Material Science

3C46

Part 1

Background

Introduction

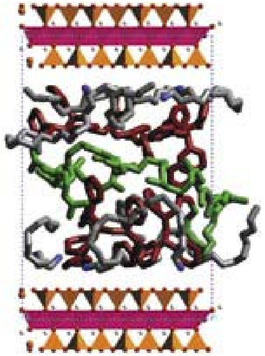
- What is Material Science?
  - The understanding of how the structure and bonding of a material controls the properties
  - The understanding of how the properties of a material can be controlled by processing
  - Material selection for a wide range of applications
- What do Material Scientists do?
  - They determine the structure of materials
  - They measure the properties of materials
  - They devise ways of processing materials
  - They think about how a material is suited to the purpose it serves and how it could be enhanced to give better performance

Material Science or Condensed Matter

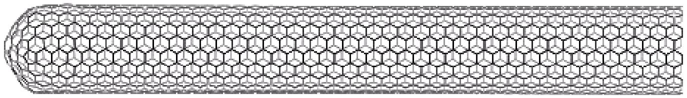
Condensed Matter Physics	**Material science**
Understanding why materials are like they are.	Science of using them for a purpose?
Why is Fe magnetic?	How do we produce a hard or soft magnet?
How does a transistor work?	How do we dope Si to be uniformly p-type?
What makes polymers hard or soft?	How do we shape hard polymers?
How does a laser work?	How can we improve the efficiency of a laser?
What is the electronic structure of Al?	When is Al best for drinks cans?
Why is Nb superconducting?	Can we make and use a high temperature superconductor?

New Materials- At research stage

- Nanostructured materials
  - Grain size ~ nm
- Nanocomposites
  - Features on scale of 10^{-9} m
  - Properties dramatically different to microcomposites
  - eg layers of silicate in a copolymer (Cornell)



- Light emitting polymers
  - Thin, flexible displays
  - Electronic news papers?
- Fullerenes and buckytubes (Nobel prize)
  - Remarkable physical and electronic propert



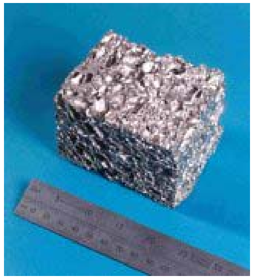
- Ceramic superconductors (Nobel prize)
  - Eg $YBa_2Cu_3O_7$ (T_c = 90 K)
  - HgBaCuO (Tc = 133K)

New Materials - Early Commercialisation

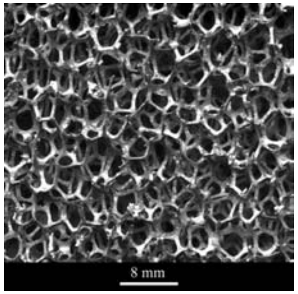
Shape-memory alloys (NiTi alloys)

  - Return to original shape on heating
  - Medical applications
  - Orthodontics

- Giant Magnetoresistance films
  - Resistance drops dramatically with applied field
  - Applications in hard drives
- Metal foams
  - Light stiff structures
  - Efficient energy adsorption
- Amorphous metals
  - Transformer cores
  - Skis, golf clubs, tennis rackets
  - Razor blades

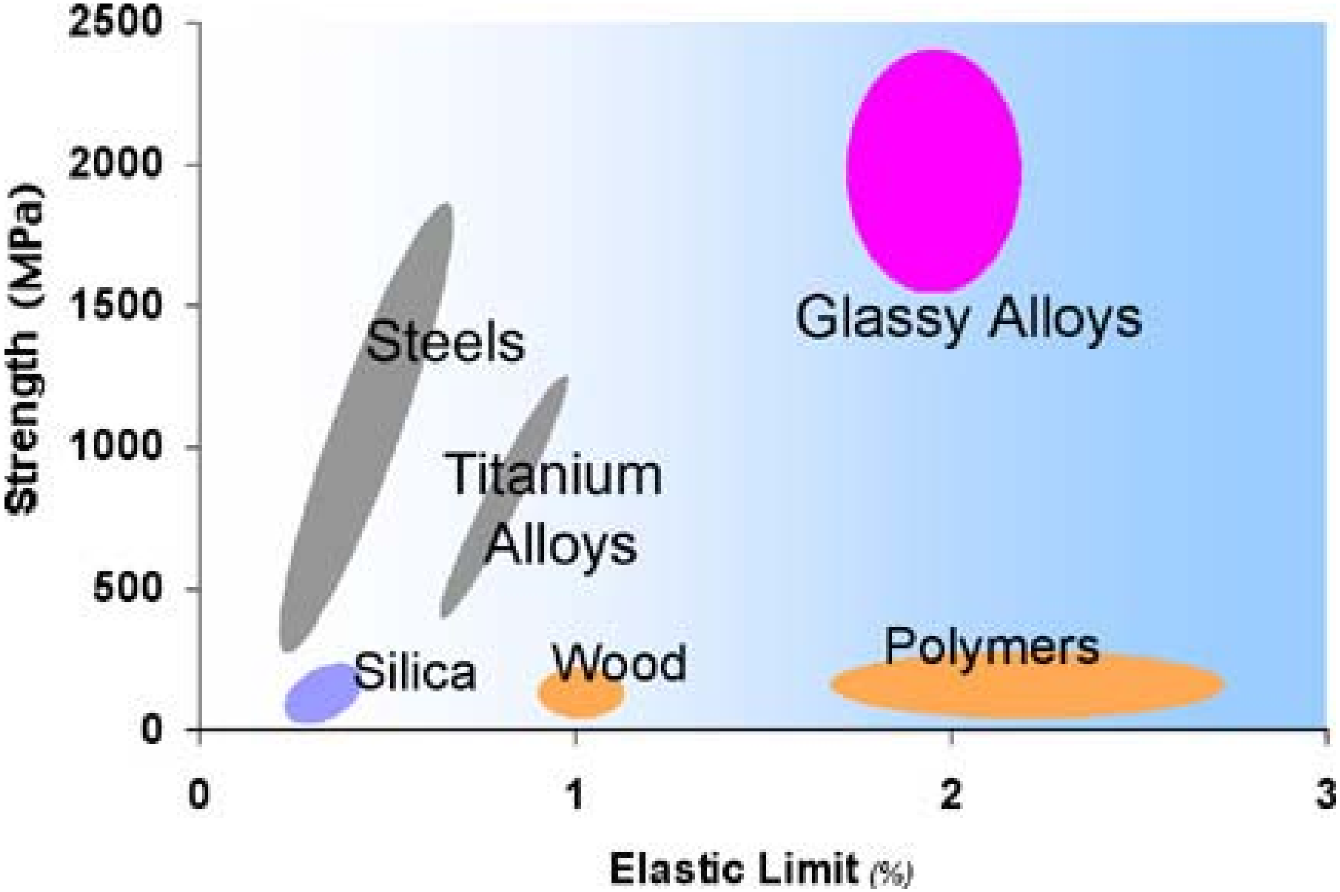


NPL



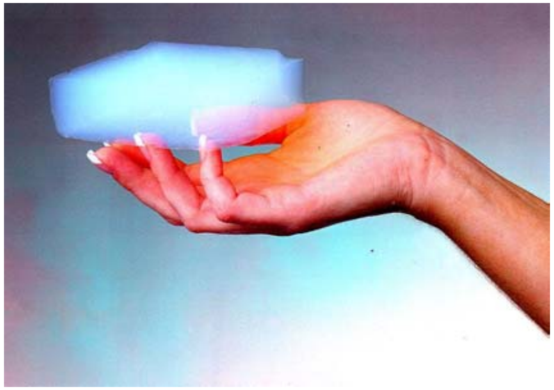
Al foam

Amorphous Metals - Properties



New Materials - Aerogels

- 99.8% air!
- Silica network with microporous structure (~10 nm)
- Prepared by removing liquid from wet gel
- Properties
  - Extremely low density
  - Exceptionally low thermal conductivity
- Applications
  - Optical Oxygen sensors (photoluminescence directly proportional to amount of Oxygen in aerogel)
  - Stardust technology – Capturing comet dust



New materials since 1960- cheap watch

- Alumina (scratch free) glass face
- Special polymers
- Liquid crystal displays
- High purity quartz for oscillators
- Microelectronic hardware

Choosing materials

- Materials have (at least one) purpose
  - Structural – it bears load or supports something
  - Functional - it does something
    - conducts electricity
    - transmits light
  - Decorative – it looks good

- Choosing the **right** material for a given purpose
  - 10000 possible materials
  - putting limits on mechanical , thermal, toxicity and other attributes (can it be shaped, joined, finished)–short list 10-50
  - Model performance - short list 5-10
  - Working prototypes - short list 1-2

Material Properties

- Economic – can we afford to use material
  - Price and availability
  - Recyclabiliy

- Physical
  - Density
  - Mechanical – is it strong/stiff enough
  - Modulus
  - Yield and tensile strength
  - Hardness
  - Fracture toughness
  - Fatigue strength

- Thermal – how will it react to temperature fluctuations
  - Thermal conductivity
  - Thermal expansion
  - Specific heat

Material Properties

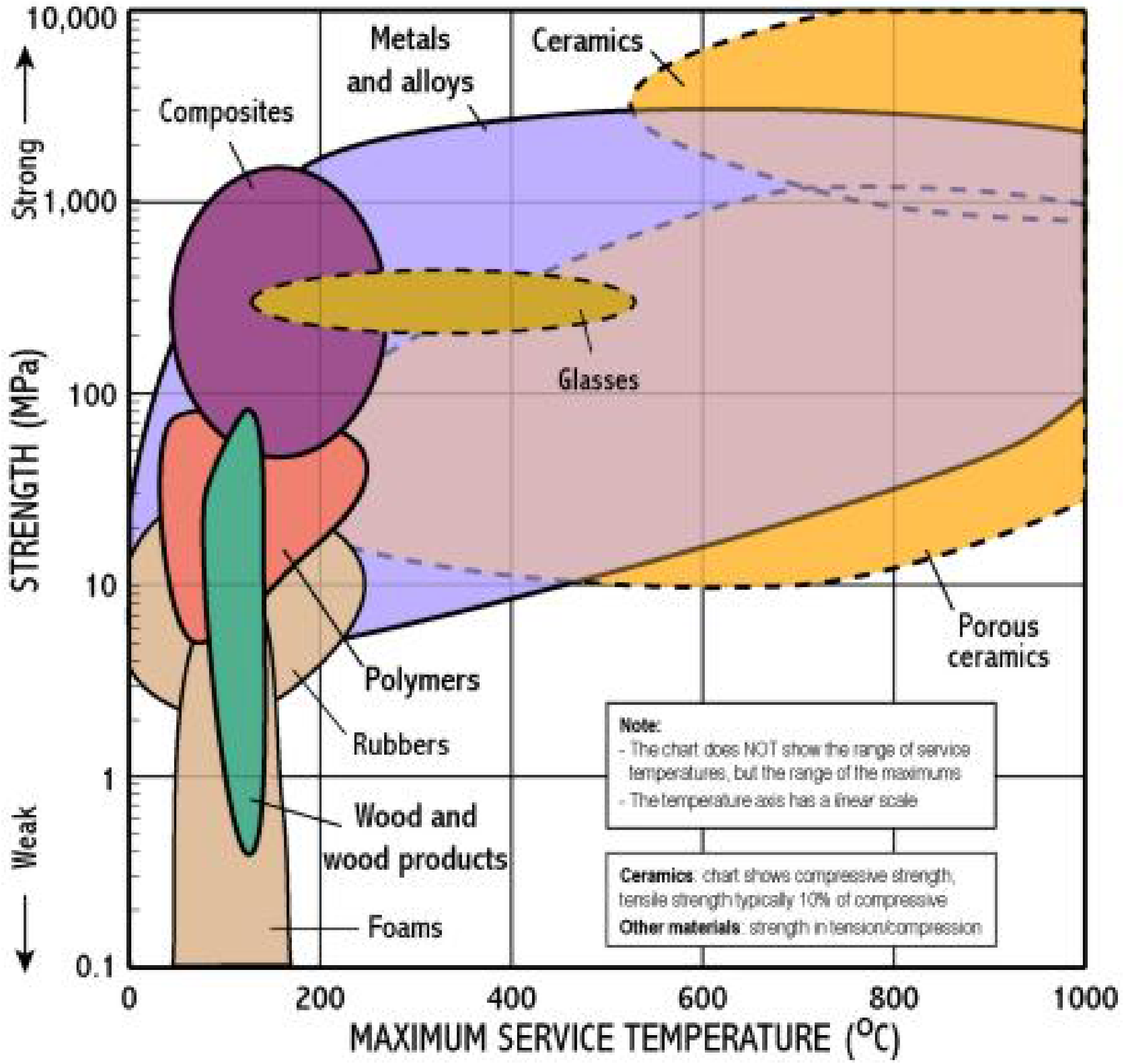
- Electrical and Magnetic – does it have the right functional properties
  - Resistivity
  - Dielectric constant
  - Magnetic permeability

- Environmental interaction – how long will it last
  - Oxidation
  - Corrosion
  - Wear

- Production – can we make it
  - Ease of manufacture
  - Joining
  - Finishing

- Aesthetic – does it look/feel nice
  - Colour
  - Texture
  - Feel

Attribute maps



Note:
- The chart does NOT show the range of service temperatures, but the range of the maximums
- The temperature axis has a linear scale

Ceramics: chart shows compressive strength, tensile strength typically 10% of compressive
Other materials: strengh in tension/compression

Types of Materials

- Metals
  - Steel
  - Light alloys (Al, Ti)

