Theoretical analysis of the momentum-dependent loss function of bulk Ag: G_0W_0-RPA calculations

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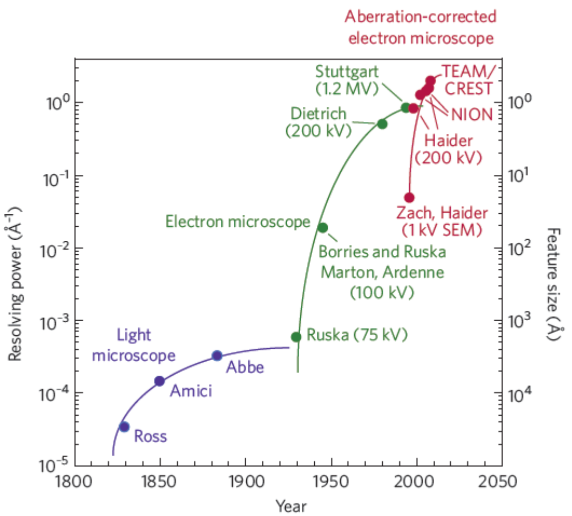
Motivation

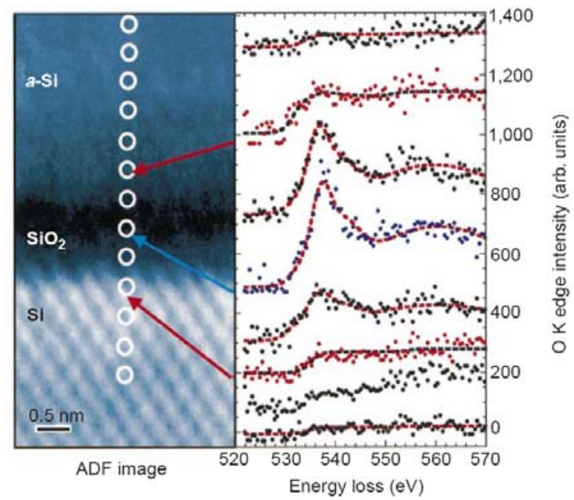
Electron energy loss spectrometry (EELS) in the transmission electron microscope (TEM) is an old and well-established technique (review: R. F. Egerton, Rep. Prog. Phys. 72, 016502 (2009)).

$$S(\mathbf{q},\omega) \sim \frac{1}{q^2}\mathrm{Im}\left\{-\frac{1}{\varepsilon(\mathbf{q},\omega)}\right\}$$

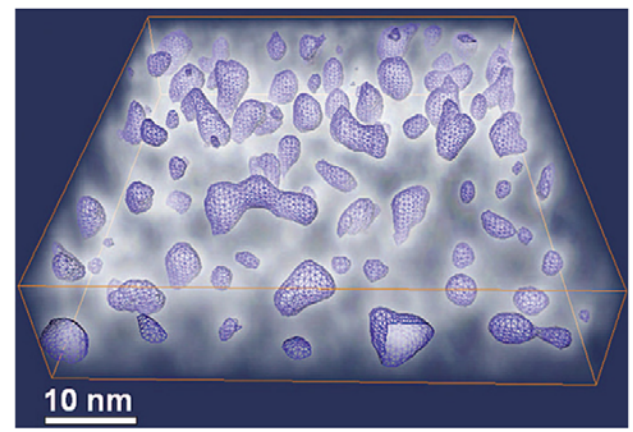
New aberration-corrected microscopes equipped with field-emission guns and monochromators achieve a very high energy resolution and a stunning (sub)atomic spatial resolution (review: review: D. A. Muller, Nature Mat. 8, 263 (2009)).



Spatial resolution of microscopes over the years (STM excluded)



Spatially-resolved (core-loss) EELS across the Si-SiO_2 interface
D. A. Muller *et al.*, Nature 399, 758 (1999)



Plasmon imaging of Si nanoparticles in the SiO_2 matrix
A. Yurtsever *et al.*, Appl. Phys. Lett. 89, 151920 (2006)

$$S(\mathbf{r},\omega) \sim \int f(\mathbf{r},\mathbf{q},\omega)\, S(\mathbf{q},\omega)\, d\mathbf{q}$$

Can accurate *q*-dependent dielectric functions be obtained using modern microscopes? (JEOL)
How well do modern theories perform for that and which level of sophistication is needed?

Joint theoretical-experimental work on a model system – Ag (next: Cu, Pd, graphite)

Outline

1. Briefly: technical details

2. The loss function from GGA-RPA

3. Analysis of the structure in the loss function: plasmon excitations and inter-band transitions

4. Why semilocal functionals fail

5. *GW* corrections: a substantial improvement

6. q-dependent loss function: GGA-RPA vs. *GW*-RPA

7. Experimental challenges

Technical details briefly

Single-scattering distribution

$$S\left(\mathbf{q},\omega\right) \sim \frac{1}{q^2}\mathrm{Im}\left\{-\frac{1}{\varepsilon(\mathbf{q},\omega)}\right\}$$

The loss function

$$L\left(\mathbf{q},\omega\right) = \mathrm{Im}\left\{-\frac{1}{\varepsilon(\mathbf{q},\omega)}\right\}$$

$$\varepsilon^{-1} = 1 + v\chi$$

Dyson's equation (RPA): $\chi = \chi_0 + \chi_0 v \chi$

$$\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) + \sum_{\mathbf{G}_1} \chi^0_{\mathbf{G},\mathbf{G}_1}(\mathbf{q},\omega) v_{\mathbf{G}_1}(\mathbf{q}) \chi_{\mathbf{G}_1,\mathbf{G}'}(\mathbf{q},\omega)$$

Dyson's equation without local fields:

$$\chi_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega) = \chi^0_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega) + \chi^0_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega) v_{\mathbf{G}}(\mathbf{q}) \chi_{\mathbf{G},\mathbf{G}}(\mathbf{q},\omega)$$

