Crystal structure, lattice dynamics and superexchange in MAgF$_3$ 1D antiferromagnets (M = K, Rb, Cs) and Rb$_3$Ag$_2$F$_7$ Ruddlesden-Popper phase

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Dedicated to Prof. M. Niezgodka at his 70th birthday

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Abstract

With the use of lattice dynamics calculation within hybrid HSE06 framework we were able to understand vibrational spectra of MAgF$_3$ (M = K, Rb, Cs) compounds. Comparative theoretical study uncovered lack of monotonicity in calculated optical phonons associated with Ag–F stretching modes which can be explained through an interplay of Lewis acidity of M(I) cation and its size. We confirm the tetragonal unit cells of MAgF$_3$ (M=Rb, Cs) at room temperature. We also theoretically predict an orthorhombic RbAgF$_3$ polymorph as a ground state at low temperature. However, we were not able to detect it by the means of low temperature PXRD (at 80 K) nor low temperature Raman (at 154 K) due to a number of constraints. We also describe a novel Ruddlesden-Popper phase of Rb$_3$Ag$_2$F$_7$ which can be regarded as quasi-0D system, where superexchange coupling constant between the nearest Ag(II) centres reaches an impressive value of $-240.2$ meV.

1. Introduction

Systems composed of silver(II) and fluorine are in many ways exceptional.¹ Silver(II) is so reactive that fluorine is the only element, which may form thermodynamically stable compounds with it. The binary AgF$_2$, on its own right, hosts many exciting phenomena such as strong mixing of Ag(d) and F(p) states,² appreciable magnetic superexchange in 2D,¹ remarkable covalence of Ag–F bonds³ and electronic structure at the verge of valence instability.⁴ These features render AgF$_2$ similar to copper(II) oxides and BaBiO$_3$, which are precursors of two important families of superconductors. Said similarity places Ag(II) fluorides in the focus of solid state chemistry, physics and materials science. Introducing the third element to the chemical composition further broadens the playground and provides us with a multitude of interesting physical phenomena to be studied.⁴–⁶

The simplest modifications of AgF$_3$ are exemplified by ternary fluoroargentates(II), M(I)AgF$_3$ and M(I)$_2$AgF$_4$. While M$_2$AgF$_4$ systems have already been thoroughly studied,⁷–⁹ the MAgF$_3$ ones (particularly M = Rb and Cs) remain explored unsatisfactorily.

Alkaline ternary fluoroargentates(II) of a general formula MAgF$_3$ (M = K, Rb, Cs) adopt a distorted perovskite structure, with alkaline atom substantially impacting level of distortion (Figure 1). Generally, smaller the alkaline metal cation, the more distant from ideal cubic lattice is the resulting structure. The early study of these compounds was conducted half a century ago, when quality of laboratory X-ray sources was much worse than nowadays. An orthorhombic (Pnma) structure was then assigned to KAgF$_3$ and tetragonal (F4/mcm) ones to RbAgF$_3$ and CsAgF$_3$ (based on Guinier pattern analysis).¹⁰ Although data quality and purity of the samples were far from good, these are the only structures of RbAgF$_3$ and CsAgF$_3$ reported so far. Only in 2013, it was possible to substantially improve purity of KAgF$_3$ specimen, which permitted more sophisticated analyses to be conducted.¹¹ However, syntheses of RbAgF$_3$ and CsAgF$_3$ have not yet been improved. There is even less research regarding other alkali fluoroargentates(II). NaAgF$_3$ is proposed to be a monoclinic or triclinic NaCuF$_3$-related post perovskite¹² while LiAgF$_3$ has not been prepared despite many attempts.¹³

The more recent study of KAgF$_3$ has showed that this compound exhibits a structural phase transition at 230 K which is of order/disorder type. The low-temperature phase is in Pnma symmetry, in agreement with the early study, but the high-temperature phase adopts Pcmn symmetry and twice smaller unit cell.¹¹ Moreover, experimental evidence of complex magnetic ordering below 66 K was also obtained.⁶ Magnetic properties of
RbAgF$_3$ and CsAgF$_3$ were only scarcely described in the structure determination paper.$^{10}$ The main obstacle while analysing magnetic properties of RbAgF$_3$ and CsAgF$_3$ was that that samples were contaminated with M$_2$AgF$_4$ and M$_3$AgF$_7$ (M = Rb, Cs) phases. The M$_2$AgF$_4$ phases are ferromagnetic,$^{4}$ thus obscuring magnetic signals from antiferromagnetic MAgF$_3$ ones.

A recent theoretical study of MAgF$_3$ compounds assumed the previously proposed crystal structures and it mostly focused on their magnetic properties. It seems that all compounds from the MAgF$_3$ family can be regarded as quasi-1D antiferromagnets, with strong AFM intra-chain superexchange, and much weaker FM inter-chain one.$^5$ The calculated intra-chain superexchange constant $J_{1D}$ is impressively large, varying between $-113$ meV for KAgF$_3$, via $-144$ meV for RbAgF$_3$, and reaching $-161$ meV for CsAgF$_3$. In all cases the inter-chain superexchange constants do not exceed $+10$ meV. Compounds exhibiting such strong magnetic interactions are rare and are of interest for solid state physics; when appropriately modified, they could be used in spintronics e.g. for data storage.

The above-mentioned theoretical study$^3$ puts in question the tetragonal unit cell of RbAgF$_3$; authors have noticed that an orthorhombic polymorph of RbAgF$_3$ has lower total energy than the tetragonal one. One possible reason for this is that experimental study$^{10}$ has been conducted at 293 K, while theoretical one corresponds formally to 0 K. Another reason might be the poor quality of old X-ray data, which did not permit to detect small orthorhombic distortion of the tetragonal cell.

In our recent work, we have studied lattice dynamics of KAgF$_3$ in order to understand its phase transition and to assign vibrational modes.$^{14}$ Very good agreement between theory and experiment was reached. Phonon calculations also proved stability of the low temperature orthorhombic polymorph of KAgF$_3$. As up to now, no lattice dynamics studies of RbAgF$_3$ and CsAgF$_3$ were performed, we have decided to conduct a joint experimental/theoretical study of these compounds. The goal of this study is to expand our recent work on KAgF$_3$ by assigning vibrational spectra of RbAgF$_3$ and CsAgF$_3$ and to gain better understanding of RbAgF$_3$ crystal structure. Moreover, by comparing the data for all three members of the MAgF$_3$ family, we aimed to detect trends in chemical bonding and vibrational structure across the series.

