EXPLORING
CRYSTAL CHEMISTRY OF BINARY SILVER CHLORIDES
With Evolutionary Algorithms And Density Functional Theory

M. Uhliar[1]*, K. Tokár[1,2], O. Kohulák[3], M. Derzsi[1,4]

[1]*ATRI Institute, MTF Slovak University of Technology in Bratislava, Slovakia*

[2]*Institute of Physics, Slovak Academy of Sciences, Slovakia*

[3] *Department of Physics, Faculty of Science, University of Ostrava, Czech Republic*

[4]*Center of New Technologies, University of Warsaw, Poland*

uhliar.matej@gmail.com

EUROPEAN UNION
European Regional Development Fund
OP Integrated Infrastructure 2014 – 2020

INTRODUCTION

- **The only know** silver chloride phase is **AgCl** with rock salt structure
- Various other stoichiometries are known among **transition metal chlorides**:

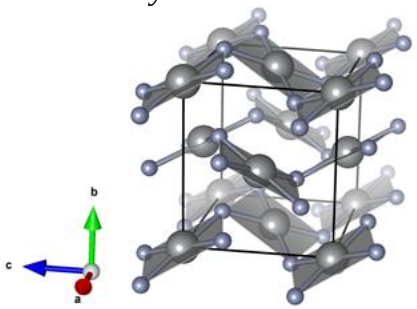
  i.e. MCl_x (x = 1 – 6), M_2Cl_5, M_3Cl_8.
- Rich phase diagram in **Ag-F system**: Ag_2F, AgF, AgF_2,Ag_2F_5, Ag_3F_8, AgF_3
- **Dichlorides** and **trichlorides** commonly observed with **coinage** metals.
- So why other **Ag-Cl** phases are not observed?
- Our **previous theoretical study** of Ag/Cl enriched/deficient AgCl models suggests existence of other phases [*Uhliar, Bsc thesis 2018*].
- **Our goal** is to **explore Ag-Cl phase diagram from ab initio** with DFT and Evolutionary Algorithms.

METHODS

- Density Functional Theory (DFT) calculation were performed in program VASP [*Kresse et. al., Phys. Rev. **59** (1999)*] with following settings:
    - GGA **PBEsol** functional,
    - plane-wave cut-off 520 eV,
    - DFT-D3 for **van der Waals** correction,
    - on site **Coulomb correlation** term U_{Ag}=5 eV in combination with Hunt exchange J_{Ag}=1 eV.
- Open source **V4p** software for electronic Density of States data reading and visualization. [*http://www.p4vasp.at/*].
- EA calculations: **XtalOpt** program using 4-step DFT+vdW optimization [*Avery, et. al., Computer Physics Communications (2017)*].
- Visualization of crystal structures was done in VESTA software [*Momma et. al., J. Appl. Crystallogr., (2011)*].

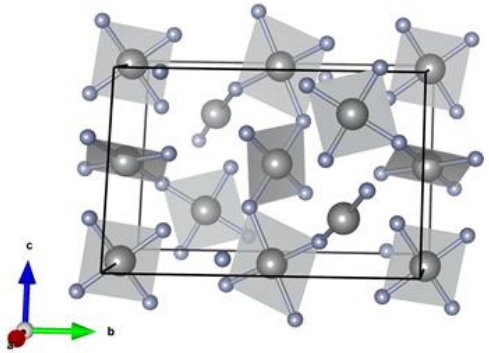
MODELLING Ag-Cl PHASES IN Ag-F STRUCTURE TYPES

