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RADIATION DAMAGE IN MATERIALS

6. Point defect structures





Introduction

- As we learnt from the previous section, irradiation creates **defects** (*defekt / kidevirhe el. kidevaurio*)
- Now we shall look in detail in the structure of the **point defects** (*punktdefekt / pistevirhe*), which are most commonly created right after irradiation
 - “Point defect” is defined as a defect without a significant extent in space
- Note that not only crystals, but also amorphous materials can have defects
 - Defining such is a bit nontrivial, but we will give examples at the end of the section
- “Crystals are like people – it is the defects in them that make them interesting”



6.1. Classification of defects

■ Defects can be classified according to their dimensionality:

■ 0D: point defects

punktdefekt / pistevirhe

■ 1D: line defects, **dislocations**

(dislokation/dislokaatio)

■ 2D: planar defects

(planära defekter / tasomainen defekti)

- Also surfaces: a surface is a defect

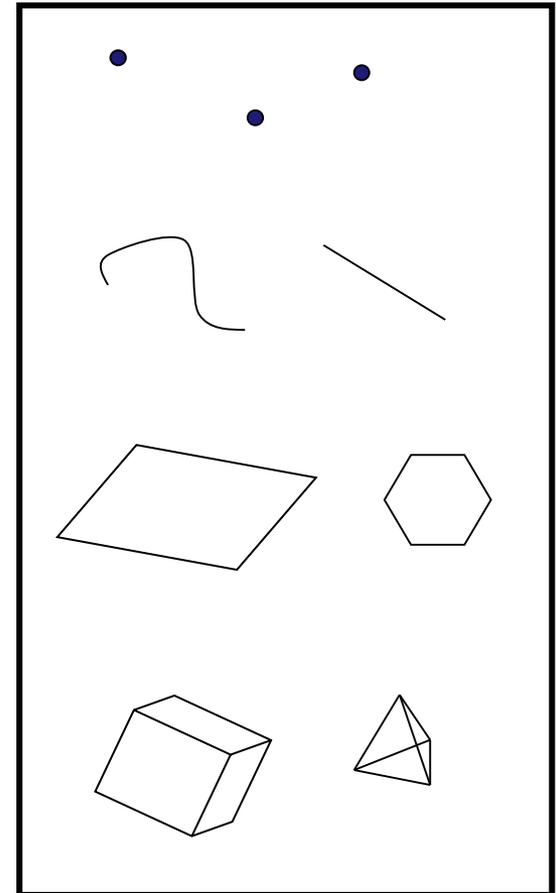
■ 3D: volume defects

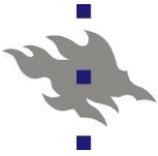
- **Voids** (*hålrum/ reikä*), **inclusions**

(inklusioner / sulkeuma), **precipitates**

(precipitat / erkauma), **amorphous**

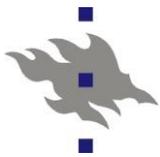
zones (*amorfa områden / amorfinen alue*)



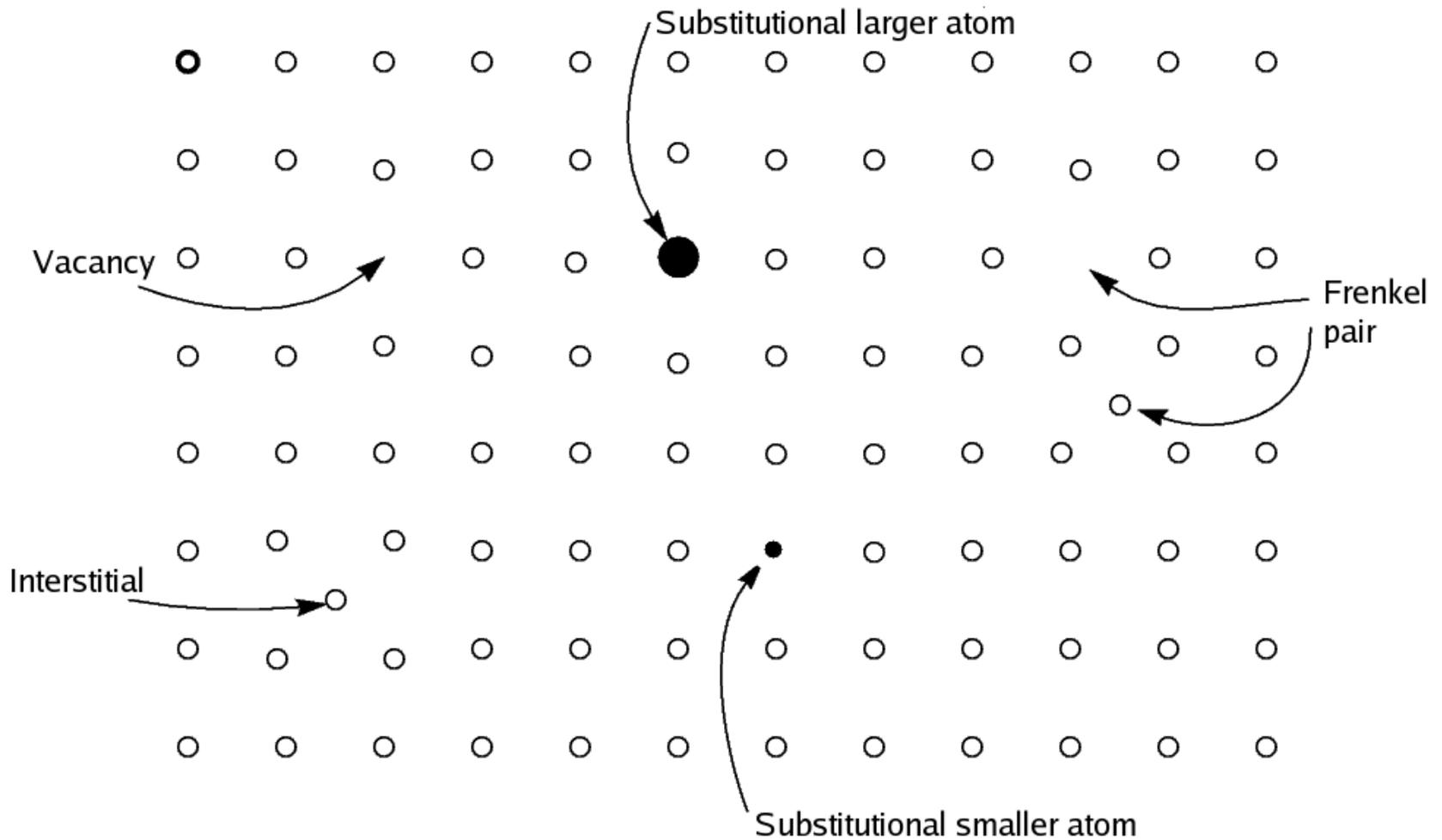


Classification of 0 D defects

- This chapter deals primarily with point defects – dislocations come later
- The upper size limit of a '0D' defect is not clear or well defined
 - But typically defects with only a few atoms not on perfect places are considered point defects
 - Since atom size roughly 2-3 Å, point defects $< \sim 1$ nm
- Another very important classification is by atom type
 - Defects without any other elements except those making up the material are called **intrinsic** (*intrinsiciska / luontainen*) defects
 - Defects which include impurity (*orenhet / epäpuhtaus*)-atoms are called **extrinsic** (*extrinsiciska / ulkonainen*) or simply impurity defects



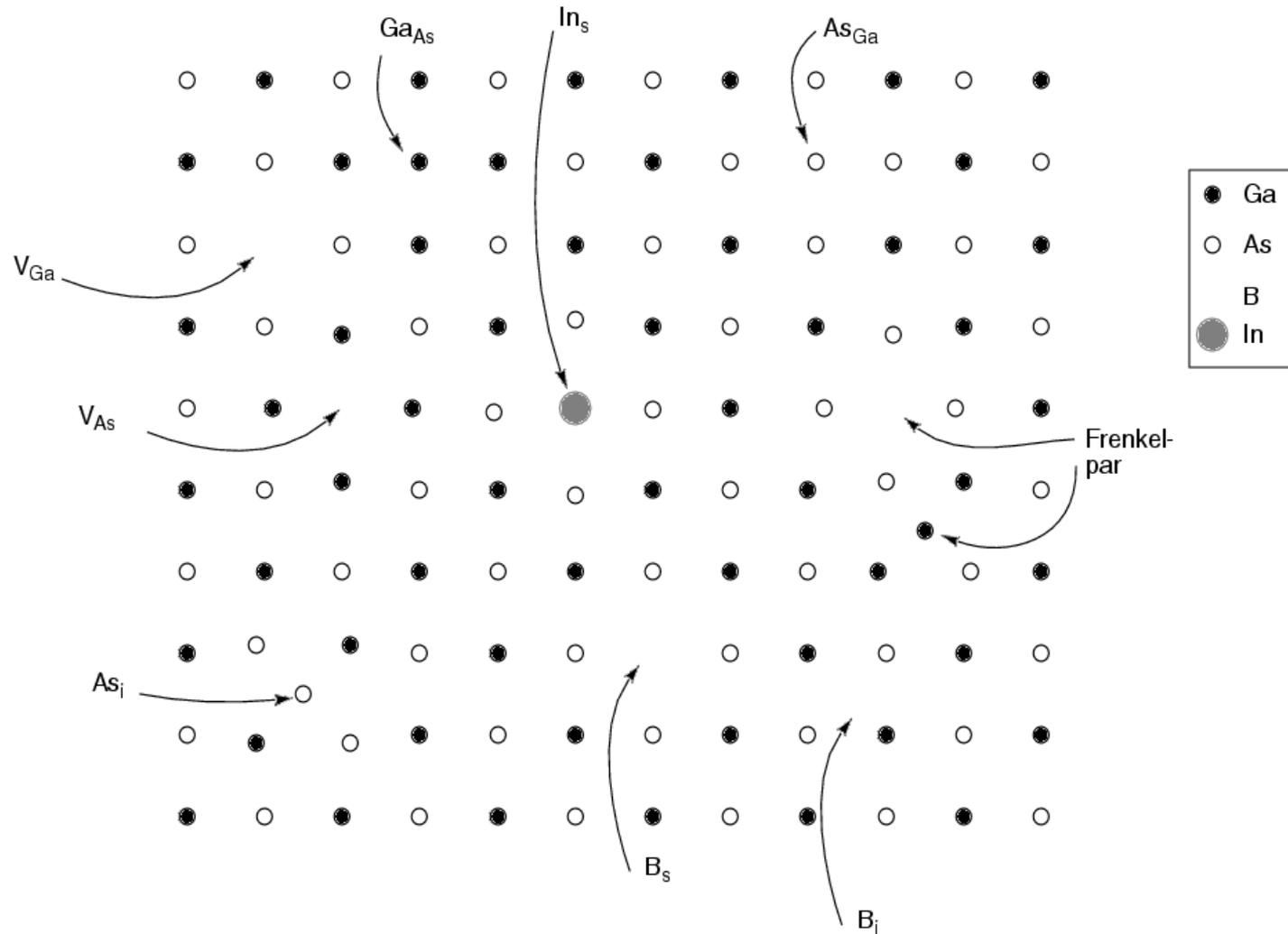
Point defect types in pure elements

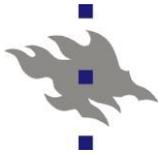


[Docent lecture of Kai Nordlund, now in wikipedia]



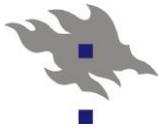
Point defect types in compounds (GaAs as an example)





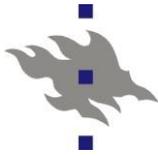
Defect notation

- The previous pictures already included some notation for defects
 - In ionic materials this notation is called Kroger-Vink notation
- V for vacancy
 - Subscript for which atom type's place is empty: V_{Ga} , V_{as}
 - V_2 for divacancy, V_3 for trivacancy, etc.
- I for any kind of interstitial defect
- As_i for As on an interstitial position, etc.
- In_s for In on a substitutional atom position
- B_i for B on an interstitial positions
- As_{Ga} for As-atoms on a Ga site: **antisite** (*motplats / vastapaikka*) defect

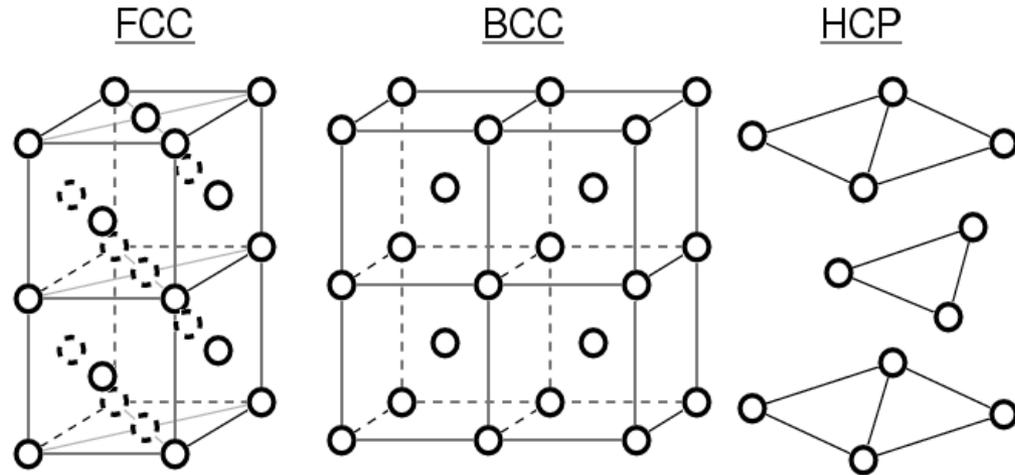


6.2. Structures of intrinsic defects in common metals and semiconductors

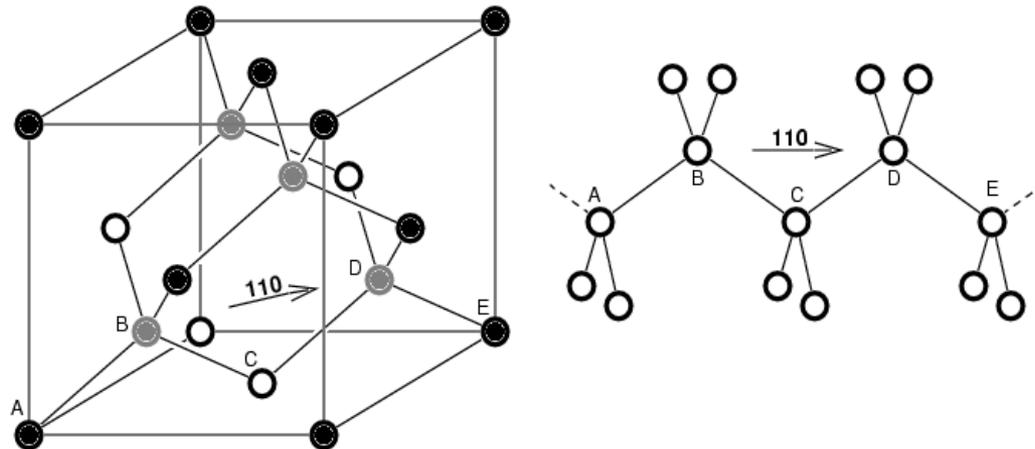
- The real structure of even simple point defects is not always as simple as the previous schematic pictures would indicate!!
 - As a matter of fact it is often not even known in many materials, even though defects are quite important for materials properties
- The following slides show the best understanding of the real structure of some of the best known intrinsic point defects in the 3 common metal structures and the diamond crystal structure.

