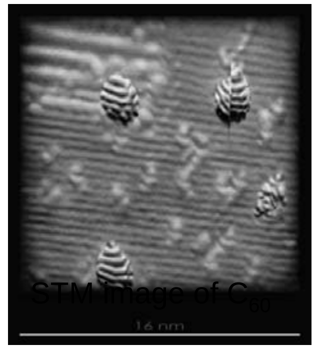
Chapter 3 (cont.)

This section will address the question “how do we determine the crystal structure of a solid sample?”



STM image of C_{60}

Some techniques used:

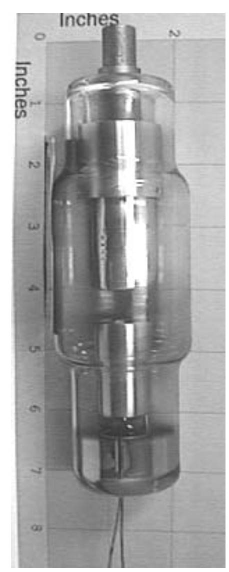
- Electron microscopy (by direct and indirect observations)
- Scanning tunneling microscope (direct observation)
- X-ray diffraction (indirect observation and analysis)

Different electromagnetic waves can be diffracted, but they have to be coherent: electron beams, laser beams, x-ray beams

X-Ray Generation

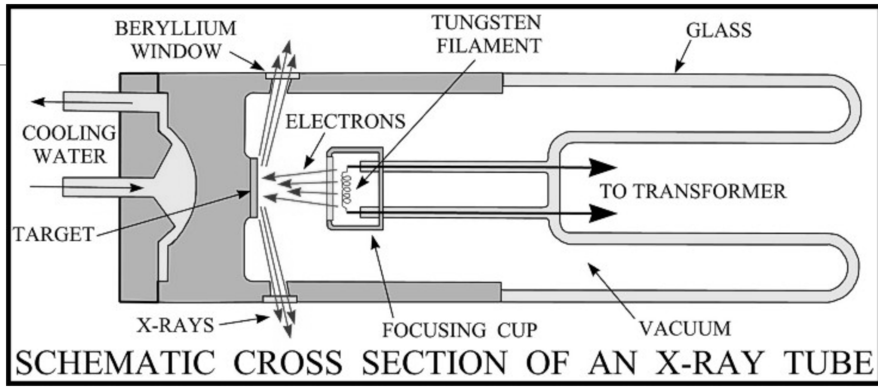
Since we are talking about X-rays, we need to know how to generate X-rays (same way as in medical applications!)

We need:
- A source of a highly energetic electron beam
- A metallic target (Cu, Co, Fe, Ni, etc.)
- A system that contains and directs the X-rays onto the specimen

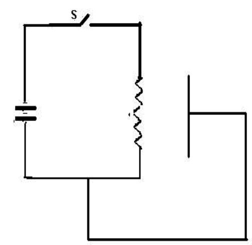


100 KV with tungsten target without shield, for medical applications

This is the x-ray tube. Notice that it is sealed under vacuum.



The W filament at very high temperature generates a highly energetic electron beam similarly to electron microscope cathodes (thermionic emission). Homework: what is *thermionic emission*? Do not confuse with *thermal emission* (pages780-781)



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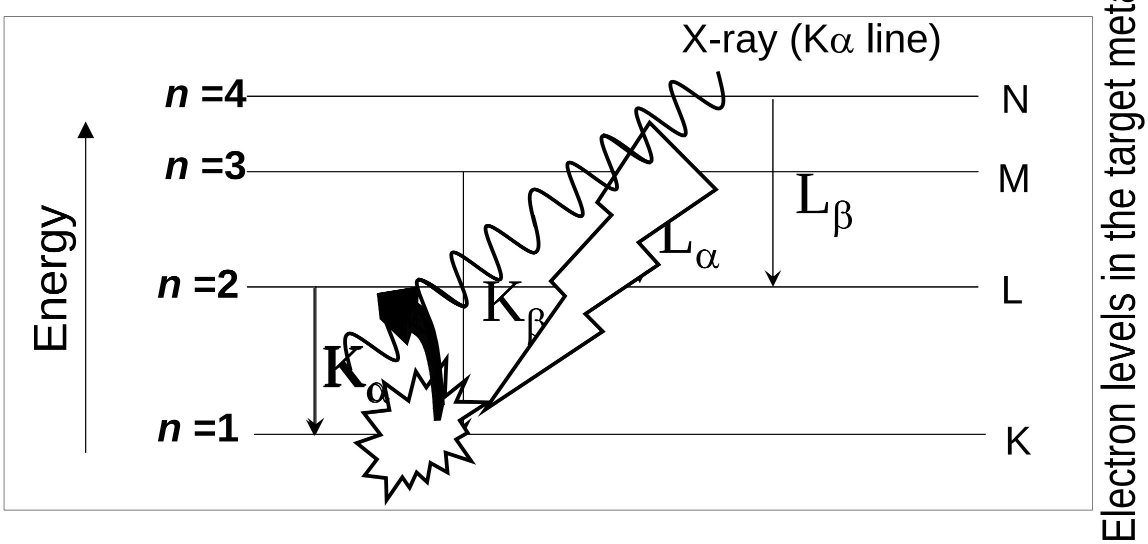
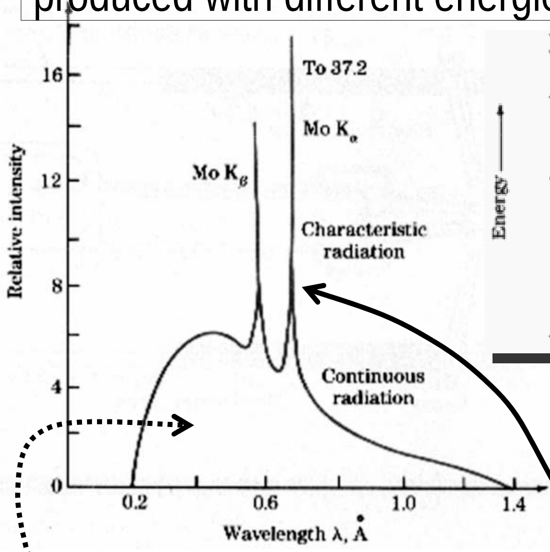
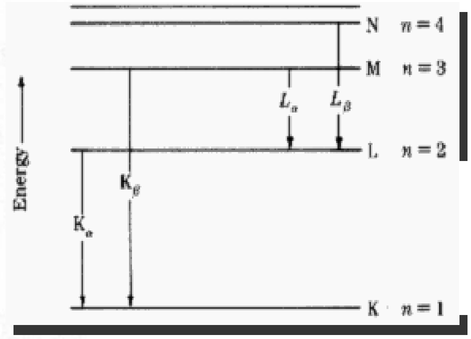
How X-rays are generated or how to knock off electrons from a target…

