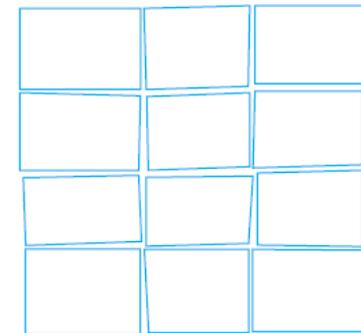
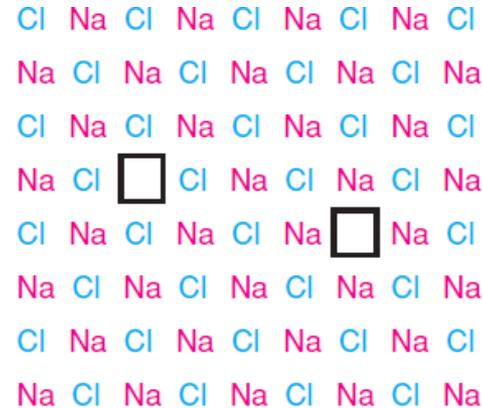


Lecture 13: Defects

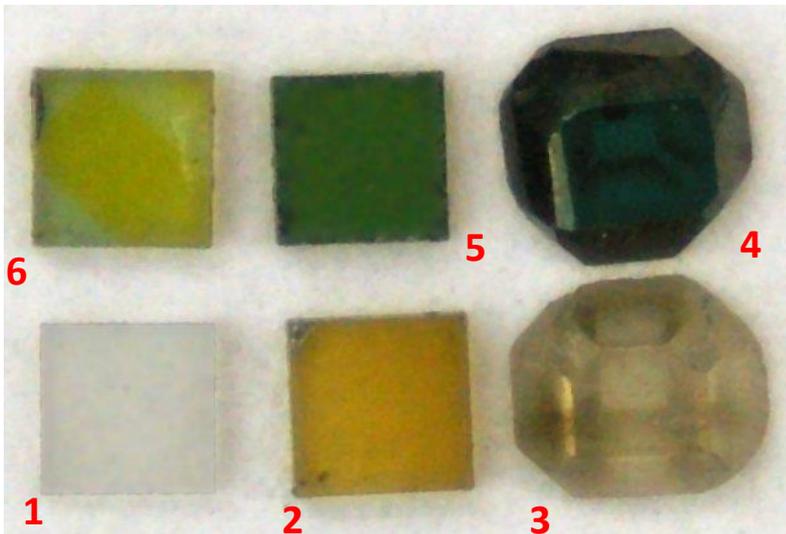
- Point defects
 - Thermodynamics of defects
 - Kröger-Vink notation for defects
 - Schottky
 - Frenkel
 - Color centers
- Non-stoichiometry
- Solid solutions
- Extended defects and dislocations



Figures: West

Defects

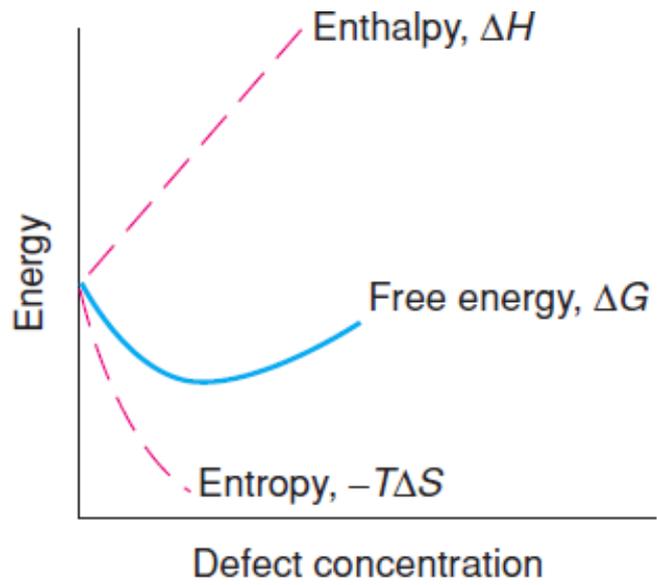
- In a perfect crystal, all the atoms are at rest on their correct lattice positions
 - Such a perfect crystal could exist only at absolute zero
- At all finite temperatures, crystals are imperfect
 - Atoms vibrate, which may be regarded as a form of defect
 - Some atoms are always misplaced
- In some crystals, the number of defects may be very small ($\ll 1\%$) as in, e.g., high-purity silicon, diamond, or quartz
- In highly defective crystals, the defects may in fact be regarded as a fundamental part of the structure rather than an imperfection



Diamonds (C), before and after irradiation and annealing. Clockwise from **left bottom**:
1) Initial (2×2 mm)
2–4) Irradiated by different doses of 2-MeV electrons
5–6) Irradiated by different doses and annealed at 800 °C.

Why do crystals have defects?