2D layers



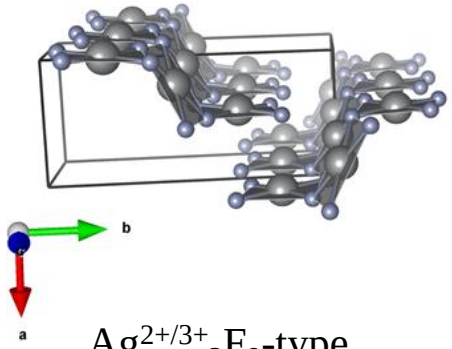
$Ag^{2+}F_2$-type

3D structure



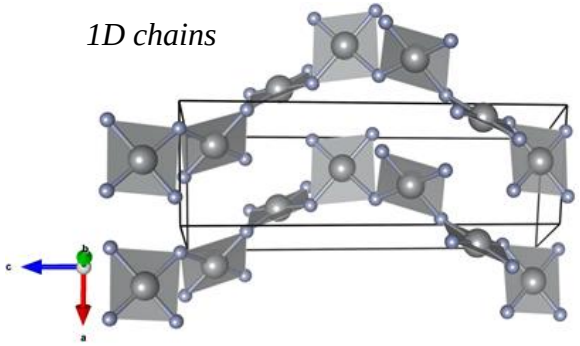
$Ag^{2+/3+}{}_2F_5$-type

1D stripes

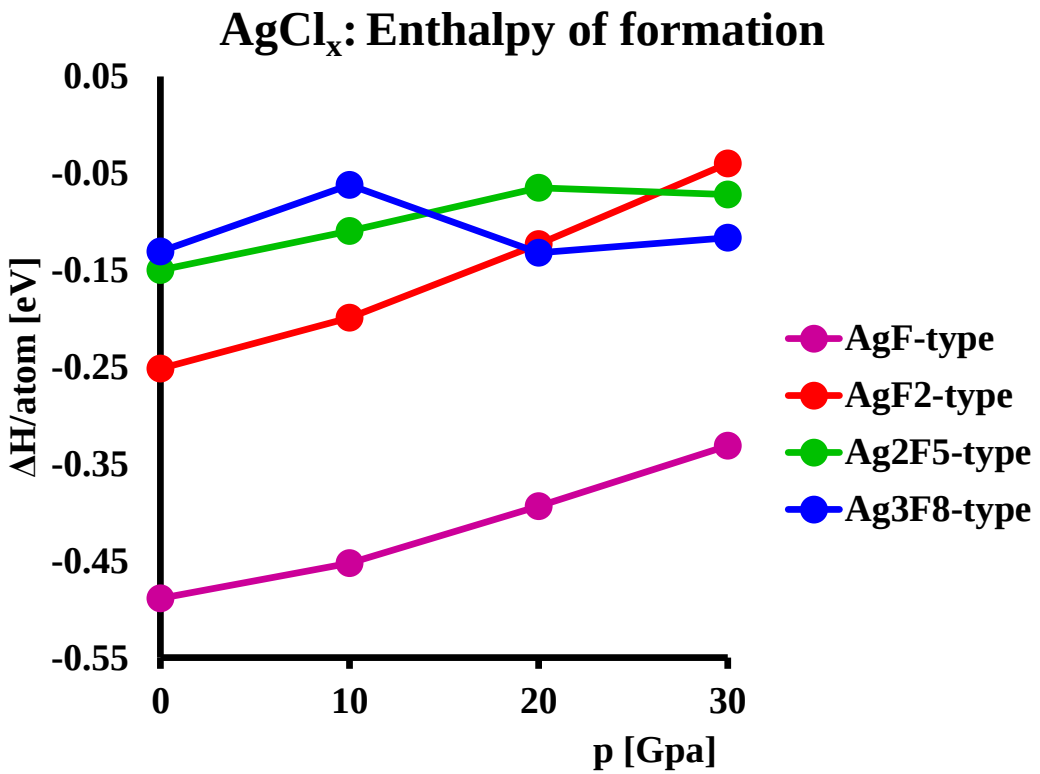


$Ag^{2+/3+}{}_3F_8$-type

1D chains



$Ag^{3+}F_3$-type

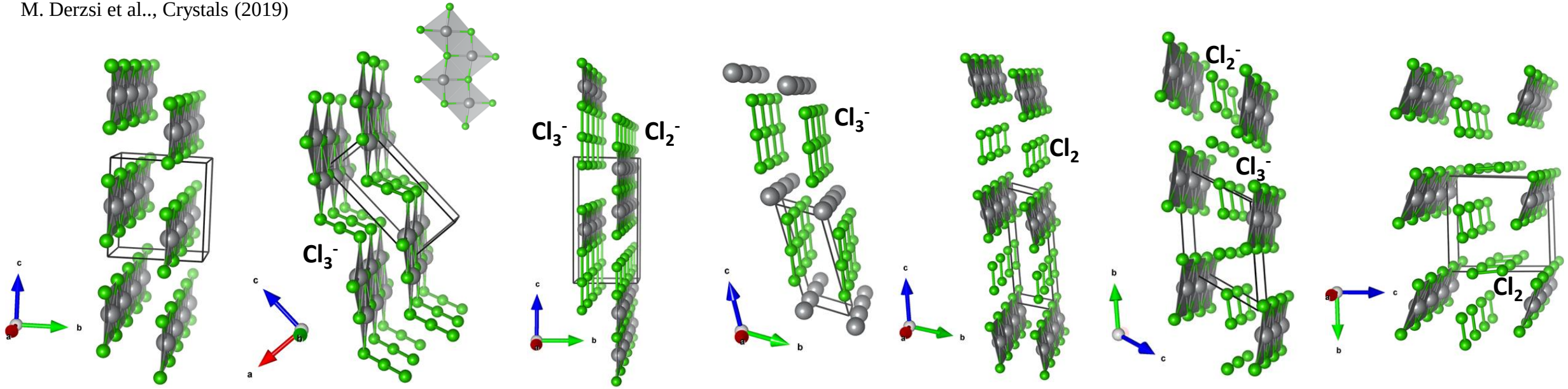


CRYSTAL STRUCTURES FROM EVOLUTIONARY ALGORITHMS

increasing Cl concertation