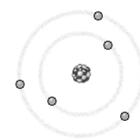


Remember that there are also subsidiary (secondary) energy levels

Since there are many striking electrons, there are many x-rays produced with different energies to create an emission spectrum.





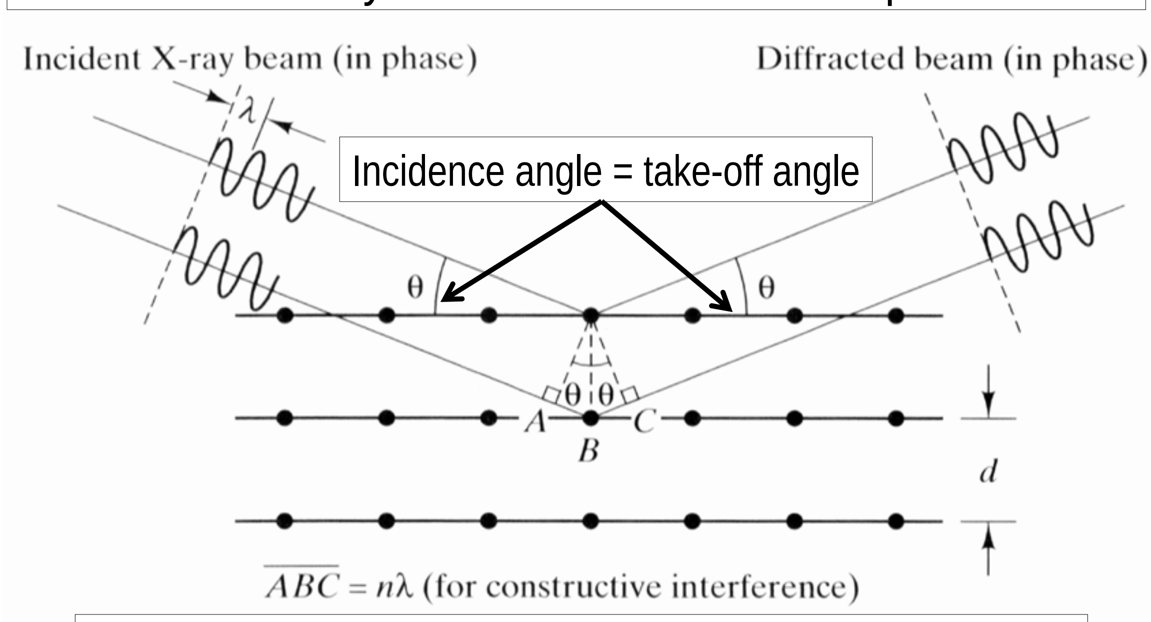


Remember Planck's equation: $E \propto \frac{1}{\lambda}$

Then for Mo: energy for Kα is 17.44KeV or λ=0.071nm

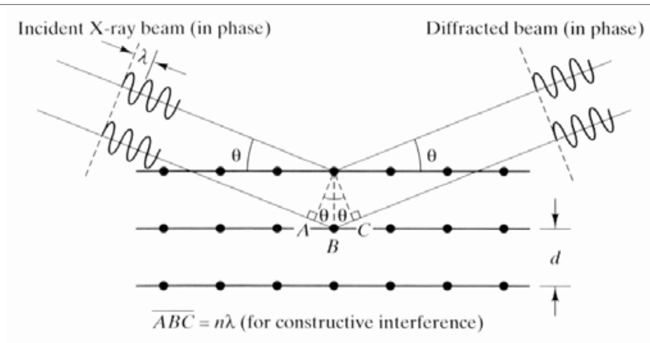
The "background" noise is the Bremsstrahlung radiation caused by the "braking" (deceleration) of x-rays when they hit the target.

