Efficient ab initio electronic transport methods

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Wednesday, 14 June, 2023

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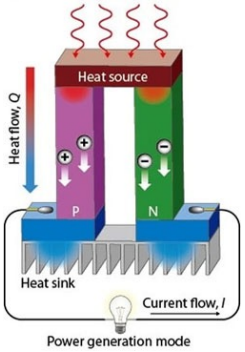
Basics of thermoelectricity



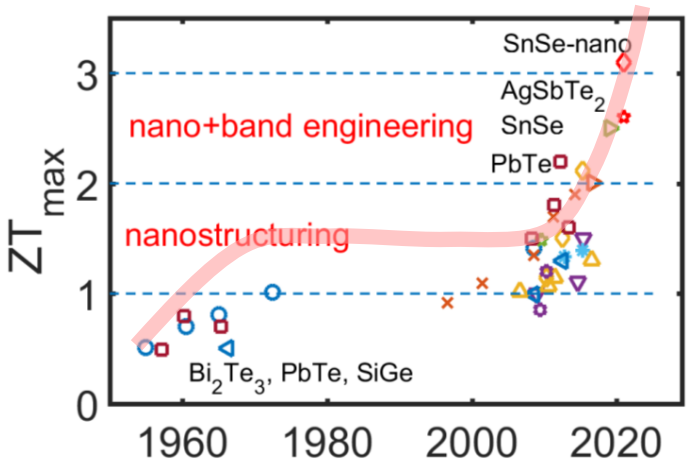
Electrical conductivity

Seebeck coefficient

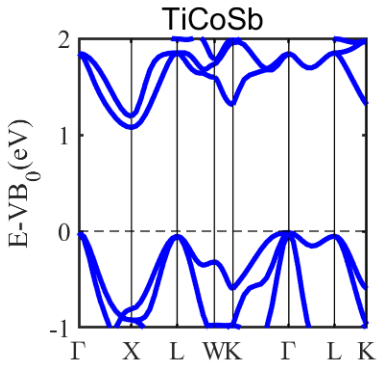
$$ZT = \frac{\sigma S^2 T}{\kappa_e + \kappa_l}$$

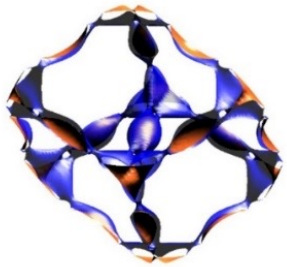
Electronic thermal conductivity

Lattice thermal conductivity

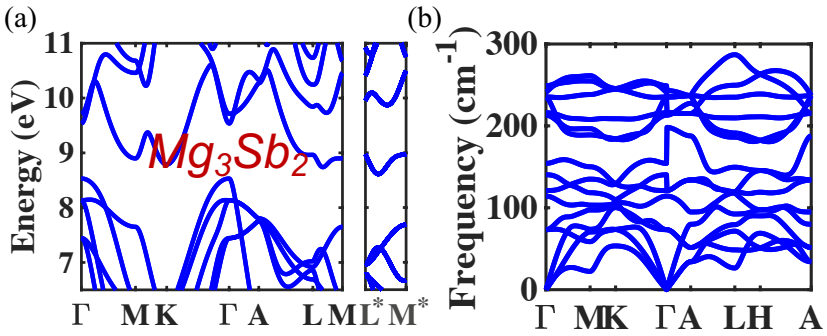


Material complexity examples





Complex bands and energy surfaces



Complex phonon spectrum and scattering

Need ab initio treatment of transport !!

Contents

I. Low field transport methods from ab initio

Constant relaxation time approximation (CRT)
Electron Phonon Wannier (EPW)
Deformation potential

II. Deformation potential beyond ADP

Non-polar materials: Case of Si
Polar materials complexities: case for Mg_3Sb_2

III. Efficiency

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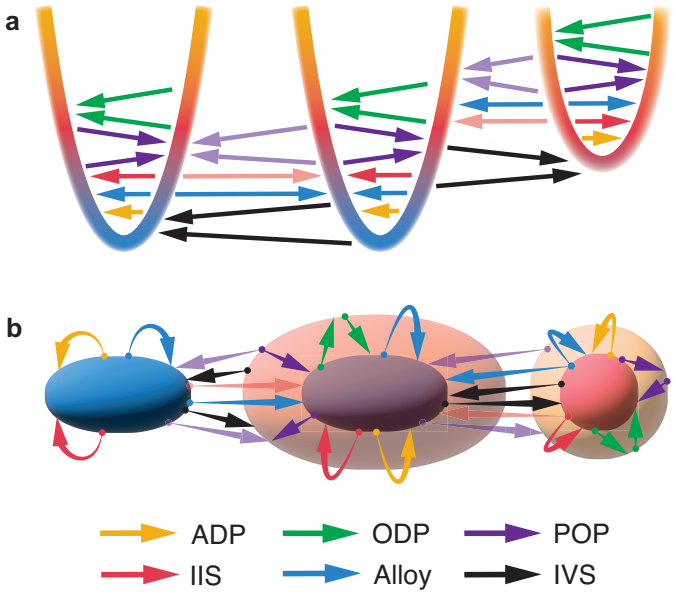
Low field transport and relaxation times

Electronic transport: DFT + BTE

BTE (Boltzmann Transport Equation)

$$\sigma = q_0^2 \int_E \Xi(E) \left(-\frac{\partial f_0}{\partial E}\right) dE$$



Transport distribution function

$$\Xi(E) = \sum_{k,n} v_{k,n,E}^2 \tau_{k,n,E} DOS_{k,n,E}$$

$$\tau(k, E, n, T, ph., imp., alloy, \dots)$$

Relaxation time?

$$\tau_{k,n,E}$$

Existing Codes

Relaxation time $\tau_{k,n,E}$

Speed

BoltzTraP

Constant **R**elaxation **T**ime (**CRT**) approximation

Avoids all tau complexity

Typically tau=15fs for all materials and T

Most commonly used

Efficiency & Accuracy ?

