Electronic Supplementary Information

Controlling Orbital Ordering of Intergrowth Structures with Flat [Ag(II)F_2] Layers to Mimic Oxocuprates(II)

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I. Structural and magnetic data of [AgF_2] layers in intergrowth compounds.

Table SI1. Structural and magnetic data for [AgF_2] layers in *Pnma* structures employing DFT+U (U_{Ag} = 5 eV) method (for J_{2D} also SCAN and HSE06).

Near to the AgF_2 layer	Short name	Formula	dAg-Ag (A) [Å]	dAg-F ax. (C) [Å]	dAg-F eq. (B1) [Å]	dAg-F eq. (B2) [Å]	Ag-F-Ag angle α [°]	B1/B2	J_{2D} [meV]		
									DFT+U	SCAN	HSE06
2xCs	Cs3	$(CsMgF_3)_2CsAgF_3$	4.18	2.49	2.09	2.09	179.80	1.00	-185.5	-212.3	---
2xCs	Cs2Rb	$(CsMgF_3)_2RbAgF_3$	4.15	2.51	2.08	2.08	179.80	1.00	-201.2	-237.7	---
2xRb	CsRb2	$(RbMgF_3)_2CsAgF_3$	4.14	2.36	2.02	2.12	175.80	0.95	-139.6	-165.3	---
2xCs	Cs2K	$(CsMgF_3)_2KAgF_3$	4.13	2.52	2.07	2.07	179.60	1.00	-211.0	-255.5	-220.6
2xK	CsK2	$(KMgF_3)_2CsAgF_3$	4.12	2.22	2.01	2.27	148.00	0.89	-29.7	+0.1	+0.5
2xRb	Rb3	$(RbMgF_3)_2RbAgF_3$	4.08	2.42	2.06	2.06	163.60	1.00	-187.0	-212.9	---
2xRb	Rb2K	$(RbMgF_3)_2KAgF_3$	4.05	2.44	2.06	2.06	159.20	1.00	-145.7	-216.2	---
2xK	RbK2	$(KMgF_3)_2RbAgF_3$	4.02	2.39	2.08	2.07	151.00	1.00	-182.6	-167.0	---
2xK	K3	$(KMgF_3)_2KAgF_3$	3.99	2.40	2.07	2.07	149.47	1.00	-147.2	-179.0	---

Table SI2. Structural and magnetic data for [AgF_2] layers in *$P2_1/c$* structures employing DFT+U (U_{Ag} = 5 eV) method.

Near to the AgF2 layer	short name	Formula	d Ag-Ag (A) [Å]	d Ag-F ax. (C) [Å]		d Ag-F eq. (B1) [Å]		d Ag-F eq. (B2) [Å]		Ag-F-Ag angle α [°]		dE of $P2_1/c$ – *Pnma* [meV/Ag]	J_{2D} [meV]	
				I layer	*II layer*	*I layer*	*II layer*	*I layer*	*II layer*	*I layer*	*II layer*		*I layer*	*II layer*
Cs, Rb	mCs2Rb	$(CsMgF_3)_2RbAgF_3$	4.17	2.51	2.32	2.08	2.01	2.08	2.16	179.87	173.80	+179.8	-178.1	-92.7
Rb, Cs	mCsRb2	$(RbMgF_3)_2CsAgF_3$	4.12	2.40	2.55	2.06	2.06	2.07	2.06	169.54	179.92	-183.7	-180.2	-207.2
Rb, K	mI_RbCsK	$RbCsKMg_2AgF_9$	4.11	2.40	2.26	2.05	2.01	2.08	2.24	169.95	150.36		-144.7	-145.3
K, Cs	mII_RbCsK	$RbCsKMg_2AgF_9$	4.11	2.24	2.58	2.01	2.05	2.24	2.05	149.88	179.94		-24.6	-169.3
Cs, Rb	mIII_RbCsK	$RbCsKMg_2AgF_9$	4.09	2.57	2.42	2.05	2.06	2.05	2.07	179.64	164.34		-218.4	-183.3
K, Cs	mCsK2	$(KMgF_3)_2CsAgF_3$	4.08	2.28	2.59	2.01	2.04	2.22	2.04	149.65	179.57	-259.6	-43.8	-191.7
Rb, K	mRb2K	$(RbMgF_3)_2KAgF_3$	4.06	2.44	2.32	2.06	2.02	2.06	2.19	160.84	149.97	+167.2	-179.6	-76.7
K, Rb	mRbK2	$(KMgF_3)_2RbAgF_3$	4.02	2.39	2.47	2.08	2.06	2.08	2.06	151.26	156.55	-168.6	-148.4	-175.2

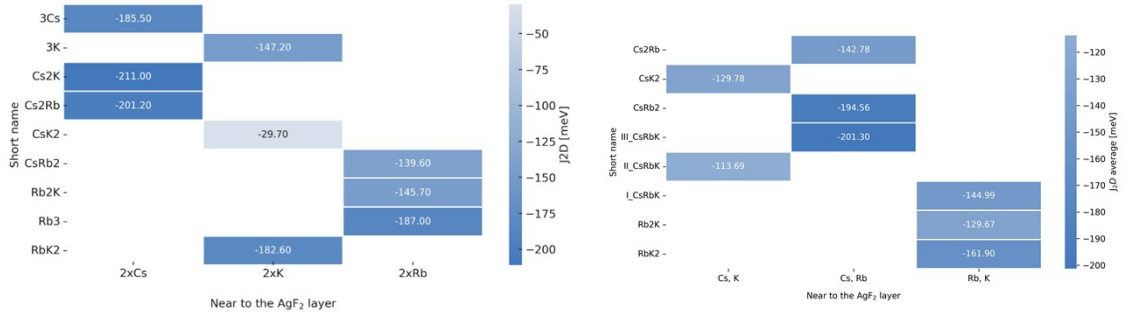

Figure SI1. J_{2D} values for [AgF_2] layer depending on the neighboring alkali metal in the *Pnma* (left) and $P2_1/c$ (right) structure for (DFT+U method).

