

# Lecture 2 - defects

# Lecture summary

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

# 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 (see lecture 5)

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Defects are often the source of interesting properties

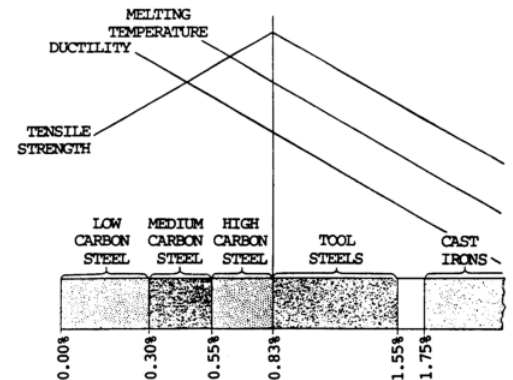
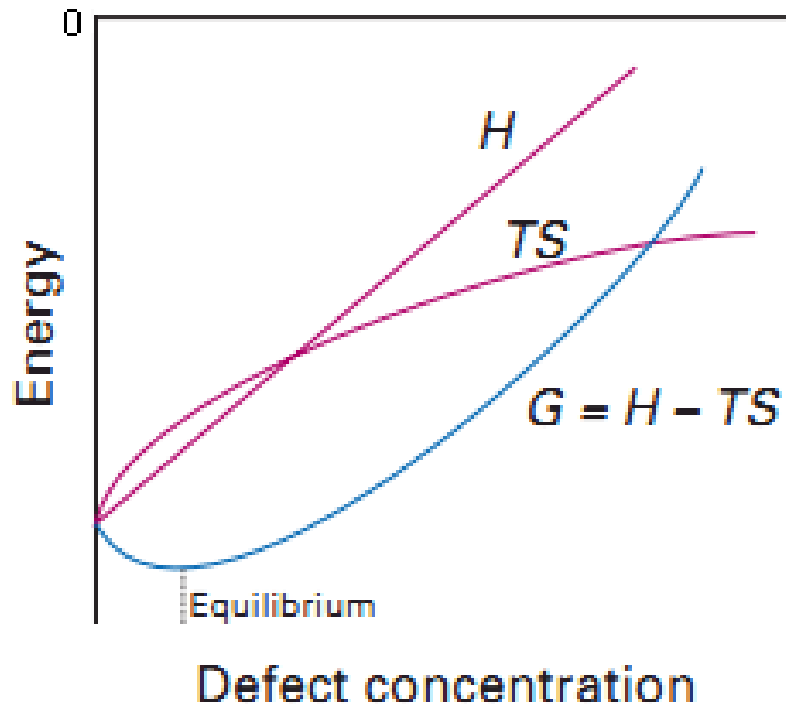


Figure 7-7. How steel qualities change as carbon is added.

# Defect amounts

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


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



Minimum in  $\Delta G$  depends on structure and bonding, but typically  $\ll 1\%$ .


# 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	M	X		X	M	X	M	X	<sup>X</sup> 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

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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		X	M	X	M	X	<sup>X</sup> 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

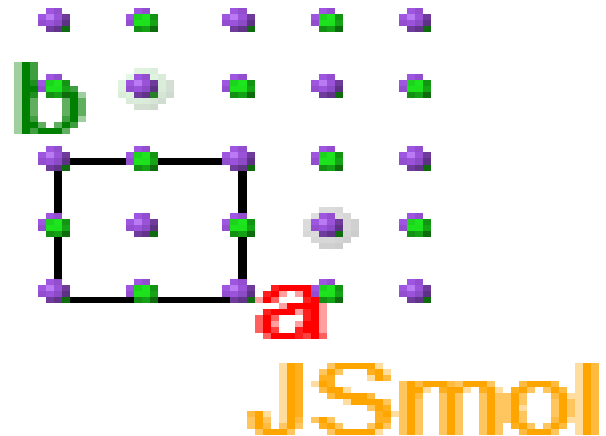
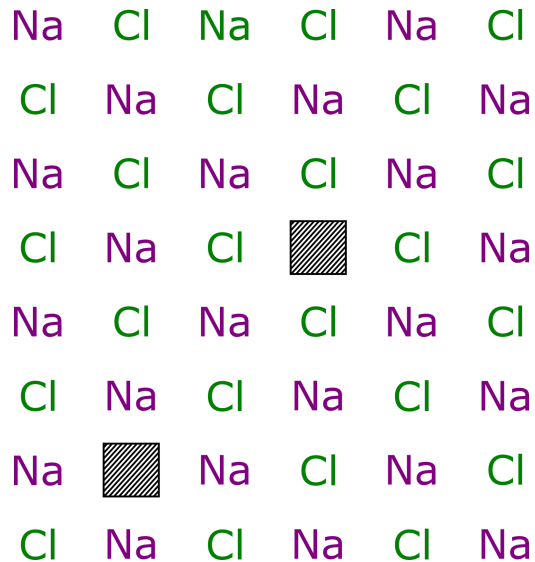


