Local and Cooperative Jahn–Teller Effect and Resultant Magnetic Properties of M₂AgF₄ (M = Na–Cs) Phases

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Supporting Information

ABSTRACT: The crystal structure, magnetic properties, heat capacity, and Raman spectra of double-perovskite M₂AgF₄ (M = K, K₁/₂Rb₁/₂, K₁/₄Rb₃/₄, and Rb) phases have been examined, adding to the body of previous results for the M = Na, Cs derivatives. The results suggest that double-perovskite K₂AgF₄ adopts a disordered orthorhombic Bmab structure with an antiferrodistortive arrangement of the elongated and tilted [AgF₆] octahedra rather than the structure with the ferrodistortive arrangement of compressed octahedra, as suggested previously (Mazej, Z.; Goreshnik, E.; Jagličić, Z.; Gaweł, B.; Łasocha, W.; Grzybowska, D.; Jaroń, T.; Kurzydłowski, D.; Malinowski, P. J.; Koźmiński, W.; Szydlowska, J.; Leszczyński, P. J.; Grochala, W. KAgF₃, K₂AgF₄ and K₃Ag₂F₇: important steps towards a layered antiferromagnetic fluoroargentate(II). CrystEngComm 2009, 11, 1702–1710). A re-examination of the previously collected single-crystal X-ray diffraction data confirms the current structure assignment, and it is also in agreement with recent theoretical calculations. High-field electron paramagnetic resonance spectra reaffirm the presence of elongated [AgF₆] octahedra in the crystal structure of all M₂AgF₄ phases studied. The local structure of the M = K derivative is most complex, with regions of the sample that are quite orthorhombically distorted, whereas other regions more closely resemble the tetragonal phase. The mixed-cation K/Rb phases are also inhomogeneous, containing regions of the pure K compound and regions of another high-symmetry phase (likely tetragonal) of a mixed (Rb-richer) compound with unknown composition. The temperature-resolved phase diagram of all K/Rb phases has been established and positioned within the entire M = Na, K, Rb, Cs series.

INTRODUCTION

Ternary fluorides of divalent silver have been known for more than 40 years,1−4 yet only recently have they attracted a large amount of interest for their potential to become a new class of high-temperature superconductors (HTSCs).5−7 These compounds, containing the Jahn–Teller (JT) active Ag⁺⁺ cation, were also investigated in the context of magneto-structural correlation.8−10 with the magnetic properties arising from the spin-¹/₂ 4d⁰ configuration of the Ag⁺⁺ cation. These efforts resulted in the experimental determination of a very strong antiferromagnetic interaction in KAgF₃,11 similar in magnitude to that found in the oxocuprate(II) precursor of the HTSCs. Compounds with M₂AgF₄ stoichiometry (M = Na, K, Rb, Cs) have attracted particular interest as their composition resembles that of La₂CuO₄, a prototypical precursor for oxocuprate(II) superconductors. This compound adopts the layered perovskite structure (Figure 1a)12 and exhibits strong...
antiferromagnetic (AFM) coupling within the \([\text{CuO}_6]^{2-}\) layers.\(^{15}\)

The cesium derivative of \(\text{M}_2\text{AgF}_4\), \(\text{Cs}_2\text{AgF}_4\), was also found to exhibit the layered-perovskite structure.\(^{14,23}\) In this compound, the elongated \([\text{AgF}_6]^{4-}\) octahedra are arranged in an antiferrodistortive pattern within the \([\text{AgF}_{4/2+2}]^{-}\) planes, a manifestation of the so-called collective Jahn–Teller effect.\(^{15,16}\) Hereinafter we will refer to such a variant of the layered-perovskite structure as AE (antiferrodistortive/elongated, Figure 1b). The cesium derivative of \(\text{M}_2\text{AgF}_4\) exhibits weak 2D ferromagnetic (FM) coupling with a magnetic ordering temperature \((T_N)\) of 14 \(K\).\(^{17,18}\)

Many experimental studies\(^{19–22}\) on the other members of the \(\text{M}_2\text{AgF}_4\) series showed that these systems exhibit a high degree of structural complexity, which leads to marked differences in magnetic properties. From electron paramagnetic resonance (EPR) measurements, the structure of \(\text{Rb}_2\text{AgF}_4\) was established to be analogous to that of \(\text{Cs}_2\text{AgF}_4\).\(^{23}\) For \(\text{K}_2\text{AgF}_4\), two polymorphs were obtained: a metastable layered perovskite phase \((\alpha)\),\(^{19}\) which will term high temperature \((HT)\), and a postperovskite \(\text{Na}_2\text{CuF}_4\)-type phase \((\beta)\),\(^{24}\) which is the ground-state polymorph at room temperature.\(^{20}\) It should be noted that the HT perovskite polymorph of \(\text{K}_2\text{AgF}_4\) is kinetically stable \((\text{metastable})\) up to 470 \(K\),\(^{20}\) therefore, its physical properties can be characterized from low temperatures up to above room temperature.

Interestingly, HT-\(\text{K}_2\text{AgF}_4\) was presumed to exhibit a ferrodistortive ordering of compressed octahedra within the \([\text{AgF}_{4/2+2}]^{-}\) layers in contrast to the rubidium and cesium derivatives. The ferrodistortive variant of the layered perovskite phase, termed by us as FC (ferrodistortive/compressed), is shown in Figure 1c. Also, for the HT-\(\text{K}_2\text{AgF}_4\) structure, tilting of the \([\text{AgF}_6]^{4-}\) octahedra was observed. Finally, for the sodium derivative, only the postperovskite \(\text{Na}_2\text{CuF}_4\)-type phase was obtained.\(^{24}\) For comparison with AE and FC layered-perovskite structures, the postperovskite \(\text{Na}_2\text{CuF}_4\)-type phase, adopted by \(\text{LT-}\text{K}_2\text{AgF}_4\) and \(\text{Na}_2\text{AgF}_4\), is shown in Figure 1d. It is characterized by chains of edge-sharing elongated octahedra with the axes of elongation being parallel for neighboring octahedra. In other words, this structure exhibits a ferrodistortive order but is distinguished from FC by a different connectivity of the Ag/F sublattice.

