Lecture 2 - defects

Return to course contents

Lecture summary

- Introduction to defects
- Types of defect
- Instrinsic 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

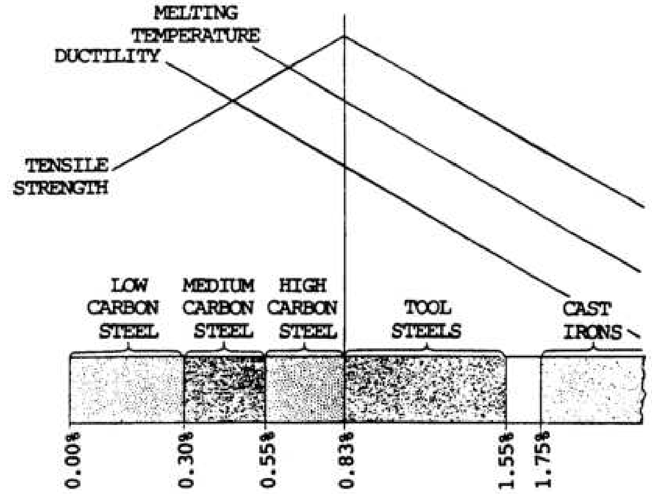


Figure 7-7. How steel qualities change as carbon is added.

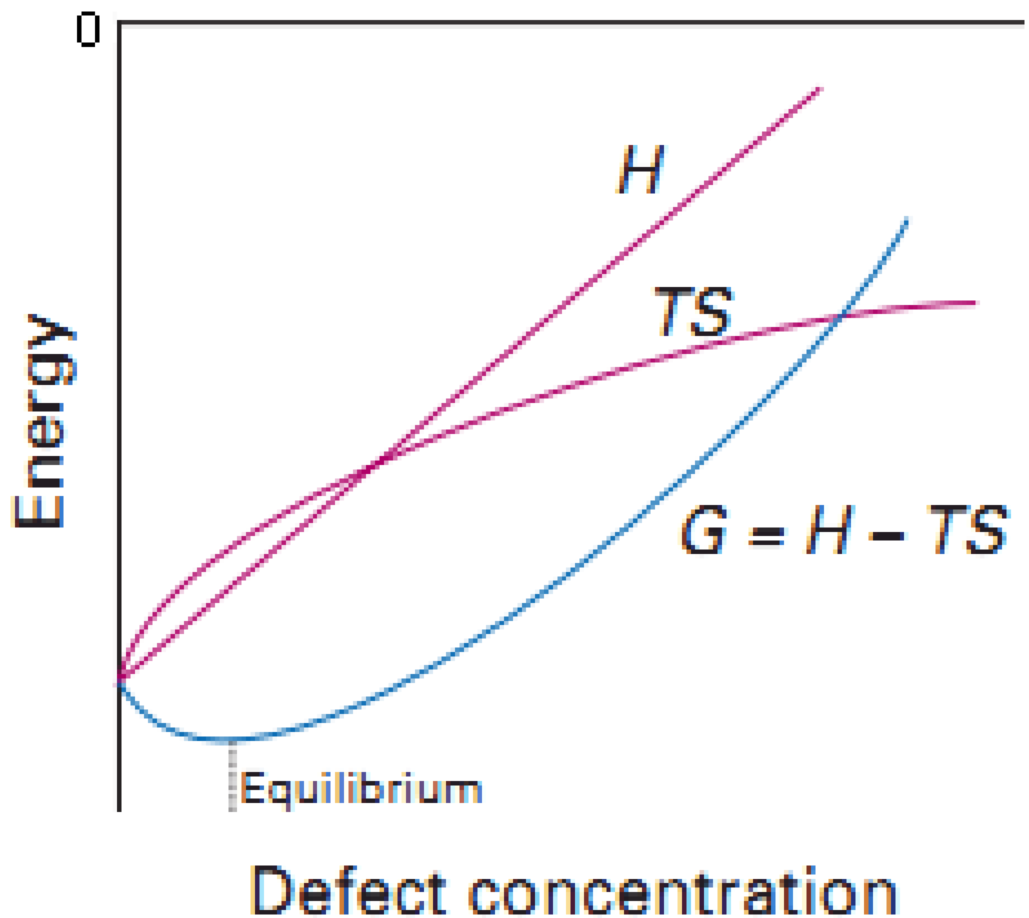
~1% Substitution in Al_2O_3

Effect of interstitial carbon on iron properties

Defect amounts

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

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



Minimum in ΔG depends on structure and bonding, but typically << 1%.

Types of defect

The three most common defect types in ionic solids are:

Vacancy	Interstitial	Substitution
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	
X M X 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 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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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								