- Ceramics
  - Pottery
  - Glass
  - Chalk

- Polymers
  - Plastic
  - Nylon

- Composites
  - Wood
  - Glass fibre

Structure of course

- Basic principles
  - Crystal structure and bonding
  - Defects
  - Diffusion
  - Thermal properties
- Mechanical properties of materials
  - Elastic and plastic deformation
  - Strength of materials
  - Strengthening mechanisms
- Phase diagrams and alloys
- Non-metals
  - Ceramics
  - Polymers
  - Composites
- Functional properties
  - Electrical properties
  - Magnetic properties
  - Optical properties

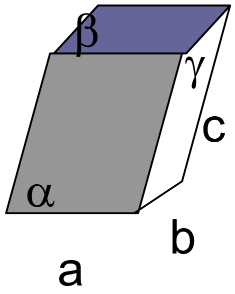
Crystal Structure and Bonding

Crystal Structure and Bonding

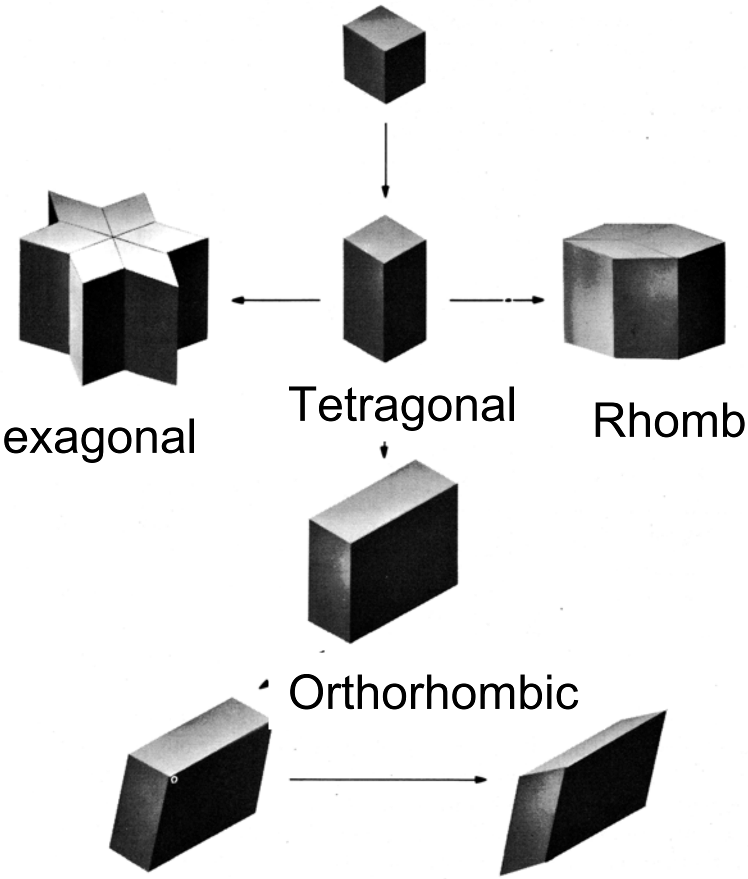
- Why do we need to know the crystal structure
  - It forms a link between the fundamental science and the real world
  - Some physical properties (e.g. slip) depend on the crystal structure
  - Crystal structures influence defect structures and associated properties
- Why do we need to know about bonding
  - Elastic properties determined by interatomic bonding
  - Interatomic bonding influences all material properties
  - Classes of materials with same bond type have similar properties (metals, ionic crystals)

Crystal Structures

- 7 classes according to the geometry of the unit cell (axial lengths a,b,c; axial angles α,β,γ)
  - Cubic : $a = b = c$; $\alpha = \beta = \gamma = 90°$
  - Hexagonal; $a=b \neq c$; $\alpha=\beta=90°$, $\gamma=120°$
  - Tetragonal; $a=b \neq c$; $\alpha=\beta=\gamma = 90°$
  - Rhombohedral; $a=b = c$; $\alpha=\beta= \gamma\neq 90°$
  - Orthorhombic; $a\neq b \neq c$; $\alpha=\beta=\gamma=90°$
  - Monoclinic; $a \neq b \neq c$; $\alpha=\gamma=90°\neq\beta$
  - Triclinic; $a \neq b \neq c$; $\alpha\neq\beta\neq\gamma\neq 90°$



Crystal Structures



Cubic

Tetragonal

Hexagonal

Rhombohedral

Orthorhombic

Monoclinic

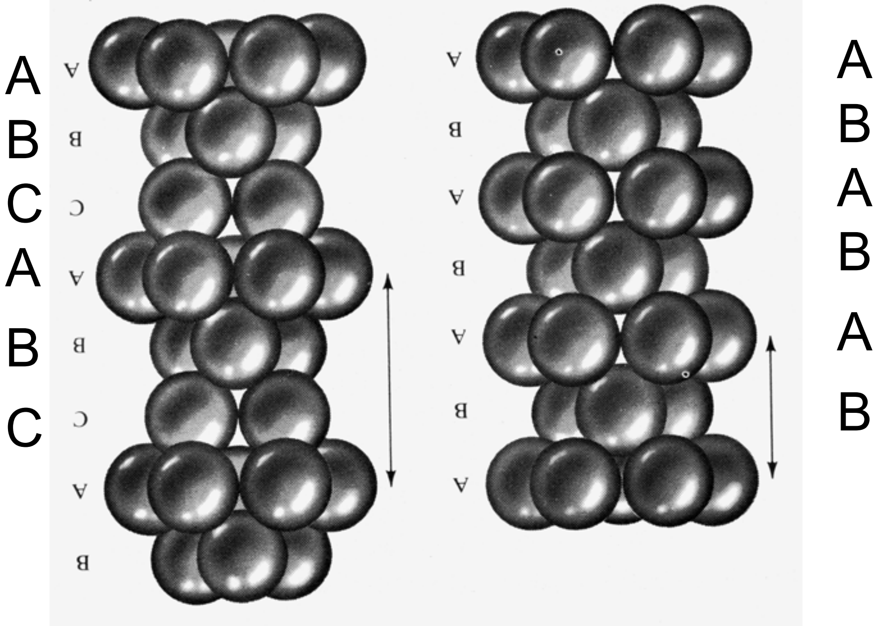
Triclinic

Metallic crystal structures

- Atomic bonding non-directional
- No restriction on number of nearest neighbours therefore dense atomic packing
- Three common structures; fcc, bcc, hcp
- Close packed crystal structures
  - fcc (cubic)- Stacking sequence ABCABCA………
  - hcp (hexagonal)- Stacking sequence ABABABA….

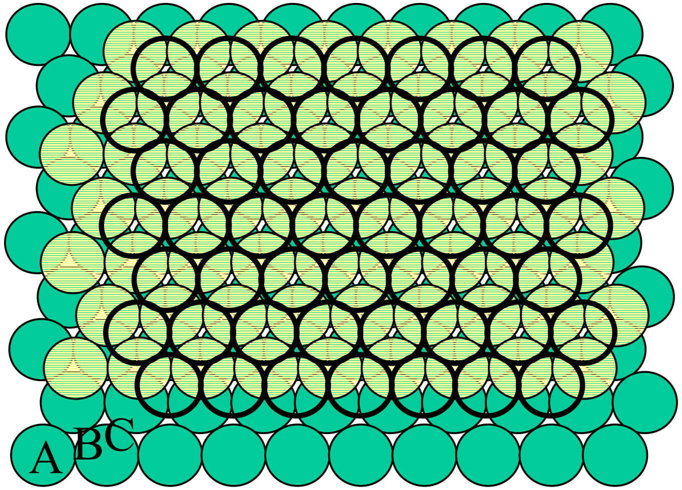
	fcc	**bcc**	**hcp**
e.g	Al, Cu, α Fe	Cr, Mo, γ Fe	Co, Zn, Ti
Coordination number	12	8	12
Atomic packing density	0.74	0.68	0.74

Close-packed structures – FCC or HCP

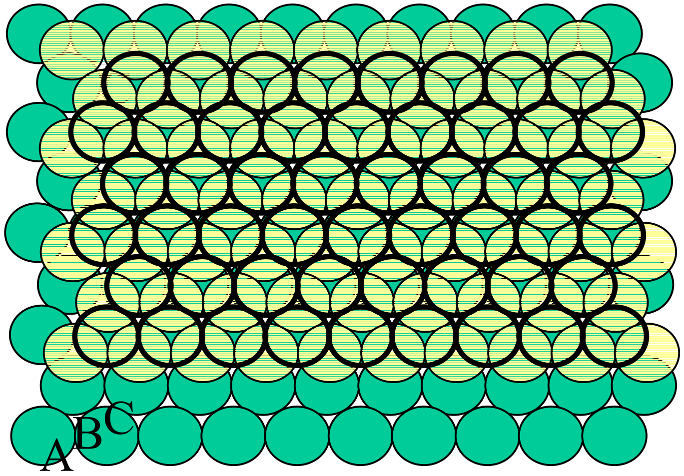


fcc

hcp



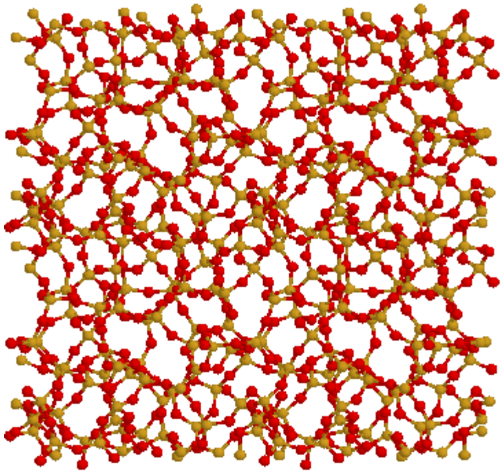
fcc



hcp

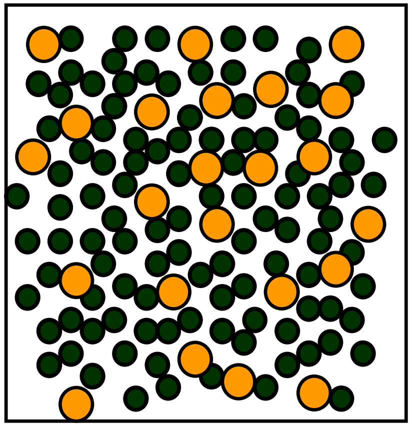
Non-crystalline structures

- SiO_2 Glass
- Continuous random network of Si atoms linked by O atoms
- 3,4,5,6,7 membered rings



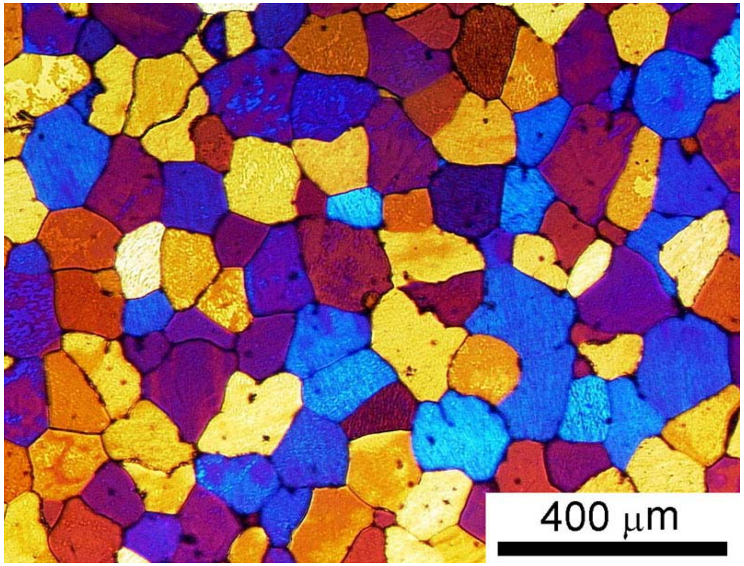
- Amorphous polymers
- Long chain molecules get entangled on cooling
- Crystallization inhibited

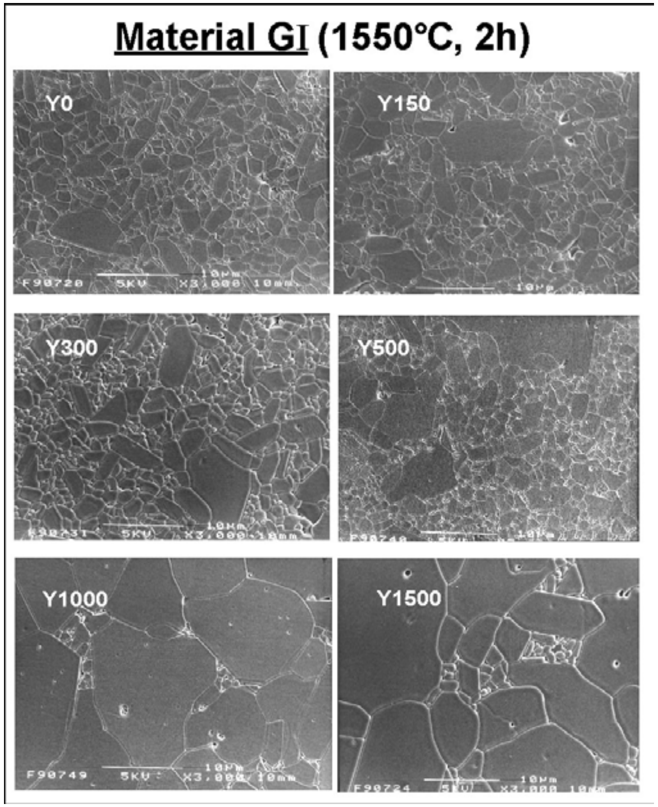
- Amorphous metals
- Alloys of metals with very different atom sizes
- Rapid quenching and size mismatch inhibits crystallization



