Elusive AuF in the solid state as accessed *via* high pressure comproportionation†‡

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Density Functional Theory (DFT) calculations indicate that AuF might be synthesized at 22.6 GPa from AuF_3 and Au (1 : 2), and subsequently quenched down to at least 5 GPa in the *Cmcm* (bent chain) structure.

The chemistry of the coinage metals is rich and surprising. One particularly interesting feature is relativistic destabilization of the 5d valence set[1] which leads to high oxidation states (usually +3 but also +5[2]) for the heaviest group 11 metal, gold. This is in contrast with the behaviour of gold's lighter congeners, which usually adopt lower oxidation states (copper +2, silver +1[3]). In spite of its attractive closed-shell $d^{10}s^0$ electronic configuration, the oxidation state +1 of gold is often unstable as it tends to disproportionate into more energetically favoured Au(+3) and Au(0). Indeed, despite numerous efforts, the 'simplest' amongst fluorides of gold, AuF, has not been synthesized in bulk (even in minute amounts) to this day. Gold monofluoride has been characterized only in its molecular form in the gas phase,[4] and the search for a successful synthetic pathway towards AuF in the solid state is still on.[5]

In this account we would like to propose a new high pressure route towards AuF. Utilization of high pressures is an attractive alternative to wet chemistry approaches since both the bonding patterns and thermodynamics of chemical reactions may be severely altered when a system is subjected to, say, 100 GPa (= 1 mln atm).[6] As we will show, the 1 : 2 mixture of AuF_3 and elemental Au is likely to transform at *ca.* 22 GPa into genuine AuF, which in turn could subsequently be decompressed to low pressures.

Inspired by previous theoretical contributions on possible ambient-pressure polymorphs of AuF,[7] in our computational study§ we have taken into account four important structure types, two cubic: NaCl (**C1**) and CsCl (**C2**), and two tetragonal: AuCl (**T1**, Fig. 1) and AuI (**T2**, Fig. 1). We have omitted the zincblende type, as it had large energy and low density as compared to other structures[7] and therefore it was not competitive in enthalpy at either ambient or elevated pressure.

Structures relaxed at 5 GPa may be arranged in order of their increasing stability: **C1** < **C2** < **T2** < **T1** (see ESI†), confirming the previously established preference for the ambient-pressure covalent chain-like structures with two-coordinate Au(I) centres over the predominantly ionic structures with large coordination numbers of Au.[7] To our surprise, calculations of the harmonic phonon frequencies for each of these structures preoptimized at 5–15 GPa§ have yielded at least one imaginary eigenvalue (see ESI†) at Γ. This suggests that all high-symmetry structures considered in previous theoretical studies[7] are not genuine local minima at these pressures.

We therefore distorted each of the parent structures along the normal mode of the imaginary phonon§ and reoptimized AuF in four new so-derived structures (see ESI† and Fig. 1). This immediately brought a decrease in enthalpy for all structures (Fig. 2). Repeating this procedure until all phonons were real, we found few additional structures (see ESI†).

Two new polymorphs: tetragonal **T3** and orthorhombic **O1** (Fig. 1), derived from **C1** and **T2**, respectively, are the most important. **O1** is *the* most stable structure of AuF at 5 GPa that we have detected,[8] since it outperforms the former **T1** candidate[7] in enthalpy by over 0.2 eV (Fig. 2). **O1** is

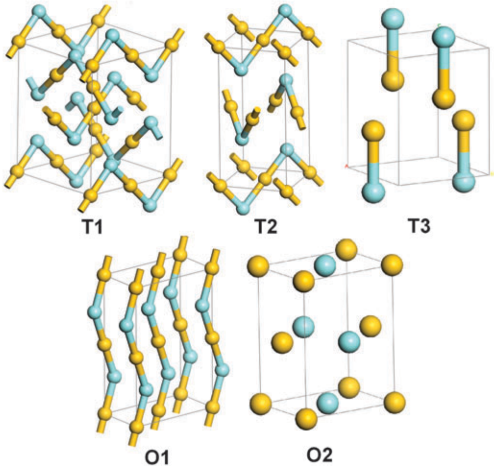

Fig. 1 Illustration of five important polymorphs of AuF at 5 GPa: **T1**, AuCl type ($I4_1/amd$, $Z = 8$), **T2**, AuI type ($P4_2/ncm$, $Z = 4$), and three new types found in this work: tetragonal **T3** ($P4/nmm$, $Z = 2$) and orthorhombic **O1** ($Cmcm$, $Z = 4$), and **O2** ($Cmmm$, $Z = 2$). Au – yellow, F – blue balls.

