FYS3410 - Vår 2011 (Kondenserte fasers fysikk)

http://www.uio.no/studier/emner/matnat/fys/FYS3410/index-eng.xml

Based on Introduction to Solid State Physics by Kittel

Course content

- Periodic structures, understanding of diffraction experiment and reciprocal lattice
- Imperfections in crystals: diffusion, point defects, dislocations
- Crystal vibrations: phonon heat capacity and thermal conductivity
- Free electron Fermi gas: density of states, Fermi level, and electrical conductivity
- Electrons in periodic potential: energy bands theory classification of metals, semiconductors and insulators
- Semiconductors: band gap, effective masses, charge carrier distributions, doping, pn-junctions
- Metals: Fermi surfaces, temperature dependence of electrical conductivity

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FYS3410 lecture schedule and exams: Spring 2011

W/19/1/2011:	Introduction and motivation. Periodicity and lattices	1h
M/24/1/2011:	Index system for crystal planes. Crystal structures	2h
W/26/1/2011:	Reciprocal space, Laue condition and Ewald construction	1h
M/31/1/2011:	Brillouin Zones. Interpretation of a diffraction experiment	2h
W/02/2/2011:	Crystal binding, elastic strain and waves	1h
M/07/2/2011:	Elastic waves in cubic crystals; defects in crystals	2h
W/09/2/2011:	Defects in crystals; case study – vacancies; diffusion	2h
M/14/2/2011:	Crystal vibrations and phonons	2h
W/16/2/2011:	Lattice heat capacity: Dulong-Petit and Einstein models	2h
M/21/2/2011:	Phonon density of states (DOS) and Debye model	2h
W/23/2/2011:	General result for DOS; role of anharmonic interactions	2h
M/28/2/2011:	Thermal conductivity and repetition of crystal vibrations	2h
W/02/3/2011:	no lectures	
M/07/3/2011:	no lectures	
W/09/3/2011:	no lectures	
M/14/3/2011:	Free electron Fermi gas in 1D and 3D – ground state	2h
W/17/3/2011:	Density of states, effect of temperature – FD distribution	1h
M/21/3/2011:	Heat capacity of FEFG	2h
W/23/3/2011:	Repetition	1h
M/28/3/2011:	Mid-term exam	

M/04/4/2011:	**Electrical and thermal conductivity in metals**	**2h**
W/06/4/2011:	**Bragg reflection of electron waves at the boundary of BZ**	**2h**
M/11/4/2011:	**Energy bands, Kronig - Penny model**	**2h**
W/13/4/2011:	**Empty lattice approximation; number of orbitals in a band**	**2h**
Påsk uppehåll		
W/27/4/2011	**no lectures**	
M/02/5/2011:	**no lectures**	
W/04/5/2011:	**no lectures**	
M/09/5/2010:	**Semiconductors, effective mass method, intrinsic carriers**	**2h**
W/11/4/2010:	**Impurity states in semiconductors and carrier statistics**	**2h**
M/16/5/2010:	**p-n junctions, Schottky contacts and heterojunctions**	**2h**
W/18/5/2010:	**Metals and Fermi surfaces**	**1h**
M/23/5/2010:	**Repetition**	**2h**
26-27/5/2010:	**Final Exam (sensor:???)**	

Lecture 7: Defects in crystals; case study - vacancies

- **defects in crystals; vacancies**
- **Configurational entropy due to vacancy**
- **Equilibrium concentration of vacancies – temperature dependence**
- **Equilibrium concentration of vacancy – pressure dependence**
- **Excess concentration and clustering of vacancies**
- **Clustering of ion implantation induced vacancies in ZnO**

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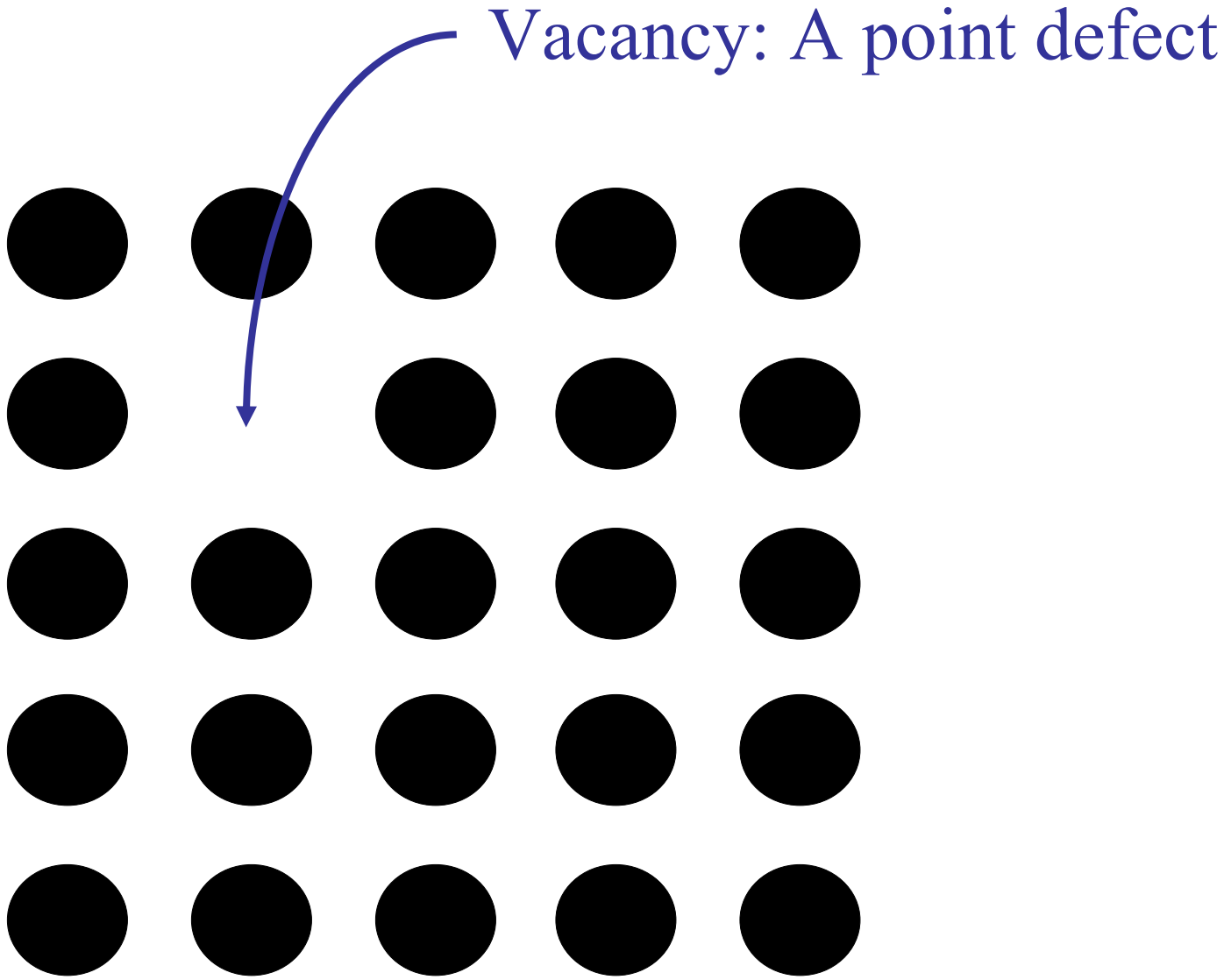

