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Thermodynamic stability, phonon anharmonicity and electronic response of antiferromagnetic and charge-transfer polymorphs of AgF2 from ab-initio

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STU MTF
SAV
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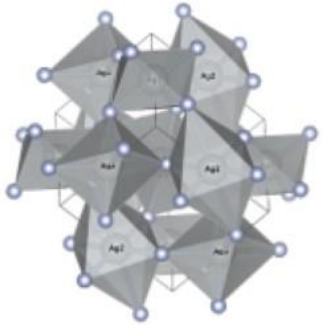
Experimental observation of phase stability in AgF2

- Common *alpha-Ag(II)F2* phase has extremely strong oxidizing and fluorinating properties, layered structure, features charge transfer insulator

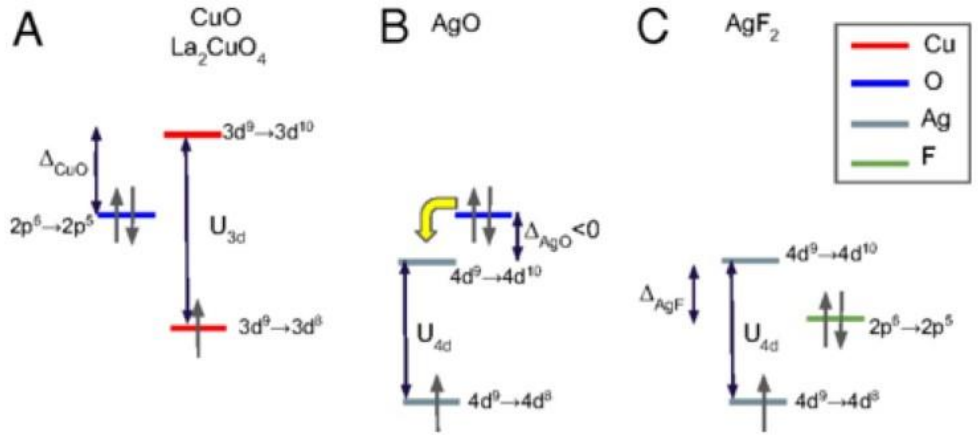
- Disproportionated ***beta*-Ag(I)Ag(III)F4** form is uncommon and has been observed before only once and a **red-brown amorphous** product of reaction of ***AgBF4*** with ***KAgF4*** in anhydrous **HF (N. Barlett)**

- ***beta*-Ag(I)Ag(III)F4 phase** undergoes a rapid exothermic conversion when **T** raised from **-80 °C to 0 °C:**



***Ag(I)Ag(III)F4* ---> *2Ag(II)F2* .**

Electronic properties of alpha AgF_2 - oxocuprates analogue



Gawraczyński et al. PNAS 116(5): 1495-1500 (2019)

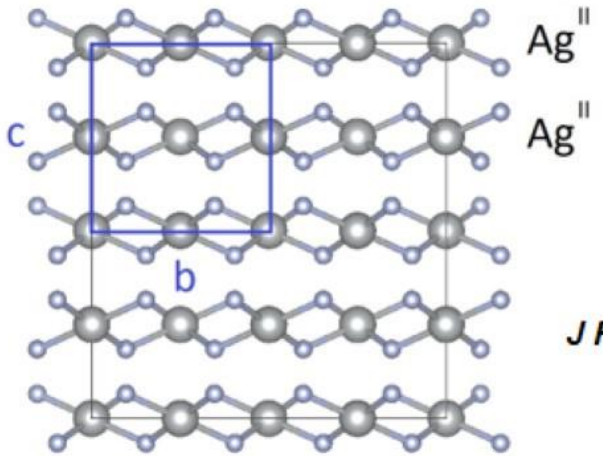
- **AgF_2** features an excellent cuprate analog with remarkably similar electronic parameters to **La_2CuO_4**

- **superexchange constant (70 meV)** reaching about **70%** of that of a typical cuprate

- structures that reduce or eliminate the buckling of the **alpha-AgF_2** planes could have an **antiferromagnetic** coupling that matches or surpasses the **cuprates**

AgF2 polymorphs – crystal structure & dielectric props

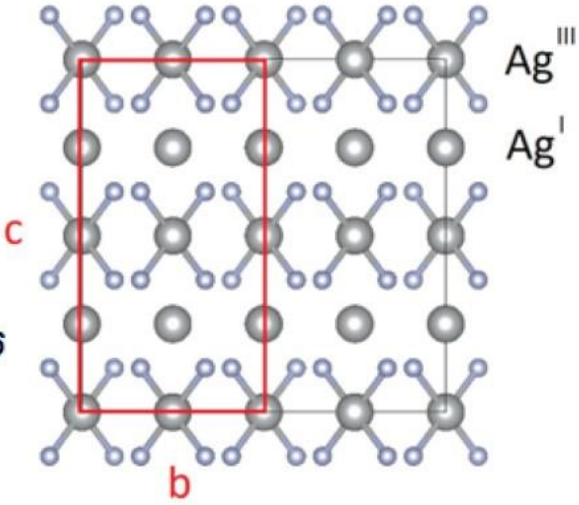
alpha-Ag(II)F2 /orthorhombic/
Pbca #61 (SC::2x2x2)



Adopted KAgF4 model structure:

Romiszewski et al.
J PHYS: COND MAT 19 (2007) 116206

beta-Ag(I)Ag(III)F4 /tetragonal/
I4/mcm #140 (SC::2x2x1)



Lattice params UC (alpha)
a = 5.055 Å
b = 5.495 Å
c = 5.325 Å

Dielectric tensor (alpha)
e_{xx} = 5.00
e_{yy} = 5.46
e_{zz} = 3.00

Lattice params UC (beta)
a = 5.025 Å
b = 5.025 Å
c = 10.704 Å

Dielectric tensor (beta)
e_{xx} = 5.49
e_{yy} = 5.49
e_{zz} = 7.84

Outlook

- Comparative theoretical and experimental study employing **Density Functional Theory (DFT) approach** and the **Raman/IR spectroscopy**

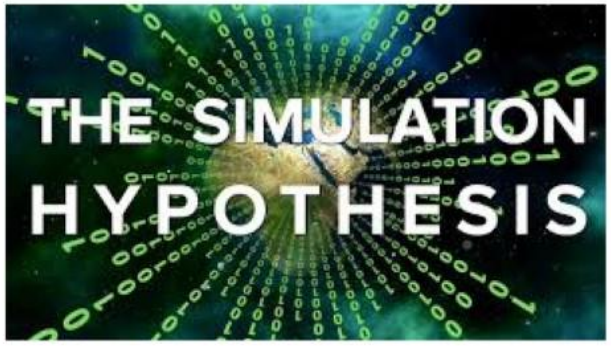
- Treating of adopted structural model that of **$KAgF_4$** type for the **beta-Ag(I)Ag(III)F4** phase

- Structural stability and lattice vibrational modes at increased external pressure **P**

- Lattice dynamics and the relative thermodynamic stability (chemical) of **alpha and beta AgF_2 phases** in **a solid state**

- Coupling of stretching phonon (**Ag-F**) to the valence ordering on **Ag** sites in **alpha**

- **Anharmonicity simulations in alpha-AgF_2 crystal at varying T from direct method**



