

Ab initio study of Silver chloride: Becquerel's photochromatic photography

Arnaud Lorin
LSI, Ecole Polytechnique

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Outline

- Introduction & Motivation
First color photography
- Silver chloride: The prototype of photography material.
- Ab initio study of band structure and optical properties.
- Conclusion and perspectives.

(A brief) History of photography

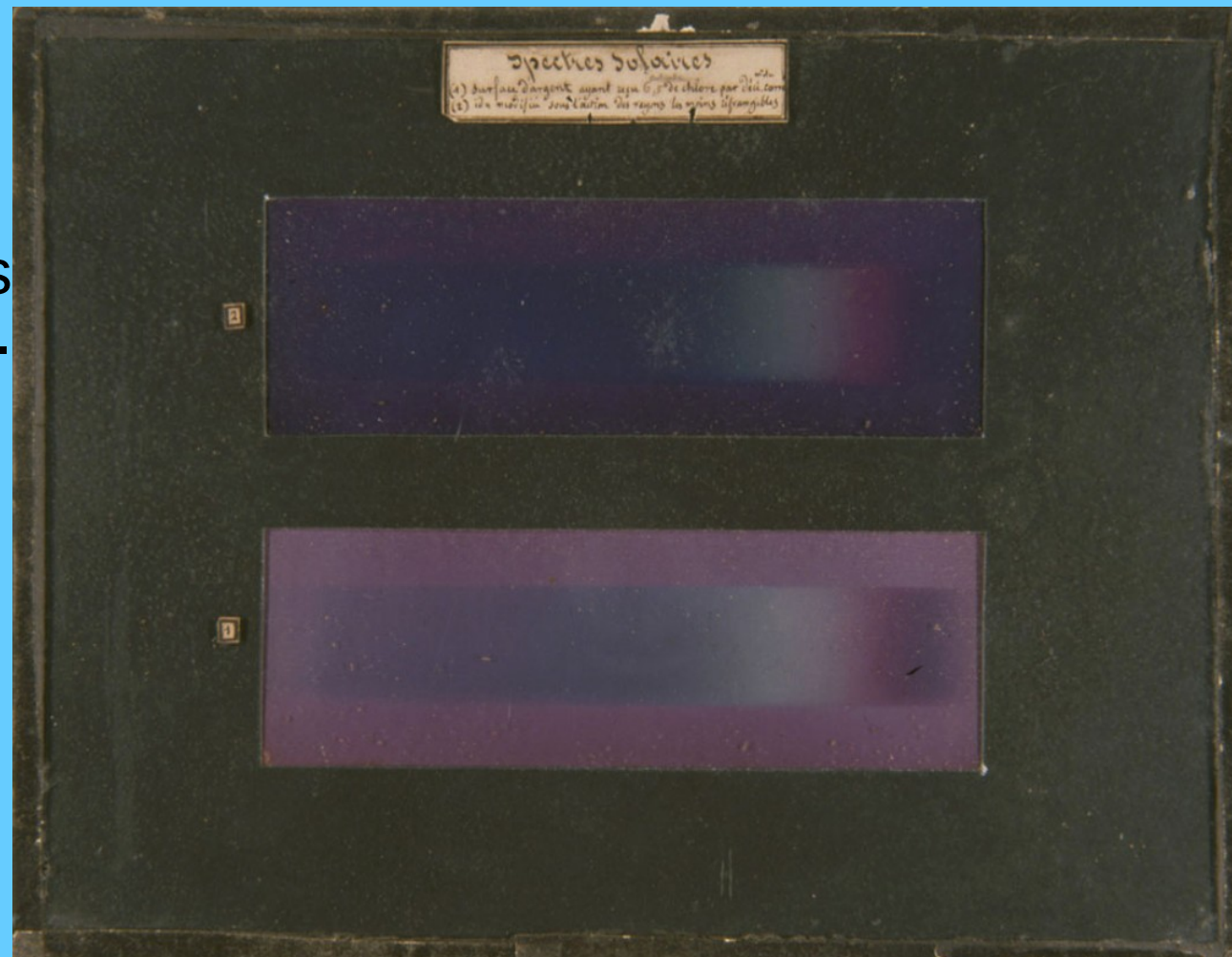
- 1826: Earliest remaining photograph by Nicéphore Niépce.
- 1839 : Black and White photography by Daguerre.
- 1848 : Color photography by Ed. Becquerel.
- 1861 : First tri-color photography.



Motivation

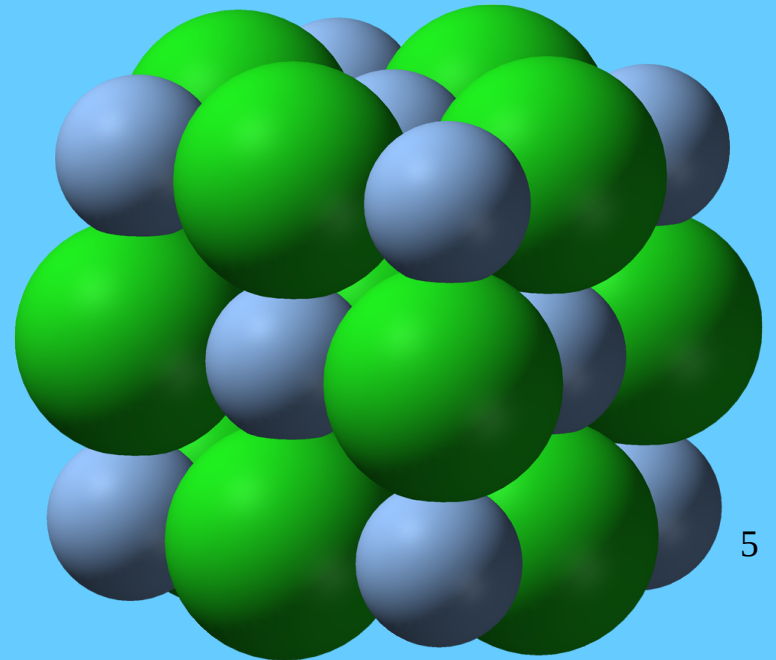
- Edmond Becquerel first color picture.
- Very fragile, process never stopped.
- Material able to adapt its color to the color of light.
- How to preserve it ?
How does it work ?
- Collaboration with the Museum national d'Histoire Naturelle (CRC).

Solar spectrum



Silver Chloride

- Perfect crystal of AgCl.
- FCC structure.
- Lattice parameter $a = 5.547\text{\AA}$.
- Widely use material:
 - Photography.
 - Electrochemistry.
 - Water cleaning.
 - Photocatalysis.
- Few theoretical studies.
- Benchmark study.



Electronic properties of AgCl Ground State

- DFT-LDA (PW)
- Parameters :
Experimental lattice parameter,
Ecut = 150Ha,
8x8x8 Monkhorst-Pack grid with 4 shifts.
- Abinit Code
<https://www.abinit.org/>



Electronic properties of AgCl

Optical Absorption

$$Abs(\omega) = \Im(\epsilon_M), \epsilon_M^{-1} = 1 + v\chi$$

- Linear response framework and TDDFT:

