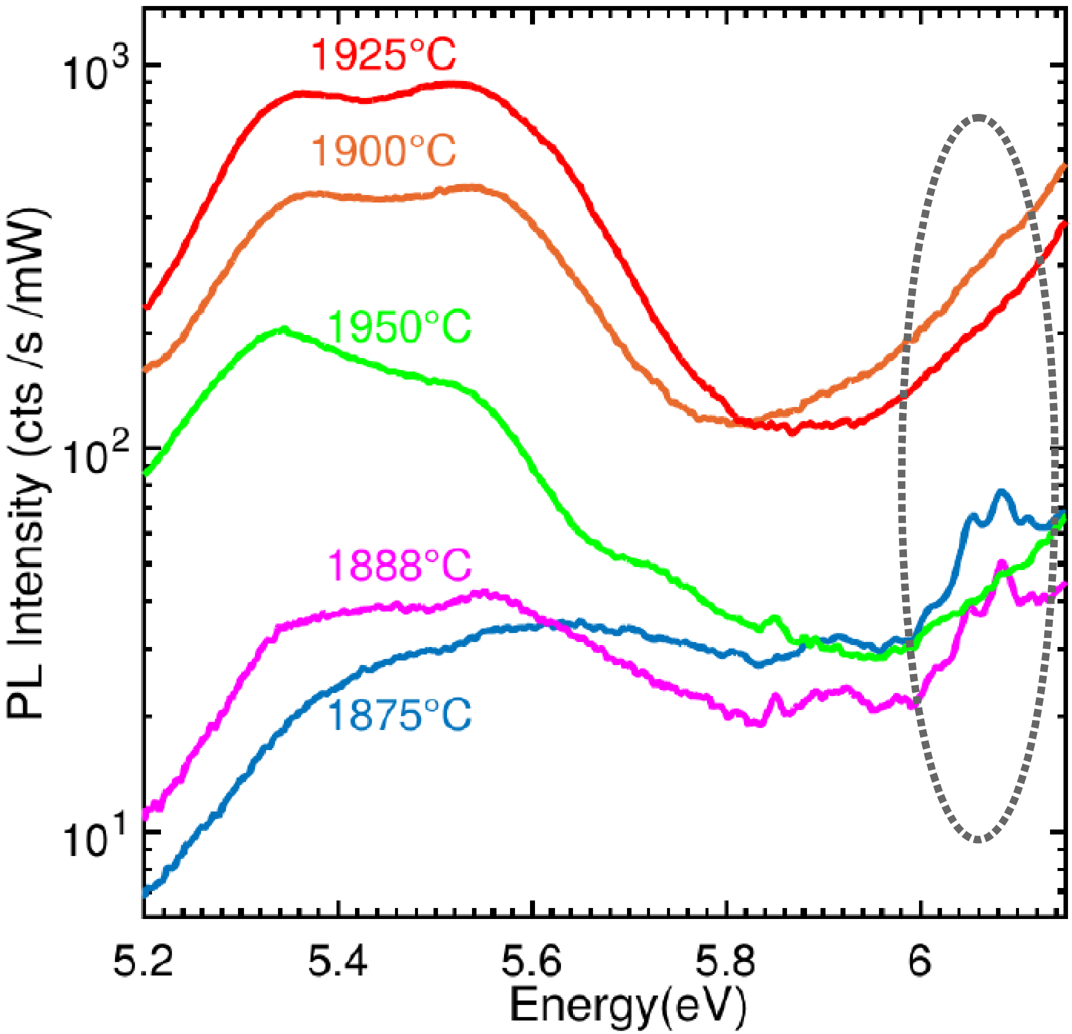
Nature Comm. **10**, 2639 (2019)

Photoluminescence in epitaxial monolayer hBN



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

Thickness dependence

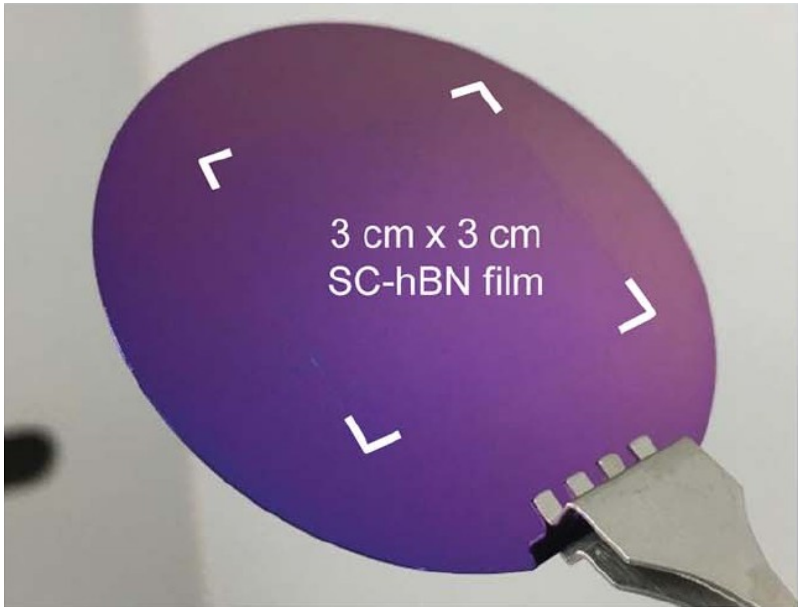


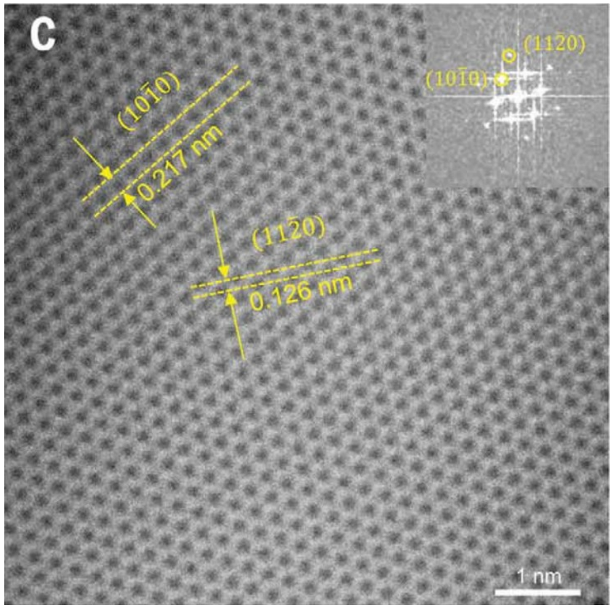
- BN coverage increases with boron-cell temperature
- Simultaneous suppression of monolayer emission

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

Recent breakthrough in CVD

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

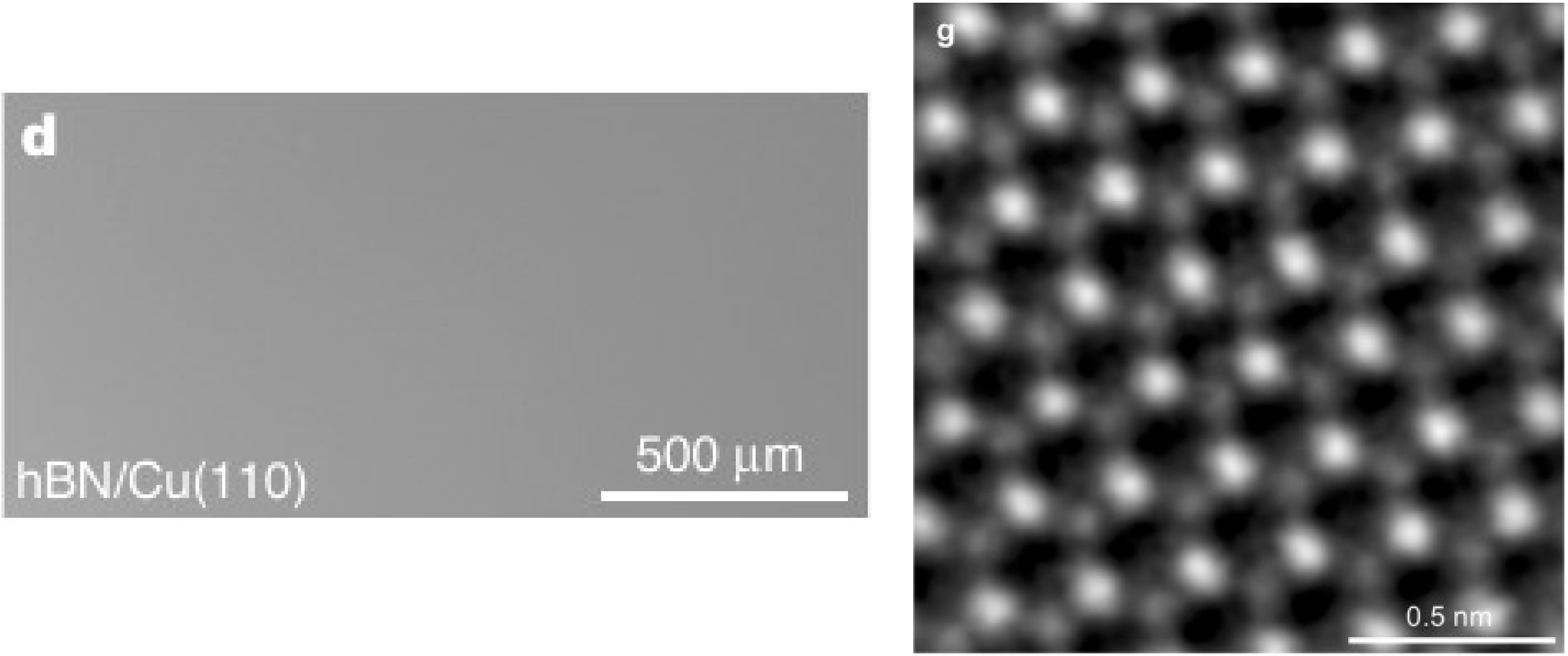




Lee, Science **362**, 817–821 (2018)

Another recent breakthrough in CVD

Wafer-scale <u>single crystal</u> of monolayer hBN (Peking Univ., China)



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

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

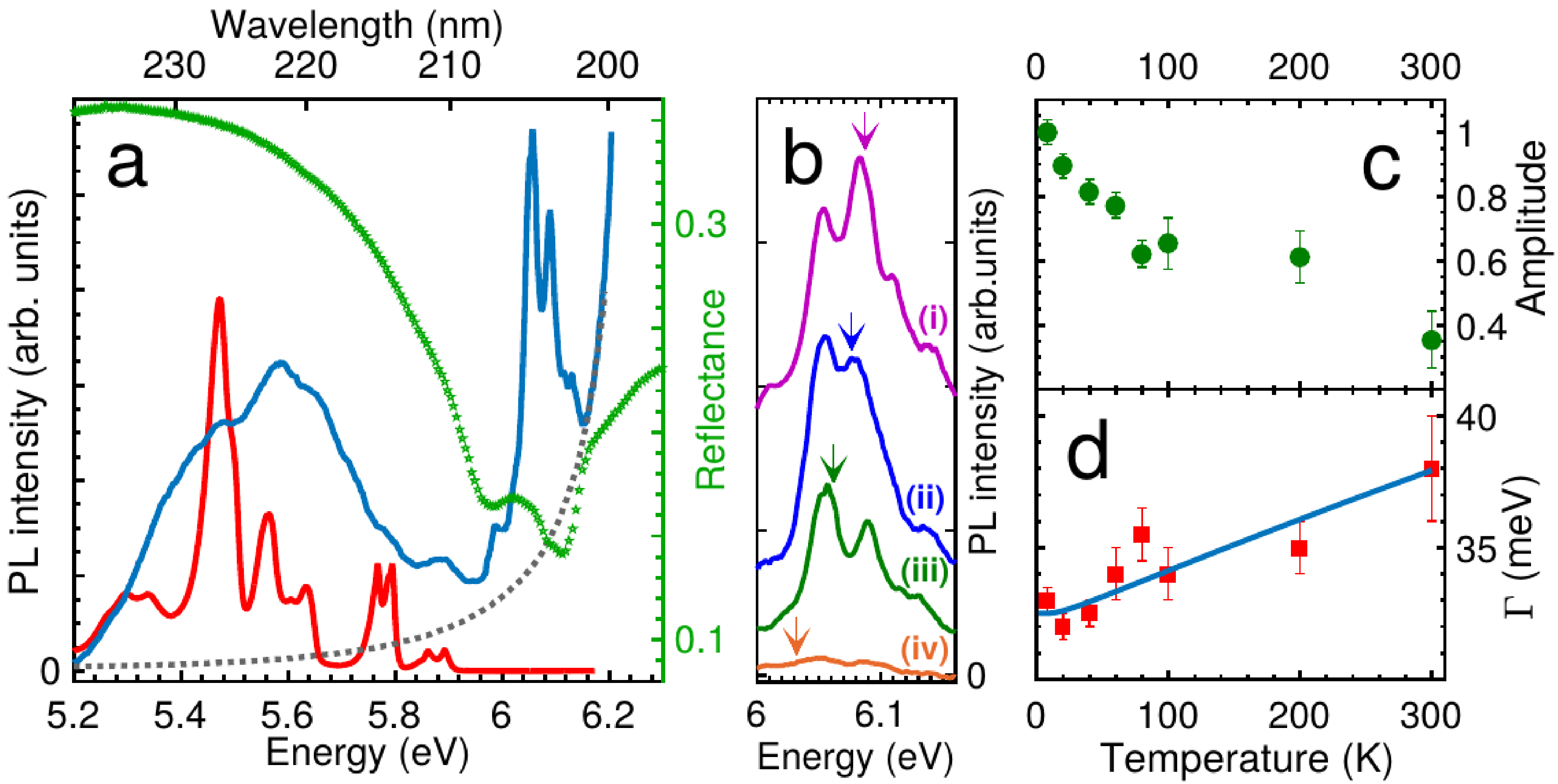
G. Cassabois

Laboratoire Charles Coulomb

CNRS / Université de Montpellier

Montpellier, France

Direct bandgap crossover in epitaxial monolayer hBN

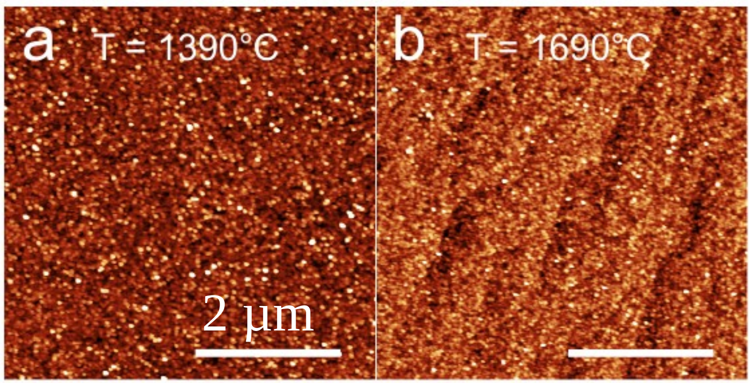


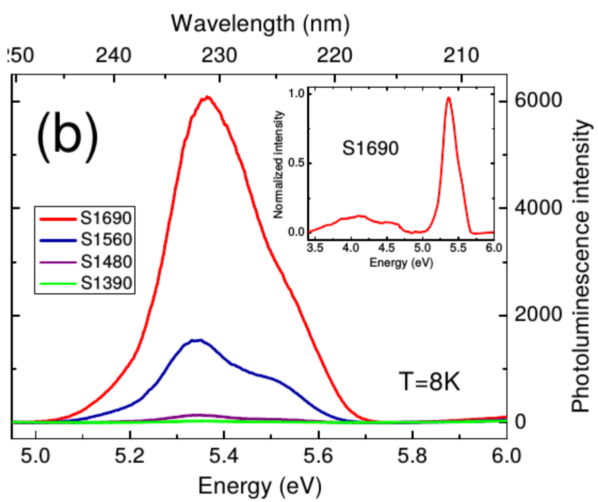
Nature Comm. **10**, 2639 (2019)

MBE

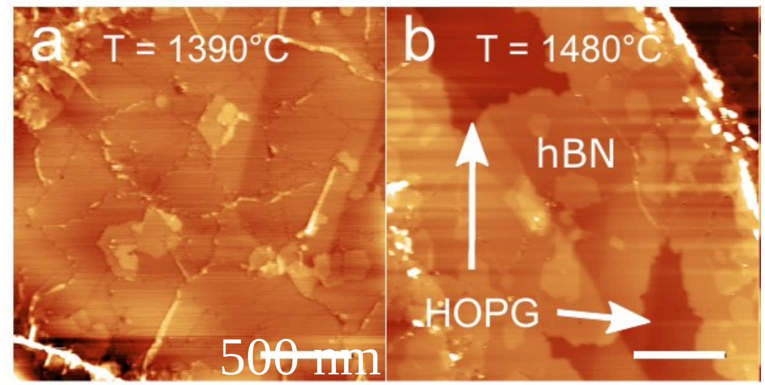
S. Novikov (Nottingham)

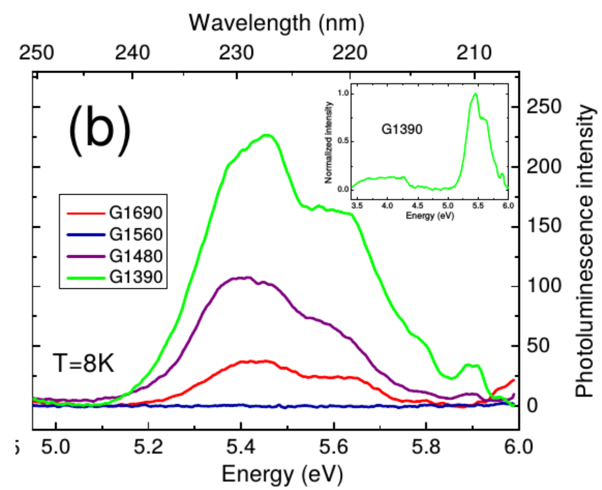
hBN on sapphire





hBN on graphite



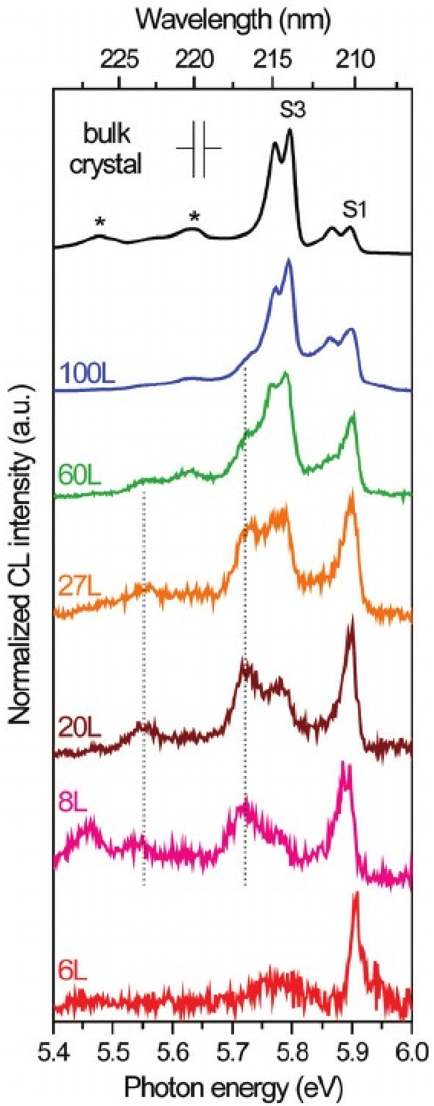


Vuong, 2D Mater. **4**, 021023 (2017)

Few-layer hBN crystals

- Cathodoluminescence down to 6 monolayers

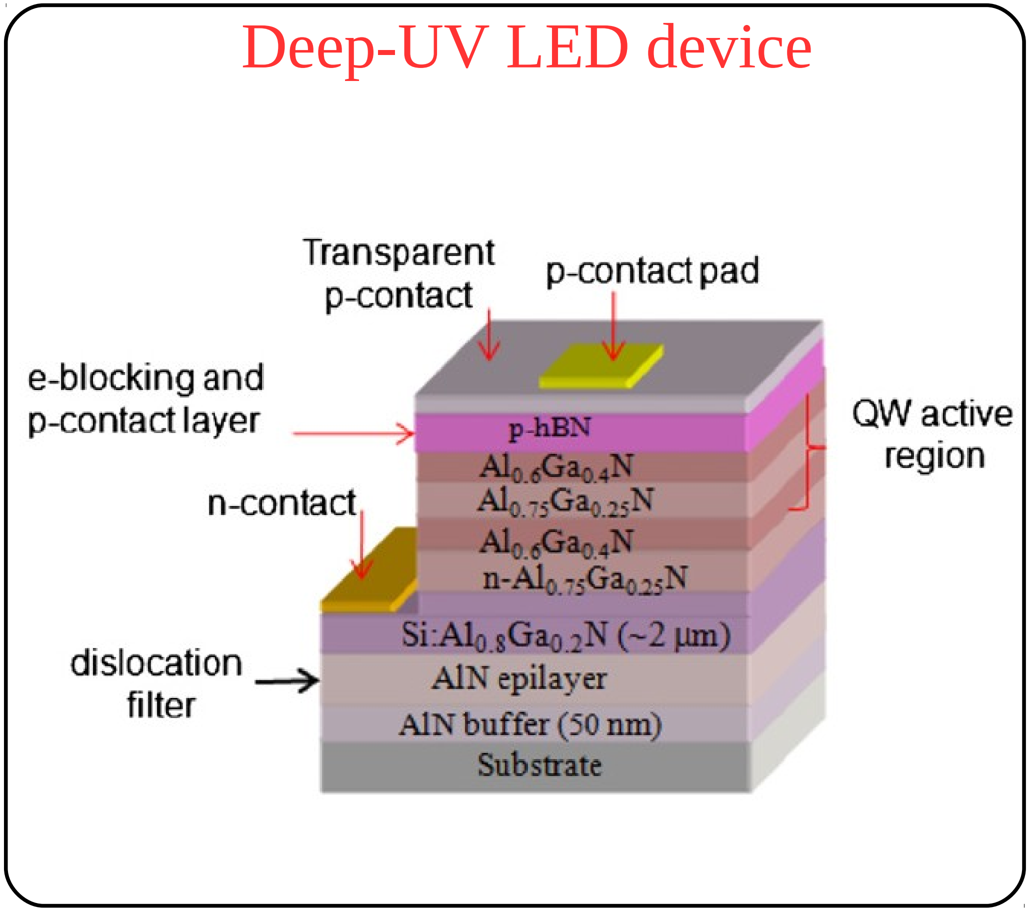
    - Exfoliated flakes
    - Modification of phonon replica intensity
    - Dominant emission at 5.9 eV (TA phonon)



