SUPPORTING INFORMATION

Crystal, electronic, and magnetic structures of M₂AgF₄ (M = Na – Cs) phases as viewed from the DFT+U method

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I. Details of the magnetic coupling calculations

For the layered perovskite phases the super-exchange-mediated magnetic coupling within the \([\text{AgF}_{4/2+2}]^{2-}\) square layers \((J_{2D})\) can be calculated with the use of the broken-symmetry

\[
\hat{H}_{ij} = -J_{ij} s_i s_j
\]

method. Taking the Heisenberg Hamiltonian in the form of \(\hat{H}_{ij} = -J_{ij} s_i s_j\) one can express the
energies of the FM(2D)/AFM(2D) spin states (Fig. S 1) in terms of \(J_{2D}\), as shown in

Table S 1. In analogy, the magnetic coupling constant within the \([\text{AgF}_{4/2+2}]^{2-}\) chains of PP can
be calculated with the knowledge of the energies of the FM(1D)/AFM(1D) states.

**Table S 1 Relations between the energy of a given spin state and the magnetic coupling
constants \((J_{1D}/J_{2D})\)**

<table>
<thead>
<tr>
<th>System</th>
<th>Energy per spin*</th>
<th>(J) value</th>
<th>Ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>(E_{\text{FM}} = -\frac{1}{2}J_{1D} + E)</td>
<td>(J_{1D} = 2(E_{\text{AFM}} - E_{\text{FM}}))</td>
<td>FM ((J_{1D} &gt; 0))</td>
</tr>
<tr>
<td></td>
<td>(E_{\text{AFM}} = \frac{1}{2}J_{1D} + E)</td>
<td></td>
<td>AFM ((J_{1D} &lt; 0))</td>
</tr>
<tr>
<td>2D</td>
<td>(E_{\text{FM}} = -\frac{1}{2}J_{2D} + E)</td>
<td>(J_{2D} = E_{\text{AFM}} - E_{\text{FM}})</td>
<td>FM ((J_{2D} &gt; 0))</td>
</tr>
<tr>
<td></td>
<td>(E_{\text{AFM}} = -\frac{1}{2}J_{2D} + E)</td>
<td></td>
<td>AFM ((J_{2D} &lt; 0))</td>
</tr>
</tbody>
</table>

* where \(E\) is the spin-independent part of the total energy.

We note that as a result of the tilting distortions present in AE\(_\beta\) and FC\(_\beta\) these phases should
be characterized by two types of super-exchange routes between nearest-neighbor Ag(II)
centers (Ag-F2a-Ag and Ag-F2b-Ag, as shown in Fig. S 2). Therefore the \(J_{2D}\) values
calculated as described above are in fact a mean of two coupling constants \((J_{2D}'\) and \(J_{2D}''\))
characterizing each coupling route. We note though that the sign of these coupling constants
should be the same as \(J_{2D}\), and their values similar. This is supported by calculations on the
FC\(_\beta\) phase of K\(_2\)AgF\(_4\) which yields \(J_{2D}' = -22.5\) meV, \(J_{2D}'' = -11.3\) meV, hence average
\(J_{2D} = -16.9\) meV.
II. Mapping the potential surface between HT-(\textit{Bmab}) and LT-
\textit{K}_2\textit{AgF}_4 (\textit{P2}_1/\textit{c}) with DFT+U

\textbf{Computational details} Using a linear-combination approach we have generated 10 model structures to map the potential surface between HT (\(a\), of \textit{Bmab} symmetry) and LT (\(\beta\), of \textit{P2}_1/\textit{c} symmetry) polymorphs of \textit{K}_2\textit{AgF}_4. The former structure form was first transformed to the LT representation with a transformation matrix (-1 0 0, 0 -1 0, 1 0 1) (Fig. S 3). Consequently, the structure parameters (coordinates and lattice vectors) of the two polymorphs were linearly combined as \(x\text{HT} + (1-x)\text{LT}\) for 10 values of \(x\) with step equal to 0.1. Such constructed models were fully optimized considering both ferromagnetic and antiferromagnetic ordering. The DFT and spin-polarized DFT+U calculations were performed in the VASP package with the DFT+U method and a plane-wave cut-off equal to 800 eV. Only results of magnetic calculations are discussed, as nonmagnetic calculations result in wrong ground state (see Fig. S 5).