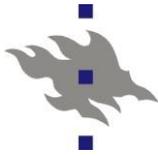


Reference: the perfect crystal structures



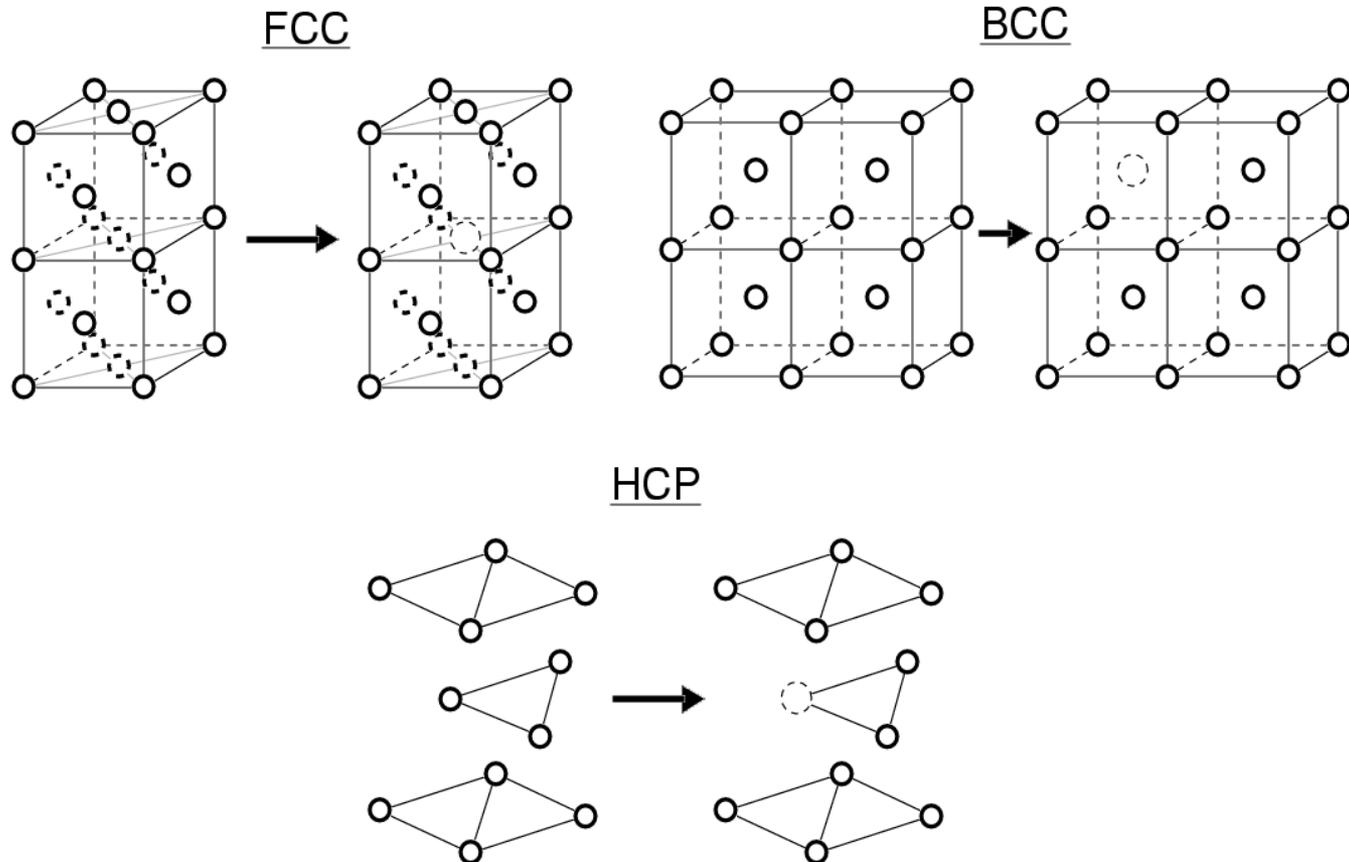
Silicon (diamond structure)

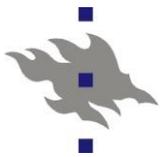




Vacancies in metals

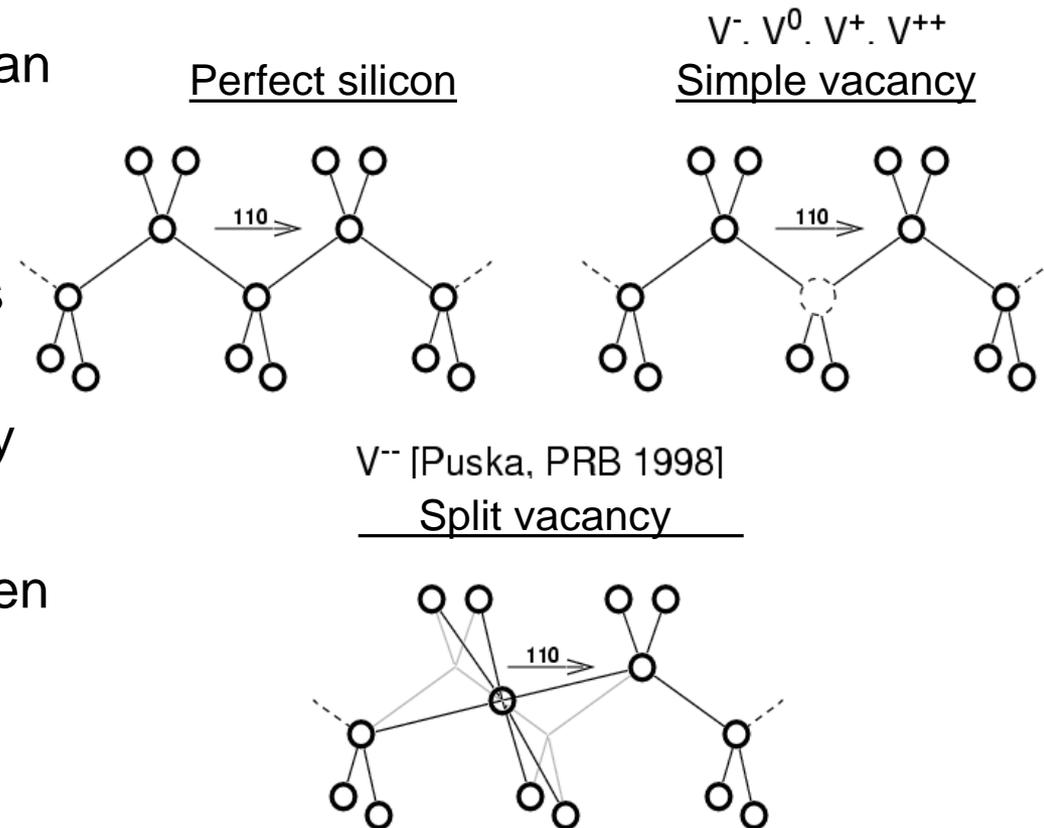
- The monovacancy in metals is simple: just an empty atom site
 - But a small relaxation of atoms around it inwards





Vacancies in silicon

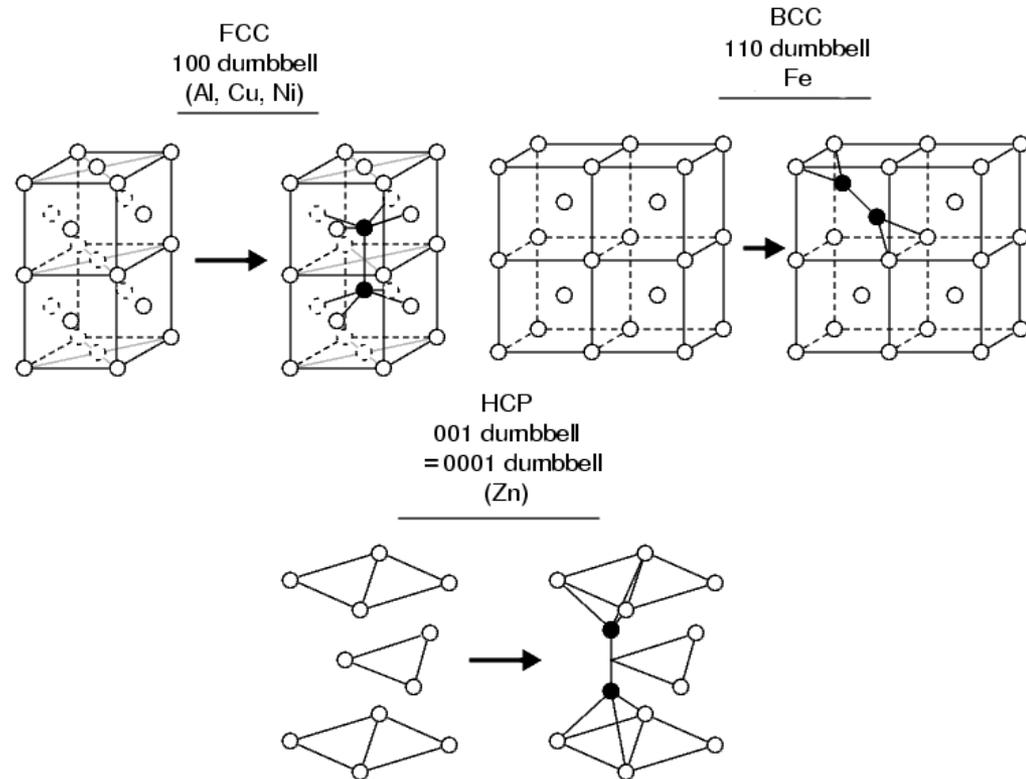
- Even though Si itself is not charged, the defects in it can be
- Already the monovacancy has 5 known charge states
 - -2, -1, 0, +1, +2
- Most of these are an empty atoms site
- But V^- has theoretically been predicted to have a split structure, see picture





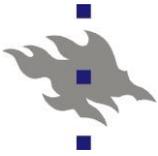
Interstitial atoms in metals

- The structure of intrinsic interstitials is in most cases a split structure where two atoms share one lattice site symmetrically around it



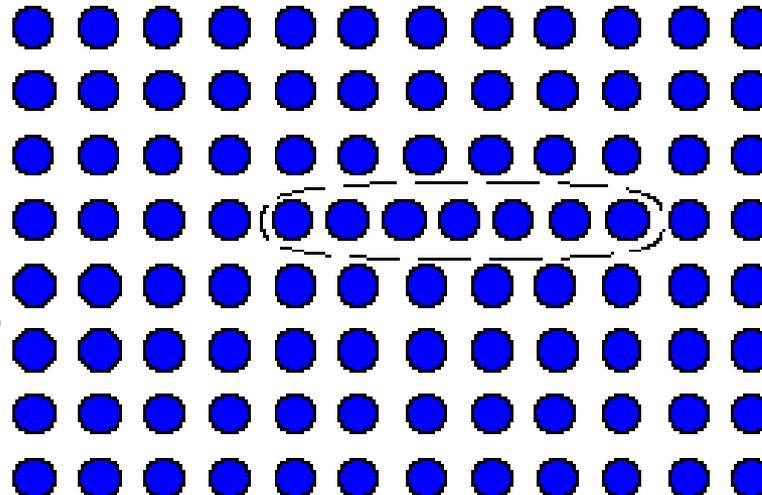
- **Dumbbell** (*hantel / käsipaino*) structure





Crowdion

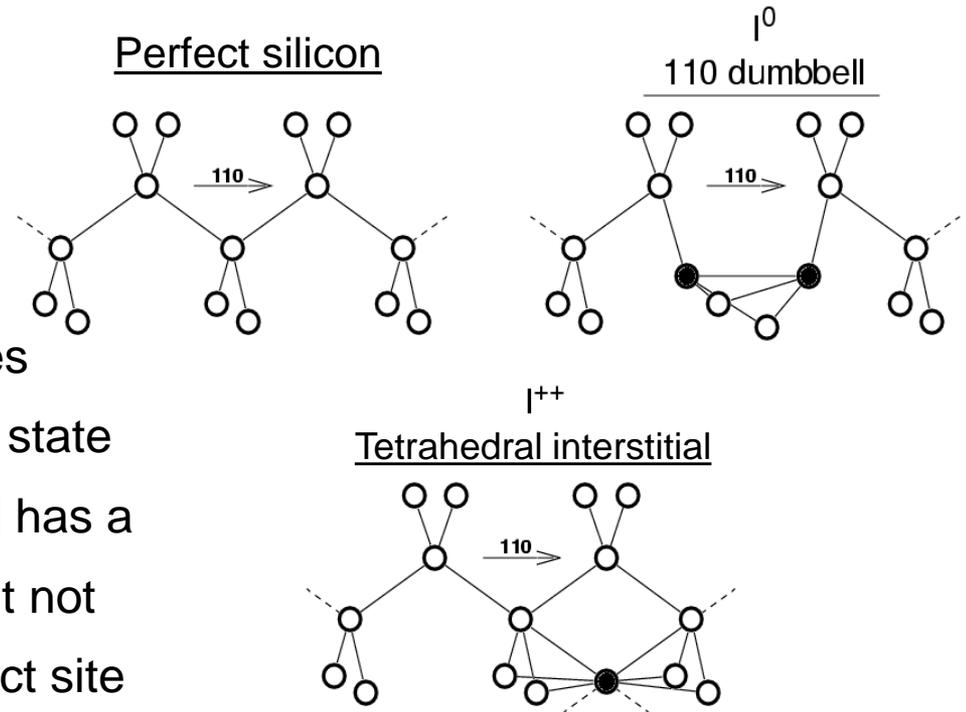
- In BCC metals except for Fe, the ground state structure of the interstitial seems to be (from DFT calculations) an extended defect along the 111 crystal direction, where one atom pushes a row of atoms on both sides into an elongated defect configuration
 - This is known as a **crowdion** (*gruppjon / kimppasija*)
 - The most recent calculations indicate that the crowdion atom row may actually not be straight, but in a slightly puckered configuration





Interstitial atoms in silicon

- In silicon life is again more complex
 - The interstitial atom has at least two different structures depending on charge state
 - The neutral interstitial has a split 110 structure, but not centered on the perfect site
 - The doubly positive interstitial has a high-symmetry tetrahedral position, with 8 nearest neighbours

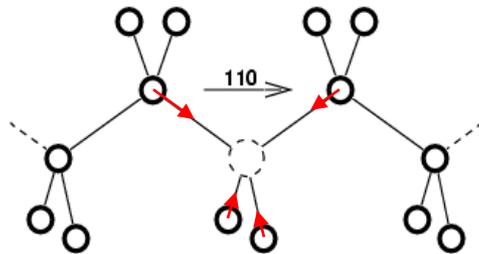




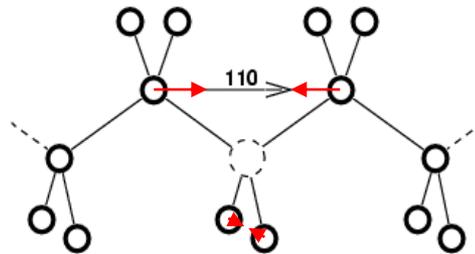
Defect reconstructions

- The same point defect may have several different varieties depending on how the neighbourhood atoms reconstruct
 - **Defect reconstruction** (*defektrekonstruktion / kidevirherekonstrukcio*)
 - Example: the 4 neighbours around the monovacancy in Si can be reconstructed in at least 3 different ways, depending on charge state and doping level of material

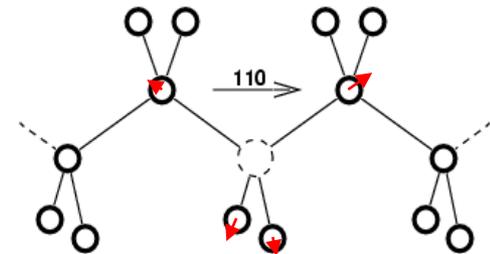
Symmetrically inwards



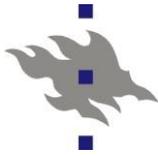
Pairwise towards each other



Symmetrically outwards(!)