$AgCl_2$ Ag_2Cl_5 Ag_3Cl_8 $AgCl_3$ $AgCl_4$ $AgCl_5$ $AgCl_6$

M. Derzsi et al.., Crystals (2019)



Common features:

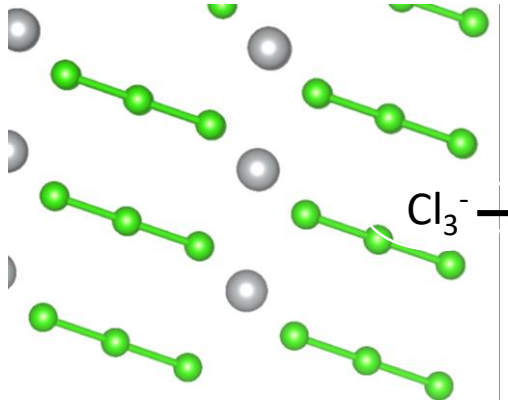
- $AgCl_2$ stripes (2-step ladder in Ag_2Cl_5)
- Cl polyanions

Distinct features:

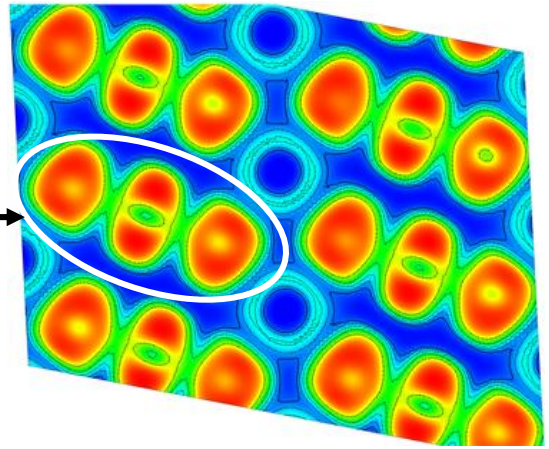
- Different connectivity of Ag with Cl polyanions

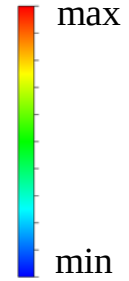
ELECTRON LOCALIZATION MAPS – ANALYSIS OF BONDS

