Lecture 13

Ch 10 Rubber Elasticity
+
Ch 6 Defects (vacancy) L1

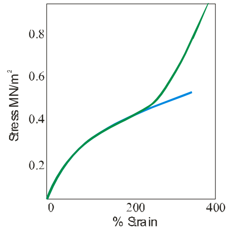
F 22.08.2025

1

1

Elastomer

Polymers with very extensive elastic deformation



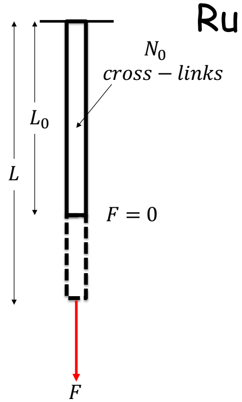
Stress-strain relationship is non-linear

Example: Rubber

2

2

Rubber Elasticity Equation



$$F = \frac{N_0 kT}{L_0}\left[\left(\frac{L}{L_0}\right) - \left(\frac{L_0}{L}\right)^2\right]$$

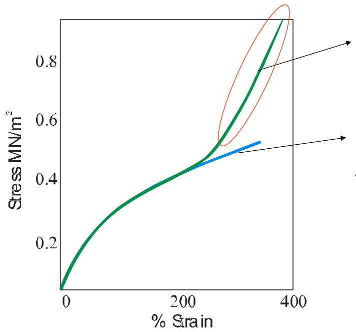
F applied tensile force
N_0 number of cross-links
k Boltzmann constant
T absolute temperature
L_0 initial length (without F)
L final length (with F)

3

3

Rubber Elasticity

Bond stretching in straightened out molecules



Experimental: Matches with Theory at low extensions but deviates at high extensions

Theory: Chain uncoiling

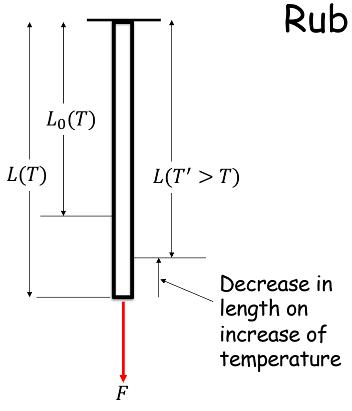
$$F = \frac{N_0 kT}{L_0}\left[\left(\frac{L}{L_0}\right) - \left(\frac{L_0}{L}\right)^2\right]$$

Good at low extensions

4

4

Rubber Elasticity Equation



$$F = \frac{N_0 kT}{L_0}\left[\left(\frac{L}{L_0}\right) - \left(\frac{L_0}{L}\right)^2\right]$$

At constant F

$$T \uparrow \Rightarrow L \downarrow$$

5

5

Elastomers have -ve thermal expansion coefficient, i.e., they CONTRACT on heating!!

EXPERIMENT 8

Section 10.3 of the textbook

6

6

Crystal Defects

Chapter 6

7

Crystal = Lattice + Motif

Is a lattice finite or infinite?

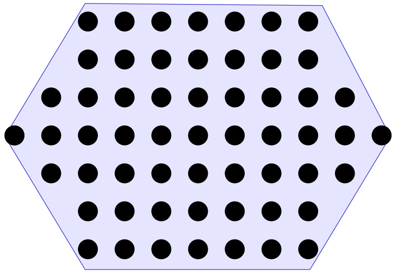
Is a lattice finite or infinite?

Abrupt ending of crystal at free surface

Free surface of a crystal is a defect

8

Free surface: a 2D defect



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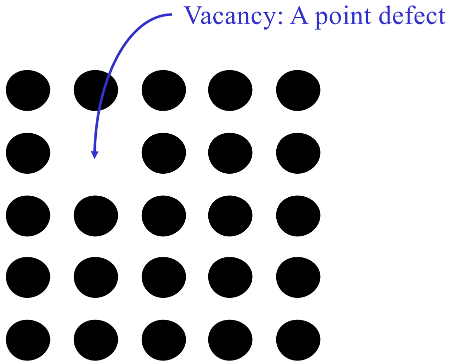

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Defects	*Dimensionality*	*Examples*
Point	0	Vacancy
Line	1	Dislocation
Surface	2	Free surface, Grain boundary Stacking Fault

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Point Defects

Vacancy

12

Point Defects: vacancy

A Guess

There *may* be some vacant sites in a crystal

Surprising Fact

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

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Equilibrium?

Equilibrium means Minimum Gibbs free energy G at constant T and P

A crystal with vacancies has a lower free energy G than a perfect crystal

What is the equilibrium concentration of vacancies?

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Gibbs Free Energy G ?

$G = H - TS$ — T Absolute temperature

H ?