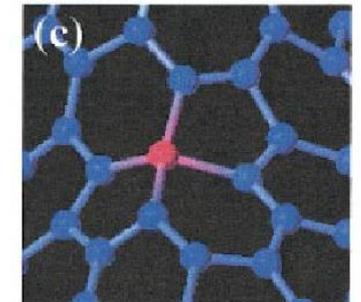
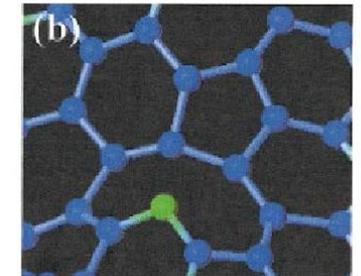
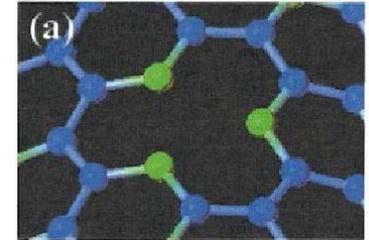


- The inwards reconstruction can be like ~10% of the bond length, the outwards less

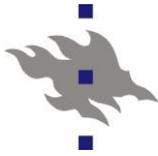


Defect reconstructions: the vacancy in graphene

- Another example is the vacancy in graphite, graphene and nanotubes
 - The obvious structure would be picking out an atom (a)
 - This has 3 unsaturated bonds
 - But there are 2 different possibilities:
 - A reconstruction where 2 unsaturated bonds meet, and one atom comes out of the plane (b)
 - A reconstruction where all unsaturated bonds meet at one atom in the middle
 - No unsaturated bonds, but high strain in them
 - It turns out that case b) is the ground state!

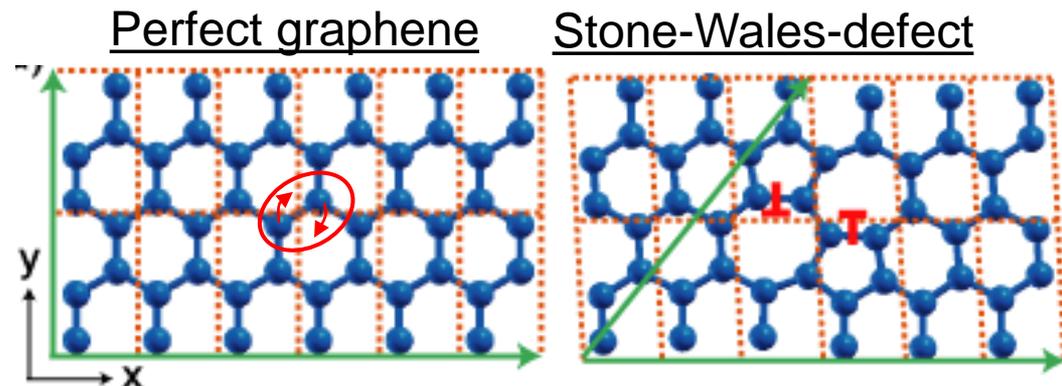
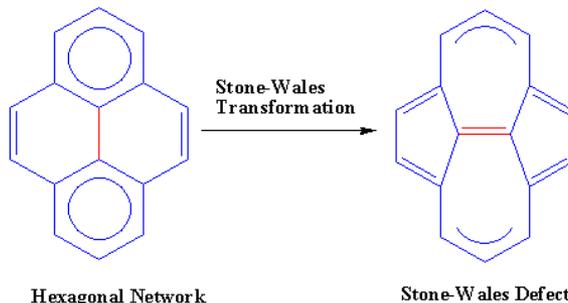


[P.M. Ajayan *et al.*,
Phys. Rev. Lett. 81
(1998) 1437].



Topological defects

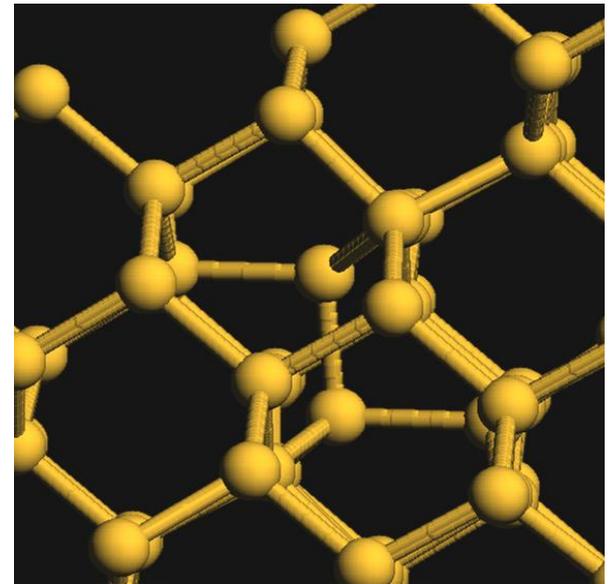
- Another variety of point defects are the **topological defects** (*topologiska defekterna / topologiset defektit*)
- This means defects where the total amount of atoms is identical to the pristine crystal, but where the bonding arrangement differs from the normal (even if the total number of bonds of each atom remains the normal value)
- Simple example: the so called Stone-Wales-defect in graphene or nanotubes
 - Instead of only 6-atom rings, two 5-atom and two 7-atom rings





Topological defects: the bond-order defect in Si

- A fairly recently found important topological defect is the so called 'bond-order' or IV pair defect in Si.
- This can be conceptually understood such that two Si atoms along the 110 row rotate about 90 degrees and then reform bonds such that all atoms still have 4 bonds, but the order is swapped
- Only fairly recently found [Tang et al, Phys. Rev. B, 55: 14279 (1997)], but now believed to be important for amorphization of Si [Donnelly, Appl. Phys. Lett. 82 (2003) 1860; Marquez, Mater. Sci. Engr. B 124-125 (2005) 72]

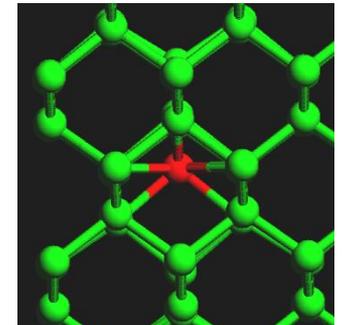
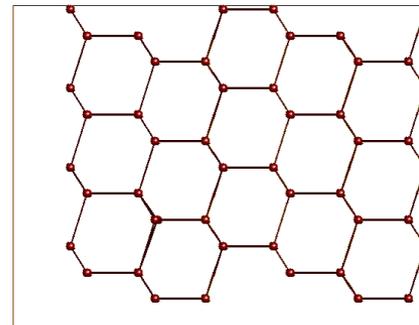


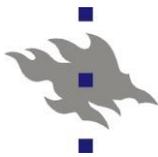
[Animation: siesta_111_20eV.avi]



Relation to irradiation

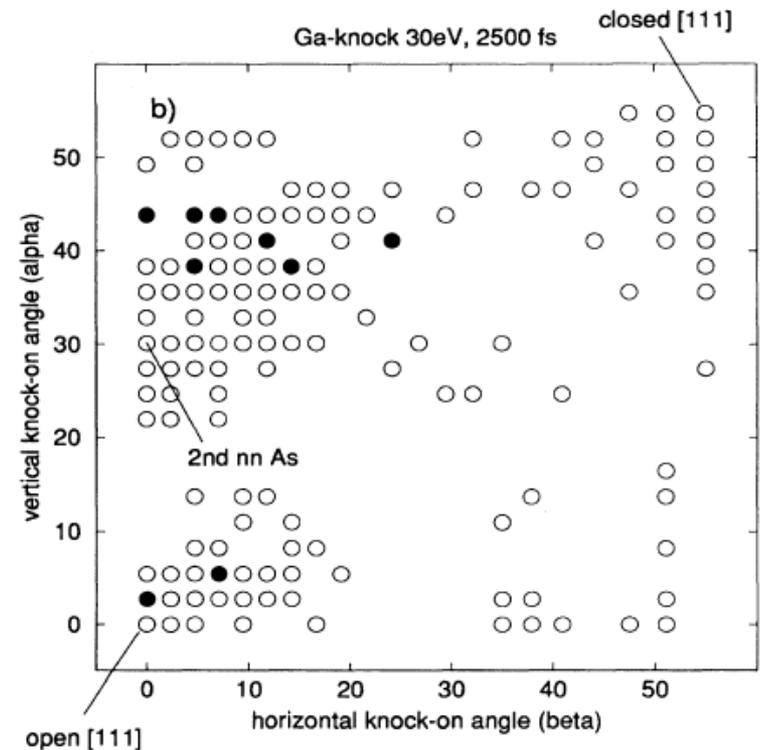
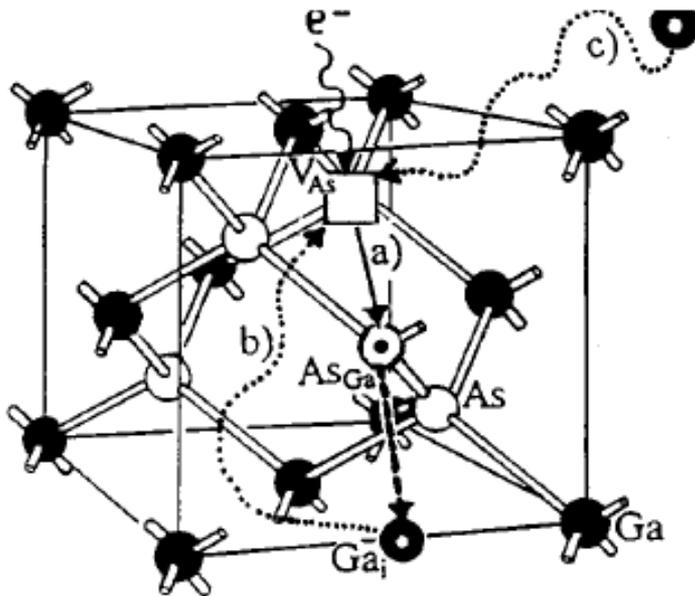
- Irradiation that gives recoil energies only just above the threshold tends to produce point defects
- Just above threshold a single Frenkel pair
 - But close FP's may be different from equilibrium structure of the vacancy+interstitial due to binding effects
 - Example: DFT MD calculations near the threshold of Si showed that in many cases the defect produced is either an IV pair, or a vacancy+tetrahedral interstitial, even though the ground state is the dumbbell interstitial! [Holmström et al, Phys. Rev. B, 78:045202, 2008]





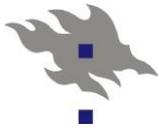
Direct antisite production

- In compound semiconductors like GaAs, it has been shown that just-above-threshold irradiation can also produce antisites directly



[Experiment: Hausmann et al, Phys. Rev. B 54, 8527]

FIG. 2. The anisotropy of antisite creation with 30 eV recoil energy (a) As and (b) Ga as the PKA. An open circle denotes the creation of one antisite of either type and a filled one the creation of two antisites.



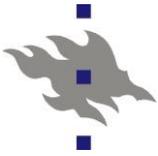
6.3. Equilibrium thermodynamics of simple point defects

- **Note: this calculation is not directly relevant to irradiation damage production rates, which is inherently nonequilibrium**
 - **But it is important for comparative calculations for irradiation**
- Consider a crystal of n vacancies and N atoms **in equilibrium** with its environment of some pressure P and temperature T

- The number can be calculated using the Gibbs free energy

$$G = U - TS + PV$$

- The volume of the crystal will now be $V = (N + n)\Omega$, where Ω is the volume per atom
- The free energy of the crystal is $F_0(n) = U - TS$
 - Now the entropy S contains a term S_0 which is the entropy without defects, and the **configurational entropy** S_c which tells in how many ways n vacancies can be arranged among the $N+n$ atom places
 - We assume $n \ll N$ so that their entropy is independent of other vacancies, and that there is no defect clustering



Thermodynamics of simple point defects

- The number of ways to arrange the atoms is

$$\binom{N+n}{n} = \frac{(N+n)!}{N!n!}$$

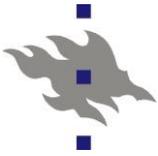
- From the definition of entropy we get the configurational entropy S^c and hence the free energy G :

$$S^c = k_B \ln \frac{(N+n)!}{N!n!}$$

$$G = F_0 - TS^c + P(N+n)\Omega$$

- By using the Stirling approximation $\ln X! \approx X \ln X - X$ we get

$$\begin{aligned} S^c &= k_B(\ln(N+n)! - \ln N! - \ln n!) \\ &= k_B((N+n) \ln(N+n) - N - n - N \ln N + N - n \ln n + n) \\ &= k_B((N+n) \ln(N+n) - N \ln N - n \ln n) \end{aligned}$$



Thermodynamics of simple point defects

- To minimize $G(n)$ we seek the point where $\partial G / \partial n = 0$. Now

$$\frac{\partial S^c}{\partial n} = k_B(\ln(N + n) + 1 - \ln n - 1) = k_B \ln \frac{N + n}{n} \approx k_B \ln \frac{N}{n}$$

as $n \ll N$ and hence

$$\frac{\partial G}{\partial n} = \frac{\partial F_0}{\partial n} + P\Omega - k_B T \ln \frac{N}{n}$$

- For $\partial F_0 / \partial n$ we can make the Taylor-approximation when $n \ll N$:

$$\frac{\partial F_0}{\partial n} = \left. \frac{\partial F_0}{\partial n} \right|_{n=0} = \varepsilon$$

where ε now is independent of n (this is saying essentially that the defect energy is the same for all vacancies, which is natural)

- ε is called the defect **formation energy** (*formationsenergi* / *muodostumisenergia*) and often denoted E^f



Thermodynamics of simple point defects

- Using $\partial G / \partial n = 0$ we now get

$$0 = \varepsilon + P\Omega - k_b T \ln \frac{N}{n}$$

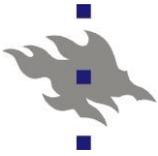
from where n can be solved and we get

$$n = N e^{-(\varepsilon + P\Omega) / k_B T}$$

which gives the equilibrium defect concentration in the lattice $c = n/N$!!

