Temperature dependence of the electronic structure of semiconductors and insulators

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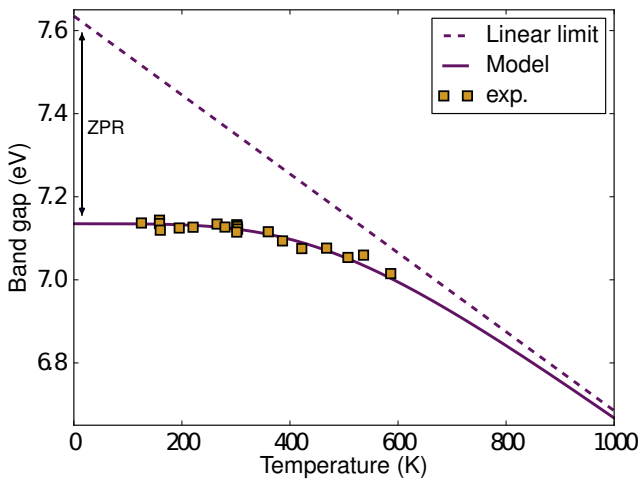
Study of the temperature dependence

The electron-phonon coupling can be probed experimentally by measuring the temperature-dependence of the electronic structure, from which the zero-point motion (ZPR) is deduced by a model.
For example, the direct bandgap diamond:



S. Logothetidis, J. Petalas, H. M. Polatoglou and D. Fuchs, Phys. Rev. B **46**, 4483 (1992)

The ZPR lies between 400 meV and 600 meV according to the analysis of various authors.

First-principles temperature dependence of eigenenergies

It can be computed by 3 types of methods

- Molecular Dynamics (MD)
  - ✓ Includes effects beyond the harmonic approx.
  - ✗ Normal MD delivers a Boltzmann statistic for phonons → no ZPR
  - ✓ But Path-Integral Molecular Dynamics (PIMD) does include Bose-Einstein statistics → ZPR is observed
  - ✗ Needs supercell for solids (molecules ok)
- Frozen-Phonon (FP)
  - ✓ Includes effects beyond the harmonic approx.
  - ✗ Supercell is required
- Diagrammatic method of many-body perturbation theory (AHC)
  - ✓ Only primitive cell is required (DFPT based)
  - ✗ Harmonic approximation
  - ✗ Rigid-ion approximation (RIA)

Temperature-dependence in the adiabatic harmonic approximation

For periodic solids

$$\Delta\varepsilon_{n\mathbf{k}}(T) = \frac{1}{N_q}\sum_{\mathbf{q}}\sum_{m}^{3N}\frac{\partial\varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}}\left(n_{m\mathbf{q}}(T)+\frac{1}{2}\right)$$

$$\frac{\partial\varepsilon_{n\mathbf{k}}}{\partial n_{m\mathbf{q}}} = \frac{1}{2\omega_{m\mathbf{q}}}\sum_{\substack{\kappa\alpha\\ \kappa'\gamma}}\sum_{ll'}\frac{\partial^2\varepsilon_{n\mathbf{k}}}{\partial R_{l\kappa\alpha}\partial R_{l'\kappa'\gamma}}e^{-i\mathbf{q}\cdot(\mathbf{R}_l-\mathbf{R}_{l'})}U^*_{m,\kappa'\gamma}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})$$

$$\varepsilon_{n\mathbf{k}} = \left\langle u^{(0)}_{n\mathbf{k}}\middle|\,\hat{H}_{\mathbf{k},\mathbf{k}}\,\middle|u^{(0)}_{n\mathbf{k}}\right\rangle$$

$\left\langle u^{(0)}_{n\mathbf{k}}\middle|\,\frac{\partial^2\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q})\partial R_{\kappa'\gamma}(\mathbf{q})}\,\middle|u^{(0)}_{n\mathbf{k}}\right\rangle$ is very difficult to compute $\rightarrow$ RIA

Temperature-dependence in the adiabatic harmonic approximation

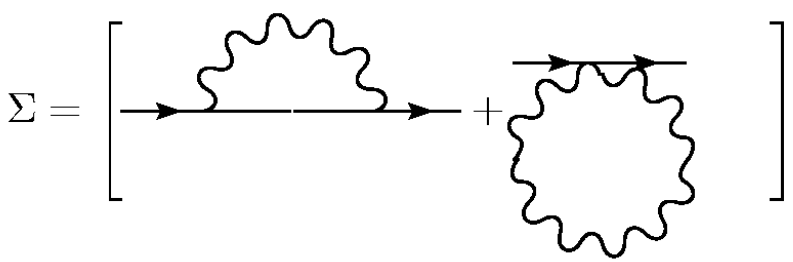
The Allan-Heine-Cardona (AHC) theory using the rigid-ion approximation:

$$\Delta\varepsilon_{n\mathbf{k}}^{(\text{adiabatic,RIA})}(T) = \frac{1}{N_q}\sum_{\mathbf{q}}\sum_{m}^{3N}\frac{1}{2\omega_{m\mathbf{q}}}\sum_{\substack{\kappa\alpha\\ \kappa'\gamma}}\sum_{n'}$$

$$\underbrace{\left\langle u_{n\mathbf{k}}^{(0)}\middle|\hat{H}^{(1)}_{\mathbf{k},\mathbf{k}}(\mathbf{q})\middle|u_{n'\mathbf{k}+\mathbf{q}}^{(0)}\right\rangle\left\langle u_{n'\mathbf{k}+\mathbf{q}}^{(0)}\middle|\hat{H}^{(1)}_{\mathbf{k},\mathbf{k}}(\mathbf{q})\middle|u_{n\mathbf{k}}^{(0)}\right\rangle}_{\text{Fan}}$$

$$\left(\frac{n_{m\mathbf{q}}(T)+1/2}{\varepsilon_{n\mathbf{k}}^{(0)}-\varepsilon_{n'\mathbf{k}+\mathbf{q}}^{(0)}+i\delta}\right)U^{*}_{m,\kappa'\gamma}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})$$

$$-\underbrace{\left\langle u_{n\mathbf{k}}^{(1)}(\mathbf{\Gamma})\middle|\hat{H}^{(1)}_{\mathbf{k},\mathbf{k}}(\mathbf{\Gamma})\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\left(n_{m\mathbf{q}}(T)+\frac{1}{2}\right)\left(U^{*}_{m,\kappa\gamma}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})+U^{*}_{m,\kappa'\gamma}(\mathbf{q})U_{m,\kappa'\alpha}(\mathbf{q})\right)}_{\text{Debye-Waller (DW) within RIA}}.$$



Fan DW

Beyond the Rayleigh-Schrödinger perturbation theory

The non-adiabatic theory take the phonon frequency into account in the denominator

$$\Delta\varepsilon_{n\mathbf{k}}^{(\text{non-adiabatic,RIA})}(T) = \frac{1}{N_q}\sum_{\mathbf{q}}\sum_{m}^{3N}\frac{1}{4\omega_{m\mathbf{q}}}\sum_{\substack{\kappa\alpha\\ \kappa'\gamma}}\sum_{n'}$$

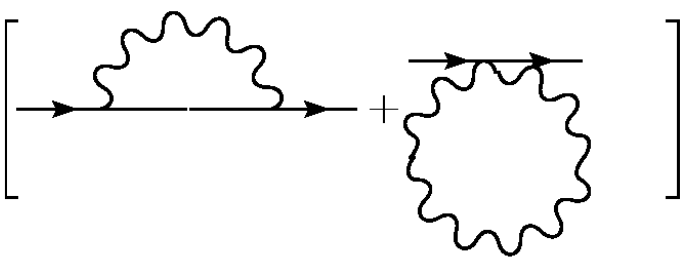
$$\left\langle u_{n\mathbf{k}}^{(0)}\middle|\hat{H}^{(1)}_{\mathbf{k},\mathbf{k}}(\mathbf{q})\middle|u^{(0)}_{n'\mathbf{k}+\mathbf{q}}\right\rangle\left\langle u^{(0)}_{n'\mathbf{k}+\mathbf{q}}\middle|\hat{H}^{(1)}_{\mathbf{k},\mathbf{k}}(\mathbf{q})\middle|u^{(0)}_{n\mathbf{k}}\right\rangle$$

