

Lecture 2 - defects

Lecture summary

- Introduction to defects
- Types of defect
- Intrinsic and extrinsic defects
- Defect equations

Defects

All crystals contain defects of some sort, for example:

- Missing atoms (*vacancies*)
- Atoms in the 'wrong' place
 - *interstitials* (between lattice sites) or *substitutions* (different atom types)
- Extended defects of lines or planes of atoms

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Defects are often the source of interesting properties

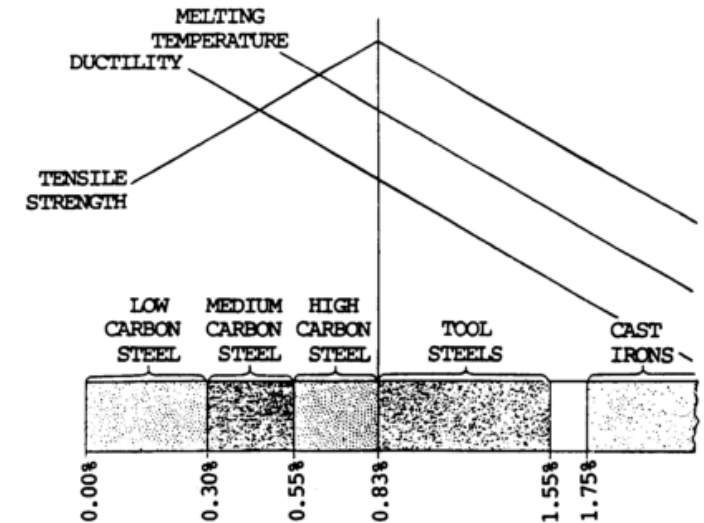
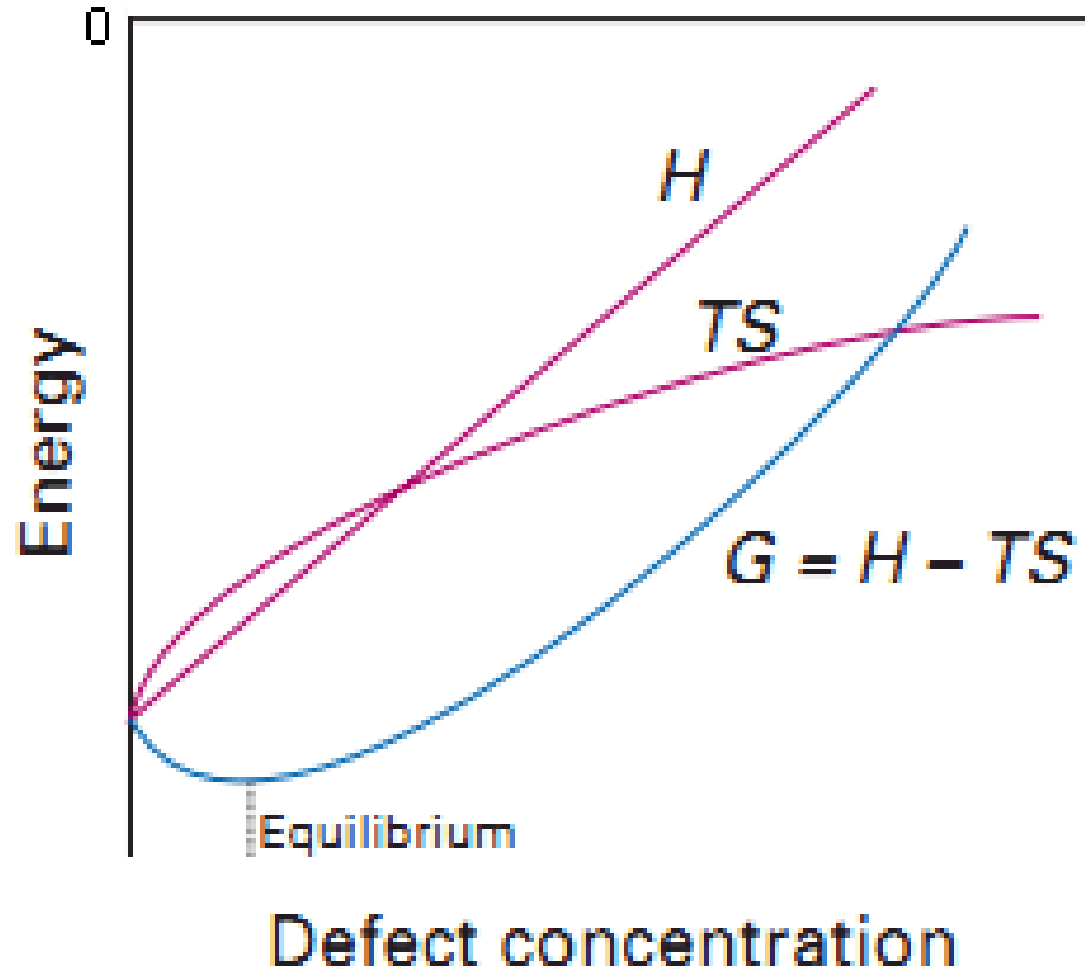