As a bonus, we have been able to determine crystal structure of Rb$_3$Ag$_2$F$_7$ Ruddlesden-Popper phase, support the space group assignment using theoretical density functional theory (DFT) calculations, and calculate the magnetic superexchange constant for discrete Ag$_2$F$_7^{3-}$ dimers present in its structure.

![Figure 1. Crystal structures of (from left): KAgF$_3$ (in low temperature $Pnma$ space group), RbAgF$_3$ (in theoretically predicted $Pmna$ space group), RbAgF$_3$ (in experimental $I4/mcm$ space group), and CsAgF$_3$ ($I4/mcm$). Colour coding: grey – silver, light blue – fluorine, violet – potassium, pink – rubidium, cyan – caesium.](image)

2. Experimental

KAgF$_3$ syntheses were conducted in three different ways: (1) annealing of ground mixture KF and AgF$_2$ at 300°C for four days in a nickel reactor under F$_2$ atmosphere, (2) thermal decomposition of KAgF$_3$ maintaining dynamic vacuum at 420°C, (3) fluorination of KAg(CN)$_2$ with stoichiometric quantity of fluorine gas at 300°C. RbAgF$_3$ sample was synthesized by annealing of hand ground RbF and AgF$_2$ mixture. This was conducted in a nickel boat in a nickel autoclave for 24 h at 310°C. After that time resultant mixture was ground again and annealed in the same reaction for additional 24 h. CsAgF$_3$ synthesis was conducted by annealing of hand ground mixture of CsF and AgF$_2$ (same conditions as RbAgF$_3$) or thermal decomposition of CsAgF$_4$ (same conditions as KAgF$_3$). Better purity CsAgF$_3$ sample was obtained from the first approach.

Infrared measurements were carried out on Bruker Vertex 80 V vacuum spectrometer using powdered samples placed on cleaned and dried HDPE windows.

Raman spectra for KAgF$_3$ and RbAgF$_3$ were obtained on a Horiba Yvon LabRam-HR Raman microspectrometer with 632.8 nm He-Ne exciting beam. Due to technical issues with abovementioned spectrometer, spectrum for CsAgF$_3$ was obtained on Renishaw inVia micro-spectrometer with 785 nm excitation beam. Because of contamination of RbAgF$_3$ and CsAgF$_3$ samples with small amounts of Rb$_2$AgF$_4$ and Cs$_2$AgF$_4$,
double perovskites, and triple perovskite Rb$_3$Ag$_2$F$_7$. Raman spectra varied somewhat from one measurement spot to another. Results chosen for further analysis were crosschecked with published data to confirm that we indeed measured spectra for MAgF$_3$ rather than M$_2$AgF$_4$ crystallites.$^{14-16}$

Low temperature Raman spectra were measured in a custom setup described in our recent work$^{14}$ using Horiba Yvon LabRam-HR Raman micro-spectrometer with 632.8 nm He-Ne exciting beam. Setup consists of FEP tube equipped with capillary holder, dry air cooled by LN$_2$ and a thermocouple.

Room temperature powder X-ray diffraction measurements were carried out on Bruker D8 Discover diffractometer, using CuK$_\alpha$ radiation. Sample was placed in heat sealed in prefluorinated 0.3 mm quartz capillary. Measurement 2$\sigma$ range spanned from 6° to 90°, with step size of 0.014°. Acquisition time used here was equal to 16 h for whole measurement in four consecutive runs to determine if sample reacted with the capillary. Low temperature measurements were conducted on Oxford Diffraction Xcalibur 2 single crystal diffractometer also using CuK$_\alpha$ radiation. Resolution of these measurements is worse than room temperature measurements, because detectors in these diffractometers are usually placed much closes to the sample. Using this setup had an advantage of reaching 80 K with high accuracy.

Room temperature powder data was refined using Rietveld method$^{17}$ in Fullprof software suite.$^{18}$ Full set of profile (including asymmetry) and atomic (positions and isotropic thermal factors) parameters were refined. Absorption correction factor of $\mu R = 1.1$ was used.

### 3. Computational details

Lattice Lattice dynamics of MAgF$_3$ (M = K, Rb, Cs) compounds was modelled using hybrid functional HSE06,$^{19}$ based on Perdew-Burke-Ernzerhof DFT-GGA functional revised for solids (PBEsol)$^{20}$ with 25% Hartree Fock exchange energy. For all calculations, projector-augmented-wave method$^{21,22}$ was used, as implemented in VASP 5.4.4 code.$^{23-25}$ Standard VASP pseudopotentials were used for description of core electrons.

All structures were optimized by performing a full relaxation of unit cell parameters and atomic coordinates. Antiferromagnetic (AFM) ordering was assumed for all structures in agreement with previous results (i.e. AFM ordering within chains propagating along the crystallographic $c$ direction, and ferromagnetic (FM) one within sheets parallel to $ab$ planes).$^{5,26}$ The cut-off energy of the plane wave basis set was equal to 520 eV with a self-consistent-field convergence criterion of $1 \cdot 10^{-7}$ eV. The k-point mesh spacing used in calculations was equal to 0.25 Å$^{-1}$. All structures were optimized until the forces acting upon each atom were smaller than 0.001 eV/Å.

Phonon calculations were conducted using finite differences method implemented in VASP. Results were then processed using Phonopy package in order to extract irreducible representations and dispersion curves, as VASP provides frequencies only in the centre of the first Brillouin zone (Γ point).$^{27}$ Animated pictures of normal modes, also generated by Phonopy, were used to assign mode types. Calculations were conducted for single unit cells, in order to limit resource usage. Phonon band structures were calculated for standardized k-path.$^{28}$ For tetragonal $I$-centered cells, primitive cells (Z=2) were used for band structure and irreducible representations calculations.