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

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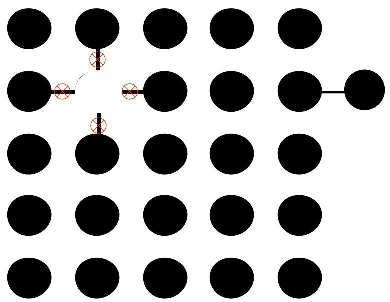
Vacancy increases H of the crystal due to energy required to break bonds



$\Delta H = n\Delta H_f$

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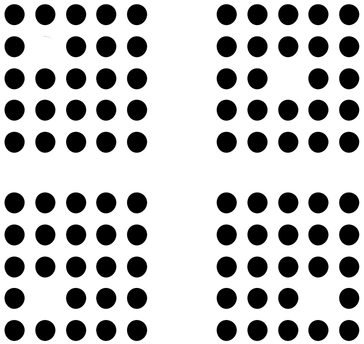
Vacancy increases S of the crystal due to configurational entropy



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Configurational entropy due to vacancy

Number of atoms: N

Number of vacacies: n

Total number of sites: $N+n$

The number of microstates:

$$W = {}^{N+n}C_n = \frac{(N+n)!}{n!N!}$$

Increase in entropy S due to vacancies:

$$\Delta S = k\ln W = k\ln\frac{(N+n)!}{n!N!}$$
$$= k[\ln(N+n)! - \ln n! - \ln N!]$$

18

Stirlings Approximation

$$\ln N! \approx N\ln N - N$$

N	$\ln N!$	$N\ln N - N$
1	0	–1
10	15.10	13.03
100	363.74	360.51

100!=93326215443944152681699238856266700490715968264381621468 5\
92963895217599993229915608941463976156518286253697920 82\
7223758251185210916864000000000000000000000000

19

$$\Delta S = k\ln W = k[\ln(N+n)! - \ln n! - \ln N!]$$

$$\ln N! \approx N\ln N - N$$

$$\Delta S = k[(N+n)\ln(N+n) - n\ln n - N\ln N]$$

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

20

Change in G of a crystal due to vacancy

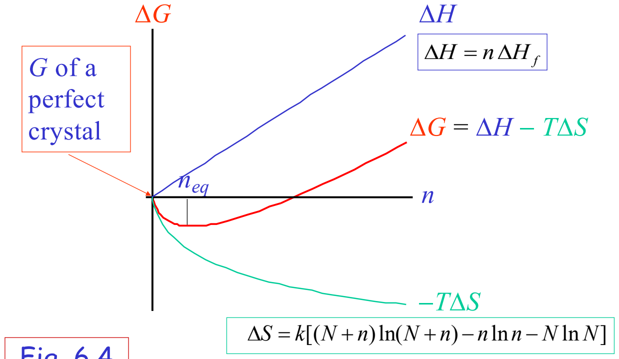

Fig. 6.4

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Equilibrium concentration of vacancy

$$\Delta S = k[(N+n)\ln(N+n) - n\ln n - N\ln N]$$

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

$$\Delta G = n\Delta H_f - Tk[(N+n)\ln(N+n) - n\ln n - N\ln N]$$

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

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

With $n_{eq} << N$

22

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

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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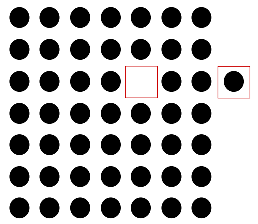
Contribution of vacancy to thermal expansion

Increase in vacancy concentration increases the volume of a crystal



A vacancy adds a volume equal to the volume associated with an atom to the volume of the crystal

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Contribution of vacancy to thermal expansion

Thus vacancy makes a small contribution to the thermal expansion of a crystal

Thermal expansion =

lattice parameter expansion

+

Increase in volume due to vacancy

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Contribution of vacancy to thermal expansion

$$V = Nv$$

V=volume of crystal
v= volume associated with one atom
N=no. of sites (atoms+vacancy)

$$\Delta V = N\,\Delta v + V\,\Delta N$$

$$\frac{\Delta V}{V} = \frac{\Delta v}{v} + \frac{\Delta N}{N}$$

Total expansion | Lattice parameter increase | vacancy

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Experimental determination of n/N

$$\frac{\Delta V}{V} = \frac{\Delta v}{v} + \frac{\Delta N}{N}$$

$$\frac{3\Delta L}{L} = \frac{3\Delta a}{a} + \frac{n}{N}$$

$$\frac{n}{N} = 3\left(\frac{\Delta L}{L} - \frac{\Delta a}{a}\right)$$

Problem 6.2

Linear thermal expansion coefficient

Lattice parameter as a function of temperature

XRD

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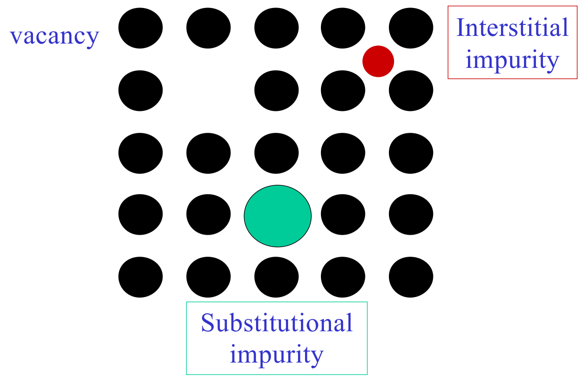
Point Defects



