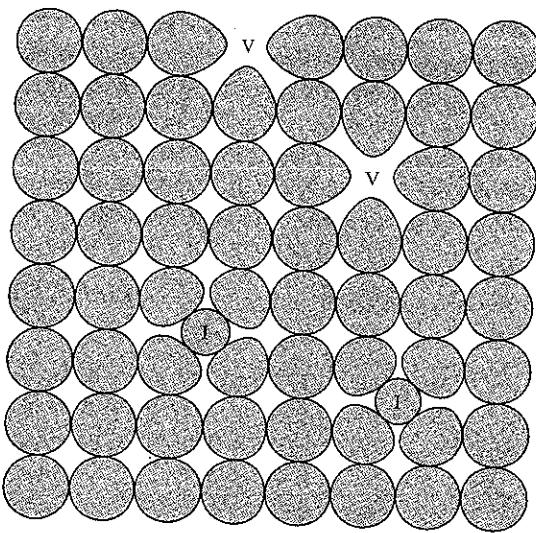


# DEFECT : POINT DEFECT (SMALL)

IN MONOTOMIC SYSTEMS



VACANCIES : SOMETHING MISSING

INTERSTITIALS : SOMETHING EXTRA

LOWER ENERGY

PERFECT CRYSTAL, NO

DEFECT, BUT NOBODY

IS PERFECT

AT  $T=0$

Read  
III-122

what about  $\textcircled{C} T > 0$  ?

SYSTEM DOES NOT MINIMIZE ENERGY BUT GIBBS FREE ENERGY

$$\text{Thermo } dE = -pdV + SdS$$

$$G = E + PV - ST \quad \text{Gibbs}$$

$$\cancel{\text{dE}} \downarrow \quad dG = dE + d(PV) - d(ST)$$

$$dG = \cancel{-pdV} + \underline{TdS} + \cancel{pdV} + Vdp - \cancel{SdT} - SdT$$

$$dG = Vdp - SdT$$

(PROPER THERMODYNAMIC

POTENTIAL TO DESCRIBE SYSTEMS at CONST Press, & Temp

at  $P=\text{const}, T=\text{const}$

$\Rightarrow$  MOST STABLE IS

min G !!!

NOT  $E$  !!

DI

DEFECTS increase Energy (strain stress order)

BUT PRESENCE OF DEFECTS INCREASE ENTROPY  
(MEASURE OF CONFUSION)

$$S = k_B \log \Omega(E)$$

BOLTZMANN DEFINITION

given  $E = \text{Energy}$ ,  $\Omega(E) = \# \text{ of states with energy } E \Rightarrow$

$$dG = VdP - SdT \Leftrightarrow G = E + PV - TS$$

per unit volume  $V=1$

pick 1 vacancy, how many possibilities?  $N!!$  atoms per unit volume.

$$\Rightarrow \sim N \text{ ways} \sim 10^{23}$$

$$\Rightarrow \underline{\Omega \approx 10^{23}} \quad S \approx 100k_B$$

$$\Rightarrow G = E + PV - 100kT !!$$

thermal temperature can be huge !!

$\Rightarrow$  DEFECTS GROW NATURALLY !!

@  $T > 0$  most stable configuration has defects!

FIGHT PERFECTION, HAVE DEFECTS

D2

How MANY DEFECTS?

TO MAKE ONE  
YOU NEED AN  
ACTIVATION ENERGY

① VACANCY  
FORMATION

IF DEFECTS ARE INDEPENDENT  $\Rightarrow$  PROBABILITY THAT  
ONE SITE HAS DEFECT IS BOLTZMANN

$$\text{prob} \sim \exp\left(-\frac{Q_{FV}}{k_B T}\right)$$

$\Rightarrow$  IF  $N_T$  AVAILABLE SITES

$$\Rightarrow N_V = N_T \exp\left(-\frac{Q_{FV}}{kT}\right)$$

in EQUILIBRIUM

$Q_{FV}$  &  $Q_{FI}$   
come from

BOOKS ~~OR~~ OR

QUANTUM MECHANICS CALCULATIONS

IF YOU WILL BE A GRAD STUDENT

IN NY GROUP



ENTROPY : <sup>IN</sup> HOW MANY WAYS I CAN PICK  
 $N_V$  ATOMS ON A POOL OF  $N_T$  ?

$$\mathcal{S} = \ln \left( \frac{N_V}{N_T} \right) = \ln \frac{N_V!}{N_T!(N_T - N_V)!}$$

$$\mathcal{S} = \ln \frac{(N_T)!}{(N_V)(N_T - N_V)!} = \frac{N_T!}{N_V!(N_T - N_V)!}$$

$$\Rightarrow S = k \log \mathcal{S} = k \left[ \log N_T! - \log N_V! - \log (N_T - N_V)! \right]$$

D3

$$\frac{S}{K} = \log N_T! - \log N_V! - \log (N_T - N_V)!$$

USING STERLING FORMULA  $\log n! \sim n(\log n - 1)$

$$= N_T \log N_T - N_T - N_V \log N_V + N_V - (N_T - N_V) \log(N_T - N_V)$$

~~+  $N_T - N_V$~~

$$= N_T \log N_T - N_V \log N_V - (N_T - N_V) \log(N_T - N_V)$$

↓

divide by  $N_T \Rightarrow N_T \left[ \log N_T - \frac{N_V}{N_T} \log N_V - \left(1 - \frac{N_V}{N_T}\right) \log(N_T - N_V) \right]$

$$= N_T \left[ \cancel{\log \frac{N_V}{N_T - N_V}} - \cancel{\frac{N_V}{N_T} \log \frac{N_V}{N_T - N_V}} - \cancel{\left(1 - \frac{N_V}{N_T}\right) \log \frac{N_T - N_V}{N_T}} \right]$$

~~res exchange and get logs together~~

$$= N_T \left[ - \log \frac{N_T - N_V}{N_T} \right]$$

$$\frac{S}{K} = N_T \left[ \log N_T - \frac{N_V}{N_T} \log N_V - \left(1 - \frac{N_V}{N_T}\right) \log(N_T - N_V) \right]$$

add and subtract  $\pm \frac{N_V}{N_T} \log N_T$

$$= N_T \left[ \log N_T \underset{(3)}{+} \frac{N_V}{N_T} \log N_T \underset{(1)}{-} \frac{N_V}{N_T} \log N_V \underset{(4)}{-} \frac{N_V}{N_T} \log(N_T - N_V) \underset{(2)}{+} \frac{N_V}{N_T} \log(N_T - N_V) \right]$$

$$= N_T \left[ - \log \frac{N_T - N_V}{N_T} \underset{(1)+(2)}{-} \frac{N_V}{N_T} \log \frac{N_V}{N_T} \underset{(3)+(5)}{+} \frac{N_V}{N_T} \log \frac{N_T - N_V}{N_T} \right]$$