$AgCl_3$

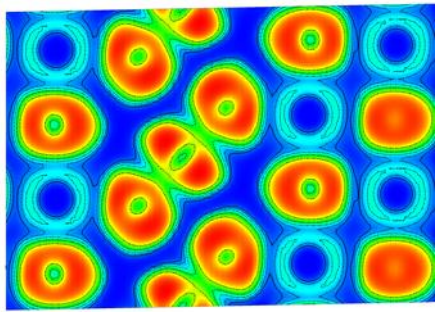


Cl_3^-

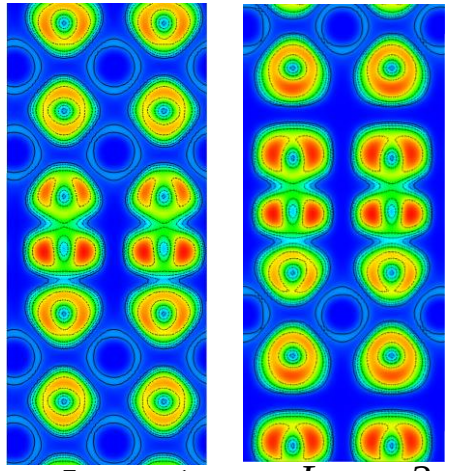




Ag_2Cl_5

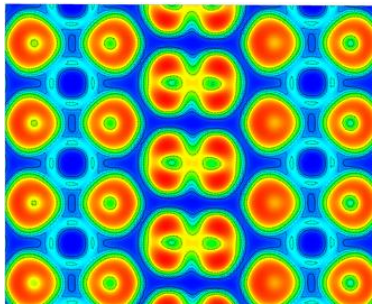


Ag_3Cl_8



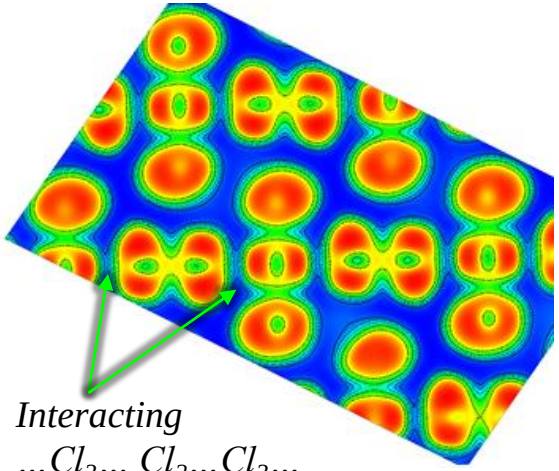
Layer 1 *Layer 2*

$AgCl_4$



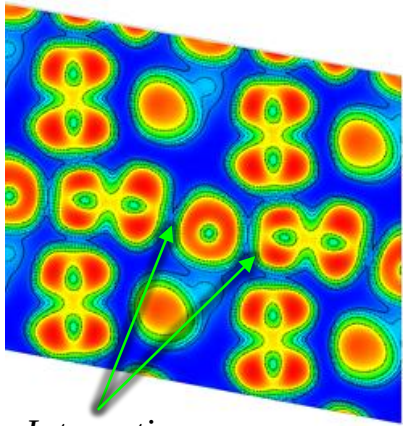
$AgCl_2$ stripes *Cl_2 molecules*

$AgCl_5$



Interacting
…Cl_3… Cl_2…Cl_3…
***1D** chlorine network*

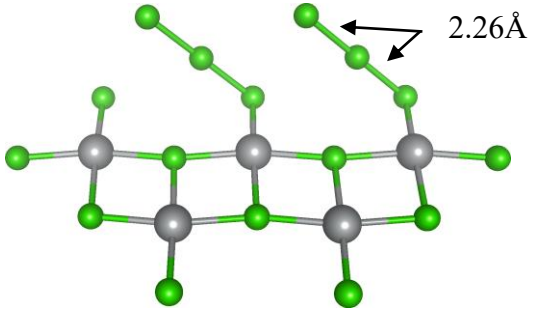
$AgCl_6$



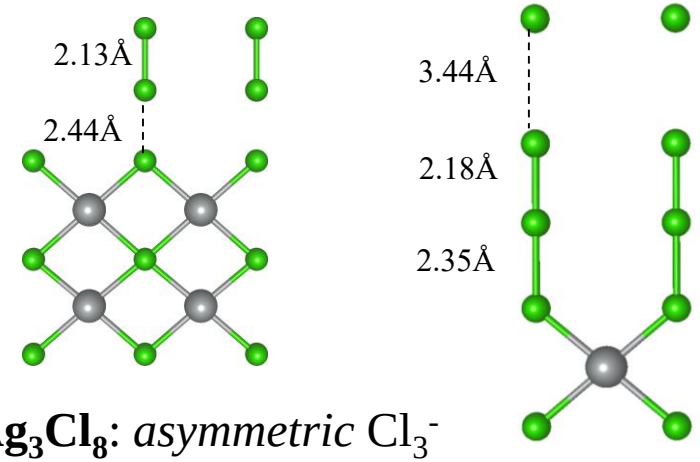
Interacting
…Cl^-… Cl_2…Cl^-…
***2D** chlorine network*

GEOMETRY OF BONDS: POLYANIONS

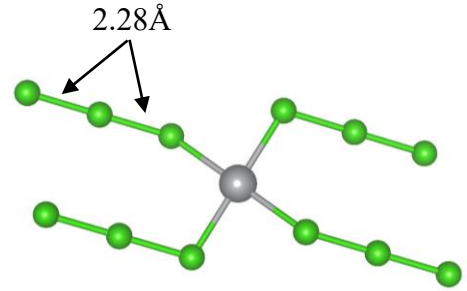
Tabulated distances	$d(Cl\text{-}Cl)_{mol}$ = 2.0 Å	Cl_3^-: d(Cl-Cl) = 2.1 - 2.6 Å	$d(Cl\text{-}Cl)_{vdW}$ = 3.6 Å