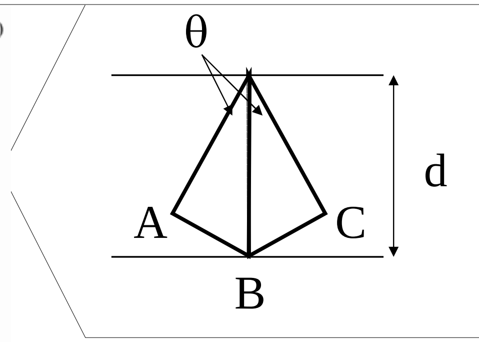
Then the x-ray beam interacts with the specimen



ABC is the only difference between both X-ray trajectories

Constructive interference helps state Bragg's law of diffraction





In order to get constructive interaction:

$$\overline{ABC} = n\lambda = 2d \cdot \sin\theta$$ where n is an integer

and d is the interplanar distance, which is calculated as (in *cubic crystals*):

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Metal Targets

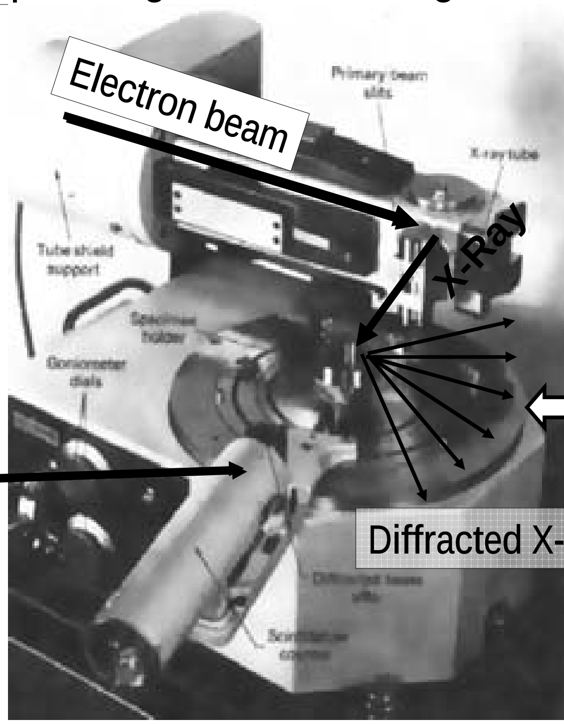
- Remember that different target metals produce different diffraction patterns (cones):

$$\lambda = 2d \cdot \sin\theta$$

- Common targets:

Target	Kα wavelength (nm)
Cr	0.229092
Fe	0.193736
Co	0.179026
Cu	0.154178
Mo	0.071069
W	0.021060

Then we need to measure not only diffracted X-rays but also the corresponding diffraction angles:

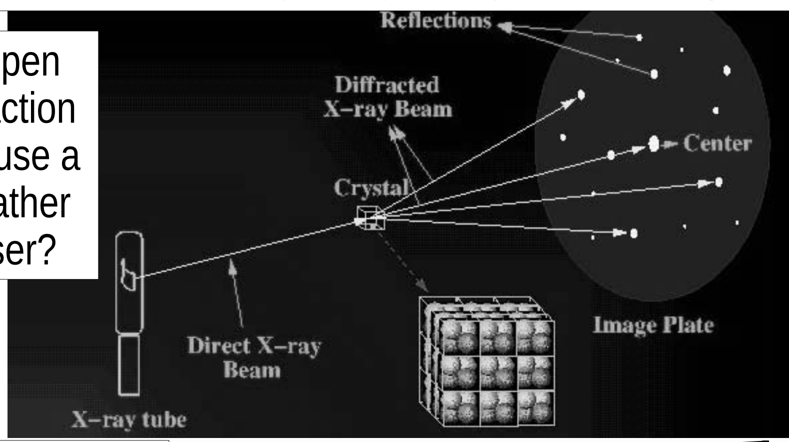


<u>The X-ray diffractometer</u> detects X-rays and records the angle at which they were detected.

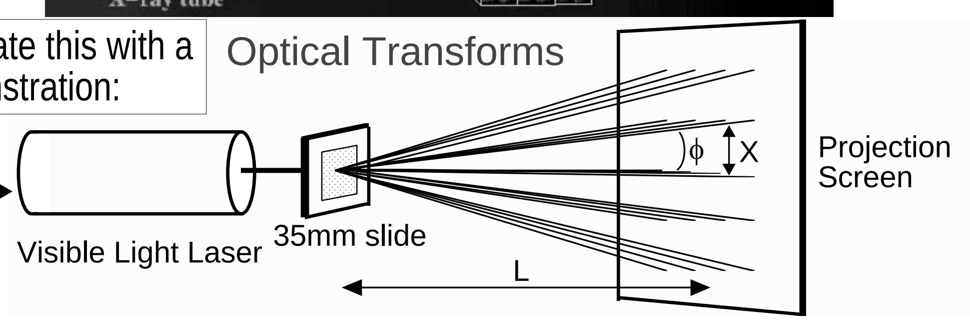
LiF diffracts Cu Kα x-rays at 2θ=44.4^{o}

The diffraction of a single crystal generates "points."