- Up to a certain limit, the presence of defects leads to a reduction of **free energy**
- Creating a single defect in a perfect crystal:
 - Requires a certain amount of energy, ΔH
 - Causes a considerable increase in entropy, ΔS , because of the large number of positions which this defect can occupy (**configurational entropy**)
- At some point, there are already so many defects that the energy required to create more defects will be larger than any subsequent gain in entropy



$$\Delta G = \Delta H - T\Delta S$$

$$S = k_B \ln W$$

W = number of possible configurations

$W \approx 10^{23}$ for one mole of sites that can host a defect!

Defect types (1)

- For a given crystal, a free energy curve can be drawn for every possible type of defect
 - The main difference between the curves is the position of the free energy minimum
- The dominant defect is the one that is the easiest to form
 - Has the smallest ΔH and the free energy minimum occurs at the highest defect concentration
- Table summarizes the defects which predominate in a variety of inorganic solids

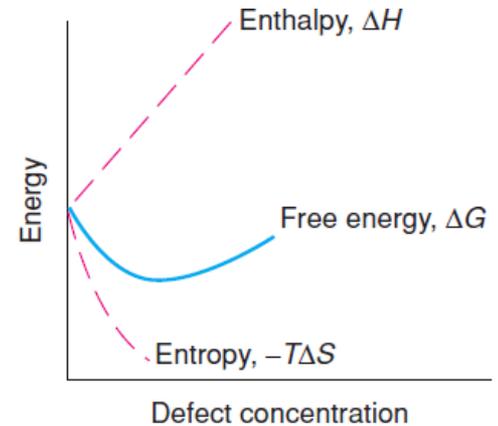


Table 2.1 *Predominant point defects in various ionic crystals*

Crystal	Crystal structure	Predominant intrinsic defect
Alkali halides (not Cs)	Rock salt, NaCl	Schottky
Alkaline earth oxides	Rock salt	Schottky
AgCl, AgBr	Rock salt	Cation Frenkel
Cs halides, TlCl	CsCl	Schottky
BeO	Wurtzite, ZnS	Schottky
Alkaline earth fluorides, CeO ₂ , ThO ₂	Fluorite, CaF ₂	Anion Frenkel

Defect types (2)

- One classification of defect types:
 - **Stoichiometric defects / intrinsic defects** in which the crystal composition is unchanged on introducing the defects
 - **Non-stoichiometric defects / extrinsic defects**, which are a consequence of a change in composition
- Another classification based on the size of the defect:
 - **point defects** involve only one atom or site, for example vacancies or interstitials (the atoms surrounding the defect are also somewhat perturbed)
 - **line defects**, that is, **dislocations**, are effectively point defects in two dimensions but in the third dimension the defect is very extensive or infinite
 - in **plane defects**, whole layers in a crystal structure can be defective
 - Sometimes the name **extended defects** is used to include all those which are not point defects

Schottky defect

- Schottky defect is a typical stoichiometric defect in ionic solids such as halides or oxides
 - Pair of vacant sites: an anion vacancy and a cation vacancy
 - Principal point defect in alkali halides
- To compensate for the vacancies, there should be two extra atoms at the surface of the crystal for each Schottky defect
- Equal numbers of anion and cation vacancies required to preserve local electroneutrality
- Vacancies attract each other and tend to associate ($\Delta H_{\text{association}} \approx 120 \text{ kJ/mol}$)
- For NaCl at room temperature, typically one in 10^{15} of the sites is vacant
- In other terms, 1 mg of NaCl ($\sim 10^{19}$ atoms) contains $\sim 10^4$ Schottky defects
- Schottky defects are responsible for the optical and electrical properties of NaCl

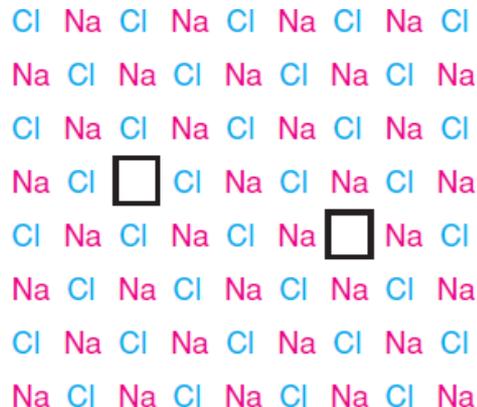
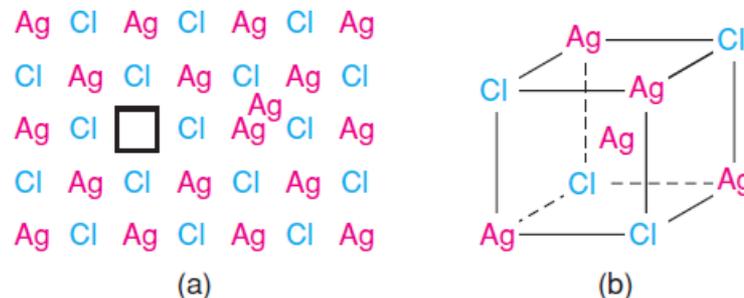


Figure 2.2 2D representation of a Schottky defect with cation and anion vacancies.

