

FYS3400 - Vår 2024 (Kondenserte fasers fysikk)

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**Pensum: Introduction to Solid State Physics
by Charles Kittel (Chapters 1-9 and 17 - 20)**

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2024 FYS3400 Lecture Plan (based on C.Kittel's Introduction to Solid State Physics, Chapters 1-9, 17-20)

Module I – Periodicity and Disorder (Chapters 1-3, 19, 20)

calender week

Mo 15/1 10-12 Introduction. Crystal bonding. Periodicity and lattices. Lattice planes and Miller indices. Reciprocal space.

3

Th 18/1 10-11 Bragg diffraction and Laue condition

Mo 22/1 10-12 Ewald construction, interpretation of a diffraction experiment, Bragg planes and Brillouin zones

4

Th 25/1 10-11 Surfaces and interfaces. Disorder. Defects crystals. Equilibrium concentration of vacancies

Mo 29/1 10-12 Mechanical properties of solids. Diffusion phenomena in solids

5

Th 1/2 10-11 Summary of Module I

Module II – Phonons (Chapters 4, 5, and 18 pp.557-561)

Mo 5/2 10-12 Vibrations in monoatomic and diatomic chains of atoms; examples of dispersion relations in 3D

6

Th 8/2 10-11 Periodic boundary conditions (Born – von Karman); phonons and its density of states (DOS)

Mo 12/2 10-12 Effect of temperature - Planck distribution; Lattice heat capacity: Dulong-Petit, Einstein, and Debye models

7

Th 15/2 10-11 Comparison of different lattice heat capacity models

Mo 19/2 10-12 Thermal conductivity and thermal expansion

8

Th 22/2 12-13 Summary of Module II

Module III – Electrons (Chapters 6, 7, 11 - pp 315-317, 18 - pp.528-530, 19, and Appendix D)

Mo 26/2 10-12 Free electron gas (FEG) versus free electron Fermi gas (FEFG); DOS of FEFG in 3D

9

Th 29/2 10-11 Effect of temperature – Fermi-Dirac distribution; Heat capacity of FEFG in 3D

Mo 4/3 10-12 DOS of FEFG in 2D - quantum wells, DOS in 1D – quantum wires, and in 0D – quantum dots

10

Th 7/3 10-11 Transport properties of electrons

Module IV – Disordered systems (guest lecture slides - Joakim Bergli)

Mo 11/3 10-12 Thermal properties of glasses: Model of two level systems

11

Th 14/3 10-11 Electron transport in disordered solids: wave localization and hopping

Mo 18/3 10-12 Advanced theory of disordered systems

12

Th 21/3 10-11 Summary of Module IV

Easter

Module V – Semiconductors (Chapters 8, 9 pp 223-231, and 17, 19)

Th 4/4 10-11 Recap of Module III

14

Mo 8/4 10-12 Origin of the band gap; Nearly free electron model; Kronig-Penney model

15

Th 11/4 10-11 Effective mass method for calculating localized energy levels for defects in crystals

Mo 15/4 10-12 Intrinsic and extrinsic electrons and holes in semiconductors

16

Th 18/4 10-11 Carrier statistics in semiconductors

Mo 22/4 10-12 p-n junctions

17

Th 25/5 10-11 Optical properties of semiconductors

Mo 29/4 10-12 Advanced photonic devices including quantum tech

18

Th 2/5 10-11 Summary of Module V

Summary and repetition

Mo 6/5 10-12 Repetition - course in a nutshell

19

Exam: oral examination

tentatively during week 20 or 21

Condensed Matter Physics



Solid State Physics of Crystals



Properties of Waves in Periodic Lattices



Elastic waves in lattices
Vibrations
Phonon DOS
Planck distribution

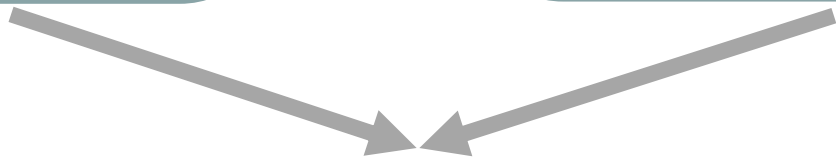


Thermal properties:
heat capacity and conductance,
thermal expansion

Electron waves in lattices
Free electrons
Electron DOS
Fermi-Dirac distribution



Electronic properties:
Electron concentration and transport,
contribution to the heat capacity



Advanced theory and novel materials properties

Condensed Matter Physics

Solid State Physics of Crystals

Disordered systems

Properties of Waves in Periodic Lattices

Elastic waves in lattices
Vibrations
Phonon DOS
Planck distribution

Disordered systems

Thermal properties:
heat capacity and conductance,
thermal expansion

Electron waves in lattices
Free electrons
Electron DOS
Fermi-Dirac distribution

Disordered system

Electronic properties:
Electron concentration and transport,
contribution to the heat capacity

Advanced theory and novel materials properties

Disordered systems

Lecture 4: Surfaces and interfaces. Point defects and diffusion in crystals

- **Surfaces and interfaces**
- **Structural defects in crystals**
- **Change in the configurational entropy due to vacancies**
- **Equilibrium concentration of vacancies – temperature and pressure dependences**
- **Watching empty lattice sites – i.e. vacancies – with positrons**

Lecture 3: Surfaces and interfaces. Point defects and diffusion in crystals

- **Surfaces and interfaces**
- Structural defects in crystals
- Change in the configurational entropy due to vacancies
- Equilibrium concentration of vacancies – temperature and pressure dependences
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Surface structure: some initial ideas

- surface is where the crystal periodicity is interrupted and chemical bonds are broken**
- surface affects a few outermost atomic layers of the crystal – surface region**
- properties of the surface differ significantly from the bulk**
- energy needed to break the bonds, so energy is needed to create a surface – surface energy**
- Broken covalent bonds are called dangling bonds**

Surface structure: surface energy

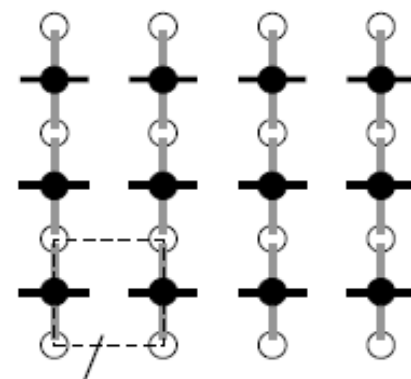
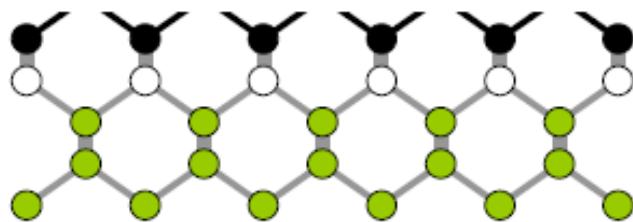
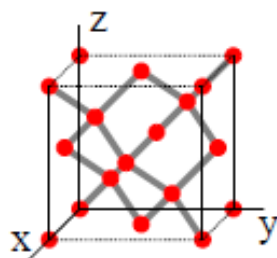
- **Surface energy is always positive, since energy is needed to break bonds**
 - **Surface always tries to minimize its energy, i.e. reduce the number of dangling bonds**
 - **Surface chemically and electrically more active due to dangling bonds**
- **Two mechanisms for minimizing surface energy when in ultrahigh vacuum**
 - **Surface relaxation**
 - **Surface reconstruction**