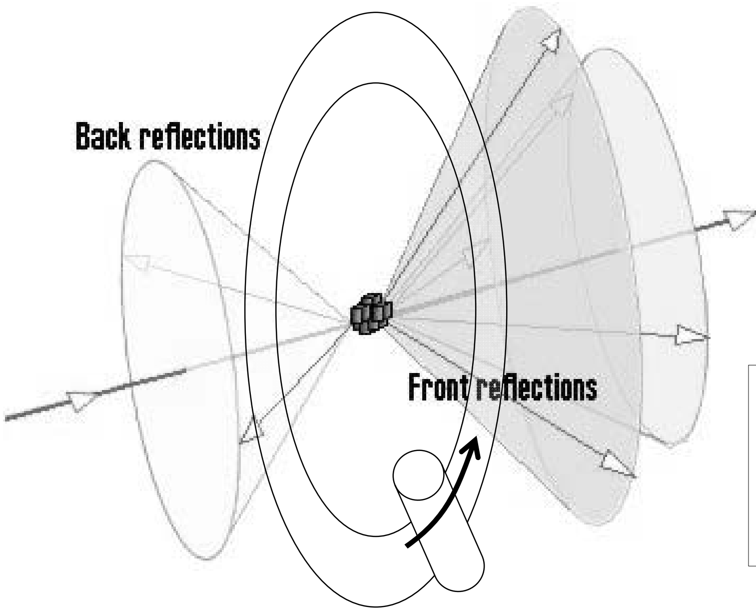
What will happen with the diffraction pattern if we use a green laser rather than a red laser?



Let's simulate this with a little demonstration:



However, if we have zillions of grains (powder form) then the sample will diffract "cones of x-rays."



Now let's cut the cones with a vertical plane and locate a detector on that plane. The detector will slide always looking at the sample

Every time the detector crosses a diffraction cone will detect a strong x-ray signal

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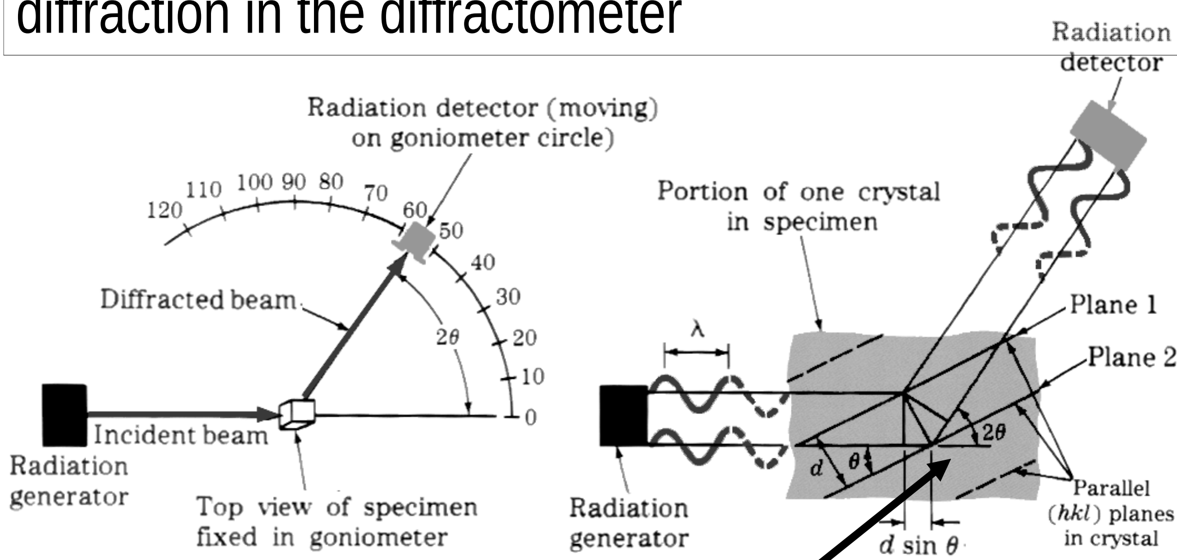
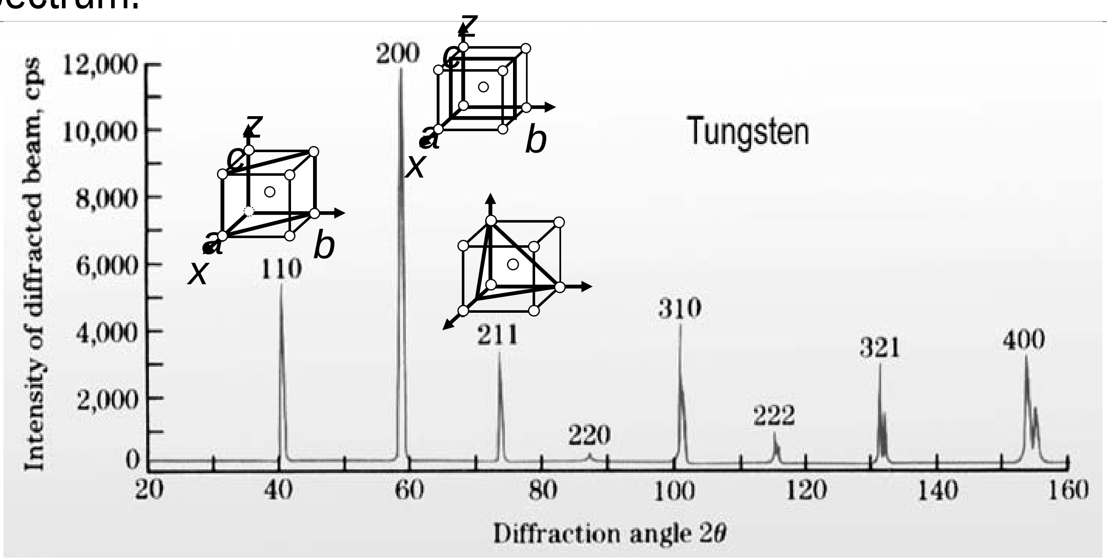
Be careful with the definition of the total angle of diffraction in the diffractometer



The total diffraction angle is 2θ!!