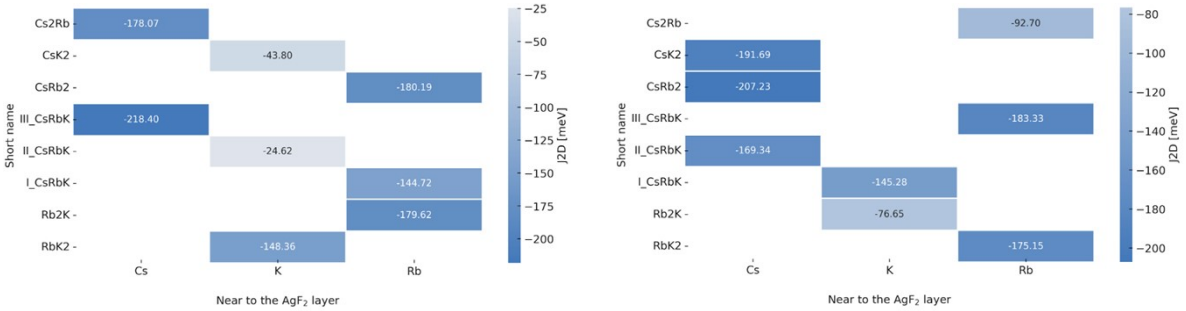

Figure SI2: J_{2D} values of the I layer [AgF_2] (left) and II layer [AgF_2] (right) as a dependence of neighboring alkali metals in the $P2_1/c$ crystal structure (DFT+U method).

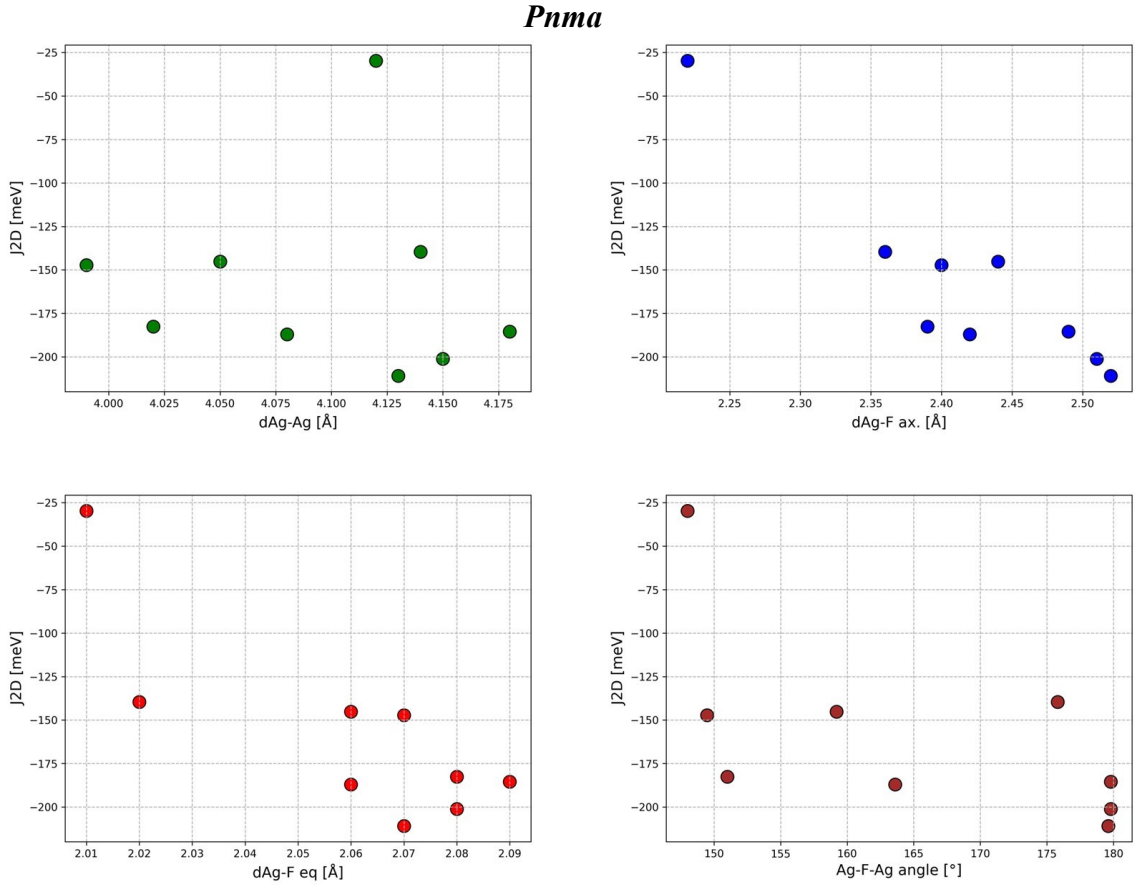

Figure SI3. J_{2D} values of [AgF_2] layers depending on the Ag-Ag, Ag-F axial and Ag-F equatorial distances and Ag-F-Ag bond angles for *Pnma* phases.