$$(4)+(6)$$

D4

$$\Rightarrow x = \frac{N_v}{N_T} = \text{concentration of vacancies}$$

$$\Rightarrow \frac{S}{V} = N_T \left[ -\log(1-x) - x \log x + x \log(1-x) \right]$$

$$= -N_T \left[ x \log x + (1-x) \log(1-x) \right]$$

$\Rightarrow$  divide per Volume  $\Rightarrow$  get per unit volume

$$\rho = N_T / V$$

$$S = -k_B \rho \underbrace{\left[ x \log x + (1-x) \log(1-x) \right]}_{<0} \quad 0 < x \leq 1$$

$$\underbrace{\qquad\qquad}_{>0 \text{ BIG} \Rightarrow}$$

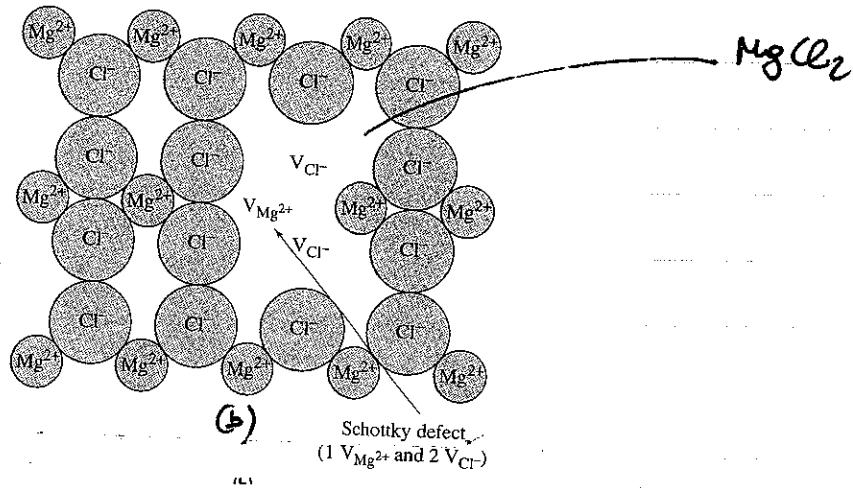
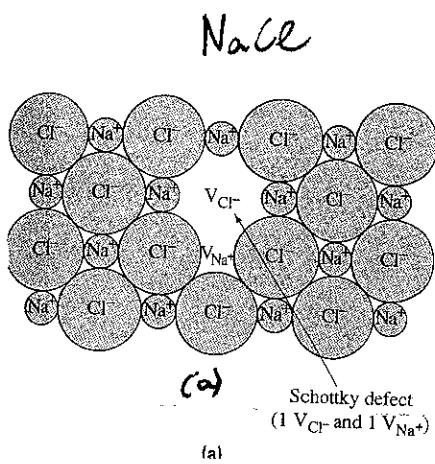
$$TS = -k_B T \rho \underbrace{\left[ x \log x + (1-x) \log(1-x) \right]}_{\text{BIGGG}}$$

DS

# DEFECT IN IONIC CRYSTALS.

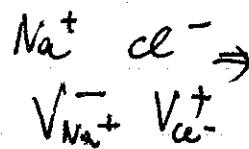
Ionic? TROUBLES

If vacancy makes non neutral  
you ~~have to~~ need two vacancies  
(CLOSE) TO get neutrality.



## SCHOTTKY DEFECTS

FOR NaCl  $\Rightarrow$  Miss 1  $Na^+$   $V_{Na^+}^-$   
& 1  $Cl^-$   $V_{Cl^-}$



For  $MgCl_2 \Rightarrow$  Miss. 1  $Mg^{2+}$   
1  $Cl^-$   
1  $Cl^-$   $\Rightarrow$   $V_{Mg^{2+}}^-$   
 $V_{Cl^-}^+$   
 $V_{Cl^-}^+$

## OTHER POINT DEFECTS IN IONICS

# FRENKEL DEFECTS !

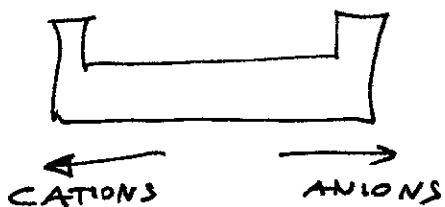
## INTERSTITIAL OF AN ION

BUT TO RESPECT NEUTRALITY YOU NEED

A VACANCY OF THE SAME ION SOMEWHERE

(WHY NOT AN INTERSTITIAL OF THE OTHER SPECIE? BECAUSE

CATIONS (+) ARE SMALL      ANIONS (-) ARE BIG



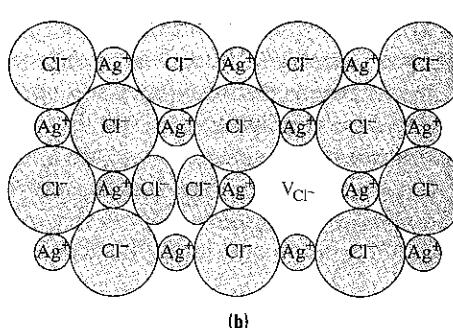
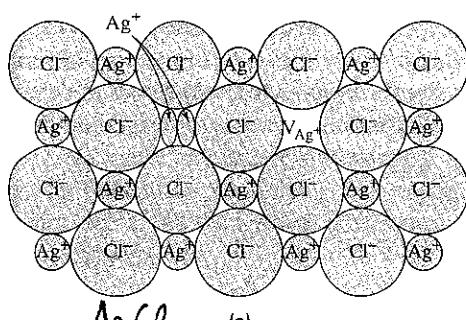
↳ ONLY CATIONS  
AVAILABLE FOR  
INTERSTITIAL

BEING HONEST: THIS IS NOT REALLY TRUE

## MATHEMATICALLY

$$\text{CY} \quad \text{IN ACT ENERGY} \quad Q_{\text{PI}}^{\text{AMON}} \quad >> \quad Q_{\text{FI}}^{\text{CATION}} \quad \text{prob:}$$

$$\Rightarrow \exp\left(-\frac{Q^{AN}}{kT}\right) \ll \exp\left(-\frac{Q^{CA}}{kT}\right)$$



**FIGURE 4.2-3** Frenkel defects in AgCl. The defect consists of vacancy/interstitial pairs. Frenkel defects involving cations (**a**) are more common than those involving anions (**b**), since cations are usually smaller.

