

PHYS-E0421 Solid-State Physics (5cr), Spring 2019

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Lecture 7, 1/4/2019

Today's topics

- Defects and diffusion (Elliott 3.1-3.4)
- Revisit homework questions and other issues

Defects in solids

“Crystals are like people: it is the defects in them which tend to make them interesting!”

– Colin Humphreys

“Like human defects, those of crystals come in a seemingly endless variety, many dreary and depressing, and a few fascinating.”

– Ashcroft & Mermin, in their textbook “Solid State Physics”

“God made the bulk; surfaces were invented by the devil.”

“One shouldn’t work on semiconductors, that is a filthy mess; who knows whether any semiconductors exist.”

– Wolfgang Pauli

Defect classification

- General definition: Deviation from the reference system
- Reference system:
 - An ideal (defect-free, infinite) crystal with translation symmetry. A defect breaks the translation symmetry, Bloch's theorem cannot be employed!
 - Amorphous solids: Continuous random network with the correct coordination number for each atom (no dangling bonds)
 - Quasicrystals: ordered but not periodic structure
- Perturbation limited to a small region

Generation of defects

- Thermal generation of defects (entropy) ➤ Intrinsic defects (unintentional)
- Fabrication process (metastable defects such as extended defects)

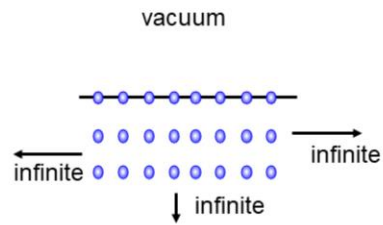
- Irradiation ➤ Extrinsic defects (intentional)
- Chemical exposure

3D defects

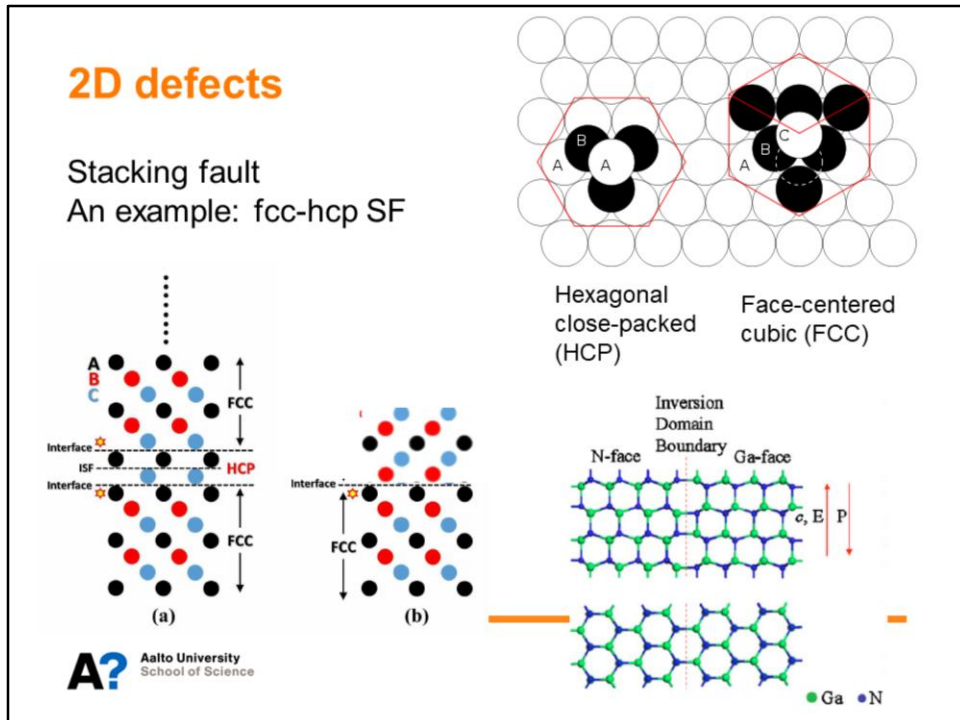
- Bulky defects
- E.g. large voids, inclusions of a different phase
- Phonons (?)

2D defects (planar)

- Surface, or interface with another material
- Breaks the translational symmetry (periodicity)
- Usually not called defects



- When is large void/inclusion 3D defect and when is it surface/interface (2D)?
- Compare surface atom to an atom next to single vacancy...

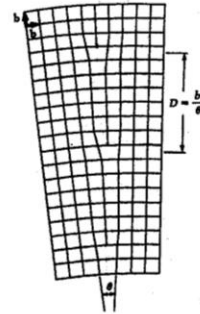
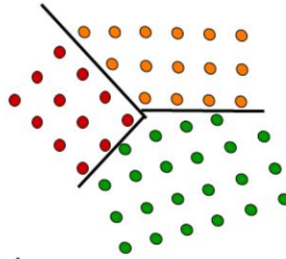


- E.g. iron can be either bcc or fcc, depending on temperature. Thus one could expect that the related energy cost is small.
- Twin boundary: domains with reflection
- Inversion domain boundary: domains with inversion. Need to have a material without inversion symmetry.
- Anti-phase boundary: connecting domains with atoms in opposite order e.g. Ga/N \rightarrow N/Ga. Necessarily leads to homopolar bonds (N-N or Ga-Ga)