- In addition to the configurational entropy, a defect can also have an 'internal' formation entropy S^f which comes for instance from how the defect changes the vibrational levels in the lattice [Peterson, J. Nucl. Mater. 69 (1978) 3]. It cannot be derived in any simple way analytically, but should be taken into account in the calculations. Hence one gets

$$c = g e^{S^f / k} e^{-(E^f + P\Omega) / k_B T}$$



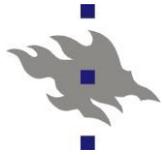
Thermodynamics of simple point defects

- To recap, the equation

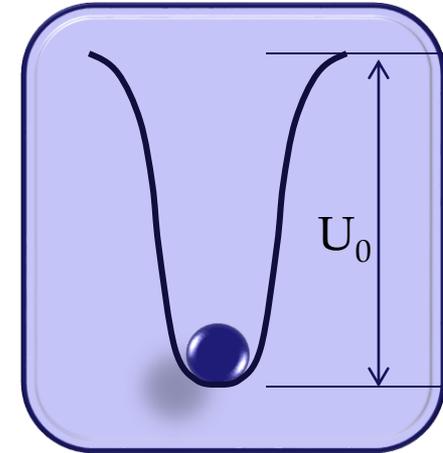
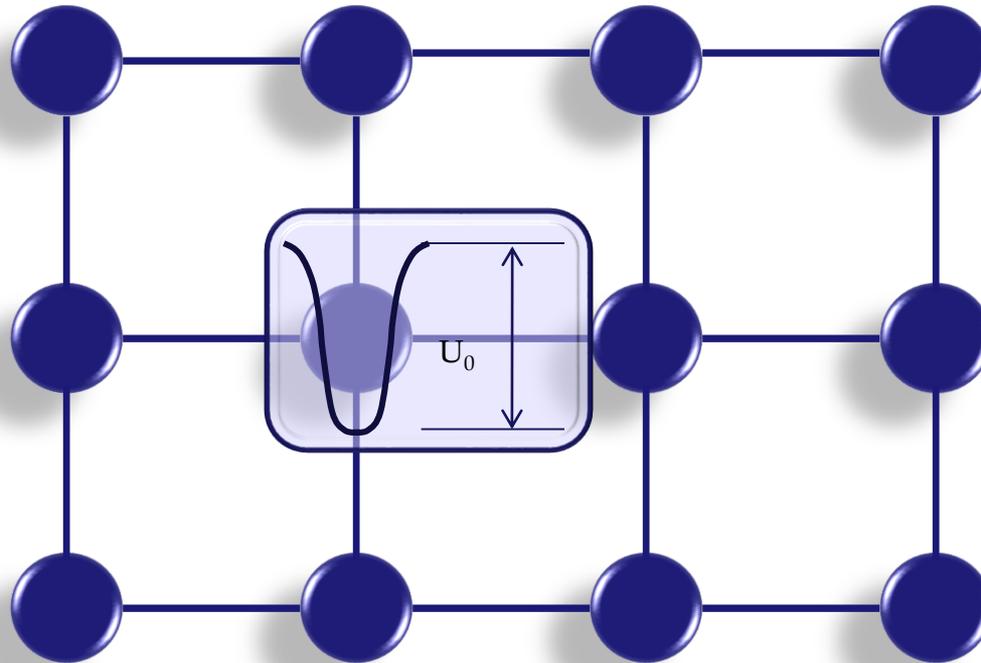
$$c = g e^{S^f/k} e^{-(E^f + P\Omega)/k_B T}$$

hence gives the concentration of vacancies in a crystal. g is a geometrical factor which tells in how many ways a defect can be placed in the same lattice sites. For simple vacancies in metals g is simply = 1.

- This E^f can be simply understood as the energy needed to insert an extra atom in a lattice



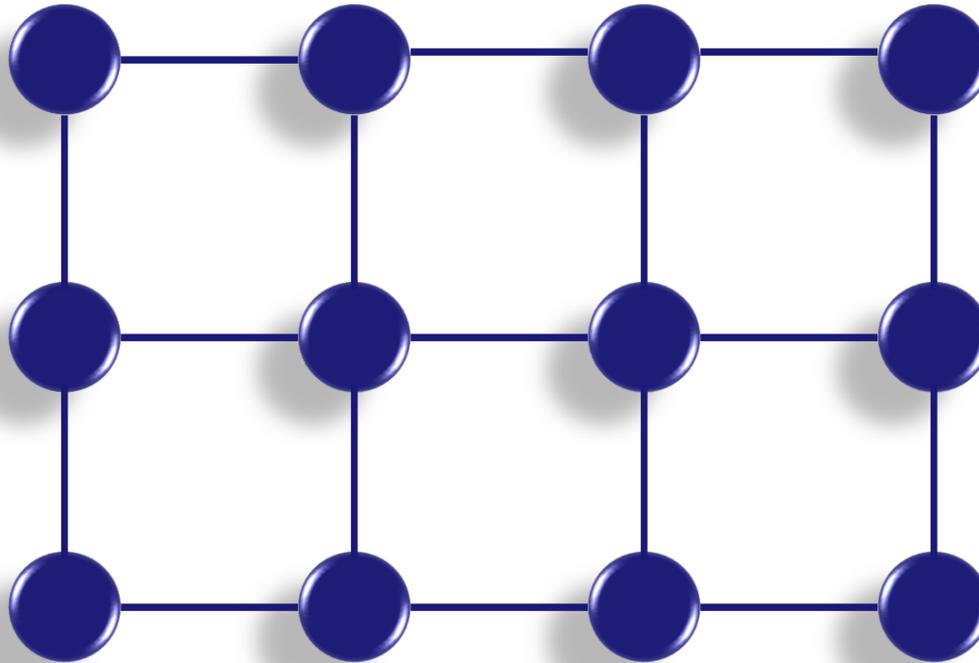
Perfect 2D metal lattice



↗ In a perfect metal crystal the atoms occupy strictly defined positions in a lattice according to interatomic interactions potential.



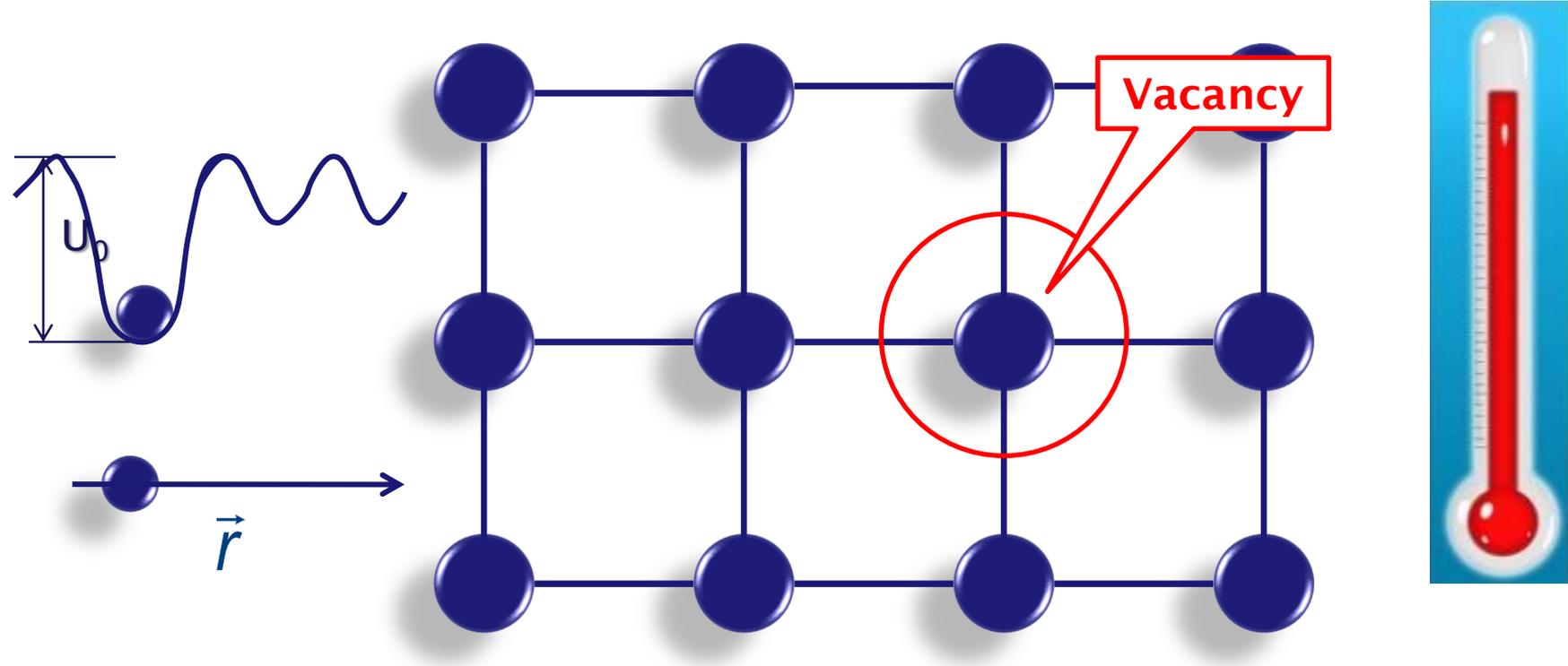
Formation of a single vacancy



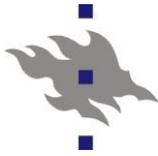
↪ Vacancies are intrinsic point defects which are always present in a crystal structure ...



Formation of a single vacancy

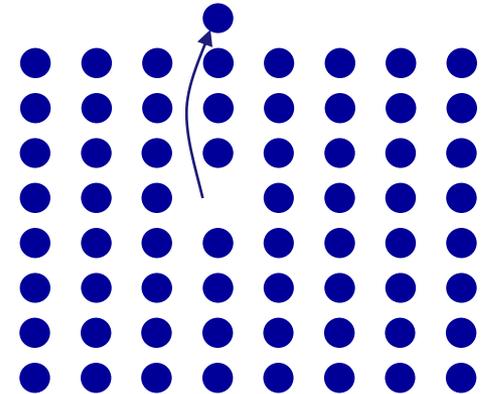


↗ Vacancies are elementary point defects which are always present in a crystal structure if the temperature of a crystal $T > 0$ K.

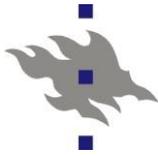


Vacancy formation energy

- In a *monatomic* system the formation energy can in principle be calculated with the following reasoning
- We imagine that we make a vacancy by taking out an atom from the system and placing it in a 'thermodynamic reservoir' on the surface
- At the surface it will have the same potential energy as a normal lattice atom: U_{pot}



- The surface energy need not be taken into account as we are in the thermodynamic limit where $n \gg 1$ (i.e. there are lots of these atoms at the surface)

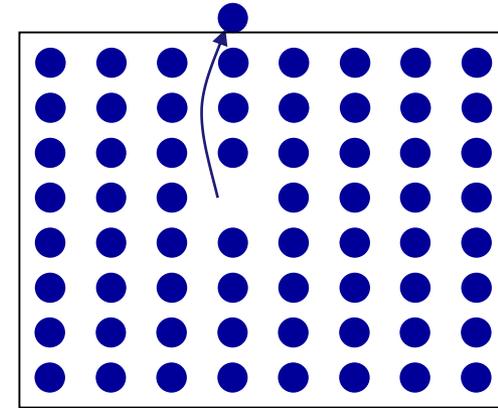


Vacancy formation energy calculation

- The energy difference in the system is now = the formation energy E^f which is now

$$E^f = U_{\text{system-with-vacancy}} + U_{\text{pot, extra atom}} - U_{\text{system-without-vacancy}}$$

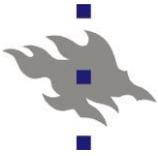
where "system" means the original system surrounded by the rectangle in the picture



- For interstitial atoms the same argument gives

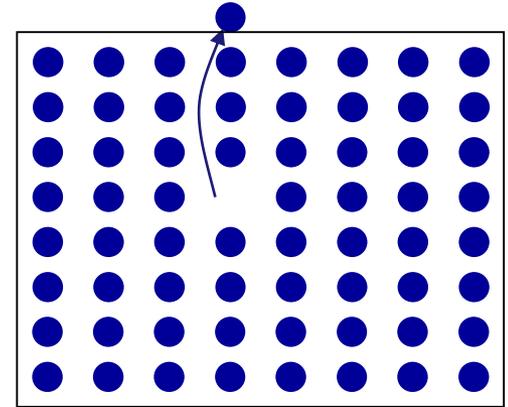
$$E^f = U_{\text{system-with-interstitial}} - U_{\text{pot, atom that is missing}} - U_{\text{system-without-interstitial}}$$

- The sign convention here is that U are all potential energies < 0 . For a ground state atom, $U_{\text{pot}} = -E_{\text{cohesive}}$, which is always positive in binding systems
- For compounds this becomes more complicated, as then the reference values should be those of the potential energy of the pure element in its ground state
 - E.g. For an As-vacancy in GaAs the reference is that of the atom in pure As, and for an N vacancy in GaN that of one of the atoms in the N_2 dimer in nitrogen gas!



