Charge ordering mechanism in silver difluoride from first principles

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Introduction

• Common ***α-Ag²⁺F₂*** **(Pbca)** structure represents an excellent silver analog of the parent compound of **high-Tc** superconducting cuprates[1].
• The existence of the ***β-Ag⁽¹⁺⁾Ag⁽³⁺⁾F₂*** mixed valence phase[2] (with proposed $KbrF_4$ structure type[3]) and its transformation to **α-phase** clearly points to competing **AFM** and **Charge Density Wave** (**CDW**) orders with different mechanisms of electron localization in ***AgF₂***.
• Charge ordered (**CO**) phase is metastable relative to the spin-ordered **AFM** phase and could be quickly destroyed thermally via intervalence charge transfer (**IVCT**)[2,4]: $Ag^{1+} + Ag^{3+} \rightarrow 2Ag^{2+}$.
• The reported experimental observation[4] indicate that the **CO** ***AgF₂*** phase may be stabilized already in an undoped regime in contrast to the superconducting copper oxides.

This work: Investigation of the mechanisms underlaying charge ordering in ***α-AgF₂*** concerned with electron-phonon coupling and its possible relation to the Kohn anomaly and Fermi surface nesting based on **Density Functional Theory (DFT)** technique and lattice dynamics modelling[5].

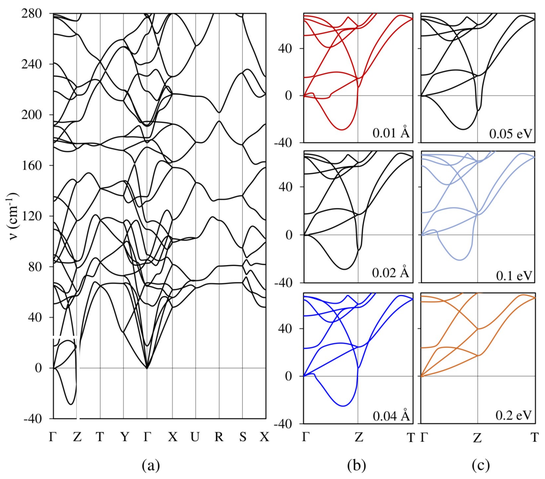
Methods

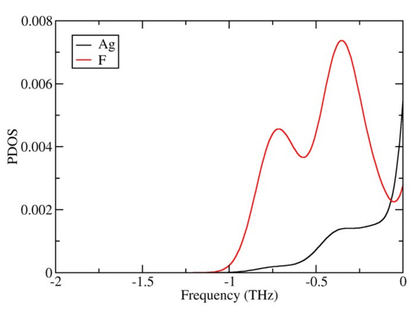
Optimization of the electronic and crystal structure of the ***α-AgF2*** have been performed using the **DFT** as implemented in ***VASP*** package. Lattice parameters and atomic positions were fully relaxed using the ***PAW*** method and the ***GGA*** approximation of ***PBEsol*** optimized for solids. The energy cutoff was set to ***520 eV***.

The occupations of electronic states close to the Fermi energy were smeared by the Gaussian method with ***σ = 0.05 eV*** dispersion. The strong electron interactions in the ***Ag(d)*** states have been included within the ***DFT + U*** method with the Coulomb parameter ***U = 5.0 eV*** and the Hund's exchange ***J = 1 eV***. For plotting the Fermi surfaces, the Wannier interpolation was performed on **DFT** calculated electronic bands using the ***WANNIER90*** software.

The phonon system and dispersion curves were obtained using the quasi-harmonic approximation with finite atomic displacements and **DFT** calculated Hellmann-Feynman forces for simulation of lattice dynamics as implemented in the ***PHONOPY*** code.