Surface structure: surface relaxation

- **Interlayer distance is changed between the 1st and 2nd layers of atoms at the surface**
 - **To minimize surface energy**
 - **The interlayer distance is often reduced**
 - **In a few cases the distance increases**
 - **Advanced theory needed to understand**
 - **Many metals experience surface relaxation**

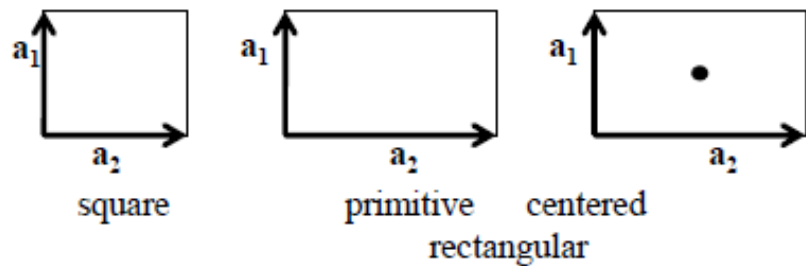
Surface structure: surface reconstruction

- **Surface atoms form a different structure than the bulk atoms**
 - The new structure is constrained by the bulk structure
 - The unit cell in the new structure is different from the bulk unit cell
 - Si(001) as an example
 - **Diamond structure**
 - **Two dangling bonds per surface atom**
 - **2-D unit cell with lattice constant $(2)^{1/2}a/2$**

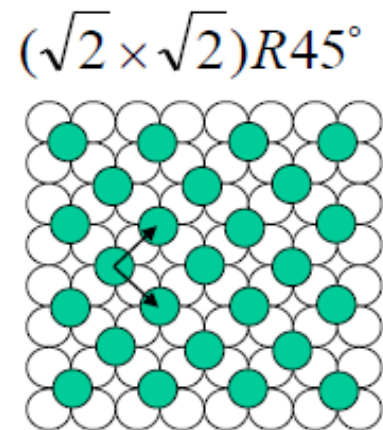
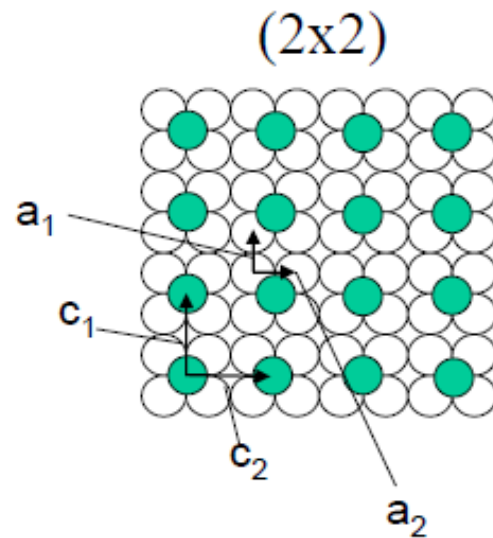
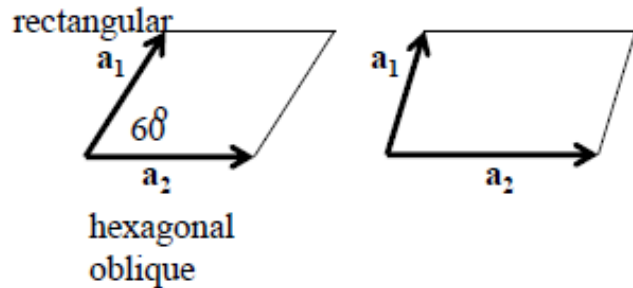


Surface unit cell

Surface structure: surface crystallography

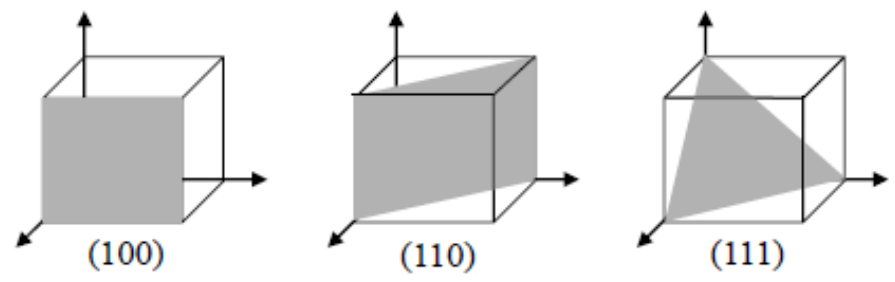


$$\begin{pmatrix} c_1 & c_2 \\ a_1 & a_2 \end{pmatrix} R\alpha$$



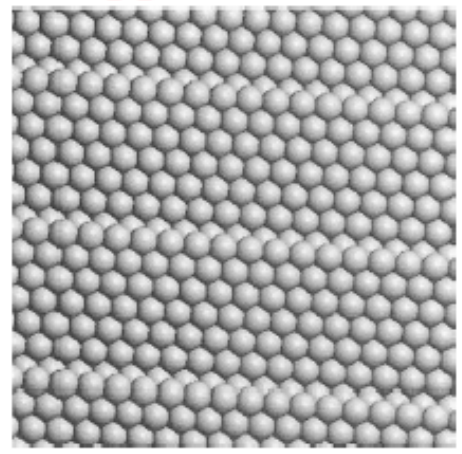
Surface structure: surface crystallography

