Electronic supplementary information

Crystal structure, lattice dynamics and superexchange in $MAgF_3$ 1D antiferromagnets (M = K, Rb, Cs) and $Rb_3Ag_2F_7$ Ruddlesden-Popper phase

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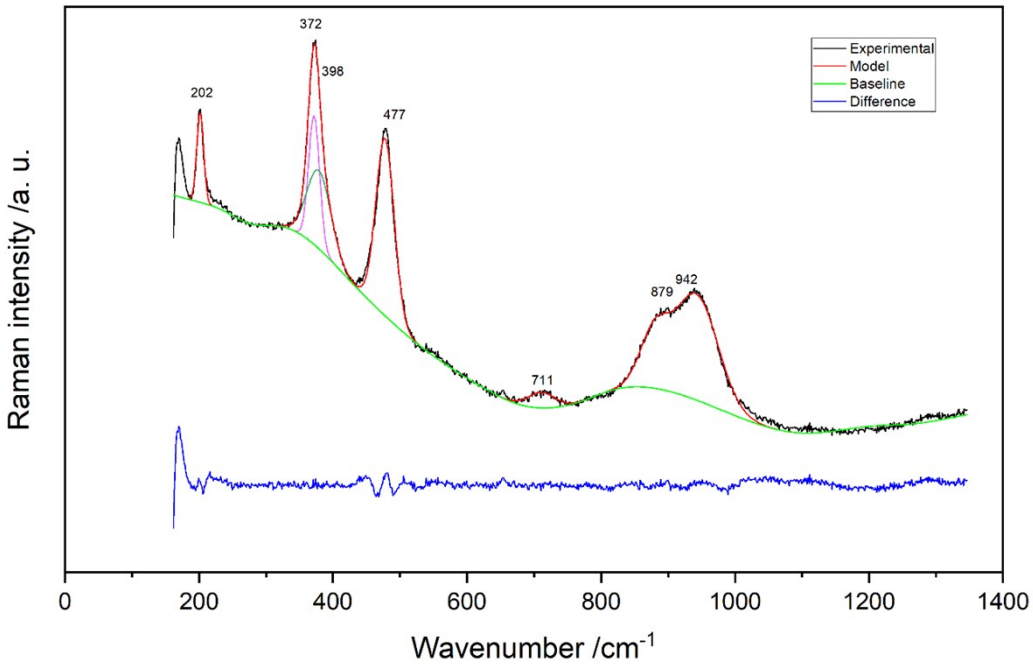

Figure S1. Deconvoluted Raman spectrum of $CsAgF_3$.

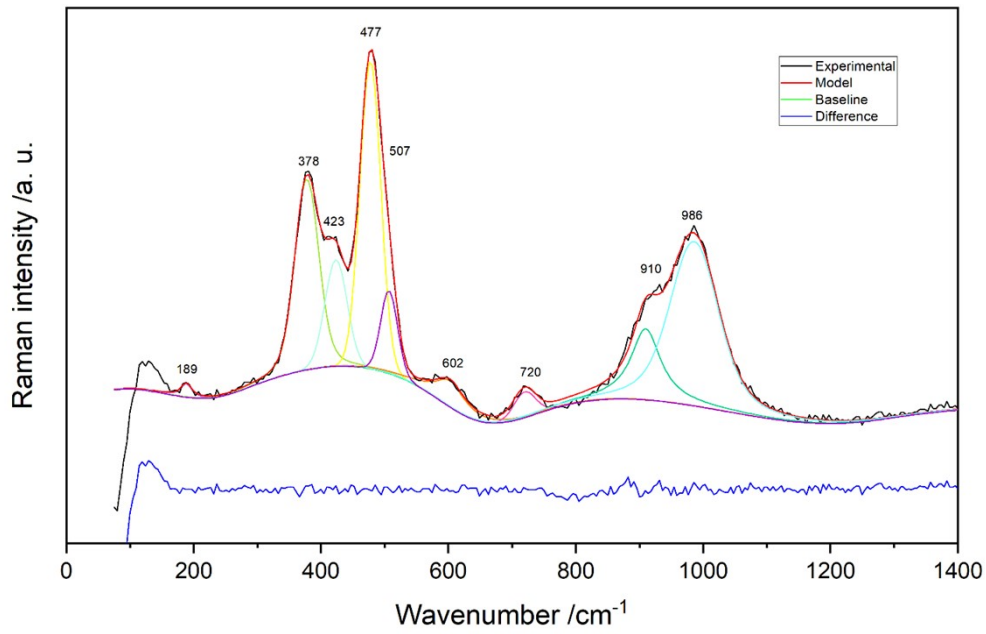

Figure S2. Deconvoluted Raman spectrum of $RbAgF_3$.