Magnetic superexchange constants were calculated using broken symmetry method mapping calculated energy values on spin Hamiltonian in a form:

$$H = -0.5 \sum_{i,j} J_{ij} S_i S_j$$

Total energy values for each magnetic configuration were obtained by the means of GGA+U by conducting single point calculations using geometry of ground state configuration. The k-point mesh spacing used in calculations was equal to 0.16 Å$^{-1}$. The cut-off energy of the plane wave basis set was equal to 800 eV with a self-consistent-field convergence criterion of $1 \cdot 10^{-7}$ eV.
4. Results and discussion

4.1. Theoretical phonon spectra.

Figure 2. Calculated phonon dispersion curves and (atomic) phonon density of states for KAgF$_3$ (blue – F, red – Ag, green – K)

Figure 3. Calculated phonon dispersion curves for tetragonal RbAgF$_3$ (left), and combined graph of dispersion curves and phonon density of states for orthorhombic RbAgF$_3$ (right) (blue – F, red – Ag, green – Rb)

Figure 4. Calculated phonon dispersion curves and (atomic) phonon density of states for tetragonal CsAgF$_3$ (blue – F, red – Ag, green – Cs)
Dispersion curves calculated for KAgF₃ using HSE06 dataset and Phonopy suite (Figure 2), remain in a good agreement with those computed recently utilizing a commercial PHONON software. All features of phonon density of states were also successfully reproduced. Therefore, for the remaining systems their phonon spectra were computed using Phonopy.

Our lattice dynamics calculations using published, tetragonal structure of RbAgF₃ show significant dynamic instability at the centre of the first Brillouin zone (Γ) but also in other special points (Figure 3, top). The presence of an imaginary branch alone is the proof that the tetragonal structure cannot be the ground state of this system. Due to that, we have used a modified model in which we have allowed for the presence of kinked $[\text{AgF}_3^-]$ chains similar to those typical of KAgF₃. Full geometry relaxation using HSE06 functional yielded a dynamically stable structure (Figure 3, bottom), that had 11.7 meV per unit cell (Z=4) lower total energy than the starting tetragonal one. That energy difference corresponds roughly to a temperature of 34 K, so it may be deduced than the orthorhombic form corresponds to a low temperature polymorph. As a result of larger ionic radius, the $[\text{AgF}_3^-]$ chains in theoretically calculated RbAgF₃ are less kinked than in calculated KAgF₃ (165.5° vs. 153.3°). This effect can also be seen by analysing density of states graph. Vibrational states of Rb are more localized than those of K signalling a larger freedom of potassium ions in KAgF₃ for rattling.

Phonon dispersion curves calculated for a primitive cell of tetragonal CsAgF₃ (Figure 4) confirm dynamic stability of this structure. A small departure of one mode from null value (img 5 cm⁻¹) stems from imperfect diagonalization of Hessian matrix, and may be considered artefactual. Localization of alkali metal vibrational states is in CsAgF₃ even more apparent meaning that caesium, with its large ionic radius, sits tightly in interstitial positions. Consequently, Ag-F-Ag angles present here are straight (i.e. 180°). This comes from the fact that among alkali metal cations, the Cs(I) cation best fulfils the geometric condition of structural stability of a perovskite structure.

Due to similarity in MAgF₃ (M = K, Rb, Cs) structures, normal modes involving similar atomic displacements can be found in each spectrum (Figure 5). In the highest wavenumber region (425-475 cm⁻¹) modes calculated for RbAgF₃ corresponding to stretching vibrations of the Ag–F bond network exhibit higher energies than those for KAgF₃ and CsAgF₃. This is an interesting feature which may be explained by considering that there are two main factors in play in the M = K, Rb, Cs series. One factor is related to the Lewis acidity of M(I) cations. K(I) cation having the largest Lewis acidity in the series leads to its strongest interaction with F⁻ ions and thus to some weakening of the Ag-F bonds. Volume of the M(I) cation is the other factor, which – particularly for the largest Cs(I) cation, may also induce weakening of the Ag–F bonds due to “negative pressure” exerted by this cation. It seems that the problem of two mutually opposing factors has an optimum and the Rb(I) salt shows the highest frequencies of Ag–F stretching modes.

![Figure 5](image-url)

**Figure 5.** Calculated wavenumber of normal modes at Γ for orthorhombic KAgF₃ (green), orthorhombic RbAgF₃ (red) and tetragonal CsAgF₃ (black). Dashed lines connect corresponding modes with similar forms of vibrations. Note that the number of modes computed for CsAgF₃ in its primitive cell is twice smaller than those for orthorhombic K and Rb ones, hence some modes do not have counterparts in the spectrum of Cs derivative.
Midrange \([AgF_6] \) octahedron stretching modes (300-425 cm\(^{-1}\)) are generally close in energy for all three compounds. However, finding the modes corresponding to one another in the spectral region below 250 cm\(^{-1}\) (e.g. lattice modes) is not that straightforward, because of significant admixture of heavy alkali metal vibrations in each mode. Generally normal modes found for RbAgF\(_3\) are softer than analogous modes of KAgF\(_3\) in agreement with the ca. twice reduced oscillator mass for the latter. Corresponding modes of CsAgF\(_3\) have comparable values to those for Rb analogue.

4.2. Assignment of vibrational spectra.

Our analysis of powder x-ray pattern shows that at room temperature RbAgF\(_3\) adopts tetragonal structure. As stated above, this is supposedly a high-temperature form, with orthorhombic one corresponding to the genuine ground state at \(T \rightarrow 0\) K. Since our spectroscopic measurements were conducted at room temperature, we have used phonons calculated for tetragonal polymorph for an interpretation of IR and Raman data.

Infrared spectrum measured for RbAgF\(_3\) consists of 8 bands, while Raman measurement yielded 6 bands (Figure 7). Group theory analysis for that compound in a primitive cell of the \(I4/mcm\) space group yields 21 distinct normal vibrational modes, including some degenerated ones (\(\Gamma_{\text{acoustic}} = A_{2u} + E_u\); \(\Gamma_{\text{optic}} = A_{1g} + 2A_{2g} + 3A_{2u} + B_{1g} + 2B_{2u} + 2B_{2g} + 5E_u + 3E_g\)); here, there are 7 Raman active (\(A_{1g}, B_{1g}, 2B_{2g}, 3E_g\)) and 8 IR-active modes (\(3A_{2u}, 5E_u\)). The remaining modes are silent. Measured spectra for CsAgF\(_3\) in \(I4/mcm\) symmetry consist of 9 infrared bands and 4 Raman bands. Obviously, the group theory predicts identical result as for the Rb salt.