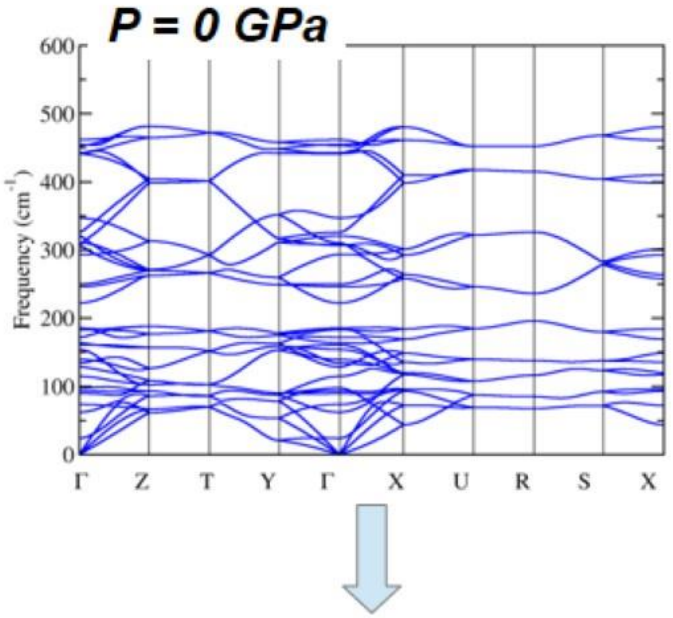
- **Vasp <5.4.4 : DFT/DFPT** calculator of electronic structure

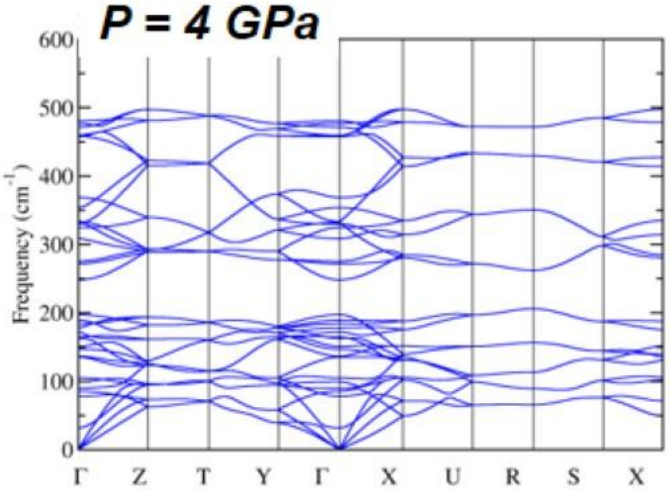
- **Phonopy 1.8.4.2-rc3: HF+DM** lattice dynamics, phonons and Quasi-harmonic approximation (**QHA**) thermodynamics

- **PhononA 7.10 –** anharmonicity effect to modes peaks

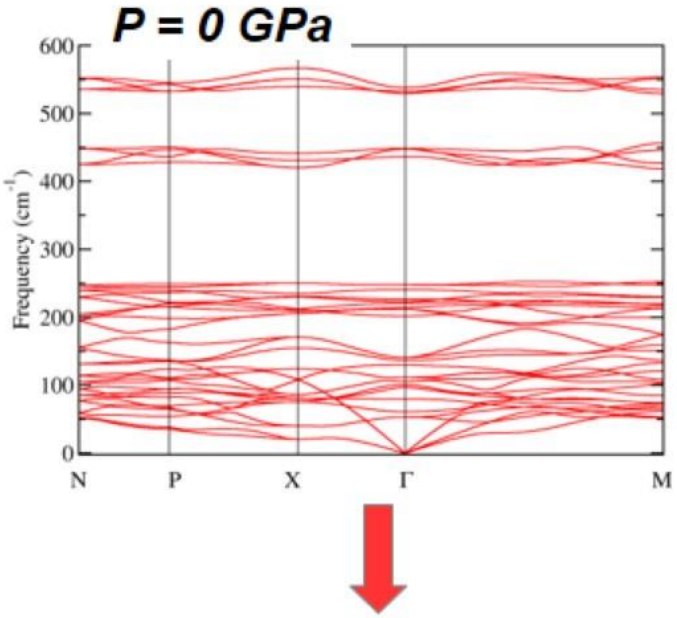
Lattice dynamics and structure stability of AgF2 phases at varying pressure

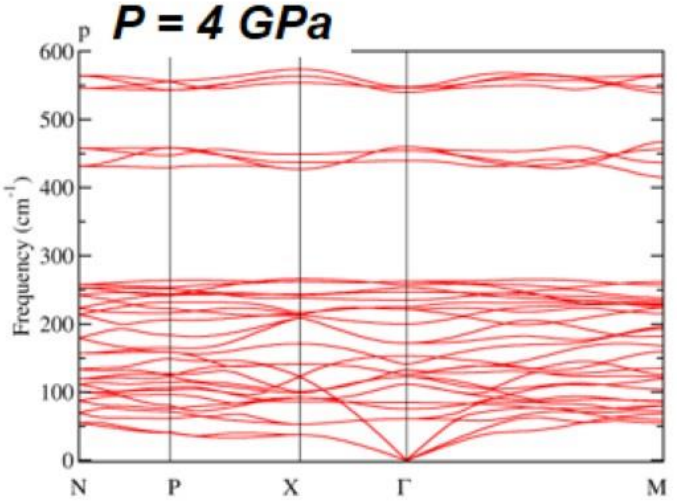
alpha-Ag(II)F2 GGA+U AFM





beta-Ag(I)Ag(III)F4 GGA+U





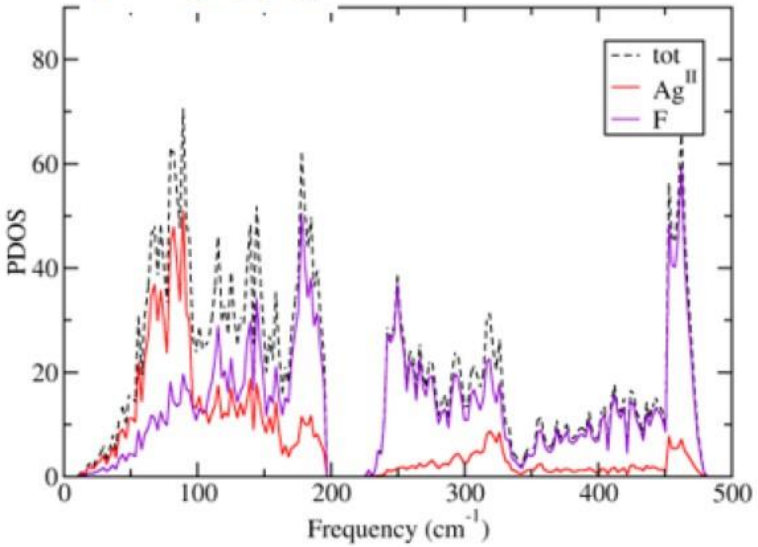
Decomposition of $Ag^{I/II/III}$ vibrational states at elevated pressure