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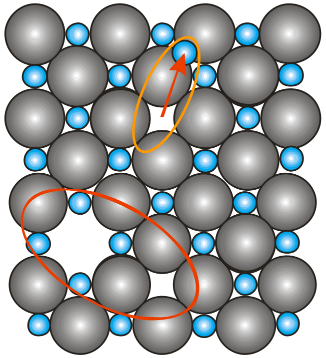
Defects in ionic solids



Frenkel defect

Cation vacancy
+
cation interstitial

Schottky defect

Cation vacancy
+
anion vacancy

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Atomic

or

statistical

interpretation of entropy

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Boltzmann's Tomb

Central Cemetery, Vienna, Austria

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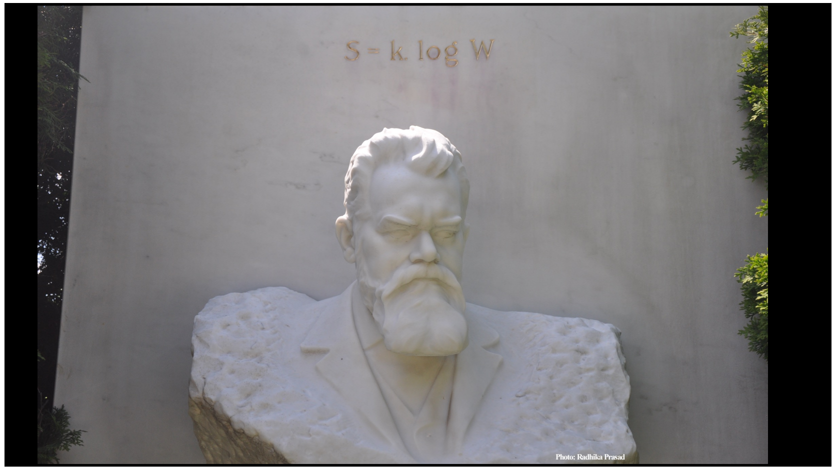

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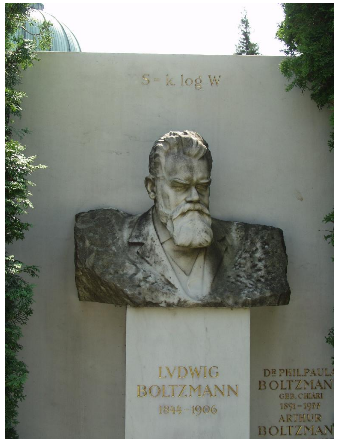
Boltzmann's Epitaph

$$S = k \ln W$$

(2.5)

W is the number of microstates corresponding to a given macrostate



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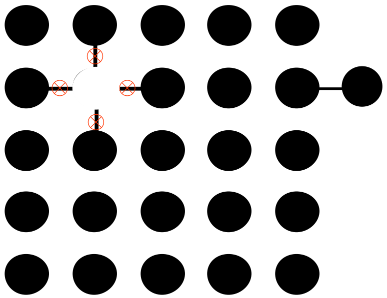
Vacancy increases H of the crystal due to energy required to break bonds



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

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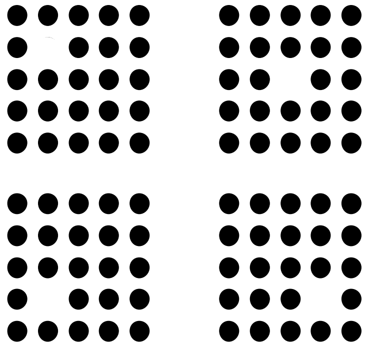
Vacancy increases S of the crystal due to configurational entropy



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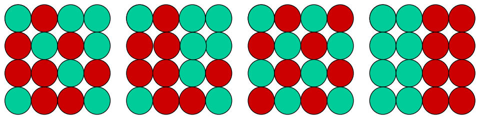
$$W = {}^{N}C_n = \frac{N!}{n!(N-n)!} \qquad (2.9)$$



***N*=16, *n*=8, *W*=12,870**

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Configurational entropy due to vacancy