P2₁/c

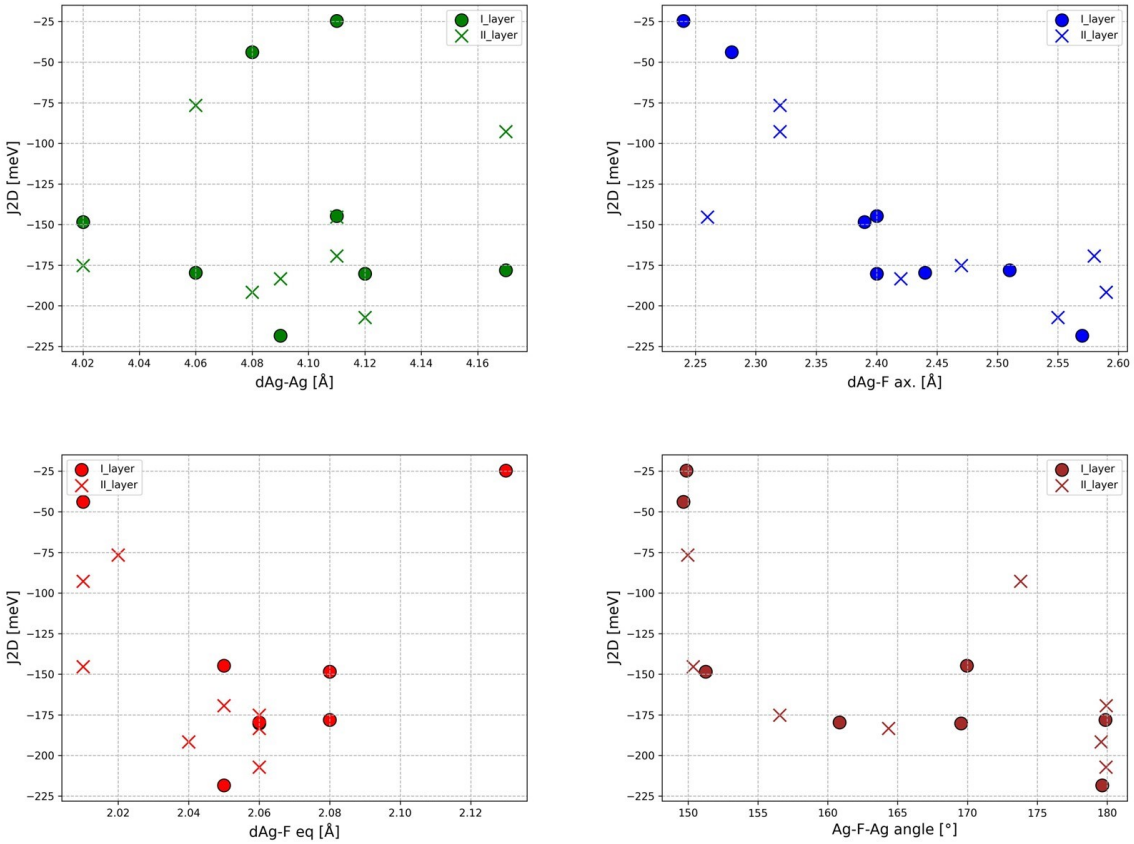

Figure SI4. J_{2D} values of [AgF_2] layers depending on the Ag-Ag, Ag-F axial and Ag-F equatorial distances and Ag-F-Ag bond angles for $P2_1/c$ phases.

II. Reactions considered and their energy effects.

For $(XMgF_3)_2XAgF3$ energy effect was calculated as follows (for X = Rb, K or Cs):

$$dE_1 = E_{(XMgF_3)_2XAgF_3} - (2E_{MMgF_3} + E_{XAgF_3})$$

$$dE_3 = E_{(XMgF_3)_2XAgF_3} - (E_{X_2AgF_4} + E_{XMgF_3} + E_{MgF_2})$$

$$dE_4 = E_{(XMgF_3)_2XAgF_3} - (E_{X_2MgF_4} + E_{XMgF_3} + E_{AgF_2})$$

For $(XMgF_3)_2YAgF_3$ energy effect was calculated as follows (for X = Rb, K or Cs and Y = Rb, K, Cs):

$$dE_1 = E_{(XMgF_3)_2YAgF_3} - (2E_{XMgF_3} + E_{YAgF_3})$$

$$dE_2 = E_{(XMgF_3)_2YAgF_3} - (E_{XMgF_3} + E_{YMgF_3} + E_{XAgF_3})$$

$$dE_3 = E_{(XMgF_3)_2YAgF_3} - (E_{X_2AgF_4} + E_{YMgF_3} + E_{MgF_2})$$

$$dE_4 = E_{(XMgF_3)_2YAgF_3} - (E_{X_2MgF_4} + E_{YMgF_3} + E_{AgF_2})$$

If X =Rb and Y = K as in $(RbMgF_3)_2KAgF_3$ compound, the energy effects were calculated as follows:

$$dE_1 = E_{(RbMgF_3)_2KAgF_3} - (2E_{RbMgF_3} + E_{KAgF_3})$$

$$dE_2 = E_{(RbMgF_3)_2KAgF_3} - (E_{RbMgF_3} + E_{KMgF_3} + E_{RbAgF_3})$$

$$dE_3 = E_{(RbMgF_3)_2KAgF_3} - (E_{Rb_2AgF_4} + E_{KMgF_3} + E_{MgF_2})$$

$$dE_4 = E_{(RbMgF_3)_2KAgF_3} - (E_{Rb_2MgF_4} + E_{KMgF_3} + E_{AgF_2})$$

For $XYZMg_2F_7AgF_2$ phases energy effect was calculated as follows (as example for X= Rb, Y = K, Z = Cs):