Deformation potential methods

AMSET, EPIC STAR

(one, 'global' acoustic deformation potential)

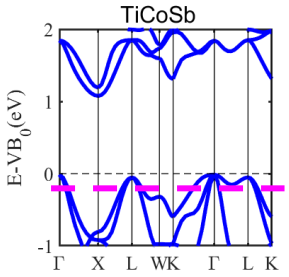
Our code: *ElecTra*

EPW®

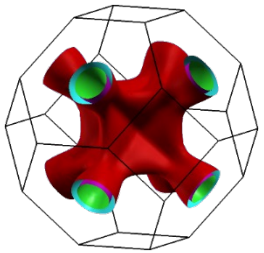
DFPT + Wannier

Accuracy

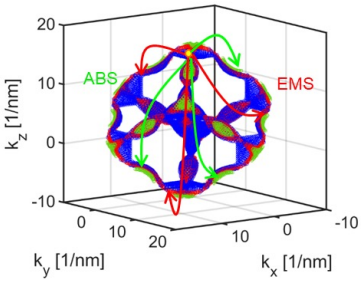
ElecTra – Electronic Transport



1) DFT bands



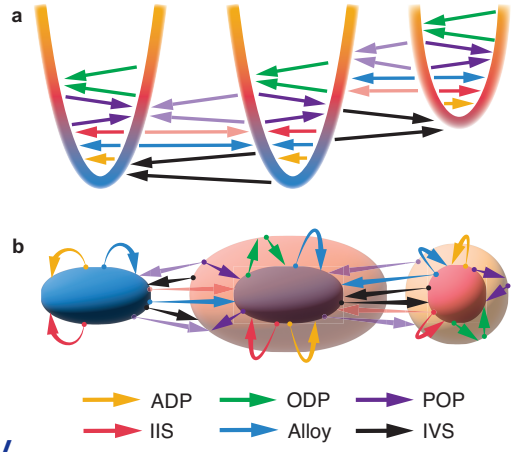
2) energy surfaces



several thousands of ***k*** points in each surface

3) discrete state-points

4) Careful consideration of scattering processes



$$\frac{1}{\tau_{x,k,n,E}^{(i)}} = \frac{1}{(2\pi)^3}\sum_{k'} |S_{k,k'}^{(i)}|\left(1-\frac{v_{x,k'}}{v_{x,k,n,E}}\right)$$

$$|S_{k,k'}^{(ADP)}| = 2\frac{\pi}{\hbar} D_{ADP}^2 \frac{k_B T}{\rho v_S^2} g_{k'}$$

$$|S_{k,k'}^{(POP)}| = \frac{\pi e^2 \omega}{|k-k'|^2 \varepsilon_0}\left(\frac{1}{k_\infty}-\frac{1}{k_S}\right)\left(N_{\omega,BE}+\frac{1}{2}\mp\frac{1}{2}\right) g_{k'}$$

$$|S_{k,k'}^{(ODP)}| = \frac{\pi D_{ODP}^2}{\rho\omega}\left(N_{\omega}+\frac{1}{2}\mp\frac{1}{2}\right) g_{k'}$$

$$|S_{k,k'}^{(IVS)}| = \frac{\pi D_{IVS}^2}{\rho\omega}\left(N_{\omega}+\frac{1}{2}\mp\frac{1}{2}\right) g_{k'}$$

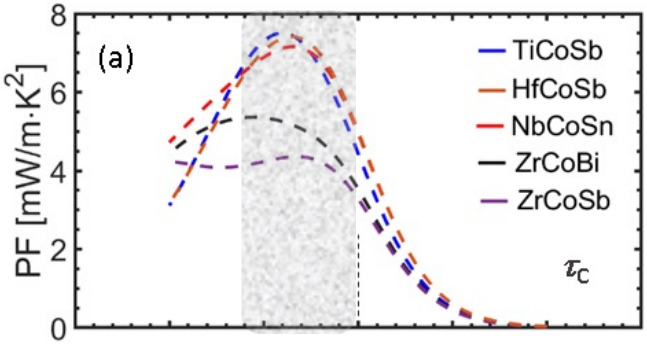
$$\left|S_{k,k'}^{(IIS)}\right| = \frac{2\pi}{\hbar}\frac{Z^2 e^4}{k_S^2 \varepsilon_0^2}\frac{N_{imp}}{\left(|k-k'|^2+\frac{1}{L_D^2}\right)^2}$$

DOI:10.5281/zenodo.5074943
https://github.com/PatrizioGraziosi/ELECTRA

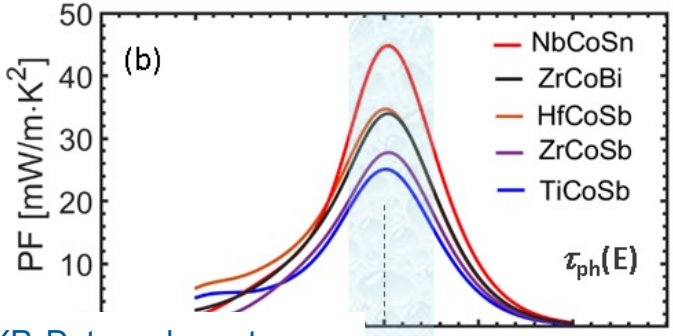
Full paper:
Graziosi, Li, NN,
Computer Physics Communications 108670, **2023**