Fan

$$\left(\frac{n_{m\mathbf{q}}(T)+f_{n'\mathbf{k}+\mathbf{q}}}{\varepsilon^{(0)}_{n\mathbf{k}}-\varepsilon^{(0)}_{n'\mathbf{k}+\mathbf{q}}+\omega_{m\mathbf{q}}+i\delta}+\frac{n_{m\mathbf{q}}(T)+1-f_{n'\mathbf{k}+\mathbf{q}}}{\varepsilon^{(0)}_{n\mathbf{k}}-\varepsilon^{(0)}_{n'\mathbf{k}+\mathbf{q}}-\omega_{m\mathbf{q}}+i\delta}\right)U^{*}_{m,\kappa'\gamma}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})$$

$$-\left\langle u^{(1)}_{n\mathbf{k}}(\mathbf{\Gamma})\middle|\hat{H}^{(1)}_{\mathbf{k},\mathbf{k}}(\mathbf{\Gamma})\middle|u^{(0)}_{n\mathbf{k}}\right\rangle\left(n_{m\mathbf{q}}(T)+\frac{1}{2}\right)\left(U^{*}_{m,\kappa\gamma}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})+U^{*}_{m,\kappa'\gamma}(\mathbf{q})U_{m,\kappa'\alpha}(\mathbf{q})\right).$$

Debye-Waller (DW) within RIA

$\Sigma =$ 

Fan DW

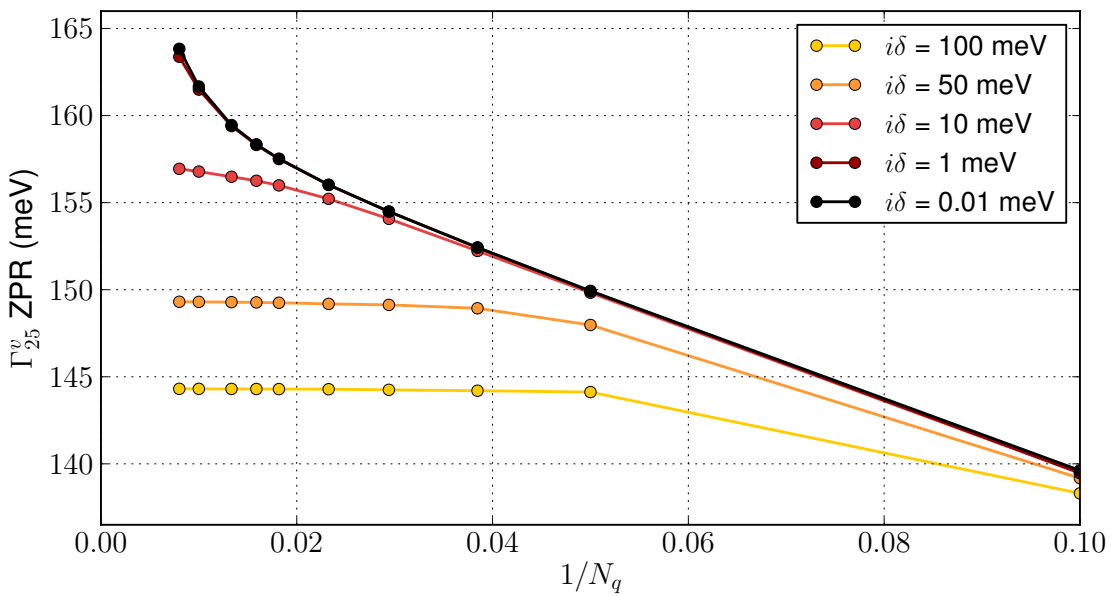
Potential breakdown of perturbation theory

$$\Delta\varepsilon_{n\mathbf{k}}^{(\text{adiabatic,RIA})}(T) \propto \sum_{\mathbf{q}} \frac{|GKK(\mathbf{q})|^2}{\varepsilon_{\mathbf{k}}^{(0)} - \varepsilon_{\mathbf{k}+\mathbf{q}}^{(0)} + i\delta}.$$

Two types of potential divergences

- when $\varepsilon_{\mathbf{k}}^{(0)} = \varepsilon_{\mathbf{k}+\mathbf{q}}^{(0)}$
- when $GKK(\mathbf{q}) \propto \frac{1}{\mathbf{q}}$ (IR-active materials or breaking of the Born effective charge neutrality sum rule)

Adiabatic ZPR of the Γ_{25}^{v} state of diamond



Restoration of the charge neutrality

$$GKK(\mathbf{q}) \propto H^{(1)}_{\mathbf{k}+\mathbf{q},\mathbf{k}}$$

$$H^{(1)}_{\mathbf{k}+\mathbf{q},\mathbf{k}} = v^{(1)}_{sep,\mathbf{k}+\mathbf{q},\mathbf{k}} + \bar{v}^{(1)}_{loc,\mathbf{q}} + \bar{v}^{(1)}_{H,\mathbf{q}} + \bar{v}^{(1)}_{xc,\mathbf{q}}$$

$$\bar{v}^{(1)}_{H,\mathbf{q}}(\mathbf{G}) = 4\pi \frac{\bar{n}^{(1)}_{\mathbf{q}}}{|\mathbf{G}+\mathbf{q}|^2}$$

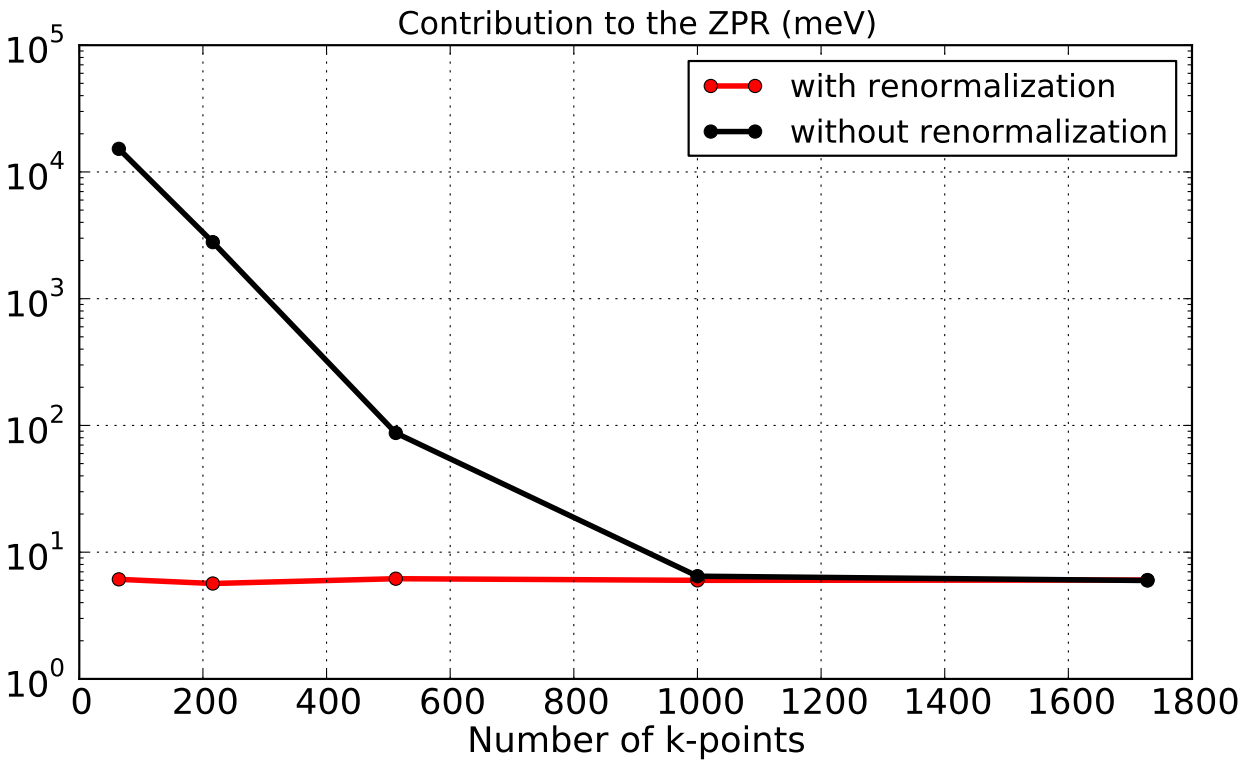
Number of **k**-points	Born effective charge
8	-2.5406
64	-0.3514
216	-0.0534
512	-0.0080
1000	-0.0011

