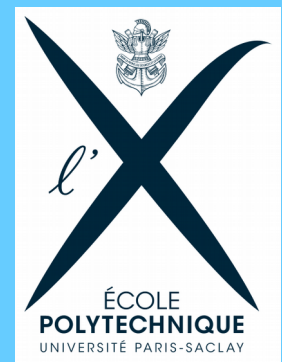


Ab initio study of Silver chloride: Becquerel's photochromatic photography

Arnaud Lorin
LSI, Ecole Polytechnique

JEELS, 11th of June, Porquerolles

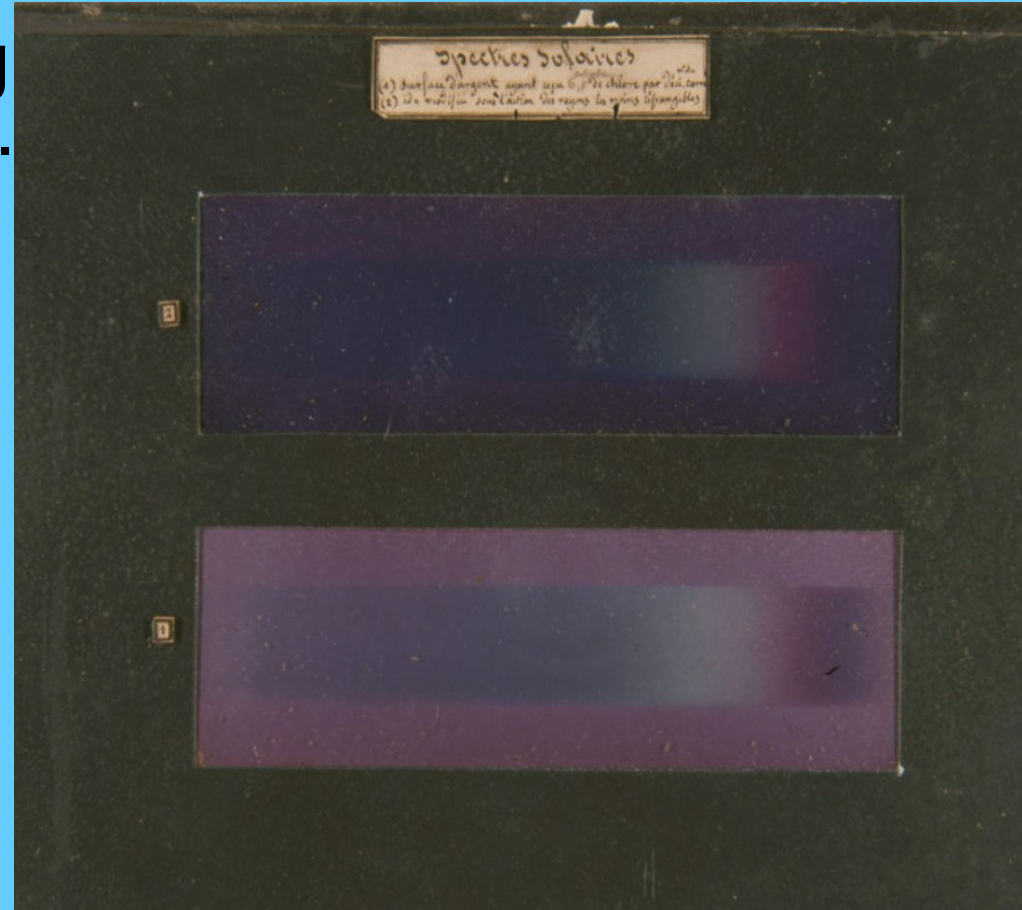


Outline

- Introduction: Silver chloride
- Ab initio study of band structure and optical properties.
- Conclusion and perspectives.

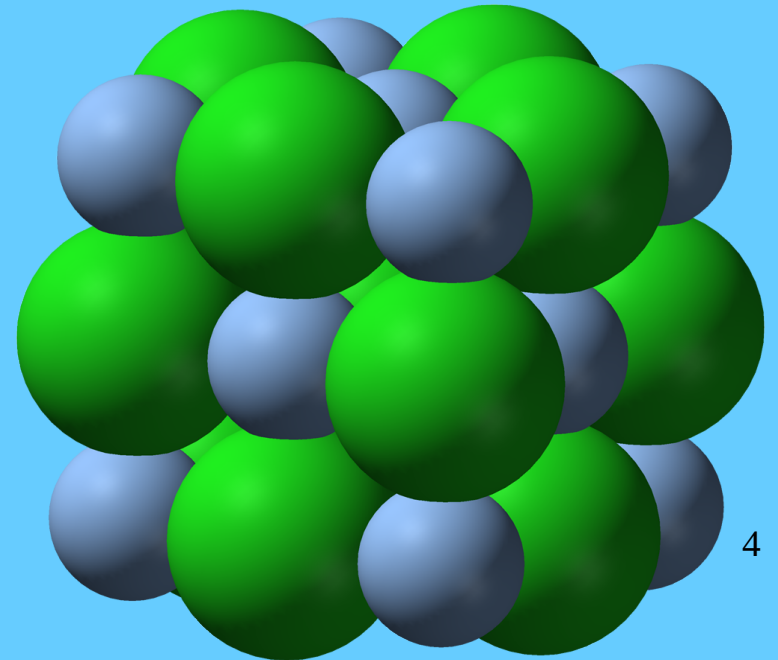
Motivation

- One of the earliest remaining color photography techniques. Edmond Becquerel 1848.
- Collaboration with Victor de Searve and the Museum national d'Histoire Naturelle (CRC).
- A theoretical study ?
 - Fragile material,
 - What is really inside the material ?
 - Experiment in the dark.



Silver Chloride

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



Electronic properties of AgCl

Electron Energy Loss

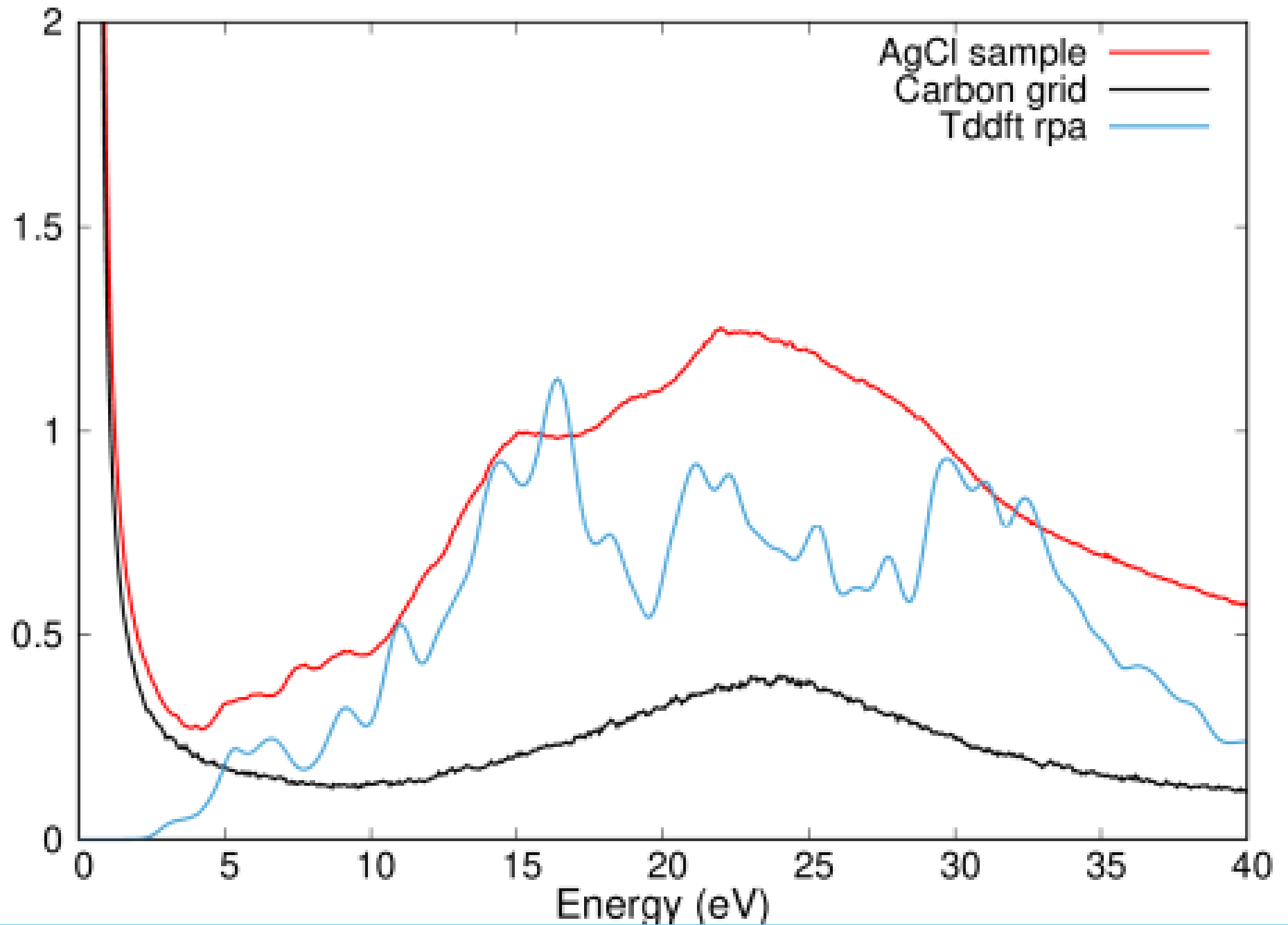
- Search for silver nanoparticles
- Reference for experiment for bulk silver chloride.
- Experiment at LPS, Orsay.
- Computation at $q \rightarrow 0$.