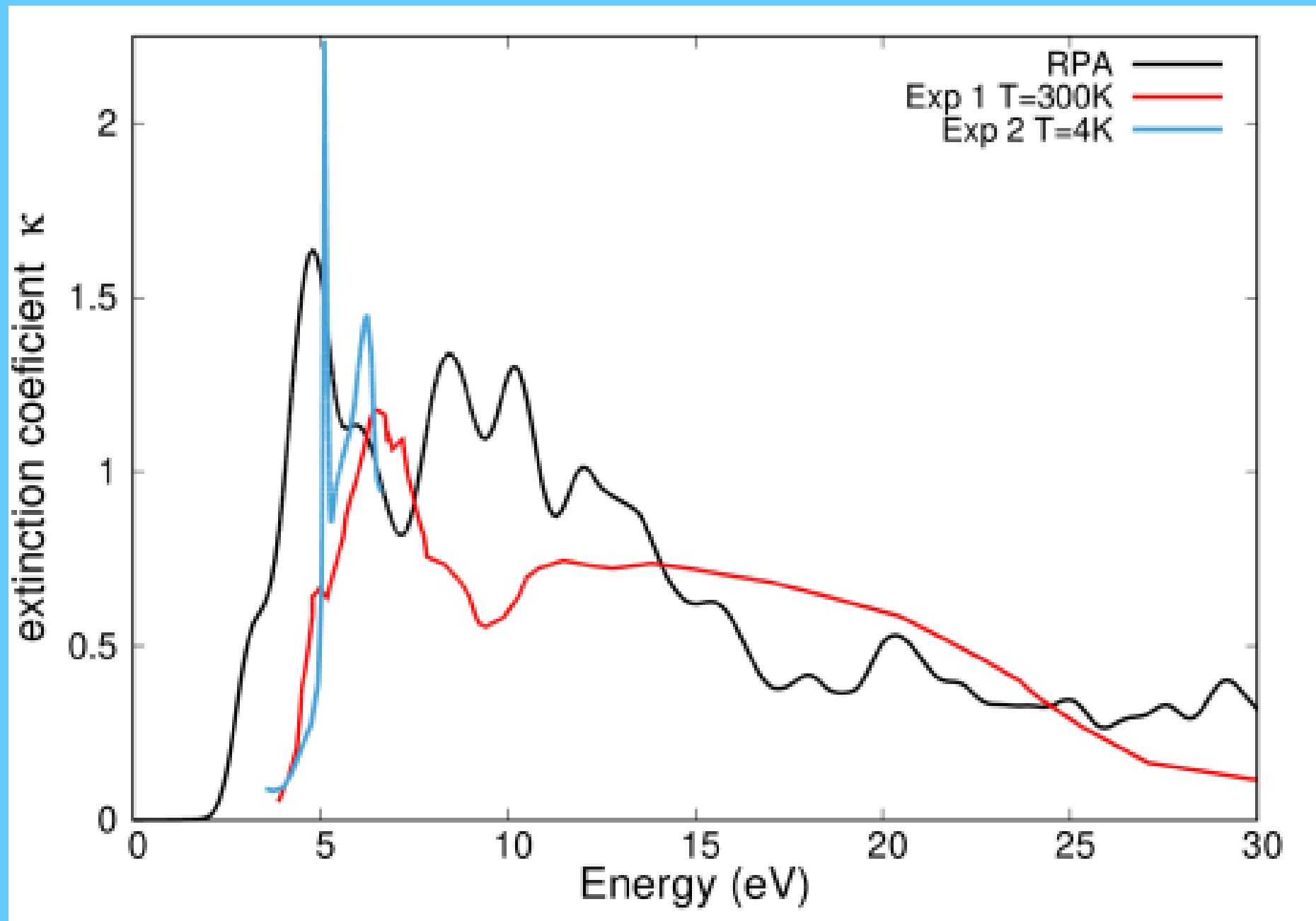
$$\chi = \chi_0 + \chi_0(v + f_{xc})\chi$$

- With Random Phase Approximation (RPA):

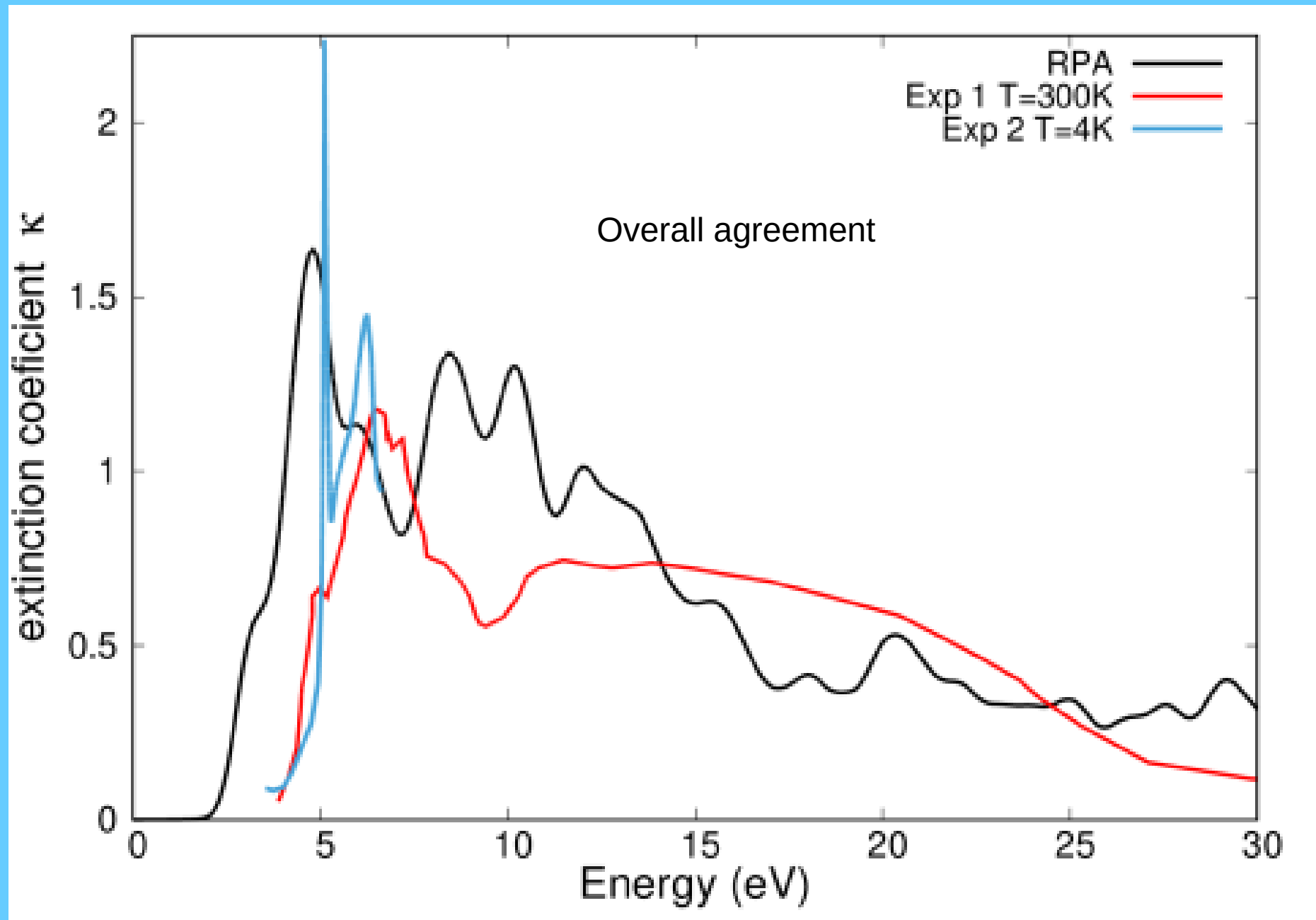
$$\chi^{RPA} = \chi_0 + \chi_0 v \chi^{RPA}$$

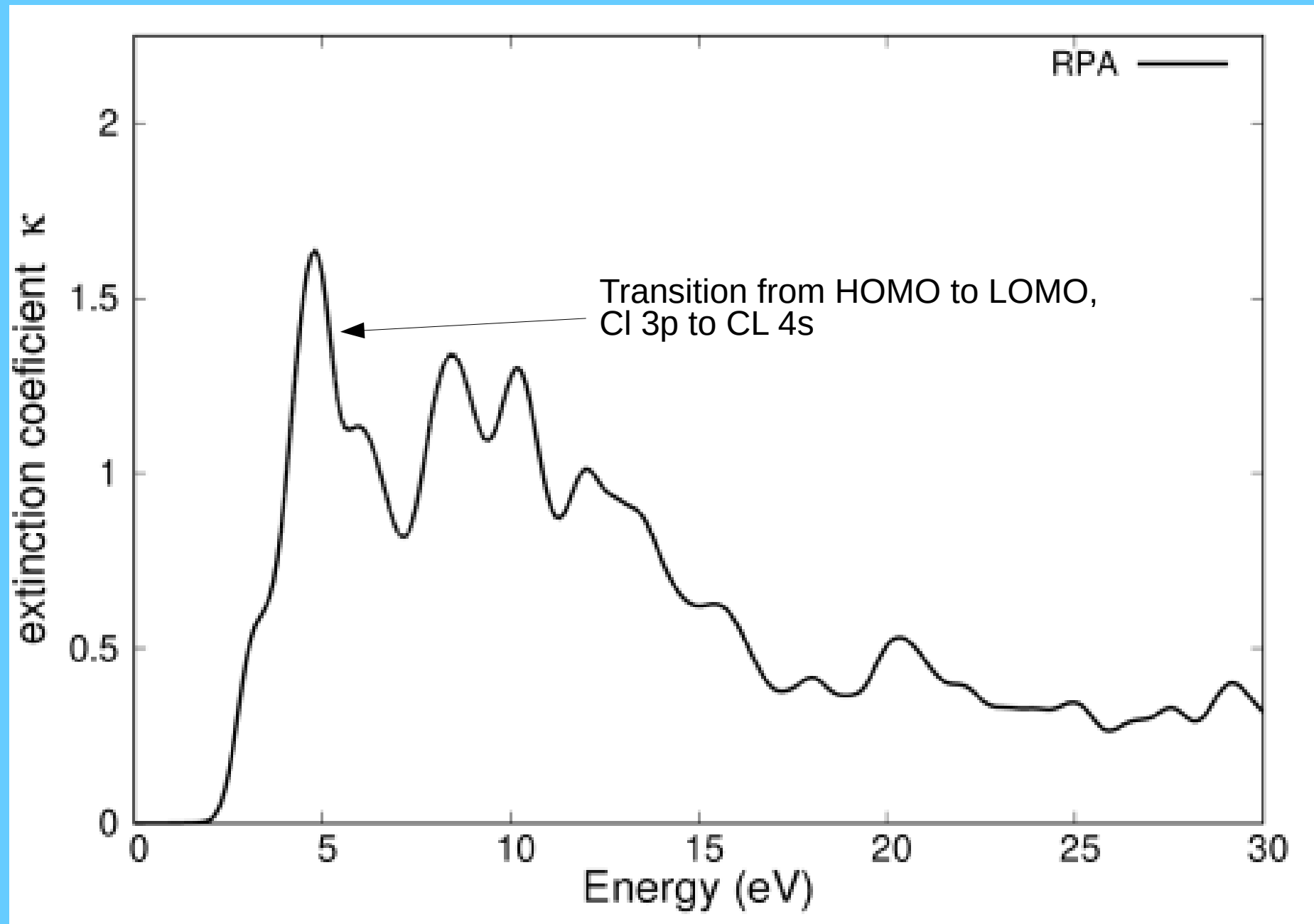
- TDDFT as implemented in the DP-code :

