Combining Theory and Experiment to Characterize the Voltammetric Behavior of Nickel Anodes in the Simons Process

Stefan Mattsson,[a] Gene Senges,[b] Sebastian Riedel,[b] and Beate Paulus[a]
Author Contributions

S.M. Formal analysis: Lead; Investigation: Lead; Methodology: Lead; Visualization: Lead; Writing - Original Draft: Lead; Writing - Review & Editing: Lead
G.S. Formal analysis: Lead; Investigation: Lead; Methodology: Lead; Visualization: Supporting; Writing - Original Draft: Supporting; Writing - Review & Editing: Supporting
S.R. Conceptualization: Supporting; Formal analysis: Supporting; Funding acquisition: Lead; Methodology: Supporting; Project administration: Lead; Supervision: Supporting; Validation: Lead; Writing - Original Draft: Supporting; Writing - Review & Editing: Supporting
B.P. Conceptualization: Lead; Formal analysis: Supporting; Funding acquisition: Lead; Methodology: Supporting; Project administration: Lead; Supervision: Lead; Validation: Supporting; Writing - Original Draft: Supporting; Writing - Review & Editing: Supporting.
1 Bulk NiF$_2$ results

We study some fundamental properties of the crystalline phase of NiF$_2$ in order to evaluate the DFT functionals used and the results are presented in Table S1. NiF$_2$ crystallizes in the rutile structure (space group P4$_2$/mnm) with two formula units in the unit cell (Figure S1). The two lattice parameters of the tetragonal unit cell, $a$ and $b$, are well reproduced by each functional although all slightly overestimate the size of the cell.

![Figure S1: Unit cell of NiF$_2$. Gray and green colors correspond to Ni and F respectively. The two inequivalent, antiferromagnetically coupling Ni$^{2+}$ ions are labeled Ni1 and Ni2. The lattice vectors are drawn with the lattice constants $|a| = |c| \neq |b|$ (tetragonal lattice).](image)

Each Ni center is six-fold coordinated by F$^-$ ions and form slightly distorted octahedra of D$_{2h}$ symmetry. The octahedra share corners along the [001] direction and edges along the [110] and [1¯10] directions. There are two different Ni-F distances at a Ni$^{2+}$ center: two pointing along [1¯10] and four pointing along the (1¯10) plane. These are calculated to be 2.0162 Å and 2.0240 Å with PBE+U and 2.007 Å and 2.015 Å with HSE06. The experimental values are 1.9961 Å and 2.0114 Å, respectively, and are well reproduced with both functionals.

Two inequivalent Ni$^{2+}$ sites are found in the center and the corner of the unit cell. Due to the largely octahedral crystal field environment, the d orbitals split into two energy levels $t_{2g}$ and $e_g$ with the two unpaired electrons (Ni$^{2+}$ has a d$^8$ configuration) populating the higher energy $e_g$ levels. This can be seen in the calculated magnetic moments ($\mu$) in Table 1, where PBE+U and HSE06 perform well, whereas PBE underestimates $\mu$ by a larger amount. Magnetic coupling between d electrons occurs according to the superexchange mechanism, where the dominant coupling is antiferromagnetic along the [110] direction. The magnetic coupling is relatively weak which results in an antiferromagnetically ordered phase below 73 K. All functionals correctly favor the antiferromagnetic phase over the ferromagnetic one, although PBE most likely overestimates the magnetic coupling due to electron density over-delocalization.

It is in the band gap that we notice another shortcoming of the PBE functional due to the intrinsic electron self-interaction. The largely underestimated band gap is problematic especially with the redox processes that are considered in this work. Furthermore, if NiF$_2$ forms an insulating film at the
anode at low potentials, the use of the PBE functional is problematic since it predicts a small-gap semi-conductor. PBE+U and HSE06 are close to the experimental value for the electronic band gap around 5 eV. These functionals are considered proper for our calculation of structural and electronic properties of NiF₂.