Vacancy: A point defect

Defects	*Dimensionality*	*Examples*
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

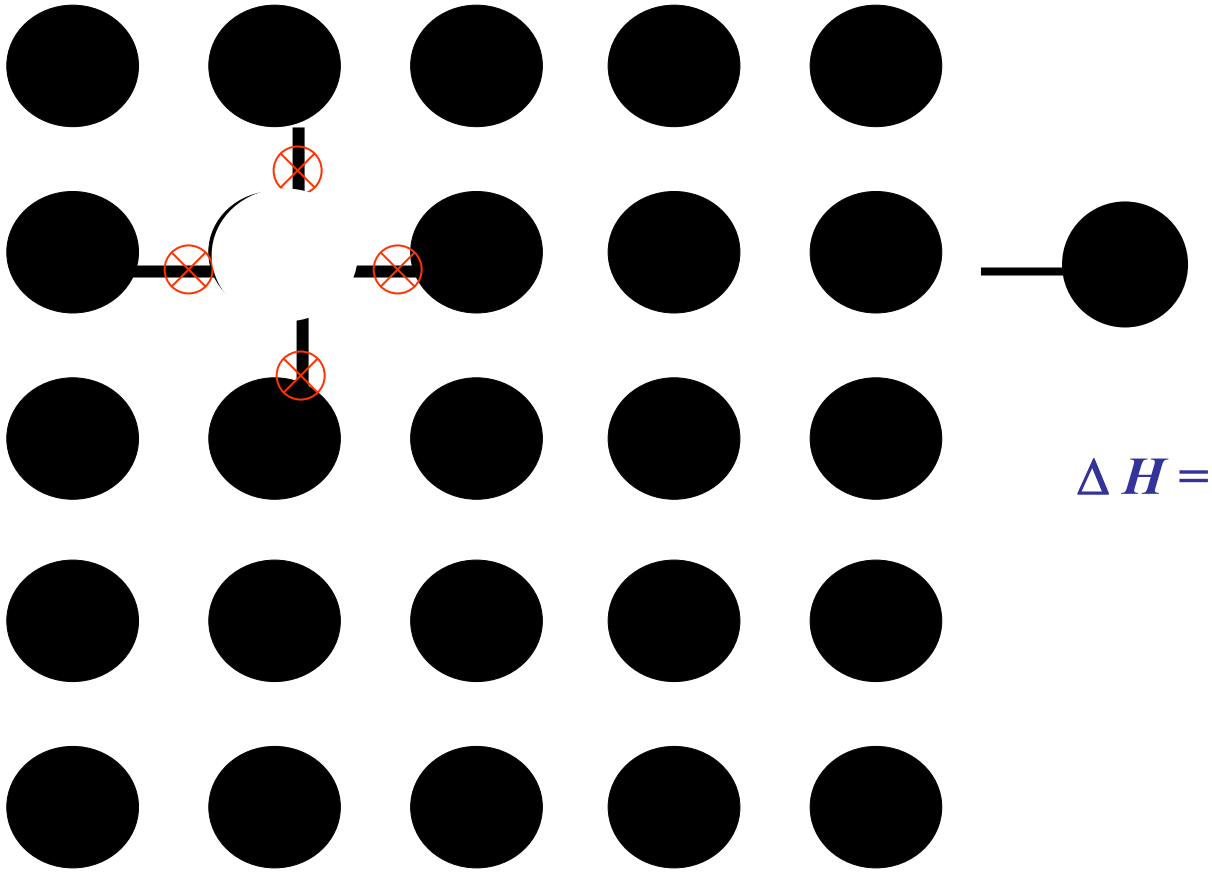
2. Entropy $S = k \ln W$

k Boltzmann constant
W number of microstates

$$G = H - T S$$

T Absolute temperature

Vacancies



$$\Delta H = n \Delta H_f$$

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

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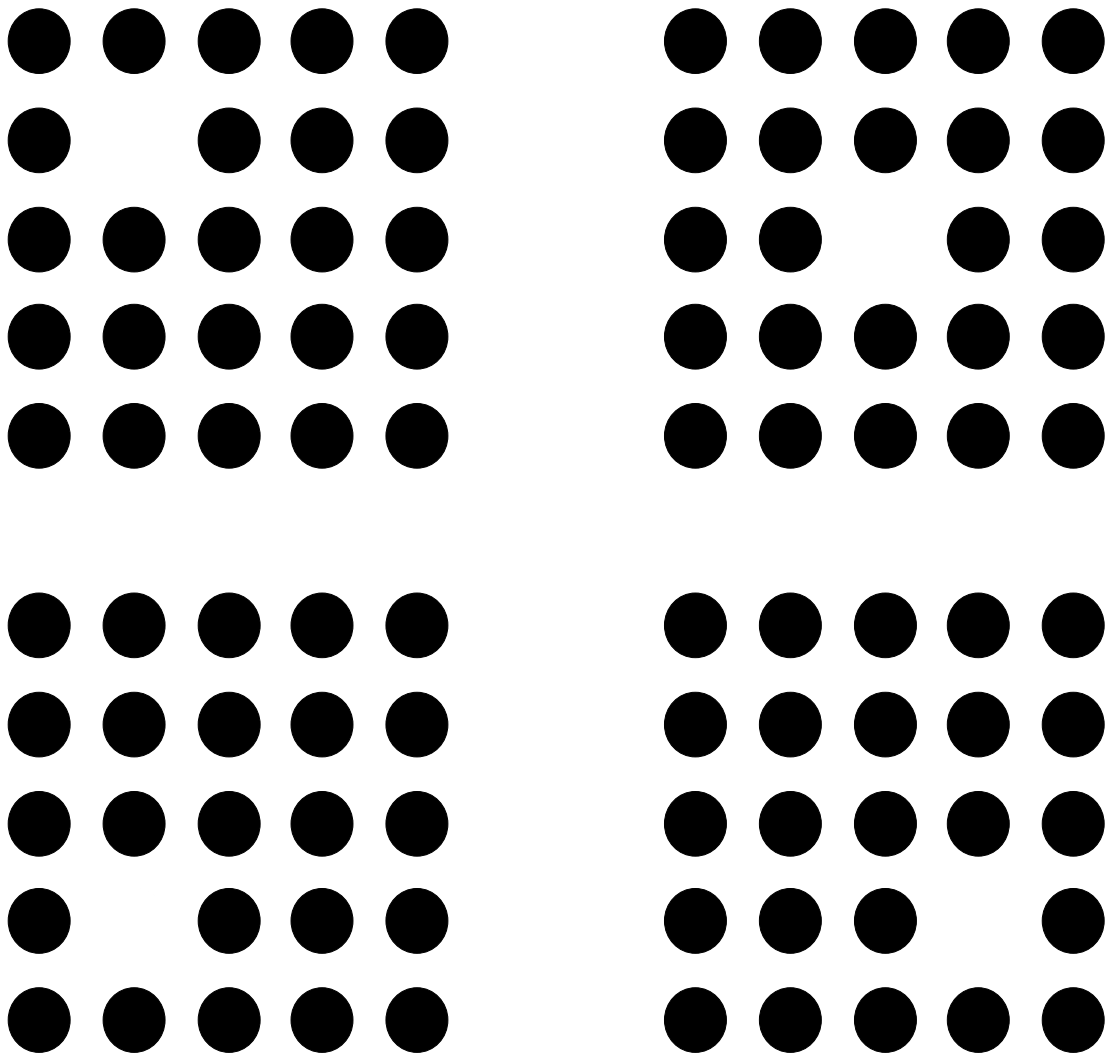
Configurational entropy due to vacancy