alpha-Ag(II)F2

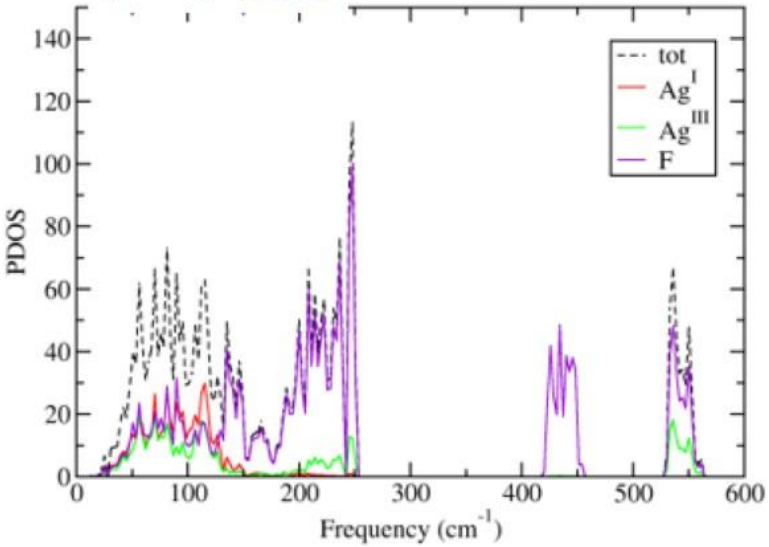
$g_{PDOS}(\omega)$

beta-Ag(I)Ag(III)F4

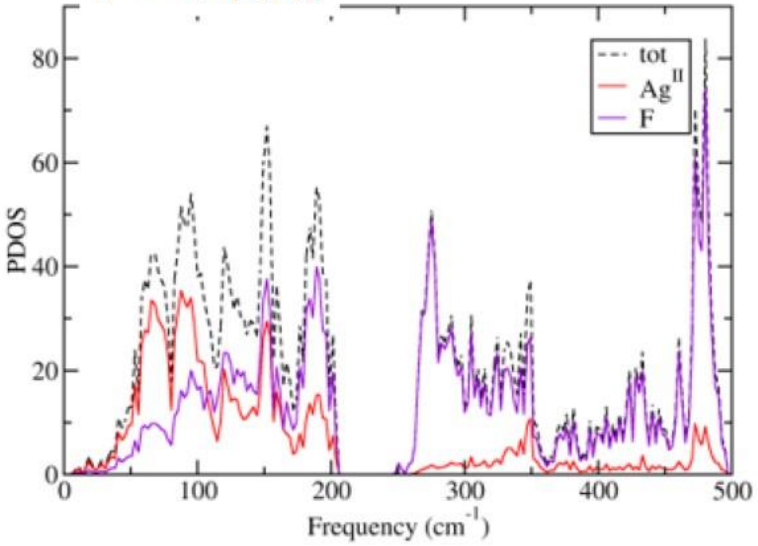
P = 0 GPa



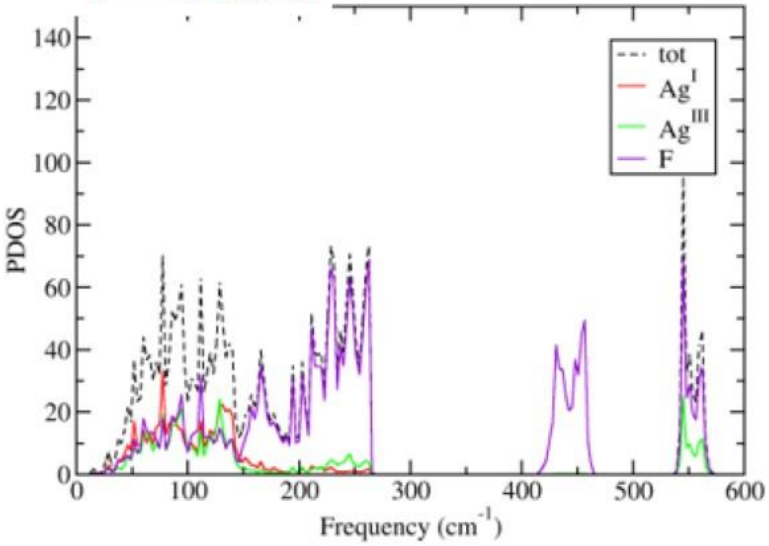
P = 0 GPa



P = 4 GPa

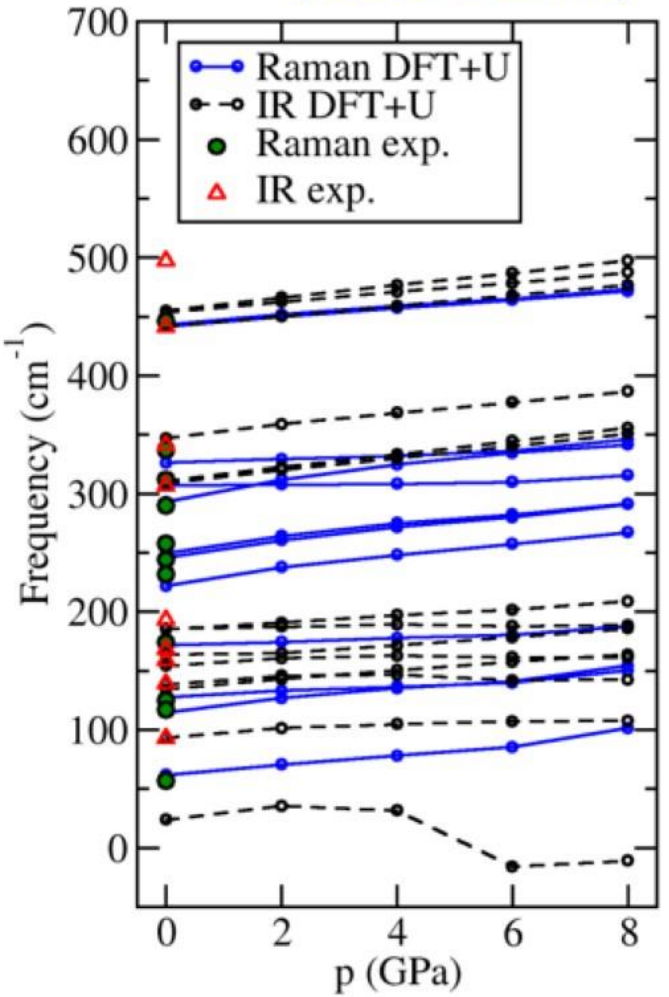


P = 4 GPa

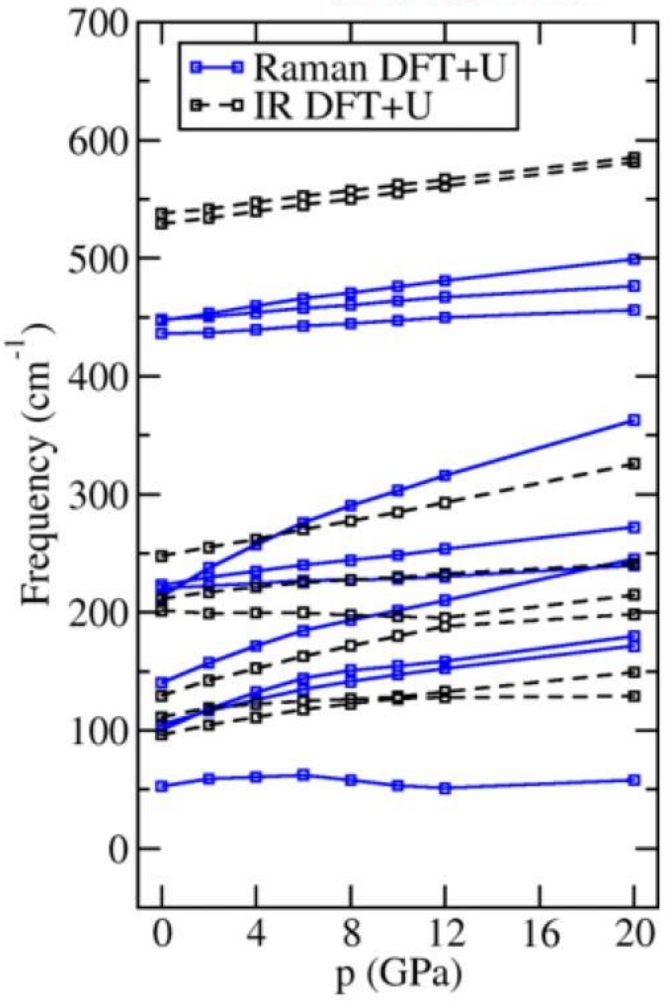


Stability of Raman and IR modes with increasing pressure

alpha-Ag(II)F2 (orthorhombic)



beta-Ag(I)Ag(III)F4 (tetragonal)