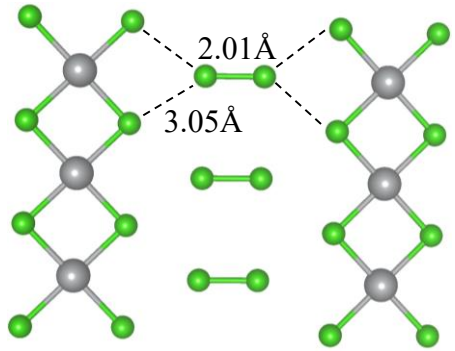
Ag_2Cl_5: *symmetric* Cl_3^-



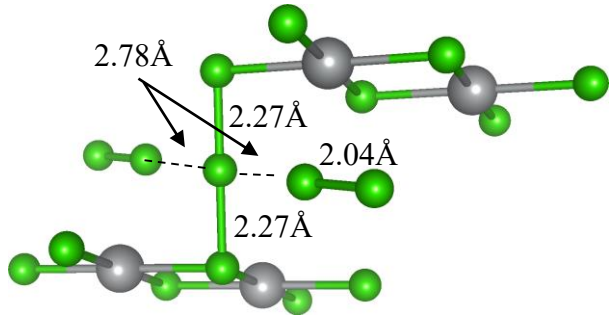
Ag_3Cl_8: *asymmetric* Cl_3^-



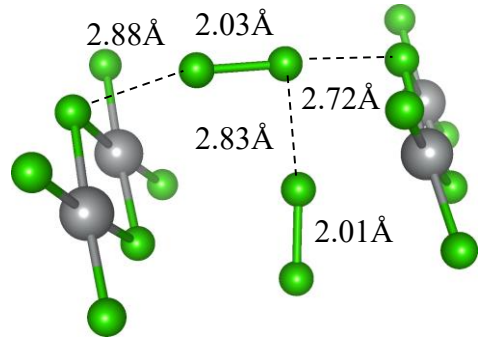
$AgCl_3$: *symmetric* Cl_3^-



$AgCl_4$: Cl_2



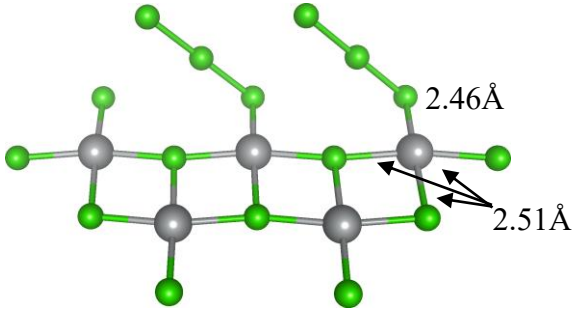
$AgCl_5$: […$(Cl_3)^-$ …Cl_2…] network



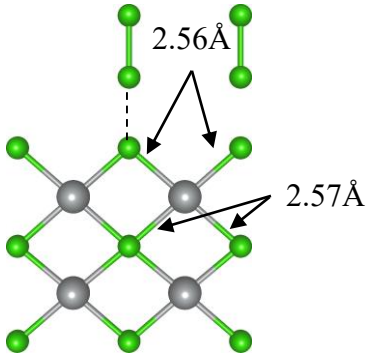
$AgCl_6$: […Cl_2 … Cl_2…] network

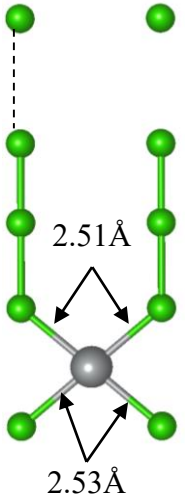
GEOMETRY OF BONDS: Ag-Cl

Tabulated distances	d(Ag^{1+}-Cl^{-}) = 2.96 Å	d(Ag^{2+}-Cl^{-}) = 2.6 Å	d(Ag^{3+}-Cl-) = 2.48 Å