$$dE_1 = E_{RbCsKMg_2AgF_9} - (E_{ZMgF_3} + E_{XAgF_3} + E_{YMgF_3})$$

$$dE_2 = E_{RbCsKMg_2AgF_9} - (E_{ZMgF_3} + E_{XMgF_3} + E_{YAgF_3})$$

$$dE_3 = E_{RbCsKMg_2AgF_9} - (E_{ZAgF_3} + E_{XMgF_3} + E_{YMgF_3})$$

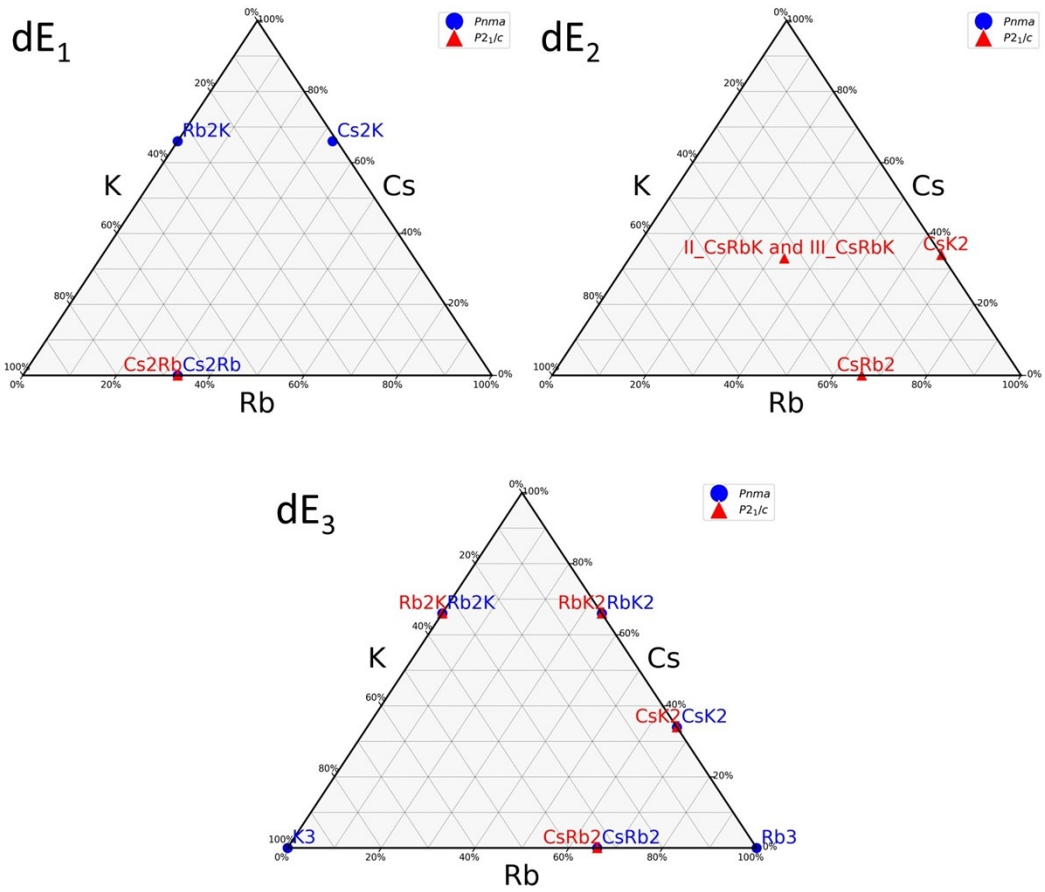

Figure SI5. Ternary phase diagram Cs-K-Rb for which dE_1, dE_2 and dE_3 are negative.