<http://www.dp-code.org/>



$$\kappa = \Im(\sqrt{\epsilon_M})$$



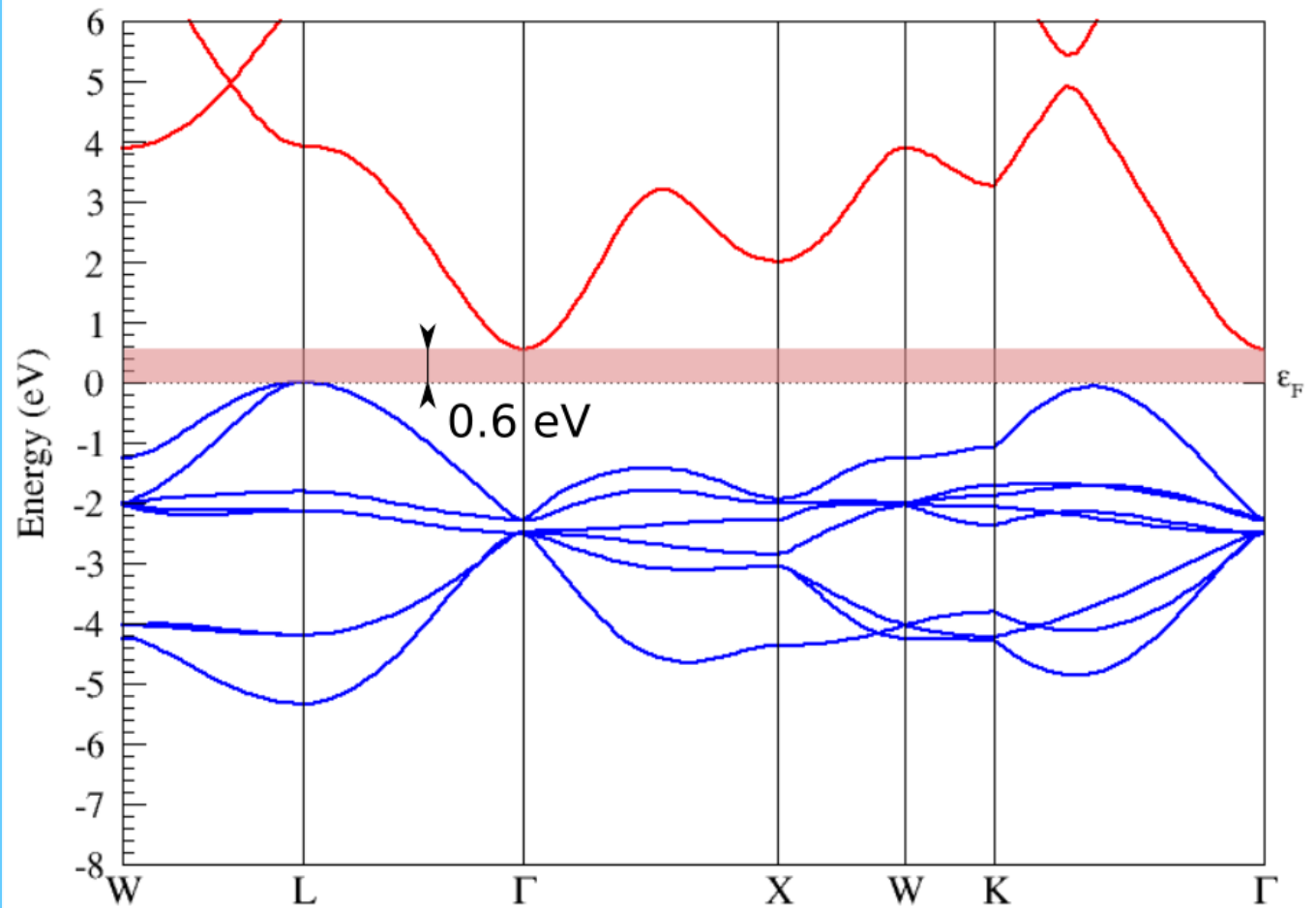


Band structure

- LDA
- $E_{\text{ind}} = 0,6 \text{ eV}$
- Transition $L \rightarrow \Gamma$
- Good agreement with other calculations:

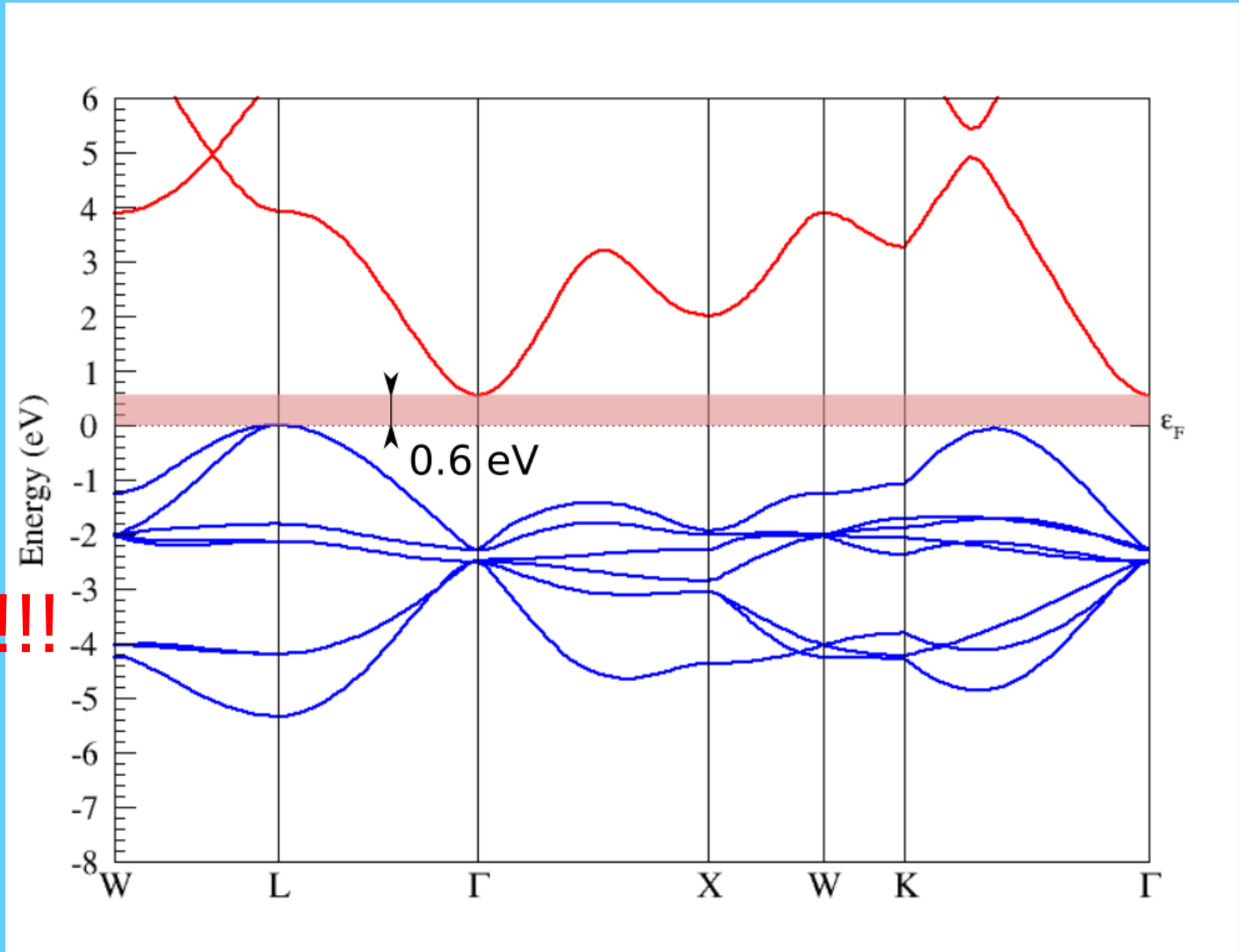
-Dirk Vogel, Peter Krüger, and Johannes Pollmann, Phys. Rev., 1998