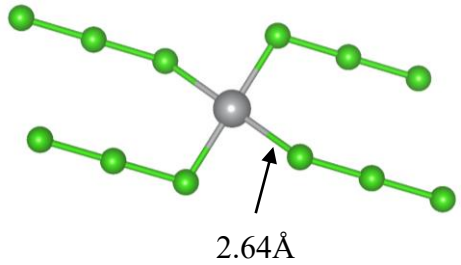


Ag_2Cl_5: $Ag^{1.5+}$

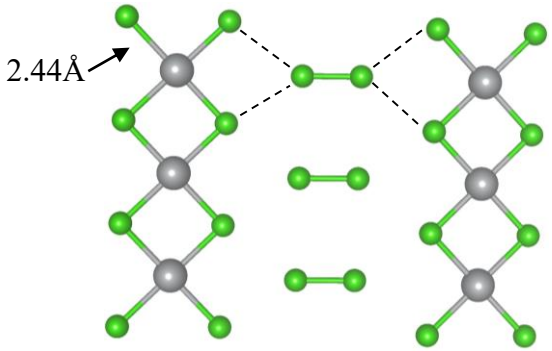




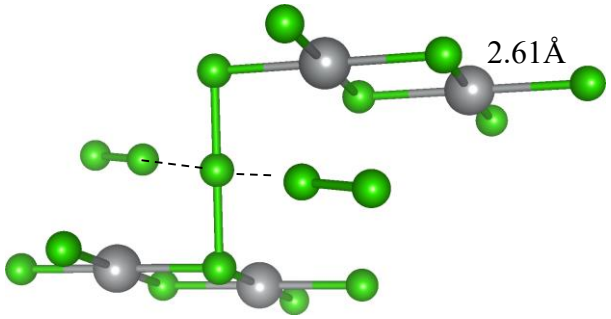
Ag_3Cl_8: Ag^{+}, Ag^{2+}



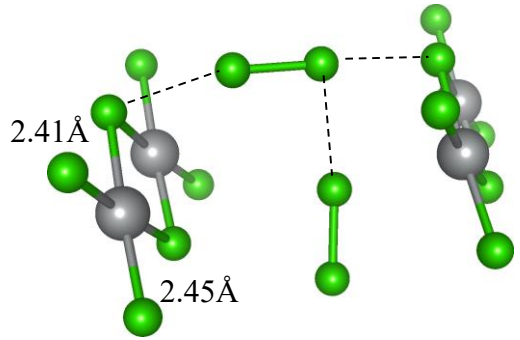
$AgCl_3$: Ag^{+}



$AgCl_4$: Ag^{2+}



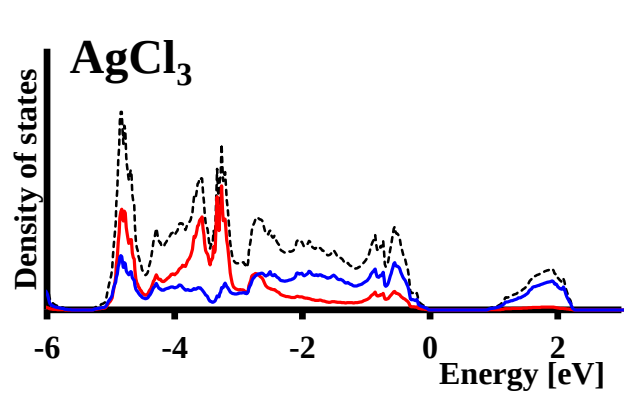
$AgCl_5$: Ag^{1+}

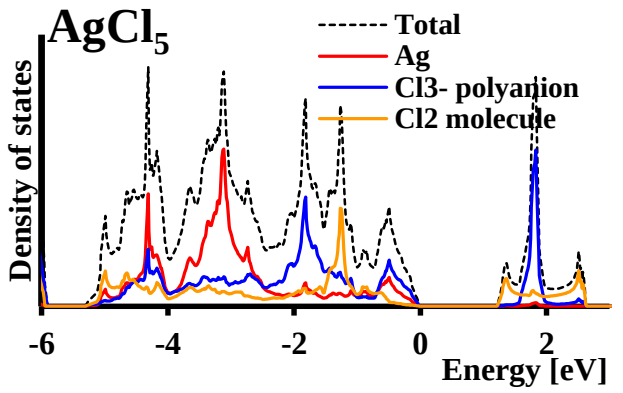


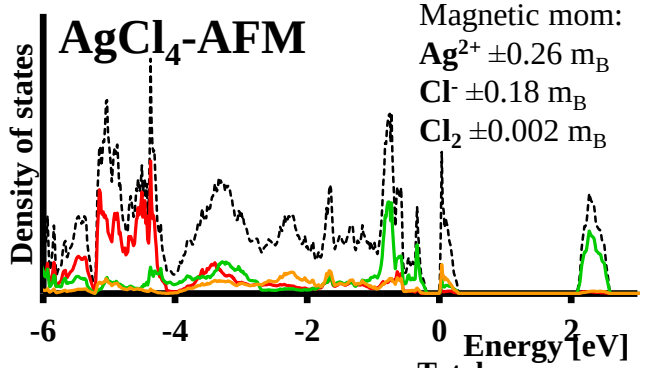
$AgCl_6$: Ag^{2+}

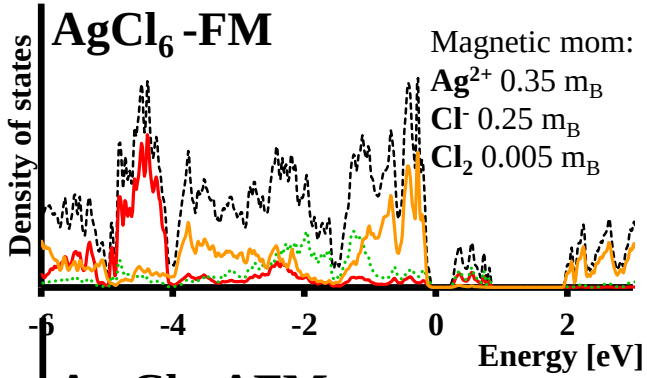
