Stable Polymorphs of Elusive AuF at High Pressure As Accessed From Phonon Calculations

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Introduction

Gold is puzzling element as its properties and chemistry differ dramatically from those of its lighter congeners. This is a result of strong relativistic effects that influence the valence electrons of gold [1]. Despite numerous attempts, and in contrast to AgF, AuF has been characterized only in the gas phase [2], and the search for a synthetic path leading to bulk AuF is still on [3]. Recently a solid state DFT study of possible polymorphs of AuF was carried out [4]. This work inspired us to investigate whether AuF could be synthesized at high pressures (>1 GPa), as the thermodynamics of chemical reactions can be severely altered in such conditions [5]. Hypothetical high pressure polymorphs of AuF have not been studied before.

Properties of gold: Basics

- Electronic configuration: $[Xe]4f^{14}5d^{10}6s^1$
- Oxidation states: 0, +1, +3, +5 (rare: –1 , +2)
- Electronegativity (Pauling): 2.54 (*vs.* carbon: 2.55)
- Au(I) often disproportionates to Au(0) and Au(III)
- Strong relativistic effects: stabilization of the 6s and destabilization of the 5d electrons

Our goals

- To verify whether the ambient pressure polymorphs of AuF [4] (NaCl type - **C1**, CsCl type - **C2**, AuCl type - **T1**, AuI type - **T2,** Fig. 1) proposed earlier are genuine minima on the potential energy surface
- To gain insight into the thermodynamic stability at high pressure of these and of other hypothetical polymorphs of AuF
- To examine the possibility of synthesizing bulk AuF from a 1:2 mixture of AuF_3 and Au under high pressure (Eq. 1) and quenching the product to ambient pressure:

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

Results

- Structures **C1**, **C2**, **T1**, **T2** exhibit large phonon instabilities (Fig. 2). This suggests that all high symmetry structures considered in previous theoretical studies [4] are not true local minima at high pressure
- By distortion of the parent structure along the normal mode of the imaginary phonon we reached four new structures (**T3**, **O1**, **O2**, **O3** Fig. 1) and subsequently optimized their geometry over a broad pressure range (Fig. 3)
- Structures **T3, O1**, **O2**, **O3** are energetically more competitive than their parent structures (Fig.3)
- More precise calculations (cut-off 600 eV, denser k-point sampling) indicate that AuF in the **O1** structure could be synthesized at 22.6 GPa ('common tangent' extrapolation)
- The **O1** structure shows no imaginary modes at 5 and 15 GPa which indicates that AuF could be quenched down from 22.6 GPa to at least 5 GPa (Fig. 3)

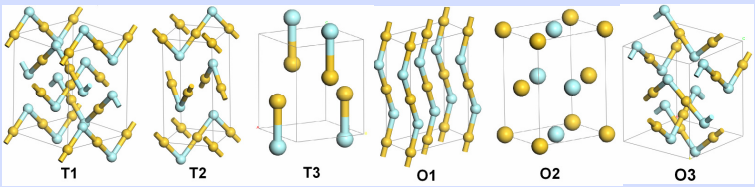

*Fig 1 Five important polymorphs of AuF at 5 GPa: **T1**, AuCl type (I4$_1$/amd, Z=8), **T2**, AuI type (P4$_2$/ncm, Z=4), and four new types found in this work: tetragonal **T3** (P4/nmm, Z=2) and orthorhombic: **O1** (Cmcm, Z=4) , **O2** (Cmmm, Z=2) and **O3** (P2$_1$2$_1$2$_1$, Z=8). Au-yellow, F-blue balls*

