Supplementary Information

High pressure behavior of silver fluorides up to 40 GPa

Adam Grzelak[a, b], Jakub Gawraczyński[a, b], Tomasz Jaroń[b], Dominik Kurzydłowski[b], Armand Budzianowski[b], Zoran Mazej[c], Piotr J. Leszczyński[b], Vitali B. Prakapenka,[d] Mariana Derzsi[b]*, Viktor V. Struzhkin[e]*, and Wojciech Grochala[b]*

[a]Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warsaw, Poland.
[b]Center of New Technologies, University of Warsaw, ul. Banacha 2C, 02-097 Warsaw, Poland.
[c]Department of Inorganic Chemistry and Technology, Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia.
[d] Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637, United States.
[e]Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington, DC 20015, United States.

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S1. Equation of state of AgF.

AgF has been previously studied under high pressure and is known to undergo a phase transition at pressure ca. 2.7 GPa from rocksalt structure to the more closely packed CsCl-type structure.[1] In one of our XRD experiments, we compressed a sample that turned out to consist mostly of AgF – a product of *in situ* decomposition of AgF_2. We studied its XRD pattern up to ca. 39 GPa and determined equation of state (EoS) parameters of the CsCl-type structure. Pressure dependence of volume of CsCl-type unit cell of AgF is shown in SI. The data was fitted with Birch-Murnaghan (B-M) EoS[2] – its parameters are given in table 1.

V_0 [Å^3]	B_0 [GPa]	B_0'	B_0 [GPa] (Ref. [1])
26.673(9)	87.1(2)	5.26(3)	110

Table S1. Birch-Murnaghan equation of state parameters for CsCl-type AgF. V_0 – reference volume, B_0 – bulk modulus, B_0' – pressure derivative of bulk modulus.

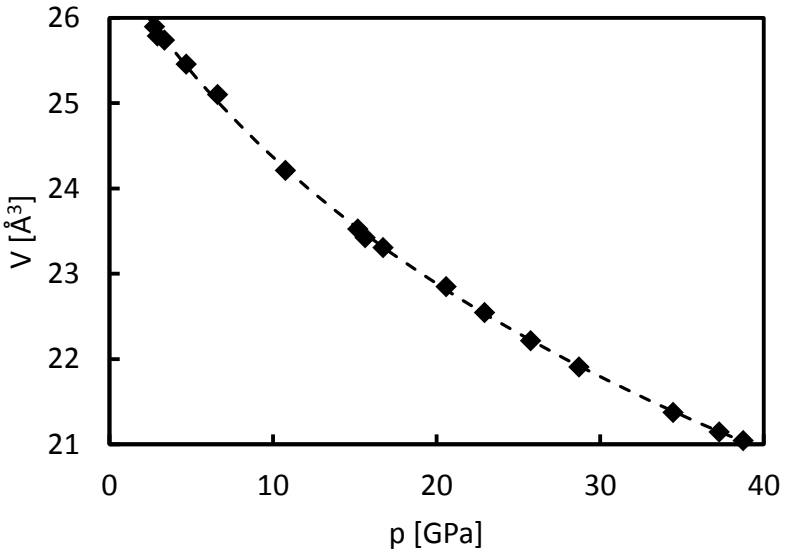


Fig. S1. Pressure dependence of volume of AgF unit cell (CsCl-type structure). Dashed line – B-M EoS fit.

S2. Rietveld fits to the collected XRDPs for characteristic pressure points.

Rietveld fits were performed using "Jana2006" software.[3]

S2.1. Rietveld fit for LP structure at 8.5 GPa.

Fit parameters and appearance is presented in Table S2.1 and Fig. S2.1.

	GOF	R_p	R_{wp}
***Pbca* (LP)**	0.53	0.81%	1.24%

Table S2.1. Fit parameters for *Pbca* (LP) structure of AgF_2 at 8.5 GPa.