$$\vec{H} = h \vec{x} + k \vec{y} + l \vec{z}$$

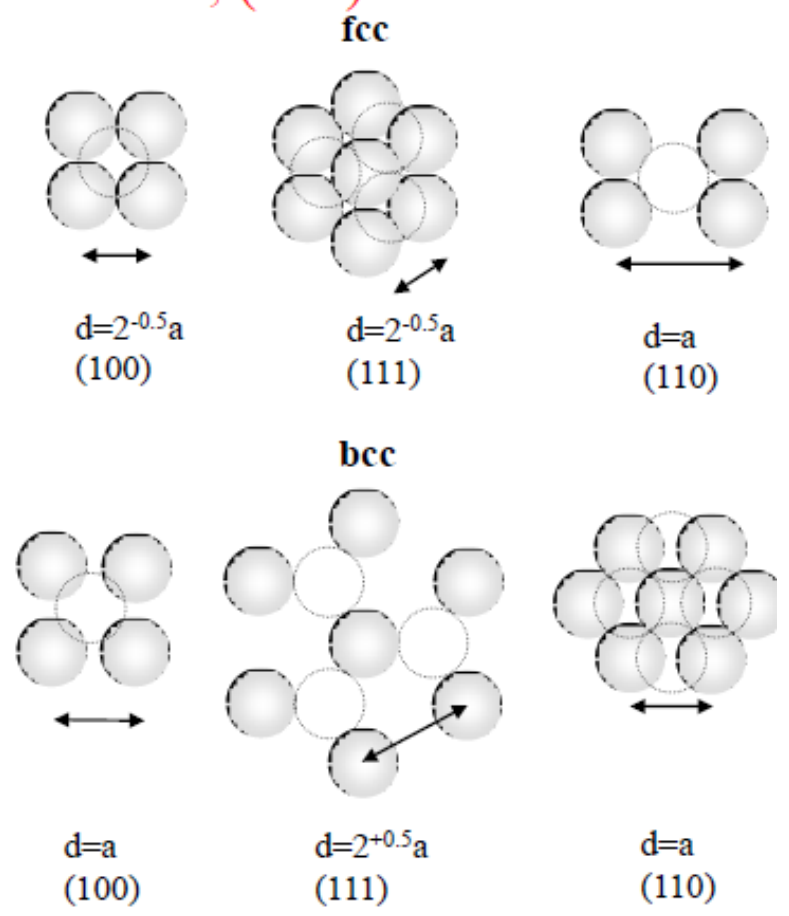


Surface density:
 fcc, (111) > 100 > 110
 fcc, (110) > 100 > 111

Stepped surfaces



fcc (755)



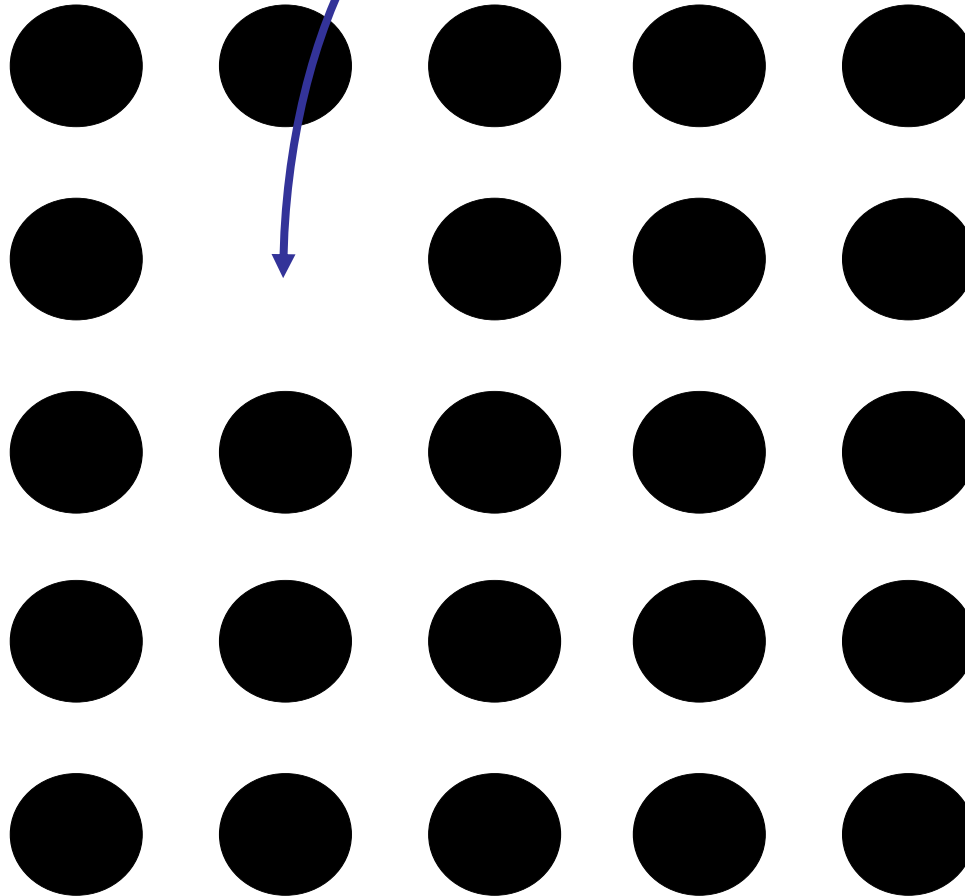
Surface states: origin

- **There exist electronic states on a semiconductor surface – surface states**
 - **The electronic states are bound to the surface**
 - **Their energy levels are within the band gap of the bulk semiconductor**
- **Dangling bonds are the origin of surface states**
 - **A dangling bond can donate its lone electron or accept another electron**
 - **It is both a donor and an acceptor**
- **Doping the surface region difficult due to compensation**
 - **Surface Fermi level doesn't move when doped – Fermi-level pinning**
 - **surface Fermi level is pinned**
 - **Since the Fermi level is horizontal, the energy bands are bent**

Lecture 4: Surfaces and interfaces. Point defects and diffusion in crystals

- Surfaces and interfaces
- **Structural defects in crystals**
- Change in the configurational entropy due to vacancies
- Equilibrium concentration of vacancies – temperature and pressure dependences
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Vacancy: A point defect



<i>Defects</i>	<i>Dimensionality</i>	<i>Examples</i>
Point	0	Vacancy
Line	1	Dislocation
Surface	2	Free surface, Grain boundary

Vacancies

Fact

There *may* be vacant sites in a crystal

Surprising Fact

There *must* be a certain fraction of vacant sites in a crystal in *equilibrium*.

Vacancies

- Crystal in equilibrium
- Minimum Gibbs free energy G at constant T and P
- A certain concentration of vacancy lowers the free energy of a crystal

Vacancies

Gibbs free energy G involves two terms:

1. Enthalpy $H = E + PV$

E internal energy

P pressure

V volume

2. Entropy $S = k \ln W$

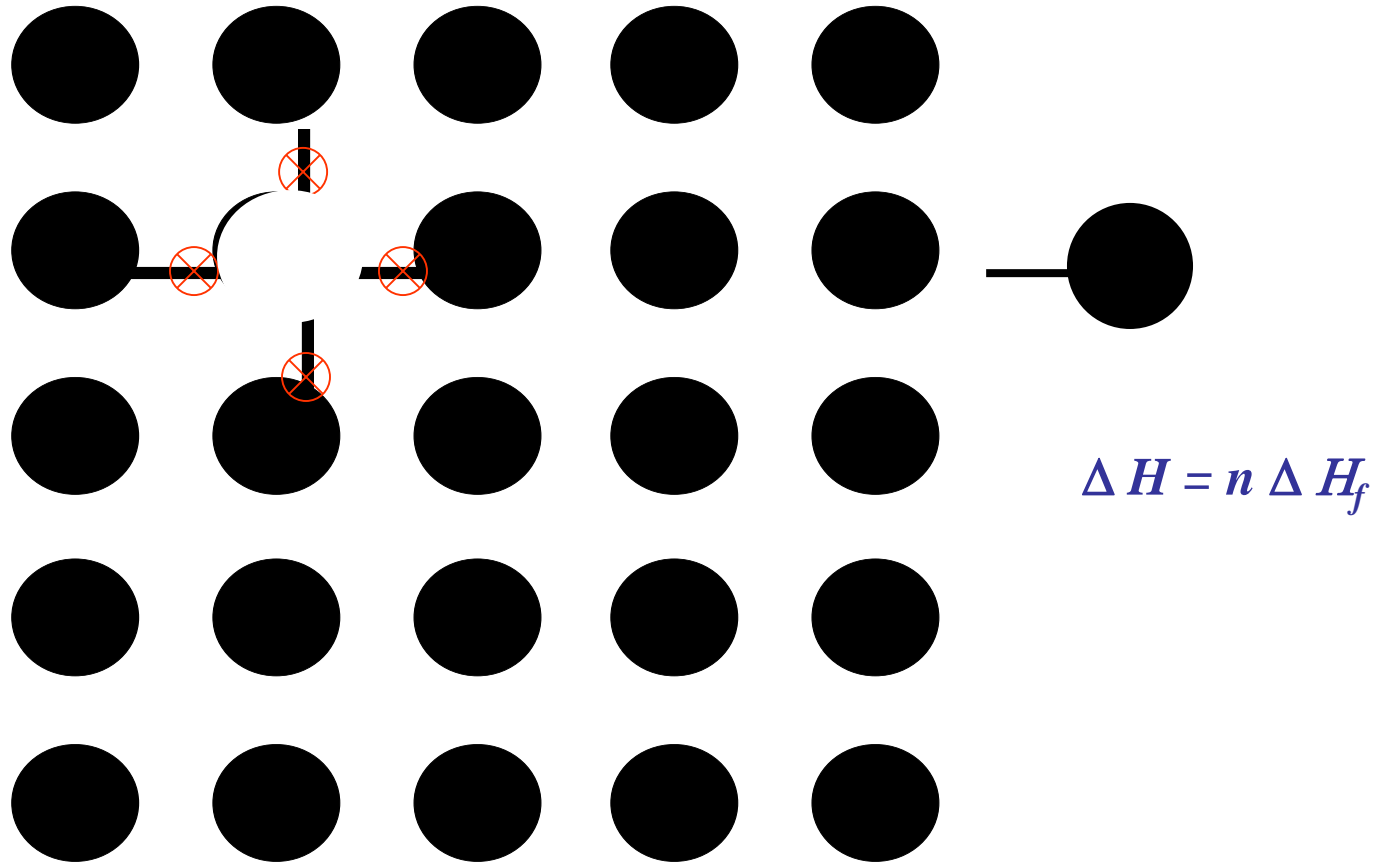
k Boltzmann constant

W number of microstates

$$G = H - T S$$

T Absolute temperature

Vacancies

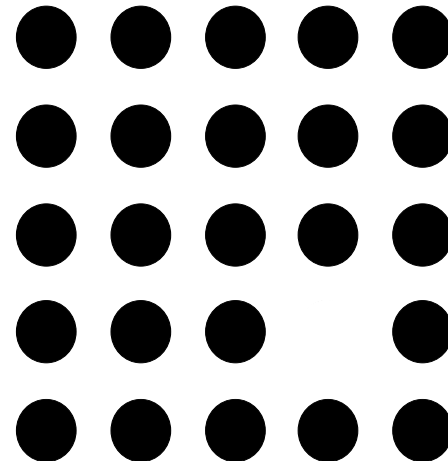
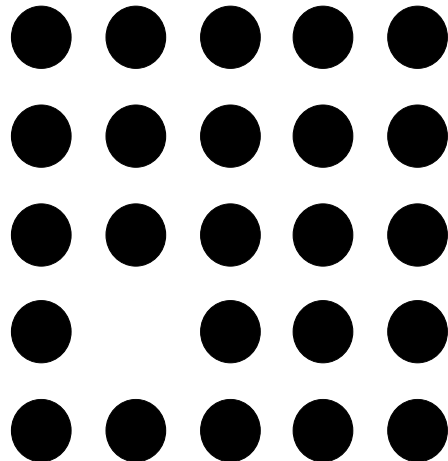
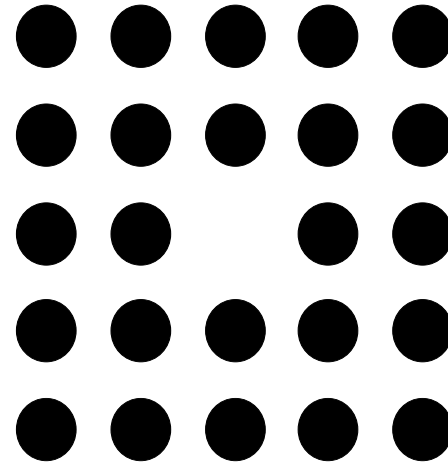
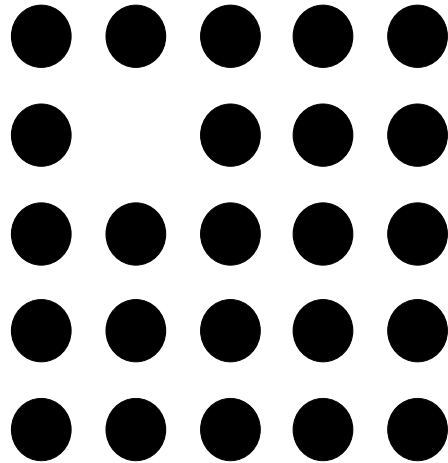


Vacancy increases H of the crystal due to energy required to break bonds

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Configurational entropy due to vacancy