The result of X-ray intensity and measured 2θ angles is an x-ray spectrum.



X-Ray diffraction pattern generated by a pure W sample, under Cu-Kα radiation (λ=0.1542nm)

Not all planes diffract in different crystals

There are rules for diffracting and non-diffracting planes

Unit Cell	**Reflections Present**	**Reflections Absent**
BCC	(*h*+*k*+*l*) = even	(*h*+*k*+*l*) = odd
FCC	(*h, k, l*) = all odd or all even	(*h, k, l*) = not all odd or not all even
SC	All	None

For other ones check the next table

	Cubic				Hexagonal	
	hkl					
$h^2 + k^2 + l^2$	Simple	Face-centered	Body-centered	Diamond	$h^2 + hk + k^2$	*hk*
1	100				1	10
2	110	. . .	110		2	
3	111	111	. . .	111	3	11
4	200	200	200		4	20
5	210				5	
6	211	. . .	211		6	
7					7	21
8	220	220	220	220	8	
9	300, 221				9	30
10	310	. . .	310		10	
11	311	311	. . .	311	11	
12	222	222	222		12	22
13	320				13	31
14	321	. . .	321		14	
15					15	
16	400	400	400	400	16	40
17	410, 322				17	
18	411, 330	. . .	411, 330		18	
19	331	331	. . .	331	19	32
20	420	420	420		20	
21	421				21	41
22	332	. . .	332		22	
23					23	
24	422	422	422	422	24	
25	500, 430				25	50
26	510, 431	. . .	510, 431		26	
27	511, 333	511, 333	. . .	511, 333	27	33
28					28	42
29	520, 432				29	

This is the sequence of planes as they show up in a spectrum from left to right (on a 2θ scale)

So we can determine the crystal structure of a given specimen!

- Look for the first two consecutive low Miller indices planes and record their diffraction angle θ, e.g. θ_1 and θ_2.
- Compute the following division: $$\frac{\sin^2\theta_1}{\sin^2\theta_2}$$
- If it is: $\frac{\sin^2\theta_1}{\sin^2\theta_2} \approx 0.50 \Rightarrow$ BCC or SC
- If it is: $\frac{\sin^2\theta_1}{\sin^2\theta_2} \approx 0.75 \Rightarrow$ FCC

This is valid only for the first two peaks! ***For other peaks and unit cells you do the math!***

Calculate the ratio for the first and second peaks in a diamond cubic cell

Now let's identify the crystal

- Once you have defined what cubic crystal it is, you have to determine its lattice constant **a**:

For a cubic unit cell: $$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

So how do you get **d** and where are you going to obtain *h*, *k*, *l*?

Identification of a Crystalline Solid

To finalize and corroborate an identification, check a table of densities ρ [g/cm^3] and do the following:

$$\Sigma A = 602.257\,\rho \cdot V$$ V: unit cell volume in nm^3

ΣA is the sum of the atomic weights of ALL the atoms in the unit cell: $$\Sigma A = n \cdot A \therefore n = \frac{\Sigma A}{A} = \frac{602.257 \rho V}{A}$$

<u>n</u> should be very close to the <u>correct</u> integer if your calculations are right.

Estimation of Crystallite Size (Scherrer's Formula)

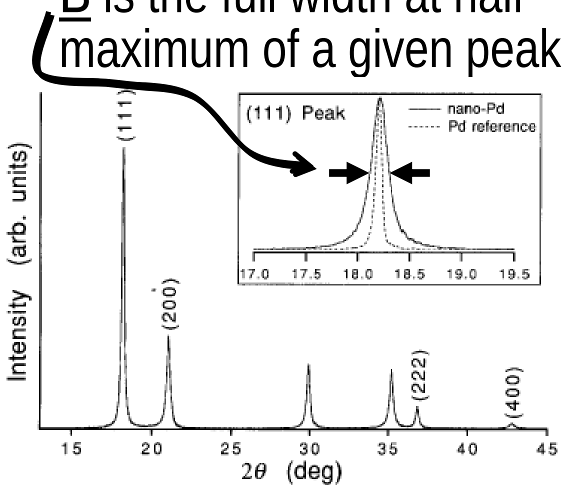
The crystallite or particle size *t* (diameter) relates to the peak broadening:

$$B = \frac{0.9\lambda}{t \cdot \cos\theta}$$

B is the full width at half maximum of a given peak

B should be in radians.

This is used to roughly estimate the size of nanoparticles in powder or aggregate form.



Nanosized Pd and regular powdered palladium (Pd) spectra.