Table S1: Calculated values for lattice parameters, band gap, magnetic phase stability (per formula unit) and Ni²⁺ magnetic moment for crystalline NiF₂ with the PBE, PBE+U and HSE06 functionals

|                | PBE   | PBE+U | HSE06 | Exp.     |
|----------------|-------|-------|-------|----------|
| `a` [Å]        | 4.7017| 4.6955| 4.6753| 4.6497   |
| `b` [Å]        | 3.1005| 3.0959| 3.0812| 3.0836   |
| `V` [Å³]       | 68.5396| 68.2575| 67.3502| 66.6665  |
| Band gap [eV]  | 1.1   | 4.6   | 5.9   | ∼5 ¹⁰    |
| `E_{AFM-FM}` [meV]| −64.9| −17.5| −19.3| AFM⁶    |
| `µ` [µB]       | 1.62  | 1.80  | 1.80  | 1.96⁸    |

2 Surface thermodynamics with an external potential

To represent a surface characterized by a Miller index (`hkl`), we employ the two-dimensional slab model. In the model, a slab of a certain thickness is constructed from the bulk structure of NiF₂ so that two of its lattice vectors, `a` and `b`, are parallel to the (`hkl`) plane (see Figure S2a).

**Figure S2:** (a) Example of a stoichiometric, symmetric slab of the NiF₂(110) surface. `a` and `b` denote the two-dimensional periodic plane whereas `c` is the non-periodic vector. (b) Surface energy convergence of the three terminations of the (110) surface versus number of stoichiometric units. Solid and dashed lines represent relaxed and unrelaxed surface energies.

The slab consists of layers of NiF₂ in its center which are terminated by (`hkl`) surfaces at its two
sides. In our work, we use symmetric slabs to avoid the build-up of dipole moments through the slab. The surface energy $\gamma$ of a slab is calculated according to

$$\gamma = \frac{1}{2A} \left[ E_{\text{slab}} - N_s E_{\text{bulk}} - \sum_i N_i \mu_i \right]$$

(1)

where $A$ is the surface area of the slab, $E_{\text{slab}}$ is the energy of the slab, $N_s$ the number of stoichiometric units in the slab and $E_{\text{bulk}}$ the energy of the bulk crystal per stoichiometric unit. The factor of $\frac{1}{2}$ is necessary since two surfaces are present on the two sides of the slab. By increasing the thickness of the slab, the center of the slab become an increasingly better representation of the bulk structure and with sufficiently many units $N_s$, $\gamma$ converges to the surface energy of the $(hkl)$ surface. The first two terms in eq. (1) describe the surface energy of a stoichiometric slab. If we are to calculate non-stoichiometric slabs, i.e. slabs with an excess or deficit of atoms $i$ (in our case $i$ are F atoms), the last term corrects the equation from the stoichiometric case by use of the chemical potential of the atom, $\mu_i$. $N_i$ denotes the excess ($N_i > 0$) or deficit ($N_i < 0$) of atom $i$ on both sides of the slab.

We consider two methods for calculating $\mu_F$. In the first method, the chemical potential of an F atom is calculated from the DFT energies of the bulk NiF$_2$ and metallic Ni

$$E_{\text{NiF}_2} = \mu_{\text{Ni}} + 2\mu_F \approx E_{\text{Ni}} + 2\mu_F$$

(2)

$$\Rightarrow \mu_F = \frac{1}{2} \left[ E_{\text{NiF}_2} - E_{\text{Ni}} \right]$$

With this method, it is not specified where the excess or deficit of F atoms is taken from or transferred to, but the surface energy of a non-stoichiometric slab is related to the formation energy of NiF$_2$ from metallic Ni.

In the second method, we assume that F atoms are available from an external reservoir. In the ECF, the fluorine source comes from the electrolysis of anhydrous HF. HF is assumed to be in equilibrium with atomic H and F and may hence be expressed in terms of the chemical potentials of H and F. H is furthermore in equilibrium with half an H$_2$ molecule

$$\mu_{\text{HF}} = \mu_{\text{H}} + \mu_F = \frac{1}{2} \mu_{\text{H}_2} + \mu_F$$

(3)

$$\Rightarrow \mu_F = \mu_{\text{HF}} - \frac{1}{2} \mu_{\text{H}_2}$$

In an experimental ECF cell, F$^-$ ions migrate to the anode and H$^+$ ions to the cathode. Here, we take advantage of the cathode half-cell reaction

$$\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2} \text{H}_2$$

and choose the cathode to be the standard hydrogen electrode (SHE), whose half-cell reaction, by construction, is an equilibrium between solvated H$^+$ and gaseous H$_2$. This allows us to relate $\mu_{\text{H}_2}$ to the chemical potentials of H$^+$ and the transferred electron

$$\mu_{\text{H}^+} + \mu_{\text{e}^-} = \frac{1}{2} \mu_{\text{H}_2}(T, V = 0)$$

(4)
Since the SHE by convention establishes the reference point for all electrode potentials, this equation refers to the SHE half-cell reaction without an external potential \((V = 0)\). If an external potential \(V\) is applied this shifts the potential energy by \(1 \, eV\) per transferred electron and an expression for a \(V\)-dependent chemical potential is acquired

\[
\frac{1}{2} \mu_{\text{H}_2}^\circ (T, V) = \frac{1}{2} \mu_{\text{H}_2}^\circ (T, V = 0) - eV
\]  