$\bar{n}^{(1)}_{\mathbf{q}} \propto |\mathbf{q}|$ when $\mathbf{q} \to \mathbf{0}$ if the charge neutrality is broken

It works ! ... for non IR-active materials

Solution (Abinit 7.11+):

$$\bar{v}^{ren(1)}_{H,\mathbf{q}}(\mathbf{0}) = \bar{v}^{(1)}_{H,\mathbf{q}}(\mathbf{0}) \frac{\sum_\gamma q_\gamma \left(Z_\kappa \delta_{\alpha\gamma} - \frac{(Z^*_{\kappa\alpha,\gamma} - \bar{Z}_{\alpha\gamma})}{\frac{1}{q^2}\sum_{\delta,\xi} q_\delta \epsilon_{\delta\xi} q_\xi} \right)}{\sum_\gamma q_\gamma \left(Z_\kappa \delta_{\alpha\gamma} - \frac{Z^*_{\kappa\alpha,\gamma}}{\frac{1}{q^2}\sum_{\delta,\xi} q_\delta \epsilon_{\delta\xi} q_\xi} \right)},$$



It works ! ... for non IR-active materials

The adiabatic AHC theory

- diverges in IR-active materials
- converges in non IR-active materials after renormalization

The non-adiabatic AHC theory

- converges in all materials

Workflow of ZPR and temperature dependence calculations

Calculation steps

1. Make response function calculation at q=0 and electric field pert.
2. Make electron-phonon matrix element calculations at q.
3. Gather the results with the `scripts/post_processing/temperature_para.py` python script (and `rf_mods.py` module) and compute the ZPR.

```
qpt       0.0 0.0 0.0
rfelfd2    2  ! DDK calculations
getddk3    2
rfelfd3    3  ! Electric-field perturbation response only
```

This will produce a DDB file that contains the Born effective charge tensor.

Warning: Abinit needs to be compiled with netCDF.

Workflow of ZPR and temperature dependence calculations

Calculation steps

1. Make response function calculation at q=0 and electric field pert.
2. Make electron-phonon matrix element calculations at q.
3. Gather the results with the `scripts/post_processing/temperature_para.py` python script (and `rf_mods.py` module) and compute the ZPR.

```
 nsym     1            # k-point sym not working
 kptopt   3            # To avoid time-reversal
 tolwfr   1.0d-28

# Ground state density
 iscf1     7

# Non self-consistent calculation with an abritrary q point
 getden2 -1
 getwfk2 -1
 iscf2   -2
 nqpt2    1
 wtq2     1.25775088986e-05                OR  ngqpt 4 4 4
 qpt2     0.0232558139535 0.0 0.0          OR  iqpt2    x
```

Workflow of ZPR and temperature dependence calculations

Calculation steps

1. Make response function calculation at q=0 and electric field pert.
2. Make electron-phonon matrix element calculations at q.
3. Gather the results with the `scripts/post_processing/temperature_para.py` python script (and `rf_mods.py` module) and compute the ZPR.

```
# Computation of the _EIGR2D at q
 getddb3  99     # Read Born effective charge
 getwfk3 -2
 getwfq3 -1
 ieig2rf3 4      # Eigenvalue correction using DFPT (Sternheimer)
                 # with control on idelta
 smdelta3 1      # For the lifetime _EIGI2D
 rfphon3  1              # Do phonon response
 rfatpol3 1 2            # Treat displacements of all atoms
 rfdir3   1 1 1          # Do all directions
 qpt13 0.0 0.0 0.0
 wtq13 1.25775088986e-05
 qpt23 0.0232558139535 0.0 0.0
```

This will produce _DDB, _EIG.nc, _EIGR2D.nc, _FAN.nc files

Workflow of ZPR and temperature dependence calculations

Calculation steps

1. Make response function calculation at q=0 and electric field pert.
2. Make electron-phonon matrix element calculations at q.
3. Gather the results with the `scripts/post_processing/temperature_para.py` python script (and `rf_mods.py` module) and compute the ZPR.

Run the python script

```
python temperature_para.py
```

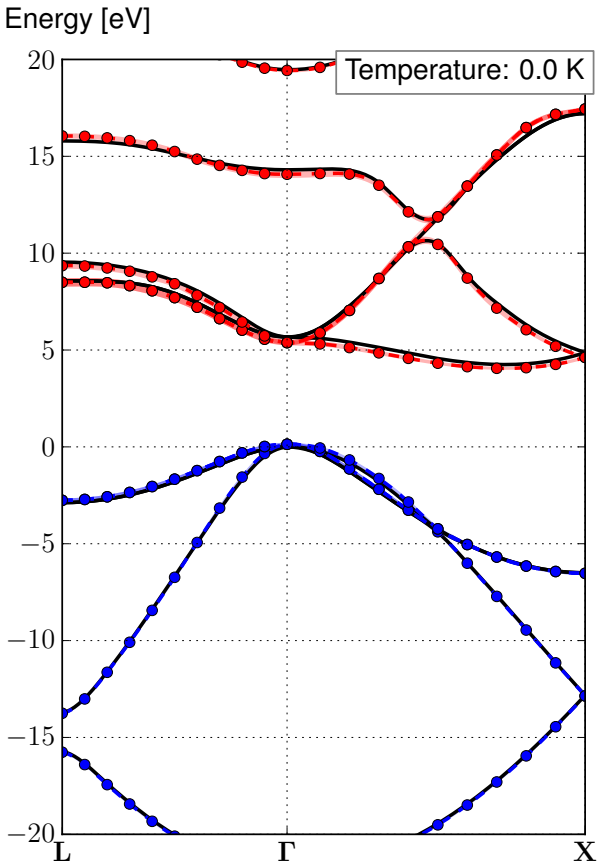
and provide the paths of the required files.

The script will produce

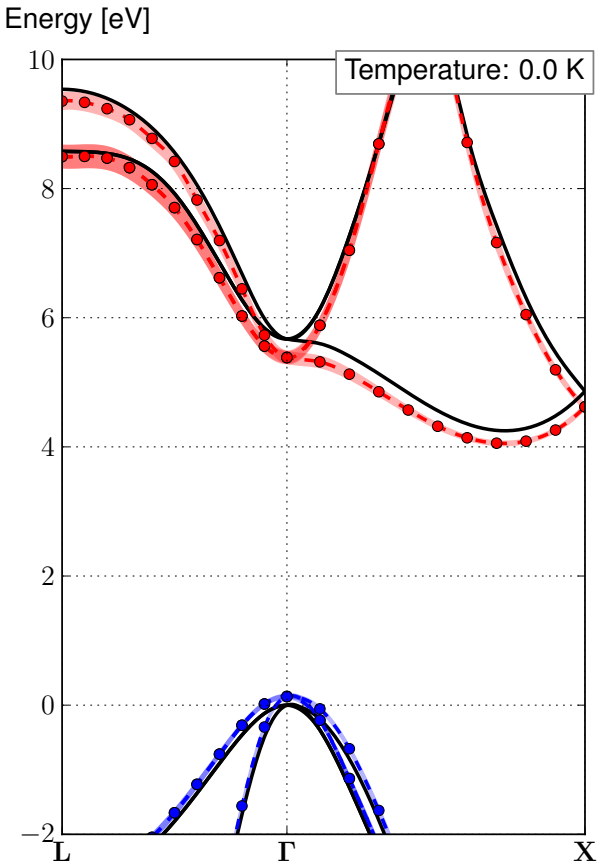
```
output_EP.nc
output_BRD.txt
output.txt
```