The magnetic properties of both \(\text{Rb}_2\text{AgF}_4\) and HT-\(\text{K}_2\text{AgF}_4\) imply ferromagnetic coupling within the \([\text{AgF}_{2/2+2}]^{2-}\) planes, with ordering temperatures close to that of \(\text{Cs}_2\text{AgF}_4\).\(^{19}\) In the postperovskite \((\text{Na}_2\text{CuF}_4\)-type) LT-\(\text{K}_2\text{AgF}_4\) and \(\text{Na}_2\text{AgF}_4\) phases, the magnetic coupling between Ag(II) centers is very weak; consequently, those compounds exhibit paramagnetic behavior even at low temperatures.\(^{20,21}\)

Theoretical studies on \(\text{M}_2\text{AgF}_4\) compounds\(^{20–29}\) managed to rationalize the tendency for the adoption of the AE-type ordering in the layered perovskite phase of \(\text{Cs}_2\text{AgF}_4\). Importantly, a recent study cast into doubt the structural assignment of the layered perovskite HT phase of \(\text{K}_2\text{AgF}_4\).\(^{29}\) These calculations showed that the experimentally derived FC-type structure has a much higher energy than a similar structure characterized by an AE-type ordering.

Here we present a reanalysis of the X-ray diffraction (XRD) data for HT-\(\text{K}_2\text{AgF}_4\) as well as the results of high-field EPR (HF-EPR) measurements, which enable an unambiguous assignment of the structure of this phase. We also perform HF-EPR measurements at selected temperatures for other members of the \(\text{M}_2\text{AgF}_4\) series \((\text{LT-}\text{K}_2\text{AgF}_4, \text{Rb}_2\text{AgF}_4, \text{Cs}_2\text{AgF}_4)\). From these, we deduce the structural evolution of these compounds with temperature. Finally, to better characterize the composition region at the borderline of stability of the layered perovskite phase, we synthesize new compounds with \(\text{K}_2–\text{Rb}_x\text{AgF}_4\) stoichiometry \((x = 0.5, 1, 1.5)\) and conduct temperature-resolved HF-EPR and XRD measurements. The obtained results enable us to fully understand and rationalize the surprising complexity of the \(\text{M}_2\text{AgF}_4\) systems.

**EXPERIMENTAL METHODS**

**Synthesis.** Most of the studied compounds were prepared from \(\text{AgF}_2\) and the corresponding alkali metal fluorides following procedures described previously.\(^{19}\) A typical synthesis included fine powdering of the reactants in stoichiometric amounts \((e.g., \text{KF/ReF}_3\) ratio of 3:1:2 for the synthesis of \(\text{K}_3\text{ReF}_6\)) in an agate mortar and placing them in a Pt boat enclosed in a nickel reactor. The synthesis was conducted at 500 \(\text{C}\) \((\text{or 300 }\text{C} \text{ in the case of } \text{LT-K}_2\text{AgF}_4)\).\(^{29}\) The most convenient synthesis route toward high-purity samples of \(\text{Na}_2\text{AgF}_4\) is the thermal decomposition of the \(\text{NaAgF}_4/\text{NaF}\) mixture under dynamic vacuum.\(^{21}\) All synthesized compounds are sensitive to moisture and were handled in a glovebox operating under an argon atmosphere.

**X-ray Powder Diffraction.** X-ray powder diffraction (XRPD) data was collected at ambient temperature on samples placed in 0.3 mm quartz capillaries with the use of a Bruker D8 Discover diffractometer with a Cu Kα X-ray tube \((\lambda = 1.5406 \text{ Å})\). The measurements were carried out in the typical range of 2θ from 10 to 120° with a 0.018° step. Cell indexing was performed with the X-Cell program embedded in the Materials Studio package (BIOVIA). Rietveld refinement was made in JANA2006.\(^{30}\)

Temperature-resolved XRPD measurements were conducted on a diffractometer equipped with a rotating Mo anode \((\lambda = 0.7093 \text{ Å})\) and a 2D MAR345 detector. Scans from a 0.3 mm quartz capillary filled with \(\text{K}_2–\text{Rb}_x\text{AgF}_4\) were collected upon heating from 80 to 330 K at 20 K/h \((\text{HT-K}_x\text{AgF}_y, \text{K}_x\text{Rb}_y\text{AgF}_z)\) and 40 K/h \((\text{K}_x\text{Rb}_y\text{AgF}_z)\) rates. The 2D images were integrated into 1D patterns with FIT2D\(^{31}\) and analyzed in the FullProf suit.\(^{32}\)

The obtained diffractograms indicated that all members of the \(\text{K}_x–\text{Rb}_x\text{AgF}_y\) series adopt the layered-perovskite structure \((\text{Figure 1a})\). An analysis of the systematic absences pointed to a statistical difference in the unit cell parameters of the \(\text{K}_x\text{Rb}_x\text{AgF}_y\) compounds. Rietveld refinement, the relative occupancy of these sites was varied, and the resulting stoichiometry was in good accordance with that derived from the Ag/F/K/Rb/F ratio used in the synthesis.
RESULTS AND DISCUSSION

Jahn–Teller Ordering in HT-K₂AgF₄. Because the X-ray scattering factor of fluorine is more than 5 times smaller than that of silver X-ray diffraction (XRD), investigations yield information only on the approximate position of fluorine atoms. Furthermore, in the case of the layered perovskite M₂AgF₄ phases, different competing JT orders are possible (Figure 1). Consequently, we found that the XRD technique is insufficient for the unambiguous determination of the JT order present in the layered perovskite phases of M₂AgF₄ compounds (in particular, Rb₆AgF₄; see the Supporting Information, section I).

In the previous single-crystal X-ray diffraction study conducted at 200 K, the crystal structure of HT-K₂AgF₄ was assigned to the FCₐ structure.⁵ The a subscript indicates the type of tilting distortion present in this structure; for details, see ref 29. Theoretical calculations show that the FCₐ structure has a much higher energy (over 0.15 eV per K₂AgF₄ unit) than the AEₐ arrangement (i.e., the AE-type structure with the same tilting distortions as for the FCₐ).⁵⁰

We therefore reanalyzed the single-crystal data by performing a refinement on the AEₐ model. To our surprise, this did not lead to a significant improvement in the goodness-of-fit parameters. We then turned to a structure that, similar to AEₐ, contained antiferrodistortive JT order and α-type tilts but additionally exhibited disorder in the orientation of neighboring octahedra. This structure, which we term AEₐ disord, exhibits the same symmetry as FCₐ. It turned out to give a much better fit to X-ray data than FCₐ (Table 1). For more details concerning AEₐ disord, see the cif file in the SI. This structure is also deposited in the ICSD database under the number 431905.