![Figure 6](image1.png)

**Figure 6.** FIR (black) and Raman (red) spectra of KAgF\(_3\) at room temperature together with marks indicating the computed wavenumbers.

![Figure 7](image2.png)

**Figure 7.** FIR (black) and Raman (red) spectra of RbAgF\(_3\) at room temperature together with marks indicating the computed wavenumbers.
KAgF₃ spectra were described in detail in our recent work based on DFT+U and HSE06 calculations. Here, in Figure 6, we show the experimental spectra overlapped with theoretically predicted modes using highly accurate hybrid HSE06 functional (without any scaling factor), so that they may be compared with those measured for its heavier analogues.

Out of eight infrared bands present in RbAgF₃ spectrum (Figure 7), six were successfully assigned to fundamentals and two to combination modes (using group theory constraints for selection rules) or impurities (Table 1). The highest wavenumber band in infrared spectrum is placed at 460 cm⁻¹ and was assigned to E_u mode representing Ag–F stretching within [AgF₂] planes. Three midrange bands at 200, 162 and 113 cm⁻¹ correspond to bending modes assigned to A2g [AgF₂] plane buckling, E_u [AgF₂] in plane bending and E_u [AgF₆] octahedron bending respectively. The lowest wavenumber bands (85 and 72 cm⁻¹) are rubidium lattice modes. The Raman spectrum features nine six of which three were assigned to fundamentals. The band at 477 cm⁻¹ has the largest intensity; it is assigned to [AgF₆] octahedron stretching mode. The second highest intensity band located at 378 cm⁻¹ was assigned to [AgF₂] plane stretching. In the lower wavenumber range, there is one band at 189 cm⁻¹ which was assigned to [AgF₆] octahedron bending mode.

Infrared spectrum of CsAgF₃ (Figure 8) consists of nine bands, six of which were successfully assigned to corresponding fundamental modes and three either to combination/overtone modes or impurities (Table 2). The highest wavenumber infrared fundamental at 448 cm⁻¹ falls very close to two predicted normal modes, leaving some ambiguity in assignment; it can either be a [AgF₂] plane stretching or [AgF⁺] chain stretching mode. Similarity to the Rb and K salt suggest preference for the former assignment. Band seen at 206 cm⁻¹ is [AgF₂] plane buckling mode, 163 cm⁻¹ is [AgF₆] octahedron bending mode, and 117 cm⁻¹ is [AgF⁺] chain bending mode. Two lowest energy bands at 86 and 80 cm⁻¹ are Cs lattice modes. Raman spectrum was deconvoluted to four major bands, of which three were assigned to fundamentals. Stretching modes are at 477 cm⁻¹ ([AgF₆] octahedron stretching) and 372 cm⁻¹ ([AgF₂] plane stretching). The third band at 202 cm⁻¹ originates from [AgF₆] octahedron bending.

The correlation between theoretically predicted and measured wavenumbers for both the Rb and Cs salt is excellent, testifying that scaling factor is nearly unity (slope factor is 0.975 for Cs, 0.995 for Rb) when using the HSE06 hybrid functional (Figure 9).

Table 1. Vibrational band assignment for tetragonal RbAgF₃ (at room temperature).

| IR /cm⁻¹ | Raman /cm⁻¹ | Type | HSE06 /cm⁻¹ | Symmetry | Assignment |
|----------|-------------|------|-------------|----------|------------|
| 602      | w           | -    | -           | -        | impurity   |
| 507      | sh          | -    | -           | -        | impurity (possible Rb₁Ag₂F₇) |
| 477      | s           | 472  | B₂g         | [AgF₆] octahedron stretching |
| 460      |              | 467  | E₉u         | [AgF₂] plane stretching |
| 423      | w           | -    | -           | -        | impurity   |
| 395      | sh          | -    | -           | -        | combination 200+189 (A₂g x E₉) or impurity |
| IR /cm\(^{-1}\) | Raman /cm\(^{-1}\) | Type | HSE06 /cm\(^{-1}\) | Symmetry | Assignment |
|---|---|---|---|---|---|
| 580 | 477 | s | 449 | B\(_{2g}\) | [AgF\(_6\)] octahedron stretching |
| 448 | s | 450 | E\(_u\) | [AgF\(_2\)] plane stretching |
| 398 | sh | – | 449 | A\(_{2u}\) | [AgF\(_2\)] chain stretching |
| 381 | sh | – | – | overtone (206 A\(_{2u}\) x A\(_{2u}\)), overtone 202 (E\(_g\) x E\(_g\)) or impurity |
| 372 | s | 370 | A\(_{1g}\) | [AgF\(_2\)] plane stretching |
| 318 | sh | – | – | combination 117+202 (E\(_u\) x E\(_g\)) or impurity |
| 206 | s | 193 | A\(_{2u}\) | [AgF\(_2\)] plane buckling |
| 202 | m | 186 | E\(_g\) | [AgF\(_6\)] octahedron bending |
| 163 | m | 162 | E\(_u\) | [AgF\(_6\)] octahedron bending |
| 117 | m | 118 | E\(_u\) | [AgF\(_2\)] chain bending |
| 86 | s | 72 | A\(_{2u}\) | Lattice (Cs out of plane) |
| 80 | sh | 72 | E\(_u\) | Lattice (Cs in plane) |

Table 2. Vibrational band assignment for tetragonal CsAgF\(_3\) (at room temperature).

Figure 9. Correlations between theoretical and experimental wavenumbers jointly for IR and Raman spectra (left – RbAgF\(_3\); right – CsAgF\(_3\); black dotted line — linear regression \(R^2\) depicted at the figure both bound to pass at (0,0)).