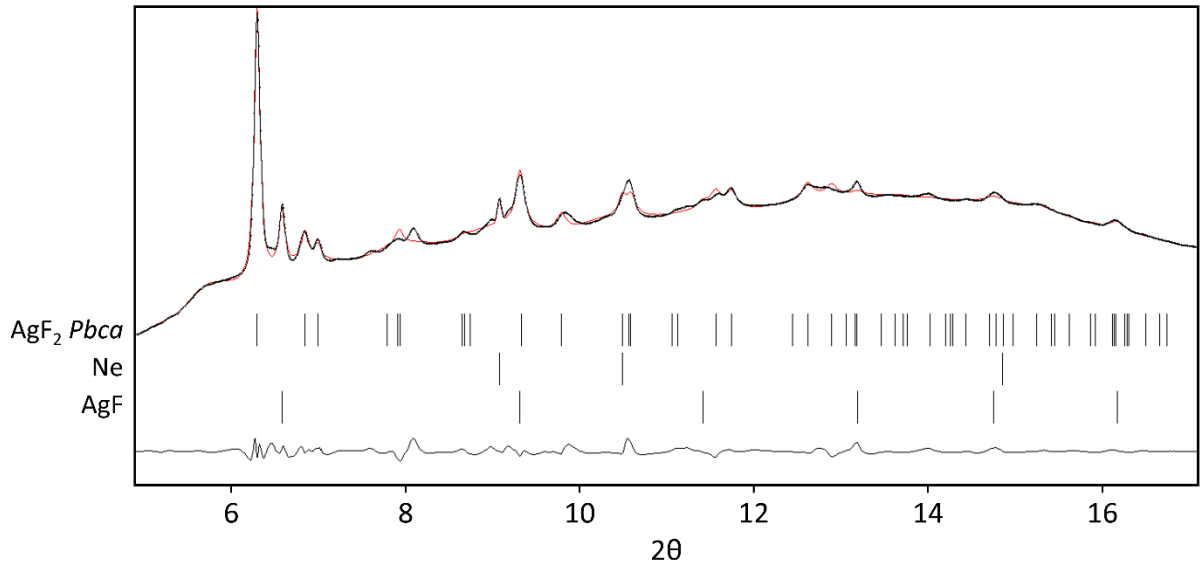


Figure S2.1. Rietveld fit at 8.5 GPa (λ = 0.3344 Å).

S2.2 Comparison of Rietveld fits for LP and HP-I structure at 11.7 GPa.

Fit parameters and appearance are compared in Table S2.2 and Fig. S2.2.

	GOF	R_p	R_{wp}
***Pbca* (LP)**	0.18	0.68%	0.96%
***Pca*2$_1$ (HP-I)**	0.13	0.51%	0.70%

Table S2.2. Fit parameters for *Pbca* (LP) and *Pca*2$_1$ (HP-I) structure of AgF_2 at 11.7 GPa.