2D defects

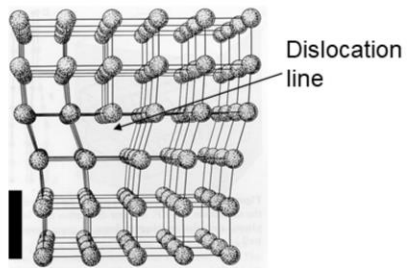
- Grain boundaries
- Domain structure
- Grain size: 1000 Å → macroscopic single crystals

- Low-angle GB consists of several edge dislocations close to each other
 - Tilt angle $\theta = b/D$



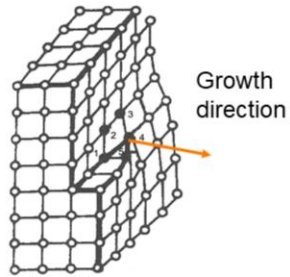
1D (line) defects

Edge dislocation



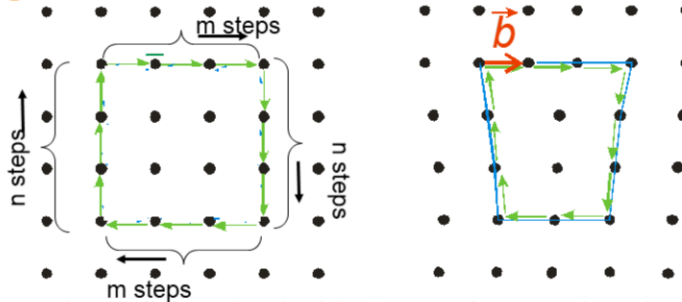
- Glide plane → mechanical strength

Screw dislocation



- Crystal growth (inexhaustible supply of edge sites)

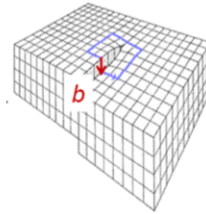
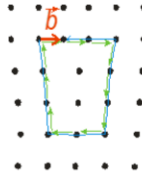
Dislocations: characterization by the Burgers vector



- If there is no dislocation inside the test loop, a closed path is achieved when moving in each direction (number of steps is the same)
- If $\mathbf{b} \neq 0$, there is a dislocation line inside the test loop

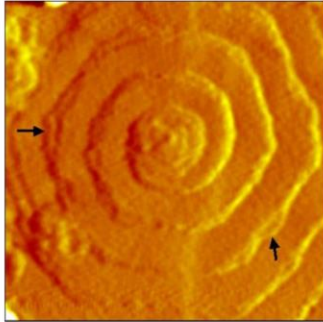
Dislocations: characterization by the Burgers vector

- Edge dislocation:
 \mathbf{b} in the plane of loop
 $\mathbf{b} \perp$ dislocation line
- Screw dislocation:
 \mathbf{b} out of the plane of loop
 $\mathbf{b} \parallel$ dislocation line



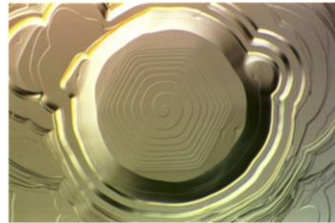
Crystal growth

Screw dislocations



Videos:

1. [Islands on a surface](#)
(simulating molecular beam epitaxy)
2. [Calcite screw dislocation under continuous CaCO₃ growth-etch solution](#)



SiC

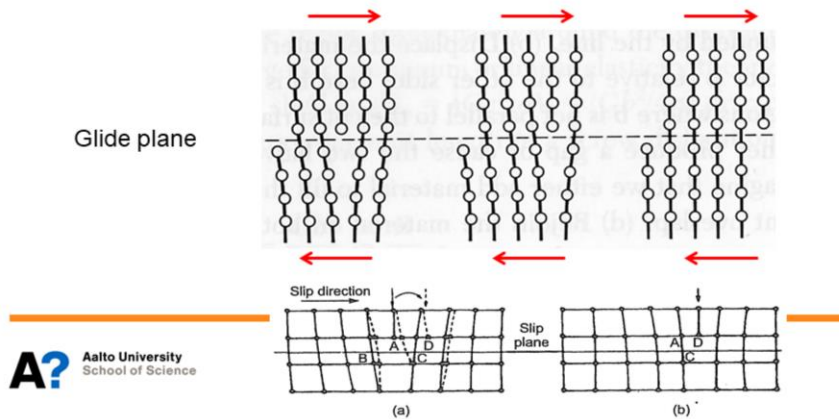


1. <https://www.youtube.com/watch?v=NsGRKSV8yH8>
2. <https://youtu.be/kpThWs8dWOI>

- Hexagonal shape further away, due to minimizing edge energy (maximizing the most stable edges). Or, alternatively, the most reactive (i.e., unstable) edges/sites grow the fastest, since the adsorption energy is highest.

Dislocations determine the mechanical strength of material

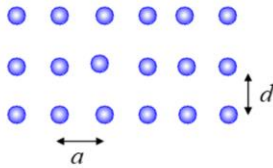
Motion of an edge dislocation under a shear tending to move the lower part of the crystal to the left. Only one row (plane) of atoms slip at a time.