Defects observed depend on both structure type and atoms involved.



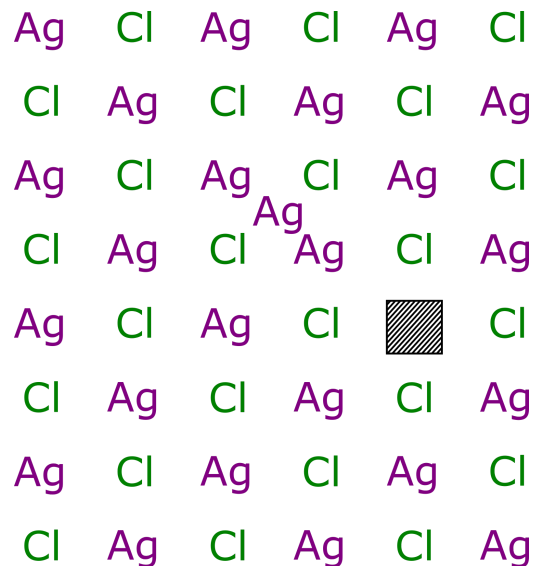
# Schottky defects

- 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 shows defect
- e.g. AgCl (NaCl-type)
  - Smaller  $\text{Ag}^+$  ion displaced to tetrahedral holes in CCP  $\text{Cl}^-$  structure



# Defect equations

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

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  - x for no net charge (sometimes omitted)
- For example:
  - Na vacancy in NaCl:  $V_{\text{Na}}'$
  - Ag interstitial in AgCl:  $\text{Ag}_i^{\bullet}$

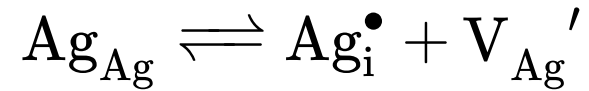
# Defect equations (2)

Defect equations must balance for:

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

# Examples

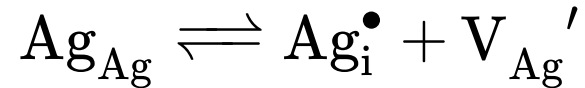
AgCl interstitial formation again:





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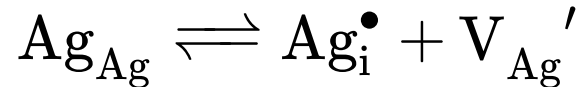


NaCl Schottky formation:



# Examples

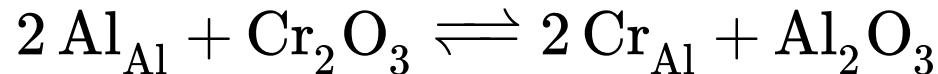
AgCl interstitial formation again:



NaCl Schottky formation:



Easily extended to substitutions, e.g. substituting  $\text{Al}^{3+}$  with  $\text{Cr}^{3+}$  in  $\text{Al}_2\text{O}_3$  (ruby):



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- 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  $\text{CaCl}_2$ :

Overall synthesis reaction:



Kroger-Vink notation:

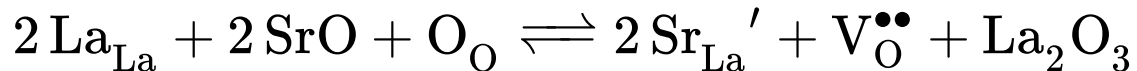


# More complex example

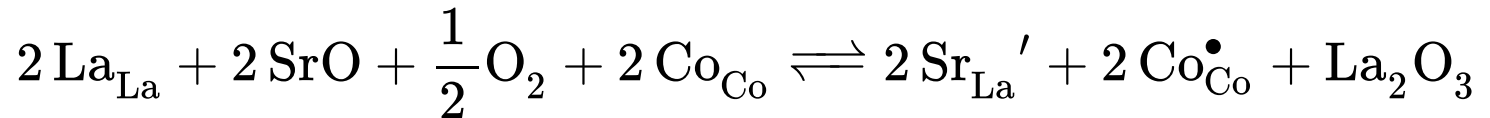
Sometimes, substitution (or 'doping') can give rise to multiple potential defects.