Necessity beyond CRT

CRT
τ_C=10 fs

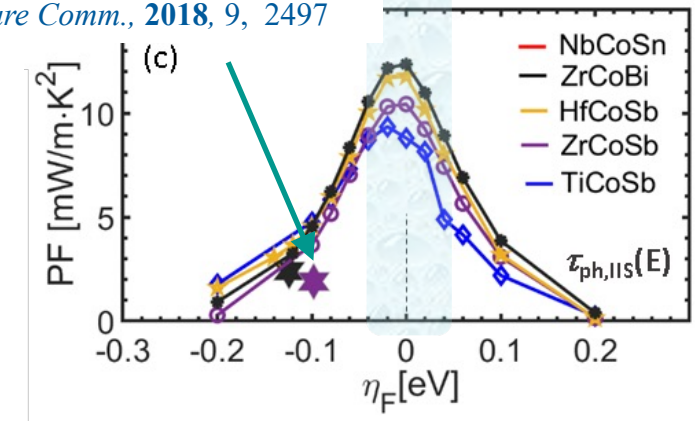


$\tau_{phonons}$

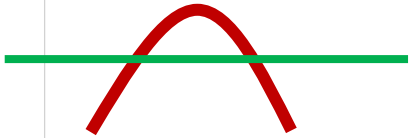


EXP. Data, polycryst.
Nature Comm., **2018**, 9, 2497

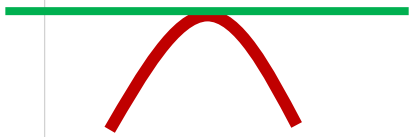
τ_{ph+IIS}



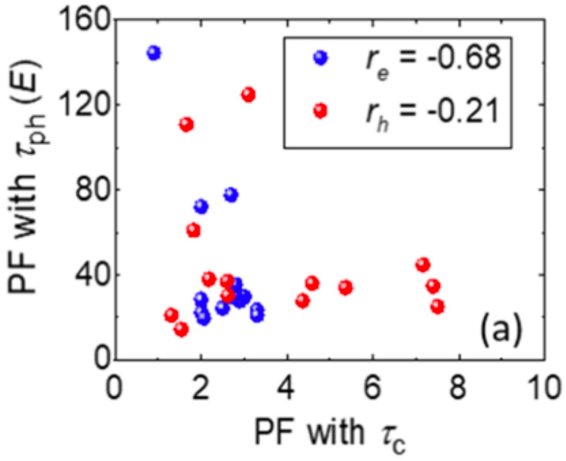
Best E_F τ_C



Best E_F τ_C



NO correlation between τ_C and $\tau_{ph(E)}$



- ✓ Difference in ranking
- ✓ Difference in optimal doping
- ✓ Different temperature trends
- ✓ Much larger PF can be achieved

P. Graziosi, el. al., *J. Appl. Phys.*, **2019**, 126, 155701;
ACS Appl. Energy Mater., **2020**, 3: 5913-5926

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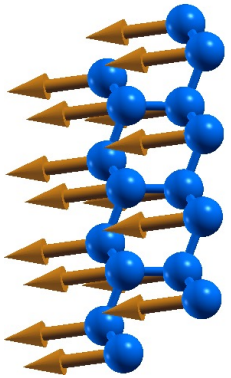
Beyond acoustic deformation potential

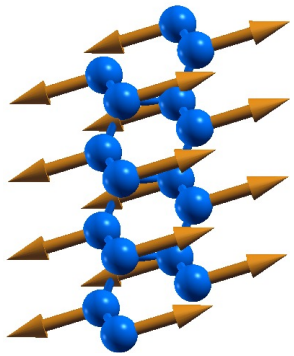
- **Acoustic deformation potential:** $D_{\mathrm{ADP}} = \frac{M^{\nu}_{mn}(\mathbf{k},\mathbf{q})}{|\mathbf{q}|}$

Acoustic phonons: Perturbing potential $V_{\mathrm{e-ph}} = D_{\mathrm{ADP}}\boldsymbol{\nabla}\cdot\boldsymbol{u}$



- **Optical deformation potential:** $D_{\mathrm{ODP}} = M^{\nu}_{mn}(\mathbf{k},\mathbf{q})$

Optical phonons: Perturbing potential: $V_{\mathrm{e-ph}} = D_{\mathrm{ODP}}\boldsymbol{u}$



- **Intervalley deformation potential:** $D_{\mathrm{IVS}} = M^{\nu}_{mn}(\mathbf{k},\mathbf{q})$

The case of Si

$$M^{\nu}_{mn}(\mathbf{k},\mathbf{q}) = <\psi_{m\mathbf{k}+\mathbf{q}}(\mathbf{r})\left|\delta_{\nu\mathbf{q}}V(\mathbf{r})\right|\psi_{n\mathbf{k}}(\mathbf{r})>$$

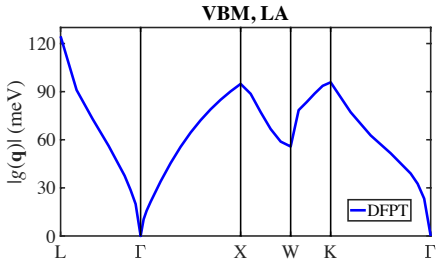
DFT calculations: *band structure, wavefunctions*

DFPT calculations: *dynamical matrix, phonon perturbation*

Z. Li, et al., *Phys. Rev. B*, **2021**, 104, 195201

Deformation potential extraction

$$g^{\nu}_{mn}(\mathbf{k},\mathbf{q}) = \sqrt{\frac{\hbar}{2m_0\omega_{\nu\mathbf{q}}}}\, M^{\nu}_{mn}(\mathbf{k},\mathbf{q}) \quad \Rightarrow \quad g^{\nu}_{mn}(\mathbf{k},\mathbf{q}) = \sqrt{\frac{\hbar}{2m_0\omega_{\nu,\mathbf{q}}}} < m,\mathbf{k}+\mathbf{q}|\delta V_{\nu,\mathbf{q}}|n,\mathbf{k} >$$



- Density Functional Theory (DFT) calculations:
  band structure, electronic wavefunctions
  using the Quantum ESPRESSO package

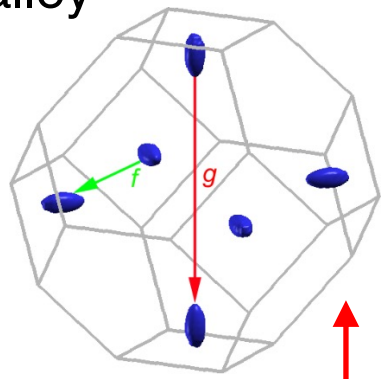
- Density Functional Perturbation Theory (DFPT) calculations:
  dynamical matrix, phonon perturbation
  using the Quantum ESPRESSO package

- Wannier Interpolation (if needed):
  e-ph coupling matrix, electron and phonon eigenvalues
  using the Electron-phonon Wannier package (EPW)