Configurational entropy due to vacancy

Number of atoms: N

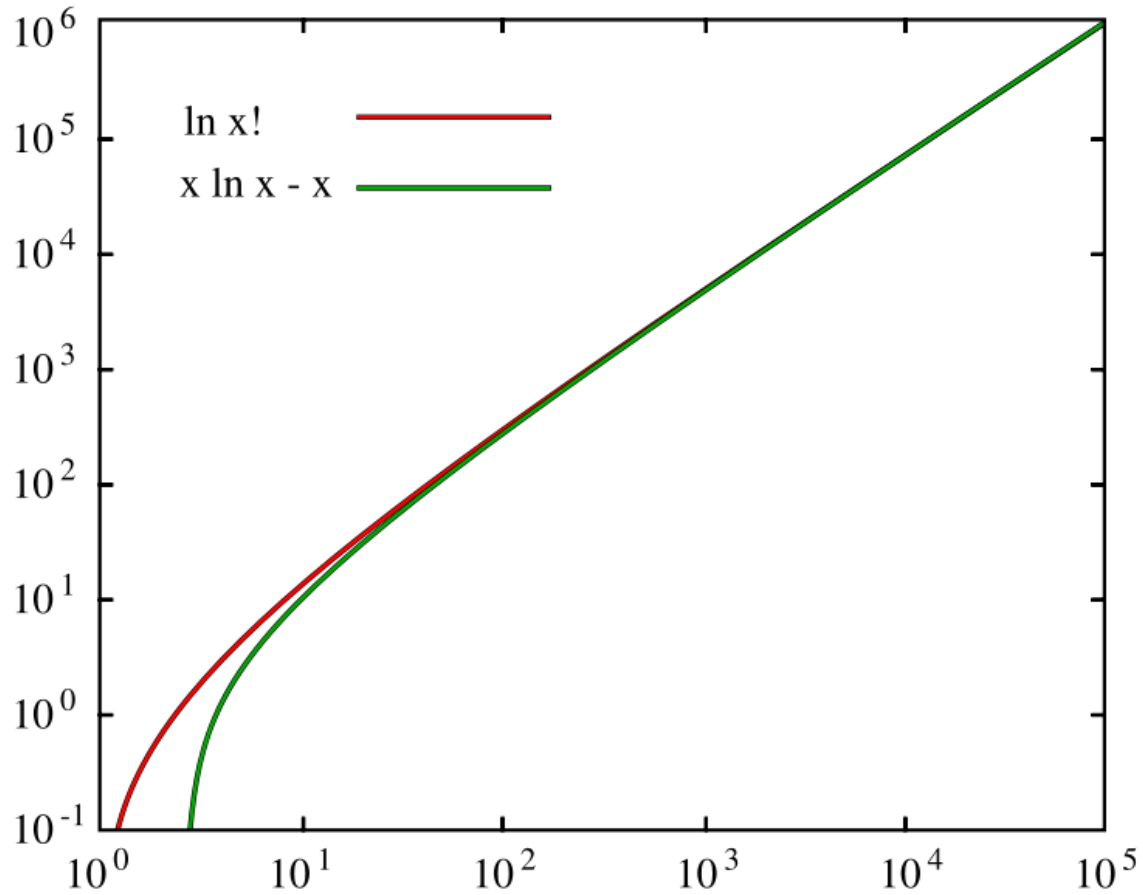
Number of vacancies: n

Total number of sites: $N+n$

How many distinguished configurations,
so called microstates?

We calculate this explicitly

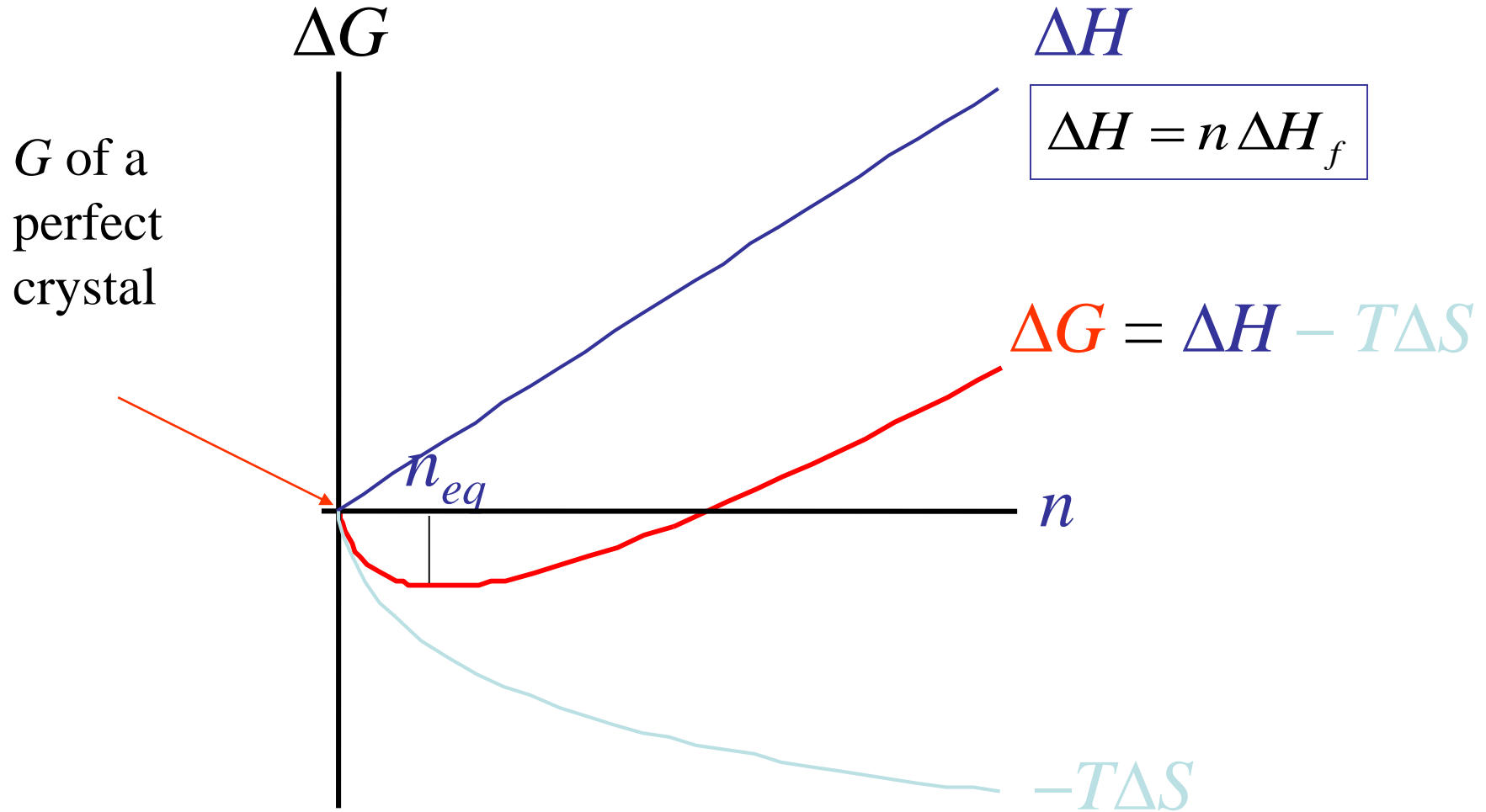
Configurational entropy due to vacancy



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Equilibrium concentration of vacancies – temperature dependence