Figure 7-7. How steel qualities change as carbon is added.

Defect amounts


The number of defects is a fine balance of entropy and enthalpy

- Defects gain entropy but have a (often large) formation energy




Types of defect

The three most common defect types in ionic solids are:

| Vacancy | Interstitial | | | | | | Substitution | | | | | |
|--|--------------|-------------|-------------|-------------|-------------|-------------|--------------|-------------|-------------|-------------|-------------|-------------|
| M X M X M X X M X M X M M X M X M X X M X  X M M X M X M X X M X M X M M X M X M X X M X M X M | M X M X M X | X M X M X M | M X M X M X | X M X M X M | M X M X M X | X M X M X M | M X M X M X | X M X M X M | M X M X M X | X M X M X M | M X M X M X | X M X M X M |

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|---|--------------------------|--|--|--|--|--|--------------|--------------------|--|--|--|--|
| M X M X M X | M X M X M X | | | | | | | M X M X M X | | | | |
| X M X M X M | X M X M X M | | | | | | | X M X M X M | | | | |
| M X M X M X | M X M X M X | | | | | | | M X M X M X | | | | |
| X M X  X M | X M X ^X M X M | | | | | | | X M X M X M | | | | |
| M X M X M X | M X M X M X | | | | | | | M X N X M X | | | | |
| X M X M X M | X M X M X M | | | | | | | X M X M X M | | | | |
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| X M X M X M | X M X M X M | | | | | | | X M X M X M | | | | |

Additionally, defects can be either

- *intrinsic* (maintaining stoichiometry) or
- *extrinsic* (non-stoichiometric)

Intrinsic defects

Two of the most common stoichiometric defects are:

Schottky

- Charge-balanced combination of anion and cation vacancies

Frenkel

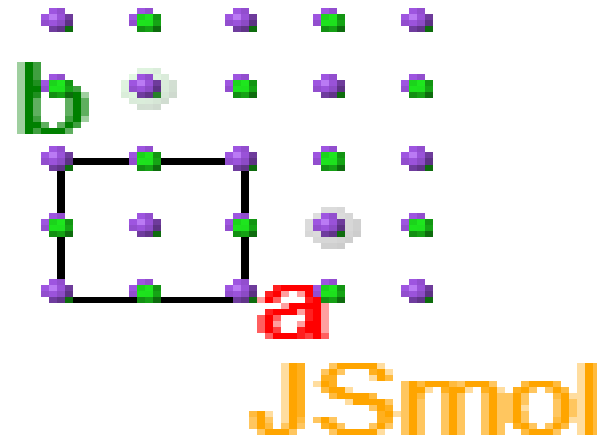
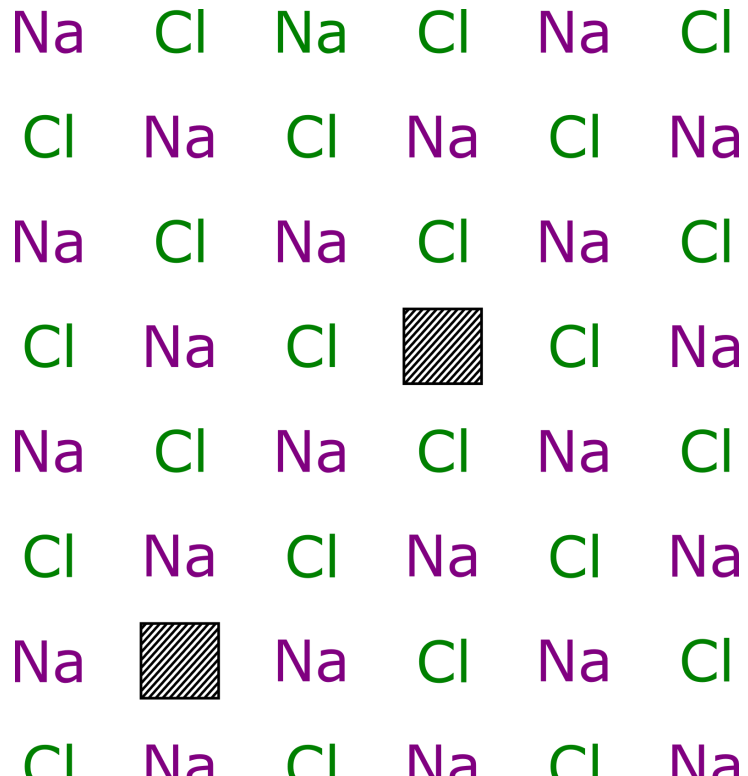
- Ions displaced to interstitial sites

Defects observed depend on both structure type and atoms involved.



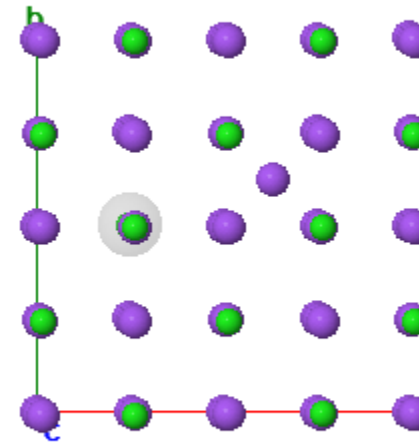
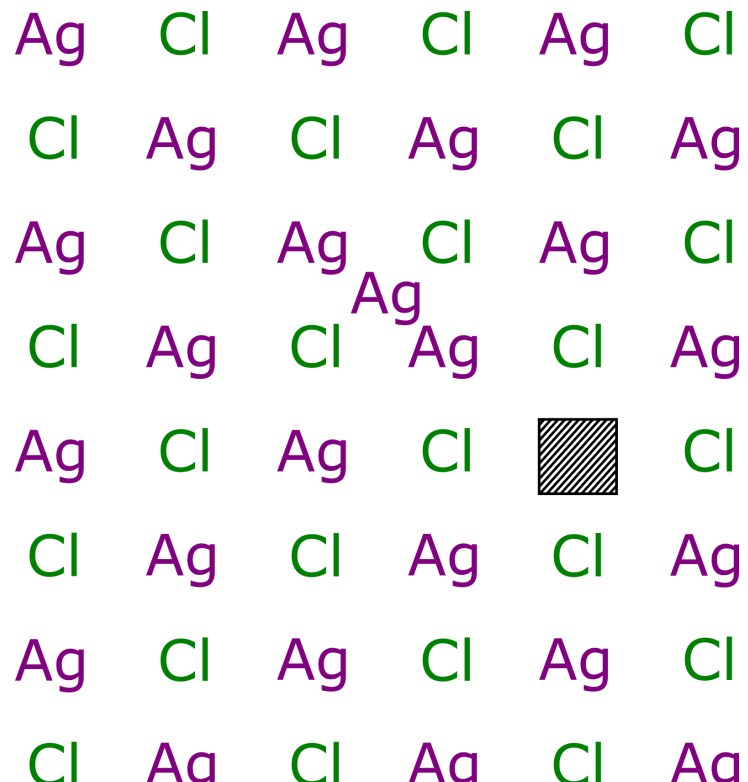
Schottky defects