4.3. Vibrational spectra and x-ray diffraction pattern for RbAgF\(_3\) at low temperature.

The calculated total energy at 0 K of tetragonal RbAgF\(_3\) is higher than total energy of orthorhombic polymorph. In order to get further insight into a possible tetragonal/orthorhombic phase transition, low temperature Raman spectrum (at 154 K) and low temperature x-ray diffraction pattern (at 80 K) were measured.

Comparison of low temperature Raman spectrum with that measured at room temperature shows the expected stiffening of all modes (Figure 10). Two features of highest energy got shifted towards higher wavenumber range (from 378 to 382 cm\(^{-1}\) and from 477 to 488 cm\(^{-1}\); a similar stiffening was observed before for the K salt\(^{14}\). Spectral features are better resolved in low-T spectra, as expected. Most new bands appear in the region above 600 cm\(^{-1}\), where no fundamentals can be found; they correspond to either combination modes or overtones (cf. ESI). These changes are not dramatic, and take place gradually while cooling down the sample.
(all spectra measured are available in ESI). While these measurements did not prove that a phase transition might occur, they also did not disprove such possibility, since the Raman spectra of orthorhombic $\text{KAfF}_3$ and of tetragonal $\text{RbAgF}_3$ do not differ markedly. Because of that, we have also conducted low temperature powder X-ray diffraction experiment at 80 K.

![Raman spectrum of RbAgF3 measured at room temperature (black) and at 154 K (red).](image1)

**Figure 10.** Raman spectrum of $\text{RbAgF}_3$ measured at room temperature (black) and at 154 K (red).

![Background-reduced powder x-ray diffraction pattern of RbAgF3 measured at room temperature (black) and at 80 K (red).](image2)

**Figure 11.** Background-reduced powder x-ray diffraction pattern of $\text{RbAgF}_3$ measured at room temperature (black) and at 80 K (red). Inset shows the three most intense peaks of the pattern.

We were able to reach temperature of 80 K in powder X-ray diffraction measurements (Figure 11). Resolution of that pattern is sufficient for the analysis of a possible tetragonal-to-orthorhombic transition. Theory predicts that a splitting of a tetragonal lattice parameter to two distinct values of 6.263 Å and 6.344 Å ($a$ and $c$ vectors in the $Pnma$ setting) will affect most strongly the 100 vs. 001, 110 vs. 011, 002 vs. 200, and related pairs of reflections. Unfortunately, they all fall in 2 theta regions where the reflections from the impurity phase are also present (see the next section). Therefore, X-ray analysis is also inconclusive with respect to a possible symmetry-lowering transition. Much purer specimen of $\text{RbAgF}_3$ and likely much lower temperature, is needed for such detection. The only unambiguous phenomenon observed is that of the thermal expansion; for example, tetragonal lattice constant of $\text{RbAgF}_3$ expands by 0.18 % upon warming while the perpendicular lattice vector by 0.33 %; such anisotropy is, obviously, not unexpected, given that $b$ is axis of propagation of the $\text{AgF}_3$ infinite chains which $a$ and $c$ are equivalent.

4.4. Crystal structure and magnetic properties of the Ruddlesden-Popper phase $\text{Rb}_3\text{Ag}_2\text{F}_7$.

One of the studied samples of $\text{RbAgF}_3$ showed significant proportion of an impurity phase. This additional phase was not only seen in PXRD measurements, but also during Raman experiments. Since Raman spectrometers equipped with microscope collect data from only a small micron-sized surface spot, it is sometimes possible to identify different phases present in the samples. We have managed, for example, to observe a distinct feature located at 504–507 cm$^{-1}$ (cf. ESI). This feature was above the range of the theoretically predicted stiffest Raman-active phonon (477 cm$^{-1}$), but its wavenumber might correspond to the
Ag–F stretching of slightly shorter Ag–F bonds than those present in RbAgF₃. This fact, together with the substantial number of unassigned reflections in the X-ray diffraction pattern, led us to more detailed study of the new phase. Indexation of the unassigned reflections yielded a strongly elongated tetragonal unit cell. Structural database search pointed out at a similar phase of the K₃AgF₇ stoichiometry, which some of us first detected two decades ago. This phase was subsequently refined in the Ccca space group. Additional research conducted over the next decade shown that the Ccca cell is certainly erroneous since it contains Ag(II) sites in an compressed rather than usual elongated octahedral environment.

A very similar conclusion was reached with respect to K₃AgF₇ double perovskite. Equipped with this knowledge, and aided by DFT+U calculations, we have been able to provide a Cmca starting model for the novel Rb₃Ag₂F₇ phase. This model was then used in Rietveld refinement of that pattern (full fit and crystallographic information file are available in ESI) and resulted in the structure which closely matched a theoretical one (cf. ESI for all theoretically derived .cif files).

Orthorhombic Rb₃Ag₂F₇ is a typical Ruddlesden-Popper phase (Figure 12), i.e. an intergrowth of the RbAgF₃ and Rb₂AgF₄ end members of the series. Its formation, while trying to prepare RbAgF₃, may be explained by partial reduction of Ag(II)F₂ to Ag(I)F upon reaction with walls of the reactor. In consequence, some RbF is left unreacted but its amount does not suffice for the formation of Rb₂AgF₄. Instead, a 50:50 compound is formed. This structure can be described as infinite [AgF₂] double (sandwich) layers interleaved with rubidium fluoride layers. Each pair of layers is rotated by 45° in respect to the neighbouring ones. The [AgF₆] octahedra are distorted in a way already known from RbAgF₃ and Rb₂AgF₄. Apical fluorides have varying atomic distances to Ag(II) of 2.19(3) and 2.104(4) Å (the shortest distance is that in between sandwich layers). There are two different equatorial Ag–F distances of 2.20(3) and 2.35(3) Å. Apical fluorides form a straight link between Ag sites, but the layers are buckled with the intrasheet Ag–F–Ag angle of 163.4(14)° angle (theoretical value 177°).

