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

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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 photography by Nicéphore Niépce.
- 1839: Black and White photography by Daguerre.
- 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).
Silver Chloride

- Perfect crystal of AgCl.
- FCC structure.
- Lattice parameter $a = 5.547\text{Å}$.
- 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

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

- Linear response framework and TDDFT:
  \[ \chi = \chi_0 + \chi_0 (v + f_{xc}) \chi \]

- With Random Phase Approximation (RPA):
  \[ \chi^{\text{RPA}} = \chi_0 + \chi_0 v \chi^{\text{RPA}} \]

- TDDFT as implemented in the DP-code:
  http://www.dp-code.org/
\[ \kappa = \mathcal{S}\left(\sqrt{\epsilon_M}\right) \]

Overall agreement

Transition from HOMO to LOMO, 
Cl 3p to CL 4s
Band structure

- LDA
- $E_{\text{ind}} = 0.6 \text{ eV}$
- Transition $L \rightarrow \Gamma$
- Good agreement with other calculations:
Band structure

- LDA
- $E_{\text{ind}} = 0.6$ eV
- Transition $L \rightarrow \Gamma$
- But experimental gap 3.25 eV !!!
✗ Shift in position
✗ Relative intensity not correct
GW correction

- Perturbative GW ($G^0W^0$)
  \[ E^{GW} = \epsilon^{LDA} + Z \langle \Sigma^{GW} - V^{LDA}_{xc} \rangle \]
- 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:
  \[ E^{GW}_{ind} = 2.5 \text{eV} \left( E^{\text{exp}} = 3.25 \text{eV}, E^{LDA} = 0.6 \text{eV} \right) \]

✔ Shift problem solved!
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

- DFT-LDA for ground states.
- TDDFT for optical properties.
- $G_0W_0$ calculation.
- Self consistent GW.
- Bethe-Salpeter equation.
- Silver nanoparticles, lattice deformation, self trapped exciton.

Present

Beyond silver chloride
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Thank you for your attention!
\[ K(\omega) = K_a(\omega) + K_e(\omega) \]

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

\[ K_a(\omega) \propto \sqrt{\hbar \omega - E_g + E_{ph}} \]
\[ K_e(\omega) \propto \sqrt{\hbar \omega - E_g - E_{ph}} \]

- From the two thresholds we can get the band gap


Pseudo potential for silver

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