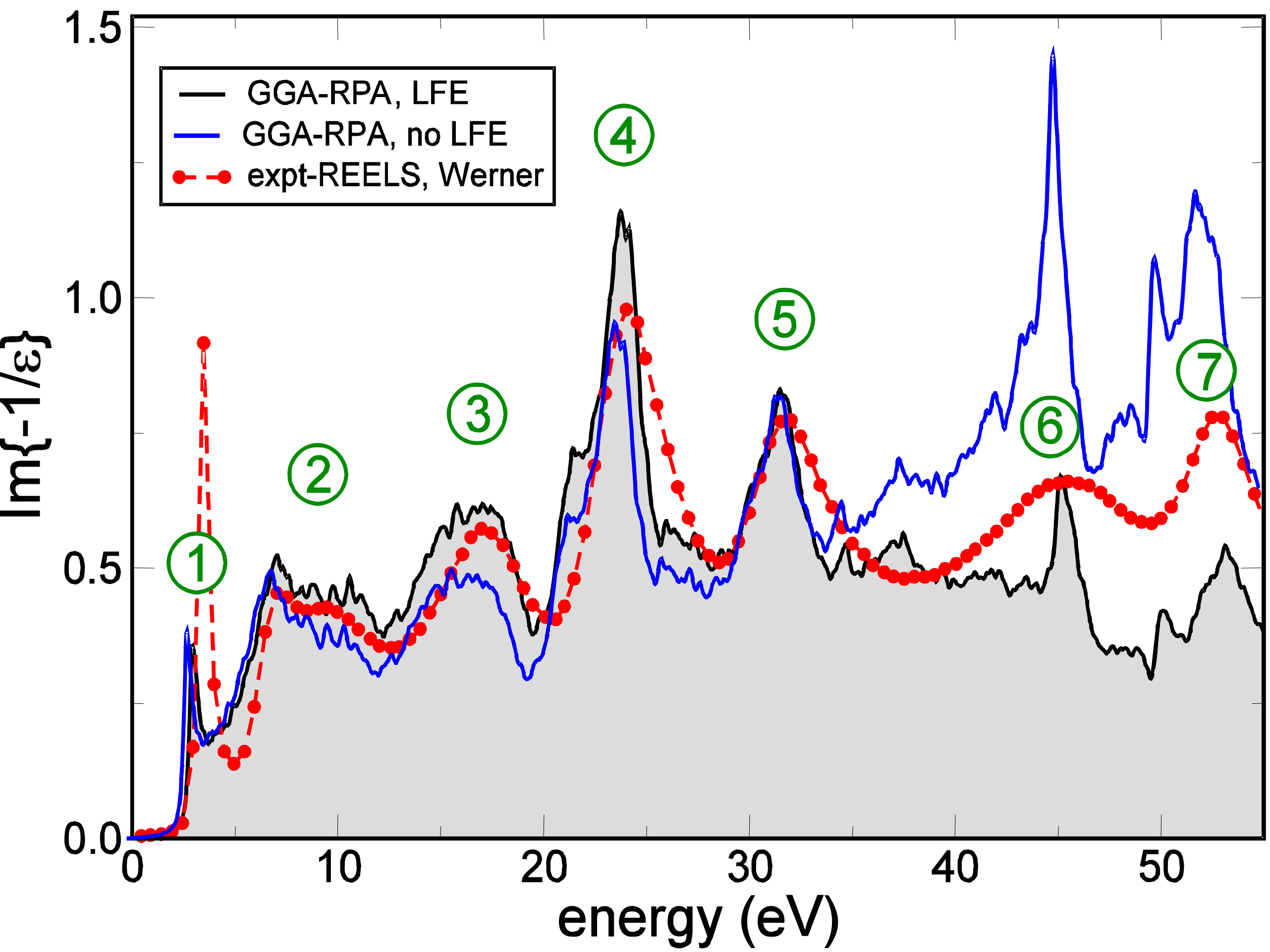
χ_0 **is calculated using Kohn-Sham orbitals; GGA (*GW*) energies**

calculations: FP-LAPW code exciting;
all-electron calculation essential at energies > 20 eV

C. Ambrosch-Draxl, S. Sagmeister, C. Meisenbichler, and J. Spitaler, exciting code; http://exciting-code.org/

Loss function at *q*=0; local-field effects

GGA-RPA vs. REELS

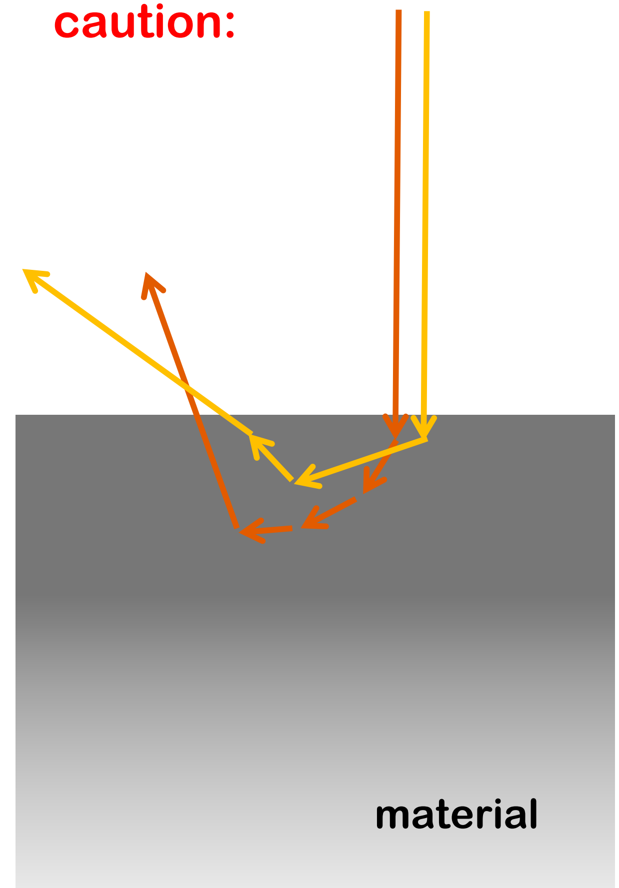


The loss function has a complex structure: it has 7 well-pronounced peaks

The inclusion of local-field effects improves the theoretical loss function

Reflection EELS: W. S. M. Werner, M. R. Went, M. Vos, K. Glantschnig, and C. Ambrosch-Draxl, Phys. Rev. B 77, 161404 (2008).

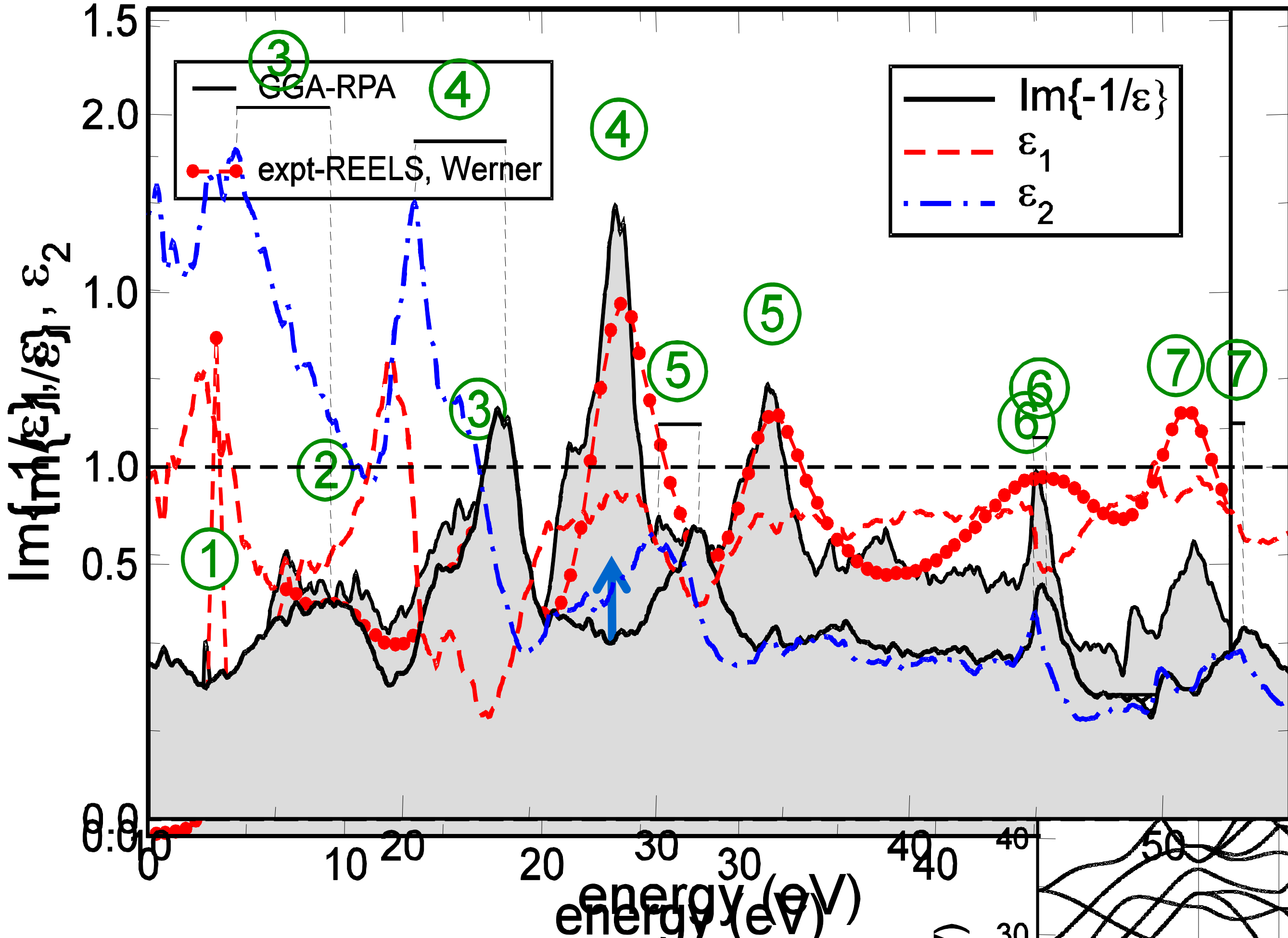
caution:



REELS:
loss function at a certain ω is an average over different **q**;
also large surface effects

comparison with q=0 is indicative;
but the loss function of Werner *et al.* so far best available

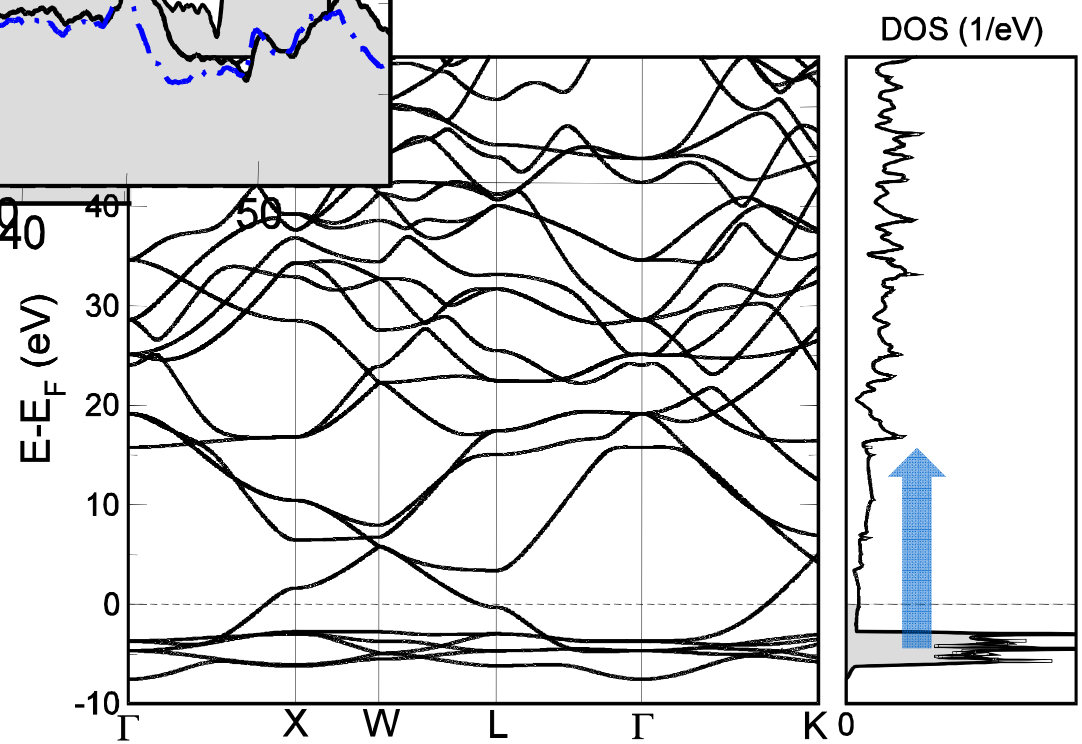
Analysis of the loss function



$$\mathrm{Im}(-1/\varepsilon) = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}$$

peaks (3)-(7): interband transitions, i.e. they are related to maxima in ε_2:

$$\tilde{\omega}_k^2 = \omega_k^2 + \frac{f_k^2 \omega_\mathrm{p}^2}{\beta}$$



peaks (1) and (2) are plasmons, i.e. they originate from zeros of in ε_1;

frequency and intensity of peak (1) is wrong; GGA-RPA: 3.0 eV; expt: 3.8 eV.

A. Alkauskas, S. Schneider, S. Sagmeister, C. Ambrosch-Draxl, and C. Hébért, submitted.

Low-energy plasmon I

Free-electron Drude frequency in Ag $\hbar\omega_{\mathrm{p}} \approx 9.2 - 9.5\,\mathrm{eV}$

The origin of the 3.8 eV plasmon has been studied before:

- H. Ehrenreich and H. R. Philipp, Phys. Rev. **128**, 1622 (1962);
- D. Pines, *Elementary excitations in solids* (1964);
- A. Otto and E. Petri, Solid State Commun. 20, 823 (1976);
- V. P. Zhukov, F. Aryasetiawan, E. V. Chulkov, I. G. De Gurtubay, and P. M. Echenique, Phys. Rev. B 61, 8033 (2000);
- M.A. Cazalilla, J. S. Dolado, A. Rubio, and P. M. Echenique, Phys. Rev. B 61, 8033 (2000).

Otto and Petri:
free electrons in the *sp* band (ω_p) + bound electrons in the *d* band; the latter yielding approximately constant contribution to ε_1 equal to ε_d.