Configurational entropy due to vacancy

Number of atoms: N

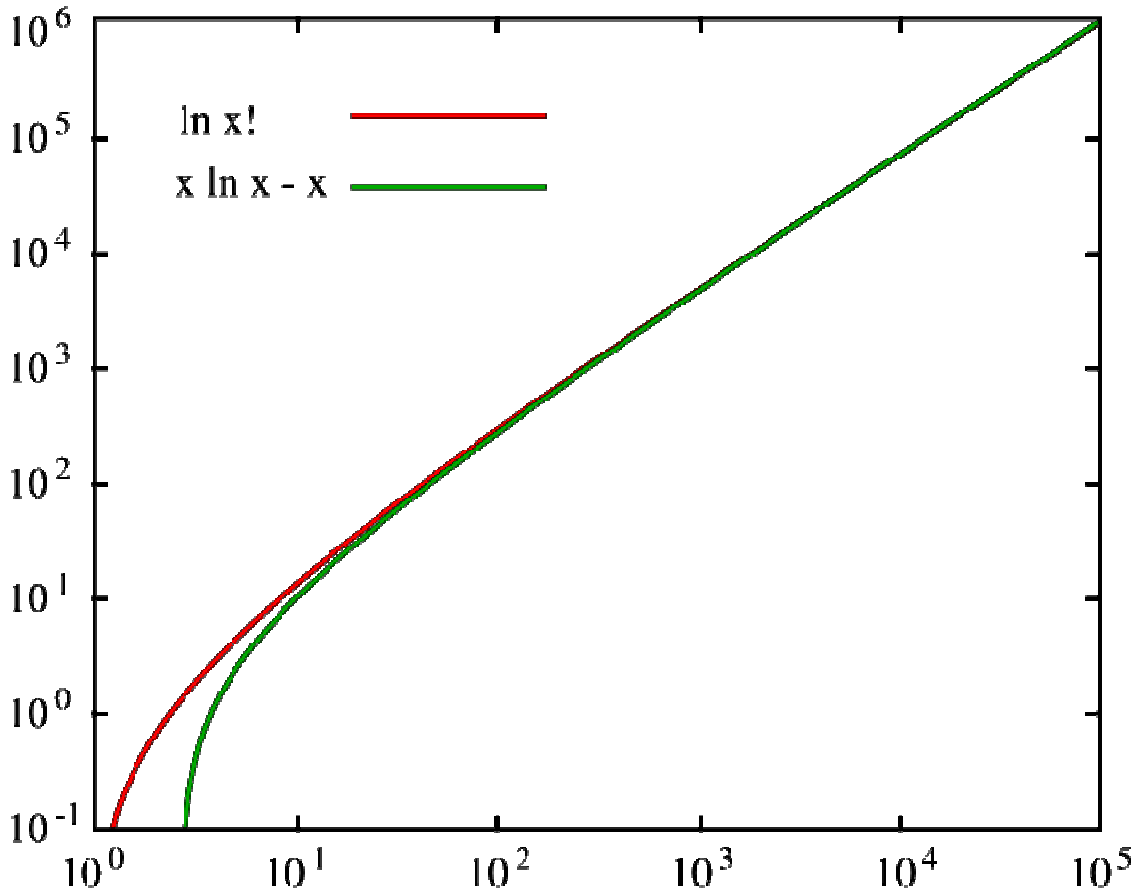
Number of vacacies: n

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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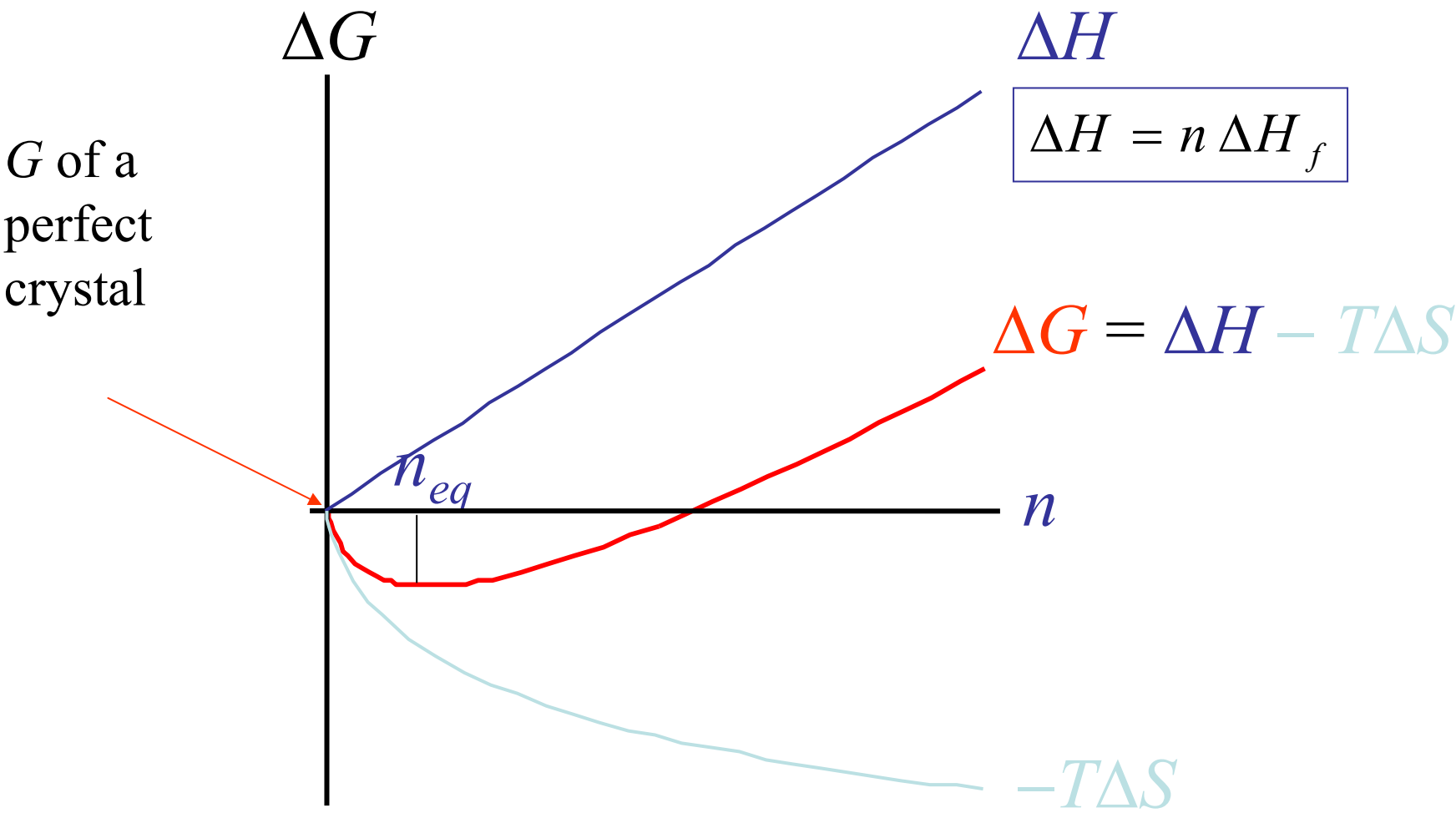
Equilibrium concentration of vacancies – temperature dependence