For example, substitution of  $\text{La}^{3+}$  for  $\text{Sr}^{2+}$  in  $\text{LaCoO}_3$  could occur:

- by creating oxygen vacancies;



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

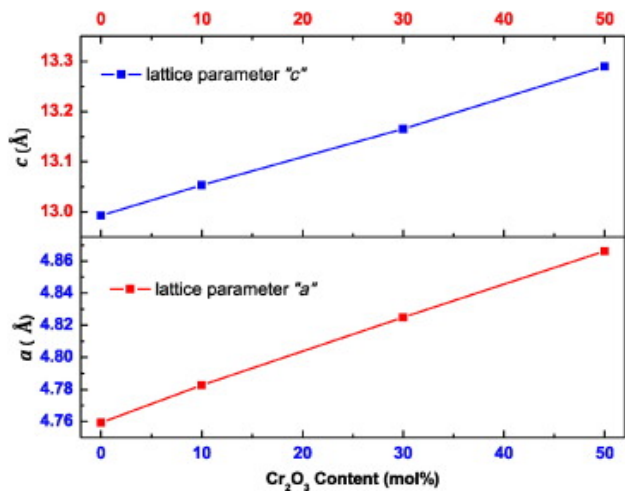
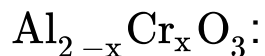


# Solid solutions

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.



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  $\text{Fe}_{1-x}\text{O}$ , 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  $\text{FeO}_{1.11}$ !

# Conductivity

- Many ionic solids conduct electricity; due to *ionic* and/or *electronic* motion.
- Most ionic solids are electrically insulating/semiconducting (localised electrons)

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- Ionic conductivity is dominated by *defects*
  - 'Ideal' lattice sites are fixed in place
- Conductivity,  $\sigma = nq\mu$ , where
  - $n$  is number of charge carriers
  - $q$  is charge
  - $\mu$  is the mobility of charge carriers

# Ion migration mechanisms

Three 'main' mechanisms of ionic migration

## 1. Vacancy mechanism

Vacancies move throughout the lattice (atoms move into vacancy)



## 2. Interstitial mechanism

Ions hop between interstitial sites



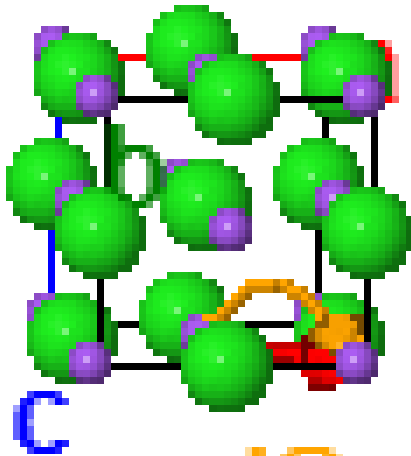
### 3. Interstitialcy (knock-on) mechanism

Interstitial ions 'push' into a neighbouring site

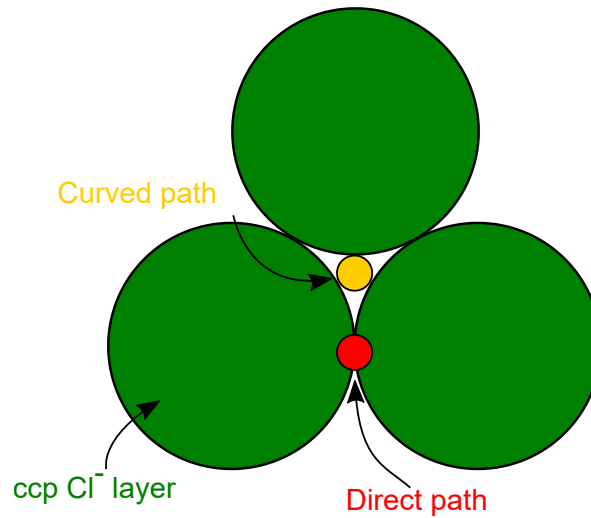


# Migration paths

Ion paths are rarely **direct**, but will take the **lowest energy route**.