(5)

Furthermore, the SHE is defined at pH 0, whereas in anhydrous HF the pH is expressed as the Hammett acidity: \(-11\). Therefore, a further correction is required according to

\[
\frac{1}{2} \mu_{\text{H}_2}^\circ (T, V, \text{pH}) = \frac{1}{2} \mu_{\text{H}_2}^\circ (T, V) - [RT\ln(10) \times \text{pH}]
\]  

(6)

where \(R\) is the universal gas constant.

The problem of both solvated protons and transferred electrons under an external potential has been simplified to a point were we only need to calculate the electronic energy and the zero-point energy of an \(\text{H}_2\) molecule using DFT. Enthalpic and entropic contributions to the chemical potential at elevated temperatures are taken from thermodynamic tables and added to the DFT energy. By following this methodology we have set up a computational hydrogen electrode (CHE), and the \(V\)-dependent chemical potential of \(\text{H}_2\) may be inserted into eq. (3).

For the chemical potential of HF, to avoid explicit calculations involving a liquid phase, the liquid phase is assumed to be in equilibrium with its vapor phase

\[
\mu_{\text{HF},\text{l}}(T) = \mu_{\text{HF},\text{g}}(T, p_{\text{vap, HF}})
\]  

(7)

The assumption is valid if the liquid HF phase contains only a low concentration of electrolytes so that the effective HF vapor pressure is close to the vapor pressure of the pure compound \((\text{cf. Raoult’s law})\). Similarly to \(\text{H}_2\), this lets us calculate the electronic energy and zero-point energy of an HF molecule at the DFT level, while adding tabulated enthalpic and entropic contributions at temperature \(T\) and pressure \(p_{\text{vap, HF}}\).

By inserting this into eq. (3), we acquire the final \(V\)-dependent expression for the surface energy

\[
\gamma(V) = \frac{1}{2A} \left[ E_{\text{slab}} - N_sE_{\text{bulk}} - N_F \left( \mu_{\text{HF}}(T, p_{\text{vap, HF}}) - \frac{1}{2} \mu_{\text{H}_2}(T, V, \text{pH}) \right) \right]
\]  

\[
= \gamma(V = 0) - \frac{N_F eV}{2A}
\]  

(8)

The equation is finally rewritten to emphasize the linear relationship that arises by using the CHE approach. As the intercept, we find the surface energy without an external potential, and the number of excess/deficit fluoride ions per area unit determines the slope of the equation. Clearly, stoichiometric surfaces \((N_F = 0)\) are independent of the external potential.
3 Example calculation of $\gamma(V)$

Table S2 shows an example calculation of the molecular quantities needed for the calculation of a potential-dependent surface energy $\gamma(V)$ from DFT results (HSE06 functional) and thermodynamic data. As example, the oxidized (110) surface is used, with $N_s = 8$ and $N_F = 2$ (8 Ni, 18 F atoms). Thermodynamic extrapolations are done to the conditions

- $V = 2\ \text{V}$
- $T = 298\ \text{K}$
- $\text{pH} = -11$ (Hammett acidity of anhydrous HF)$^{12}$
- $p_{\text{H}_2} = p^\circ = 1\ \text{bar}$
- $p_{\text{HF}} = p_{\text{cap, HF}}(298\ \text{K}) = 1.197\ \text{bar}$

The derivation of the model is presented in Section 2. Equations used that are not included above are

$$\Delta \mu^\circ_{0\rightarrow T} = \Delta H^\circ_{0\rightarrow T} - T \Delta S^\circ_{0\rightarrow T}$$

$$\mu^\circ(T) = E_{\text{el}} + E_{\text{ZPE}} + \Delta \mu^\circ_{0\rightarrow T}$$

$$\mu(T, p) = \mu^\circ(T) + R T \ln \frac{p}{p^\circ}$$

For HF, the extrapolation of the DFT results ($E_{\text{el}} + E_{\text{ZPE}}$) to the chemical potential of the liquid phase at 298 K lowers the energy by $-0.4430\ \text{eV}$. 99% of this comes from the $T$ extrapolation, which means the approximation in Eq. (7) for the $p$ extrapolation only has a minor impact on the results.