Frenkel defect

- An atom displaced off its lattice site into an interstitial site that is normally empty
- AgCl (with the NaCl crystal structure) has predominantly this defect (interstitial Ag)
- There is probably some covalent interaction between the interstitial Ag^+ ion and its four Cl^- neighbours which stabilizes the defect
 - Due to this, AgCl prefers Frenkel defects over Schottky defects
- Comparison with NaCl: Na^+ is a “harder” cation and there would be high energetic cost to have it surrounded by four other Na^+ ions
 - Frenkel defects do not occur to any significant extent in NaCl
- Calcium fluoride, CaF_2 , has predominantly *anion* Frenkel defects in which F^- occupies interstitial sites
- As with Schottky defects, the vacancy and interstitial are oppositely charged and may attract each other to form a pair



Ref: West p. 85

Figure 2.3 (a) 2D representation of a Frenkel defect in AgCl; (b) interstitial site showing tetrahedral coordination by both Ag and Cl.

Color centers (1)

- The best known example of a color center is the F-center (**Farbzentrum**), which is an electron trapped on an anion vacancy
- F-centers can be prepared by heating an alkali halide in vapor of an alkali metal
- NaCl heated in Na vapor becomes slightly non-stoichiometric due to the uptake of Na to give $\text{Na}_{1+\delta}\text{Cl}$ ($\delta \ll 1$), which has a greenish yellow color
- The trapped electron provides a classic example of an “electron in a box”.
 - A series of energy levels are available for the electron within this “box”
 - The energy required to transfer the electron from one level to another falls in the visible part of the electromagnetic spectrum

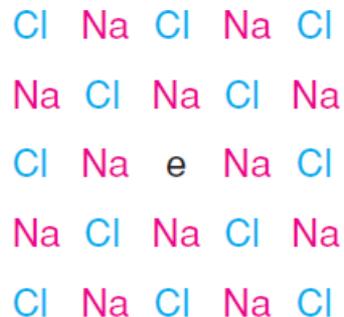


Figure 2.5 *The F-centre, an electron trapped on an anion vacancy.*

Color centers (2)

- Many other color centers have been characterized in alkali halide crystals
- H- and V-center containing the chloride molecule ion Cl_2^- are shown in the figure
 - The V-center occurs on irradiation of NaCl with X-rays
- Other defect centers identified in the alkali halides include
 - F'-center: two electrons trapped on an anion vacancy
 - F_A -center: an F-center, where one of six cationic neighbors is a foreign monovalent cation (for example, K^+ in NaCl)
 - M-center: a pair of nearest neighbor F-centers
 - R-center: three nearest neighbor F-centers located on a (111) plane
 - Ionized or charged cluster centers, such as M^+ , R^+ and R^-



Figure 2.6 (a) H-centre and (b) V-centre in NaCl.

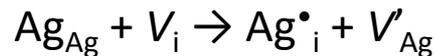
The Kröger–Vink notation for crystal defects

- Kröger and Vink developed a notation that is very useful for discussing point defects, the sites involved, and the effective charges on the defects
- Each defect is represented by a combination of three symbols
 - the symbol for the atom involved, or V if the site is vacant
 - a superscript indicating the net charge:
 - for charge +1,
 - x for zero net charge
 - ' for charge -1
 - a subscript to indicate the nature of the site in an ideal crystal, with i for an interstitial site and s for a surface site

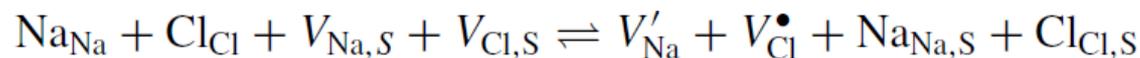
Examples:	V'_{Na}	a sodium ion vacancy (in e.g. NaCl), net charge -1
	V_{Cl}^{\bullet}	a chloride ion vacancy (in NaCl), net charge +1
	$\text{Na}_{\text{Na}}^x, \text{Cl}_{\text{Cl}}^x$	Na and Cl ions on regular lattice sites, no net charge
	$\text{Cd}_{\text{Na}}^{\bullet}$	a substitutional Cd ion on a Na site, charge +1
	Ag_i^{\bullet}	an interstitial Ag^+ ion in AgCl, charge +1
	F'_i	an interstitial F^- ion in CaF_2 , charge -1.