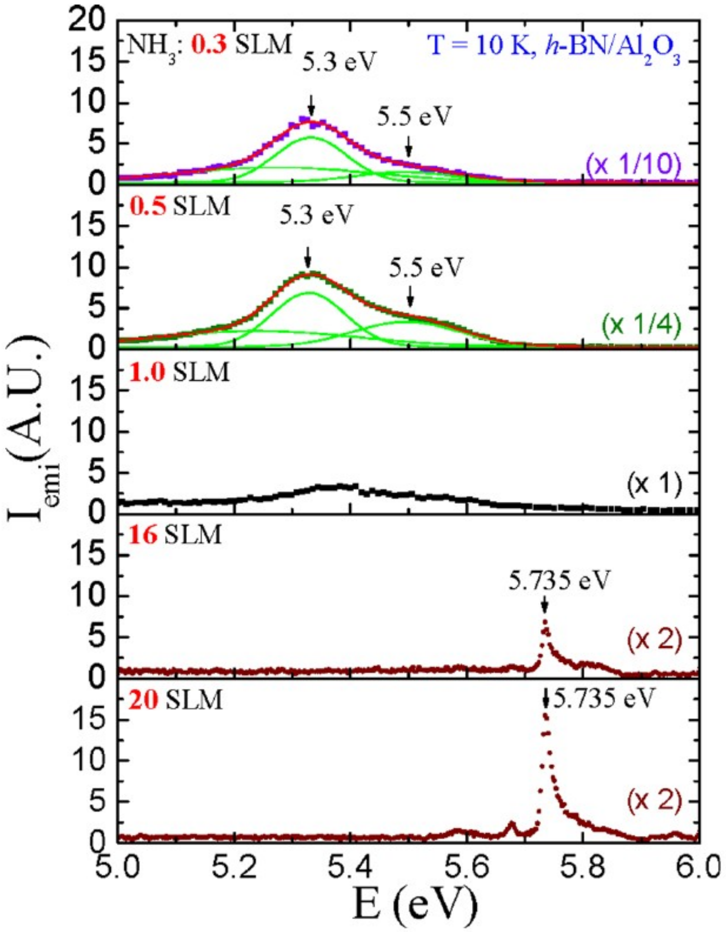
Schué, Nanoscale, 10.1039/C6NR01253A

MOCVD

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



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

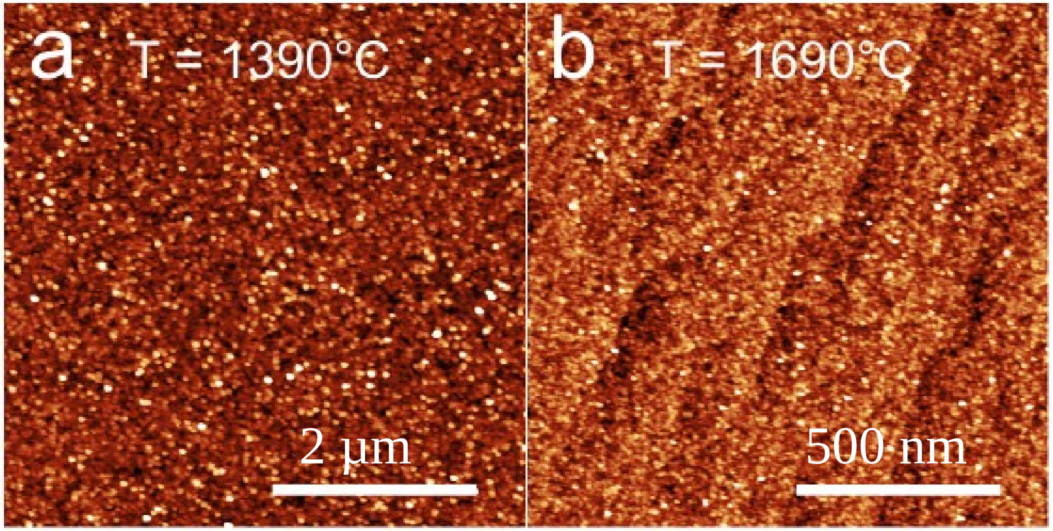


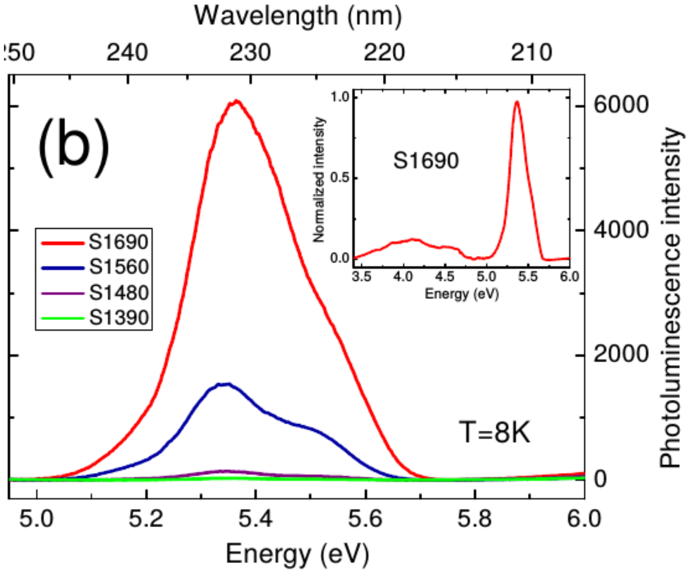
Du, APL **108**, 052106 (2016)

MBE

S. Novikov (Nottingham)

hBN on sapphire

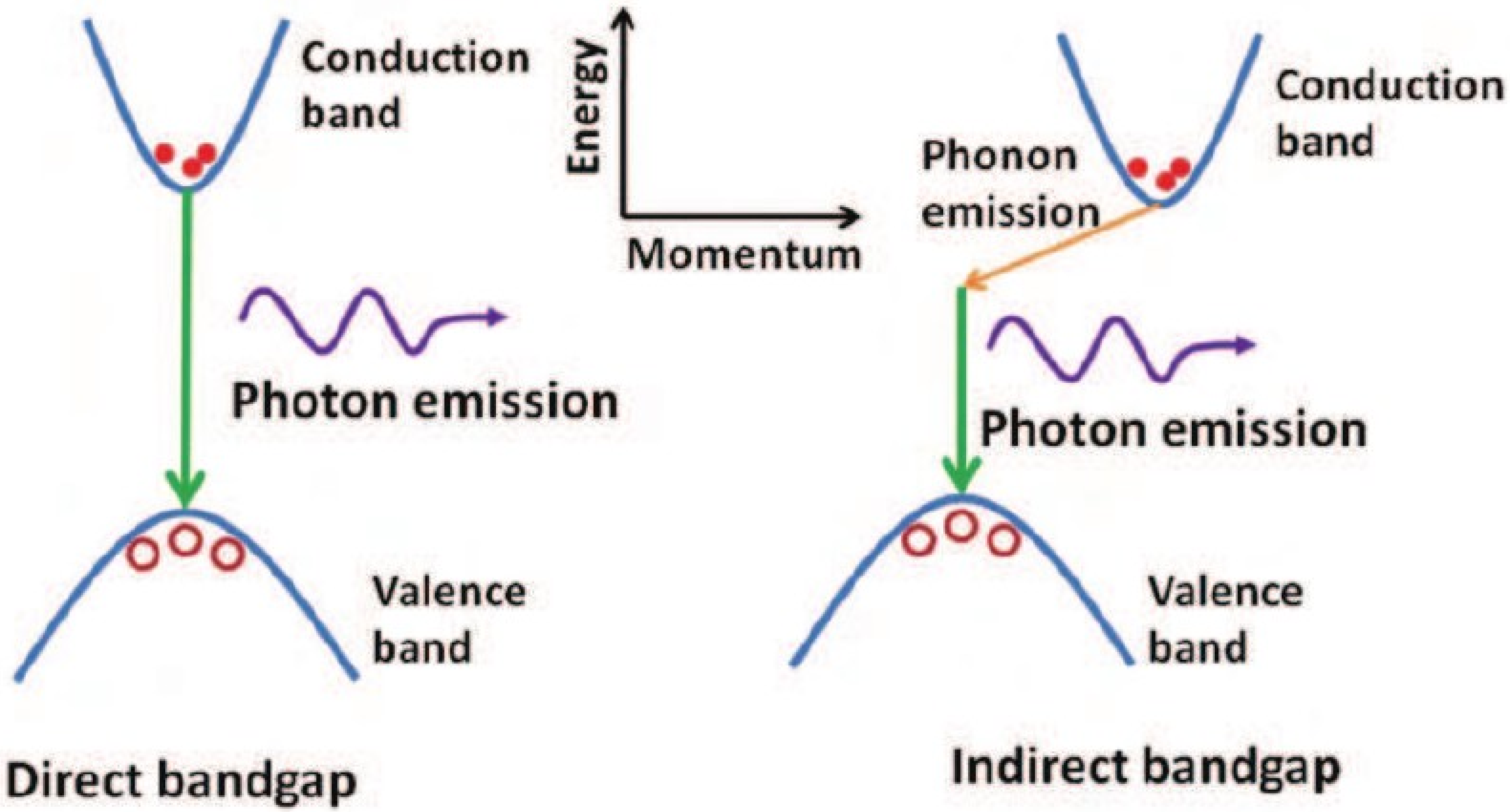




Vuong, 2D Mater. **4**, 021023 (2017)

Direct versus indirect recombination

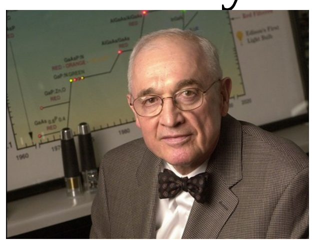
Direct | Indirect



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 → EQE; injection efficiency → IE; internal quantum efficiency → IQE; extraction efficiency → EE

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

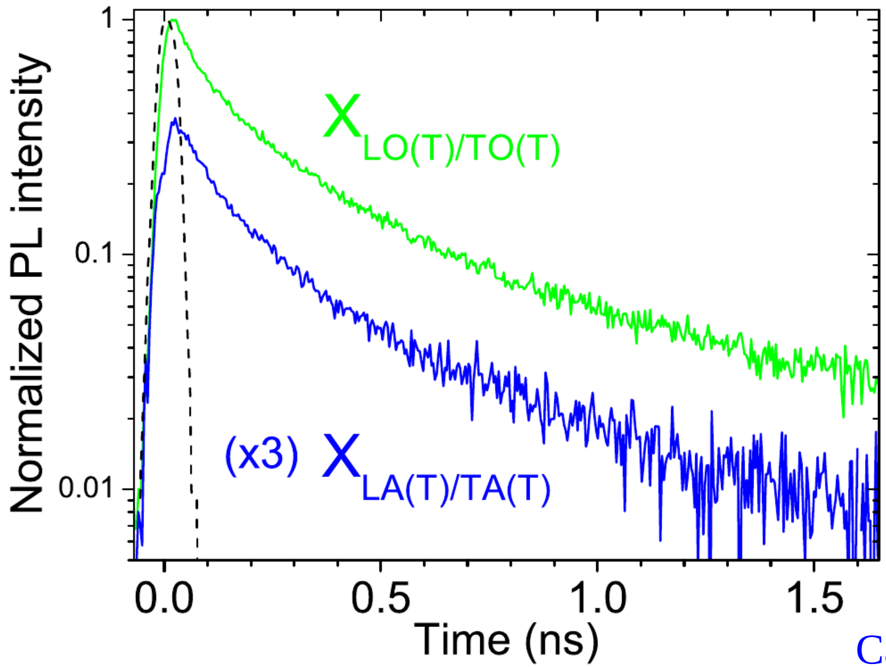
- $$IQE = \frac{\gamma_{rad}}{\gamma_{rad} + \gamma_{nrad}}$$

  - 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.

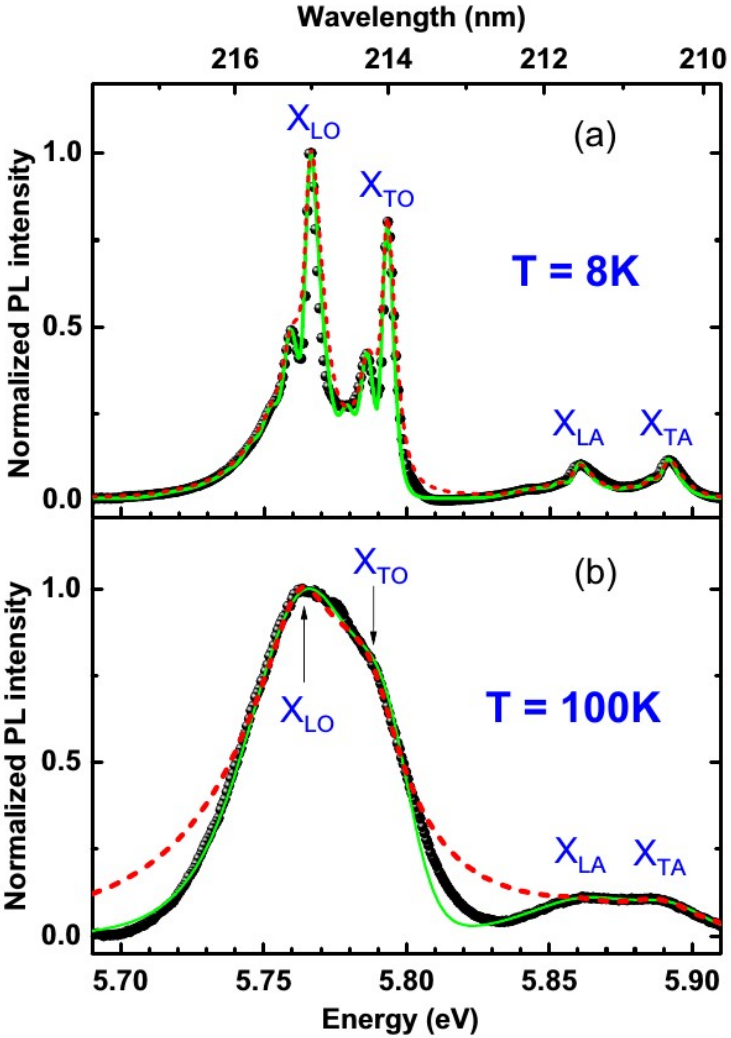
Strong coupling

Gaussian profile
+ width increasing as $\sqrt{T}$

Weak coupling

Lorentzian profile
+ width increasing as T

Gaussian lineshape

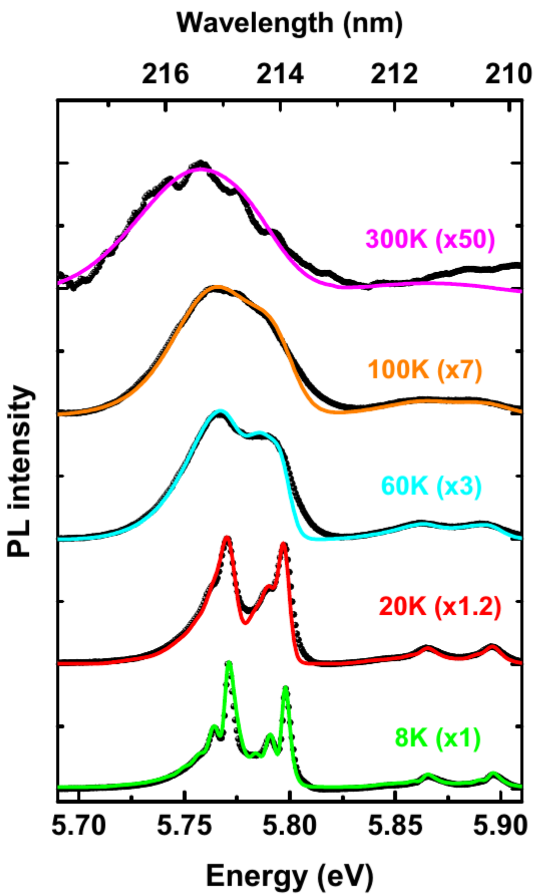


Gaussian profile

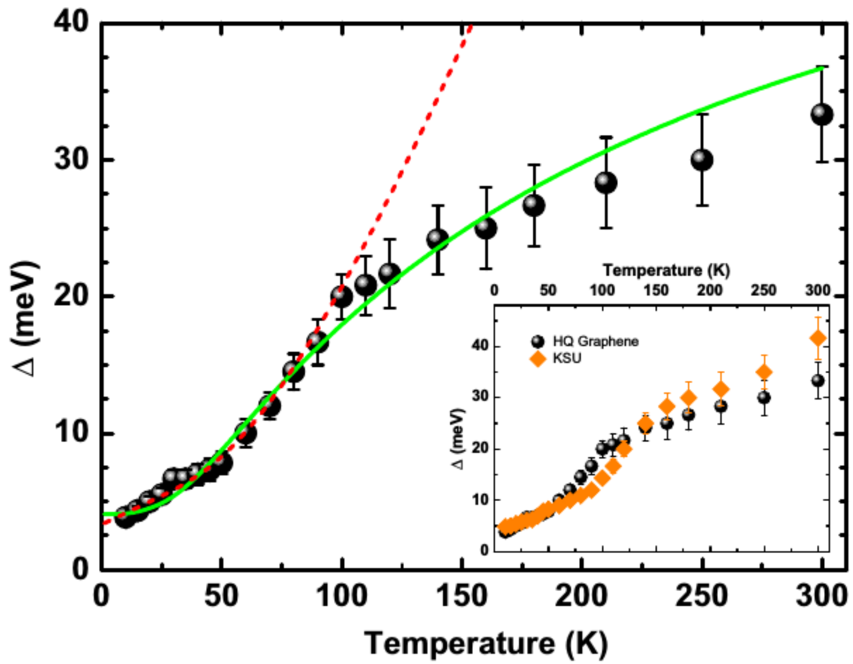
- at low temperature
- AND at high temperature