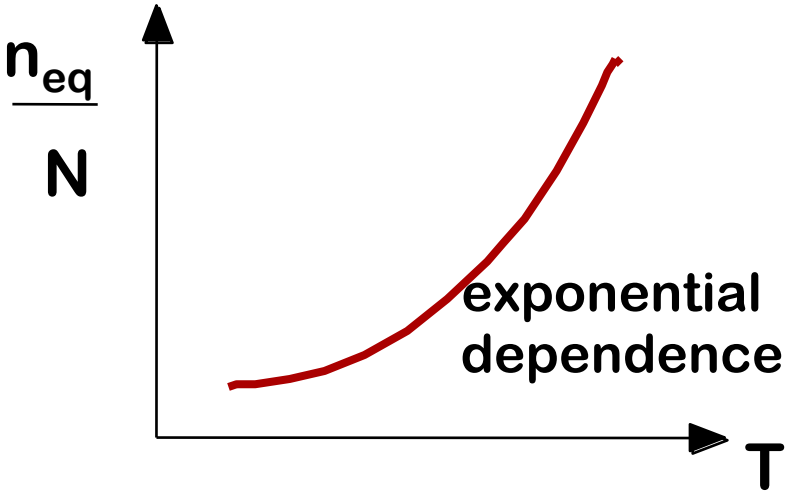
Equilibrium concentration of vacancies – temperature dependence

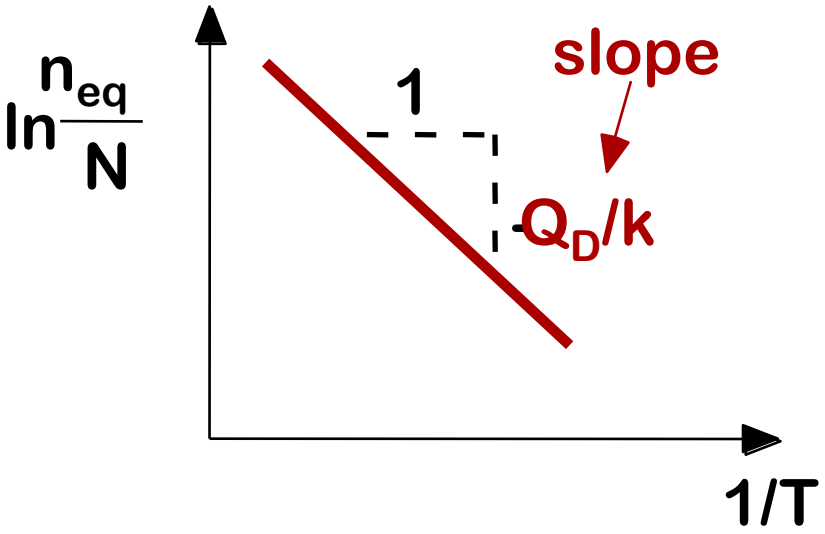
$$\left.\frac{\partial \Delta G}{\partial n}\right|_{n=n_{eq}} = 0$$

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

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 ºC

H_f = 0.9 eV/at A_{Cu} = 63.5 g/mol ρ = 8400 kg/m^{-3}

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

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

$N =$

units Check ☑

$$N \rightarrow \frac{(at/mol)(kg/m^3)}{kg/mol} = \frac{at}{m^3}$$

Equilibrium concentration of vacancies – temperature dependence

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

- Now apply the Arrhenius relation @1000 ºC

$$N_v = N \exp\left(-\frac{H_f}{kT} \right)$$

$$= 7.97 \times 10^{28} \exp\left[\frac{-0.9 eV / at}{\left(8.62 \times 10^{-5} eV / at - K\right) 1273 K} \right]$$

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

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}

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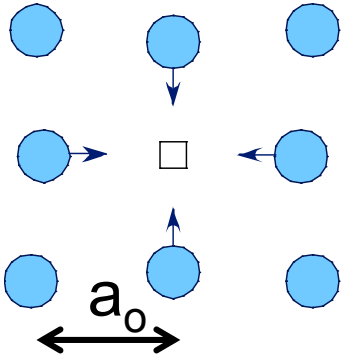
Equilibrium concentration of vacancy – pressure dependence

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



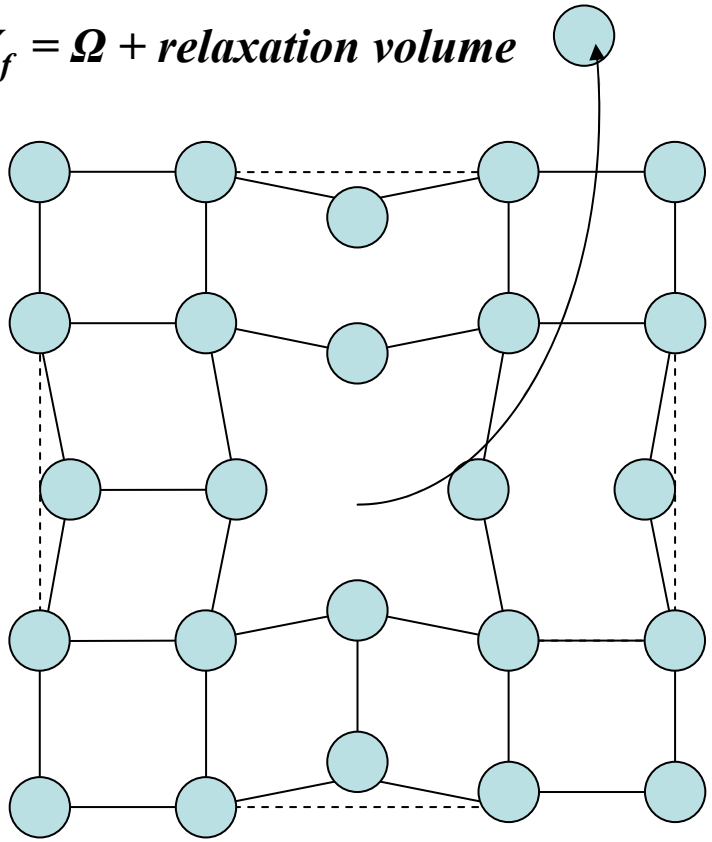
- Neighboring atoms tend to move into the vacancy, which creates a tensile stress field
- The stress/strain field is nearly spherical and short-range.

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

Equilibrium concentration of vacancy – pressure dependence

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

$V_f = \Omega +$ ***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

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

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?