From the above, we can conclude that indeed HT-K₂AgF₄ exhibits AE-type Jahn–Teller ordering, similar to that in Rb₆AgF₄ and Cs₆AgF₄ and in accordance with DFT + U calculations.²⁹ To further confirm this result, we turned to a complementary nondiffraction technique that can provide information on the Jahn–Teller distortion by conducting high-field electron paramagnetic resonance (HF-EPR) measurements for all members of the M₂AgF₄ family that exhibit the layered perovskite structure (Cs₆AgF₄, Rb₆AgF₄, HT-K₂AgF₄, as well as mixed K/Rb compounds described further below). As can be seen in Figure 2, all three pure compounds exhibit very similar axial spectra, with just two g-tensor components: the measured perpendicular and parallel values are approximately 2.25(g₂) and 2.07(g₁), respectively. The resonance fields were determined at various microwave frequencies from 24 to 406 GHz and at 200 K to avoid complications associated with magnetic ordering (see below). The extrapolated plots of the resonance fields versus frequency pass through the origin (B = 0, ν = 0), meaning that the equation 2μBν/g₂μ₀B is obeyed, there is no zero-field splitting of the levels involved in the EPR transitions, and no measurable internal magnetic field is present (SI, Section II).

The relative magnitudes of the g-tensor components seem to indicate at first glance the presence of the compressed form of

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Table 1. Comparison of the Structure Parameters of FCₐ and AEₐ disord Models of HT-K₂AgF₄.

<table>
<thead>
<tr>
<th>space group</th>
<th>FCₐ b</th>
<th>AEₐ disord c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>4</td>
<td>2.47%/5.91%</td>
</tr>
<tr>
<td>R₁/wR₁^a</td>
<td>3.06%/7.89%</td>
<td>2.76%/8.18%</td>
</tr>
<tr>
<td>a (Å)</td>
<td>6.182(3)</td>
<td>6.1835(5)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>6.436(3)</td>
<td>6.4372(5)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.632(5)</td>
<td>12.634(1)</td>
</tr>
<tr>
<td>K</td>
<td>0.5; 0.190(2); 0.1431(1)</td>
<td>0.126(2); 0.0193(2); 0.1432(1)</td>
</tr>
<tr>
<td>Fq</td>
<td>0.0; 0.0; 0.0</td>
<td>0.0; 0.0; 0.0</td>
</tr>
<tr>
<td>Feq</td>
<td>0.0; 0.0; 0.0</td>
<td>0.0; 0.0; 0.0</td>
</tr>
<tr>
<td>RAg-1 (Å)</td>
<td>2.086(6)</td>
<td>2.090(4)</td>
</tr>
<tr>
<td>Req</td>
<td>2.259(1)</td>
<td>2.149(9)</td>
</tr>
</tbody>
</table>

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For each atom, the fractional (x, y, z) position is given along with the Wyckoff site label, the site occupancy, and the isotropic displacement factor. bReference 19. cThis work.  dNonstandard setting of the cell parameters used for the refinement in the P1 space group, which retains the c lattice vector as perpendicular to the [AgF₄/2+2] sheets. eRI = ΣFᵢl − |Fᵢl|/ Σ|Fᵢl| for I > 2σ(I), wR₂ = Σ((Fᵢl − |Fᵢl|)w)/ Σ(Fᵢl)w for I > 2σ(I).

Electron Paramagnetic Resonance (EPR). High-field, high-frequency EPR spectra at temperatures ranging from ca. 3 to 290 K were recorded on a home-built spectrometer at the EMR facility of the NHMFL. The instrument is equipped with a superconducting solenoid (Oxford Instruments) capable of reaching a field of 17 T. Microwave frequencies over the range of 52–416 GHz were generated by a phase-locked Virginia Diodes source, producing a base frequency of 13 ± 1 GHz, which was multiplied by a cascade of frequency multipliers. The instrument is a transmission-type device and uses no resonance cavity. A liquid He-cooled InSb bolometer (QMC Instruments Ltd.) was used as a microwave detector. All spectra were recorded in derivative, df/DB (where B is the absorption intensity), mode using field modulation and a phase-sensitive lock-in detection scheme.

Because the samples are tremendously moisture-sensitive, they were packed in sample holders (ϕᵣ = 7 mm, ϕᵢ = 9 mm, l = 26 mm) made from perfluoropolymer and protected with two tightly fitting PTFE (Teflon) stoppers (l = 28 mm; see the SI for a photograph of a holder).

Magnetic Measurements. Magnetic measurements were performed using Quantum Design MPMS-XL-5 SQUID and MPMS SQUID VSM magnetometers. The temperature dependence of the susceptibility was measured between 2 and 300 K in a magnetic field of 1 kOe. The obtained data has been corrected for an empty sample holder (quartz/TEP for XL-5/VSM) as well as for temperature-independent diamagnetism of inner shell electrons.⁴³

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Inorganic Chemistry

Article
Elongated Geometry, with the Unpaired Electron in the d
Cs2AgF4. The red spectrum is the best simulation of the Cs2AgF4 data
combined in fact, the spectra of all three compounds can be explained by the
experimental spectra are not due to the isolated molecules. In
AE (or AE
resonance in Figure 2 should occur at a higher
gT. It is thus apparent that the
experimentally observed
may be reduced due to covalence. Thus,
gβ > gγ for the compressed case and gβ > gγ for the elongated case.

Table 2. Intrinsic g-Tensor Components Expected for Ag2+
in a JT Compressed Octahedral Geometry, For Which the
Unpaired Electron Resides in the dz^2 Orbital, and in a JT
Elongated Geometry, with the Unpaired Electron in the dx^2 − y^2 Orbital

<table>
<thead>
<tr>
<th></th>
<th>JT compressed</th>
<th>JT elongated</th>
</tr>
</thead>
<tbody>
<tr>
<td>gβ</td>
<td>2.0023</td>
<td>2.0023</td>
</tr>
<tr>
<td>gδ</td>
<td>2.0023</td>
<td>2.0023</td>
</tr>
<tr>
<td>gε</td>
<td>2.0023</td>
<td>2.0023</td>
</tr>
</tbody>
</table>

“The spin–orbit coupling constant λ for Ag^2+ equals –1844 cm\(^{-1}\) but may be reduced due to covalence. Thus, gβ > gε for the compressed case and gβ > gγ for the elongated case.

be exactly equal to g0 (= 2.0023); therefore, the corresponding resonance in Figure 2 should occur at a higher field of ca. 11.65 T. It is thus apparent that the gβ values seen in the experimental spectra are not due to the isolated molecules. In fact, the spectra of all three compounds can be explained by the combined influences of the AE orbital ordering and exchange averaging (hence the “ex” superscript on the experimental g values), similar to what has previously been found for K2CuF4.35