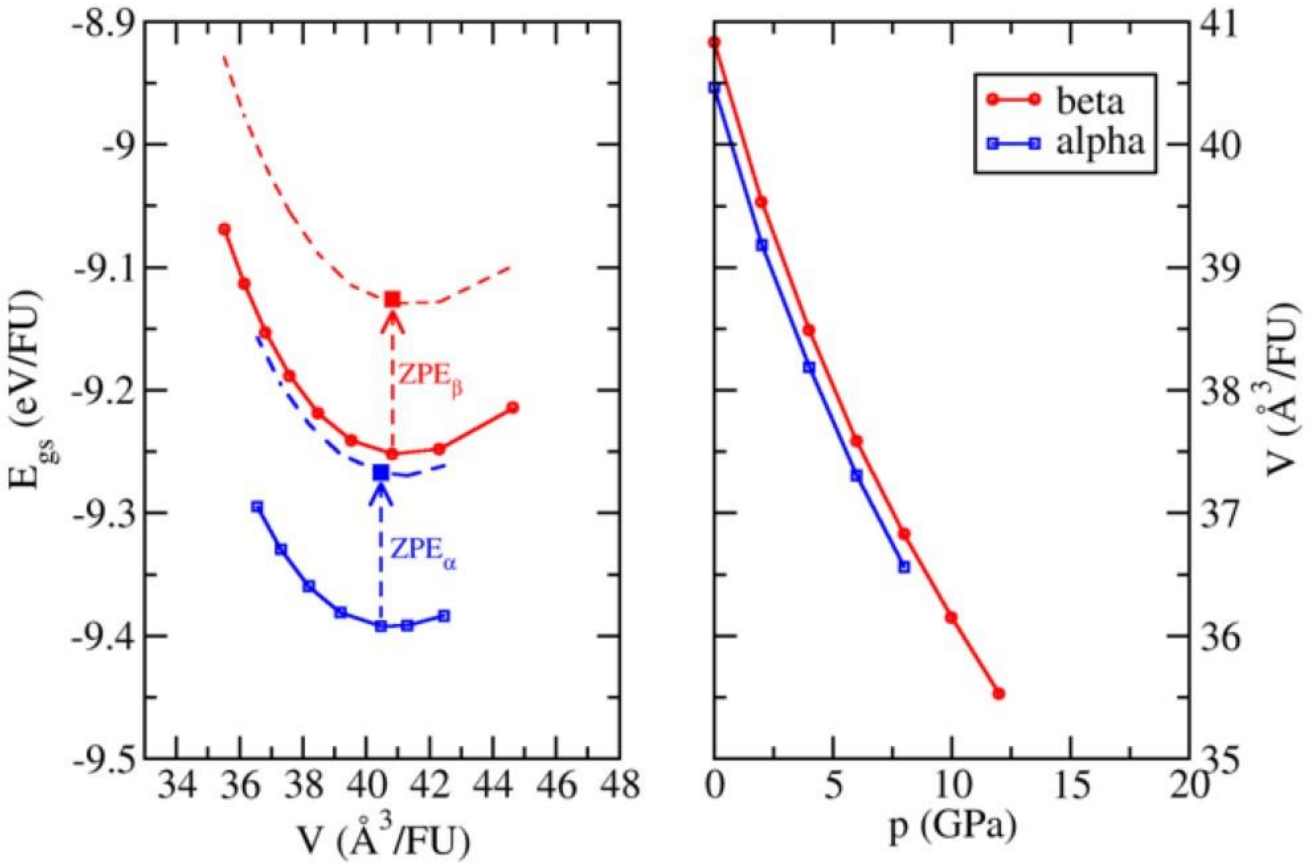
exp.: PNAS 116(5): 1495-1500 (2019)

S : 6Au
IR: 5B1u+5B2u+5B3u
R: 3Ag+3B1g+3B2g+3B3g

S : A1u+3B1u+B2u
IR: 4A2u+5Eu
R: 2A1g+B1g+2B2g+4Eg

Calculated Stability: up to 8 GPa | up to 20 GPa

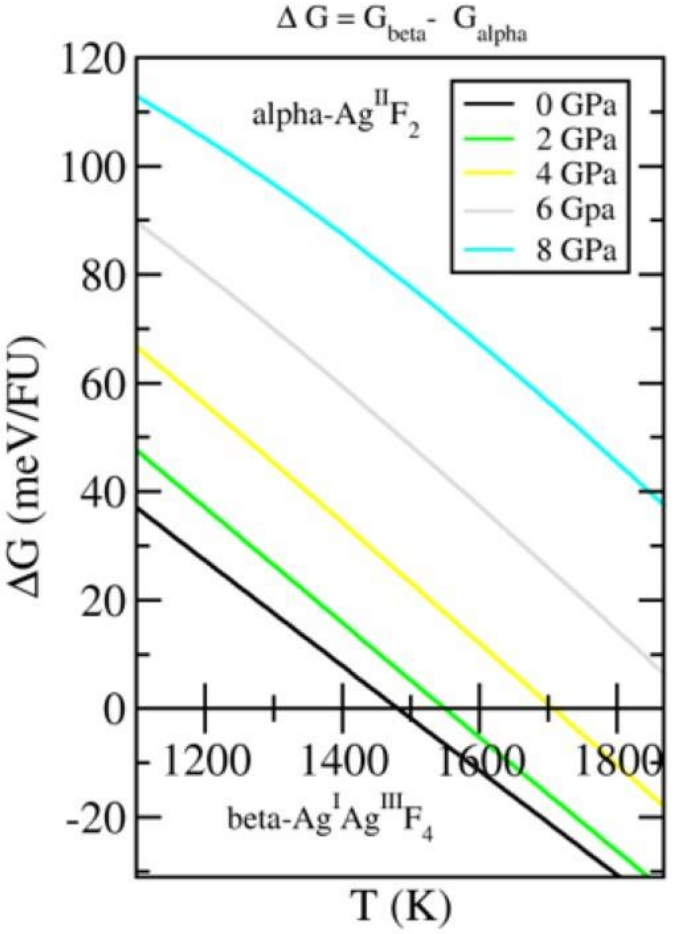
Polymorphs equations of state and zero-point energy contribution



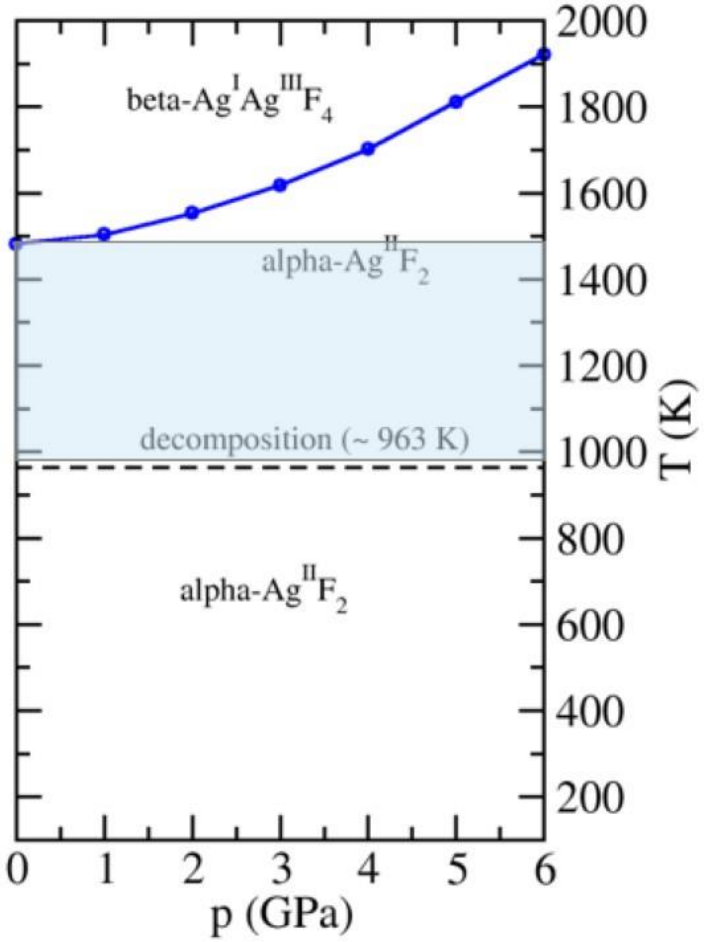
Phase (p=0 GPa)	Ground-state energy $E_{gs}(V)$	ZPE	Free energy $F_{tot}(T,V)$ (p=0 GPa, T=0 K)
beta	-9.248 eV/FU	0.122 eV/FU	-9.126 eV/FU
alpha	-9.392 eV/FU	0.125 eV/FU	-9.267 eV/FU
E-difference	**0.146 eV/FU**		**0.141 eV/FU**