Phonon coupling impact on CDW orders – Kohn anomaly





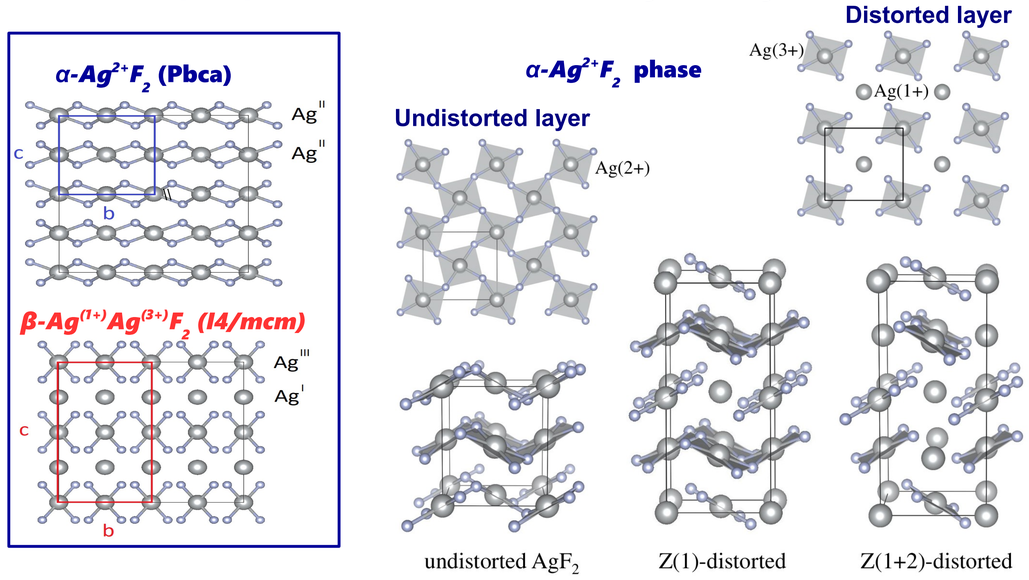
Top panel shows atomic projections of the imaginary phonon density of states with dominant contribution from F atoms.
The panel in left highlights the doubly degenerated Z-mode.

a) Phonon dispersion relations in ***α-AgF₂*** calculated with the atomic displacement **u = 0.02 Å** within the GGA. The electronic state is metallic without any magnetic order and a phonon instability in the form of a sharp dip reminiscent of a **Kohn anomaly** develops at the Z-point.
b) Evolution of soft phonon mode with the increasing atomic displacement magnitude **u** indicating sensitivity of **C-CWD (**connected with $q_z = (0, 0, 0.5)$ commensurate vector) to atomic displacement.
c) Impact of electron occupation smearing width on the **C-CDW** and **I-CDW** ($q_z = (0, 0, 0.37)$) modes stabilization by electronic temperature along the Z-direction calculated for the nonmagnetic state with the pure GGA approximation.

Metallic ***α-AgF₂*** state would first transform to an incommensurate **I-CDW** phase and subsequently to a commensurate **C-CDW** phase with decreasing temperature via **IVCT**:

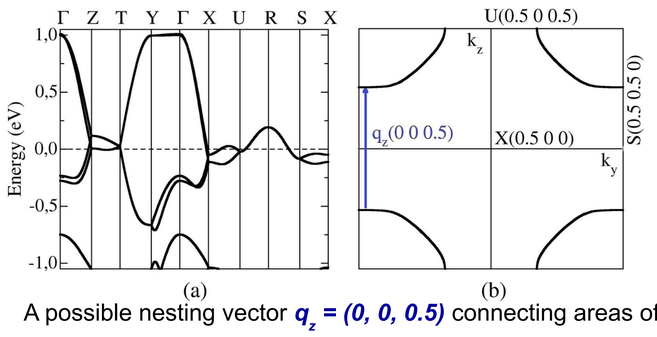
$$Ag^{2+}F_2 \rightarrow \textit{incommensurate } Ag^{1+/3+}F_2 \rightarrow \textit{commensurate } Ag^{1+/3+}F_2.$$