Simple first estimate of the formation energy

- We will now estimate this energy with a simple "bond-counting"-argument
 - Typical metals have a cohesive energy of ~ 3 eV
 - Close packed metals have 12 nearest neighbours
 - Assume all bonding is in nearest-neighbour bonds



(which is not very accurate in metals so this is really only a rough estimate)

- Consider a crystal with N atoms and the cohesive energy U_{pot}
 - If there would be no bonding of atoms, the formation energy would be

$$E^f = (N - 1)U_{pot} + U_{pot} - NU_{pot} = 0$$

- But in reality the 12 nearest neighbours lose a bond. The energy per a bond is $-U_{pot}/12$ because 12 bonds would give the normal cohesive energy
- Hence the system with the vacancy gets an energy change of $-12*U_{pot}/12$ so:

$$E^f = -12U_{pot} / 12 + (N - 1)U_{pot} + U_{pot} - NU_{pot} = -U_{pot}$$



Simple first estimate of the formation energy

- This result should be modified by the chemical observation from Linus Paulings theory of chemical bonding, that if one bond is lost the other bonds tend to strengthen
 - Hence the true loss per bond is $< -U_{pot}/12$
 - In addition, the atoms can be relaxed somewhat in towards the vacancy, which also reduces the energy loss
 - Hence the estimate $E^f = -U_{pot}$ is an upper limit, and the end resultat is
$$E^f \leq -U_{pot}$$
- Note the signs: $U_{pot} < 0, E^f > 0$
 - ($E^f < 0$ would imply it is energetically favourable to form vacancies, which would imply the crystal structure is inherently unstable => not possible)
- For typical binding energies $U_{pot} \sim -3$ eV we can hence make an order-of-magnitude estimate $E_v^f \sim 1$ eV

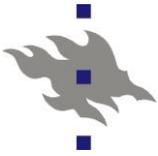


The pressure term

- Let us now consider the pressure-dependent term $P\Omega$. At normal pressures, say the order of kbar and less, we can easily estimate the magnitude of the term

$$1 \text{ kbar} = 10^8 \text{ Pa} = 10^8 \frac{\text{J}}{\text{m}^3} = 6 \times 10^{-4} \frac{\text{eV}}{\text{\AA}^3}$$

- For a typical atomic volume of 10 \AA^3 we get $P = 6$ milli-eV.
- But above we estimated that the formation energy is of the order of 1 eV
- Hence the pressure term $P\Omega$ will be vanishingly small in normal cases
 - Only at pressures around ~ 0.1 Mbar may it become significant
- Note that considering atom relaxation around the defect, this term is actually $P\Delta V$, where ΔV is the defect relaxation volume (*relaxationsvolym / relaksaatioilavuus*)



Formation energy in different forms

- When the pressure term can be neglected and $g=1$, we can write simply

$$c = e^{S^f/k} e^{-E_v^f/k_B T}$$

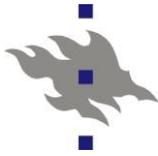
- For interstitial atoms one can similarly derive

$$c_i = g e^{S_i^f/k} e^{-E_i^f/k_B T}$$

and for Frenkel pairs

$$c_{FP} = g_i^{1/2} e^{(S_i^f + S_v^f)/2k} e^{-(E_i^f + E_v^f)/2kT}$$

(the factor 2 comes from the fact that the derivation needs to consider a product of the configurations of vacancies and interstitials)



Typical values

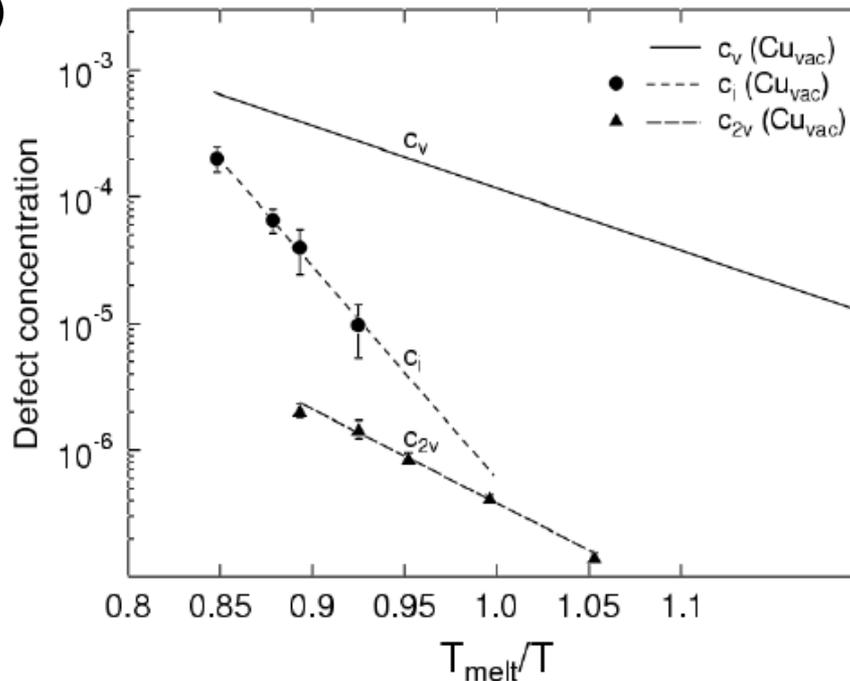
- For vacancies measurements in pure metals typically give
 - $E_v^f \sim 1 \text{ eV}$ and $S_v^f \sim 2 k_B$
 - Note that this same derivation in many textbooks completely ignores the S_v^f . In that case the result is wrong by $\sim e^2 \sim 10$
- For interstitials measured values in metals are
 - $E_i^f \sim 3\text{-}5 \text{ eV}$.
 - S_i^f is not well established but recent works indicate $\sim 10 k_B$
[recent work by A. V. Granato et al]

Metal	E_v^f	E_i^f
Al	0.66	3.2
Cu	1.31	2.2
Pt	1.43	3.5
Mo	1.30	
Zn	0.45	



Typical values

- The formation energy of the vacancy is the lowest of all defects in metals at room temperature, so they dominate in equilibrium
 - Near the melting temperature the divacancy and interstitial may become significant
 - Example: Cu (experiment for vacancy, simulation for divacancy $2v$ and interstitial i)



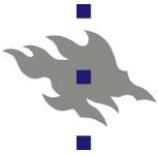


Binding energy of composite defects

- For composite defects another very important quantity is the binding energy.
- It is defined as the difference in energy between splitting up the composite defect into its individual counterparts
- For instance, for the defect reaction $V + V \rightarrow 2V$ the binding energy can be written

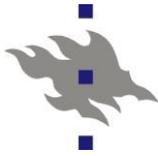
$$E_{2v}^b = E_{2v}^f - 2E_v^f$$

- If now the formation energy of the vacancy is 1.0 eV and the divacancy 1.5 eV, the divacancy binding energy is -0.5 eV
 - In this case the divacancy is binding, because it takes less energy to form a divacancy than two single vacancies
- **NOTE:** the sign convention in this context is varying in the literature, some use the opposite convention that positive binding energies are binding => **always define clearly which one you use!**



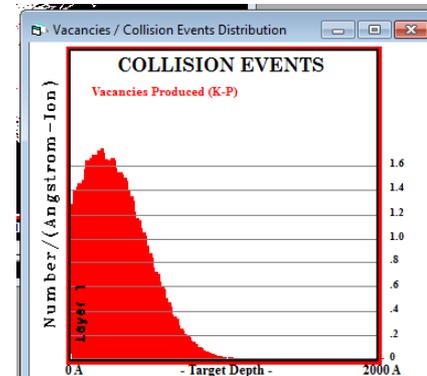
6.4. Concentration of radiation defects

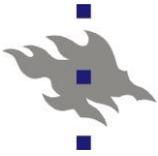
- Note that the previous calculations were all for the equilibrium defect concentration
- Radiation is **NOT** equilibrium, and hence the radiation defect concentrations can be orders of magnitude higher
- For instance, in Cu the numbers given in the table above and assuming a formation entropy of 2 for the vacancy and 10 for an interstitial, gives at room temperature equilibrium concentrations of 7×10^{-22} for vacancies and 7×10^{-33} for interstitials => completely negligible!



Example: SRIM estimate of defect concentration

- To give an idea of typical irradiation defect concentrations (order-of-magnitude), consider 100 keV Ar irradiation of Cu with SRIM
- SRIM gives about 1.6 vacancies/(Å ion) at the damage maximum at a depth of roughly 200 Å.
- For a typical fluence of 10^{14} ions/cm² = 0.01 ions/Å² this means a defect concentration of 0.016 vacancies/Å³.
- Comparing with the atomic density of Cu of 4 atoms/3.62 Å³ (one FCC unit cell) = 0.084 atoms/ Å³ , one hence gets a defect concentration of ~ 0.2
 - And same for interstitials!
- Hence irradiation values ~ 23 and 33 **orders of magnitude** higher than equilibrium concentrations at room temperature!





Interstitials and irradiation...

- We saw that even at up to the melting point the equilibrium concentration of interstitials is extremely low => interstitials exist mainly due to irradiation at low temperatures, and any study of interstitials is often assumed to be associated with radiation effects



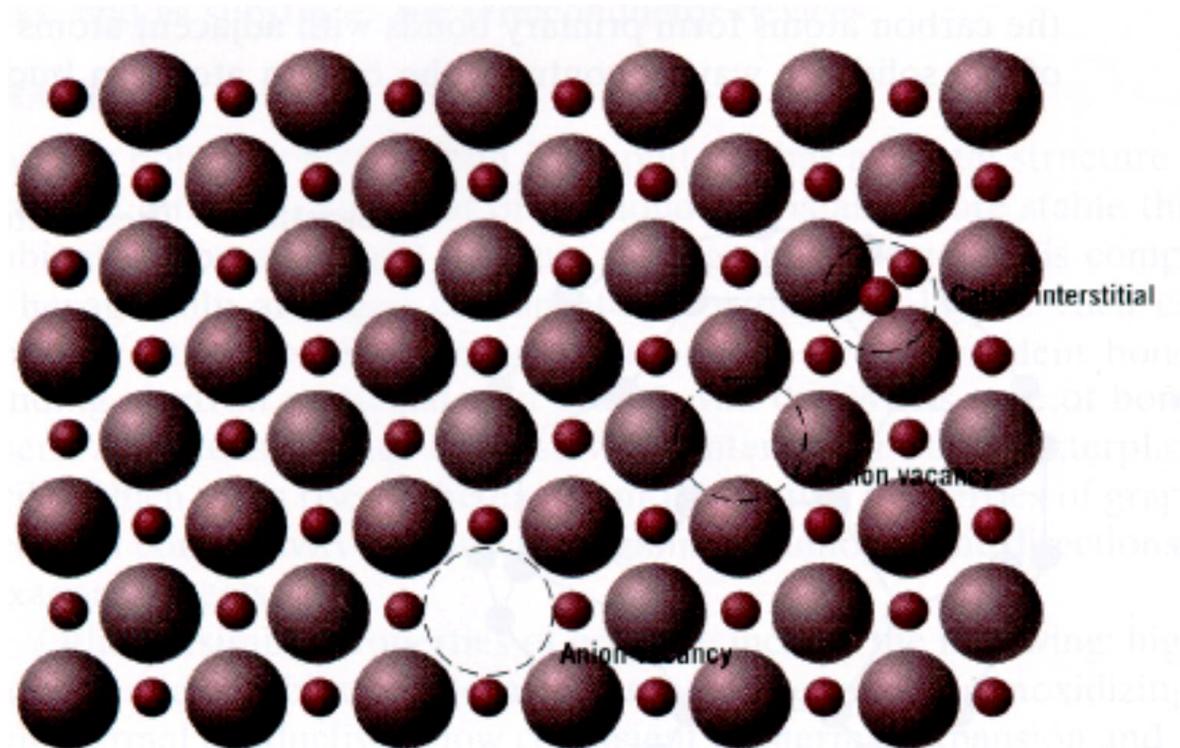
6.5. Defects in ionic crystals

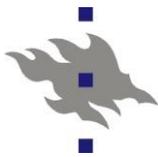
- In principle all the kinds of defects discussed above can also be assumed to exist in ionic crystals
- But the ionicity adds some additional criteria for which defects can be considered energetically sensible
 - The defects must be charge-neutral
 - The Anions are much bigger than the cations -> the anion interstitials are unlikely (at least in close-packed ionic materials)



Simple point defects in ionic crystals

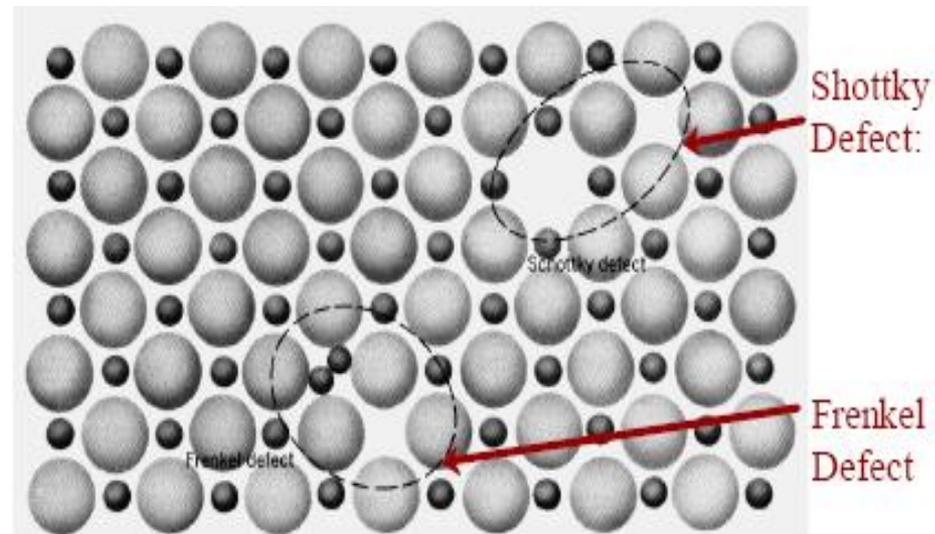
- The simple point defects are hence
 - Anion vacancy
 - Cation vacancy
 - Cation interstitial





Charge neutrality

- But to achieve charge neutrality these have to be somehow grouped
- Obvious examples:
 - Frenkel pair of cation vacancy and –interstitial
 - **Schottky-defect**: pair of vacancies!
 - Note: in pure elements a Schottky defect means a single vacancy