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‡ This paper is dedicated to Peter A. Schwerdtfeger, in recognition of his landmark contributions to the theoretical chemistry of heavy elements.

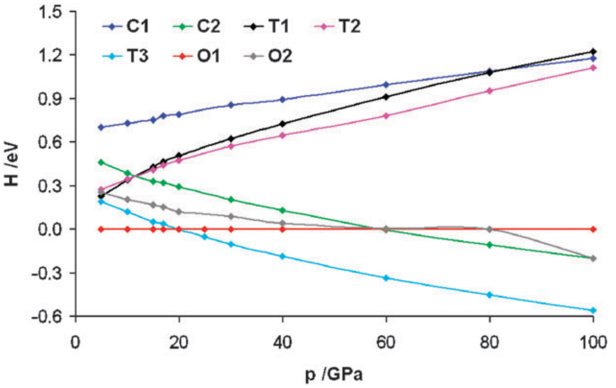

Fig. 2 Enthalpy per one AuF unit (H/eV) *vs.* pressure (p/GPa) for seven polymorphs of AuF. Enthalpies are referenced at each pressure to that for the **O1** structure. Note the phase transition from **O1** to **T3** at 20 GPa.

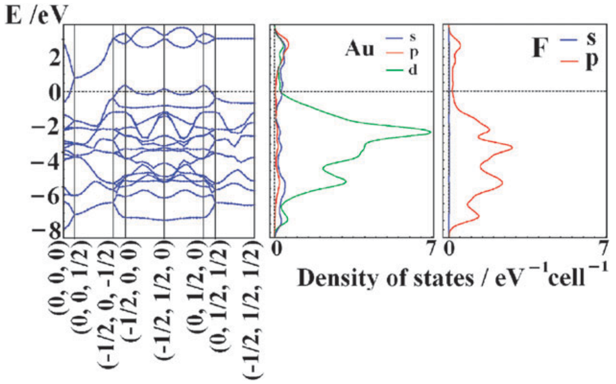

Fig. 3 Electronic band structure and atomic contributions to the electronic DOS, F(s,p) and Au(s,p,d), for AuF in the **O1** structure (5 GPa).

predominant in the phase diagram of AuF up to 20 GPa, when a phase transition to the **T3** polymorph is expected.

Crystal structure **O1** at 5 GPa (Fig. 1) exhibits infinite one-dimensional chains of the AuF stoichiometry similar to those found in the other two covalent structures studied.[7] AuF thus has a polymeric nature, with perfectly linear $[AuF_2]$ dumbbells sharing every F atom. The chain is bent at the F bridges, with a AuFAu angle of 143°. On the other hand **T3** has a pseudo-molecular structure with the isolated [AuF] units interacting with one another *via* secondary Au···F contacts; the [AuF] units may be derived from linear $[AuF_{2/2}]_\infty$ chains *via* a Peierls-like pairing distortion. As the **T3** becomes more compact at higher pressures ($>$20 GPa), the Au–Au separations decrease and the puckered [Au] sheets may be formally distinguished (Fig. 5).

The covalent structures of AuF (Fig. 1) differ in the mutual orientation of the $[AuF_{2/2}]_\infty$ chains. The chains run in two perpendicular directions for **T1** and **T2**, but they are aligned in the same direction for **O1** and **T3**. The shortest Au–Au separation seen for **O1** and **T3** (2.85 Å) is much shorter than twice the ambient pressure van der Waals radius of the Au atom (2 × 1.66 Å), and comparable to the calculated Au–Au bond length in fcc gold (2.923 Å at 5 GPa). The strength of the aurophilic interactions[9] which stabilize these structures at a modest compression should be tested using methods which explicitly treat the weak interactions.