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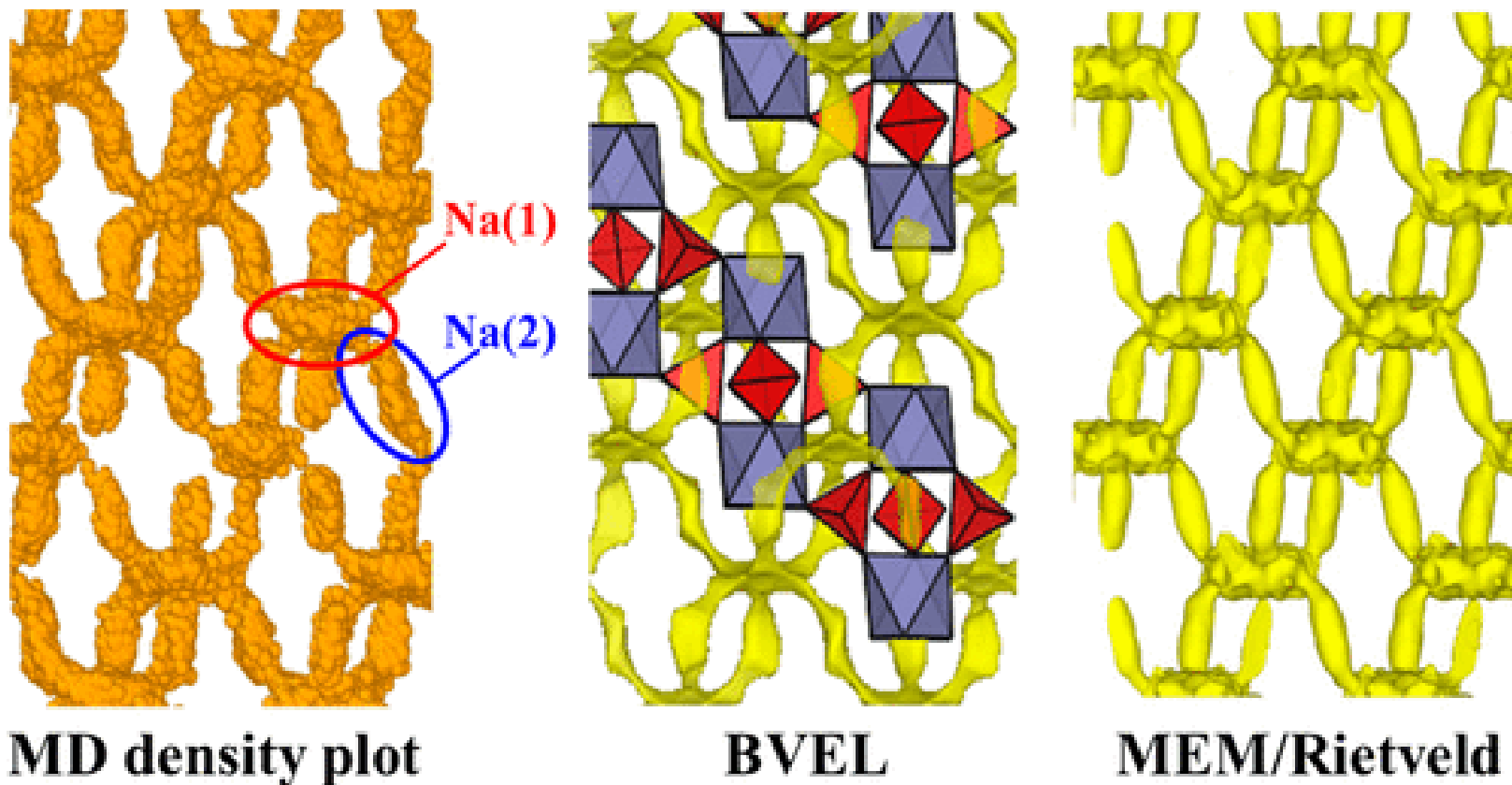




# Pathways can be complex

- Migration pathways can be calculated and/or experimentally determined

e.g. **NASICON**  $\text{Na}^+$  conductor,  $\text{Na}_3\text{Zr}_2(\text{SiO}_4)_2(\text{PO}_4)$ :

