# Lecture 3 - Ionic Conductivity

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# Lecture summary

- Recap of defect types
- Ionic conductivity
- Conduction mechanisms
- Ionic migration paths
- Energetics of conduction

# Defect recap


Wooclap Code: SUJNYY

# Defect recap results

wooclap

Quiz results will be available here
after the lecture

# 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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- Most ionic solids are electrically insulating/semiconducting (localised electrons)
- Ionic conductors are important!

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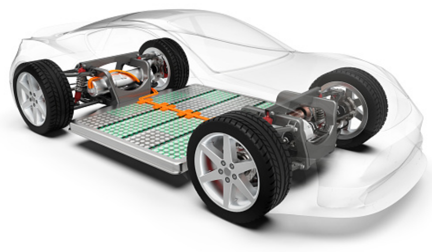
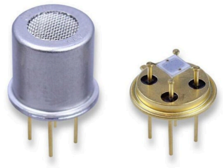
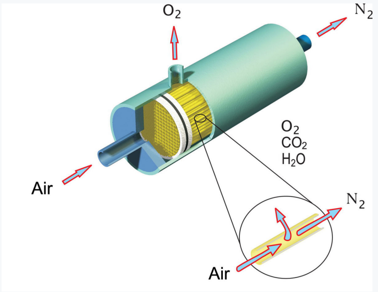
|  |  |
| Batteries (Lecture 4) | Sensors |
|   |  |
| Separation Membranes | Fuel Cells (Lecture 6) |

# Origin of ionic conduction

- Ionic conductivity is dominated by **defects**
    - In an ideal crystal, ions can't easily move
    - vacancies and/or interstitials are the main charge carriers

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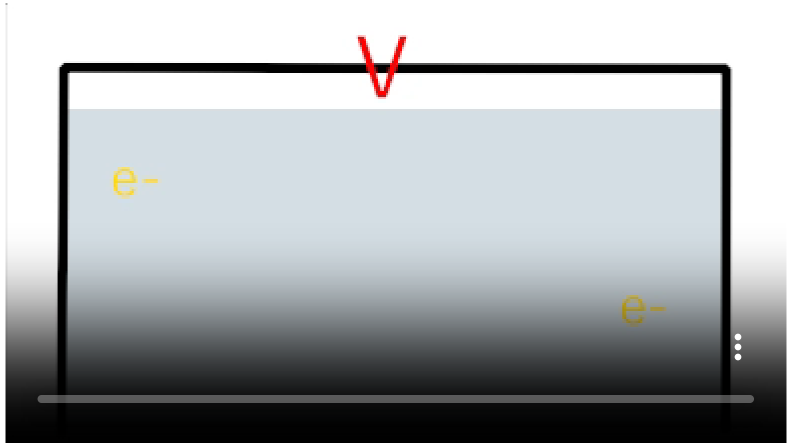
- In ionic solids, conductivity covers $10^{-16}\ \mathrm{S\,m^{-1}} - 10^{3}\ \mathrm{S\,m^{-1}}$
  - most solids are limited to around $10^{-2}\ \mathrm{S\,m^{-1}}$
  - Liquid electrolytes typically $10^{-1}$–$10^{3}\ \mathrm{S\,m^{-1}}$

# Measuring Conductivity

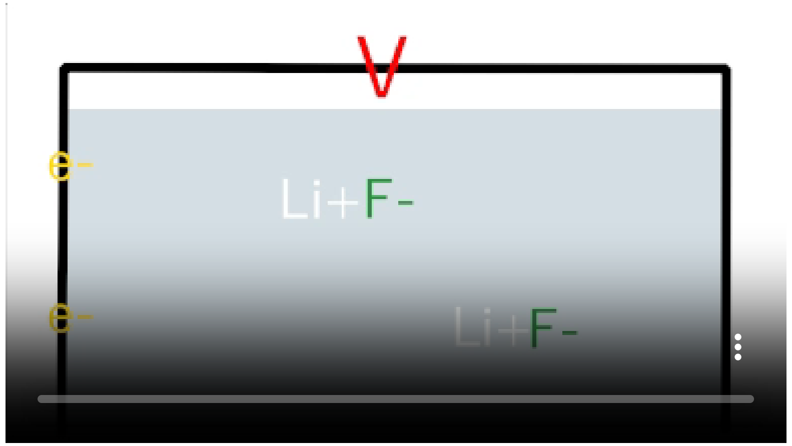
- For electronic conductors, this is simple:
  - Apply a voltage $(V)$ and measure the resulting current $(I)$
  - Resistance (in $\Omega$) is found through Ohm's law; $V = IR$
  - Resistivity (in $\Omega\ cm$) of the material calculated from geometry
- Resistivity $\rho$ (in $\Omega\ cm$) = $\frac{1}{\text{Conductivity } \sigma \text{ (in S cm}^{-1})}$