Thermodynamic stability and phase boundaries from QHA

Temperature - energy differences



P-T phase diagram



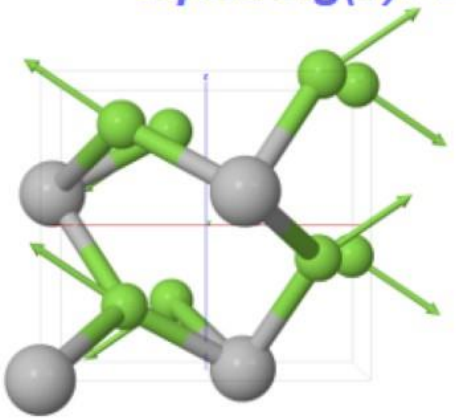
Ag(I)Ag(III)F4 ---> 2Ag(II)F2
decomposition

Distortion of Ag-F generated by B_{2g} phonon mode

B_{2g} polarization vector (AFM+U)
f = 442 cm-1

Q - amplitude parametrization of **Ag-F** distortion
Q = 0 – 0.500

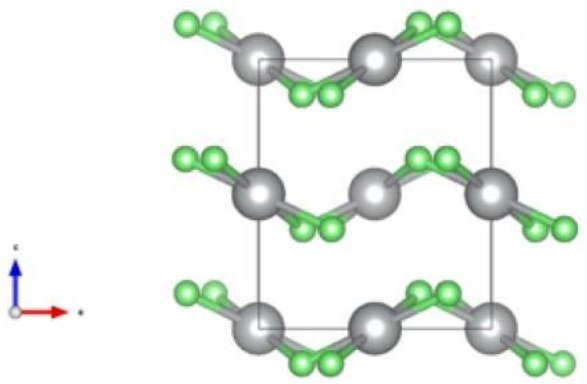
alpha-Ag(II)F2



Only F atoms move!

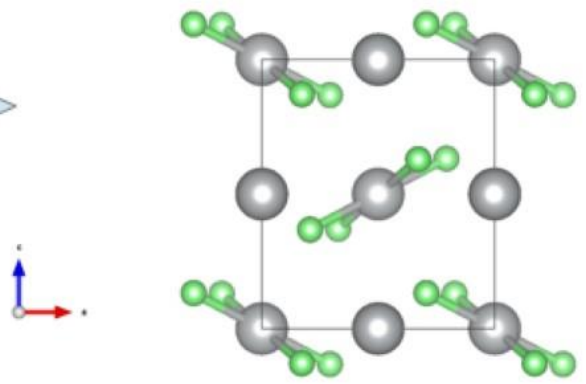
Ag-F Bond lengths variating

(undistorted **Q=0**)



Q

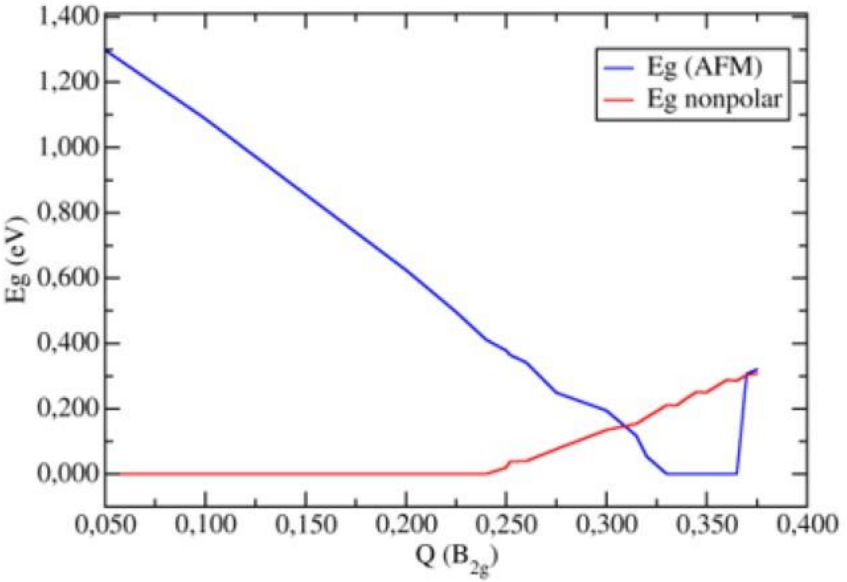
(distorted **Q=0.375**)



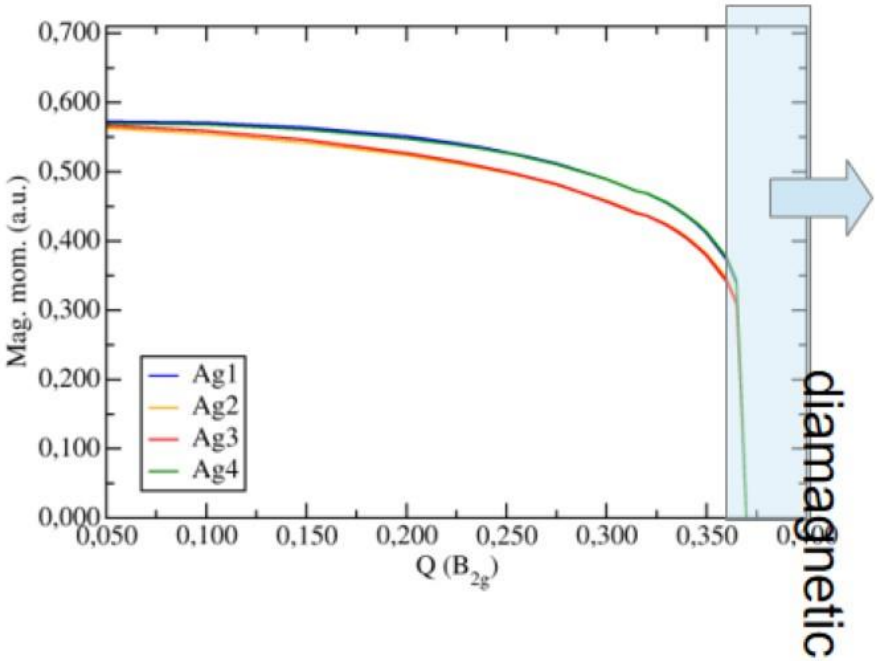
Q – distortion amplitude parametrization

Electronic bang gap and magnetic moment along B_{2g} mode

alpha-Ag(II)F2 (orthorhombic)