Nonpolar material: the case of Si

6-fold
intra-valley
inter-valley

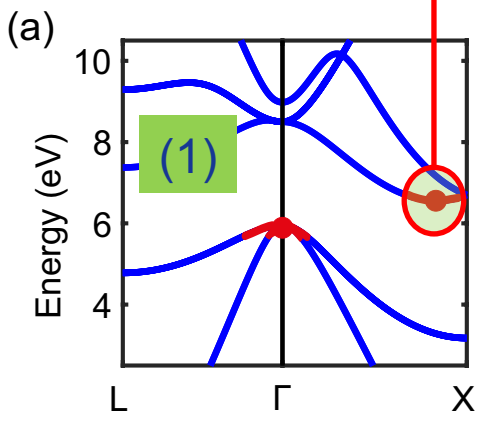
(2)



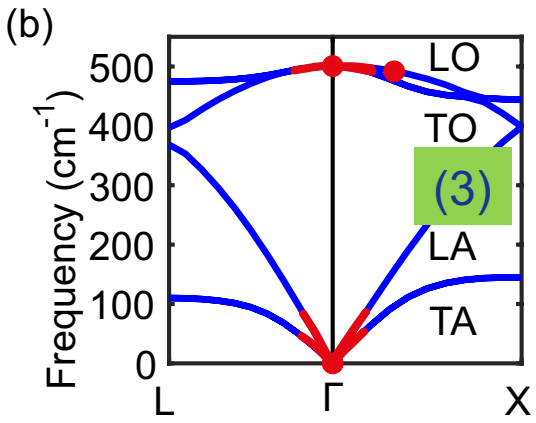
Steps:

1. Identify band extrema and energy range
2. Identify different possible transitions (intra/inter-valley)
3. Identify phonon modes that satisfy energy/momentum conservation
4. Extract matrix elements and *D*'s for all transitions

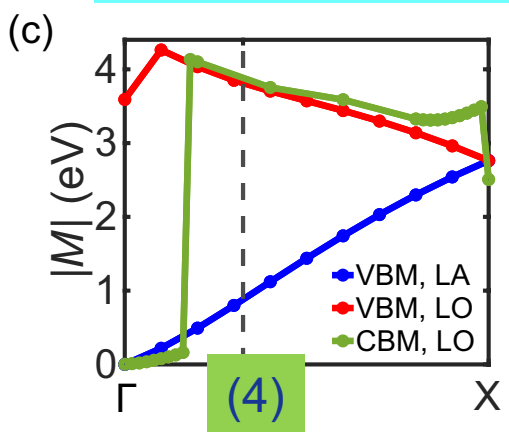
band-structure



phonon spectrum



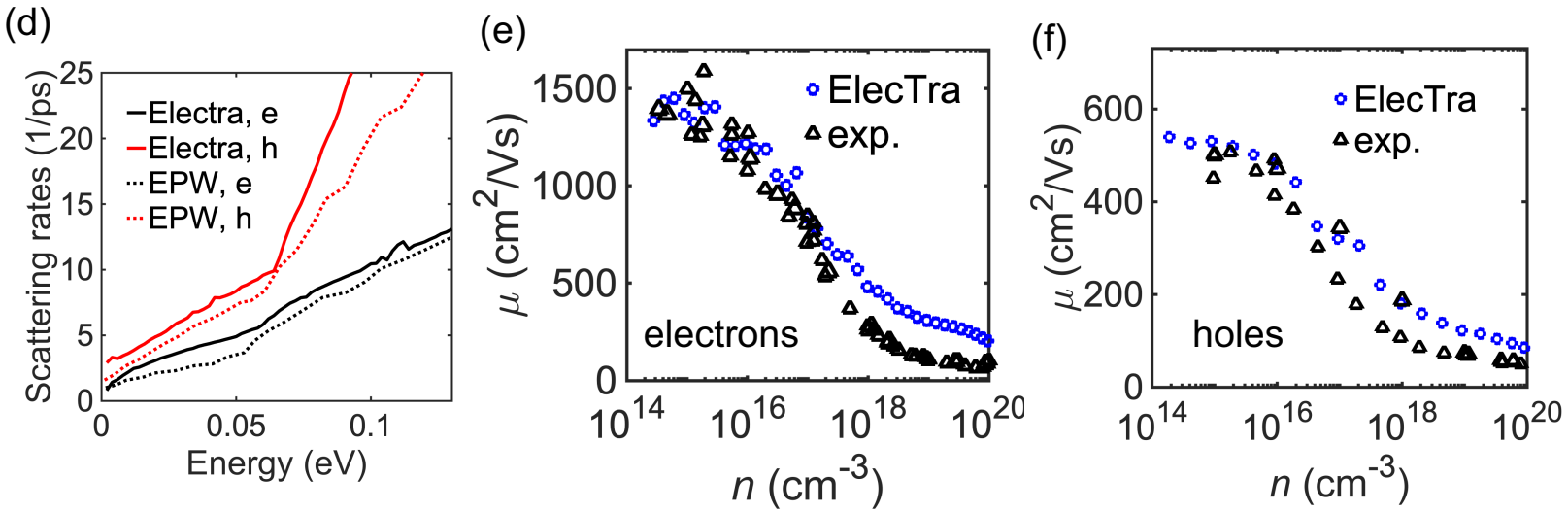
matrix elements



Z. Li, et al., *Phys. Rev. B*, **2021**, 104, 195201

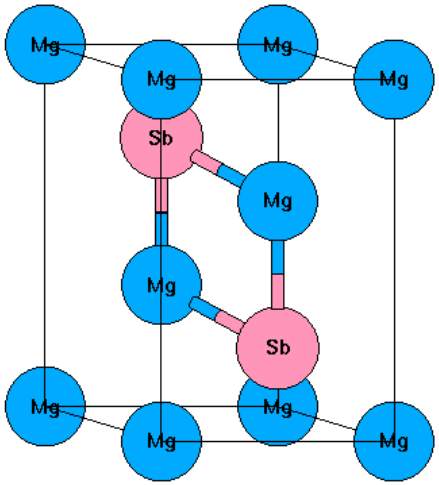
Si mobility from fully ab initio

Good agreement between our method and DFPT+Wannier / exp.