In reality, we normally use two wires for V and two for I

# Measuring Ionic Conductivity

- Ions cannot flow round a circuit, so current drops with a constant applied voltage



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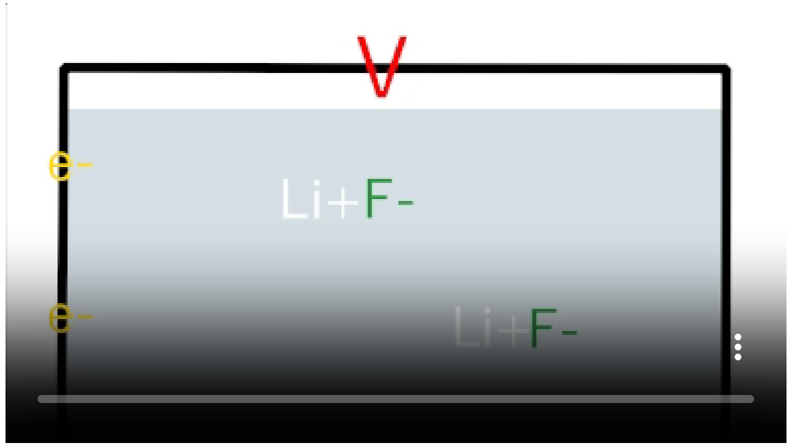
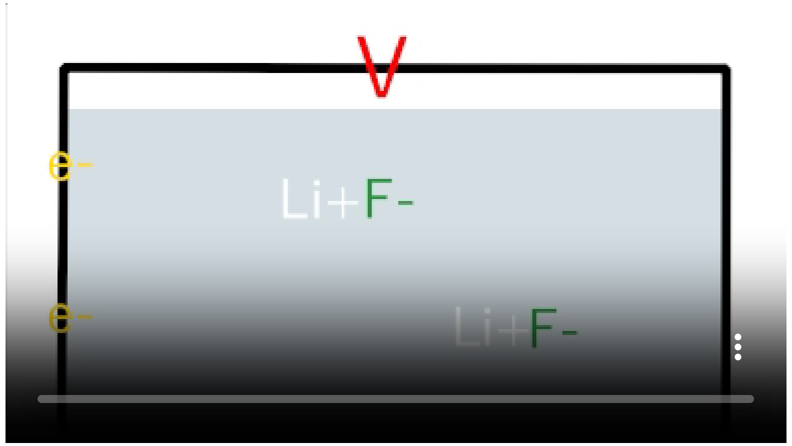



- Instead, we use an alternating voltage - this is called Impedance spectroscopy (see lecture 5)



# 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

# Vacancy, Interstitial or Interstitialcy?

**What technique(s) could you use to distinguish the mechanism?**

Write your answer...