Collapse
Q ~ 0.370

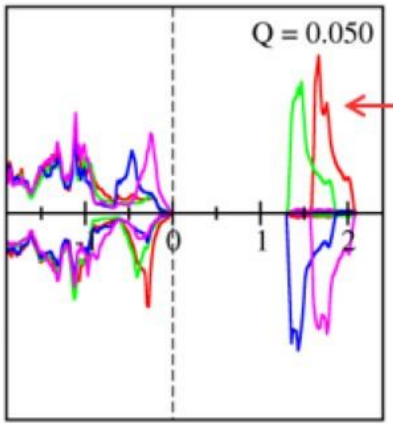


- **AFM+U= 5** – band gap closes with amplitude of B2g distortion

- **Nonpolar (U)** – in metallic regime at Q > 0.250 opens

Onset of intervalence charge transfer

up



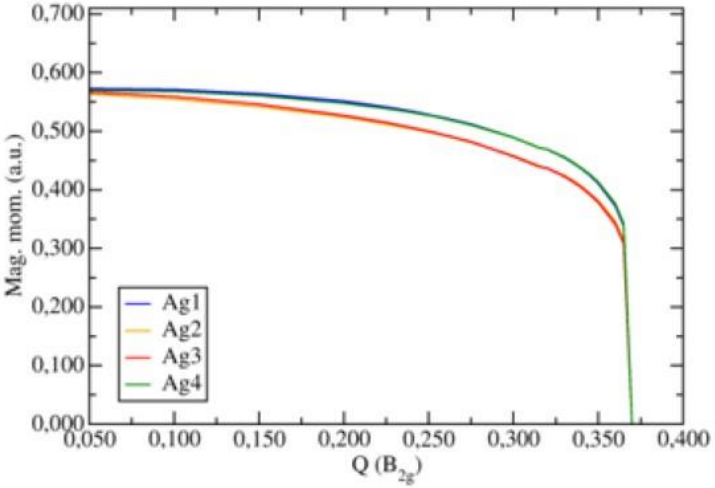
down

Unoccupied **d**-orbitals **E>E$_F$**
Ag1 Ag2 Ag3 Ag4

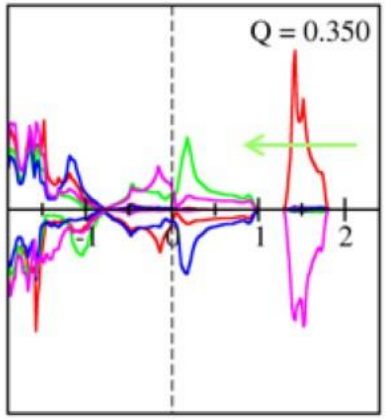
Q=0.050

Band gap = 1.1 eV

Magnetic moments collapse
Q ~ 0.370



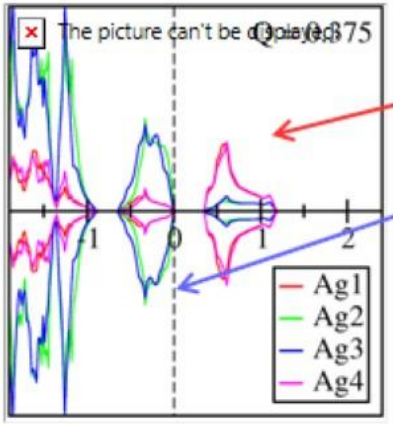
up



down

Q=0.360
metallic

up



down

Unoccupied d
Ag1 Ag4

Occupied d
Ag2 Ag3

Q > 0.375
Band gap reopening
Eg ~ 0.3 eV

\+ Charge transfer to **d**(Ag2+Ag3)

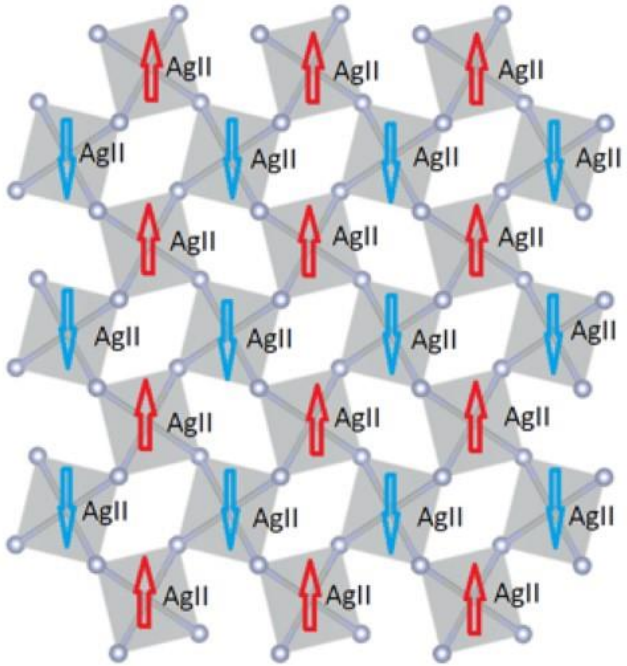
Valence d-states
Reordering

Ag^{II} → Ag^{I} Ag^{III}

Diamagnetic state

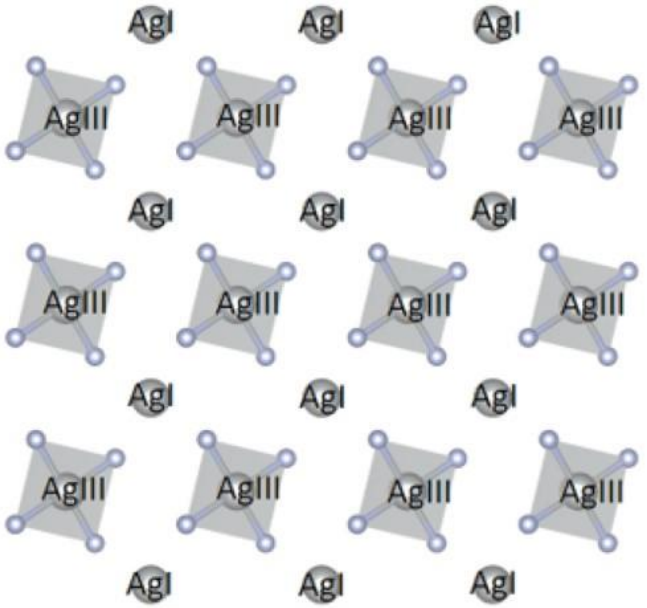
Intervalence charge transfer and valence ordering

AFM $Ag^{II}Ag^{II}F_4$ valence ordering



Q=0.050

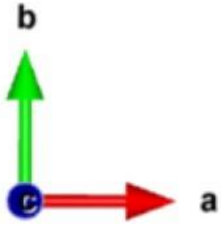
Nonmagnetic $Ag^{I}Ag^{III}F_4$ valence ordering



Q

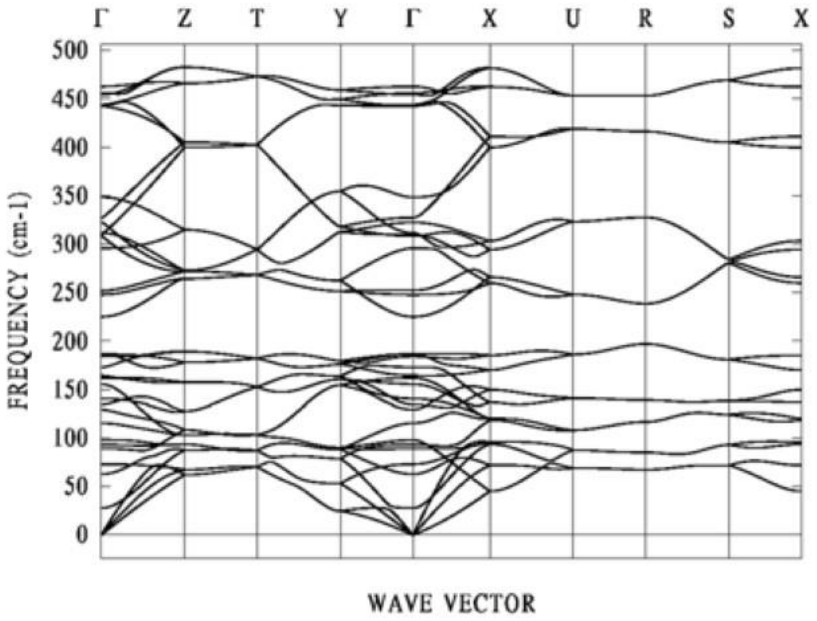
Q=0.375

NOT beta-Ag(I)Ag(III)F4 phase!!