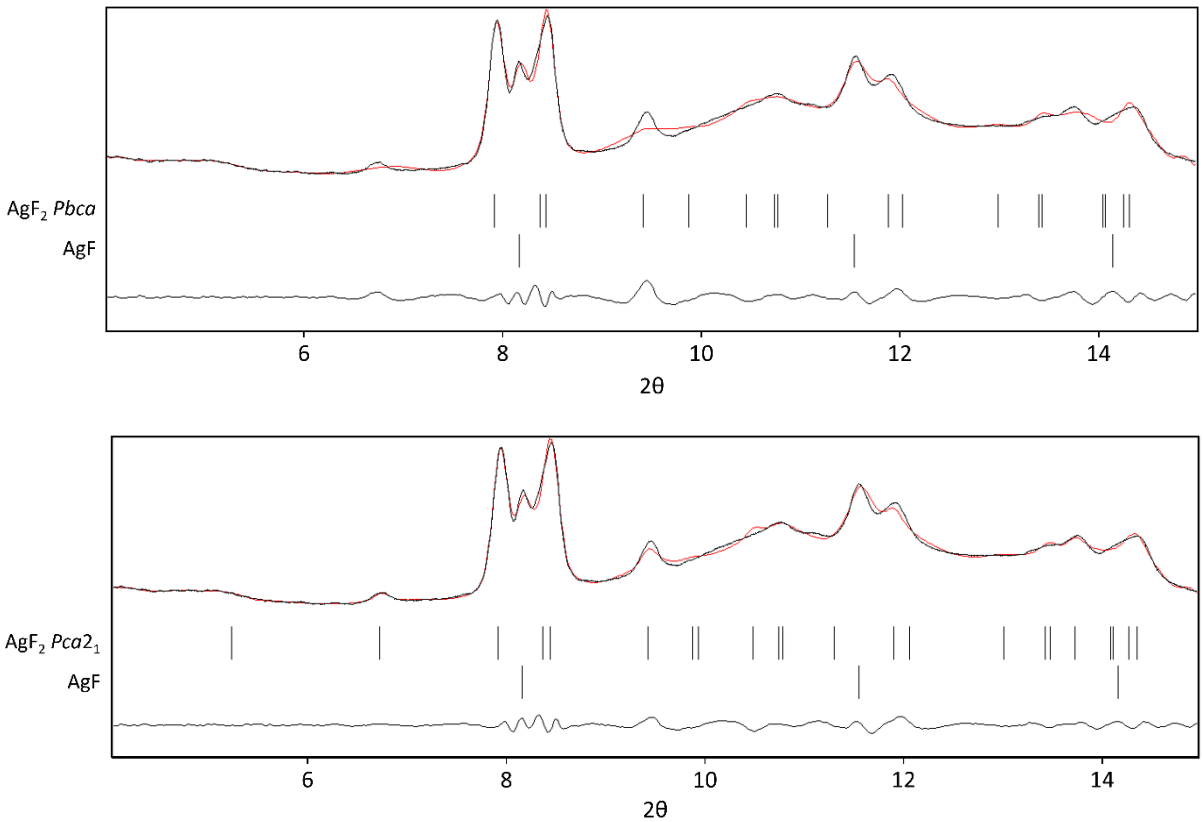


Figure S2.2. Rietveld fits at 11.7 GPa. Top: LP (*Pbca*); bottom: HP-I (*Pca*2$_1$) (λ = 0.4113 Å).

S2.3. Rietveld fit for HP-II structure at 36.2 GPa.

Fit parameters and appearance is presented in Table S2 and Fig. S2.

	GOF	R_p	R_{wp}
***Pbcn* (HP-II)**	0.30	0.29%	0.44%

Table S2.3. Fit parameters for *Pbcn* (HP-II) structure of AgF_2 at 36.2 GPa.

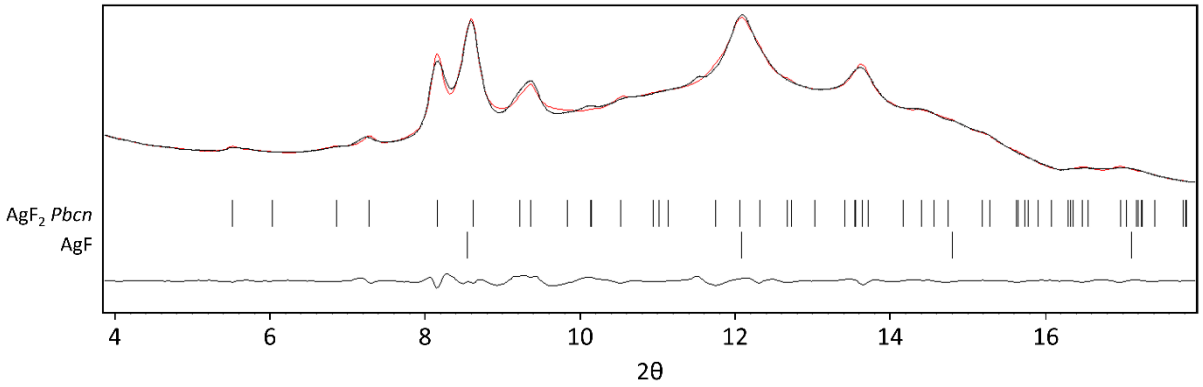


Figure S2.3. Rietveld fit at 36.2 GPa (λ = 0.4113 Å).

S3. Lattice constants of AgF_2 at different pressures obtained from XRD experiments.

