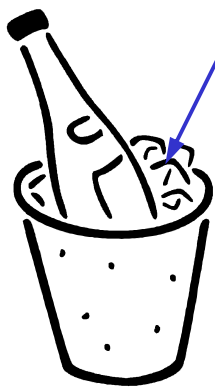# Crystal Structures

D. K. Ferry, J. P. Bird,
D. Vasileska and G. Klimeck

Crystal Structures

Matter comes in many different forms—the three we are most used to are solid, liquid, and gas.
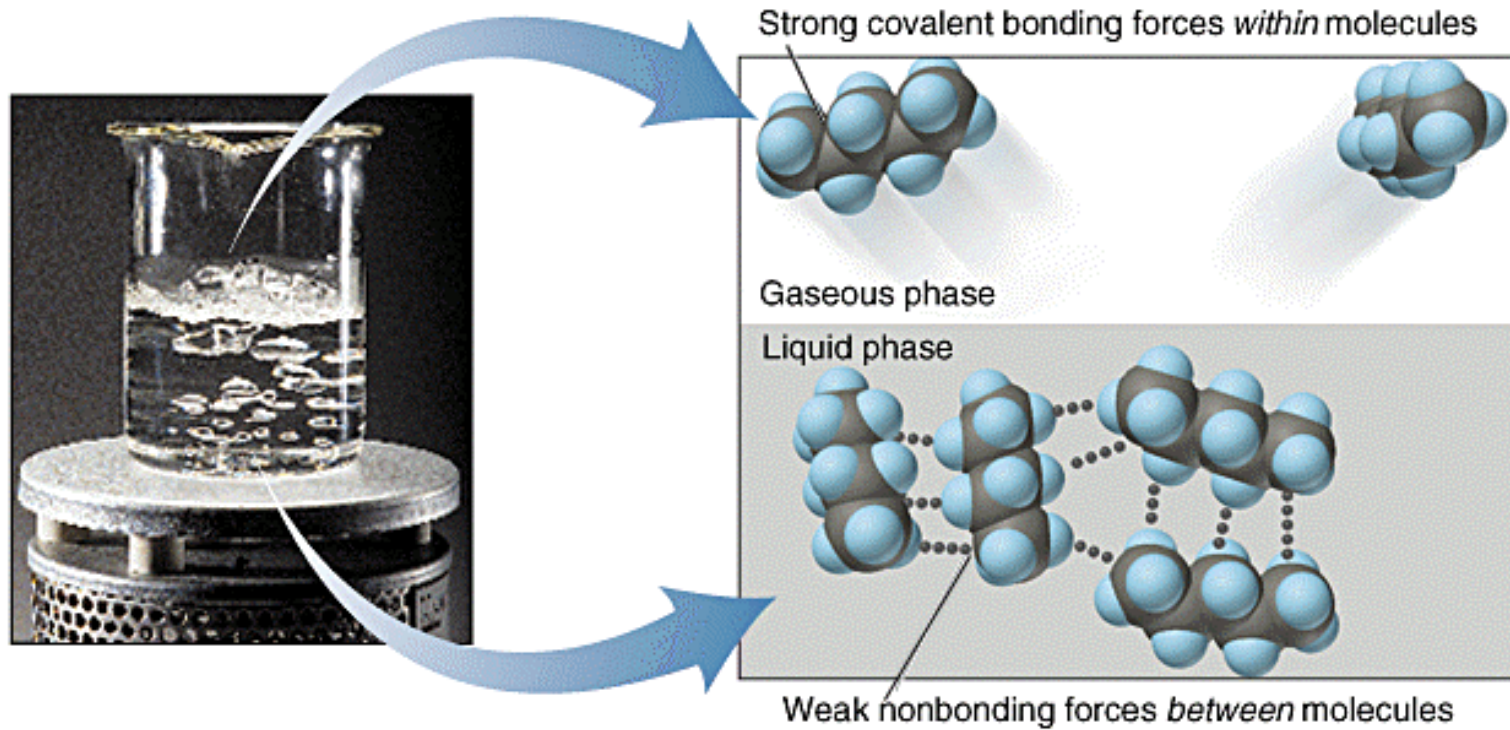
water

ice

**Air
Water vapor
etc.**

Matter in its Many Forms

Strong covalent bonding forces *within* molecules

Gaseous phase
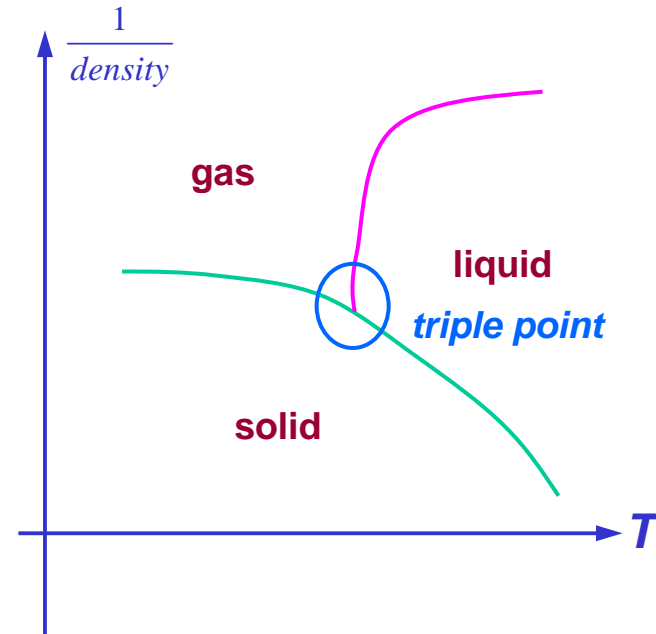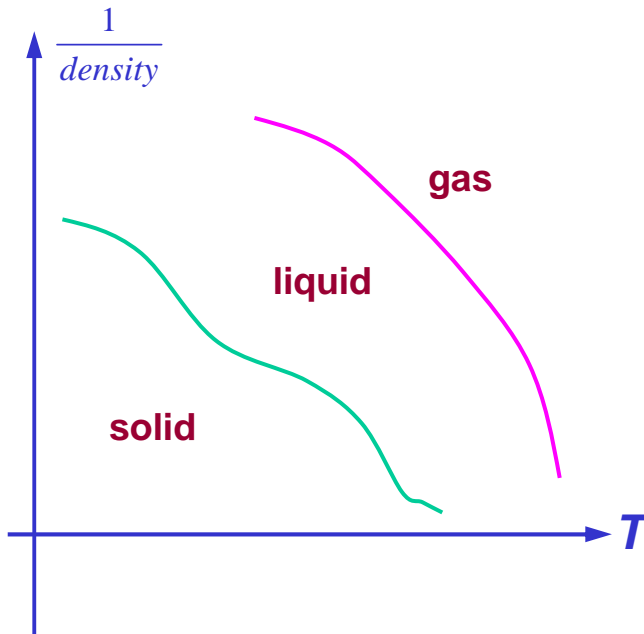
Liquid phase

Weak nonbonding forces *between* molecules

Matter in its Many Forms

Heating ice produces water (T > 0 C, 32 F – melting point)

**Heating water produces steam (water vapor) (T > 100 C, 212 F)**

These transitions are *phase transitions*.

**Some materials have *triple points*, where all three forms can exist together at the same time.**

Matter in its Many Forms

• In **LIQUIDS** the density of molecules is very much higher than that of gases

    * **BUT** the molecular interaction is **STILL** relatively weak

        ⇒ **NO** structural stability

• **SOLIDS** may have a similar molecular density to that of liquids

    * **BUT** the interaction between these molecules is now very **STRONG**

        ⇒ The atoms are **BOUND** in a correlated **CRYSTAL** structure

        ⇒ Which exhibits **MECHANICAL STABILITY**
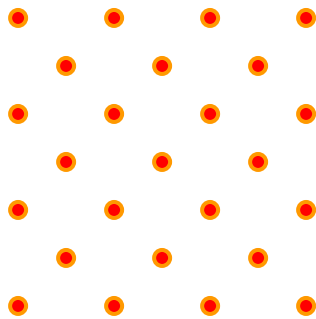
*IN SOLID MATTER THE STRONG INTERACTION BETWEEN DIFFERENT ATOMS MAY BIND THEM INTO AN ORDERED CRYSTAL STRUCTURE*
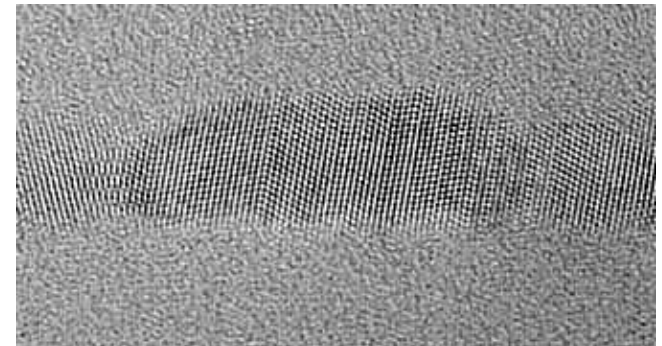
Classifying Solids

• **An issue concerns the classification of ORDER in crystal materials**

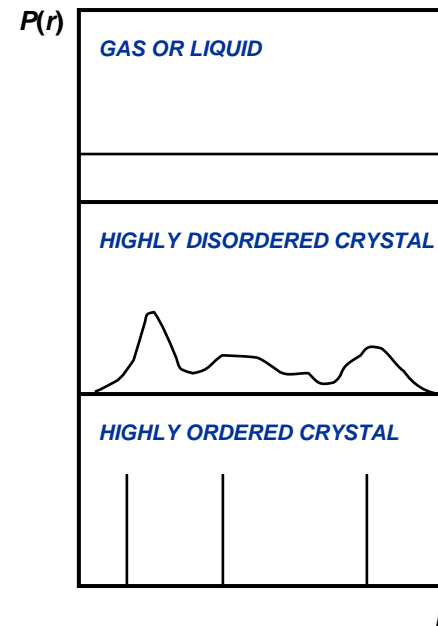   * **In order to achieve this we can define the RADIAL DISTRIBUTION FUNCTION**

        ⇒ **Which tells us WHERE we should find atoms in the material**

        ⇒ **This parameter can be measured experimentally**

r
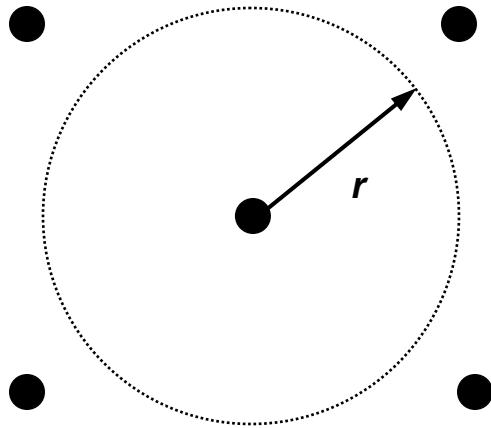
P(r) IS THE POSITION AVERAGED PROBABILITY OF FINDING ANOTHER ATOM AT A DISTANCE r FROM SOME REFERENCE ATOM

P(r)