![Figure 12. Crystallographic unit cell of novel Rb₃Ag₂F₇ phase (pink – rubidium, grey – silver, blue – fluorine).](image)

| Formula | Rb₃Ag₂F₇ |
|---------|----------|
| Colour  | brown    |
| Space group | Cmca (No. 64) |
| Z       | 4        |
| V /Å³   | 879.524(18) |
| a /Å    | 21.7577(5)  |
| b /Å    | 6.35844(9)   |
| c /Å    | 6.35747(9)   |
| α /°    | 90       |
| β /°    | 90       |
| γ /°    | 90       |
| Positions | Rb1 0.68404(15) 0.00000 0.00000 0.00000 0.00000 0.00776 Ag1 -0.09670(16) 0.00000 0.00000 0.00000 0.00000 0.00000 F1 0.8028(13) 0.00000 0.00000 0.00000 0.00000 0.00000 F2 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 F3 0.5899(7) 0.291(4) 0.274(5) |
The shortest Ag–F distance of 2.104(4) Å is slightly shorter than the shortest distance of 2.10935(3) Å seen in tetragonal RbAgF$_3$ at a room temperature. This, together with the different reduced mass factor, might explain why the corresponding oscillator for Rb$_2$Ag$_5$F$_7$ is stiffer by 5% than that seen for RbAgF$_3$, as explained above.

Consideration of Goodenough–Kanamori–Anderson rules leads us to the notion, that magnetic interaction between two [AgF$_2$] layers within a sandwich must be very strong and antiferromagnetic. Indeed, the computed magnetic ground state of Rb$_2$Ag$_5$F$_7$ turns out to feature an antiferromagnetic spin ordering in [AgF$_2$] dimers, ferromagnetic within [AgF$_2$] layers, and also weakly ferromagnetic between sandwich layers (i.e. in a (AB)(BA) manner). Because of that, we have simplified calculations by assuming two dominant superexchange pathways: Ag–F–Ag within a dimer along crystallographic $a$ axis (this coupling constant is labelled $J_{0D}$), and an intralayer Ag–F...Ag one (labelled $J_{perp}$). Superexchange constants are expressed by equations:

$$J_{0D} = \frac{E_{A2} - E_{A1}}{8}, \quad J_{perp} = \frac{E_{A1} - E_{FM}}{2}$$

($E_{A1}$ is total energy of the ground state, $E_{A2}$ is total energy ordered antiferromagnetically in dimers, antiferromagnetically in layers, $E_{FM}$ is total energy of ferromagnetic solution; energy values per unit cell).

Calculated values are $J_{0D} = -240.2$ meV, $J_{perp} = 10.9$ meV. The $J_{0D}$ value is comparable with those for other strongly coupled Ag(II)-based antiferromagnets calculated to date. Related fluoroargentate(II) systems showing low magnetic dimensionality are Ag$_2$ZnZr$_2$F$_{14}$ ($J_{0D} = -313$ meV), HPII-Ag$_2$F$_2$ ($J_{0D} = -250$ meV) phase,$^{38}$ AgFBF$_4$ ($J_{0D} = -298$ meV)$^3$ and CsAgF$_3$ ($J_{0D} = -161$ meV)$^5$. On the other hand, $J_{perp}$ is ferromagnetic and comparable to a several meV values typical for MAgF$_3$$^6$ and M$_2$AgF$_4$$^8$. The ratio of $J_{perp}$ and $J_{0D}$ is ca. 0.045 and permits us to label this system as quasi-0D because dimers interact with each other quite weakly.

5. Conclusions

Theoretical calculations have led us to conclusion, that at the T → 0 K limit, the previously published structure of RbAgF$_3$$^{10}$ is not dynamically stable (in a harmonic approximation). We have been able to propose orthorhombic candidate for the low temperature polymorph, that is isostructural to low-temperature form of KAgF$_3$. Main structural difference between both forms reveals itself in Ag–F–Ag chains, which in tetragonal RbAgF$_3$ are completely straight, and kinked in orthorhombic RbAgF$_3$. There is also an associated puckering of the [AgF$_2$] sheets in the orthorhombic polytype. Total energy of that orthorhombic phase is 11.7 meV lower than that of the known tetragonal counterpart (HSE06, per Z=4 unit cell), which corresponds to 0.3 kJ mol$^{-1}$ or 34 K.

In order to experimentally confirm a possible existence of low temperature RbAgF$_3$ polymorph, low temperature Raman and powder X-ray diffraction study were conducted. Unfortunately, both methods were inconclusive. Colling to liquid helium temperatures and preparing of a purer specimen is needed to confirm or refute the postulated phase transition. Orthorhombic RbAgF$_3$ should be searched for at LHe temperatures.

Comparative theoretical analysis of lattice dynamics of MAgF$_3$ (M = K, Rb, Cs) compounds was performed. Phonon dispersion curves, phonon density of states and full list of vibrational modes were calculated for orthorhombic RbAgF$_3$ and tetragonal CsAgF$_3$ as a development of our recent study for the K analogue.$^{14}$
Analysis of phonon density of stated graph yielded conclusion, that having larger cation in interstitial positions in a distorted perovskite lattice causes significant localization of certain phonons. We have also compared corresponding theoretically predicted modes to understand trends observed in that series of compounds.

Although at 0 K the orthorhombic RbAgF₃ is more stable, in order to analyse room temperature spectral data it was necessary to calculate normal modes for tetragonal structure. Using that, and predicted phonons for CsAgF₃ we have assigned specific vibrations to most bands present at IR and Raman spectra. We have reached very good accuracy of the correlation between experimental and theoretical data, thus supporting our assignment.

One of analysed samples of RbAgF₃ contained significant portion of contamination phase. Upon indexation, DFT+U modelling, and subsequent Rietveld refinement we have proposed a novel Rb₂Ag₃F₇ phase. This new compound constitutes the second known Ruddlesden-Popper phase in fluoroargentate(II) family. Rb₂Ag₃F₇ crystallizes in Cmca (No. 64) space group (21.7577(5) 6.35844(9) 6.35747(9) 90 90 90). Its structure best described as sandwich layers of \([\text{AgF}_2]\) stacked at 45°, interleaved with rubidium cations. According to the DFT calculations, this compound features one of the shortest Ag–F bonds known, and it hosts a very strong antiferromagnetic superexchange (\(J_{\text{SD}} = -240.2 \text{ meV}\)) within the sandwich layers.