Excess concentration and clustering of vacancies

Radiation

Chemical reactions

The amount of single vacancies exceed the ”solubility” limit and vacancies may start cluster

$$\frac{\partial[V_n]}{\partial t} = \underbrace{4\pi R D_V [V_{n-1}][V]}_{\textbf{generation}} - \underbrace{[V_n] \cdot C_0 \exp(-E_b/kT)}_{\textbf{dissociation}}$$

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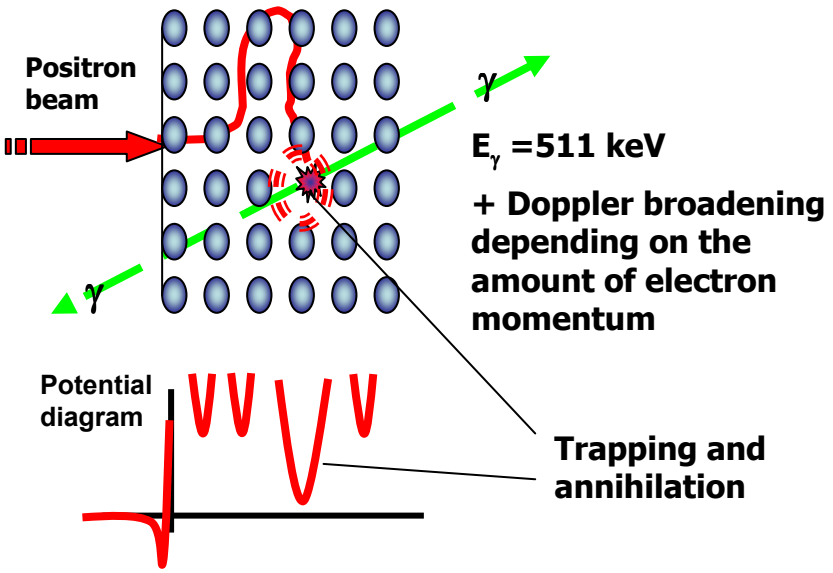
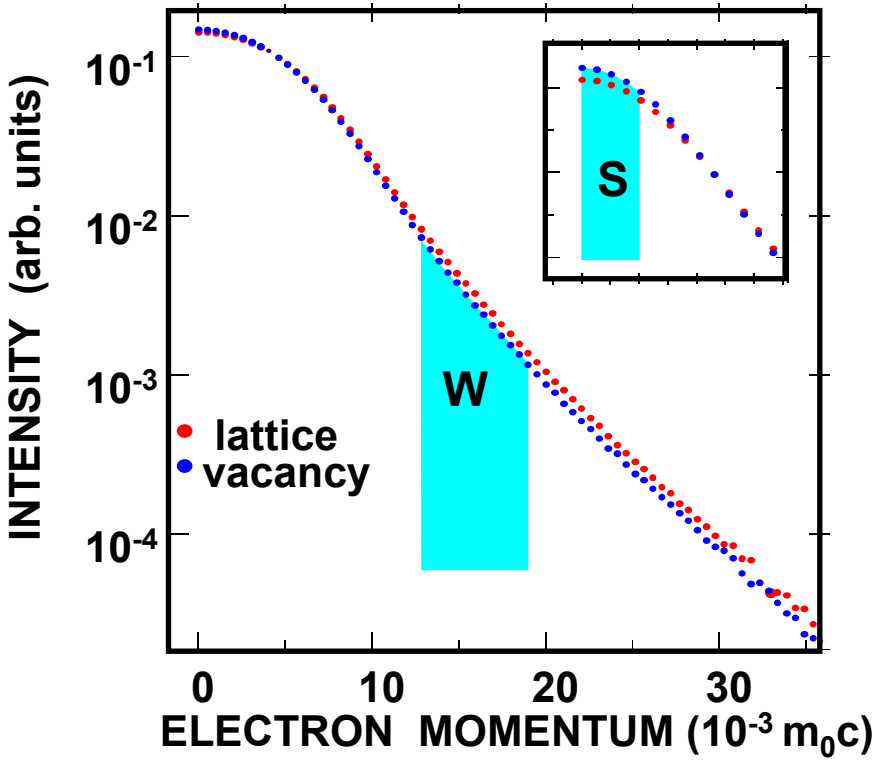
Positron probing of vacancies in semiconductors