GAS OR LIQUID

HIGHLY DISORDERED CRYSTAL

HIGHLY ORDERED CRYSTAL

r

Classifying Solids
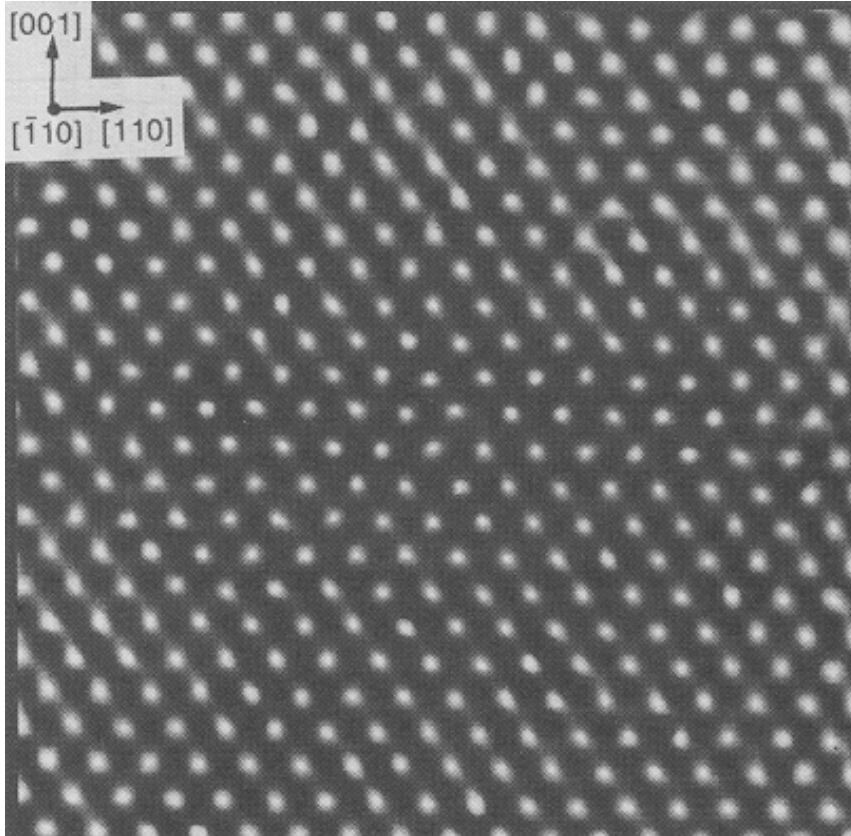
A transmission electron microscope (TEM) image of a highly ordered crystal of Si. We will learn soon about how to discribe the different directions in such a crystal as this.

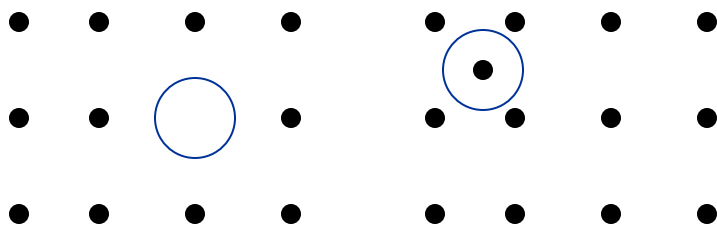# Classifying Solids--Crystals

• In reality very **FEW** materials exhibit perfect crystalline order

    * Most materials develop **IMPERFECTIONS** during their fabrication process

       ⇒ Unwanted **IMPURITY** atoms
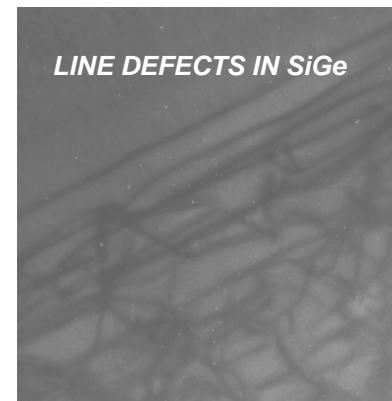
       ⇒ **POINT** and **LINE DEFECTS**

       ⇒ Thermodynamics and **ENTROPY**

VACANCY   *INTERSTITIAL DEFECT*

EXAMPLES OF LINE DEFECTS

LINE DEFECTS IN SiGe

Classifying Crystals

• A large number of materials exhibit **POLYCRYSTALLINE** order

    * These materials consist of regions with **NEARLY PERFECT** order

        ⇒ That are separated by thinner **DISORDERED** regions

        ⇒ The **RELATIVE** orientation of the **CRYSTALLITES** is **RANDOM**
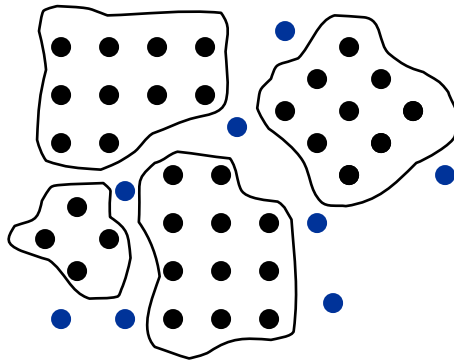
SCHEMATIC ILLUSTRATION OF POLYCRYSTALLINE ORDER

DISORDERED Si
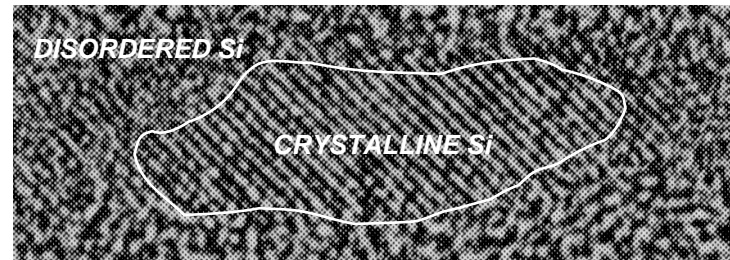
CRYSTALLINE Si

TRANSMISSION ELECTRON MICROGRAPH SHOWING A 10 nm Si CRYSTALLITE EMBEDDED IN DISORDERED Si

Classifying Crystals

• Other materials are referred to as **AMORPHOUS**

    * These are solids in which the molecules are almost **RANDOMLY** arranged

        ⇒ **LITTLE** or no long range order exists

        ⇒ These materials are essentially **HIGHLY VISCOUS** liquids

        ⇒ **GLASS** is an example of an *amorphous solid*
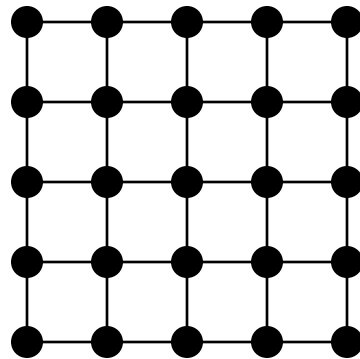
A PERFECT CRYSTAL STRUCTURE

AN AMORPHOUS ATOMIC ARRANGEMENT

Classifying Solids
Transistors in our Integrated Circuit

90 nm Generation Transistors

NiSi Layer

Silicon Gate
Electrode

50nm

1.2 nm SiO$_2$
Gate Oxide

Let's look closer in here
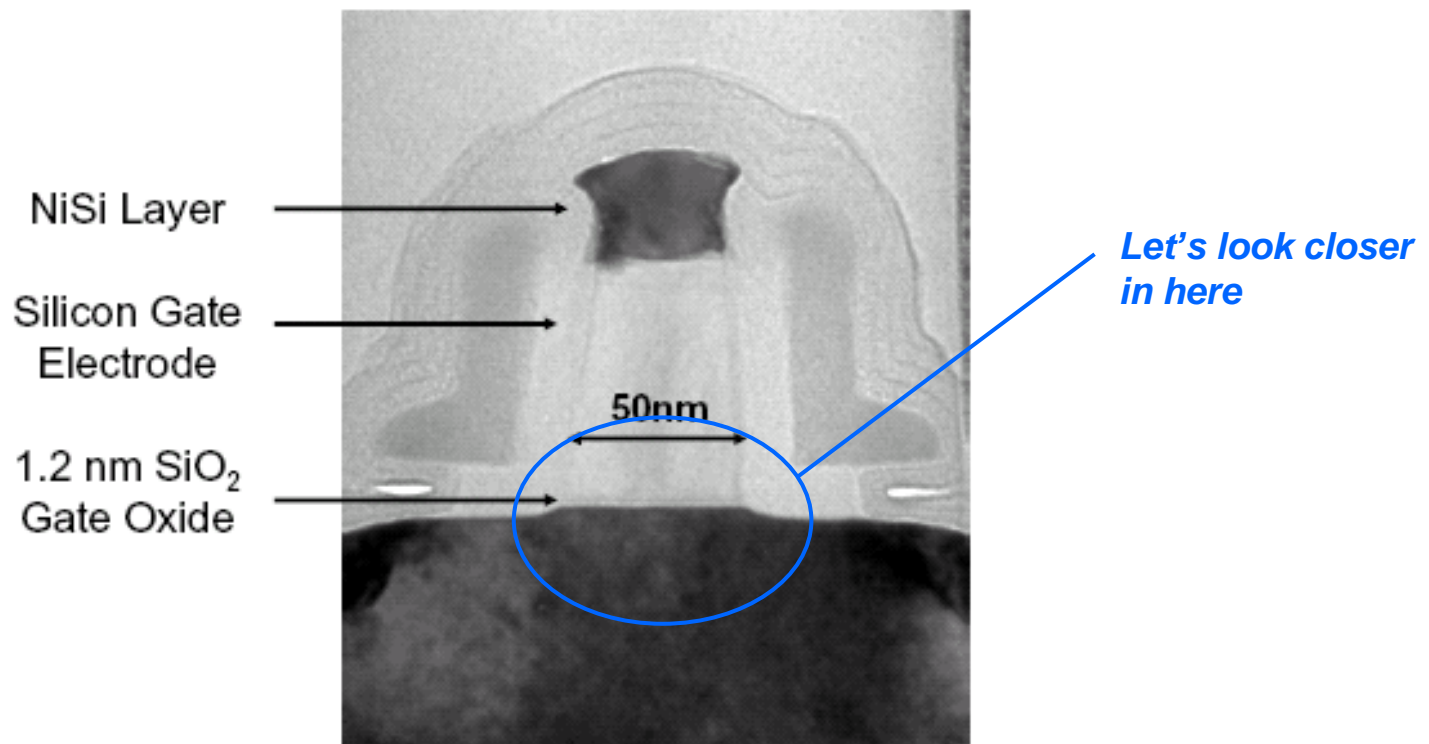
Classifying Solids
Transistors in our Integrated Circuit

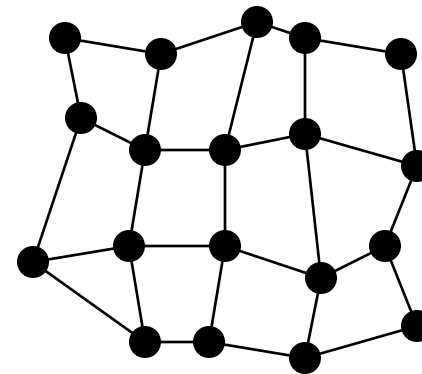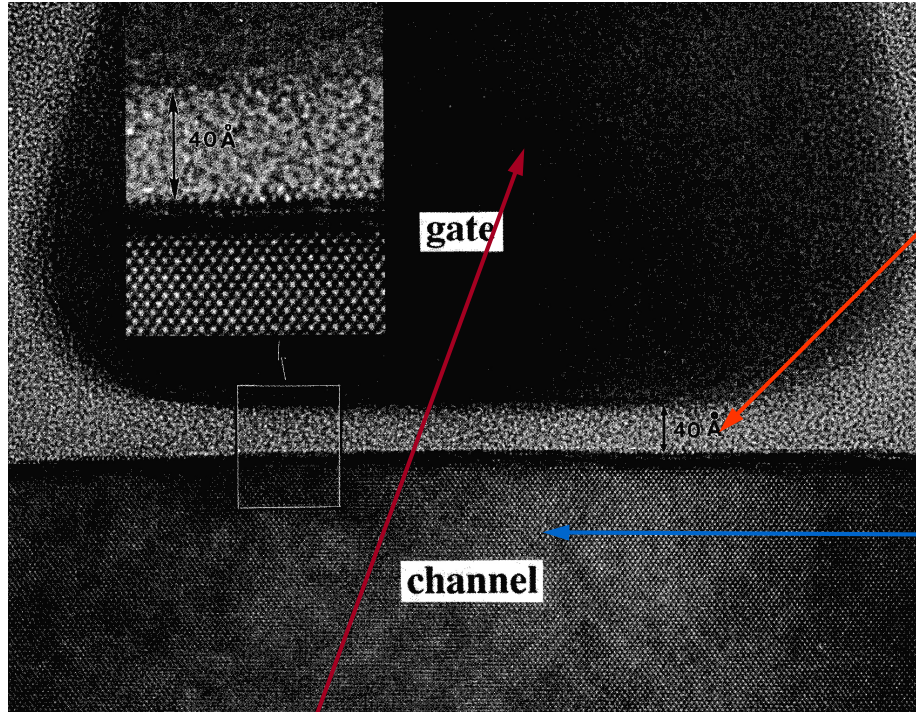SiO$_2$ is an amorphous material which is used for the insulator--it grows naturally on Si at high temperature.