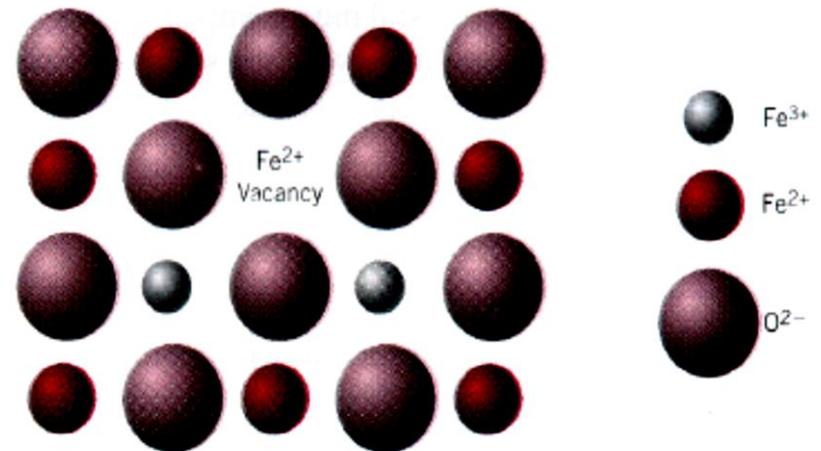
Stoichiometry

- All defects which preserve the relative number of cations and anions, preserve the charge neutrality
- At the same time, they preserve the **stoichiometry** (*stökiometrin / stökiometrian*), i.e. the K:A ratio 1:1
 - E.g. the Schottky- and Frenkel-defects obviously preserve the stoichiometry
- But there are defect types which lead to **nonstoichiometric** (*ickestökiometriska / eistökiometrinen*) compounds even though the charge neutrality is preserved
 - This is possible if the two elements can have different charge states



Nonstoichiometric compounds: FeO

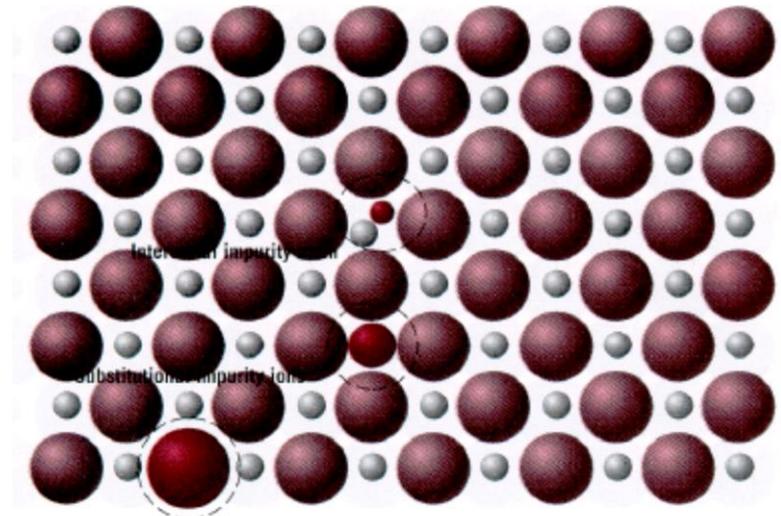
- An example is FeO:
 - Fe can have two charge states Fe^{2+} and Fe^{3+}
 - In normal stoichiometric FeO the O has the charge 2- and hence the Fe the charge 2+
 - But if two Fe^{3+} are near to each other, the charge neutrality can be preserved by one Fe^{2+} -ion being missing!
 - Hence V_{Fe} can be charge neutralized with two Fe^{3+}
- But with such defects the system becomes Fe-deficient
- This is common, and often FeO is denoted as Fe_{1-x}O with $0 < x \ll 1$

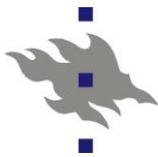




Impurities in ionics

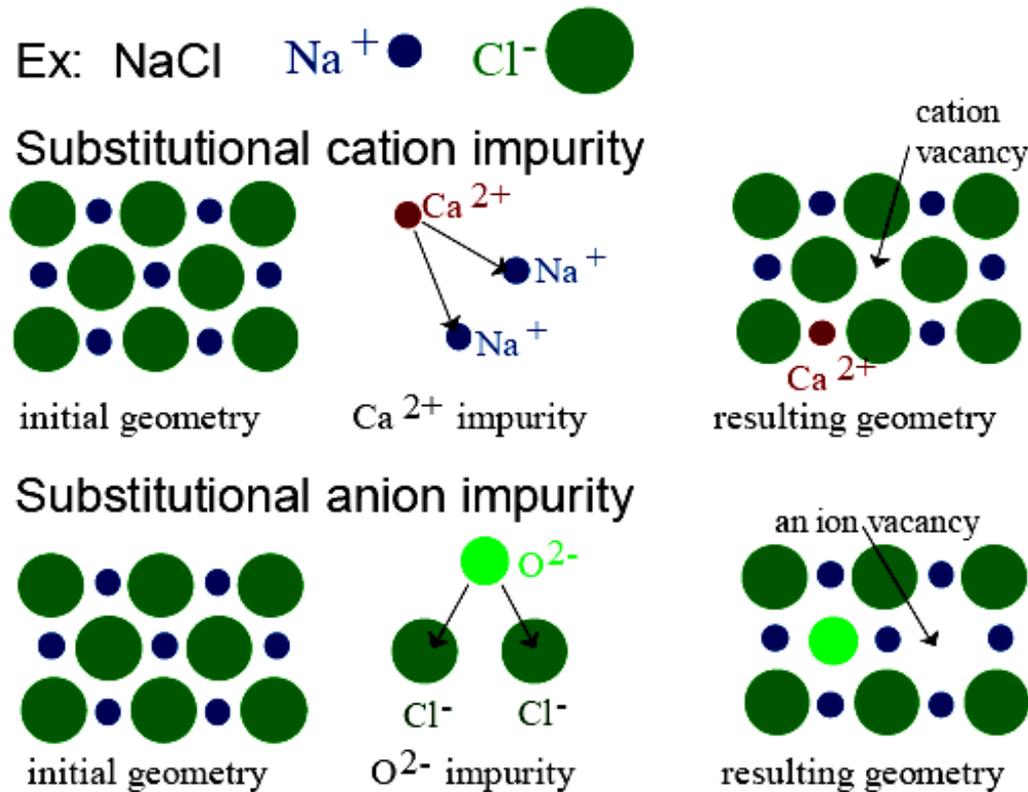
- Impurities in ionic materials can be either on interstitial or substitutional sites
 - But interstitial atoms must by necessity have relatively small atomic radii compared to the anions to fit in
 - Substitutional atoms are on sites with the same charge state as they themselves; otherwise the local charge becomes too large
- Impurities with the same charge state and about the same size as the lattice atoms can of course easily replace them





Impurities in ionics

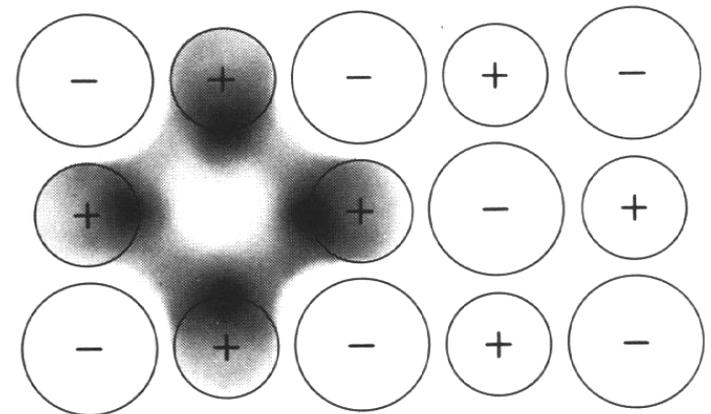
- Ex: NaCl with Ca^{2+} and O^{2-} - impurities:
 - To get charge neutrality additional atoms are needed for each impurity





Electrons and holes as charge neutralizers

- But there is also a completely different way of achieving charge neutrality than with other atoms
- Individual electrons or holes can get bound to a defect!
 - Hole = lack of an electron, a positive pseudoparticle
- Example: an anion vacancy can be neutralized by having an electron bound to the atoms around it
 - One can think that the electron is bound to the surrounding positive atoms and hence neutralized





Kroger-Vink notation for the defects

- All of the defects mentioned above can be described with the so called Kroger-Vink-notation
 - Same basic idea as that described earlier, but charge states included
- A perfect lattice is described with a 0

Table 1.19 Summary of Kroger–Vink Notation

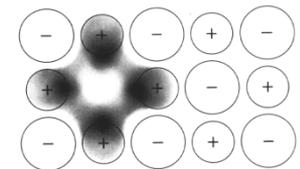
The Notation...	Represents a(n)...
V	Lattice vacancy
h	Free hole
e	Free electron
M (e.g., Ca, Al...)	Cation atom
X (e.g., O, Cl...)	Anion atom
<i>Subscripts</i>	
i	Interstitial lattice position
M	Cation lattice position
X	Anion lattice position
<i>Superscripts</i>	
•	Positive charge
'	Negative charge



Colour centers

- One of the reasons point defects in ionic crystals are so important is their optical properties
 - Many of them simply affect the colour of the crystal
- Hence they are also known as **colour centers** (*färgcentra* / *värikeskus*)
- The simplest colour centre is the so called F-center
 - Name comes from the name for colour in German: *Farbe*
 - F centra are simply an anion vacancy which has captured an electron
- Example: F-centers in CaF_2 makes it violet

[http://www.minsocam.org/msa/collectors_corner/arc/color.htm]





More F-centers

- There are many variations on F-centers:
 - F_n -centers: many F-centers next to each other diagonally
 - F_n^+ / F_n^- -centers: charge state specified
 - $F_A / F_B / F_C$ – centra: cation impurity A/B/C next to the F-center
- Example: $(F_2^+)_A$ – center: two F-centers with a cation impurity, charge +1

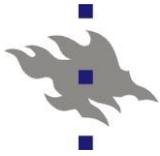


Other centers

- Other centers in alkali halides
 - H-center: Cl^{2-} - ion on a lattice site
 - V-center: Cl^{2-} - ion on two lattice sites
- Hole centers in quartz:
 - A metal impurity stabilizes an electron too little for oxygen: a hole
 - Example:
 - Al^{3+} - impurity => "smoky quartz"
(*rökkvarts* / *savukvarts*)
 - Fe^{3+} - impurity in quartz => amethyst



=> Many precious stones (jewels) are defined by the defects in them!



Examples on the atomic structures of centers

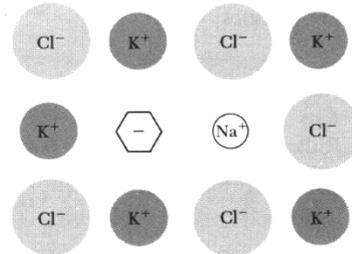


Figure 9 An F_A center in KCl: one of the six K^+ ions which bind an F center is replaced by another alkali ion, here Na^+ .

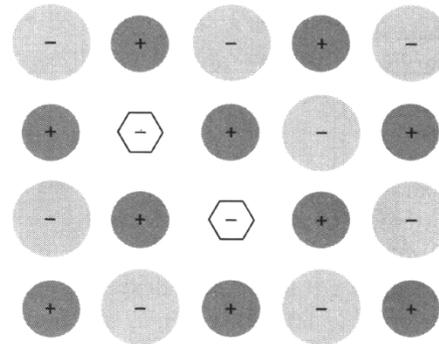


Figure 10 An M center consists of two adjacent F centers.

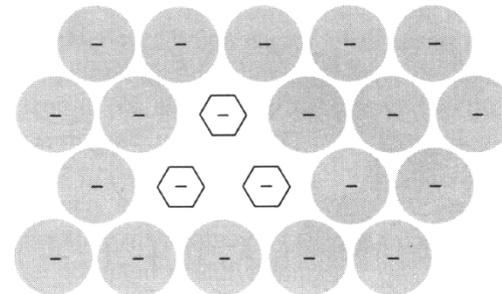
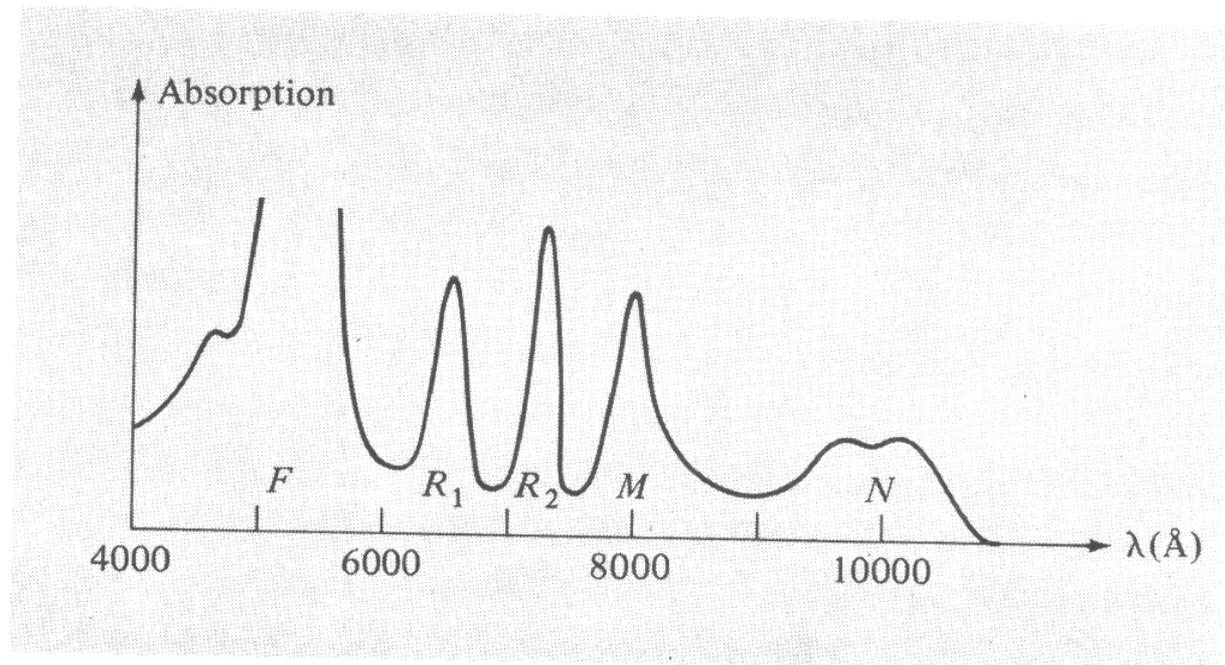


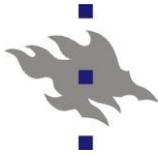
Figure 11 An R center consists of three adjacent F centers; that is, a group of three negative ion vacancies in a $[111]$ plane of the NaCl structure, with three associated electrons.



The effect on the absorption spectrum

- Different centers have different light absorption bands, and this defines them and can be used to measure them.