$\rightarrow V_{ce}^+$  &  $I_{ce}^-$   
are more  
RARE

四

$V_g^+$  &  $I_{A_g^+}^+$  Frequent

## CONCENTRATIONS OF DEFECTS

FRENKEL  $\downarrow$  Concentration

$$C_V = \frac{N_V}{N_T} = \exp\left(-\frac{\Phi_{FV1}}{2RT}\right) = \frac{N_i}{N_T} = c_i$$

$\uparrow$   
because 2 defects are built

SCHOTTKY

$$C_{V,\text{corr}} = \frac{N_{V,\text{corr}}}{N_T} = \exp\left(-\frac{\Phi_{FVP}}{2RT}\right) = \frac{N_{V,\text{AN}}}{N_T} = c_{AN,\text{corr}}$$

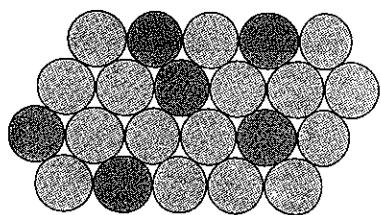
CAN BE PROOVED FOR SCHOTTKY IN  $M_nX_p$  compounds

$M_nX_p \xrightarrow{\text{?}} pC_{V,\text{corr}} = nP \left[ -\frac{\Phi_{FVC}}{(n^2 + p^2)RT} \right] = nC_{V,\text{AN}}$

## IMPURITIES IN CRYSTALS

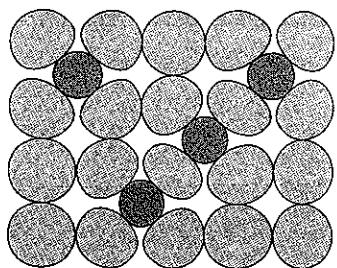
Matrix of atom = SOLVENT  
+ SOLUTE

SUBSTITUTION (SOLUTE)  
INTERSTITIAL (SOLUTE)



○ = Solvent atom  
● = Solute atom

SUBSTITUTIONAL  
MUST BE  
SIMILAR SIZES



○ = Solvent  
● = Interstitial (solute)

INTERSTITIAL  
MUST BE  
COMPATIBLE  
SIZES

## SUBSTITUTIONAL

EXAMPLE : Steel (IRON + C)

C > Fe dimension 0.022% @ 725°C  
1000 K

Big C makes IRON STRONGER

(prevents movement  
of DISLOCATIONS)

OTHER IMPURITIES

H, O, N → small, BAD

But if AlN → BIG PARTICLES  
SYSTEM VERY STRONG

RULES

HUME-ROTHERY

1) Δ size  $\leq 15\%$

2) similar electronegativity (giving, to  $\text{by } \text{e}^-$ )

3) similar valence (how many electrons)

4) same crystal structure (for bonds)  
(relax condition)

FCC & HCP can exist

NO 1)  $\Rightarrow$  STRAIN

NO (2,3)  $\Rightarrow$  different BOND CHARACTERISTICS

NO 4)  $\Rightarrow$  Because atoms prefer similar environments

STEEL : Fe is BCC @ T<sub>room</sub>, BCC HAS BRITTLE TRANSITION FRACTURES TEMPERATURE

add Ni, (2  $\Rightarrow$  SOLID SOLUTION}  
8% 18% FCC @ T<sub>room</sub>)  $\left. \begin{array}{l} \text{BETTER} \\ \text{ELECTRICAL} \\ \text{PROPERTIES:} \\ \text{BETTER} \\ \text{CORROSION RESISTANCE} \end{array} \right\}$

D9

## ASSIGNMENT

- DO IMPURITIES IN POLYMERIC CRYSTALS 119

→ 4.3-2 EXAMPLE

4.3-1

IMPURITIES IN IONIC CRYSTALS  $\Rightarrow$  need to measure  
electroneutrality.

- EXAMPLE 4.3-3

- STUDY 111 - 122

~~WELL~~



# LINEAR DEFECTS

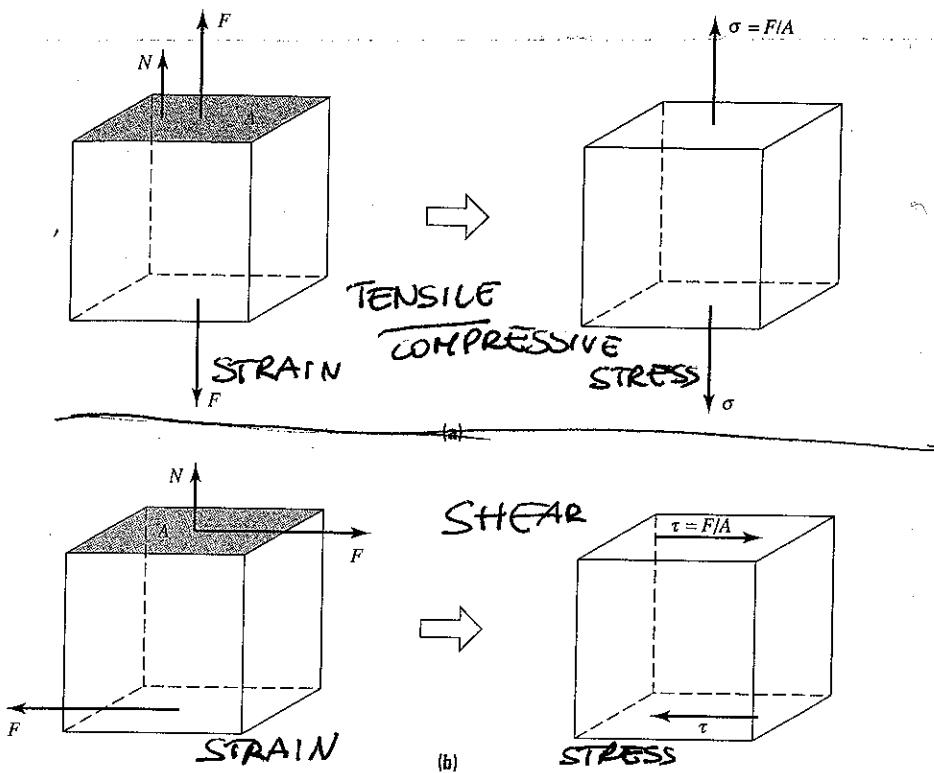


FIGURE 5.2-1 Illustration of (a) a normal stress, given the symbol  $\sigma$  and defined as  $F/A$  when  $F$  is parallel to the plane normal  $N$ ; and (b) a shear stress, given the symbol  $\tau$  and defined as  $F/A$  when  $F$  is perpendicular to  $N$ .