Non-adiabatic ZPR of diamond

The ZPR is integrated on a 75x75x75 **q**-grid for δ extrapolated to 0

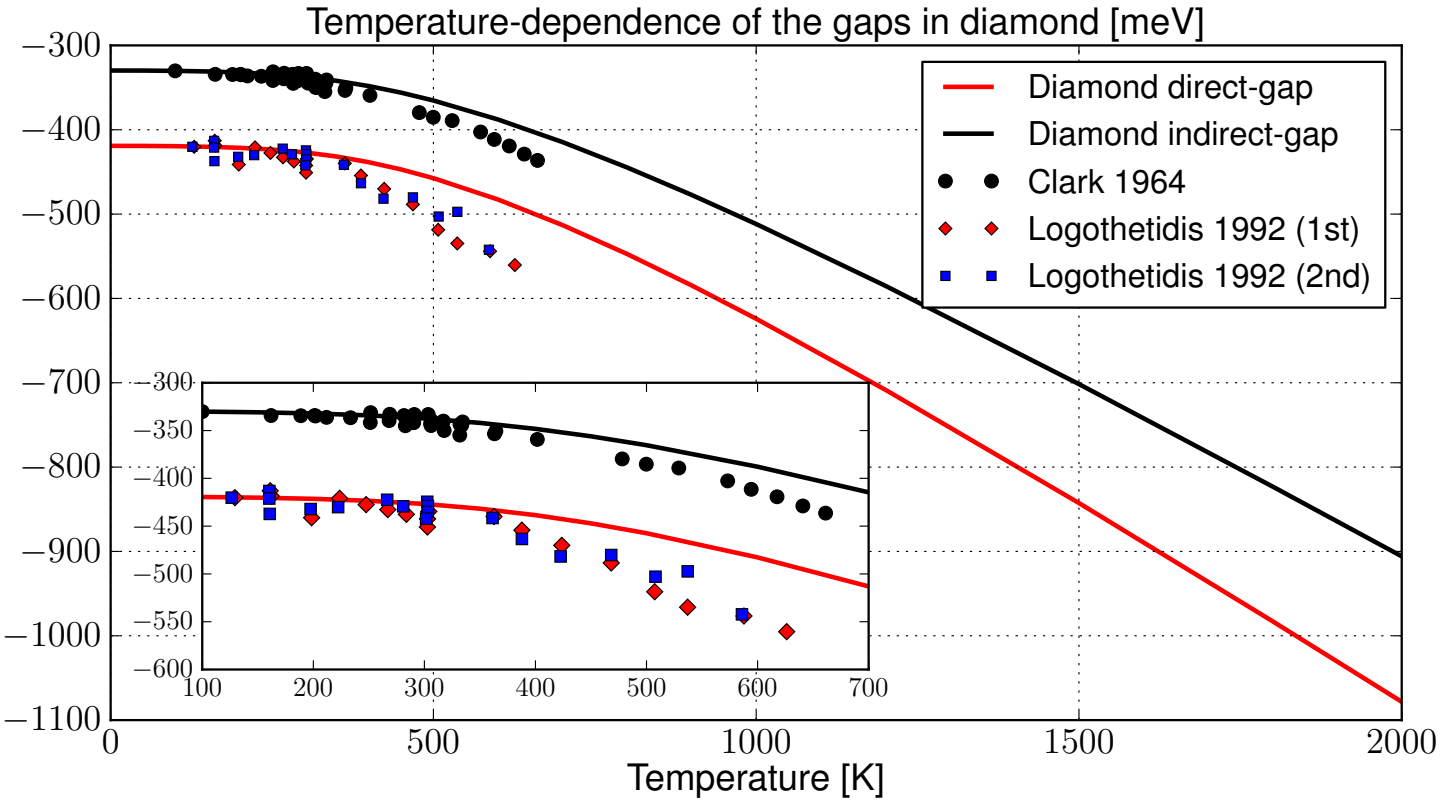


Diamond bandstructure at 0K.



Zoom of the left-hand side figure.

Non-adiabatic temperature dependence of diamond



Exp. are shifted to match with the theoretical one at 4 K.

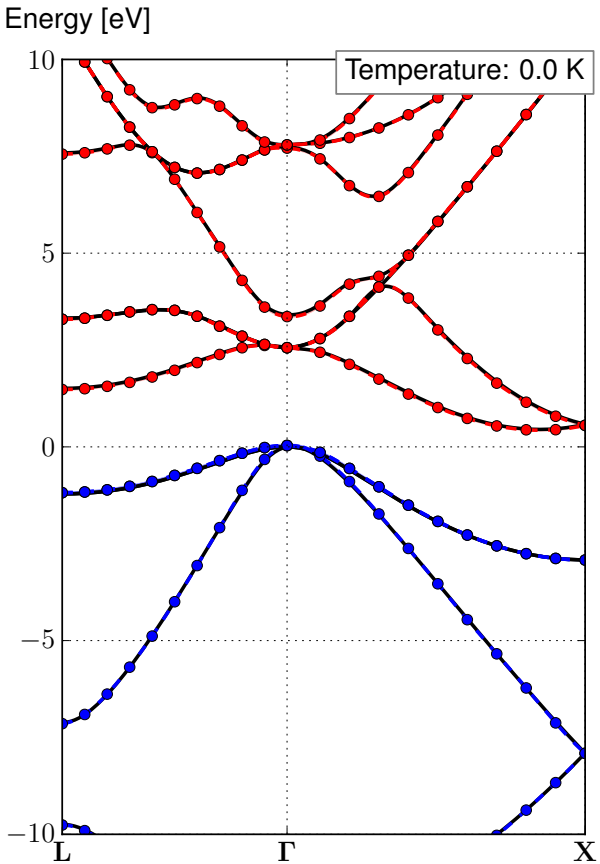
- The slopes at high temperature are -0.504 meV/K for the direct gap of diamond and -0.435 meV/K for the indirect one.

Exp: C. D. Clark *et al.*, P. Roy. Soc. Lond. A Mat.**227** (1964).

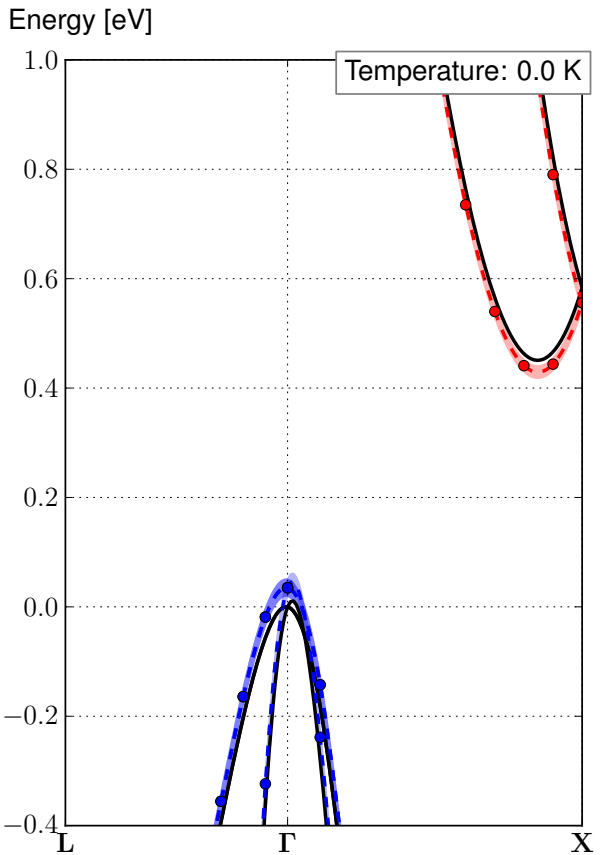
S. Logothetidis *et al.*, Phys. Rev. B **46**, 4483 (1992).

