Nitrides and other semiconductors

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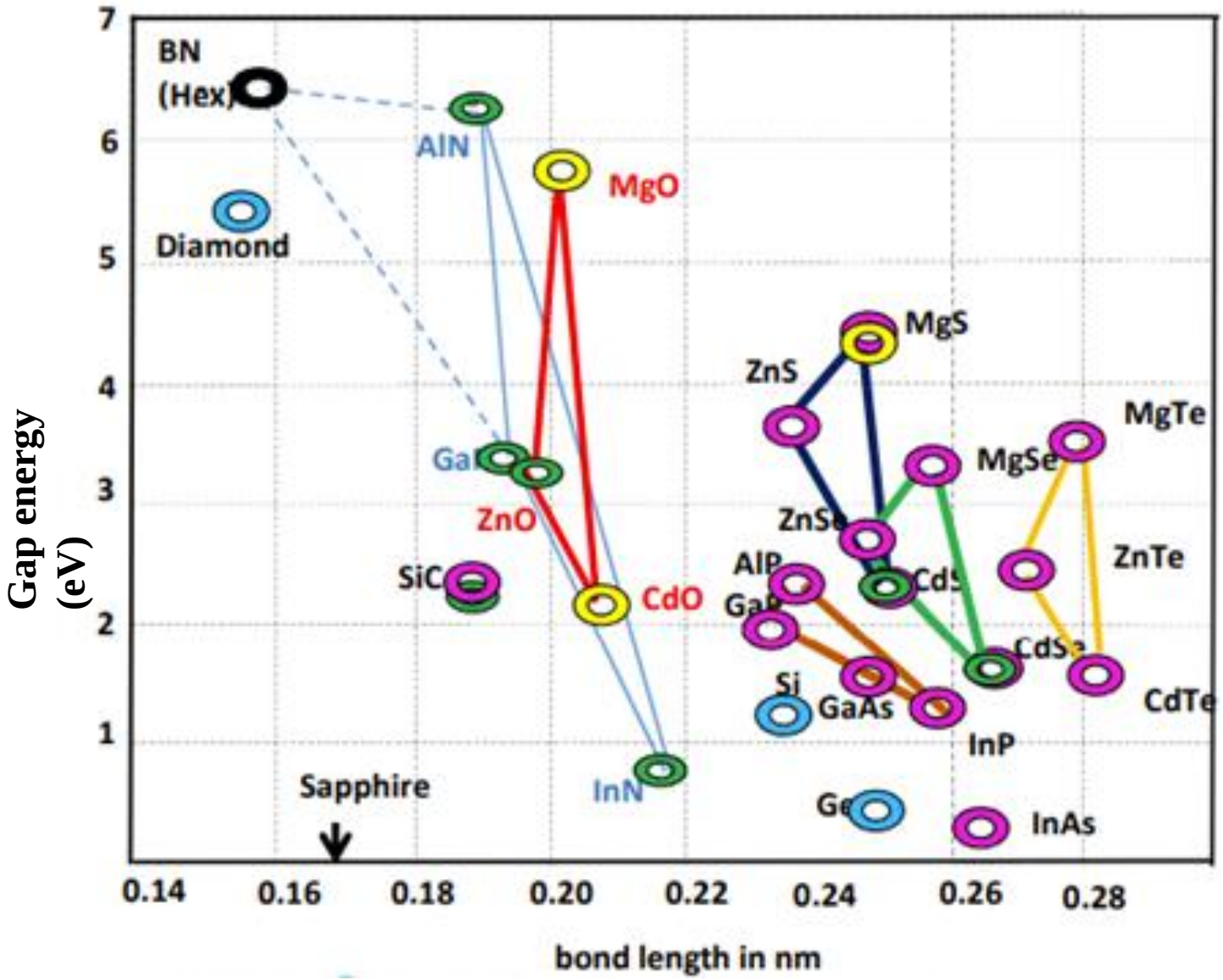

Main industrial semiconductors

1-Si
2-Ge
3-SiC
4-GaN
4-GaAs
5-InP
6-InAs
7-GaSb
8-CdTe
9-HgCdTe

IV
III-V
II-VI

	GaN	AlN	InN	GaAs	Si	Diamond
Bond length (A)	1.95	1.90	2.15	2.44	2.34	1.54
Bond energy (eV)	8.9*	11.5	7.7	6.5	4.7	7.4
Cohesive energy (eV/atom)	2.24	2.88	1.93	1.63	2.32	4.62
Melting point (K)	2791	3487	2146	1513	1687	3770

* About 10 meV less for the cubic phase: less stable from thermodynamics

Thermal stability

Chemical inertness

Radiation hardness

CRHEA

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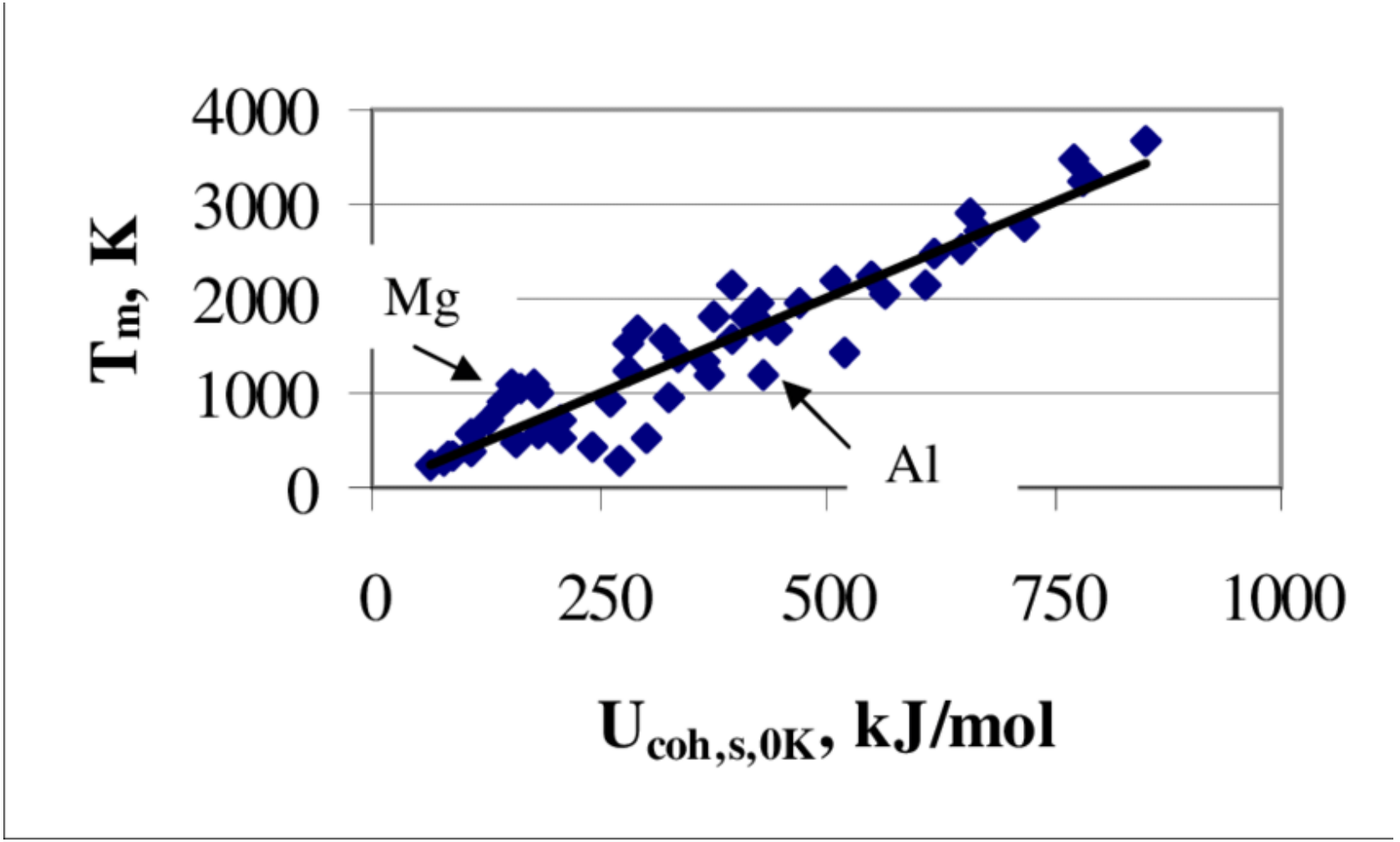
Melting temperature and cohesive energy



Ionic/covalent bond

Bond character depends on atom electronegativity

For instance for group V elements :

$\chi_N >> \chi_P >> \chi_{As} >> \chi_{Sb}$

Bonds in nitrides are more ionic than in many other SC

How does the validity of tight binding methods vary along this table ?

	Ionicity
Si	0
C (diamond)	0
AlAs	0.274
AlP	0.307
GaAs	0.310
GaP	0.327
InAs	0.357
InP	0.421
AlN	**0.449**
GaN	**0.500**
InN	**0.558**
NaCl	0.9

* J.C. Phillips, *Bonds and Bands in Semiconductors*, 1973

Polarization in heterostructures

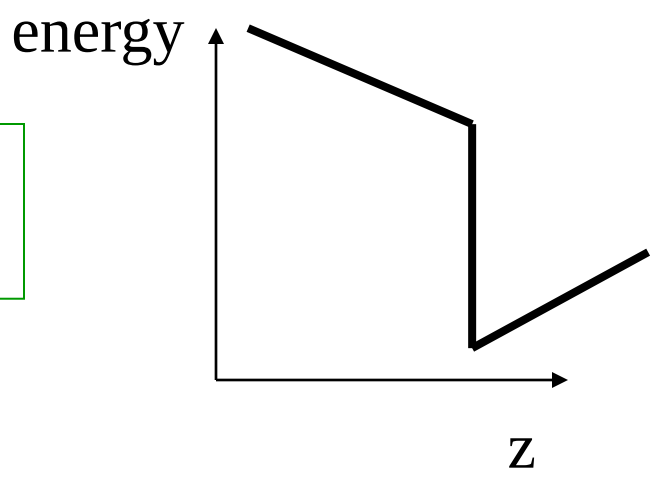
What is important is the differences in polarization between two materials (the absolute value may even not be defined (C. van de Waal)

$$E(z) = -\frac{1}{\varepsilon_0 \varepsilon_r} P(z)$$

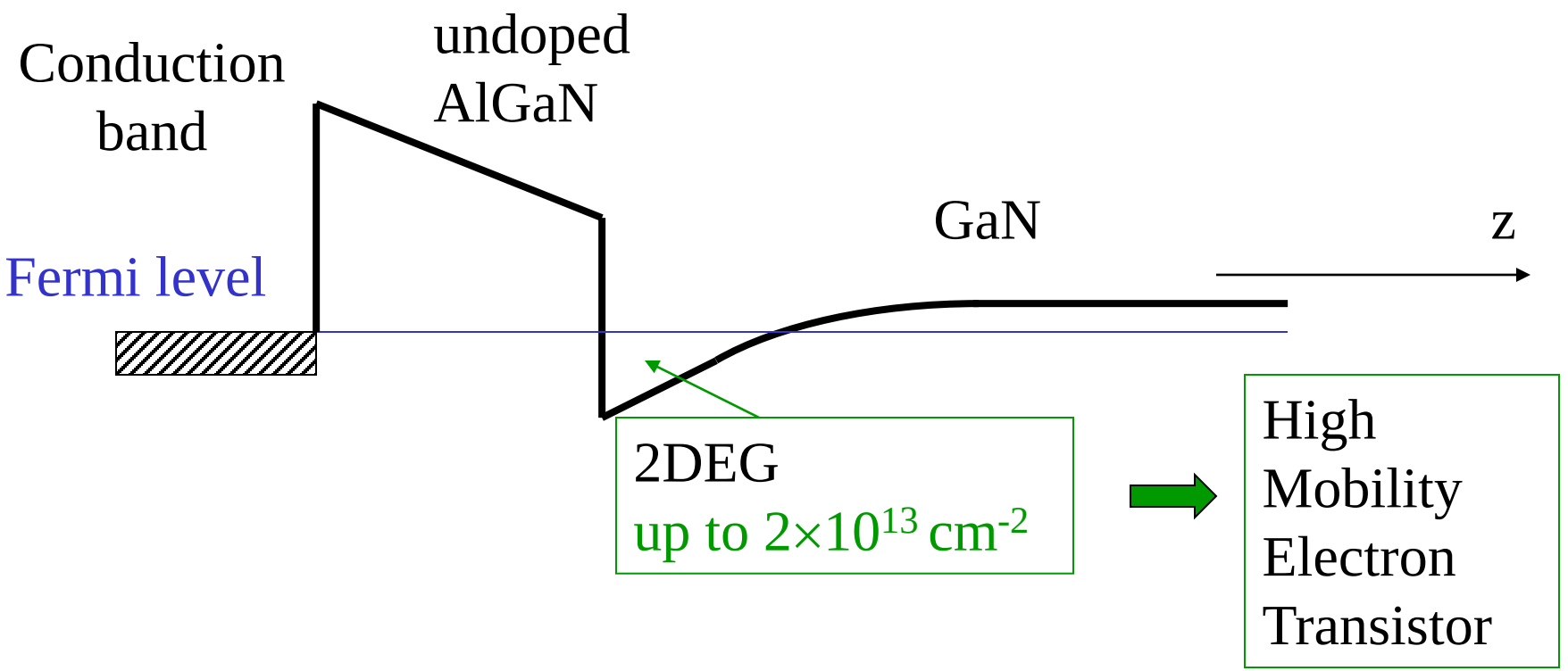
$\Delta P = P_{AlN} - P_{GaN} \approx$ 0.05-0.1 C/m^2

$\Delta E = E_{AlN} - E_{GaN} \approx \Delta P / \varepsilon_0 \varepsilon_r \approx$ 6-12 MV/cm

Enormous internal field discontinuity at the interface !