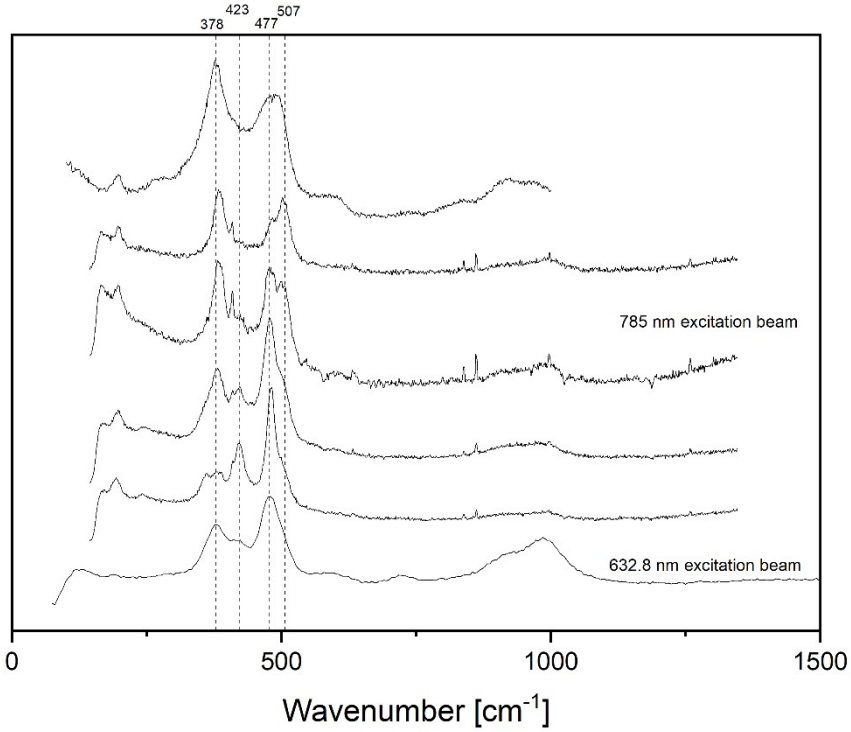

Figure S3. Different Raman spectra collected for of $RbAgF_3$.