Defect reactions using Kröger–Vink notation

- Formation of Frenkel defects in AgCl:



- Important to keep the balance of masses, sites, and charges
- Can be used to study the thermodynamics of defects
- For example, Schottky equilibria in a crystal of NaCl can be treated by assuming that a pair of ions is removed from the crystal interior, leaving vacancies, and relocated at the crystal surface, as follows

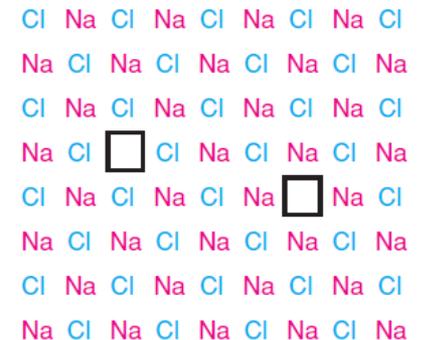
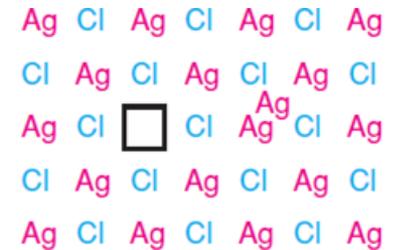


$$K = \frac{[V'_{\text{Na}}][V_{\text{Cl}}^{\bullet}][\text{Na}_{\text{Na,S}}][\text{Cl}_{\text{Cl,S}}]}{[\text{Na}_{\text{Na}}][\text{Cl}_{\text{Cl}}][V_{\text{Na,S}}][V_{\text{Cl,S}}]}$$

- After some manipulations, the number of vacancies, N_v , is

$$N_v = N \times \text{constant} \times \exp(-\Delta H/2RT)$$

- The equilibrium concentration of Schottky defects increases exponentially with temperature



Investigating defect structures

- Diffraction methods yield **average** crystal structures.
- For non-stoichiometric and defective crystals, the average structure may represent very poorly the actual structure in the region of the defect.
- In order to determine defect structures, techniques are needed that are sensitive to **local** structure -> spectroscopic techniques
- However, the spectra are not usually informative about the structure extending beyond the immediate coordination environment of a particular atom
- Modern approach: electron microscopy, possibly combined with modelling
 - Example: Annular Dark-field Scanning Transmission Electron Microscopy of MoS₂

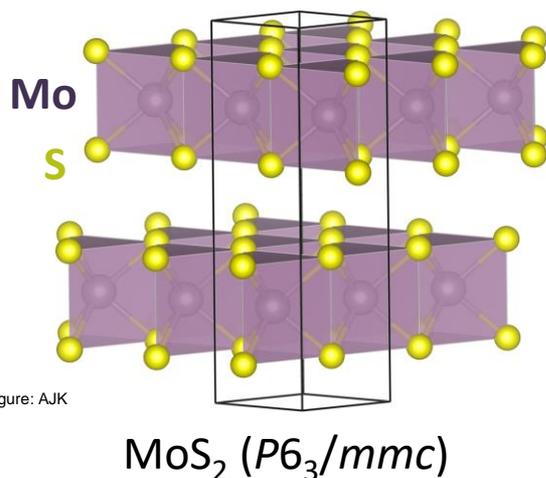
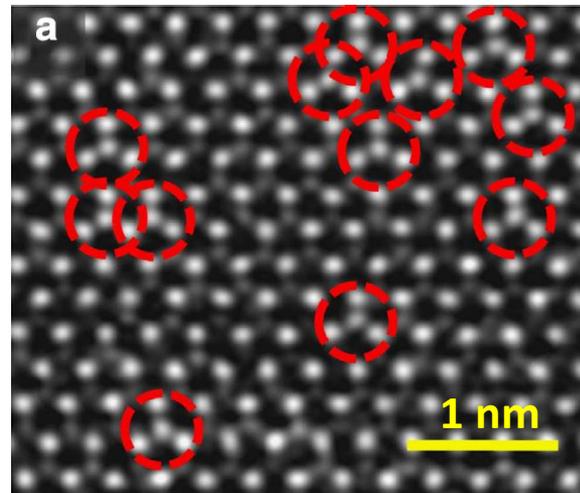


Figure: AJK



Antisite defects in MoS₂ monolayers

Figure: Hong et al. *Nature Commun.* 2015, 6, 6293 (DOI).

Defects in non-stoichiometric crystals

- Schottky and Frenkel defects are **intrinsic** and occur in stoichiometric crystals
- Defects can also occur due to variation in composition -> **extrinsic** defects.
- Extrinsic defects may arise on doping pure crystals with **aliovalent impurities**
 - Impurity atoms which have a different valency to those in the host crystal
- For instance, NaCl may be doped with CaCl₂ to give crystals of formula $\text{Na}_{1-2x}\text{Ca}_x\text{V}_{\text{Na},x}\text{Cl}$
- In these, the *ccp* Cl⁻ arrangement is retained but the Na⁺, Ca²⁺ ions and V_{Na} are distributed over the octahedral cation sites.
- The overall effect of doping NaCl with Ca²⁺ ions is to increase the number of cation vacancies
- The vacancies that are controlled by the **impurity level** are extrinsic defects, in contrast to the thermally created intrinsic defects such as Schottky pairs.