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

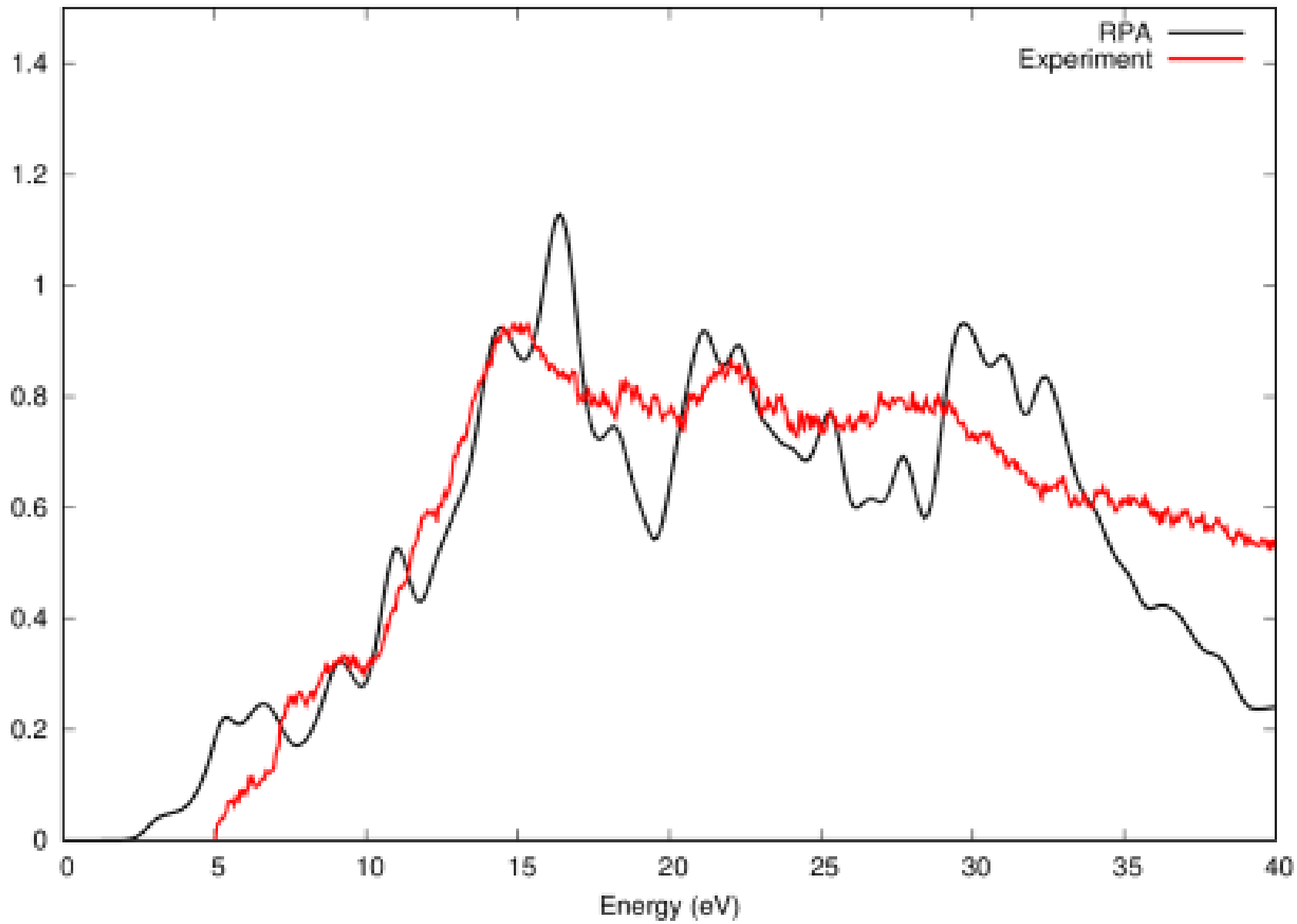
Linear response framework and TDDFT, with Random Phase Approximation (RPA):

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

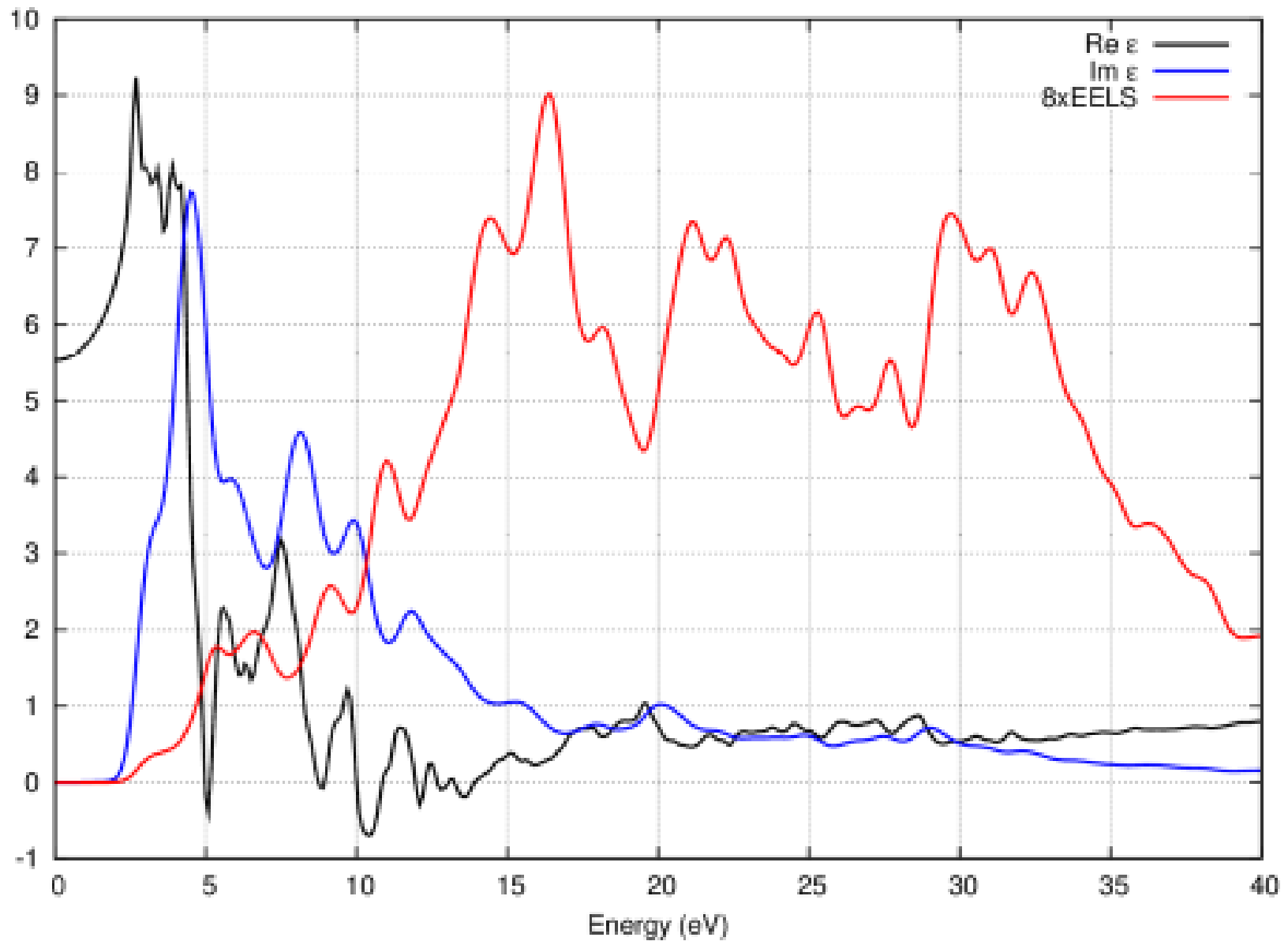
- TDDFT as implemented in the DP-code.

