CompMatPhys Project Report:
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Contents

I: Formation Energy of Crystalline TeO$_3$

Procedure

General Details

- Quantum Espresso (QE) was used to perform DFT calculations, using a Generalized Gradient Approximation exchange-correlation functional, specifically PBE.
- Cif2Cell was used to convert the original CIFs into QE input files.
- Free energies per unit cell/molecule were calculated for the following (after performing a geometry optimization in each case):
    - Elemental Te (solid crystal)
    - Elemental O (diatomic gas)
    - TeO$_3$ (solid crystal)
- These quantities were used to calculate the formation energy of the TeO$_3$ crystal.

Elemental Te

- The CIF used was that with ID 1531230 in the Crystallography Open Database (COD; crystallography.net/cod/1531230.cif).
- The pseudopotential (like the O and H pseudopotentials used below) was taken from the MaterialsCloud's Efficiency library (materialscloud.org/discover/sssp/table/efficiency).
- In this and all subsequent calculations, the following precision settings were used:
    - **ecutwfc=87**
    - **ecutrho=435** (i.e. **ecutwfc** × 5)
- In this and all subsequent crystalline calculations, the k-mesh density was $3 \times 3 \times 3$.
- The calculations were non-spin-polarized, as were all subsequent calculations in this project.
- First, atomic positions within the unit cell were optimized (QE keyword **calculation='relax'**).
- A full geometric optimization was then performed (**calculation='vc-relax'**), covering the size and shape of the unit cell in addition to the atomic positions within the cell (using as an initial state the atomic coordinates optimized in the previous step).
- A static calculation (**calculation='scf'**) using the resulting lattice parameter, cell parameters and atomic positions was then performed to confirm the optimized unit cell's free energy.

Elemental O

- No existing CIF was used; instead, a CIF with P1 symmetry was created manually with the following dimensions:
    - Cell shape: cubic ($\alpha = \beta = \gamma = 90°$)
    - Cell side length: 9 Å ($a = b = c = 9$)
    - Bond length: 1.208 Å (one atom at $x = y = z = 0$; another at $x = y = 0$, $z = 0.134\,222$)
- In this and all subsequent gas phase calculations, the k-mesh density was $1 \times 1 \times 1$
- First, the bond length was optimized (**calculation='relax'**).
- Using the resulting bond length, a static calculation was then performed to confirm the optimized molecule's free energy.

Crystalline TeO₃

- The CIF used had COD ID 7035629 (crystallography.net/cod/7035629.cif).
- As described above for crystalline Te:
    - Atomic positions within the unit cell were optimized;
    - These positions then formed the basis for a full geometry optimization;
    - A static electronic relaxation was then performed on this optimized geometry.

Results

The QE-calculated free energies of the optimized structures were as follows:
- Tri-atomic unit cell of crystalline Te: $-79.494\ 152\ 95$ Ry
- Gaseous O_2: $-82.966\ 469\ 61$ Ry
- TeO₃ crystalline unit cell with stoichiometry Te_2O_6: $-302.441\ 522\ 69$ Ry

Analysis

- Let variables be defined as follows:
    - d = free energy /Ry of optimized elemental Te unit cell with three atoms
    - e = free energy /Ry of optimized O_2 molecule
    - f = free energy /Ry of optimized compound unit cell with stoichiometry Te_2O_6
    - E_{form} = compound formation energy /Ry per minimum stoichiometric unit (TeO₃)
    - E_{comp} = free energy /Ry of crystal per TeO₃ unit
    - E_{Te} = free energy /Ry per atom of elemental Te
    - E_O = free energy /Ry per atom of elemental O
- By definition, $E_{form} = E_{comp} - 3E_O - E_{Te}$
- The first result calculated above using DFT was $d = 3E_{Te}$, which re-arranges to $-E_{Te} = -\frac{d}{3}$
- The second calculated result was $e = 2E_O$, which re-arranges to $-3E_O = -\frac{3e}{2}$
- The third result was $f = 2E_{Comp}$, which re-arranges to $E_{Comp} = \frac{f}{2}$;
- Substituting accordingly: $E_{form} = \frac{f}{2} - \frac{3e}{2} - \frac{d}{3} = \frac{3f - 9e - 2d}{6}$
- Substituting the values obtained above:

$$E_{form} = \frac{3(-302.441\ 522\ 69) - 9(-82.966\ 469\ 61) - 2(-79.494\ 152\ 95)}{6}$$
$$= \frac{9(82.966\ 469\ 61) + 2(79.494\ 152\ 95) - 3(302.441\ 522\ 69)}{6}$$
$$\approx -0.273\ 005\ 946\ 7$$

- The PBE-predicted formation energy (per minimum stoichiometric unit) of crystalline TeO₃ with respect to solid crystalline Te and molecular O_2 is thus -0.273 Ry to 3 s. f.