ELECTRONIC STRUCTURE: DENSITY OF STATES

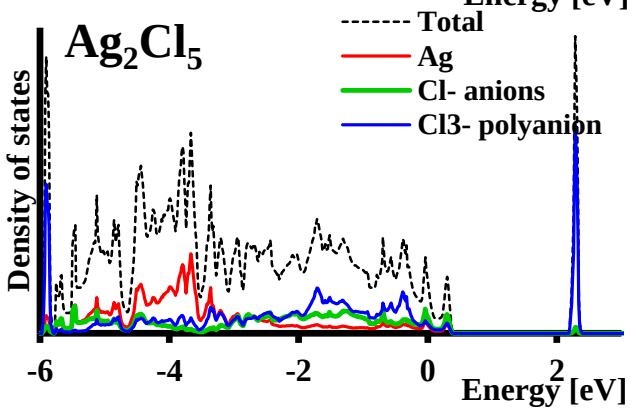
Phase	Stoichiometry	Ground state
$AgCl_3$	$Ag^{+}Cl_3^{-}$	semiconductor
$AgCl_5$	$Ag^{+}Cl_3^{-}Cl_2$	semiconductor
$AgCl_4$	$Ag^{2+}Cl^{-}_2Cl_2$	AFM semiconductor
$AgCl_6$	$Ag^{2+}Cl^{-}_2(Cl_2)_2$	FM semiconductor
Ag_3Cl_8	$Ag^{2+}Cl^{-}Cl_3^{-}$ (layer 1) $Ag^{1+}_2Cl^{-}Cl_3^{-}$ (layer 2)	AFM metal
Ag_2Cl_5	$Ag^{1.5+}_2(Cl^{-})_2Cl_3^{-}$	metal