Crystalline Si is used as the base material for all processing in the integrated circuit world.

Poly-crystalline Si, or a metal such as Al, is used to make the "gate" of the transistor (we will learn later just what the gate does).

Preparing the Silicon for VLSI

• **Most materials may actually exist in ALL three different states**

  * **Depending on the manner in which they were FABRICATED**

  * **Crystalline materials are the most DIFFICULT to make**

  ⇒ **And typically require special processes**
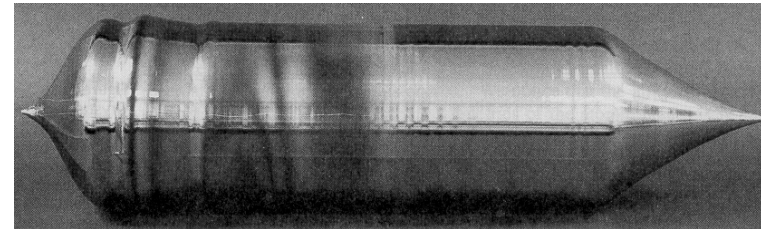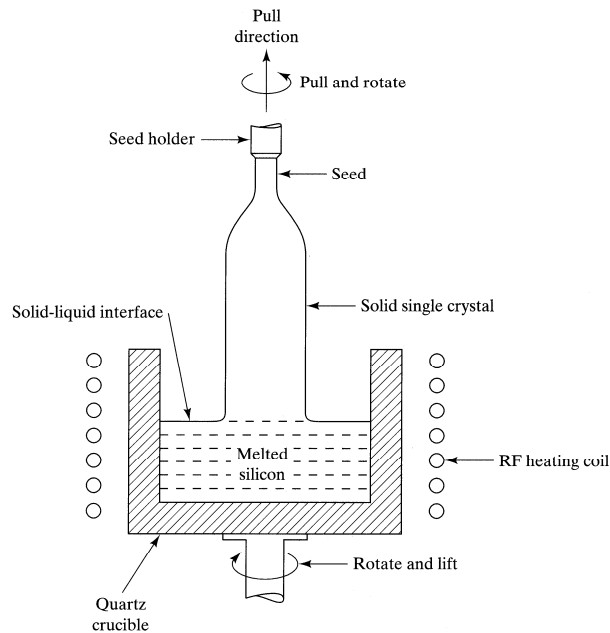
SINGLE CRYSTAL SILICON IS GROWN BY THE CZOCHRALSKI METHOD
AN 8-in DIAMETER INGOT OF SINGLE CRYSTAL SILICON IS SHOWN ABOVE

Now, crystals can be made in many shapes. You can even do it at home.

Silicon crystals have to have very high purity—no defects, vacancies, or random non-silicon atoms. This is done via the *CZOCHRALSKI METHOD*.

A special machine for the vertical growth of crystals via the Czochralski method.

- Seed
- Silicon Ingot
- Quartz crucible
- Water cooled jacket
- Heat shield
- Carbon heater
- Graphite crucible
- Crucible support
- Spill tray
- Electrode

Cz crystal pulling furnace
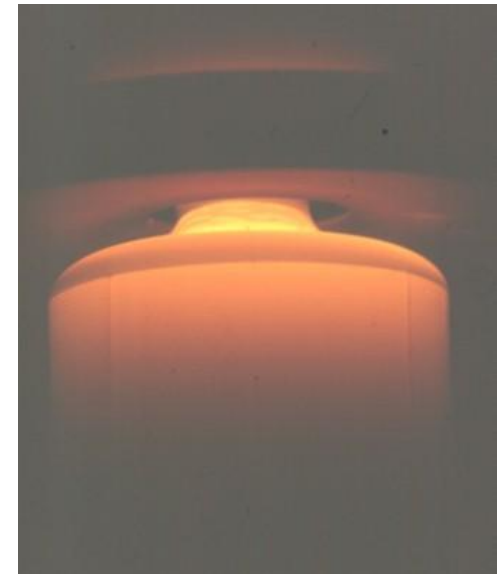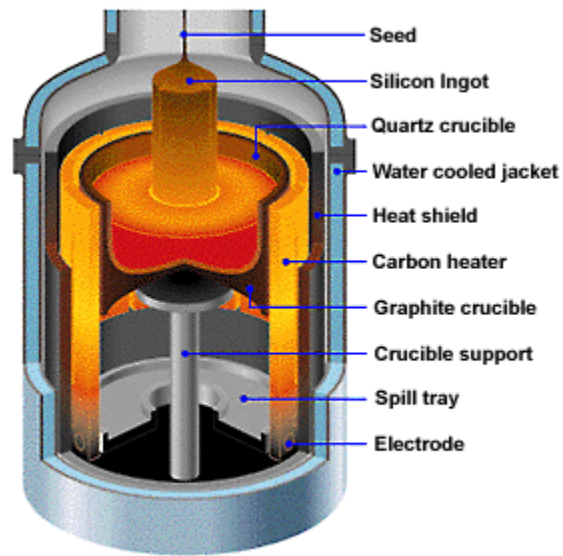
Preparing the Silicon for VLSI
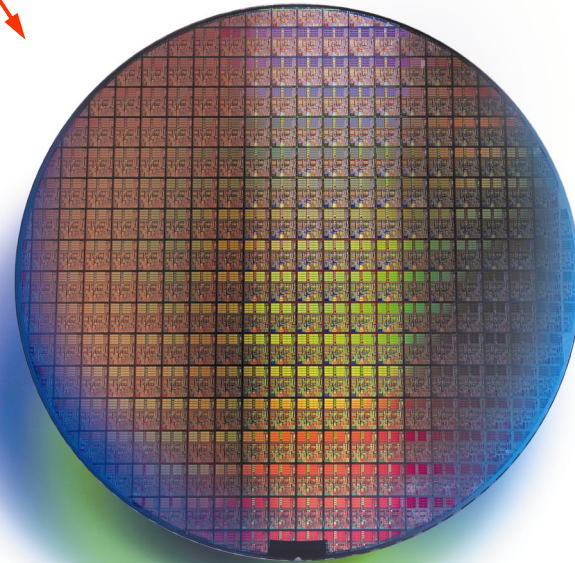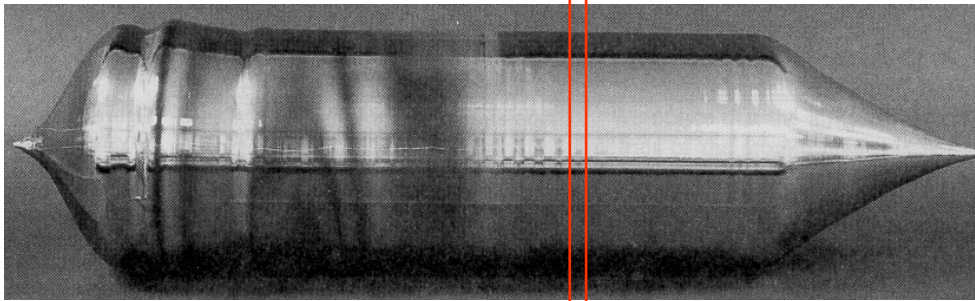
A very thin wafer of the ingot is used to process and create the integrated circuit. More than 200 individual chips will be made on each wafer.

Five years ago: We used 8" wafers.

This Year: The Intel facilities in Chandler all use 12" wafers!

Classifying Materials

• **Not all materials are easily classified using the schemes described above**

   * **Liquid crystals are HIGHLY VISCOUS liquids containing LONG molecules**

   ⇒ **With STRONG and PERMANENT electric dipole moments**

   * **In the absence of an electric field the molecules are RANDOMLY oriented**

   ⇒ **But an electric field may be used to ALIGN their dipoles**

IN THEIR UNALIGNED STATE WE MAY PICTURE THE MOLECULES OF THE LIQUID CRYSTAL ARRANGED AS THE LOGS IN THIS PHOTOGRAPH

Covalent bonds – the key to life (and semiconductors)!

atoms

SHARING OF ELECTRONS

molecule

covalent bond

● *Electron from carbon*
● *Electron from hydrogen*
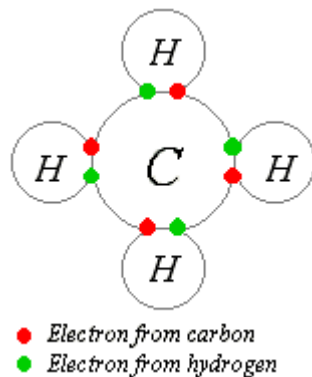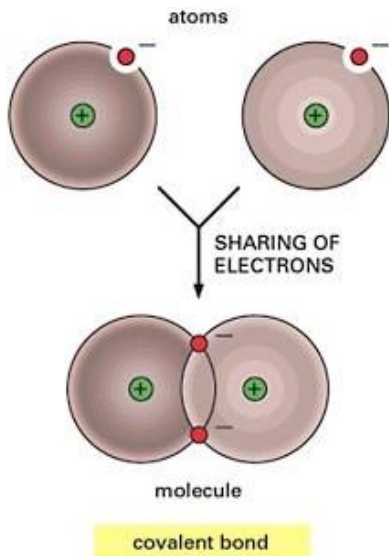
Highly directional

4 *hybrids* of *s*- and *p*- electrons form

Since the hybrids are composed of electrons, they repel each other – most uniform result is tetrahedral shape