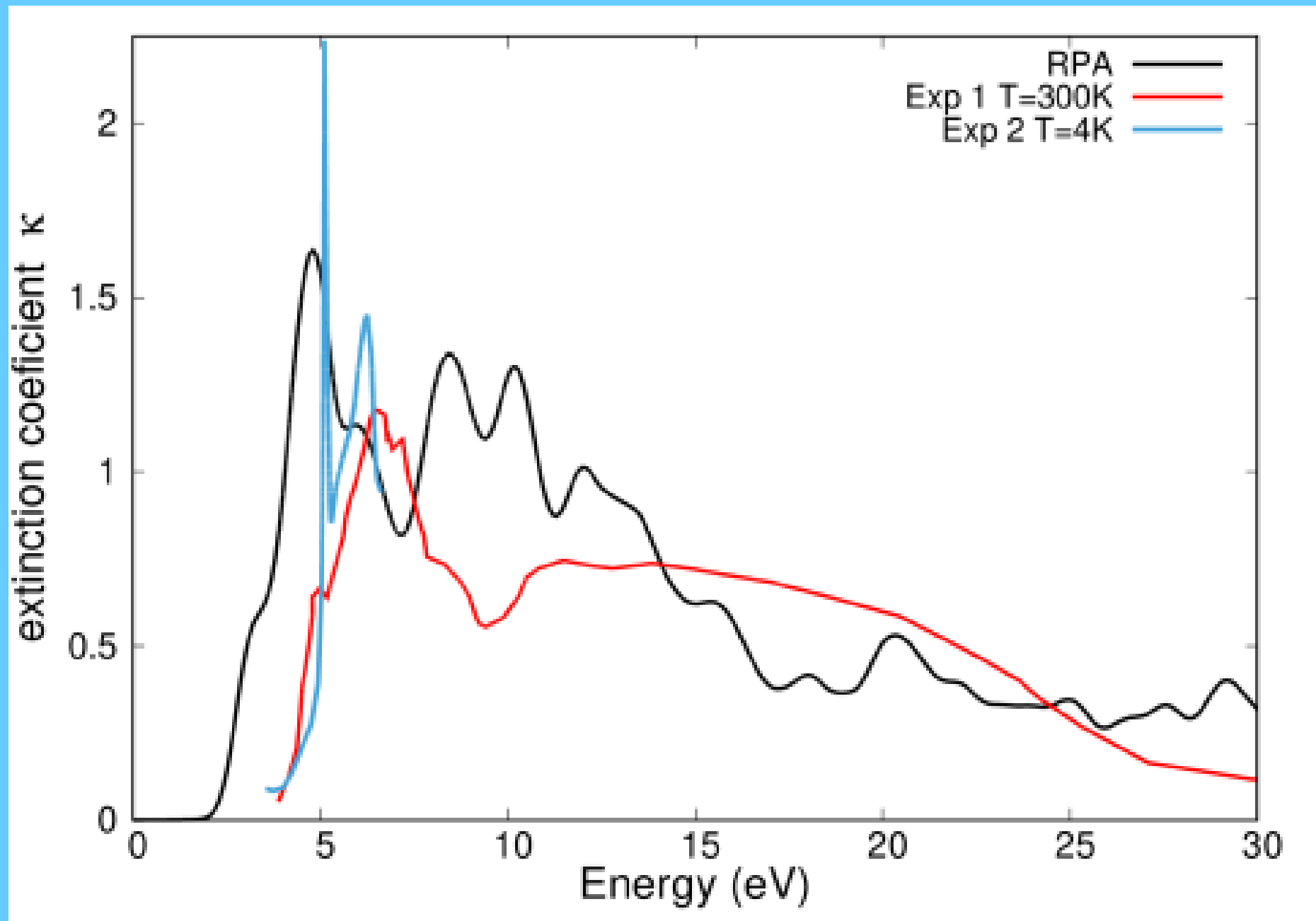


- Experiment at the LPS with Victor de Seauve (CRC) and Mathieu Kociak (LPS)