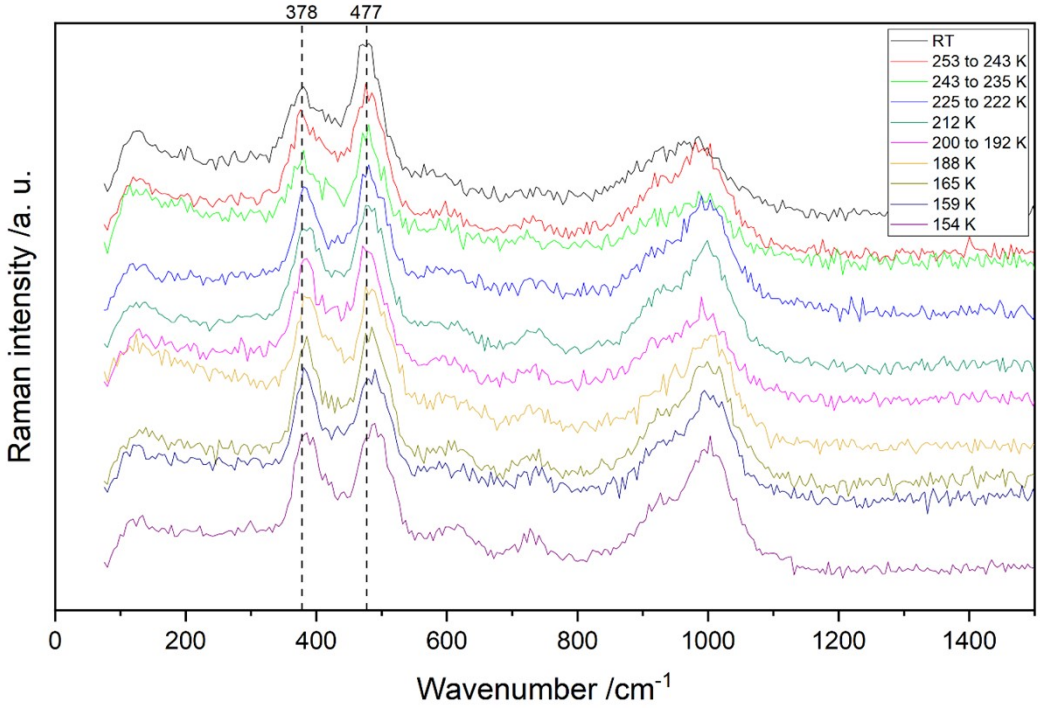

Figure S4. Full set of Raman spectra at low temperature for RbAgF3.

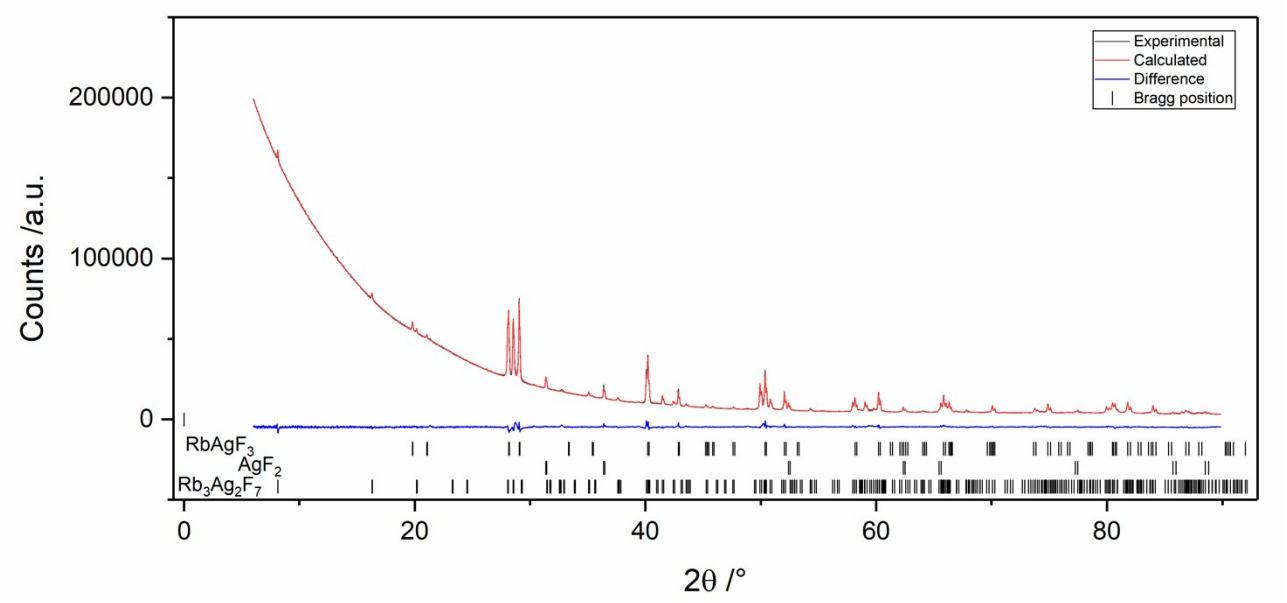

Figure S5. X-ray diffraction pattern of $RbAgF_3$ sample containing novel $Rb_3Ag_2F_7$ phase and the results of the Rietveld refinement. Bottom part shows simulated Bragg positions for each present phase (from top to bottom: $RbAgF_3$, AgF and $Rb_3Ag_2F_7$).

Table S1. Crystallographic data for $RbAgF_3$.