$\left(0, \frac{1}{2}, \frac{1}{2}\right)$

$\left(\frac{1}{2}, 0, \frac{1}{2}\right)$

$\left(\frac{1}{2}, \frac{1}{2}, 0\right)$

$(0,0,0)$
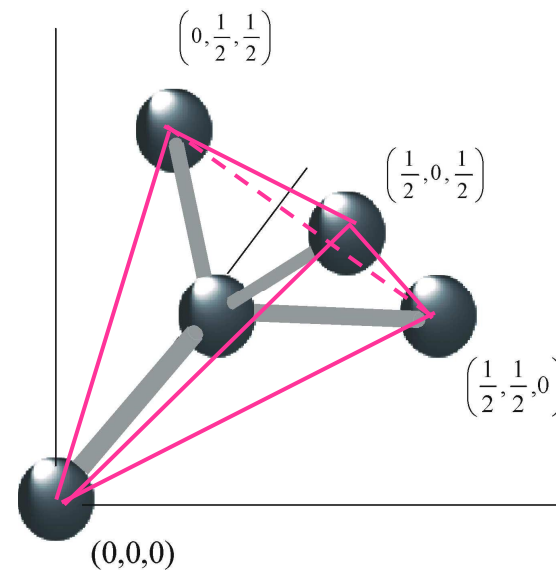
Array of Atoms in Diamond Lattice
(diamond, silicon, germanium, grey tin, …)

	IVB	VB
Symbol E_s E_p	**C** -17.52 -8.97	**N**

	IIIB	IVB	VB
	Al -10.11 -4.86	**Si** -13.55 -6.52	**P** -17.1 -8.33
IIB	**Ga** -11.37 -4.9	**Ge** -14.38 -6.36	**As** -17.33 -7.91	VIB

IIB	IIIB	IVB	VB	VIB
Cd -7.7 -3.38	**In** -10.12 -4.69	**Sn** -12.5 -5.94	**Sb** -14.8 -7.24	**Te** -17.11 -8.59
Hg -7.68 -3.48				

Group IVB: 4 outer electrons
1 *s*-electron, 3-*p* electrons

Compounds from these two groups can form with an *average* of 4 electrons per atom.

GaAs
GaP
InP
AlAs
InAs
GaN

Compounds from these two groups can form with an *average* of 4 electrons per atom.

	IIB	IIIB	IVB	VB	VIB
Symbol E_s E_p					
			C -17.52 -8.97	N	
		Al -10.11 -4.86	Si -13.55 -6.52	P -17.1 -8.33	
		Ga -11.37 -4.9	Ge -14.38 -6.36	As -17.33 -7.91	
	Cd -7.7 -3.38	In -10.12 -4.69	Sn -12.5 -5.94	Sb -14.8 -7.24	Te -17.11 -8.59
	Hg -7.68 -3.48				

Crystalline Order
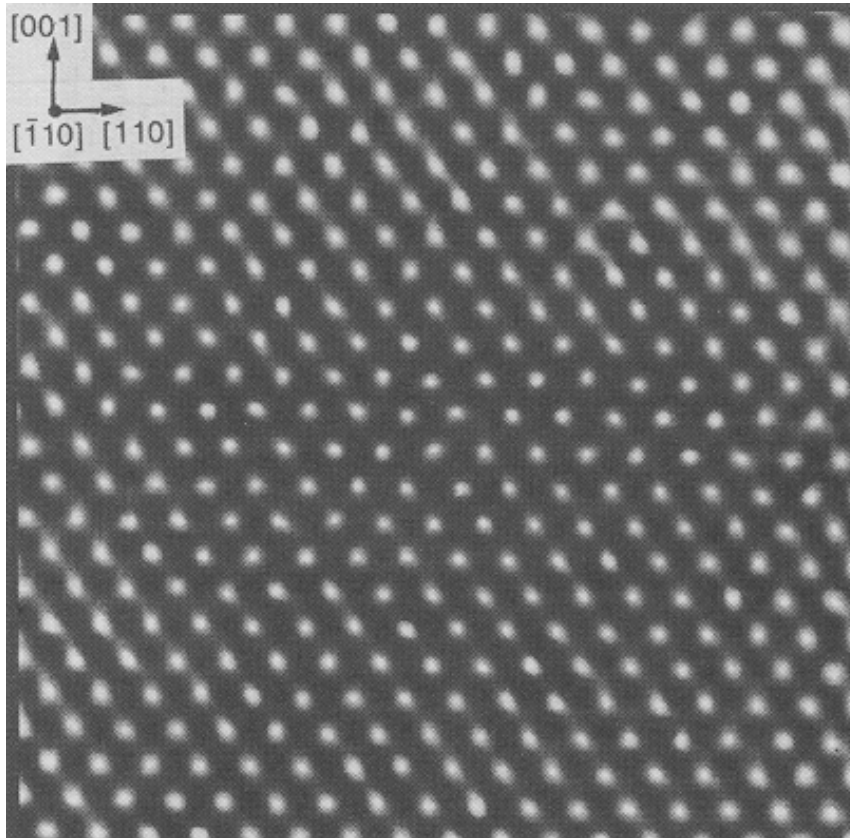
The high degree of order in this TEM picture of Si is apparent.
[http://cst-www.nrl.navy.mil/lattice/struk/a4.html]

The order is more apparent when we understand how this picture is made through a process known as *lattice plane imaging*. Diffraction of the electrons occurs from each plane of atoms; the diffracted beams of electrons form a Fourier transform in the microscope, and this is re-transformed to give the image.

For those interested, a review of lattice plane imaging technology is found at:
http://www.xray.cz/ms/bul2001-1/karlik.pdf

First, however, not everything is crystalline: Crystalline Order

• We have seen that crystalline systems may exhibit varying degrees of ORDER

    * In AMORPHOUS materials there is little order at all

    * In POLYCRYSTALLINE materials the order is INTERMEDIATE
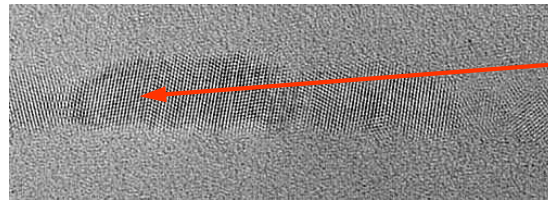
Poly-crystalline grain of Si embedded in amorphous Si

•

• In many cases though it is convenient to assume the crystalline order is PERFECT

GaAs

AlAs

3 Å
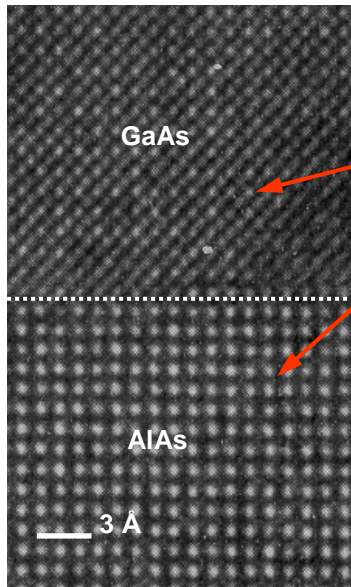
THIS ATOMICALLY PRECISE SANDWICH OF SEMICONDUCTOR MATERIALS (GaAs & AlAs) EXHIBITS HIGH CRYSTALLINE ORDER AND WAS GROWN BY A TECHNIQUE KNOWN AS MOLECULAR BEAM EPITAXY. NOTE THE ALMOST PERFECT ARRANGEMENT OF INDIVIDUAL ATOMS IN THIS FIGURE
This precision is achievable because both GaAs and AlAs have the same lattice constant.

By crystal structure, we mean the regular (or not) arrangement of the atoms.

[001]

[$\bar{1}$10] [110]
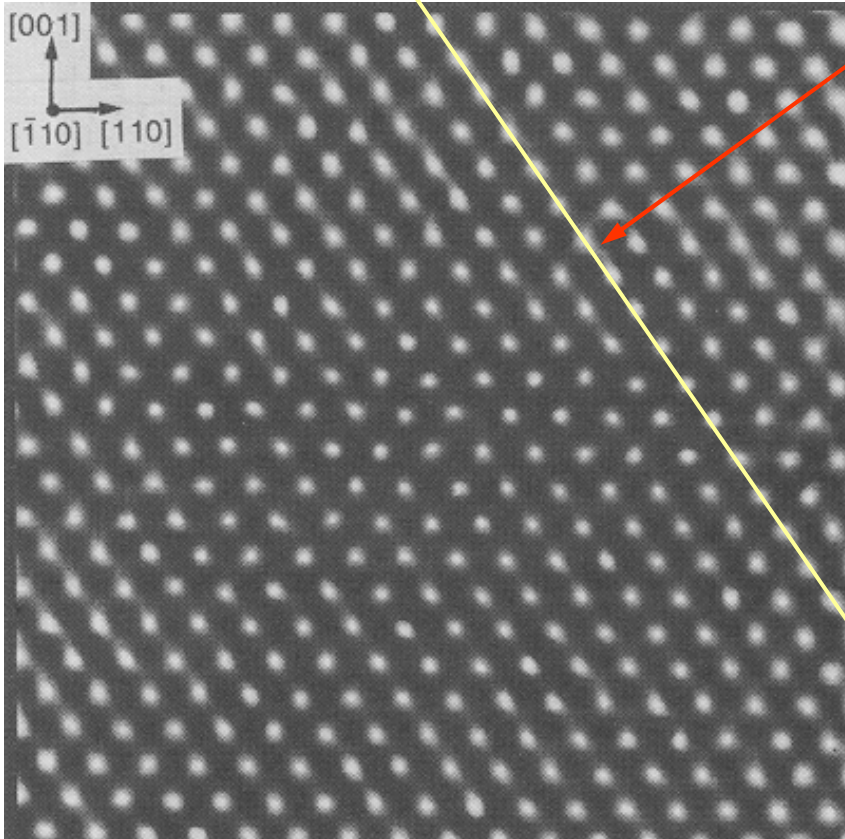
We can talk about "planes" of atoms (which are rows in this 2D projection of the 3D lattice. [http://cst-www.nrl.navy.mil/lattice/struk/a4.html]

These planes define directions relative to the planes—each plane has a surface normal vector which defines the plane.

$\vec{a}_N$

Describing Crystal Structures

How do we identify various crystals, and tell two materials apart from their crystal properties?

We need a method by which we can describe the crystal in terms of its basic properties.

This can be done in one sense, because there are only a few types of crystal lattice. Hence, identifying this structure tells us a lot about the crystal.

Describing Crystal Structures

• An **IDEAL** crystal is an **INFINITE** repetition of **IDENTICAL** structural units in space

    * These units may range from **single atoms to complex molecules**

• We therefore need **TWO** important quantities to **DESCRIBE** a given crystal structure

    * A multi-dimensional **LATTICE**: a set of **POINTS** in space

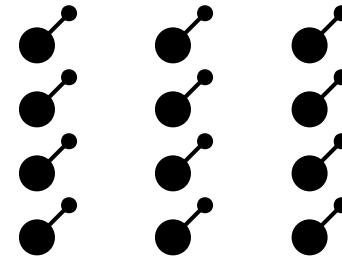   * A suitable **BASIS**: the unit that will be placed at **EACH** lattice point
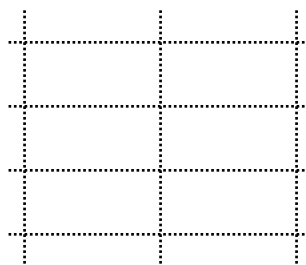
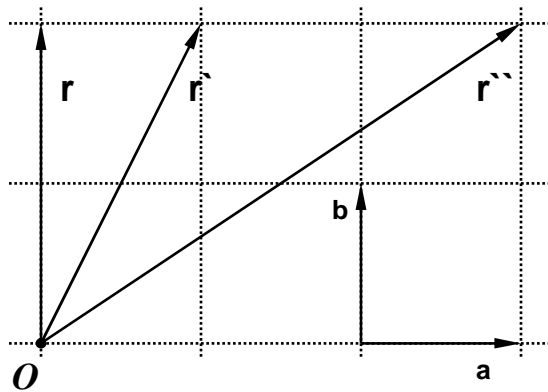*2-D LATTICE*   *BASIS*   *2-D CRYSTAL*

The "basis" may be a single atom,
or a small group of atoms.