Non-adiabatic ZPR of silicon

The ZPR is integrated on a 75x75x75 **q**-grid for δ extrapolated to 0

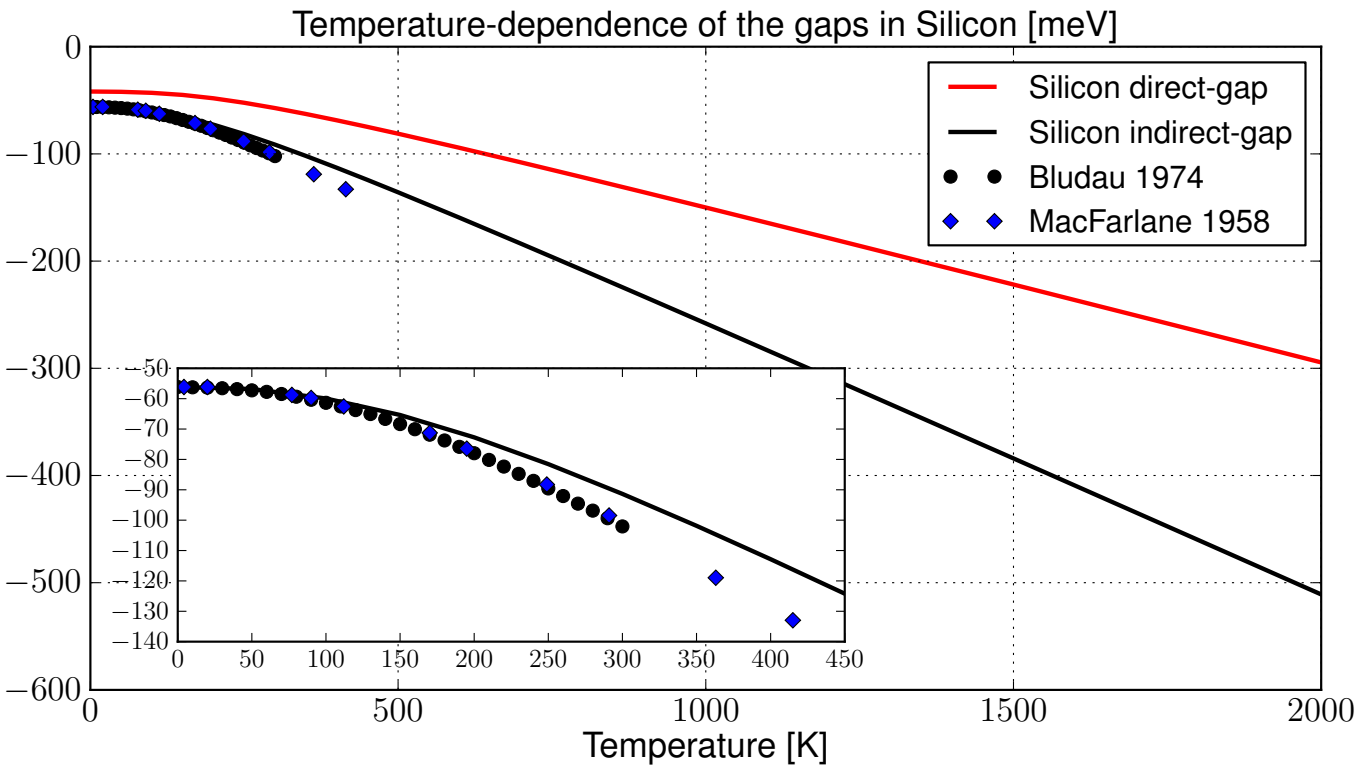


Silicon bandstructure at 0K.



Zoom of the left-hand side figure.

Temperature dependence in Silicon



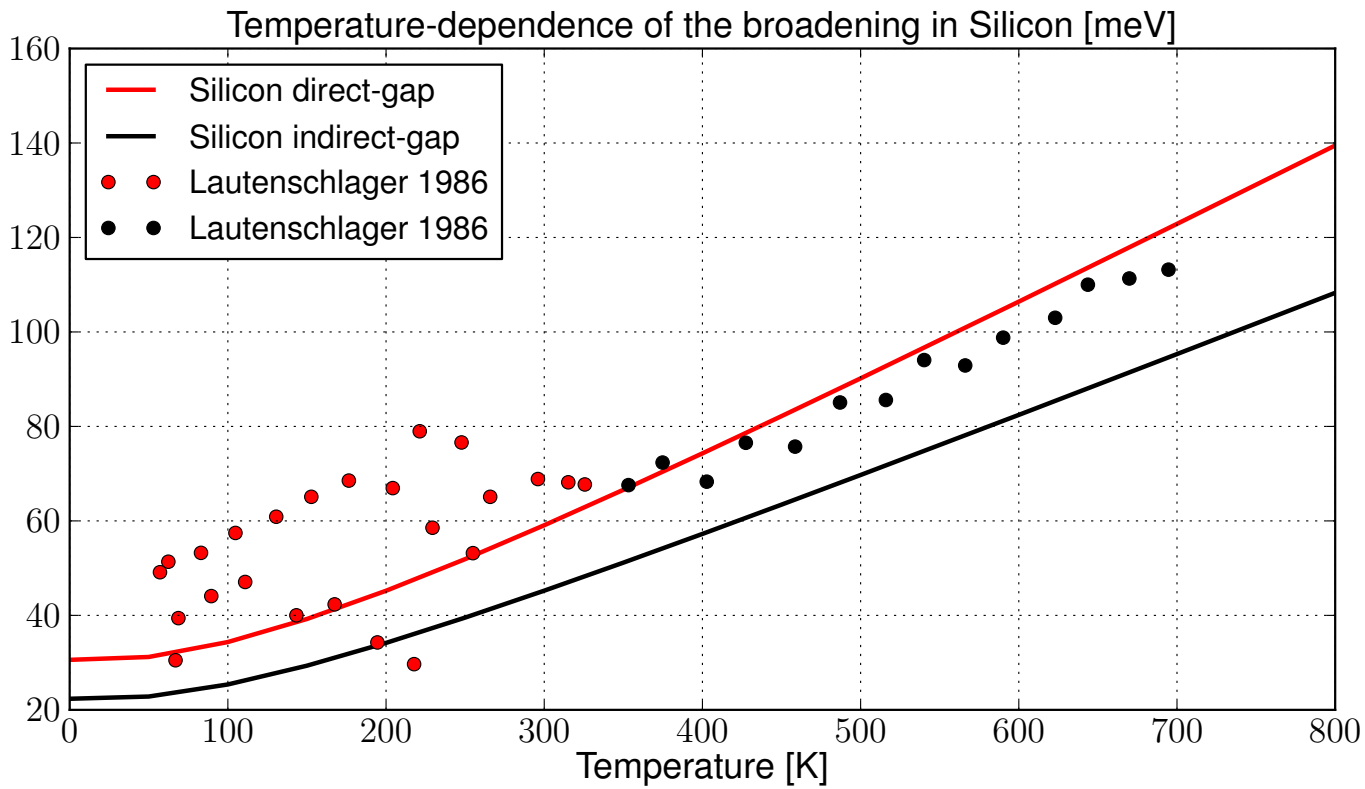
Exp. are shifted to match with the theoretical one at 4 K.

- The slopes at high temperature are -0.147 meV/K for the direct gap of silicon and -0.255 meV/K for the indirect one.

Exp: W. Bludau *et al.*, J. Appl. Phys. **45**, 1846 (1974).