At 200 K, the M = Cs and Rb compounds adopt AE structures that are tetragonal (b/a = 1.00 to within the experimental accuracy, see SI Section III and ref 15), with no discernible tilting of the [AgF6]^4– octahedra out of the layers. Consequently, the JT elongation axis (local z) of a given ion will be parallel to one of the short axes (local x) of its four nearest neighbors within the same plane, whereas the other short axes of the neighbors (local y) are oriented perpendicular to the plane (Figure 1b). For this high-symmetry case, the intrinsic Ag(II) g-tensor components (gβ, gδ, gε) combine according to eqs 1 and 2 to give an exchange-averaged effective g tensor that is tetragonal, in accordance with the experimental observations:

\[
g_{ex}^z = g_y \\
g_{ex}^x = \frac{1}{2}(g_x + g_z) \\
g_{ex}^y = \frac{1}{2}(g_y - g_x)\cos \alpha
\]

Equation 2 implies an exact perpendicular arrangement of the Z axes of the interacting ions. With an angle of α ≠ 90° between the Z axes of interacting ions, eq 2 can be generalized as follows:

\[
g_{ex}^x = \frac{g_x + g_z + (g_y - g_x)\cos \alpha}{2} \\
g_{ex}^y = \frac{g_x - g_y + (g_y - g_x)\cos \alpha}{2}
\]

Nonaxial EPR spectra are thus expected for α ≠ 90°. Two different perpendicular g components should be seen as a result of the tilting.

If one then assumes local g tensors corresponding to the JT elongated case in Table 2 (i.e., gβ = gε and gγ > gγ), then the intrinsic g-tensor components can be extracted from the exchange-averaged ones in Figure 2, giving gex = ca. 2.07 and gε = ca. 2.44. These values are in excellent agreement with those previously determined at 130 K for Cs2AgF4 (gβ = 2.07, gγ = 2.42) and Rb2AgF4 (gβ = 2.07, gγ = 2.43) and postperovskite LT-K2AgF4 (gβ = 2.42, gγ = 2.10) at 150 K.20 In this work, values of gβ = 2.427, gγ = 2.100, and gδ = 2.077 were determined at 200 K for LT-K2AgF4 (Table 3). This suggests that very similar coordination spheres of Ag2+ exist in both HT and LT phases of K2AgF4.

The exchange-averaging phenomenon may be further understood by modeling the system as a simple dimer composed of two exchange-coupled, octahedrally coordinated Ag(II) centers, with long and short Ag–F bonds oriented in a way that mimics the actual structure. This dimer unit corresponds to the elementary building block within the 2D layers, and although its spatial symmetry is low, the symmetry of the corresponding spin Hamiltonian is tetragonal,

\[
\hat{H} = \mu_B \sum_j \vec{g}_j \cdot \vec{\hat{S}}_j + \mu_B \sum_j \vec{g}_j \cdot \vec{\hat{S}}_j - J\hat{S}_1 \cdot \hat{S}_2
\]

where \(\hat{S}_j\) and \(\vec{g}_j\) (j = 1, 2) correspond respectively to the local spin operators and intrinsic g tensors at the two sites within the

Table 3. Diagonal gβ-Tensor Components Determined Experimentally at 200 K for the Layered-Perovskite Structures

<table>
<thead>
<tr>
<th></th>
<th>LT-K2AgF4^a</th>
<th>HT-K2AgF4</th>
<th>K0.5Rb0.5AgF4</th>
<th>KRbAgF4</th>
<th>K0.5Rb1.5AgF4</th>
<th>RbAgF4</th>
<th>Cs2AgF4</th>
</tr>
</thead>
<tbody>
<tr>
<td>gβ</td>
<td>2.077</td>
<td>2.259</td>
<td>2.260</td>
<td>2.258</td>
<td>2.259</td>
<td>2.255</td>
<td>2.252</td>
</tr>
<tr>
<td>gγ</td>
<td>2.100</td>
<td>2.259</td>
<td>2.260</td>
<td>2.258</td>
<td>2.259</td>
<td>2.255</td>
<td>2.252</td>
</tr>
<tr>
<td>gδ</td>
<td>2.427</td>
<td>2.072</td>
<td>2.075</td>
<td>2.076</td>
<td>2.075</td>
<td>2.075</td>
<td>2.073</td>
</tr>
</tbody>
</table>

^aLT-K2AgF4 exhibits ferrodistortive order (Figure 1d), and gβ components reflective of the intrinsic values are directly observed. All of the others are AE (or AEi disabled) ordered, and axial exchange-coupled gβ values are given.
dimer, and $J$ is the exchange coupling strength. The structure then dictates that $g_{xx} = g_{yy} = 2.44$, $g_{zz} = 2.07$, and $g_{xy} = g_{yx} = 2.07$, where the coordinates are now referenced to the dimer frame (i.e., $x$ and $y$ correspond to the JT elongation axes on sites 1 and 2, respectively, and $z$ represents the normal to the layers). Taking the experimental value of $J = 30 \text{ cm}^{-1}$ for Cs$_2$AgF$_4$, an axial $(g^a_x = g^a_y)$ simulated spectrum is obtained, in accord with the experimental results (see Figure 2, top).

The HT-K$_2$AgF$_4$ compound, meanwhile, adopts the distinctly orthorhombic $A_{E_{\text{disord}}}$ structure, with an orthorhombic phase at 200 K. This should give rise to a nonaxial exchange-averaged $g$ tensor (i.e., $g^a_x$ should be different from $g^a_y$). According to eqs 1a and 1b, these $g^a_x$ and $g^a_y$ values should be centered on the $g^a_{xy} = (g_x + g_y)/2 = 2.26$ value, which is observed at 200 K for all samples (Figure 2). The degree of splitting will depend on the precise details of the local coordination at different Ag(II) sites in the lattice, which is not well established from XRD studies. Meanwhile, the disorder associated with the $A_{E_{\text{disord}}}$ structure will likely further complicate matters, as some regions of the crystal are more orthorhombic than others. Consequently, a continuous distribution of $g^a_x$ and $g^a_y$ values may be expected, centered on 2.26, thus explaining the single broad $g^a_{xy}$ component observed for the HT-K$_2$AgF$_4$ compound at high temperatures. The fact that this resonance is substantially broader than all other features in Figure 2 seems to support this hypothesis, which is further confirmed by the low-temperature spectra (see below).

Therefore, on the basis of the analysis of HFEPR data we have concluded that the HT-K$_2$AgF$_4$ polymorph exhibits a layered perovskite structure with an antiferrodistortive ordering of elongated octahedra analogous to that found in Cs$_2$AgF$_4$. The only difference between Cs$_2$AgF$_4$ and HT-K$_2$AgF$_4$ would be the disorder and presence of tilting distortions in the latter. This is further supported by the striking similarities in the Raman spectra of HT-K$_2$AgF$_4$/Rb$_2$AgF$_4$ and Cs$_2$AgF$_4$ (SI, Section V). This finding, which reconciles the available experimental and theoretical results, should be confirmed in the future with the neutron diffraction measurements.