→ PULL TOO MUCH  
YOU GET  
DEFORMATION

SLIP PLANE  
SLIP DIRECTION

SLIP  
SYSTEM.  
(NOT ONLY BY  
SHEAR)

DIO

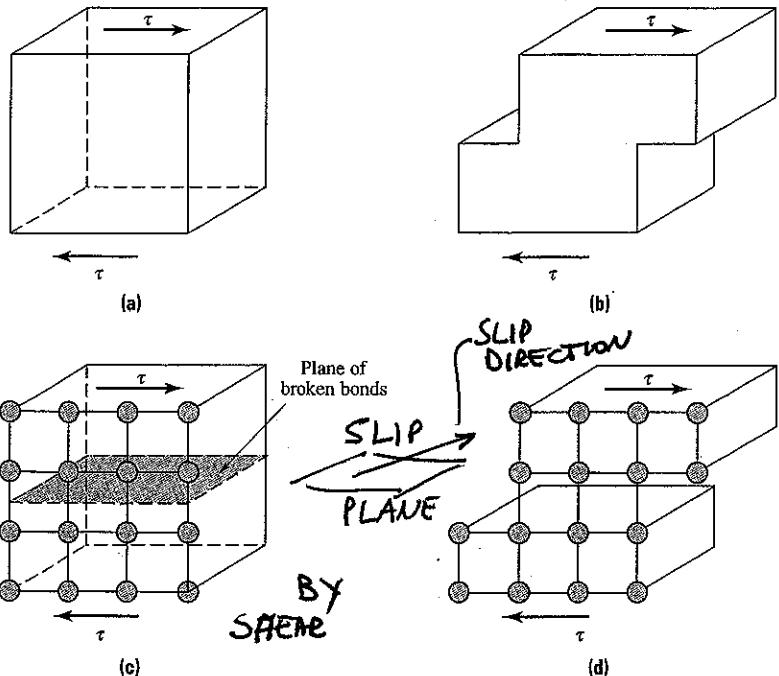
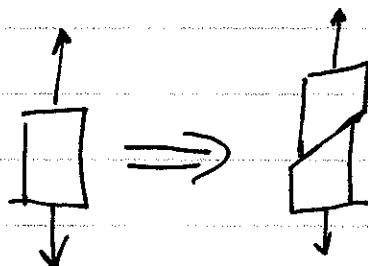
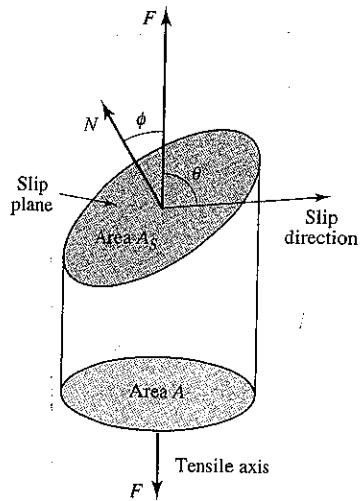


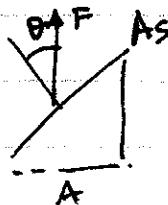
FIGURE 5.2-3 Model for computation of the theoretical critical resolved shear strength. Under the application of a shear stress  $\tau$ , the top plane of atoms is assumed to slide over the bottom plane as a unit to produce permanent offset. Parts (a) and (b) represent a macroscopic view, while parts (c) and (d) represent an atomic scale view, of the process. As discussed in the text, this model requires that an entire plane of bonds be broken simultaneously.

TENSILE STRESS PRODUCES SLIP TOO !!



DEFORMATION

$\theta = \text{angle FORCE} \wedge \text{SLIP DIRECTION}$   
 $\phi = \text{angle FORCE} \wedge \text{NORMAL SLIP PLANE}$



$$A_s = \frac{A}{\cos \phi} \Rightarrow \text{area of the slip plane.}$$

$F_s = F \cos \theta \Rightarrow \text{Force parallel to the slip plane}$   
~~in the direction of~~  
~~the slip direction.~~

$$\tau = \frac{F_s}{A_s} = \frac{F \cos \theta}{A / \cos \phi} = \sigma \cos \theta \cos \phi$$

in critical shear

$\Rightarrow$  to get slip  $\Rightarrow$  stress  
 critical tensile to get  
 deformation

Metal	Experimental	Theoretical ( $E/10$ )
Cu	0.10	$1.03 \times 10^3$
Ag	0.37	$9.2 \times 10^3$
Al	0.73	$7.0 \times 10^3$
Fe	2.44	$21.0 \times 10^3$
Ti	3.72	$11.0 \times 10^3$

$\approx E/10$

THEORETICAL

BAD!! need defects

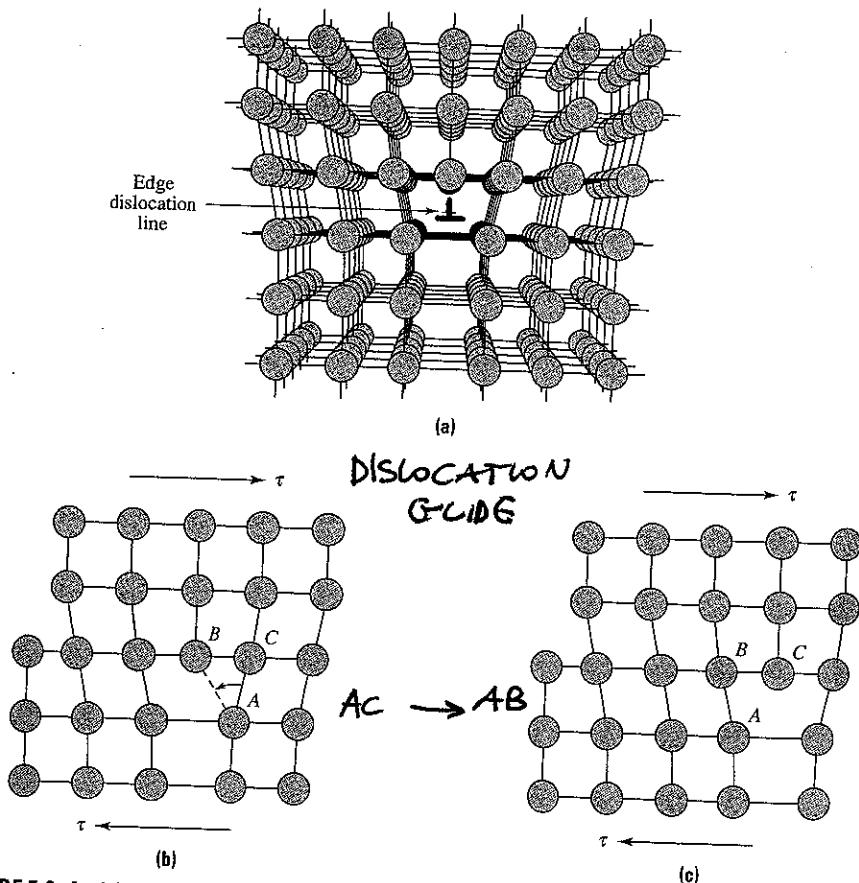
BAD THEORY

SCHMID'S LAW

$$\sigma_{CR} = \frac{\tau_{CR}}{\cos \theta \cos \phi}$$

# SLIP IS MUCH EASIER THAN THEORETICAL

→ HAVE DEFECTS.