$$\Omega_{\mathrm{p}} \approx \frac{\omega_p}{\sqrt{\varepsilon_d}}$$

From optical absorption / GGA-RPA: $\varepsilon_d \approx 5 - 7$

$$\Omega_{\mathrm{p}} \approx 3.9\,\mathrm{eV}$$

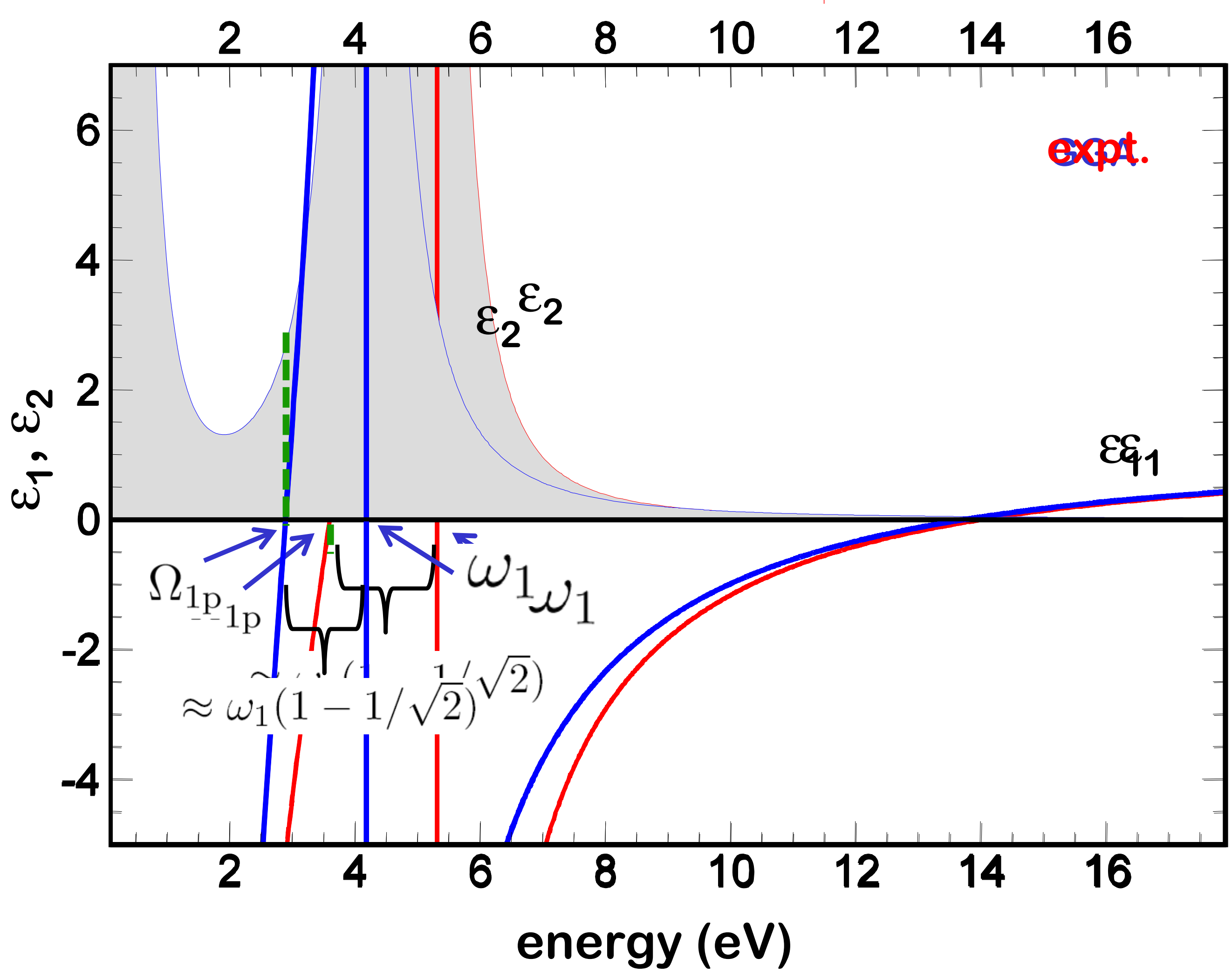
However, the failure of GGA is difficult to understand within this picture.

Low-energy plasmon II

free electrons in the *sp* band (ω_p) coupled to one narrow optical band (ω_1)
C. B. Wilson, Proc. Phys. Soc. LXXVI, 481 (1960).

$$\varepsilon_1(\omega) = 1 - \frac{\omega_\mathrm{p}^2 f_0}{\omega^2} + \frac{\omega_\mathrm{p}^2 f_1}{\omega_1^2 - \omega^2}$$

plasmons: $$1 - \frac{\omega_\mathrm{p}^2 f_0}{\Omega^2} + \frac{\omega_\mathrm{p}^2 f_1}{\omega_1^2 - \Omega^2} = 0.$$



if $\omega_1 \ll \omega_\mathrm{p}$

$$\Omega_{1\mathrm{p}} \approx \frac{\omega_1}{\sqrt{2}} \qquad \Omega_{2\mathrm{p}} \approx \sqrt{2}\omega_\mathrm{p}$$

GGA: ω_1≈4.2 eV

Ω_{1p}≈3.0 eV

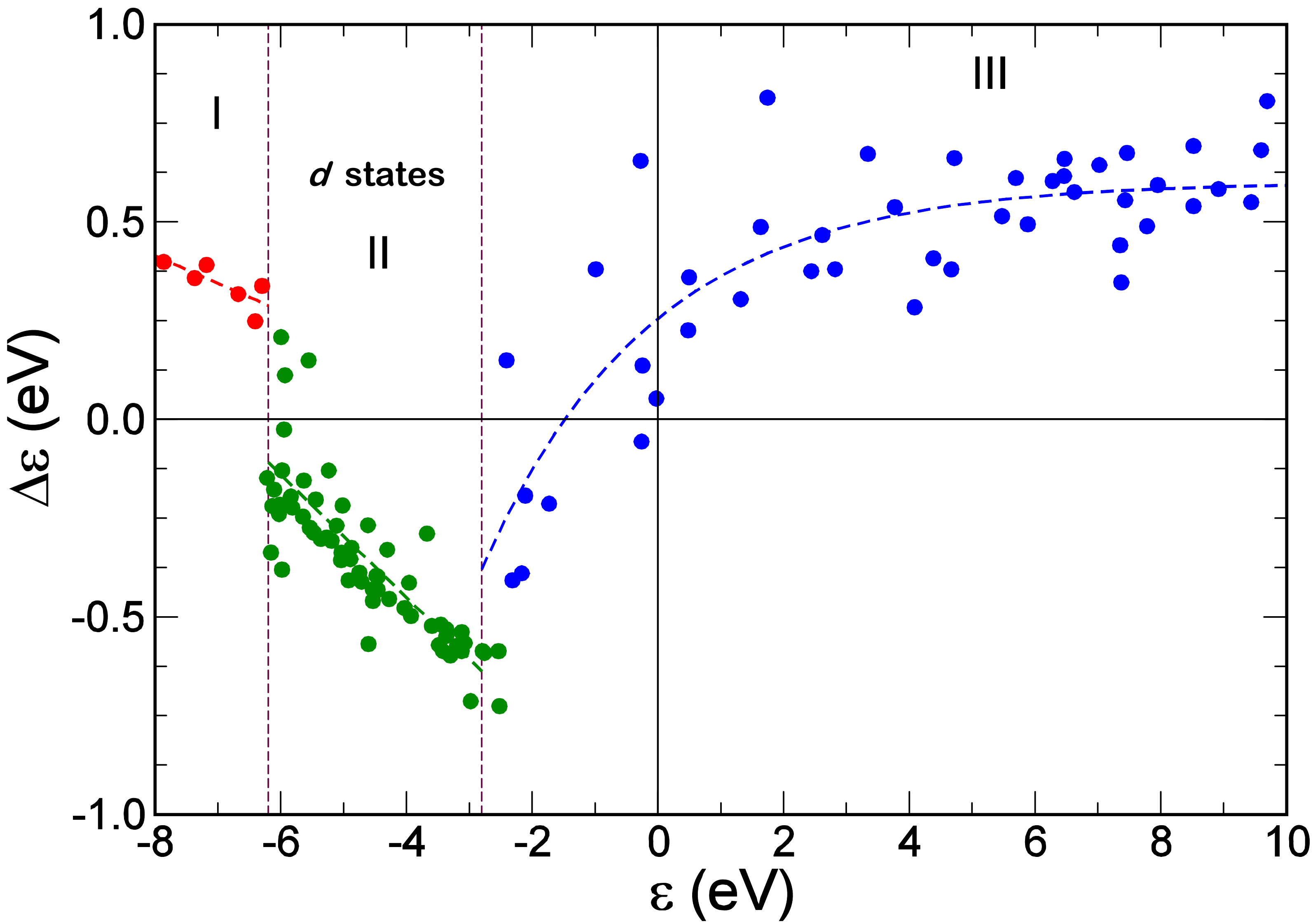
expt: ω_1≈5.3 eV

Ω_{1p}≈3.7 eV

$$\mathrm{Im}(-1/\varepsilon) = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}$$