Table 3 collects values of the diagonal components of the $g^{ex}_x$ tensors determined at 200 K by HFEPR for layered perovskite structures in the M$_2$AgF$_4$ family (M = K, Rb, Cs), also including the mixed K/Rb phases (cf. next section). With the exception of LT-K$_2$AgF$_4$, all of the tensors are axial/tetragonal, with $g^a_x = g^a_y > g^a_{xy}$ reflecting the AE structures. Meanwhile, LT-K$_2$AgF$_4$ possesses a postperovskite structure with chains of ferrodistortively ordered octahedra (Figure 1d). Therefore, the experimental g-tensor components correspond exactly to the intrinsic axially JT elongated values in Table 2, with a slight distortion of the $[\text{AgF}_4]^{4-}_{\text{ex}}$ octahedra giving rise to a rhombic g-tensor with $g^a_x \neq g^a_y$.

** Tilting Distortions and the Phase Diagram of the K$_2$−Rb$_2$AgF$_4$ System. ** Having established the structural characteristics of HT-K$_2$AgF$_4$, we decided to explore the nature of the tilting distortions in the layered-perovskite K$_2$−Rb$_2$AgF$_4$ systems. We synthesized three new compounds exhibiting different $a$ and $b$ lattice vectors (a/b ratio of approximately 1.01). We will refer to this phase as LTO (low-temperature orthorhombic). Upon heating, the b/a ratio remains nearly constant up to 110 K. Above this temperature, a drastic increase in the b/a ratio is seen (up to approximately 1.03). This marks the entrance into the LTO phase (low-temperature orthorhombic). This transition is accompanied by a volume discontinuity suggesting that it is a first-order transition.

Upon further heating, the b/a ratio of LTO decreases down to a value of 1.005 at 330 K and remains nearly constant above this temperature. At this point, the measured difference between $a$ and $b$ is below the resolution of the XRPD measurements, and thus we conclude that, above 330 K, the cell is tetragonal ($a = b$). Therefore, at this temperature we observe the transition into the high-temperature tetragonal phase (HTT). The LTO-HTT transition seems to be continuous with no volume discontinuity and only a small change in the slope of the c vs T dependence.

We followed the changes in the lattice parameters of the mixed-cation compounds as well as those of HT-K$_2$AgF$_4$ and Rb$_2$AgF$_4$ by performing XRD measurements in the temperature range from 80 to 340 K (we found that above 340 K the studied compounds reacted with the walls of the quartz capillaries). Note that although HT-K$_2$AgF$_4$ is a metastable phase its transition to the ground-state LT-K$_2$AgF$_4$ polymorph is kinetically hindered and requires temperatures in excess of 470 K.

In the studied temperature-composition range, we found evidence for three types of phases. In the investigated temperature window, all three of them are observed for K$_2$RbAgF$_4$ (Figures 3 and 4). At 80 K, this compound is characterized by an orthorhombic cell with very similar lengths of the $a$ and $b$ lattice vectors (a/b ratio of approximately 1.01). We will refer to this phase as LTO (low-temperature less orthorhombic). Upon heating, the b/a ratio remains nearly constant up to 110 K. Above this temperature, a drastic increase in the b/a ratio is seen (up to approximately 1.03). This marks the entrance into the LTO phase (low-temperature orthorhombic). This transition is accompanied by a volume discontinuity suggesting that it is a first-order transition.

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Measurements of compounds with lower Rb content (HT-K\textsubscript{2}AgF\textsubscript{4}, K\textsubscript{1.5}Rb\textsubscript{0.5}AgF\textsubscript{4} – see SI, Section III) revealed the presence of only the LTLO-LTO transition in the studied temperature range, which appears with decreasing Rb content at progressively higher temperature and with greater hysteresis. For systems with high Rb content (K\textsubscript{0.5}Rb\textsubscript{1.5}AgF\textsubscript{4}, Rb\textsubscript{2}AgF\textsubscript{4}) we observed by XRPD only the LTO-HTT transition (SI, Section III). The temperature of this transition decreases with increasing Rb content. Heat capacity measurements conducted in the 2\textdegree-300 K temperature range (SI, Section IV) did not indicate any additional structural phase transitions apart from those observed by XRPD. The temperature dependence of the magnetic susceptibility (Figure 5) suggests that all perovskite K\textsubscript{2-x}Rb\textsubscript{x}AgF\textsubscript{4} phases exhibit paramagnetic behavior above 20 K, consistent with a model for a 2D spin-1/2 system\textsuperscript{36} and 2D FM properties below \textasciitilde20 K with ordering temperatures increasing slightly from K\textsubscript{2}AgF\textsubscript{4} (13.4 K) to Rb\textsubscript{2}AgF\textsubscript{4} (17.5 K). We have not found any evidence for anomalous behavior of the magnetic susceptibility in the vicinity of the structural phase transitions. On the other hand, the HFEPR spectra of the three phases differ significantly, as discussed in the next section (SI, Section VI).

HFEPR Studies of the Magnetic Ordering. As a microscopic probe, HFEPR can provide important information concerning the magnetic ordering in the M\textsubscript{2}AgF\textsubscript{4} family, which in turn can give further insights into the low-temperature structures. It is most straightforward to first consider the simplest M = Cs and Rb cases, particularly the former as it maintains a tetragonal structure (HTT) all the way down to 5 K.\textsuperscript{15} As seen in Figure 6, Cs\textsubscript{2}AgF\textsubscript{4} displays axial spectra both at high (200 K) and low (3 K) temperatures, with just two resonances corresponding to parallel (\//z) and perpendicular (\//xy) mode excitations. However, the anisotropy, as measured by the spacing between these two resonances, is significantly stronger (by approximately a factor of 2 at 326 GHz) at low temperature.