**FIGURE 5.2-4** (a) A 3-D representation of an edge dislocation. The dislocation is not the extra half plane of atoms that has been inserted but rather the line that runs along the bottom of the extra half plane. Parts (b) and (c) illustrate the motion of an edge dislocation in response to the application of a shear stress  $\tau$ . The details of this motion are described in the text.

## DISLOCATION

↗ ↘

## EXTRA PLANE

THEY FORM

1) NATURALLY  
GROWING CRYSTAL

2) OTHER DEFEATS  
RELEASING  
ENERGY

3) INTERACTIONS  
BETWEEN  
DISLOCATION

↓

SINCE ↗

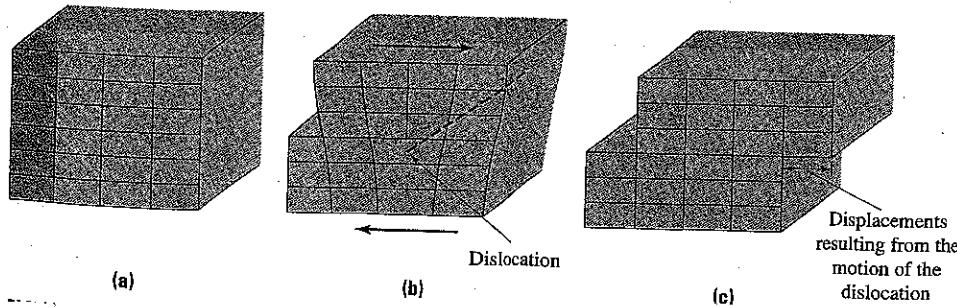
MOVEMENT

IS EASIER

DEFORMATION

ONE PLANE AT  
EACH TIME

DISLOCATION GLIDE → MOVES (IF FORCE APPLIED)  
UNTIL IT'S OUT OF THE CRYSTAL



# HOW TO MEASURE DISLOCATIONS?

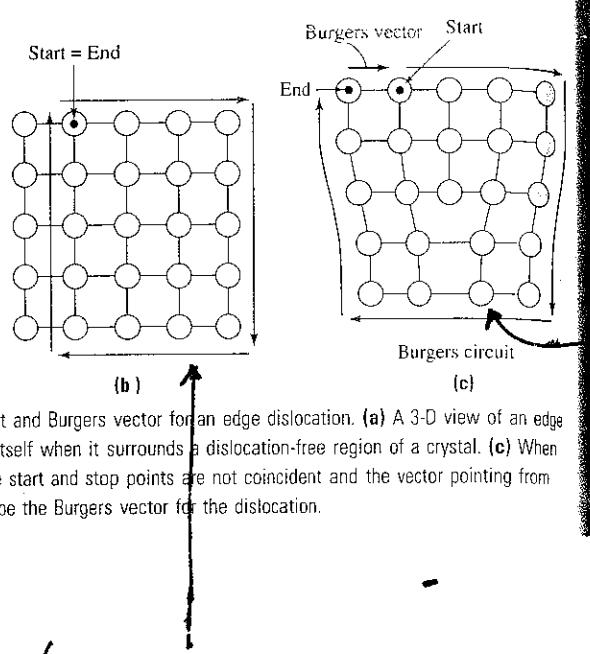
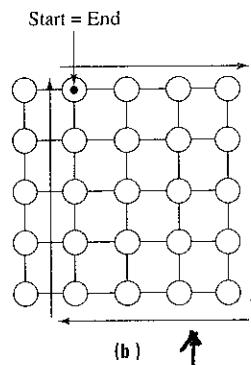
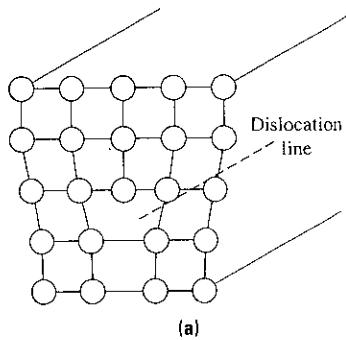
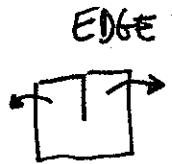
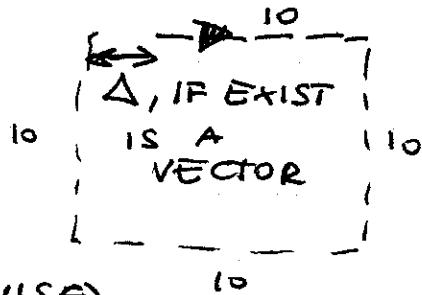
MAKE A CIRCLE ~~IN~~ AROUND ATOMS AND SEE  
WHAT IS LEFT :



~~BURGER~~

BURGER CIRCLE (CLOCKWISE)

$\Rightarrow$  BURGER VECTOR!



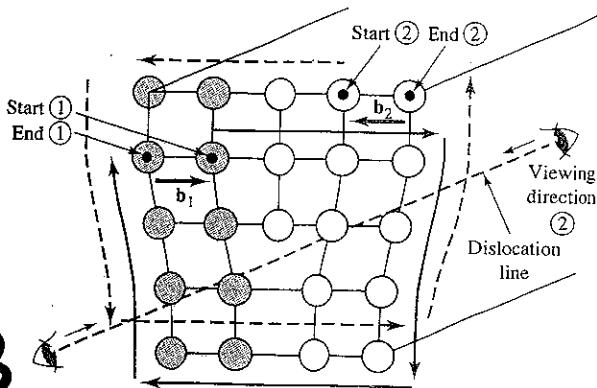
BURGER  
IS  
INVARIANT

DEFECT  
 $b = \rightarrow$

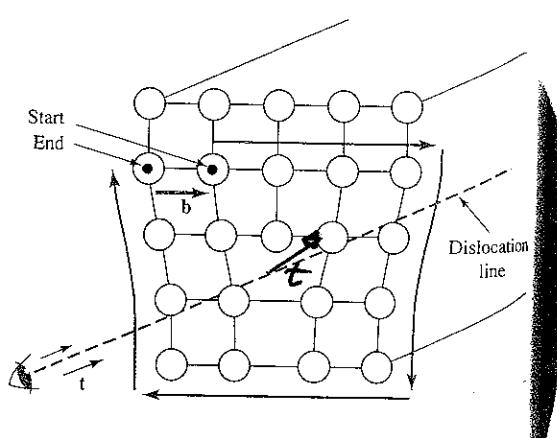
CLOCKWISE RESPECT

PERFECT  $\Rightarrow b = 0$

TO THE SCREW DRIVER RULE APPLIED TO THE  
UNIT TANGENT VECTOR  $t$ , TANGENT TO THE  
DISLOCATION, LOCALLY  $\Rightarrow$



D13



b

v

$b \perp t$  all are in the slip plane

(EDGE  
 $b \perp t$ )