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

Thermal broadening

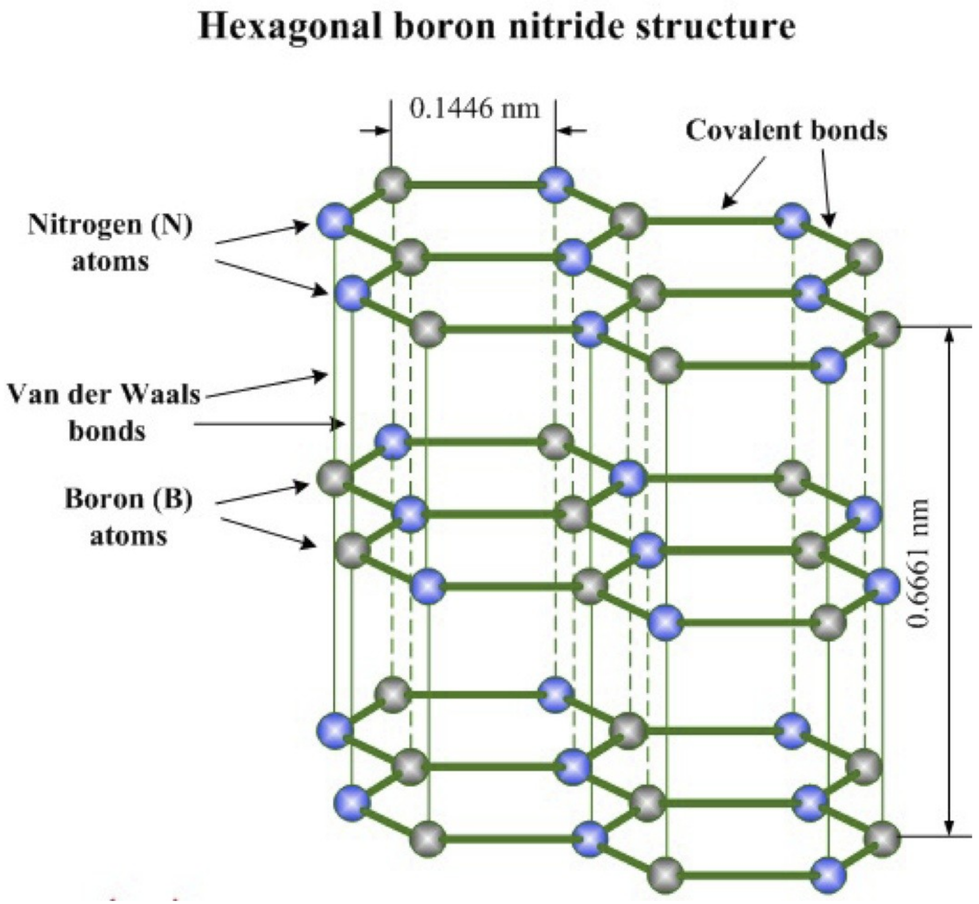


width increasing as $\sqrt{T}$

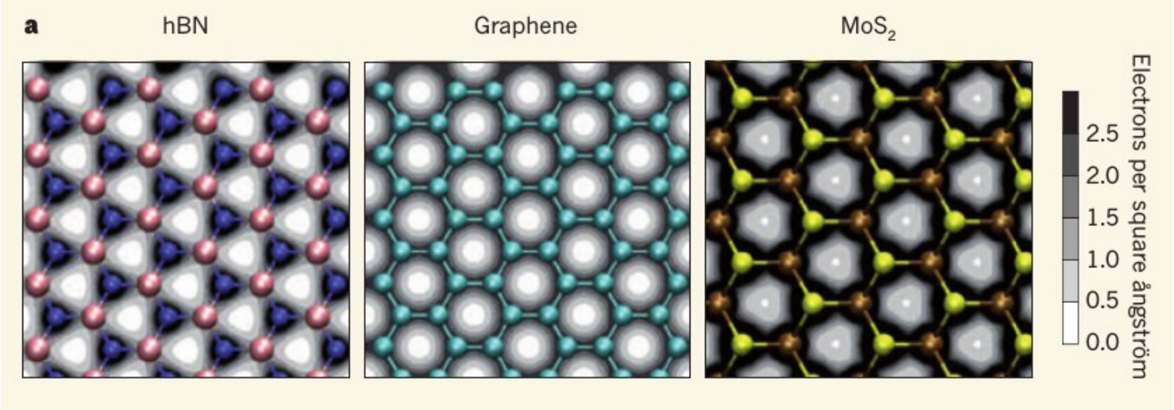


Vuong, PRB **95**, 201202(R) (2017)

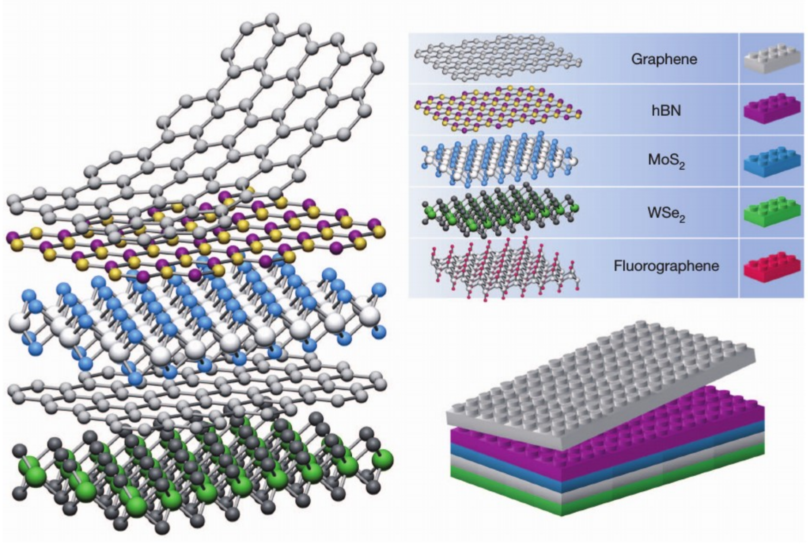
“White graphite”



Beyond graphene

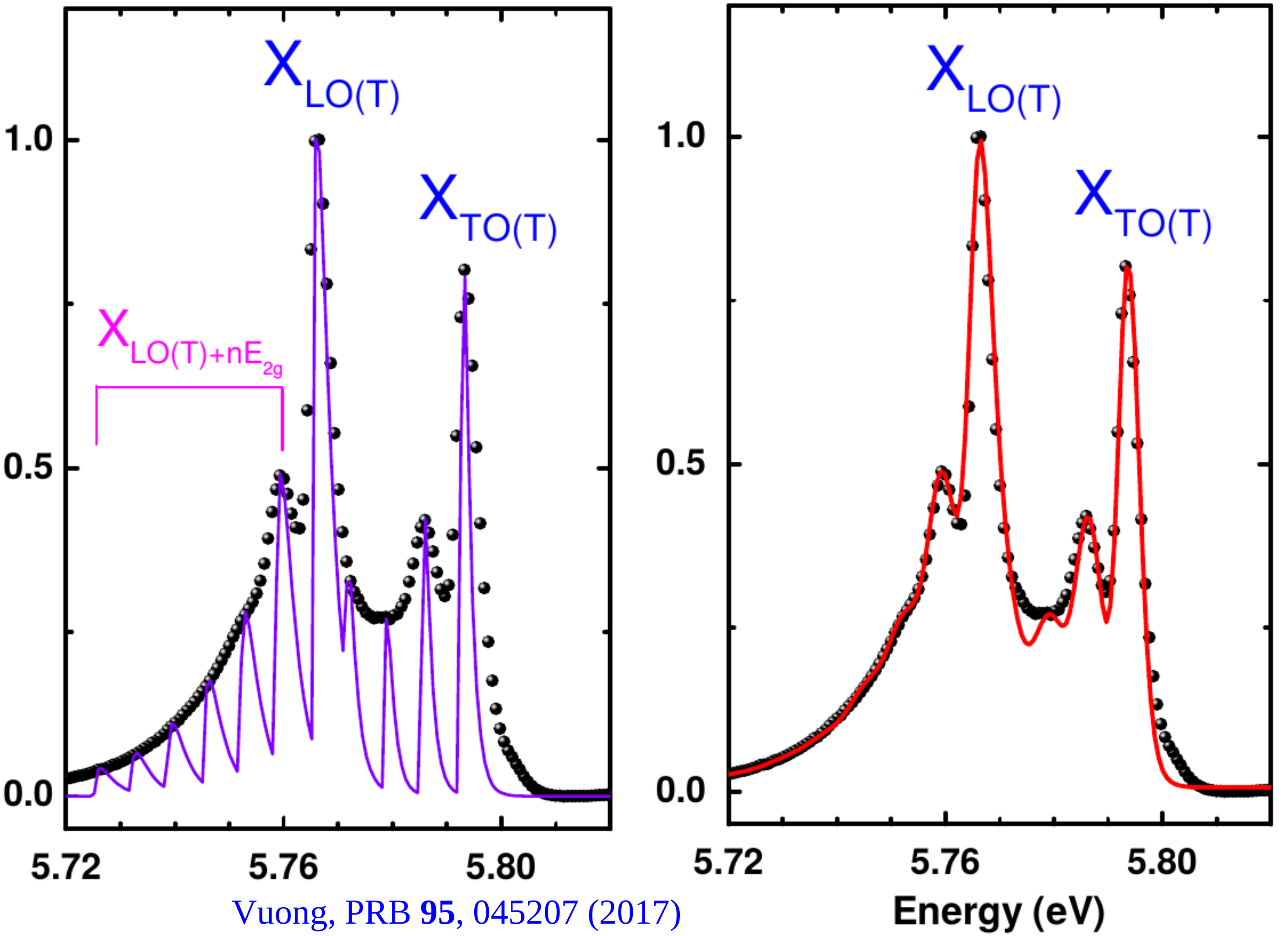


Van der Waals heterostructures



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

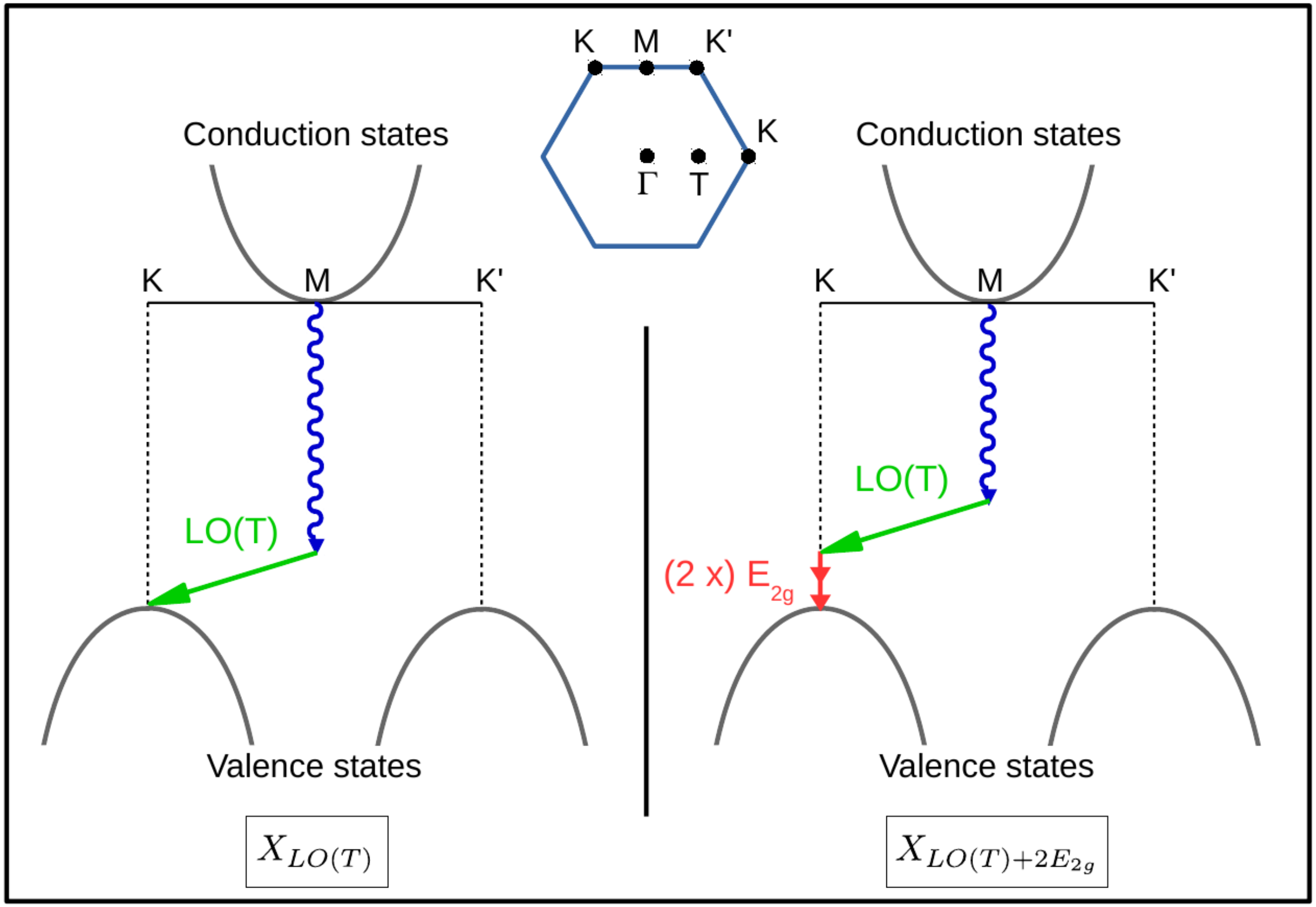
Raman overtones



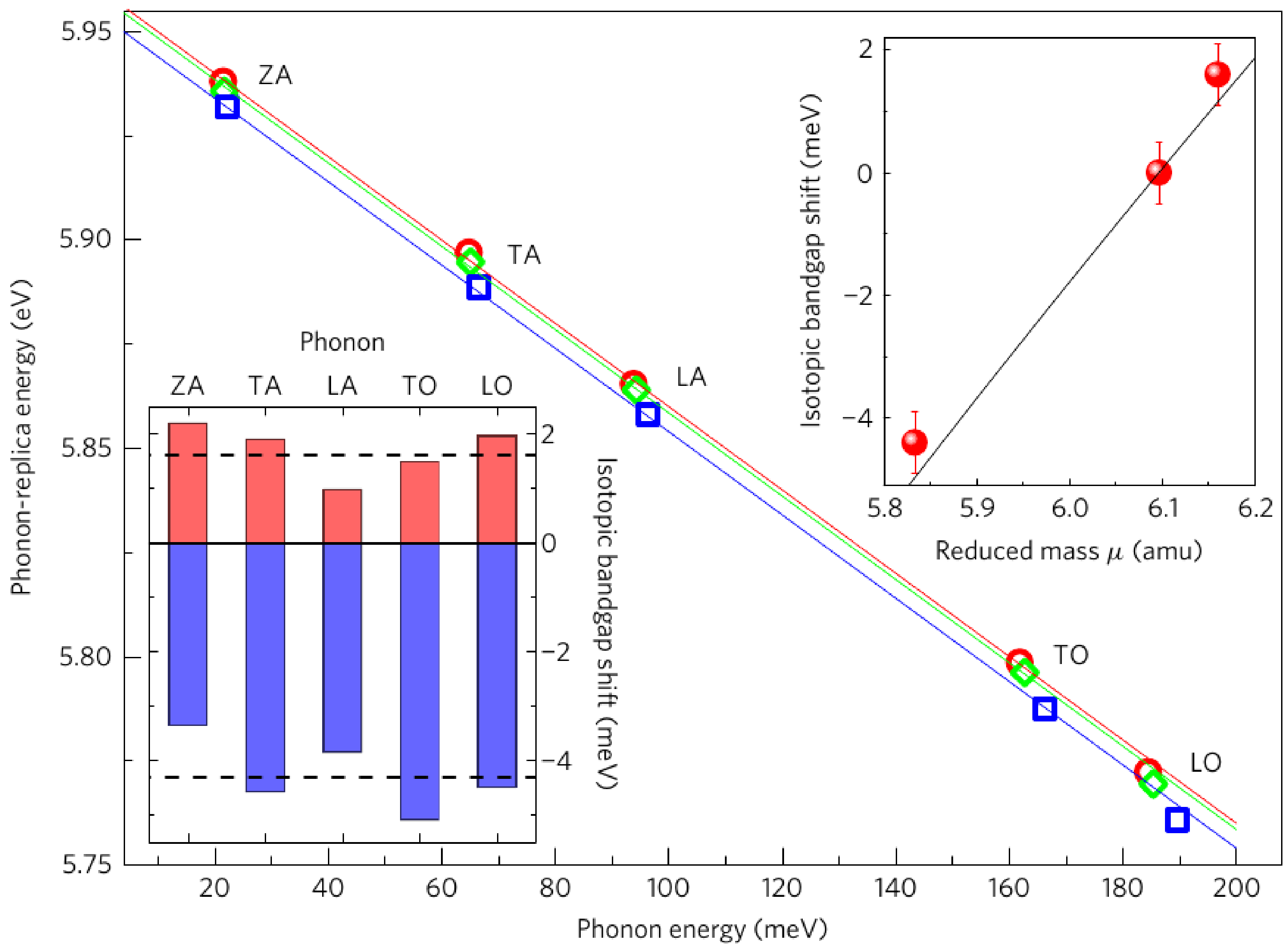
Vuong, PRB **95**, 045207 (2017)

High-order phonon-assisted processes

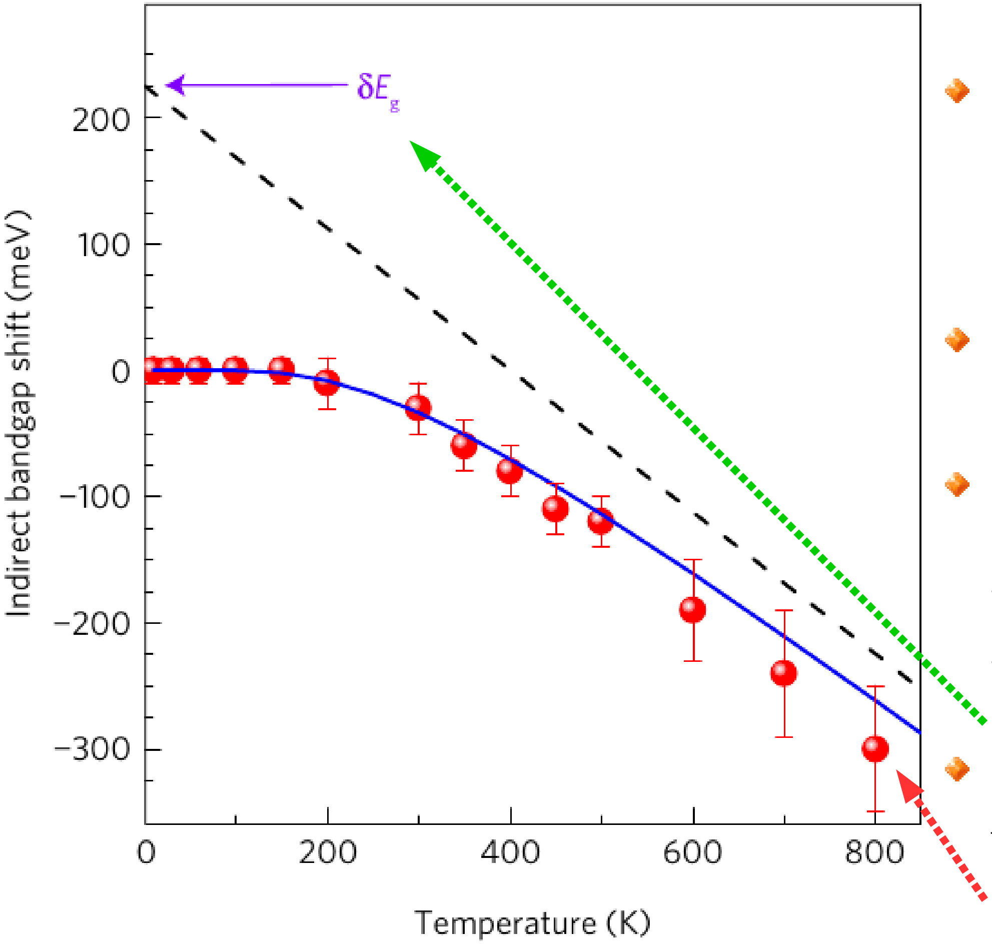
- low-energy Raman-active mode @ zone center
- no momentum change



Isotopic tuning of phonon replicas

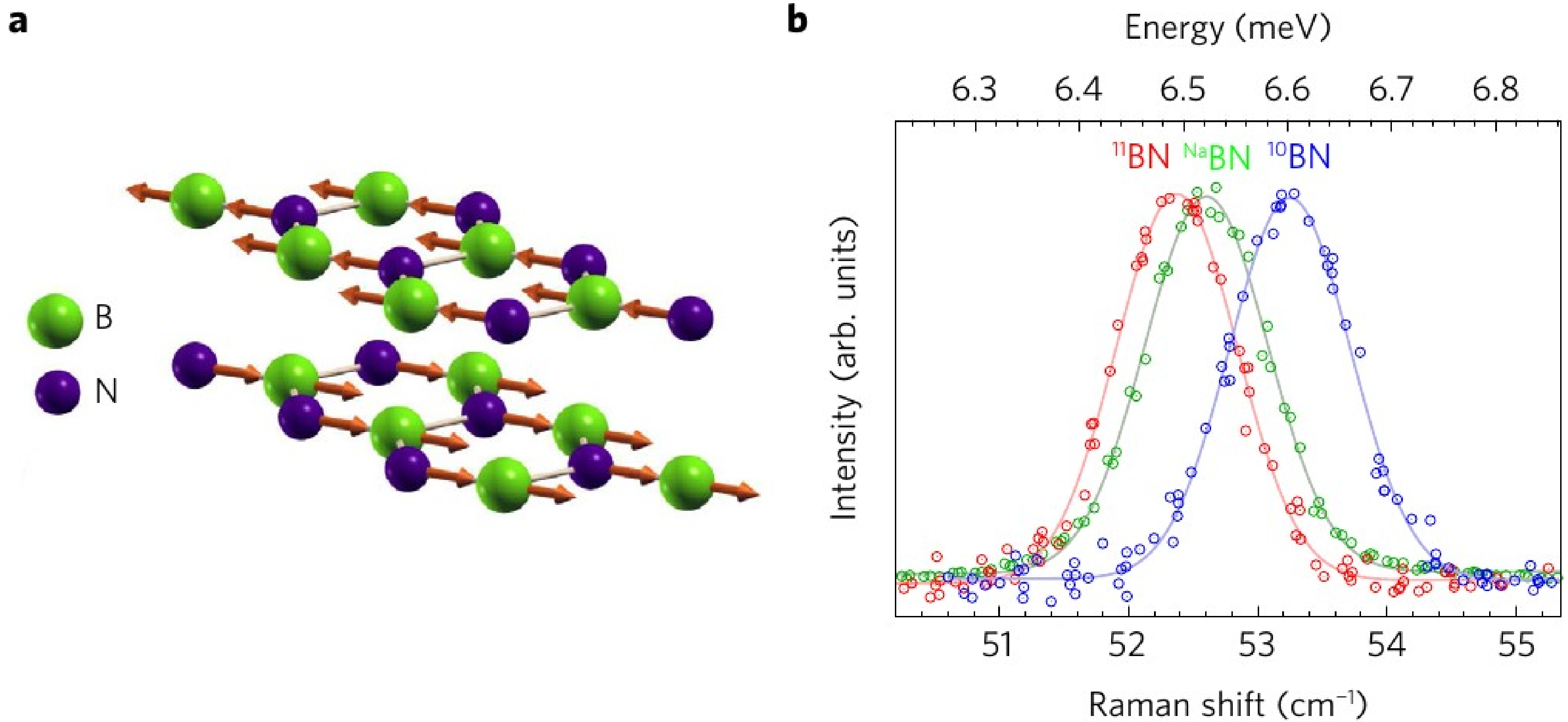


Bandgap renormalization



- 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)