solution: correcting ω_1 (the position of d states) - *GW*

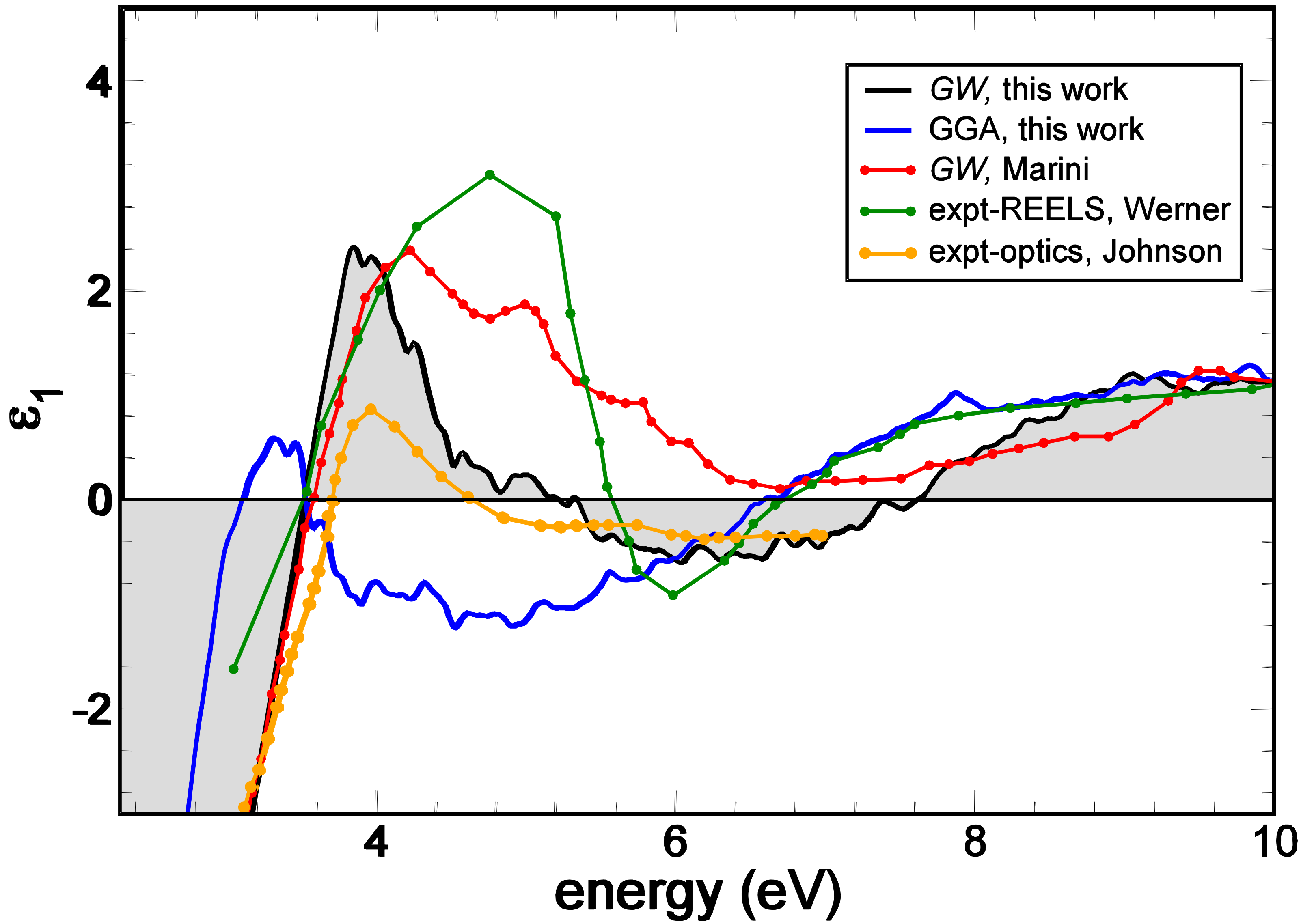
GW corrections



analytical fit to: A. Marini, R. Del Sole, and G. Onida, Phys. Rev. B 66, 115101 (2002)

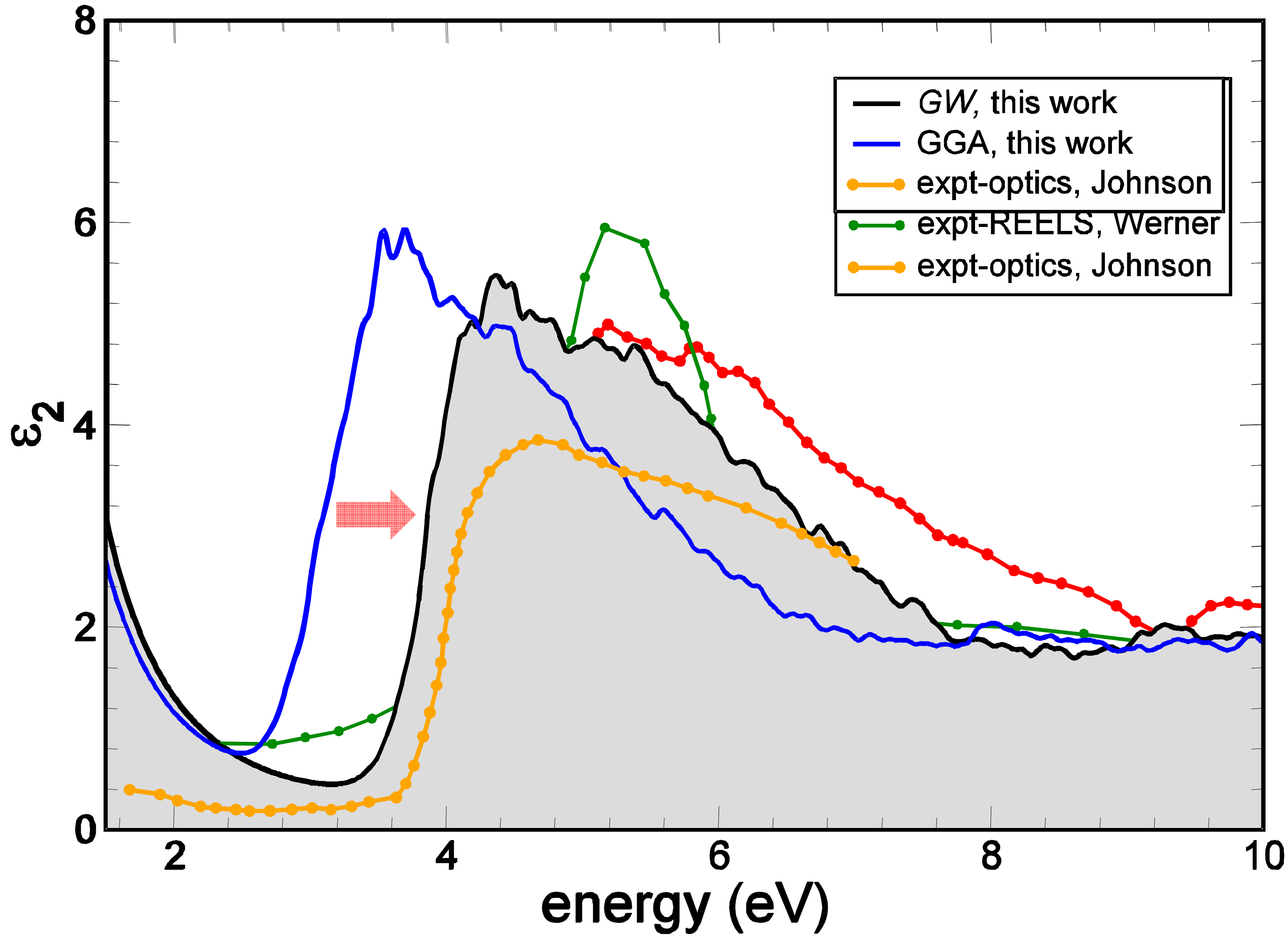
results are not sensitive to the analytical form of the fit as long as main features are reproduced (the position of *d* states)