Describing Crystal Structures

• The crystal **LATTICE** may be defined using appropriate **TRANSLATION VECTORS**

 * If we know where **ONE** lattice point is situated in the crystal

  ⇒ These vectors determine the position of **OTHER** lattice points

• *STARTING FROM AN ARBITRARY ORIGIN O WE MAY USE TRANSLATION VECTORS a & b TO MAP TO ANY OTHER LATTICE POINT:*

$$\Rightarrow \mathbf{r} = 2\mathbf{b}$$

$$\Rightarrow \mathbf{r}' = \mathbf{a} + 2\mathbf{b}$$

$$\Rightarrow \mathbf{r}'' = 3\mathbf{a} + 2\mathbf{b}$$

 * Here *a* and *b* are referred to as **PRIMITIVE** translation vectors

 * Since they can be used to determine the position of **ALL** lattice points

Describing Crystal Structures

* A 2-D crystal structure consists of a rectangular lattice with primitive translation vectors *a* and 2*a* in the horizontal and vertical directions. The basis unit of this crystal consists of two different atoms that are placed at (*a*/2)[x, y] and (*a*/2)[x,-y] relative to each lattice point. Draw the crystal.

a

2*a*

LATTICE

+

BASIS

=

CRYSTAL STRUCTURE
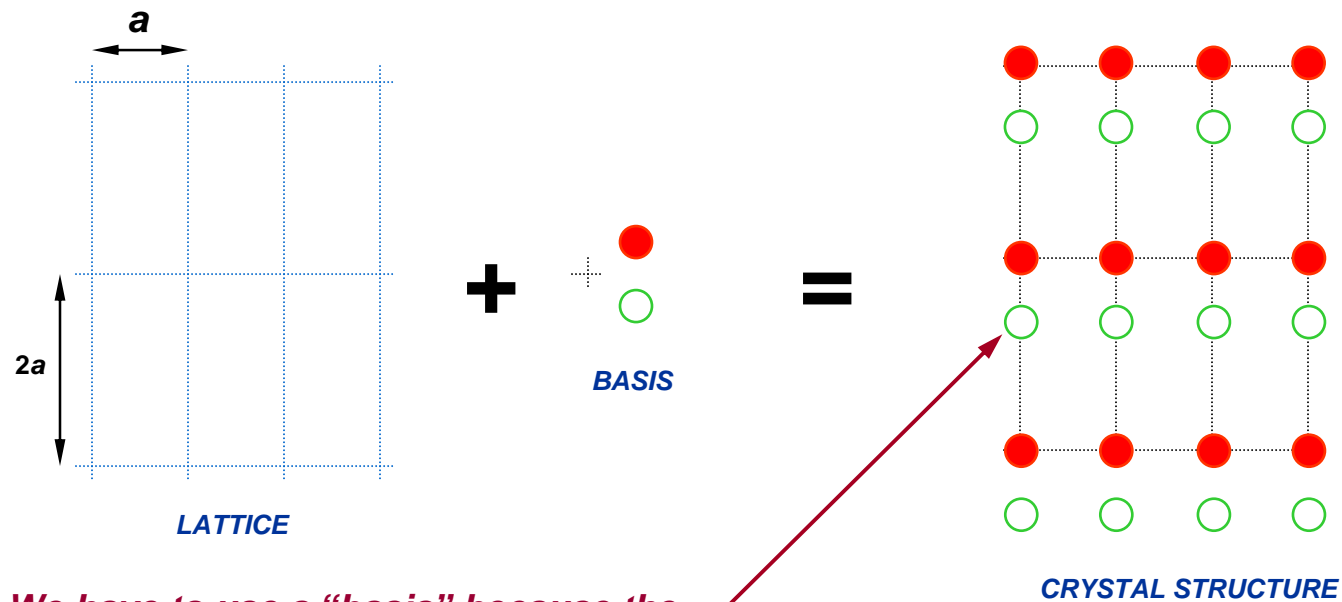
We have to use a "basis" because the atoms themselves don't form a proper lattice

Typical 3D Lattice Types

• While the number of materials exhibiting crystal order is very **LARGE** in nature

    * The number of lattice **TYPES** encountered is actually quite small

    * Here we discuss the most important lattice types found in nature

• Real crystal structures are **THREE-DIMENSIONAL** in nature

    * In a **SIMPLE CUBIC** lattice the three primitive vectors have **EQUAL** length
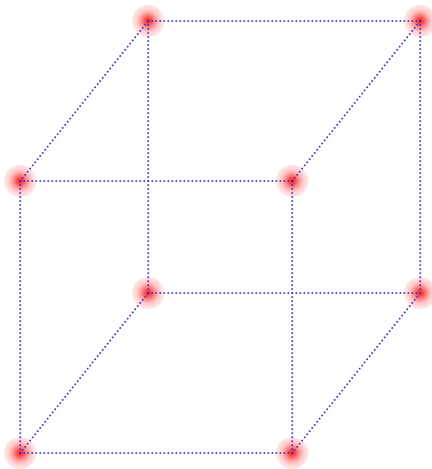
• *REMEMBER THIS IS JUST THE LATTICE!*

• *THE BASIS OF ATOMS WE ADD TO EACH LATTICE POINT DETERMINES WHAT MATERIAL WE FINALLY END UP WITH*

• *FOR EXAMPLE, ADDING MANGANESE ATOMS TO EACH LATTICE POINT WOULD GIVES CRYSTALLINE MANGANESE*

Typical 3D Lattice Types

• The **BODY CENTERED CUBIC** lattice is formed by adding an **ADDITIONAL** lattice point

* To the **CENTER** of each cube defined by the simple cubic lattice

* This lattice may be considered as **TWO** interlocking simple cubic lattices
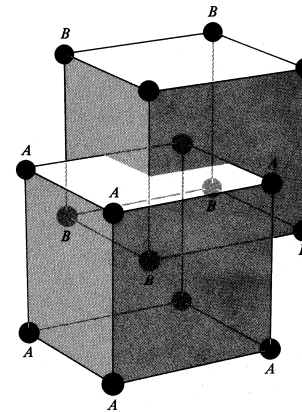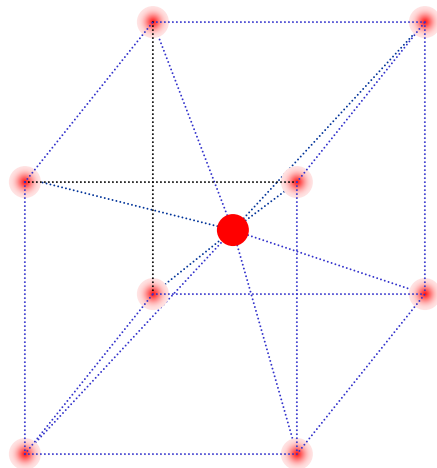
ELEMENTS WITH THE MONATOMIC BODY-CENTERED CUBIC CRYSTAL STRUCTURE

ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ba	5.02	Li	3.49 (78 K)	Ta	3.31
Cr	2.88	Mo	3.15	Tl	3.88
Cs	6.05 (78 K)	Na	4.23 (5 K)	V	3.02
Fe	2.87	Nb	3.30	W	3.16
K	5.23 (5 K)	Rb	5.59 (5 K)		

Typical 3D Lattice Types

For the **BODY CENTERED CUBIC** lattice, we must be careful to define the primitive translation vectors to include the new atom at the center of the cube.
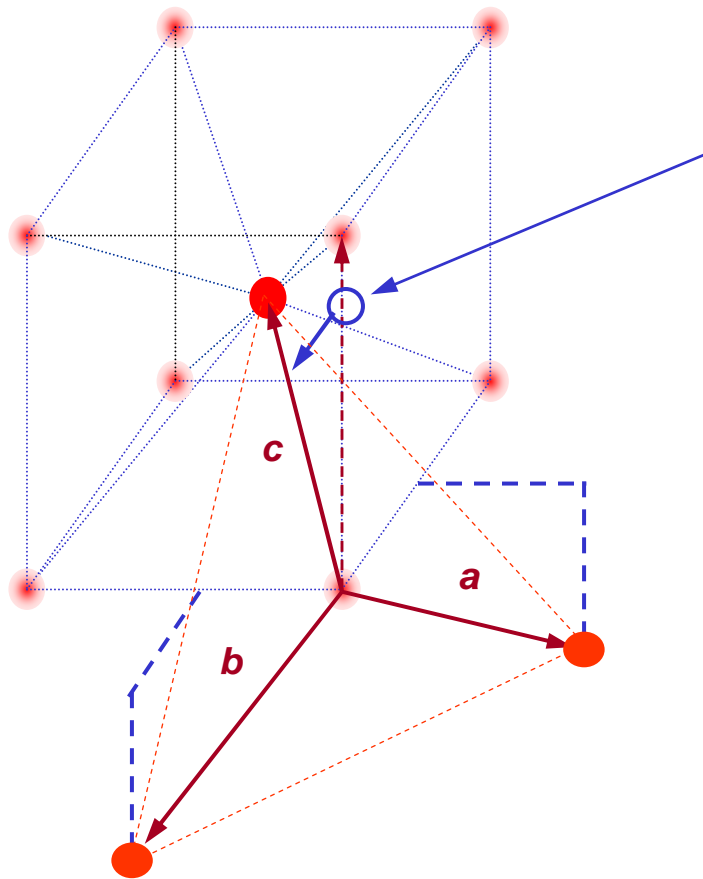
Each **direction** is rotated to a new body-centered atom. Now, these vectors can be translated to define any point in the lattice. These three atoms form a smallest tetrahedron along with the single corner atom.

Typical 3D Lattice Types

• The **FACE CENTERED CUBIC** lattice is formed by adding an **ADDITIONAL** lattice point

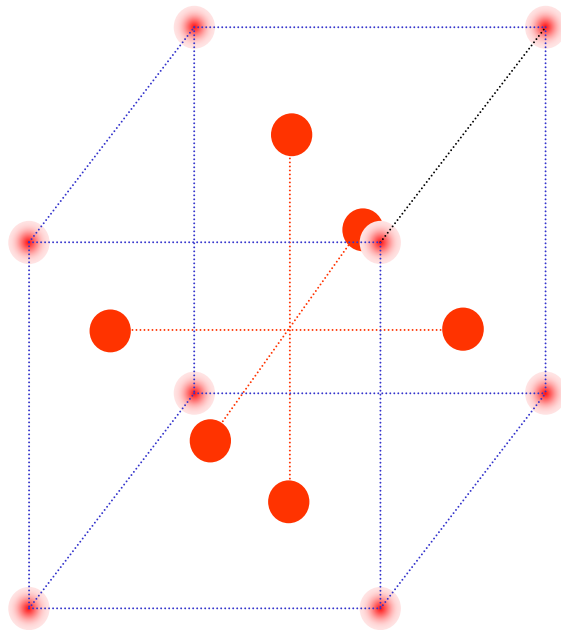 * To the **CENTER of EACH** face of the cube formed in a simple cubic lattice

ELEMENTS WITH THE MONATOMIC FACE-CENTERED CUBIC CRYSTAL STRUCTURE

ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ar	5.26 (4.2 K)	Ir	3.84	Pt	3.92
Ag	4.09	Kr	5.72 (58 K)	δ-Pu	4.64
Al	4.05	La	5.30	Rh	3.80
Au	4.08	Ne	4.43 (4.2 K)	Sc	4.54
Ca	5.58	Ni	3.52	Sr	6.08
Ce	5.16	Pb	4.95	Th	5.08
β-Co	3.55	Pd	3.89	Xe (58 K)	6.20
Cu	3.61	Pr	5.16	Yb	5.49

Data in Tables 4.1 to 4.7 are from R. W. G. Wyckoff, *Crystal Structures*, 2nd ed., Interscience, New York, 1963. In most cases, the data are taken at about room temperature and normal atmospheric pressure. For elements that exist in many forms the stable room temperature form (or forms) is given. For more detailed information, more precise lattice constants, and references, the Wyckoff work should be consulted.