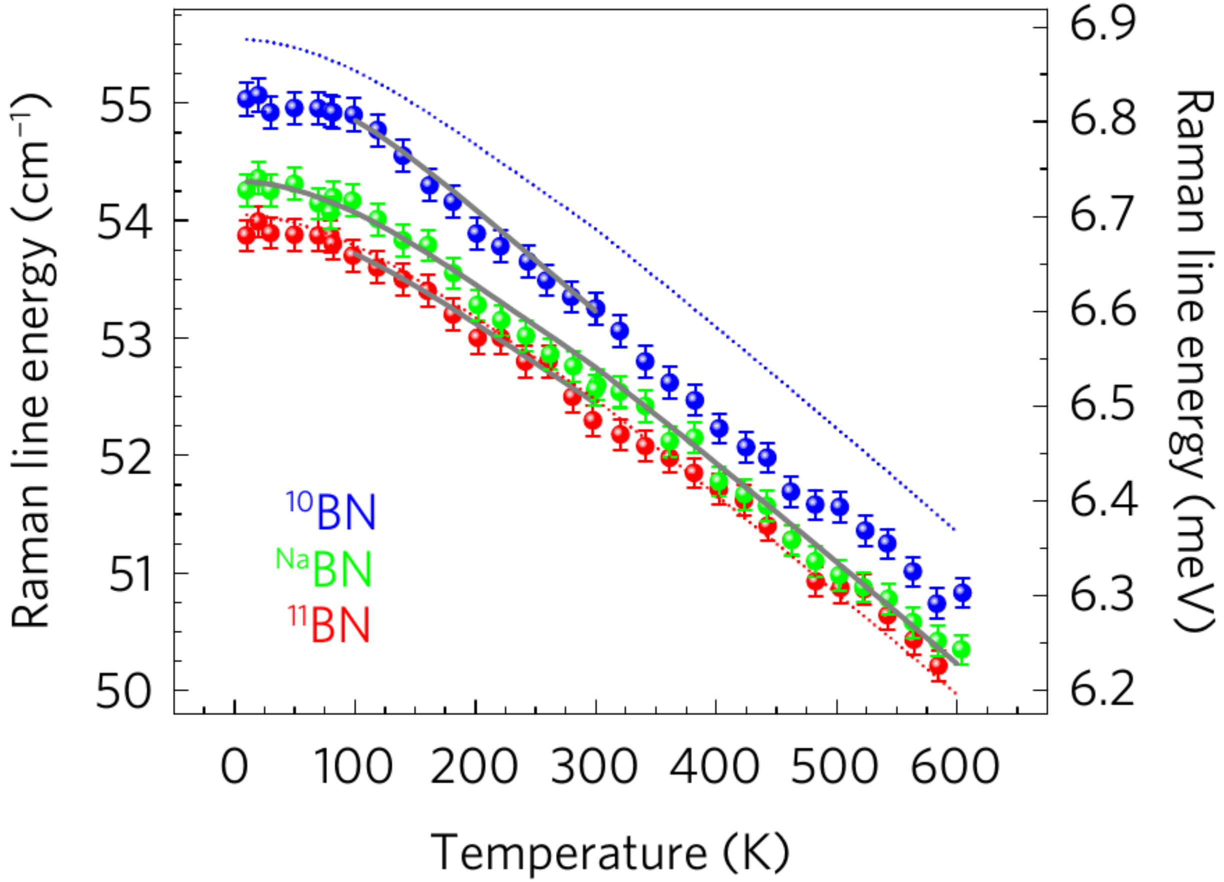
Interlayer shear mode



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

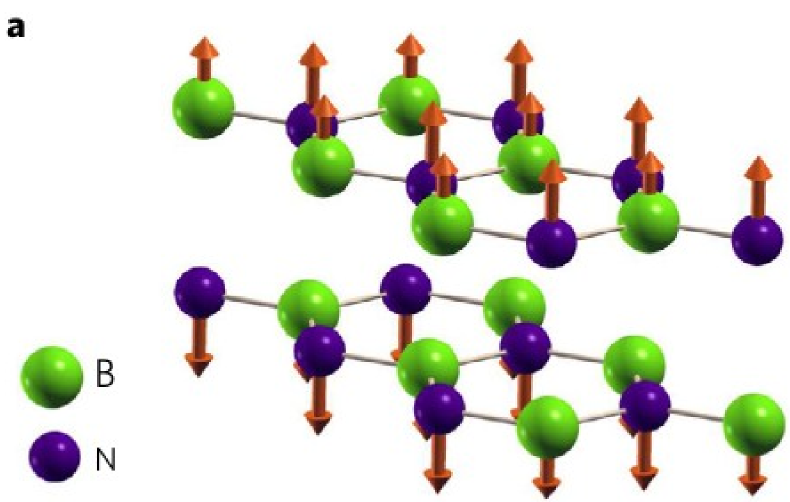
The lower the B mass, the higher the phonon energy : again, BUT...

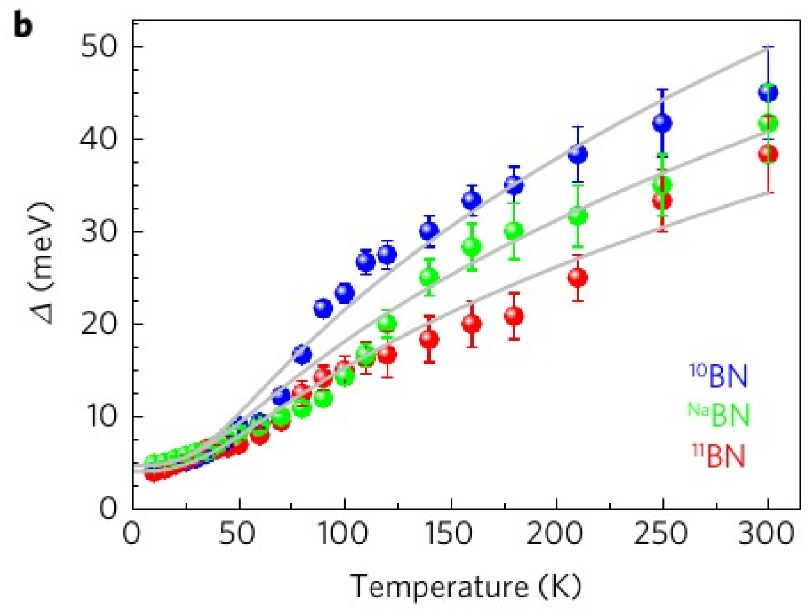
Isotope-dependent thermal shift



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

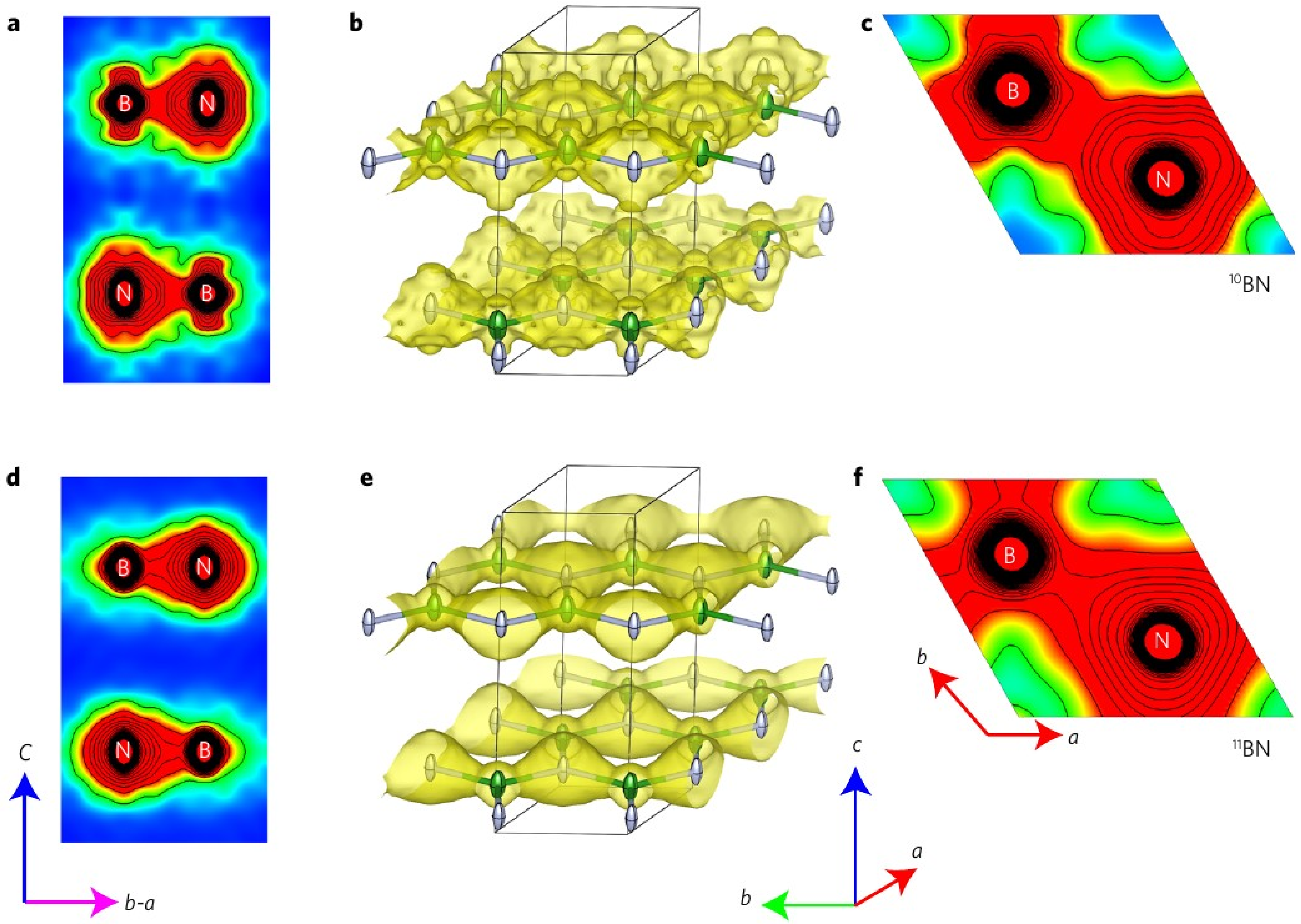
Interlayer breathing mode





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

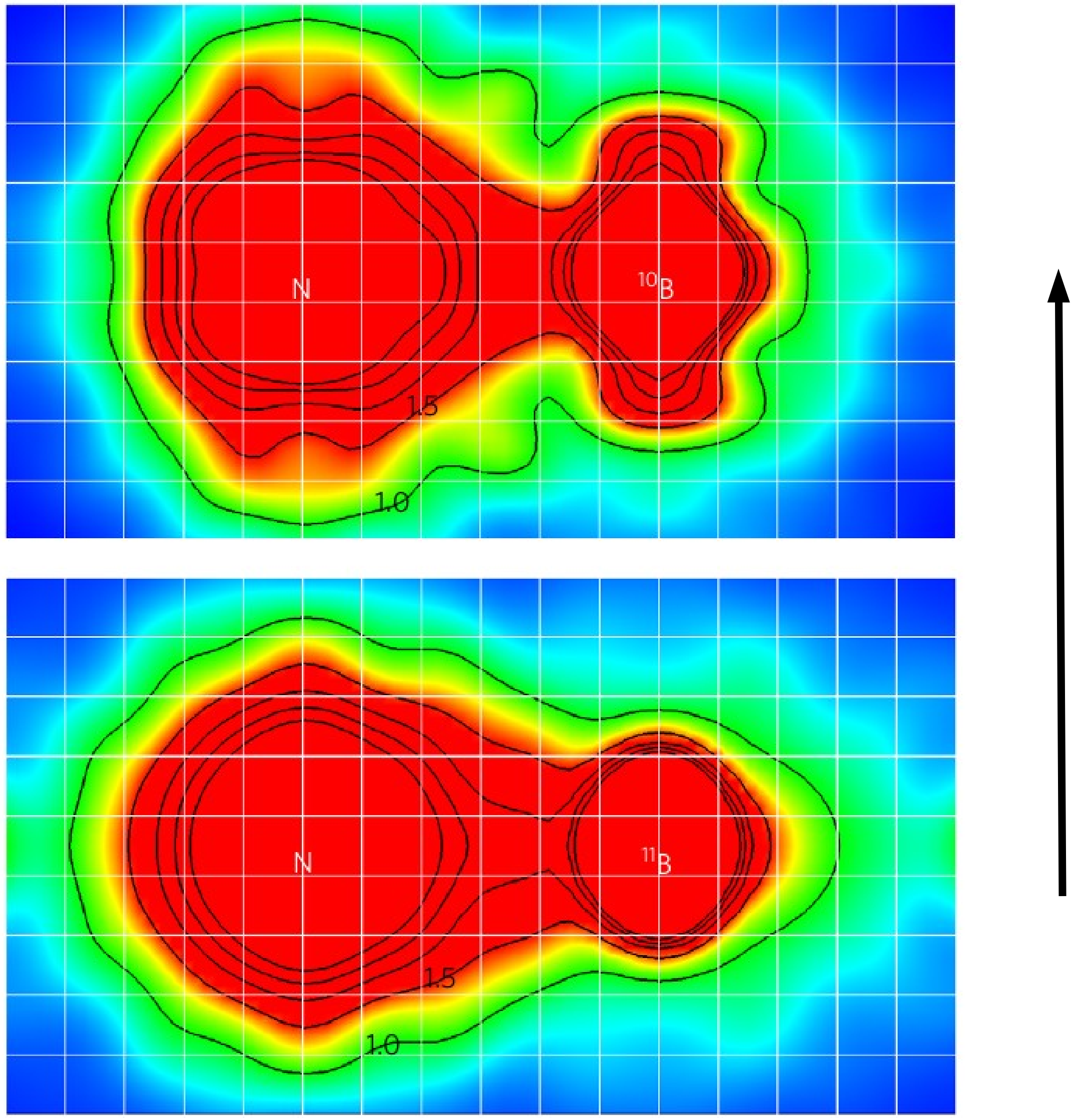
X-ray diffraction experiments



Isotope-dependent electronic distribution

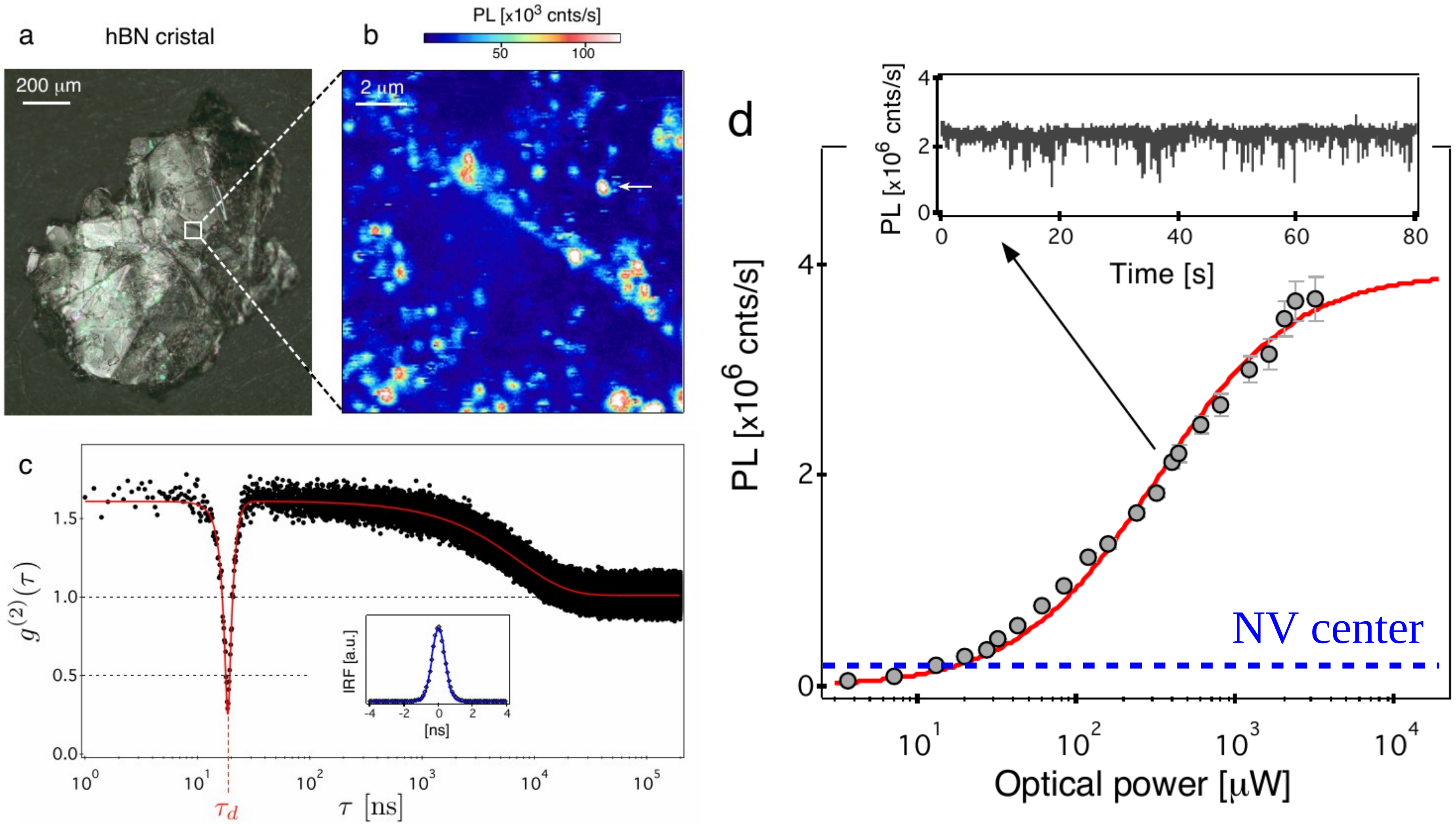
^{10}BN

^{11}BN



c-axis

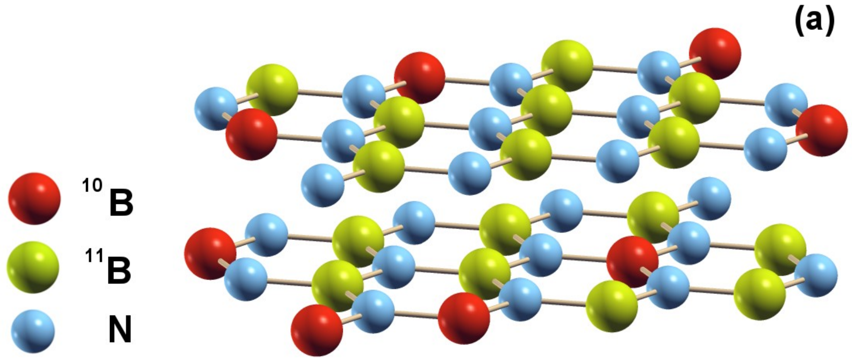
Point defects in hBN as bright single-photon sources



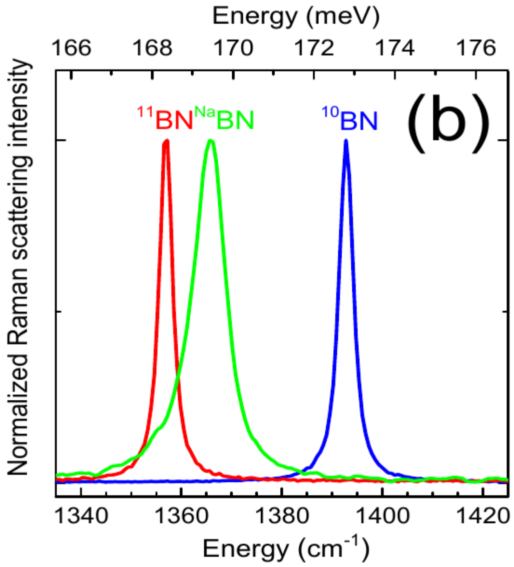
Phys. Rev. B **94**, 121405(R) (2016)

Isotopic purification

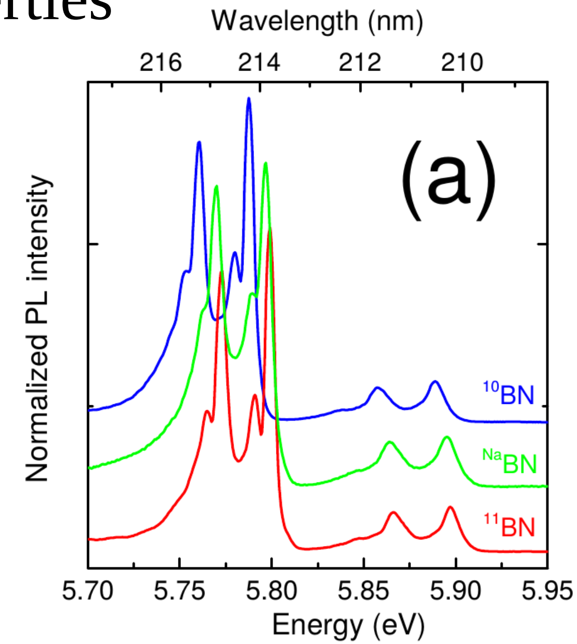
- Isotopic mixture



- Impact on vibrational and electronic properties



submitted for publication



Applications

Powder

« white graphite »

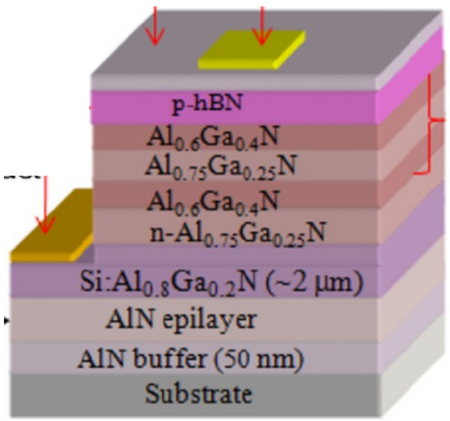
- many industrial applications
- solid lubricant, thermal coating, additive in plastics, cosmetics...

