

# Experimental determination of the H–Hf phase diagram using *in situ* neutron diffraction

Maxime Dottor<sup>a</sup>, Jean-Claude Crivello<sup>a</sup>, Laetitia Laversenne<sup>b</sup>, Jean-Marc Joubert<sup>a,\*</sup>

<sup>a</sup> Univ Paris Est Creteil, CNRS, ICMPE, UMR 7182, 2 rue Henri Dunant, 94320 Thiais, France

<sup>b</sup> University Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, 38000 Grenoble, France

\* Corresponding author. [jean-marc.joubert@cnr.fr](mailto:jean-marc.joubert@cnr.fr)

## Figures

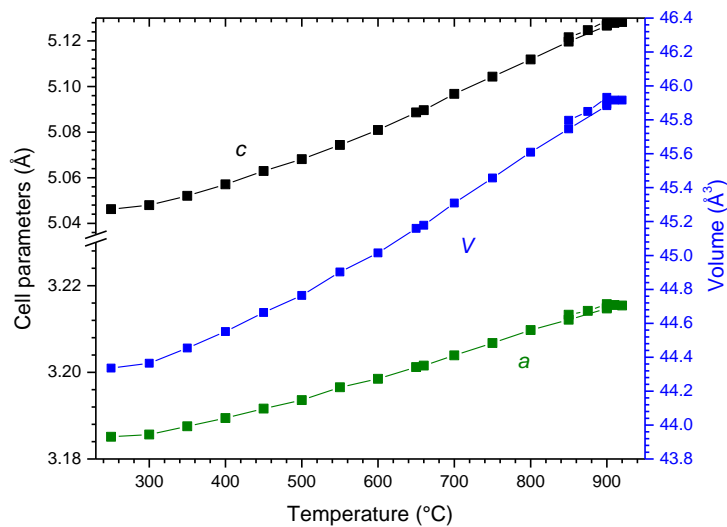


Figure S1. Cell parameters and volume of the  $\alpha$ -Hf phase as a function of temperature in a sample of initial composition HfD<sub>0.217</sub> (experiment 1). For cell parameters, error bars (0.001 Å) are commensurate with the symbol size.

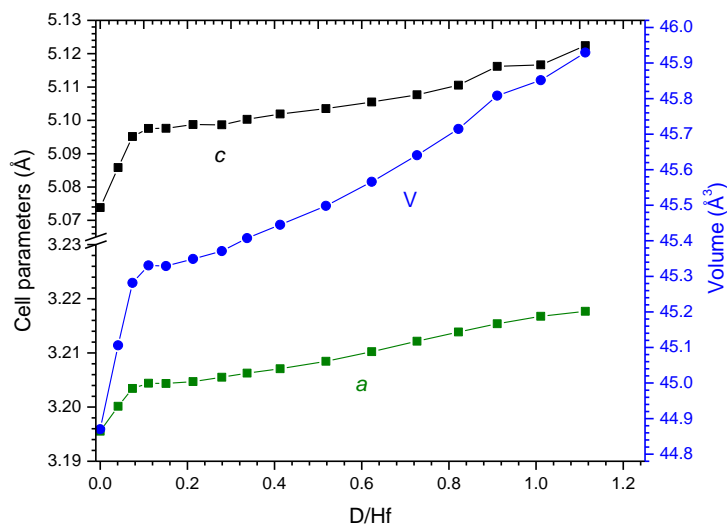


Figure S2. Cell parameters and volume of  $\alpha$ -Hf phase as a function of overall deuterium content at 700 °C (experiment 1). For cell parameters, error bars (0.001 Å) are commensurate with the symbol size.

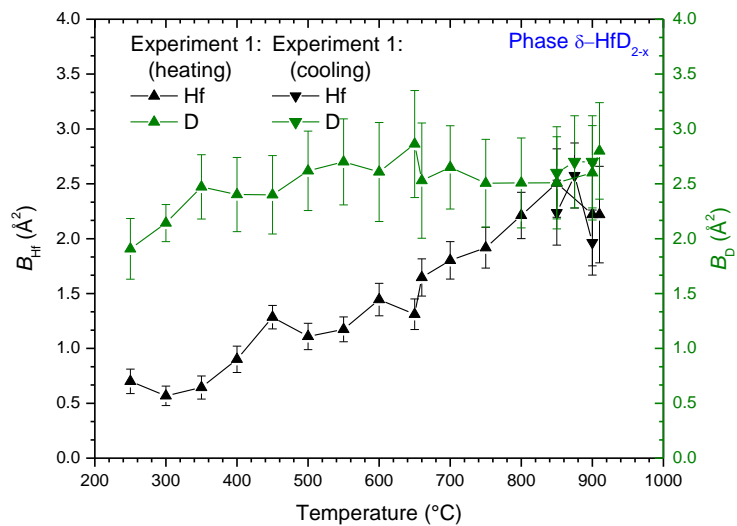


Figure S3. Displacement parameters of the  $\delta\text{-HfD}_{2-x}$  phase as a function of temperature (experiment 1).

