



Computational Solid State Chemistry 2

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Contents and Plan

Modelling defects and dopants in ionic crystals

- Calculation of energies of formation of defects in crystals
- Modelling ion migration
- Doping: substitution and solution energies

Defects: revision

- We are usually interested in studying the formation of:
 - Vacancies
 - Interstitials
 - Substitutional defects (e.g. Dopants)
- Point defects and defect clusters
- Finite defect concentrations

Point defects and defect clusters

- The basis of the method used to calculate the formation energy of point defects and defect clusters is the **Mott-Littleton Approximation**.
 - NF Mott, MJ Littleton, *Trans. Faraday Soc.*, 1938, **34**, 485
 - A meeting was held in 1988 to mark 50 years since the publication of the paper!
 - *Faraday Trans. II*, 1989, **85**, 335-579

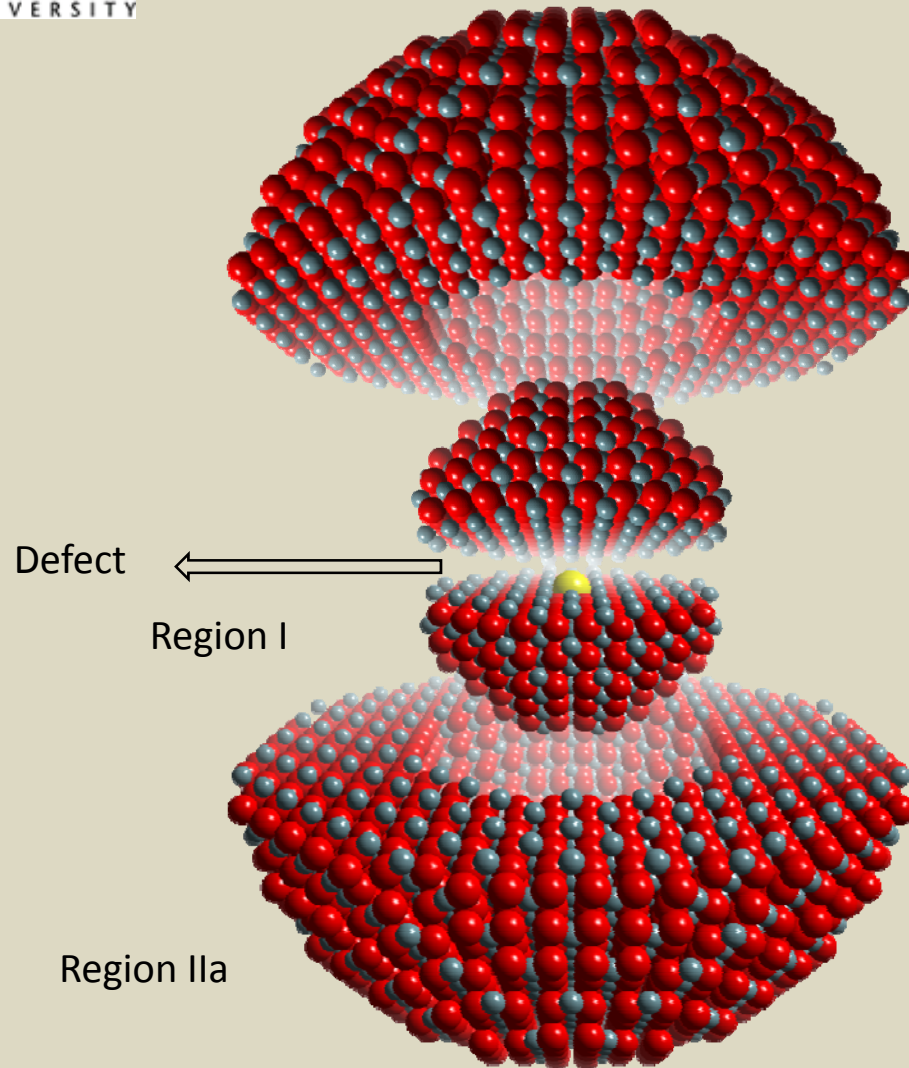


"Simulation of Defects in Polar Solids,"
on the 50th Anniversary of the Mott-Littleton Paper.
Polar Solids Group, Royal Society of Chemistry,
Oxford, 29 March, 1988.

N F Mott

Mott-Littleton approximation

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Region I

Ions are strongly perturbed by the defect and are relaxed explicitly with respect to their Cartesian coordinates.

Region II

Ions are weakly perturbed and therefore their displacements, with the associated energy of relaxation, can be approximated.



Calculating the formation energy of defects in ionic crystals – (i)

- Using the Mott-Littleton Approximation, the radii of regions I and IIA are specified (in Å), and the centre of the defect.
- In GULP this is done as follows (in UO_2):
size 10 15
centre 0.0 0.0 0.0
vacancy 0.0 0.0 0.0
- This will create a vacancy at the O site.



Calculating the formation energy of defects in ionic crystals – (ii)

- Running the GULP program with this information added to the basic dataset (from part 1), plus a few modifications to the initial keywords, will calculate the formation energy of an oxygen vacancy in UO_2
- Defect clusters are treated in a similar way, except that the centre of the **cluster** can be specified.