Polycrystals

Watanabe, Nature Mater. 3, 404 (2004)

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

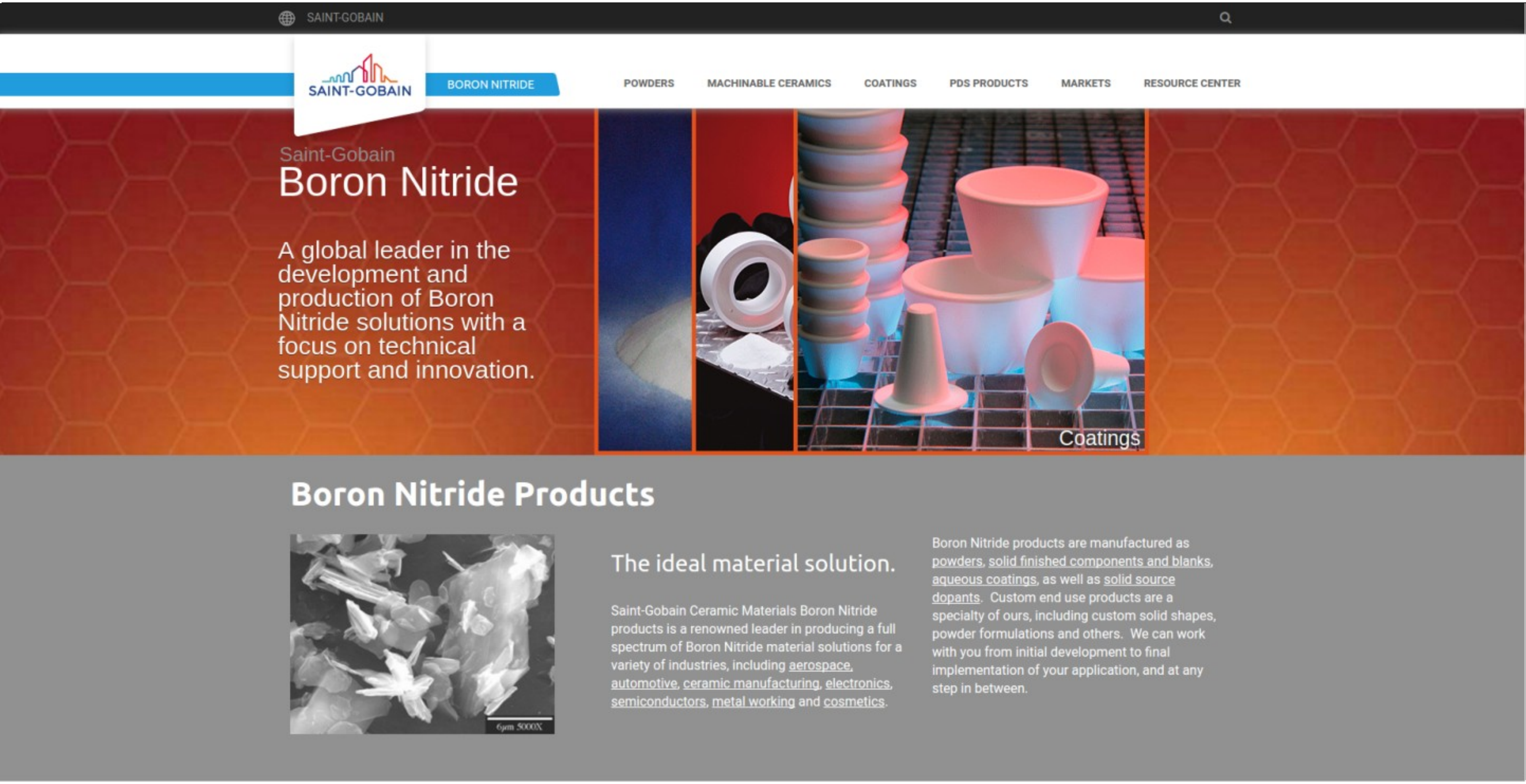
Epilayers



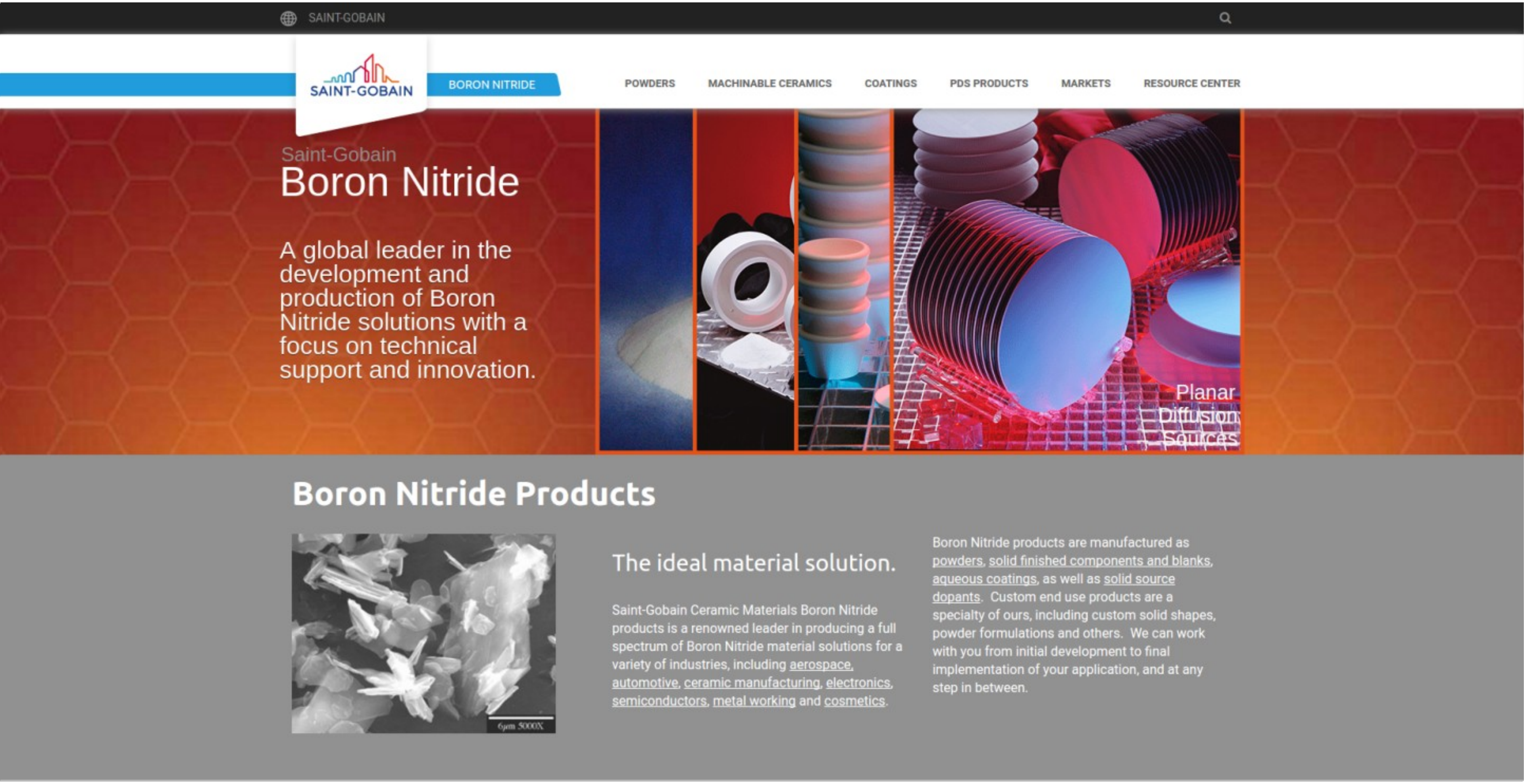
Jiang, Semicond. Sci. Technol. 29, 084003 (2014)

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

hBN in the industry

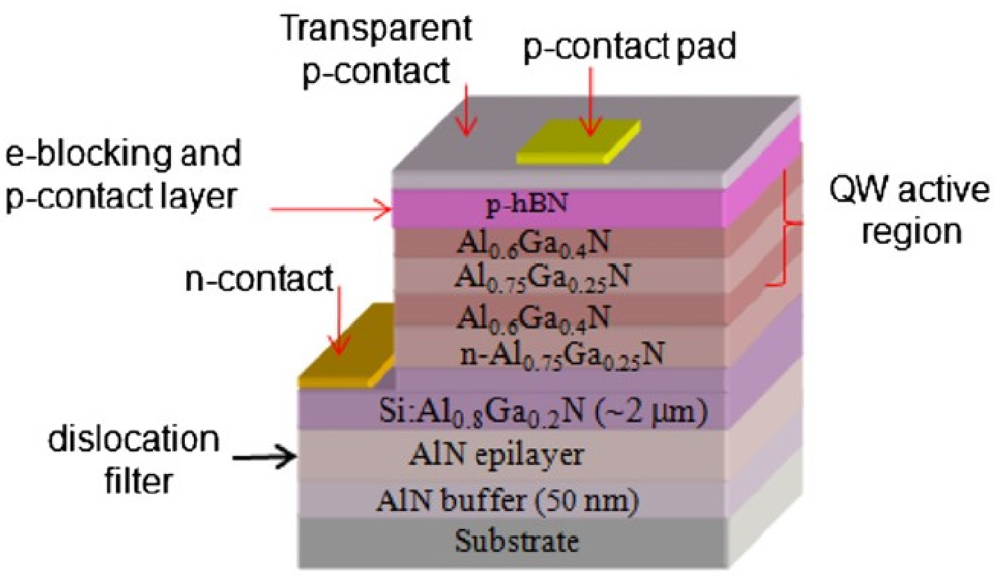


hBN in the industry

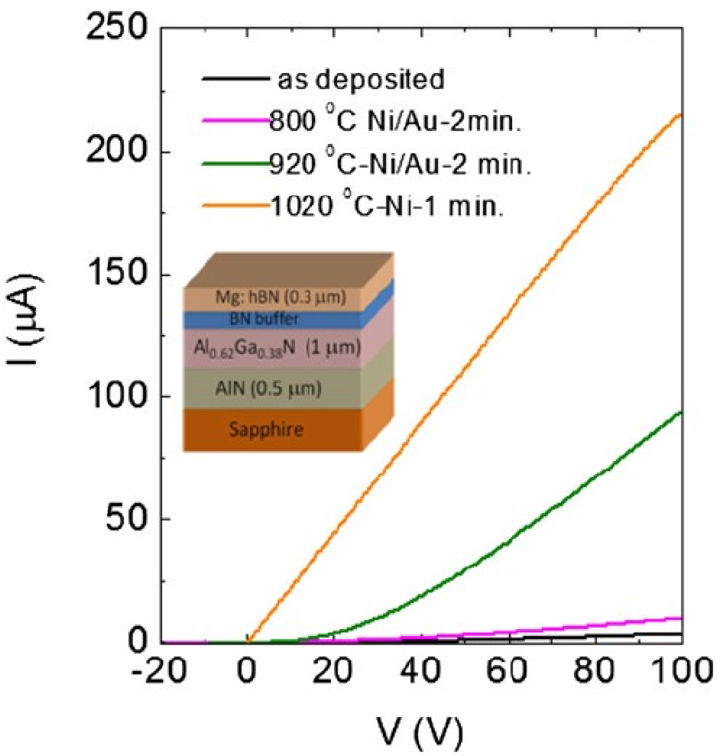


Highly conductive p-type hBN layer

Deep-UV LED device

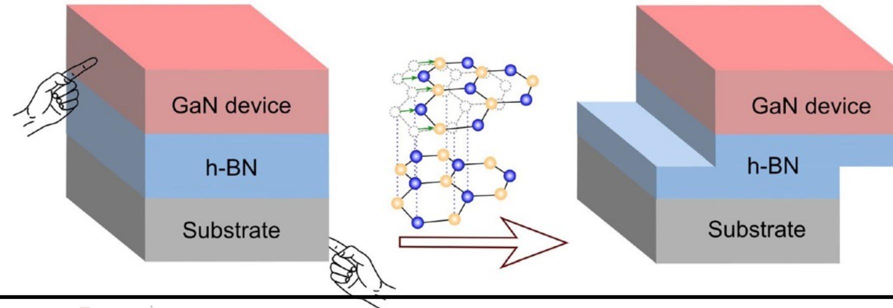


p-BN:Mg /n-AlGaN structure

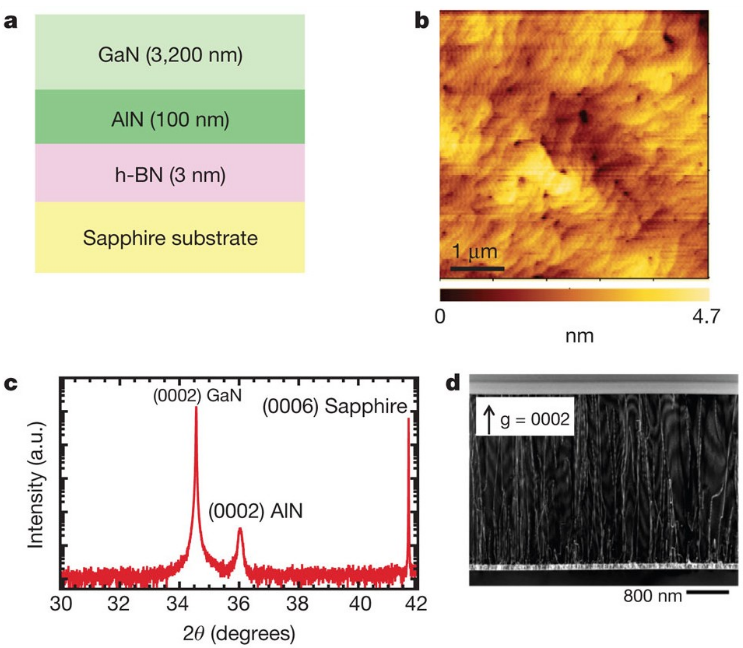


Jiang, Semicond. Sci. Technol. 29, 084003 (2014)

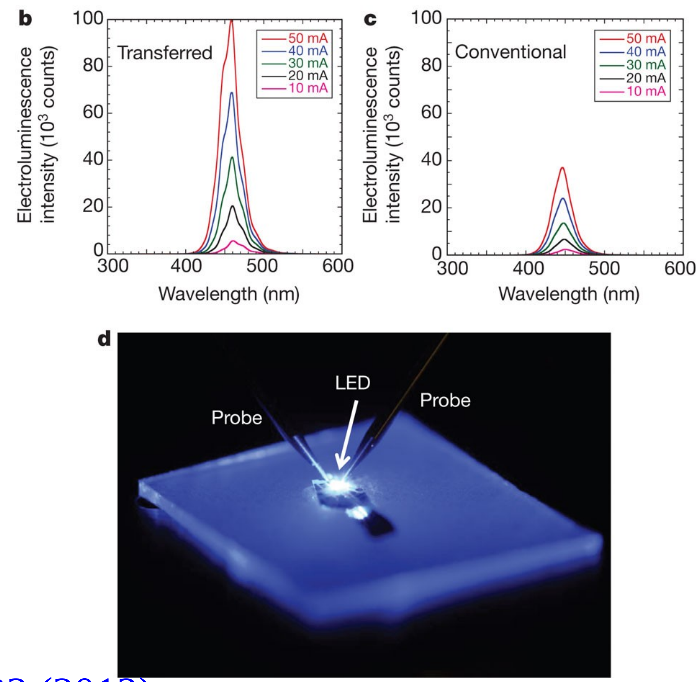
hBN as release layer for mechanical transfer



Growth of AlN on hBN



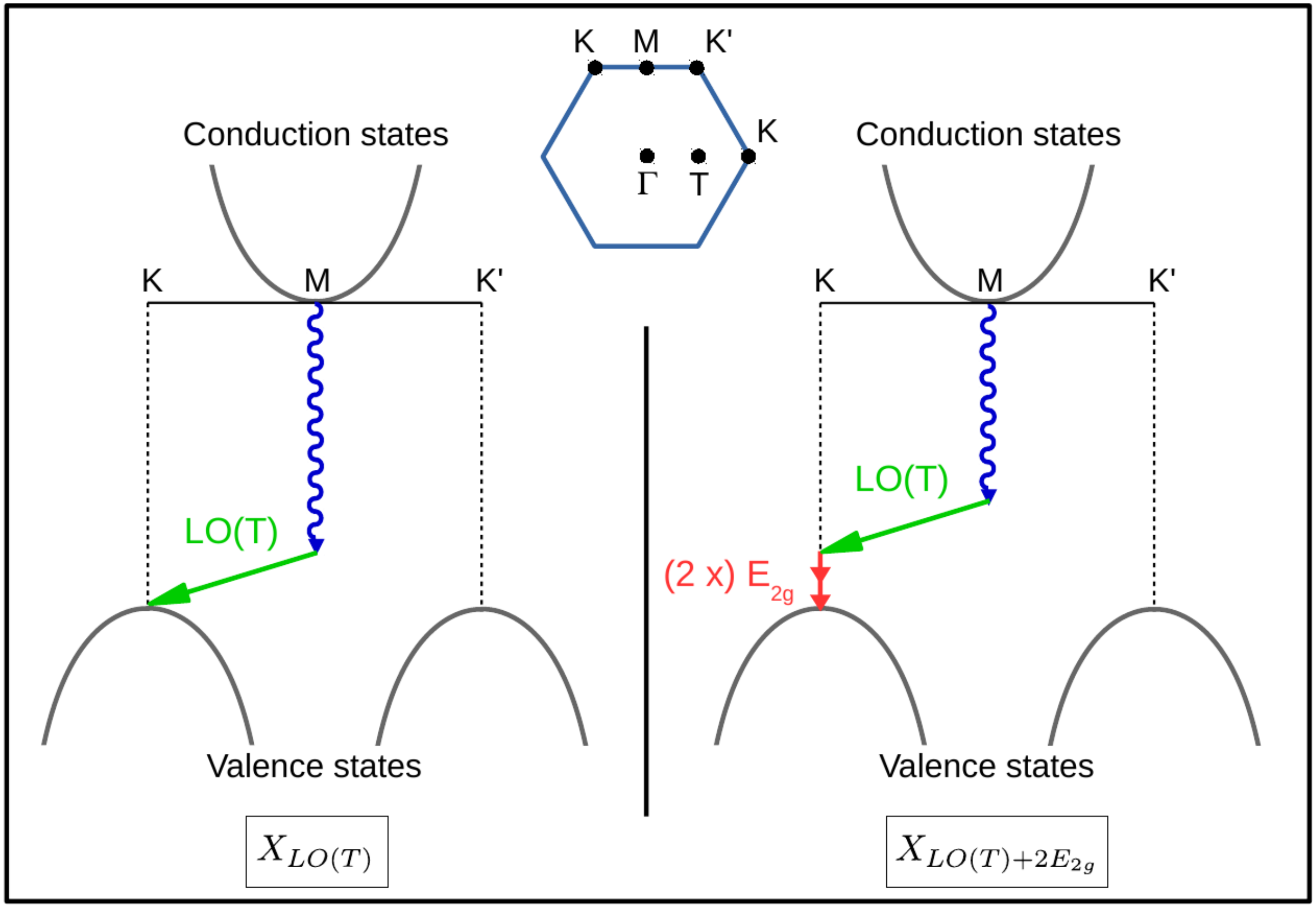
Multi-quantum well LED



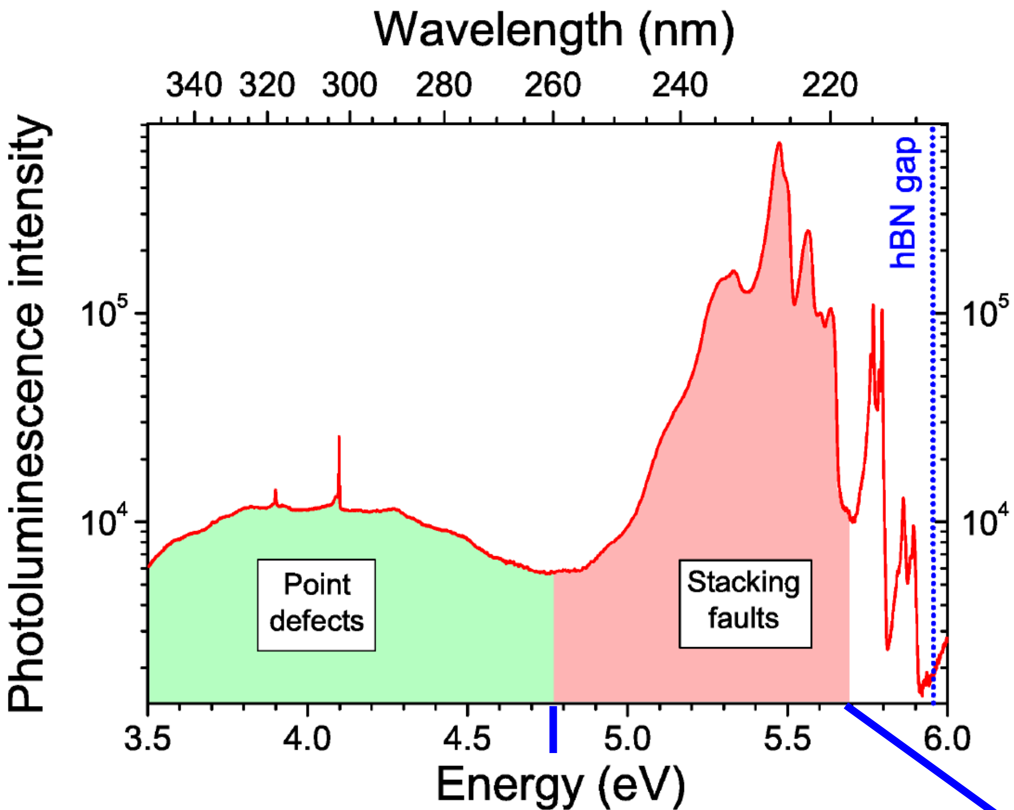
Kobayashi, Nature 484, 223 (2012)