Analysis of the electronic band structure and electronic DOS for the **O1** structure at 5 GPa (Fig. 3) reveals that AuF should be metallic. The bands cross the Fermi level: one close to Γ (orbital 19 in the ESI†) and another one close to T, Y, X and U (orbital 18). Band 18 is built mostly from the combination of $d(z^2)_{Au}$, s_{Au} and p_F orbitals with charge density propagating along the $[AuF_{2/2}]_\infty$ chains (see ESI†). Apparently, two of four ($Z = 4$) relativistically-stabilized $6s_{Au}$ orbitals firmly penetrate the $5d_{Au}$ set. Band 19 has a large dispersion and, accordingly, significant overlap of diffuse atomic orbitals of Au may be seen in two directions perpendicular to the $[AuF_{2/2}]_\infty$ chains. The charge on F in a *monofluoride* of gold at 5 GPa (−0.40 e) is similar to one found for a *difluoride* of Ag at 50 GPa,[10] and even less negative than that computed for the infinite-layer AgF_2 at ambient pressure (−0.50 e),[11] testifying to unusually large covalence of the Au(I)–F bond. Indeed, bands directly above the Fermi level have a substantial share of F(p) states. This feature is anomalous but not unexpected for chemical connections of *the* most electronegative transition metal.

Analysis of the phonon dispersion curves and phonon density of states (DOS) for **O1** at 5 GPa (Fig. 4) helps to identify major phonon branches. The highest-frequency Au···F stretching modes appear at 407–498 cm^{-1} reconfirming that the covalent Au–F bonds are quite stiff at 5 GPa.

The **O1** structure seems to be a viable candidate for the lowest-enthalpy structure of AuF in a low pressure regime (5–20 GPa). But how could AuF be synthesized?

The simplest reaction path for the synthesis of AuF seems to be that of comproportionation between Au and AuF_3.[13]

$$2/3\ \mathrm{Au} + 1/3\ \mathrm{AuF_3} \rightarrow \mathrm{AuF} \qquad (1)$$

The reaction described by eqn (1) is not favoured at 5 GPa (Fig. 5) because of the positive value of the reaction enthalpy. Therefore disproportionation of AuF is facilitated thermodynamically at 5 GPa and certainly also at ambient pressure. The fate of reaction (1) could, however, be reversed under pressures larger than 22 GPa (Fig. 5), resulting in formation of AuF in the **T3** structure. Since the pressure of the **O1**/**T3** phase transition is comparable to the pressure of AuF formation, we

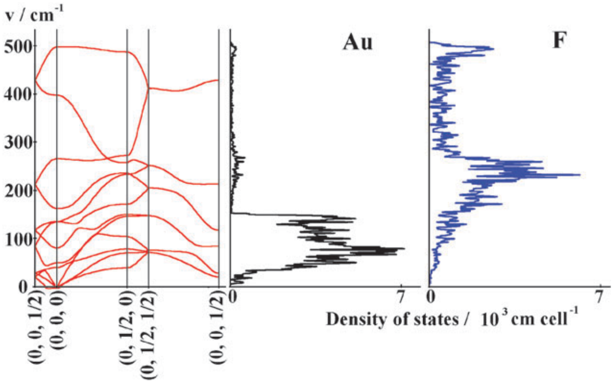

Fig. 4 Phonon dispersion curves and atomic contributions to the phonon DOS for AuF in the **O1** structure (5 GPa).[12]