Table S3.1. XRD-A data (compression only).

	p AgF	Δp	a	Δa	b	Δb	c	Δc	V	ΔV
LP	4.9	0.1	5.485	0.001	5.656	0.001	4.965	0.002	154.03	0.10
	8.5	0.2	5.477	0.003	5.592	0.003	4.831	0.003	147.93	0.03
HP-I	10.0	0.5	5.475	0.007	4.704	0.006	5.564	0.006	143.32	0.10
	13.5	0.6	5.572	0.008	4.513	0.007	5.523	0.007	138.88	0.09
HP-II	16.9	0.6	5.475	0.013	8.350	0.022	5.693	0.015	260.2	1.3
	21.8	1.0	5.300	0.016	8.234	0.018	5.714	0.017	249.4	1.7
	25.9	1.8	5.198	0.023	8.137	0.031	5.716	0.017	241.8	2.4

Table S3.2. XRD-B (compression and decompression).

	p AgF	Δp	a	Δa	b	Δb	c	Δc	V	ΔV
HP-I	11.7	0.5	5.585	0.007	4.500	0.008	5.634	0.007	141.58	0.08
HP-II comp	14.8	0.6	5.475	0.010	8.331	0.015	5.787	0.007	264.0	1.1
	25.3	0.8	5.301	0.010	8.100	0.016	5.777	0.009	248.1	1.2
	32.7	1.2	5.197	0.017	7.947	0.019	5.821	0.010	240.4	1.4
	36.2	0.8	5.129	0.010	7.849	0.011	5.803	0.007	233.6	0.8
HP-II decomp	34.4	0.6	5.141	0.007	7.905	0.011	5.802	0.006	235.8	0.8
	32.8	1.1	5.173	0.015	7.920	0.020	5.810	0.010	238.1	1.4
	28.5	0.7	5.198	0.010	7.951	0.013	5.833	0.007	241.1	0.9
	24.6	0.9	5.250	0.015	8.011	0.020	5.858	0.010	246.4	1.5
	20.1	0.4	5.322	0.012	8.128	0.015	5.851	0.005	253.1	0.4
	16.5	0.3	5.355	0.009	8.305	0.013	5.836	0.010	259.5	0.4

S4. Theoretical enthalpies of the relevant structures.

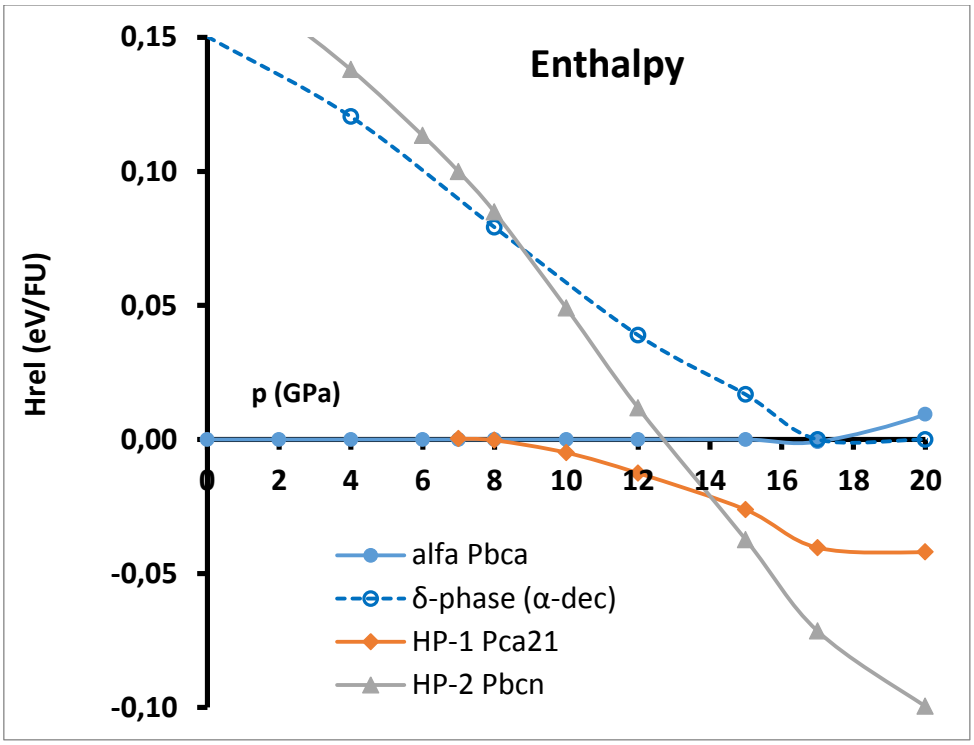


Figure S4.1. Pressure dependence of relative enthalpies of AgF_2 structures (compared to LP-*Pbca* structure) in a narrower p range. δ phase stands for flat layer form theorized in Ref.6.