- Typically occur when anions and cations have similar size (e.g. NaCl structure)
- Reduced density compared with the ideal material
- e.g. NaCl - equal numbers of Na and Cl vacancies



Frenkel defects

- Smaller ion normally displaced
- Only one ion type shows defect
- e.g. AgCl (NaCl-type)
 - Smaller Ag^+ ion displaced to tetrahedral holes in CCP Cl^- structure



Defect equations

Useful to write equation for defects, using **Kroger-Vink** notation:

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- Charges shown relative to the ideal host site:
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- For example:
 - Na vacancy in NaCl: V_{Na}'
 - Ag interstitial in AgCl: Ag_i^{\bullet}

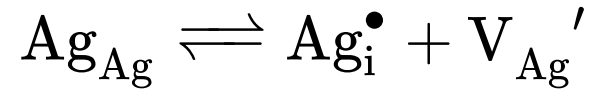
Defect equations (2)

Defect equations must balance for:

- mass (atoms)
- charge
- sites
 - positions created/destroyed must balance

Examples

AgCl interstitial formation again:



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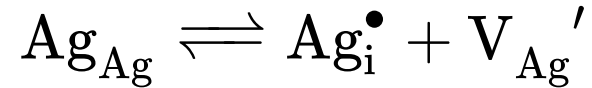


NaCl Schottky formation:



Examples

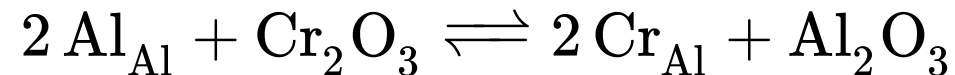
AgCl interstitial formation again:



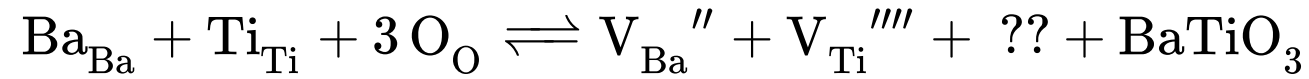
NaCl Schottky formation:



Easily extended to substitutions, e.g. substituting Al^{3+} with Cr^{3+} in Al_2O_3 (ruby):



Quick test - BaTiO₃ Schottky Formation

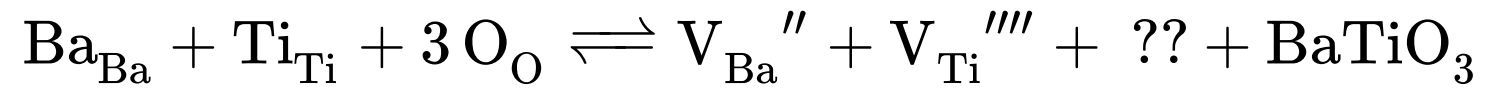


What is missing?

$3 \text{V}_{\text{O}}^{\bullet\bullet}$ ☐ A

$3 \text{O}_{\text{i}}''$ ☐ B

$3 \text{O}_{\text{O}}^{\times}$ ☐ C



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Ionic Substitution

- Ions of similar size can often replace each other

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- While an integer number are substituted across a crystal, the average can be non-stoichiometric
 - often represented by a variable such as x :
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 - i.e. Ruby is $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ ($0 \leq x \leq 2$)
- Substitution can dramatically affect properties:
 - e.g. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$:
 - semiconducting for $x = 0$
 - superconducting (below 40 K) for $x = 0.15$

Extrinsic defects

Substitution can also drive formation of defects, e.g. doping NaCl with CaCl₂:

Overall synthesis reaction:



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Overall synthesis reaction:



Kroger-Vink notation:



More complex example

Sometimes, substitution (or 'doping') can give rise to multiple potential defects.