II: Molecular Formation Energies

Procedure

General Details

- As in part I, QE and Cif2Cell were used.
- Free energies per atom were calculated for the following gasses (after performing a geometry optimization in each case):
  - Elemental H (diatomic)
  - TeO_4
  - $TeO_3(OH)$
  - $TeO_2(OH)_2$
- These quantities were used to calculate the formation energy of each compound molecule.

Elemental H

- A CIF was created manually, with the cell shape and size described in Part I above for O_2.
- The initial bond length was $0.74\,\text{Å}$ (one atom at $x = y = z = 0$; another at $x = y = 0$, $z = 0.082\,222$)
- First, the bond length was optimized (**calculation=relax**).
- Using the resulting bond length, a static calculation was then performed to confirm the optimized molecule's free energy.

TeO₄

- A CIF was created manually, with P1 symmetry and a rectangular cuboidal unit cell:
  - The molecule's shape was a square-based pyramid, with the Te at the apex and an O at each of the four corners.
  - The initial length of each of the four Te–O bonds was set to $1.9\,\text{Å}$
  - The minimum distance along any one Cartesian axis between each atom and the nearest atom in a mirror-image molecule was set to $8\,\text{Å}$ (for instance, the maximum x-axis separation between two atoms within the molecule was $\Delta x = 1.9\,\text{Å}$, so the unit cell's side-length in the x-direction was $8\,\text{Å} + 1.9\,\text{Å} = 9.9\,\text{Å}$).
  - For the precise cell dimensions and atomic positions (before and after geometric optimization, see the appendix at the end of this report).
- As tellurate is a dianion (pubchem.ncbi.nlm.nih.gov/compound/Tellurate), the total charge was set to **tot_charge=–2**.
- First, the bond lengths and angles were optimized (**calculation=relax**).
- All bond lengths were allowed to relax but some of the bond angles were fixed at $90°$, so that the overall pyramidal shape was approximately retained.
- Using the resulting atomic positions, a static calculation was then performed to confirm the free energy of the optimized molecule.

TeO₃OH

- Again, a P1 CIF was created manually:
    - The optimized tellurate dianion structure generated above was retained, but one hydrogen cation was added, creating a hydrogen-tellurate anion.
    - This hydrogen was attached to one of the oxygen atoms, with an initial O–H bond length of 0.95 Å.
    - The unit cell was expanded to enforce the 8 Å separation along each axis between molecule and periodic mirror-molecule.
- As hydrogen-tellurate is an anion (pubchem.ncbi.nlm.nih.gov/compound/ hydrogentellurate), the total charge was set to **tot_charge=–1**.
- As before, the atomic positions were optimized (with some bond angles fixed), then a static calculation was performed on the optimized molecule to determine its free energy.

TeO₂(OH)₂

- For tellursaeure the optimized hydrogen-tellurate anion structure was retained, but another hydrogen cation was added, creating a neutral tellursaeure molecule.
- The hydrogen was attached to one of the three remaining un-bonded oxygen molecules, with an initial O–H bond length of 0.95 Å.
- Tellursaeure is a neutral molecule (pubchem.ncbi.nlm.nih.gov/compound/61609).
- After relaxing all bond lengths and most bond angles, a static calculation was performed to determine the free energy of the optimized geometry.

Results & Analysis

The QE-calculated free energies of the optimized gas molecules were as follows:
- H_2: $-2.333\,249\,14$ Ry
- TeO_4: $-193.154\,220\,62$ Ry
- $TeO_3(OH)$: $-194.171\,568\,65$ Ry
- $TeO_2(OH)_2$: $-195.048\,232\,87$ Ry

TeO₄

- Let variables be defined as follows:
    - d = free energy /Ry of optimized elemental Te unit cell with three atoms
    - e = free energy /Ry of optimized O2 molecule
    - f = free energy /Ry of optimized TeO4 dianion
    - E_{form} = formation energy /Ry per molecule of TeO4
    - E_{mol} = free energy /Ry per molecule of TeO3
    - E_{Te} = free energy /Ry per atom of elemental Te
    - E_O = free energy /Ry per atom of elemental O
- By definition, $E_{form} = E_{mol} - 4E_O - E_{Te}$.
- Using the known values: $(E_{mol},\ -4E_O,\ -E_{Te}) = \left(f,\ -2e,\ -\dfrac{d}{3}\right)$
- Substituting accordingly: $E_{form} = f - 2e - \dfrac{d}{3} = \dfrac{3f - 6e - d}{3}$
- Substituting the values: $E_{form} = \dfrac{3(-193.154\,220\,62) - 6(-82.966\,469\,61) - (-79.494\,152\,95)}{3}$

$$= \dfrac{6(82.966\,469\,61) + 79.494\,152\,95 - 3(193.154\,220\,62)}{3} \approx -0.663\,230\,416\,7$$

- The PBE-predicted formation energy per molecule of anionic $(TeO_4)^{2-}$ with respect to solid crystalline Te and molecular O_2 is thus -0.663 Ry to 3 s. f.