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

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

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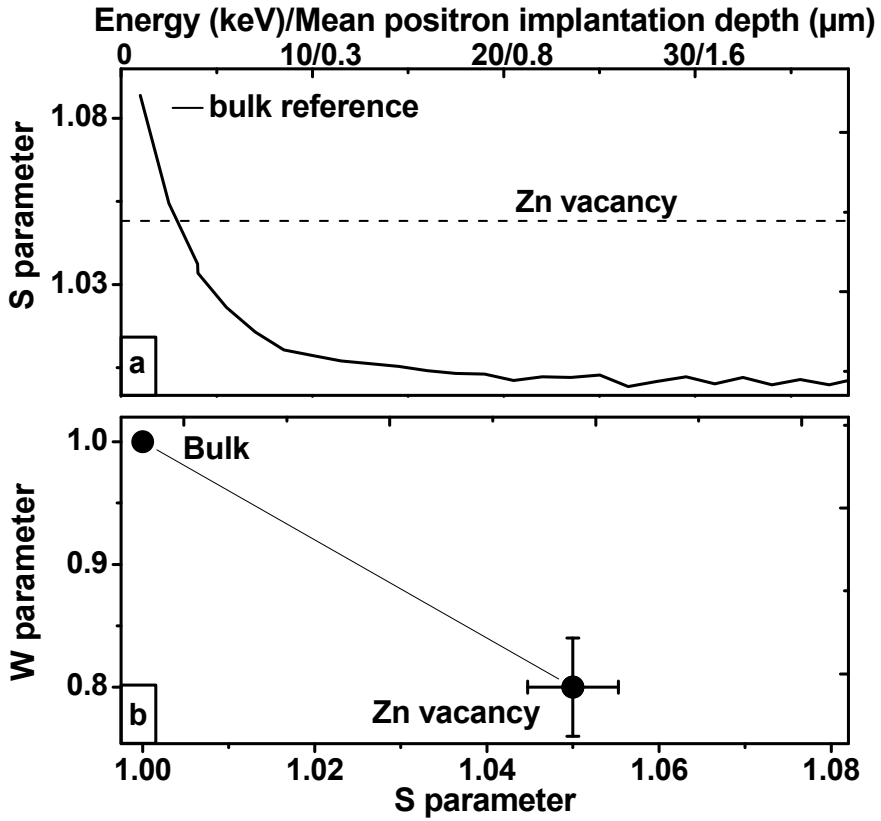
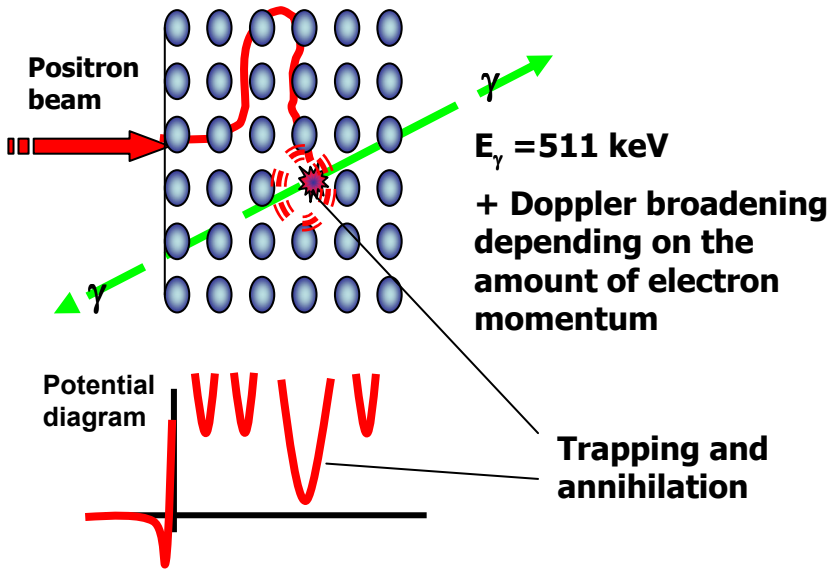
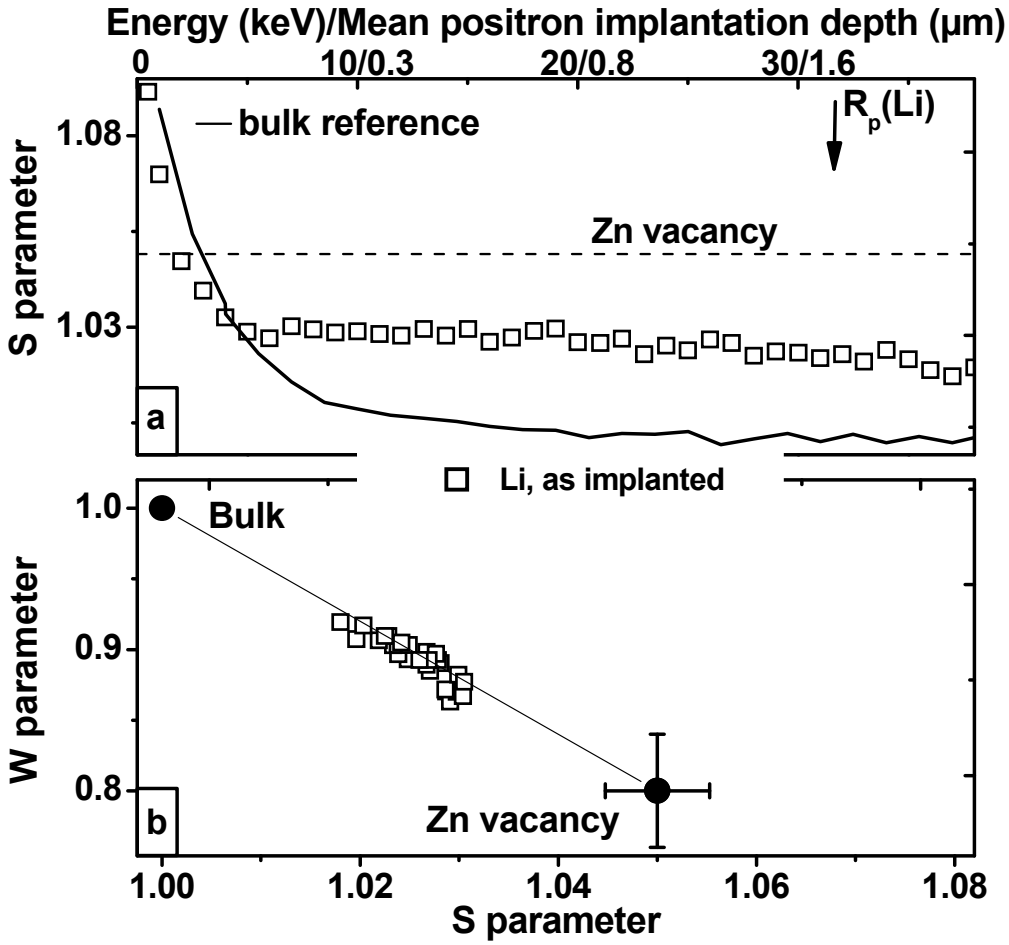




Experimental points group around a line in the W-S plane if there are only two annihilation states vailable in the sample

Clustering of ion implantation induced vacancies in ZnO



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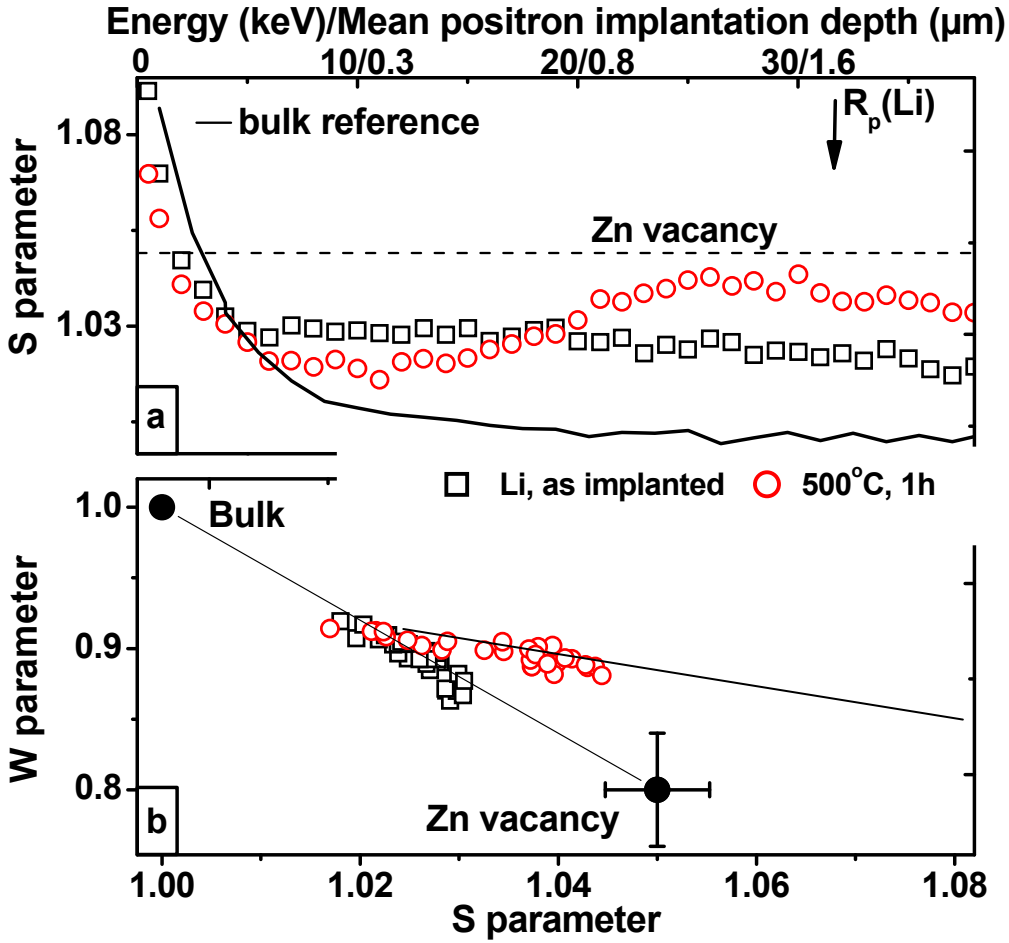