Typical Lattice Types

For the **FACE CENTERED CUBIC** lattice, we have to define the three lattice vectors so that they fully account for the atoms at the face centers.
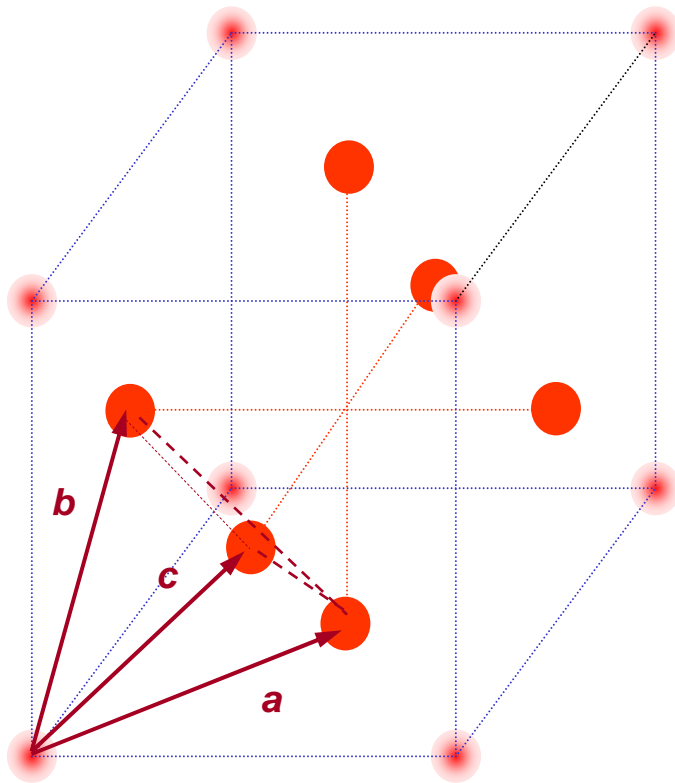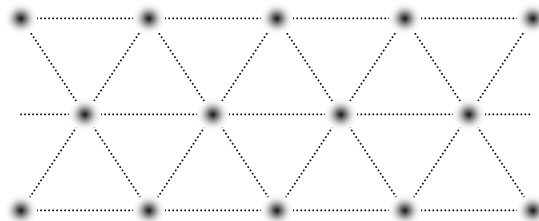
The three primitive vectors run from a corner atom to the three adjacent faces of that corner. Again, these form a tetrahedron.
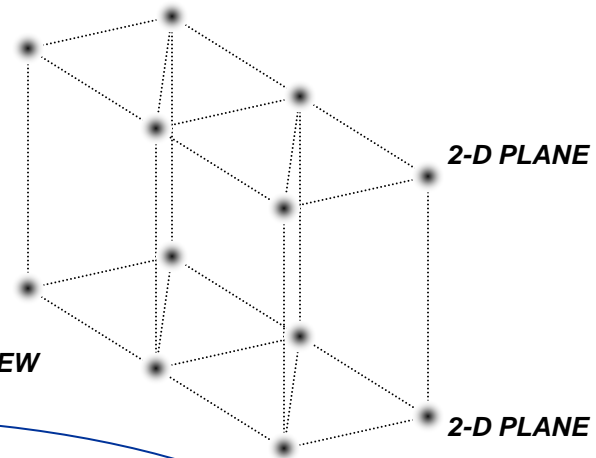
Typical Lattice Types

• In addition to cubic lattices **HEXAGONAL** lattices are also frequently found in nature

    * A **SIMPLE** hexagonal lattice is built from **TWO-DIMENSIONAL** nets

    ⇒ Stacked **DIRECTLY** above each other

VIEW FROM ABOVE
ONE 2-D PLANE

3-D VIEW

2-D PLANE

2-D PLANE

IN THE HEXAGONAL BRAVAIS LATTICE
TWO-DIMENSIONAL TRIANGULAR
NETS ARE STACKED DIRECTLY
ON ONE ANOTHER. HOWEVER,
*THE LAYERS MAY NOT BE DIRECTLY ALIGNED.*

Typical Lattice Types

• **A modified version of the hexagonal lattice is the CLOSE-PACKED hexagonal lattice**
[web]

* **This can be viewed as TWO simple hexagonal lattices**

⇒ **Which INTERPENETRATE each other**

ELEMENTS WITH THE HEXAGONAL CLOSE-PACKED CRYSTAL
STRUCTURE

| ELEMENT	a (Å)	c	c/a	ELEMENT	a (Å)	c	c/a
Be	2.29	3.58	1.56	Os	2.74	4.32	1.58
Cd	2.98	5.62	1.89	Pr	3.67	5.92	1.61
Ce	3.65	5.96	1.63	Re	2.76	4.46	1.62
α-Co	2.51	4.07	1.62	Ru	2.70	4.28	1.59
Dy	3.59	5.65	1.57	Sc	3.31	5.27	1.59
Er	3.56	5.59	1.57	Tb	3.60	5.69	1.58
Gd	3.64	5.78	1.59	Ti	2.95	4.69	1.59
He (2 K)	3.57	5.83	1.63	Tl	3.46	5.53	1.60
Hf	3.20	5.06	1.58	Tm	3.54	5.55	1.57
Ho	3.58	5.62	1.57	Y	3.65	5.73	1.57
La	3.75	6.07	1.62	Zn	2.66	4.95	1.86
Lu	3.50	5.55	1.59	Zr	3.23	5.15	1.59
Mg	3.21	5.21	1.62				
Nd	3.66	5.90	1.61				
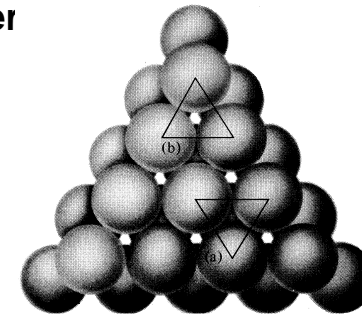
VIEW FROM ABOVE
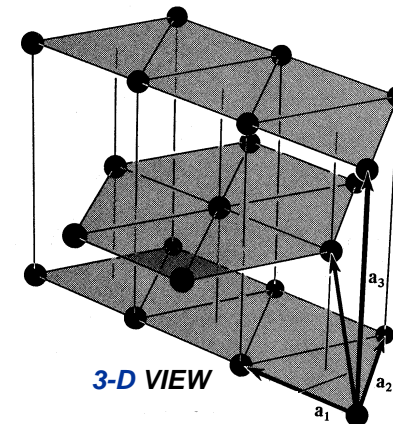
3-D VIEW

Crystal Structure of Diamond

• **Here we consider some important crystal structures encountered in nature**

   * **The first of these is the DIAMOND crystal structure**

      ⇒ **Which is one of the crystal forms of CARBON**

• **In crystallography it is typical to break crystals down to their PRIMITIVE CELL**

   * **A basic BUILDING BLOCK that can be used to construct the crystal**

   * **The cell of the diamond structure, shown below, IS NOT THE PRIMITIVE CELL**


*THE **NORMAL** CELL OF DIAMOND*
***FOUR** ATOMS ARE CONTAINED*
***WITHIN** THIS CELL MAKING IT*
*EXTREMELY **COMPLEX**!*
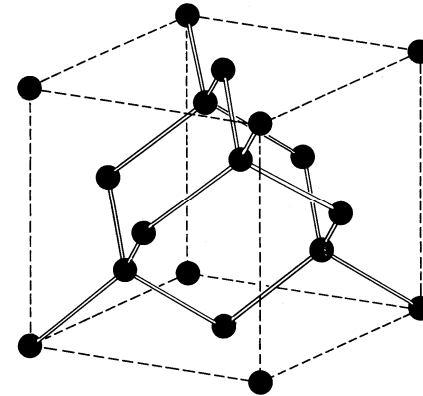
The PRIMITIVE CELL is formed by the primitive vectors and the basis. The normal cell is larger, but is more suitable for building the lattice.
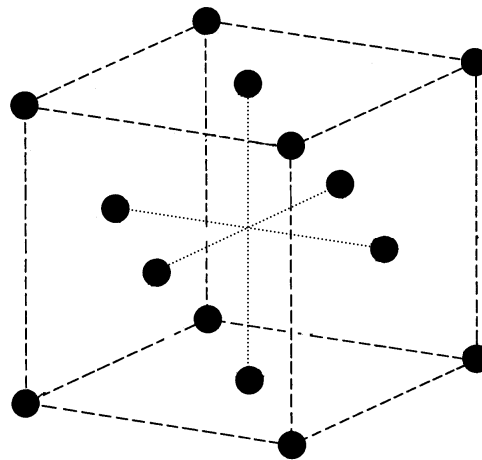
Crystal Structure of Diamond

• To classify the crystal structure of diamond we must define its **LATTICE** and **BASIS**

  * The lattice is actually one of the simple forms we have discussed already

  $\Rightarrow$ A **FACE-CENTERED CUBIC** lattice

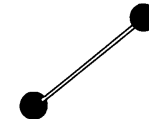 * While the basis is **DIATOMIC** and consists of **TWO** carbon atoms
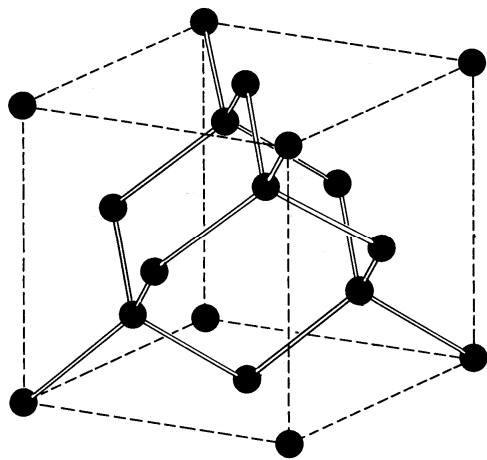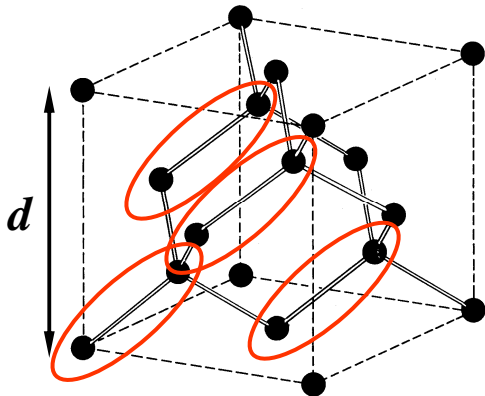