Number of atoms: N

Number of vacacies: n

Total number of sites: $N+n$

The number of microstates:

$$W = {}^{N+n}C_n = \frac{(N+n)!}{n!N!}$$

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     59296389521759999322991560894146397615651828625369792082\
     7223758251185210916864000000000000000000000000
```

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$$\Delta S = k \ln W = k[\ln(N+n)! - \ln n! - \ln N!]$$

$$\ln N! \approx N \ln N - N$$

$$\Delta S = k[(N+n)\ln(N+n) - n \ln n - N \ln N]$$

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

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Change in G of a crystal due to vacancy

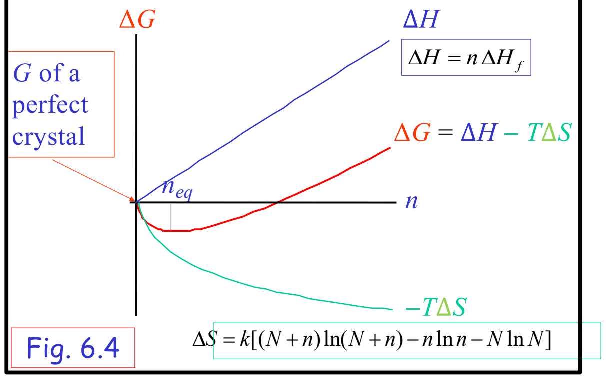

Fig. 6.4

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Equilibrium concentration of vacancy

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Ni	0	$5.59\text{x}10^{-30}$	$1.78\text{x}10^{-10}$

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

$$\frac{n_{eq}}{N} = \exp\left(-\frac{\Delta H_f}{RT}\right)$$ ΔH_f *per mole of vacancy*

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Lecture 14

+

Ch 6 Defects L2: Dislocations

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Line Defects

Dislocations

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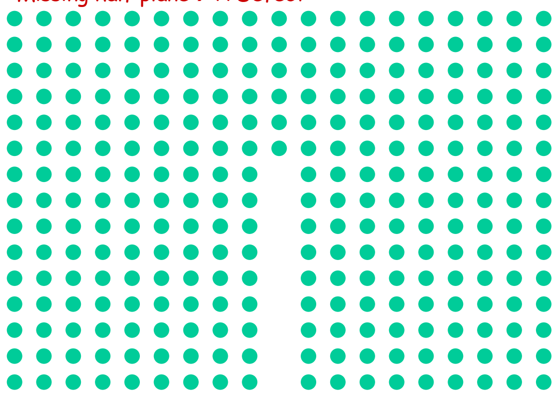
Missing half plane→ A Defect



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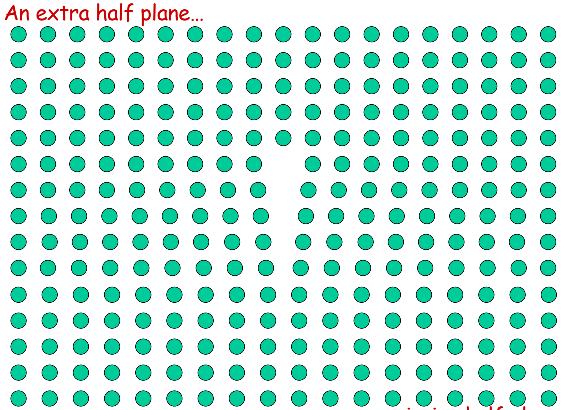
An extra half plane…



…or a missing half plane

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What kind of defect is this?

A line defect?

Or a planar defect?

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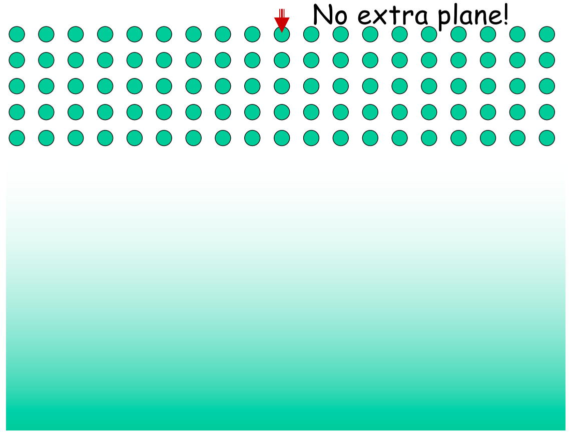

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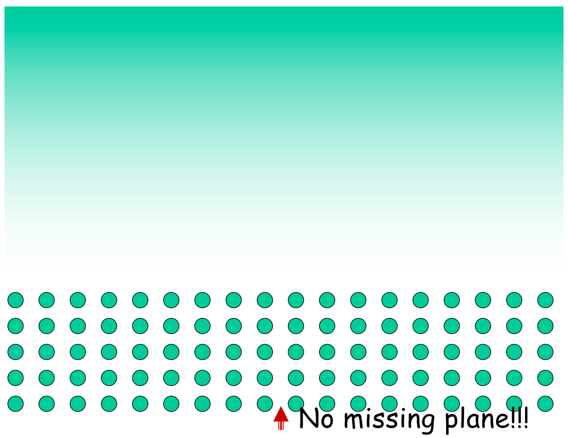

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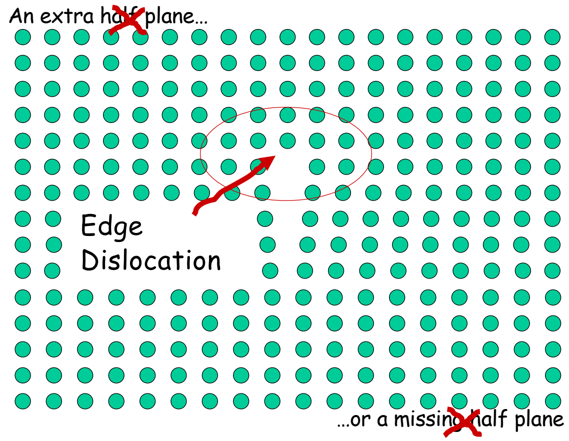

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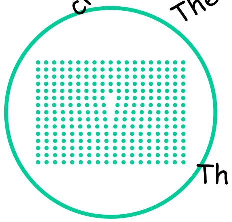
If a plane ends abruptly inside a crystal, we have a defect.

The whole of abruptly ending plane is not a defect