Non-stoichiometric 3d metal oxides

Table 5.5 Approximate composition ranges for some non-stoichiometric compounds

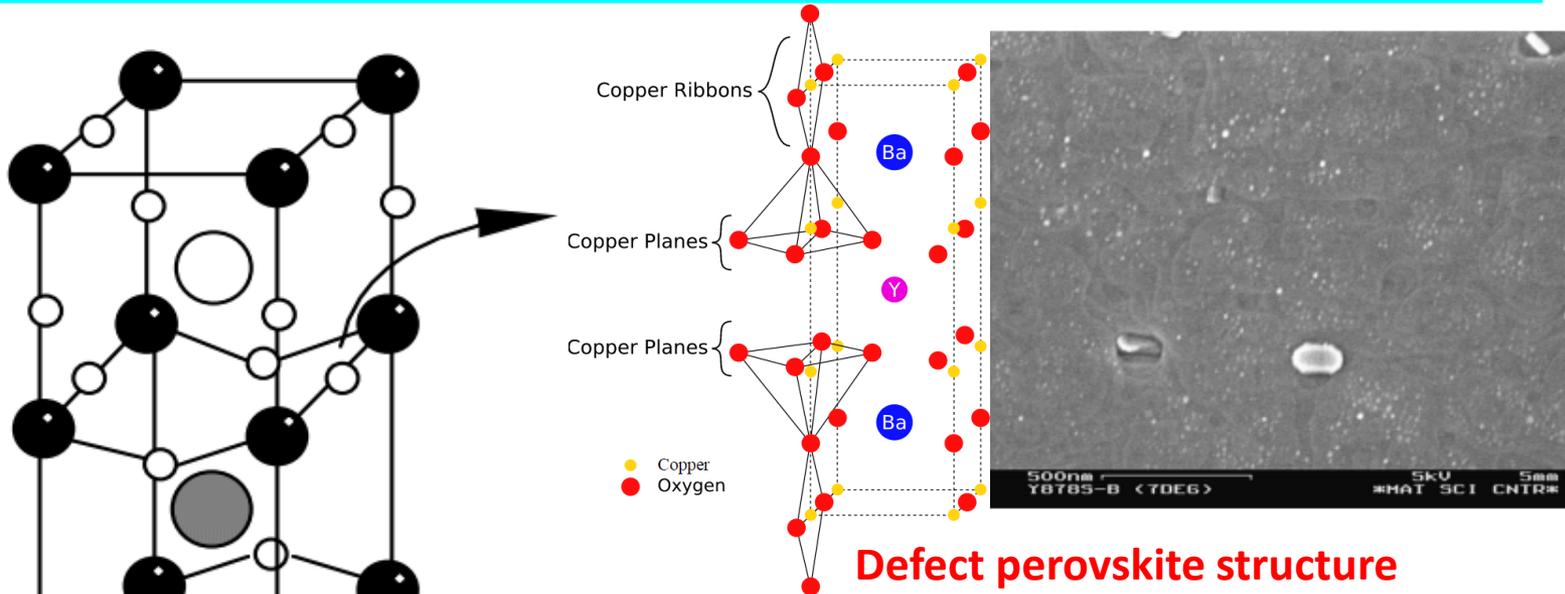
<i>Compound</i>		<i>Composition range*</i>
TiO _x	[≈TiO]	0.65 < x < 1.25
	[≈TiO ₂]	1.998 < x < 2.000
VO _x	[≈VO]	0.79 < x < 1.29
Mn _x O	[≈MnO]	0.848 < x < 1.000
Fe _x O	[≈FeO]	0.833 < x < 0.957
Co _x O	[≈CoO]	0.988 < x < 1.000
Ni _x O	[≈NiO]	0.999 < x < 1.000
CeO _x	[≈Ce ₂ O ₃]	1.50 < x < 1.52
ZrO _x	[≈ZrO ₂]	1.700 < x < 2.004
UO _x	[≈UO ₂]	1.65 < x < 2.25
Li _x V ₂ O ₅		0.2 < x < 0.33
Li _x WO ₃		0 < x < 0.50
TiS _x	[≈TiS]	0.971 < x < 1.064
Nb _x S	[≈NbS]	0.92 < x < 1.00
Y _x Se	[≈YSe]	1.00 < x < 1.33
V _x Te ₂	[≈VTe ₂]	1.03 < x < 1.14

* Note that all composition ranges are temperature-dependent and the figures here are intended only as a guide.

YBCO

Figure: Nina Heinig + Wikipedia

High temperature superconductors, like $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, have electrical properties controlled by oxygen stoichiometry.