Formula	$RbAgF_3$
Colour	brown
Space group	*I*4/*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)
α /°	90
β /°	90
γ /°	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)	
B_{2u}	471	A_{2u}	484	E_u	450
A_u	470	B_{2g}	472	B_{2g}	449
B_{3g}	467	E_u	467	A_{2u}	449
B_{1u}	464	A_{1g}	381	A_{1g}	370
B_{3u}	464	B_{2g}	312	B_{2g}	302
A_u	462	B_{1u}	233	B_{1u}	227
B_{2u}	461	E_g	184	A_{2u}	193
B_{2g}	449	A_{2u}	183	E_u	186
B_{1g}	414	E_u	181	E_g	186
A_g	380	E_u	159	E_u	162
B_{1g}	365	A_{2g}	144	B_{1u}	155
B_{3g}	303	B_{1u}	139	A_{2g}	150
B_{3u}	271	E_u	124	E_u	118
B_{1u}	240	A_{2g}	69	B_{1g}	95
B_{3u}	205	A_{2u}	67	E_g	88
A_g	201	E_u	66	A_{2u}	72
B_{2g}	200	E_g	65	E_u	72
B_{1u}	199	E_g	26	A_{2g}	65
B_{2u}	186	A_{2u}	-1	E_g	56
B_{2g}	182	E_u	-2	A_{2u}	-5
B_{1u}	175	B_{1g}	-39	E_u	-5
B_{3u}	174				
A_u	174				
A_u	164				
B_{2u}	162				
B_{3u}	161				
B_{1u}	157				
B_{3g}	153				
B_{2u}	146				
A_u	146				
B_{1g}	139				
B_{1u}	139				
B_{3g}	134				
B_{3u}	134				
B_{3u}	129				
B_{2g}	125				
B_{1u}	118				
A_g	98				
A_g	87				
B_{1g}	86				
B_{1u}	82				
A_g	78				
B_{3g}	77				
A_u	76				
B_{3u}	76				
B_{2u}	74				
B_{2g}	73				
B_{2u}	71				
A_g	69				
B_{3u}	68				
B_{1u}	65				
A_u	64				
B_{2g}	60				
B_{1g}	50				
A_u	49				
B_{2g}	34				
A_g	33				
B_{2u}	-1				
B_{1u}	-1				

B_{3u}	-2				

Cif files of structures used in lattice dynamics calculations

$RbAgF_3$ *Pnma* (HSE06)

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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

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_atom_site_fract_symmform
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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
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$RbAgF_3$ *I4/mcm* (HSE06)

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8 y,x,-z+1/2
9 -x,-y,-z
10 -x,y,z+1/2
11 x,-y,z+1/2
12 x,y,-z
13 y,x,z+1/2
14 y,-x,-z
15 -y,x,-z
16 -y,-x,z+1/2
17 x+1/2,y+1/2,z+1/2
18 x+1/2,-y+1/2,-z
19 -x+1/2,y+1/2,-z
20 -x+1/2,-y+1/2,z+1/2
21 -y+1/2,-x+1/2,-z
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23 y+1/2,-x+1/2,z+1/2
24 y+1/2,x+1/2,-z
25 -x+1/2,-y+1/2,-z+1/2
26 -x+1/2,y+1/2,z
27 x+1/2,-y+1/2,z
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Rb1 Rb 4 a 0.00000 0.00000 0.25000 1.00000 0,0,0
F1 F 4 b 0.00000 0.50000 0.25000 1.00000 0,0,0
F2 F 8 h 0.22870 0.72870 0.00000 1.00000 Dx,Dx,0

$CsAgF_3$ *I*4/*mcm* (HSE06)

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6 -y,x,z
7 y,-x,z
8 y,x,-z+1/2
9 -x,-y,-z
10 -x,y,z+1/2
11 x,-y,z+1/2
12 x,y,-z
13 y,x,z+1/2
14 y,-x,-z
15 -y,x,-z
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29 y+1/2,x+1/2,z
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_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 0.00000 0.50000 0.25000 1.00000 0,0,0
F2 F 8 h 0.22363 0.72363 0.00000 1.00000 Dx,Dx,0

$Rb_3Ag_2F_7$ *Cmca* (GGA+U)

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5 -x,-y,-z
6 -x,y,z
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
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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 0,0,0
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 0,0,0
F3 F 16 g 0.09527 0.26940 0.23077 1.00000 Dx,Dy,Dz