X	M	X		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	N	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	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

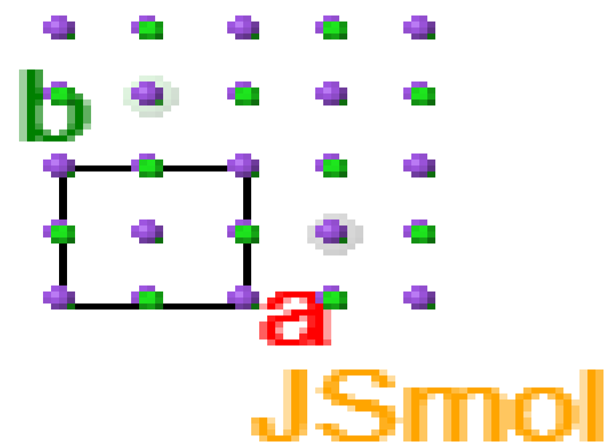
Defects observed depend on both structure type and atoms involved.

Top: Walter Schottky (1886-1976) Bottom: Yakov Frenkel (1894-1952)

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

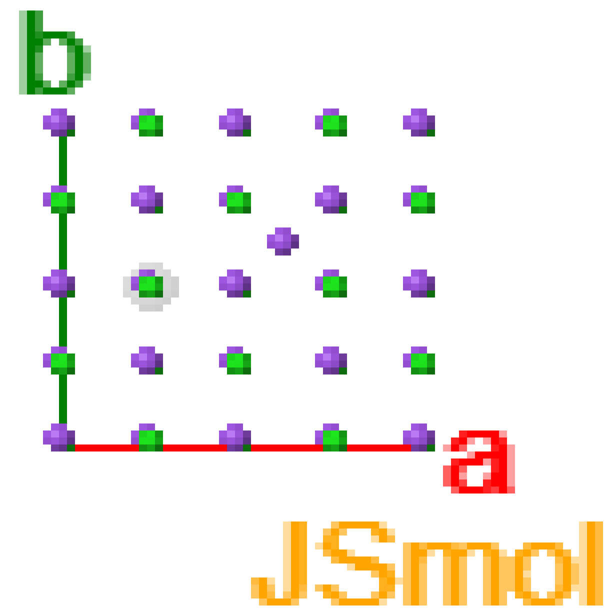
Na	Cl	Na	Cl	Na	Cl
Cl	Na	Cl	Na	Cl	Na
Na	Cl	Na	Cl	Na	Cl
Cl	Na	Cl		Cl	Na
Na	Cl	Na	Cl	Na	Cl
Cl	Na	Cl	Na	Cl	Na
Na		Na	Cl	Na	Cl
Cl	Na	Cl	Na	Cl	Na



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

Ag	Cl	Ag	Cl	Ag	Cl
Cl	Ag	Cl	Ag	Cl	Ag
Ag	Cl	Ag	Cl	Ag	Cl
		Ag			
Cl	Ag	Cl	Ag	Cl	Ag
Ag	Cl	Ag	Cl		Cl
Cl	Ag	Cl	Ag	Cl	Ag
Ag	Cl	Ag	Cl	Ag	Cl
Cl	Ag	Cl	Ag	Cl	Ag