Chapter 4

Imperfections in the Atomic and Ionic Arrangements

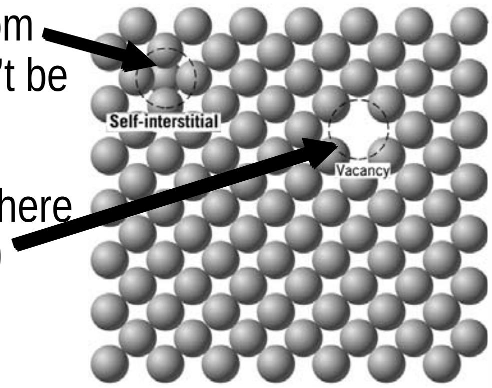
Crystalline Imperfections

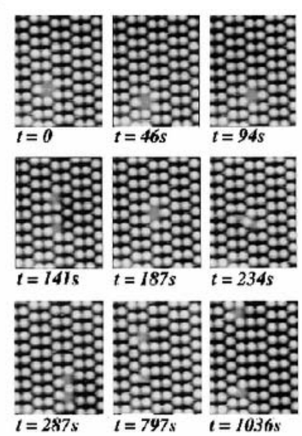
We will differentiate three types of imperfections:

- Zero-dimension imperfections (point defects)
- One-dimension imperfections (linear defects)
- Two-dimension imperfections (surface defects)

There are two main types of point defects in a pure solid element:

- Interstitialcy (one atom where there shouldn't be any)
- Vacancy (no atom where there should be one)





STM image of vacancy movement in Ge

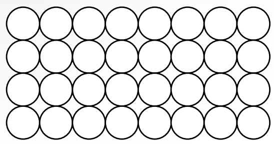
All point defects distort the surrounding atomic arrangement.

What does this tell you about the lattice energy?

How do we calculate the equilibrium concentration of point defects?

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

- No. of defects: N_D
- Activation energy: Q_D
- Temperature: T
- No. of potential defect sites: N
- Boltzmann's constant: k
  - (1.38 x 10^{-23} J/atom K)
  - (8.62 x 10^{-5} eV/atom K)



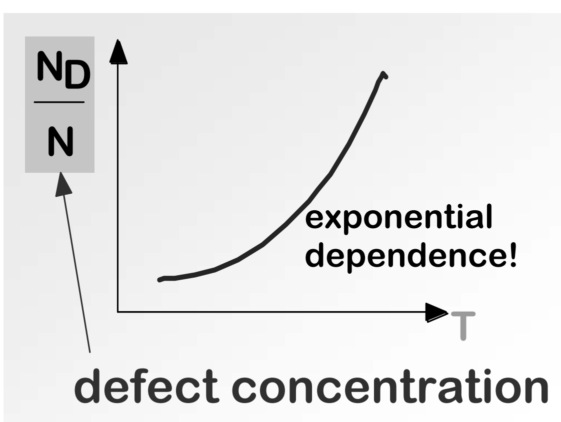
Each lattice site is a potential vacancy site

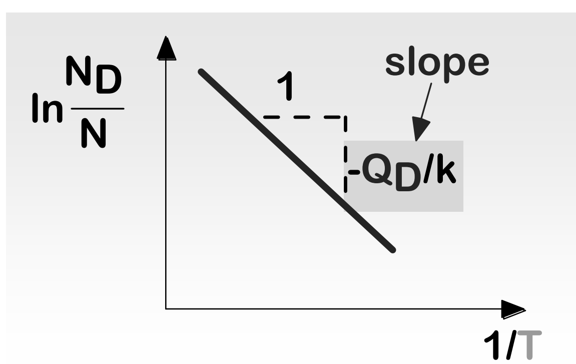
These are "thermally activated defects" because the equilibrium concentration varies with temperature!

But what is the activation energy Q_D? A threshold or an energy barrier

$$\frac{N_D}{N} = \exp\left(\frac{-Q_D}{kT}\right)$$

- We can get Q from an experiment.
  - Measure this...
  - Replot it...

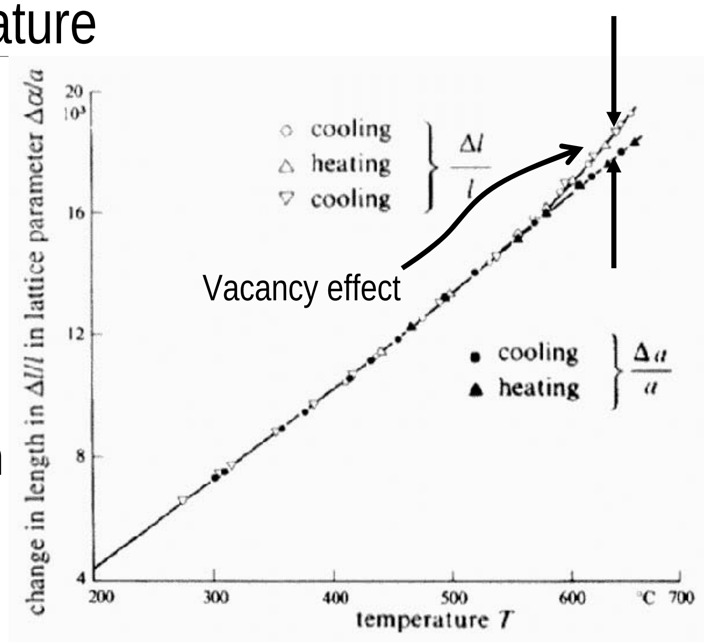




There is another manifestation of vacancies as a function of temperature

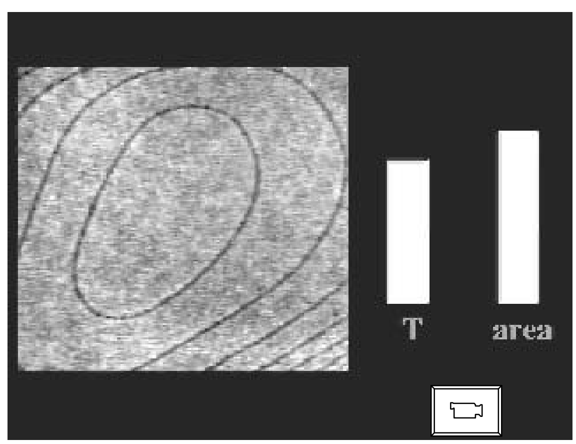
Difference between macroscopic measurements of length changes and microscopic determination of lattice constant changes for aluminum