Bond disproportionation within layers by soft modes

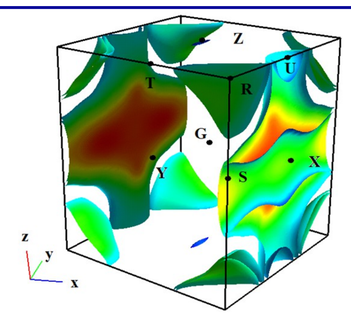


Charge disproportionation and cell doubling induced by the doubly degenerate phonon mode branches at the Z-point:
Undistorted ***α-AgF₂*** (left); distorted by one Z(1) arm (**AFM-CDW** phase, middle) and conjunction of both Z(1 + 2) arms of the Z-mode (**CDW** phase, right). Ag atoms with no connections to F atoms (middle and right panels) are those around which the intralayer **Ag-F** bonds are elongated by the Z-mode. The remaining **Ag-F** bonds within the same layer are contracted. The ***AgF₂*** layer distorted by the Z mode is illustrated in the top right corner, which can be compared with an undistorted ***AgF₂*** layer shown in top middle.

Fermi nesting and Kohn anomaly for AgF_2 metallic solution

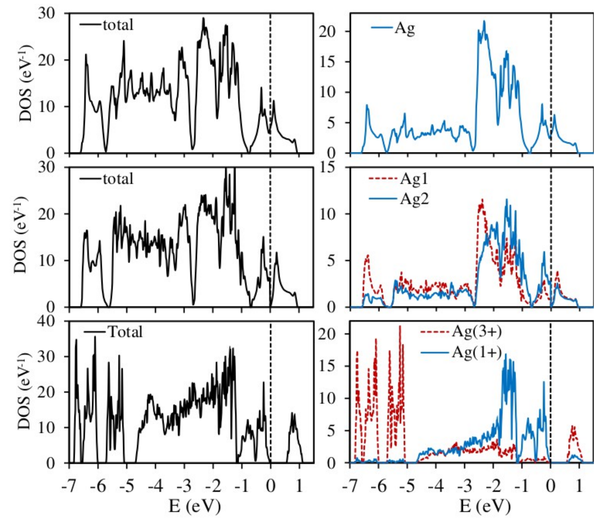


A possible nesting vector $q_z = (0, 0, 0.5)$ connecting areas of the corner pockets can support the formation mechanism of **CDW** regime.
a) Electronic band structure at the vicinity of the Fermi level describing four partially filled bands below the Fermi energy.
b) The cross-section of the Fermi surface along the U-X-S directions.



Merged Fermi surfaces of four bands crossing the Fermi level reduced to the first Brillouin zone as calculated in GGA for ***α-AgF₂*** metallic state. The nesting vector connects R-corner centered pockets.

Electronic structure and Ag(d_{x2-y2}) bands segregation



Total and atom (Ag)-projected density of states for:

a) Undistorted ***α-AgF₂*** structure calculated at DFT GGA level.

b) ***α-AgF₂*** distorted along the imaginary Z-mode calculated at DFT GGA level. Formation of two silver (Ag1, Ag2) cations is highlighted.

c) The complete charge transfer: $2Ag^{2+} \rightarrow Ag^{1+} + Ag^{3+}$ takes place at Coulomb electronic correlations GGA+U regime with Hubbard's parameter $U_{Ag} = 5$ ***eV***.

Conclusions

• The phonon-driven mechanism of electron localization might compete with the **AFM** interactions and promotes charge disproportionation in ***α-AgF₂***.
• Uncovered **CDW** mechanism underneath the **AFM** spin ordering at realistic values of on-site electron correlations.
• There exists soft phonon mode in ***α-AgF₂*** structure related to the Kohn anomaly enhanced by Fermi surface nesting.
• Shown possibility of tuning the electronic structure between charge ordering and spin ordering regimes, e. g. by strain or alloying.

References

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