TeO$_3$(OH)

- In addition to the variables defined above, let:
  - g = free energy /Ry of optimized H2 molecule
  - E_H = free energy /Ry per atom of elemental H
- By definition, $E_{form} = E_{mol} - E_H - 4E_O - E_{Te}$ and $g = 2E_H$
- Using the known values: $(E_{mol}, -E_H, -4E_O, -E_{Te}) = \left(f, -\frac{g}{2}, -2e, -\frac{d}{3}\right)$
- Substituting accordingly: $E_{form} = f - \frac{g}{2} - 2e - \frac{d}{3} = \frac{6f - 3g - 12e - 2d}{6}$
- Substituting the values obtained above:

$$E_{form} = \frac{6(-194.171\,568\,65) - 3(-2.333\,249\,14) - 12(-82.966\,469\,61) - 2(-79.494\,152\,95)}{6}$$

$$= \frac{3(2.333\,249\,14) + 12(82.966\,469\,61) + 2(79.494\,152\,95) - 6(194.171\,568\,65)}{6}$$

$$\approx -0.573\,953\,876\,7$$

- The PBE-predicted formation energy per molecule of anionic (TeO$_3$OH)$^-$ with respect to solid crystalline Te, molecular O$_2$ and molecular H$_2$ is thus -0.574 Ry to 3 s. f.

TeO$_2$(OH)$_2$

- For the neutral molecule, $E_{form} = E_{mol} - 2E_H - 4E_O - E_{Te}$
- Using the known values: $(E_{mol}, -2E_H, -4E_O, -E_{Te}) = \left(f, -g, -2e, -\frac{d}{3}\right)$
- Substituting accordingly: $E_{form} = f - g - 2e - \frac{d}{3} = \frac{3f - 3g - 6e - d}{3}$
- Substituting the DFT-calculated values:

$$E_{form} = \frac{3(-194.171\,568\,65) - 3(-2.333\,249\,14) - 6(-82.966\,469\,61) - (-79.494\,152\,95)}{3}$$

$$= \frac{3(2.333\,249\,14) + 6(82.966\,469\,61) + 79.494\,152\,95 - 3(194.171\,568\,65)}{3}$$

$$\approx -0.592\,670\,693\,3$$

- The PBE-predicted formation energy per molecule of TeO$_2$(OH)$_2$ with respect to solid crystalline Te, molecular O$_2$ and molecular H$_2$ is thus -0.593 Ry to 3 s. f.

III: Appendix: Atomic Coordinates

- In all unit cells below, $\alpha = \beta = \gamma = 90°$
- The coordinates which were fixed in place during the optimization are shaded in blue

	Initial Configuration	Optimized Configuration

TeO₄ Unit Cell:
 	
- $a = 9.9\,\text{Å}$
- $b = 10.687\,006\,\text{Å}$
- $c = 9.9\,\text{Å}$
	Atomic Positions
	- Te: $x = y = z = 0$
	- O no. 1:
	  - $\frac{x}{a} = 0.191\,919$
	  - $y = z = 0$
	- O no. 2:
	  - $\frac{x}{a} = 0.095\,960$
	  - $\frac{y}{b} = -0.125\,714$
	  - $\frac{z}{c} = 0.095\,960$
	- O no. 3:
	  - $x = y = 0$
	  - $\frac{z}{c} = 0.191\,919$
	- O no. 4:
	  - $\frac{x}{a} = 0.095\,960$
	  - $\frac{y}{b} = 0.125\,714$
	  - $\frac{z}{c} = 0.095\,960$
		Atomic Positions
		- Te: $x = y = z = 0$
		- O no. 1:
		  - $\frac{x}{a} = 0.193\,314\,571\,1$
		  - $y = z = 0$
		- O no. 2:
		  - $\frac{x}{a} = -0.079\,325\,317\,6$
		  - $\frac{y}{b} = 0.855\,543\,239\,8$
		  - $\frac{z}{c} = -0.079\,325\,317\,6$
		- O no. 3:
		  - $x = y = 0$
		  - $\frac{z}{c} = 0.193\,314\,571\,1$
		- O no. 4:
		  - $\frac{x}{a} = -0.079\,325\,317\,6$
		  - $\frac{y}{b} = 0.144\,456\,760\,2$
		  - $\frac{z}{c} = -0.079\,325\,317\,6$