6. Acknowledgements

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7. Notes and references

Further details of the crystal structures reported here may be obtained from Fachinformationszentrum Karlsruhe (76344 Eggenstein-Leopoldshafen, Germany; fax (+49)7247-808-666; e-mail: crysdata@fizkarlsruhe.de) on quoting their CSD numbers: 2122449 for RbAgF₃ and 2122450 for Rb₃AgF₇.

‡ Ionic radius of MAgF₃ (M = K, Rb, Cs) compounds increases in the series starting from 1.64 Å for potassium, through 1.72 Å for rubidium, to 1.88 Å for caesium (all for coordination number XII).

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Electronic supplementary information

Crystal structure, lattice dynamics and superexchange in MAgF$_3$ 1D antiferromagnets (M = K, Rb, Cs) and Rb$_3$Ag$_2$F$_7$ Ruddlesden-Popper phase

Kacper Koteras,$^{1, *}$ Jakub Gawraczyński,$^{1}$ Gašper Tavčar,$^{2}$ Zoran Mazej,$^{2}$ Wojciech Grochala$^{1}$

Figure S1. Deconvoluted Raman spectrum of CsAgF$_3$.

Figure S2. Deconvoluted Raman spectrum of RbAgF$_3$.
Figure S3. Different Raman spectra collected for of RbAgF$_3$.

Figure S4. Full set of Raman spectra at low temperature for RbAgF$_3$. 
Figure S5. X-ray diffraction pattern of RbAgF$_3$ sample containing novel Rb$_3$Ag$_2$F$_7$ phase and the results of the Rietveld refinement. Bottom part shows simulated Bragg positions for each present phase (from top to bottom: RbAgF$_3$, AgF and Rb$_3$Ag$_2$F$_7$).

Table S1. Crystallographic data for RbAgF$_3$.

| Formula      | RbAgF$_3$           |
|--------------|---------------------|
| Colour       | brown               |
| Space group  | $I4/mcm$ (No. 140)  |
| $Z$          | 4                   |
| $V$ /Å$^3$   | 338.991(6)          |
| $a$ /Å       | 6.33855(6)          |
| $b$ /Å       | 6.33855(6)          |
| $c$ /Å       | 8.43740(11)         |
| $\alpha$ /° | 90                  |
| $\beta$ /°  | 90                  |
| $\gamma$ /° | 90                  |
| Positions    | Rb1 0.00000 0.00000 0.25000 Ag1 0.00000 0.50000 0.00000 F1 0.00000 0.50000 0.25000 F2 0.240(4) 0.740(4) 0.00000 |
| Reliability factors | Not corrected for background (all data) $R_p = 0.84$ % $R_{wp} = 1.78$ % |
|              | Corrected for background (all data) $cR_p = 27.86$ % $cR_{wp} = 15.16$ % |
|              | R Bragg factor (this phase) $R_{Bragg} = 9.53$ % |
| Atomic distances /Å | Ag–F (apical) 2.10935(3) |
|              | Ag–F (equatorial) 2.33(3) 2.15(3) |
Table S2. Theoretically calculated modes.

| RbAgF$_3$ Pnma (HSE06) | RbAgF$_3$ I4/mcm (HSE06) | CsAgF$_3$ I4/mcm (HSE06) |
|-------------------------|--------------------------|--------------------------|
| B2u                     | A2u                      | E_u                      |
| 471                     | 484                      | 450                      |
| A_u                     | B3g                      | B2g                      |
| 470                     | 472                      | 449                      |
| B3g                     | E_u                      | A3u                      |
| 467                     | 467                      | 449                      |
| B1u                     | A1g                      | A1g                      |
| 464                     | 381                      | 370                      |
| B3u                     | B3g                      | B3g                      |
| 464                     | 312                      | 302                      |
| A_u                     | B1u                      | B1u                      |
| 462                     | 233                      | 227                      |
| B2u                     | E_u                      | A2u                      |
| 461                     | 184                      | 193                      |
| B2g                     | A3u                      | E_u                      |
| 449                     | 183                      | 186                      |
| B1g                     | E_u                      | E_u                      |
| 414                     | 181                      | 186                      |
| A_u                     | E_u                      | E_u                      |
| 380                     | 159                      | 162                      |
| B1g                     | A2g                      | B1u                      |
| 365                     | 144                      | 155                      |
| B3g                     | B1u                      | A2g                      |
| 303                     | 139                      | 150                      |
| B3u                     | E_u                      | E_u                      |
| 271                     | 124                      | 118                      |
| B1u                     | A2g                      | B1g                      |
| 240                     | 69                       | 95                       |
| B3u                     | A2g                      | E_u                      |
| 205                     | 67                       | 88                       |
| A_u                     | E_u                      | A3u                      |
| 201                     | 66                       | 72                       |
| B2g                     | E_u                      | E_u                      |
| 200                     | 65                       | 72                       |
| B1u                     | E_u                      | A2g                      |
| 199                     | 26                       | 65                       |
| B2u                     | A2u                      | E_u                      |
| 186                     | -1                       | 56                       |
| B2g                     | E_u                      | A3u                      |
| 182                     | -2                       | -5                       |
| B1u                     | B1g                      | E_u                      |
| 175                     | -39                      | -5                       |
| B3u                     | 174                      |                           |
| A_u                     | 174                      |                           |
| A_u                     | 164                      |                           |
| B2u                     | 162                      |                           |
| B3u                     | 161                      |                           |
| B1u                     | 157                      |                           |
| B3g                     | 153                      |                           |
| B2g                     | 146                      |                           |
| A_u                     | 146                      |                           |
| B1g                     | 139                      |                           |
| B1u                     | 139                      |                           |
| B3g                     | 134                      |                           |
| B3u                     | 134                      |                           |
| B3u                     | 129                      |                           |
| B2g                     | 125                      |                           |
| B1u                     | 118                      |                           |
| A_u                     | 98                       |                           |
| A_u                     | 87                       |                           |
| B1g                     | 86                       |                           |
| B1u                     | 82                       |                           |
| A_u                     | 78                       |                           |
| B3g                     | 77                       |                           |
| A_u                     | 76                       |                           |
| B3u                     | 76                       |                           |
| B2u                     | 74                       |                           |
| B2g                     | 73                       |                           |
| B2u                     | 71                       |                           |
| A_u                     | 69                       |                           |
| B3u                     | 68                       |                           |
| B1u                     | 65                       |                           |
| A_u                     | 64                       |                           |
| B2g                     | 60                       |                           |
| B1g                     | 50                       |                           |
| A_u                     | 49                       |                           |
| B2g                     | 34                       |                           |
| A_u                     | 33                       |                           |
| B2u                     | -1                       |                           |
| B1u                     | -1                       |                           |
| B3u                     | -2                       |                           |
Cif files of structures used in lattice dynamics calculations