**30** remaining

You can answer multiple times

Submit

# Suggestions

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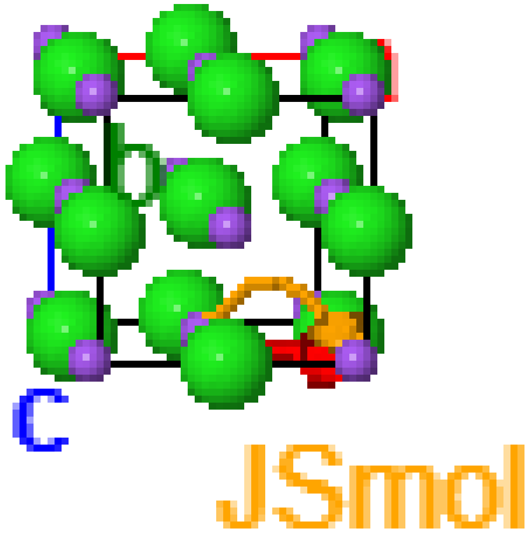
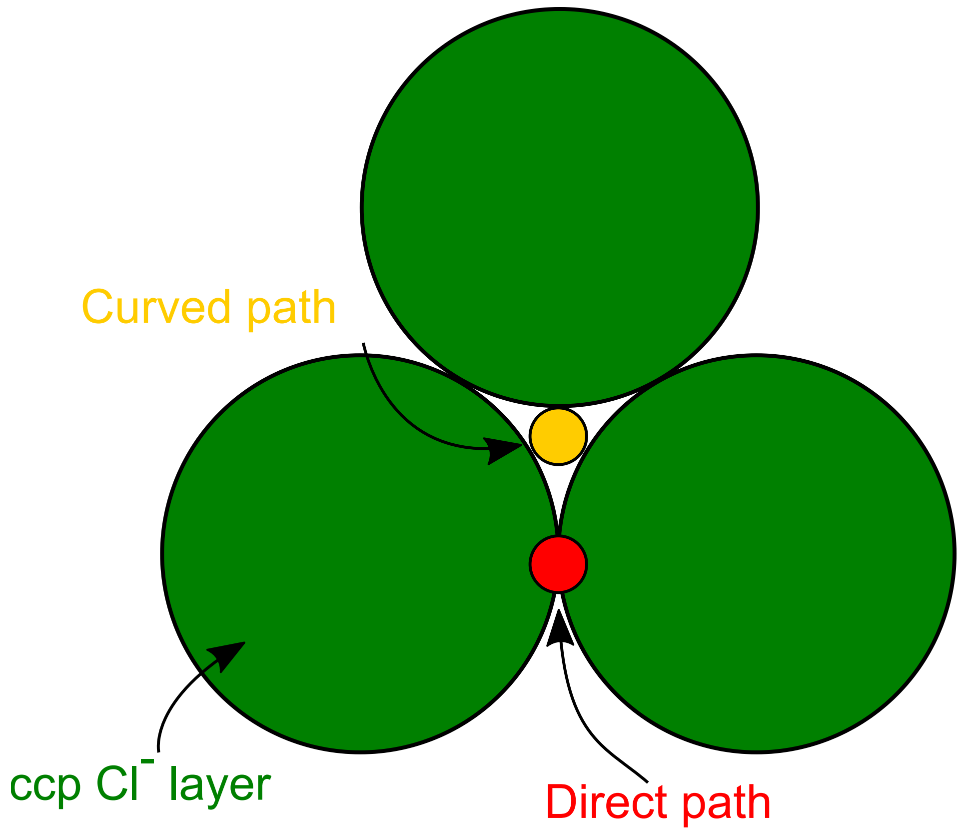
Quiz results will be available here
after the lecture