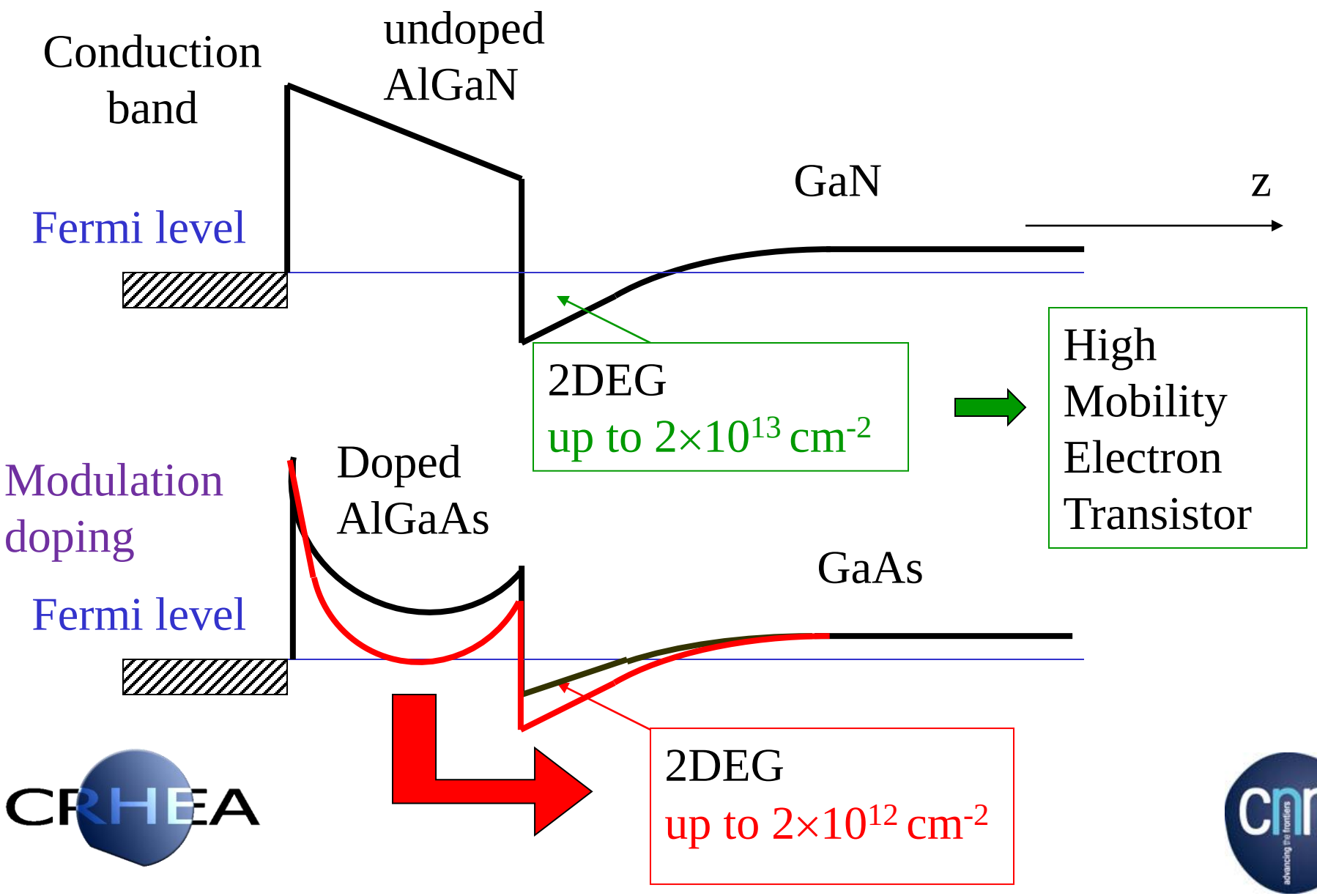


Polarization in wurzite nitrides



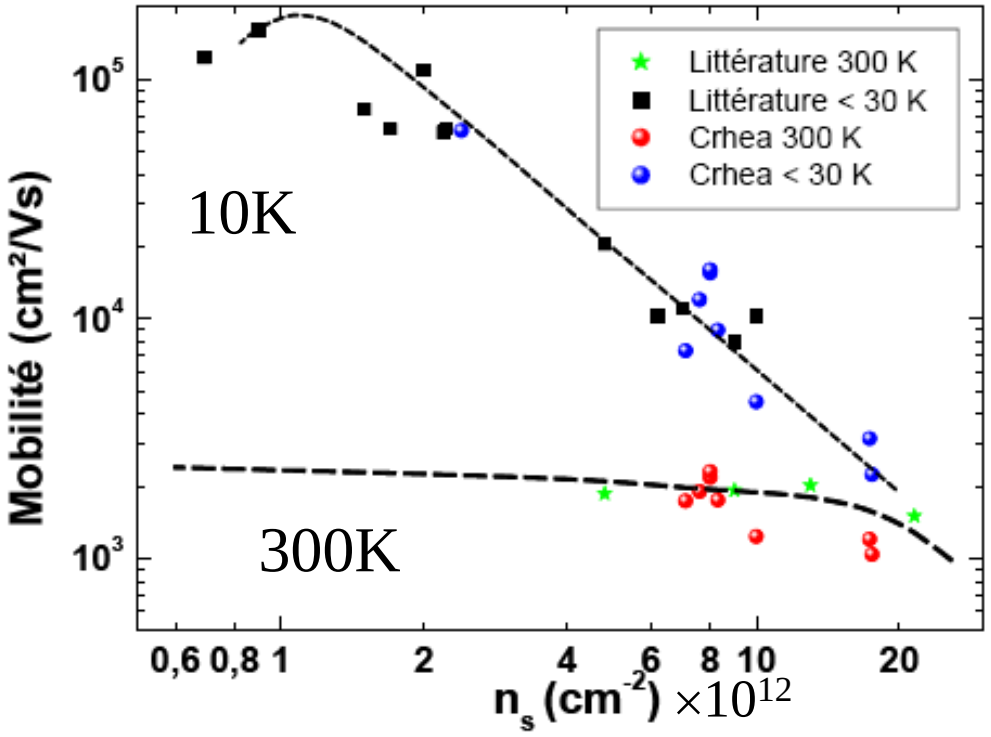
Can you get 2D gases without polarization field ?

Polarization in wurzite nitrides



Best of - GaN 2DEG

	n_s ($10^{12}cm^{-2}$)
GaN/AlGaN	36
GaN/AlInN	42
GaAs/AlGaAs	2
InGaAs/AlInAs	8.5



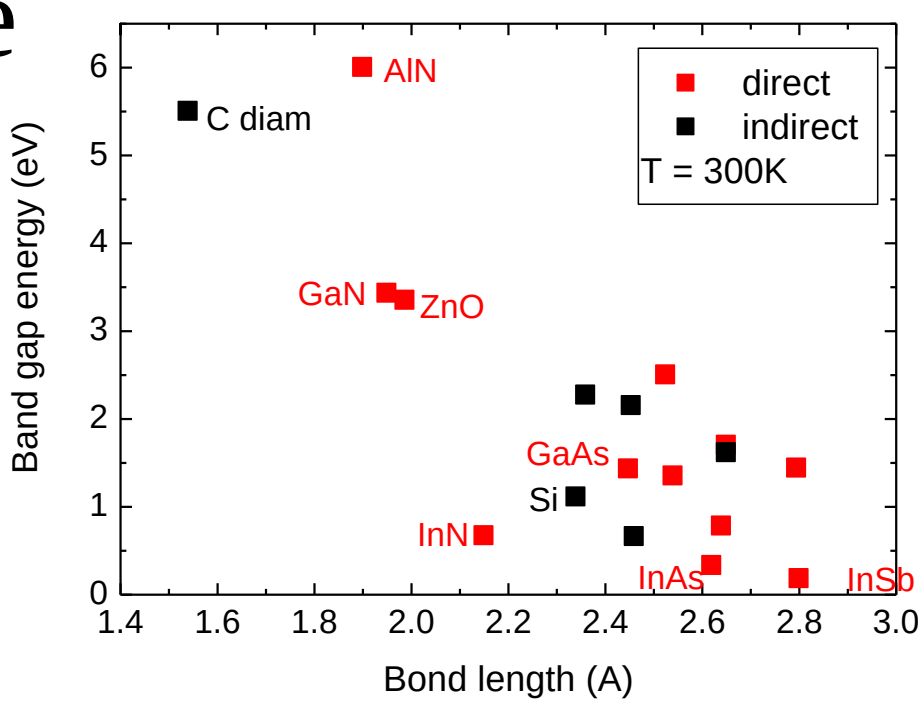
	μ(300K) cm^2/Vs	n_s (300K) cm^{-2}	μ (<4K) cm^2/Vs	n_s (<4K) cm^{-2}
GaN/AlGaN	2500	$4\text{-}6\times10^{12}$	10^5	2×10^{12}
GaAs/AlGaAs	10000	2×10^{11}	3×10^7	2×10^{11}

Why is μ smaller in GaN than in GaAs ?

Band structure

Small atoms, short bonds:

⇒ large band gap energy

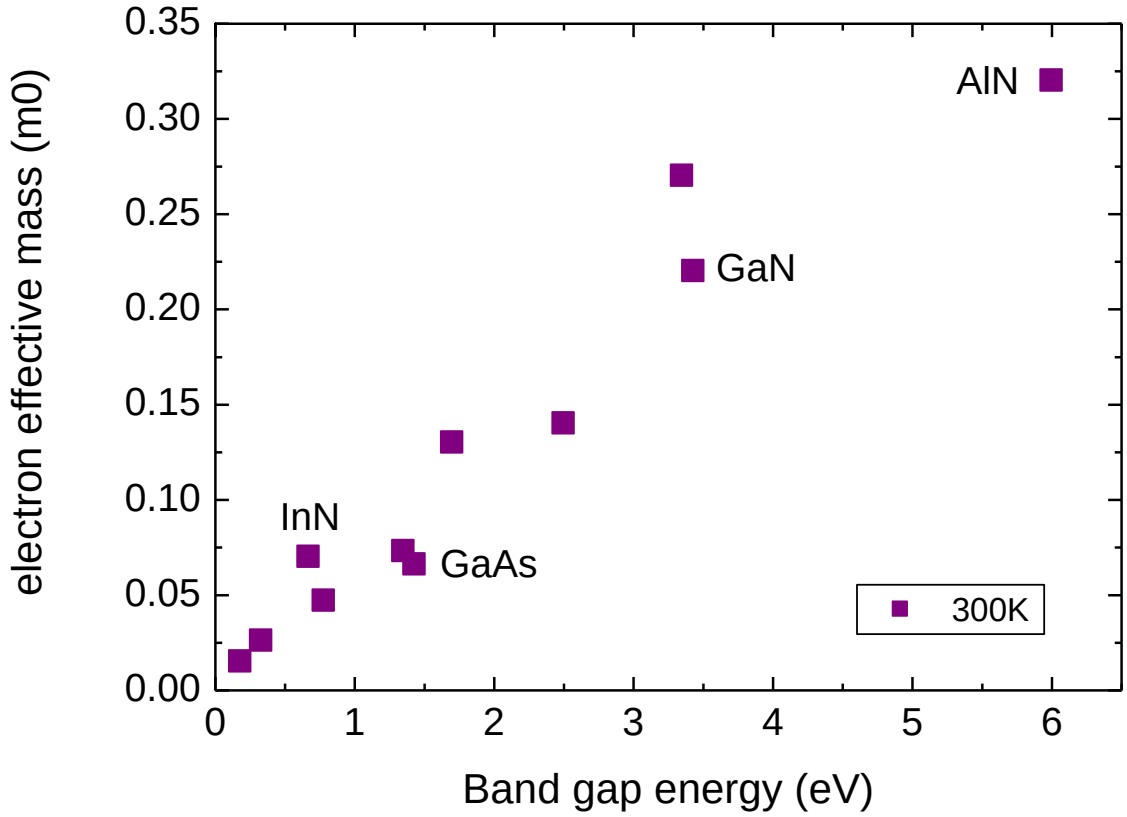


Material	c-GaN	w-GaN	AlN	InN
Band gap (300K)	3.3 eV	3.43 eV	6.0 eV	0.67 eV

All direct gap materials ! Optoelectronics from IR to UV IR: (InN:1.85 µm) , visible (InGaN) , to UV (AlN:0.206 µm).