G. Macfarlane *et al.*, Phys. Rev. **111**, 1245 (1958).

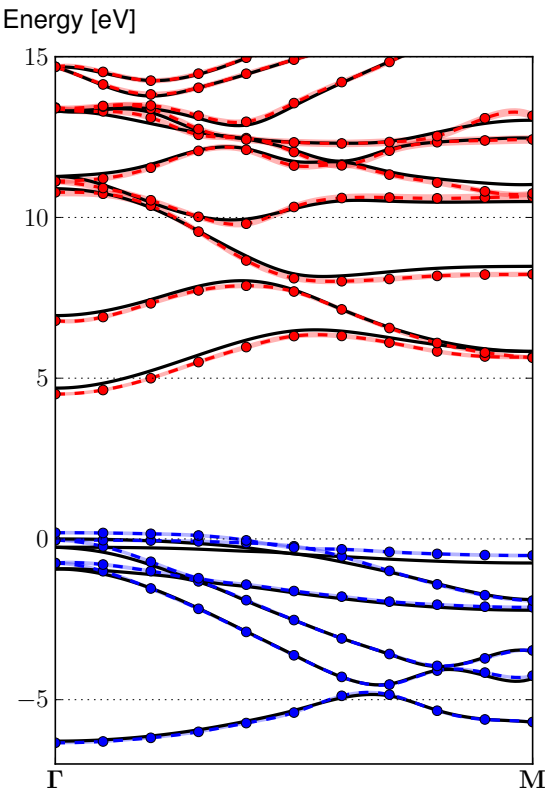
Temperature dependence of the silicon broadening



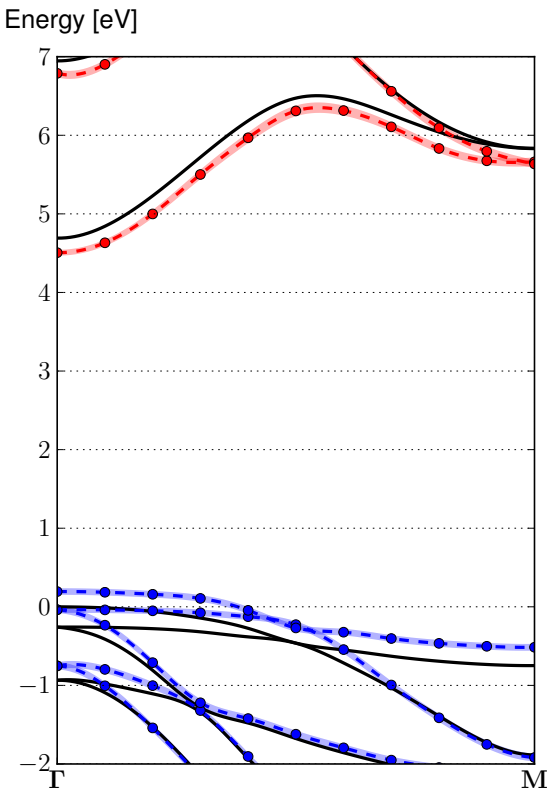
Exp: P. Lautenschlager *et al.*, Phys. Rev. B **33**, 5501 (1986).

Non-adiabatic ZPR of hexagonal α-AlN

The ZPR is integrated on a 34x34x34 **q**-grid for δ extrapolated to 0

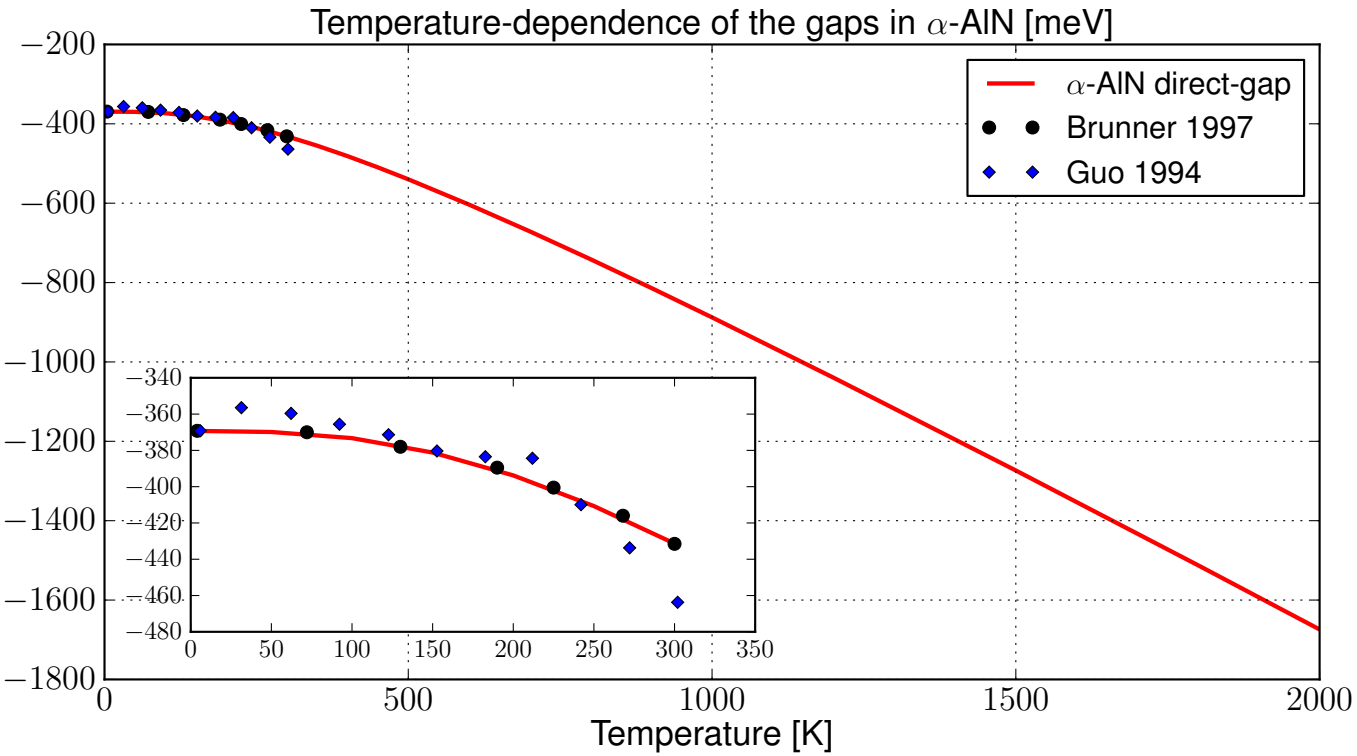


α-AlN bandstructure at 0K.



Zoom of the left-hand side figure.

Temperature dependence in α-AlN



Exp. are shifted to match with the theoretical one at 4 K.

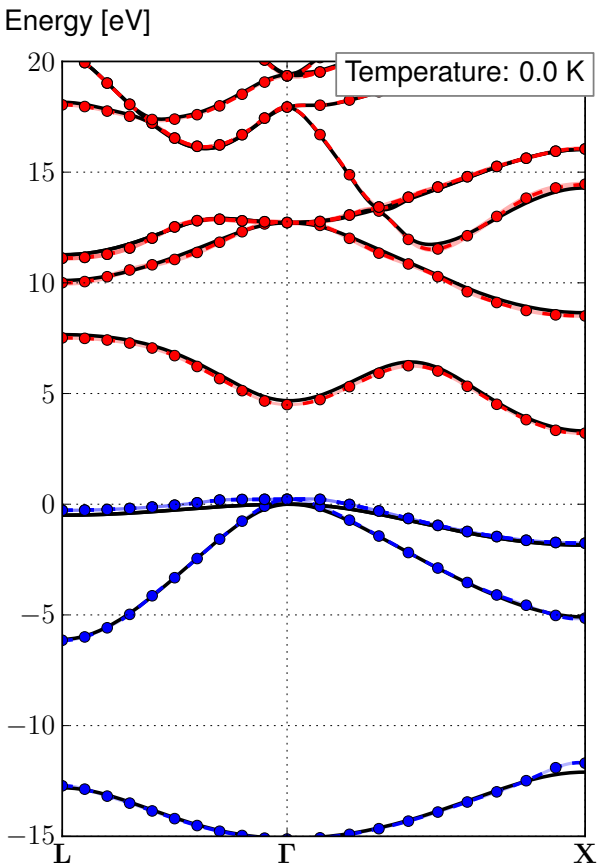
- The slope at high temperature is -0.772 meV/K for the direct gap of α-AlN.

Exp: D. Brunner *et al.*, J. Appl. Phys. **82**, 5090 (1997).