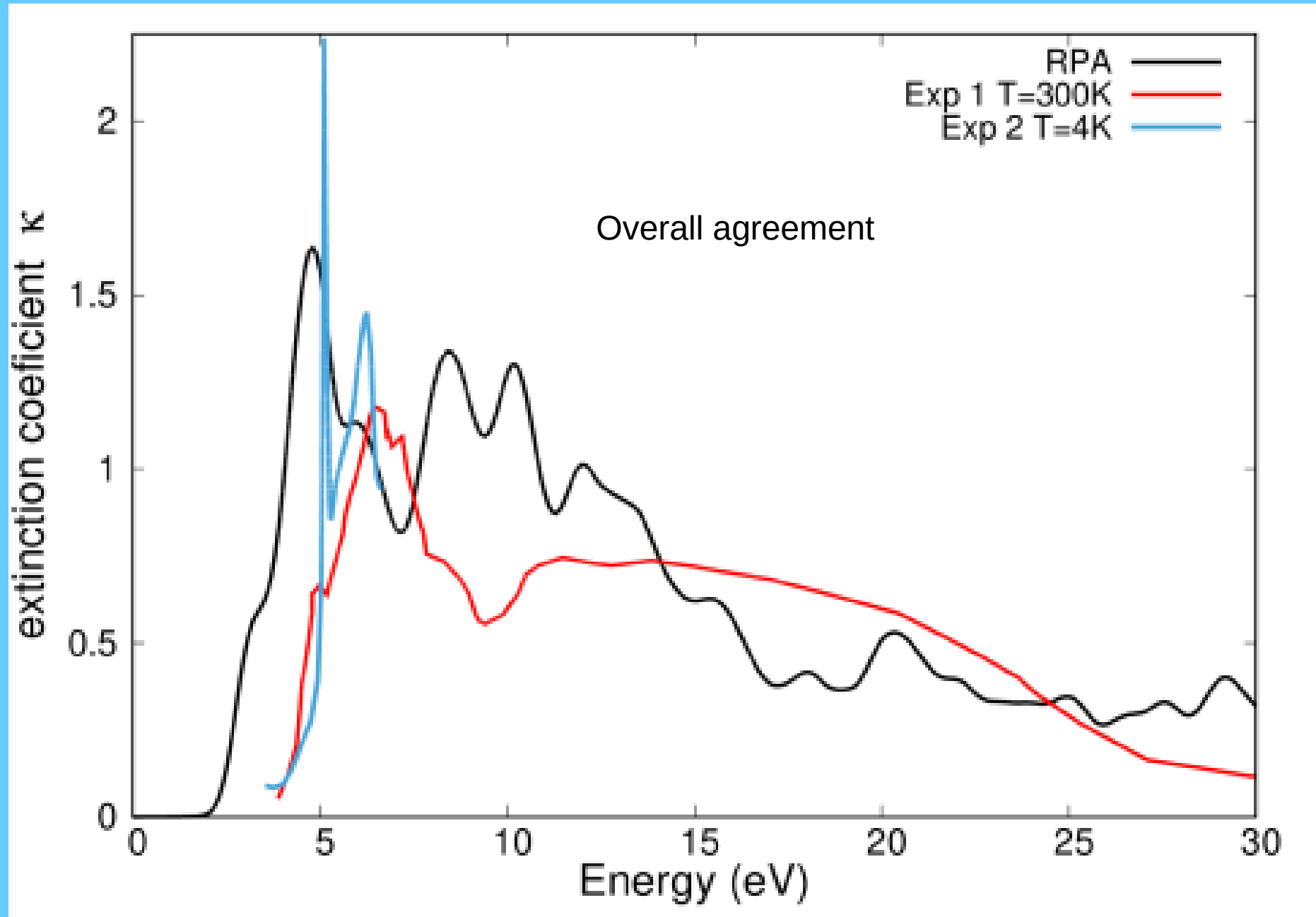


Optical absorption





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

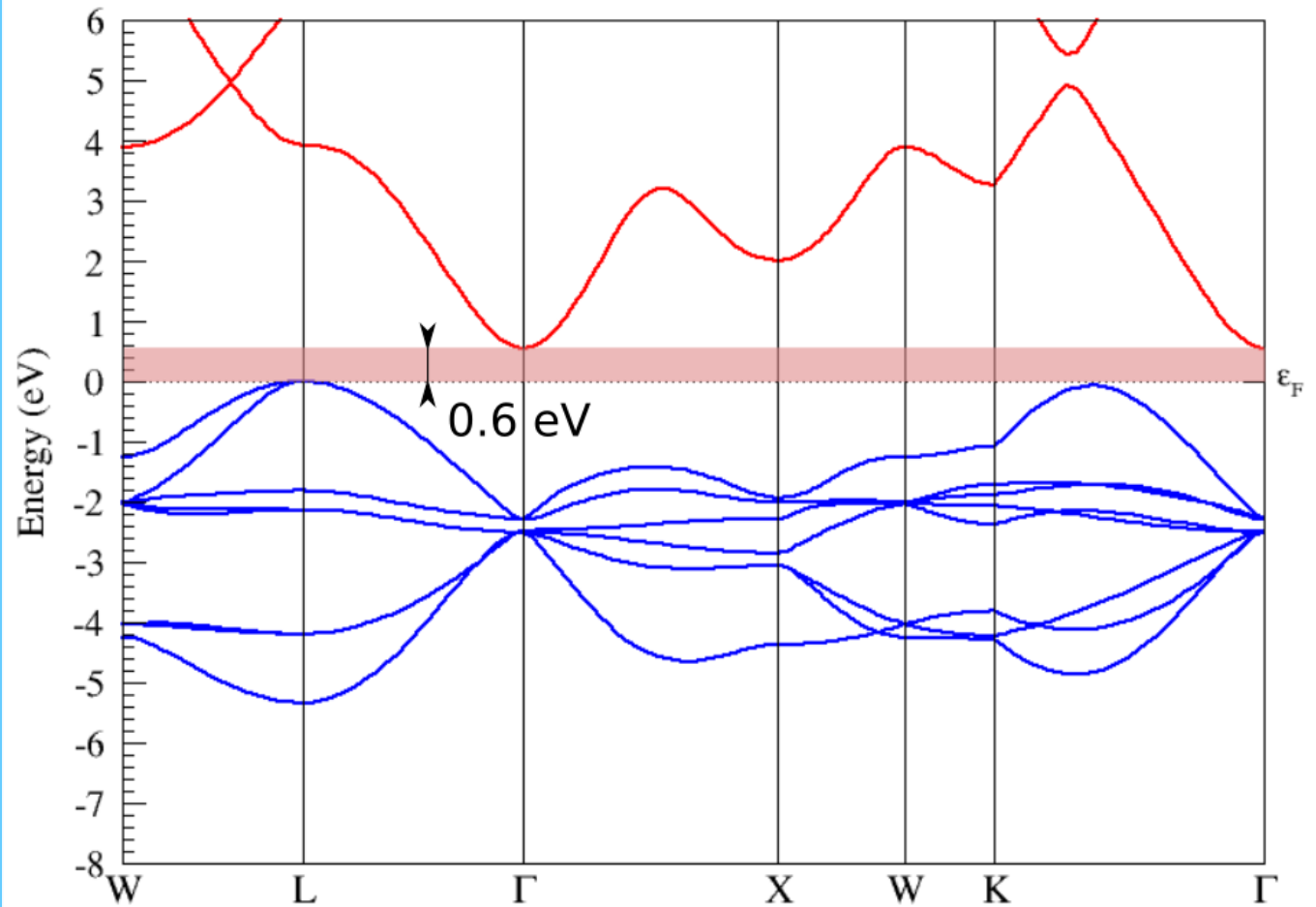


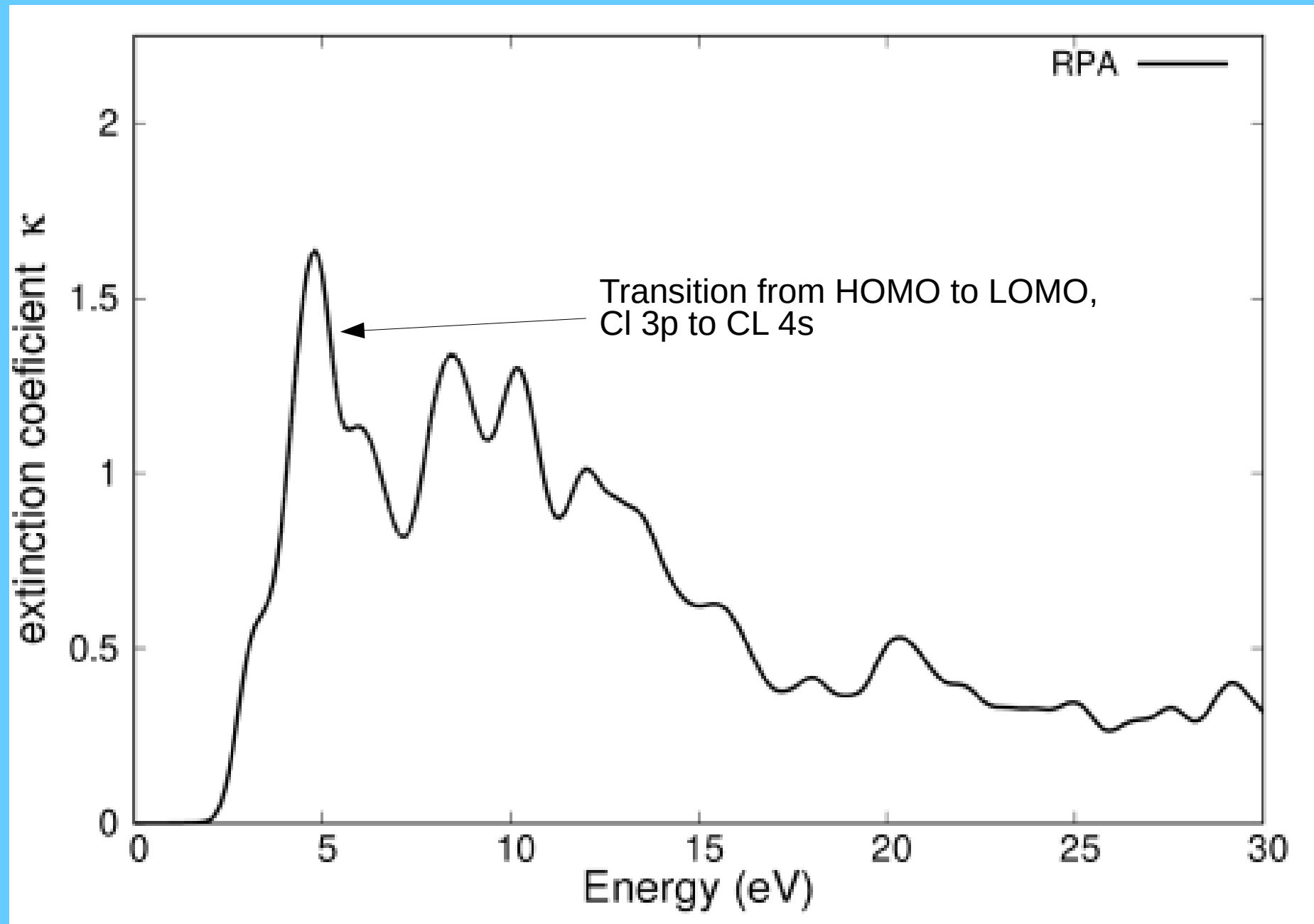
Band structure

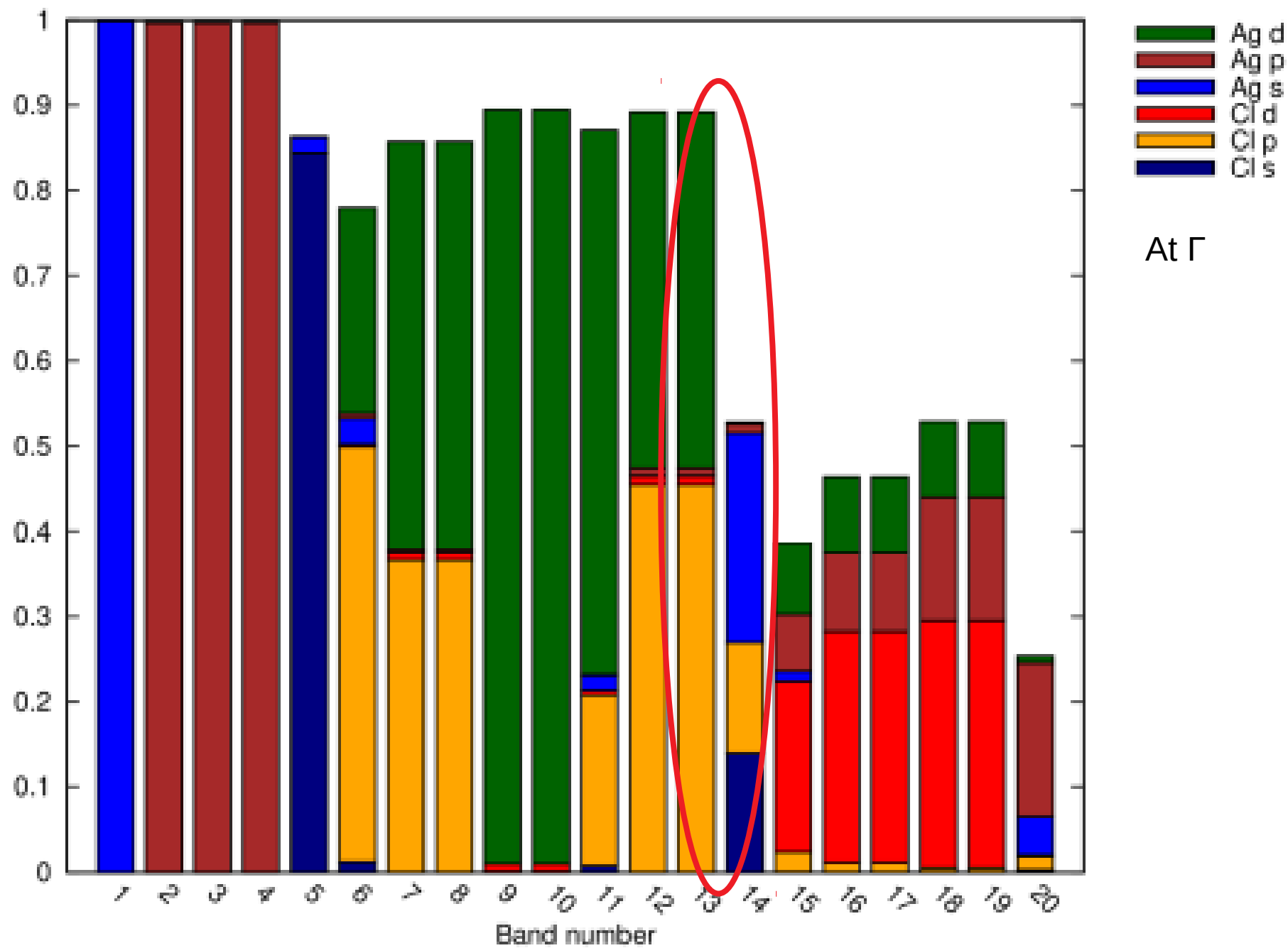
- LDA
- $E_{\text{ind}} = 0,6 \text{ eV}$
- Transition $L \rightarrow \Gamma$
- Good agreement with other calculations:

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

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

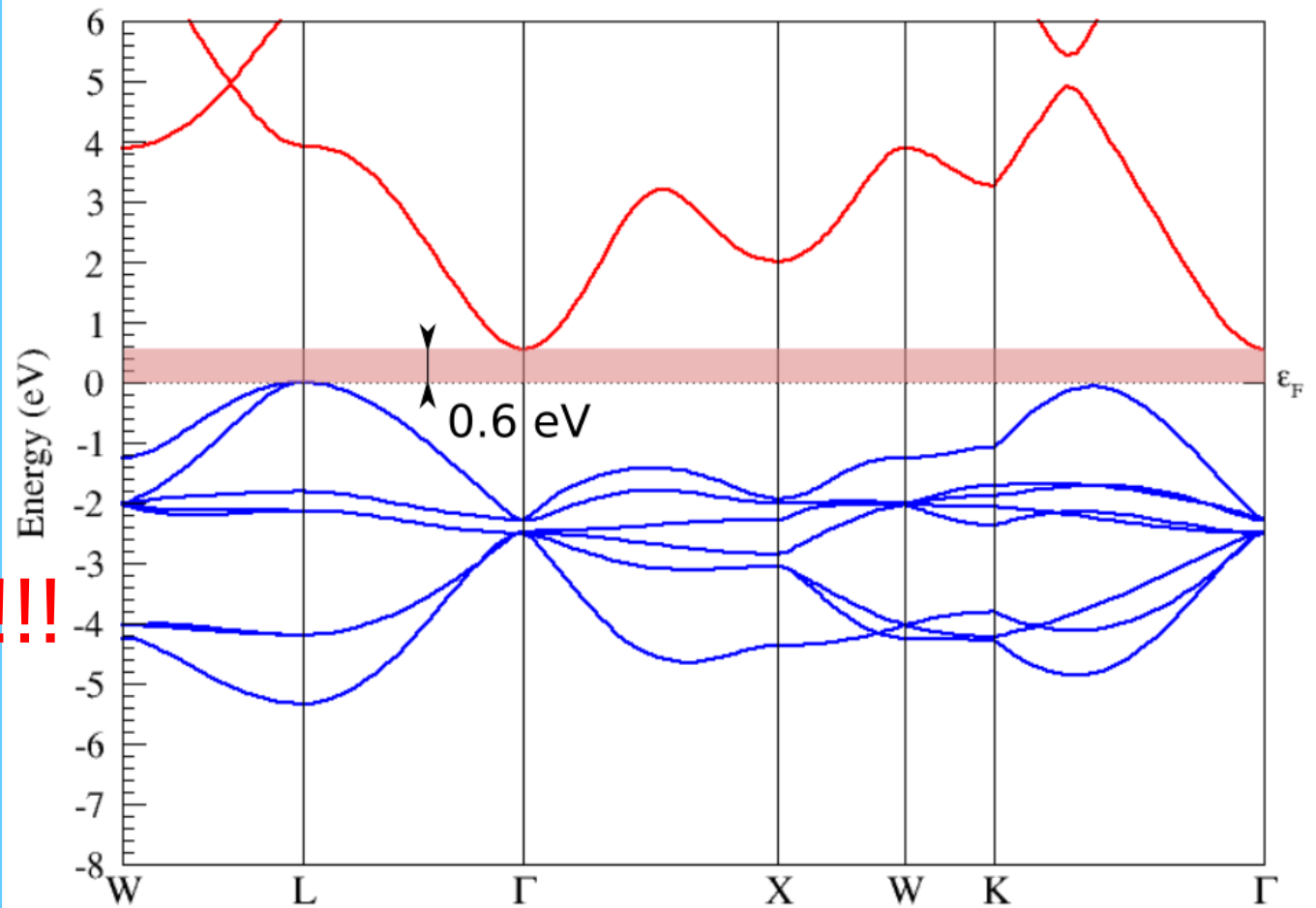


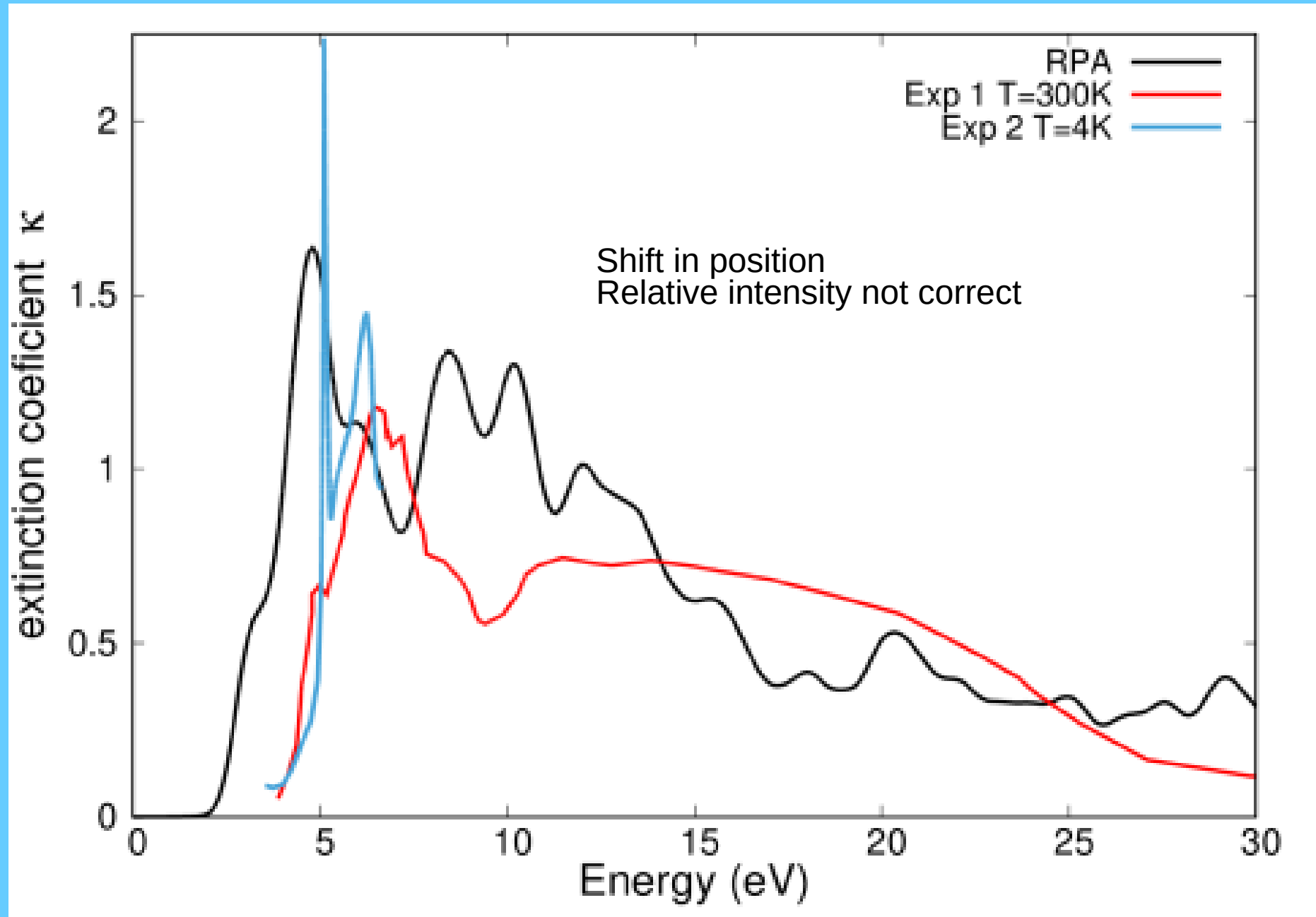




Band structure

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



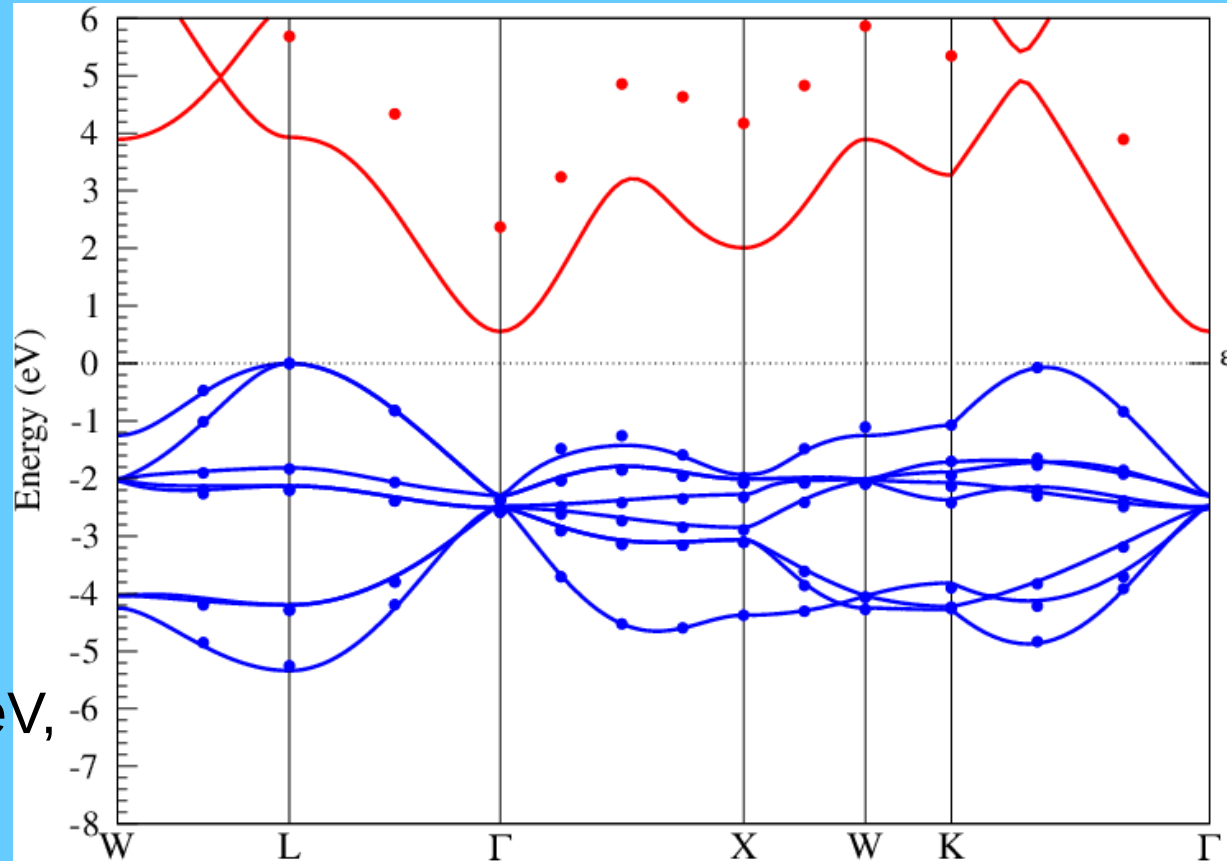


GW correction

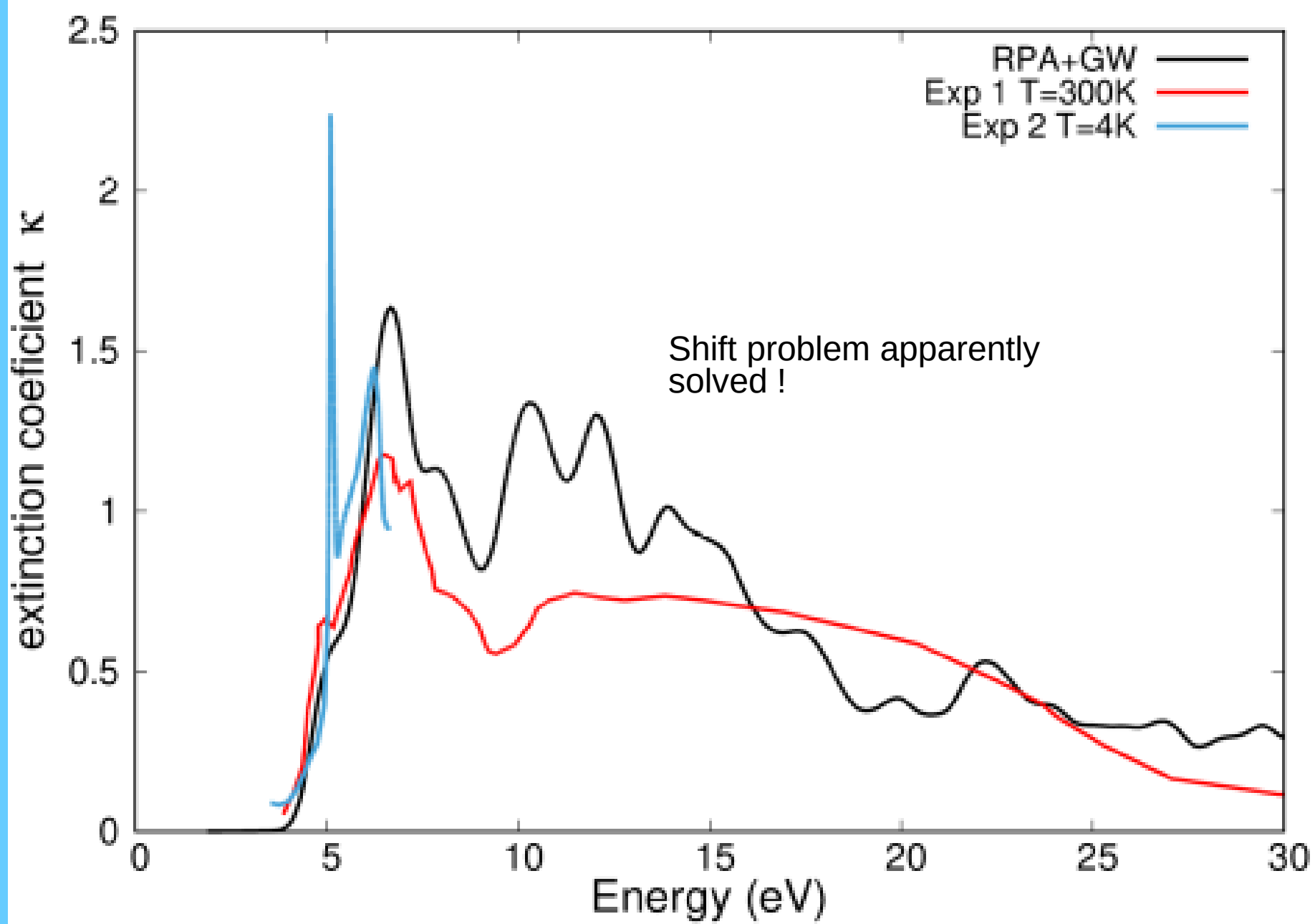
- Perturbative GW (G^0W^0)