Only the edge of the plane can be considered as a defect



This is a line defect called an
EDGE DISLOCATION

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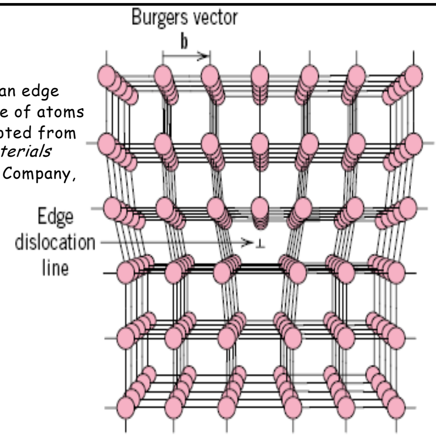
Callister FIGURE 4.3

The atom positions around an edge dislocation; extra half-plane of atoms shown in perspective. (Adapted from A. G. Guy, *Essentials of Materials Science*, McGraw-Hill Book Company, New York, 1976, p. 153.)



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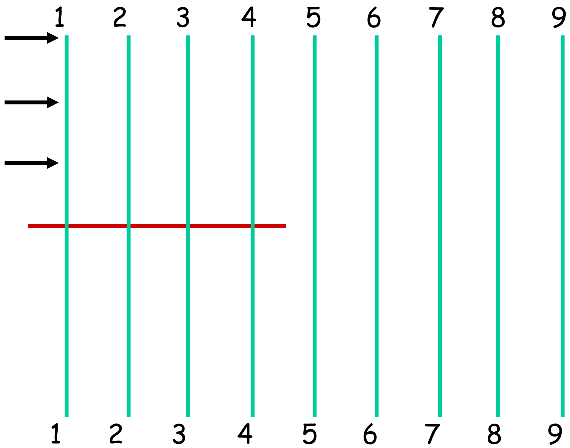

Disloca-
tion as
boundary
between
slip and
no slip
regions
of a slip
plane

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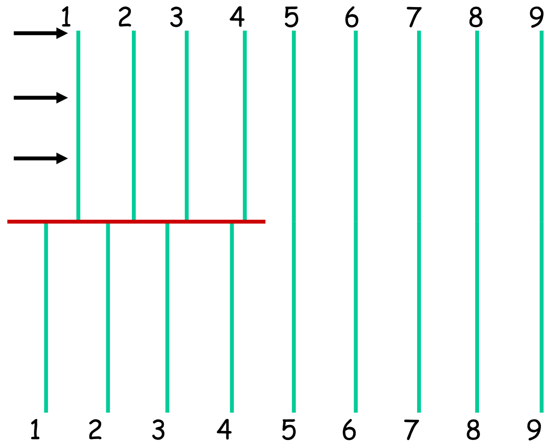

Disloca-
tion as
boundary
between
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of a slip
plane

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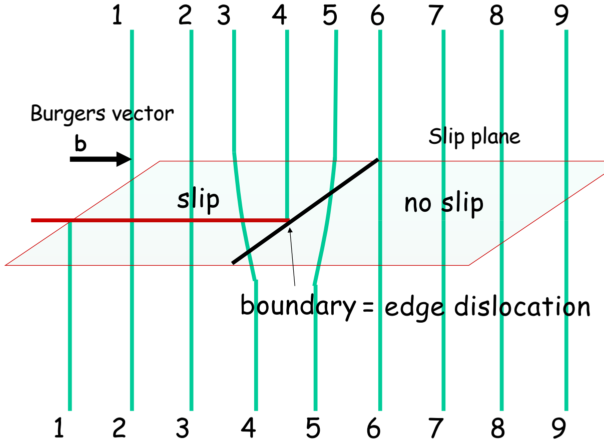

Disloca-tion as boundary between slip and no slip regions of a slip plane

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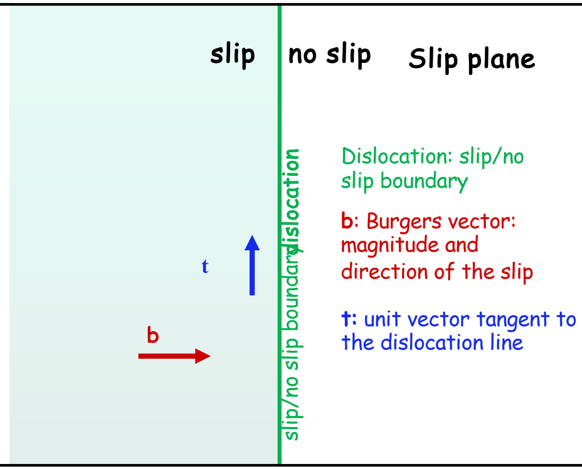

Dislocation as boundary between slip and no slip regions of a slip plane

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Dislocation Line:
A dislocation line is the boundary between slip and no slip regions of a crystal

Burgers vector:
The magnitude and the direction of the slip is represented by a vector **b** called the Burgers vector,

Line vector
A unit vector **t** tangent to the dislocation line is called a tangent vector or the line vector.

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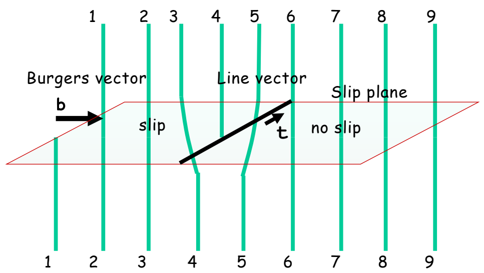
Two ways to describe an EDGE DISLOCATION

1. Bottom edge of an extra half plane
2. Boundary between slip and no-slip regions of a slip plane



What is the relationship between the directions of b and t?

$\boxed{\mathbf{b} \perp \mathbf{t}}$

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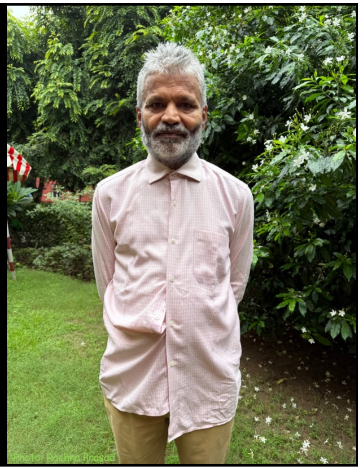
Edge Dislocation in the shirt of a careless professor



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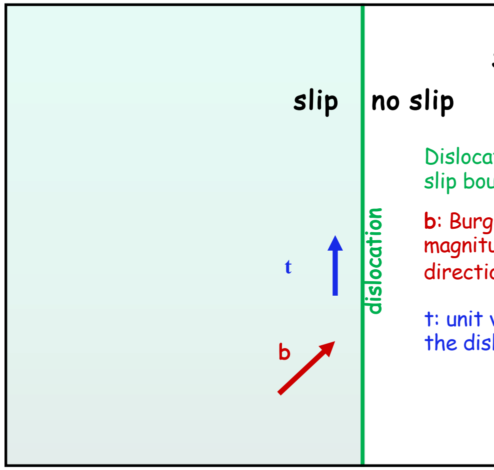
Slip plane



Dislocation: slip/no slip boundary