Band structure

Electron effective mass: follows the m∝Eg rule

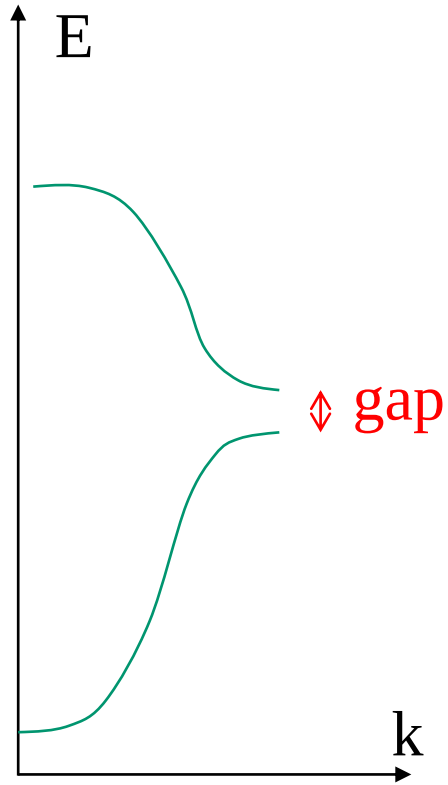


Large effective masses in nitrides

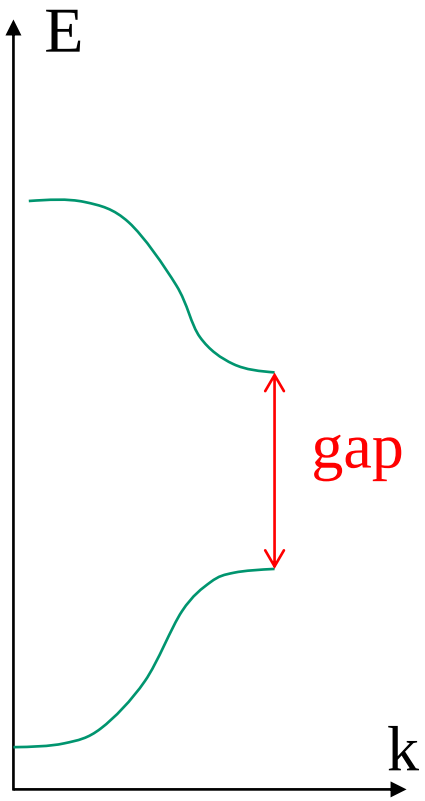
Mobilities smaller than in other III-vs

Effective mass versus band gap

$$\frac{1}{m} = \frac{\partial^2 E}{\partial k^2}$$

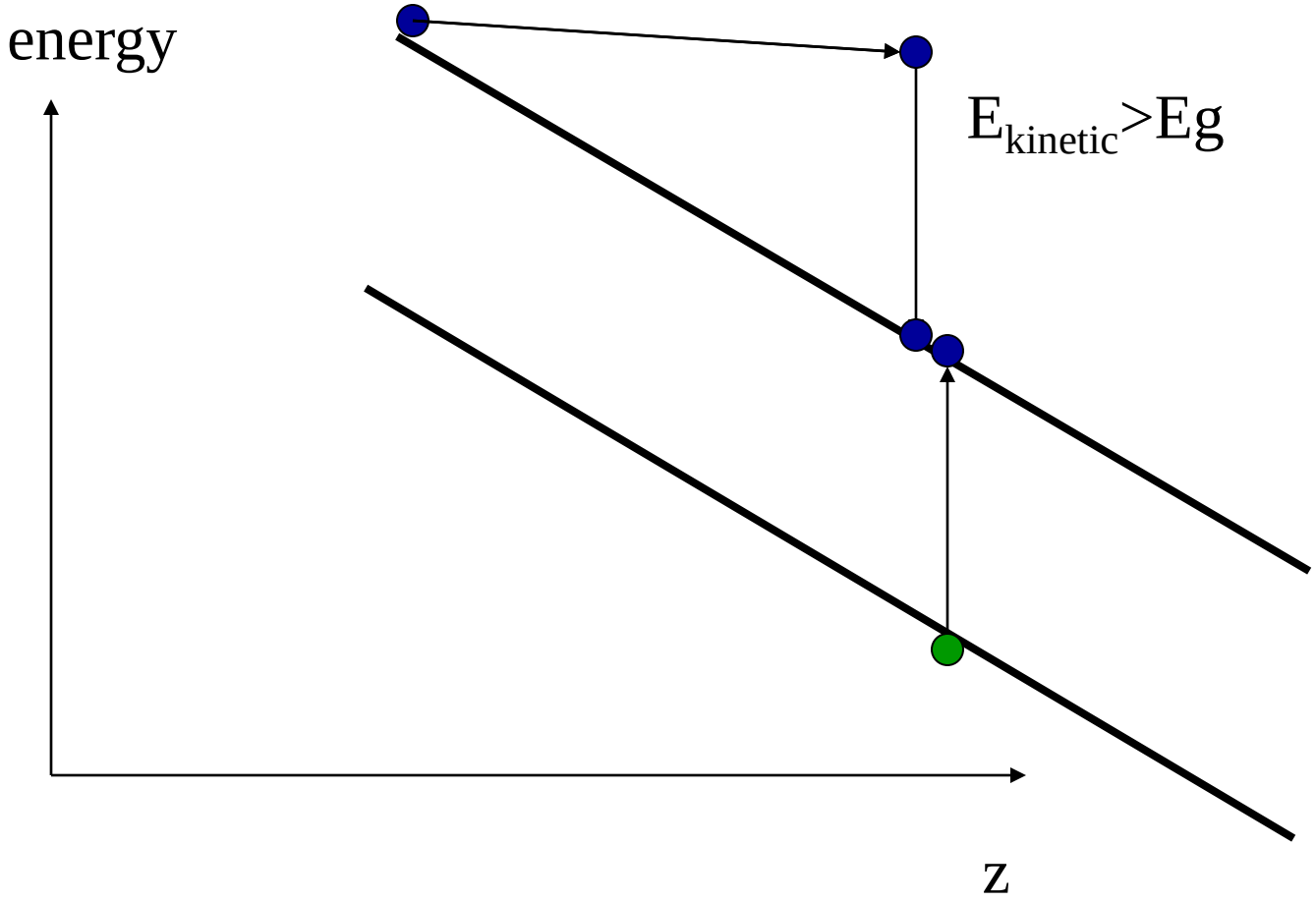


m small



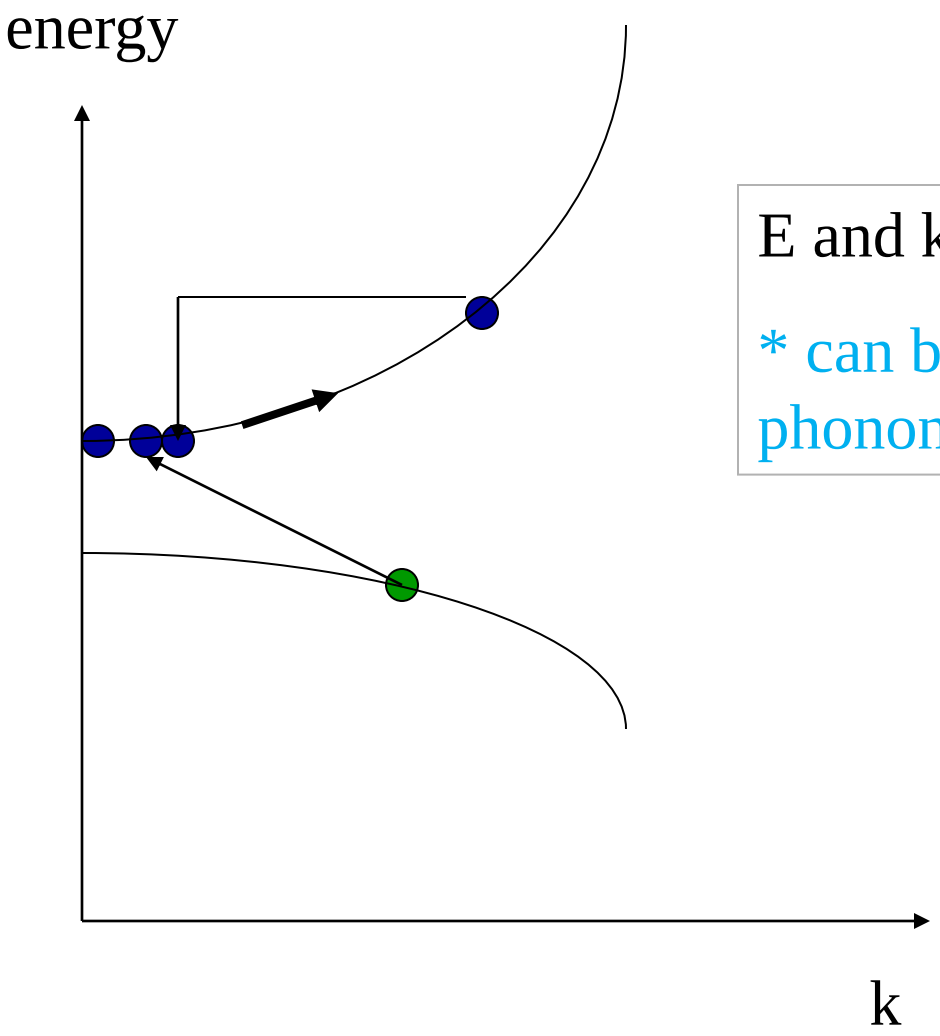
m large

Impact ionisation



On so on…avalanche breakdown (requires a minimal thickness L so that $\alpha L=1$!!)

Impact ionisation

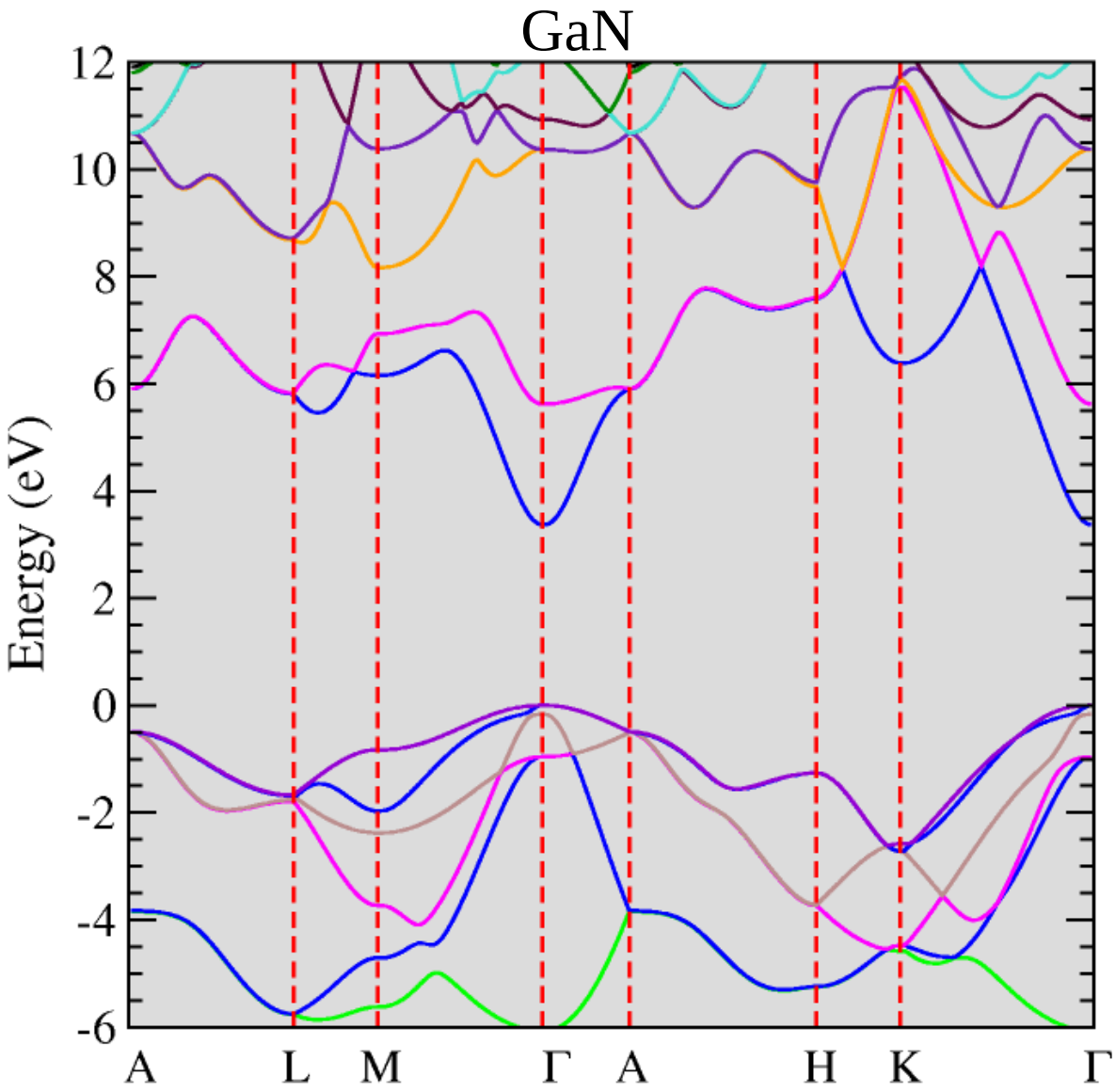


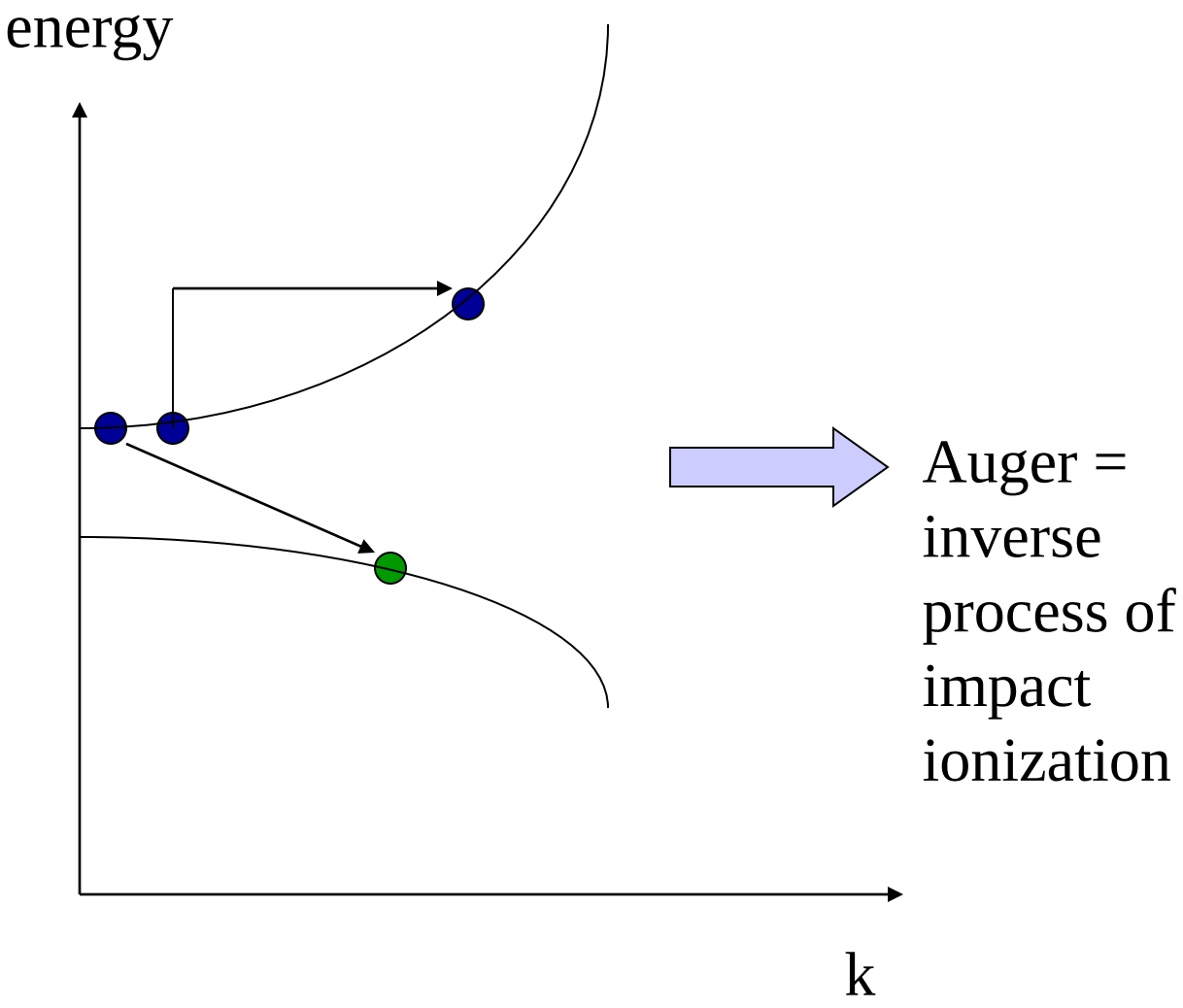
E and k conservation*

* can be relaxed if phonon assisted

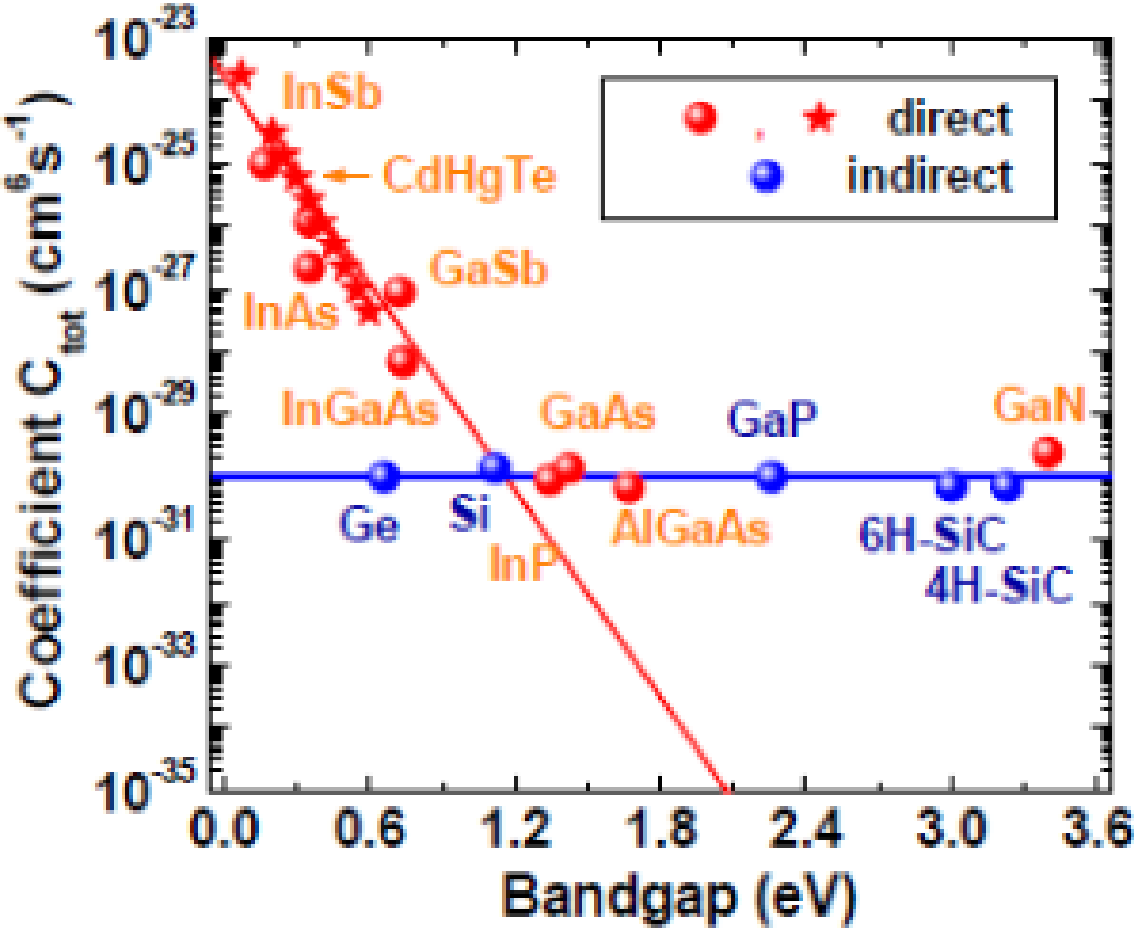
Impact ionisation

Not so easy to obey E and k conservation: ionization is weaker in wider band gap materials