Polycrystalline Materials

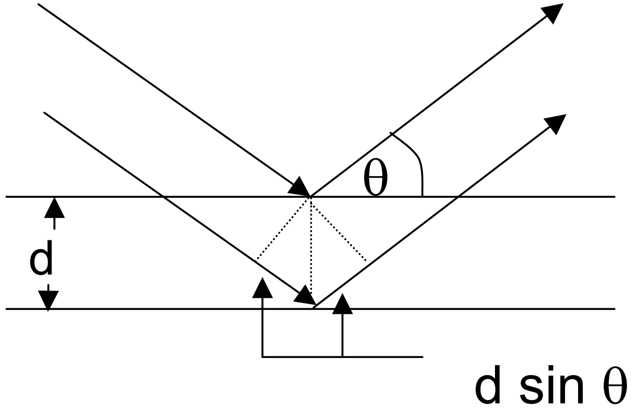
- Single crystals have regular geometric shape indicative of crystal structure and flat faces (eg diamonds)
- Most materials made from small crystals with random orientations separated by grain boundaries



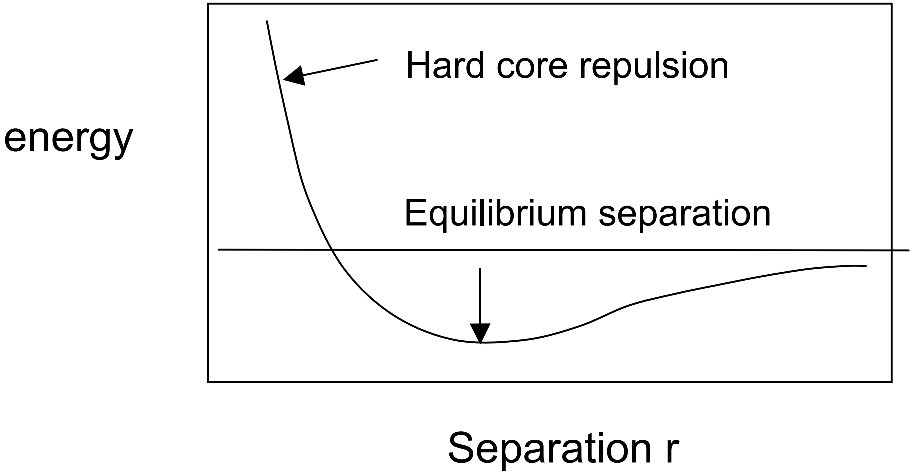


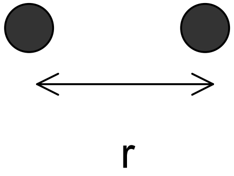
Determination of Crystal Structure

- X-ray diffraction – x-rays scattered from regular arrays of atoms show peaks at certain angles according to Bragg’s Law
  - $n\lambda = 2\, d_{hkl} \sin\theta$: n=1,2,3…….:
  - d_{hkl} is the interplanar spacing



Interatomic bonding





$$U = A / r^m - B / r^n$$

$$F = dU/dr = - Am/r^{m+1} + Bn/r^{n+1}$$

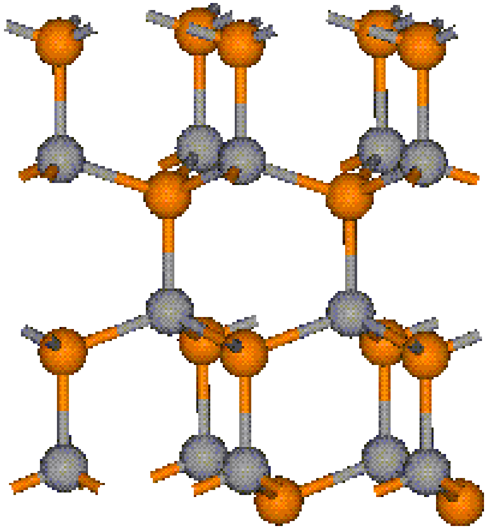
$$n<m$$

$$m \sim 12$$

m depends on type of bond

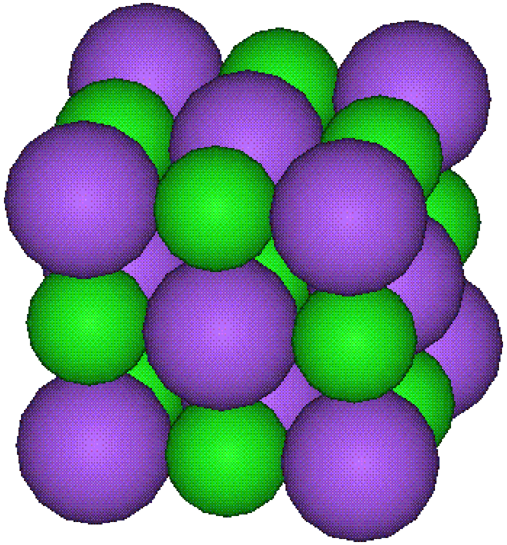
Interatomic bonding -Covalent

- Atoms shares electrons
- Strong and directional
- Low density
- Stiff and hard and brittle
- eg SiC
  - Diamond structure
  - Si bonded to 4 C
  - C bonded to 4 Si
  - Very hard



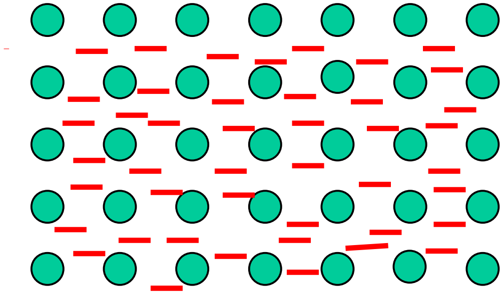
Interatomic bonding -Ionic

- Electrons transferred between atoms.
- n=1
- Strong non-directional
- Eg NaCl
  - Rocksalt (cubic) structure
  - Each Na^+ surrounded by 6 Cl^-
  - Each Cl^- surrounded by 6 Na^+
- In general ionic bonds are partially covalent
  - % ionic = $\{1-\exp[0.25(X_A-X_B)^2\}\times 100$
  - X_A and X_B are electronegativities of the 2 components A and B



Interatomic bonding - Metallic

- A lattice of positive ions in a sea of delocalized (mobile) electrons
- Non-directional
  - Favours close packed structures (fcc, hcp)
- Range of strength (0.7eV for Hg 8.8 eV for W)
- Transition metals have some directional bonding (favours non-close packed bcc)



Interatomic bonding – Van der Waals

- Sometimes called secondary bonding
- Dipole-dipole interactions
  - Permanent dipoles
  - Induced dipoles (London dispersion) $E_{attr} = -A/r^6$
- Weak (0.2 eV)
- Interaction between covalently bonded molecules
- Strength increases with molecule size
  - Significant in polymers
  - Melting point increases with molecule size

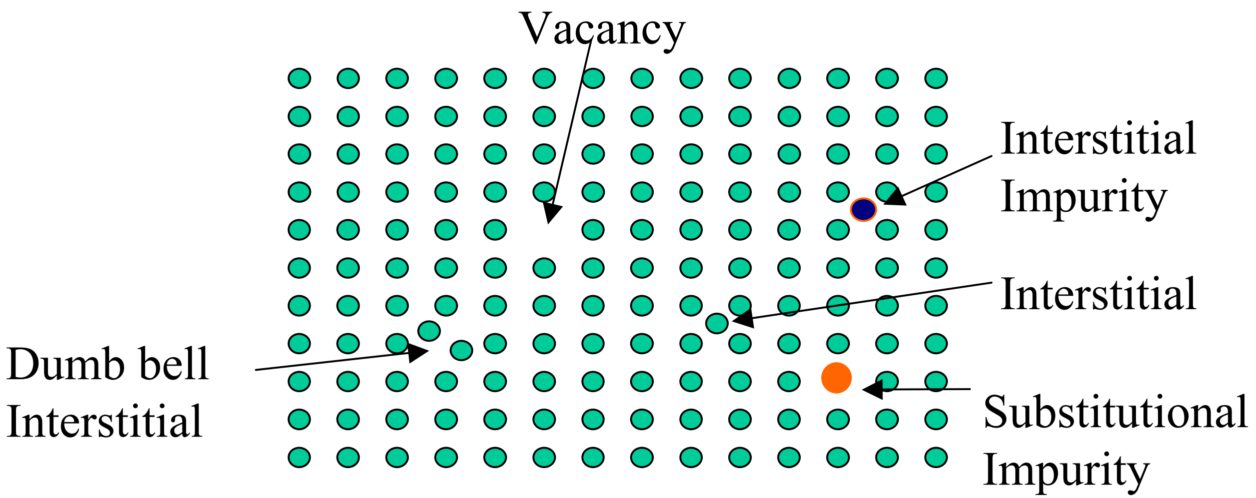
Defects

Defects in crystals

- Why study defects?
  - All material properties (physical, optical, electronic) are affected or even dominated by defects
  - Defects often give materials their desired properties
    - Colours of gem stones – impurities
    - Doping in semi-conductors
    - Dislocations in metals – plasticity
- Classes of defect
  - Point defects
  - Line defects
  - Planar defects

Point defects

- Vacancies – missing atoms
- Self-interstitials – atoms occupy void in structure not normally occupied.
- Impurities
  - Substitutional – impurity atom replaces atom of host crystal
  - Interstitial – small impurities can occupy interstitial positions



Concentration of Point defects

- Equilibrium number of vacancies increases with temperature
- $N_c = N \exp(-Q_v/kT)$
- For metals $N_c/N \sim 10^{-4}$ just below melting point
- Defects may be introduced during processing – not necessarily in equilibrium
- Self interstitials are rare in close-packed (metal) structures
  - Atoms are significantly larger than small void space

Point Defects in Ionic Crystals

- In ionic crystal have extra constraint that total defect charge must be zero
  - Frenkel defects
    - Anion vacancy + anion interstitial
    - Cation vacancy + cation interstitial
  - Schottky defect
    - Anion vacancy + Cation vacancy

Impurities

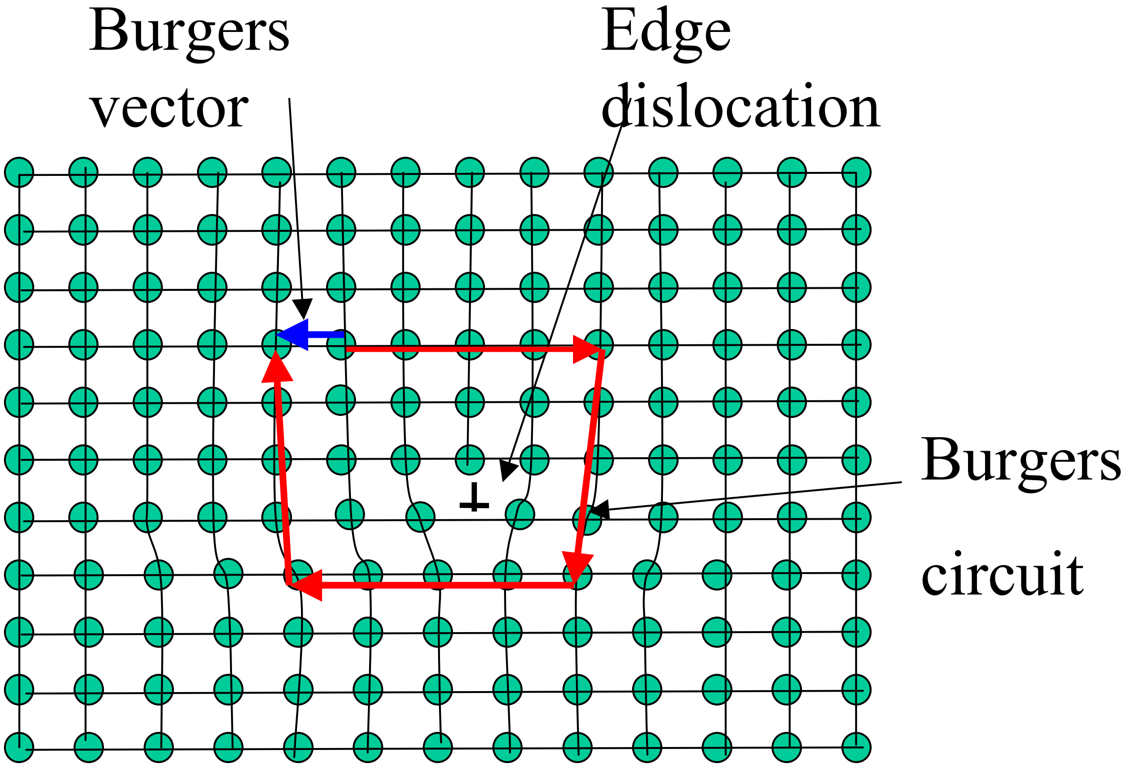
- Addition of impurity atoms results in either
  - A second phase
  - A solid solution
- A solid solution forms when the impurities are homogenously dispersed throughout material
- The solubility depends on
  - The atomic size – appreciable solubility if size difference < 15%
  - Crystal structure – same crystal structure increases solubility
  - Valences – a metal has a greater tendency to dissolve another metal of higher valence
- Cu / Ni soluble in one another in all proportions