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

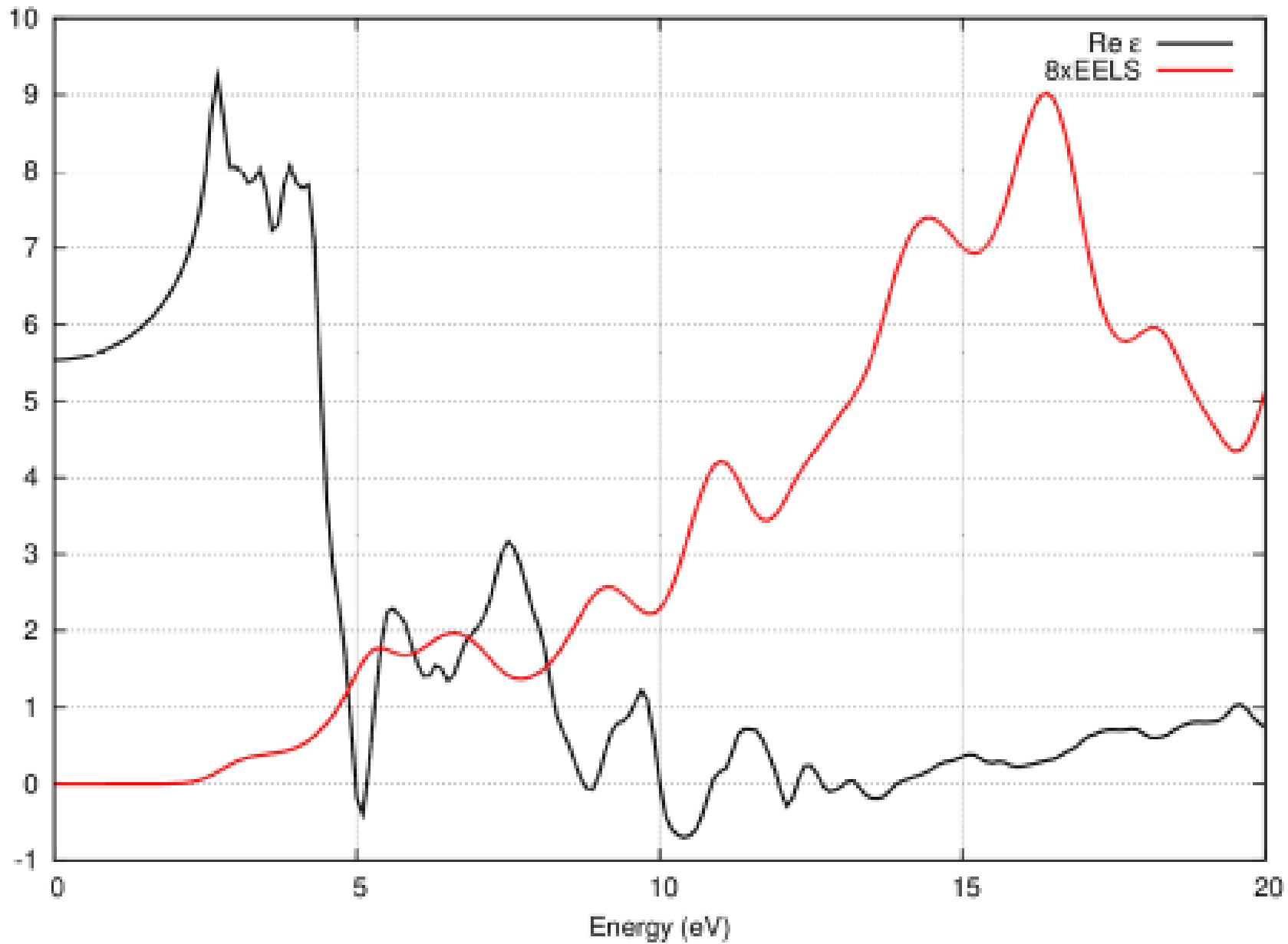
- Code Abinit
- 620 bands (330eV),
- Plasmon pole approximation.
- Effective Energy Technique.
 - 120 bands
 - 5% error
- Direct gap correction at Γ : 1.9eV,
at L: 1.6eV
- Indirect gap correction:



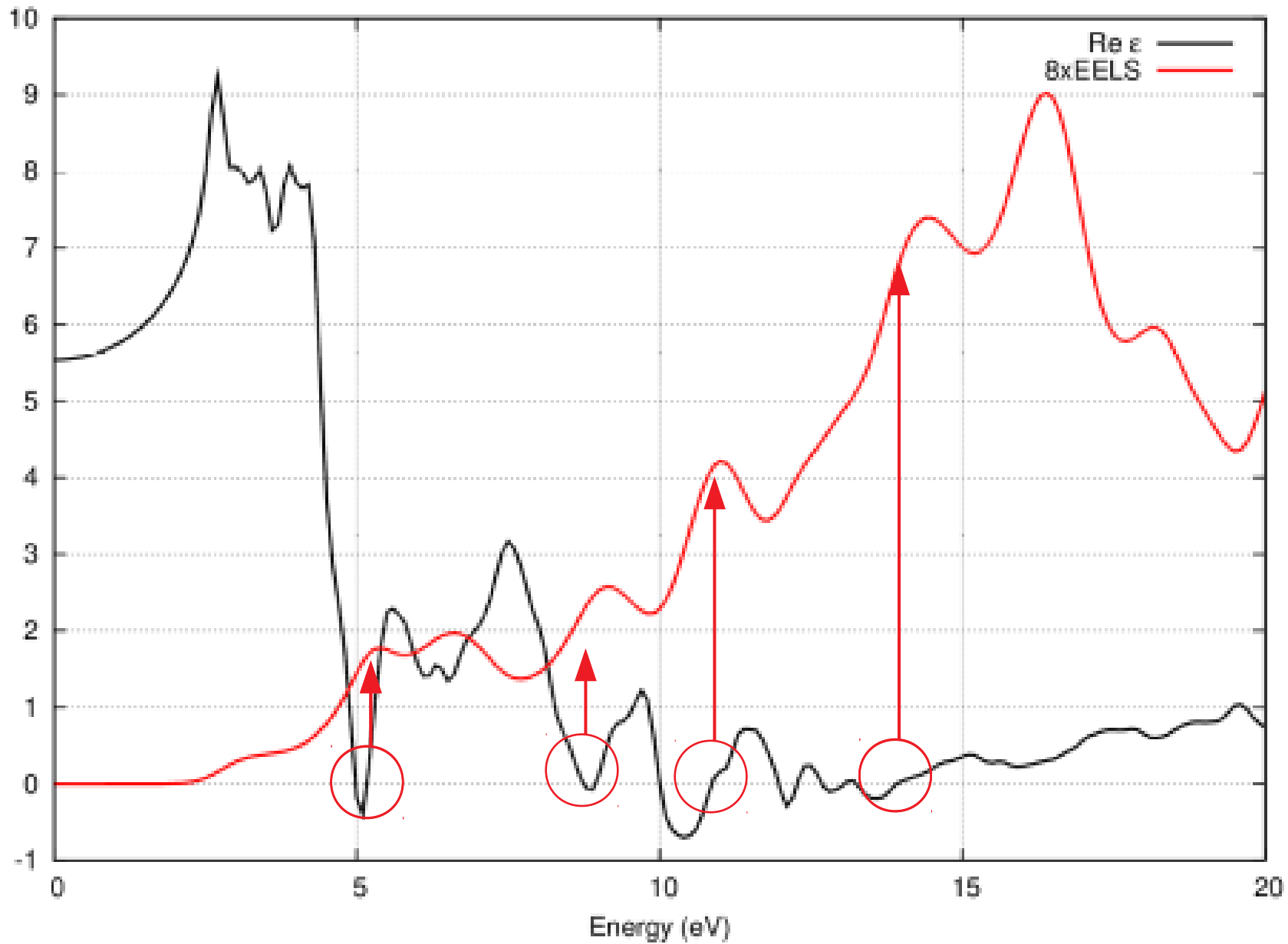
$$E_{ind}^{GW} = 2.5 \text{ eV} \left(E^{\text{exp}} = 3.25 \text{ eV}, E^{LDA} = 0.6 \text{ eV} \right)$$