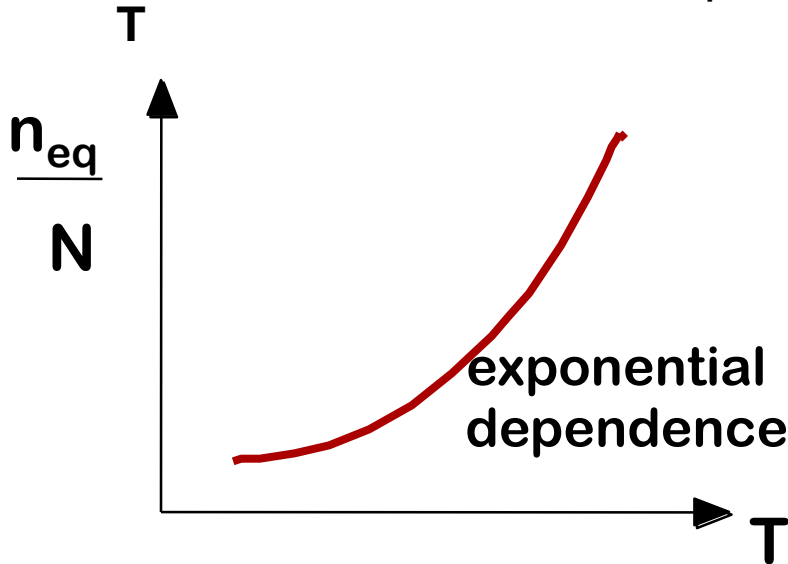
Equilibrium concentration of vacancies – temperature dependence

$$\left. \frac{\partial \Delta G}{\partial n} \right|_{n=n_{eq}} = 0$$

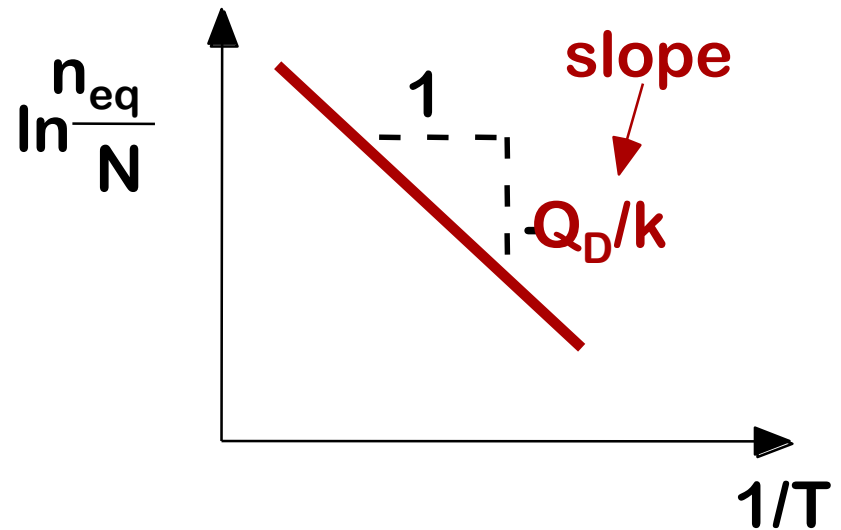
$$\frac{n_{eq}}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$$

Equilibrium concentration of vacancies – temperature dependence

Measure a material property which is dependent on n_{eq}/N vs T



$$\frac{n_{eq}}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$$



Find the activation energy from the slope

Equilibrium concentration of vacancies – temperature dependence

– Copper at 1000 °C

$$H_f = 0.9 \text{ eV/at} \quad A_{\text{Cu}} = 63.5 \text{ g/mol} \quad \rho = 8400 \text{ kg/m}^{-3}$$

First find N in atoms/ m^{-3}

$$N = \frac{N_A \rho}{A_{\text{Cu}}} = \frac{(6.023 \times 10^{23})(8400)}{0.0635}$$

$$N =$$

units Check

$$N \rightarrow \frac{(\cancel{\text{at/mol}})(\cancel{\text{kg/m}^3})}{\cancel{\text{kg/mol}}} = \frac{\text{at}}{\text{m}^3} \quad \boxed{\checkmark}$$

Equilibrium concentration of vacancies – temperature dependence

$$N = 7.97 \times 10^{28} \quad \text{at} - \text{sites} / \text{m}^3$$

- Now apply the Arrhenius relation @ 1000 °C

$$\begin{aligned} N_v &= N \exp\left(-\frac{H_f}{kT}\right) \\ &= 7.97 \times 10^{28} \exp\left[\frac{-0.9 \text{ eV} / \text{at}}{(8.62 \times 10^{-5} \text{ eV} / \text{at} - \text{K}) 1273 \text{ K}}\right] \end{aligned}$$

$$N_v = 2.18 \times 10^{25} \text{ vac} / \text{m}^3$$

Equilibrium concentration of vacancies – temperature dependence

$$\frac{n_{eq}}{N} = \exp\left(-\frac{\Delta H_f}{kT}\right)$$

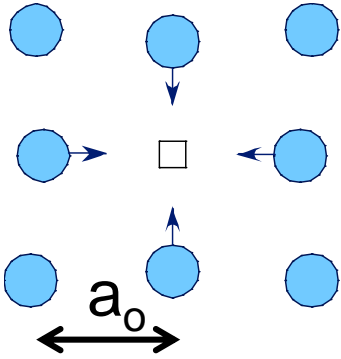
Al: $\Delta H_f = 0.70$ eV/vacancy

Ni: $\Delta H_f = 1.74$ eV/vacancy

n/N	0 K	300 K	900 K
Al	0	1.45×10^{-12}	1.12×10^{-4}
Ni	0	5.59×10^{-30}	1.78×10^{-10}

Equilibrium concentration of vacancy – pressure dependence

$$H_f = E_f + PV_f \quad \longrightarrow \quad \Delta G_f = E_f + PV_f - TS_f$$



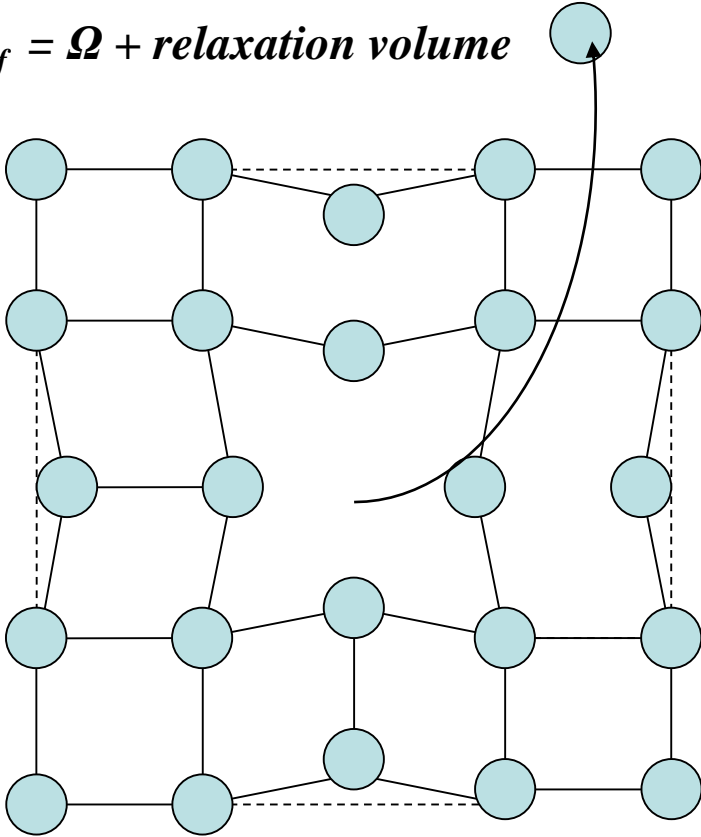
- Neighboring atoms tend to move into the vacancy, which creates a tensile stress field
- The stress/strain field is nearly spherical and short-range.