Dislocations

1-dimensional defects

Line defects – edge dislocations

- Crystal contains an extra half plane of atoms
- Burgers vector perpendicular to dislocation line

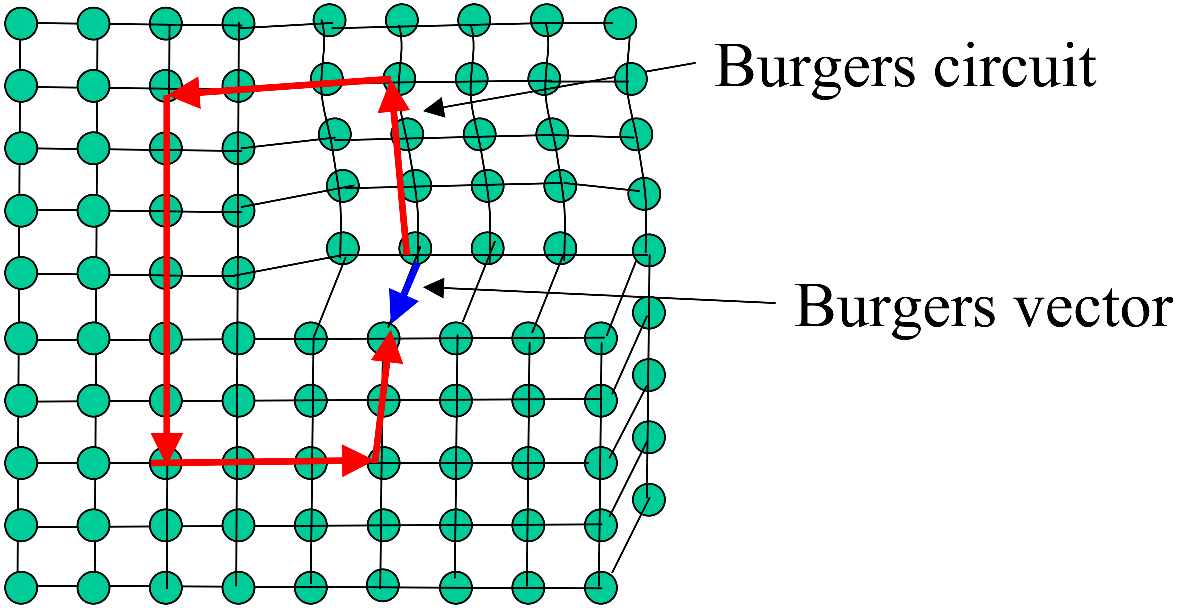


Burgers vectors

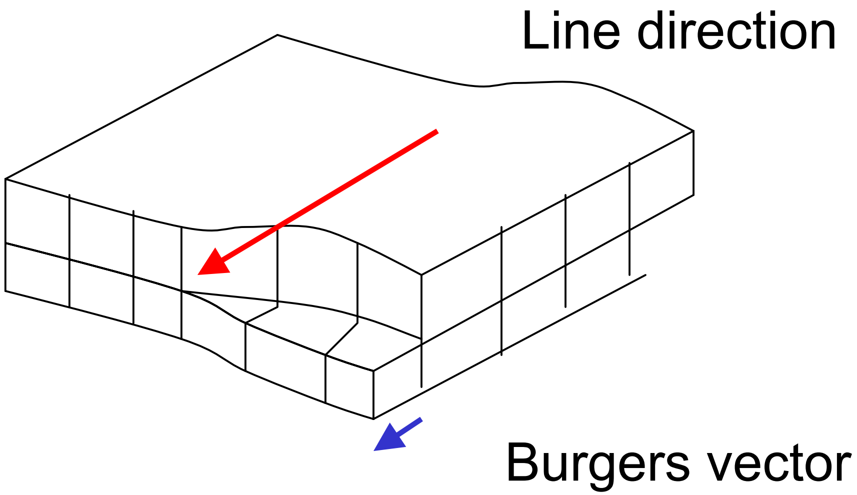
- Perform atom to atom circuit around the dislocation line returning to starting point
- Choice of line direction is arbitrary but once line direction is chosen the circuit is done in a right hand sense
- Repeat atom to atom circuit in a perfect crystal
- Circuit does not close
- <u>b</u> goes from finish to start of circuit
- Burgers vector is always a lattice vector of crystal

Line defects – screw dislocations

- Atoms of one side of crystal displaced with respect to atoms on other side in part of crystal
- Burgers (displacement) vector parallel to dislocation line
- Screw dislocations cause surface steps - growth



Screw dislocation



Most dislocations are mixed – they have some edge component and some screw component

Combining dislocations

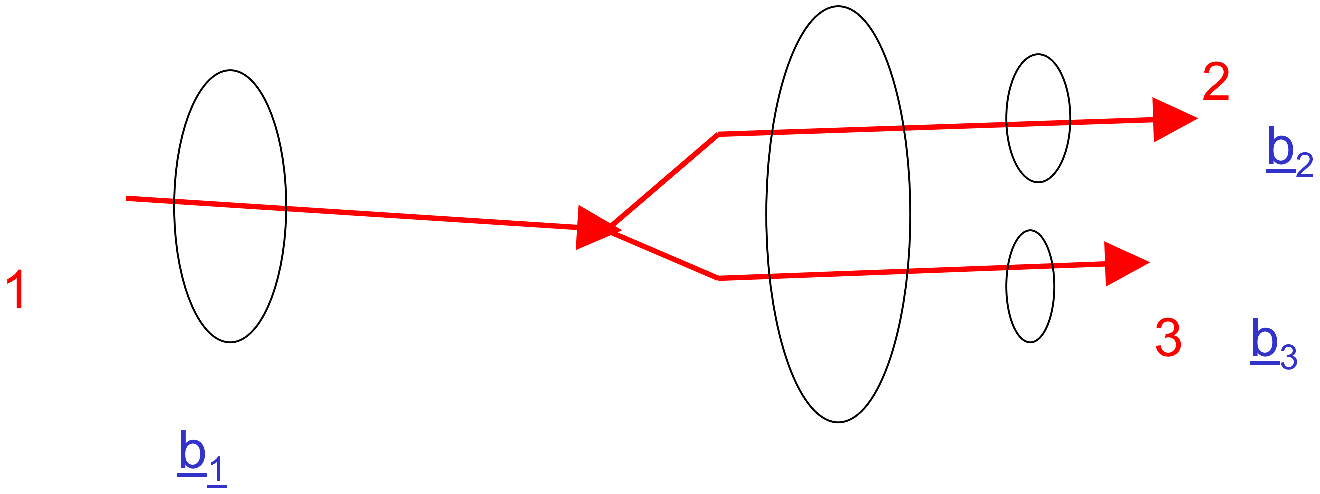
- Dislocations never end within a crystal
  - Burgers vector is constant along the whole length of the dislocation
  - Character of dislocation may change (eg from edge to mixed to screw) as it changes direction

- When 2 dislocations combine the resulting dislocation has the sum of the Burgers vectors : $\underline{b}_3 = \underline{b}_1 + \underline{b}_2$
  - eg annihilation $\underline{b} - \underline{b} = 0$

Dislocation nodes

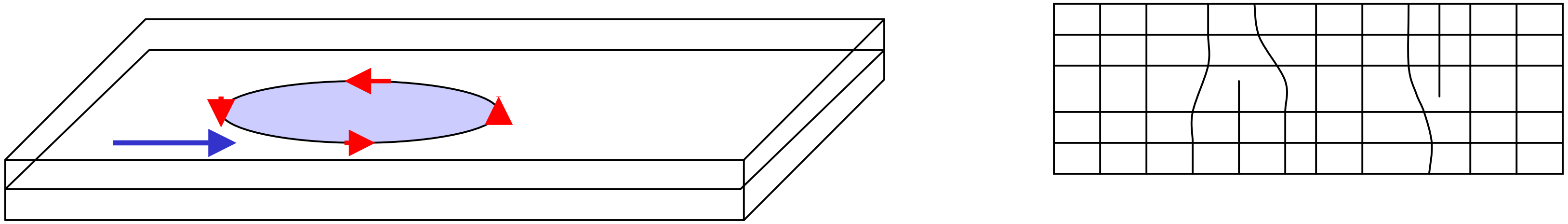
Dislocations can combine/split in a crystal

Total Burgers vector must be conserved



$$\underline{b}_1 = \underline{b}_2 + \underline{b}_3$$

Dislocation loops



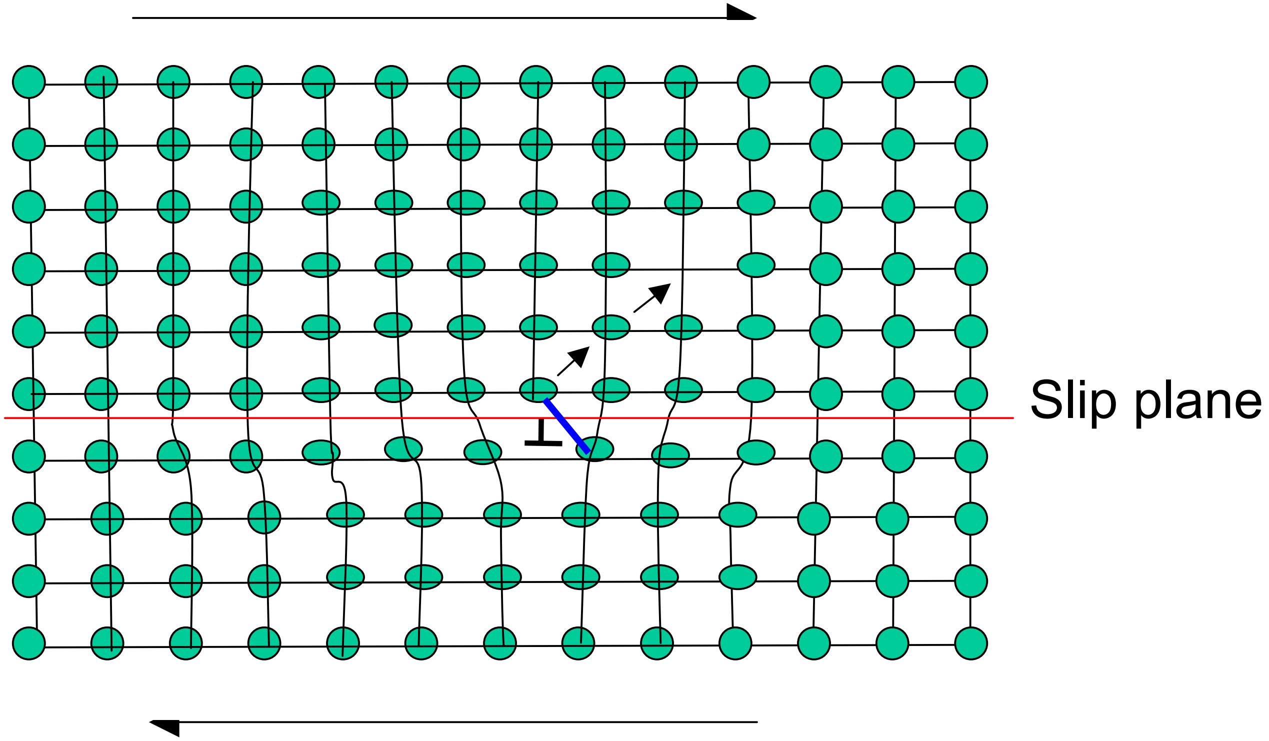
Dislocation loops form when enclosed patch of material slips on slip plane

Dislocation character changes from edge type to screw type

Shear stress acting on the loop will either expand or contract it

Dislocation motion

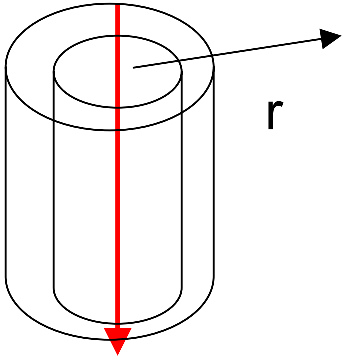
- The application of stress to crystals causes dislocations to move (plastic deformation)
- Dislocation climb requires vacancy diffusion
- Slip plane – easy direction for dislocation motion
  - Close packed direction of crystal (eg (111) in fcc)



Stresses and Strains around Dislocations

- Dislocations disrupt the crystal structure therefore they cost energy
- The energy comes from 2 sources
  - The long range stress field that can be analysed using linear elasticity
  - A core region in which strains (distortions) are too large to be analysed using linear elasticity
- The long range elastic stress field controls how dislocations interact with
  - Other dislocations
  - Solute atoms
  - Applied stresses
- The core structure is associated with dislocation dissociation and core spreading

Stress / Strain field of a Screw Dislocation



$$\varepsilon_{\theta z} = \varepsilon_{\theta z} = b/2\pi r$$

$$\sigma_{\theta z} = \sigma_{\theta z} = G\,b\,/2\pi r$$

Stress and strain fields are pure shear

Fields have radial symmetry

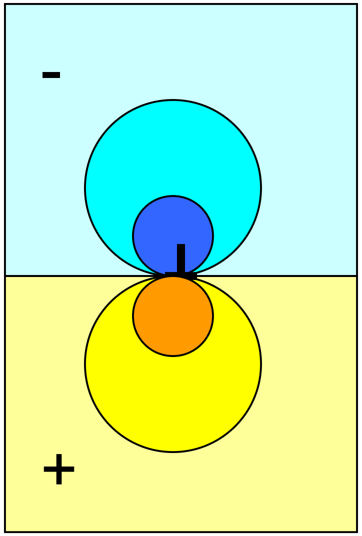
Stress and strain proportional to 1/r

Stress and strain tend to infinity as r-> 0

Stress / Strain Field of Edge Dislocation

More complicated than screw dislocation

Not pure shear – hydrostatic component



Energy of a dislocation

Elastic energy / unit volume= $\frac{1}{2} \sigma \varepsilon$

$= Gb^2 / 8\pi r^2$

Elastic energy of a shell $= Gb^2 / 4\pi r \, \delta r$

Total elastic energy $= Gb^2/4\pi \ln(R/r_o)$ per unit length

$\sim Gb^2/2$

Typically 1-4 nJ m^{-1}

Core energy – estimate as equivalent to one broken bond per atom spacing along core