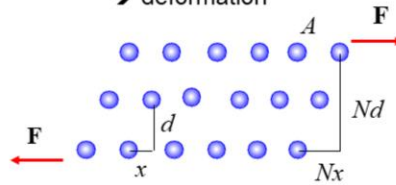
- Dislocations cannot be healed locally. Need to heal the lattice from dislocation all the way to the edge, or glide the dislocation to the edge.

Plastic deformation

Ideal crystal
in equilibrium



External shear
→ deformation



Hooke's law :

$G = \text{shear modulus} \sim 2 \times 10^{10} \frac{\text{N}}{\text{m}^2}$

$$\sigma = \frac{F}{A} = G \frac{x}{d}$$

Shear stress Strain

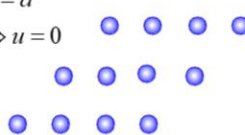
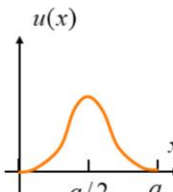
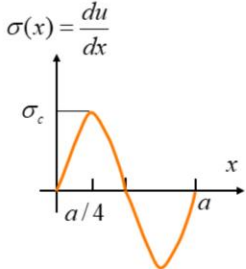
OK for $x \ll a$

- Force/area = energy/volume

Shear energy: $\frac{U}{V} = u = \frac{1}{V} \int_0^{Nx} \mathbf{F} \cdot d\mathbf{x}' \Rightarrow \sigma(x) = \frac{V}{A} \frac{du}{dx}$

for $x \ll a$: $u \propto x^2$

$x = a$
 $\Rightarrow u = 0$

Critical shear stress σ_c : $\sigma > \sigma_c \Rightarrow$ Irreversible deformation

Estimate: $\sigma = C \sin(2\pi x/a)$; $x \rightarrow 0 \Rightarrow \sigma = G \frac{x}{d} = C \frac{2\pi x}{a} \Rightarrow C = \sigma_c = \frac{Ga}{2\pi d} \approx \frac{G}{6}$

$\sigma_c(\text{Experiments}) \approx \sigma_c(\text{Theory})/10^2 \dots 10^6$ Discrepancy \leftarrow Dislocations

Exceptions: Nanocrystals, Carbon nanotubes

A? Aalto University
School of Science

- Force is derivative of energy $\Rightarrow \sigma = 1/A \cdot dU/dx$

Plastic deformation

Table 1 Comparison of shear modulus and elastic limit

	Shear modulus G , in dyn/cm ²	Elastic limit σ_e , in dyn/cm ²	G/σ_e
Sn, single crystal	1.9×10^{11}	1.3×10^7	15,000
Ag, single crystal	2.8×10^{11}	6×10^6	45,000
Al, single crystal	2.5×10^{11}	4×10^6	60,000
Al, pure, polycrystal	2.5×10^{11}	2.6×10^8	900
Al, commercial drawn	$\sim 2.5 \times 10^{11}$	9.9×10^8	250
Duralumin	$\sim 2.5 \times 10^{11}$	3.6×10^9	70
Fe, soft, polycrystal	7.7×10^{11}	1.5×10^9	500
Heat-treated carbon steel	$\sim 8 \times 10^{11}$	6.5×10^9	120
Nickel-chrome steel	$\sim 8 \times 10^{11}$	1.2×10^{10}	65

Handwritten notes: 10^{10} N/m^2 under the first two columns, and $\frac{1}{10} \frac{\text{N}}{\text{m}^2}$ under the last two columns.

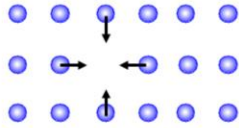
After Mott.

- Elastic limit (yield strength) depends on dislocation density. Usually, small grains have smaller density. Moreover, dislocations can not easily move from one grain to another. Thus polycrystalline has higher elastic limit.
- Dislocation motion can also be affected by alloying and introducing impurities/precipitates

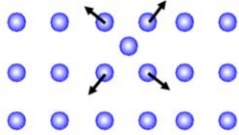
0D defects

- Point defects (intrinsic)

- Vacancy

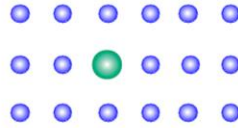


- Interstitial

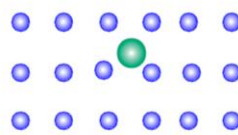


- Impurities

- Substitutional



- Interstitial



- Antisite in compounds, e.g. Ga in As site of GaAs lattice.