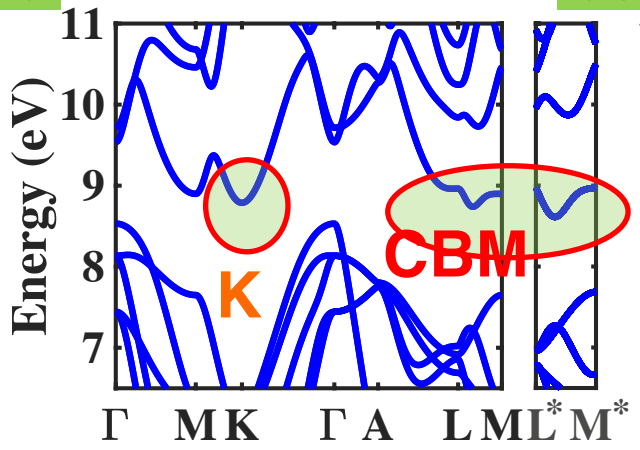


[1] Z. Li, et al., *Phys. Rev. B*, **2021**, 104, 195201
[2] J. Ma, et al., Phys. Rev. B 97, 045201 (2018)
[3] J. C. Irvin, Bell Syst. Tech. J. 41, 387 (1962).
[4] F. Mousty, et al., J. Appl. Phys. 45, 4576 (1974)
[5] W. R. Thurber, No. 64. US Department of Commerce, National Bureau of Standards (1981)
[6] G. Masetti, et al., IEEE Trans. Electron Devices 30, 764 (1983)
[7] C. Jacoboni, et al., Solid State Electron. 20, 77 (1977)

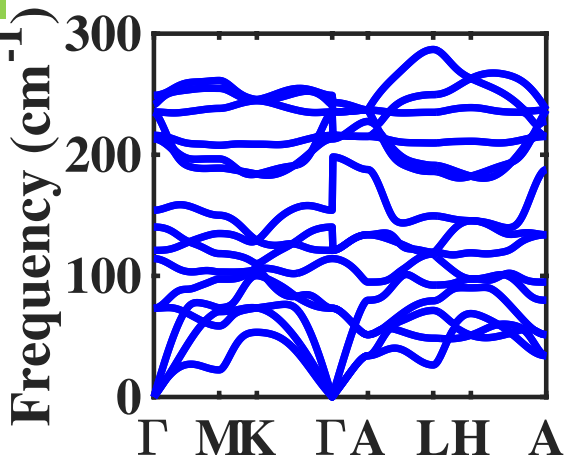
Polar material: the case of Mg_3Sb_2

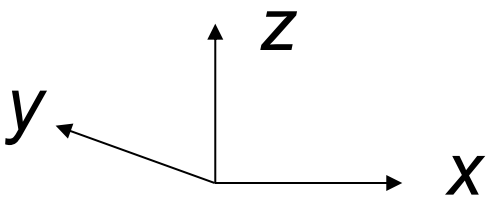


(1)



(3)

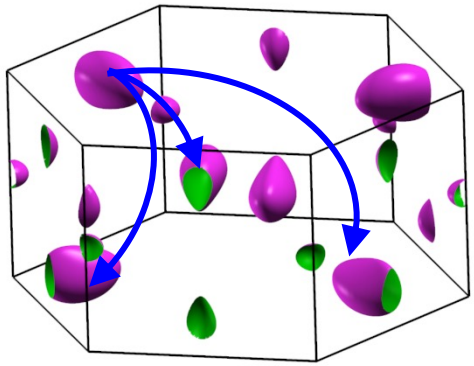


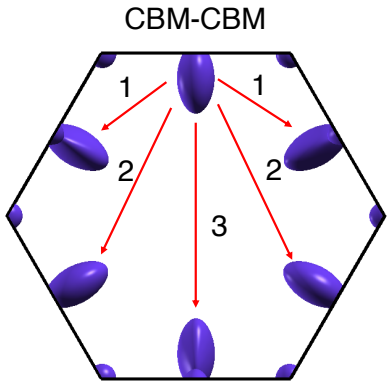


Hexagonal lattice

a = 4.592 Å

(2)

