FYS3410 - Vår 2010 (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
- Crystal binding, elastic strain and waves
- **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 2010

M/18/1/2010:	**Introduction and motivation. Periodicity and lattices**	**2h**
W/20/1/2010:	**Index system for crystal planes. Crystal structures**	**1h**
M/25/1/2010:	**Reciprocal space, Laue condition and Ewald construction**	**2h**
W/27/1/2010:	**Brillouin Zones. Interpretation of a diffraction experiment**	**1h**
M/01/2/2010:	**Crystal binding, elastic strain and waves**	**2h**
W/03/2/2010:	**Elastic waves in cubic crystals; defects in crystals**	**1h**
M/08/2/2010:	**Defects in crystals; case study - vacancies**	**2h**
W/10/2/2010:	Atomic diffusion	1h
M/15/2/2010:	Crystal vibrations and phonons	2h
W/17/2/2010:	Crystal vibrations and phonons	1h
M/22/2/2010:	Planck distribution and density of states	2h
W/24/2/2010:	Debye model	1h
M/01/3/2010:	Einstein model and general result for density of states	2h
W/03/3/2010:	Thermal conductivity	1h
M/08/3/2010:	Free electron Fermi gas in 1D and 3D – ground state	2h
W/10/3/2010:	Density of states, effect of temperature – FD distribution	1h
M/15/3/2010:	Heat capacity of FEFG	2h
W/17/3/2010:	Repetition	1h
22/3/2010:	Mid-term exam	

M/14/4/2010:	Electrical and thermal conductivity in metals	2h
W/12/4/2010:	Bragg reflection of electron waves at the boundary of BZ	1h
M/19/4/2010:	Energy bands, Kronig - Penny model	2h
W/21/4/2010:	Empty lattice approximation; number of orbitals in a band	1h
M/26/4/2010:	Semiconductors, effective mass method, intrinsic carriers	2h
W/28/4/2010:	Impurity states in semiconductors and carrier statistics	1h
M/03/5/2010:	p-n junctions and heterojunctions	2h
W/05/5/2010:	surface structure, surface states, Schottky contacts	2h
M/10/5/2010:	no lectures	
W/12/5/2010:	no lectures	
W/19/5/2010:	Repetition	2h
W26/5/2010:	Repetition	2h

28/5/2010: Final Exam (sensor: Prof. Arne Nylandsted Larsen at the Århus University, Denmark, http://person.au.dk/en/anl@phys.au.dk)

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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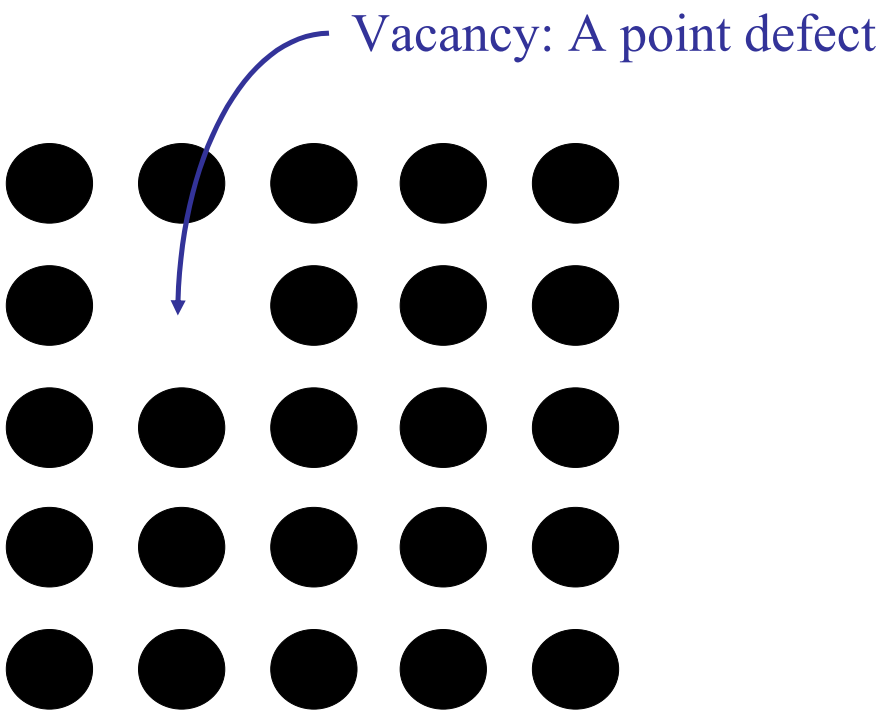