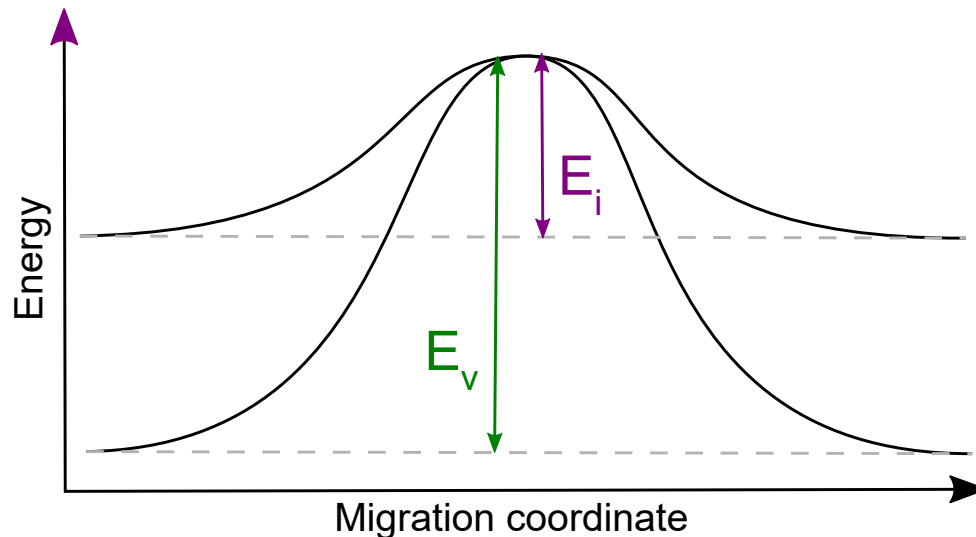


# Migration energetics

- Defect mobility is a thermally-activated process:

$$\mu = \mu_0 \exp\left(-\frac{E_a}{RT}\right)$$

- interstitial sites are higher energy than vacancies, so smaller energy barrier ( $E_i < E_a$ ) - dominates



# Variation with temperature

As  $\sigma = nq\mu$  and  $\mu$  is thermally-activated,

$$\begin{aligned}\sigma &= nq\mu_0 \exp\left(-\frac{E_a}{RT}\right) \\ &= A \exp\left(-\frac{E_a}{RT}\right)\end{aligned}$$

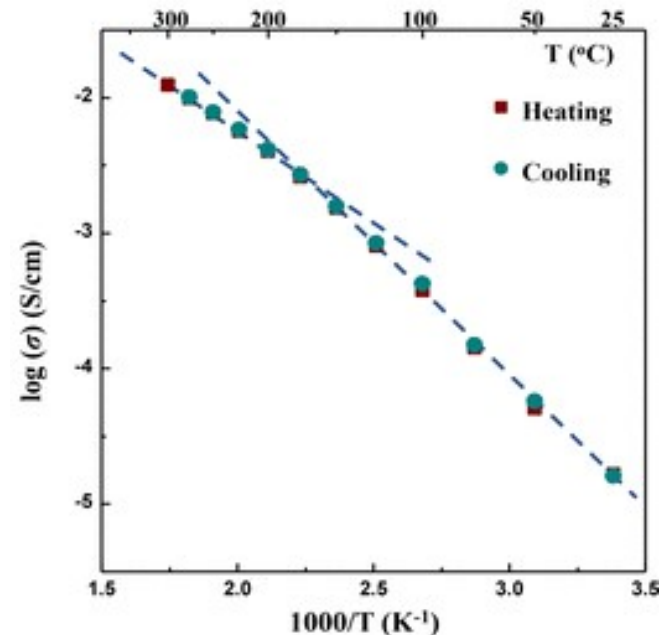
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Plotting  $\ln \sigma$  vs.  $\frac{1}{T}$  (or more commonly  $\log_{10} \sigma$  vs  $\frac{1000}{T}$  for high temperature measurements) should give a straight line

- gradient =  $-\frac{E_a}{R}$  (or  $-\frac{E_a}{2303R}$ ).



# 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
- Defects can give rise to ionic conduction
  - Occurs by three main mechanisms:
    - Vacancy hopping
    - Interstitial hopping
    - interstitialcy (knock-on) cooperation
- Ionic conductivity is thermally-activated
  - shows Arrhenius-like behaviour