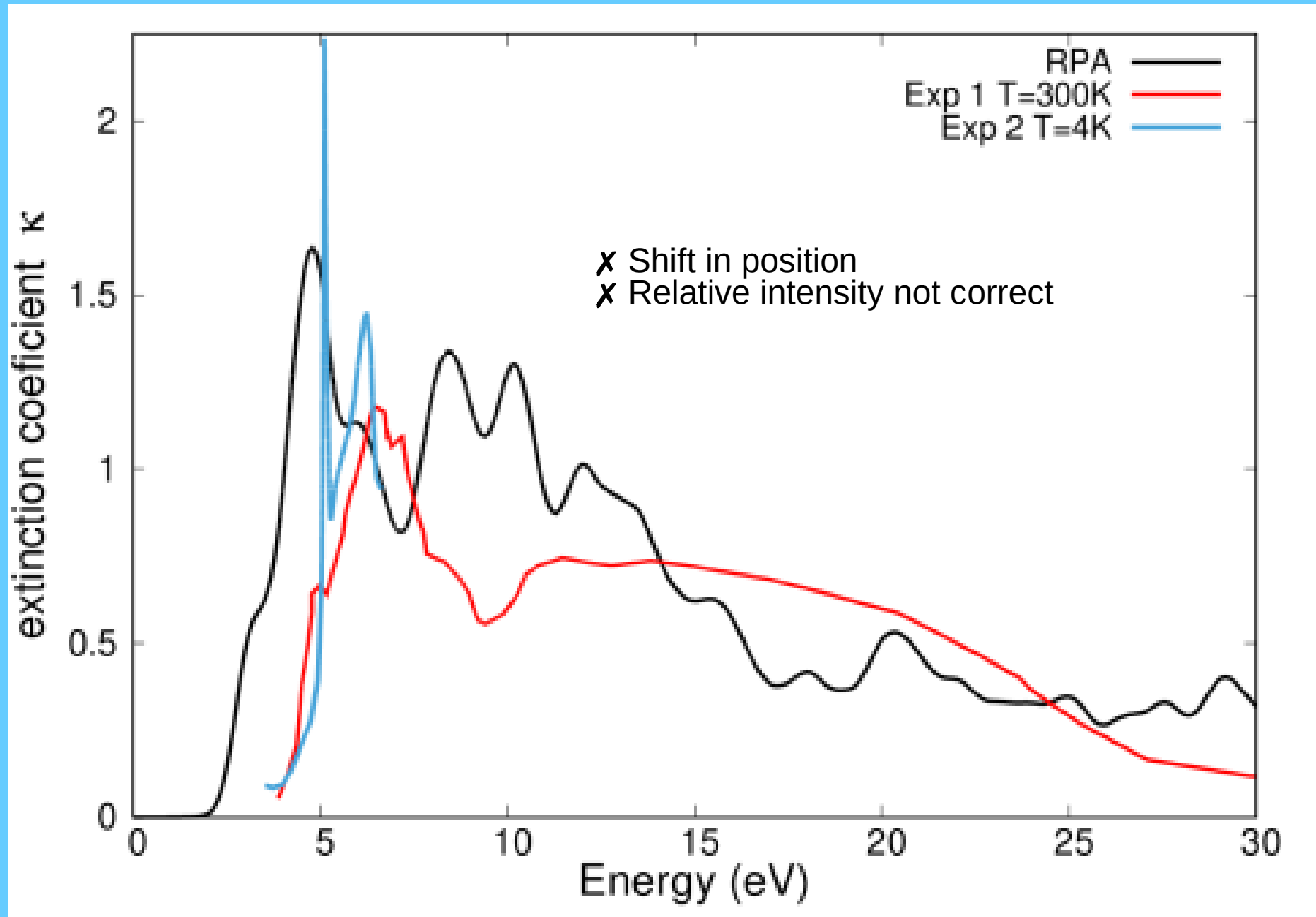
-de Boer and de Groot, *J. Phys. Chem. A*, 1999



Band structure

- LDA
- $E_{\text{ind}} = 0,6 \text{ eV}$
- Transition $L \rightarrow \Gamma$
- **But experimental gap 3.25 eV !!!!**