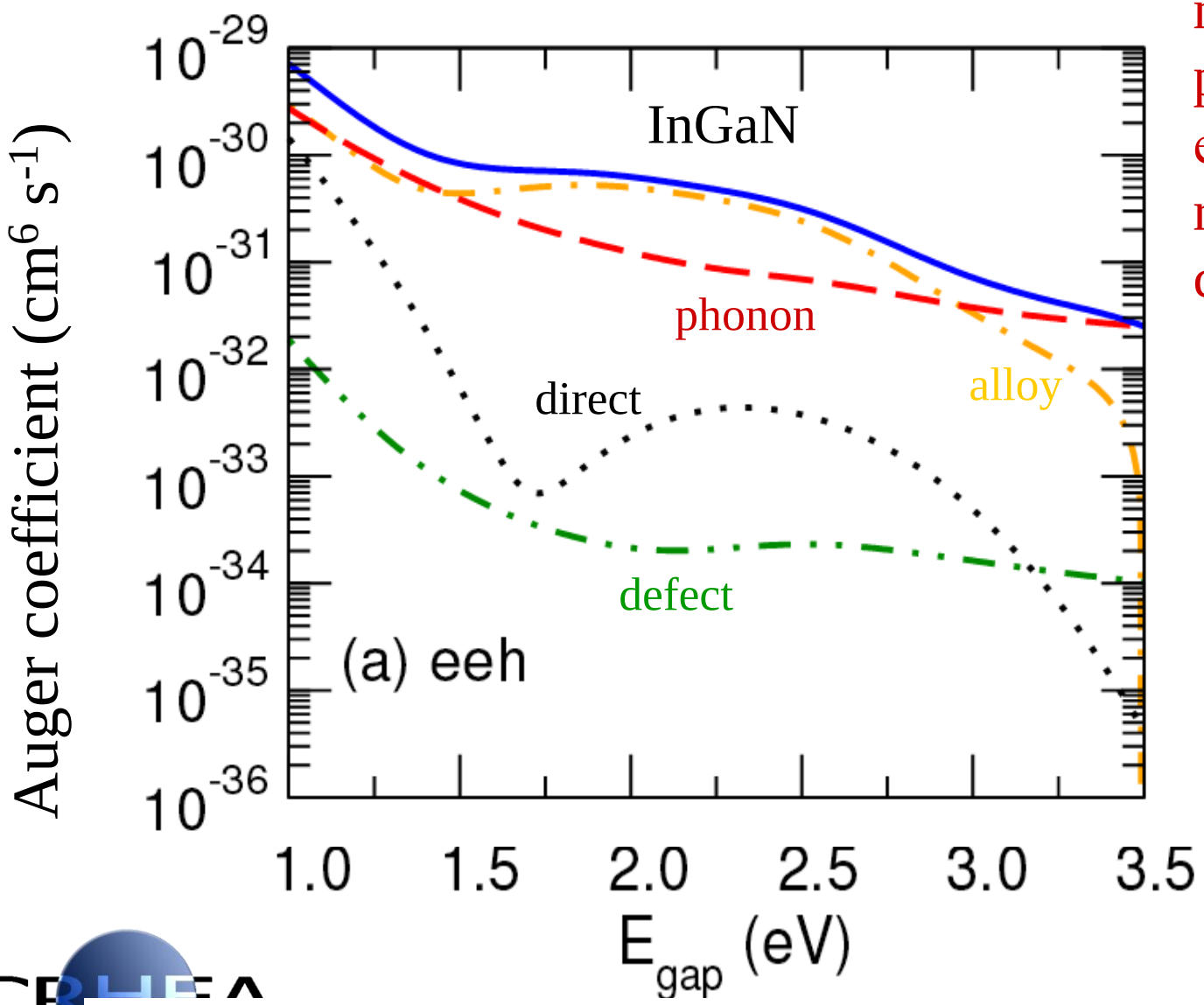

energy
k
Auger =
inverse
process of
impact
ionization

Auger



The Auger coefficient does not decrease with band gap above 1.4 eV (wide band gap are similar to normal band gap materials. Why ?)

Auger

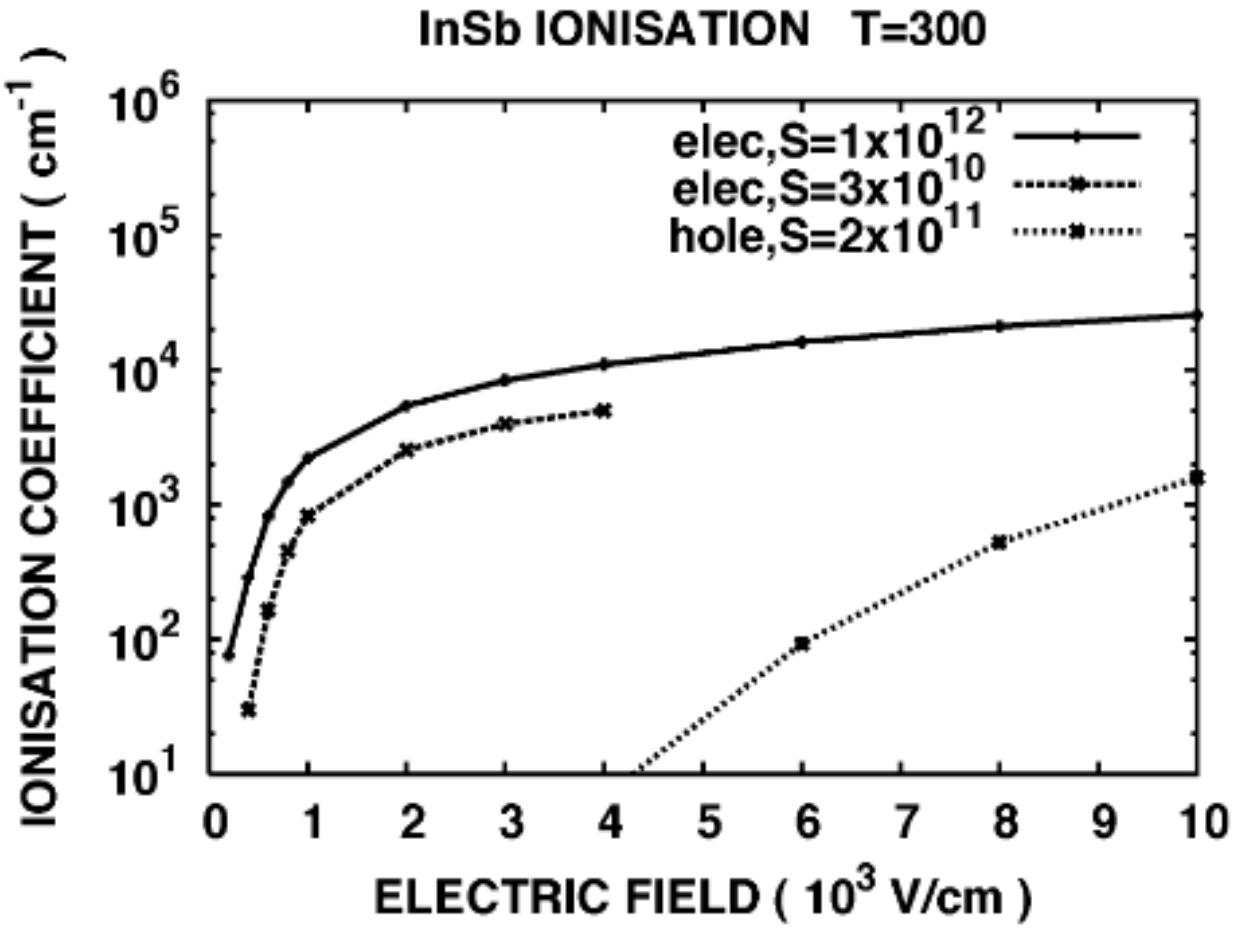


Extrinsic Auger mediated by phonons, etc…which relaxes the E-k conservation rule

First-principles calculations of indirect Auger recombination in nitride semiconductors, E.Kioupakis,…, Chris.Van de Walle, Phys. Rev. B 92, 035207 (2015)

Ionisation coefficient

InSb Eg=0.17 eV

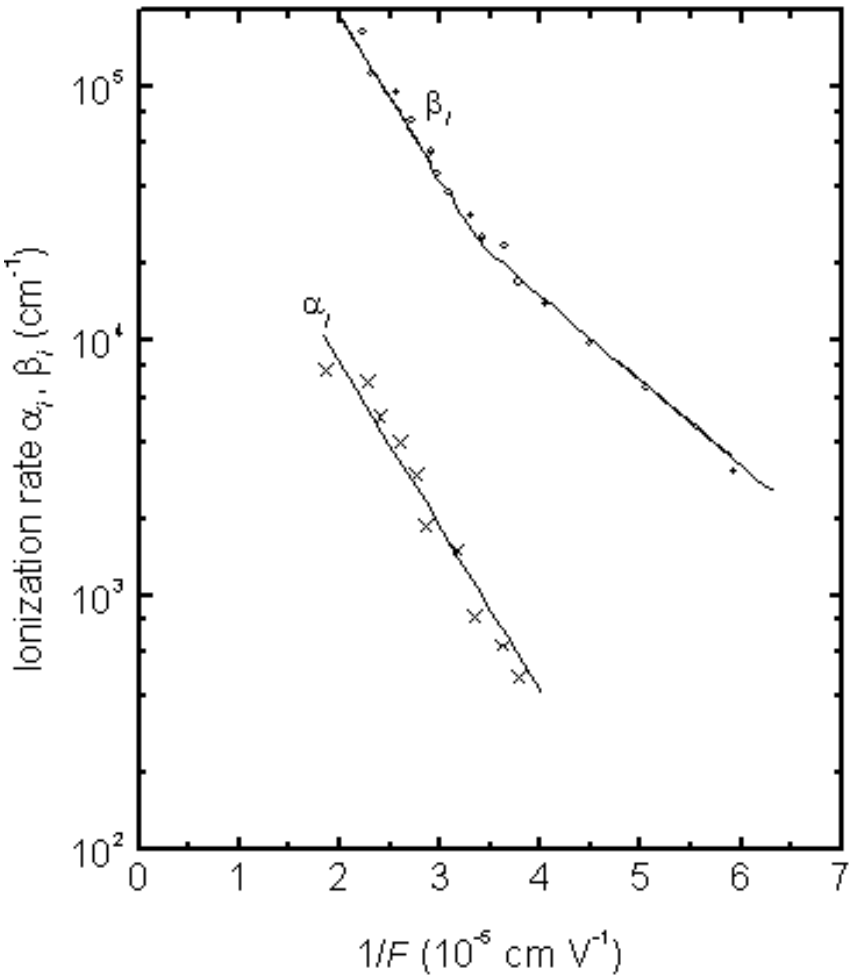


Mikhailova, M. P., A. A. Rogachev, and I. N. Yassievich, *Sov. Phys. Semicond.* **10**, 8 (1976) 866-871

Ionisation coefficient

InAs

Eg=0.35 eV

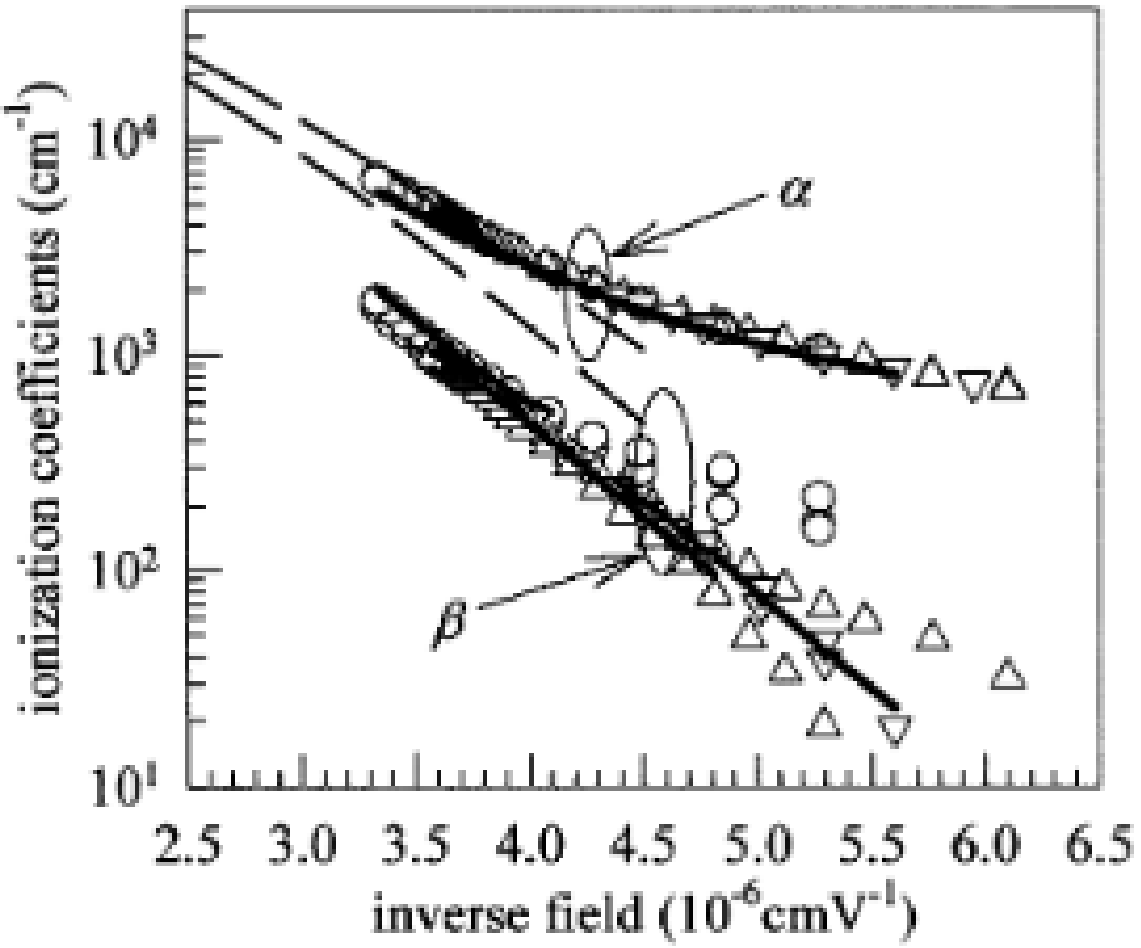


Mikhailova, M. P., A. A. Rogachev, and I. N. Yassievich, *Sov. Phys. Semicond.* **10**, 8 (1976) 866-871

Ionisation coefficient

$In_{0.53}Ga_{0.47}As$

Eg=0.8 eV

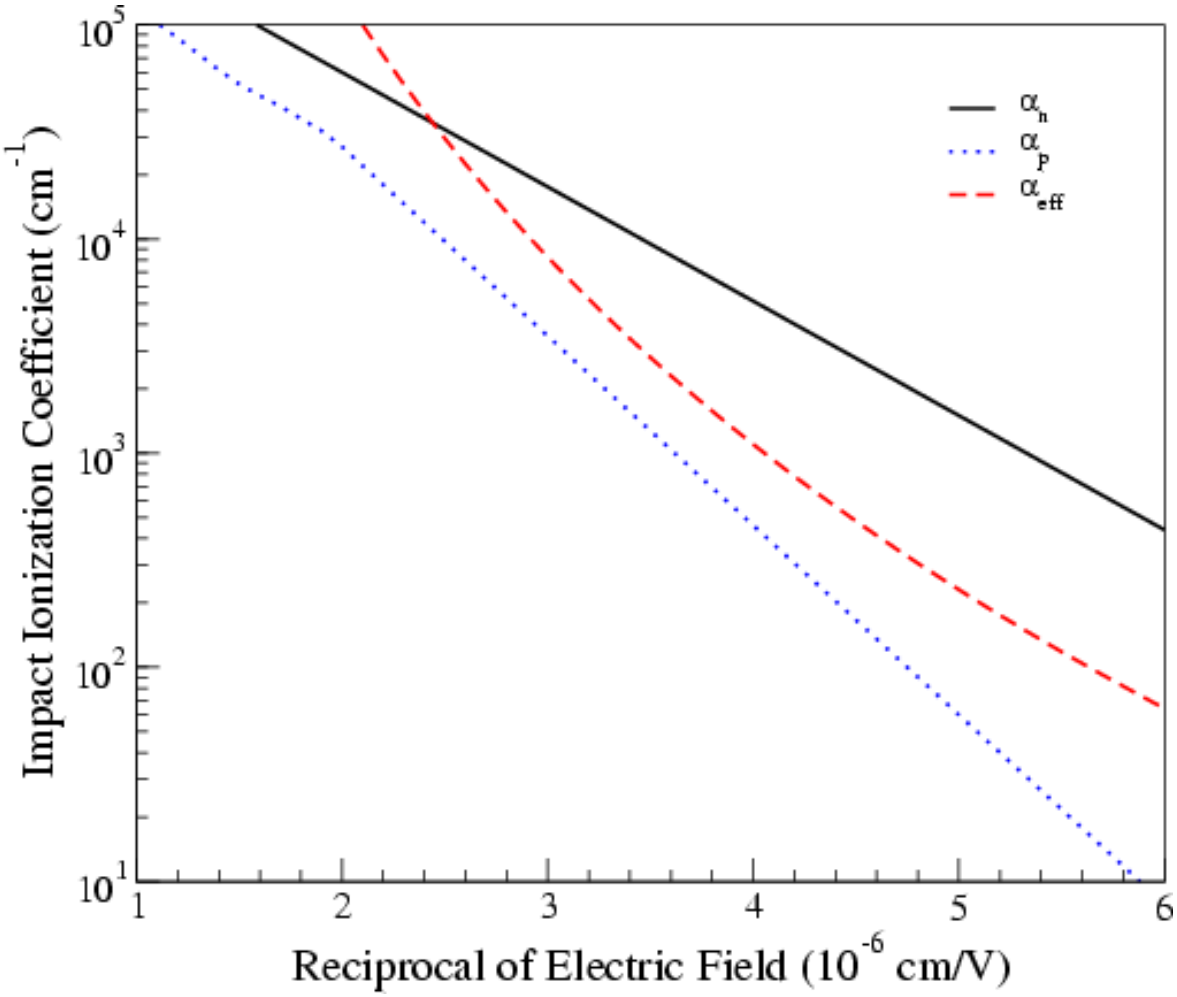


S. Ng et al, Field Dependence of Impact IonizationCoefficients in In0:53Ga0:47AsJ. S. Ng IEEE TRANSACTIONS ON ELECTRON DEVICES, VOL. 50, NO. 4, APRIL 2003