From measurements performed at multiple frequencies (Figure 6, main panel), we ascertain that the additional contribution to the low-temperature anisotropy is due primarily to a field-independent interaction. In other words, the field-dependent Zeeman interaction is more or less unchanged between 200 and 3 K, with very similar g factors deduced from the slopes of linear fits to the data in Figure 6 (see also Tables 3 and 4). Note that the g\textsubscript{z} value for HT-K\textsubscript{2}AgF\textsubscript{4} does change from 2.26 at 200 K to 2.30 at 3 K but remains unchanged in the compounds containing Rb and Cs.
Field-independent magnetic anisotropy can have several sources. At the single-site level, spin–orbit coupling gives rise to so-called zero-field-splitting interactions, although only for spin $s > \frac{1}{2}$. Meanwhile, both short- and long-range intersite magnetic interactions can be modeled in terms of an anisotropy field, $B_{\text{int}}$, internal to the sample. Indeed, such effects may be strong in ferromagnetically ordered materials. For an ordered uniaxial crystal, assuming only second-order contributions to the magnetic anisotropy, this gives rise to modified ferromagnetic resonance (EMR) conditions for fields applied parallel and perpendicular to the tetragonal axis.\(^\text{37}\)

\[
\text{parallel: } h\nu = g_s \mu_B (B + B_{\text{int}}^\parallel)
\]

\[
\text{perpendicular: } h\nu = g_s \mu_B \left( B - \frac{1}{2} B_{\text{int}}^\parallel \right)
\]

Here, $B_{\text{int}}^\parallel$ refers to the uniaxial component of the anisotropy field so as to distinguish it from the perpendicular component, $B^\perp$, appropriate to the rhombic cases discussed further below. $B$ represents the local magnetic induction, which may include an isotropic internal contribution, $B_{\text{iso}}$, such that $B = B^\parallel + B_{\text{iso}}$, where $B^\parallel$ is the externally applied magnetic field. The above expressions assume $B_{\text{iso}}^\parallel$ to be constant (i.e., that the sample magnetization is saturated), requiring $B^\parallel > B_{\text{iso}}^\parallel$. An examination of the zero-frequency intercepts in Figure 6 (see inset) reveal values of +0.59 T and −0.21 T for the parallel and perpendicular modes, respectively. These are not so far from being in the 2:–1 ratio predicted on the basis of eqs 4 and 5, suggesting that $B_{\text{iso}}^\parallel$ is relatively weak in comparison to $B_{\text{iso}}^\perp$. Taking the difference of these two intercepts and dividing by $\frac{1}{2}$ gives a value of $B_{\text{iso}}^\parallel \approx 0.53$ T, from which one can deduce that $B_{\text{iso}}^\parallel \approx 0.06$ T. In fact, the signs of the intercepts dictate a negative value of $B_{\text{iso}}^\perp$, indicating an easy-plane character to the field-independent anisotropy (easy $xy$ plane and hard $z$ axis) (i.e., the same symmetry as the field-dependent spin–orbit anisotropy) as measured by the exchange-averaged $g$ tensor ($g_{xy} > g_z$, see Table 3).

The anisotropy field $B_{\text{int}}^\parallel$ can have contributions from\(^\text{37}\) (i) dipole–dipole interactions, (ii) macroscopic demagnetizing fields, and (iii) spin–orbit-mediated exchange processes. The first two contributions to $B_{\text{int}}^\parallel$ would not be expected to exceed $\mu BM_{\text{sat}}$, where $M_{\text{sat}}$ is the saturation magnetization, with an upper bound of −0.1 T for the $\text{M}_2\text{AgF}_4$ family determined on the basis of the known structures and unit cell parameters (SI).

### Table 4. Diagonal $g^{\alpha\beta}$-Tensor Components and Anisotropy (A) Fields Determined Experimentally at 3 K for the Layered-Perovskite Structures

<table>
<thead>
<tr>
<th></th>
<th>LT-$\text{K}_2\text{AgF}_4$</th>
<th>HT-$\text{K}_2\text{AgF}_4$</th>
<th>$\text{K}_x\text{Rb}_y\text{AgF}_4$</th>
<th>KRBaAgF$_4$</th>
<th>$\text{K}_x\text{Rb}_y\text{AgF}_4$</th>
<th>$\text{Rb}_2\text{AgF}_4$</th>
<th>Cs$_2$AgF$_4$</th>
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<tbody>
<tr>
<td>$g_{xx}$</td>
<td>2.067</td>
<td>2.303</td>
<td>2.254</td>
<td>2.270</td>
<td>2.268</td>
<td>2.26</td>
<td>2.257</td>
</tr>
<tr>
<td>$g_{yy}$</td>
<td>2.093</td>
<td>2.22</td>
<td>2.254</td>
<td>2.270</td>
<td>2.268</td>
<td>2.26</td>
<td>2.257</td>
</tr>
<tr>
<td>$g_{zz}$</td>
<td>2.431</td>
<td>2.075</td>
<td>2.077</td>
<td>2.076</td>
<td>2.077</td>
<td>2.077</td>
<td>2.077</td>
</tr>
<tr>
<td>$B_{\text{int}}^{\perp}$</td>
<td>0.45 T</td>
<td>0.50 T</td>
<td>0.52 T</td>
<td>0.54 T</td>
<td>0.58 T</td>
<td>0.53 T</td>
<td></td>
</tr>
<tr>
<td>$B_{\text{int}}^{\parallel}$</td>
<td>0.35 T</td>
<td>0</td>
<td>0</td>
<td>0.11 T</td>
<td>0.09 T</td>
<td>0</td>
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*LT-$\text{K}_2\text{AgF}_4$ exhibits ferrodistortive order (Figure 1d), and $g_{xx}$ components reflective of the intrinsic values are directly observed. All others are AE or $\text{AE}_{\text{obs}}$ ordered, and axial exchange-coupled $g_{xx}$ values are given. *Estimated; see the ext. *Values associated with minor species. *The maximum value associated with a broad distribution.*
Section VI. In fact, for the employed powder samples, one would not anticipate any appreciable magnetic anisotropy arising from demagnetizing fields because the crystallography in the powder are, on average, spherical and the sample itself has an aspect ratio that gives a demagnetizing factor similar to that of a sphere. Spherical geometry makes only an isotropic contribution to the internal field of $6B_{\text{int}}^\text{iso} = \frac{2}{3}\mu_0 M$, suggesting a value of about 0.07 T at saturation, which is remarkably close to the estimate above. We thus conclude that the overwhelming contribution to $B_{\text{int}}^{\text{int}}$ must be due to spin–orbit-mediated anisotropic exchange processes between Ag(II) sites, giving rise to a non-Heisenberg exchange Hamiltonian, $H = \hat{\tau}_i \cdot \hat{\tau}_j \cdot \hat{\tau}_k$, where the interaction $\hat{J}_0$ is now a tensor. The details of this physics are beyond the scope of this article, and the reader is instead referred to refs 37, 39, and 40 for an in-depth discussion.