GULP dataset for oxygen vacancy calculation in UO_2

```
conp opti compare prop defe regi
# UO2 Structure parameters obtained from:
# Barrett, S.A.; Jacobson, A.J.; Tofield, B.C. and Fender, B.E.F.
# Acta Crystallographica B (1982) 38, 2775-2781
cell
5.4682 5.4682 5.4682 90.0 90.0 90.0
fractional 4
U core 0.00 0.00 0.00 -2.54
U shel 0.00 0.00 0.00 6.54
O core 0.25 0.25 0.25 2.40
O shel 0.25 0.25 0.25 -4.40
space
225
# U-O potential from Read & Jackson , Journal of Nuclear Materials, 406 (2010) 293–303
buck
U shel O shel 1027.6 0.4026 0.0 0.0 15.0
buck4
O shel O shel 11272.6 0.1363 134.0 0.0 1.2 2.1 2.6 15.0
spring
U core U shel 110.75
O core O shel 296.2
vacancy 0.25 0.25 0.25
size 10 15
centre 0.25 0.25 0.25
```

Modelling ion migration – (i)

- For example, in solid electrolytes, ions can migrate via the **vacancy mechanism**, whereby an ion moves into a neighbouring vacant site, creating a vacancy which is then available for another ion to move into.
- This can be modelled by having two vacancies, with the migrating ion represented by an **interstitial ion**.

Modelling ion migration – (ii)

- The migration **pathway** can be modelled by moving the ion between the two vacancies, or the **saddle point** (usually the mid point) configuration can be calculated.

- For O migration in UO_2 :

centre 0.25 0.0 0.0

vacancy 0.0 0.0 0.0

vacancy 0.5 0.0 0.0

interstitial **O** 0.25 0.0 0.0

Note that the migrating ion must be identified



Calculating activation energies for ion migration

- Once the energy of the saddle point configuration has been calculated, the activation energy for ion migration is calculated from:

$$\text{Activation energy} = \text{saddle point energy} - \text{vacancy formation energy}$$

- This energy can be compared with experimental energies.

Dopants in crystals

- We may be interested in calculating the energy involved in substituting a different ion in a structure (where that ion adds functionality, e.g. in optical/sensor materials, or in YSZ (Y stabilised ZrO_2))
- We will consider the process of substitution, and calculation of the **substitution energy** and the **solution energy**.

Introducing dopants – (i)

- To introduce dopants into the structure, the impurity keyword is used in GULP.
- In UO_2 , consider substituting a Pu (4+) ion at the U site:

centre 0.25 0.25 0.25

impurity Pu 0.25 0.25 0.25

- In this case the charges are the same, so no **charge compensation** is needed.

Introducing dopants – (ii)

- If there is a charge difference between the substituting and substituted ion, a charge compensating defect has to be included.
- This can be done as a separate calculation, or the defect can be included in the calculation as part of a defect cluster.
- Consider substituting a Mg (2+) ion into the UO₂ structure (at the U site):

How charge compensation is included

- In this case we could calculate the substitution energy from:

centre 0.25 0.25 0.25

impurity Mg core 0.25 0.25 0.25

- Charge compensation could be via a O^{2-} vacancy; this energy could be calculated separately or included as an extra line:

vacancy 0.0 0.0 0.0

Substitution and solution energies

- Substitution energies do not give information about trends, since they do not take into account all the energetic terms involved in the solution process.
- We will consider the 2 cases already mentioned, and list all the energy terms involved.
- Expressions for the **solution energy** (E_{sol}) will be obtained.

(i) Pu in UO₂

- Start with the oxide PuO₂, and mix it with UO₂.
 - Term 1: - E_{latt} (PuO₂) (produces ions of Pu⁴⁺ and O²⁻)
 - Term 2: substitution energy, E_{subs} (Pu_U) (from GULP)
 - Term 3: E_{latt} (UO₂) (the displaced U ion and the O combine)

- The solution equation is then:

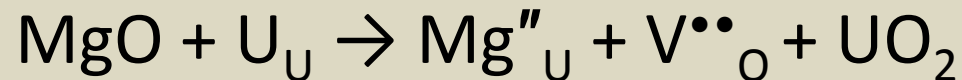


➤ $E_{\text{sol}} = - E_{\text{latt}} (\text{PuO}_2) + E_{\text{subs}} (\text{Pu}_U) + E_{\text{latt}} (\text{UO}_2)$

(ii) Mg in UO_2

- We follow a similar procedure to (i), but this time the vacancy formation energy term is included.

- Solution equation:



Note: Kroger-Vink notation employed

- Solution energy expression:

$$E_{\text{sol}} = -E_{\text{latt}}(\text{MgO}) + E_{\text{subs}}(\text{Mg}''_\text{U}) + E(\text{V}^{\bullet\bullet}_\text{O}) + E_{\text{latt}}(\text{UO}_2)$$

Bound and unbound defects

- In case (ii), the solution energy can be calculated using values of the substitution and vacancy formation energies calculated separately or together.
- In the second case, the defect **binding energy** is included in the calculation.
- Tables of bound and unbound solution energies can be found in papers.

Finite defect concentrations

- When considering doping, it is useful to be able to consider solution of more than one dopant ion in an infinite lattice (which is what has been presented so far).
- A new method has been developed which enables solution energies to be calculated as a function of dopant concentration.
- This will be presented in my talk tomorrow!

Conclusions for part 2

- Defects have been briefly revised.
- The procedure for calculating point defect formation energies has been explained.
- The calculation of activation energies for ion migration has been explained.
- The calculation of substitution energies has been explained, and solution energies introduced.