b: Burgers vector: magnitude and direction of the slip

t: unit vector tangent to the dislocation line

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Types of dislocation based on angle between b and t

$\mathbf{b} \perp \mathbf{t}$ $\quad \theta = 90^\circ$ Edge dislocation

$\mathbf{b} \,||\, \mathbf{t}$ $\quad \theta = 0^\circ, 180^\circ$ Screw dislocation

$\mathbf{b} \not\perp \mathbf{t}$ $\quad \theta \neq 90^\circ$
$\mathbf{b} \not\parallel \mathbf{t}$ $\quad \theta \neq 0^\circ, 180^\circ$ Mixed dislocation

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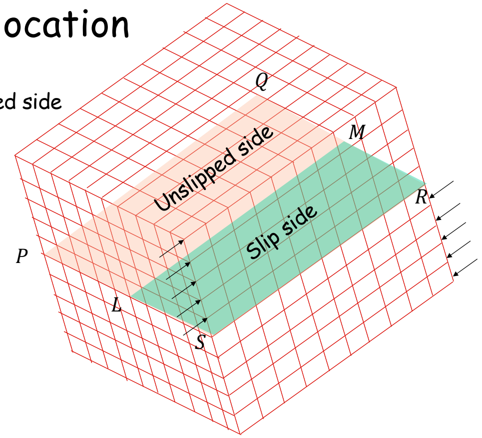
An RH screw dislocation

$PQRS$: Slip plane

$LMRS$: Slip side $LPQM$: Unslipped side



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An RH screw dislocation

$PQRS$: Slip plane

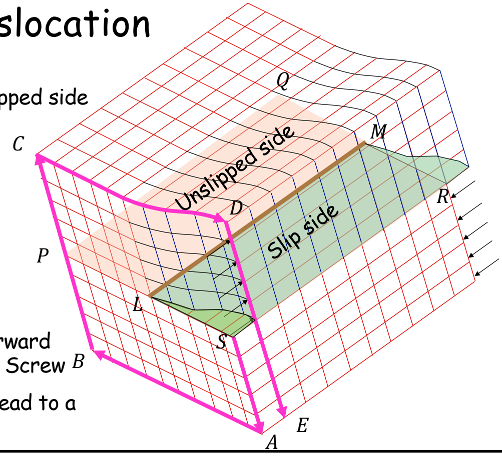
$LMRS$: Slip side $LPQM$: Unslipped side

LM: Boundary between slipped and unslipped side
$\equiv$ *Dislocation Line*

Distinct ∥ planes ⊥ to the dislocation line have become a single helicoidal surface like that of a screw

Clockwise rotation leads to forward movement: Right-Handed (RH) Screw

Slip in opposite direction will lead to a left-handed screw.



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	Positive	Negative
Edge Dislocation	Extra half plane ***above*** the slip plane $\perp$	Extra half plane ***below*** the slip plane $\top$
Screw Dislocation	Left-handed Left-handed screw	Right-handed Right-handed screw

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Lecture 15
+
Ch 6 Defects L3: Dislocations

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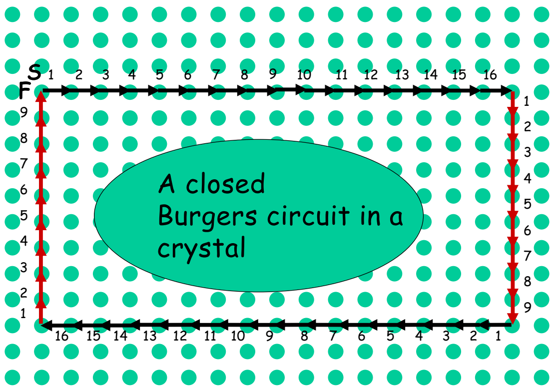
Burgers Circuit



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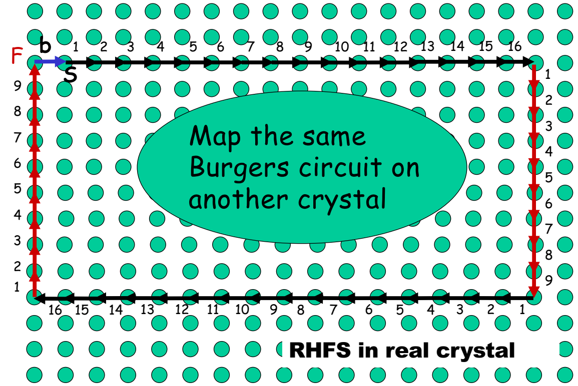

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Two interpretations of Burgers Vector

Magnitude and direction of slip

Closure failure of a Burgers circuit

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Burgers vector

Johannes Martinus BURGERS

~~Burger's vector~~

Burgers vector

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Burgers Circuit and Burgers Vector