Now, you understand why the *theoretical* density has that name

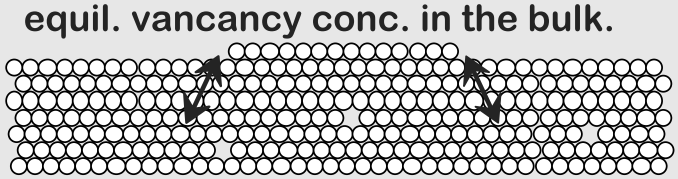


Can we observe those vacancies?

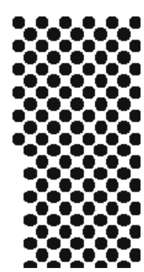
- Low energy electron microscope view of a (110) surface of NiAl.
- Increasing T causes surface island of atoms to grow.
- Why? The equivalent vacancy concentration increases via atom motion from the crystal to the surface, where they join the island.



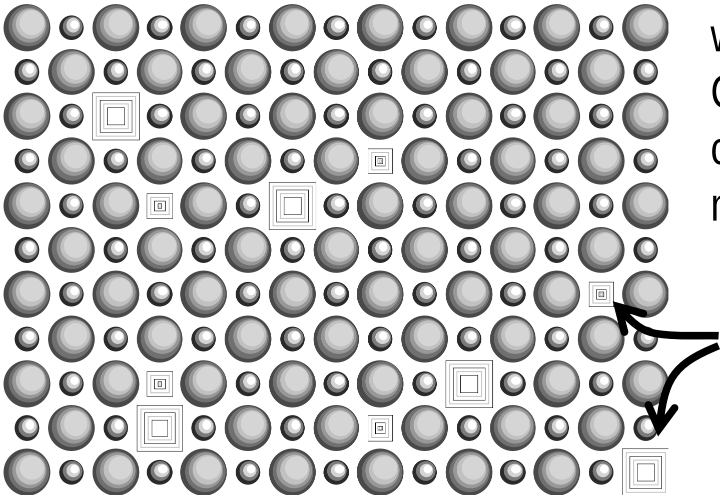
Island grows/shrinks to maintain equil. vancancy conc. in the bulk.



We'll see in the next chapter how vacancies "move."



In ionic crystals point defects are somewhat different:

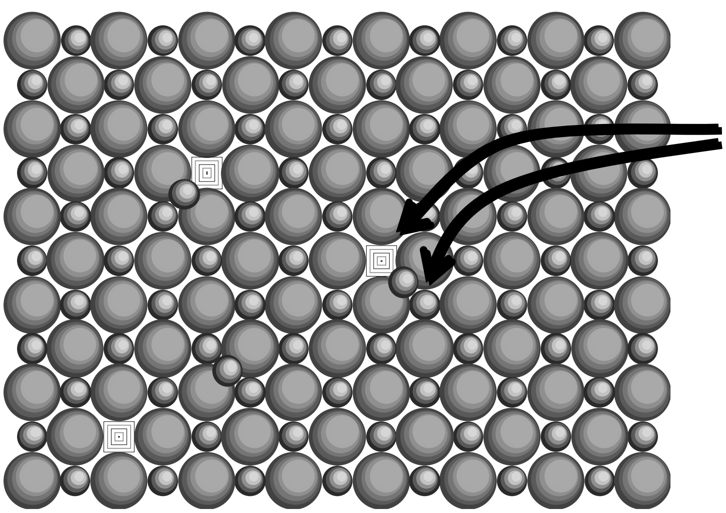


One main difference with respect to metals: Charge Neutrality of the crystal needs to be maintained!

<u>Schottky</u> defects are like vacancies in metals

So, any ideas how to make “ionic electrical conductors”?

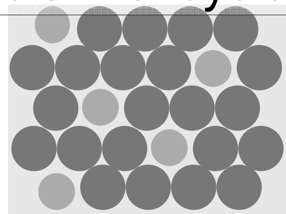
Point defects in ionic crystals:



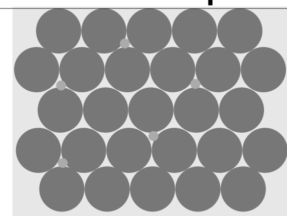
Then <u>Frenkel</u> defects are like interstitials and vacancies in metals. Again, charge neutrality is preserved.

Again, any ideas how to make “ionic electrical conductors”?