Formation energy

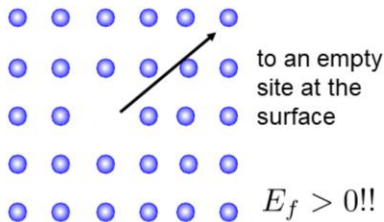
- Schottky defect (= vacancy)

Formation energy:

$$E_f = E(\text{with defect}) - E(\text{pristine}) + E(\text{atom})$$

$$= E(\text{with defect}) - \frac{N-1}{N} E(\text{pristine})$$

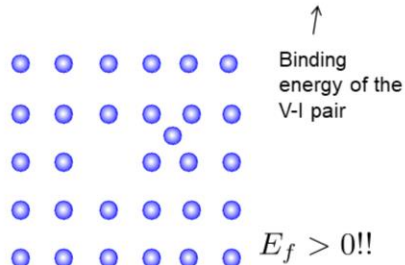
N-1 atoms N atoms 1 atom



- Frenkel defect

$$E_f = E(N \text{ with V-I pair}) - E(N)$$

$$= E_f(\text{vac}) + E_f(\text{inter}) - E_b$$



- $E(N)$ is the total (binding) energy of the system with N atoms
- Connection to cohesive/atomization energy $E(\text{coh})$
- With covalent materials, if each atom has four bonds $E(\text{bond}) = E(\text{coh})/4$. Then, very approximately, $E_f = E(\text{bond}) \cdot \#(\text{broken bonds}) = E(\text{coh})$. In Si, $E(\text{coh}) = 4.6$, $E_f = 3.6$. Difference arising from relaxation of atom positions and rebonding.

Thermodynamics of point defects

Finite temperature \rightarrow Always point defects

Example: Schottky defects

In equilibrium :

Gibbs free energy $G = U - TS + PV$ minimized

$V \approx \text{constant} \Rightarrow$

Helmholtz free energy $F = U - TS$ minimized

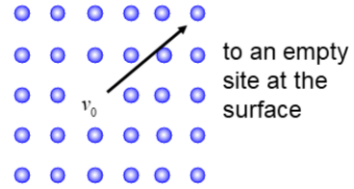
$F = U - TS_{\text{vib}} - TS^{\text{conf}}$ Configuration entropy

Structural entropy \leftarrow phonons

$F(n) = F_0(n) - TS^{\text{conf}}(n)$; $S^{\text{conf}}(n) \propto$ # of ways to choose n vacancies from N sites
 # of ways to choose n interstitials from N' sites

Boltzmann Lotto

$$S^{\text{conf}}(n) = k_B \ln P = k_B \ln \frac{N!}{n!(N-n)!}$$



- $U = n \cdot E_f$

Stirling : $\ln x! \approx x(\ln x - 1) \Rightarrow$

$$S^{conf} = k_B [N \ln N - N - n \ln n + n - (N - n) \ln(N - n) + N - n]$$

Mimimize : $\frac{dF}{dn} = \frac{dF_0}{dn} - T k_B [-\ln n - 1 + \ln(N - n) + 1]$

$$F_0(n) = n(\Delta h_f + T \Delta s_{vib}), \quad \Delta h_f \approx E_f$$

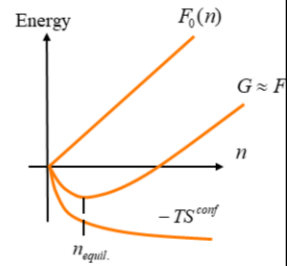
$\Delta h_f =$ Schottky def. formation energy ; $\Delta s_{vib} =$ formation entropy

$$\Rightarrow \frac{dF}{dn} = \Delta h_f + T \Delta s_{vib} + k_B T \ln \frac{n}{(N - n)} = 0$$

$$\Rightarrow n = N \exp\left(-\frac{\Delta h_f}{k_B T}\right) \exp\left(\frac{\Delta s_{vib}}{k_B}\right)$$

$$\Delta E \sim 1 \dots 4 \text{ eV} \quad ; \quad \exp\left(\frac{\Delta s_{vib}}{k_B}\right): T\text{-independent t, phonons \& band softening} \Rightarrow \Delta s_{vib} > 0$$

$$\Delta s_{vib} \sim 1 \dots 10 k_B$$



Examples

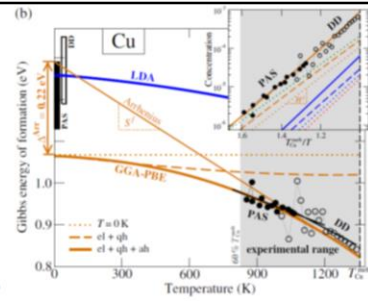
$$n = N \exp(-\Delta h_f / k_B T) \exp(\Delta s_{\text{vib}} / k_B) = N \exp(-\Delta g_f / k_B T)$$

$$\Delta g_f = \Delta h_f + T \Delta s_{\text{vib}}$$

		Δh_f (eV)	$\Delta s_{\text{vib}} / k_B$
e ⁺ experiments	Al	0.75	2.4
	Cu	1.18	1.6-3.0
ab - initio calculations	Si	3.3-3.6	5-10

E.g. V_{Al}: $c_v = \frac{n}{N} = \exp(2.4) \exp(-0.75 \text{ eV} / k_B T)$ T = 300 K $\Rightarrow c_v = 3 \times 10^{-12}$
 (T_m = 933 K) T = 800 K $\Rightarrow c_v = 2 \times 10^{-4}$

Quenching = fast cooling e.g. to room temperature \Rightarrow high non - equilibrium c_v

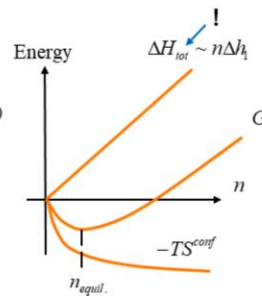


- $\exp(2.4)=11$, but (here) temperature independent

Defect thermodynamics

Point defects (0D):