# Migration paths

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

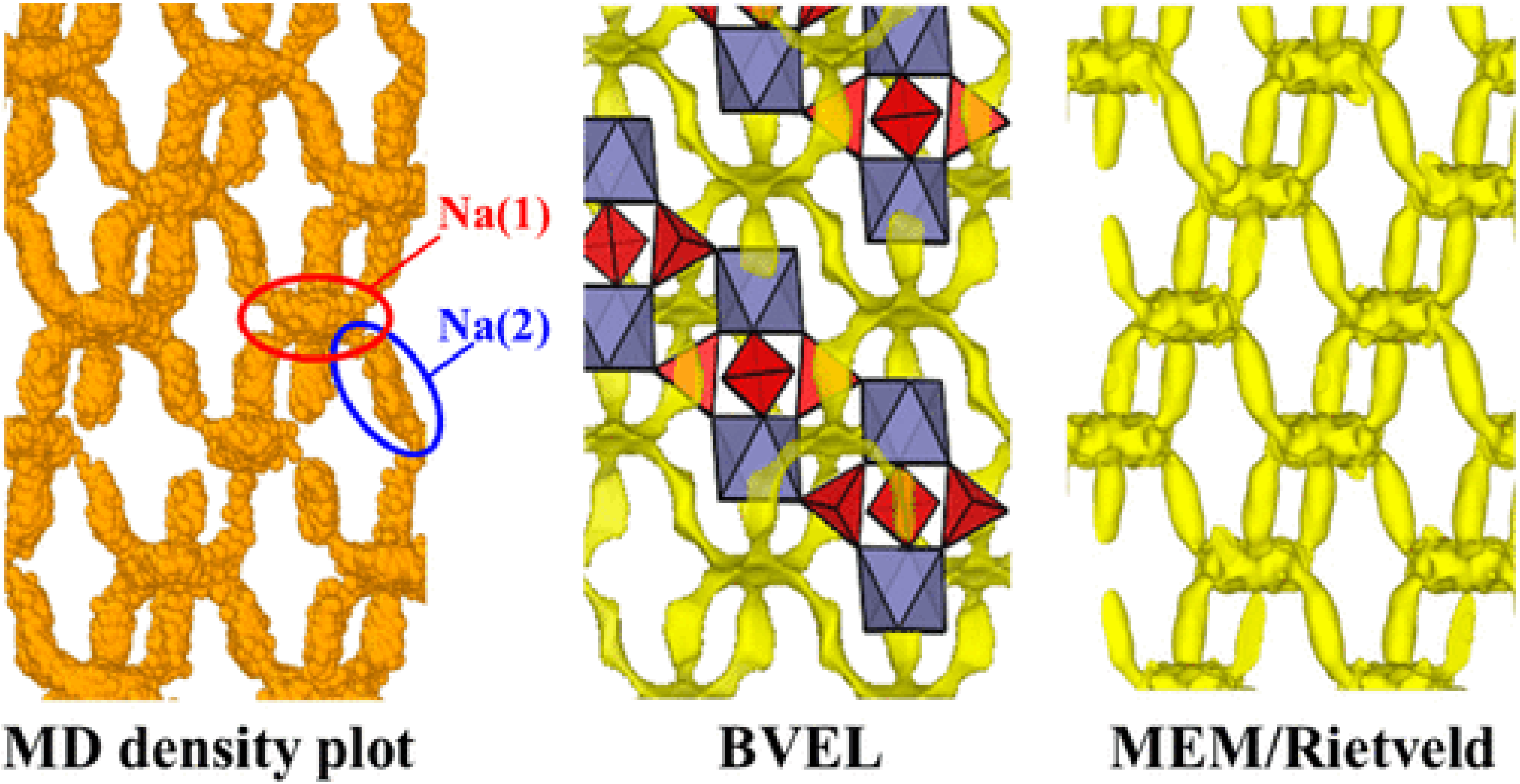


# Pathways can be complex

- Migration pathways can be calculated and/or experimentally determined

*e.g.* **NASICON** $Na^+$ conductor, $Na_3Zr_2(SiO_4)_2(PO_4)$:



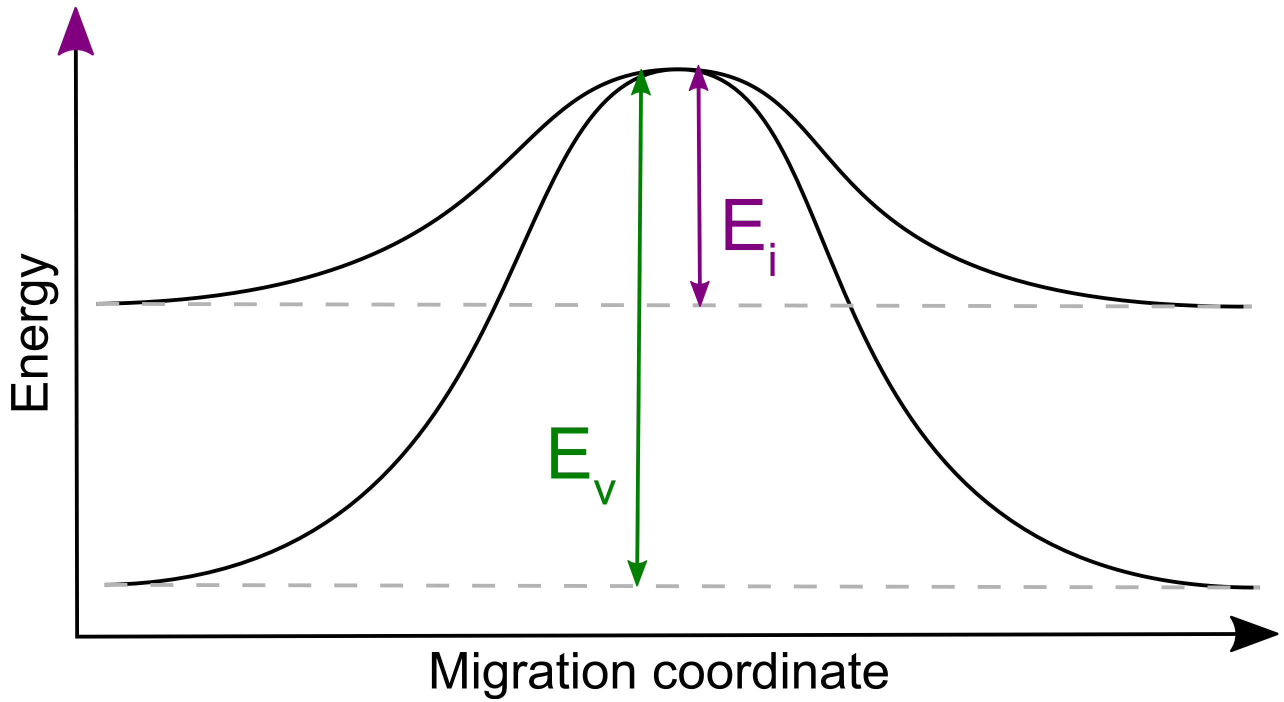

Y. Deng, *Chem. Mater.*, 2018, 2618.

# Migration energetics

- Defect mobility $(\mu)$ is a thermally-activated process:

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

- interstitial sites are higher energy than vacancies, so will be more mobile.



# Variation with temperature

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

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

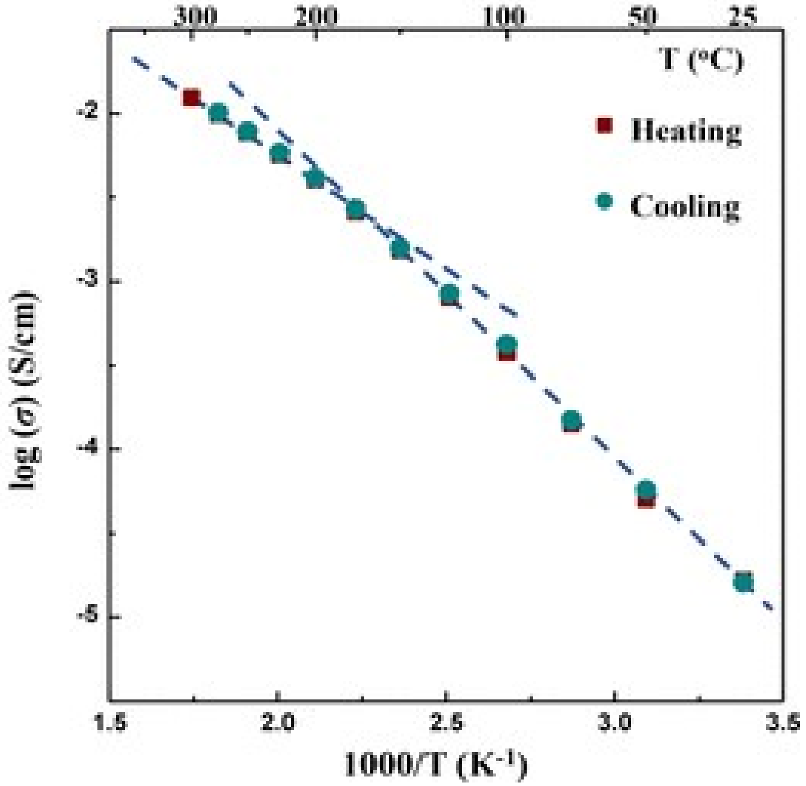
# Variation with temperature

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

$$\sigma = nq\mu_0 \exp\left(-\frac{\mathrm{E_a}}{\mathrm{RT}}\right)$$
$$= A \exp\left(-\frac{\mathrm{E_a}}{\mathrm{RT}}\right)$$

