Electronic Supplementary Information

Elusive AuF in the Solid State as Accessed via High Pressure Comproportionation

by Dominik Kurzydłowski and Wojciech Grochala

Contents.

1. Unit cell vectors, fractional atomic coordinates and enthalpy for C1, C2, T1 and T2 structures, as optimized for p=5 GPa (300 eV cutoff, 0.05 $Å^{-1}$ k-point grid).

Structure	Enthalpy /eV	Unit cell vectors /Å	Au(x,y,z)	F(x,y,z)
C1 (Fm-3m)	-1577.79	a = 4.999	0.0 0.0 0.0	0.5 0.5 0.5
C2 (Pm-3m)	-1578.03	a = 3.035	0.0 0.0 0.0	0.5 0.5 0.5
T1 ($I4_1$/amd)	-1578.27	a = 6.124 c = 7.711	0.0 0.0 0.0	0.0 0.25 0.192
T2 ($P4_2$/ncm)	-1578.21	a = 4.078 c = 8.430	0.0 0.0 0.0	0.25 0.25 0.187

2. Imaginary phonon frequencies at Γ for the T1 and T2 structures, as optimized with VASP at p=15 GPa.

Structure	Imaginary phonons /cm^{-1}
T1	-35; -27; -1*
T2	-169; -2*

* Deviation from 0 cm^{-1} for phonons with wavenumbers –5 cm^{-1} < ν < +5 cm^{-1} is within accuracy of the computational method. **C1** and **C2** do not have imaginary phonons at Γ.

3. Unit cell vectors, fractional atomic coordinates and enthalpy for O1, O2, O3, O4, O5, O6, O7, H1 and T3 structures, as optimized with CASTEP for p=5 GPa (300 eV cutoff, 0.05 Å^{-1} k-point grid).

Structure	Enthalpy /eV	Unit cell vectors /Å	Au(x,y,z)	F(x,y,z)
T3 (P4/nmm)[1]	-1578.30	a = b = 3.554 c = 4.616	0.0 0.5 0.355	0.0 0.5 0.876
O1 (Cmcm)[2]	-1578.49	a = 2.849 b = 5.304 c = 8.121	0.0 0.0 0.0	0.0 0.872 0.25
O2 (Cmmm)[3]	-1578.26	a = 5.128 b = 2.893 c = 3.887	0.0 0.0 0.0	0.5 0.0 0.5
O3 ($P2_12_12_1$)[4]	-1578.26	a = 6.284 b = 6.306 c = 7.472	0.249 0.250 0.001 0.5 0.499 0.251	0.513 0.247 0.440 0.999 0.221 0.189
O4 (Pmmn)[5]	-1578.46	a = 4.997 b = 2.898 c = 4.269	0.0 0.0 0.909	0.0 0.0 0.413
O5 (Pnma)[6,7]	-1578.45	a = 8.506 b = 5.017 c = 2.905	0.501 0.25 0.25	0.251 0.25 0.303
O6 (Cmcm)[6]	-1578.45	a = 5.034 b = 2.905 c = 8.495	0.0 0.5 0.0	0.0 0.446 0.25
O7 ($Pmn2_1$)[8]	-1578.49	a = 5.031 b = 8.178 c = 3.005	0.0 0.25 0.25	0.0 0.5 0.043
H1 (P6/mmm)[6]	-1578.48	a = b = 2.911 c = 4.249 γ = 120.0	0.0 0.00 0.0	0.0 0.0 0.5