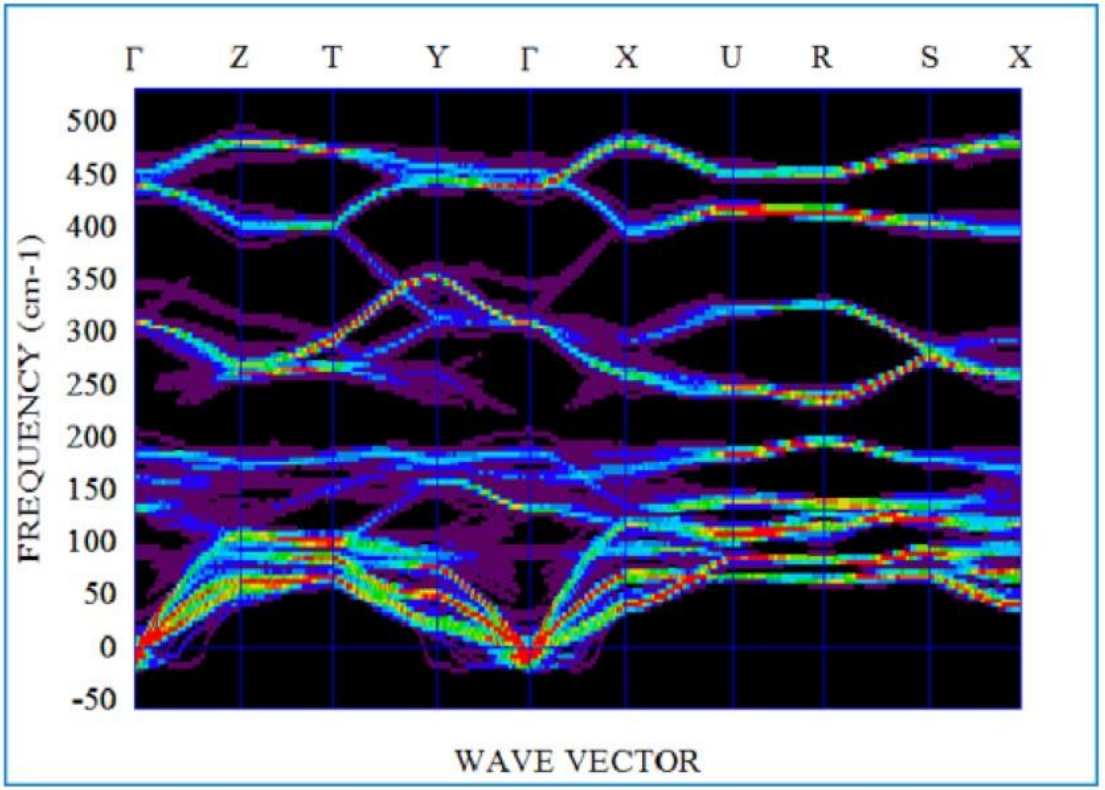


Anharmonicity effects in alpha-AgF2 crystal

Harmonic approximation



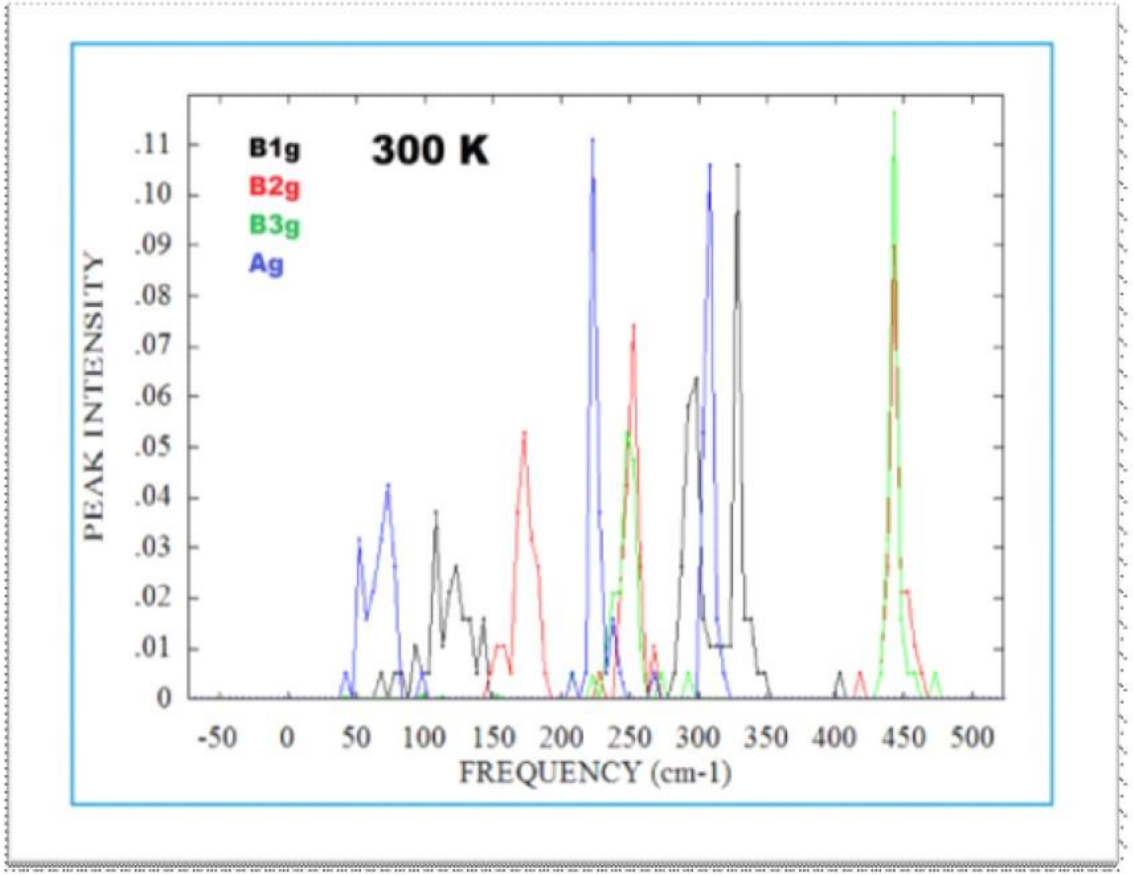
Anharmonic approximation
T=300 K :: Phonon intensity map



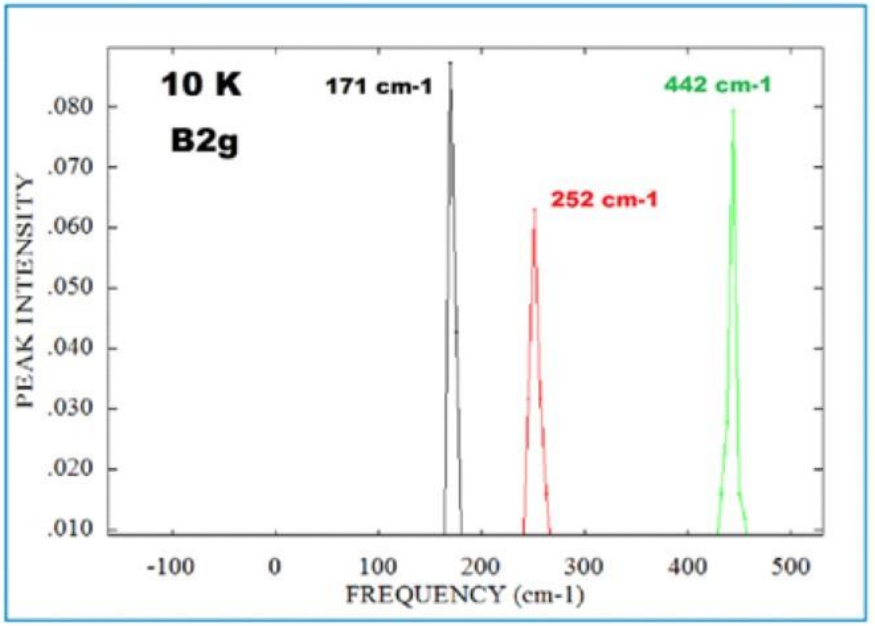
Computing Tool: PhononA ver7.10 (Parlinski, PRB B 98, 054305 (2018))
Principle:
- Mapping of crystal's PES with harmonic atoms displacements at varying T
- Scanning of phonon spectra in displaced patterns
- Evaluation of thermodynamic potentials and transport properties