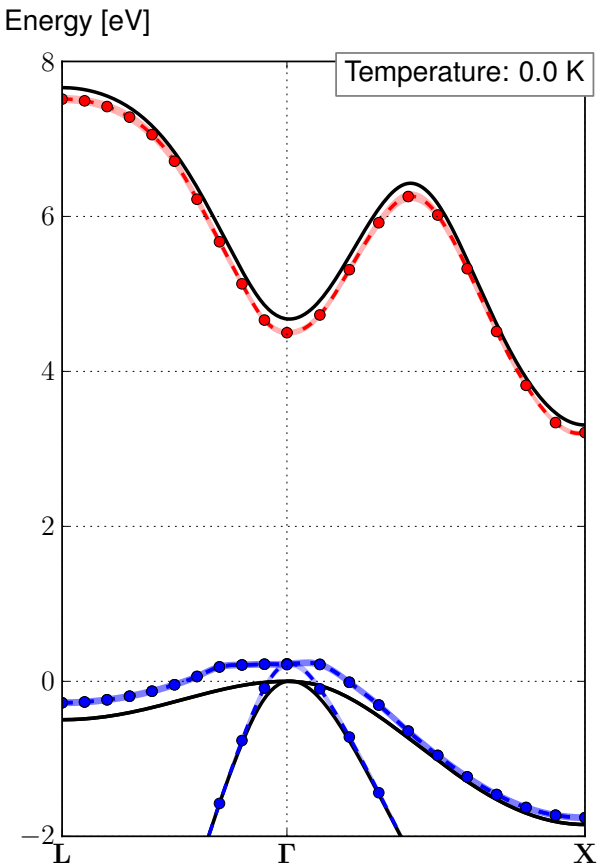
Q. Guo and A. Yoshida, Jap. J. Appl. Phys. **33**, 2453 (1994).

Non-adiabatic ZPR β-AlN

The ZPR is integrated on a 75x75x75 **q**-grid for δ extrapolated to 0



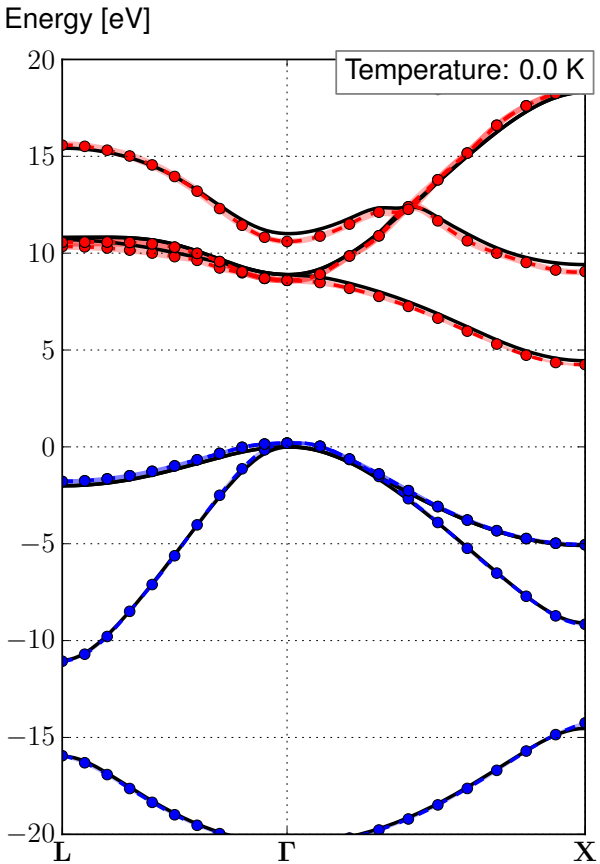
β-AlN bandstructure at 0K.



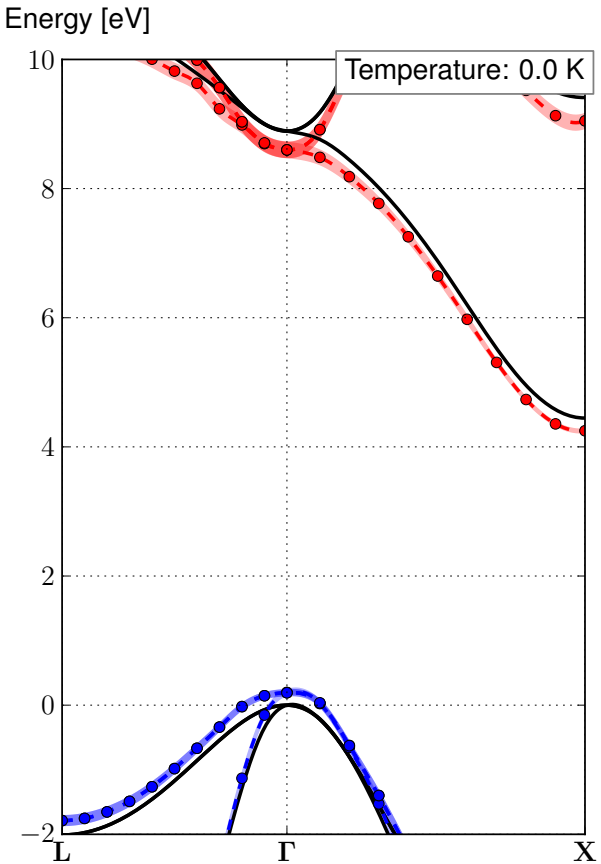
Zoom of the left-hand side figure.

Non-adiabatic ZPR c-BN

The ZPR is integrated on a 75x75x75 **q**-grid for δ extrapolated to 0



c-BN bandstructure at 0K.



Zoom of the left-hand side figure.

Summary

The ZPR, slope at high temperature as well as lifetime are all underestimated with respect to experiment (need GW).

		ZPR [meV]			Slope high T [meV/K]		Broadening [meV]	
Comp.	Gap	Adia	Non-adia	Exp.	Non-adia.	Exp.	Adia.	Exp.
α-AlN	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-	-377.7	**-239**	-0.772	-0.83	117	
β-AlN	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-	-413.6		-0.763		118	
	$\mathbf{\Gamma} - \mathbf{X}$	-	-334.4		-0.521		108	
c-BN	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-	-502.0		-0.639		315	
	$\mathbf{\Gamma} - \mathbf{X}$	-	-405.6		-0.521		136	
C	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-438.6	-415.8	-450	-0.504	-0.60	180	
	$\mathbf{\Gamma} - 0.7\mathbf{X}$	-379.3	-329.8	-364	-0.435	-0.54	63	
Si	$\mathbf{\Gamma} - \mathbf{\Gamma}$	-47.1	-42.1		-0.147		31	
	$\mathbf{\Gamma} - 0.8\mathbf{X}$	-64.3	-56.2	-64	-0.255	-0.32	22	$\sim$35

For experimental ref. see S. Poncé *et al.* arXiv:1504.05992

Conclusions

- Restoration of the charge neutrality $\rightarrow$ speed up **k**-convergence
- The adiabatic AHC theory breakdowns in IR-active materials.
- GW adds a significant electron-phonon coupling contribution.
- 5 semiconductors have been studied (C, Si, α-AlN,β-AlN, c-BN)
- All the results are underestimated wrt experiment but allow for comparison between materials

Related papers

- S. Poncé *et al.*, Comp. Mater. Sci. **83**, 341 (2014).
- G. Antonius *et al.*, Phys. Rev. Lett. **112**, 215501 (2014).
- S. Poncé *et al.*, Phys. Rev. B **90**, 214304 (2014).
- A. Marini *et al.*, Phys. Rev. B (submitted) (2015) [arXiv:1503.00567].
- S. Poncé *et al.*, J. Chem. Phys. (submitted) (2015) [arXiv:1504.05992].