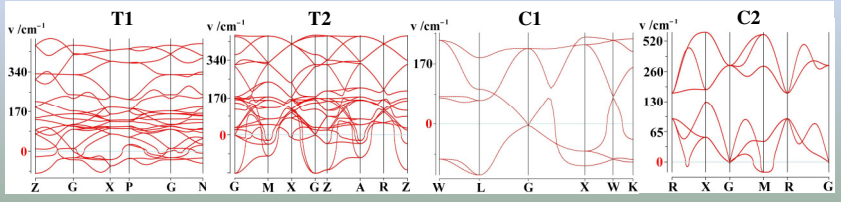

*Fig. 2 Phonon dispersion curves for four hypothetical polymorphs of AuF at 15 GPa: **T1**, **T2**, and at 5 GPa: **C1**, **C2***

Conclusions

- Elusive AuF in the solid state might be obtained via comproportionation of Au(0) and AuF_3 at p > ~22 GPa (such pressures are now routinely achieved in diamond anvil cells) [6]
- The reaction product is likely to survive a low temperature decompression; the **O1** polymorph of AuF is metastable at 5 GPa [6]

Outlook

- Possibility of an adduct formation between AuF and Xe is currently under investigation in our laboratory

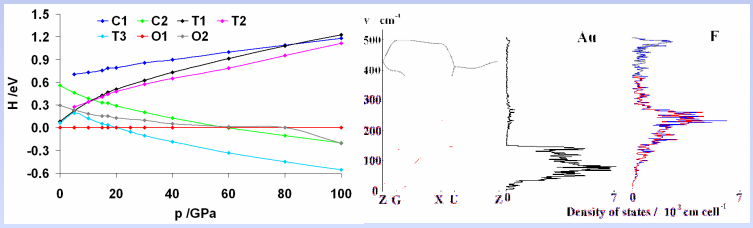

*Fig. 3 Enthalpy per one AuF unit (H /eV) vs. pressure (p /GPa) for seven polymorphs od AuF (left). Enthalpies are referenced at each pressure to that for the **O1** structure (300 eV cut-off). Phonon dispersion and atomic contributions to phonon DOS for AuF in the **O1** structure (right) (400 eV cut-off)*

Methodology

- Geometry optimization: CASTEP, VASP; phonon frequencies: linear response method (PHONON)
- Density Functional Theory within the GGA approximation
- Perdew-Burke-Ernzerhof exchange-correlation functional
- Ultrasoft Vanderbilt-type relativistic pseudopotentials
- Typical spacing of k-points: 0.05 $Å^{-1}$; SCF tolerance: $2 \cdot 10^{-6}$ eV/atom
- Kinetic energy cut-off: 300 eV (CASTEP) and 400 eV (VASP); 600 eV (CASTEP) for electronic band structure calculations and for precise 'common tangent' extrapolations
- Supercells used in PHONON: 4x2x2 for **O1** (Z=64), 2x2x1 for **T1** (Z=32), 2x2x1 for **T2** (Z=16), 3x3x2 for **T3** (Z=36), 2x2x2 for **C1** (Z=32) and 3x3x3 for **C2** (Z=27)

References

[1] P. Pyykkö, Angew. Chem. Int. Ed. Engl. **43** (2004) 4412.

[2] K. L. Saenger and C. P. Sun, Phys. Rev. A **46** (1992) 670; P. Schwerdtfeger *et al.*, Angew. Chem. Int. Ed. Engl., **33** (1994) 212; C. J. Evans and M. C. L. Gerry, J. Amer. Chem. Soc. **122** (2000) 1560; F. Mohr, Gold Bull. **37** (2004) 164.

[3] S. Seidel and K. Seppelt, Science **290** (2000) 117.

[4] T. Sohnel, H. Hermann and P. Schwerdtfeger, Angew. Chem. Int. Ed. Engl., **40** (2001) 4382; T. Sohnel, H. Hermann and P. Schwerdtfeger, J. Phys. Chem. B. **109** (2005) 526.

[5] W. Grochala, R. Hoffmann, J. Feng, and N. W. Ashcroft, Angew. Chem. Int. Ed. Engl. **46** (2007) 3620

[6] D. Kurzydłowski and W. Grochala, manuscript submitted to Chem. Comm.