[1] derived from **C1** by following an imaginary (-114 cm^{-1}) phonon at X (at 5 GPa); [2] derived from **T2** by following an imaginary (-169 cm^{-1}) phonon at Γ (at 5 GPa); tighter symmetry constraints lead to the **M2** C2/c structure, which in fact has a nearly identical H *vs.* p plot as **O1**; [3] derived from **C2** by following an imaginary (-22 cm^{-1}) phonon at M (at 5 GPa); [4] derived from **T1** by following an imaginary (-75 cm^{-1}) phonon at Z (at 5 GPa); [5] derived from **T3** by following an imaginary (-75 cm^{-1}) phonon at Z (at 5 GPa); **O4** has no imaginary phonons at Γ; [6] all three structures derived from **O4** by following an imaginary (-78 cm^{-1}) phonon at Z (at 5 GPa) and subsequent symmetry recognition at various thresholds; [7] following the imaginary -32 cm^{-1} phonon at Γ formally yields a monoclinic **M1** ($P2_1/c$) structure, which in

fact is nearly identical with **O5**; **M1** was not analyzed in detail; [8] derived from **O5** by following an imaginary (-158 cm^{-1}) phonon at Γ (at 5 GPa).

4. Unit cell vectors, fractional atomic coordinates and enthalpy for AuF_3 and Au, as optimized with CASTEP at p=5 GPa (300 eV cutoff, 0.05 $Å^{-1}$ k-point grid).

Structure	Enthalpy /eV	Unit cell vectors /Å	Au(x,y,z)	F(x,y,z)
Au (Fm3m)	-917.07	a = 4.134134	0.0 0.0 0.0	n. a.
AuF_3 ($P6_122$)	-2901.65	a = 5.058 b = 5.058 c = 17.063 γ = 120.0	0.482 0.241 0.083	0.797 0.325 0.004 0.151 0.0 0.0

5. Unit cell vectors, fractional atomic coordinates, and enthalpy for O1 and T3 structures, as optimized with CASTEP at p=5 GPa (increased accuracy, 600 eV cutoff, 0.04 $Å^{-1}$ k-point grid).

Structure	Enthalpy /eV	Unit cell vectors /Å	Au(x,y,z)	F(x,y,z)
O1	-1578.955	a = 2.887 b = 5.128 c = 8.089	0.0 0.0 0.0	0.0 0.871 0.25
T3	-1578.851	a = 3.710 c = 4.380	0.0 0.5 0.377	0.0 0.5 0.889

6. Population analysis and the closest interatomic separations for O1 and T3 structures, as optimized with CASTEP at p=5 GPa (increased accuracy, 600 eV cutoff, 0.04 $Å^{-1}$ k-point grid).

Structure	q(Au) /e	q(F) /e	R(AuF) /Å	R(AuAu) /Å
O1	0.40	-0.40	2.127	2.887 2.942
T3	0.42	-0.42	2.141	2.834

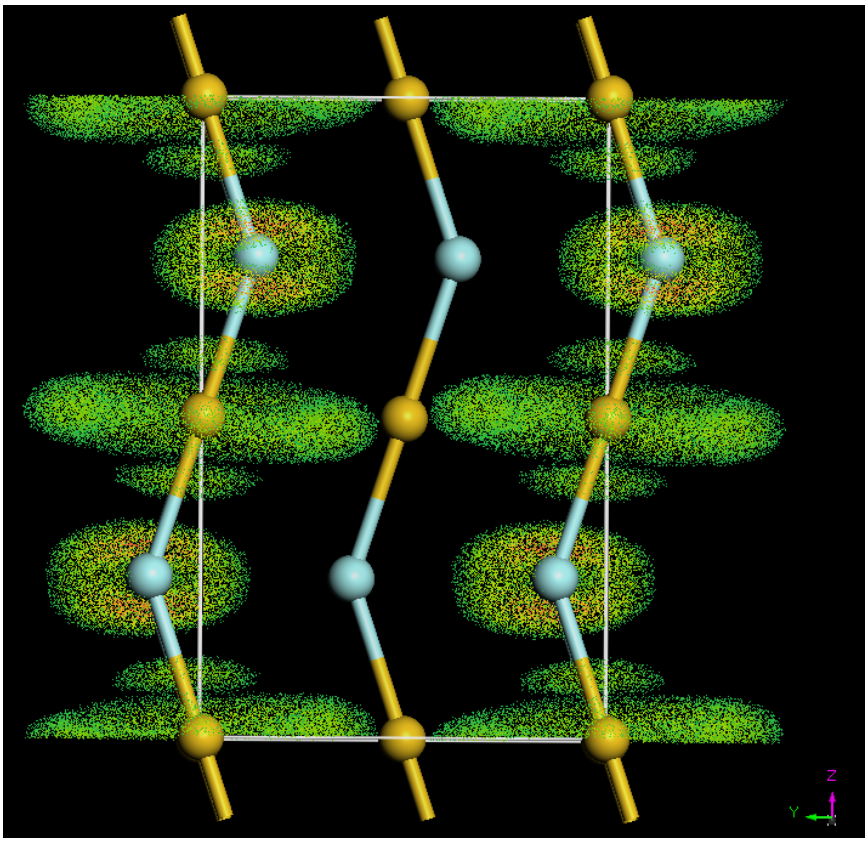
7. Phonon wavenumbers (ν) at Γ for the O1 structure at p=5 GPa (symmetry point group: D_{2h}).