Ionisation coefficient

Si

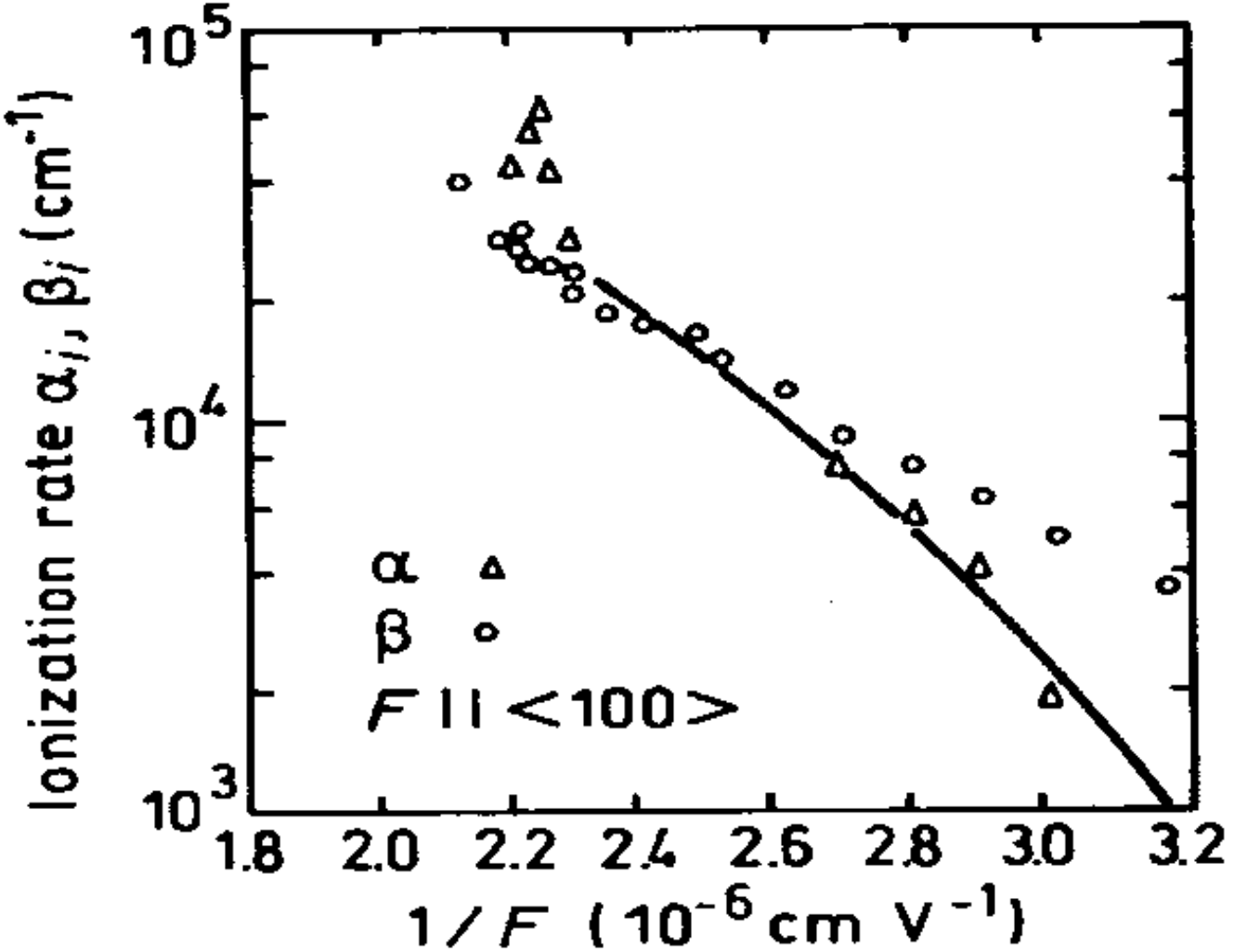
Eg=1.11 eV



Ionisation coefficient

GaAs

Eg=1.41 eV

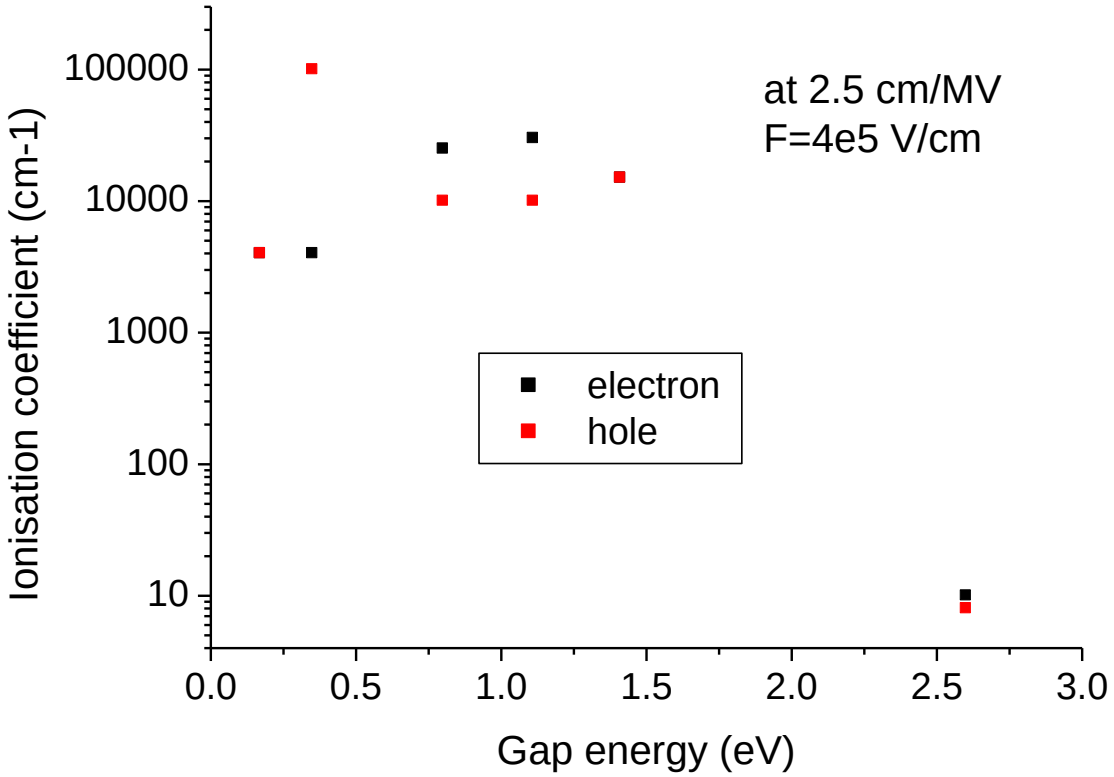


Pearsall, T. P., F. Capasso, R. E. Nahory, M. A. Pallack, and J. Chelikowsky, *Solid State Electron.* **21**, 1 (1978) 297-302

Ionisation coefficient

At high field, all material have similar ionisation coefficients (saturation)

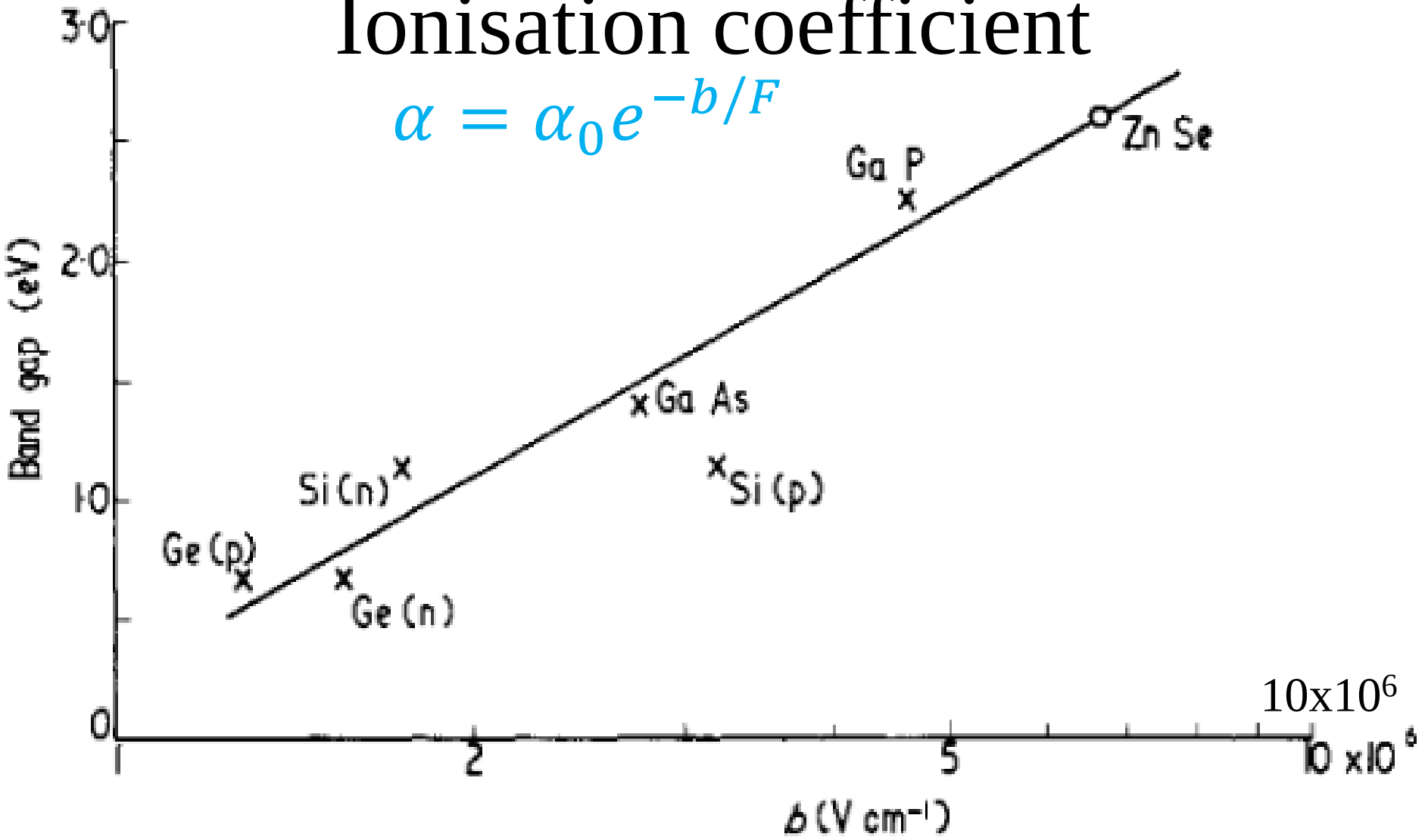
Only ZnSe is not saturated at 4e5V/cm



What is more interesting is the dependence on F

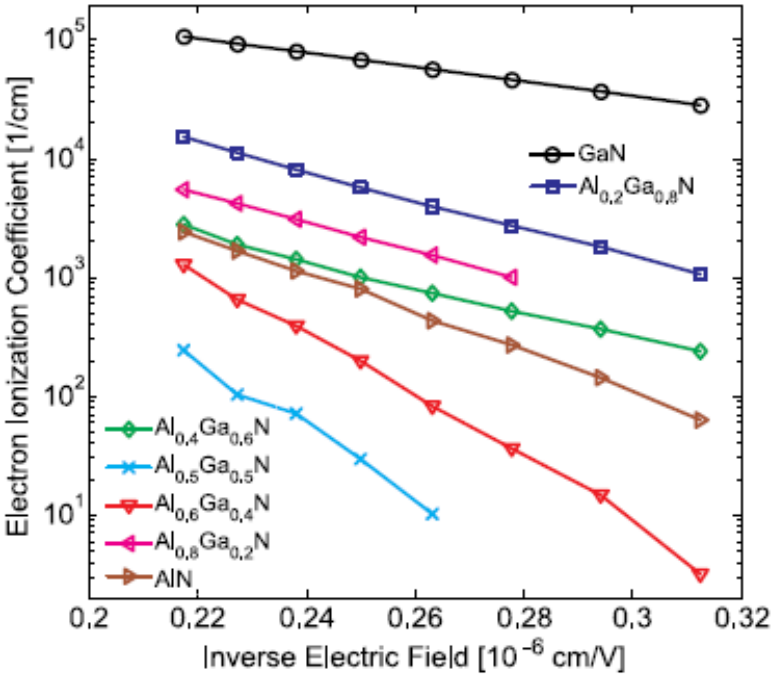
Ionisation coefficient

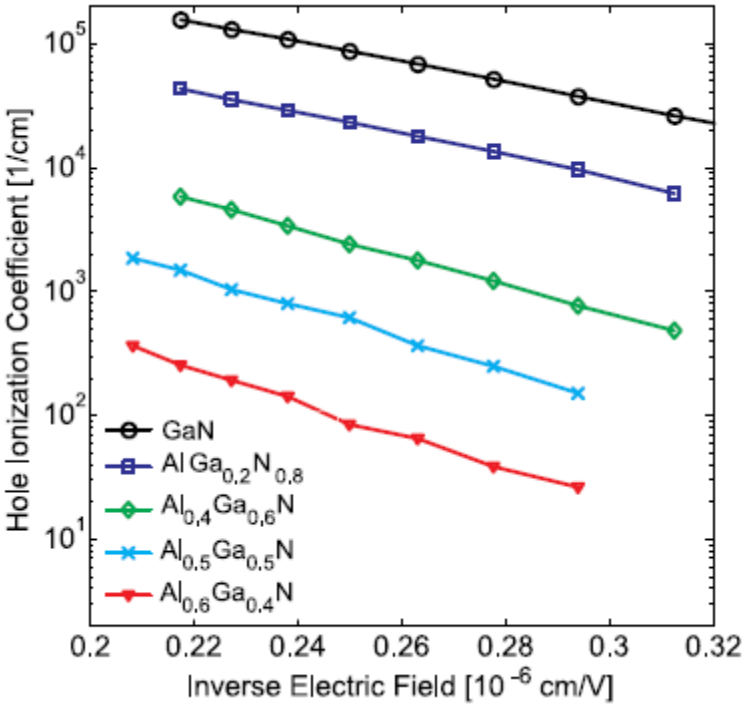
$$\alpha = \alpha_0 e^{-b/F}$$



What about nitrides ?