GW corrections: ε_1



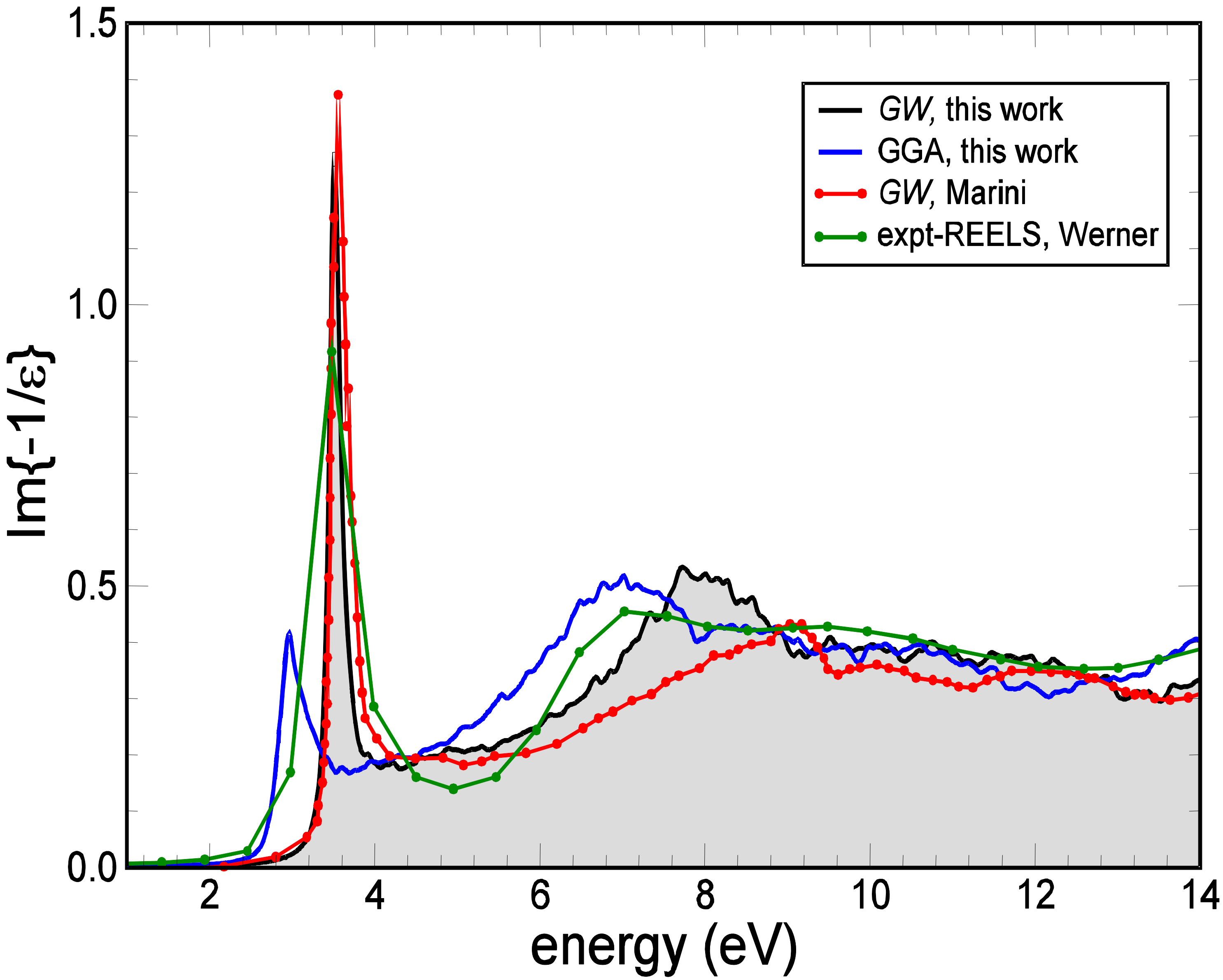
REELS: W. S. M. Werner et al., Phys. Rev. B 77, 161404 (2008);
optical measurements: B. Johnson and R. W. Christy, Phys. Rev. B 6, 4370 (1972);
GW: A. Marini, R. Del Sole, and G. Onida, Phys. Rev. B 66, 115101 (2002).

GW corrections: ε_2



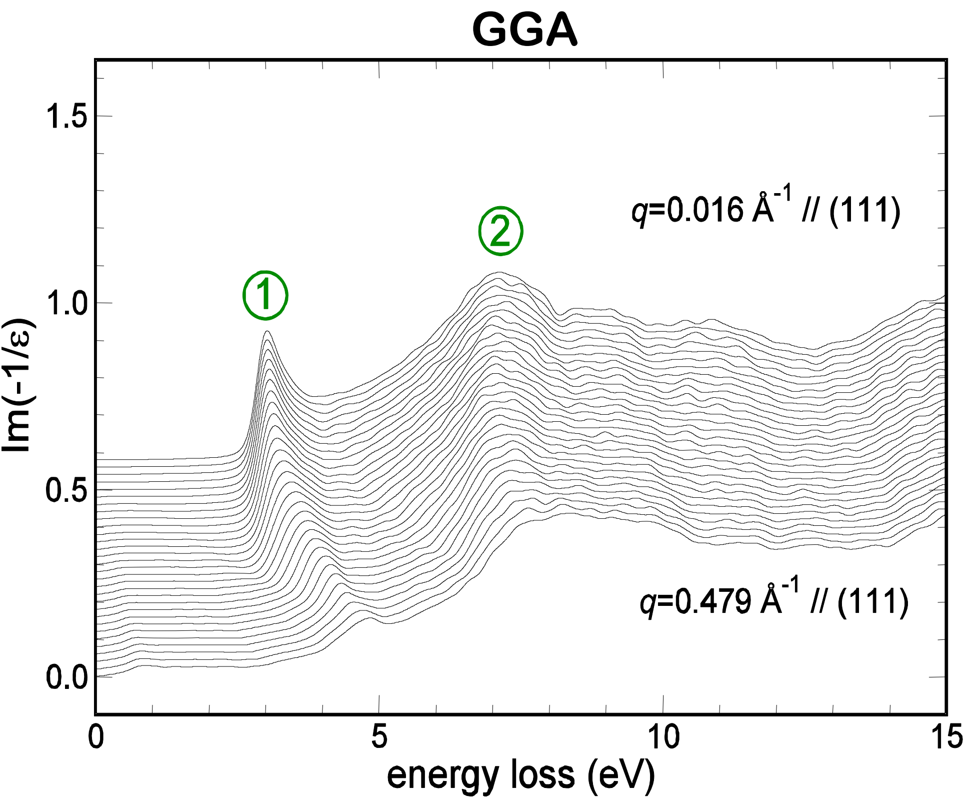
REELS: W. S. M. Werner et al., Phys. Rev. B 77, 161404 (2008);
optical measurements: B. Johnson and R. W. Christy, Phys. Rev. B 6, 4370 (1972);
GW: A. Marini, R. Del Sole, and G. Onida, Phys. Rev. B 66, 115101 (2002).