TeO₃OH Unit Cell:
 	
- $a = 11.649\,137\,\text{Å}$
- $b = 11.087\,624\,\text{Å}$
- $c = 11.649\,137\,\text{Å}$
	Atomic Positions
	- Te: $x = y = z = 0$
	- O no. 1:
	  - $\frac{x}{a} = 0.164\,288$
	  - $y = z = 0$
	- H no. 1:
	  - $\frac{x}{a} = 0.245\,839$
	  - $y = z = 0$
	- O no. 2:
	  - $\frac{x}{a} = -0.067\,415$
	  - $\frac{y}{b} = -0.139\,237$
	  - $\frac{z}{c} = -0.067\,415$
	- O no. 3:
	  - $x = y = 0$
	  - $\frac{z}{c} = 0.164\,288$
	- O no. 4:
	  - $\frac{x}{a} = -0.067\,415$
	  - $\frac{y}{b} = 0.139\,237$
	  - $\frac{z}{c} = -0.067\,415$
		Atomic Positions
		- Te: $x = y = z = 0$
		- O no. 1:
		  - $\frac{x}{a} = 0.171\,514\,453\,4$
		  - $y = z = 0$
		- H no. 1:
		  - $\frac{x}{a} = 0.253\,907\,555\,7$
		  - $y = z = 0$
		- O no. 2:
		  - $\frac{x}{a} = 0.956\,261\,725\,7$
		  - $\frac{y}{b} = 0.858\,377\,356$
		  - $\frac{z}{c} = 0.925\,695\,157\,6$
		- O no. 3:
		  - $x = y = 0$
		  - $\frac{z}{c} = 0.160\,245\,629\,4$
		- O no. 4:
		  - $\frac{x}{a} = 0.956\,261\,725\,7$
		  - $\frac{y}{b} = 0.141\,622\,644$
		  - $\frac{z}{c} = 0.956\,261\,725\,7$

	Initial Configuration	Optimized Configuration

TeO$_2$(OH)$_2$ Unit Cell:
 	
• $a = 11.467\,320$ Å
• $b = 11.140\,521$ Å
• $c = 11.692\,123$ Å
	<u>Atomic Positions</u>
	• Te: $x = y = z = 0$
	• O no. 1:
	  ○ $\frac{x}{a} = 0.174\,234$
	  ○ $y = z = 0$
	• H no. 1:
	  ○ $\frac{x}{a} = 0.257\,934$
	  ○ $y = z = 0$
	• O no. 2:
	  ○ $\frac{x}{a} = -0.044\,432$
	  ○ $\frac{y}{b} = -0.140\,95$
	  ○ $\frac{z}{c} = -0.074\,032$
	• O no. 3:
	  ○ $x = y = 0$
	  ○ $\frac{z}{c} = 0.159\,657$
	• H no. 2:
	  ○ $x = y = 0$
	  ○ $\frac{z}{c} = 0.241\,747$
	• O no. 4:
	  ○ $\frac{x}{a} = -0.044\,432$
	  ○ $\frac{y}{b} = 0.140\,95$
	  ○ $\frac{z}{c} = -0.074\,032$
		<u>Atomic Positions</u>
		• Te: $x = y = z = 0$
		• O no. 1:
		  ○ $\frac{x}{a} = 0.166\,695\,415\,7$
		  ○ $y = z = 0$
		• H no. 1:
		  ○ $\frac{x}{a} = 0.250\,670\,422\,7$
		  ○ $y = z = 0$
		• O no. 2:
		  ○ $\frac{x}{a} = 0.947\,491\,270\,5$
		  ○ $\frac{y}{b} = 0.853\,922\,057\,9$
		  ○ $\frac{z}{c} = 0.948\,463\,738$
		• O no. 3:
		  ○ $x = y = 0$
		  ○ $\frac{z}{c} = 0.163\,562\,270\,7$
		• H no. 2:
		  ○ $x = y = 0$
		  ○ $\frac{z}{c} = 0.245\,931\,902\,4$
		• O no. 4:
		  ○ $\frac{x}{a} = 0.947\,491\,270\,5$
		  ○ $\frac{y}{b} = 0.146\,077\,942\,1$
		  ○ $\frac{z}{c} = 0.948\,463\,738$