ν /cm^{-1}	**Assignement**	**Symmetry**	**IR/Raman**
-4*	Acoustic (z)	B_{1u}	+/-
-3*	Acoustic (x)	B_{3u}	+/-
-2*	Acoustic (y)	B_{2u}	+/-
40	Bending of the FAuF angle	A_u	-/-
50	Bending of the FAuF angle	B_{1u}	+/-
81	Hindered rotation of the AuF chains	B_{1g}	-/+
135	Bending of the zigzag chain out of plane	B_{2u}	+/-
135	Bending of the zigzag chain out of plane	B_{3u}	+/-
163	Bending of the zigzag chain within its plane + symmetric stretch of the AuF bonds	A_g	-/+
266	Antisymmetric stretch and deformation of the AuF bonds	B_{2u}	+/-
398	Symmetric stretch of the AuF bonds	B_{3g}	-/+
498	Antisymmetric stretch of the AuF bonds	B_{1u}	+/-

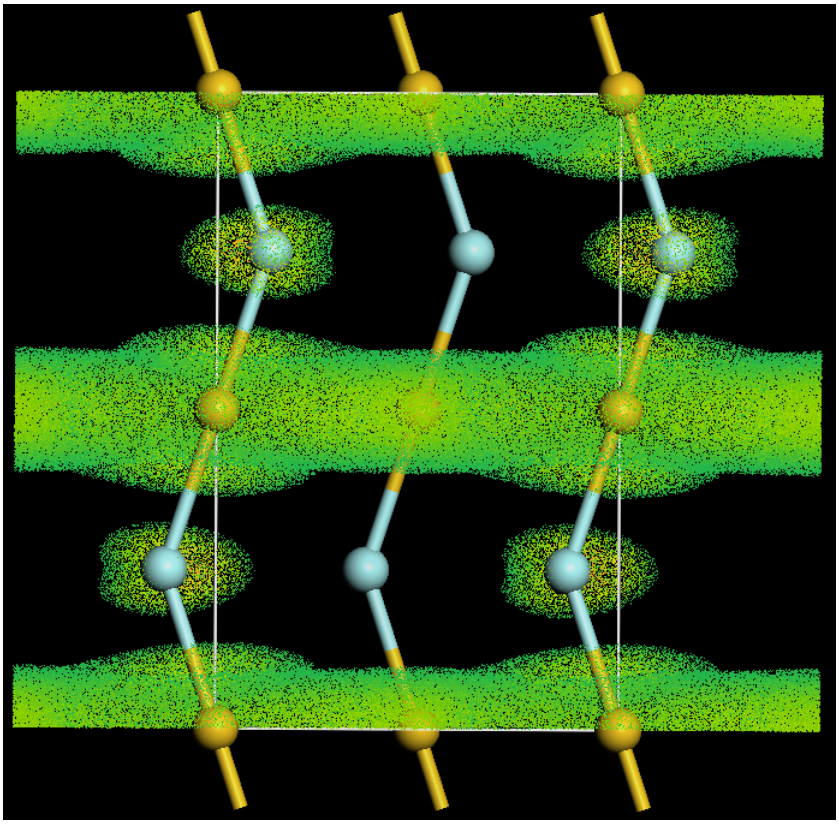
* Deviation from 0 cm^{-1} for phonons with wavenumbers –5 cm^{-1} < ν < +5 cm^{-1} is within accuracy of the computational method.