Defect equations

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

- Normal chemical symbols used for atoms, and V for vacancies

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    - $'$ for $1-$, $''$ for $2-$, etc.;
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- For example:
  - Na vacancy in NaCl: $\mathrm{V_{Na}}'$
  - Ag interstital in AgCl: $\mathrm{Ag_i^{\bullet}}$

Defect equations (2)

Defect equations must balance for:

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

Examples

AgCl interstitial formation again:

$$\mathrm{Ag_{Ag}} \rightleftharpoons \mathrm{Ag_i^{\bullet}} + \mathrm{V_{Ag}}'$$

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

$$2\,\mathrm{Al_{Al}} + \mathrm{Cr_2O_3} \rightleftharpoons 2\,\mathrm{Cr_{Al}} + \mathrm{Al_2O_3}$$

Quick test - $BaTiO_3$ Schottky Formation

$$Ba_{Ba} + Ti_{Ti} + 3\,O_O \rightleftharpoons v_{Ba}'' + v_{Ti}'''' + \;?? + BaTiO_3$$

Mentimeter

What is missing?

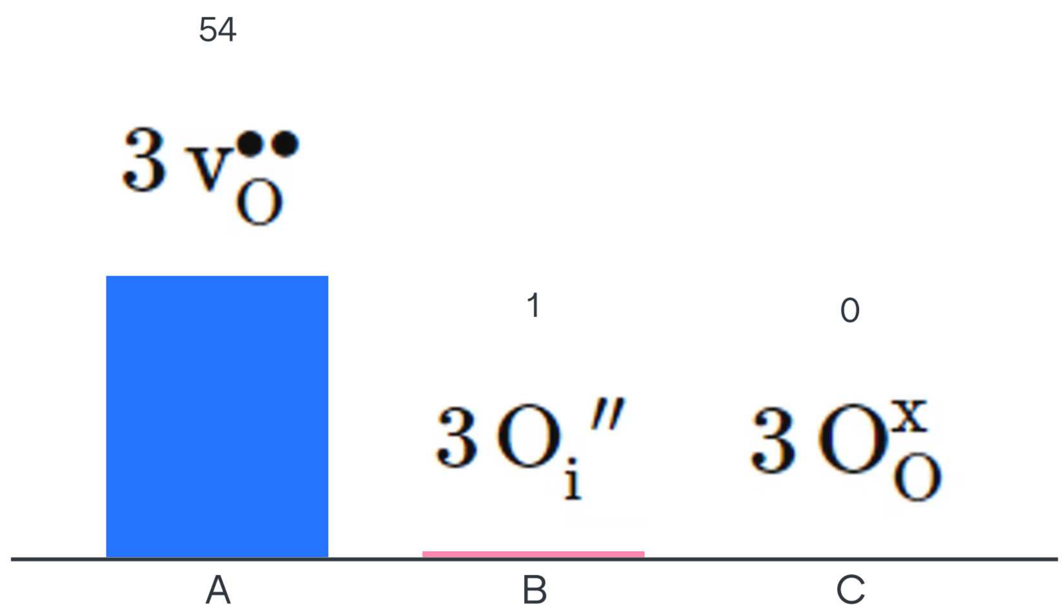
- $3\,v_O^{\bullet\bullet}$ ○ A
- $3\,O_i''$ ○ B
- $3\,O_O^x$ ○ C

Submit

$$\mathrm{Ba_{Ba}} + \mathrm{Ti_{Ti}} + 3\,\mathrm{O_O} \rightleftharpoons \mathrm{v_{Ba}}'' + \mathrm{v_{Ti}}'''' + \; ?? + \mathrm{BaTiO_3}$$

Go to **www.menti.com** and use the code

What is missing?