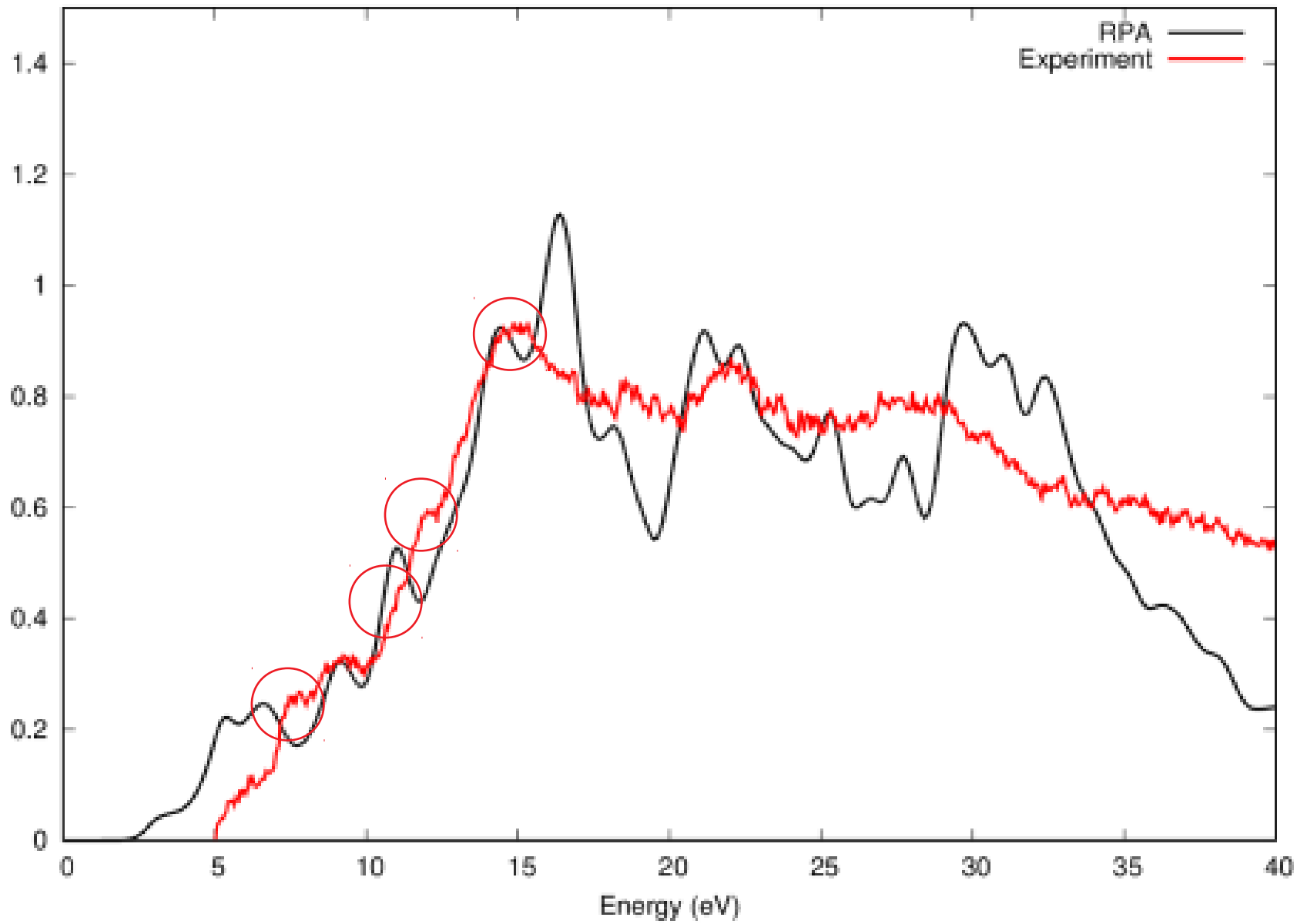


Plasmon study



Plasmon study





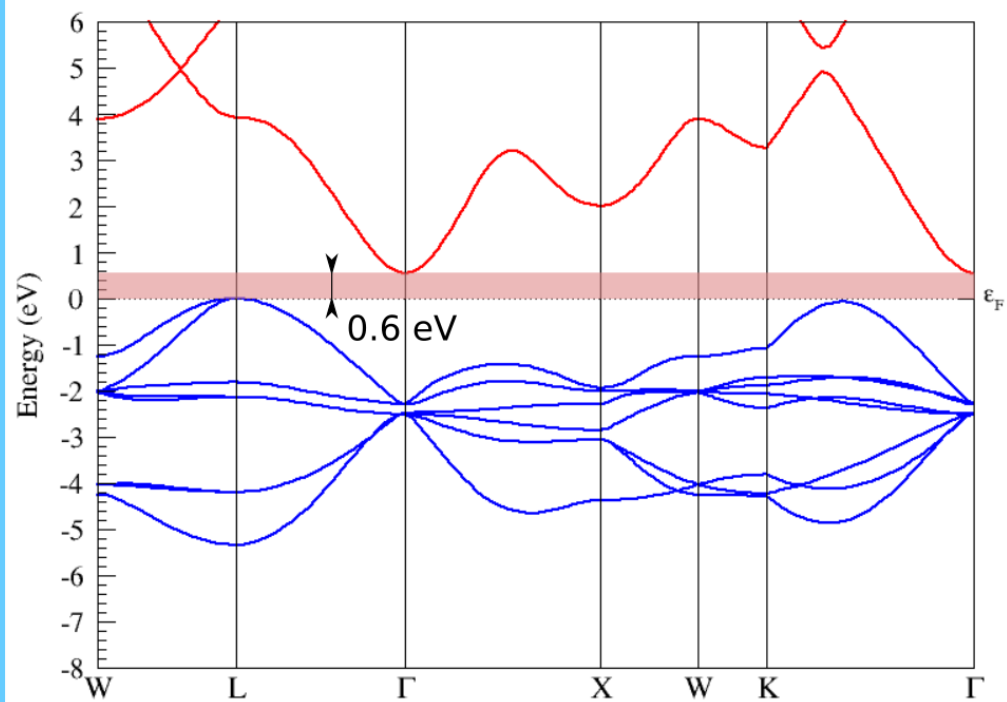
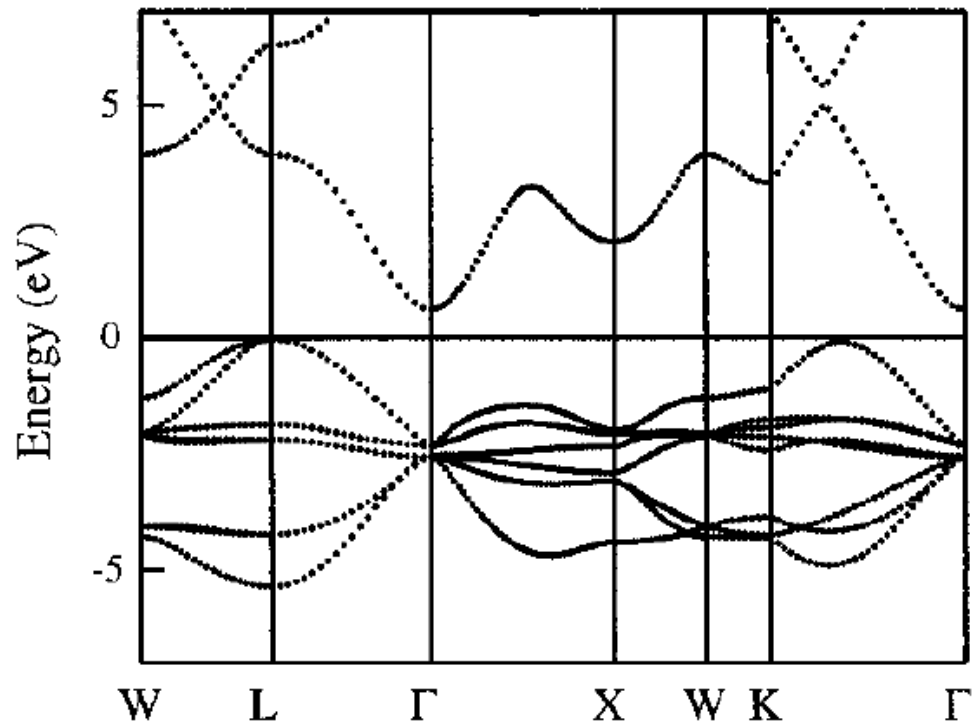
Conclusion