$T > 0$



Line defects (1D): $\Delta H_1 \sim N^{1/3}$

Plane defects (2D): $\Delta H_1 \sim N^{2/3} \Rightarrow n_{equil.} \rightarrow 0$, i.e. metastable defects

Annealing: $T \uparrow \leq T_m \Rightarrow$ defect migration and recombination $c_{1D}, c_{2D}, c_{3D} \downarrow$

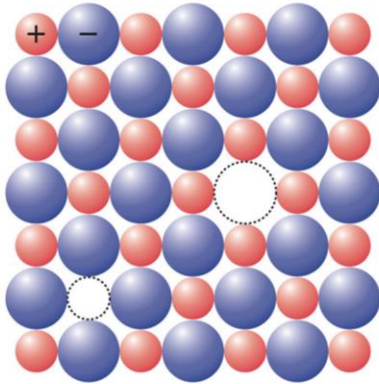
Slow cooling \Rightarrow small $c_{equil.}$ (c.f. quenching: $c_{0D} \uparrow$)

Examples: high - quality Si and Ge: $c_{1D} \sim 10^6$ dislocations/m² ($d \sim 1$ mm)

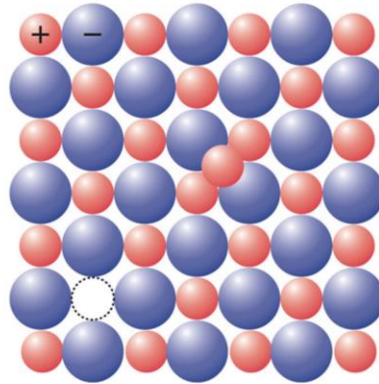
deformed metal: $c_{1D} \sim 10^{16}$ dislocations/m² ($d \sim 10$ nm)

- N is the number of atoms in the material. $\ln(n)$ has very slow dependence on n .
- Can only form if N is very small, or e.g. the material is very thin, say, graphene, whereby 1D defects become point defects.

Point defects and defect pairs in ionic crystals: charge neutrality condition



(a) Schottky defect

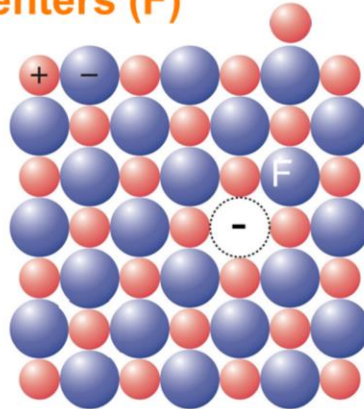


(b) Frenkel defect

- Fig 3.5a is wrong in Elliott

Point defects in ionic crystals: production of Color centers (F)

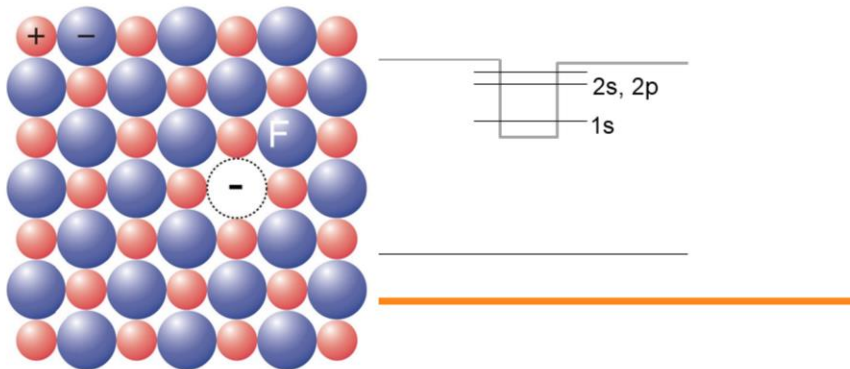
- Heating in Na atmosphere
 - Na deposited on the surface
 - Na is very reactive, really wants to get rid of its electron
 - Cl⁻ diffuses to surface
 - Leaves behind vacancy that is filled by the electron from Na
- The system obtains distribution of "alternating charges" that is the most stable



- Na can not localize the electron next to it on the surface, but it can be localized on the vacancy, surrounded by positive ions

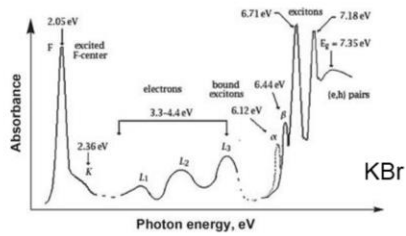
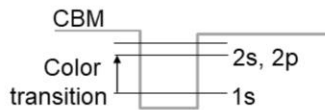
Electronic structure of Cl vacancy

- Potential well (quantum well) due to the positively charged Na ions around the site
- The one left-over electron is captured by the well



Why "color"?