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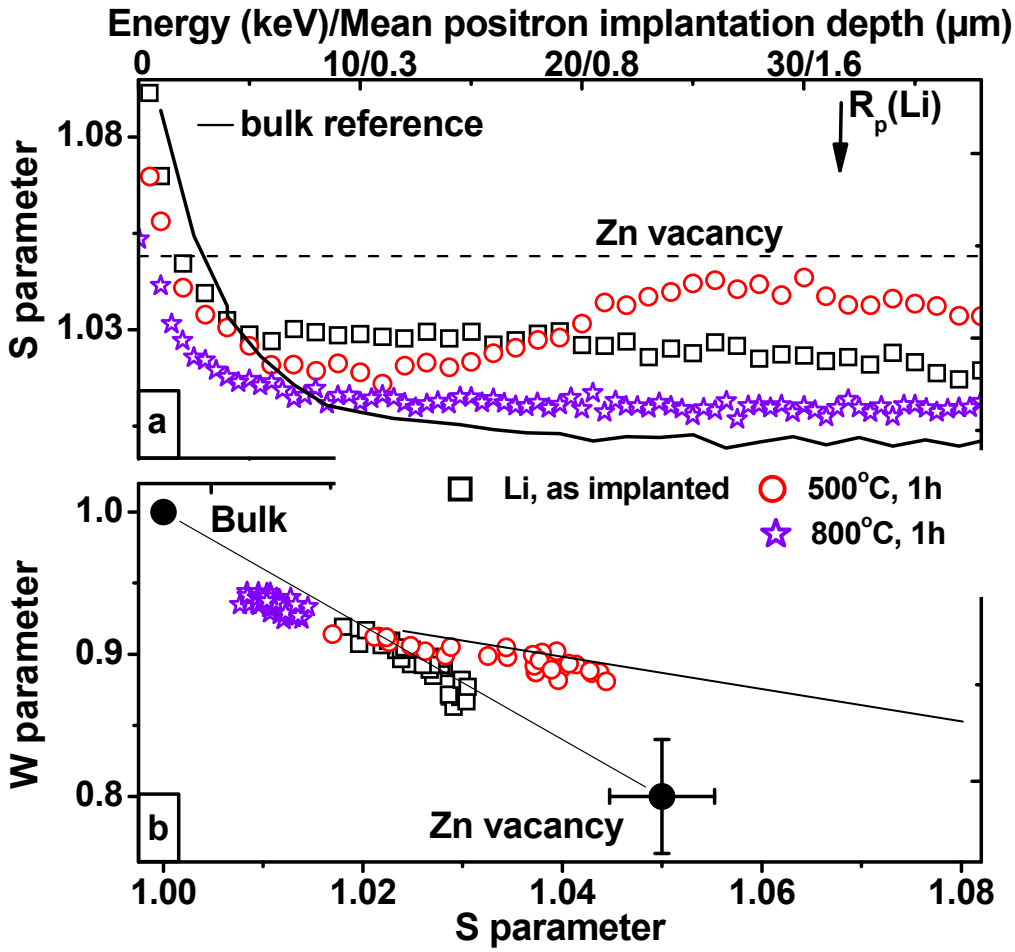

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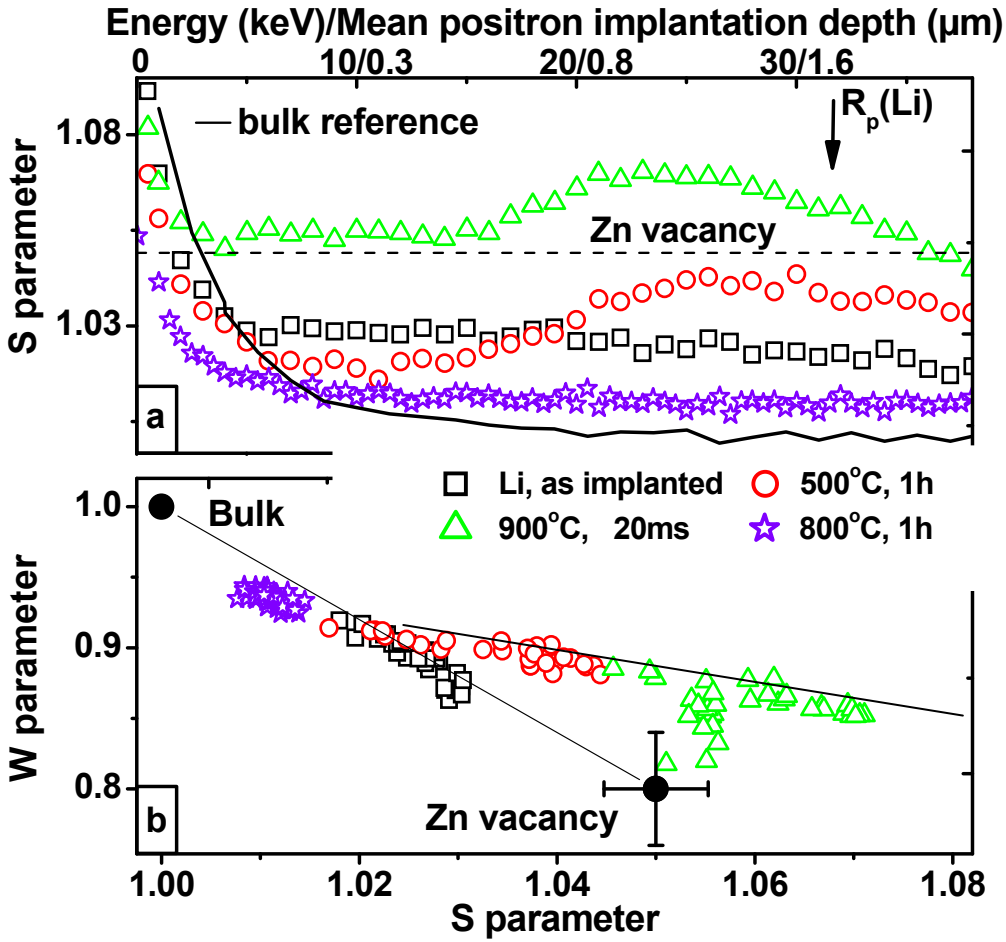