Plotting $\ln \sigma$ *vs.* $\frac{1}{\mathrm{T}}$ should give a straight line

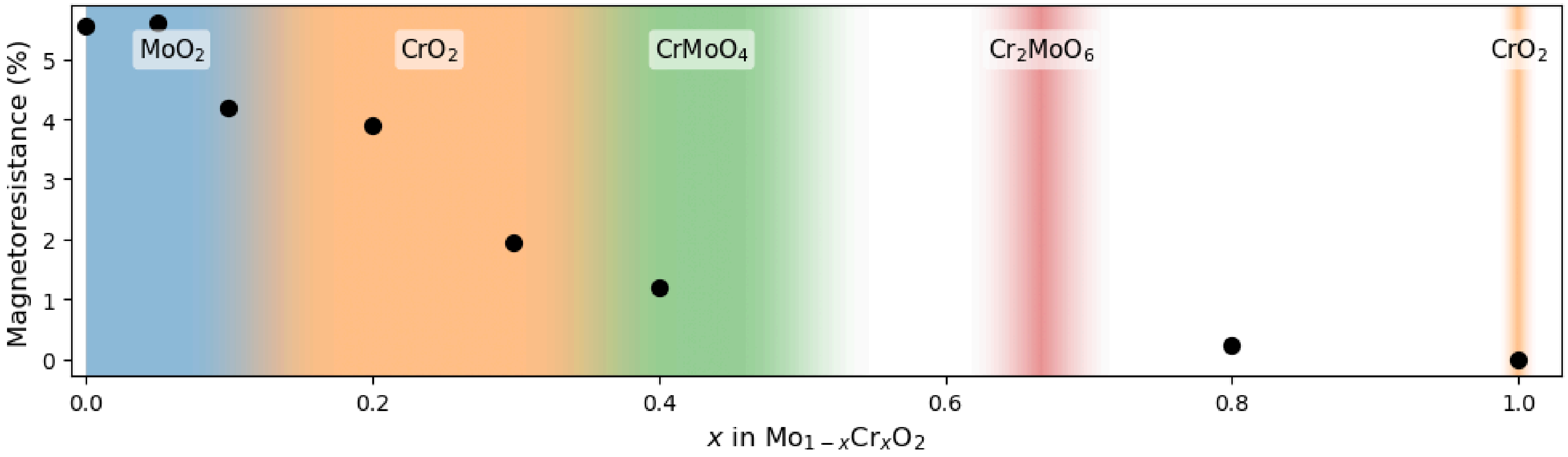
- more commonly we plot $\log_{10} \sigma$ *vs.* $\frac{1000}{\mathrm{T}}$ for high temperature measurements
- gradient is $\frac{-E_a}{R}$ (or $\frac{-E_a}{2303R}$ using base 10).

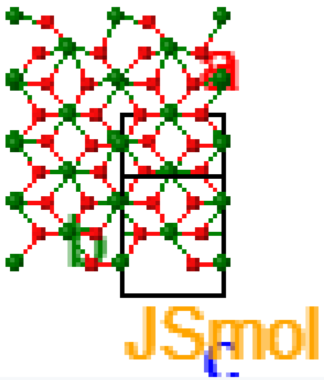
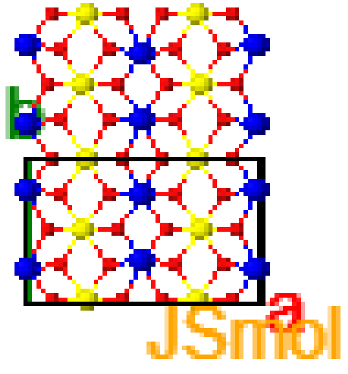
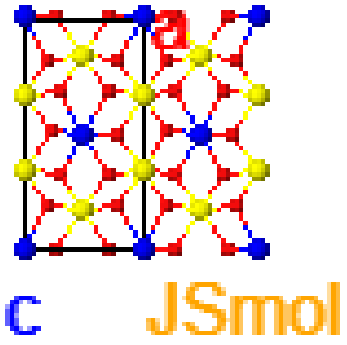
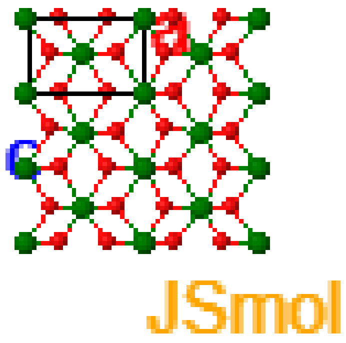