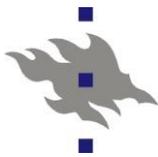




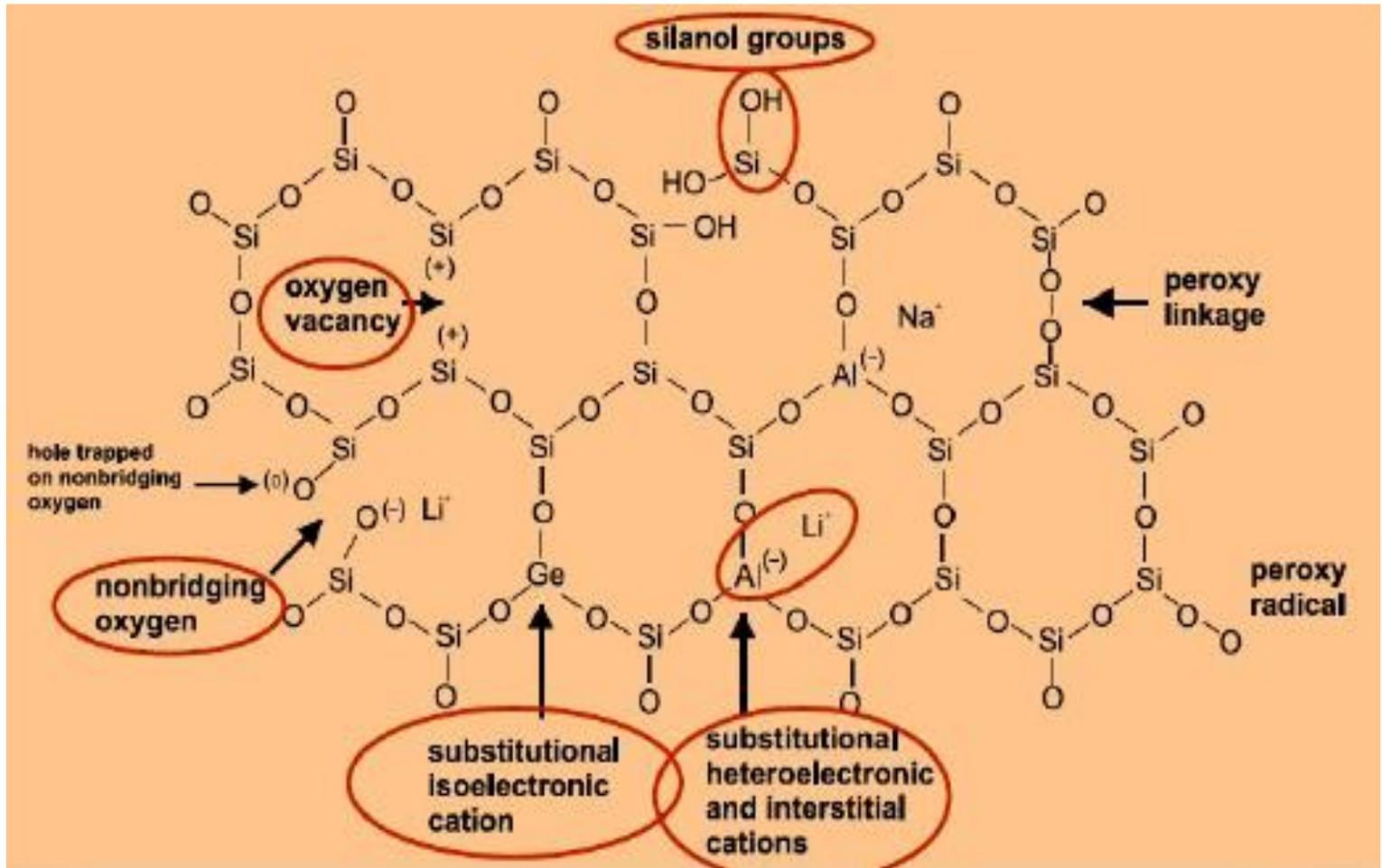
Centers in quartz

- A summary of how different centra affect quartz:

Materials Added (impurities)	Effect
Iron	Green
Barium	Brilliance
Soda Ash	Fogging
Manganese oxide	Violet or Blue
Cobalt oxide	Blue
Copper chloride	Red
Sulfur and iron oxide	Yellow to ruby amber
Neodymium oxide	Yellow sunglasses
Selenium	Ruby glass
Gold chloride and tin oxide	Ruby glass



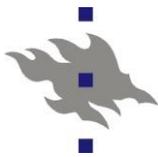
Defects in quartz (2D schematic)





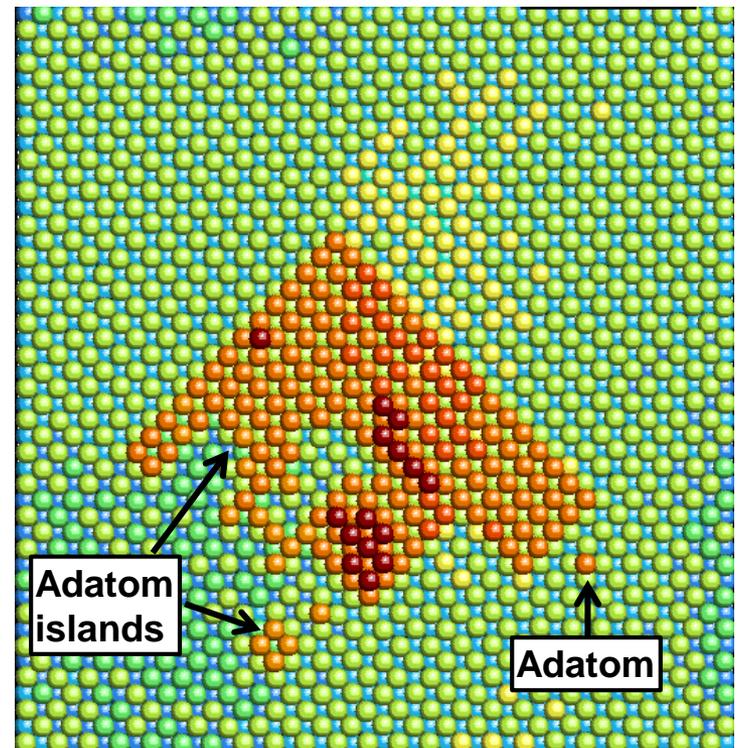
6.6. Defects in amorphous materials

- The defects in quartz are defined by bond breaking and impurities => many of them can be present also in an amorphous material
 - E.g. peroxy radical, peroxy linkage, silanol group etc.
- But also in pure elements it is possible to define defects
- In metals they can exist in a transient manner, defined by e.g. defect relaxation volume
- Example 1: positron measurements have detected vacancies in amorphous Si [Roorda et al, J. Appl. Phys. 72 (1992) 5145]
- Example 2: MD simulation of defects in amorphous Cu (details not important) gave defect relaxation volumes [Nordlund et al, Europhys. Lett. 71 (2005) 625]

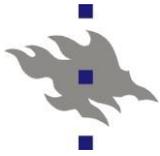


6.7. Surface defects

- Surfaces can have vacancies and atoms on top of the surface = adatoms
- As in bulk, surface vacancies and adatoms can cluster.
- Many adatoms are called **adatom islands** (*adatomö* /*adatomisaareke*)
- Example: adatoms (orange and red) on Cu formed by a 50 keV irradiation event



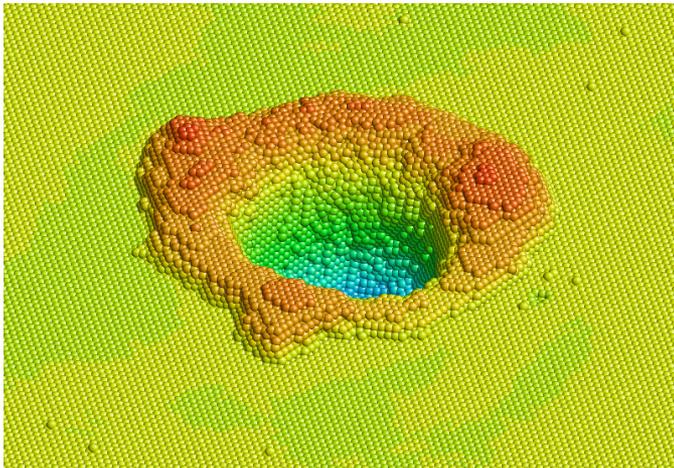
[Nordlund et al, Nature **398**, 49 1999]



Craters

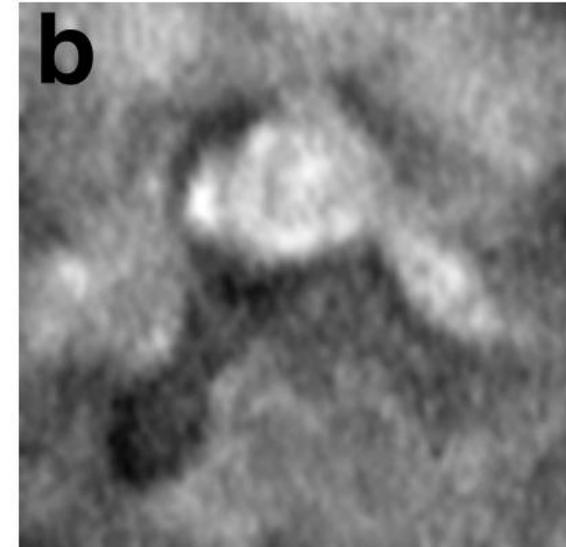
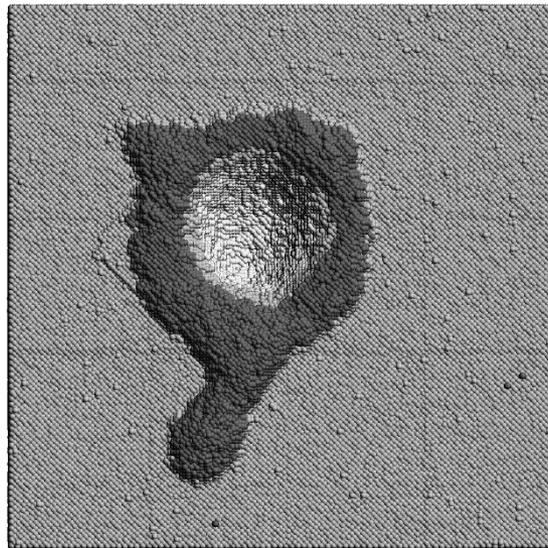
- As explained in the previous section, heat spikes can produce craters on surfaces
 - These can sometimes have nontrivial irregular shapes

Simulation



[Nordlund, Physics World 14, 22 (2001)]

Experiment



[Nordlund, Tarus, Keinonen, Donnelly, Birtcher, NIM B 2003]

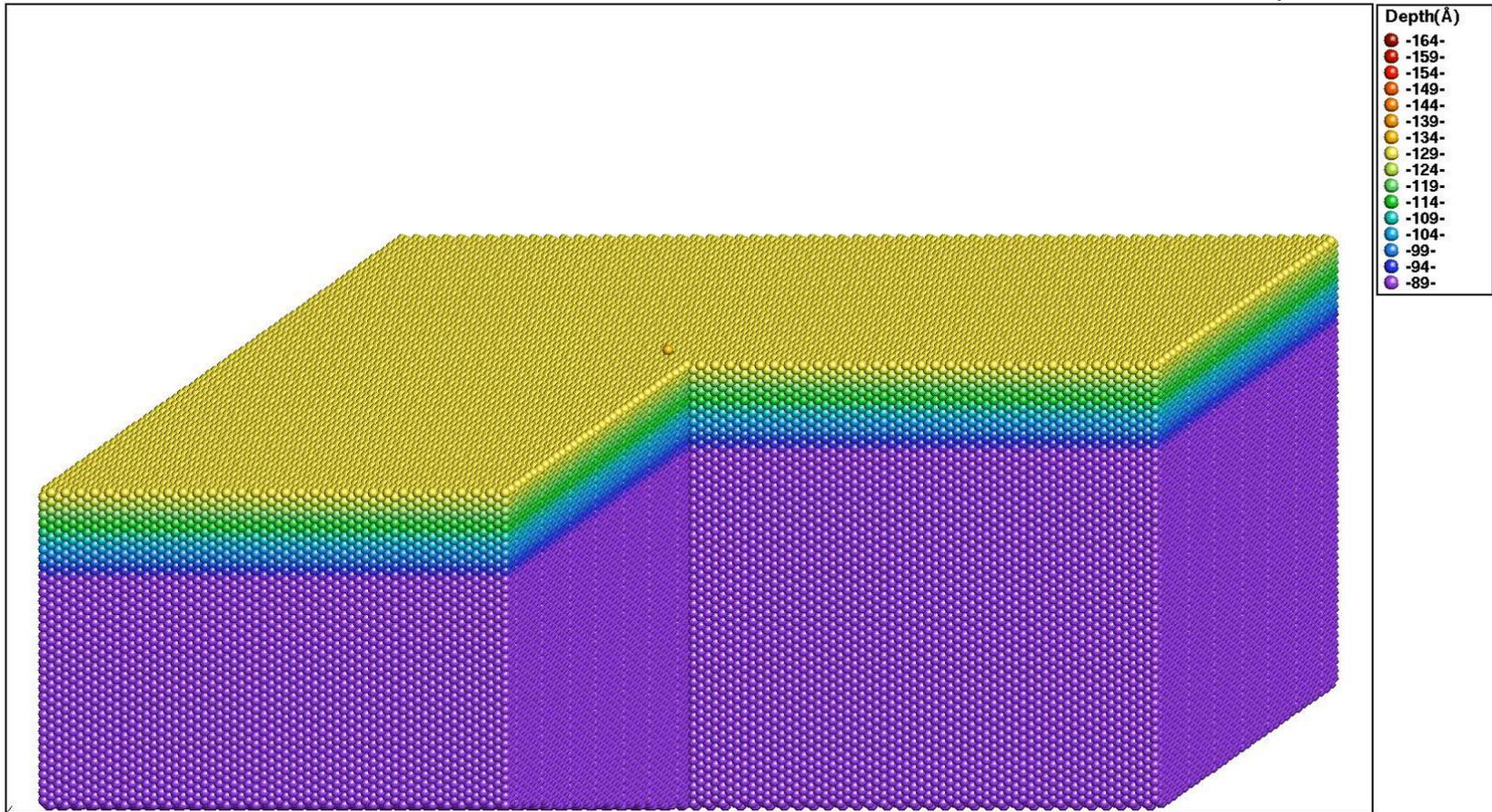


Crater formation animation

- An animation (Cut of 3 quadrants) of crater formation by a 50 keV Xe heat spike on Au (height colors)