Only the anisotropic part of this interaction influences the FMR mode frequency, thus contributing to shifts in the spectral peak positions. However, these shifts vanish at elevated temperatures because thermal fluctuations suppress local spin–spin correlations (i.e., $\langle \hat{S}_1 \cdot \hat{S}_2 \rangle \rightarrow 0$ or, more precisely, $\langle \hat{S}_1 \cdot \hat{S}_2 \rangle \rightarrow 0$, with $\eta = x, y, z$). In this sense, $B_{\text{int}}^{\text{int}}$ really looks like an internal field because it emerges as the ordered ferromagnetic moment appears. One expects stronger relativistic spin–orbit effects in Ag(II) compounds than in Cu(II) compounds, and it is notable that an anisotropy field of $\sim 0.2$ T has previously been estimated from powder EPR studies in the ordered state of AE K$_2$CuF$_4$. $^{23,35}$ It is therefore likely that these anisotropies have the same origin, with the heavier Ag(II) ions manifesting stronger spin–orbit coupling $|B_{\text{int}}^{\text{int}}| = 0.53$ T.

We next turn to the M = Rb compound that has a tetragonal (HTT) structure at room temperature but transitions to an orthorhombic (LTO) structure at $\sim 105$ K (Figure 4). This is clearly borne out by the HFEPR spectra in Figure 7a. At 100 K and above, an axial spectrum is observed, with just two peaks corresponding to parallel ($/z$) and perpendicular ($/xy$) mode excitations, having $g$ values essentially identical to those of the M = Cs compound (Table 3 and Figure 8a). However, below 100 K, the perpendicular part of the spectrum starts to exhibit fine structure indicative of a breaking of the tetragonal (i.e., $x \equiv y$) symmetry. The only complication is that three perpendicular features are observed at low temperatures.

For a small rhombic magnetic anisotropy, one would expect the $B_{/xy}$ portion of the spectrum to split into two components positioned symmetrically about the location of the axial $xy$ resonance: the lower-field component should appear as a peak, with the higher-field component having a derivative shape (crossing through the spectral baseline). A comparison between the 3 K spectra for M = Cs and Rb in Figure 8b shows that this is indeed the case (i.e., that the low-field ($x$-field) and high-field ($y$-field) components of the M = Rb perpendicular spectrum are located symmetrically about the single $xy$ resonance for the M = Cs compound. However, there is also a peak in the middle, suggesting perhaps that the LTO phase is inhomogeneous, with some regions remaining in the HTT phase or transitioning to the LTLO phase. We thus conclude that the overwhelming contribution to the internal field $B_{\text{int}}^{\text{int}}$ must be due to spin–orbit-mediated anisotropic exchange processes between Ag(II) sites, giving rise to a non-Heisenberg exchange Hamiltonian, $H = \hat{\tau}_i \cdot \hat{\tau}_j \cdot \hat{\tau}_k$, where the interaction $\hat{J}_0$ is now a tensor. The details of this physics are beyond the scope of this article, and the reader is instead referred to refs 37, 39, and 40 for an in-depth discussion.

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as expected on the basis of the XRPD studies (Figure 4) and that $B_{gxy}^{ex}$ increases slightly (Table 4); the central perpendicular resonance is also weaker in comparison to the rhombic ones, suggesting reduced amounts of the tetragonal phase, and there is also a hint of an additional peak at ∼9.8 T that we explain further below.

We conclude by considering the remaining $K_{x-y-Rb}_xAgF_4$ compounds ($x \leq 1$) together with the pure HT-K$_2AgF_4$ system. As noted already, although they all start out in the LTO phase at 200 K, the rhombic anisotropy cannot be resolved in the high-temperature spectra. At low temperature, meanwhile, all of the $x \leq 1$ compounds transition to the LTO phase. However, at first glance, the 3 K spectra appear to be more rhombic than those of the $x > 1$ compounds (Figures 7 and 8 and SI, Section VI), with a pair of well-separated low-field resonances. However, the clearest clue to what is likely happening can be seen upon comparing spectra for the mixed K/Rb and pure HT-K compounds in Figure 8b. We believe that the mixed phases are again inhomogeneous, containing regions of the pure K compound and regions of another high-symmetry phase (likely tetragonal) of a mixed (Rb-richer) compound with unknown composition. Thus, the 9.8 T perpendicular resonance is due to the pure K compound, whereas the resonance occurring at 10.1 T is due to the high-symmetry (LTLO) mixed phase. Although appreciably broader, one sees that this latter resonance has the same shape and is located at exactly the same position as the M = Cs perpendicular mode, suggesting that this phase could be very close to tetragonal, with approximately the same axial anisotropy field (Table 4). Moreover, one can clearly observe that the intensity of the peak ascribed to K, relative to the one due to the mixed K/Rb phase, decreases with decreasing K concentration, being barely discernible in the $x = 1.5$ compound. From Table 4, one also sees that, with the exception of HT-K$_2AgF_4$, the symmetries of the majority phases (as determined by zero or nonzero $B_{gxy}^{ex}$) of the mixed compounds are in agreement with the phase diagram of Figure 4.

One of the remaining puzzles concerns the form of the low-temperature HT-K$_2AgF_4$ spectra. Below 150 K, the spectrum is clearly rhombic whereas the one obtained for the K$_{1.5}Rb_{0.5}AgF_4$ compound (SI, Section VI) is not, even though it has an almost identical b/a ratio at this temperature. This may be due to differences in the tilting of [AgF$_6$]$^{4-}$ octahedra in the two compounds and/or the disordered nature of the JT elongation axes within the 2D layers of the HT-K$_2AgF_4$ compound that could result in regions of the sample that are quite distorted, with other regions more closely resembling the tetragonal AE phase.

More interesting is the behavior upon cooling further into the supposed LTLO phase. XRPD data suggest that the b/a ratio approaches 1.00 (to within the precision of the measurements) at the lowest temperatures, yet the HT-K$_2AgF_4$ FMR spectra become even more rhombic. The evolution of the FMR spectrum from 100 to 3 K reveals that the lowest-field ($x$-) component shifts appreciably to lower field and remains sharp/well-defined; the z component exhibits similar behavior, although shifting to higher field. In contrast, the intermediate ($y$) component seen at ∼10.5 T at 50 K essentially washes out (i.e., it spreads apart into a series of successively smaller peaks with decreasing temperature). However, one can just about see one remaining component at ∼10.5 T at the lowest temperature in Figures 7c and 8b. If one associates this with the $y$ component of the spectrum, one then sees that the $x$ and $y$ resonances again split symmetrically about the axial position of the M = Cs compound. In other words, it appears that the axial saturation anisotropy field, $B_{gxy}^{ex}$, is the same as in the other layered compounds whereas the perpendicular component (associated with at least part of the sample), $B_{gxy}^{ex}$, is about a factor of 3 stronger than found for the orthorhombic LTO phase (Table 4).