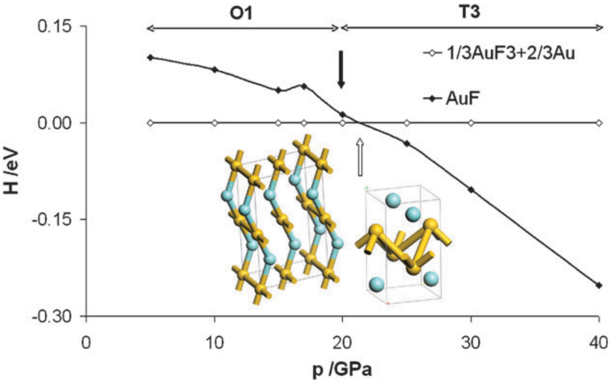

Fig. 5 Enthalpy, H/eV, of AuF (filled diamonds) for its **O1** polymorph up to 20 GPa (filled arrow), and **T3** at larger pressures, as referred to enthalpy of the [2/3 Au + 1/3 AuF_3] mixture (empty diamonds). Comproportionation is expected at about 22 GPa (empty arrow). The structures of **O1** and **T3** at 20 GPa are also shown.

have recalculated both values with more accuracy (600 eV cutoff, denser k-point grid, and smaller SCF tolerance, see ESI†) using the standard 'linear tangent' method. It turns out that the pressure of the **O1**/**T3** phase transition is in fact larger than the pressure of formation of AuF in the **O1** structure (22.6 GPa),[14] which means that AuF should adopt the **O1** structure upon formation. Importantly, no imaginary phonons are detected for **O1** at 5 GPa (Fig. 4) and thus **O1** should be metastable at this pressure (it should *not* undergo the thermodynamically-preferred decomposition to 2/3 Au and 1/3 AuF_3, Fig. 5).

In conclusion, we have shown that the elusive AuF in the solid state might be obtained *via* comproportionation of Au(0) and Au(+3) at $p > \sim 22$ GPa; such pressures are now routinely achieved in diamond anvil cells.[6] The product is likely to survive a careful low-temperature decompression down to near-ambient pressures, yielding a metastable **O1** polymorph of AuF.

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Notes and references

§§ Our DFT calculations were performed within the general gradient approximation (GGA), using the Perdew–Burke–Ernzerhof exchange-correlation functional, and the ultrasoft Vanderbilt-type relativistic potentials, as implemented in the CASTEP code (Materials Studio). For each structure under a given pressure (from 5 to 100 GPa) we have relaxed the unit cell vectors and fractional atomic positions, while keeping the symmetry constraints, and we have calculated the total enthalpy. The k-point sampling was generated *via* the Monkhorst–Pack scheme with a uniform spacing of about 0.05 $Å^{-1}$ for all structures (volume dependent setting). We used 300 eV cut-off for the kinetic energy of the plane waves, and SCF tolerance of 2×10^{-6} eV per atom. The electronic band structure and DOS (at k-point grid of 0.025 $Å^{-1}$) were calculated for the **O1** structure which was first reoptimized with 600 eV cut-off, k-point grid (0.04 $Å^{-1}$), and SCF tolerance of 10^{-6} eV per atom (ESI†). Our calculations took into account only the electronic contribution to the total energy without correction for zero-point vibrational energy. No spin polarization was used, as is customary for closed-shell species. The calculations of the phonon dispersion and phonon density of states were performed using PHONON code (MedeA). We used supercells constructed from conventional cells preoptimized with the cut-off of 400 eV using VASP. We used the following supercells: $4 \times 2 \times 2$ for **O1** ($Z = 32$), $2 \times 2 \times 1$ for **T1** ($Z = 32$), $2 \times 2 \times 1$ for **T2** ($Z = 16$), $3 \times 3 \times 2$ for **T3** ($Z = 36$), $2 \times 2 \times 2$ for **C1** ($Z = 32$) and $3 \times 3 \times 3$ for **C2** ($Z = 27$). While distorting the high-symmetry structures we have usually followed the imaginary phonons of the largest absolute frequency. The values of partial DOS (Figs. 3 and 4) are shown for four atoms of each type together ($Z = 4$). Formation of AuF_2 and of various mixed valence fluorides of gold was not taken into account in our study. Fluorides of Au(II) are scarce[15] and AuF_2 should have an unusually strong tendency to disproportionate.[10,16] Possible phase transitions for AuF_3 were not considered, except for the RuO_3-like polymorph, which is not competitive in enthalpy over the entire pressure range studied.

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