Typically 0.1 – 1 nJ m^{-1}

Forces between dislocations

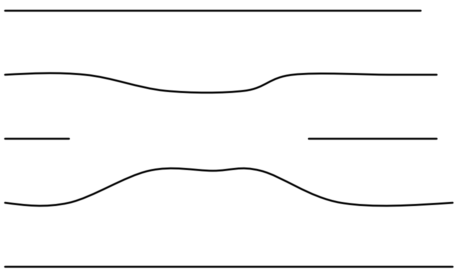
- Dislocations with same line vectors and same Burgers vectors repel each other
- Dislocations with same line vectors and opposite Burgers vectors attract each other
- Application of shear stress exerts a force on a dislocation
  - $F = \tau b$

Origin and Multiplication of Dislocations

- Dislocations introduced during the growth process

- Typical dislocation densities
  - 10^6 cm^{-2} for well annealed crystals
  - 10^{11} cm^{-2} after plastic deformation

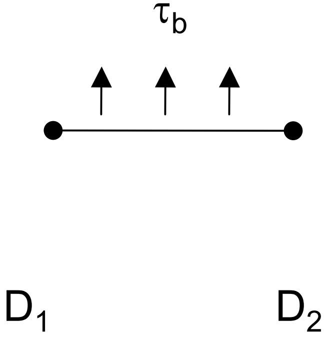
- Dislocations can be created from the collapse of vacancy loops



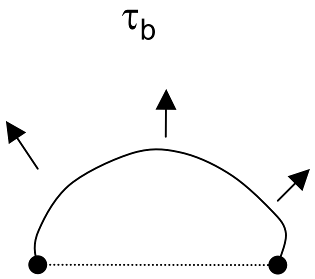
- Dislocations created at regions of local stress (eg inclusions)

Sources of Dislocations

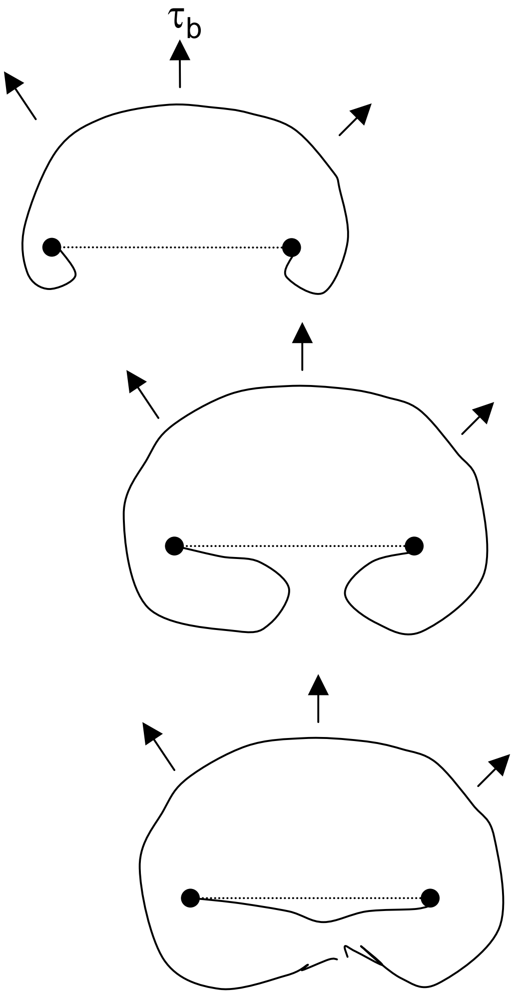
Frank-Read Sources



Dislocation fixed at $D_1$and D_2 by obstructions



The application of a stress makes the dislocation bow outward



Frank-Read Source

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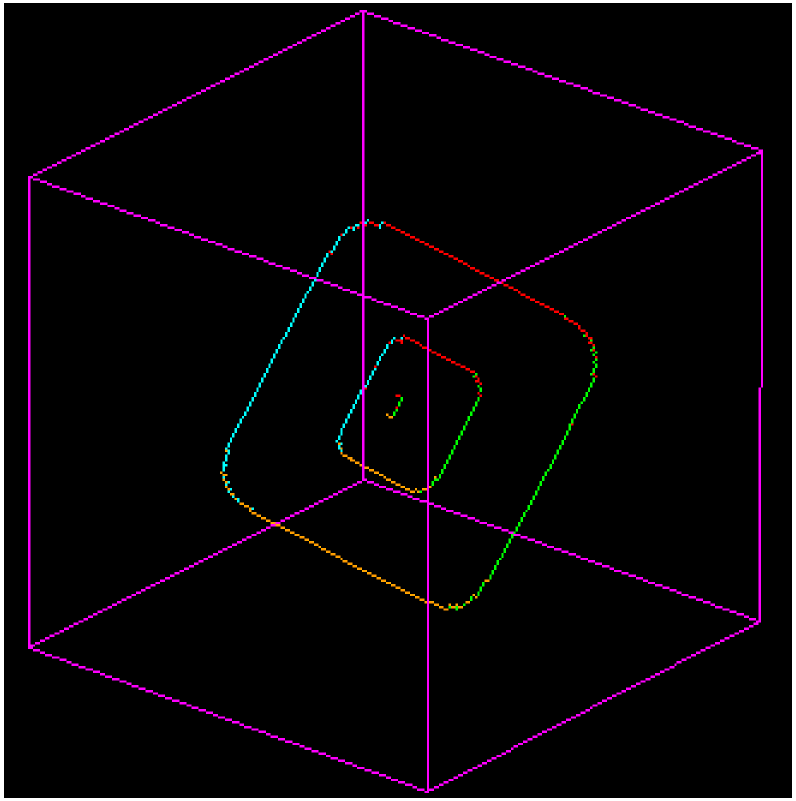


Planar / Interfacial Defects

- Free surfaces
  - Solid air interface
- Phase boundaries
  - Separate regions of different chemical composition and/or atomic structure
- Grain boundaries
  - Separate regions of different crystal orientation

Grain Boundaries

- Most material are polycrystalline
  - Grain size depends on processing (rate of cooling from melt)
  - Grain boundary population never in equilibrium
- The interfaces between the grains (grain boundaries)
  - Dominate many material properties
  - Contribute to the energy of a lattice
- The properties of grain boundaries depend on the misorientation angle between the grains

Characterisation of Grain Boundaries

- Characterised by 3 parameters
  - The normal to the interface
  - The rotation axis (common crystallographic axis between 2 grains)
  - The misorientation angle (θ)

- 2 types of boundary
  - Tilt – rotation axis perpendicular to boundary plane normal
  - Twist – rotation axis parallel to boundary normal

Misorientation angle (θ)

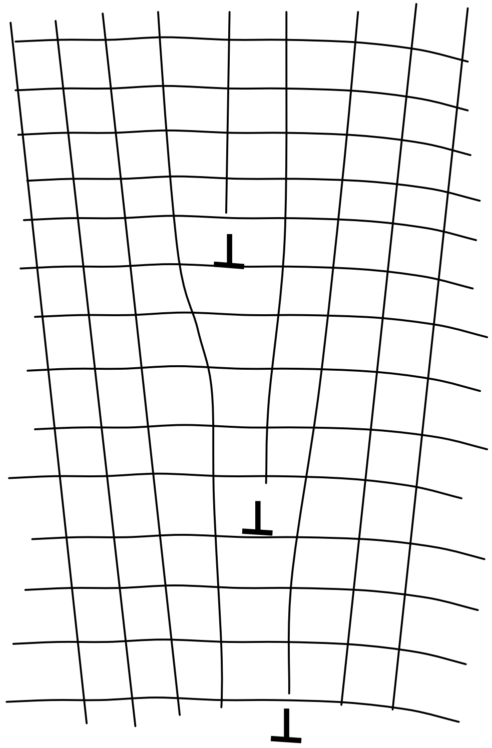
- Low angle grain boundaries – $\theta < 15°$
  - Small lattice mismatch concentrated along discrete lines in boundary
  - Arrays of dislocations

- High angle grain boundaries – $\theta > 15°$
  - Crystal structure disordered in boundary plane

- Special grain boundaries
  - For certain orientations there is good matching between the atoms in boundary plane
  - Relatively low energy

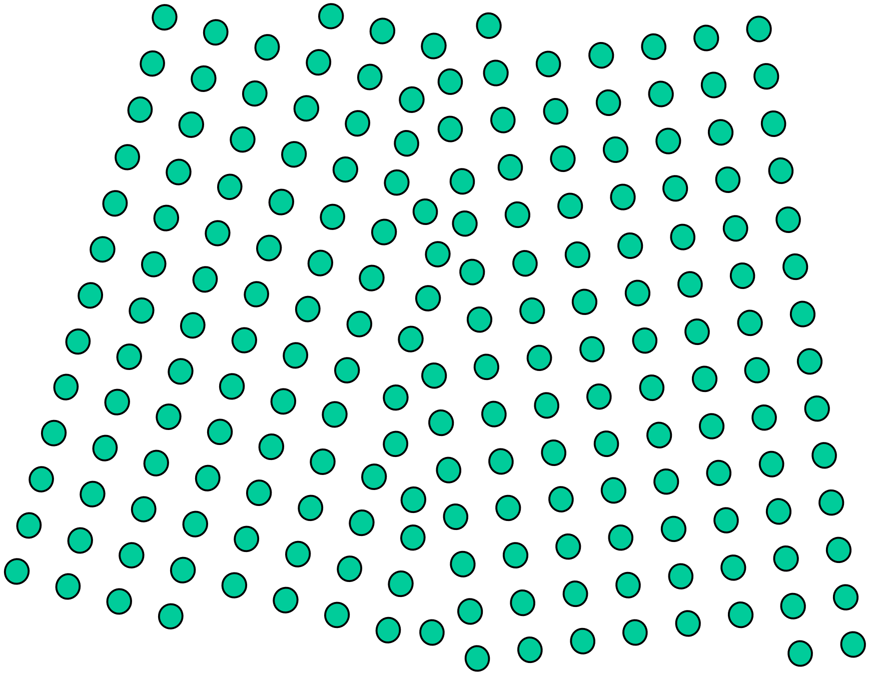
Low angle grain boundaries

- Widely spaced arrays of dislocations
- Perfect lattice between dislocations
- Angle (θ) : sin $\theta \sim \theta = |b|/d$
- Energy increases with angle
- Edge dislocations – tilt boundary
- 2-dimensional arrays of screw dislocations – twist boundary



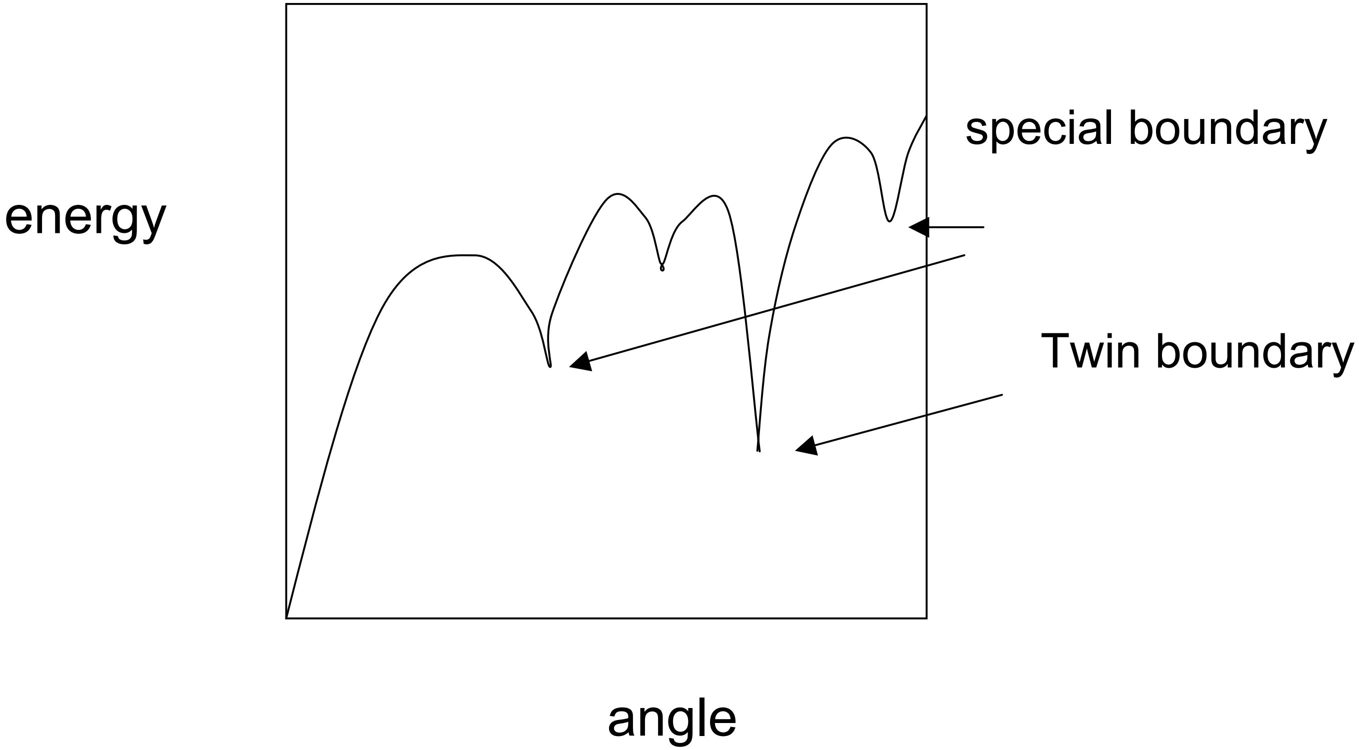
High angle Grain Boundaries

- When θ > 15 then the dislocations become so close together that the cores overlap
- Individual dislocations can no longer be identified
- Energy becomes independent of angle (with the exception of special orientations)