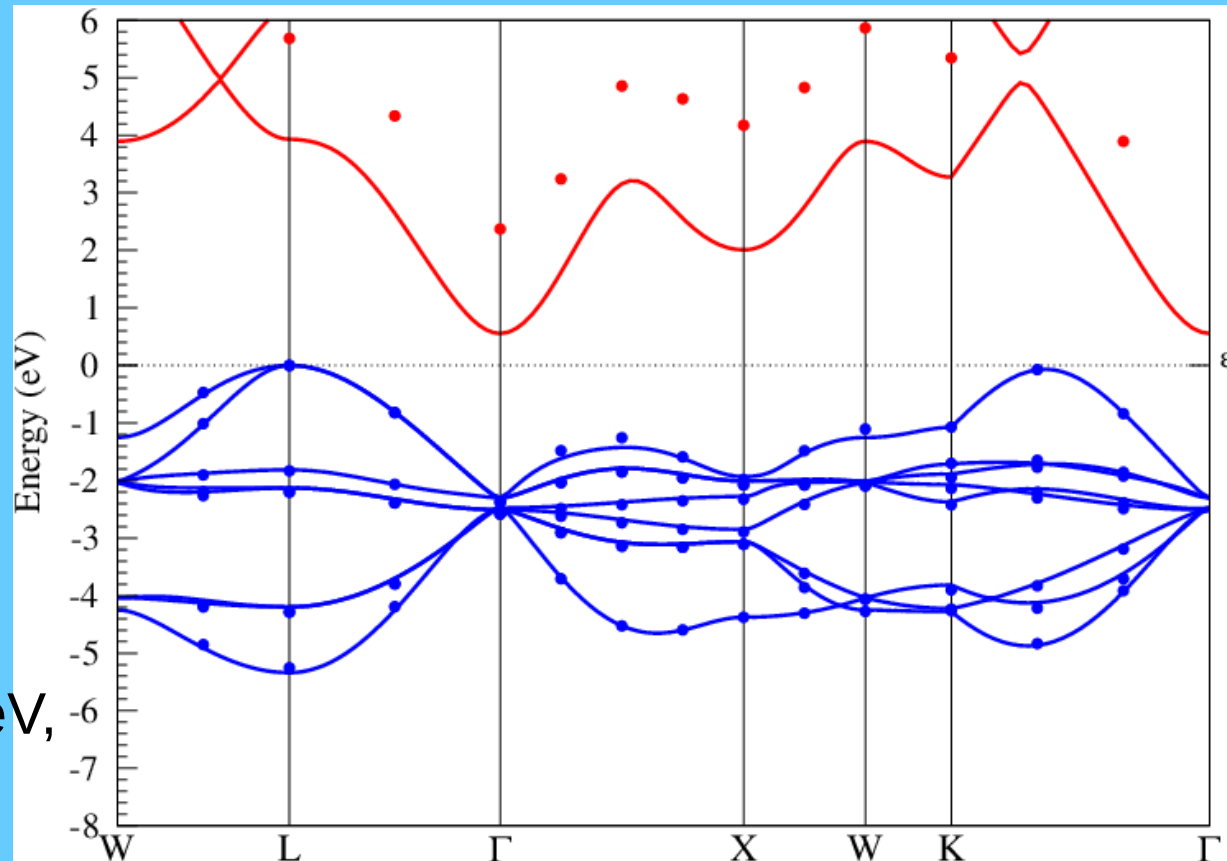
GW correction

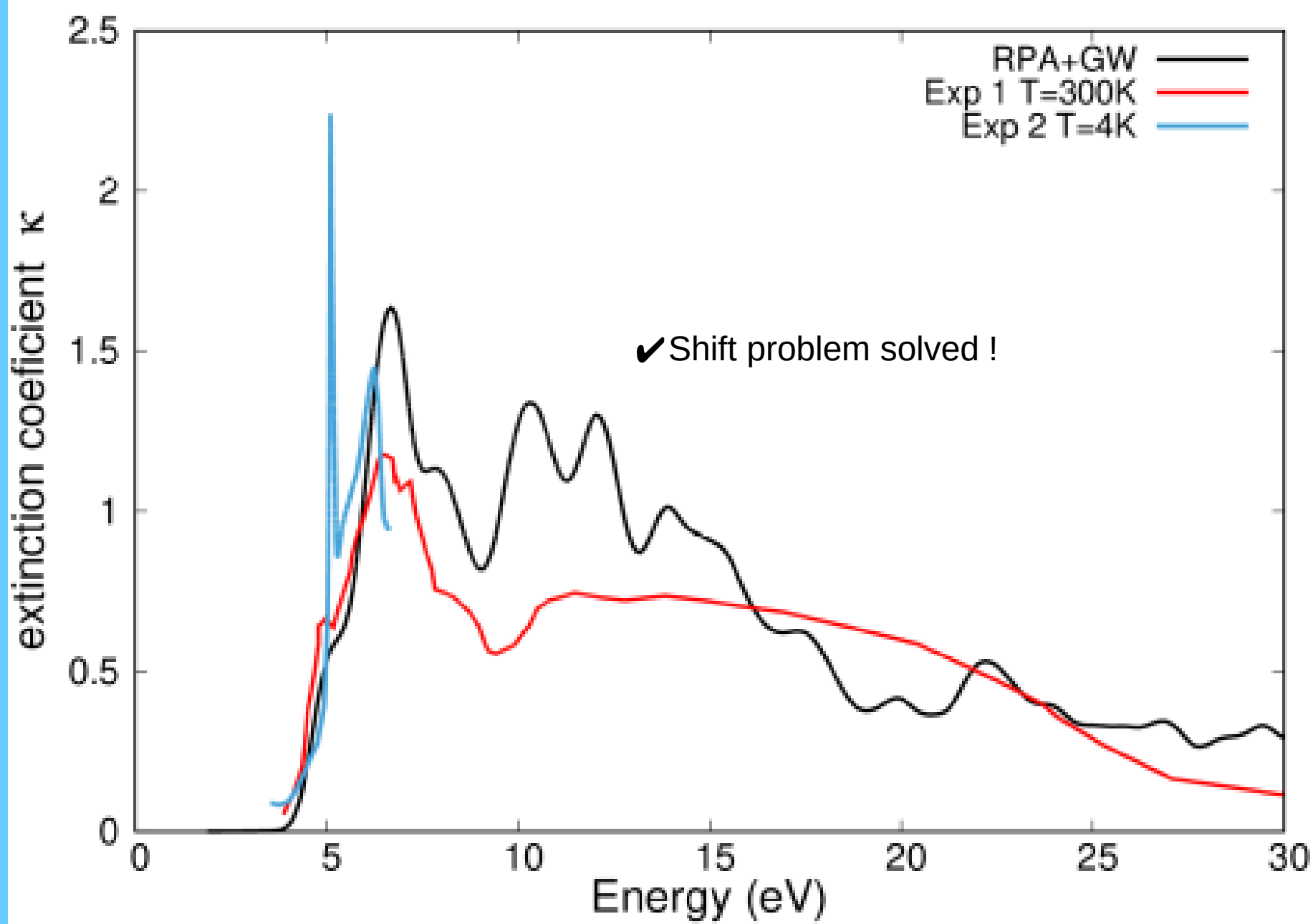
- Perturbative GW (G^0W^0)

$$E^{GW} = \epsilon^{LDA} + Z \langle \Sigma^{GW} - V_{xc}^{LDA} \rangle$$

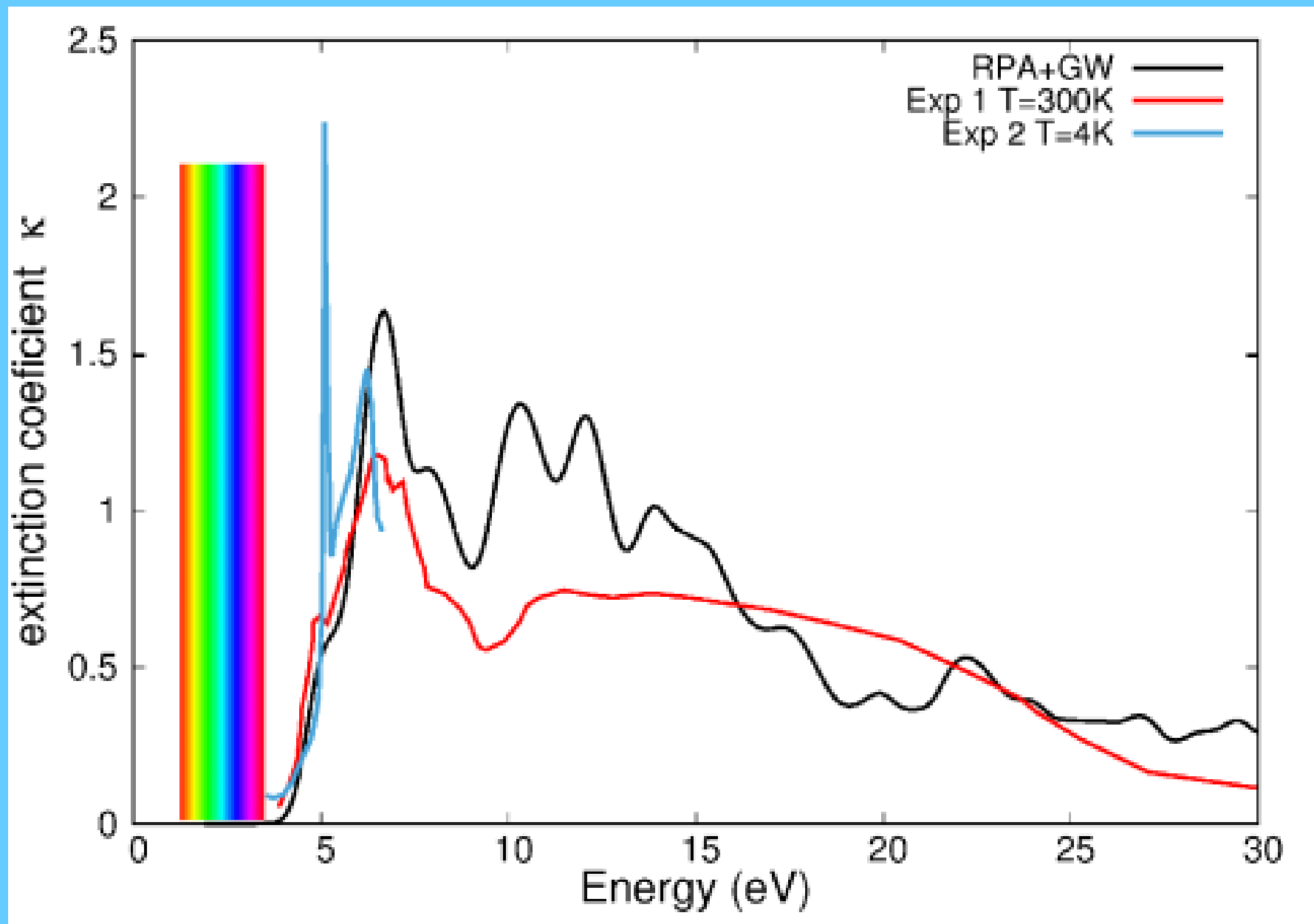
- Code Abinit
- 620 bands (330eV),
- Plasmon pole approximation.
- Effective Energy Technique.
 - 120 bands
 - 5% error
- Direct gap correction at Γ : 1.9eV,
at L: 1.6eV
- Indirect gap correction:

$$E_{ind}^{GW} = 2.5 eV (E^{exp} = 3.25 eV, E^{LDA} = 0.6 eV)$$





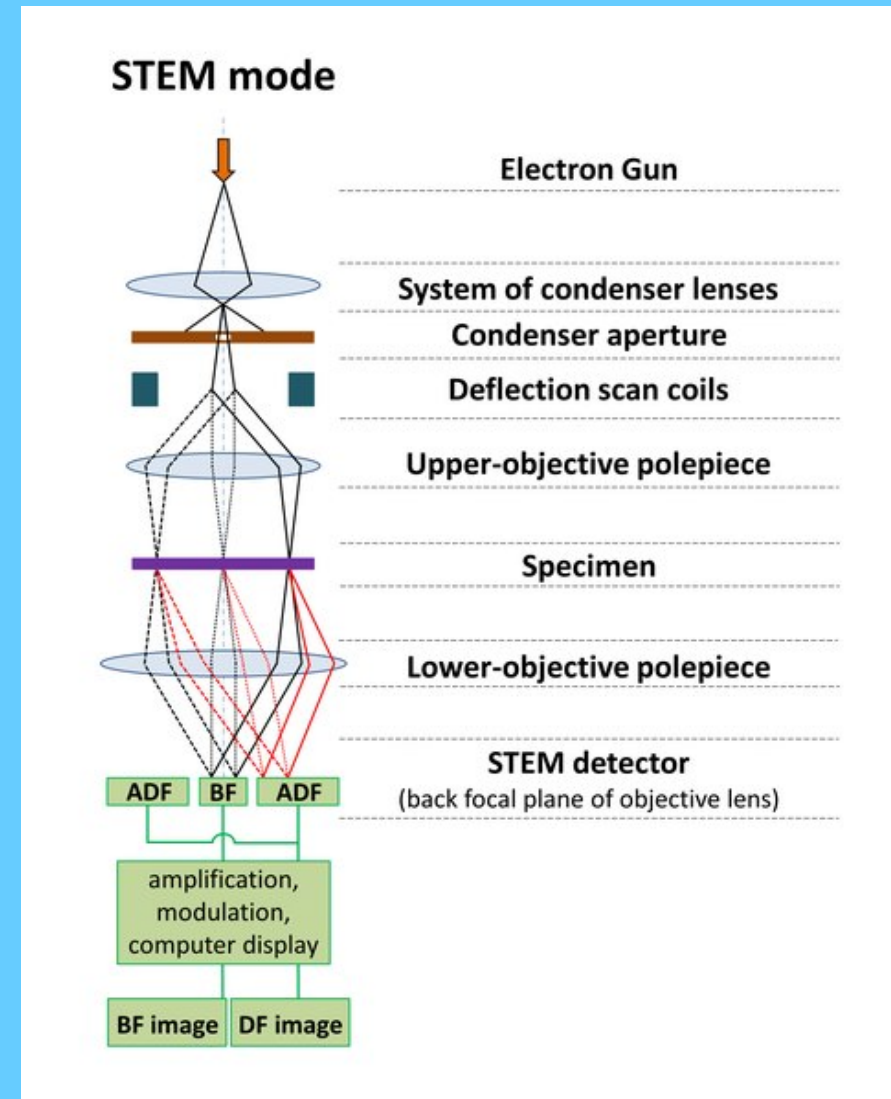
A little problem

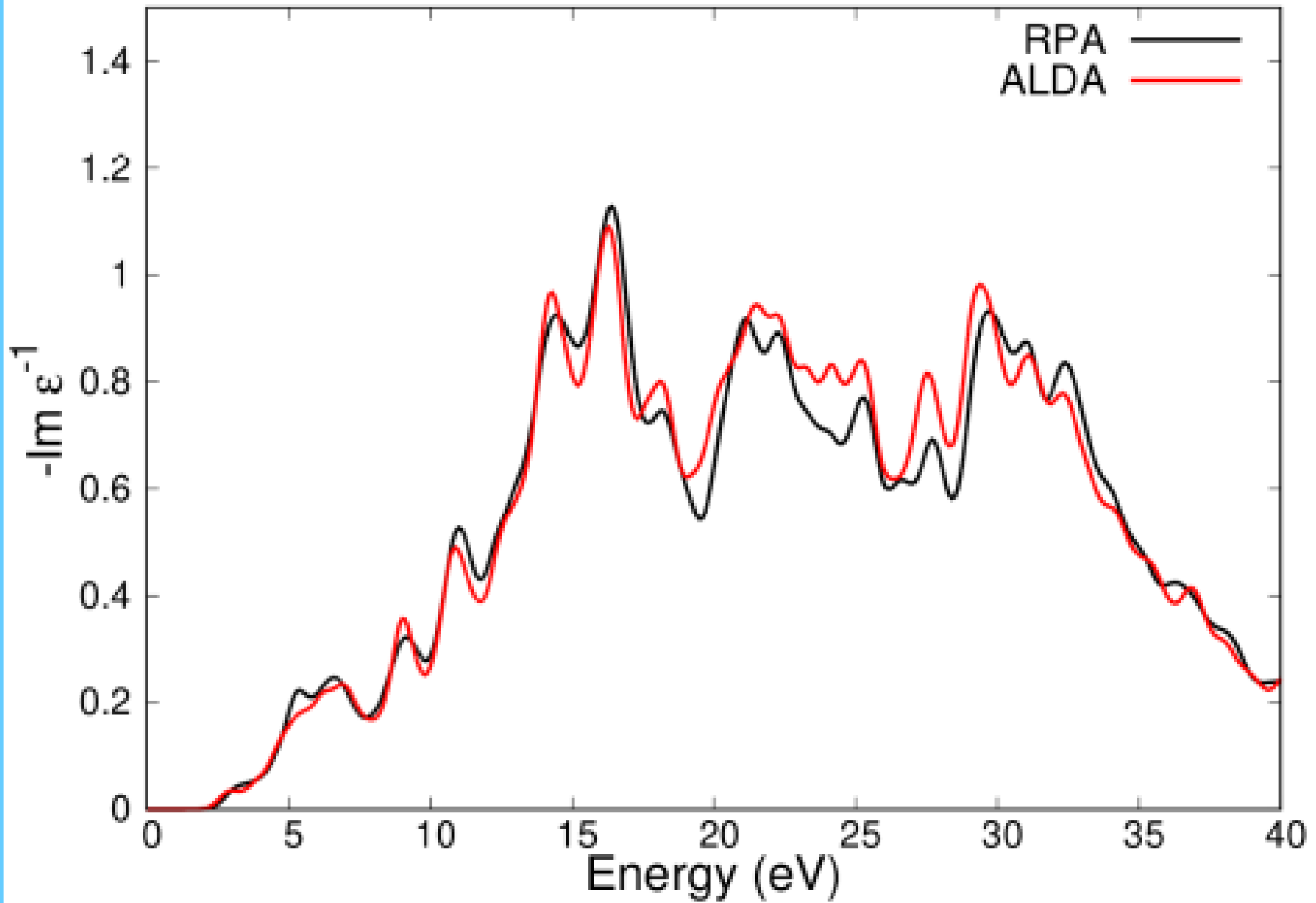


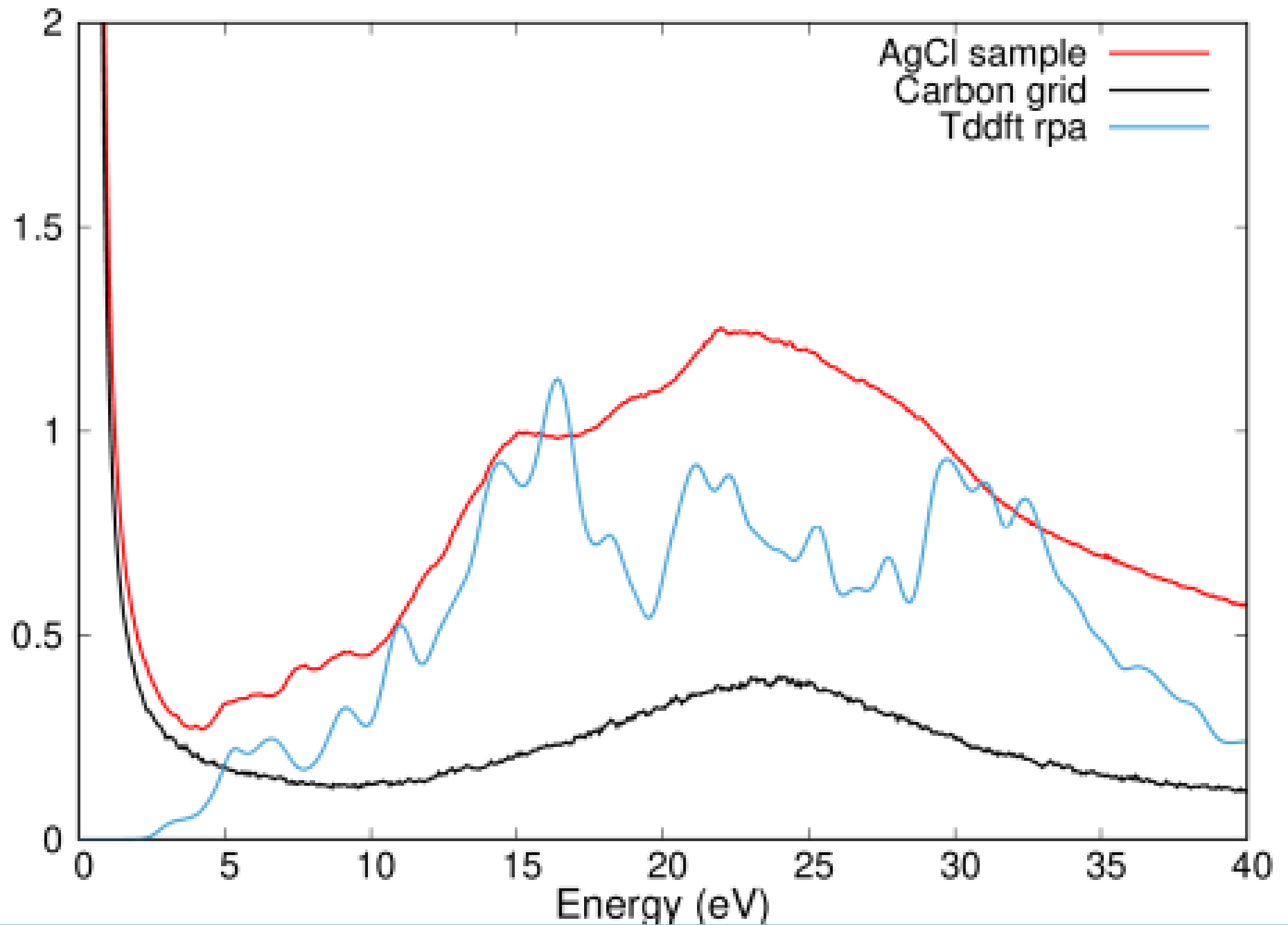
Electronic properties of AgCl

Electron Energy Loss

- Search for silver nanoparticles
- Reference for bulk silver chloride for experiment.
- Experiment at LPS, Orsay.
- Computation at $q \rightarrow 0$.
- $EELS(\omega) = -\Im(\epsilon_M^{-1})$