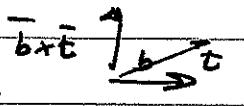
⇒ MILLER INDICES OF

SLIP PLANE IN CUBIC SYSTEMS ARE  $\bar{b} \bar{x} \bar{t}$

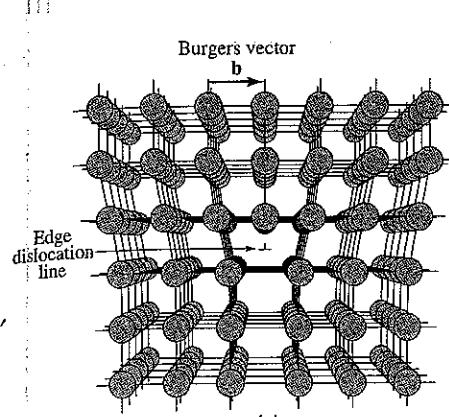
because

PLANE  $(h+k+l) \perp$  direction  $(h+k+l)$

in CUBIC SYSTEMS



## SCREW DISLOCATION

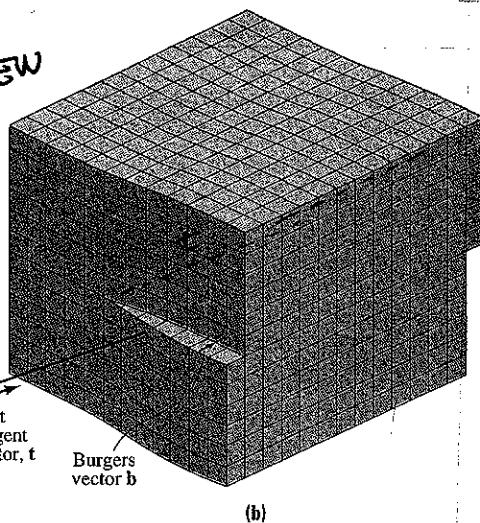


SCREW  
 $b//t$

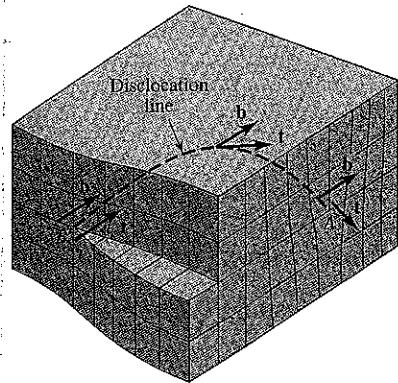
Dislocation line

Unit tangent vector,  $t$   
Burgers vector  $b$

(a)

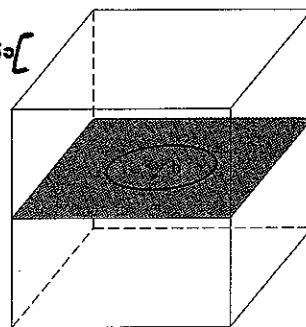


(b)



(c)

MIXED  
 $b^2 t \epsilon \rightarrow 0, g_0$



(d)

BURGER IS INVARIANT

SCREW

$b//t$

MIX

MIXED,

loop

DIS

FIGURE 5.2-8 Illustrations of four types of dislocations: (a) an edge dislocation, (b) a screw dislocation, (c) a mixed dislocation, and (d) a dislocation loop. (Source: (b) William D. Callister, Jr., Materials Science and Engineering, 2nd ed., Copyright © 1991 by John Wiley & Sons. Used with permission of John Wiley & Sons, Inc. (c) James F. Shackelford, Introduction to Materials Science for Engineering, 3rd ed. Copyright © Macmillan Publishing Company, Inc. Used with permission of Macmillan College Publishing Company.)

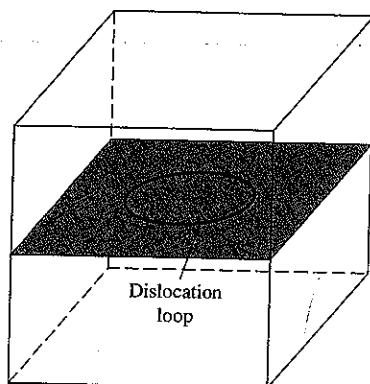
D14

- BURGER VECTOR IS INVARIANT!!
- DISLOCATION ENDS IN ANOTHER DISL. ON ITSELF, OR AT THE SURFACE

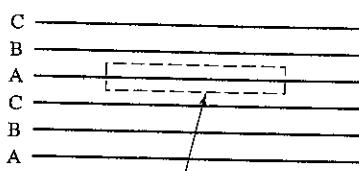
loops

DISLOCATION

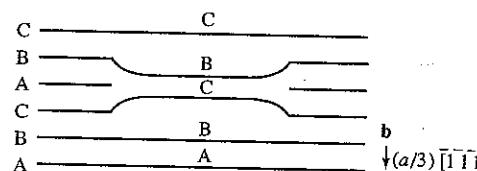
loop



(a)



(b)



(c)

CLIMBING!!

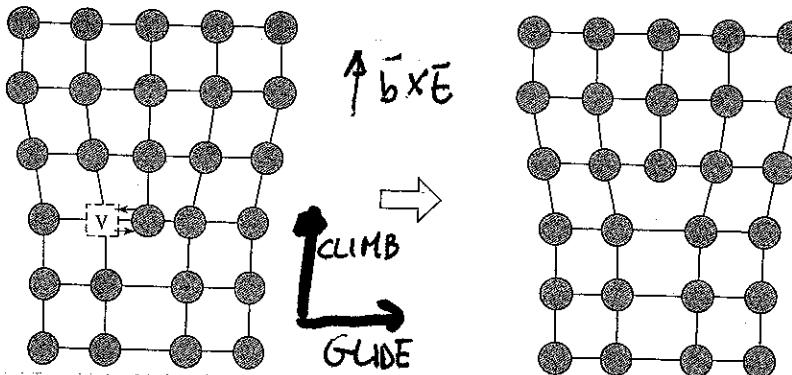


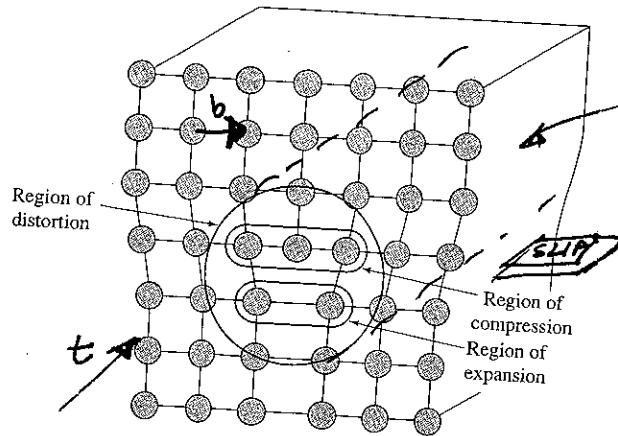
FIGURE 5.2-10 Climb of edge dislocation. The dislocation moves up one atomic spacing when it absorbs a vacancy.