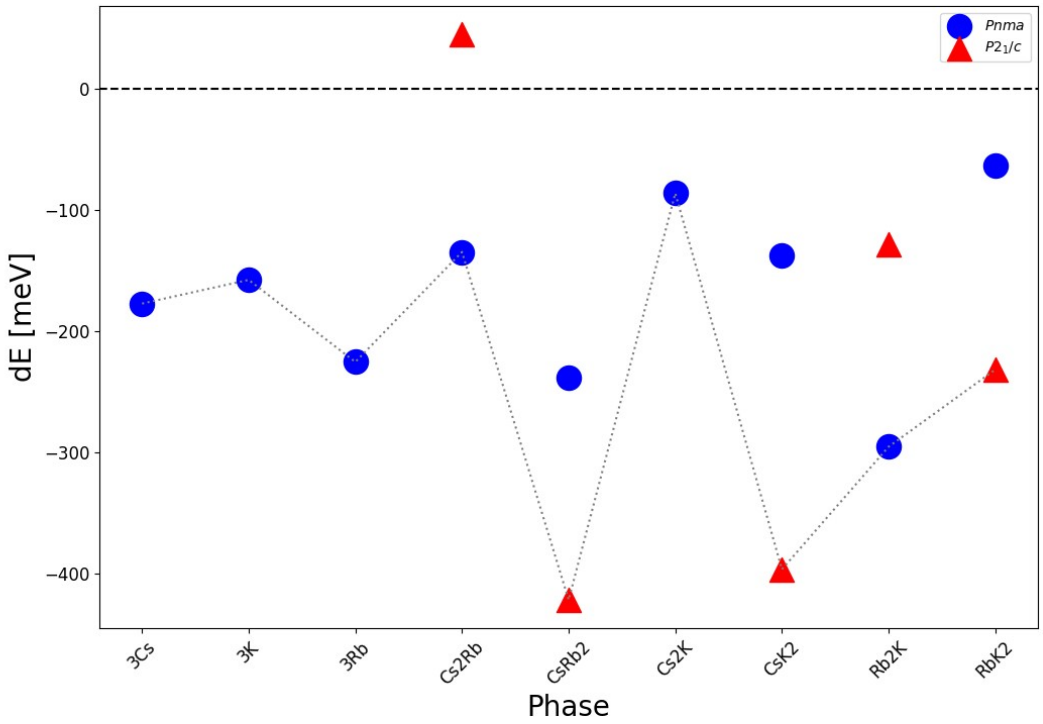

Figure SI6. Formation energy (dE_4) vs phase (in $P2_1/c$ and *Pnma* systems, if applicable)

III. Density of states for selected compounds – magnetic and non-magnetic solutions. Electronic band structure for Cs2K.

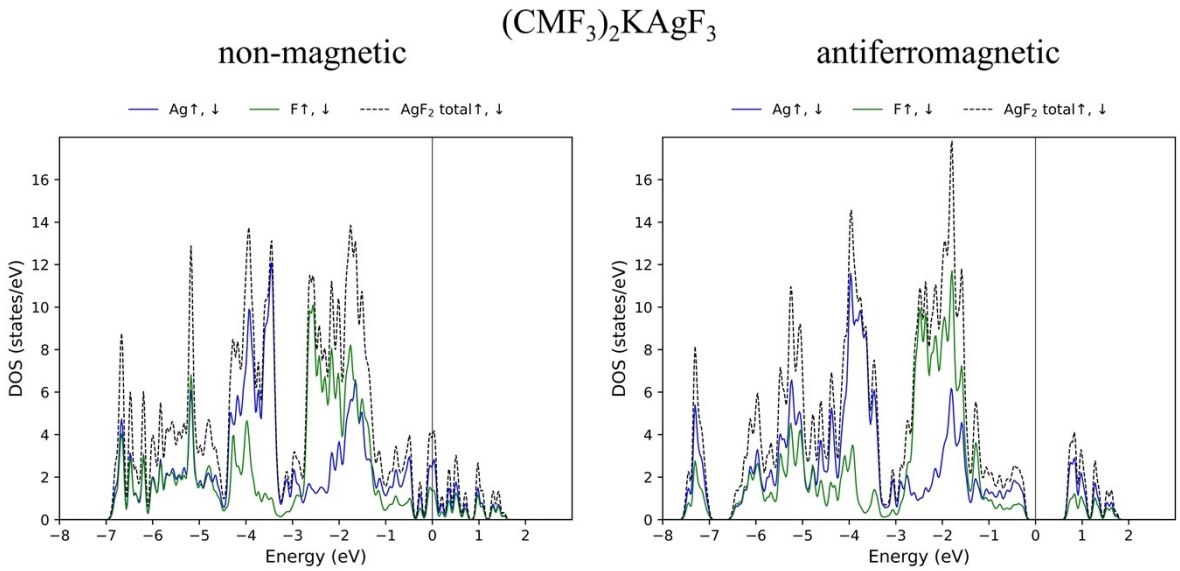

Figure SI7. DOS for Cs2K without spin-polarization (non-magnetic solution) on left and in antiferromagnetic solution on right. Only Ag and F states are presented.