Defect perovskite structure

$\text{YBa}_2\text{Cu}_3\text{O}_6$ = antiferromagnetic insulator

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ = metallic conductor

Non-stoichiometry, highest T_c (95 K) for $x = 0.07$

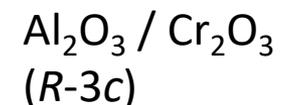
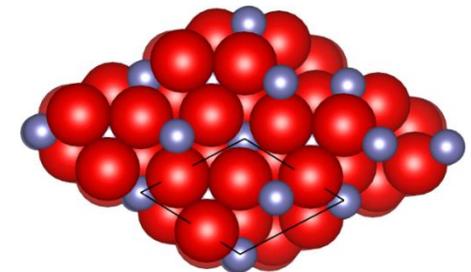
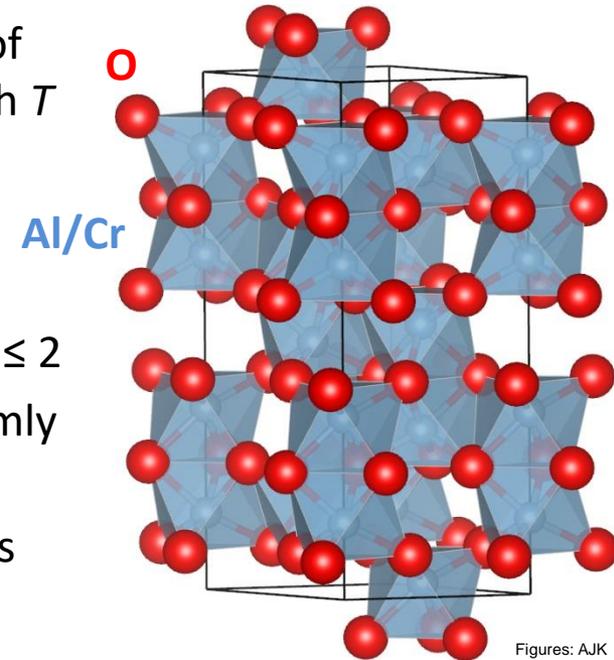
single crystal films have much higher critical currents than bulk single crystals.

Solid solutions

- In extrinsic defects associated with dopants or impurities, the dopants either occupy interstitial sites or substitute for atoms or ions in the parent lattice
- As the dopant concentration rises, above $\sim 0.1\text{--}1\%$, it is common practice to refer to the materials as **solid solutions** rather than as doped materials, but these two terminologies are interchangeable
- A solid solution is basically a crystalline phase that can have variable composition
- As with doped crystals, simple solid solutions are one of two types:
 - in **substitutional** solid solutions, the atom or ion that is being introduced directly replaces an atom or ion of the same charge in the parent structure
 - in **interstitial** solid solutions, the introduced species occupies a site that is normally empty and no ions or atoms are left out
- Starting with these two basic types, a considerable variety of more complex solid solution mechanisms may be derived

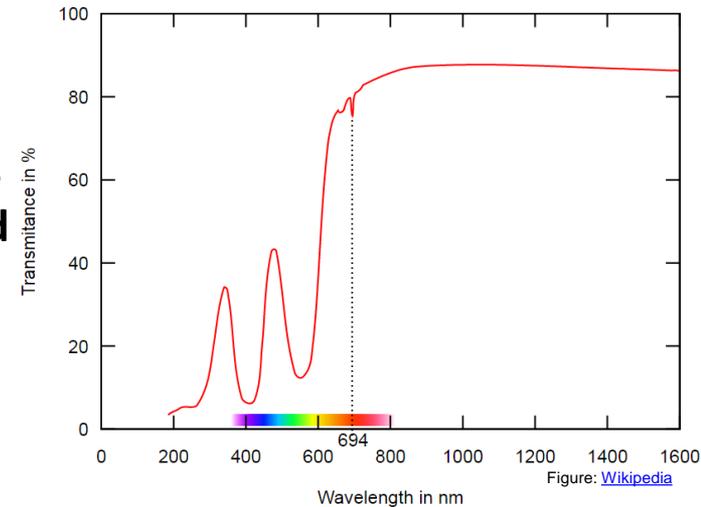
Substitutional solid solution (1)

- An example of a substitutional solid solution is the series of oxides formed on reacting together Al_2O_3 and Cr_2O_3 at high T
- Both **end members** have the corundum structure: approximately *hcp* oxide ions with Al^{3+} and Cr^{3+} ions occupying two-thirds of the available octahedral sites
- The solid solution may be formulated as $(\text{Al}_{2-x}\text{Cr}_x)\text{O}_3$: $0 \leq x \leq 2$
- At intermediate x , Al^{3+} and Cr^{3+} ions are distributed randomly over the octahedral cation sites
 - The probability that a site contains either Cr^{3+} or Al^{3+} is related to x
- When the structure is considered as a whole and the occupancy of all the sites is averaged, it is useful to think of each site as being occupied by an “average cation”
 - Properties, atomic number, size, etc., are intermediate between those of Al^{3+} and Cr^{3+}



Substitutional solid solution (2)

- The $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system illustrates how **properties** may change on doping or solid solution formation.
- Al_2O_3 is a white, insulating solid, but with small amounts (<1%) of Cr^{3+} substitutions, the color becomes **bright red**
- This is the composition of the **ruby** gemstone and was the material in which the principle of **laser** action was first demonstrated
- The red color is lost if too much Cr^{3+} is added and the solid solutions then revert to the green color of Cr_2O_3 .