Defects	*Dimensionality*	*Examples*
Point	0	Vacancy
Line	1	Dislocation
Surface	2	Free surface, Grain boundary

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

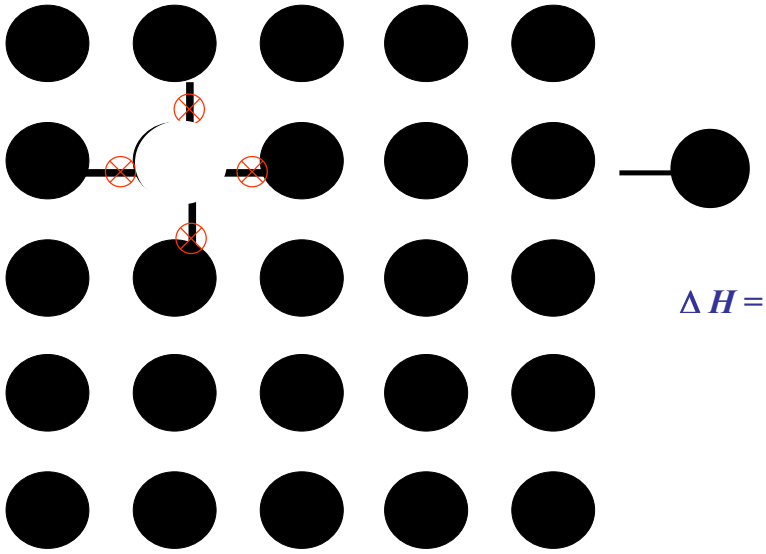
2. Entropy $S = k \ln W$

k Boltzmann constant
W number of microstates

$$G = H - TS$$

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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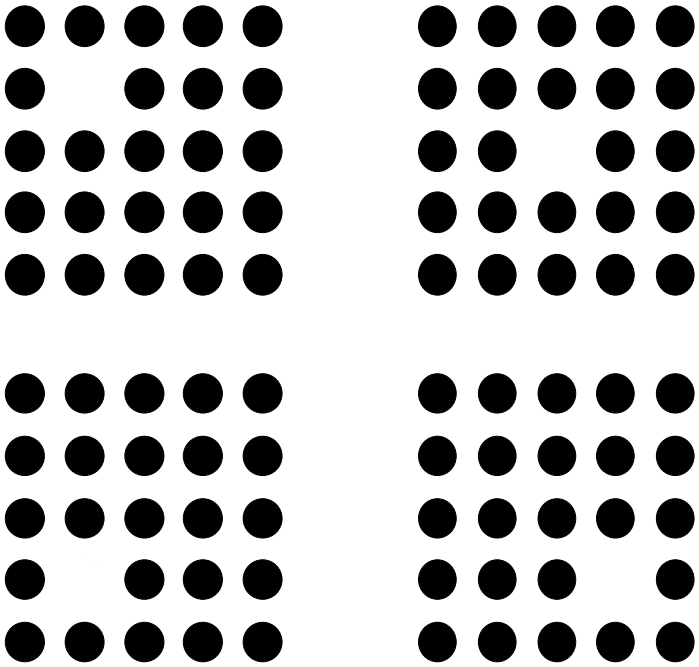
Configurational entropy due to vacancy