Ionisation coefficient





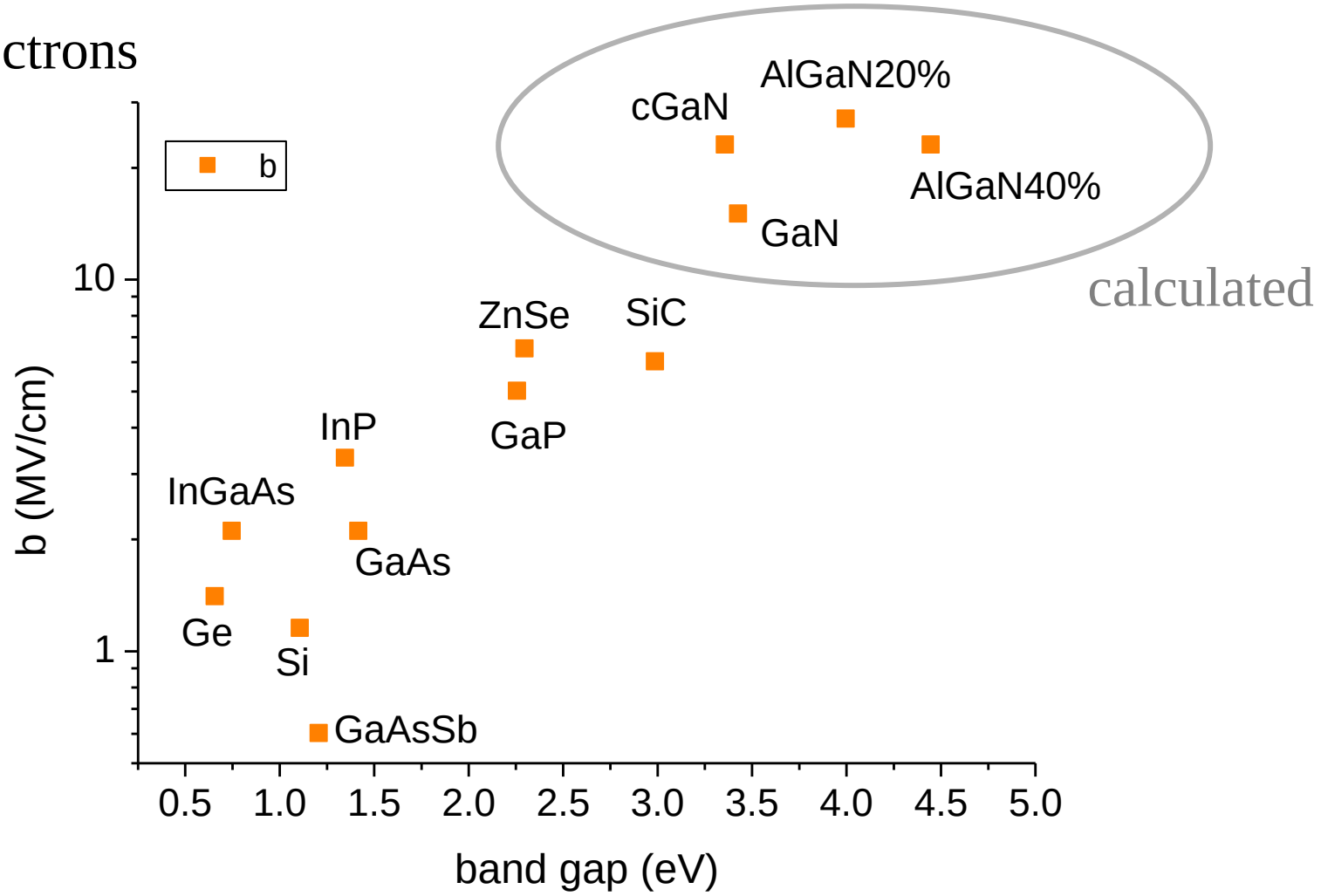
Calculated ionisation rates very weak in nitrides

Phonon assisted ionization not included (may be important in the k conservation; also phonon interaction strong in nitrides)

E. Bellotti and F. Bertazzi, J. Appl. Phys. 111, 103711 (2012)

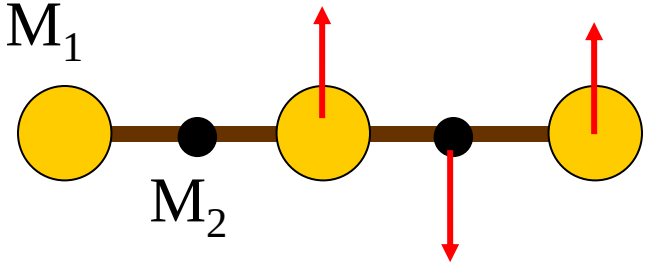
Ionisation coefficient

For electrons

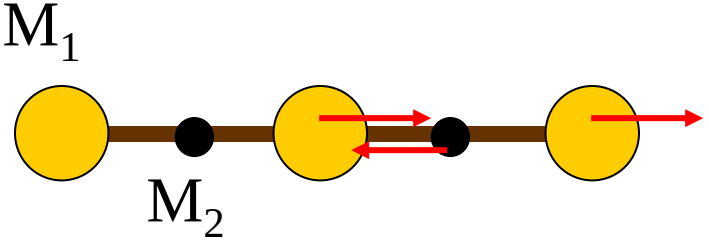


All materials reach similar ionization coefficients, but not for the same fields ! Nitrides have larger breakdown fields than many other SCs

Phonons



TO- Transverse optic

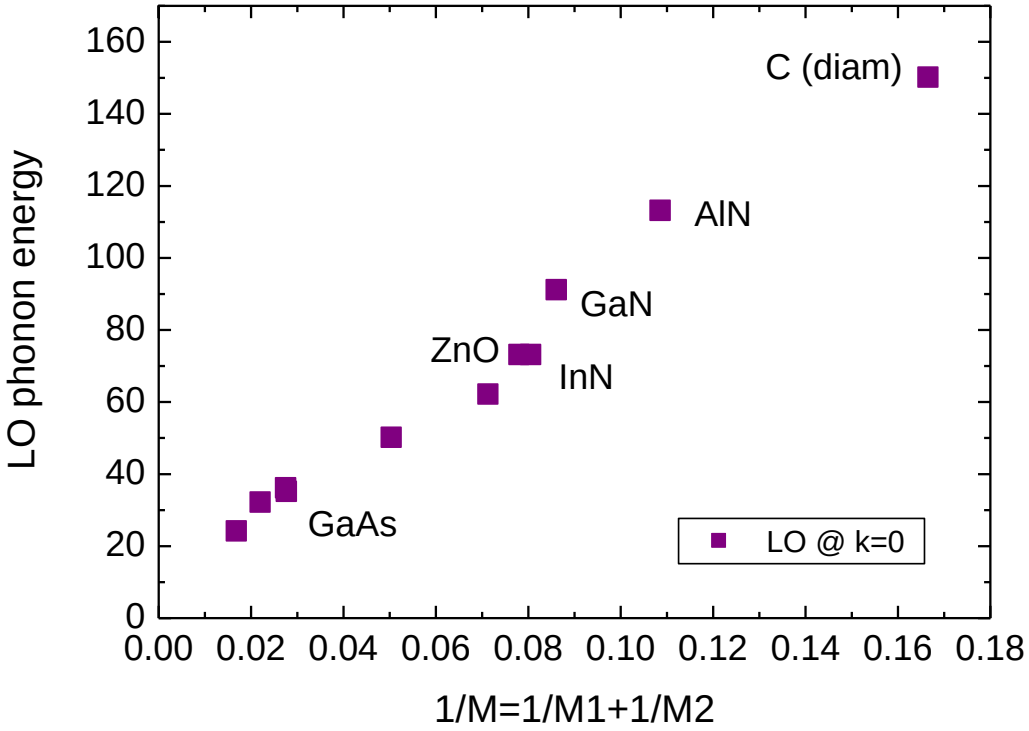


LO- Longitudinal optic

Simple model:

$$\omega^2 = \frac{2C}{M}$$

$$\frac{1}{M} = \frac{1}{M_1} + \frac{1}{M_2}$$



M is small in nitrides $\Rightarrow$ ω is large

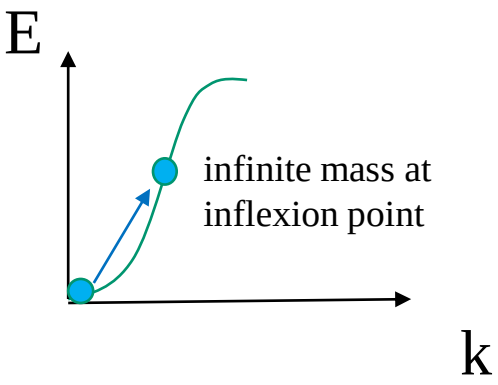
E_{LO}=91 meV, E_{TO}=70 meV in GaN

Saturation velocities

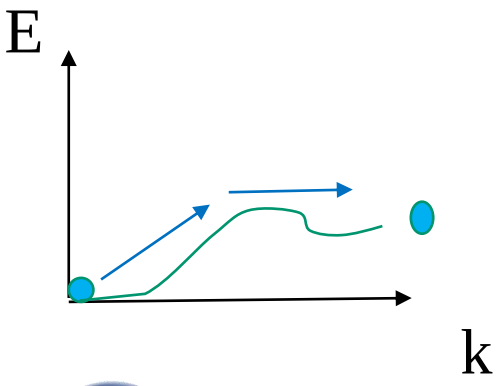
$$\hbar \boldsymbol{dk} = \boldsymbol{F} dt$$

$$v_g = \frac{1}{\hbar} \nabla_k E$$

GaAs

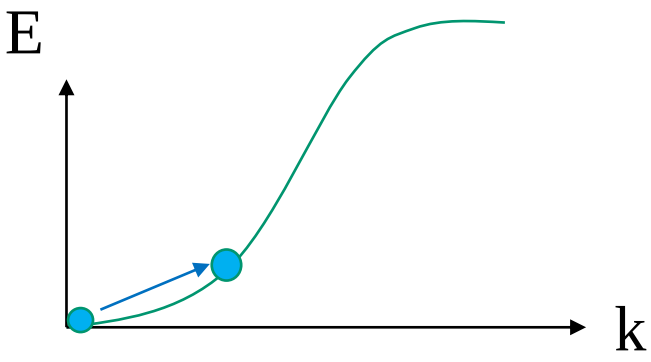


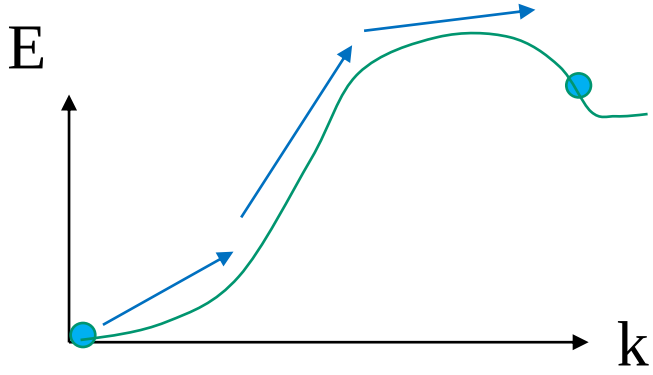
Non parabolicity, band curvature



valley transfer

GaN

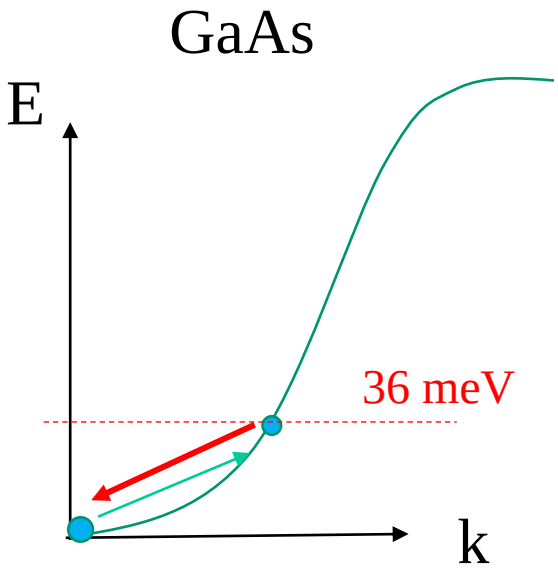




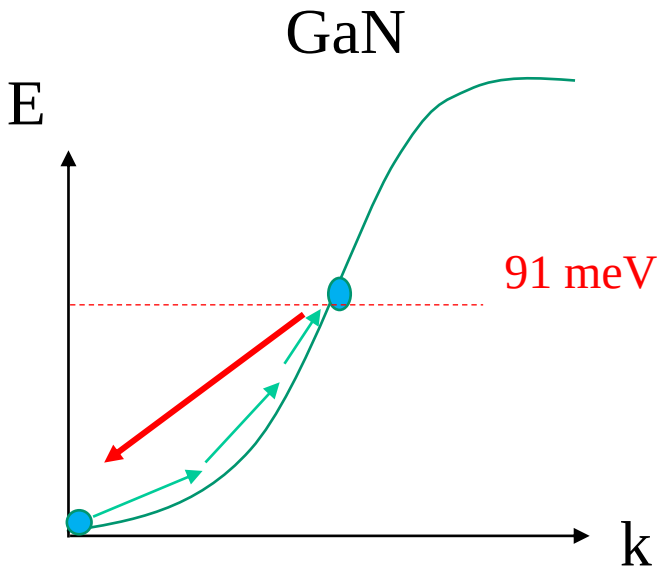
Velocity saturation is reached for higher fields in nitrides