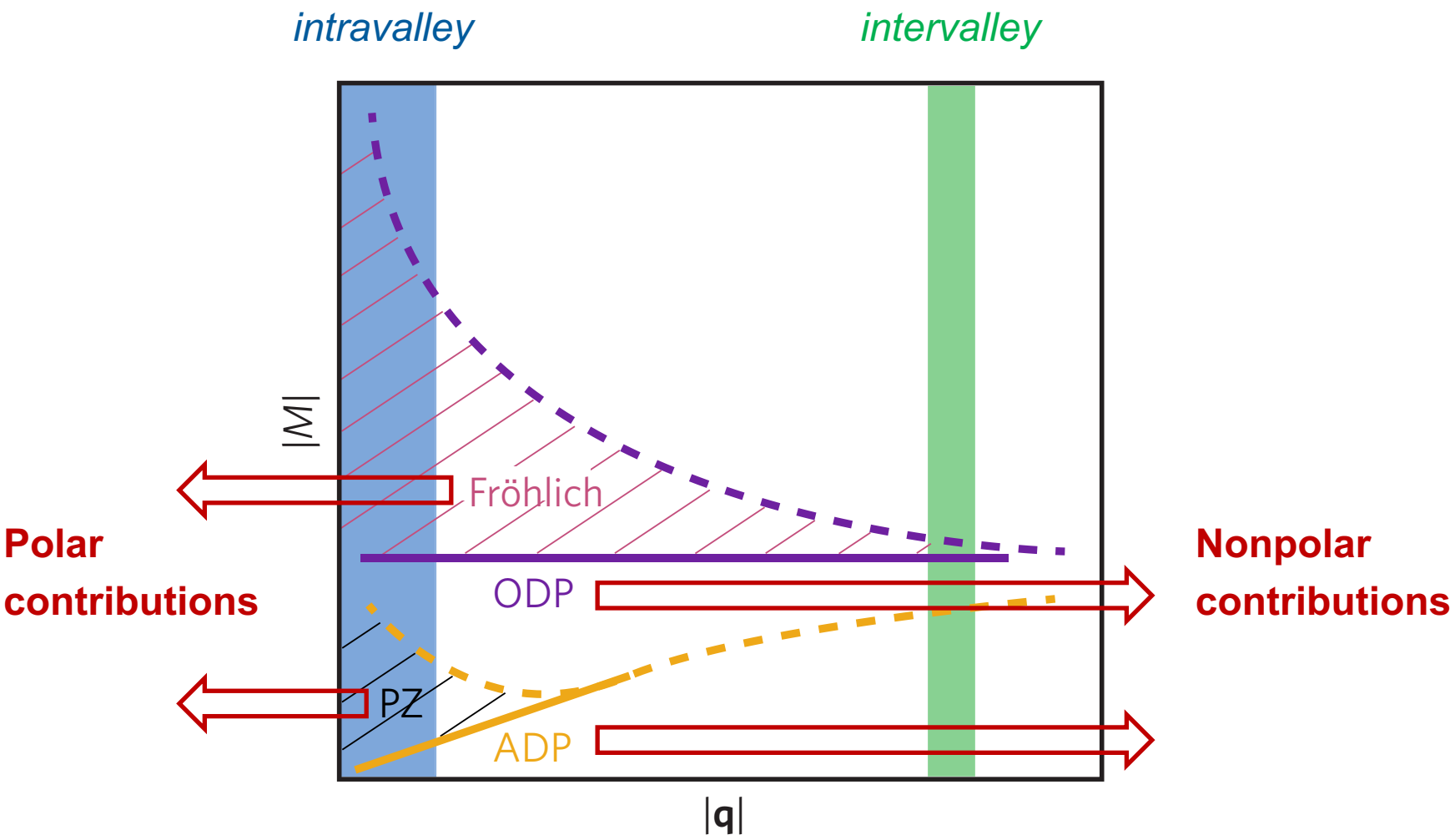




20 times more cost compared to Si
(makes EPW methods extraordinary expensive)

CBM to CBM: 6 valleys,
three transition types

Polar material



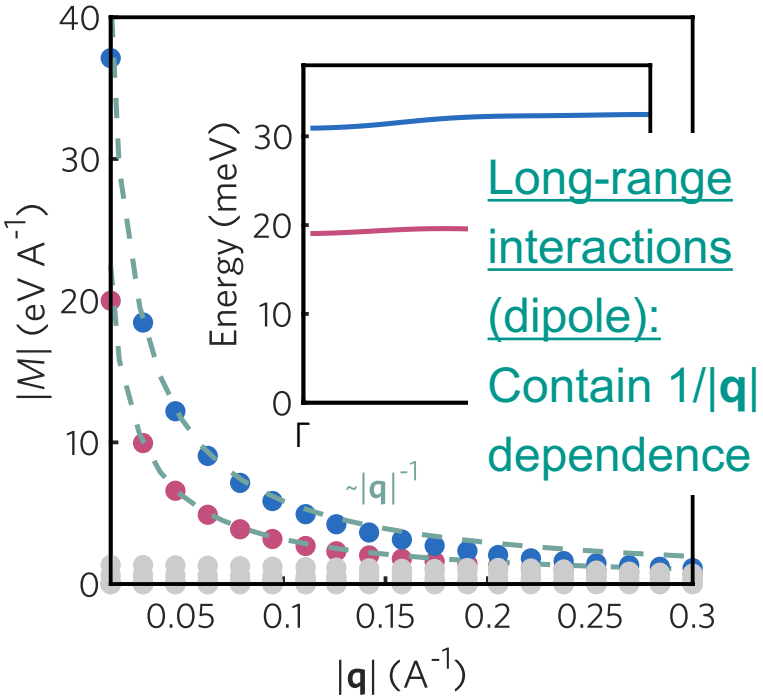
Various scattering channels at room temperature

Polar optical phonon treatment

➢ ***major scattering channel at room temperature***: Fröhlich interaction

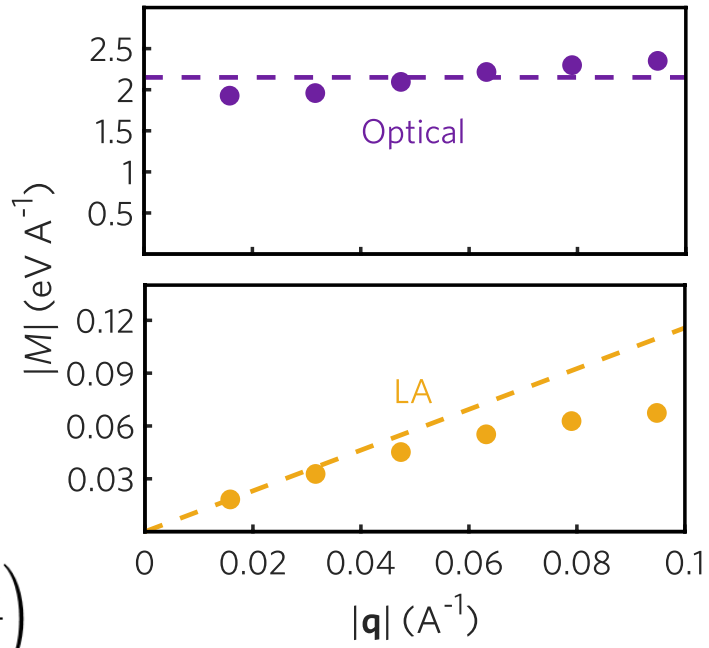
(1) Subtract this long range (dipole) part from the total

$$g^{L}_{mnv}(\mathbf{k},\mathbf{q}) = i\frac{4\pi}{\Omega}\frac{e^2}{4\pi\varepsilon_0}\sum_k\left(\frac{\hbar}{2NM_k\omega_{\mathbf{q}v}}\right)^{1/2}\times\sum_{\mathbf{G}\neq-\mathbf{q}}\frac{(\mathbf{q}+\mathbf{G})\cdot\mathbf{Z}^*_k\cdot e_{kv}(\mathbf{q})}{(\mathbf{q}+\mathbf{G})\cdot k_\infty\cdot(\mathbf{q}+\mathbf{G})}\times<\psi_{m\mathbf{k}+\mathbf{q}}(\mathbf{r})\left|e^{i(\mathbf{q}+\mathbf{G})r}\right)\left|\psi_{n\mathbf{k}}(\mathbf{r})>$$