Configurational entropy due to vacancy

Number of atoms: N

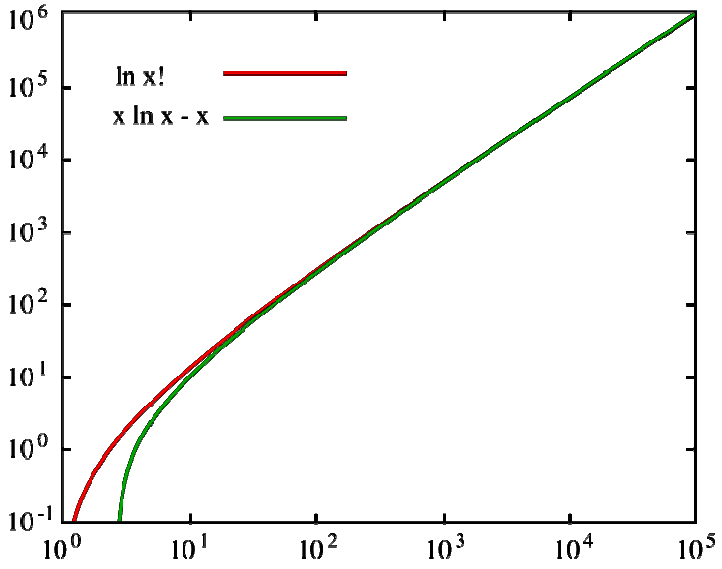
Number of vacancies: n

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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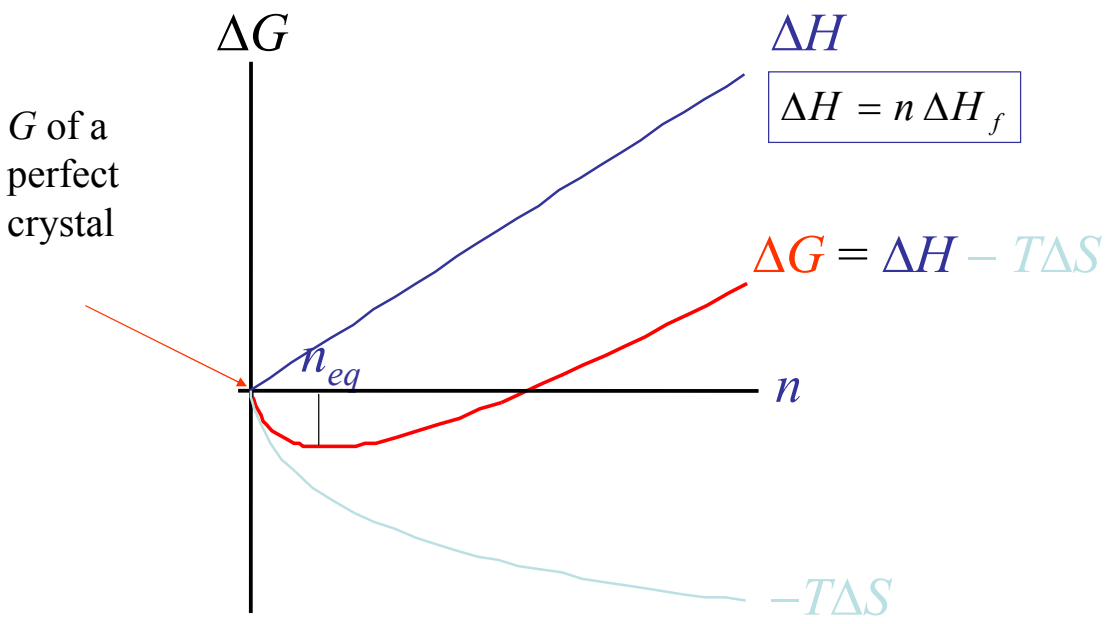
Equilibrium concentration of vacancies – temperature dependence



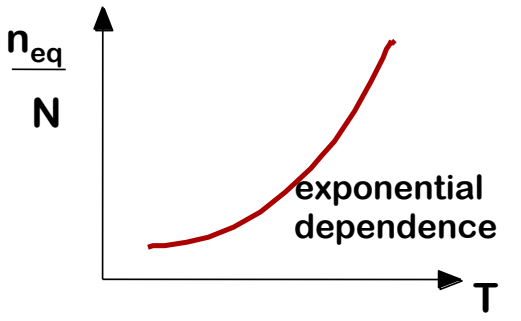
Equilibrium concentration of vacancies – temperature dependence

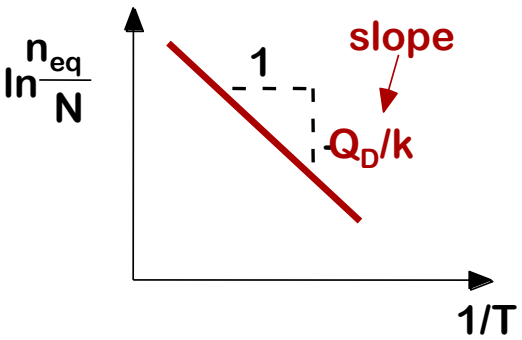
$$\left.\frac{\partial \Delta G}{\partial n}\right|_{n=n_{eq}} = 0$$