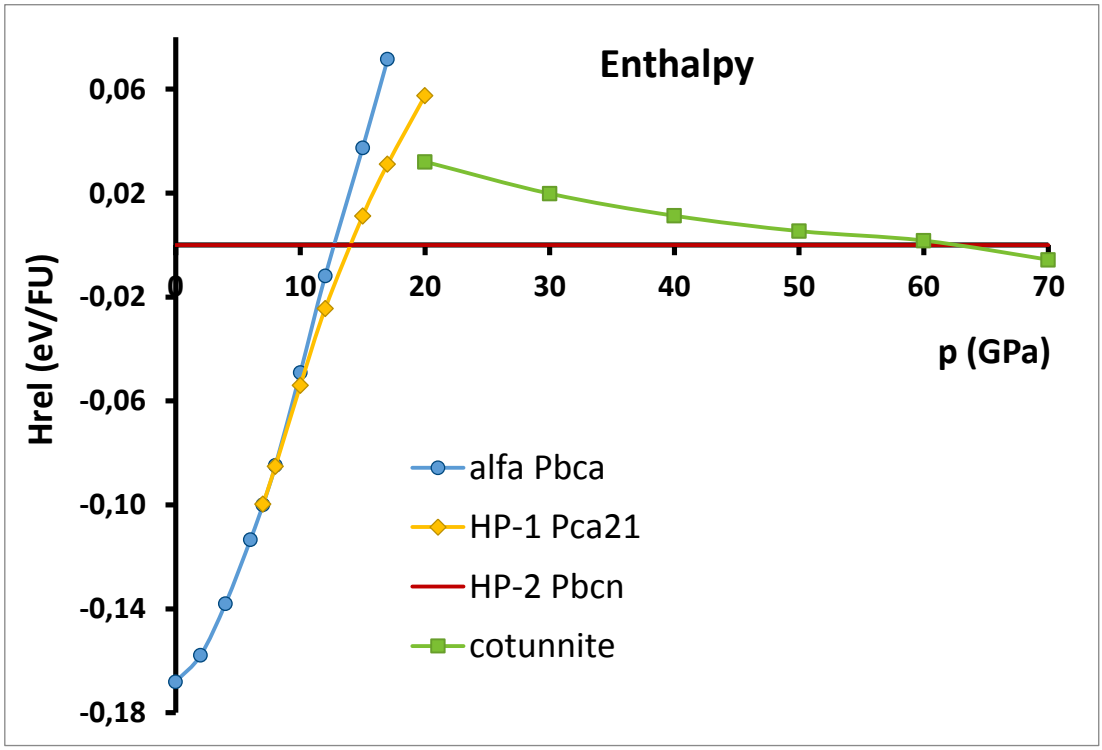


Figure S4.2. Pressure dependence of relative enthalpies of AgF_2 structures (compared to HP-II structure) in a broader p range.

S5. The closest F…F contacts in the observed crystal structures.

Table S5. Selected F…F contacts and torsional AgFFAg angle in the **HP-I** structure as calculated with DFT+U. See **Figure S5** below for geometry of the F…F contacts and the in-plain Ag-F…F-Ag angle. Within the pressure range 0-6 GPa the **HP-I** converges to the higher-symmetry **LP** phase. Note, twice the vdW radius of F is 2.96 Å at 1 atm.