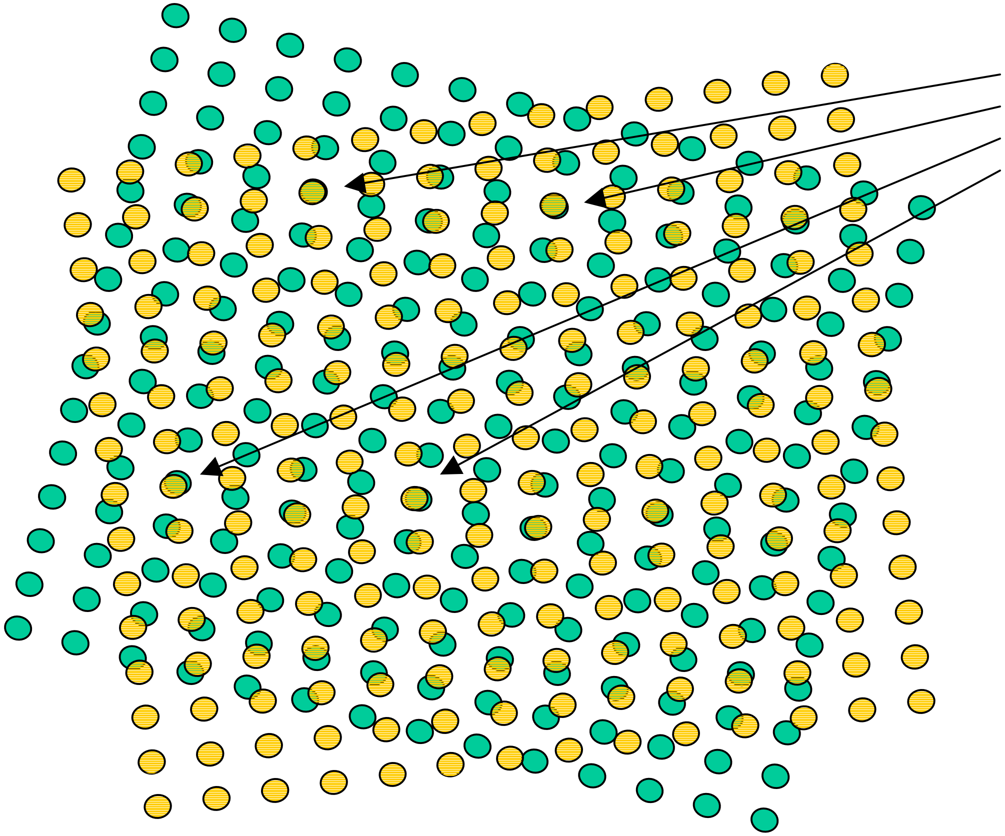
Grain Boundary Energy

Energy of a low angle grain boundary = G θ/2



Special grain boundaries

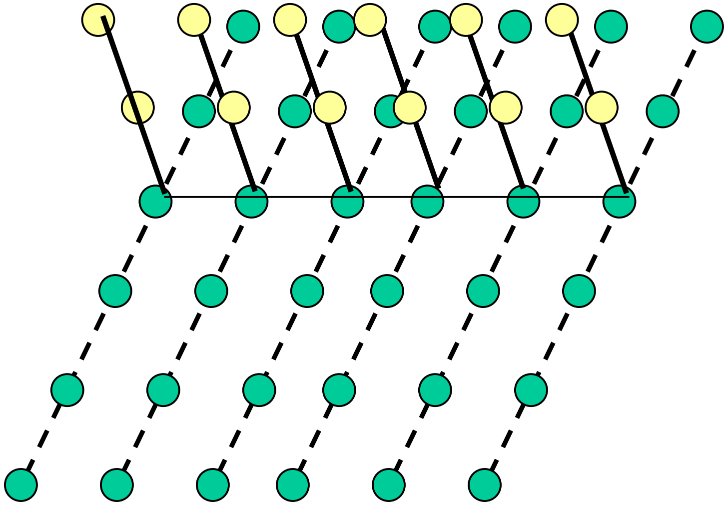
- Low energy boundaries when 2 lattices have a high density of coincident points



Coincidence sites

Twin Boundaries

- Twin boundaries separate 2 grains that are related by mirror symmetry (eg ABCABACBA in fcc lattice)



Crystal	γ_{twin} mJ m^{-2}	γ_{gb} mJ m^{-2}
Cu	21	623
Ag	8	377
Fe-Cr-Ni	19	835

Effects of grain boundaries

- Electrical properties
  - Scatter electrons
  - Acquire charge in ionic crystals

- Magnetic properties
  - Inhibit domain wall motion

- Thermal properties
  - Scatter phonons

- Physical properties
  - Inhibit dislocation motion
  - Increase creep
  - Act as a sink/source for point defects

Observing defects

- Optical microscopy – up to 2000 x magnification
  - Reflecting mode for opaque samples
  - Surface preparation (polishing and etching) shows up grains because of different surface texture
  - Grooves form along grain boundaries

- Electron microscopy
  - TEM – beam passes through specimen (> 10^6 magnification) – thin specimens
  - SEM – Electron beam scanned across surface

Diffusion

The natural tendency for atoms to be transported under a concentration gradient

Why study diffusion

- Heat treatment of materials
- Doping in semi-conductors
- Creep
- Solid state sensors, solid state batteries
- Diffusion bonding

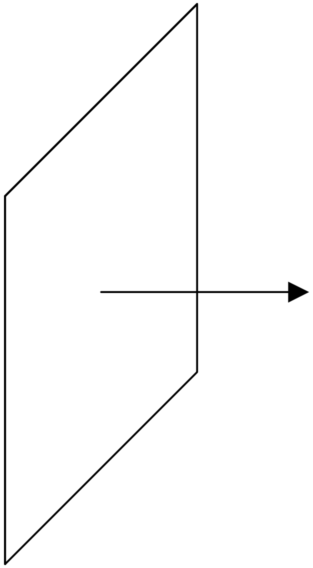
Definitions - Flux

Flux (J)

the mass (or number) of atoms passing through and perpendicular to a unit cross-section area of a material per unit time

$J = M/At$

$J = 1/A \, dM/dt$



Units

kg m^{-2} s^{-1}

or atoms m^{-2} s^{-1}

Fick's law (1st Law)

Steady state – Concentration does not change with time

Steady state diffusion

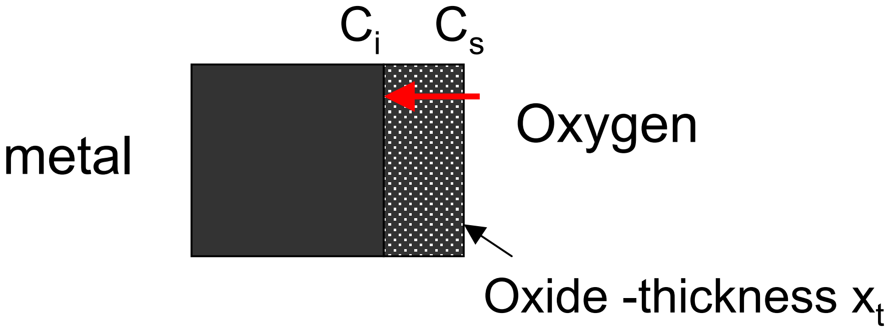
$$J = -D\, dC/dx$$

The flux (J) of diffusing particles is proportional to the gradient of concentration (C)

The coefficient of proportionality D is called the diffusion coefficient (units $m^2\ s^{-1}$)

Example of Fick's 1st law

- Oxidation of metals
  - Diffusion of oxygen through scale of thickness x_t
  - Outer oxygen concentration constant C_s
  - Inner oxygen concentration C_i
  - Flux of oxygen through scale $J = D\,(C_s - C_i)/x_t$
  - However x increases at rate proportional to J
  - $dx_t/dt = K\ J$ (K constant of proportionality)
  - $dx_t/dt = DK\,(C_s - C_i)/x_t \qquad \int x_t\,dx_t = DK\,(C_s - C_i)\int dt$
  - $x_t^2 = DK\,(C_s - C_i)\,t$: Parabolic oxidation



Fick's Laws - 2nd Law

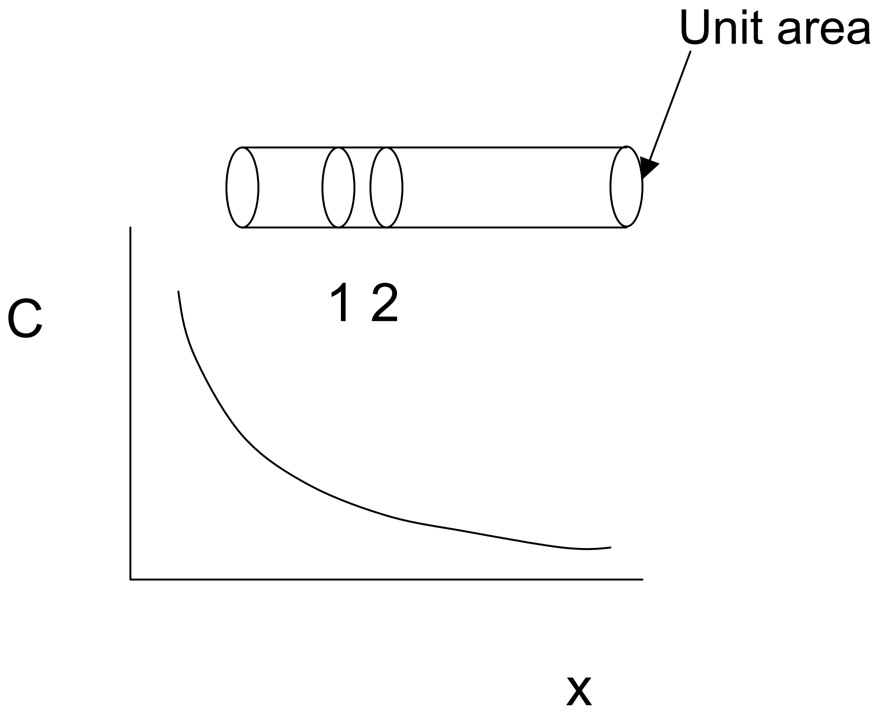
Non-steady diffusion

Non-uniform concentration gradient

$$\delta C/\delta t = D \ \ \delta^2 C/\delta x^2$$

Most practical diffusion situations are non-steady state

Fick's 2nd law - Derivation



Consider volume between 1 and 2

Flux in is – D $\{\delta C/\delta x\}_1$

Flux out is – D $\{\delta C/\delta x\}_2$

$= -D(\{\delta C/\delta x\}_1 + \delta x (\{\delta^2 C/\delta x^2\}$

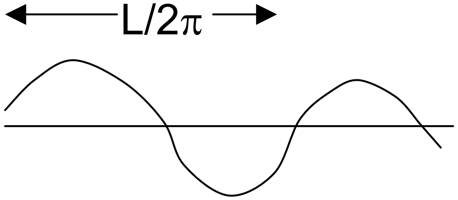
In the time interval δt the net change in concentration ($\delta C \delta x$) is (flux in – flux out)δt

Therefore

$\delta C/\delta t = D\, \delta^2 C/\delta x^2$

Example of Fick's 2nd law

- Rapidly changing concentration fluctuations are rapidly damped



  - $C(x,t) = a(t) \sin(x/L)$
  - $dC/dt = D\, d^2C/dx^2 = - D\, C/L^2$
  - Solving differential equation $\int 1/C\, dC = - \int D/L^2\, dt$
  - $\ln(C) = -(D / L^2)\, t$
  - $C = \exp -(D / L^2)\, t = \exp -t/\tau$ (τ relaxation time)

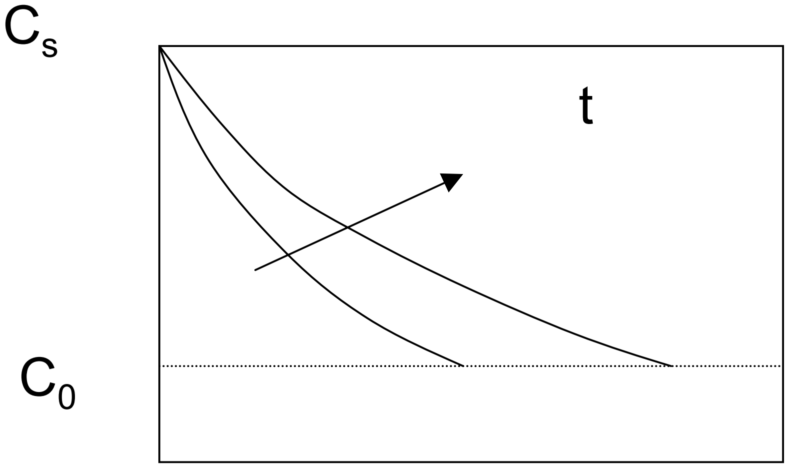
- Small L gives small relaxation time and rapid decay of fluctuations