DIAMOND STRUCTURE = *FACE-CENTERED CUBIC* LATTICE + *DIATOMIC* BASIS: 2 CARBON ATOMS

[web]

Crystal Structure of Diamond

• **Recall that when describing lattice structures we used TRANSLATION VECTORS**

   * **That allow us to MAP from one lattice point to another**

• **We must also introduce translation vectors to describe the BASIS unit of the crystal**

   * **These vectors indicate the spatial relation of atoms WITHIN the basis unit**

   * **The translation vectors for the basis unit of diamond are shown below**

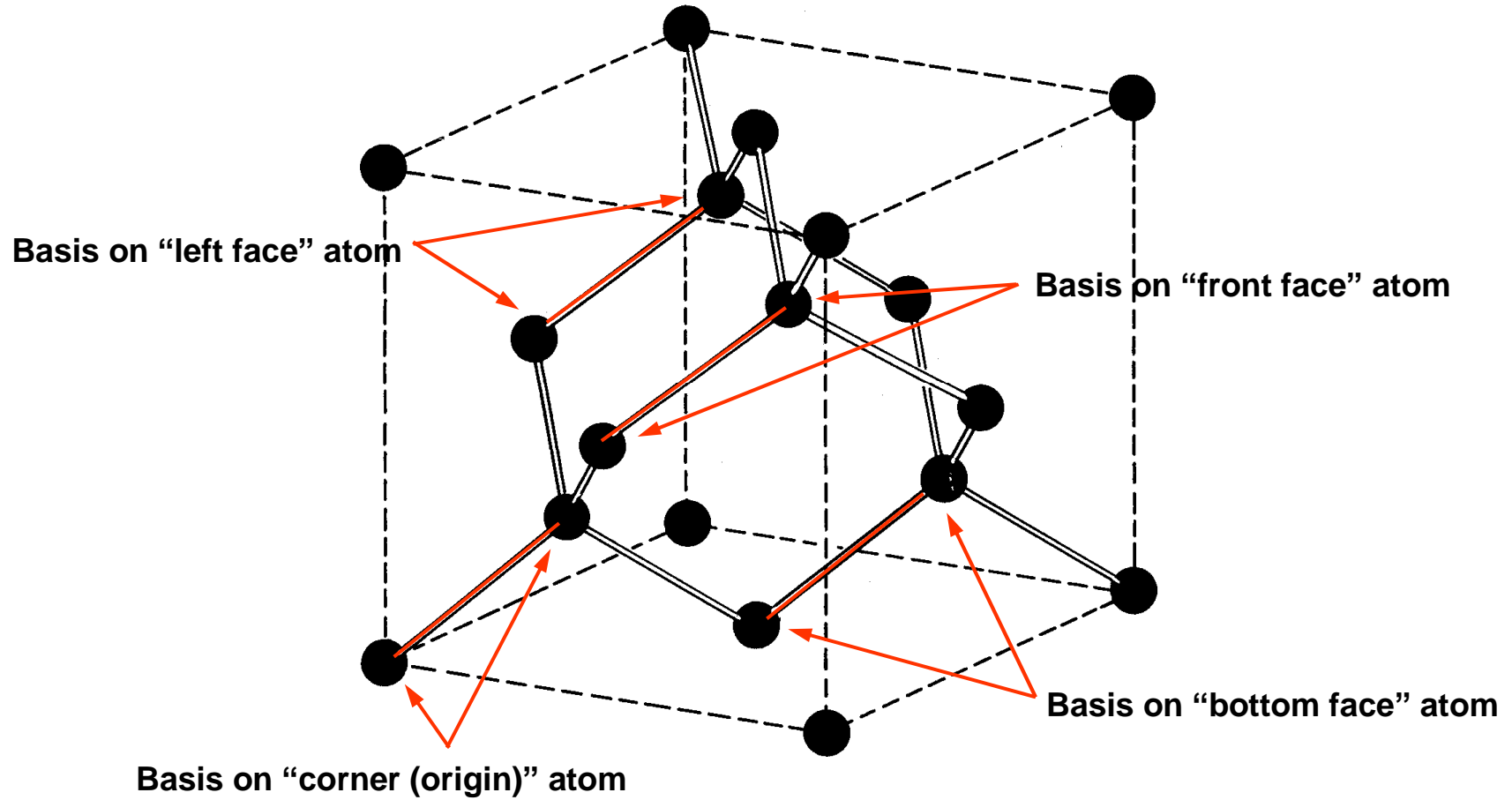   ⇒ **Where we have assumed the primitive cell size is *a***

• **Relative to each lattice point:**

   * **The FIRST atom of the basis is located at:** $[0,0,0]$

   * **The SECOND atom of the basis is located at:** $\dfrac{d}{4}[\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}]$

Crystal Structure of Diamond

Basis on "left face" atom

Basis on "front face" atom

Basis on "corner (origin)" atom
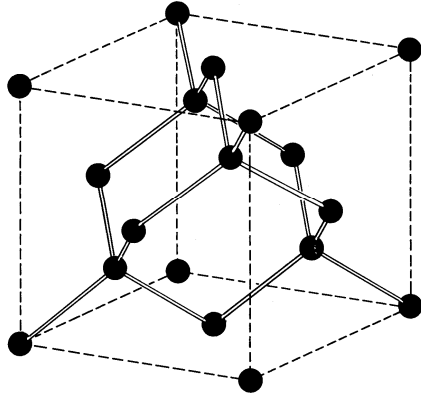
Basis on "bottom face" atom

Crystal Structure of Diamond

The "basis" results in 4 new atoms in the face-centered cubic cell (BUT only 4 as the new structure is not "close packed" but rather open):
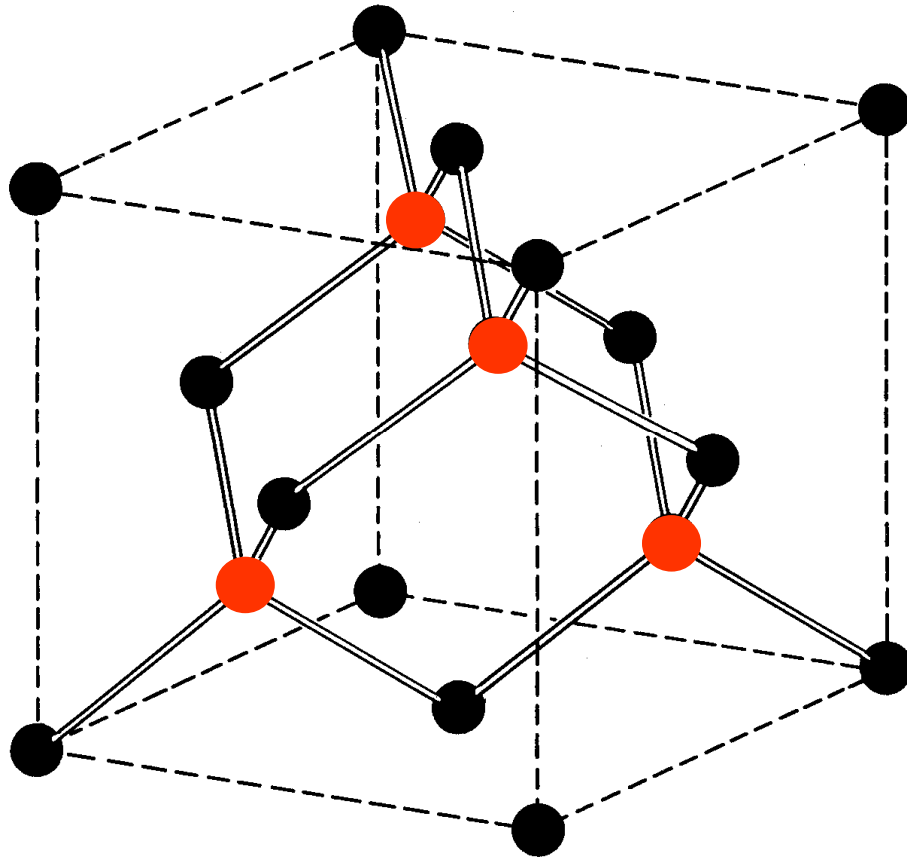
Crystal Structure of Diamond

There are 8 corner atoms, each shared with 8 cubes, so that this contributes 8 X (1/8) = 1 atom

There are 6 faces, each shared with two cubes, so that this contributes 6 X (1/2) = 3 atoms

There are the 4 new atoms, which are not shared, so that this contributes 4 X 1 = 4 atoms

The basic DIAMOND cubic cell then has

1 + 3 + 4 = 8 atoms

Crystal Structure of ~~Diamond~~ Silicon

The inter-atomic distance is twice the **covalent radii**, or **2.346 Angstrom** in Si.

The **PRIMITIVE LATTICE** vector has a length that is

$$2\sqrt{2/3}$$

times the nearest neighbor distance, or **3.83 Angstrom** in Si.

$\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$

$\left(\frac{1}{2},\frac{1}{2},0\right)$

(0,0,0)

(1,0,0)
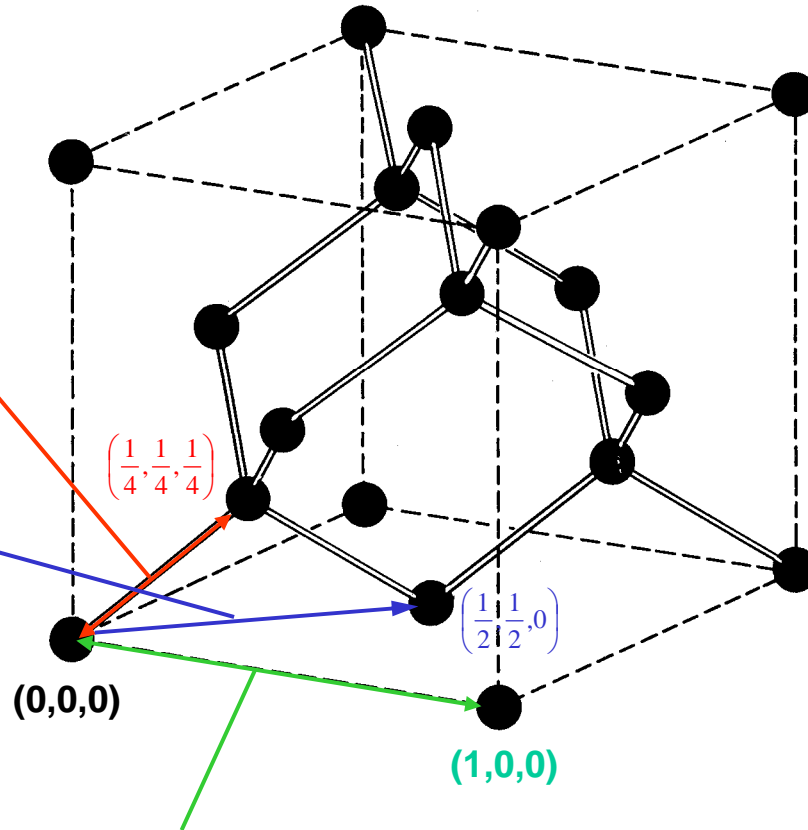
The edge of the **NORMAL CELL** is $4/\sqrt{3}$ times the inter-atomic spacing or **5.418 Angstrom** in Si.