- Like quantum well or H atom
- Excited localized levels
- Absorption with light with frequency ω at which the perfect crystal is transparent



- NaCl irradiated with x-rays

Gemstones

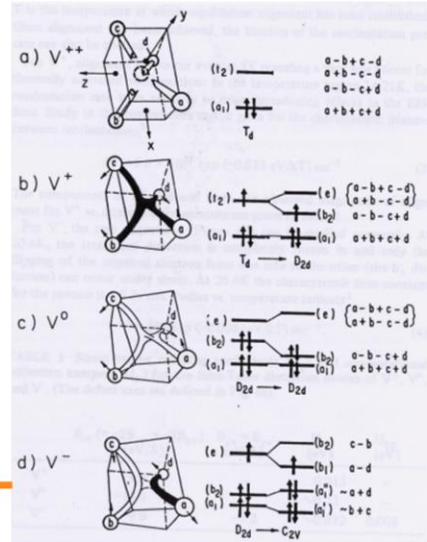
- Corundum = Crystalline aluminum oxide Al_2O_3
 - Ruby = corundum with Cr
 - Sapphire (purple) = with V
 - Sapphire (yellow) = with Fe
 - Sapphire (blue) = with Fe and Ti
- Emerald = Beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$) with Cr and V
- Amethyst = SiO_2 with Fe
- Diamond (yellow, brown) = with N
- Diamond (blue) = with B



- E.g. ruby absorbs yellow-green light, thus appears as red.

Charge states of the vacancy in Si

- 4 dangling bonds (sp³-hybridized) near ~mid-gap
- In neutral state occupied by 4 electrons
- Additional bonding between dangling bonds
 - Energy gain when electrons occupy bonding states
 - Energy cost due to structural distortion
 - Jahn-Teller effect: system with partially occupied degenerate states will always distort to lower its symmetry
- Defect symmetry depends on the number of electrons occupying the defect states



G. D. Watkins

- Due to interaction of electrons in the defect, it's not possible to have Si vacancy with charge state +4 or -4, or even +3

Interactions between point defects

- If defects migrate fast, it's important to know if they might cluster

- Interactions:

Elastic interactions
Covalent bonds (semicond., insulators)
Electrostatic forces (semic., ionic solids)

} → Defect pairs

- Examples:

- Divacancies in metals ← lowering of strain (sharing)
- Schottky defect in ionic crystals, (ordered defect compounds)

- ODC: e.g. in CuInSe_2 , the formation energy of Cu vacancy (-1 charge) and $\text{In}@_{\text{Cu}}$ antisite (+2 charge) are so low that their concentration can be ~10%. Due to Coulomb interaction, the defects are ordered similar to ionic crystals.

Diffusion of defects in solids

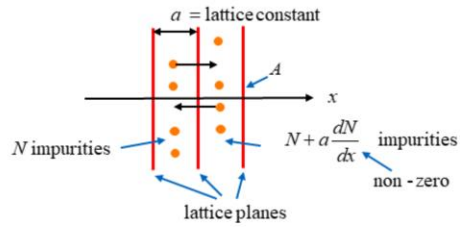
- self-diffusion, diffusion of (dopant) impurities
- ➔ agglomeration, recombination, smoothing of dopant profiles
- measurement: radioactive tracers, isotope-enriched layers + secondary-ion mass spectrometry (SIMS), on surfaces STM, HR-TEM

Fick's law: $\mathbf{J} = -D\nabla n$; \mathbf{J} = current density ; $[\mathbf{J}] = 1/\text{m}^2\text{s}$; $[n] = 1/\text{m}^3$
→ D = diffusion constant ; $[D] = \text{m}^2/\text{s}$

Continuity equation: $\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{J} = 0 \Rightarrow \frac{\partial n}{\partial t} = \nabla \cdot (D\nabla n)$ Diffusion equation (for n)
 $\left(\frac{\partial n}{\partial t} = D\nabla^2 n \quad \text{if } D = \text{constant, i.e., homogeneous sample} \right)$

Microscopic classical picture of diffusion

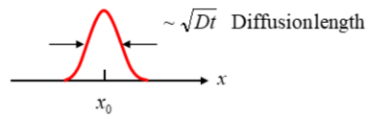
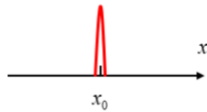
Microscopic quantities $\Rightarrow D$



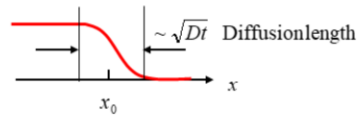
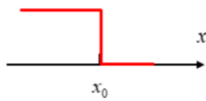
Current density ($n = N/aA$):
$$J = \frac{1}{A} \left[\overbrace{N}^{\text{hopping rate}} v - \left(N + a \frac{dN}{dx} \right) v \right] = -\frac{1}{A} a v \frac{dN}{dx} = -a^2 v \frac{dn}{dx} = -D \frac{dn}{dx}$$

Diffusion: one-dimensional examples (see also exercises)

$$n(x, t=0) = N\delta(x-x_0) \quad \Rightarrow \quad n(x, t) \propto \exp\left[-(x-x_0)^2 / 4Dt\right]$$



$$n(x, t=0) = n_0[1 - \Theta(x-x_0)] \quad \Rightarrow \quad n(x, t) = n_0 \operatorname{erfc}\left[x / (4Dt)^{1/2}\right]$$