Example of Fick's 2nd law

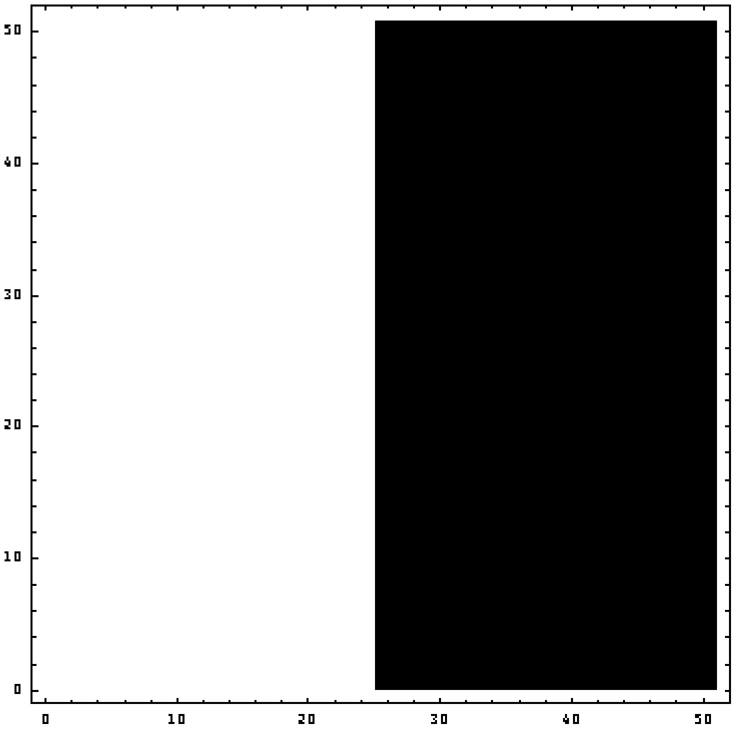
Semi-infinite solid in which surface concentration is fixed

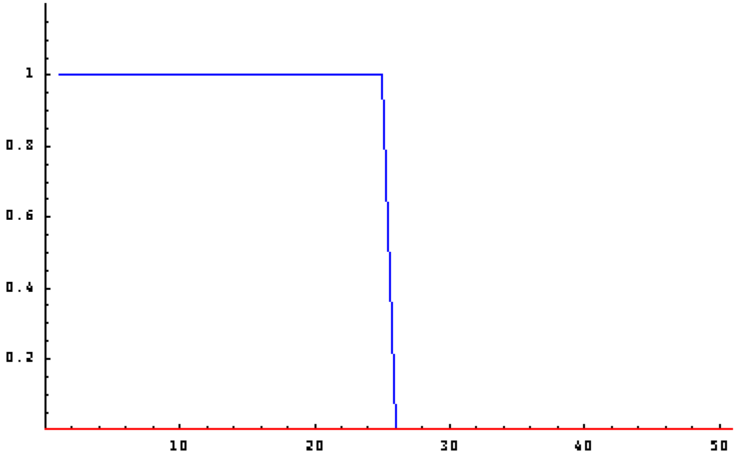
Eg Carburisation and decarburisation processes

$$(C_x - C_0)/(C_s - C_0) = 1 - \mathrm{erf}(x/2\sqrt{Dt})$$



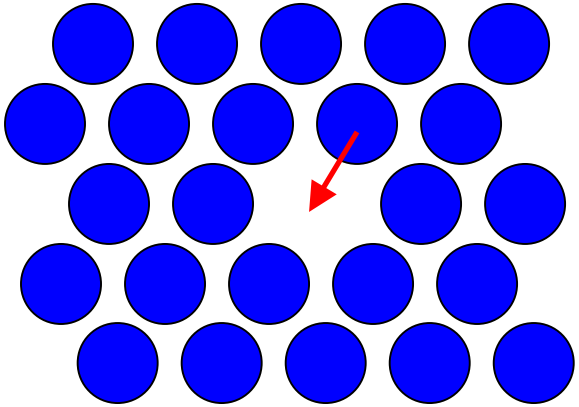
Interdiffusion



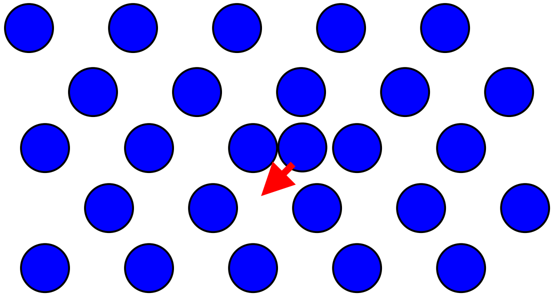


Diffusion mechanisms

- Diffusion is the stepwise migration of atoms in the lattice
  - Vacancy diffusion

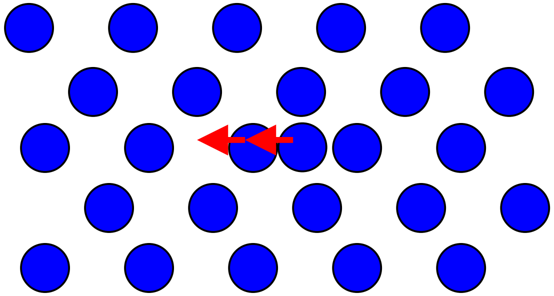


  - Interstitial mechanism

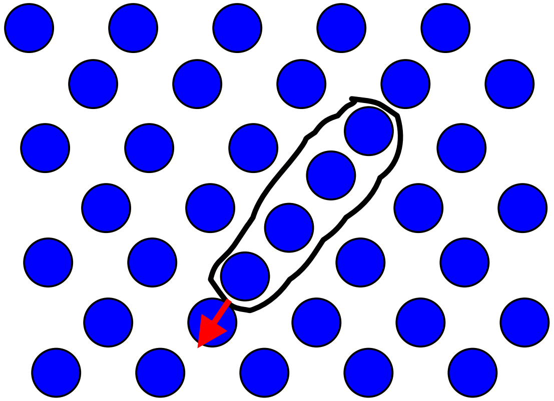


Diffusion mechanisms

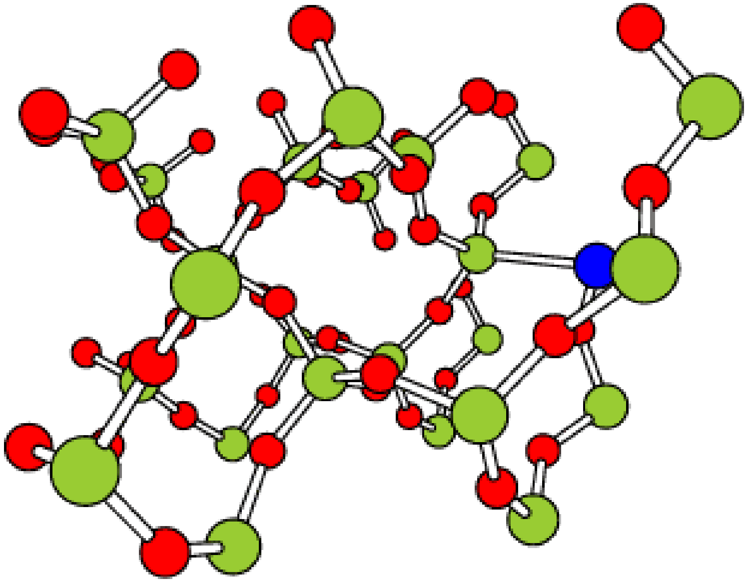
- Indirect interstitial mechanism – interstitial moves into lattice site and displaces atom into interstitial site



- Extended interstitial mechanism (crowdion) mechanism
  - Low activation energy



Interdiffusion of Si in α-quartz

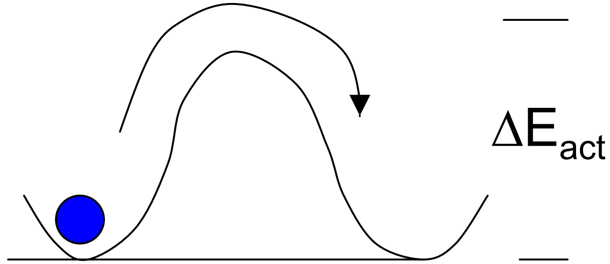


From http://www.ensiacet.fr/E-Materials/diffusion/limoge/limoge1.html

Activation energies

All the diffusion processes have an associated activation barrier

Barrier is associated with local lattice distortion



Initial state

final state

Attempt frequency ν_0

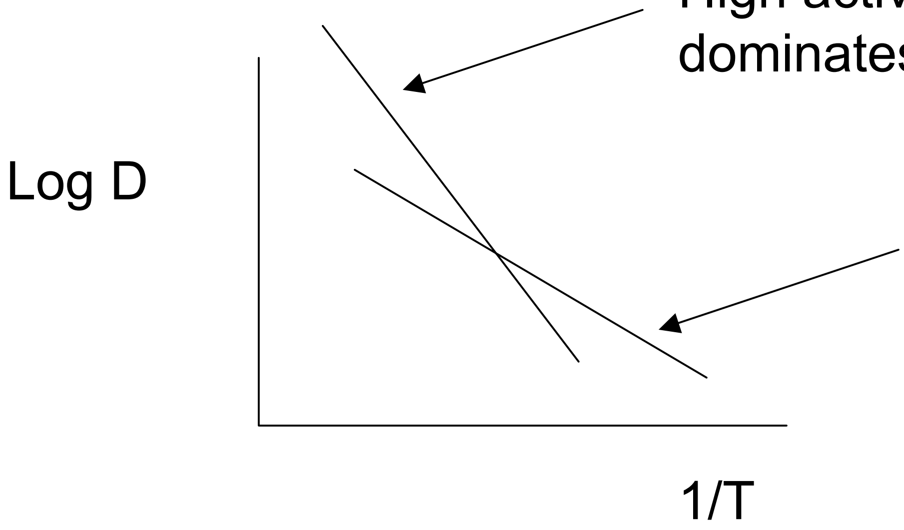
Successful attempts

$\nu = \nu_0 \exp - (G_{act}/kT)$

$= \nu_0 (\exp (S_{act}/k)) \exp - (H_{act}/kT)$

However $D \propto \nu$ Therefore $D = D_0 \exp - (H_{act}/kT)$

Diffusion vs temperature plots



High activation energy – dominates at high T

Low activation energy – dominates at low T

$$D = D_0 \exp - (H_{act}/kT)$$

Different diffusion processes have different activation energies and different pre-factors

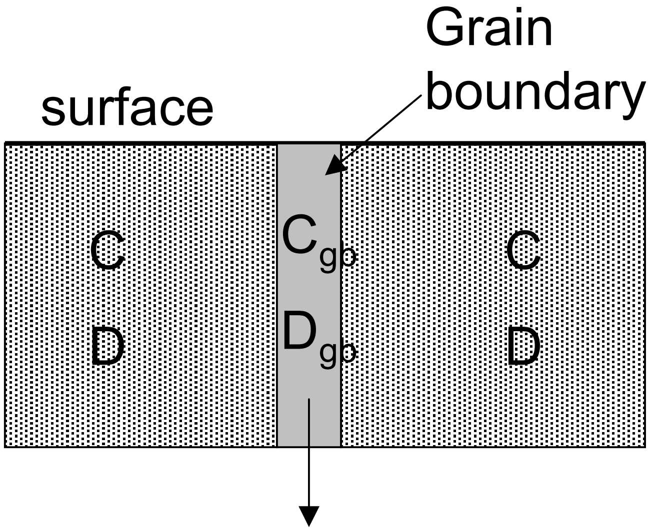
Typical values H_{act} ~1-5 eV $D_0 \sim 10^{-4}\ cm^2 s^{-1}$

Grain Boundary Diffusion

Activation energies for diffusion often found to be much less than expected for bulk defect diffusion

Atomic disorder and lower density around grain boundaries gives rise to lower activation energies

Density of defects also higher close to grain boundaries



$C_{gb} > C$

$D_{gb} > D$

Therefore grain boundary diffusion dominates at low temperatures

Examples of Diffusion

- Inter-diffusion of alloys
- Grain boundary diffusing in sintering
- Creep
- Changes of Phase
- Fast ion conduction (solid state batteries)

Li ion Batteries

- Driving force for better (smaller, lighter, cheaper, better recyclability) batteries is considerable.
- Li is good potential material because of strong reducing properties (loses electrons easily)
- Early Li batteries used Li metal but these were withdrawn due to safety considerations
- Modern methods use intercalation – Li ions are repeatedly inserted into available sites in the host structure framework

Thermal properties

Heat Capacity

Thermal conductivity

Thermal expansion

Why study thermal properties

Need to know how much a material will expand/contract on heating/cooling

Need to know how fast energy will be transported through a material from a heat source

Heat capacity

Definition:

The amount of heat required to raise the temperature of a mole of a material by a unit of temperature.

$$C = dQ/dT$$

Units $\quad$ $\mathrm{J\ mol^{-1}\ K^{-1}}$

Specific heat capacity

heat capacity per unit mass ($\mathrm{J\ kg^{-1}\ K^{-1}}$)