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)

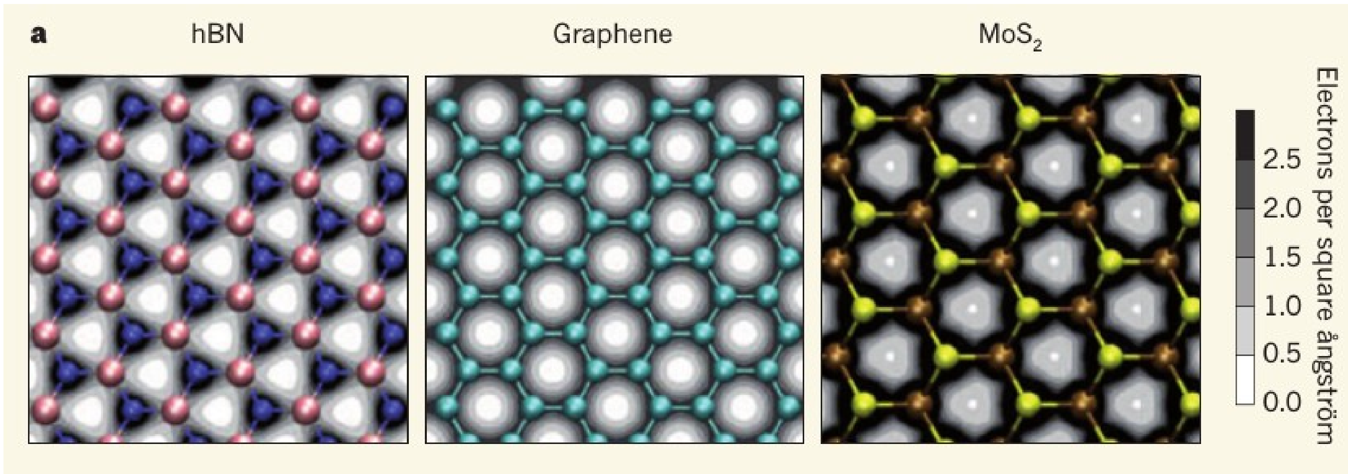
poster 1.160 by P. Vuong

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

Direct vs indirect bandgaps

- 2D crystals

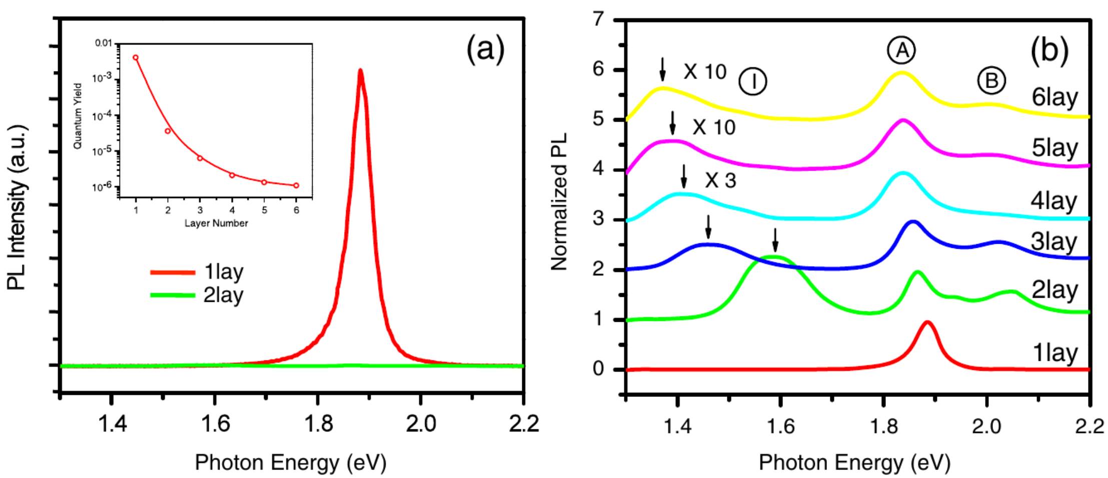
Geim, Nature 499, 419 (2013)



- Monolayer = direct bandgap

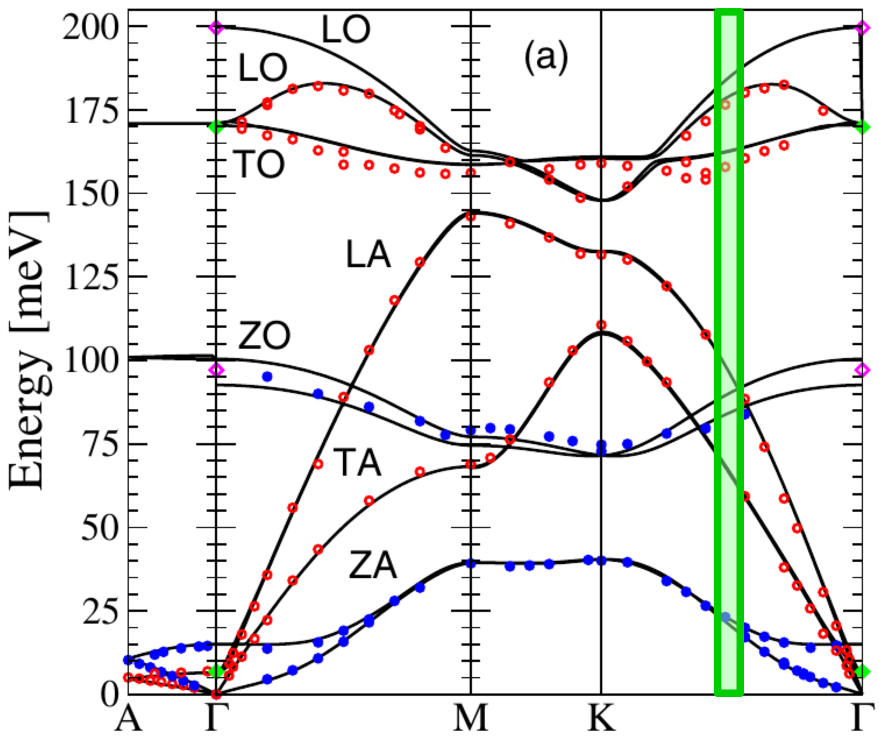
Mak, PRL 105, 136805 (2010)

MoS_2

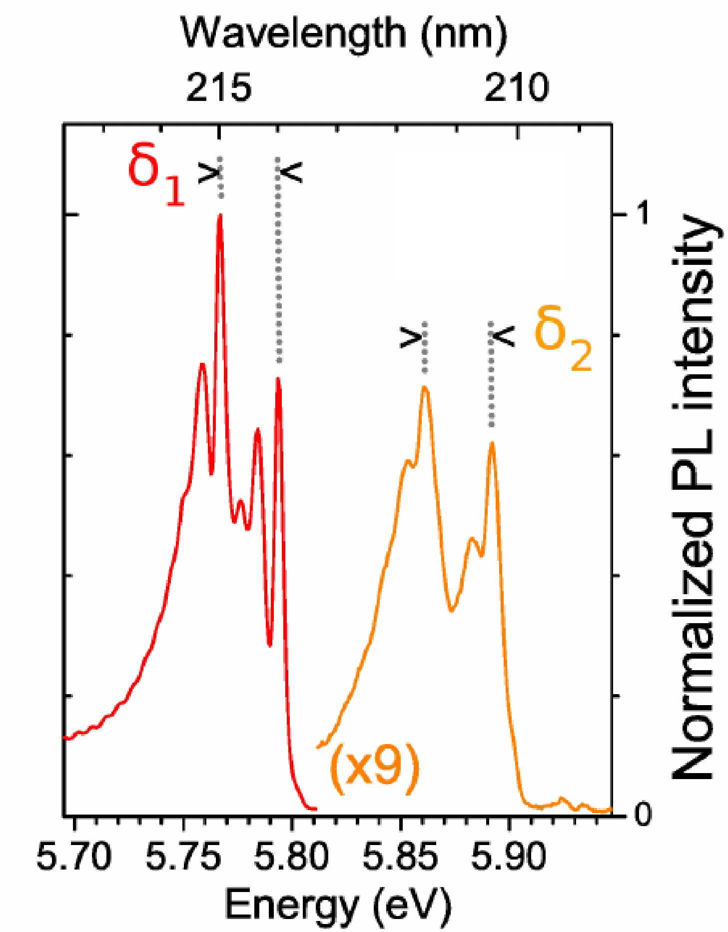


Phonon group velocity & multiplet visibility

Phonon band-structure



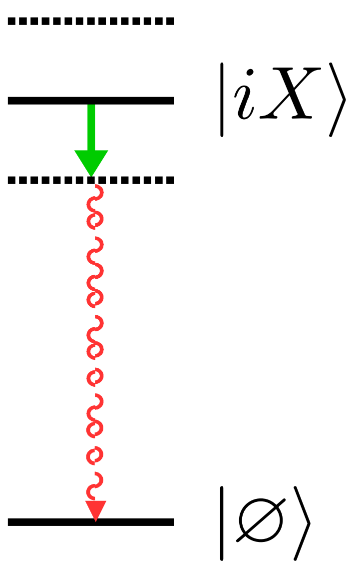
Serrano, PRL 98, 095503 (2007)

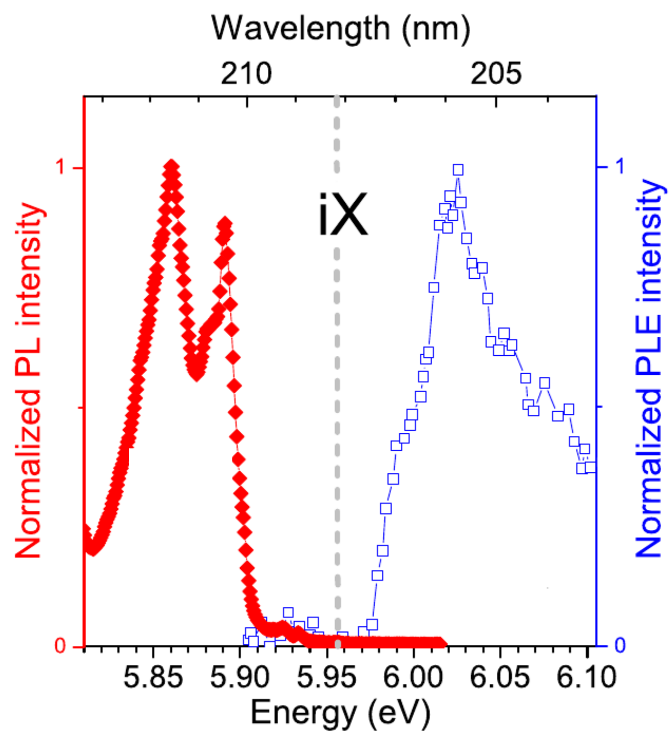


Mirror symmetry between emission and absorption

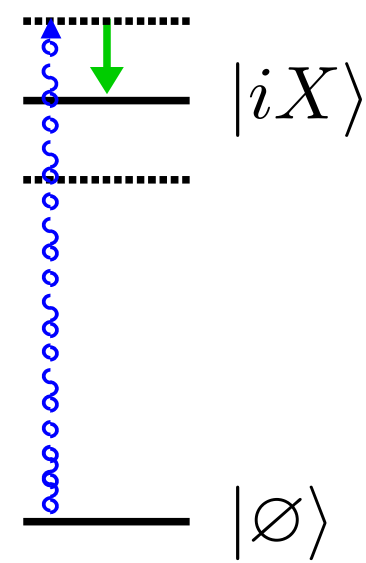
- Phonon-assisted recombination = red-shifted by phonon energy
- Phonon-assisted absorption = blue-shifted by phonon energy

Phonon-assisted recombination



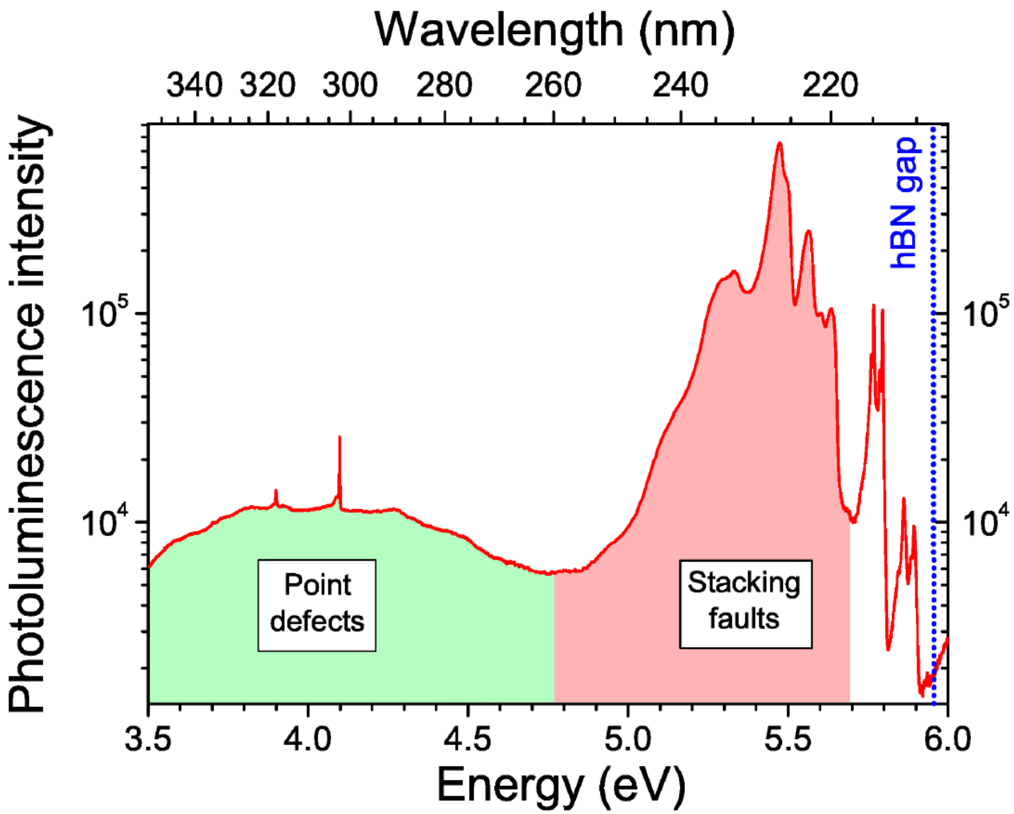


Phonon-assisted absorption



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

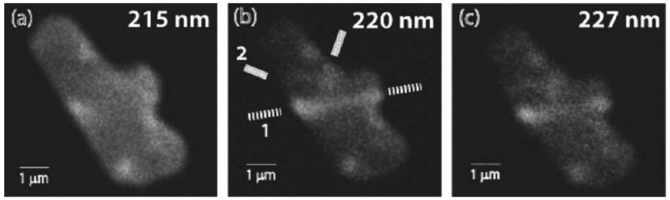
Outline



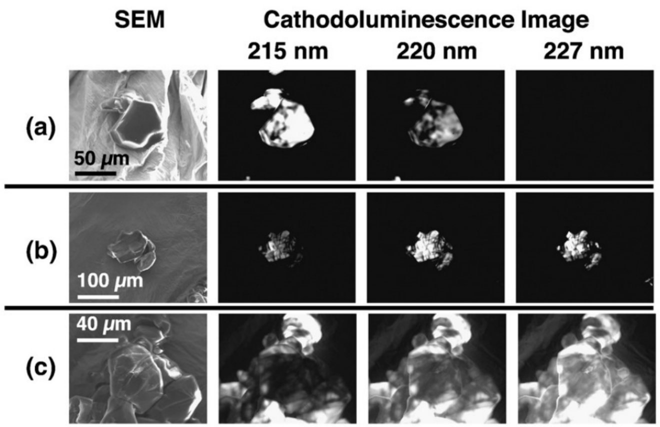
- Phonon replicas (at the band edge)
- Intervalley scattering (stacking faults)
- Phonon-photon mapping (point defects)

Spatially-resolved cathodoluminescence

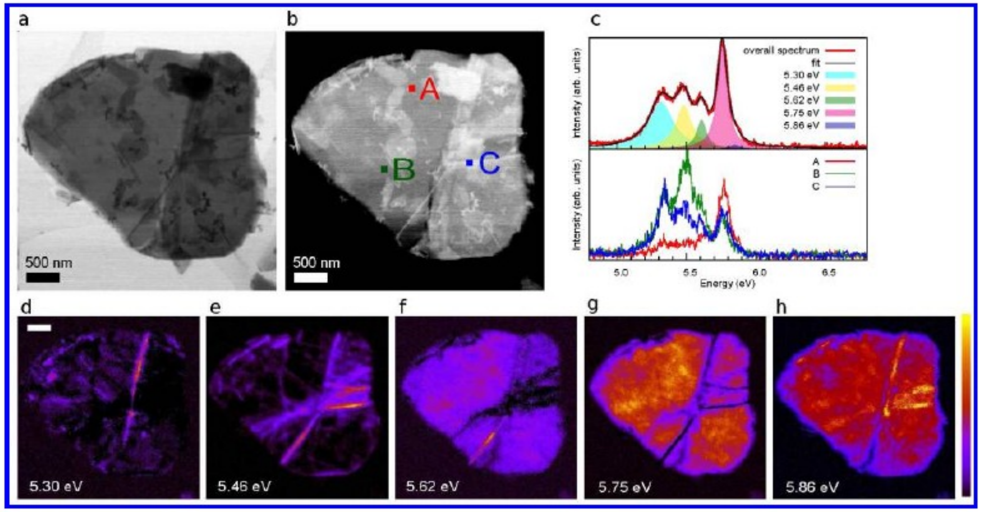
localization at defects of luminescence below 5.7 eV



Jaffrenou, JAP 102, 116102 (2007)