Circuit closed in an ideal crystal, Or vice-versa

Fails to close in a real crystal

The closure failure ➔ dislocation

Finish to Start vector ➔ Burgers vector

Or Start to Finish

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Attendance on

https://rollcall.iitd.ac.in

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Conventions for Burgers vector

Closure failure: Real crystal or Ideal crystal

RH or LH

MLL100
RHFS Real Crystal

F->S or S->F

2x2x2=8 conventions

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b for an RH screw dislocation

$PQRS$: Slip plane

$LMRS$: Slip side $LPQM$: Unslipped side

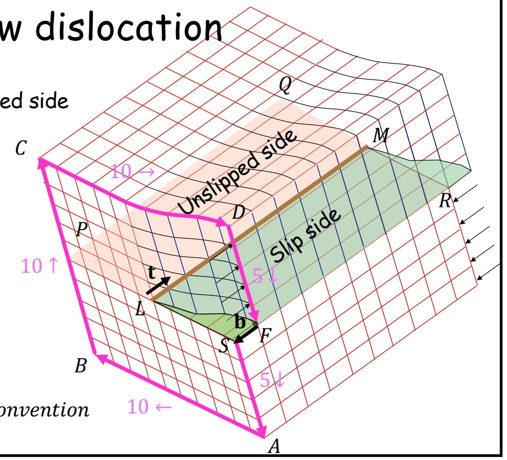
LM: Boundary between slipped and unslipped side $\equiv$ *Dislocation Line*

t: tangent vector

$SABCDF$: RH Burgers circuit wrt to **t**

FS: Burgers Vector **b**

$$\mathbf{b} = -b\mathbf{t}$$ *in our RHFS convention*



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Two equivalent classes of $\mathbf{b}$ conventions

For RH screw dislocation

$$\mathbf{b} = -b\mathbf{t}$$

$\mathbf{b}$ antiparallel to $\mathbf{t}$

$$\mathbf{b} = b\mathbf{t}$$

$\mathbf{b}$ parallel to $\mathbf{t}$

RHFS convetion of MLL100

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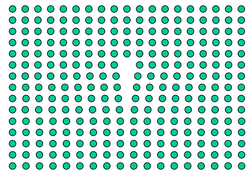
Two types of edge dislocations

$+ve$ ($\perp$)

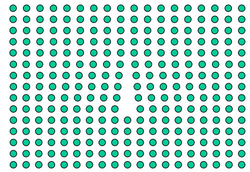


Half plane above the slip plane

180°

You can rotate a $+ve$ edge dislocation to become a $-ve$ edge dislocation

$-ve$ ($\top$)



Half plane below the slip plane

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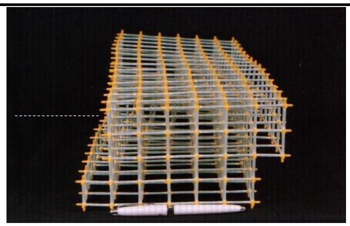
Prof. S. Ranganathan
IISc, Bangalore



SR: Is this an RH or LH dislocation?

RP: Sir, that depends upon the way you look at it.

Conference on Perspectives in Physical Metallurgy and Materials Science, Indian Institute of Science, Bangalore, 12-14 July, 2001.
R. Prasad, "*Dislocation Models for Classroom Demonstrations*"

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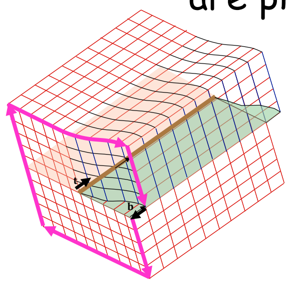
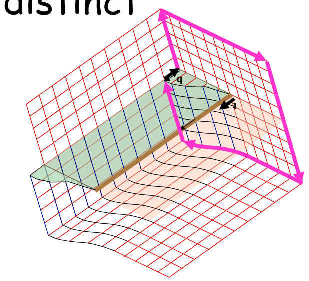