Dulong and Petit Law

The specific heats of many materials at room temperature are the same

Equipartition of energy

Energy per mole = 3 k T N_A

N_A is Avogadro's number

$C_v = \delta E/\delta T = 3\ k\ N_A$ /mole = 24.94 J $mol^{-1}\ K^{-1}$

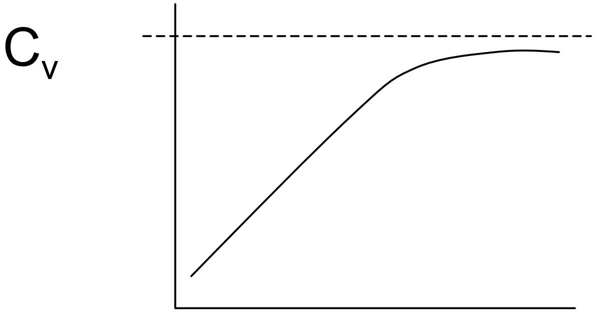
Cu : C_V = 24.6 J $mol^{-1}\ K^{-1}$

Pb : C_V = 26.5 J $mol^{-1}\ K^{-1}$

Al : C_V = 24.3 J $mol^{-1}\ K^{-1}$

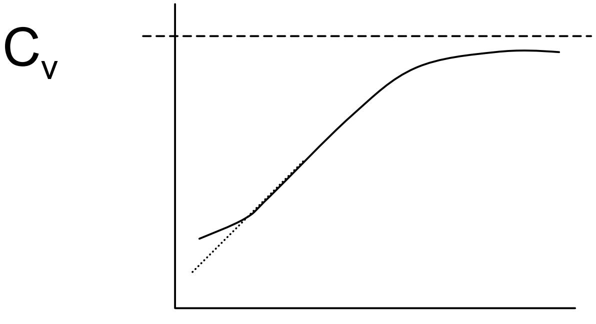
Au : C_V = 25.6 J $mol^{-1}\ K^{-1}$

Low temperature specific heat



Silicon

$C_v \propto T^3$



Copper

Departs from $C_v \propto T^3$ at very low T

At low temperatures the phonon contribution becomes important

Bose-Einstein statistics

Debye theory: $C_v = 12/5\ \pi^4 Nk\ (T/T_D)^3$

Metals – electronic contribution Fermi – Dirac statistics

Einstein Debye: $C_{electrons} = \pi^2 N_A k^2 T / 2E_F$

Specific Heat Capacity

Typical values (J kg^{-1} K^{-1})

Metals	~ 300 – 900
Ceramics	~ 700 – 900
Polymers	~ 1000 - 2000

Thermal Expansion

Definition:

The fraction change in length/volume per unit temperature rise

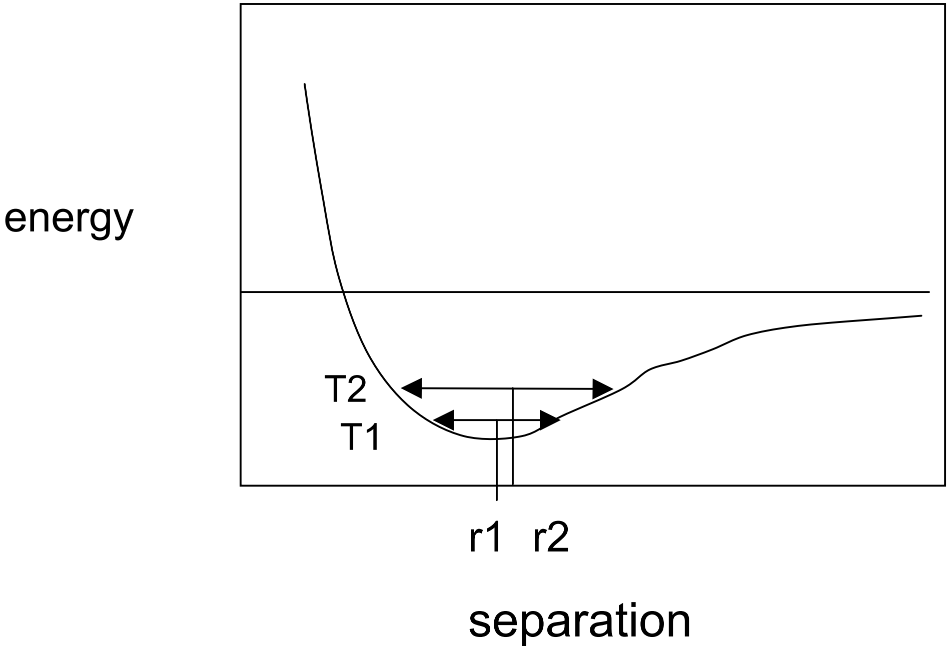
Length $\alpha_L = \Delta l / l_0 / \Delta T$

Volume $\alpha_v = \Delta V / V_0 / \Delta T$

Origin of expansion

Thermal expansion caused by increase in average distance between atoms

Increase arises from anharmonicity of interatomic potentials



Thermal expansion

Typical values (x 10^{-6} K^{-1})

Metals	~ 5-25
Special alloys (FeNi, invar)	< 1
Ceramics	~ 0.5 – 15
Polymers	~ 50 – 300

Invar Effect

- Guillaume (1897) noted that Fe Ni(35%) exhibits anomalously low thermal expansion over a wide range of temperatures

- Other properties (heat capacity, modulus and magnetisation) also show anomalous behaviour

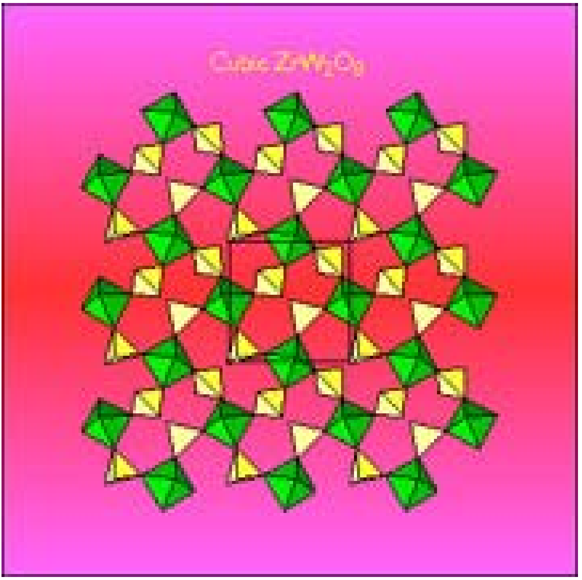
- Effect related to magnetism but full understanding is still lacking

- Change in magnetic alignment with volume – anomalous volume dependence of binding energy

- Applications
  - Electronic devices – Cathode ray tubes
  - Aircraft controls
  - Bimetal strips in household appliances

Negative expansion materials

- Certain complex ceramics were found to have a negative coefficient of expansion
- Example – ZrW_2O_8 – Negative coefficient from 0 – 1050 K
- Origin of effect
  - Structure composed of linked (nearly) rigid octahedral and tetrahedra
  - Rotation of these units causes shrinkage
  - Increasing temperature increases rotation



From http://www.esc.cam.ac.uk /astaff/dove/zrw2o8.html

Zero-expansion Materials

- Recent Nature paper (Salvador et al.Nature, **425**, 702 (2003)) reported an alloy (YbGaGe) with zero thermal expansion coefficient

- Unlike negative expansion materials this alloy is conducting

- Origin of effect is electronic (not magnetic)
  - With increasing temperature electrons move from Yb to Ga
  - Yb shrinks but Ga remains unchanged
  - Counteracts normal thermal expansion

Thermal conductivity

Definition

Thermal conduction is the phenomenon whereby heat is transported from regions of high temperature to regions of low temperature

$q = -\kappa\, dT/dx$ (cf Fick's law for diffusion)

κ is the thermal conductivity - units $W\ m^{-1}\ K^{-1}$

q is the heat flux per unit area per unit time ($W\ m^{-2}$)

Mechanisms of heat transport

Phonons – dominates in insulators

$\kappa = 1/3\, C_v\, v\, \lambda$ (cf diffusion)

v is phonon velocity

λ is phonon mean free path

-Limited by

- Other phonons
- Impurities
- Defects – vacancies, dislocations
- Grain boundaries

Mechanisms of heat transport

Free electrons – dominates in metals

$$\kappa = 1/3\ C_v\ v\ \lambda$$

Wiedemann-Franz law

At a given temperature the Thermal conductivity of a metal is proportional to the electrical conductivity

$$\kappa/\sigma = LT$$

Thermal conductivity increases with T – increased velocity

Electrical conductivity decreases with T – increased scattering

L (Lorentz number) should be independent of T and same for all metals

($2.44 \times 10^{-8}\ \Omega W K^{-2}$) if heat energy entirely transported by free electrons

Typical values of κ ($W\ m^{-1}\ K^{-1}$)

Metals	~	100 - 400
Ceramics	~	1 – 40
Polymers (good insulators)	~	0.1 – 0.2
Diamond	~	2000

Conductivity can be reduced by making porous materials

-Styrofoam cups (foamed polystyrene)

-Porous ceramics

-Foamed metals

Thermal stress

- Stresses induced by temperature changes
  - eg brass rod heated but prevented from lengthening
  - Compressive stress $\sigma = E\alpha(T-T_0)$

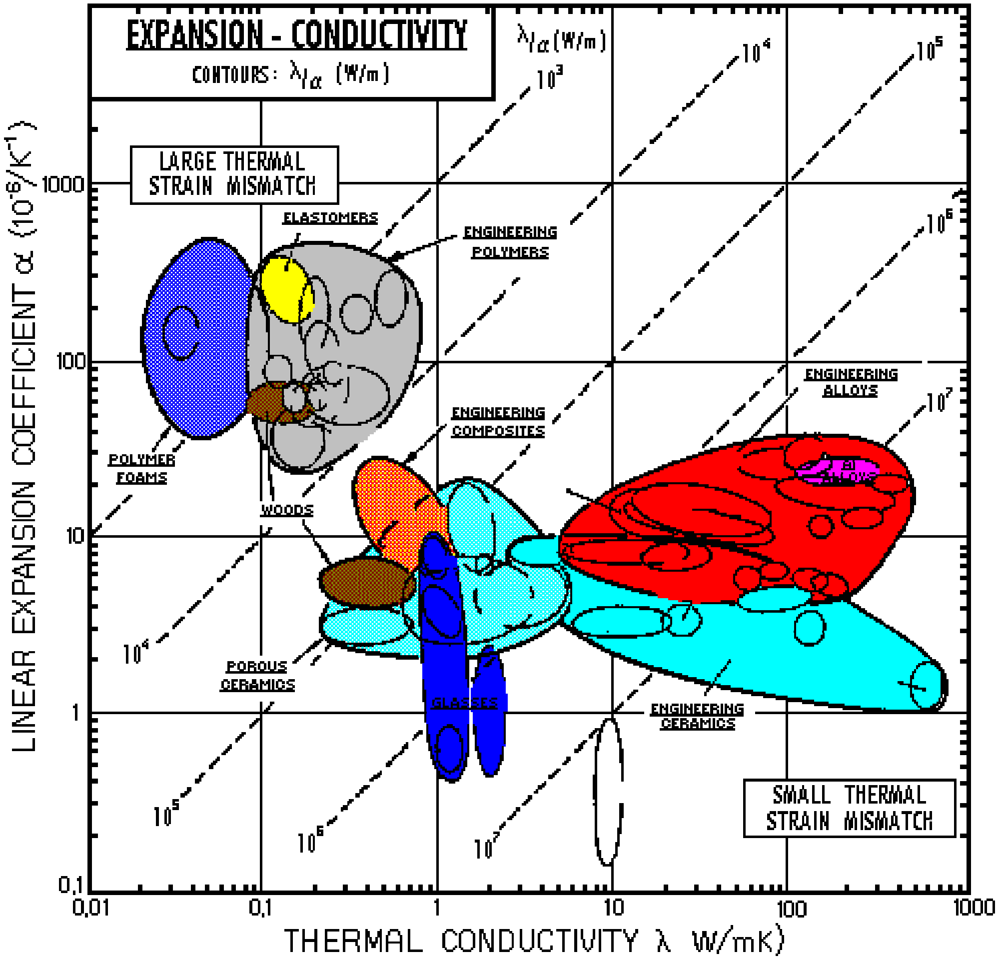
- Thermal stresses may cause fracture in brittle materials (ceramics)
  - Surface cools rapidly and tries to contract
  - Interior cools more slowly
  - Residual stresses

- Fracture most likely to occur during cooling

Thermal Shock Resistance

Figure of Merit

$$\frac{\text{Strength x Thermal Conductivity}}{\text{Young's Modulus x Thermal Expansion}}$$



Thermal Shock Resistance

- Spark plugs
- Engine components
- High voltage insulators
- Crucibles
- Furnace linings
- Cookware
- Cookers / hobs

Applications

- Heat sinks
  - Electronic components – size of electronic devices often limited by rate at which energy can be removed from unit
- Insulators
  - Homes
  - Refrigeration
- Thermal barriers
  - Plasma spayed coating of ZrO_2 8%Y_2O_3 on aero-engine components (low thermal conductivity, good thermal shock resistance)
  - Space shuttle solid rocket components (Carbon fibre based material, ceramics reinforced with carbon nanotubes)

Part 1 - Summary

- Revision of / Introduction to
  - Crystal structure, bonding
    - From these we can estimate fundamental crystal properties (modulus, ideal strength)
  - Microstructure – dislocations, grain boundaries
    - The microstructure varies with processing
    - The microstructure influences all properties of real materials

- Diffusion
  - The transport of atoms in materials
  - Materials processing depends on moving atoms in materials

- Thermal properties
  - How materials behave when subjected to high temperatures / sudden temperature changes