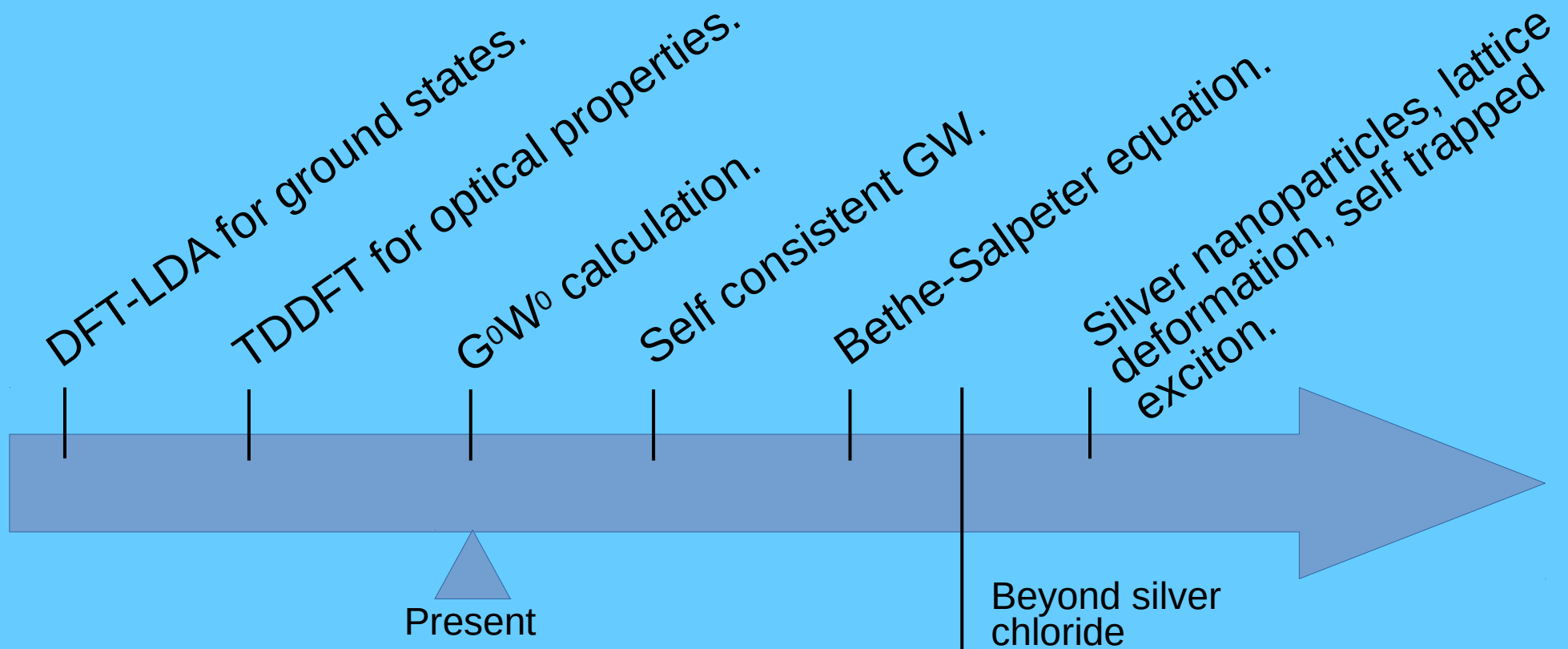






- Experiment at the LPS with Victor de Seauve (CRC) and Mathieu Kociak (LPS)

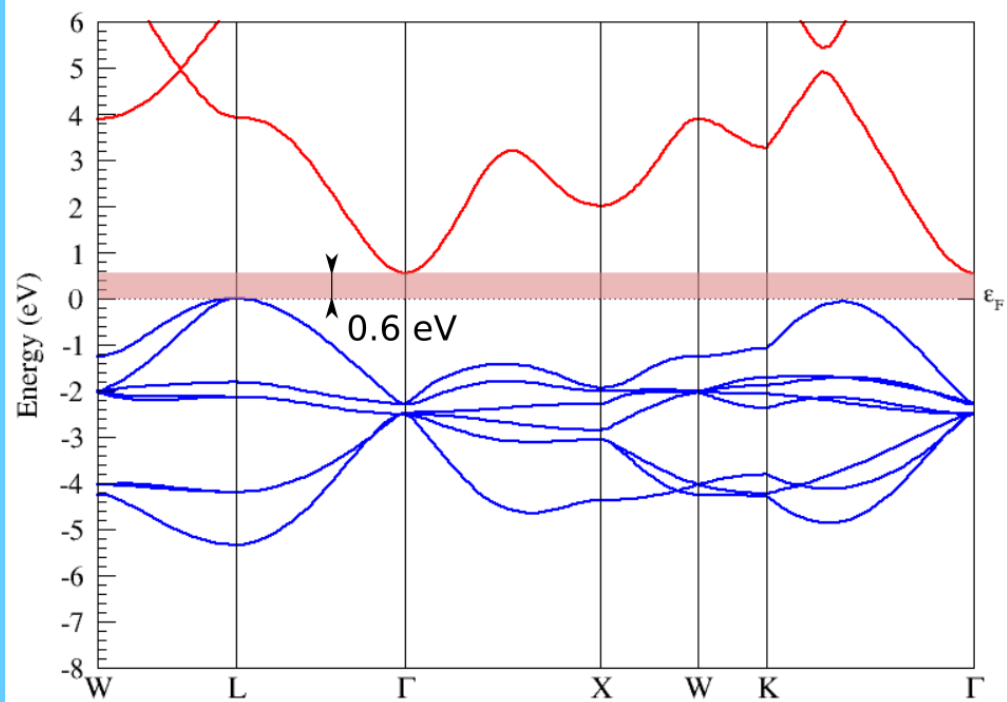
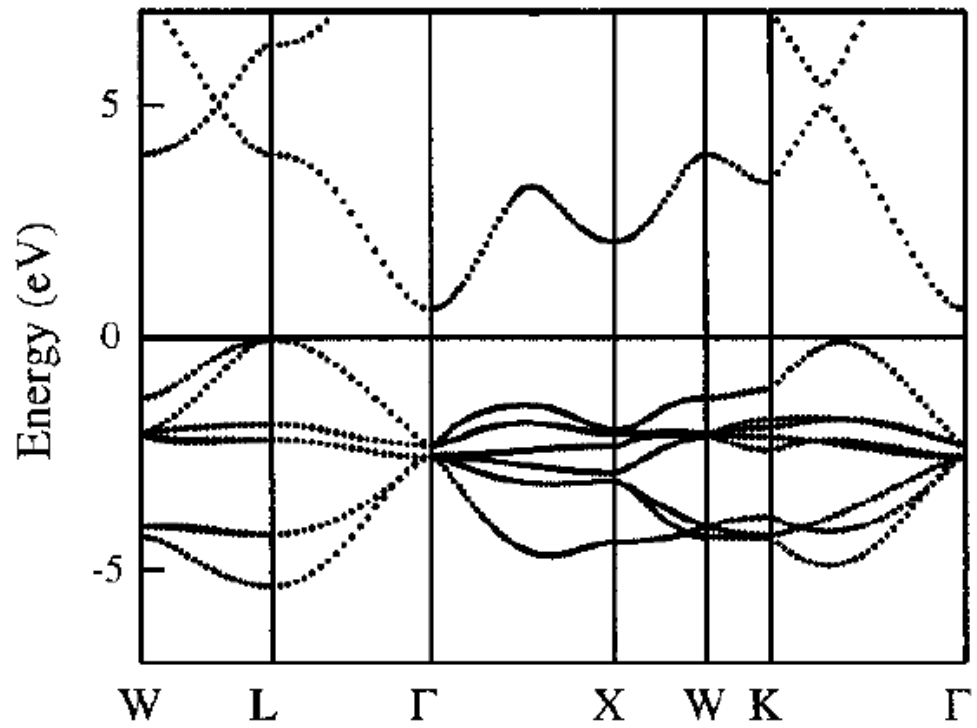
Conclusion and perspective