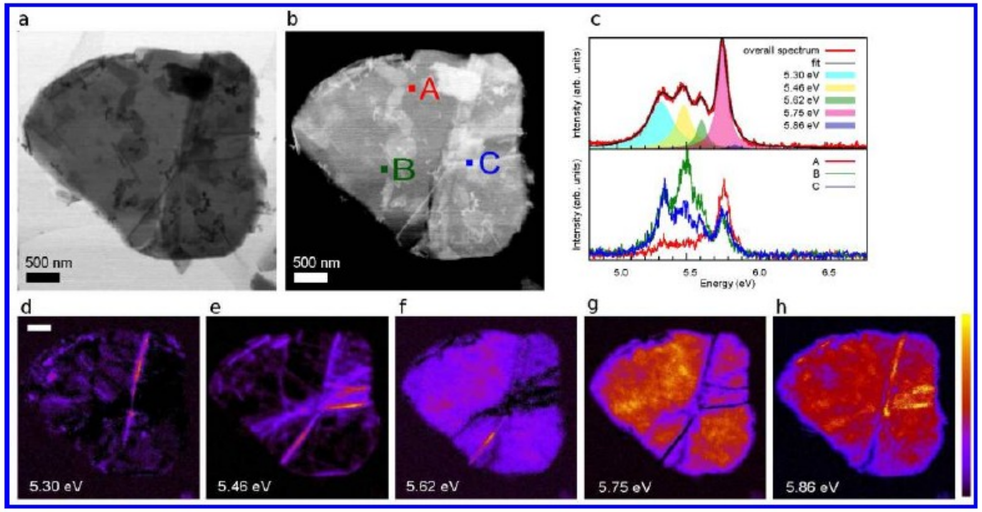


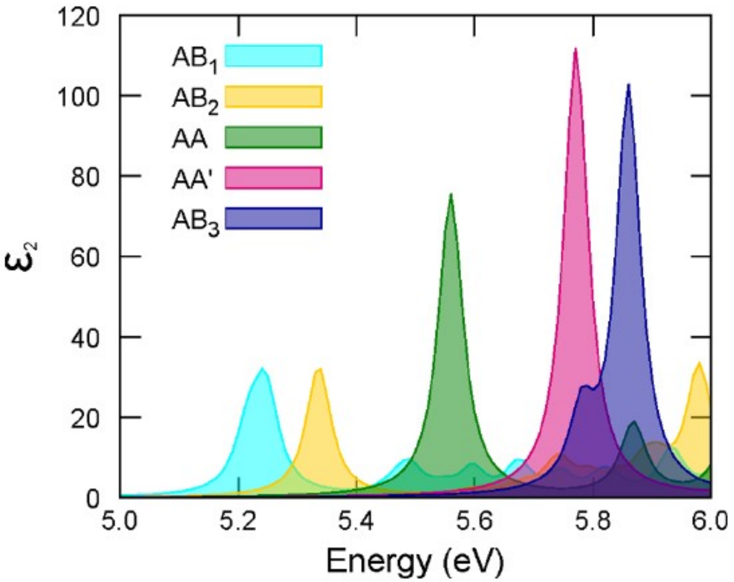
Watanabe, Diam. Rel. Mat. 20 849 (2011)



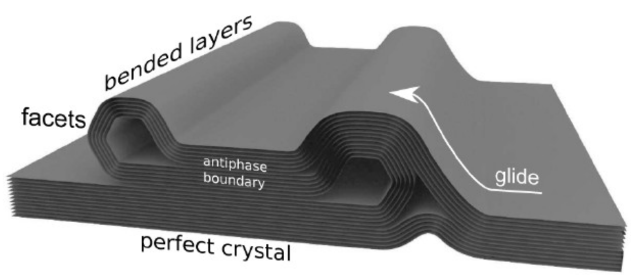
Bourrelier, ACS Photonics 1, 857 (2014)

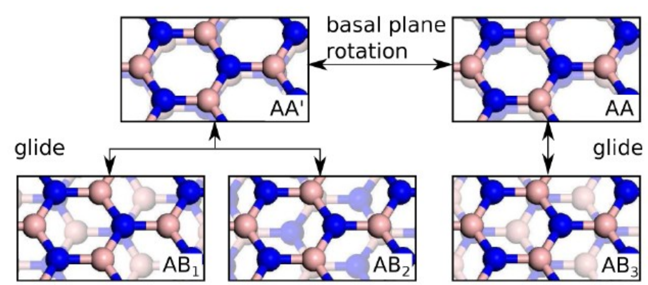
Defect-related emission band



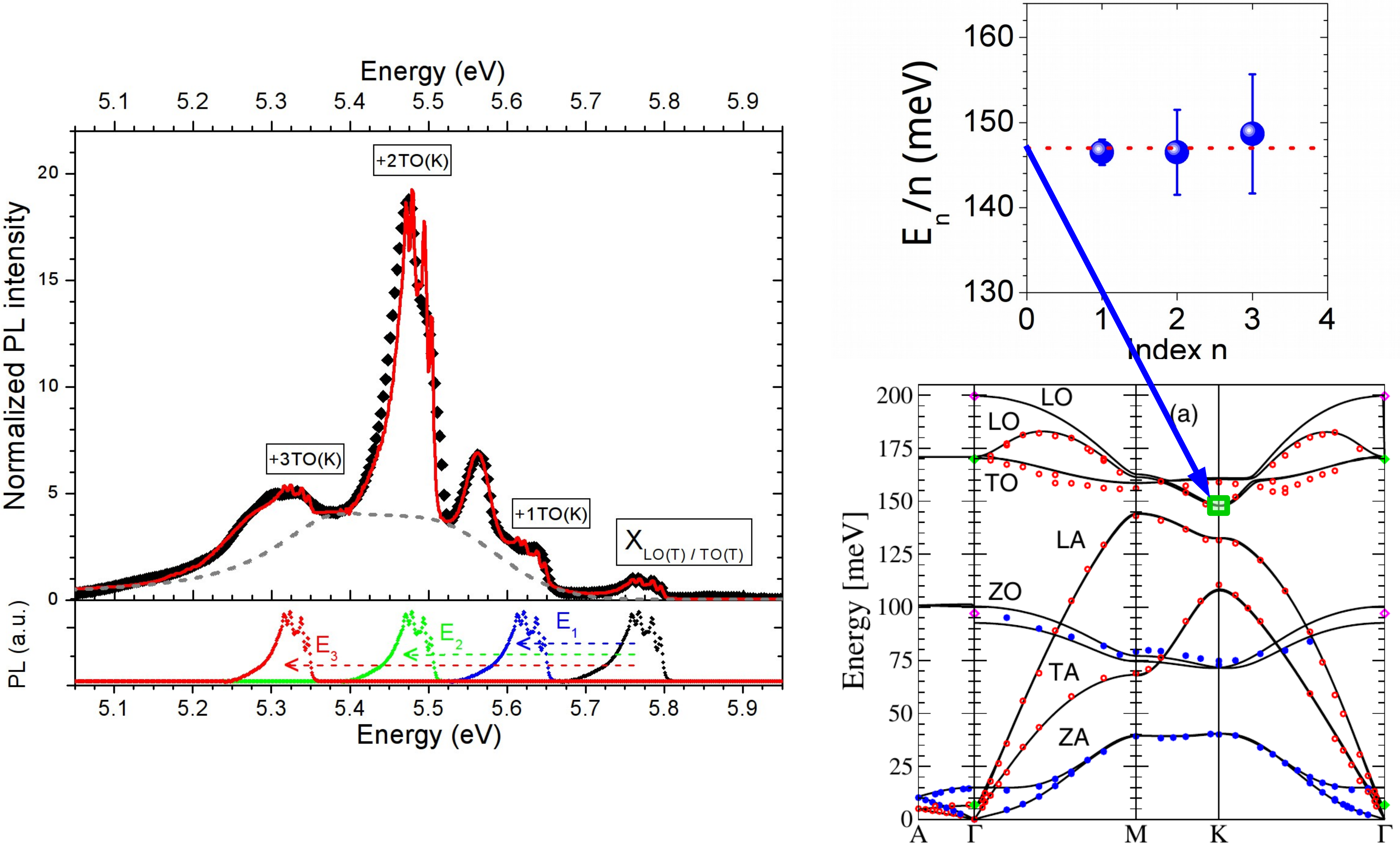


Bourrelier, ACS Photonics 1, 857 (2014)

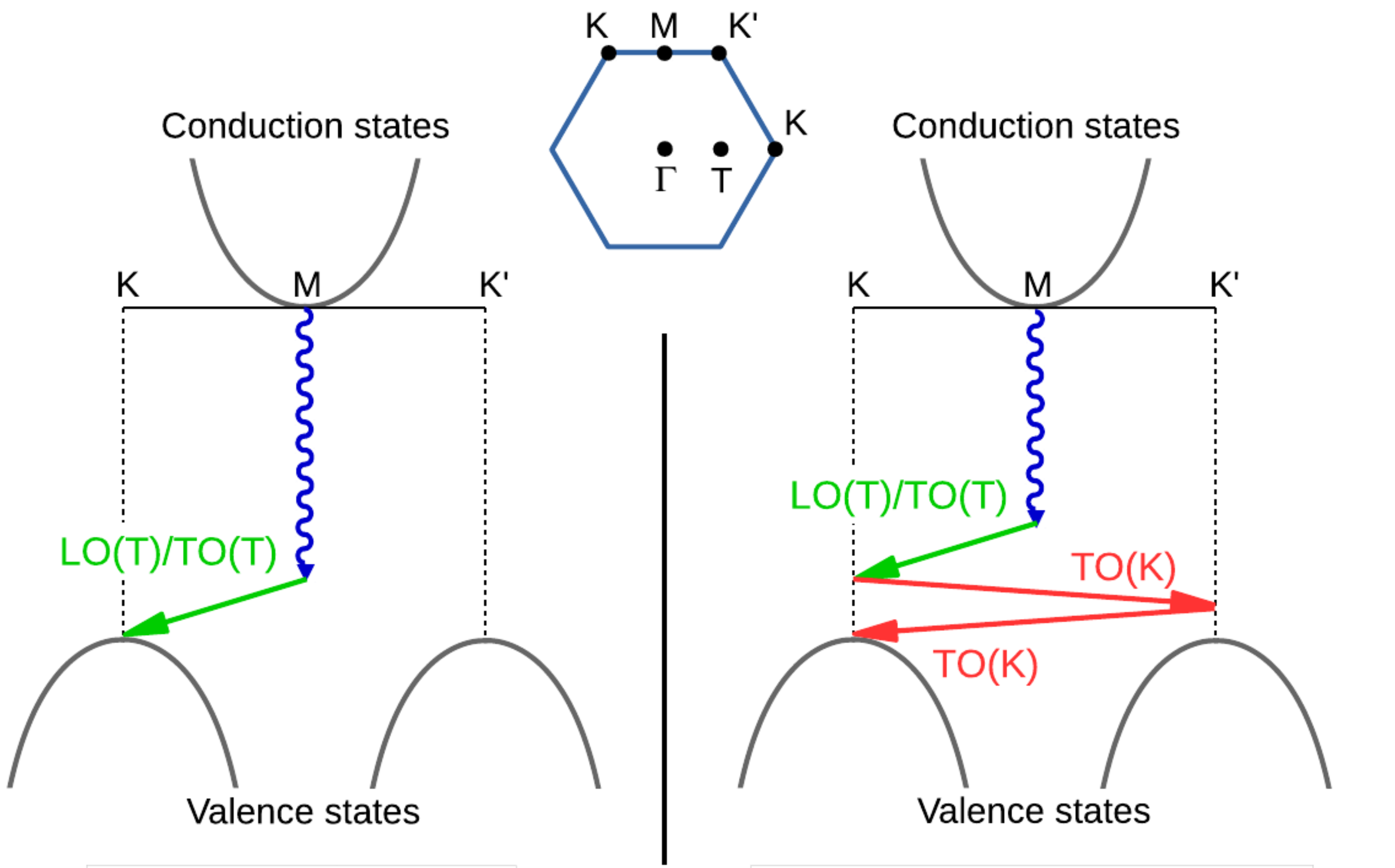




Phonon replicas...again



Intervalley scattering



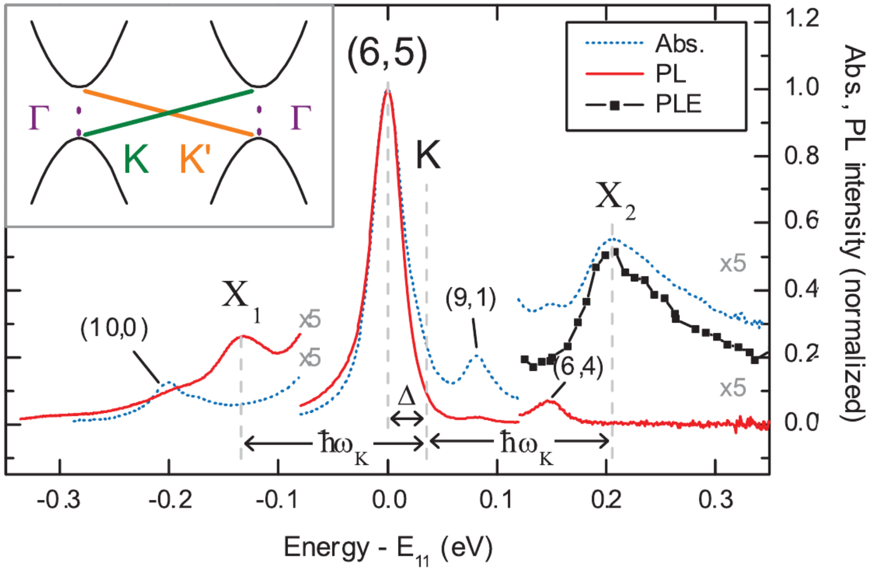
$X_{LO(T)/TO(T)}\ (5.76eV)$

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

TO(K)-assisted intervalley scattering

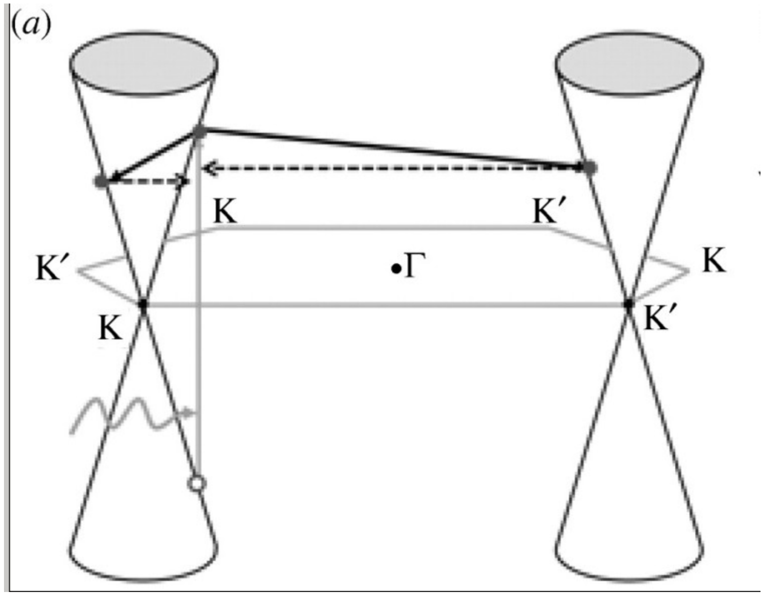
same TO(K) phonon found in two similar systems

Carbon nanotubes
(emission of valley-dark exciton)



Torrens, PRL 101, 157401 (2008)

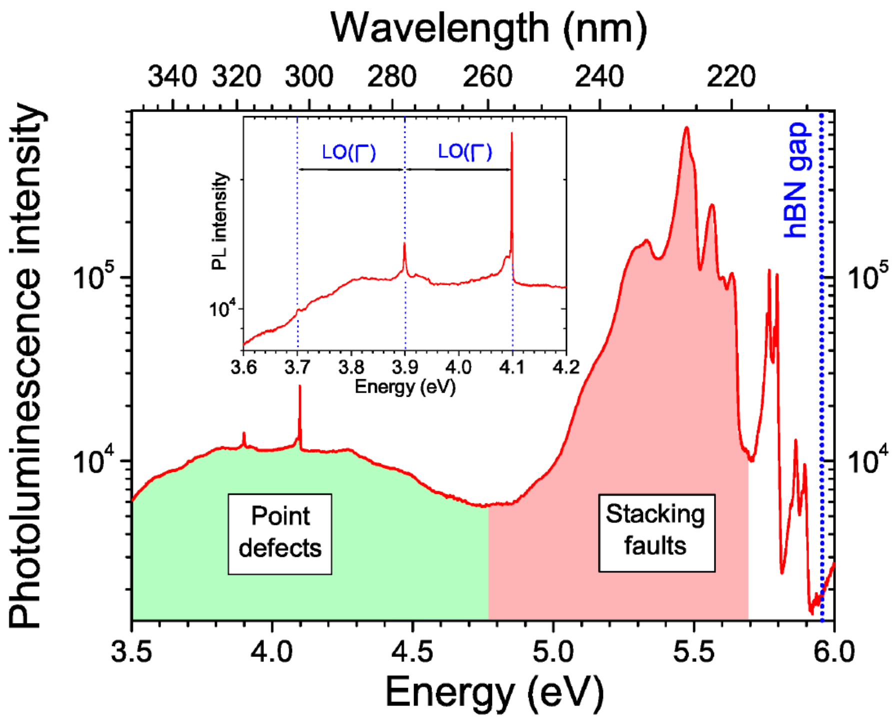
Graphene
(Raman D band)



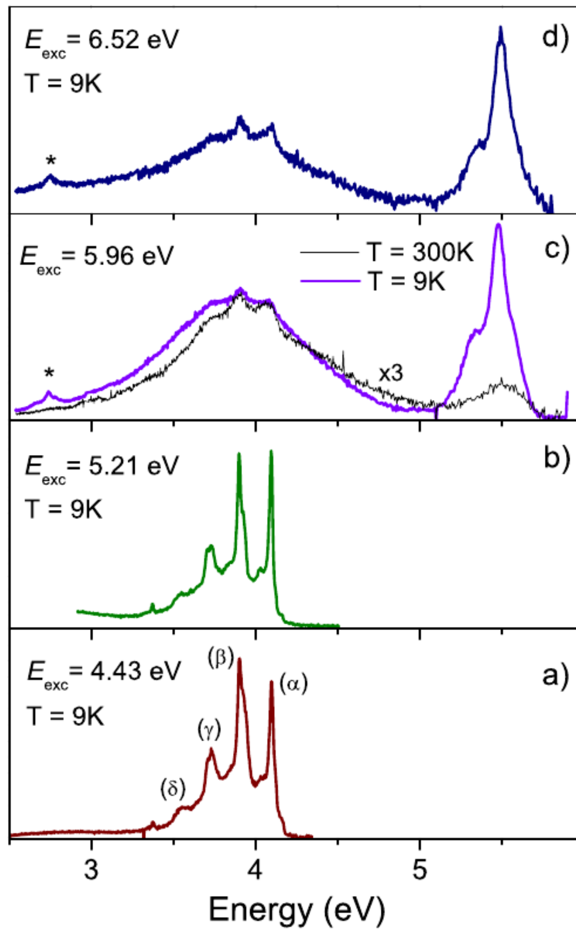
Thomsen, PRL 85, 5214 (2000)

Excitation spectroscopy

above bandgap excitation

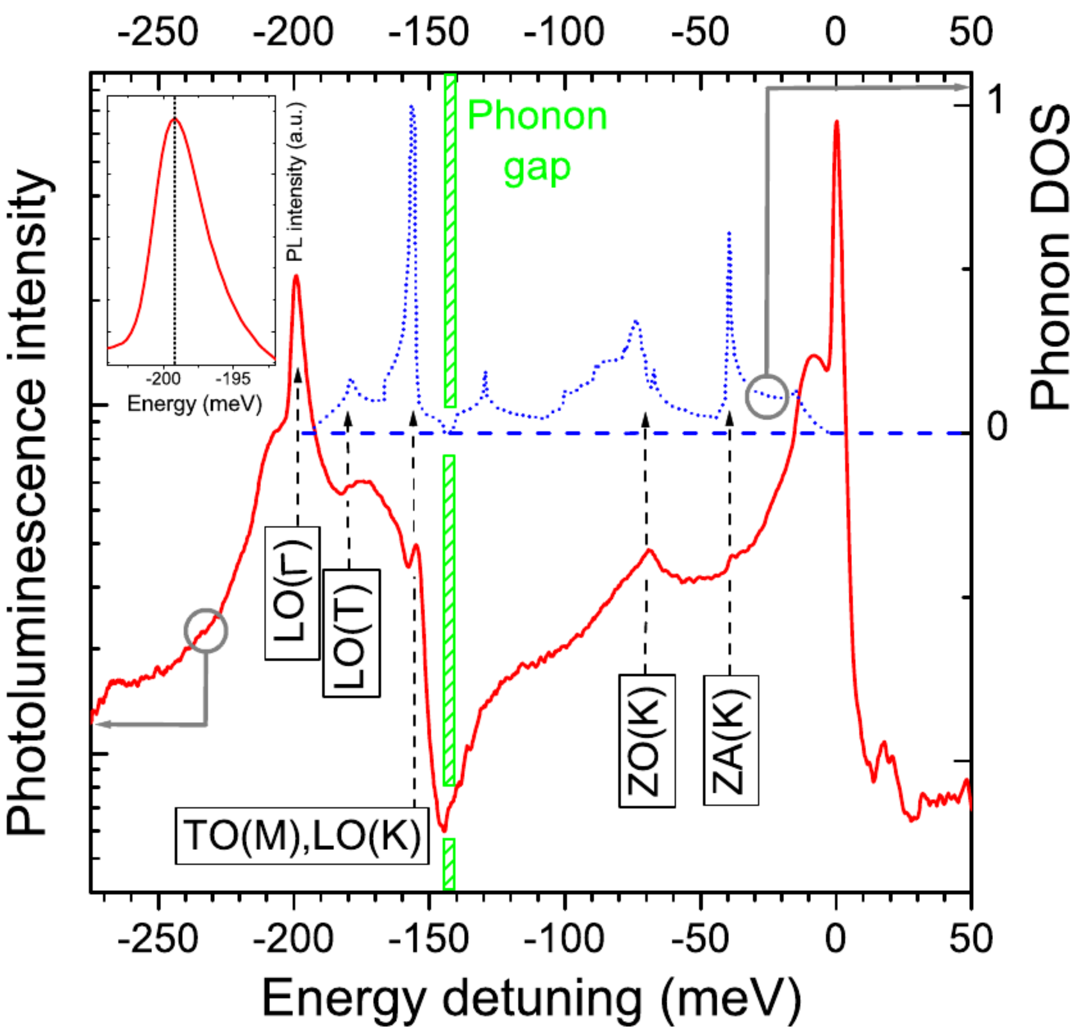


below bandgap excitation



Museur, PRB 78, 155204 (2008)