$$C_V^{eq} = e^{-\Delta G_f / kT} = e^{S_f / k} e^{-E_f / kT} e^{\sigma V_f / kT}$$

Equilibrium concentration of vacancy – pressure dependence

$$C_V^{eq} = e^{-\Delta G_f/kT} = e^{S_f/k} e^{-E_f/kT} e^{\sigma V_f/kT}$$

$V_f = \Omega + \text{relaxation volume}$



How big the pressure should be to make a measurable effect on vacancy concentration?

Compare

ΔH_f

σV_f

Equilibrium concentration of vacancy – pressure dependence

101.325 kPa is “one standard atmosphere” and **1 Pa** = 1 N/m²

$$1 \text{ J} = 1 \text{ N} \cdot \text{m} = \left(\frac{\text{kg} \cdot \text{m}}{\text{s}^2} \right) \cdot \text{m} = \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2} = \text{Pa} \cdot \text{m}^3 = 1 \text{ W} \cdot \text{s}$$

1 eV = 1.602176487×10⁻¹⁹ Joule

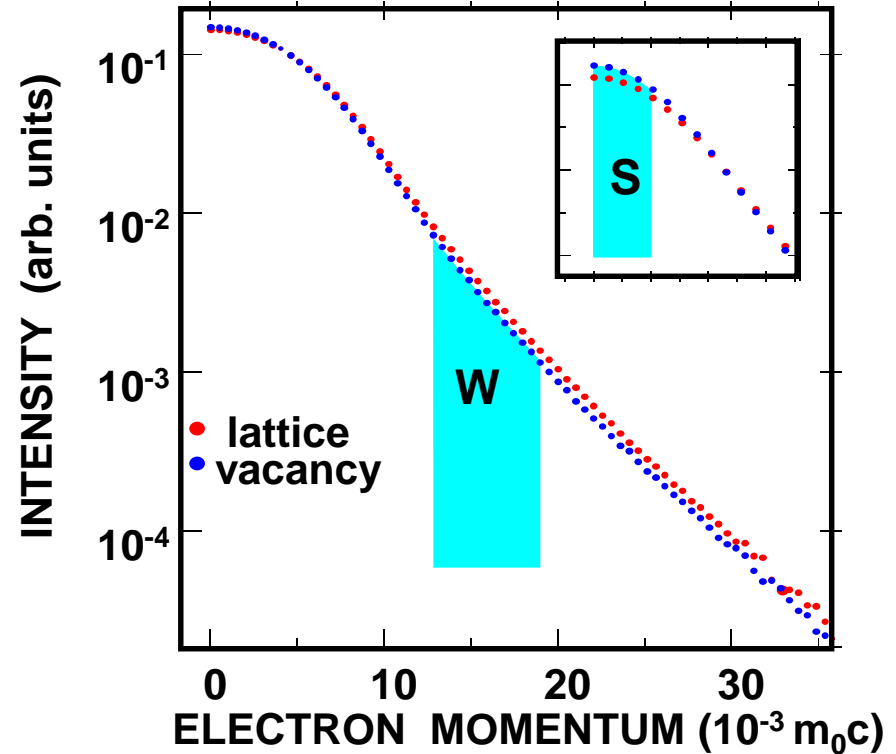
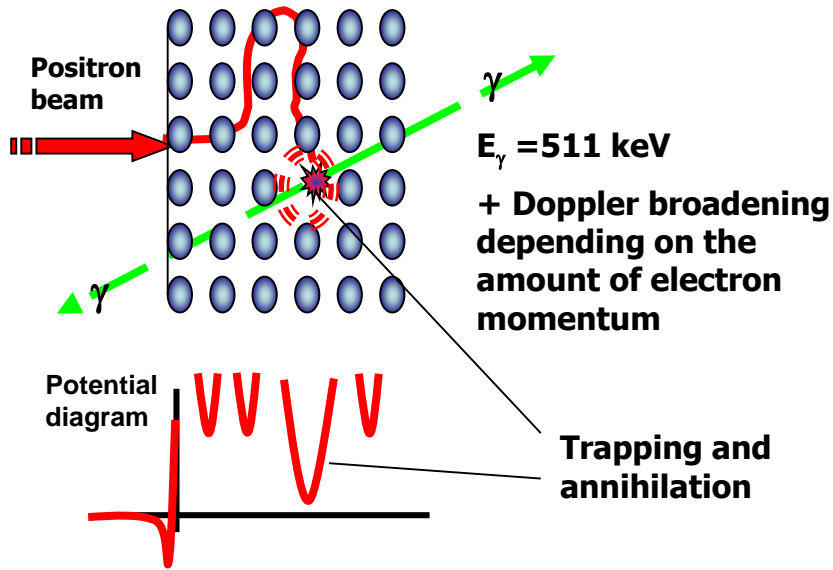
As we calculate the effect of pressure/stress on vacancy concentration starts to be significant at quite high values – in the range of 100 MPa.

Are these conditions available in real “life” or happens only in a laboratory experiment?