Transmittance of ruby



Figure: [Wikipedia](#)

Corundum
(Al_2O_3)



Figure: [Wikipedia](#)

Ruby
($\text{Al}_{2-x}\text{Cr}_x$) O_3 : $x < 1\%$



Figure: [Wikipedia](#)

Eskolaite
(Cr_2O_3)

Substitutional solid solution (3)

- For a range of simple substitutional solid solutions to form, there are certain requirements that must be met:
- The ions that replace each other must have the same charge. Otherwise, structural changes such as vacancies or interstitials would be required for **electroneutrality**
- The ions that replace each other must be fairly **similar in size**.
 - For *metal alloys*, the radii of the metal atoms may differ max $\sim 15\%$
 - For *non-metallic systems*, even differences larger than 15% are feasible
 - Solid solution formation is often very temperature dependent
 - The enthalpy term may, or may not, favor solid solution
 - Entropy term favors solid solutions in higher temperatures
- An important factor is the **crystal structure** of the two end members
- For a **complete solid solution**, it is essential that the end members are isostructural
 - Even if two phases are isostructural they do not always form solid solutions!
 - e.g. LiF and CaO both have NaCl structure but do not form solid solutions.

Substitutional solid solution (4)

- Let's see some practical examples of ions which can and cannot replace each other in solid solution formation
- Using [Shannon](#) and Prewitt radii for octahedral coordination, based on an oxide ion radius of 1.26 Å, monovalent alkali metal and silver ions have radii:
 - Li: 0.88, Na: 1.16, Ag: 1.29, K: 1.52, Rb: 1.63 and Cs: 1.84 Å.
- The radii of K/Rb and Rb/Cs pairs are both within 15% of each other and it is common to obtain solid solutions between pairs of corresponding Rb/Cs salts.
- K⁺ ion is ~30% larger than Na⁺, but Na/K salts sometimes form solid solutions with each other, especially at high temperatures (for example, KCl and NaCl at 600°C)
- The size difference of Li⁺ and K⁺ is too large and these ions do not generally replace each other in solid solutions.
- The Ag⁺ ion is similar in size to Na⁺ and solid solutions between pairs of corresponding Na/Ag salts are common (for example, NaCl and AgCl).

Substitutional solid solution (5)

- Some divalent ions, with octahedral radii:
 - Mg: 0.86, Ca: 1.14, Sr: 1.30, Ba: 1.50, Mn: 0.96 (HS), Fe: 0.91 (HS), Co: 0.88 (HS), Ni: 0.84, Cu: 0.87, Zn: 0.89 and Cd: 1.09 Å
- It is common to find solid solutions in which the divalent transition metal ions, Mn..Zn, substitute for each other
 - Mg also commonly forms solid solutions with them and is of similar size
 - Ca does not form solid solutions with them because it is 20–30% larger
- Similar considerations apply to trivalent ions
- Similar-sized Al, Ga, Fe and Cr (octahedral radii 0.67–0.76 Å) commonly substitute for each other
- So do many of the trivalent lanthanides (octahedral radii 0.99–1.20 Å)

Some extended defects

- Stacking faults are plane defects that are common in materials with layered structures, especially those that exhibit polytypism
 - For example: Co metal exhibits both polytypism and stacking faults. It occurs in two main polytypes, either ccp (ABC) or hcp (AB).
 - Stacking disorder occurs when the normal stacking sequence is interrupted by the presence of 'wrong' layers, e.g. . . . ABABABA**BCA**BABA
- Subgrain boundaries and antiphase domains (boundaries)
 - Within the domains, typically $\sim 10\,000\text{ \AA}$ in size, the structure is relatively perfect, but at the interface between domains there is a structural mismatch
 - Another type of boundary, an antiphase boundary, involves a relative lateral displacement of two parts of the same crystal

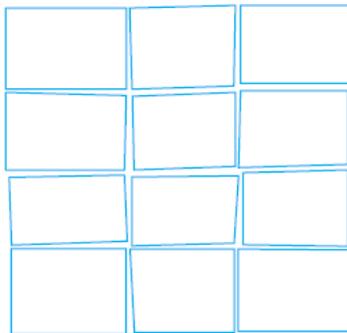
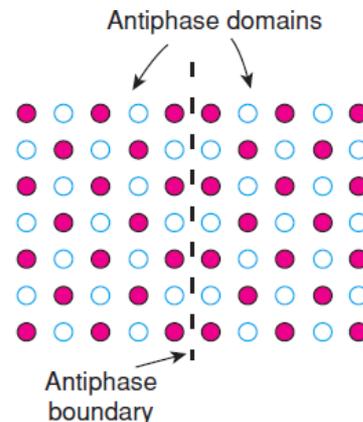


Figure 2.18 Domain texture in a single crystal.



Ref: West p. 110

Figure 2.19 Antiphase domains and boundaries in an ordered crystal AB: A, open circles; B, closed circles.