Diffusion mechanisms

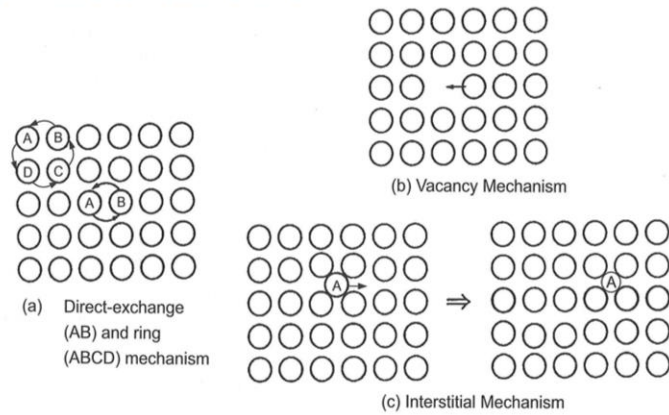
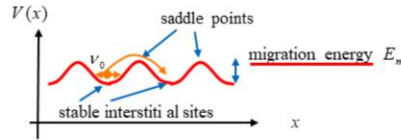


Fig. 3.30 Schematic illustration of three mechanisms of atomic transport in solids: (a) direct-exchange (ring) mechanism; (b) vacancy mechanism; (c) interstitial mechanism. (Borg and Dienes (1988). Reproduced by permission of Academic Press, Inc.)

- Direct exchange tends to be quite rare as it requires lot of space

Microscopic classical picture of diffusion

e.g., an interstitial impurity, high temperature



$$\text{probability } E_{kin} > E_m : P = \frac{1}{Z} \int_{E_m}^{\infty} dE D(E) \exp(-E/k_B T) = \exp(-E_m/k_B T)$$

$$Z = \int_0^{\infty} dE D(E) \exp(-E/k_B T)$$

Assume harmonic potential wells: trial frequency for hopping $v_0 = \text{constant}$

$$\Rightarrow \text{Hopping rate } v = v_0 \exp(-E_m/k_B T) \quad ; \quad v = z v_0 \exp(-E_m/k_B T)$$

3D, 2D: several hopping directions = $z = \text{coordination number}$

- Classical treatment should probably yield same result: i.e., consider particles with MB velocity distribution and see how many have sufficient kinetic energy to overcome the barrier.
- Potential energy landscape, but no dynamical effects. In reality, the hop might be possible in principle, but require that the positions and velocities of all particles are just right, and thus the prefactor would be very low.
- v_0 typically $\sim 10^{12}$ 1/s
- Activation energy = defect formation energy + migration barrier. Relevant if defects are (spontaneously) generated before migrating.

Arrhenius law

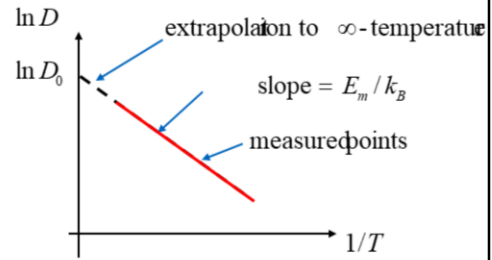
Current density ($n = N/aA$): $J = \frac{1}{A} \left[Nv - \left(N + a \frac{dN}{dx} \right) v \right] = -\frac{1}{A} a v \frac{dN}{dx} = -a^2 v \frac{dn}{dx} = -D \frac{dn}{dx}$

Hopping rate $v = v_0 \exp(-E_m/k_B T)$

$\Rightarrow D = a^2 v = a^2 v_0 \exp(-E_m/k_B T)$

prefactor D_0

Activation energy



Diffusion in solids

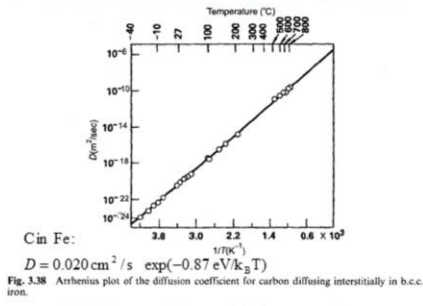
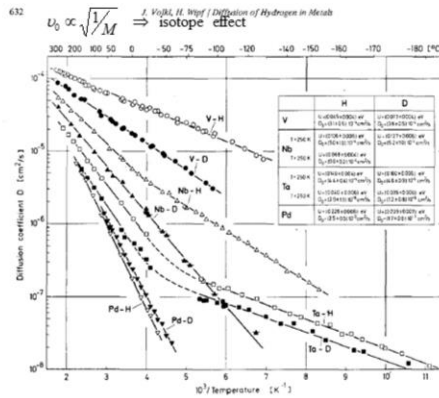


Table 3.4 Pre-exponential factors and activation energies of diffusion for various diffusing species in a range of crystals

Host crystal	Diffusing atom	$D^0 (\text{m}^2 \text{ s}^{-1})$	$E_D (\text{eV})$
Cu	Cu	2×10^{-3}	2.04
Ag	Ag	4×10^{-5}	1.91
Ag	Cu	1.2×10^{-4}	2.00
Na	Na	2.4×10^{-7}	0.45
Si	Al	8.0×10^{-4}	3.47
Si	Ga	3.6×10^{-4}	3.51
Si	As	3.2×10^{-3}	3.56
Si	Li	2×10^{-5}	0.66
Ge	Ge	1.0×10^{-3}	3.1
Fe	C	2.0×10^{-6}	0.87

(After Kittel (1996). Reprinted by permission of John Wiley & Sons Inc.)