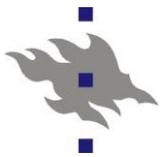
50 keV Xe impact on Au

time 0 ps



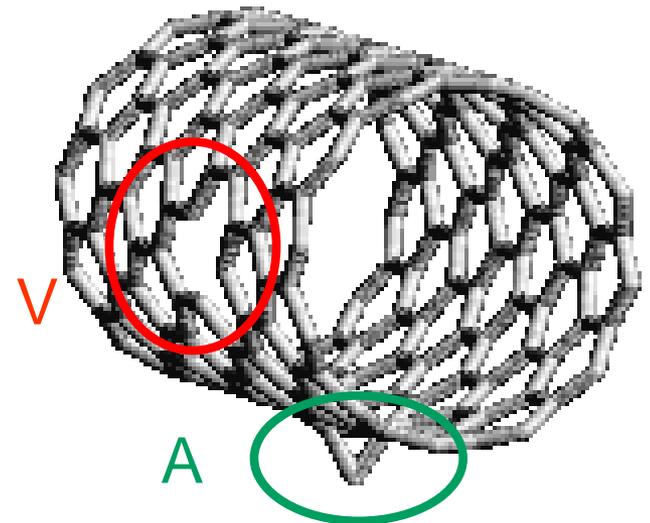
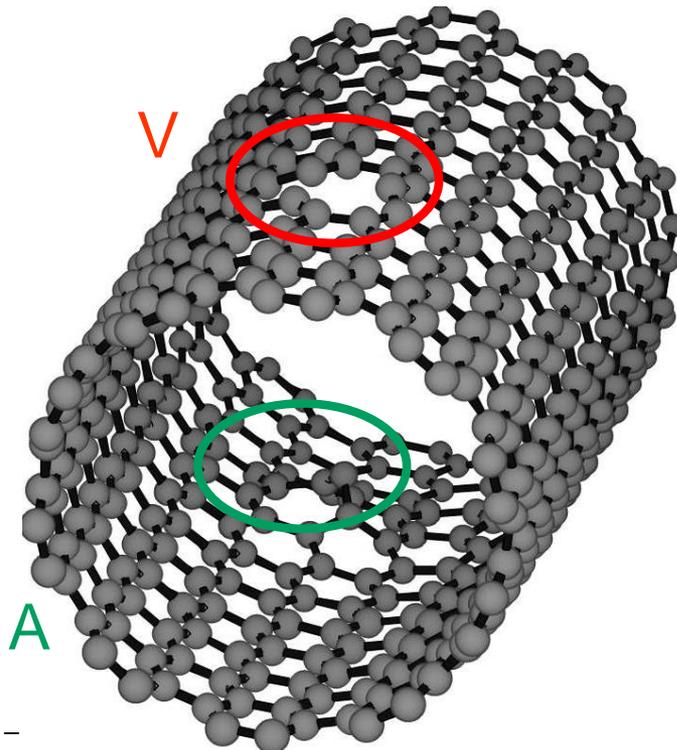
Radiation damage: x (-190 - 190) y (-80 - 300) z (-190 - 190)

(Kai Nordlund 1998, 2016)



Surface defects on nanotubes

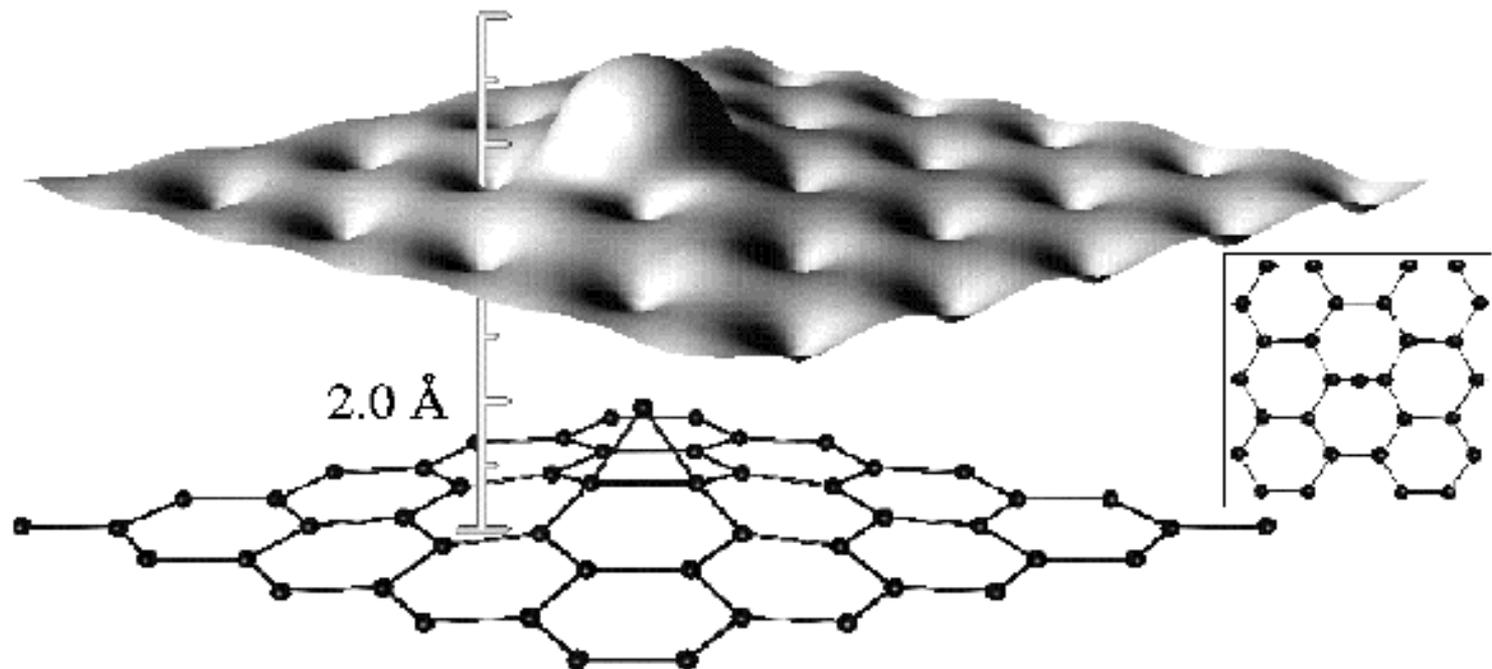
- Single-walled carbon nanotubes have a special kind of adatom defect formed by a triangle of atoms where one atom is 'on top of' two regular ones inside or outside the tube
 - No interstitial exists (chemically too unstable)





The nanotube adatom ('D3 defect')

- This defect can also be created on graphite by irradiation
- A zoom-in including the electronic structure of the outermost levels

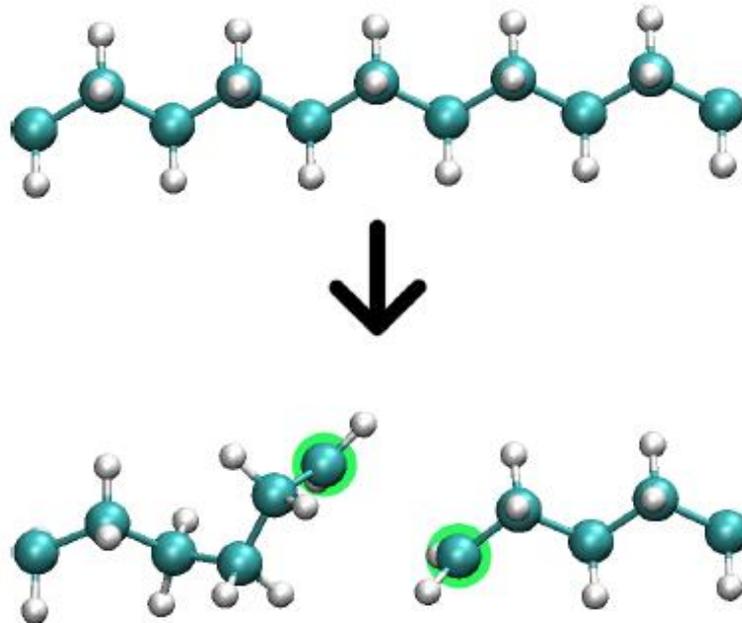


[Nordlund et al, Phys. Rev. Lett. 77 (1996) 699]



6.8. Defects in polymers

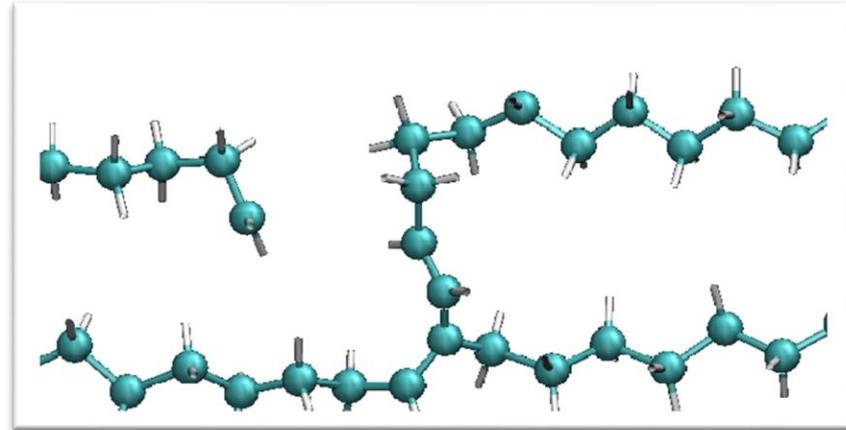
- As noted earlier, defect formation mechanisms in polymers are poorly understood
- However, some defect types are clearly known:
- **Chain breaking (scission)** is fairly obvious:





Crosslinking

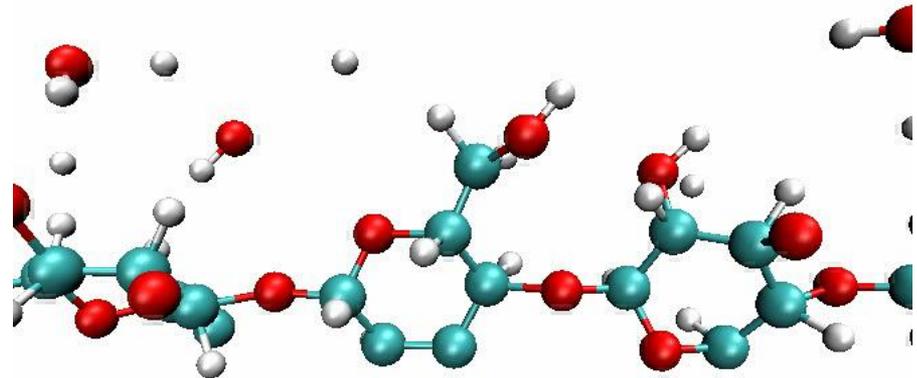
- **Cross-linking** (*korslänkning / ristisitoutuminen*), i.e. joining the C chains in two different polymer strands, has a major effect on polymer properties (“rubber boots go bad if stored for long times in sunshine”)
- Can be induced by any kind of irradiation, but also by chemical processes





Free molecule formation

- Naturally irradiation can lead to the formation of free molecules
- Example: single atomic recoil in cellulose
 - Only small segment of simulation cell shown
 - One OH and one CH₂ radical formed



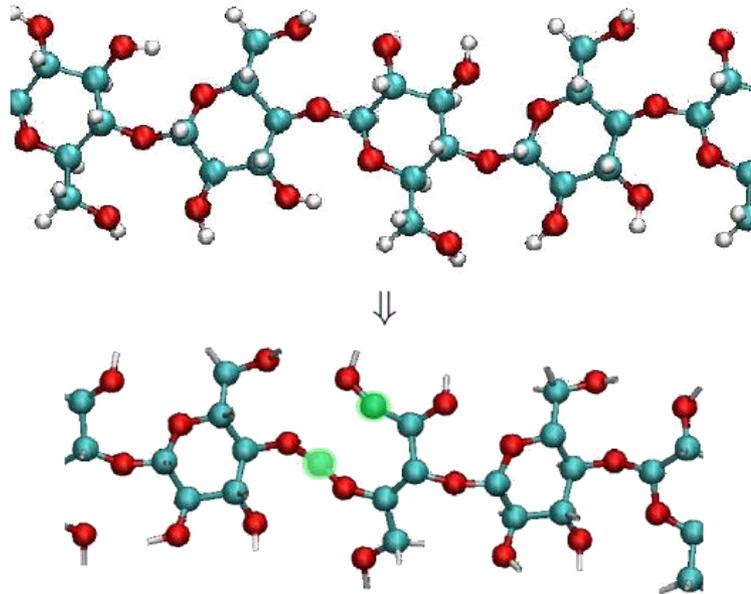
[Animation: cellulose_recoil.wmv]



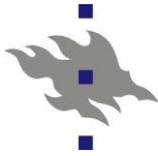
Ring breaking

- In polymers with ringlike structures within the chain, the ring may break without breaking polymer main chain

Glucose ring breaking in cellulose



J. Polvi and K. Nordlund, *J. Appl. Phys.* **115**, 023521 (2014).



6.9. Non-atomic defects

- Finally, there are defects which are not atomic at all
- **Polarons** (*polaroner / polaroni*) are extra electrons in an ionic crystal, which are not associated with any atomic defect. But they induce a deformation of the crystal (which can be understood as a polarisation) to reduce the electrostatic energy of the electron
- A even more subtle 'defect' is simple an excited electronic state, which can move in an ionic crystal. Such defects are called **excitons** (*excitoner / excitoni?*)
- In metals the free electrons can be considered to form an electron plasma. An excitation in this plasma is called a **plasmon** (*plasmon / plasmoni*).
 - Surface plasmons are important for optical properties of nanocrystals

[These definitions are from Ashcroft-Mermin, Solid State Physics]



References: general review articles

- The study of defects in solids is a huge field, and somewhat split between the metals, semiconductors, ceramics and nanomaterials communities. Hence there is no single authoritative book on the topic. The following references are pretty good overviews especially for metals:
 - P. Ehrhart, K. H. Robrock, and H. R. Shober, Basic Defects in Metals, in Physics of Radiation Effects in Crystals, edited by R. A. Johnson and A. N. Orlov, page 3-, Elsevier, Amsterdam, 1986
 - P. Ehrhart, Properties and interactions of atomic defects in metals and alloys, Vol. 25 of Landolt-Börnstein, New Series III, chapter 2, page 88, Springer, Berlin, 1991
 - P. Jung, Production of atomic defects in metals, volume 25 of Landolt-Börnstein, New Series III, chapter 1, pages 1--86, Springer, Berlin, 1991



What should you have learned from this section?

- You know the basic types of defects both in elemental, compound and ionic materials
- You understand the difference between equilibrium and irradiation defect formation
- Combining chapters 5 and 6, you understand roughly how irradiation produces the defects
- You know the concept of color centers
- You know the notation convention for defects in nonionic and ionic crystals
- You know that also surface and amorphous materials can have defects