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

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 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}

$$N = \frac{N_A \rho}{A_{Cu}} = \frac{(6.023\times10^{23})(8400)}{0.0635}$$

$N =$

units Check

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

☑

Equilibrium concentration of vacancies – temperature dependence

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

- Now apply the Arrhenius relation @1000 ºC

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

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

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

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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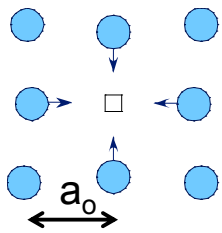
Equilibrium concentration of vacancy – pressure dependence

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



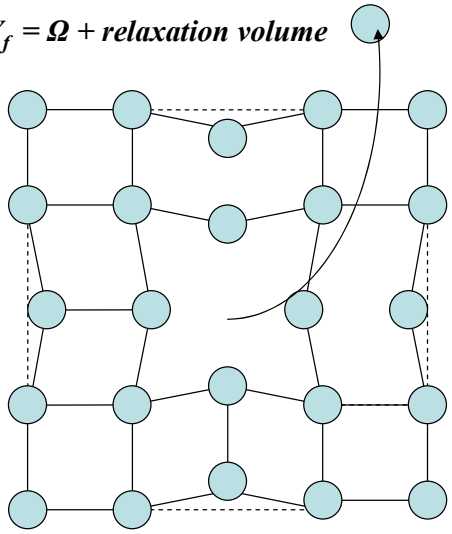
- Neighboring atoms tend to move into the vacancy, which creates a tensile stress field
- The stress/strain field is nearly spherical and short-range.

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

Equilibrium concentration of vacancy – pressure dependence

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

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



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

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

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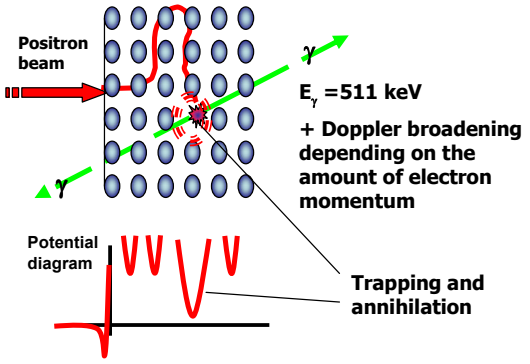
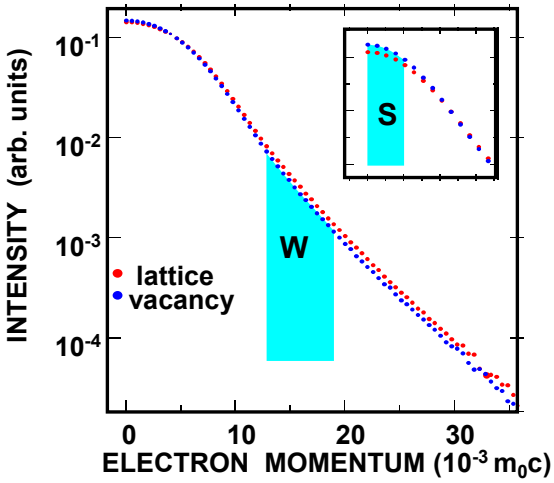
Positron probing of vacancies in semiconductors