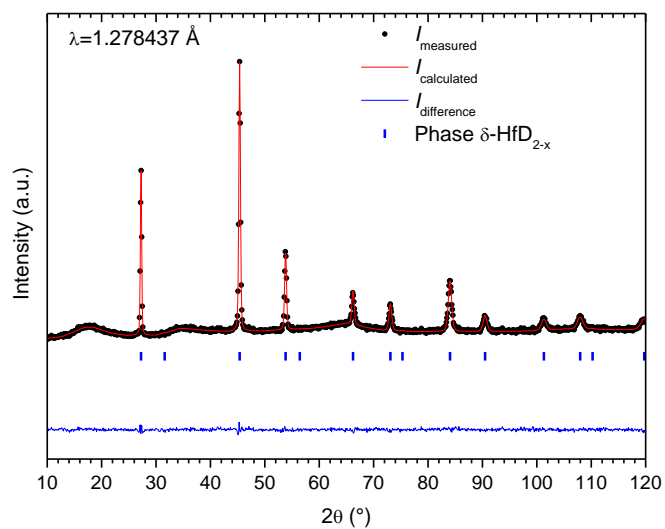


Figure S4. ND pattern of  $\text{HfD}_{1.215}$  at  $700^{\circ}\text{C}$  (experiment 1).

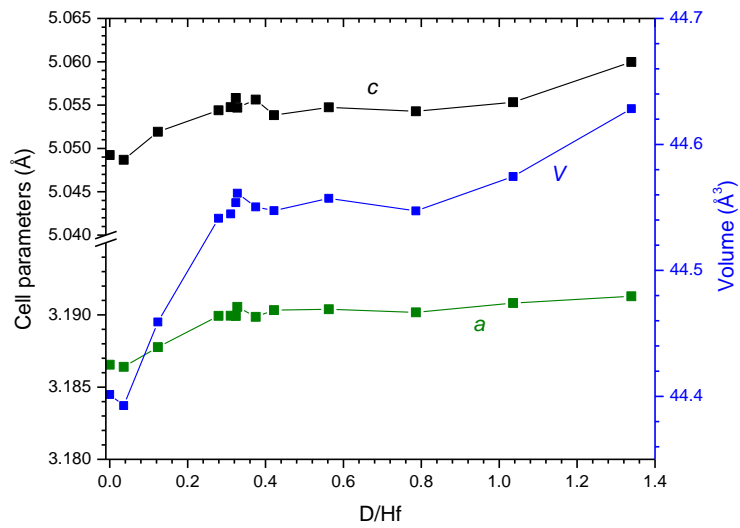


Figure S5. Cell parameters and volume of  $\alpha$ -Hf phase as a function of overall deuterium content at 250 °C (experiment 2). For cell parameters, error bars (0.001 Å) are commensurate with the symbol size.

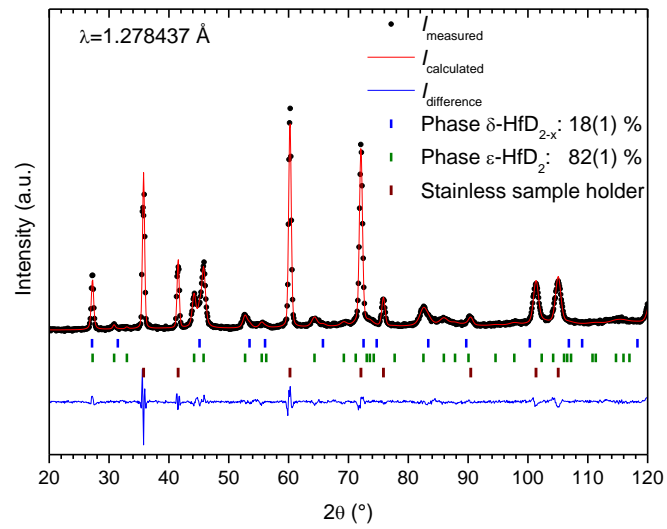


Figure S6. ND pattern of HfD<sub>1.92</sub> at 300 °C (experiment 2).