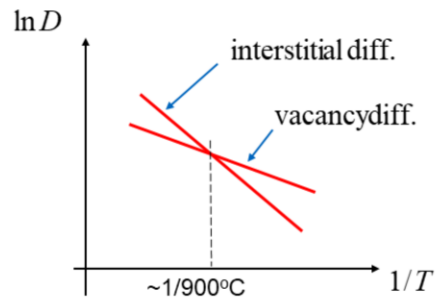
H in Nb:
 $T > 0 \text{ C: } D = 5 \times 10^{-4} \text{ cm}^2/\text{s} \exp(-0.106 \text{ eV}/k_B T)$
 $T < 0 \text{ C: } D = 0.9 \times 10^{-4} \text{ cm}^2/\text{s} \exp(-0.068 \text{ eV}/k_B T)$



- C in Fe at RT: $D=10e-20 \Rightarrow L=\sqrt{Dt}=1 \text{ \AA}$ in 1s, 10 $\mu\text{m/s}$ in 700C, surface hardening of iron.
- H in V at RT: $D=1e-4 \Rightarrow L=0.1\text{mm}$ in 1s. It's difficult to contain hydrogen with metal tanks (I guess carbon fiber something is usually used).

Diffusion mechanisms

- An example: Si
T > 900°C: interstitial diff.
dominates
T < 900°C: vacancy diff.
dominates



Are defects in solids good or bad?



- Deterioration of mechanical properties (e.g. via movement of dislocations)
- Scattering of charge carriers and phonons
- Undesirable changes in colors (e.g. in diamonds), non-radiative recombination centers
- Fermi-level pinning

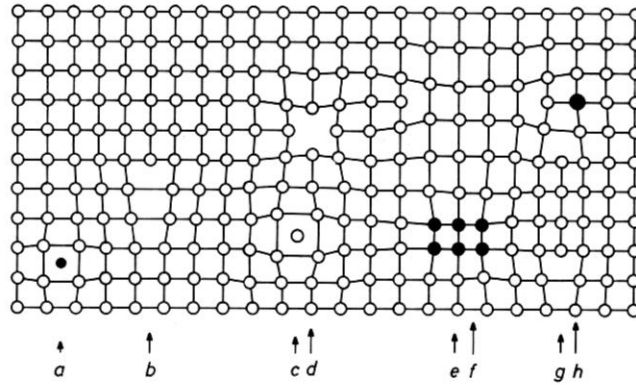


- Improvement of mechanical properties (e.g. precipitates block dislocation movement)
- Creating and controlling charge carriers by impurity doping
- Providing bright colors (e.g. rubies), recombination in indirect materials
- Pinning of magnetic vortices in type II superconductors

Examples from my research

- If time allows

Summary (identify the defects)

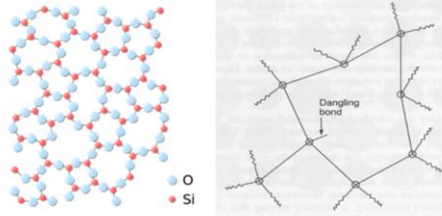


a) Interstitial impurity atom, b) Edge dislocation, c) Self interstitial atom, d) Vacancy, e) Precipitate of impurity atoms, f) Vacancy type dislocation loop, g) Interstitial type dislocation loop, h) Substitutional impurity atom

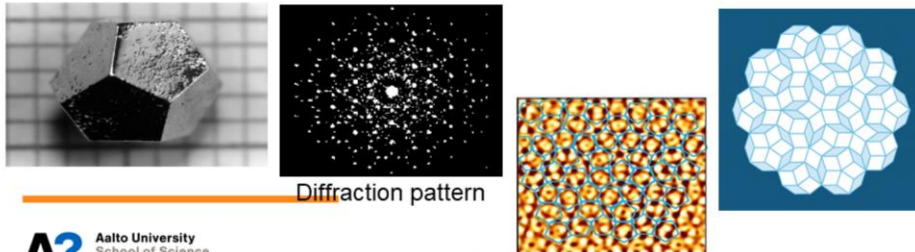
Quasicrystals and amorphous solids

- Which types of defects are not possible?
- Any new types of defects?

Amorphous solid:
e.g. glasses, SiO_2



Quasicrystal: 2011 Nobel Prize in Chemistry for Daniel Shechtman



A? Aalto University
School of Science

Fig. 1 $100 \times 100 \text{ nm}^2$ image of the five-fold surface of the icosahedral Al-Pd-Mn quasicrystal with a Penrose P1 tiling superimposed.

- Defects in amorphous material: dangling bonds, wrong bonds (e.g. Si-Si). No dislocations, stacking faults, etc. How about vacancies/interstitials?
- In quasicrystals, the same as in periodic lattices. Dislocations, stacking faults possible (?)

Near future and period V

- Exercises this Friday (deadline to be agreed on)
- 1st Midterm exam:
Tuesday 9 April 2019 at 16:30-19:30, Hall A/B/C (check)
- Lecturer during period V:
Martti Puska
- First lecture on 15 April