For $\text{H}_2$, the $T$ extrapolation accounts for a lowering of the DFT energy by $-0.3158\ \text{eV}$ whereas the $\text{pH}$ extrapolation raises it by 0.6502 eV. The relatively high amount (62.8 kJ/mol) is sensible as the chemical activity is expected to be large for anhydrous HF. A change from pH -11 to pH -10 changes the oxidation potential ($V_{\text{ox. (hkl)}}$) of the (110) surface from 3.20 V to 3.18 V, meaning $V_{\text{ox. (hkl)}}$ is still fairly insensitive to the pH parameter.

The most significant contribution to the over-all chemical potential comes from the $V$ term (see Eq. (5)). At $+2\ \text{V}$ it lowers the chemical potential by $-4\ \text{eV}$. This linear relation is presented in Eqs. (4) and (5) and is easily understood as, for each transferred electron, a lowering of 1 eV per V (one $\text{H}_2$ molecule requiring two transferred electrons to form from protons at the cathode). Phrased differently, an electron under a potential $V$ carries $eV$ chemical energy.
Table S2: Example calculation of the quantities needed for $\gamma(V)$. All electronic energies ($E_{el}$) and zero-point vibrational energies ($E_{ZPE}$) are calculated in vacuum at 0 K with the HSE06 functional. The NiF$_2$ bulk and slab structures are optimized with PBE+U whereas H$_2$ and HF are optimized with HSE06. Extrapolations to experimental conditions are done using thermodynamic tables. The energies refer to one stoichiometric unit for bulk NiF$_2$, HF and H$_2$ and the total energy of the NiF$_2$ slab ($N_s = 8$).

| Term | Energy/chem. pot. [eV] | Source |
|------|------------------------|--------|
| Bulk NiF$_2$ | | |
| $E_{el}$ | -20.2757 | DFT |
| Oxidized NiF$_2$(110) slab | | |
| $E_{el}$ | -167.4041 | DFT |
| Liquid HF | | |
| $E_{el}$ | -10.0314 | DFT |
| $E_{ZPE}$ | 0.2602 | DFT |
| $\Delta H_{0\to T}^0$ | 0.0891 | CODATA$^{14}$ |
| $T\Delta S_{0\to T}^0$ | 0.5367 | NIST$^{13}$ |
| $\Delta \mu_{0\to T}^0$ | -0.4475 | Eq. (9) |
| $\mu^0(T)$ | -10.2188 | Eq. (10) |
| $\mu(T, p_{\text{cap},HF})$ | -10.2142 | Eq. (11) |
| Gaseous H$_2$ | | |
| $E_{el}$ | -7.8317 | DFT |
| $E_{ZPE}$ | 0.2751 | DFT |
| $\Delta H_{0\to T}^0$ | 0.0878 | CODATA$^{14}$ |
| $T\Delta S_{0\to T}^0$ | 0.4036 | NIST$^{15}$ |
| $\Delta \mu_{0\to T}^0$ | -0.3158 | Eq. (9) |
| $\mu^0(T)$ | -7.8724 | Eq. (10) |
| $\mu^0(T,V)$ | -11.8724 | Eq. (5) |
| $\mu^0(T,V,pH)$ | -11.2220 | Eq. (6) |

The quantities are used to calculate the $\gamma(V)$ according to Eq. (8) and presented in Table S3. The area of the slab, $A$, is 20.5579 Å$^2$. 


Table S3: Calculation of $\gamma(V)$ for the NiF$_2$(110) surface from the quantities in Table S2. A potential $V = 2$ eV is used.

| Term              | Surface energy (J/m$^2$) |
|-------------------|--------------------------|
| $\gamma(V = 0)$   | 3.120                    |
| $\frac{N_{FeV}}{2A}$ | 1.558                   |
| $\gamma(V)$       | 1.562                    |