Dislocations

- Dislocations are an extremely important class of crystal defect
 - They are responsible for the relative **weakness of pure metals** and in certain cases (after work-hardening) for just the opposite effect of extra hardness
 - The mechanism of crystal growth from either solution or vapor appears to involve dislocations
 - Reactions of solids often occur at active surface sites where dislocations emerge from the crystal
- Dislocations are **stoichiometric line defects**
- Dislocations can be one of two extreme types, **edge** or **screw** dislocations, or can have any degree of intermediate character

Edge dislocation

- A simple edge dislocation is an extra half-plane of atoms, i.e. a plane of atoms that goes only part of the way through a crystal structure
- To understand the effect of dislocations on the mechanical properties, consider the effect of applying a shearing stress to a crystal that contains an edge dislocation
 - Top half of the crystal is pushed to the right and the bottom half to the left
 - All that is now needed is an easy means of generating half-planes and, by a process of repetition, the crystal will eventually shear completely

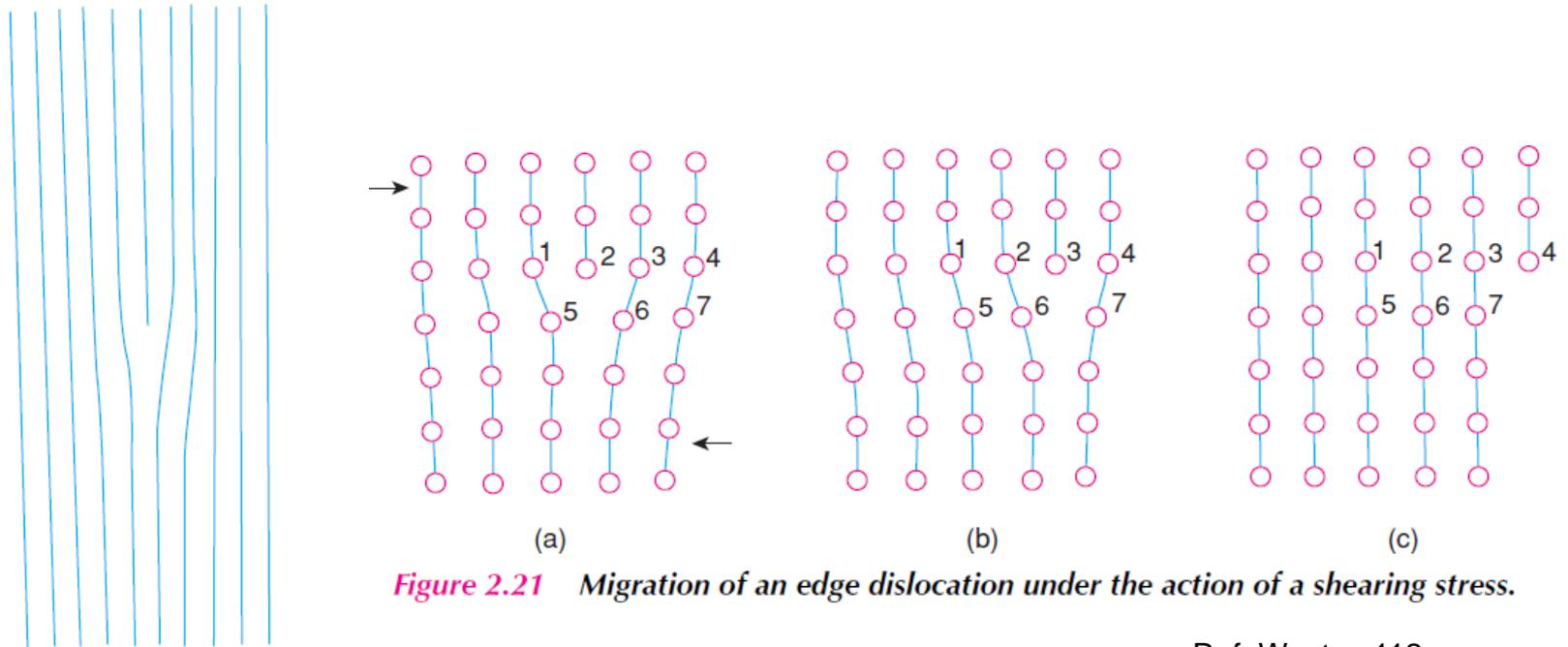
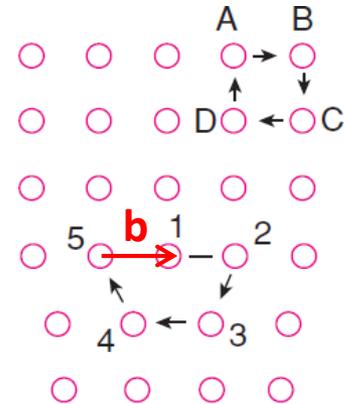


Figure 2.21 Migration of an edge dislocation under the action of a shearing stress.

Burgers vector

- Dislocations are characterised by a vector, the *Burgers vector*, \mathbf{b} .
- To find the magnitude and direction of \mathbf{b} , it is necessary to make an imaginary atom-to-atom circuit around the dislocation
- In normal regions of the crystal, a circuit such as ABCDA, involving one unit of translation in each direction, is a closed loop and the starting point and finishing point are the same, A.
- However, the circuit 12345 which passes round the dislocation is not a closed circuit because 1 and 5 do not coincide.
- The magnitude of the Burgers vector is given by the distance 1–5 and its direction by the direction 1–5 (or 5–1).



Defining Burgers vector