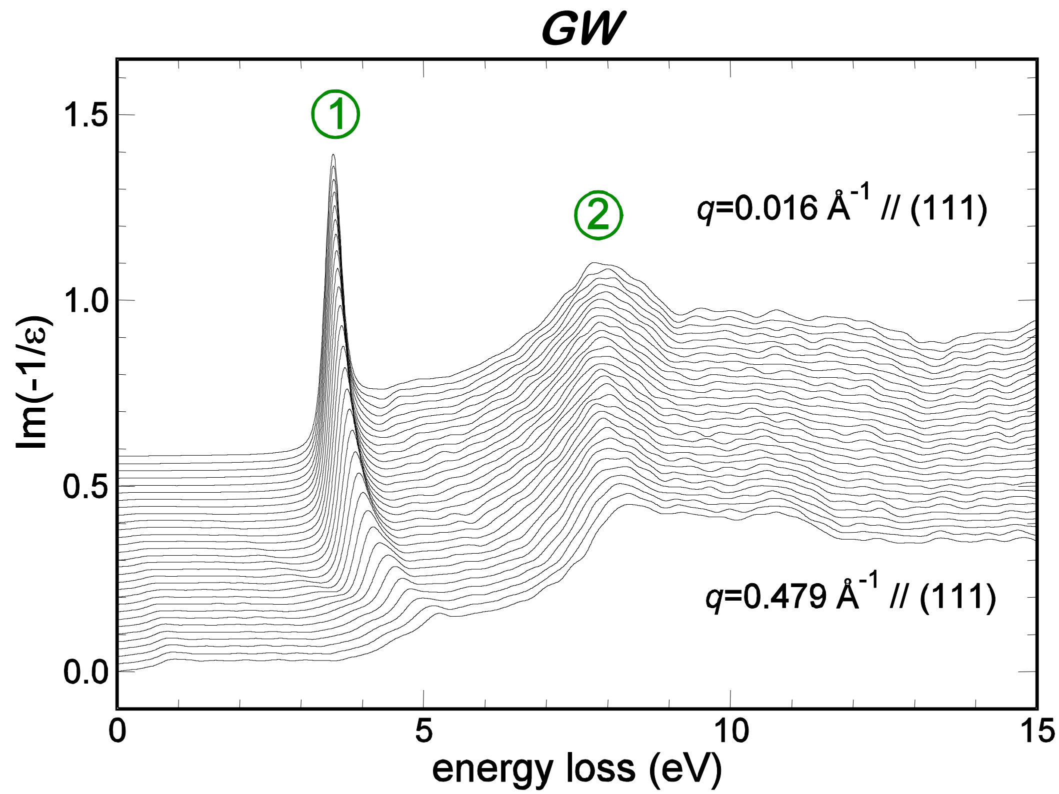
GW corrections: loss function

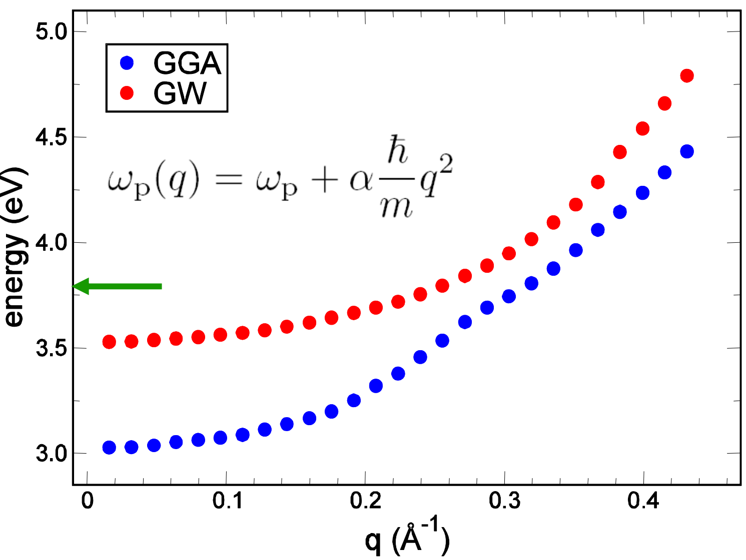


REELS: W. S. M. Werner et al., Phys. Rev. B 77, 161404 (2008);
optical measurements: B. Johnson and R. W. Christy, Phys. Rev. B 6, 4370 (1972);
***GW*: A. Marini, R. Del Sole, and G. Onida, Phys. Rev. B 66, 115101 (2002).**

q-dependent loss function: plasmon dispersion







$$\omega_{\mathrm{p}}(q) = \omega_{\mathrm{p}} + \alpha \frac{\hbar}{m} q^2$$

	$q<0.4$ Å^{-1}	$q<0.2$ Å^{-1}
GGA	**1.02**	**0.83**
GW	**0.83**	**0.49**
free elec.	**--**	**0.47**
expt.	**0.8±0.1** **0.76±0.03**	**--**

$$\alpha = (3/5)(E_{\mathrm{F}}/\hbar\omega_{\mathrm{p}})$$

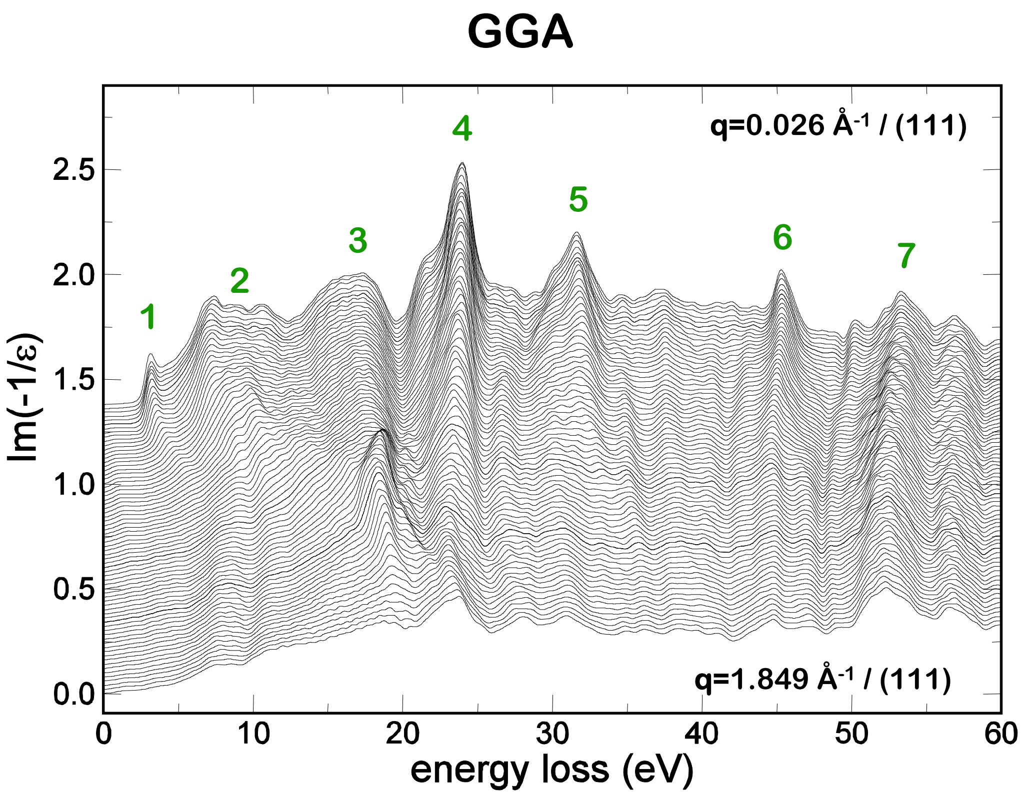
expt.:

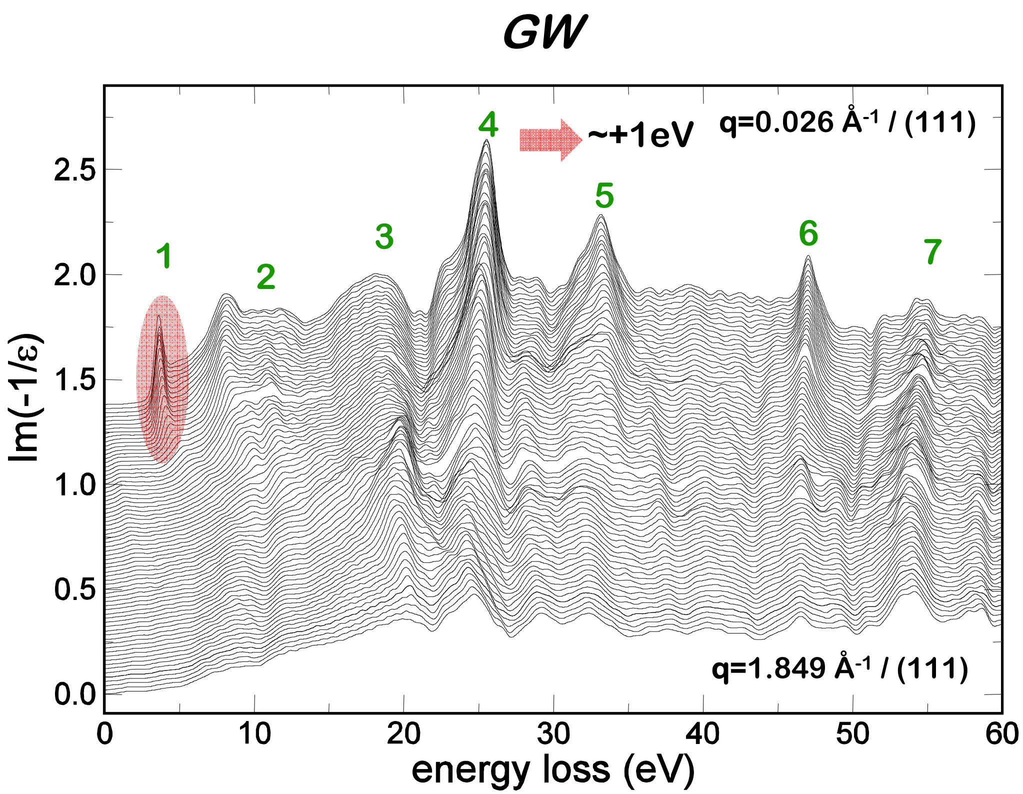
P. Zacharias and K. L. Kliewer, Solid State Commun. 18, 23 (1976).

A. Otto and E. Petri, Solid State Commun. 20, 283 (1976).

for comparison Al: ω_1=14.95±0.05 eV, α=0.38±0.02, q_c≈1.3 Å^{-1}

q-dependent loss function: inter-band transitions





-peak (1) is a low-energy plasmon;
-peaks (3)-(7) caused by inter-band transitions are almost dispersionless (~1eV);
however, they decay with q differently;
-peak (2) has the most complicated behaviour, retaining both inter-band and plasmon character.

GW corrections affect most dramatically the low-energy plasmon;

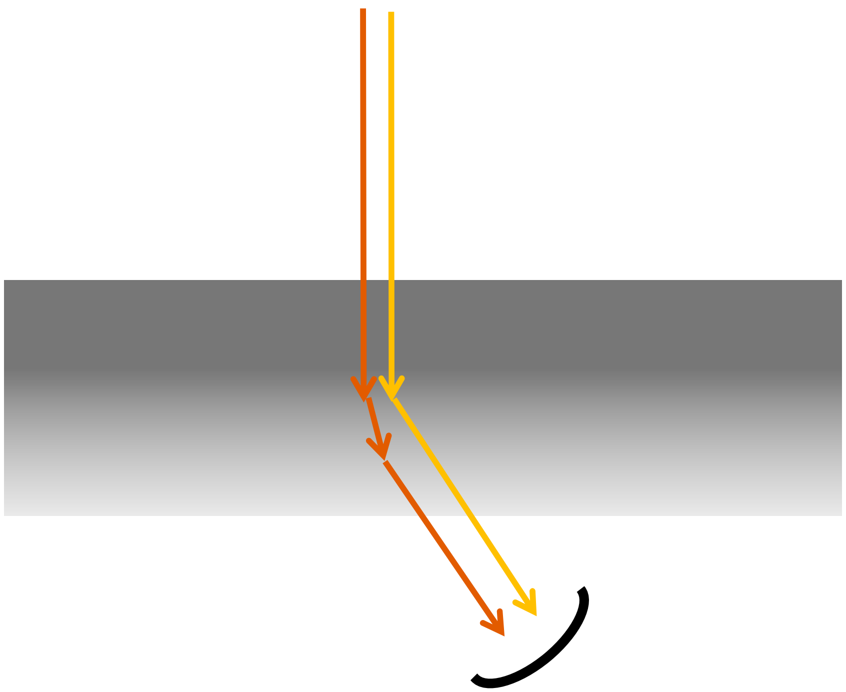
inter-band transitions simply shift to slightly larger energies.

Challenges for experiment

S. Schneider at CIME/EPFL (first half of 2010)

(i) sample preparation – thin free-sanding layers

(ii) multiple scattering

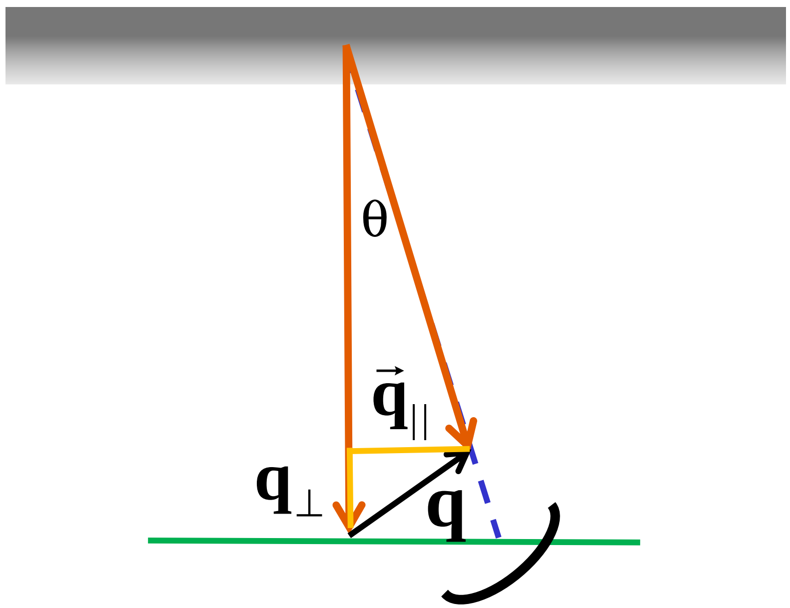


Fourier-log deconvolution if all **q**-dependent information is available;

if not, tricks are needed:
P. E. Batson and J. Silcox, Phys. Rev. B 27, 5224 (1983);

alternatively: theoretical loss function to simulate multiple scattering + adjusting of parameters.

(iii) ω-dependent **q**



For a given scattering angle θ, **q** depends on energy loss ω;
for a fixed $\vec{\mathbf{q}}_{||}$, $\mathbf{q}_{\perp}$ increases with ω

Conclusions and outlook

Conclusions

The loss function of Ag in the low-loss region has a complex structure: plasmons and inter-band transitions

GGA-RPA fails to predict the position and the width of the low-energy plasmon due to the underbinding of d states

Approximate *GW* corrects this deficiency

Outlook

Detailed experimental work

Single-scattering distribution from experimental measurements

Lifetimes

Experimental loss functions and problems involved in obtaining them will indicate which level of theoretical sophistication is needed to reproduce measurements

end