	HP-I		LP		F_2†	
GPa	F…F	$F…F^{shortest}$	F…F	$F…F^{shortest}$	F…F	$F\text{-}F^{intramolecular}$
	in-plain	out-plain	in-plain	out-plain		
0	-	-	-	-	3.014	1.388
2	-	-	-	-		
4	-	-	-	-		
6	-	-	-	-		
7	2.891	2.914	2.891	2.914		
8	2.852	2.718	2.852	2.718		
10	2.766	2.664	2.766	2.664	2.394	1.383
12	2.679	2.605	2.679	2.605		
15	2.602	2.553	2.602	2.553		
17	2.570	2.534	2.570	2.534		
20	2.535	2.519	2.535	2.519	2.275	1.379

†Values for solid F_2 under high pressure were calculated by Kurzydłowski and Zaleski-Ejgierd.[4]

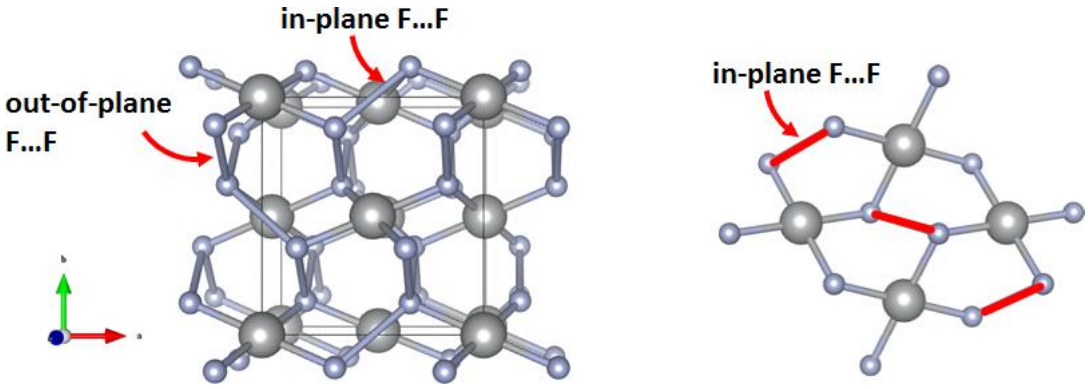


Fig. S5. Illustration of the in-plane and the shortest out-of-plain F…F contact between F atoms belonging to different AgF_4 squares in the HP-I structure: 3D structure showing one unit cell (left) and single AgF_2 layer (right). The in-plain F…F contact corresponds to the chalcogenide bond in cobaltite CoAsS. The in-plain Ag-F…F-Ag torsional angle is also highlighted (right). This figure should be read together with **Table S4**.

S6. Raman spectroscopy of AgF and AgF_2

To our knowledge, high-pressure Raman spectra of AgF have not been previously reported. Raman spectra of the high-pressure (CsCl-type) phase of AgF have been collected up to 27 GPa (see ESI). The most prominent feature of these spectra is the first overtone of the band assigned to infrared-active T_{1u} mode. Pressure dependence of this band is plotted in fig. S6.

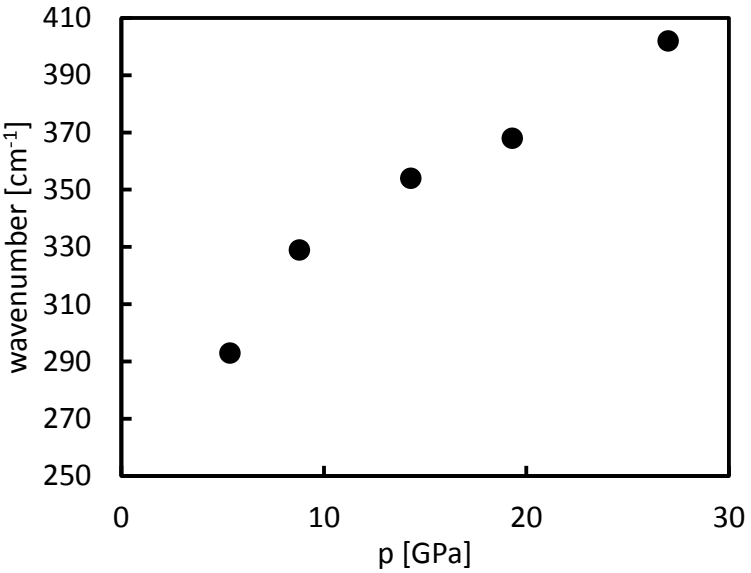


Fig. S6. Pressure dependence of the wavenumber of the Raman-active first overtone of the IR-active T_{1u} mode of CsCl-type AgF phase.