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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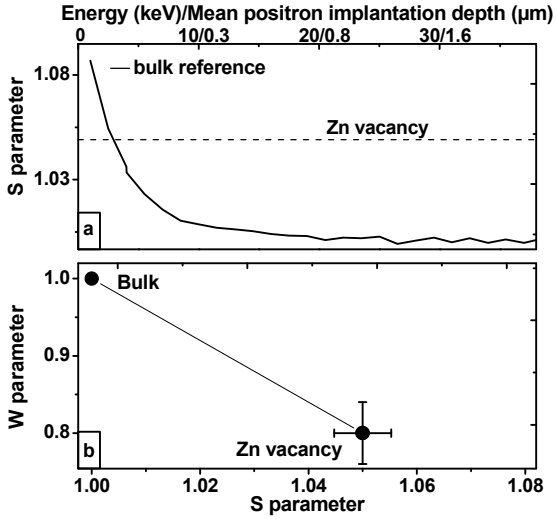
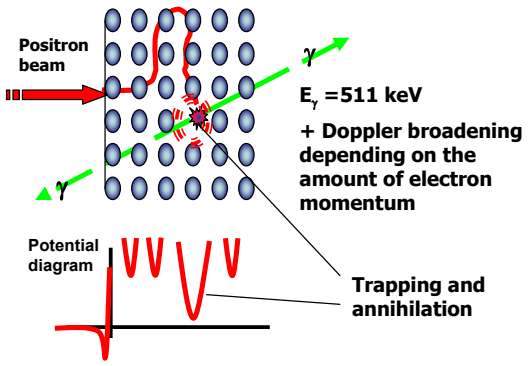
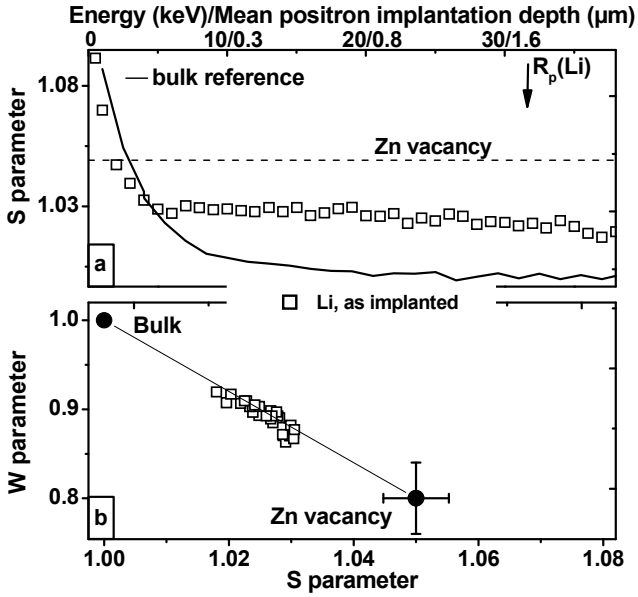




Experimental points group around a line in the W-S plane if there are only two annihilation states vailable in the sample

Clustering of ion implantation induced vacancies in ZnO



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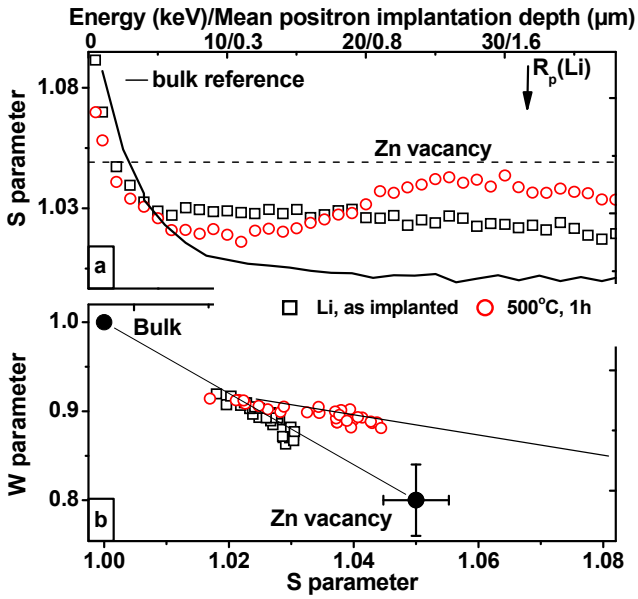

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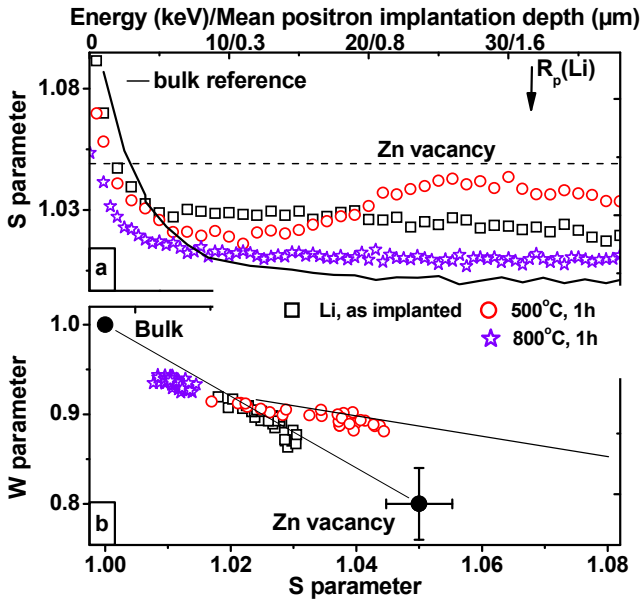