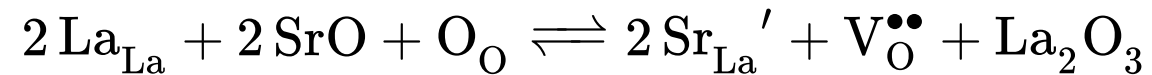
For example, replacing La^{3+} by Sr^{2+} in LaCoO_3 could occur:

More complex example

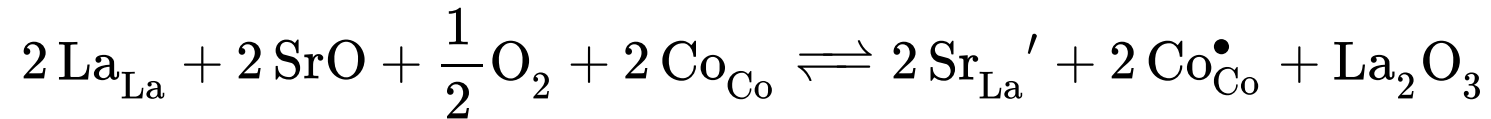
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For example, replacing La^{3+} by Sr^{2+} in LaCoO_3 could occur:

- by creating oxygen vacancies;



- or by oxidising Co^{3+} to Co^{4+}



Quiz 2 - Extrinsic defects

At high pressure, oxygen vacancies in Mg_2SiO_4 can react with H_2O to form new defects.

 **Mentimeter**

Assign these as reagents / products / not used

| | | |
|-----------------------|-----------|-------------------------------------|
| H_2O | | <input type="button" value="Skip"/> |
| | 1 Reagent | |
| 1 | | 3 |
| Reagent | | Product |
| H_i^\bullet | | <input type="button" value="Skip"/> |
| | 1 Reagent | |
| 1 | | 3 |
| Reagent | | Product |
| OH_o^\bullet | | <input type="button" value="Skip"/> |

Results - Extrinsic defects

Go to www.menti.com and use the code 2153 6400

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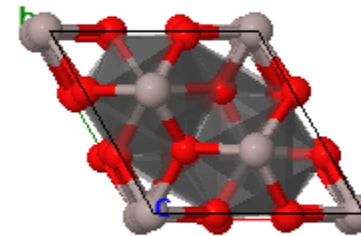
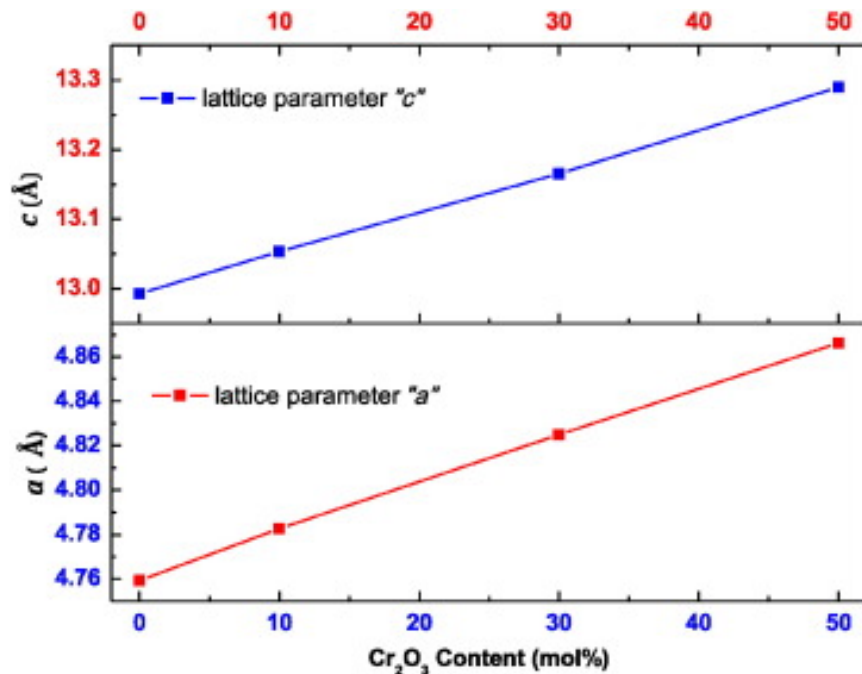
Assign these as reagents / products / not used