55

Ionic Substitution

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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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- Substitution can dramatically affect properties:
    - e.g. $\mathrm{La_{2-x}Sr_xCuO_4}$:
        - 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 $\mathrm{CaCl_2}$:

Overall synthesis reaction:

$$(1-2\,\mathrm{x})\mathrm{NaCl} + \mathrm{xCaCl_2} \longrightarrow \mathrm{Na_{1\,-2\,x}Ca_x\,Cl}$$

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Kroger-Vink notation:

$$2\,\mathrm{Na_{Na}} + \mathrm{CaCl_2} \rightleftharpoons \mathrm{Ca^{\bullet}_{Na}} + \mathrm{V_{Na}}' + 2\,\mathrm{NaCl}$$

More complex example

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

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

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

- by creating oxygen vacancies;

$$2\,\mathrm{La_{La}} + 2\,\mathrm{SrO} + \mathrm{O_O} \rightleftharpoons 2\,\mathrm{Sr_{La}}' + \mathrm{V_O^{\bullet\bullet}} + \mathrm{La_2O_3}$$

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

$$2\,\mathrm{La_{La}} + 2\,\mathrm{SrO} + \frac{1}{2}\mathrm{O_2} + 2\,\mathrm{Co_{Co}} \rightleftharpoons 2\,\mathrm{Sr_{La}}' + 2\,\mathrm{Co_{Co}^{\bullet}} + \mathrm{La_2O_3}$$

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 reagants / products / not used