Saturation velocities

$$\hbar \boldsymbol{dk} = \boldsymbol{F} dt$$

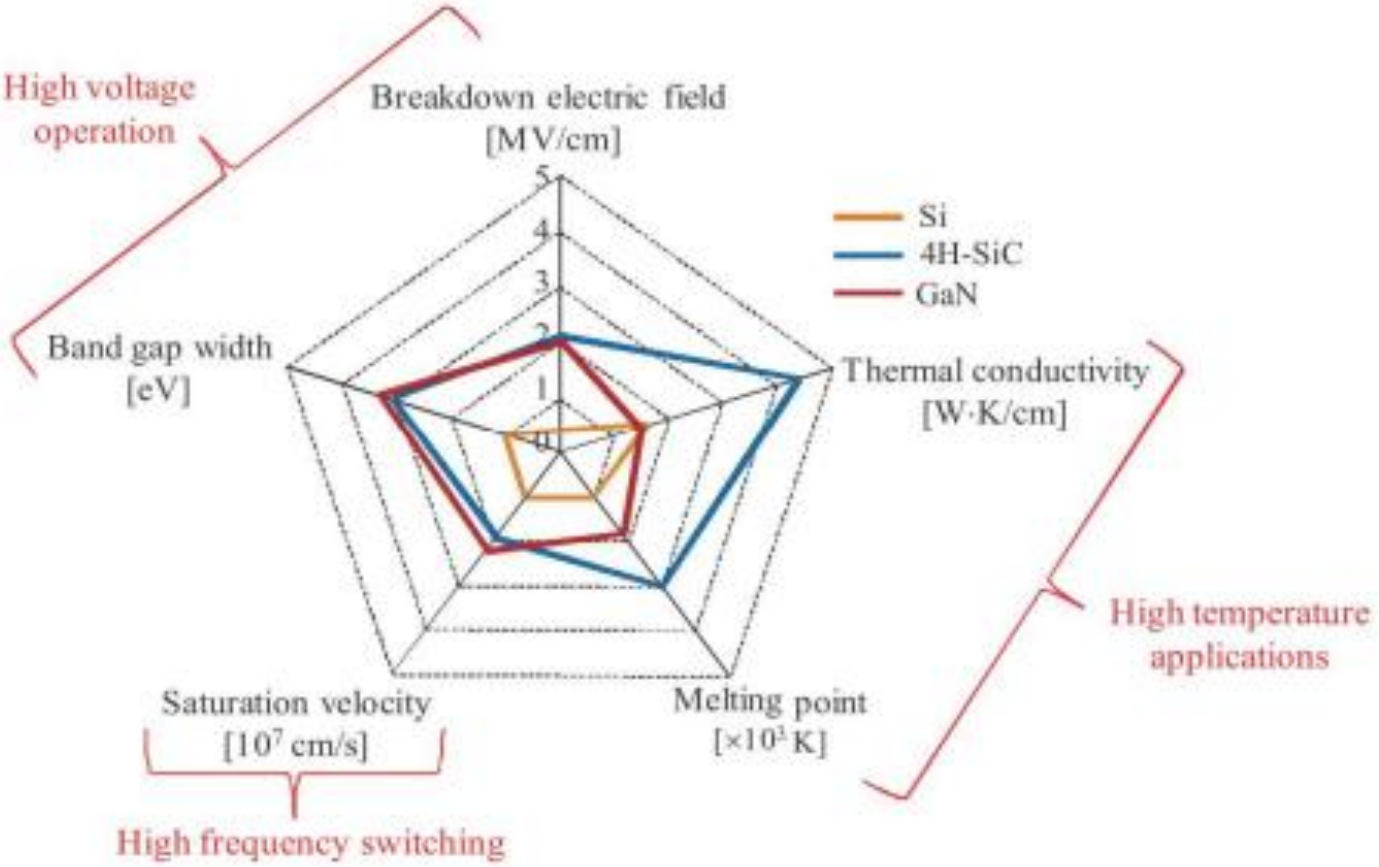


LO phonon emission



Velocity saturation is reached for higher fields in nitrides

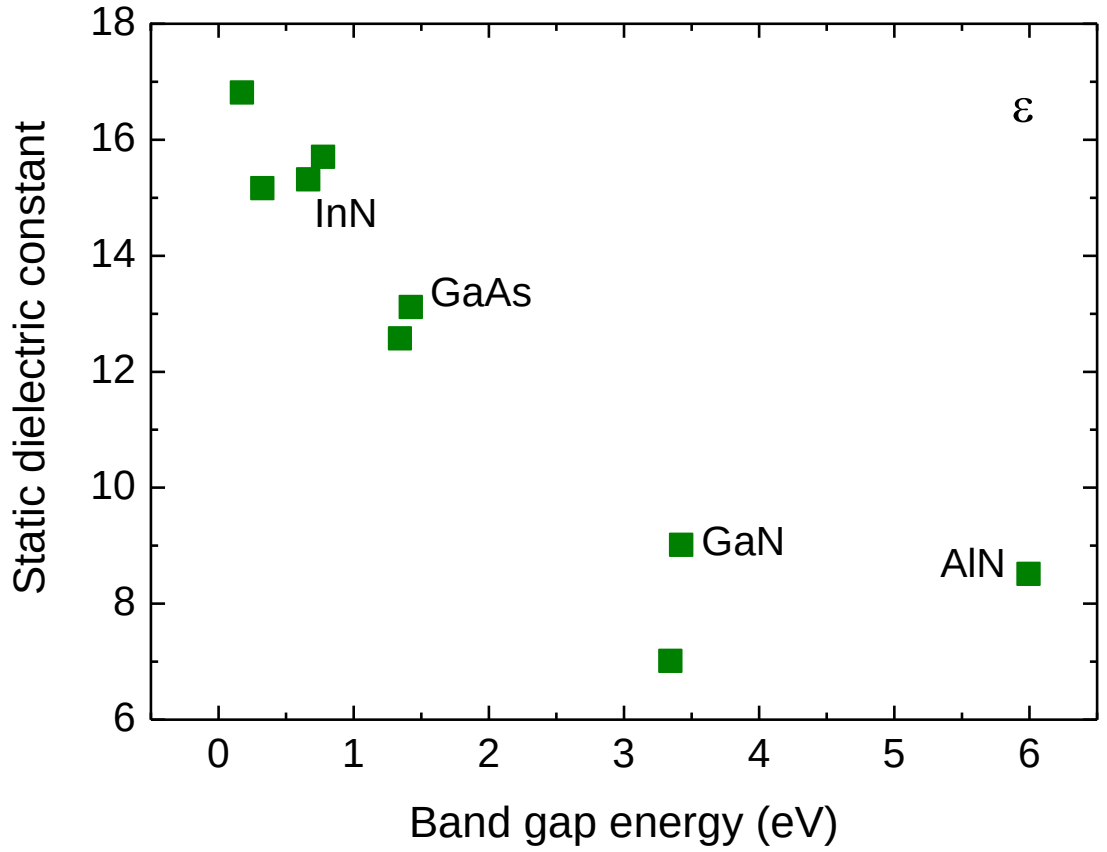
Semiconductors for electronics



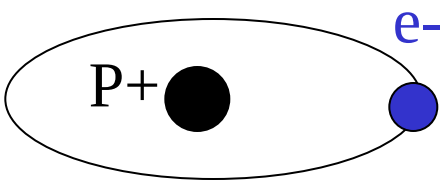
Static dielectric constant

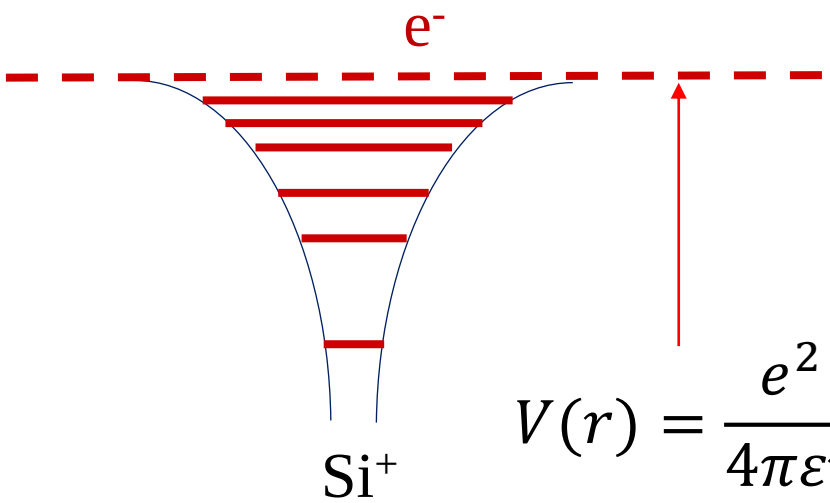
Shorter bonds, less polarizable by a constant external field :

$\Rightarrow$ small dielectric contant



Hydrogenoid model





$1/\mu = 1/m_e + 1/m_P$

$$E = \frac{\mu e^4}{32\pi^2\hbar^2\varepsilon^2} = \frac{\mu}{m_0}\frac{1}{\varepsilon_r^2}R_y$$

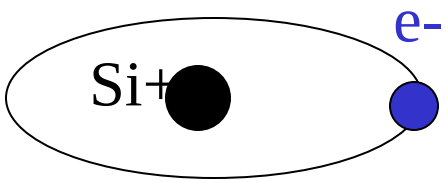
with R_y=13.6 eV

Static relative dielectric constant

$$V(r) = \frac{e^2}{4\pi\varepsilon r}$$

NB: Hydrogenoid model accurate only for large Bohr radii (r>2×cell) i.e. small energies (E<50 meV)

Donors



$1/\mu = 1/m_e + 1/m_{Si} \approx 1/m_e$

$$E = \frac{m_e}{m_0}\frac{1}{\varepsilon_r^2}R_y$$

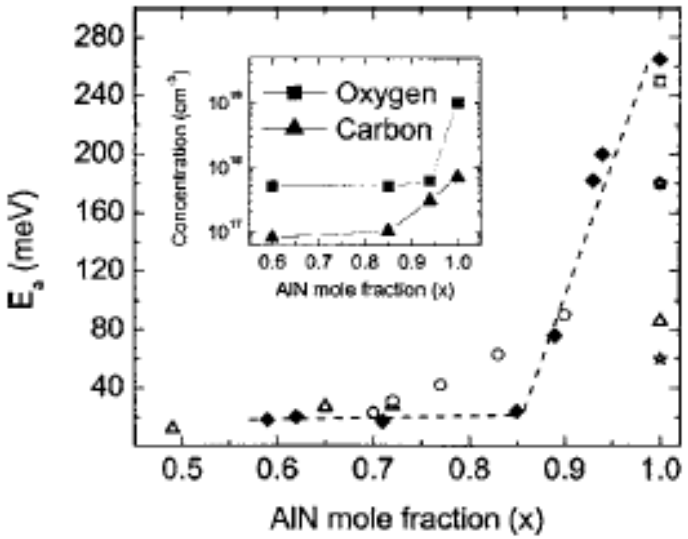
Large donor energies are expected in nitrides (37 meV)

O : shallow donor in GaN (26 meV) but deep level in AlGaN

Si: shallow donor in GaN (25 meV), deeper in AlGaN

	GaAs	GaN	AlAs	AlN
E_{Si} measured (meV)	5.8	25	70	250/60

B. Borisov, APL 87,132106 (2005)

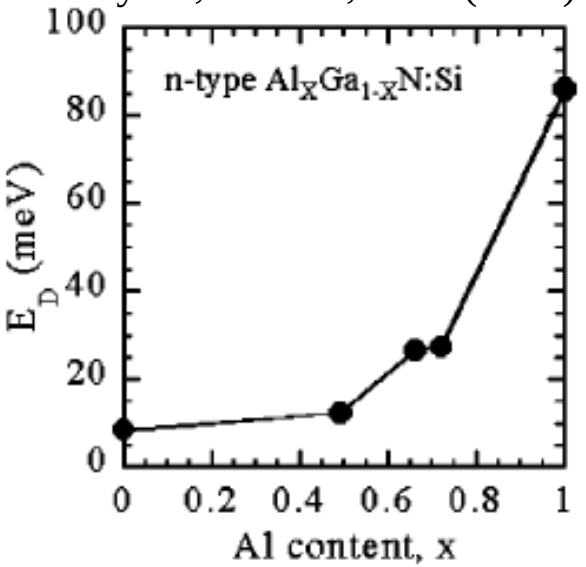


Donor energy renormalized at high concentration

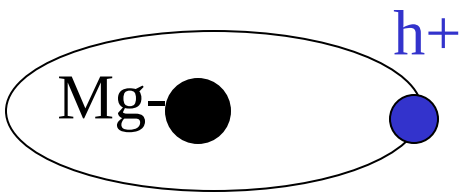
$E=E_0-\beta n^{1/3}$

$\beta=10^{-8}$ eV/cm

Taniyasu, APL 81, 1255 (2002)



Acceptors



$1/\mu = 1/m_h + 1/m_{Mg} \approx 1/m_h$

$$E = \frac{m_e}{m_0}\frac{1}{\varepsilon_r^2}R_y$$

Very large acceptor energies are expected in nitrides (168 meV with m_h=1): not hydrogenoid !

E_{Mg} = 220 meV

⇒Low ionization ratio

⇒Large Mg densities necessary: 5×10^{19} cm^{-3} for p=5×10^{17} cm^{-3}

Doping in semiconductors

	GaN	SiC	ZnO	Diamond	GaAs	Si
n-type dopant	Si on Ga site (~ 15 meV)	N on C site (~ 85 meV)	B on Zn (~30-60 meV)	N (~ 1.7 eV)	Si 6meV	P 45meV
p-type dopant	Mg on Ga site (160 meV) Zn ~ 340 meV	Al on Si site (~ 200 meV)	N on O site (~ 170-200 meV)	B (~ 370 meV)	C (Be) ~28 meV	B 40meV
n-conductivity*	~ 0.002 Ωcm	~ 0.01 Ωcm	~ 0.02 Ωcm	> 1000 Ωcm	~ 0.001 Ωcm	
p-conductivity*	0.2-2 Ωcm	0.5-2 Ωcm	0.5-40 Ωcm	10-100 Ωcm		

* Experimental values

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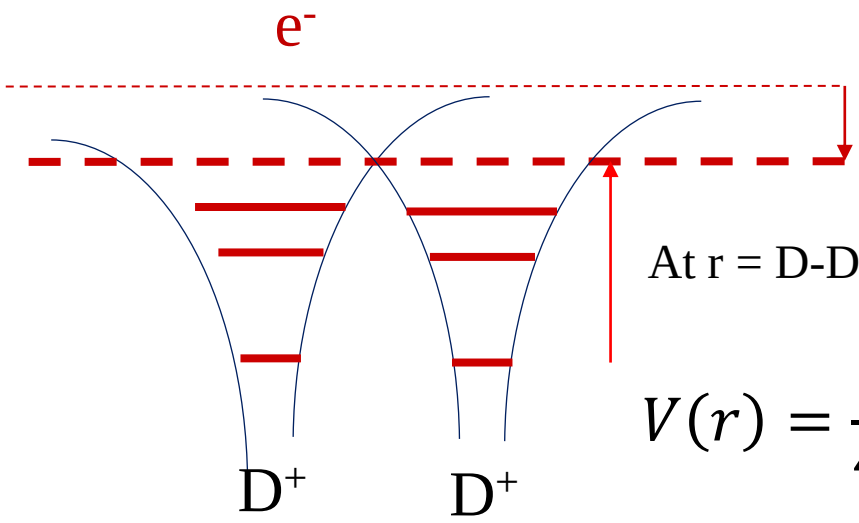
Variation of donor and acceptor energy among samples, with doping.

Renormalization, screening…of the binding energy ?

What are we talking about ?

Activation energy of donors



At r = D-D distance = $[D]^{-1/3}$

$$V(r) = \frac{e^2}{4\pi\varepsilon r} = \frac{e^2[D]^{1/3}}{4\pi\varepsilon}$$

E_D is decreased by $\beta[D]^{1/3}$ with $\beta = \frac{e^2}{4\pi\varepsilon} = 1.6 \times 10^{-8} eVcm$

Rigorous calculation should include the shift of the 1s state but finally leads to the same result !

Experiments: β=1.6×10^{-8} eVcm on Ge [A Ajay *et al* 2016 *J. Phys. D: Appl. Phys.* **49** 445301],
β=2×10^{-8} eVcm on Si [B. Meyer et al, Solid State Com, 95, 9, 597-600 (1995)]

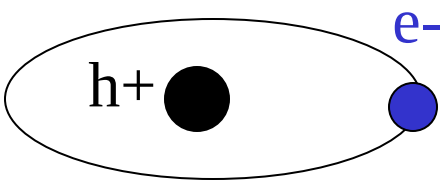
Examples:

GaN: [Si]=3×10^{17} cm^{-3}, E_D= 25-1.6×10^{-5}×(3×10^{17})$^{1/3}$ = 25-11=14 meV

$Al_{0.7}Ga_{0.3}N$, [Si]= 5×10^{19} cm^{-3}, E_D= 60-1.6×10^{-5}×(5×10^{19})$^{1/3}$=60-58=2 meV