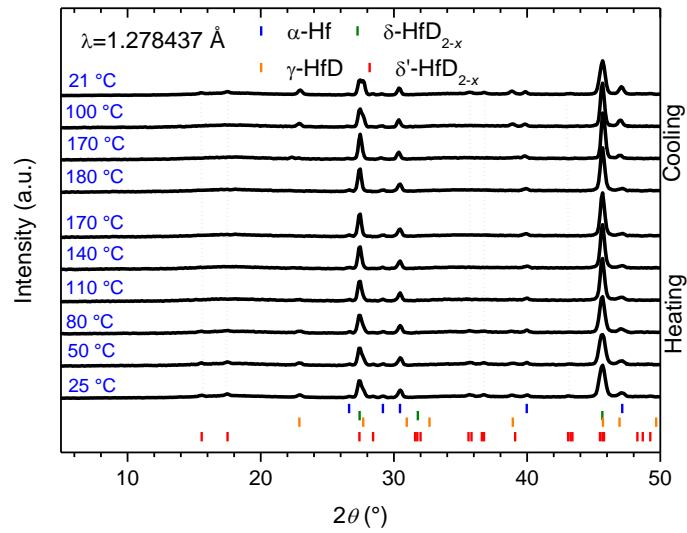


Figure S7. ND patterns of  $\text{HfD}_{0.994}$  sample during heating and cooling where the dotted lines represent the superstructure peaks of the  $\delta'$ - $\text{HfD}_{2-x}$  phase (experiment 3).

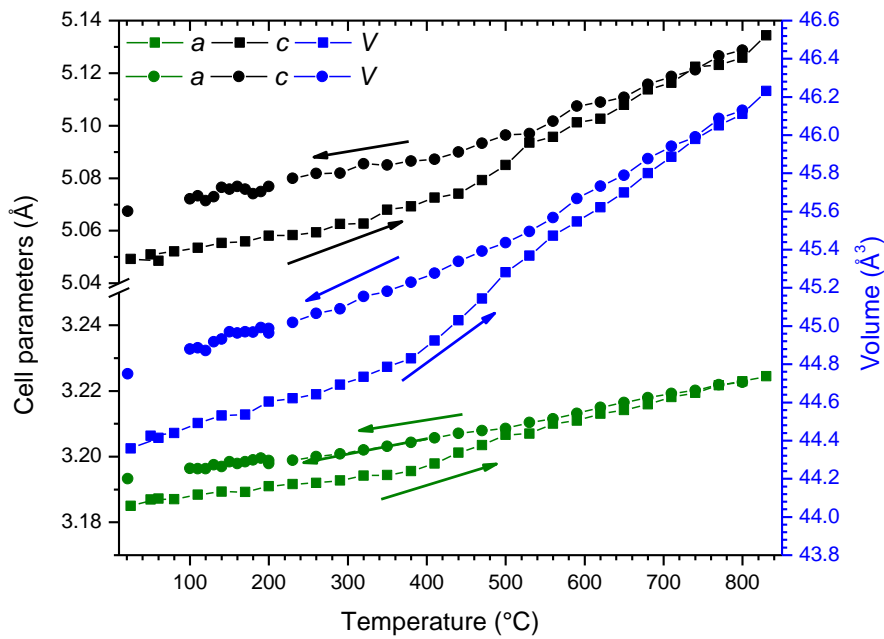


Figure S8. Cell parameters and volume of  $\alpha$ -Hf as a function of temperature in a sample of initial composition  $\text{HfD}_{0.994}$  (experiment 3). For cell parameters, error bars ( $0.001 \text{ \AA}$ ) are commensurate with the symbol size.

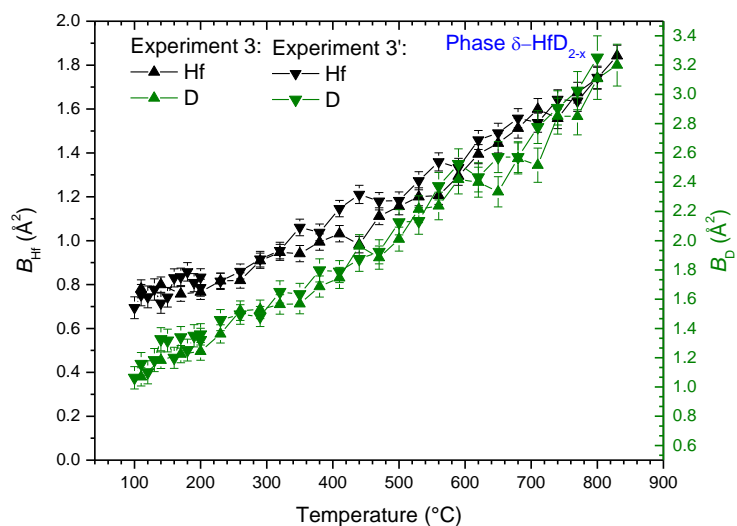


Figure S9. Displacement parameters of the  $\delta$ -HfD<sub>2-x</sub> phase as a function of temperature (experiment 3).