RH and LH Screw dislocations are physically distinct



180°



An RH screw dislocation remains RH even after any rotation

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Positive and negative edge dislocations can be superimposed on each other by $180°$ rotation about the dislocation line

LH and RH screw dislocations cannot be superimposed on each other by rotation.

They can be superimposed on each other by a reflection. Hence, they are chiral pair.

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Slip Plane

A plane containing b and t is called the slip plane of the dislocation line.

Edge dislocation: $\mathbf{b} \perp \mathbf{t} \Rightarrow$ A unique slip plane

Screw dislocation: $\mathbf{b} \parallel \mathbf{t} \Rightarrow$ Non unique slip planes: Any plane passing through both b and t is possible slip plane

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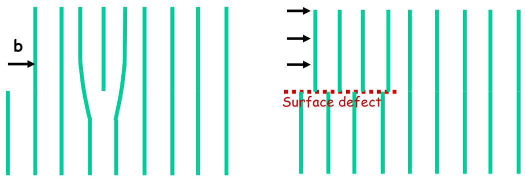
b is a lattice translation



If **b** is not a complete lattice translation then a surface defect (stacking fault) will be associated along with the line defect.

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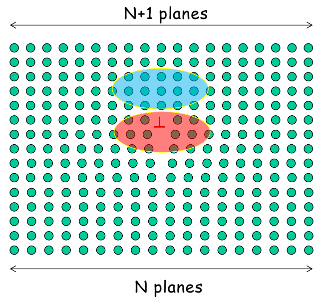
Elastic strain field associated with an edge dislocation



Compression

Above the slip plane

Tension

Below the slip plane

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Line energy of a dislocation

Elastic energy per unit length of a dislocation line

$$E = \frac{1}{2}\mu b^2$$

μ	Shear modulus of the crystal
b	Length of the Burgers vector

Unit: J m^{-1}

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b is the shortest lattice translation

Energy of a dislocation line is proportional to b^2. $E = \frac{1}{2}\mu b^2$

Thus dislocations with short b are preferred.

b is a lattice translation

b is the shortest lattice translation

90

b is the shortest lattice translation

SC	$\langle 100\rangle$
BCC	$\frac{1}{2}\langle 111\rangle$
FCC	$\frac{1}{2}\langle 110\rangle$
DC	$\frac{1}{2}\langle 110\rangle$
NaCl	$\frac{1}{2}\langle 110\rangle$
CsCl	$\langle 100\rangle$

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