3.1 Surface energies

In this study, we focus on the low-index surfaces of NiF$_2$ ($h$, $k$ and $l \leq 1$). Of those, five inequivalent cuts are possible with the Miller indices (110), (100), (101), (001) and (111). Depending on the surface cut, there are 1-4 different terminations (listed in Table S4). Some of these cuts yield slabs with $n$ Ni and $2n$ F atoms. Since these slabs maintain the stoichiometry of NiF$_2$, we refer to these slabs as stoichiometric slabs. The construction of stoichiometric slabs does not involve any redox reactions – i.e. the Ni atoms at the surface as well as in the center of the slabs are all in the oxidation state +II. The remaining terminations lead to an excess (or deficit) of F$^-$, the slabs are no longer stoichiometric with respect to NiF$_2$ and F$^-$ ions are added (or removed) at the surface of the slab, thus changing the oxidation state of the surface layer Ni. We label surfaces with an excess of fluoride ($hkl$)+F$^-$ and slabs with a deficiency of fluoride ($hkl$)−F$^-$. Ni ions in the center of the slab maintain the same bulk-like structure and the +II oxidation state. Throughout all slab calculations, the Ni centers show antiferromagnetic coupling analogous to the bulk magnetic phase, also between Ni$^{2+}$ and Ni$^+$ or Ni$^{3+}$ centers in non-stoichiometric slabs.

The convergence of the relaxed and unrelaxed zero-potential surface energies is shown for the three terminations of the (110) surface in Figure S2b. All investigated surface energies converge after around 8 stoichiometric units within an accuracy of 0.01 J/m$^2$. Surface energies are calculated according to Eq. (8) and further surface energies in this report refer to relaxed slabs.
Table S4: NiF$_2$ surfaces and their relaxed surface energies without an external potential. The fluoride source is HF, according to method 2 above. The slabs were optimized with PBE+U. Surface energies are also calculated with the HSE06 functional using the same structures.

| Index | Termination | Excess F$^-$ ($\frac{N_{F^2}}{A}$) | CN, surface Ni | $\gamma(V = 0)$ [J/m$^2$] | PBE+U | HSE06 |
|-------|-------------|----------------------------------|----------------|--------------------------|-------|-------|
| (110) | 1           | +1                               | 6, 6           | 2.95                     | 3.12  |
|       | 2           | 0                                | 6, 5           | 0.55                     | 0.62  |
|       | 3           | −1                               | 4, 5           | 1.55                     | 1.90  |
| (100) | 1           | +1                               | 6              | 3.91                     | 4.10  |
|       | 2           | 0                                | 5              | 0.60                     | 0.69  |
|       | 3           | −1                               | 3              | 1.98                     | 2.34  |
| (101) | 1           | +2                               | 6, 6           | 4.19                     | 4.41  |
|       | 2           | 0                                | 5, 5           | 0.66                     | 0.73  |
|       | 3           | −2                               | 4, 4           | 2.02                     | 2.34  |
| (001) | 1 (ads.)    | +1                               | 5              | 2.71                     | 2.92  |
|       | 1           | 0                                | 4              | 0.88                     | 0.95  |
|       | 1 (des.)    | −1                               | 3              | 1.59                     | 1.87  |
| (111) | 1           | +1                               | 6, 5           | 1.91                     | 2.00  |
|       | 2           | 0                                | 5, 4           | 0.98                     | 1.08  |
|       | 3           | 0                                | 5, 4           | 1.01                     | 1.13  |
|       | 4           | −1                               | 5, 3           | 1.34                     | 1.57  |

3.1.1 Non-stoichiometric surfaces

Defluorination of stoichiometric surfaces leads to reduced Ni$^+$ surface motifs while fluorination yields oxidized surface Ni$^{3+}$ ions. For all surface cuts, defluorinated surfaces are considerably higher in energy than fluorinated surfaces. There is a linear relation between zero-potential surface energies and number of excess (deficit) of fluoride per surface area ($\frac{N_{F^2}}{A}$), as presented in Figure S3. This indicates that the energetics involved in the investigated (de)fluorinated surfaces are not, to any large extent, governed by the atomistic surface structure, such as adsorption sites and steric factors. An exception to this is the (111)+F$^-$ surface, of which the surface energy falls somewhat lower than the linear fit. This surface also shows the lowest surface energy among the fluorinated surfaces at zero-potential. This is due to the aforementioned cavity in the (111) surface, providing a pocket for more efficient F$^-$ adsorption.
Figure S3: Calculated surface energies for relaxed non-stoichiometric surfaces as a function of the excess or deficit of fluoride ions per surface area ($\frac{N_F}{2A}$). The values refer to surface energies without an external potential. Linear fits are made for both series, not including the (111)+F$^-$ point. Surface energies are calculated using HSE06 with the structures optimized using PBE+U.