H_2O Skip

1 Reagent

1 Reagent … 3 Product

$H_i^{\bullet}$ Skip

1 Reagent

1 Reagent … 3 Product

$OH_O{}'$ Skip

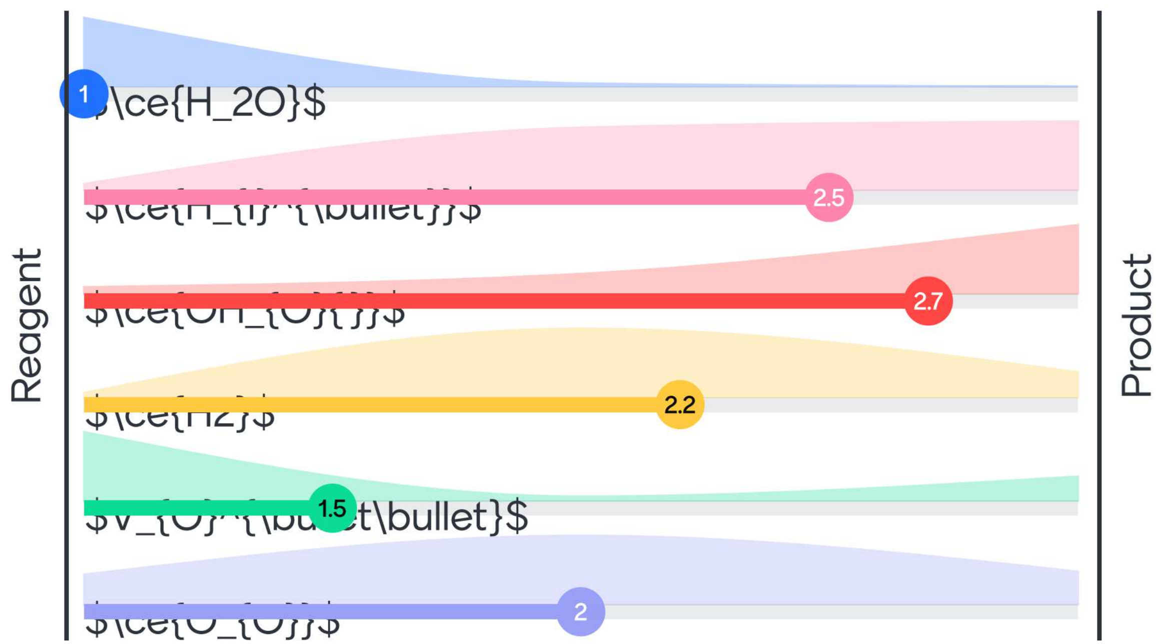
1 Reagent

1 … 3

Results - Extrinsic defects

Go to **www.menti.com** and use the code

Assign these as reagants / products / not used

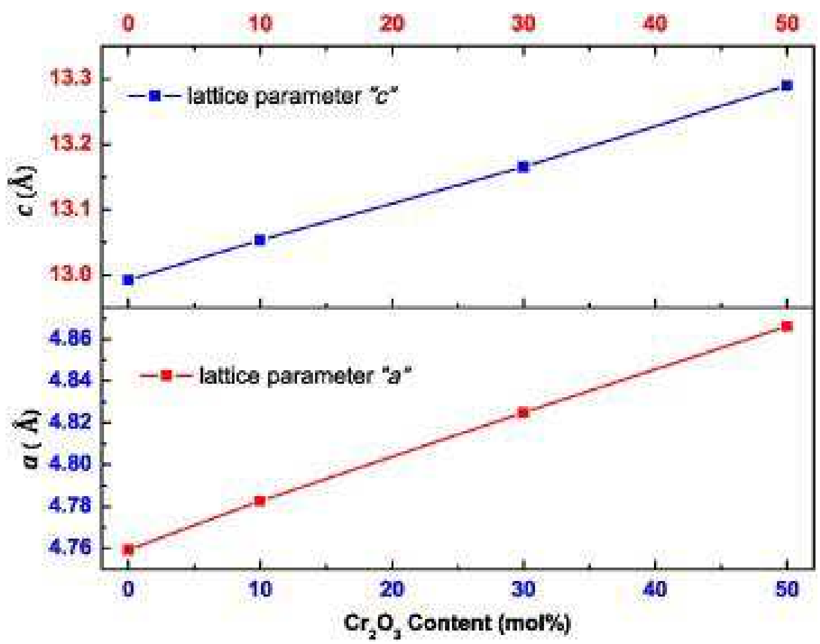


44

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. $Al_{2-x}Cr_xO_3$:



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 $\mathrm{Fe_{1\ -x}O}$, with $0.05 \leq x \leq 0.15$

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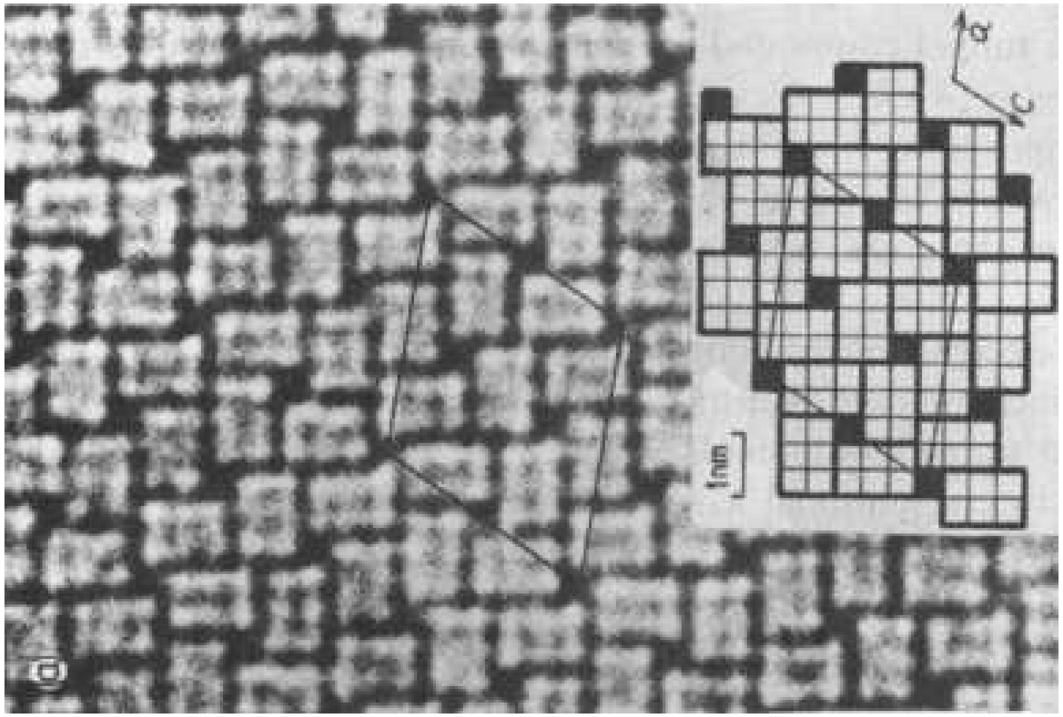
N.B. From cation:anion ratio alone you cannot determine the defect types
e.g. Fe:O ratio of 0.9 could equally be $\mathrm{Fe_{0\ \cdot 9}O}$ or $\mathrm{FeO_{1\ \cdot 11}}$!