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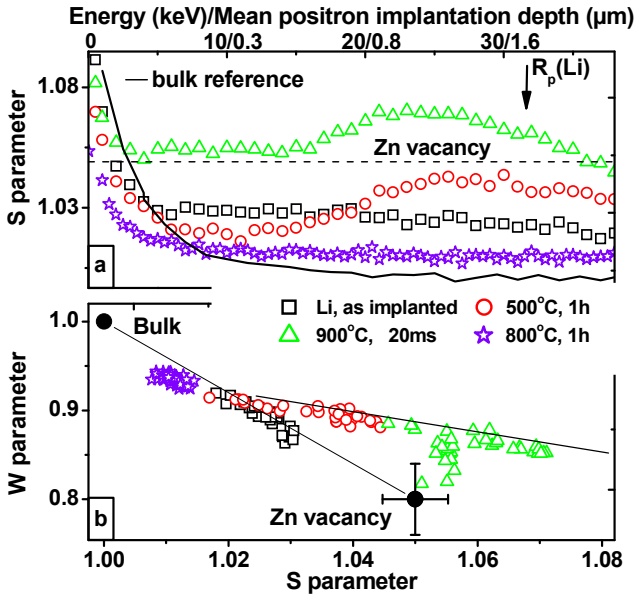

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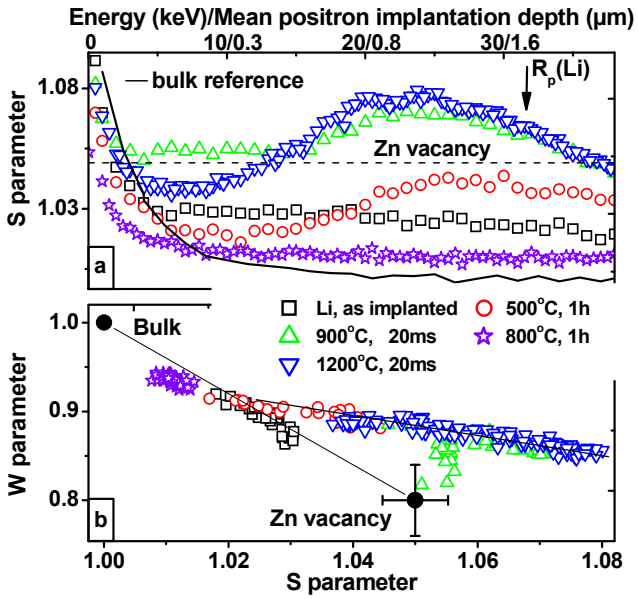

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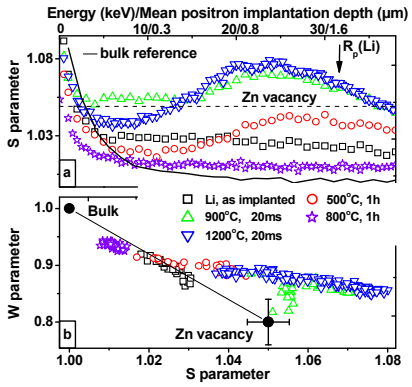
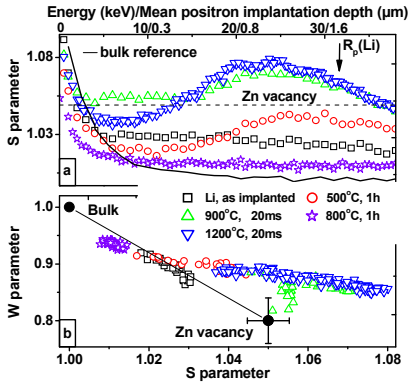


vacancies build clusters consisting of at least 3–4 V_{Zn}

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

Clustering of ion implantation induced vacancies in ZnO



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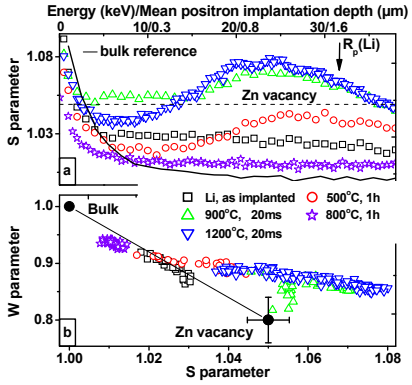
- **clustering take place as long as the vacancy diffusivity (D_v), supersaturation level ([V]), and clustering reaction radii (R) are high enough**
- ***E_b* – dissociation energy – determines the dissociation rate at a given temperature**

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)