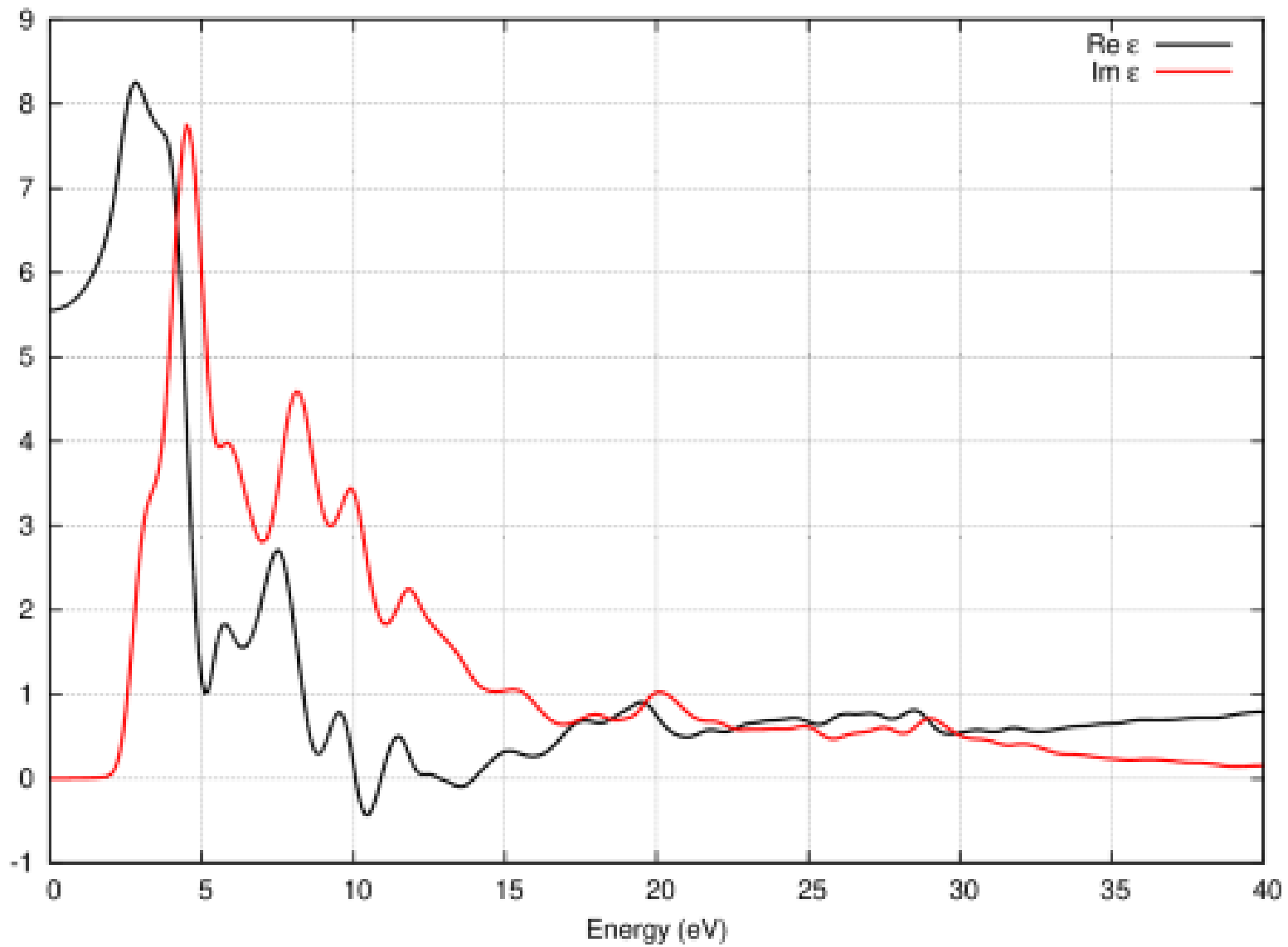
- Ab-initio using DFT-LDA for ground states and optical properties. GW correction under work.
- Plasmon structure understood.
- Most probably presence of a strong exciton in the material.
- Basic theory is not enough, need for more sophisticated theory.

Acknowledgement:

- Lucia Reining, Francesco Sottile, Matteo Gatti (LSI)
- Victor de Seauve, Marie-Angélique Languille (CRC)
- Mathieu Kociak (LPS)

Thank you for your attention !



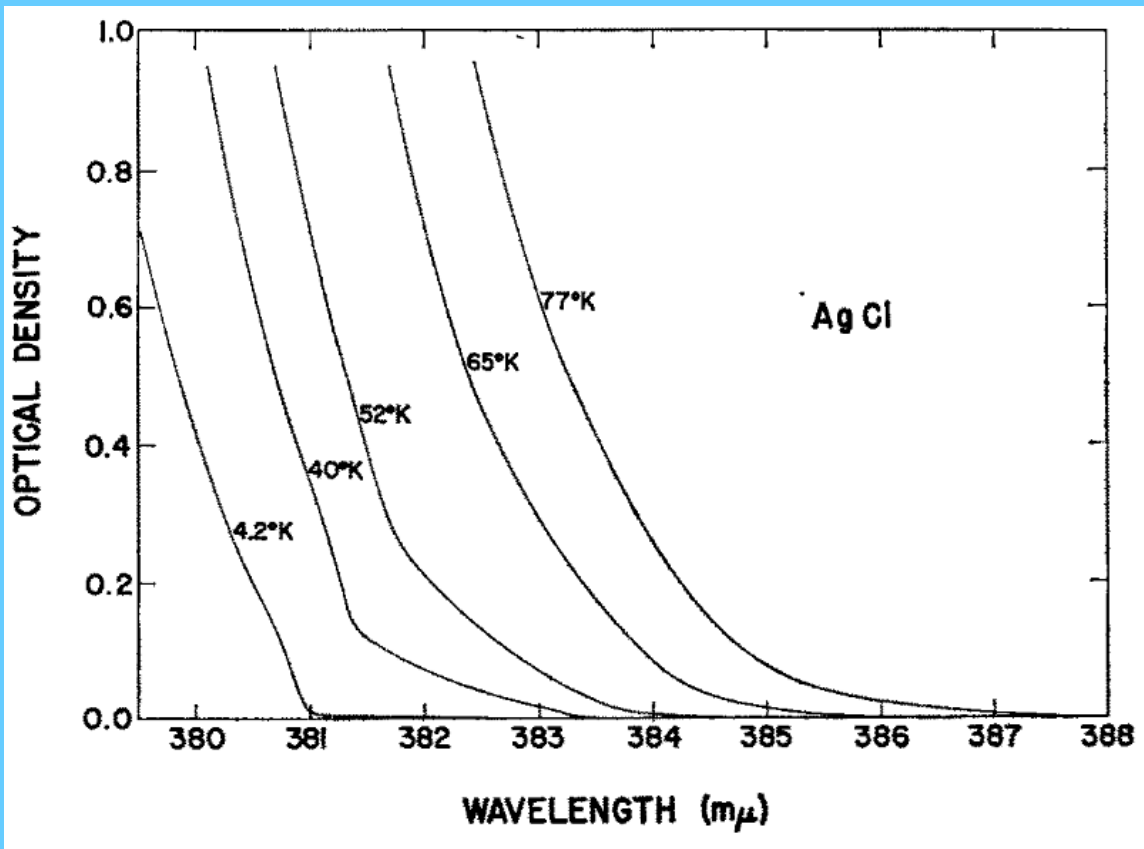
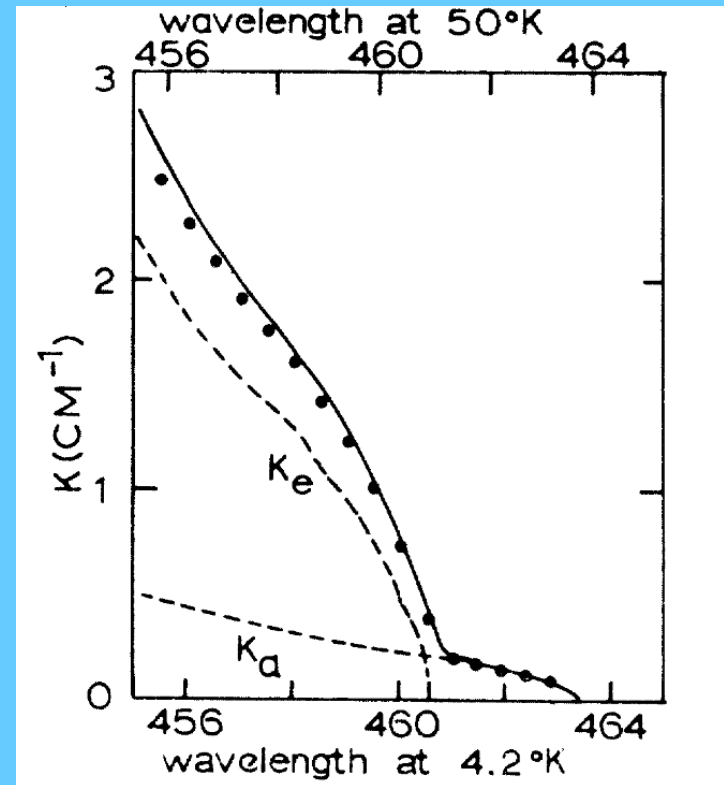


$$K(\omega) = K_a(\omega) + K_e(\omega)$$

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.