Defect ordering

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

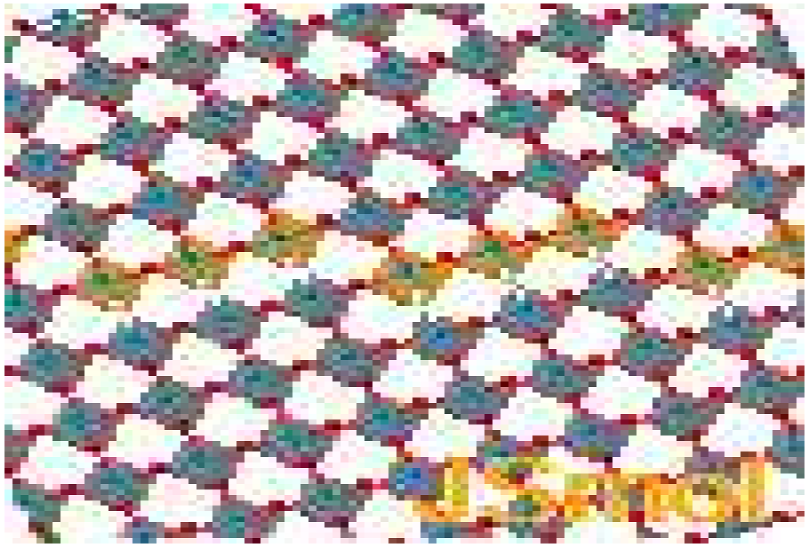
Often seen in microscopy, e.g. $\mathrm{ZrNb_{24}O_{62}}$ shows 2D order in two directions:



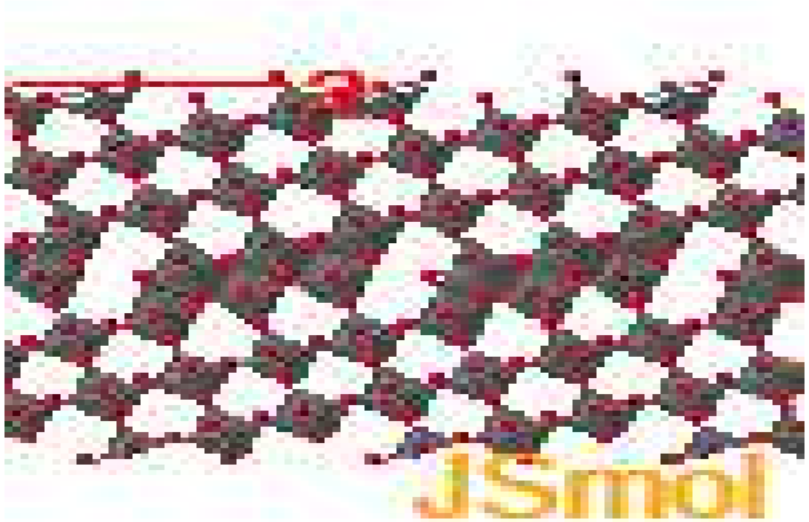
Example - WO_3

Plane-like defects often described as shear phases

WO_3



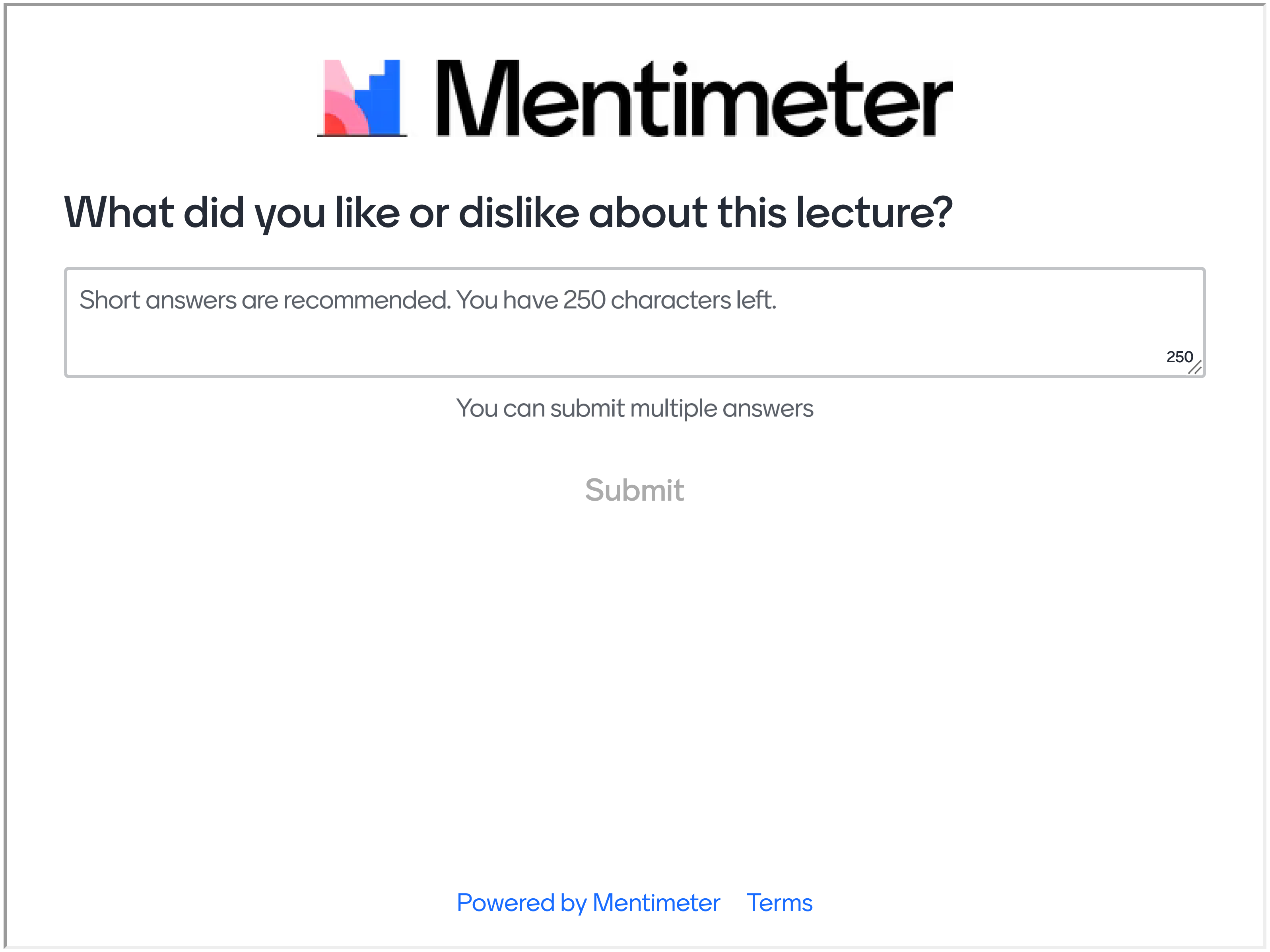
$WO_{2.90}$ or $W_{10}O_{29}$



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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