DIS

# SLIP PLANES (where is?)

WHERE DOES IT MOVE?

dislocation = elastic energy in a region



CYLINDER CONTAINING  
"DISTORTIONAL" ENERGY

RADIUS  $\propto |\vec{b}|$

$\Rightarrow$  ~~stack~~

Volume per UNIT LENGTH  
 $\propto |\vec{b}|^2$

$E_{\text{dislocation}} \propto |\vec{b}|^2 \Rightarrow$  MINIMUM ENERGY

$\Rightarrow$  MINIMUM BURGERS VECTORS

BURGER VECTOR: ~~Minimum energy~~

vector contained in the slip plane, vector connecting two ~~atoms~~  $\Rightarrow$  look for shortest possible in  $\{hkl\}$  planes

FCC LATTICE ATOMS

POSSIBLE BURGERS VECTORS CONTAINED IN  $\{111\}$  PLANE

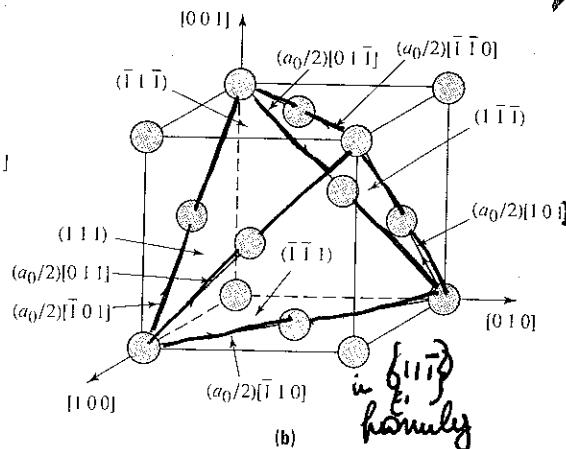
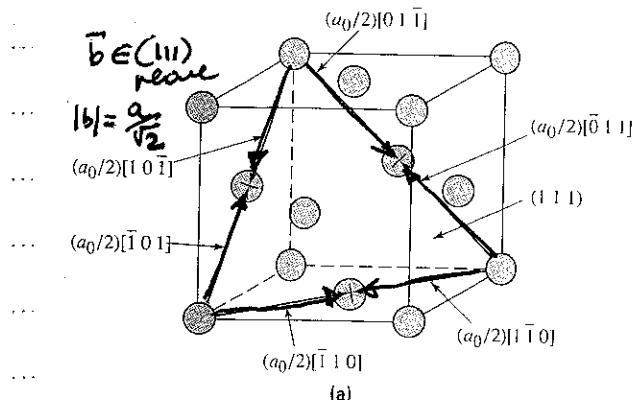


FIGURE 5.2-12 Burgers vectors and slip systems in the FCC structure: (a) an FCC unit cell showing the location of the  $(111)$  slip plane and the six valid Burgers vectors in the  $(111)$  plane. Note that the Burgers vectors occur in pairs, such that only three of the Burgers vectors are independent. (b) The tetrahedron formed by four members of the  $\{111\}$  family of planes in the FCC structure, including the three independent Burgers vectors in each plane.

FOR FCC  $\{111\}$  FAMILY D16

$\Rightarrow \{b\}$  in  $\{11\bar{1}\}$  family of planes:  
 $\rightarrow (111)(11\bar{1})(1\bar{1}1)(\bar{1}11)(1\bar{1}\bar{1})(\bar{1}\bar{1}1)(\bar{1}1\bar{1})(1\bar{1}\bar{1})$   
 FAMILY

$|b|$  in such family is  $a/\sqrt{2}$  long.

there are 12 possible BURGERS VECTORS

IN FCC 12 POSSIBLE BURGERS VECTORS  
 in  $\{111\}$  family,  $\Rightarrow$  SLIP PLANE IS ONE  
 OF THE PLANES in  $\{111\}$

SLIP DIRECTION IS ONE OF THE DIRECTION

OF BURGERS.  $\Rightarrow \frac{a}{2} <110>$  family of direction!

$\Rightarrow$  12 slip systems FCC  
 (directions + PLANES)

< more > where you want  
 and put  $\pm 1 \Rightarrow 1 \text{ or } \bar{1}$   
 everywhere !!

BCC is NOT CLOSED PACKED  $\Rightarrow$  SOLUTION IS COMPLICATED

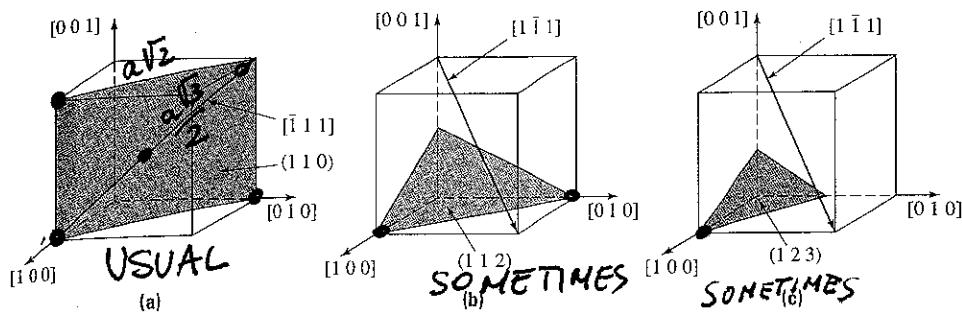


FIGURE 5.2-13 Slip planes and directions in the BCC structure: (a) a member of the  $\{110\}\{111\}$  system, (b) a member of the  $\{112\}\{111\}$  system, and (c) a member of the  $\{123\}\{111\}$  system.

from  $\{110\}$   
 family get  
 42, then  
 36 from  
 others

$\Rightarrow$  a total of 48 slip systems

D17

IN SPECIFICATIONS, MURPHY'S LAW  
 SUPERSEDES OHM'S.

HCP. (a mess!)

SLIP ALONG BASAL PLANES.

+ ~~skip~~  
OTHER SLIP DEPENDS  
ON LOADING

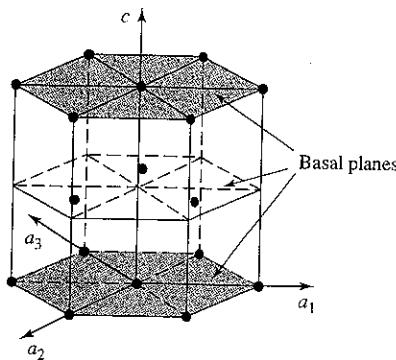


FIGURE 5.2-14 The slip planes and directions in the HCP structure are the basal planes and the  $a$  directions.

TABLE 5.2-2 Primary slip systems in the BCC, FCC, and HCP systems.