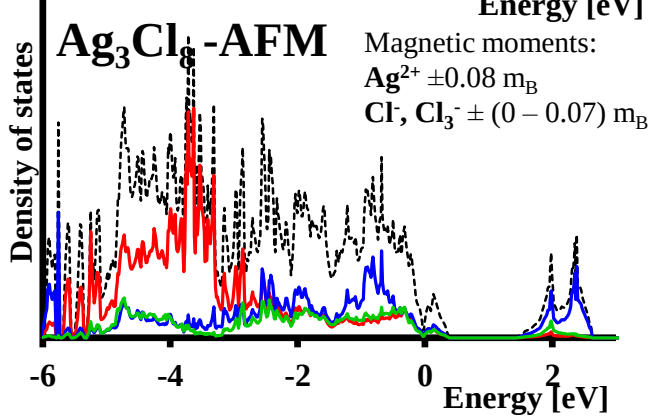




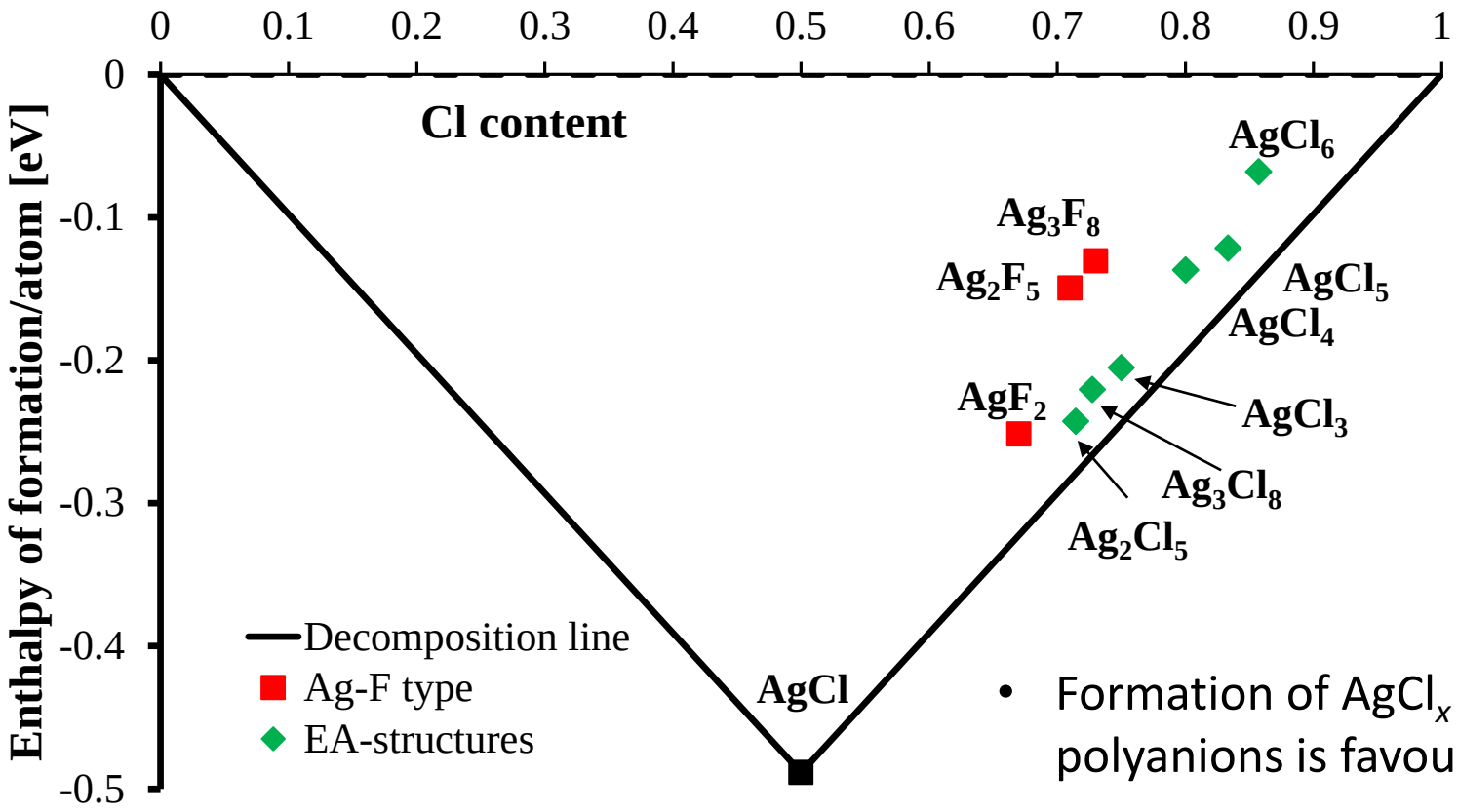








CONVEX HULL



- Formation of $AgCl_x$ structures containing Cl polyanions is favoured over AgF_x type structures
- All phases are metastable relative to AgCl

CONCLUSIONS

- **Ag-Cl phases** were modelled in **Ag-F types** of crystal structures at low and high pressures.
- **Evolutionary algorithms** were used to calculate crystal structures of: $AgCl_3$, $AgCl_4$, $AgCl_5$, $AgCl_6$, Ag_2Cl_5, Ag_3Cl_8.
- Our calculations predict **formation of chlorine polyanions** in all phases with higher chlorine content (>0.7).
- Ag-Cl containing Cl polyanions are energetically **preferred over the Ag-F** type structures.
- The **highest oxidation** state of silver found in the predicted phases is $\mathbf{Ag^{2+}}$.
- The phases containing $\mathbf{Ag^{+}}$ cations are predicted as **semiconductors**.
- The phases containing higher oxidation states are predicted to be **magnetic metals** or **semiconductors**.
- **All** predicted structures were computed to be **metastable** relative to the known AgCl.

ACKNOWLEDGEMENTS

- The European Regional Development Fund, Research and Innovation Operational Programme, for project No. ITMS2014+: 313011W085.
- Scientific Grant Agency of the Slovak Republic, grant No. VG 1/0223/19.
- The Slovak Research and Development Agency, grant No. APVV-18-0168.
- Aurel supercomputing infrastructure in CC of Slovak Academy of Sciences acquired in projects ITMS 26230120002 and 26210120002 funded by ERDF.

Thank you for your attention!