When E_D=0, Mott transition towards metallic behavior

Excitons



$$E = \frac{\mu}{m_0}\frac{1}{\varepsilon_r^2}R_y = 30meV$$ expected

$1/\mu = 1/m_e + 1/m_h$

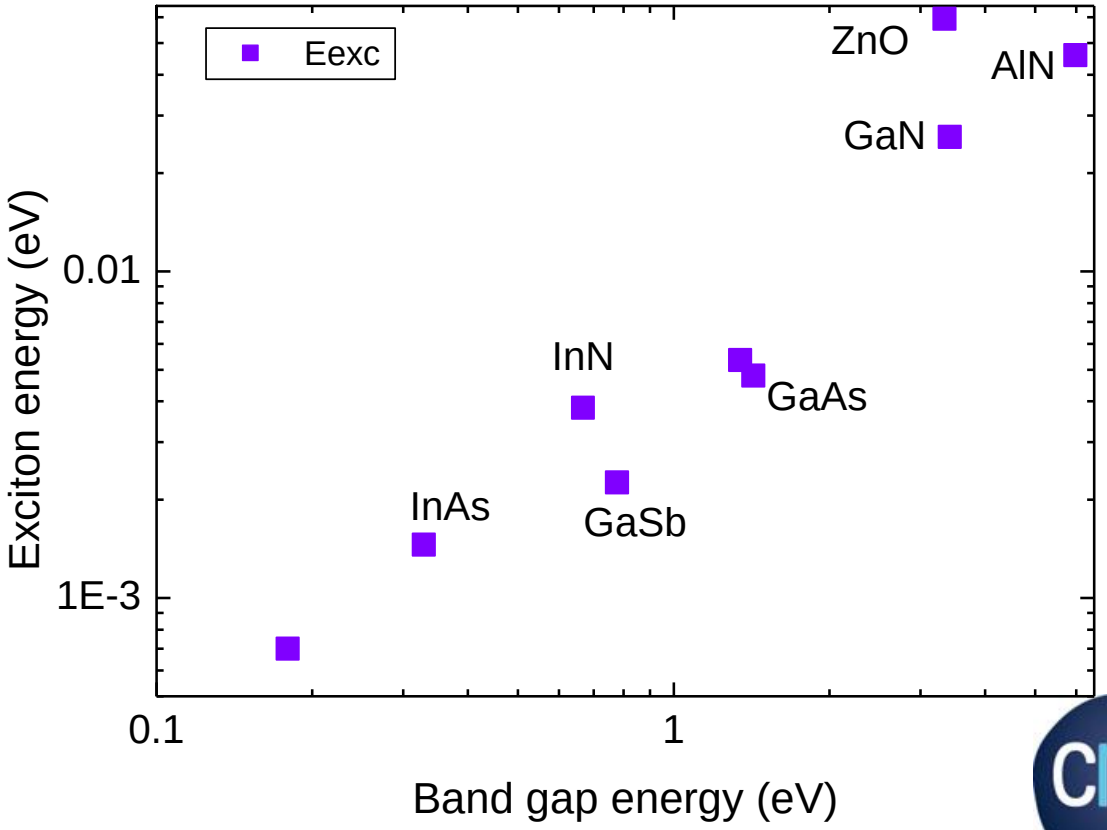
$$E = \frac{\mu}{m_0}\frac{1}{\varepsilon_r^2}R_y$$

$$E \propto \frac{E_{gap}}{\varepsilon_r^2}$$

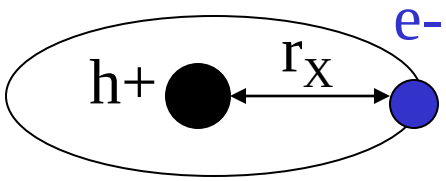
Decreases with gap

$$E \propto (E_{Gap})^n$$

with n>1



Excitons



E_x (GaN) = 26 meV ≈ kT @ 300K

⇒ Exciton stable at room temperature

$$E = \frac{e}{8\pi\varepsilon r_X}$$

$$r_X = r_{Hydro}\frac{m}{\mu}\varepsilon_r^2$$

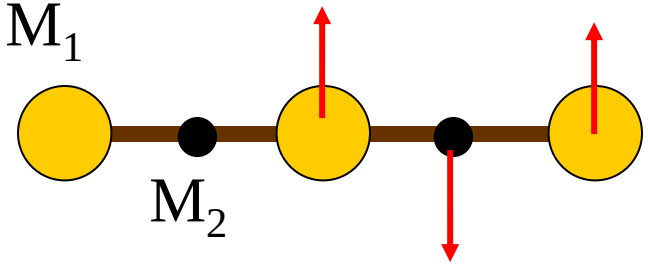
r_X small ⇒ exciton stable at high density

	Bohr radius	**Mott density**
GaAs	11.6nm	$3\text{-}12\times10^{16}$ cm^{-3}
GaN	2.8nm	2×10^{18} cm^{-3}

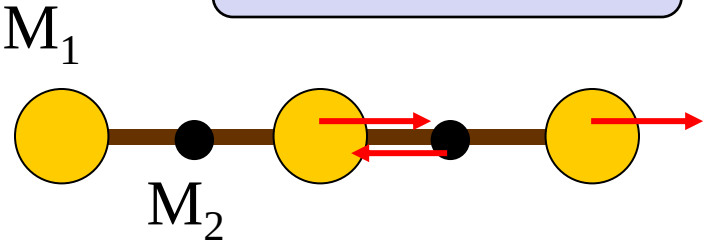
Absorption and emission in nitrides are dominated by excitons (A,B,C)

Phonons

Already shown



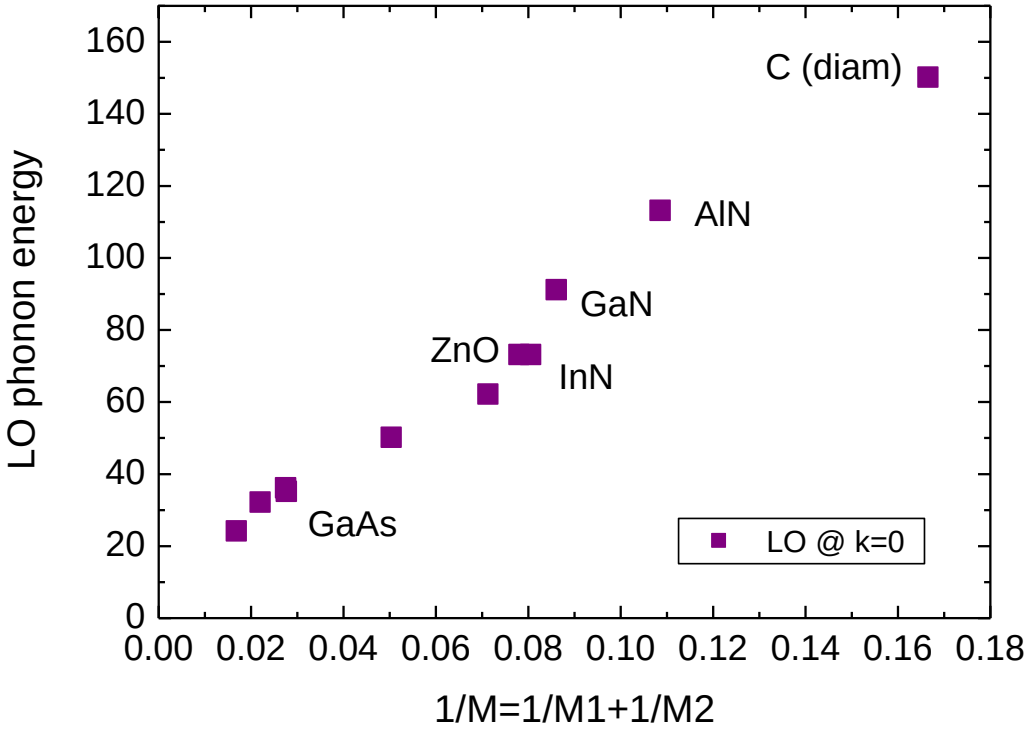
TO- Transverse optic



LO- Longitudinal optic

$$\omega^2 = \frac{2C}{M}$$

$$\frac{1}{M} = \frac{1}{M_1} + \frac{1}{M_2}$$



M is small in nitrides $\Rightarrow$ ω is large

E_{LO}=91 meV, E_{TO}=70 meV in GaN

Phonons and dielectric constant

ω_{LO}=91 meV
ω_{TO}=70 meV

$$\left(\frac{\omega_{LO}}{\omega_{TO}}\right)^2 = 1.69$$

What is the difference between ε_{static} and ε_∞ ?

$$\varepsilon_{static} = 9$$

$$\varepsilon_\infty = n^2 = 2.3^2$$

$$\frac{\varepsilon_{static}}{\varepsilon_\infty} = 1.69$$

What a nice coincidence !!!??

Lyddane–Sachs–Teller relation

$$\left(\frac{\omega_{LO}}{\omega_{TO}}\right)^2 = \frac{\varepsilon_{static}}{\varepsilon_\infty}$$

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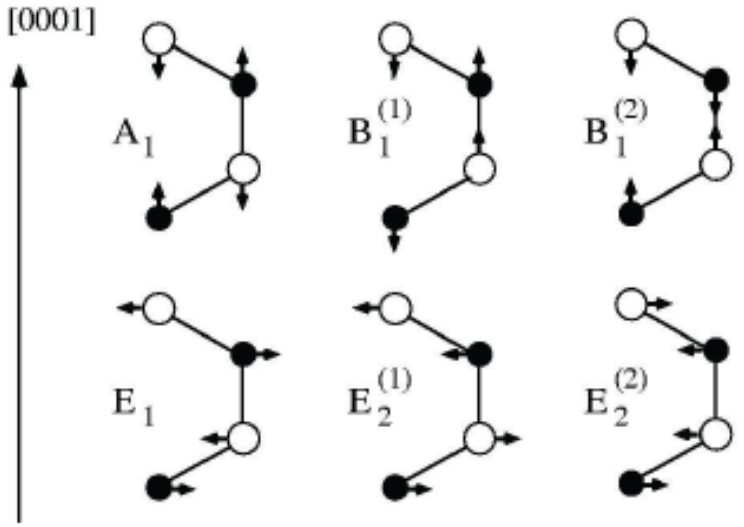
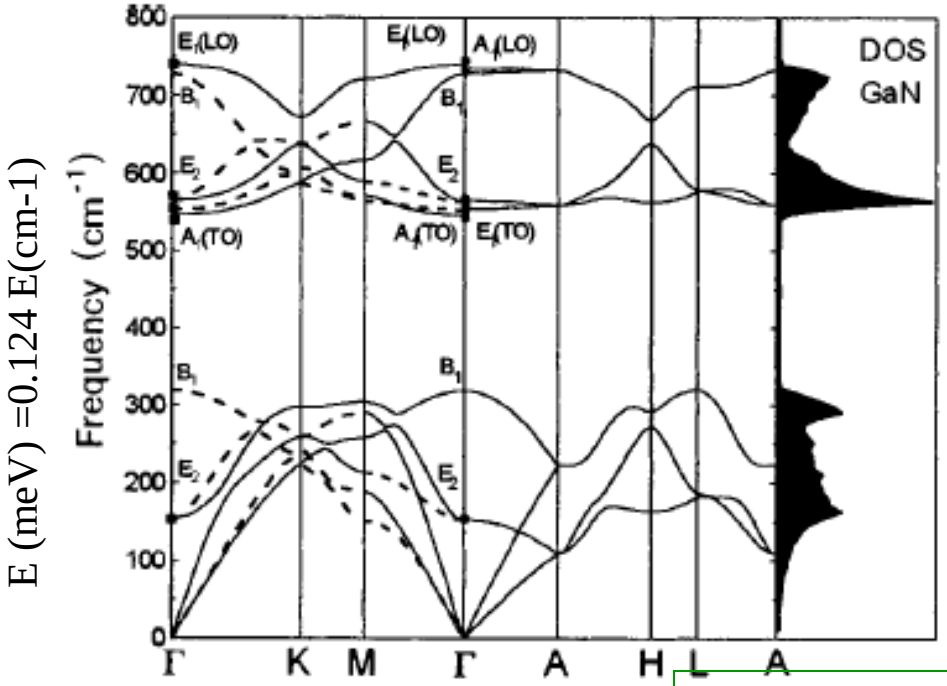
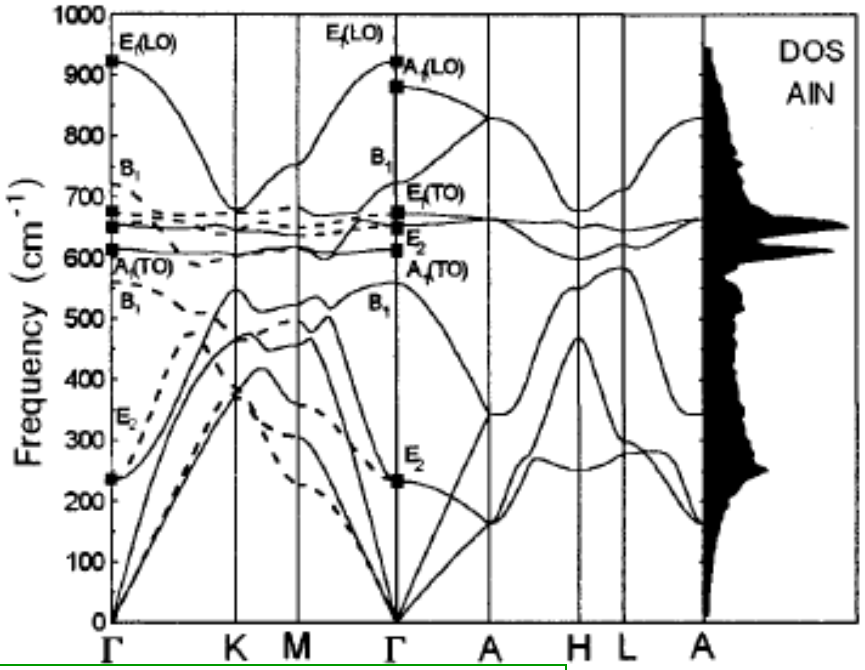
Phonons

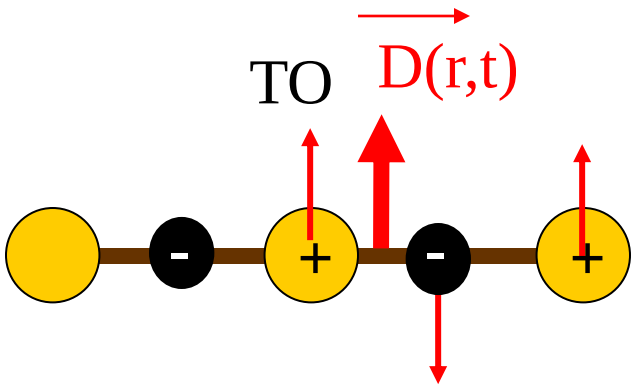


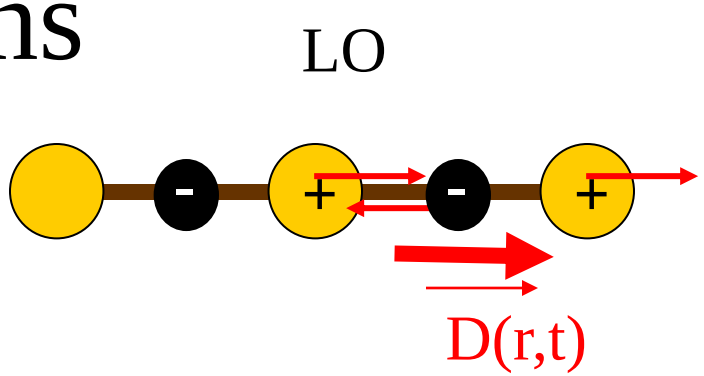


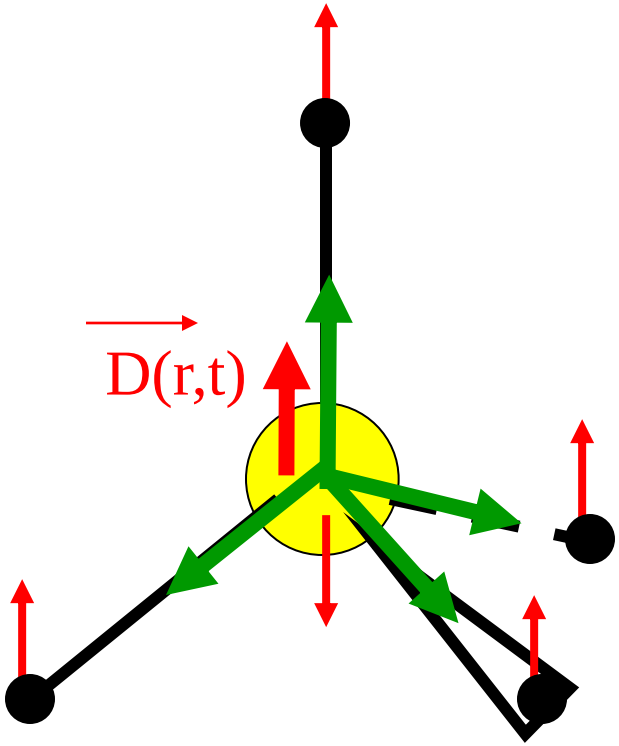


Dispersion but $E_{LO} \approx 91$ meV
Mixing LO-TO

Phonons







Polar atomic bond ⇒ phonons are associated with an electric polarization ⇒ strong coupling with electrons

Pure TO do not couple with electrons *, however mixt TO-LO in nitrides couple (but coupling 10^3 smaller than for LO)

$\tau_{e\text{-}LO}$ GaN =1/10 $\tau_{e\text{-}LO}$ GaAs = a few 10 fs

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* $V_{Frohlich} \propto \vec{\delta} \cdot \vec{q} / q^2 e^{i(\vec{q}\cdot\vec{r} - \omega t)}$

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Summary

Most nitride properties can be estimated by rules of thumb or an educated guess, and compared with those of other SCs

- Wide band gap energy and large band offsets
- Chemical inertness and thermal stability
- Large effectives masses
- Low mobilities and large saturation velocities
- Excitonic effects and large oscillator strengths
- Ionic bonds and large internal fields
- Deep donors and acceptors
- High energy optical phonons strongly coupled with charged carriers

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