8. Electron density integrated over bands No.18 (from –1.990 eV to +0.358 eV), No.19 (from –0.674 eV to +3.064 eV) and No.20 (from +0.786 eV to +3.707 eV) for the O1 structure at 5 GPa. View along the crystallographic a axis is shown. Bands 18 and 19 cross the Fermi level (displayed density: 0.02 eV/ Å ^{3} and higher).

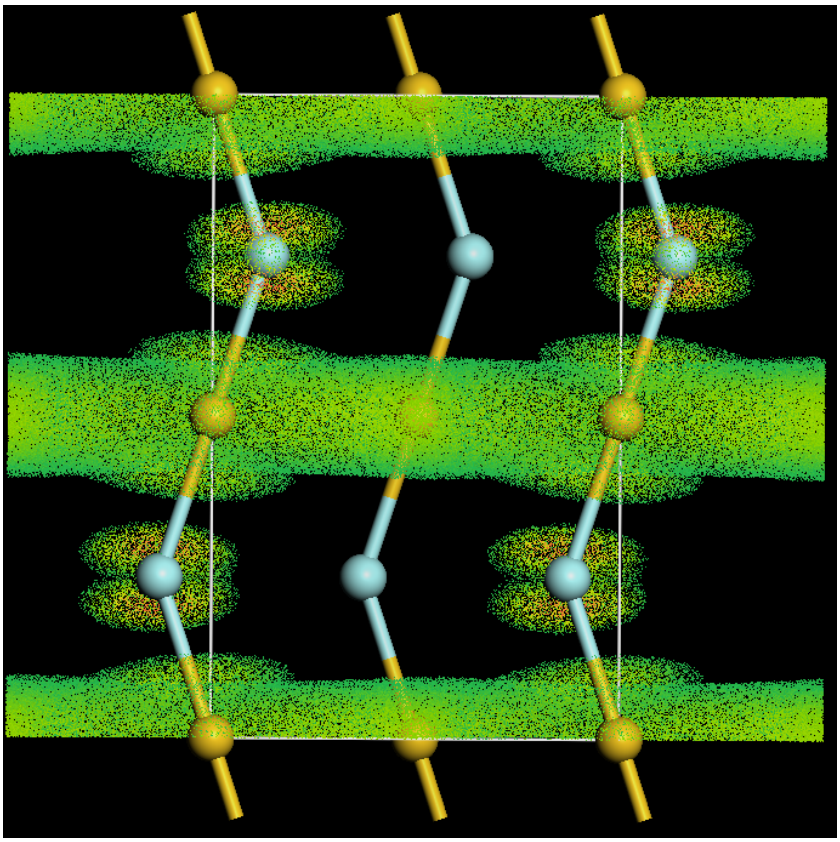
No.18:



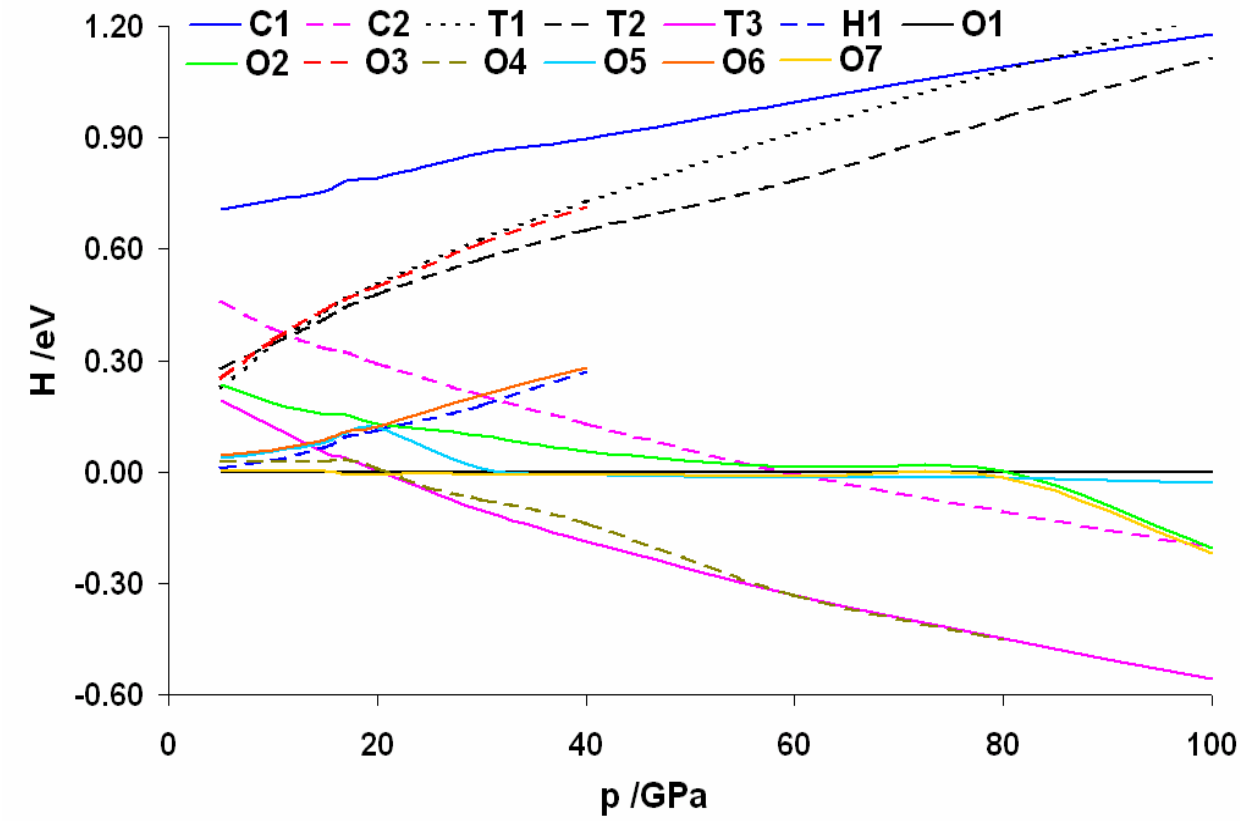
No.19:



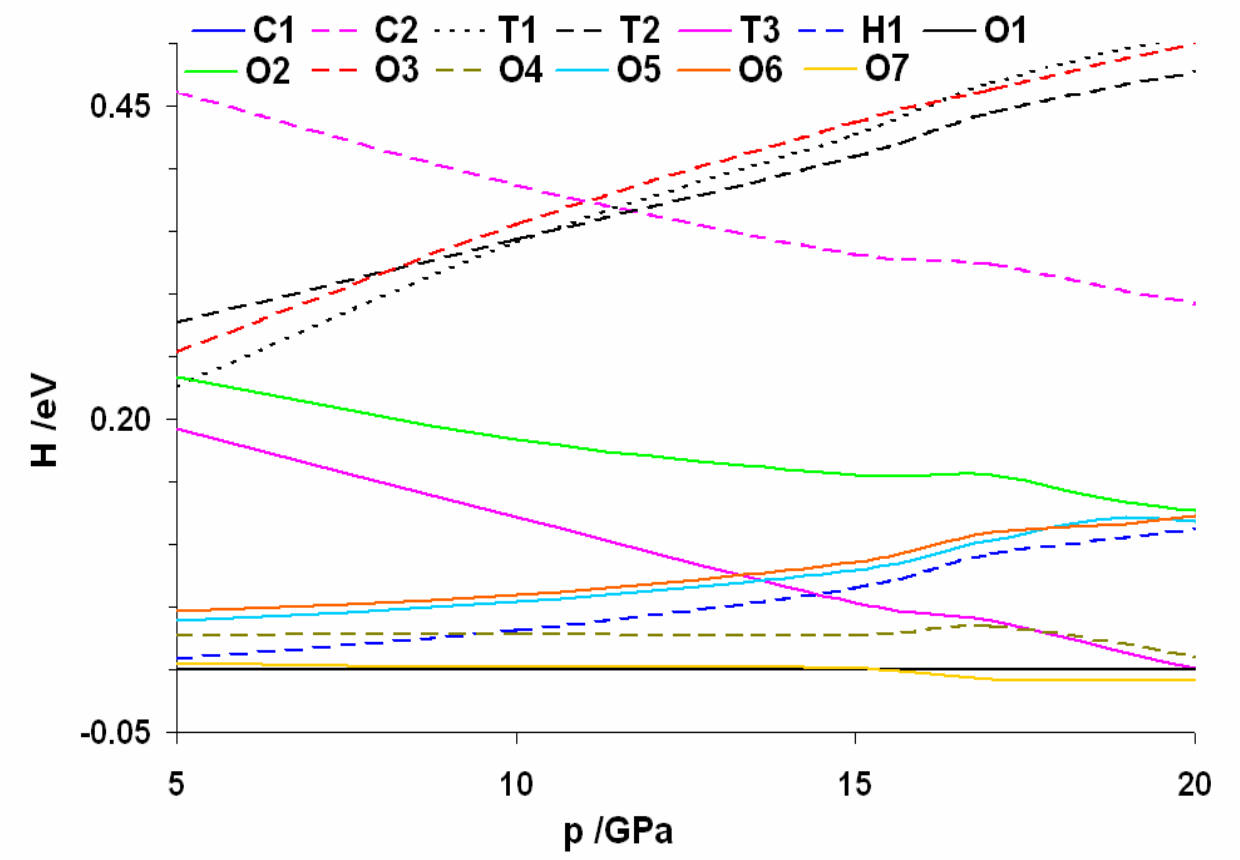
No.20:



9. Plot of enthalpy for all structures studied for 5 GPa ≤ p ≤ 100 GPa.



Zoom at the 5–20 GPa region:



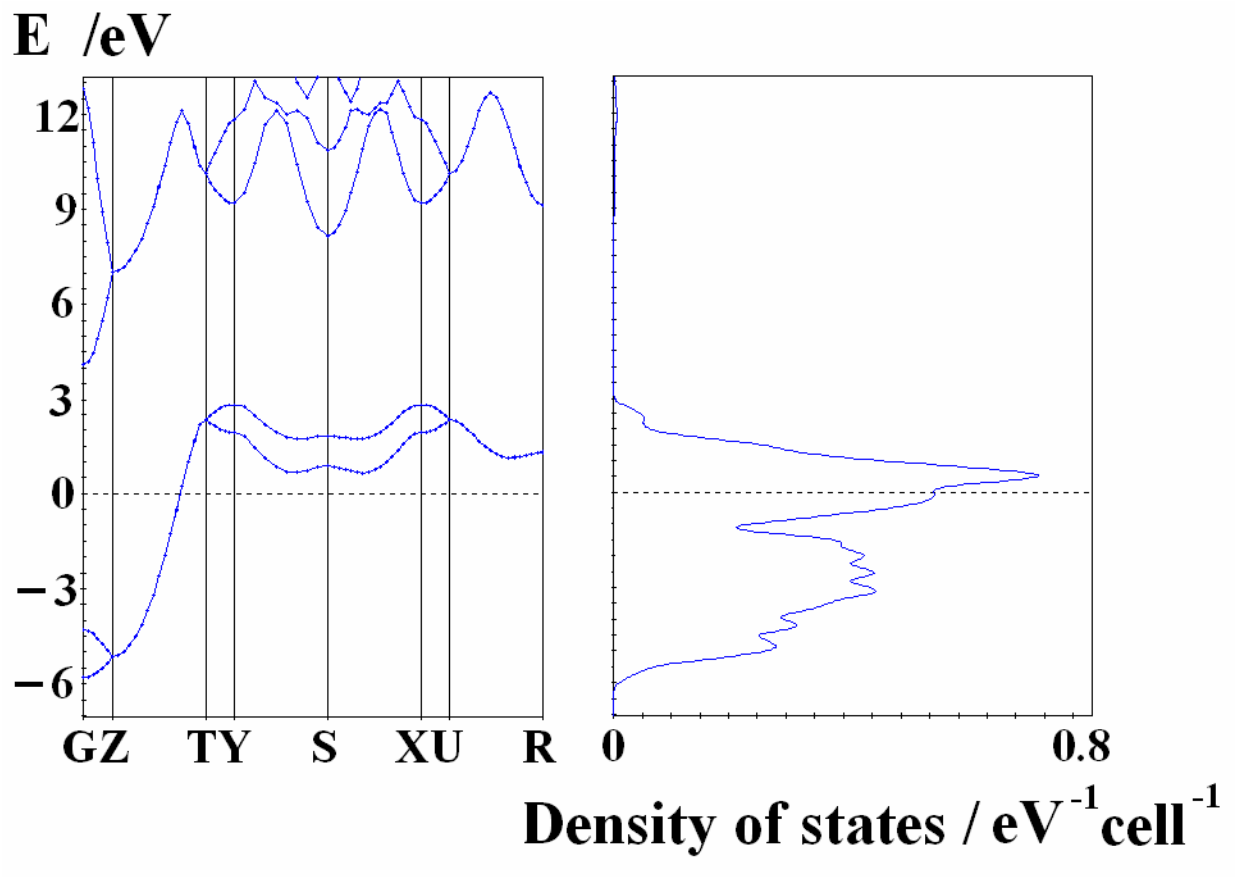
10. Estimate of the formation pressure of AuF using the common tangent method (increased accuracy, 600 eV cutoff, 0.04 $Å^{-1}$ k-point grid).

ΔH(products/substrates) @ 5 GPa = 0.10 eV
ΔV(products/substrates) @ 5 GPa = –0.95 $Å^3$
P(formation) = 5 – 160.2177 x ΔH/ΔV = 22.6 GPa

Product (AuF) was assumed to adopt the **O1** structure. Analogous calculation shows that the **T3** structure is *not* preferred in the low-pressure regime, in contrast to calculations using 300 eV cutoff; the estimated pressure of the **O1**/**T3** phase transition is as large as 86.7 GPa.

11. Band structure and DOS for cell containing H atoms in the O1 structure at p=5 GPa.

The O1 structure was modified in such way, that all F atoms were removed and all Au atoms were substituted with H atoms, while keeping the fractional atomic positions. Then the unit cell vectors were decreased in such way that the ratio of the shortest resulting H…H distance to the shortest initial Au…Au distance was identical as the ratio of the van der Waals radii of H and Au atoms. Then, the electronic band structure and DOS were calculated, yielding the following result:



The partially–occupied bands originating mainly from the 1s orbitals of H resemble a lot the set of two partially occupied and two unoccupied bands originating mainly from the 6s orbitals of Au (detected for the AuF in the O1 structure) in terms of dispersion of these bands along the **k** vector. The striking similarity testifies that Au indeed resembles H, as pointed out in many papers by P. Pyykkö.