| Reagent | | Product |
|-------------------------------|--|---------|
| H_2O | | |
| H_i^\bullet | | |
| OH_o^\bullet | | |
| H_2 | | |
| $\text{V}_o^{\bullet\bullet}$ | | |
| O_o | | |

Solid solutions

Frequently, substitutional defect concentrations can exceed 1%

- known as a 'solid solution'
- Very important for tuning properties *via* synthesis
- Often useful to think of the "average ion" properties at each site
 - e.g. ionic radius, resulting in *Vegard's Law*
 - Lattice parameter is weighted average of the end-members, e.g. $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$:



JSmol

Non-stoichiometry

Some materials are naturally non-stoichiometric even without extrinsic defects

- Very common in transition metal compounds
 - multiple oxidation states available
- Example: FeO (wustite, NaCl structure) cannot actually form stoichiometrically at ambient pressure
 - Actually Fe_{1-x}O , with $0.05 \leq x \leq 0.15$

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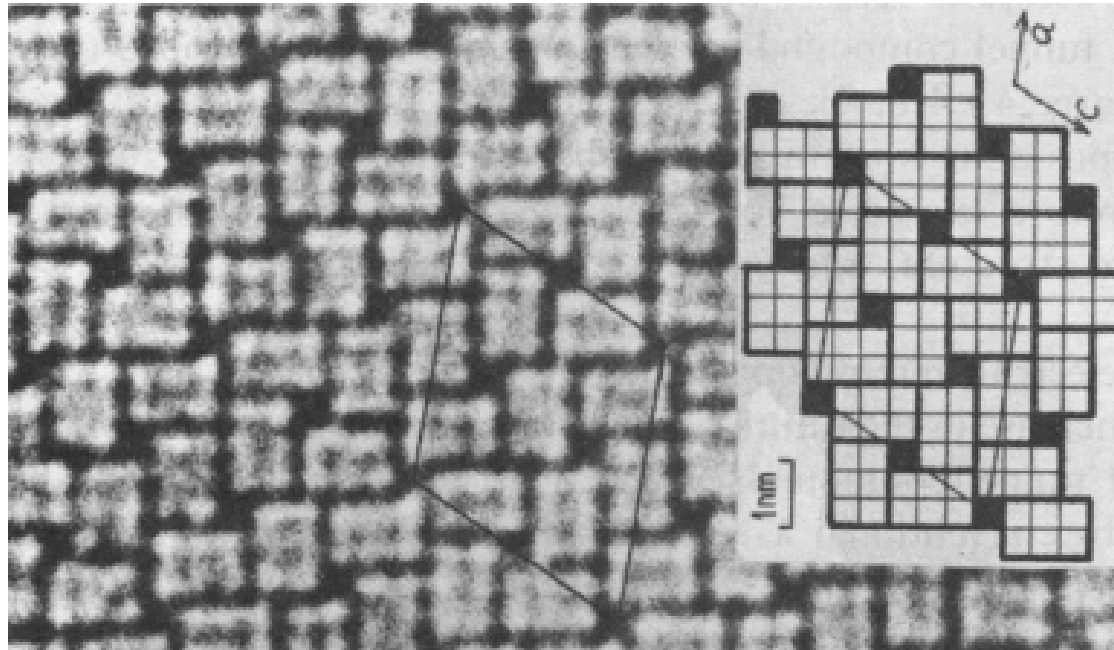
N.B. From cation:anion ratio alone you cannot determine the defect types

e.g. Fe:O ratio of 0.9 could equally be $\text{Fe}_{0.9}\text{O}$ or $\text{FeO}_{1.11}$!