Throughout all surfaces, the oxidation potential $V_{\text{ox},(hkl)}$ decreases with increasing stoichiometric surface surface energy $\gamma_s$ (which is $V$-independent). In fact, for all surfaces except (111) there is a linear relationship between the stoichiometric surface energy and $V_{\text{fl}}$. The linear relationship intuitively means that the less stable stoichiometric surface cuts are more easily fluorinated. Due to its special F$^-$ binding environment, the fluorination of the (111) surface is more favorable than the other surface cuts.

Figure S4: Fluorination potential for all surfaces as a function of the stoichiometric surface energy. A linear fit is made using all points except (111)+F$^-$. Surface energies are calculated using HSE06 with the structures optimized using PBE+U.
4 Structures and absolute energies

The structures used for the calculations are included in a zip file as part of the Supporting Information. The file format is POSCAR (VASP format) and may be browsed with, for example, VESTA.

All energies are calculated with the HSE06 functional and the further parameters specified in the paper. The reported absolute energies are extrapolated to 0 K by the VASP program (the E0 output) to minimize Gaussian smearing artifacts to the energy.

The absolute energies of the HF and H\textsubscript{2} molecules are −1.003144E+01 eV and −7.83168 eV, respectively. The absolute energy of bulk NiF\textsubscript{2} is −4.055139E+01 eV.

Table S5: Absolute DFT energies of the slabs used for all surface energy calculations in the publication. All calculations are done with the HSE06 functional.

| Index | Termination | Filename | Energy [eV] |
|-------|-------------|----------|-------------|
| (110) | 1           | 110ox    | −1.6740408E+02 |
|       | 2           | 110s     | −1.6061501E+02 |
|       | 3           | 110red   | −1.4413422E+02 |
| (100) | 1           | 100ox    | −1.4770505E+02 |
|       | 2           | 100s     | −1.4068430E+02 |
|       | 3           | 100red   | −1.2447403E+02 |
| (101) | 1           | 101ox    | −1.7407405E+02 |
|       | 2           | 101s     | −1.5979820E+02 |
|       | 3           | 101red   | −1.6861518E+02 |
| (001) | 1 (ads.)    | 001ox    | −1.8765422E+02 |
|       | 1           | 001s     | −1.7987135E+02 |
|       | 1 (des.)    | 001red   | −1.6413300E+02 |
| (111) | 1           | 111ox    | −1.4759392E+02 |
|       | 2           | 111s1    | −1.3787147E+02 |
|       | 3           | 111s2    | −1.3768418E+02 |
|       | 4           | 111red   | −1.6337961E+02 |
References

1. Perdew, J. P., Burke, K. and Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

2. Dudarev, S. L., Botton, G. A., Savrasov, S. Y., Humphreys, C. J. and Sutton, A. P. *Phys. Rev. B* **1998**, *57*, 1505.

3. Krukau, A. V., Vydrov, O. A., Izmaylov, A. F. and Scuseria, G. E. *J. Chem. Phys.* **2006**, *125*, 224106.

4. Costa, M. M. R., Paixão, J. A., de Almeida, M. J. M. and Andrade, L. C. R. *Acta Cryst.* **1993**, *B49*, 591-599.

5. Goodenough, J. B. *Annu. Rev. Mater. Sci.* **1998**, *28*, 1-27.

6. Richards, P. L. *J. Appl. Phys.* **1963**, *34*, 1237-1238.

7. Cooke, A. H. *Proc. Phys. Soc.* **1965**, *85*, 967-977.

8. Strempfer, J., Rütt, U., Bayrakci, S. P., Brückel, T. and Jauch, W. *Phys. Rev. B* **2004**, *69*, 014417.

9. Das, H., Kanungo, S. and Saha-Dasgupta, T. *Phys. Rev. B* **2012**, *86*, 054422.

10. Olalde-Velasco, P., Jiménez-Mier, J., Denlinger, J. D., Hussain, Z. and Yang, W. L. *Phys. Rev. B* **2011**, *83*, 241102.

11. Bao, J. I., Gagliardi, L. and Truhlar, D. G. *J. Phys. Chem. Lett.* **2018**, *9*, 2353-2358.

12. Cotton, F. A. and Wilkinson, G. In Advanced Inorganic Chemistry vol. 4; John Wiley & Sons, New York: **1980**, pp 238.

13. https://webbook.nist.gov/cgi/cbook.cgi?ID=C7664393&Mask=1, accessed December 18, 2019.

14. http://www.codata.info/resources/databases/key1.html, accessed December 18, 2019.

15. https://webbook.nist.gov/cgi/cbook.cgi?Name=h2&cTG=on, accessed December 18, 2019.