Crystal structure	Slip planes	Slip directions	Number of slip systems
FCC	{1 1 1}	<1 1 0>	12
BCC	{1 1 0}	<1 1 1>	12
	{2 1 1}	<1 1 1>	12
	{3 2 1}	<1 1 1>	24
HCP	Basal	$a$	3

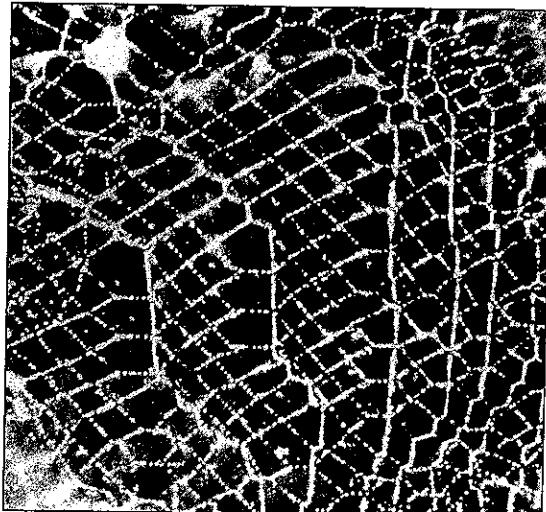
ANYWAY: THE  
MOST COMMON  
IS THE BASAL  
(B SYSTEMS)  
SLIP

SUMMARY: HINTS

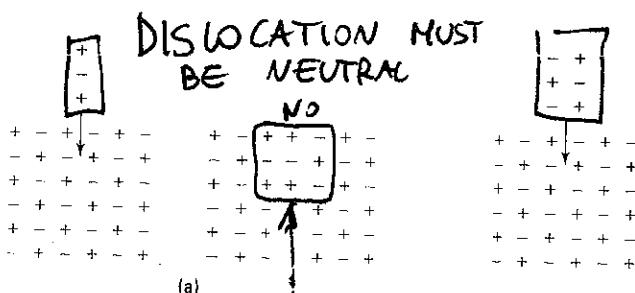
FOR THE EXAM YOU  
MUST BE ABLE TO  
CALCULATE  
 $|b|$  &  $\bar{e}$  FOR THIS  
SYSTEMS LISTED  
HERE

# DISLOCATIONS IN IONS

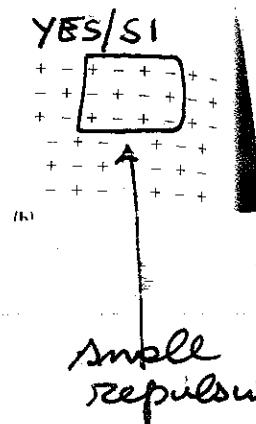
Always remember that BURGER VECTOR  
MUST CONNECT EQUIVALENT POINTS = N.O.



KCL



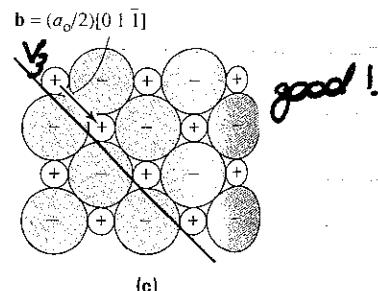
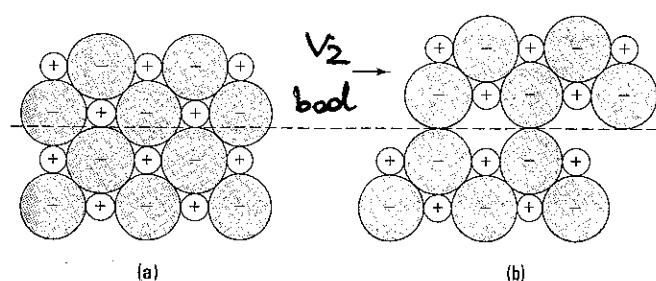
Bad  
Repulsion



N.O.  
V<sub>2</sub> NOT good way?  
 $|V_3| < |V_2|$

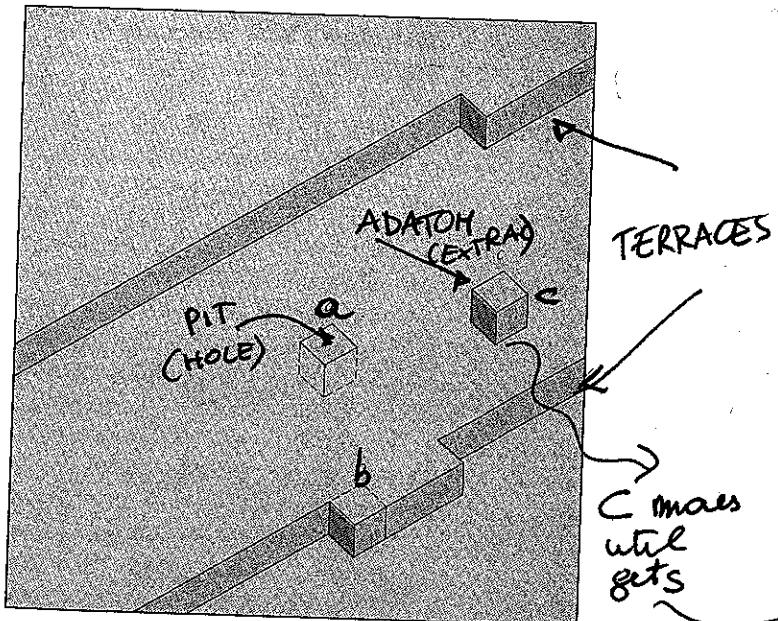
$\uparrow b$

ASSIGNMENT  
Ex: 5.2-4  
Burgers for CsCl



DIG

# PLANAR DEFECTS



**FIGURE 5.3-1** Schematic illustration of atoms (assumed to be cubes) adsorbed at a free surface. The lowest-energy location for adsorption is at *a*, since the atom is attached with a reduction in the surface area and, hence, a reduction in the surface energy. At position *b* the surface energy remains unchanged, while at *c* the energy increases, since the surface area increases. The site at *b* is a "repeatable step," since the process may be repeated continually with no change in energy.

MIMIMIZE SURFACE ENERGY  
(PROP  $\propto$  NUMBER OF OPEN BONDS)

absorbed by a terrace  
(b) USUALLY

ADATOM & PIT HAVE HIGH ENERGY  $\Rightarrow$  TRY TO GET  
ADSORBED BY TERRACES  
REMEMBER THAT @  $T > 0$   
NEED FOR DEFECTS SINCE ENTROPY!!!!

TERRACES GROWTH-!!

ASSIGNMENT STUDY  $\rightarrow$  S.3.1  
S.3.2  
S.3.3 (NO S.3.4)  
S.3.5  
S.4 //

D20