Lecture 4: Surfaces and interfaces. Point defects and diffusion in crystals

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- **Watching empty lattice sites – i.e. vacancies – with positrons**

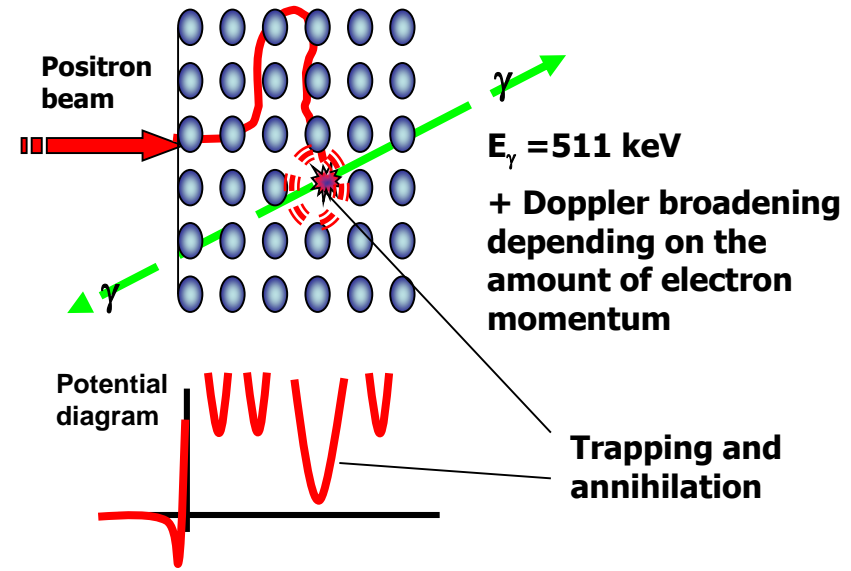
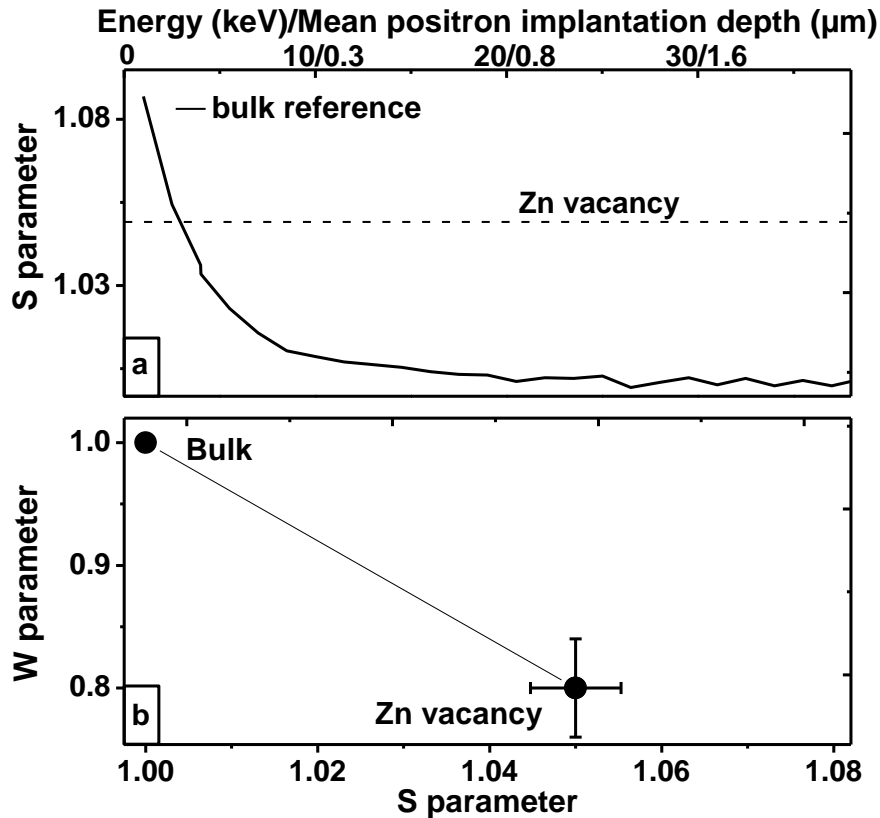
Positron probing of vacancies in semiconductors



S-parameter characterizes annihilation with low momentum valence electrons. Increase in S-parameter is naturally interpreted as an increase in vacancy concentration

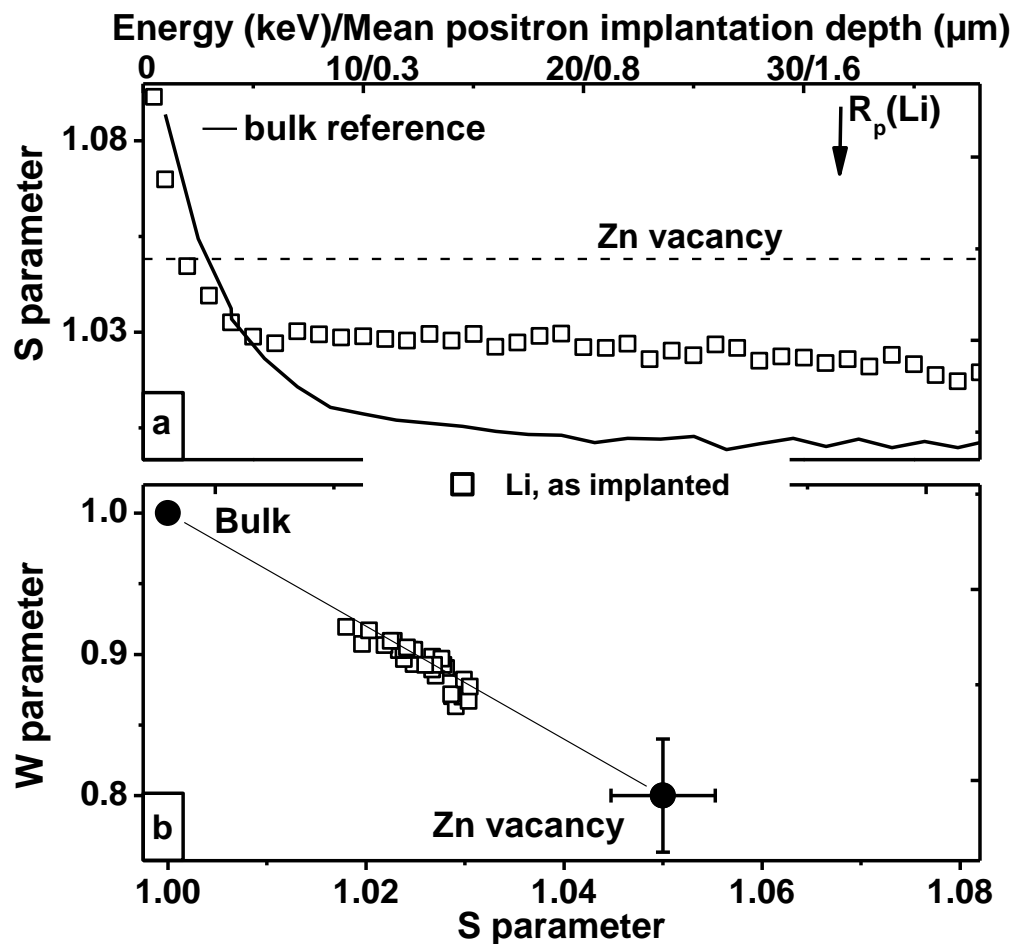
W-parameter characterizes annihilation with high momentum core electrons and increase in vacancy concentration results in decrease of W-parameter

Clustering of ion implantation induced vacancies in ZnO



Experimental points group around a line in the W-S plane if there are only two annihilation states available in the sample

Clustering of ion implantation induced vacancies in ZnO



Clustering of ion implantation induced vacancies in ZnO