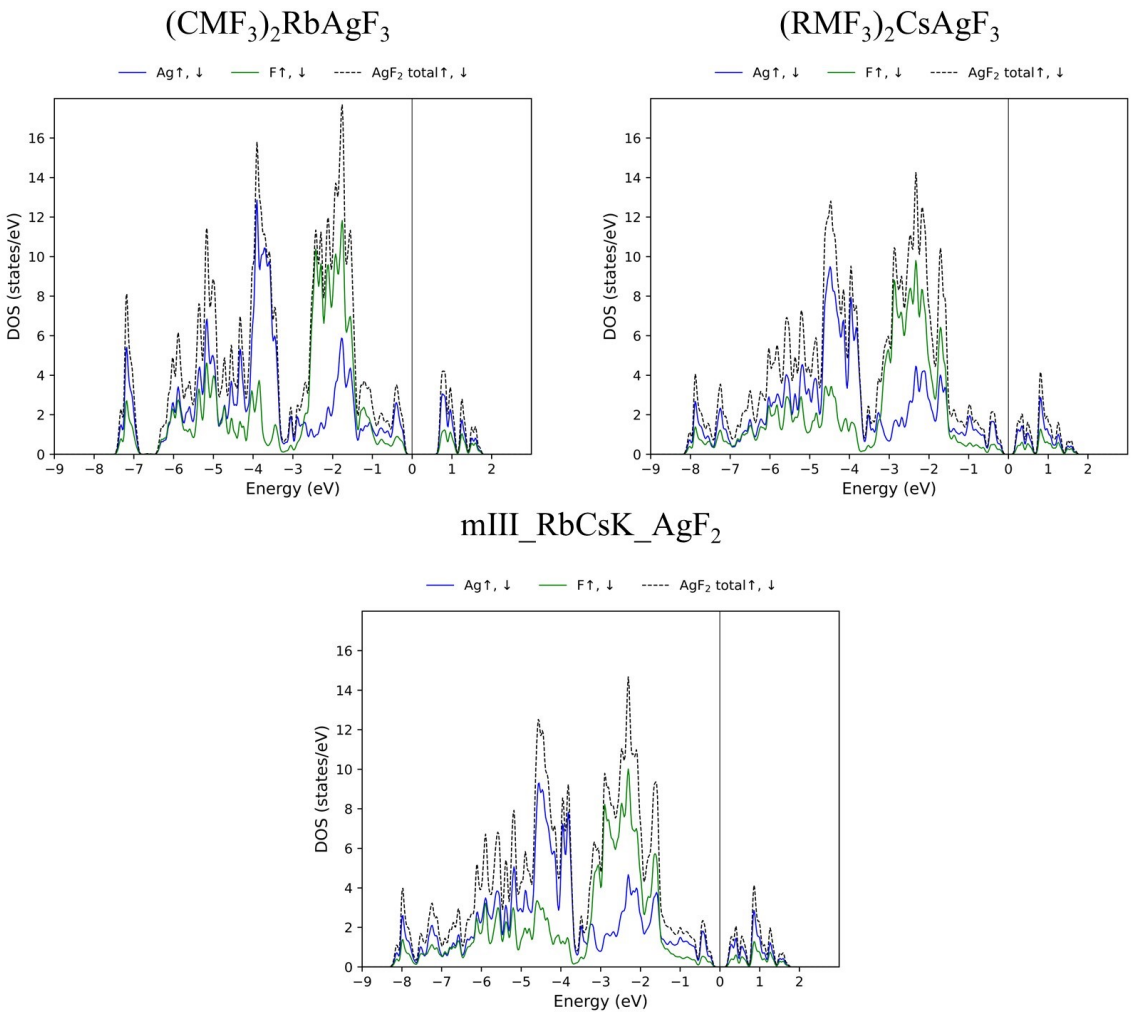

Figure SI8. DOS for **Cs2Rb, Rb2Cs** and **mIII_RbCsK** in antiferromagnetic solution. Only Ag and F states are presented.

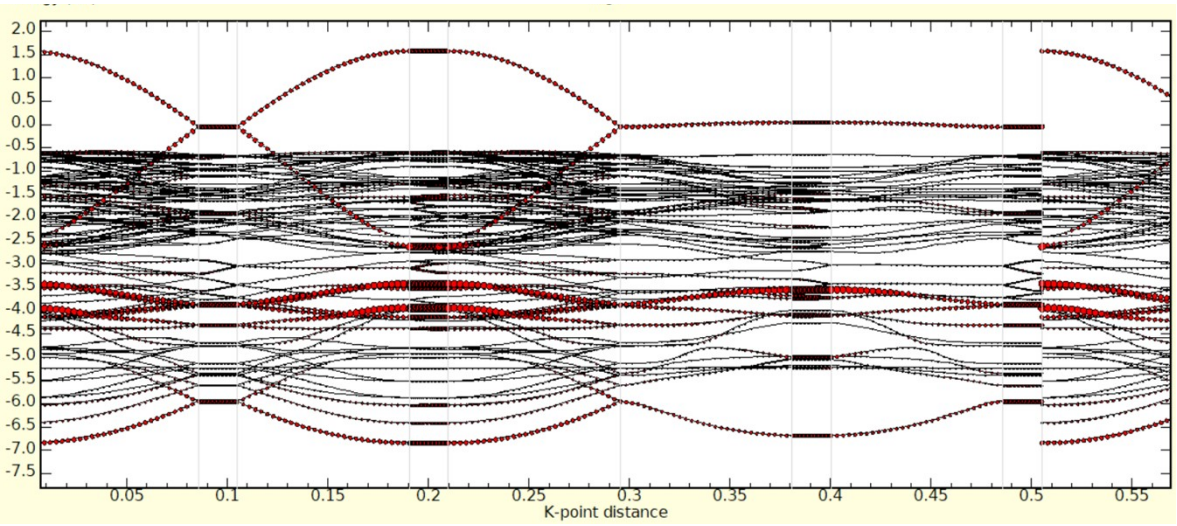

Figure SI9. Band structure for Non-magnetic solution of **Cs2K** (*Pnma* phase). Red dots correspond to the contribution from Ag*d* states from [AgF_2] layer.

IV. Doping of Cs2K.

Table SI3 Structural, magnetic, and electronic parameters for Cs2K compounds in scenarios of gradual replacement of K^+ by Ba^{2+}. **A** for Ag-Ag distance, **C** for Ag-F apical bond, **B1** and **B2** for Ag-F equatorial bonds and **α** for Ag-F-Ag angle, **D** for distance between [AgF_2] layer to M^+/M^{2+} cation. UHB is the width of the Upper Hubbard Band. Doping level, $\delta n_{Ag(UHB)}$, refers to the populated part of UHB.