Nasicon conductivity

# Defect ordering

More defects increase conductivity, but interaction can form new phases, *e.g.* $Mo_{1-x}Cr_xO_2$:



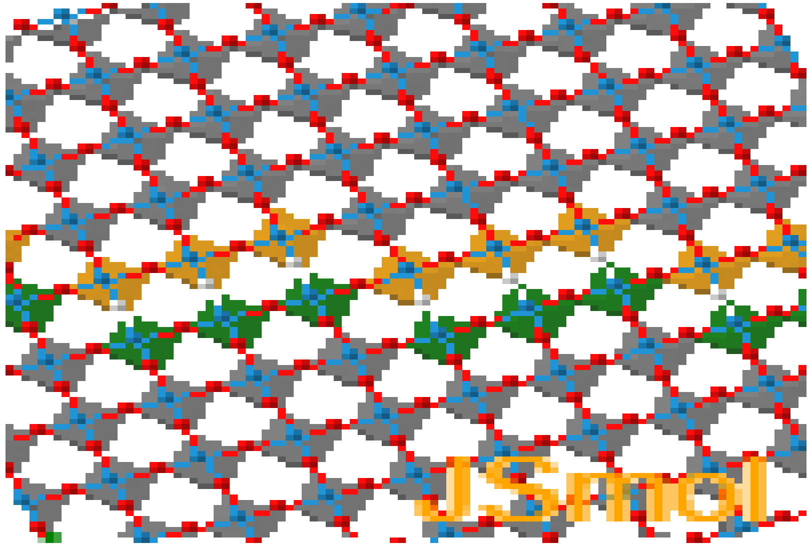

| $MoO_2$ | $CrMoO_4$ | $Cr_2MoO_6$ | $CrO_2$ (rutile) |
|---|---|---|---|
|  |  |  |  |

# Vacancy ordering

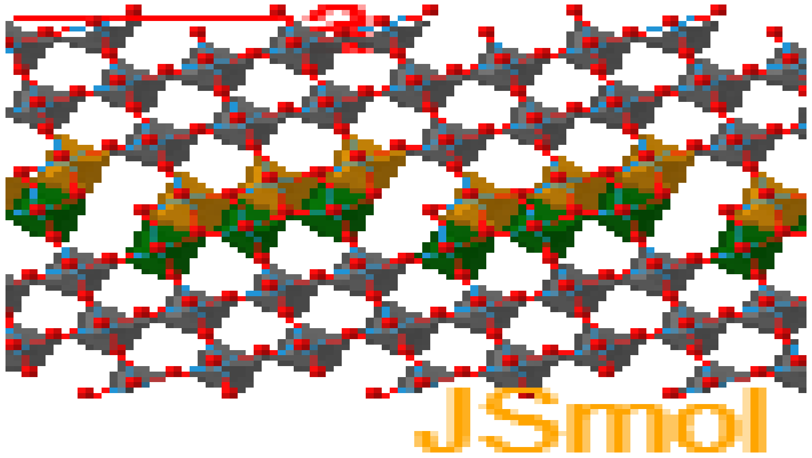
Vacancies can order in lines/planes, leading to structural 'collapse'.

Plane-like defects are often described as *shear phases*

$WO_3$




$WO_{2\cdot 90}$ or $W_{10}O_{29}$



# Lecture recap

- 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
- Different defects have different conduction energetics
  - Pathways can sometimes be determined experimentally
- Ordering of defects can sometimes give rise to new crystal phases with different conduction properties

# Feedback

**What did you like or dislike about lecture 3?**

Write your answer...

Submit