Figure 9. (Main panel) Comparison of 3 K, 326 GHz absorption spectra for (a) Cs$_2AgF_4$ and HT-K$_2AgF_4$ that were obtained through integration of the EPR spectra (b). The spectra have been normalized by comparing the 200 K paramagnetic spectra in order to correct for the total number of spins in each sample. The inset in panel a displays low-field EPR spectra of HT-K$_2AgF_4$ measured at 5 K and the indicated low microwave frequencies.

Very similar trends to those noted above can be seen in the inset to Figure 9a, which shows low-temperature, field-dependent spectra for HT-K$_2AgF_4$. A rhombic spectrum is seen at the lowest field/frequency, with clearly discernible $x$ and $y$ resonances, although their separation is considerably less than at high fields due to a reduction in the Zeeman interaction. Upon increasing the field, the $y$ resonance again washes out in essentially the same way that it does for the high-field spectra upon cooling. This clearly indicates that the vanishing of the intermediate component of the spectrum is connected to the saturation of the ordered FM moment and the resulting perpendicular anisotropy field, $B_{gxy}^{ex}$ (and associated exchange interactions).

How this happens is seen most clearly in the main panels of Figure 9, which compare normalized 3 K spectra for the M = Cs and HT-K compounds in both absorption (a) and derivative (b) modes. The axial (and presumably well-ordered) Cs compound shows a strong onset of absorption at 10.1 T that is due to the perpendicular ($xy$) component of the g tensor. A much (9-fold) weaker onset is seen at 9.8 T for the biaxial AE disord K compound and hence the much weaker $g_{ex}^{ex}$ peak in Figure 9b, suggesting that a relatively small fraction of the sample experiences the maximal $B_{gxy}^{ex}$ field reported in Table 4. Note that this is not the case for the parallel ($z$) components. The maximum g value measured from the slope of the frequency dependence at the low-field end of the spectra is $g_{ex}^{ex} = 2.30$ (Figure S2). Because $g_{ex}^{ex} = 2.26$ was observed at 200 K,
the minimum $g_{xx}$ value should be around 2.22, according to eqs 2a and 2b. The difference between $g_{xx}$ (200 K) and $g_{xx}$ (3 K) also implies an $\sim 13^\circ$ tilt from the perfect perpendicular arrangement in good agreement with a value of 16.2 deg derived from DFT+U calculations. The disorder in the HT-arrangement in good agreement with a value of 16.2 deg ∼ the observed phase transitions should originate solely from α-orientation of the elongated [AgF$_6$]$^{4-}$ feature in the derivative spectrum. The fact that the parallel component does not appear to be affected confirms that the disorder is confined mainly to the $xy$ plane. This could be due to a complete switching of the sign of the exchange (from FM to AFM) along the $xy$ plane. This would affect not only the local exchange anisotropy but also would give rise to spin frustration, resulting in a local suppression of spin correlations ($\hat{J}_{ij}$). Disorder associated with the tilting of the [AgF$_6$]$^{4-}$ octahedra may also influence the local exchange anisotropies, although the effects of the abnormally oriented JT axes will likely have a much stronger influence.

**More on Tilting Patterns.** Because of the previously mentioned problems of discerning the type of JT order present in M$_2$AgF$_4$ by the powder X-ray diffraction method, we cannot conclude from those data what kind of ordering scenario is present in the LTLO, LTO, and HTT phases. Previous DFT + U calculations show that FC-type phases are over 100 meV/fu higher in energy than the AE-type structures. Such an energy difference corresponds to temperatures above 1100 K and thus indicates that in the studied temperature range the K$_{1/2}$Rb$_{1/2}$AgF$_4$ phases should exhibit AE-type structures. Thus, the observed phase transitions should originate solely from differences in tilting distortions, possibly from the transition from $\alpha$-type distortions to $\beta$-type ones. (The differences between these distortion types is discussed in ref 29.)

**CONCLUSIONS AND OUTLOOK**

We have studied the M$_2$AgF$_4$ series (M = K, K$_{3/4}$Rb$_{1/4}$, K$_{1/2}$Rb$_{1/2}$, K$_{1/4}$Rb$_{3/4}$, Rb, Cs) using temperature-resolved X-ray diffraction and heat capacity measurements, magnetometry, and HFEPR spectroscopy. Our results suggest that all double-perovskite fluorargentates(II) phases, including HT-K$_2$AgF$_4$, adopt structures consisting of an antiferrodistortive arrangement of the elongated [AgF$_6$]$^{4-}$ octahedra, in agreement with recent theoretical calculations. The HFEPR spectra show that the structures of the M$_2$AgF$_4$ phases are most complex, with local distortions and possibly even composition inhomogeneity, despite their seemingly single-phase character in powder X-ray diffraction.

The temperature-resolved phase diagram of the $M = K/Rb$ phases has been investigated in the 2−350 K temperature window, adding to the existing data for the $M = Na$ to Cs members. This phase diagram shows a systematic trend in the temperatures of the phase transitions involving two orthorhombic phases and one tetragonal phase, which most probably arises from various tilting distortions within the doubleperovskite structure. The phase diagram is further complicated by the thermodynamic preference for the 1D postperovskite structure for $M = Na$, K.

The importance of the correct assignment of the JT order in Ag(II) fluorides lies in the strong dependence of the magnetic properties on the structure of these compounds. As calculations show, the AE distortion induces FM coupling within the [AgF$_4$]$^{2-}$ planes of the layered-perovskite phases and FC ordering would lead to antiferromagnetic (AFM) interactions. The fact that M$_2$AgF$_4$ compounds adopt AE-type structures and hence are FM at low temperatures makes them dissimilar from La$_2$CuO$_4$. Therefore, the present study offers experimental evidence that the M$_2$AgF$_4$ systems are unlikely to constitute good precursors for HTSCs. Still, the connectivity of the Ag/F sublattice might be modified by the application of high pressure, by analogy to studies on K$_2$CuF$_4$. The results of our high-pressure studies on M$_2$AgF$_4$ will be published shortly elsewhere.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02037.

Room-temperature XRDP of Rb$_2$AgF$_4$; frequency dependence of the field components of the EPR spectra obtained for HT-K$_2$AgF$_4$; temperature-resolved XRDP measurements for K$_{1-x}$Rb$_x$AgF$_4$; heat capacity measurements for K$_{1-x}$Rb$_x$AgF$_4$; Raman measurements; HFEPR spectra of K$_{1-x}$Rb$_x$AgF$_4$ and K$_{0.5}$Rb$_{1.5}$AgF$_4$; XRDP diffractograms at 80 K; comparison between X-band and HFEPR spectra; photograph of a holder for conducting HFEPR measurements; and HT-K$_2$AgF$_4$ structure (AE$_{\text{disord}}$) in CIF format (PDF)

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