**RbAgF₃, Pnma (HSE06)**

data_findsym-output
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  _cell_length_c  6.3443100000
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  _cell_angle_beta  90.0000000000
  _cell_angle_gamma 90.0000000000
  _cell_volume  332.1058636297

  _symmetry_space_group_name_H-M "P 21/n 21/m 21/a"
  _symmetry_Int_Tables_number 62
  _space_group.reference_setting '062:-P 2ac 2n'
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    _space_group_symop_operation_xyz
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    2 x+1/2,-y+1/2,-z+1/2
    3 -x,y+1/2,-z
    4 -x+1/2,y,z+1/2
    5 -x,-y,-z
    6 -x+1/2,y+1/2,z+1/2
    7 x,-y+1/2,z
    8 x+1/2,y,-z+1/2

  loop_
    _atom_site_label
    _atom_site_type_symbol
    _atom_site_symmetry_multiplicity
    _atom_site_Wyckoff_label
    _atom_site_fract_x
    _atom_site_fract_y
    _atom_site_fract_z
    _atom_site_occupancy
    _atom_site_fract_symmform
    Ag1  Ag   4 a 0.00000 0.00000  0.00000 1.00000 0,0,0
    Rb1  Rb   4 c 0.00381 0.25000  0.49913 1.00000 Dx,0,Dz
    F1   F    4 c 0.49600 0.25000  0.45836 1.00000 Dx,0,Dz
    F2   F    8 d 0.26645 -0.02118 0.27814 1.00000 Dx,Dy,Dz

**RbAgF₃, I4/mcm (HSE06)**

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  _cell_angle_alpha 90.0000000000
  _cell_angle_beta  90.0000000000
  _cell_angle_gamma 90.0000000000
  _cell_volume  333.1304144144

  _symmetry_space_group_name_H-M "I 4/m 2/c 2/m"
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    _space_group_symop_operation_xyz
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    2 x,-y,-z+1/2
CsAgF<sub>3</sub> \( I4/mcm \) (HSE06)

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_cell_angle_gamma 90.0000000000
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 2 x,-y,-z+1/2
 3 -x,y,-z+1/2
 4 -x,y,z
 5 -y,-x,-z+1/2

Ag1 Ag   4 d 0.00000 0.50000 0.00000 1.00000 0,0,0
Rb1 Rb   4 a 0.00000 0.00000 0.25000 1.00000 0,0,0
F1  F    4 b 0.22870 0.72870 0.00000 1.00000 DxD,0
F2  F    8 h 0.22870 0.72870 0.00000 1.00000 DxD,0
loop
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  _atom_site_type_symbol
  _atom_site_symmetry_multiplicity
  _atom_site_Wyckoff_label
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_occupancy
  _atom_site_fract_symmform
Ag1 Ag   4 d 0.00000 0.50000 0.00000 1.00000 0,0,0
Cs1 Cs   4 a 0.00000 0.00000 0.25000 1.00000 0,0,0
F1  F    4 b 0.22363 0.72363 0.00000 1.00000 Dx,Dx,0
F2  F    8 h 0.22363 0.72363 0.00000 1.00000 0,0,0

Rb3Ag2F7 Cmca (GGA+U)

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  _cell_length_c 6.2937100000
  _cell_angle_alpha 90.0000000000
  _cell_angle_beta 90.0000000000
  _cell_angle_gamma 90.0000000000
  _cell_volume 858.6781972783
  _symmetry_space_group_name_H-M "C 2/m 2/c 21/a"
  _symmetry_Int_Tables_number 64
  _space_group.reference_setting '064:-C 2ac 2'
  _space_group.transform_Pp_abc a,b,c;0,0,0

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  _space_group_symop_operation_xyz
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2 x,-y,-z
3 -x+1/2,y,-z+1/2
4 -x+1/2,-y+1/2
5 -x,-y,-z
6 -x,y,z
\[
\begin{align*}
7 & \ x+1/2,-y,z+1/2 \\
8 & \ x+1/2,y,z+1/2 \\
9 & \ x+1/2,y+1/2,z \\
10 & \ x+1/2,-y+1/2,-z \\
11 & \ -x,y+1/2,-z+1/2 \\
12 & \ -x,y+1/2,z+1/2 \\
13 & \ -x+1/2,-y+1/2,-z \\
14 & \ -x+1/2,y+1/2,z \\
15 & \ x,-y+1/2,z+1/2 \\
16 & \ x,y+1/2,-z+1/2 \\
\end{align*}
\]

| Loop Atom Site Label | Atom Site Symbol | Wyckoff Multiplicity | Fract X | Fract Y | Fract Z | Symmetry Form |
|---------------------|------------------|----------------------|---------|---------|---------|---------------|
| Ag1 Ag              | 8 d              | 0.40284 0.00000 0.00000 1.00000 | Dx,0,0  |
| Rb1 Rb              | 8 d              | 0.18085 0.00000 0.00000 1.00000 | Dx,0,0  |
| Rb2 Rb              | 4 a              | 0.00000 0.00000 0.00000 1.00000 | 0,0     |
| F1 F                | 8 d              | 0.30625 0.00000 0.00000 1.00000 | Dx,0,0  |
| F2 F                | 4 b              | 0.50000 0.00000 0.00000 1.00000 | 0,0     |
| F3 F                | 16 g             | 0.09527 0.26940 0.23077 1.00000 | Dx,Dy,Dz |