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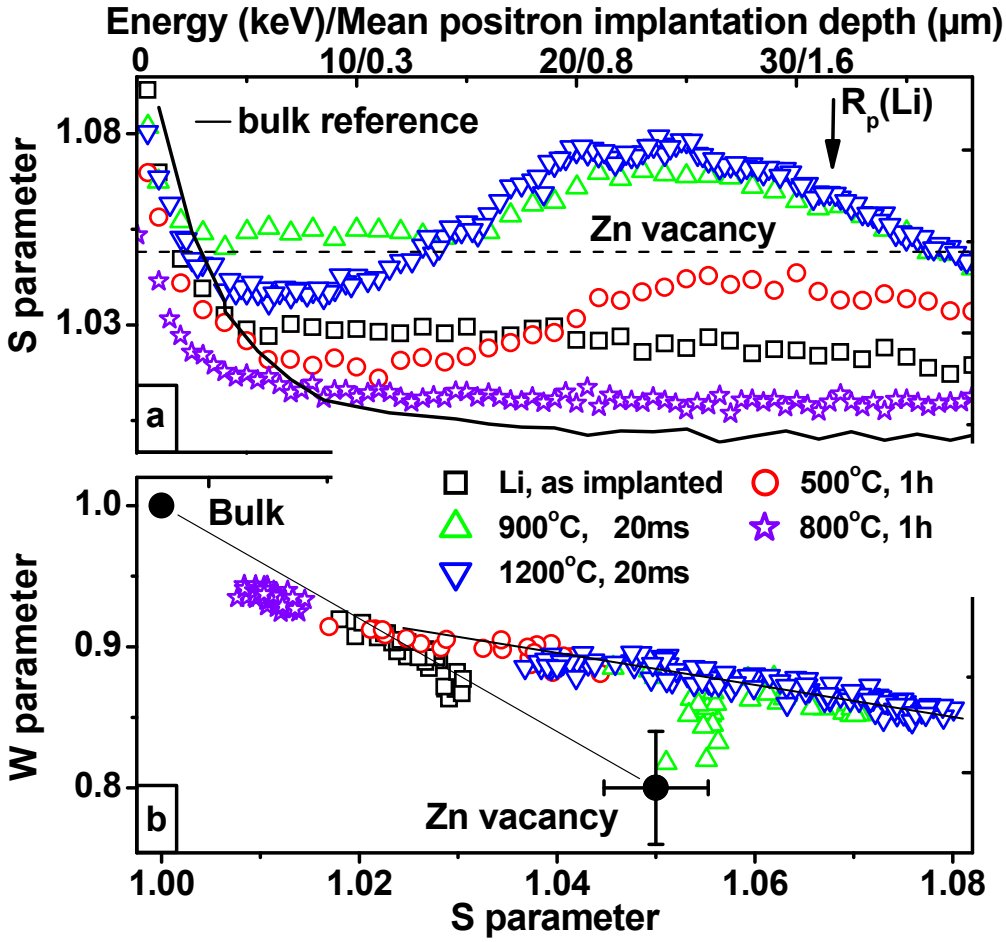

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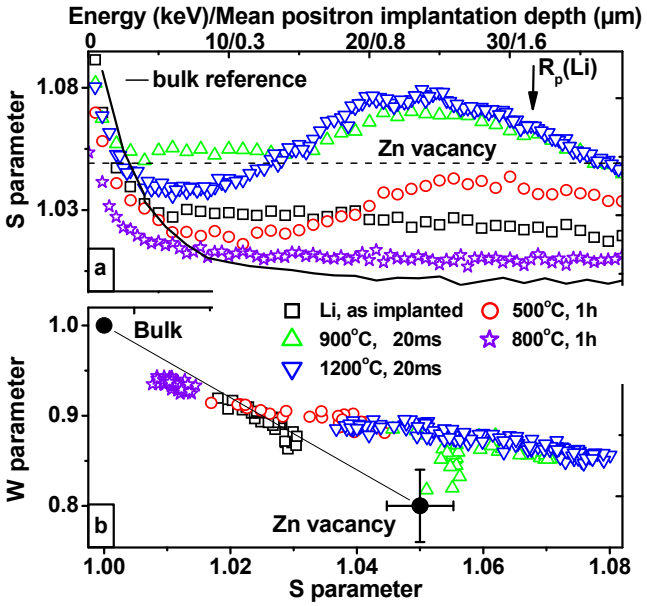
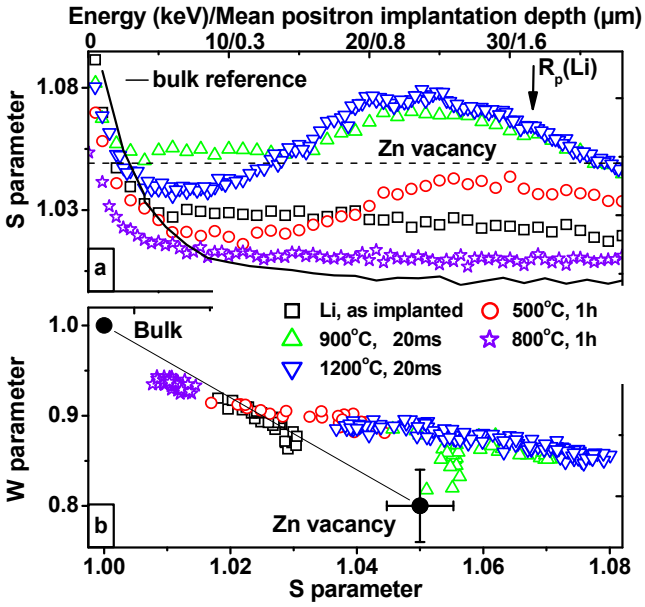


vacancies build clusters consisting of at least 3–4 V_{Zn}

Why clusters do not survive 1h anneals at ≥ 800 °C?

Clustering of ion implantation induced vacancies in ZnO



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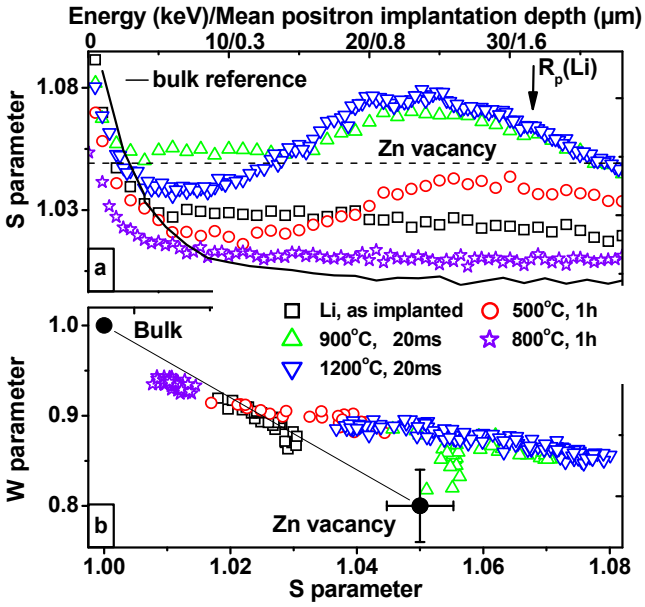
Why clusters do not survive 1h anneals at ≥ 800 °C?

$$\frac{\partial[V_n]}{\partial t} = \underbrace{4\pi R D_V [V_{n-1}][V]}_{\text{generation}} - \underbrace{[V_n]\cdot C_0 \exp(-E_b/kT)}_{\text{dissociation}}$$

- **clustering take place as long as the vacancy diffusivity (D_V), supersaturation level ([V]), and clustering reaction radii (R) are high enough**
- ***E_b* – dissociation energy – determines the dissociation rate at a given temperature**

Clustering of ion implantation induced vacancies in ZnO



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temperature (°C)	500	800	900	1200	1400
clusters survive	1h		20 ms	20 ms	20 ms
clusters dissolve		1h			

→ **E_b = 2.6 ± 0.3 eV**

T.M. Børseth, *et al* Phys.Rew. B 89, (2006)