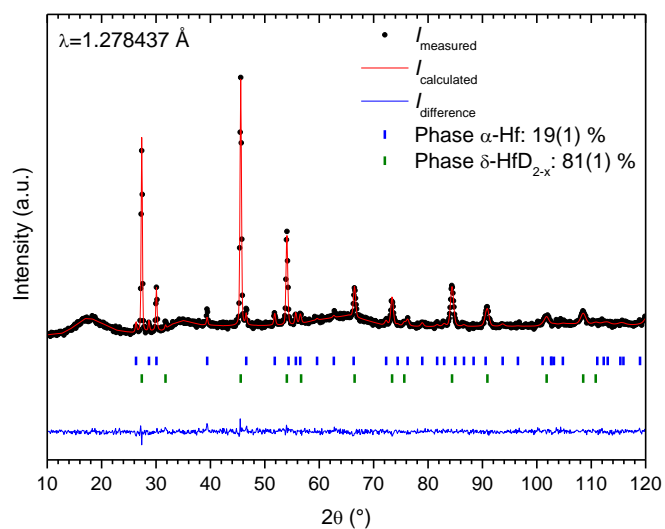


Figure S10. ND pattern of HfD<sub>0.944</sub> at 830°C (experiment 3).

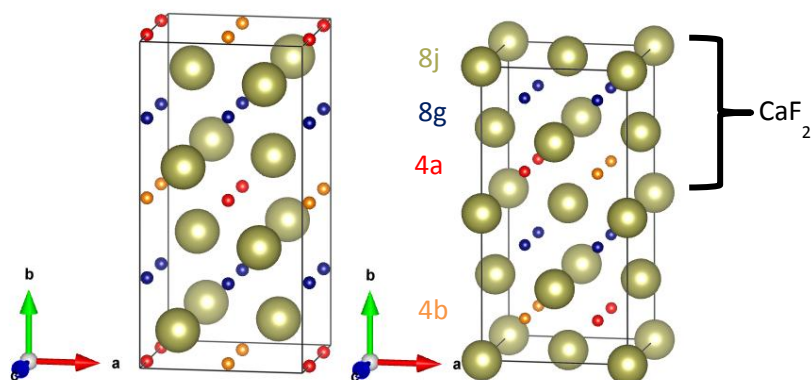


Figure S11. HfH<sub>1.5</sub> structure. The left figure shows the structure as determined in the present work. The right figure shows the same structure after an origin shift allowing to compare with the CaF<sub>2</sub> crystal structure.

Table

Table S1. Phase distribution of the hydrogenated and deuterated hafnium powder sample determined *ex situ* by Rietveld refinement of XRD data.

| Sample                     | Hydrogenation/Deuteration temperature | Phase                         | Percentage (wt%) |
|----------------------------|---------------------------------------|-------------------------------|------------------|
| <b>HfH<sub>1.000</sub></b> | 400 °C                                | $\delta'$ -HfD <sub>2-x</sub> | 49 (1)           |
|                            |                                       | $\gamma$ -HfD                 | 19 (1)           |
|                            |                                       | $\alpha$ -Hf                  | 32 (1)           |
| <b>HfD<sub>1.001</sub></b> | 400 °C                                | $\delta'$ -HfD <sub>2-x</sub> | 48 (1)           |
|                            |                                       | $\gamma$ -HfD                 | 18 (1)           |
|                            |                                       | $\alpha$ -Hf                  | 34 (1)           |
| <b>HfD<sub>0.994</sub></b> | 400 °C (Before PND)                   | $\delta'$ -HfD <sub>2-x</sub> | 58 (1)           |
|                            |                                       | $\gamma$ -HfD                 | 28 (1)           |
|                            |                                       | $\alpha$ -Hf                  | 14 (1)           |
|                            | 400 °C (After PND)                    | $\delta'$ -HfD <sub>2-x</sub> | 31 (1)           |
|                            |                                       | $\gamma$ -HfD                 | 34 (1)           |
|                            |                                       | $\alpha$ -Hf                  | 35 (1)           |