Point defects in alloys are related to composition:



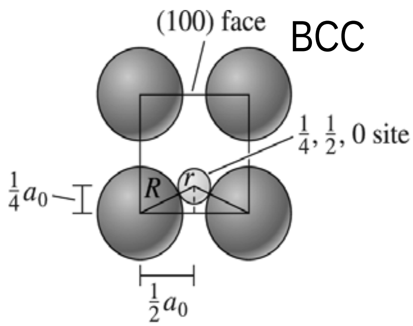
OR



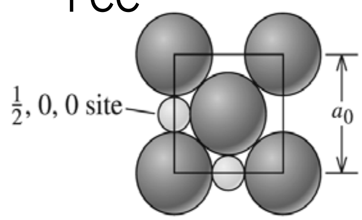
Substitutional alloy (e.g., Cu in Ni) Interstitial alloy (e.g., C in Fe)

Calculate the maximum size of interstitials that can be dissolved in:

BCC



FCC



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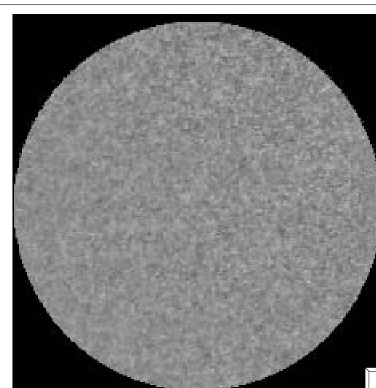
When alloying atoms move on a surface

- Low energy electron microscope view of a (111) surface of Cu.
- Sn islands move along the surface and "alloy“ the Cu with Sn atoms, to make "bronze".
- The islands continually move into "unalloyed“ regions and leave tiny bronze particles in their wake.
- Eventually, the islands disappear.



Field of view is 1.5 mm and the temperature is 290K.

Let's Run Some Numbers

- Calculate the number of atoms in 1 g of nickel. Data:
  - Atomic mass of Ni: 58.71 (units?)
  - $N_A = 6.023 \cdot 10^{23}$ atoms/mol
- In an alloy containing 15g of Pd and 85g of Ni, calculate the weight percent of Pd and Ni and their atomic percent.
- Create a formula to convert back and forth from wt.% $\rightarrow$ at.% and from at.% $\rightarrow$ wt.%

Let's calculate the composition of a (binary) alloy or mixture

Definition: Amount of impurity (B) and host (A) in the system.

Two descriptions:

- Weight %

$$C_B = \frac{\text{mass of B}}{\text{total mass}} \times 100$$

- Atom %

$$C'_B = \frac{\text{\# atoms of B}}{\text{total \# atoms}} \times 100$$

- Conversion between wt % and at% in an A-B alloy:

$$C_B = \frac{C'_B A_B}{C'_A A_A + C'_B A_B} \times 100$$

$$C'_B = \frac{C_B / A_B}{C_A / A_A + C_B / A_B}$$

- Basis for conversion:

mass of B = moles of B x A_B ← atomic weight of B

mass of A = moles of A x A_A ← atomic weight of A

Let’s talk more about solid solutions

- So, what’s a solution?
- Examples?

The same situation in solid state represents a solid solution.

Two or more metallic or non-metallic elements atomically dispersed in a single-phase structure.

There are two types of solid solutions

Two different types:

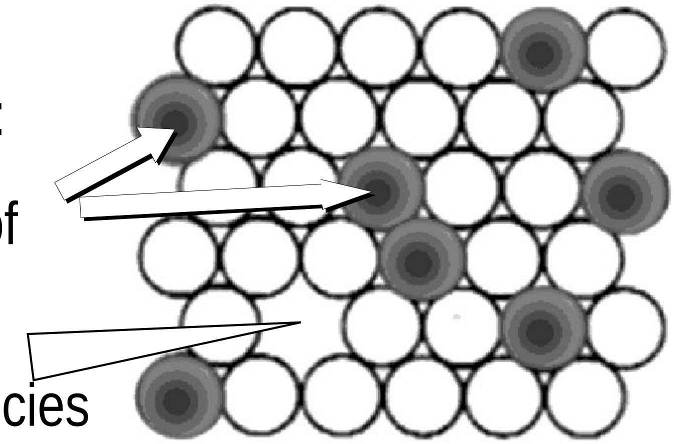
- Substitutional solid solutions
- Interstitial solid solutions

Different conditions for the atoms intervening in the solution.

Solute and solvent have different characteristics.

Substitutional Solid Solutions

Example: (111) plane in an FCC solvent ("white atoms") dissolving another metal ("red atoms")



Two characteristics:

- Random location of solute atoms
- Presence of vacancies

Substitutional Solid Solutions (cont.)

The conditions for better substitutional solubility between two elements according to Hume-Rothery are:

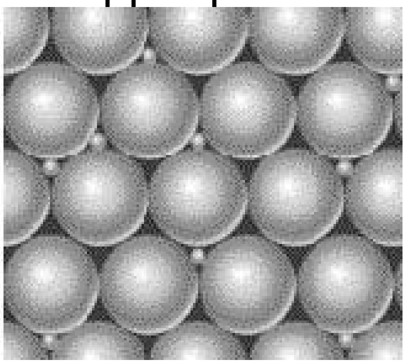
- Similar atomic sizes: diameters not more than 15% in difference
- Similar crystal structures
- No significant difference in electronegativities
- Solvent and solute must have similar valence

Interstitial Solid Solutions

Now the main condition is the size of the solute atom

For interstitials look in the upper part of the periodic table:

- Hydrogen
- Nitrogen
- Carbon
- Oxygen



Compare both solid solutions in the graph