Raman spectra obtained from compressed AgF_2 were collected using 514.5 nm laser line. The spectra are dominated by a band which appears at 420 cm^{-1} at ambient pressure. The frequency of this band increases with compression up to 540 cm^{-1} at 40 GPa. Interestingly, this band does not normally feature in Raman spectra of AgF_2, but it has been reported in spectra of fluoroargentates such as $KAgF_3$ and K_2AgF_4, which contain complex $[AgF_3]^-$ or $[AgF_4]^{2-}$ anions.[5] It is possible that the sample compressed in this experiment decomposed as a result of irradiation with 514.5 nm laser, yielding a fluoroargentate product. More detailed studies of irradiated samples of AgF_2 are needed in order to elucidate the structure of this yet-unknown species.

S7. Electronic band gap at the Fermi level (theoretical DFT+U data).

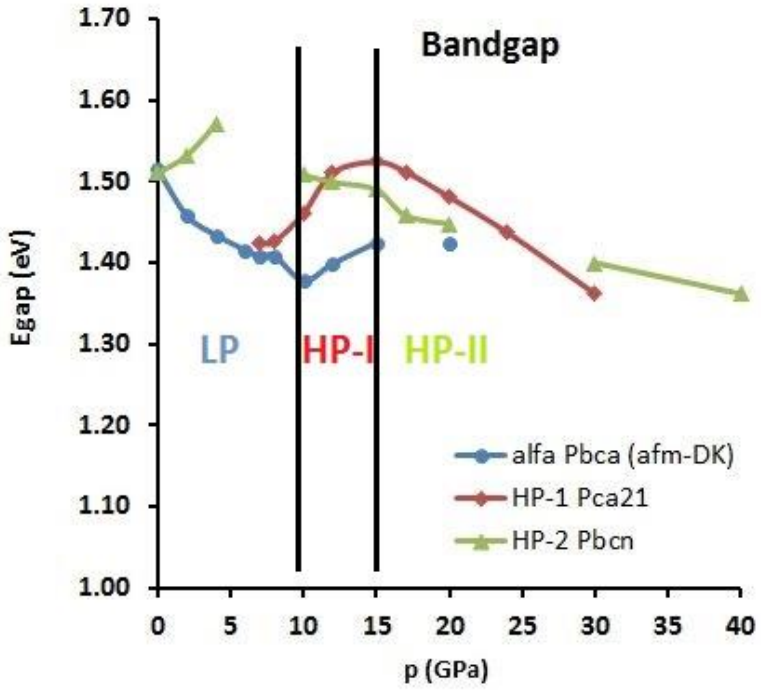
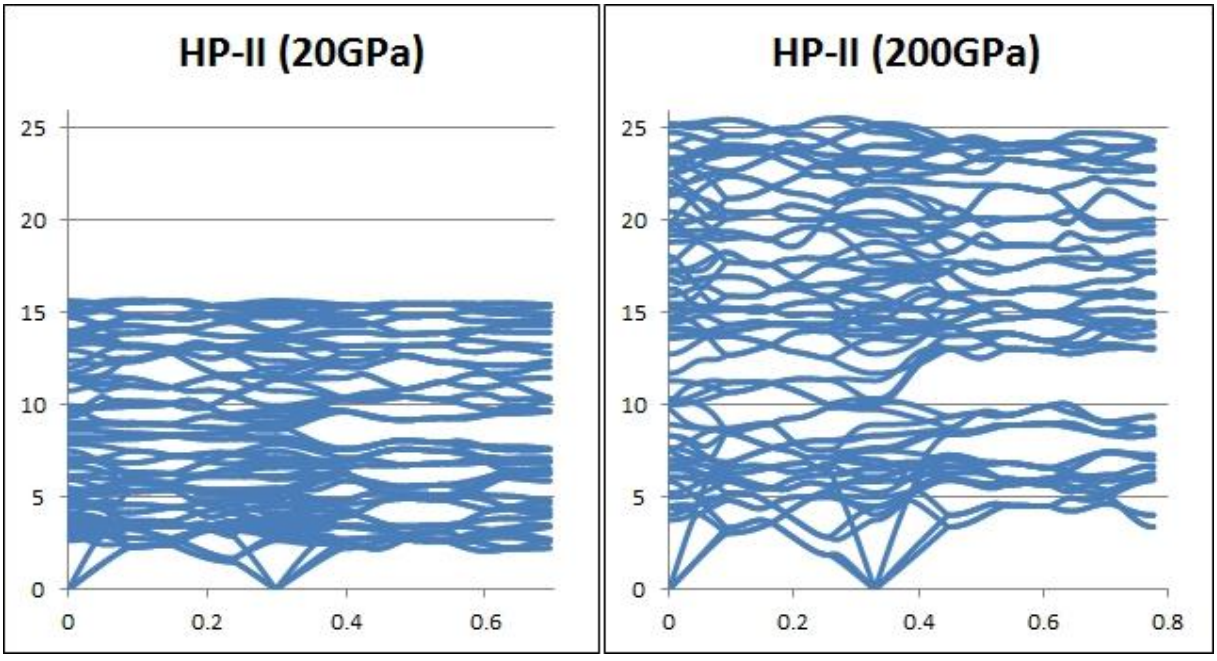