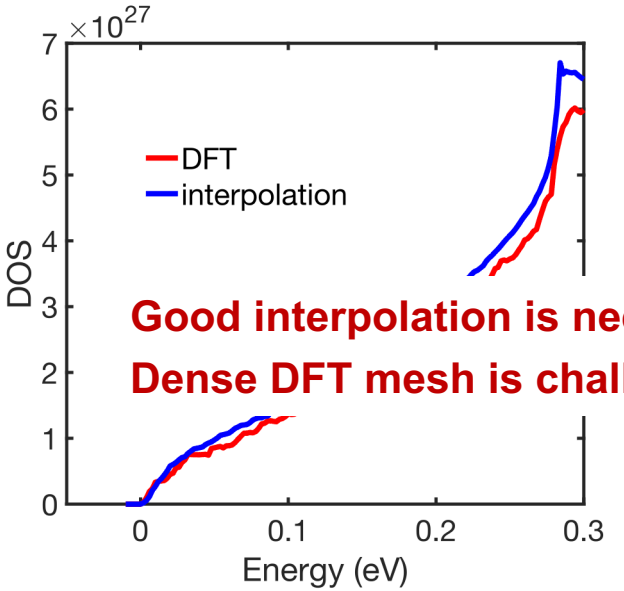
Long-range interactions (dipole): Contain 1/|**q**| dependence

(2) Use the remaining part to extract *D*'s



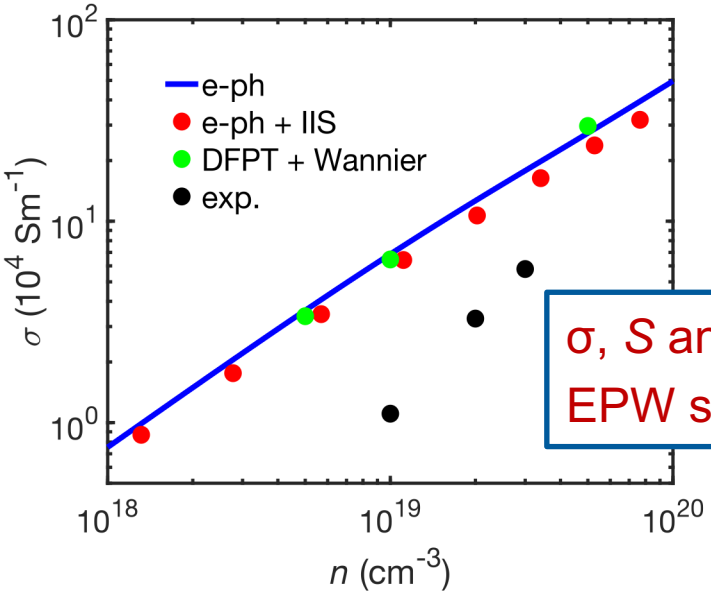
$$\left|S_{\boldsymbol{k},\boldsymbol{k}'}{}^{(\mathrm{POP})}\right| = \frac{\pi e^2\omega}{|\boldsymbol{k}-\boldsymbol{k}'|^2\varepsilon_0}\left(\frac{1}{k_\infty}-\frac{1}{k_s}\right)\left(N_{\omega,BE}+\frac{1}{2}\mp\frac{1}{2}\right)$$

Transport properties for Mg_3Sb_2

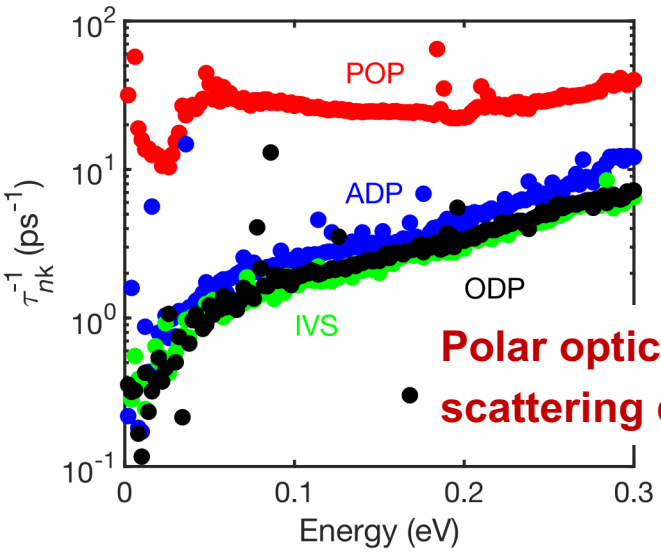


Good interpolation is needed.

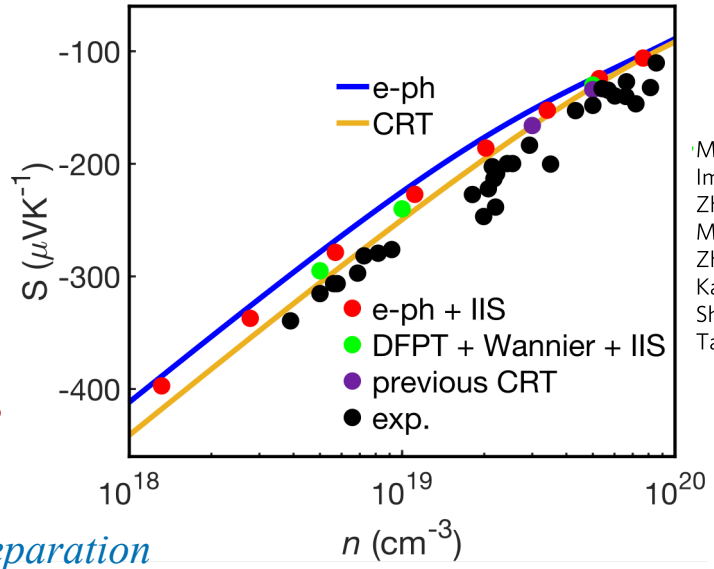
Dense DFT mesh is challenging.