% Ba	a=c [Å]	b [Å]	V [Å³]	D [Å]	A [Å]	C [Å]	B1=B2 [Å]	α [°]	Ag mag. mom. [μ_B]	Doping level, $\delta n_{Ag(UHB)}$ [%]	UHB [eV]
0	5.842	25.975	886.312	7.12	4.13	2.53	2.07	179.60	0.48	0.0	1.242
1	5.839	26.053	888.176	7.14	4.13	2.54	2.06	179.97	0.48	6.0	1.262
2.5	5.839	26.083	889.344	7.14	4.13	2.55	2.06	179.96	0.47	6.7	1.301
5	5.840	26.136	891.498	7.16	4.13	2.57	2.06	179.93	0.46	12.1	1.319
10	5.842	26.244	895.763	7.18	4.13	2.61	2.07	179.90	0.42	13.9	1.377
15	5.845	26.351	900.218	7.21	4.13	2.65	2.07	179.86	0.38	13.7	1.435
20	5.849	26.445	904.592	7.23	4.14	2.68	2.07	179.89	0.34	18.4	1.515
25	5.854	26.532	909.206	7.25	4.14	2.71	2.07	179.91	0.29	22.8	1.592

Doping level is calculated following formula below. Therefore it is the part (%) of UHB band occupied, as a result of K^+ by Ba^{2+} replacement in the Cs2K structure.

$$\delta n_{Ag(UHB)}\% = \frac{\int_{E_0(UHB)}^{E_F(UHB)} (eDOS)dE}{\int_{E_0(UHB)}^{E_1(UHB)} (eDOS)dE} * 100\%$$

E_0 – lower part of UHB, E_F – Fermi level, E_1 – upper part of UHB.

Table SI4 Structural, magnetic, and electronic parameters for Cs2K compounds in scenarios of gradual replacement of Mg^{2+} by Li^+. **A** for Ag-Ag distance, **C** for Ag-F apical bond, **B1** and **B2** for Ag-F equatorial bonds and **α** for Ag-F-Ag angle, **D** for distance between [AgF_2] layer to [$Li^+/Mg^{2+}F_2$] layer. Doping level, $\delta n_{Ag(\beta - dx^2 - y^2)}$, δn_F, for depopulation level of apical fluorine atoms $p_{(z)}$ and , $\delta n_{Ag(dz^2)}$ – depopulation level of Ag$d_{(z^2)}$ states.

% Li	a=c [Å]	b [Å]	V [Å³]	D [Å]	A [Å]	C [Å]	B1=B2 [Å]	α [°]	Ag mag. mom. [μ_B]	F apical mag. mom [μ_B]	Doping level [%]		
											$\delta n_{Ag(\beta - dx^2 - y^2)}$	$\delta n_{Ag(dz^2)}$	δn_F
0	5.842	25.975	886.312	4.54	4.13	2.53	2.07	179.60	0.48	0.00	0	0	0
1	5.838	26.037	887.462	4.55	4.13	2.53	2.06	179.89	0.48	0.01	0.2	0.5	0.2
2.5	5.839	26.026	887.441	4.55	4.13	2.53	2.06	179.94	0.48	0.01	1.1	1.6	0.5
5	5.845	25.924	885.810	4.52	4.13	2.49	2.07	179.99	0.48	0.00	1.1	3.6	7.9
10	5.857	25.715	882.229	4.47	4.14	2.40	2.07	180.00	0.47	0.01	1.4	4.4	7.4
15	5.866	25.602	880.898	4.45	4.15	2.34	2.07	180.00	0.47	0.02	1.4	5.7	6.7
20	5.873	25.543	880.994	4.45	4.15	2.26	2.08	180.00	0.44	0.03	1.3	11.0	6.6
25	5.923	25.417	891.813	4.44	4.19	2.07	2.09	180.00	0.51	0.12	*	*	*

* rearrangement of geometry, consideration not applicable

$$\delta n_{Ag(\beta - dx^2 - y^2)}\% = \frac{\int_{E_F(LHB)}^{E_1(LHB)} (eDOS)dE}{\int_{E_0(LHB)}^{E_1(LHB)} (eDOS)dE} * 100\%$$

E_0 – lower part of LHB, E_F – Fermi level, E_1 – upper part of LHB. This formula was applied to calculate depopulation level of β– $d_{(x2-y2)}$ of silver, and also to calculate depopulation level of F$p_{(z)}$ and Ag$d_{(z2)}$ orbitals.

Electronic density of states for 25% of Li doping level.