Defect ordering

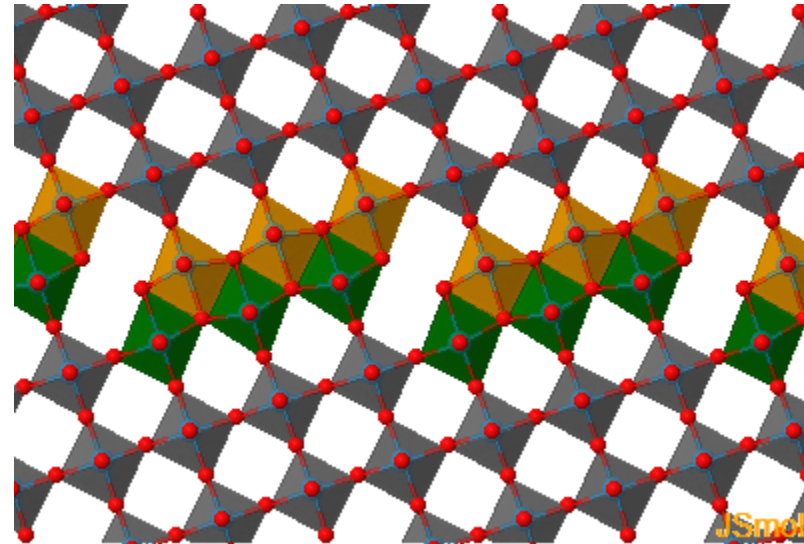
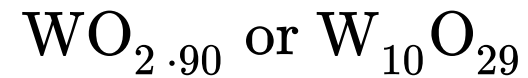
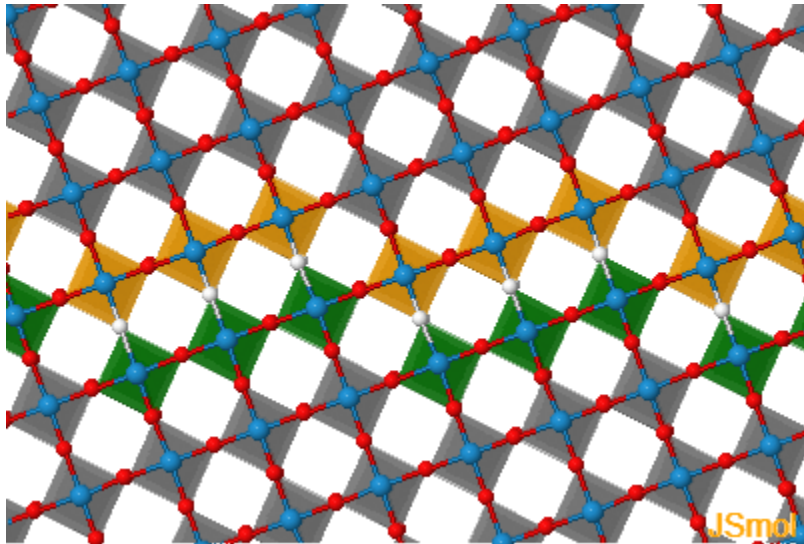
- At large defect concentrations, defects can interact
 - minimises enthalpy
- Can occur as
 - clusters ('0D')
 - lines ('1D')
 - planes ('2D')

Often seen in microscopy, e.g. $\text{ZrNb}_{24}\text{O}_{62}$ shows 2D order in two directions:



Example - WO_3

Plane-like defects often described as shear phases



Lecture recap

- Crystals are never perfect!
 - defects favoured at higher temperature
- Three main types of defect:
 - vacancy (called Schottky if stoichiometry maintained)
 - interstitial (called Frenkel if stoichiometry maintained)
 - substitution
- Kroger-Vink notation is a way to write defect equations
- Some materials can form solid solutions and/or non-stoichiometric compositions
- If defects order, this can lead to new stoichiometric structure types

Feedback



What did you like or dislike about this lecture?

Short answers are recommended. You have 250 characters left.

250

You can submit multiple answers

Submit