Theory of bandgap temperature dependence

The Allan-Heine-Cardona (AHC) theory using the translation invariance and the rigid-ion approximation:

$$\Delta\varepsilon_{n\mathbf{k}}^{(\text{static,RIA})}(T) = \frac{1}{N_q}\sum_{\mathbf{q}}\sum_{m}^{3N}\left(n_{m\mathbf{q}}(T)+\frac{1}{2}\right)\frac{1}{2\omega_{m\mathbf{q}}}\sum_{\substack{\kappa\alpha\\ \kappa'\gamma}}\Bigg[\sum_{n'=1}^{M}{}'\frac{\left\langle u_{n\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q})}\middle|u_{n'\mathbf{k}+\mathbf{q}}^{(0)}\right\rangle\left\langle u_{n'\mathbf{k}+\mathbf{q}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle}{\varepsilon_{n\mathbf{k}}^{(0)}-\varepsilon_{n'\mathbf{k}+\mathbf{q}}^{(0)}+i\delta}$$

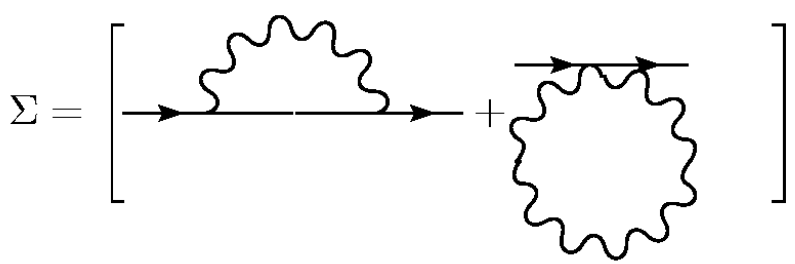
$$+\left\langle P_{c\mathbf{k}+\mathbf{q}}\frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{q})}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\Bigg]U_{m,\kappa'\gamma}^{*}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})$$

Fan

$$-\frac{1}{2}\Bigg[\sum_{n'=1}^{M}{}'\frac{\left\langle u_{n\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{\Gamma})}\middle|u_{n'\mathbf{k}}^{(0)}\right\rangle\left\langle u_{n'\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{\Gamma})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle}{\varepsilon_{n\mathbf{k}}^{(0)}-\varepsilon_{n'\mathbf{k}}^{(0)}+i\delta}$$

Diagonal Debye-Waller (DDW) within RIA

$$+\left\langle P_{c\mathbf{k}}\frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{\Gamma})}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{\Gamma})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\Bigg]\left(U_{m,\kappa\gamma}^{*}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})+U_{m,\kappa'\gamma}^{*}(\mathbf{q})U_{m,\kappa'\alpha}(\mathbf{q})\right).$$



Fan DDW

Dynamical Fan self-energy beyond the Rayleigh-Schrödinger perturbation theory

$$\Delta\varepsilon_{n\mathbf{k}}^{(\text{non-adiabatic,RIA})}(T) = \Re\frac{1}{N_q}\sum_{\mathbf{q}}\sum_{m}^{3N}\frac{1}{2\omega_{m\mathbf{q}}}\sum_{\substack{\kappa\alpha\\ \kappa'\gamma}}$$

$$\left[\sum_{n'=1}^{M}\left\langle u_{n\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q})}\middle|u_{n'\mathbf{k}+\mathbf{q}}^{(0)}\right\rangle\left\langle u_{n'\mathbf{k}+\mathbf{q}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\right.$$

$$\left(\frac{n_{m\mathbf{q}}(T)+f_{n'\mathbf{k}+\mathbf{q}}}{\omega-\varepsilon_{n'\mathbf{k}+\mathbf{q}}^{(0)}+\omega_{m\mathbf{q}}(T)+i\delta\,\mathrm{sgn}(\varepsilon_{n\mathbf{k}})}+\frac{n_{m\mathbf{q}}(T)+1-f_{n'\mathbf{k}+\mathbf{q}}}{\omega-\varepsilon_{n'\mathbf{k}+\mathbf{q}}^{(0)}-\omega_{m\mathbf{q}}+i\delta\,\mathrm{sgn}(\varepsilon_{n\mathbf{k}})}\right)$$

$$\left.+\left\langle P_{c\mathbf{k}+\mathbf{q}}\frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{q})}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\left(n_{m\mathbf{q}}(T)+\frac{1}{2}\right)\right]$$

$$U_{m,\kappa'\gamma}^{*}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})$$

$$-\frac{1}{2}\left[\sum_{n'=1}^{M}\frac{\left\langle u_{n\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{\Gamma})}\middle|u_{n'\mathbf{k}}^{(0)}\right\rangle\left\langle u_{n'\mathbf{k}}^{(0)}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{\Gamma})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle}{\varepsilon_{n\mathbf{k}}^{(0)}-\varepsilon_{n'\mathbf{k}}^{(0)}+i\delta}\right.$$

$$\left.\left.+\left\langle P_{c\mathbf{k}}\frac{\partial u_{n\mathbf{k}}}{\partial R_{\kappa\alpha}(\mathbf{\Gamma})}\middle|\frac{\partial\hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{\Gamma})}\middle|u_{n\mathbf{k}}^{(0)}\right\rangle\right]\left(U_{m,\kappa\gamma}^{*}(\mathbf{q})U_{m,\kappa\alpha}(\mathbf{q})+U_{m,\kappa'\gamma}^{*}(\mathbf{q})U_{m,\kappa'\alpha}(\mathbf{q})\right),$$

Phonon-induced lifetime broadening in the adiabatic limit

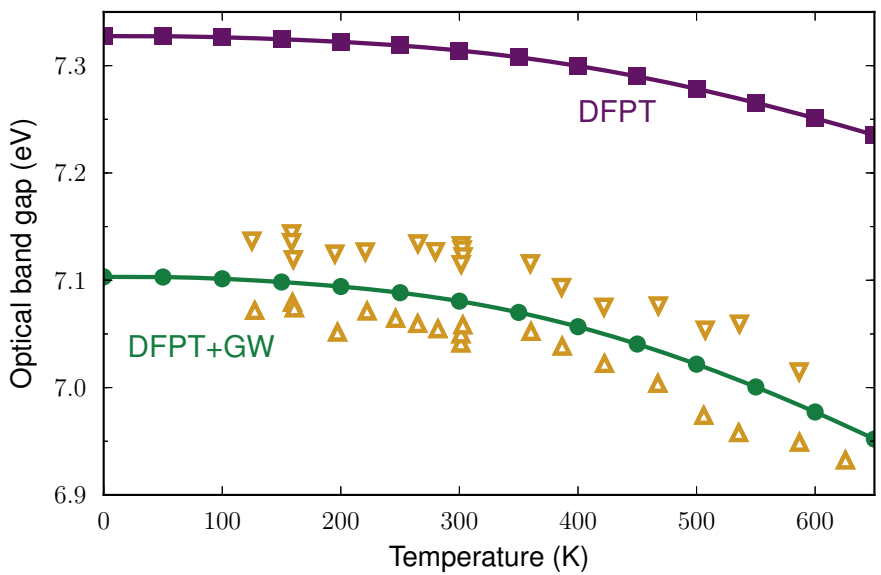
By taking the adiabatic limit ($\omega_{m\mathbf{q}} << \omega - \varepsilon_{n'\mathbf{k}+\mathbf{q}}$) of the imaginary part of the previous equation, we obtain

$$\frac{1}{2\tau_{n\mathbf{k}}^{(\text{static,RIA})}} = \frac{\pi}{N_q} \sum_{\mathbf{q}} \sum_{m}^{3N} \frac{1}{2\omega_{m\mathbf{q}}} \left(n_{m\mathbf{q}}(T) + \frac{1}{2} \right) \sum_{\substack{\kappa\alpha \\ \kappa'\gamma}} \sum_{n'=1}^{M}{}' \left\langle u_{n\mathbf{k}}^{(0)} \middle| \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa\alpha}(-\mathbf{q})} \middle| u_{n'\mathbf{k}+\mathbf{q}}^{(0)} \right\rangle \left\langle u_{n'\mathbf{k}+\mathbf{q}}^{(0)} \middle| \frac{\partial \hat{H}_{\mathbf{k},\mathbf{k}}}{\partial R_{\kappa'\gamma}(\mathbf{q})} \middle| u_{n\mathbf{k}}^{(0)} \right\rangle \delta(\varepsilon_{n\mathbf{k}}^{(0)} - \varepsilon_{n'\mathbf{k}+\mathbf{q}}^{(0)}) U_{m,\kappa'\gamma}^{*}(\mathbf{q}) U_{m,\kappa\alpha}(\mathbf{q}).$$

The ZPR using AHC underestimates experiment

The Abinit results with AHC do not reproduce experiment well ... and it should not !

- Calculation made on a 32x32x32 **q**-grid with DFPT AHC leads to -404 meV gap renormalization.
- Many-body G_0W_0 correction: -209 meV on the ZPM



See G. Antonius *et al.* Phys. Rev. Lett. **112**, 215501 (2014)