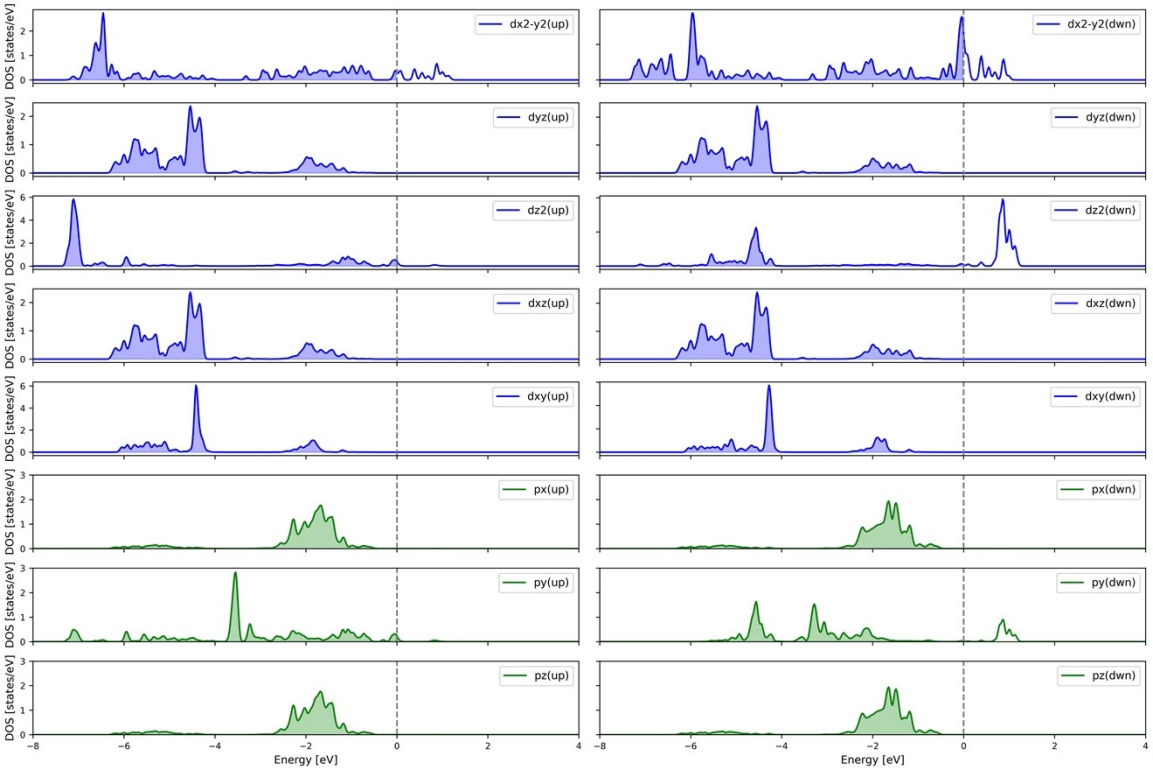

Figure SI10. Electronic density of states AgF_2 for 25% Li doping level. Ag states in blue, F states in green

V. Hole doping of LCO

Table SI5 Structural, magnetic, and electronic parameters for LCO (La_2CuO_4) compounds in scenarios of gradual replacement of La^{3+} by Ba^{2+}. **A** for Cu-Cu distance, **C** for Cu-O apical bond, **B1** and **B2** for Cu-O equatorial bonds and **α** for Cu-O-Cu angle. Doping level stems for depopulation of Cu x^2-y^2 states, $\delta n_{(Cu(\beta - dx2 - y2))}$, depopulation of apical oxygen states, δn_O, and depopulation of Cu$d_{(z^2)}$ states, $\delta n_{Cu(dz^2)}$. The doping level was calculated in the same manner as in the previous chapter.

% Ba	a [Å]	b [Å]	c [Å]	V [Å³]	A [Å]	C [Å]	B1= B2 [Å]	α [°]	Cu mag. mom [μ_B]	F apical mag. mom [μ_B]	Doping level [%]		
											$\delta n_{(Cu(\beta - dx$	$\delta n_{Cu(dz^2)}$	δn_O

0	5.271	5.408	12.994	370.420	3.78	2.42	1.89	172.35	0.52	0.01	0	0	0
5	5.290	5.360	13.081	370.883	3.77	2.39	1.88	174.70	0.52	0.01	1.4	4.7	7.3
10	5.314	5.317	13.142	371.320	3.76	2.36	1.88	179.44	0.51	0.02	1.8	6.3	7.9
15	5.325	5.327	13.162	373.370	3.77	2.34	1.88	179.99	0.51	0.04	1.7	6.7	8.4

VI. Cif file for Cs2K.

Cs2K

```
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      0.0000000000     25.9749107361      0.0000000000
      0.0000000000      0.0000000000      5.8420829773
  Ag  Mg  Cs  K  F
   4   8   8  4  36
Direct
     0.000000000       0.000000000       0.000000000
     0.500000000       0.000000000       0.500000000
     0.000000000       0.500000000       0.000000000
     0.500000000       0.500000000       0.500000000
     0.000020000       0.825380027       0.000000000
     0.999979973       0.174619973       0.000000000
     0.499980003       0.174619973       0.500000000
     0.500020027       0.825380027       0.500000000
     0.999979973       0.325380027       0.000000000
     0.000020000       0.674619973       0.000000000
     0.500020027       0.674619973       0.500000000
     0.499980003       0.325380027       0.500000000
     0.000060000       0.908309996       0.500020027
     0.999939978       0.091689996       0.499979973
     0.499940008       0.091689996       0.000020027
     0.500060022       0.908309996       0.999979973
     0.999939978       0.408309996       0.499979973
     0.000060000       0.591690004       0.500020027
     0.500060022       0.591690004       0.999979973
     0.499940008       0.408309996       0.000020027
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     0.000040000       0.750000000       0.499859989
     0.500039995       0.750000000       0.000140011
     0.499960005       0.250000000       0.999859989
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     0.249960005       0.175660014       0.750029981
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     0.249960005       0.324339986       0.750029981
     0.750039995       0.675660014       0.249970004
     0.250039995       0.675660014       0.250029981
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     0.250050008       0.675759971       0.749979973
     0.749949992       0.324240029       0.250020027
     0.249949992       0.324240029       0.249979973
     0.750050008       0.675759971       0.750020027
     0.749949992       0.175759971       0.250020027
     0.250050008       0.824240029       0.749979973
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0.249949992	0.175759971	0.249979973
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0.250779986	0.000150000	0.750779986
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0.500029981	0.902700007	0.500199974
0.499970019	0.097300000	0.499800026
0.999970019	0.097300000	0.000199974
0.000029981	0.902700007	0.999800026
0.499970019	0.402700007	0.499800026
0.500029981	0.597299993	0.500199974
0.000029981	0.597299993	0.999800026
0.999970019	0.402700007	0.000199974
0.499960005	0.250000000	0.500419974
0.500039995	0.750000000	0.499580026
0.000039995	0.750000000	0.000419974
0.999960005	0.250000000	0.999580026