Fig. S7. The calculated band gap (DFT+U) for three experimentally observed forms of AgF_2; the vertical lines mark the approximate stability ranges.

S8. Analysis of phonons of HP-II phase at 20 GPa and 200 GPa.



No imaginary modes have been detected for the HP-II phase at 200 GPa.

S9. The .cif file of the HP-II structure at 250 GPa (theoretical DFT+U data).

```
_pd_phase_name                  'HP-II 250 GPa DFT'
_cell_length_a                  5.37061
_cell_length_b                  6.69718
_cell_length_c                  4.17178
_cell_angle_alpha               90
_cell_angle_beta                90
_cell_angle_gamma               90
_symmetry_space_group_name_H-M  'Pbcn'
_symmetry_Int_Tables_number     60

loop_
  _atom_site_label
  _atom_site_occupancy
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_B_iso_or_equiv
  _atom_site_type_symbol
  Ag1    1.0   0.572494   0.381317   0.015398   Biso  1.000000 Ag
  F1     1.0   0.250000   0.385745   0.821412   Biso  1.000000 F
  F2     1.0   0.404499   0.151591   0.141401   Biso  1.000000 F
```

References:

(1) Hull, S.; Berastegui, P. High-Pressure Structural Behaviour of silver(I) Fluoride. *J. Phys. Condens. Matter* **1998**, *10*, 7945–7955.

(2) Birch, F. Finite Elastic Strain of Cubic Crystals. *Phys. Rev.* **1947**, *71*, 809–824.

(3) Petříček, V.; Dušek, M.; Palatinus, L. Crystallographic Computing System JANA2006: General Features. *Zeitschrift für Krist. - Cryst. Mater.* **2014**, *229*, 345–352.

(4) Kurzydłowski, D.; Zaleski-Ejgierd, P. Hexacoordinated nitrogen(V) Stabilized by High Pressure. *Sci. Rep.* **2016**, *6*, 36049.

(5) Mazej, Z.; Goreshnik, E.; Jagličić, Z.; Gaweł, B.; Łasocha, W.; Grzybowska, D.; Jaroń, T.; Kurzydłowski, D.; Malinowski, P.; Koźminski, W.; et al. $KAgF_3$, K_2AgF_4 and $K_3Ag_2F_7$: Important Steps towards a Layered Antiferromagnetic fluoroargentate(II). *CrystEngComm* **2009**, *11*, 1702–1710.

(6) Romiszewski, J.; Grochala, W.; Stolarczyk, L. Z. Pressure-Induced Transformations of $Ag^{II}F_2$ — towards an “infinite Layer” d^9 Material. *J. Phys. Condens. Matter* **2007**, *19*, 116206.