![Fig. S 3 Unit cell of HT- and LT-K\textsubscript{2}AgF\textsubscript{4} used as starting structures for generation of 10 model structures via linear combination approach. The HT form is visualized in a LT (\(\textit{P2}_1/\textit{c}\)) representation.](image-url)
Results

Main structural changes along HT → LT transformation path

All obtained structures are visualized in Fig. S 4. The important structural changes along the HT → LT transformation path account for change in the AgF₆ octahedra and their orbital ordering pattern. First, the contracted AgF₆ octahedron changes to elongated one and simultaneously the ferrodistortive ordering pattern of \( d(x^2-y^2) \) orbitals along the \( ab \) plain changes to antiferrodistortive one (\( x=0.1–0.4 \)). Next, the \( d(x^2-y^2) \) orbitals reorient in such a way as to form parallel stacking that propagates along \( a \) axis (\( x=0.5 \)). Such stacking leads to considerable reduction of the LT angle by 20°. These features (the parallel stacking and LT angle approaching 90°) are reminiscent of the LT polymorph with the exception that the potassium atoms are not located at the central positions of the van der Waals cavities between the AgF₆ octahedra. Respective shifts in the potassium sub-lattice enforce a butterfly coordination around Ag atoms and it take place for \( x=0.6 \). Once the potassium atoms are shifted the parallel stacking of the \( d(x^2-y^2) \) orbitals recovers and the LT polymorph is stabilized (\( x=0.7–0.9 \)).

Fig. S 4

Fig. S 4 All optimized ferromagnetic models shown along axes \( a \) (top), \( b \) (middle) and \( s \) (bottom) of the LT-K₂AgF₄ representation.

Energy barrier along HT → LT transformation path

The energy barrier calculated for ferromagnetic models is shown in Fig. S 5. Change of the contracted AgF₆ octahedron to
elongated one and simultaneous change of the ferrodistortive ordering pattern of \( d(x^2-y^2) \) orbitals to the antiferrodistortive one amounts for large energy decrease by 180 meV/FU (x=0 \( \rightarrow \) x=0.1). This transition is another indication of the tendency for \( \text{K}_2\text{AgF}_4 \) to adopt the AE-type arrangement in the layered perovskite structure. The elongated octahedra and the antiferrodistortive ordering is preserved in following three structures (x=0.2-0.4) which differ in energy maximally by 40 meV/FU. These order of magnitude smaller energy changes can be assigned to slight changes in relative tilting of the AgF\(_6\) octahedra. The perovskite type structures are separated from the LT polymorph by an energy barrier of 180 meV/FU, which accounts mainly for changes in potassium sub-lattice.

![Fig. S 5 Energy barrier between HT (Bmab) and LT (P2\(_1\)/c) polymorphs calculated for nonmagnetic and FM models. Note that the true barrier height may differ from that calculated for x=0.6.](image)

Generally speaking, all linear combinations of HT and LT polymorphs resulted in AE and PP types of structures.

In order to obtain more detailed information about the potential energy surface of the perovskite and post-perovskite forms of \( \text{K}_2\text{AgF}_4 \) we have additionally calculated a monoclinic variants of the Bmab structure (FM C2/c and AFM P2\(_1\)/c), another variant with infinite linear AgF chains (AFM P4\(_4\),mc), post-perovskite structure with contracted AgF\(_6\) octahedra and the contraction taking place along the direction of the octahedral stacking (Pbam) and finally perovskite structure with ideally flat AgF\(_2\) layers considering both contracted and elongated ocrahedra (FM I4/mmm and AFM C2/c). The analysis presented below focuses on general trends considering also these additional polymorphs.
**Coordination / Jahn-Teller distortions** Structures with 2+2+2 and 4+2 (with both elongated and contracted octahedra) coordination were obtained. In all structures with 2+2+2 coordination, the difference between the two sets of equatorial Ag-F distances is maximally 0.06 Å, while the difference between axial and equatorial distances is usually by one order of magnitude larger. The amount of the distortion \( d(Ag-F)_{eq}/d(Ag-F)_{ax} \) translates to energetic stabilization of the structures - the energy decreases with the increase of the octahedral distortion (Figure 4). The distortion is the largest for elongated octahedra (0.44–0.70) and it is considerably smaller for contracted octahedra (0.06–0.32). In consequence, the solutions with contracted octahedra are separated from the solutions with elongated octahedra by 100 meV/FU gap. There is one solution that strongly deviates from this linear trend in Fig. S 6. This is a \( C2/c \) cell with 2D AFM ordering. Its high energy suggests that the 2D AFM ordering is substantially disfavoured (see below).