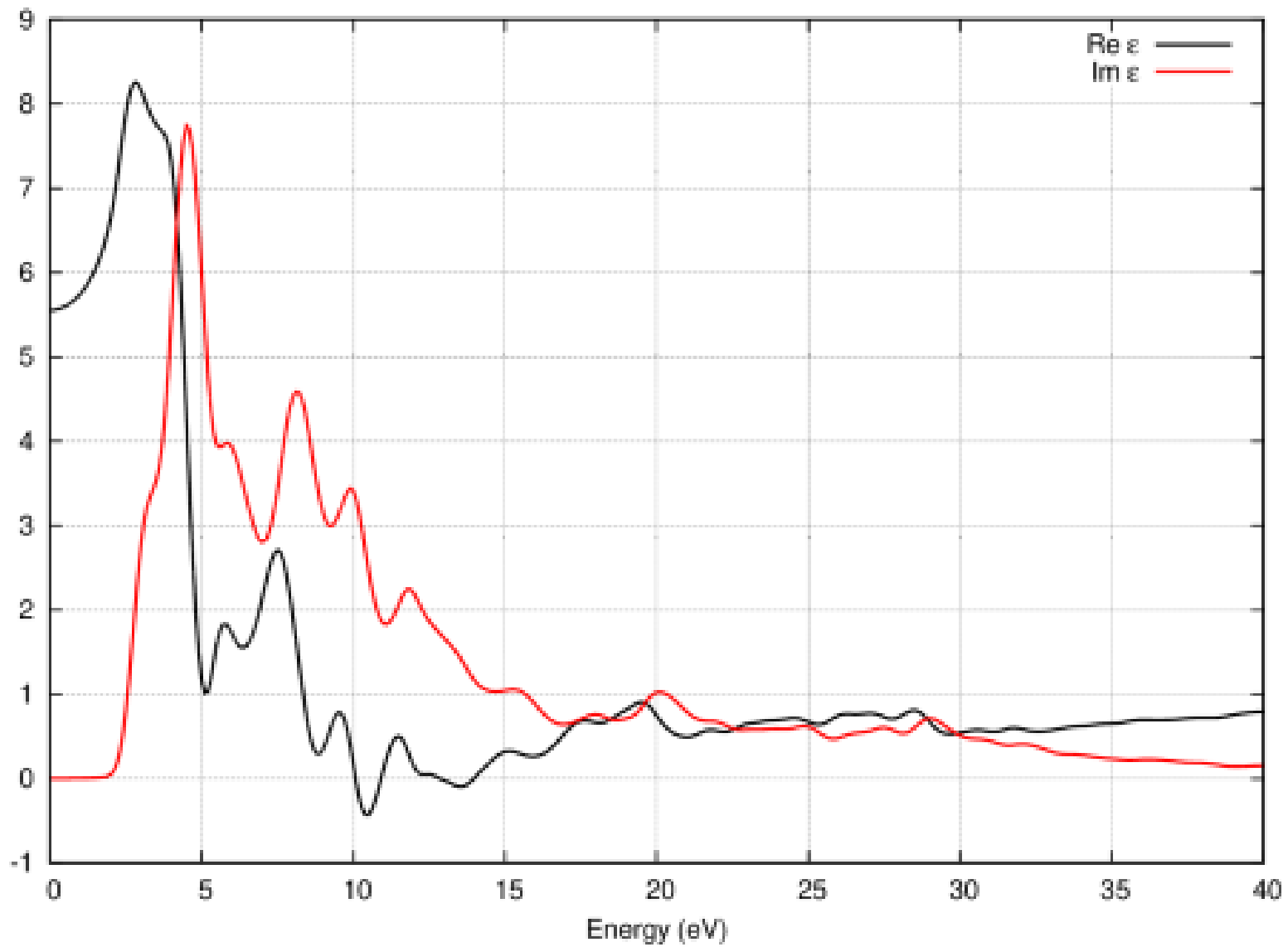


Acknowledgement:

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- Victor de Seauve, Marie-Angélique Languille (CRC)
- Mathieu Kociak (LPS)

Thank you for your attention !



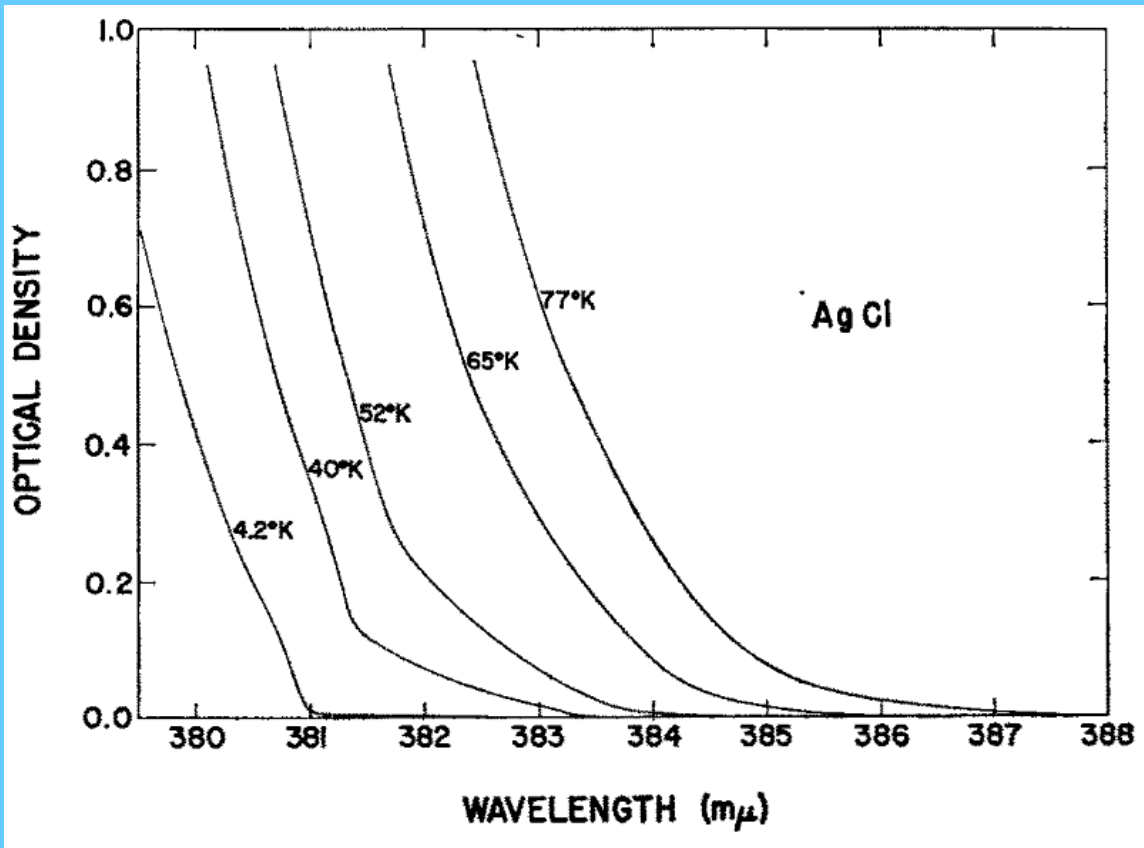
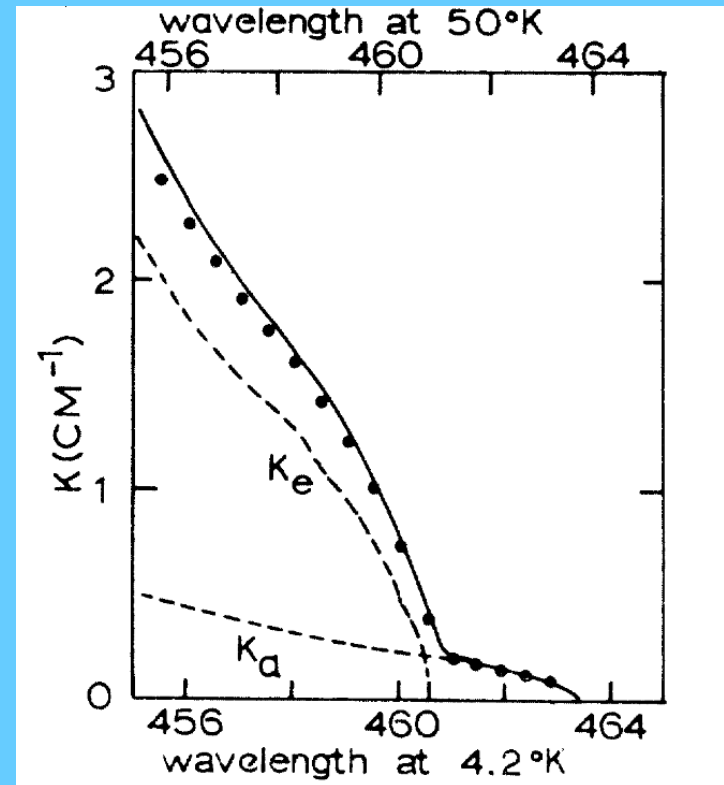


$$K(\omega) = K_a(\omega) + K_e(\omega)$$

Close to gap we have, with one phonon emitted or absorbed:

$$K_a(\omega) \propto \sqrt{h\omega - E_g + E_{ph}}$$

$$K_e(\omega) \propto \sqrt{h\omega - E_g - E_{ph}}$$



- From the two thresholds we can get the band gap

F. Brown, T. Masumi, and H. Tippins, Journal of Physics and Chemistry of Solids, 1961.

B. L. Joesten and F. C. Brown Phys. Rev. 1966

Pseudo potential for silver

- ^{47}Ag : $[\text{Ar}]4s^23d^{10}4p^65s^14d^{10}$
- Ionized Silver.
- Including the semi-core of silver 4p and 4s.
- Full shell included in the valence band.