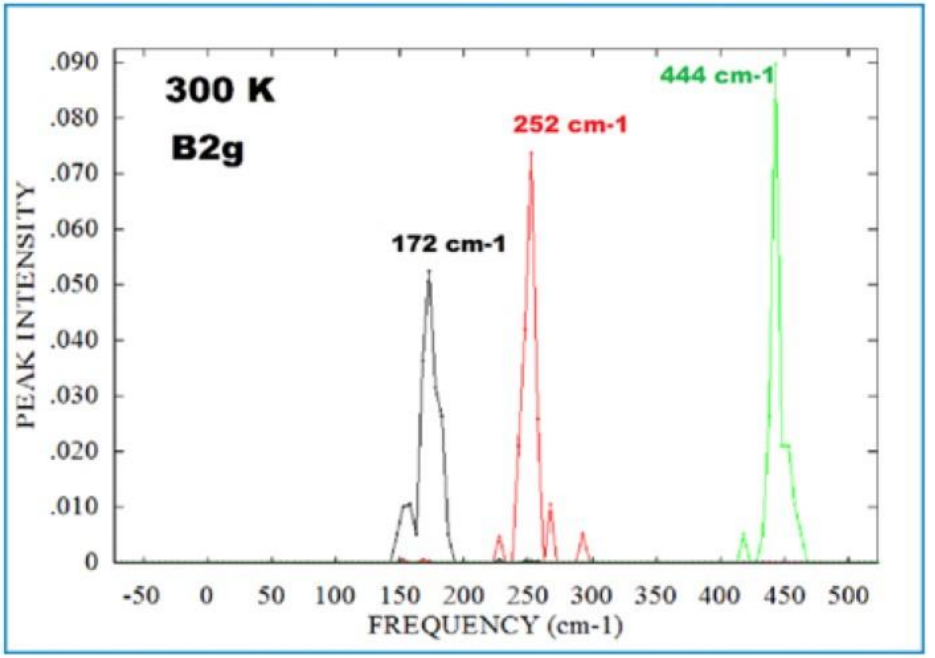
FWHM of anharmonic modes corresponded to Raman active

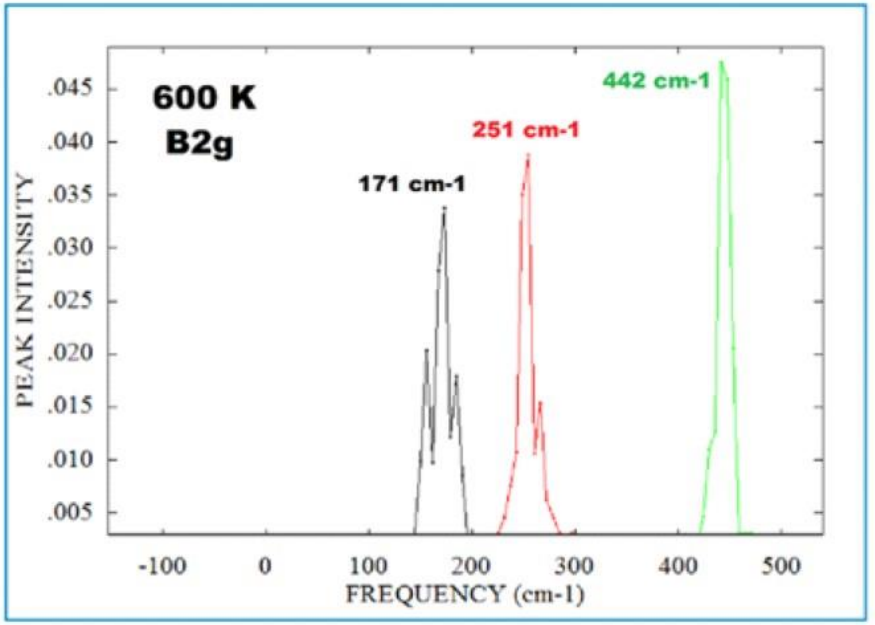
Raman modes simulated in anharmonic regime at T=300 K

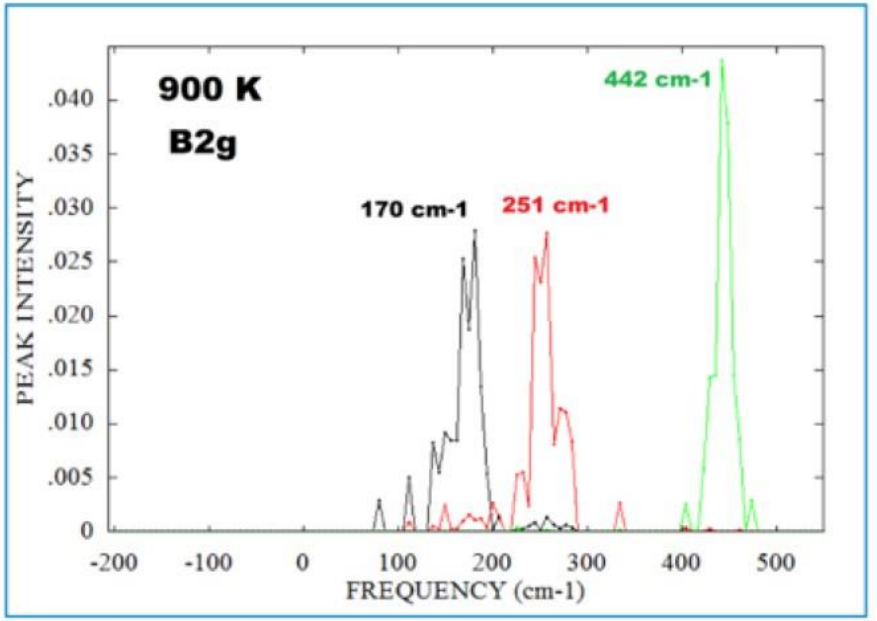


B2g anharmonic modes temperature dependence









Conclusions and Observations

- Both ***alpha-AgIIF2*** and ***beta-AgIAgIIIF4*** phases crystal structures are calculated to be mechanically stable at zero temperature ***T=0*** up to high pressures ***~ 8 GPa and 20 GPa*** respectively.

- The orthorhombic ***alpha-AgIIF2*** phase should be thermodynamically preferred over **beta** also at high pressures. Computed results are in line with **Barlett** observation: ***beta-AgIAgIIIF4*** phase in the ***AgF2*** **system** may be obtained as a **metastable** species when starting from ***Ag(I)*** and ***Ag(III)F4*** precursors.

- Phonon **B2g** mode induces progress from antiferromagnetic $Ag^{II}Ag^{II}F_4$ to diamagnetic mixed-valence $Ag^{I}Ag^{III}F_4$ state accompanied by bandgap closure and subsequent reopening.

- Anharmonic phonon band maps of ***alpha-AgIIF2*** were calculated up to **900 K** near decomposition. FWHMs of B2g peaks under consideration have tendency to increase with temperature.

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EURÓPSKA ÚNIA
Európsky fond regionálneho rozvoja
OP Integrovaná infraštruktúra 2014 – 2020

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Thank you for attention

Raman active modes on temperature

B1g (cm-1)	FWHM (cm-1)	B2g (cm-1)	FWHM (cm-1)	B3g (cm-1)	FWHM (cm-1)	Ag (cm-1)	FWHM (cm-1)
10 K							
113	**42**	171	**28**	250	**35**	41	**157**
296	**31**	252	**28**	440	**33**	210	**135**
327	**40**	442	**30**			310	**58**
300 K							
116	**51**	172	**33**	246	**53**	64	**62**
295	**31**	252	**35**	443	**47**	225	**31**
330	**39**	444	**31**			305	**37**

Construction of AgF2 crystals thermodynamics T >0K

Quasi-harmonic Approximation (QHA)

$F_{phon}(T,V) = F\{g_{PDOS}(\omega),T,V\}$ ==> *free energy of phononic contribution*

$G_{AgF2}(T,p) = E_{gs}(V) + F_{phon}(T,p) + p.V$ ==> *Gibbs energy*

$G_{alpha}(T,p) = G_{beta}(T,p)$ ==> *phases equilibrium condition*

$\Delta G = G_{beta}(T,p) - G_{alpha}(T,p)$

Siegel A. et al., PRB 74 (2006), 104116
Tokar et al., PHYS CHEM MIN 40 (2013) 251-257