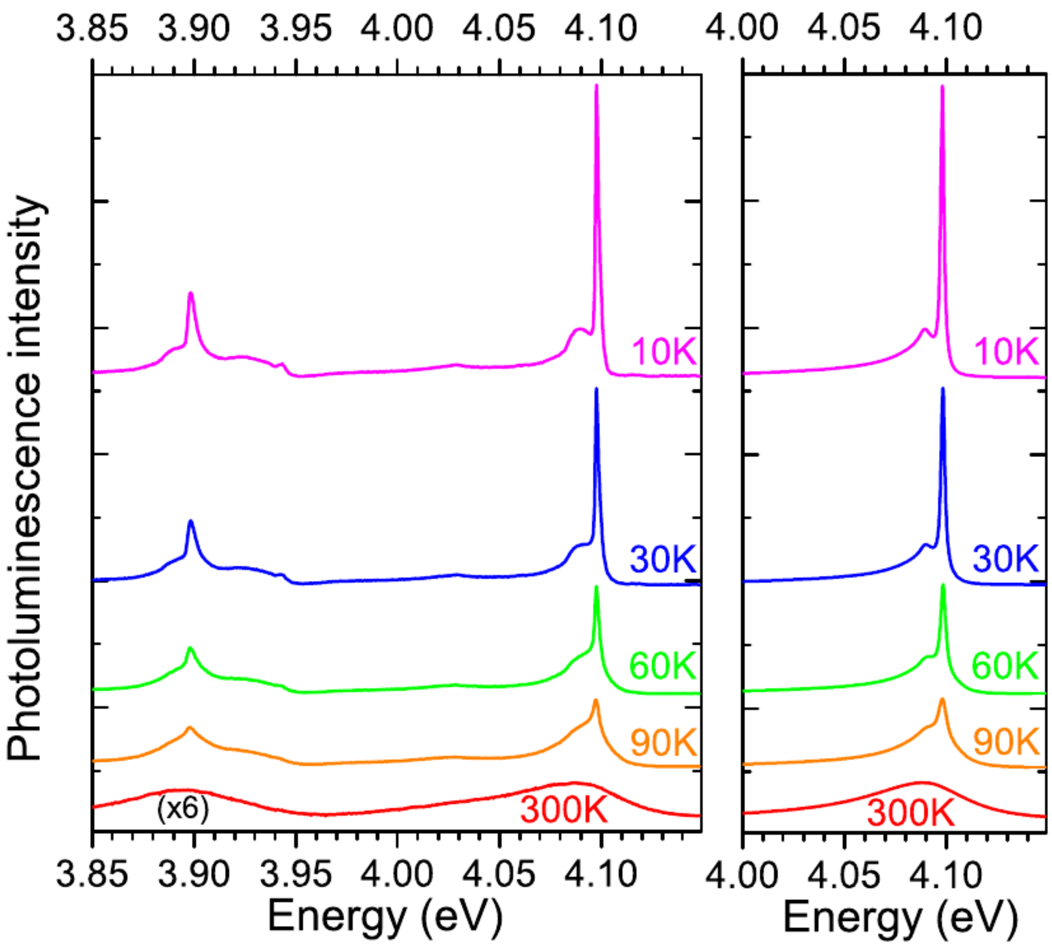
PL spectrum vs phonon DOS



- 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

experiments theory



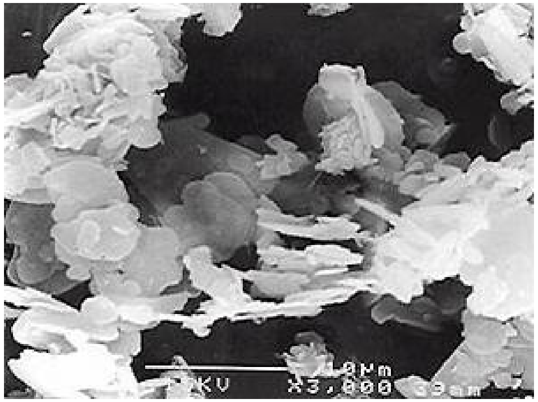
- non-perturbative calculations of LA phonon sidebands
- excellent agreement from 10K to room temperature
- deformation potential
  D ~ 11 eV
- defect size ~ 2 Å

White graphite

an old story ...

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

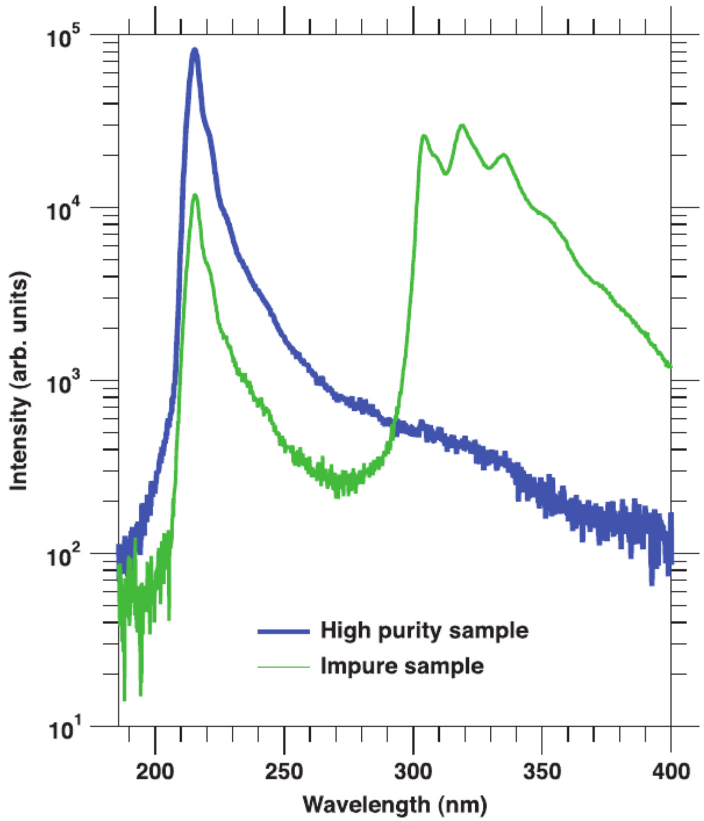
widely used as :
- solid lubricant
- thermal coating
- additive in plastics, ceramics
- cosmetic powder



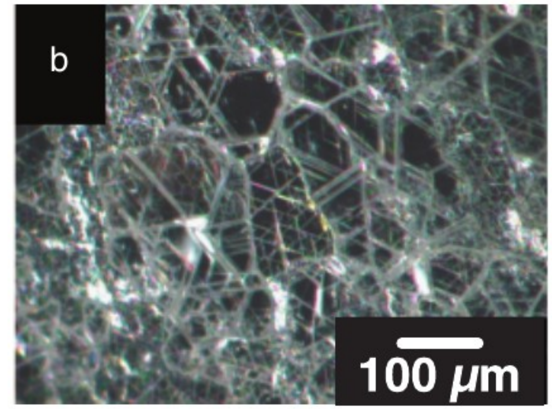
High-quality monocrystals

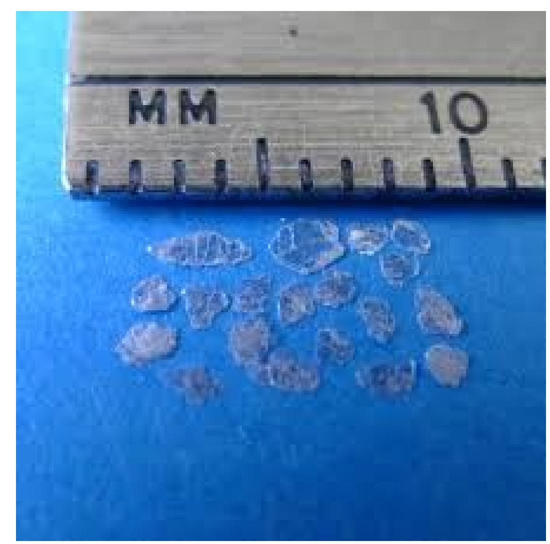
2004-breakthrough by Watanabe & Taniguchi

(N



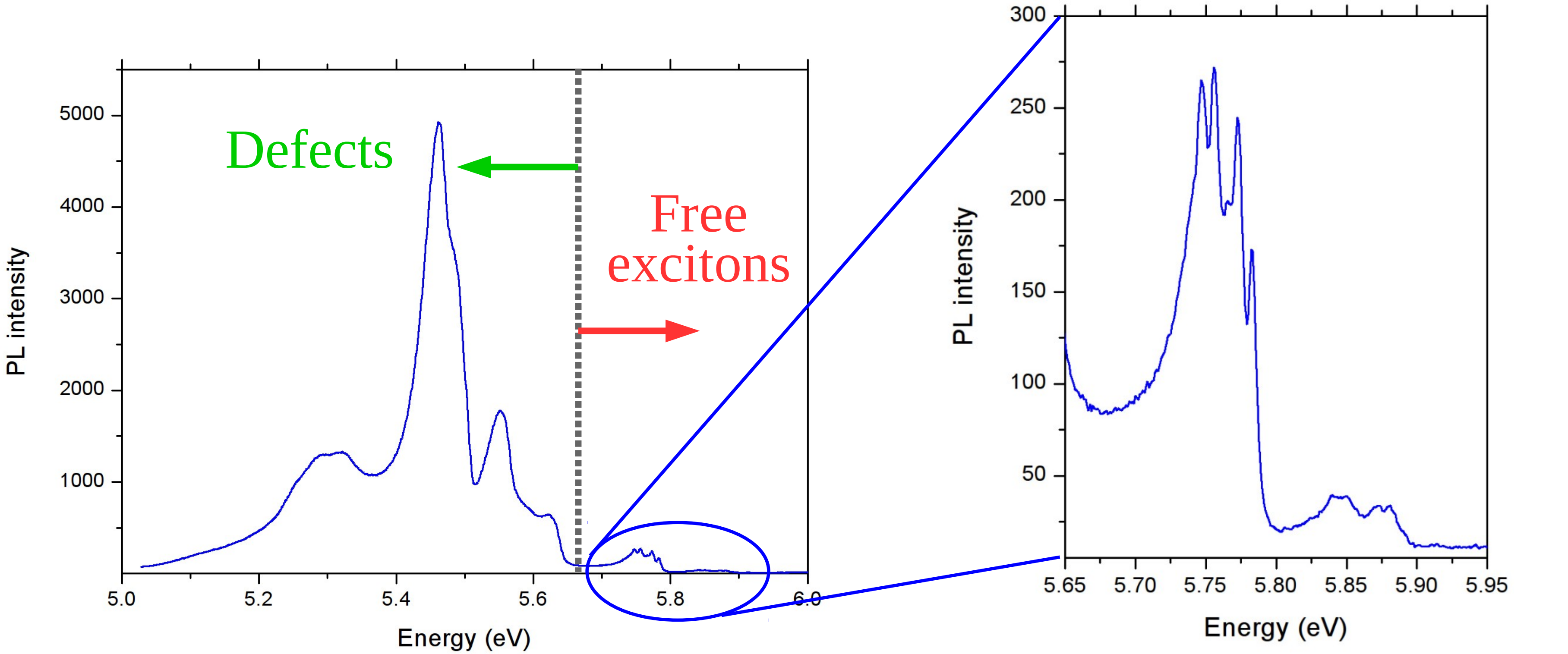
Watanabe, Int. J. Appl. Ceram. Technol. 8, 977 (2011)



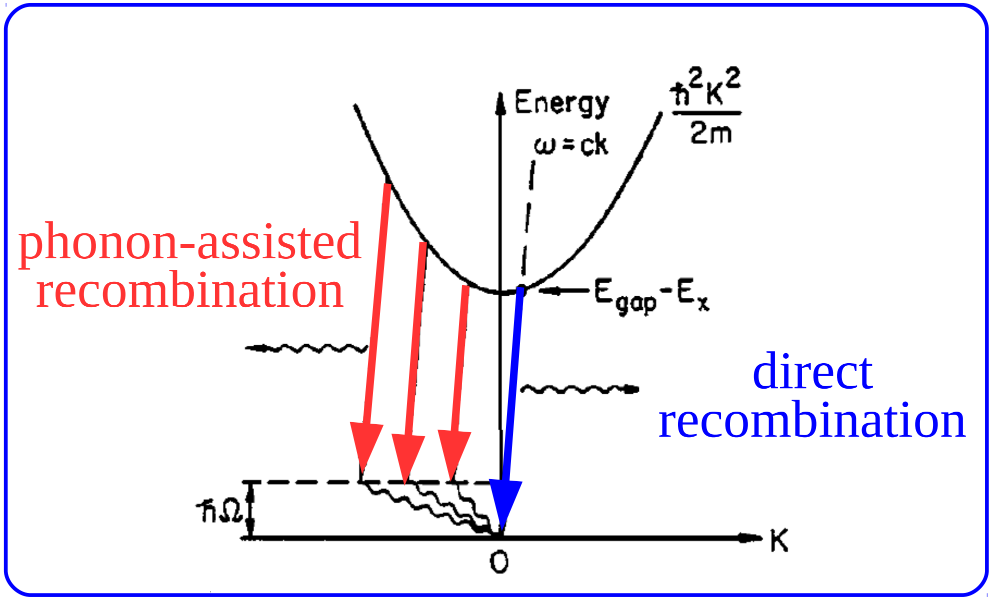


Photoluminescence spectrum

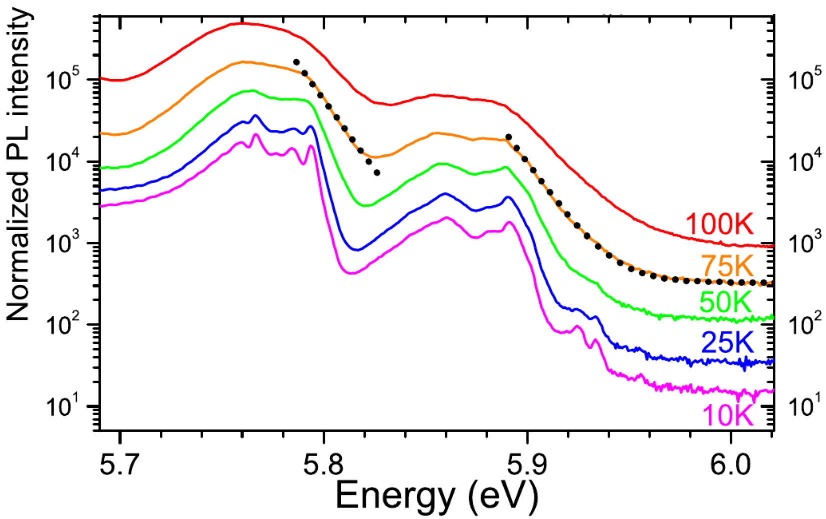
- hBN sample from HQ Graphene (www.hqgraphene.com)
- PL spectroscopy at 10K under laser excitation @ 6.3 eV

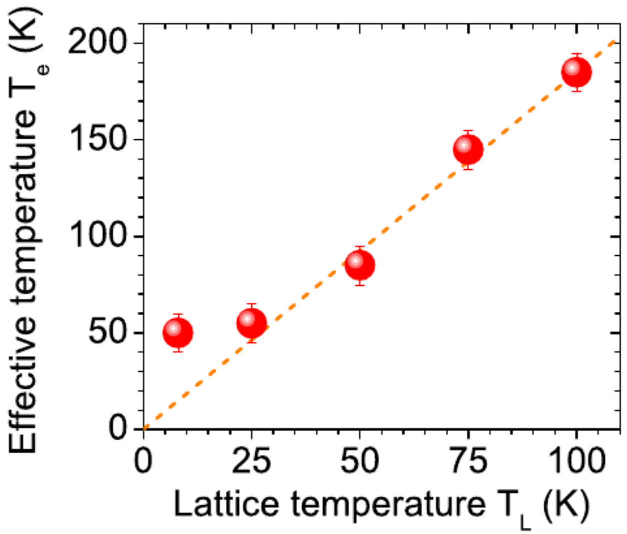


Monitoring the thermalization of high-K excitons



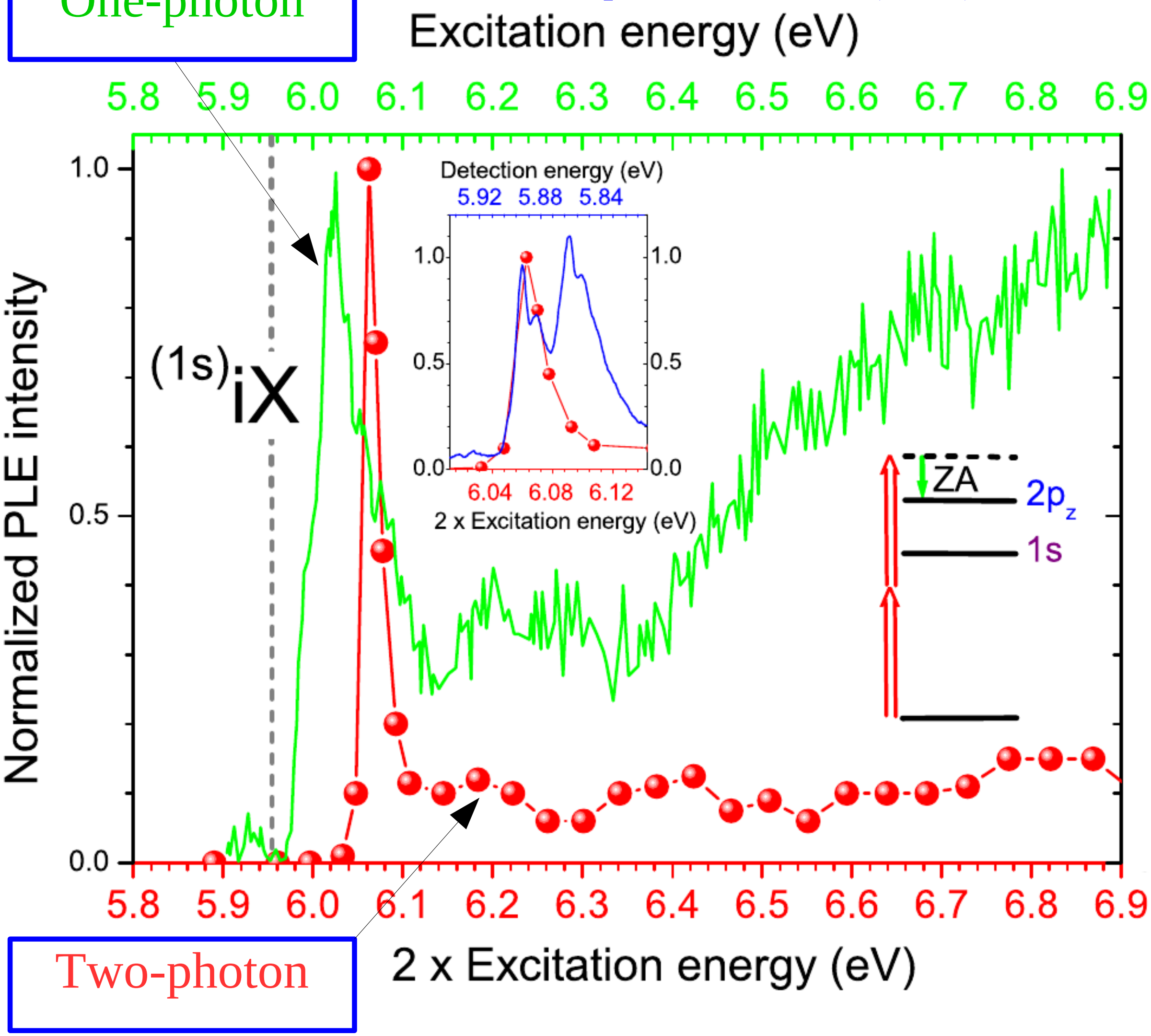
- direct recombination probes excitons at K~0
- thermal distribution of high-K excitons only monitored in phonon replicas





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