σ, *S* and *μ* match EPW studies well



Polar optical phonon scattering dominates



Meng et al. 2020, calc., EPW
Imasato et al. 2018, exp.
Zhang et al. 2017, exp.
Mao et al. 2017, exp.
Zhang et al. 2017, exp.
Kanno et al. 2018, exp.
Shi et al. 2019, exp.
Tamaki et al. 2016, exp.

in preparation

Contents

I. **Low field transport methods from ab initio**
   - Constant relaxation time approximation (CRT)
   - Electron Phonon Wannier (EPW)
   - Deformation potential

II. **Deformation potential beyond ADP**
   - Non-polar materials: Case of Si
   - Polar materials complexities: case for Mg_3Sb_2

III. **Efficiency**

Efficiency

High performance computing clusters: 1 node = 16 CPUs

EPW

Meshes:

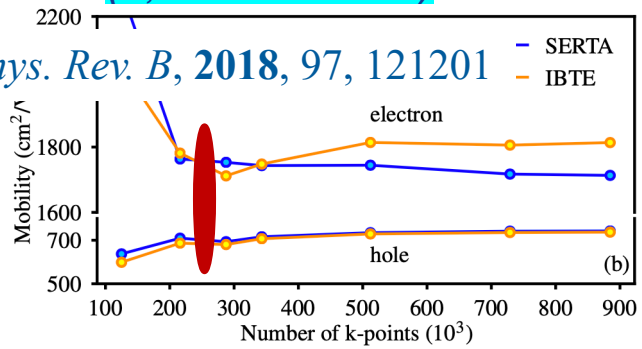
- ✓ DFT wavefunctions/ DFPT calc.
- ✓ 12×12×12 k-mesh, 6×6×6 q-mesh
- ✓ Interpolate k-mesh with Wannier

Transport- EPW (main cost):

- ✓ *Several millions of* matrix elements
- ✓ compute transport

Cost: 64×64×64: *< 20 hr on 16 nodes*

✓ *(5,000 CPU hrs)*



this method

Meshes:

- ✓ DFT wavefunctions/ DFPT calc.
- ✓ gives the 'original' k-mesh, q-meshe
- ✓ DFT bands or Wannier interp. bands
  - ✓ *(if DFT-a few hundred CPU hrs)*

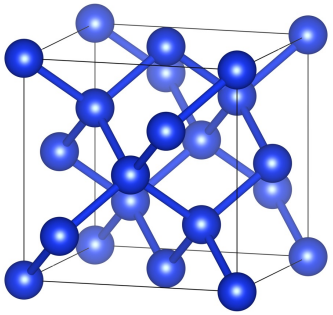
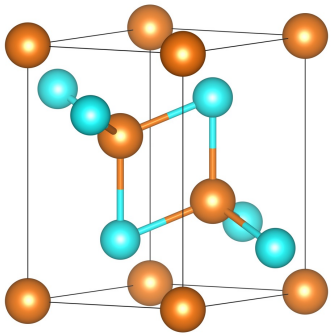
Transport:

- ✓ *A few matrix elements (100s)*
  - ✓ *DFPT (50 hrs on 1 node, 30min/element)*
  - ✓ *or EPW (2hrs on 1 node)*
- ✓ *Deformation pot. (minimal time)*

Transport cost: < 24 hrs on 1 node

✓ *(400 CPU hrs)*

Complexity for Mg_3Sb_2

	Si	Mg_3Sb_2
		
Lattice system	cubic	hexagonal
Number of atoms (primitive cell)	2	5

DFT calculations for Mg_3Sb_2: 20× the time of Si

Too difficult for fully ab initio calculations of transport for Mg_3Sb_2

Conclusions

Novel formalism for electronic transport in complex materials

1) Newly developed numerical simulator for BTE in complex TE materials:

Allows the incorporation of e-ph, ionized impurity, and alloy scattering, etc.;

ElecTra: 10.5281/zenodo.5074944
P. Graziosi, et al., *ACS Appl. Energy Mater.*, **2020**, 3, 5913-5926
Z. Li, et al., *Crystals*, **2022**, 12, 11, 1591 (invited)
P. Graziosi, el. al., *Comput. Phys. Commun.*, **2023**, 108670

2) First-principles framework to extract el-ph. scattering rates:

Extract acoustic, optical, and intervalley deformation potentials for use in BTE;

Z. Li, et al., *Phys. Rev. B,* **2021**, 104, 195201

Truly enabling, <u>accurate</u>, and <u>computationally efficient</u> method:

Middle ground between the CRT and fully first-principles Wannier-type methods.

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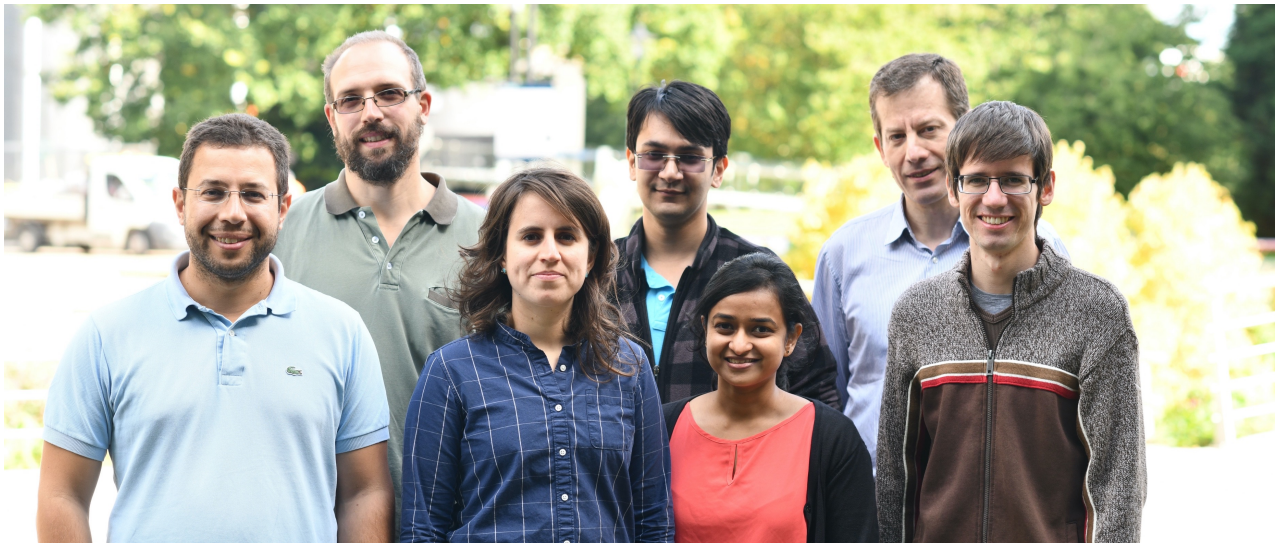

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