![Amount of octahedral distorsion vs E](image)

**Fig. S 6** Energy of all calculated \( K_2AgF_4 \) models plotted as a function of an amount of octahedral distortion calculated as \( d(Ag-F)_{eq}/d(Ag-F)_{ax} \), where \( d(Ag-F)_{eq} \) stands for average equatorial Ag-F distance and \( d(Ag-F)_{ax} \) for average axial Ag-F distance.

**Orbital ordering** In all obtained structures, the relative orientation of the nearest-neighbour highest-occupied \( d \) orbitals is such as to minimize their overlap. Thus, in structures with elongated \( AgF_6 \) octahedra the highest occupied \( d(x^2-y^2) \) orbitals exhibit antiferrodistortive ordering and in the structures with contracted \( AgF_6 \) octahedra, the highest occupied \( dz^2 \) orbitals exhibit parallel ordering. In structures with antiferrodistortive ordering of the magnetic \( d(x^2-y^2) \) orbitals, the extremely large JT distortion \( (abs(d(Ag-F)_{eq}/d(Ag-F)_{ax}) > 0.44) \) that controls their separation prevents stabilization of the AFM solution.
Table S2: List of all calculated K$_2$AgF$_4$ models ordered in respect to their increasing relative energy $\Delta E = E - E_0$. For each structure orbital ordering pattern (OO) and Ag-F distances are listed. AE = antiferrodistortive ordering of elongated octahedra. FC = ferrodistortive ordering of contracted octahedra. PP-E – post-perovskite with elongated octahedra. PP-C – post-perovskite with contracted octahedra.

<table>
<thead>
<tr>
<th>mag</th>
<th>symm</th>
<th>$\Delta E$</th>
<th>OO</th>
<th>Ag-F1</th>
<th>Ag-F2</th>
<th>Ag-F3</th>
</tr>
</thead>
<tbody>
<tr>
<td>FM 1D</td>
<td>$P2_1/c$ (LT)</td>
<td>0.000</td>
<td>PP-E</td>
<td>2.130</td>
<td>2.112</td>
<td>2.816</td>
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<tr>
<td>FM 2D</td>
<td>$Pbc$</td>
<td>0.047</td>
<td>AE</td>
<td>2.130</td>
<td>2.120</td>
<td>2.615</td>
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<tr>
<td>FM 2D</td>
<td>$P-1$ no.1</td>
<td>0.060</td>
<td>AE</td>
<td>2.124</td>
<td>2.123</td>
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<td>FM 2D</td>
<td>$P-1$ no.2</td>
<td>0.074</td>
<td>AE</td>
<td>2.120</td>
<td>2.138</td>
<td>2.571</td>
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<tr>
<td>FM 1D</td>
<td>$Pbam$</td>
<td>0.174</td>
<td>PP-C</td>
<td>2.395</td>
<td>2.395</td>
<td>2.078</td>
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<tr>
<td>AFM 1D</td>
<td>$Pbam$</td>
<td>0.176</td>
<td>PP-C</td>
<td>2.395</td>
<td>2.395</td>
<td>2.078</td>
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<tr>
<td>FM</td>
<td>$C2/c$</td>
<td>0.218</td>
<td>FC</td>
<td>2.307</td>
<td>2.285</td>
<td>2.105</td>
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<tr>
<td>AFM 2D</td>
<td>$P2_1/c$ (from $C2/c$)</td>
<td>0.221</td>
<td>FC</td>
<td>2.324</td>
<td>2.289</td>
<td>2.091</td>
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<tr>
<td>FM</td>
<td>$Bmab$ (HT)</td>
<td>0.228</td>
<td>FC</td>
<td>2.286</td>
<td>2.286</td>
<td>2.108</td>
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<td>AFM 2D</td>
<td>$P2_1/c$ (from Cmca)</td>
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<td>FC</td>
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<td>2.299</td>
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<td>AFM 2D</td>
<td>$P42mc$</td>
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<td>FC</td>
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<td>2.278</td>
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<td>FM</td>
<td>$I4/mmm$</td>
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<td>FC</td>
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<td>2.217</td>
<td>2.155</td>
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<td>AFM 2D</td>
<td>$C2/c$ (from $I4/mmm$)</td>
<td>0.457</td>
<td>FE</td>
<td>2.125</td>
<td>2.125</td>
<td>2.350</td>
</tr>
</tbody>
</table>

III. References