Crystal Structure of Silicon, Diamond, Germanium,…

The shared bonding electrons have their charge density between the atoms, along the tetrahedral directions:



(1,1,0) plane

Ge

Ge

A

B

10

25

20

10

12

2
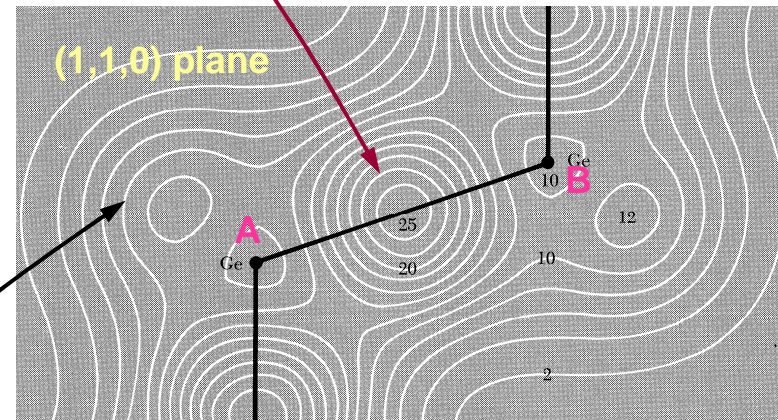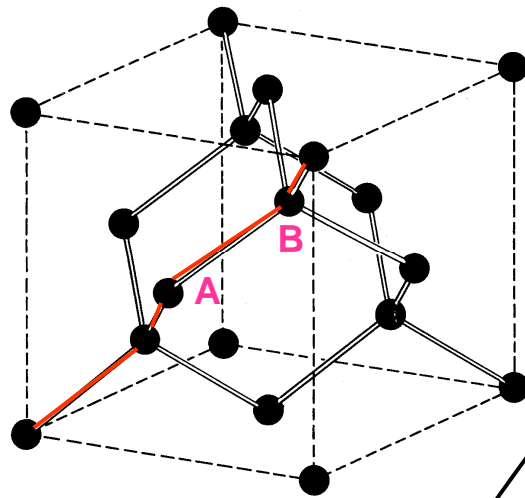
NOTE THE *ABSENCE* OF BONDING IN THE REGIONS INDICATED

CONTOUR LINES SHOW THE *CHANCE* OF FINDING ELECTRONS IN COVALENTLY BONDED GERMANIUM WHICH ALSO SHOWS THE DIAMOND STRUCTURE

# Crystal Structure of Silicon, Diamond, Germanium,…

These two bonds form a plane, which is a (110) plane

The two back bonds form a plane, which is at right angles to the first plane—THE PLANE OF THE BONDS ROTATE TO FORM THE TETRAHEDRON.
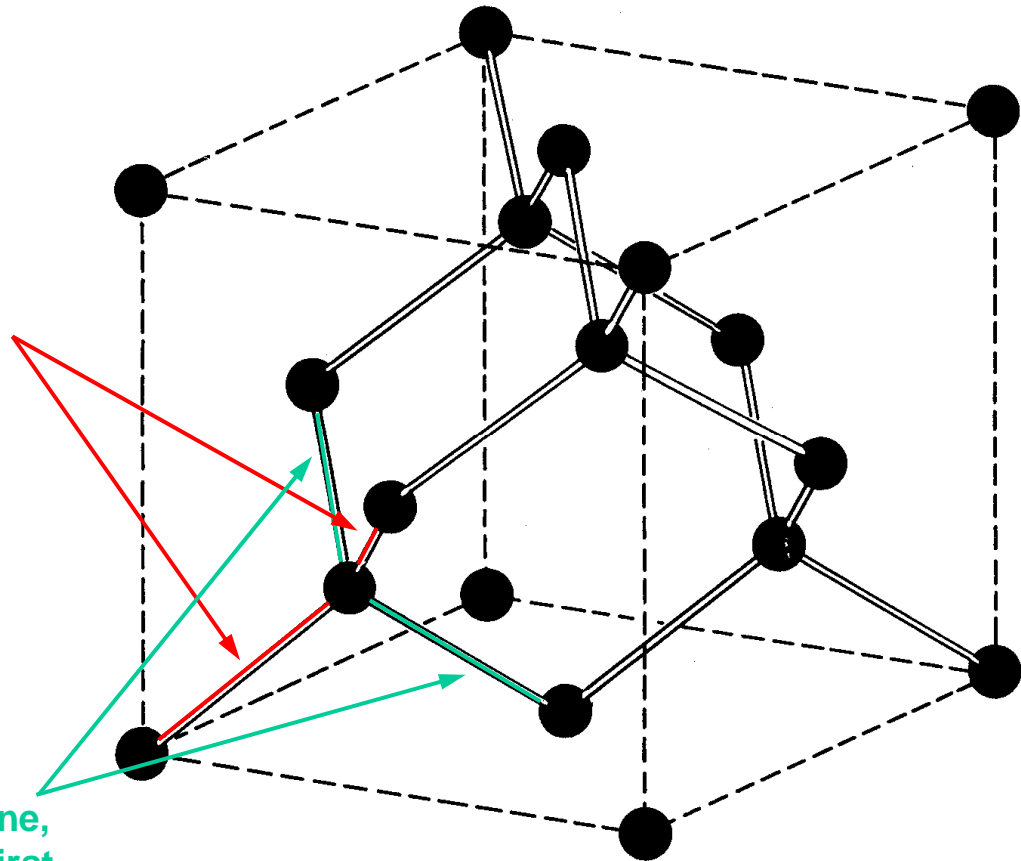
The basic tetrahedral coordination dominates covalent bonding.

Covalent bonding is the basis for our semiconductors, but also of all carbon-based lifeforms.
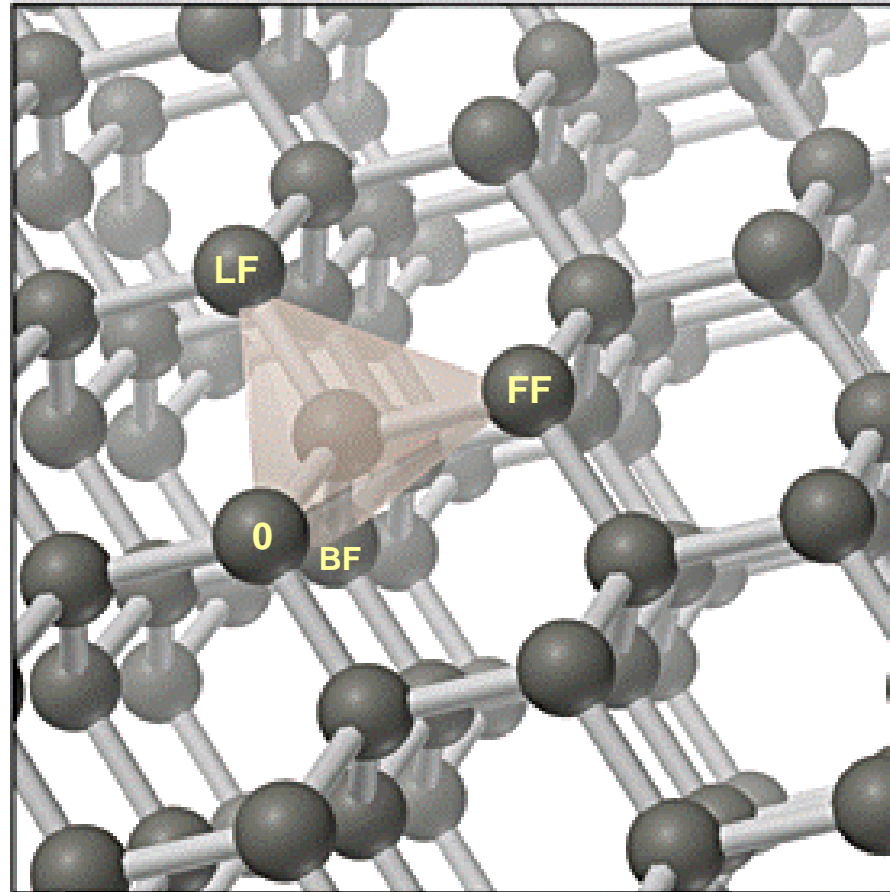
Determining Crystal Structures
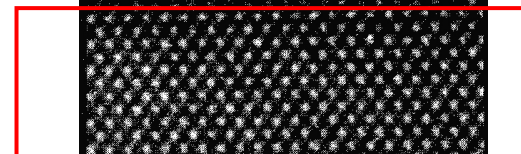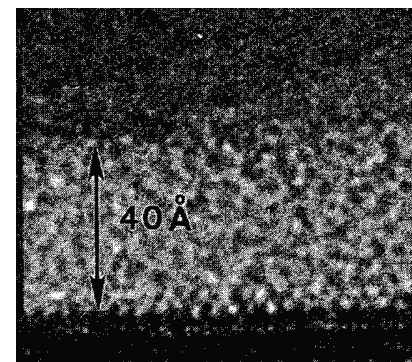
* **Crystal diffraction**

  ⇒ **Crystal planes**

  ⇒ **Bragg's law**

* **X-ray diffraction**
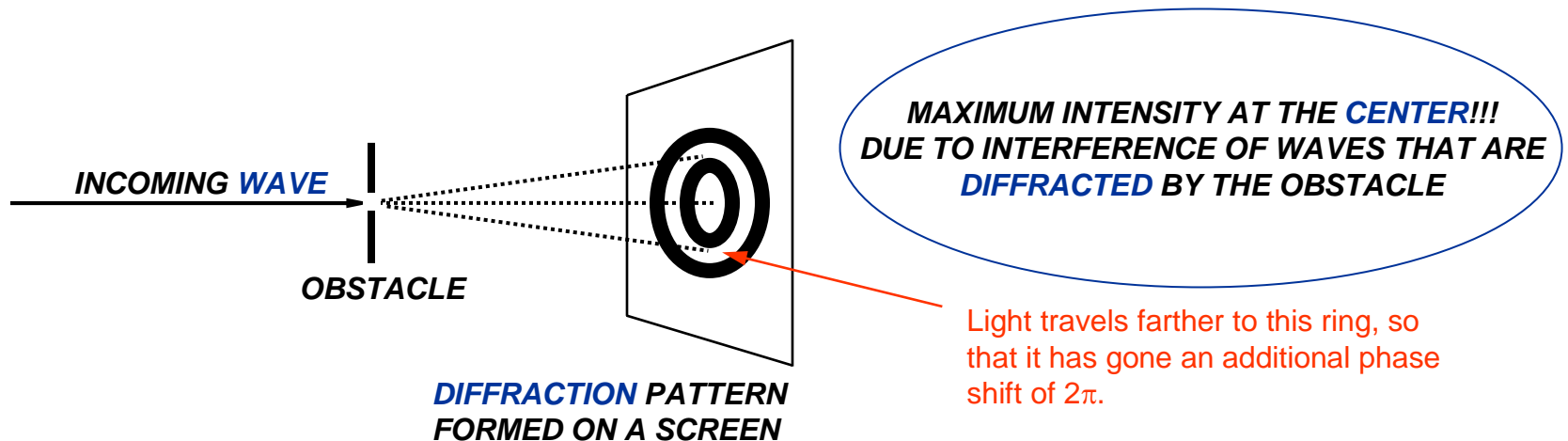
  ⇒ **Practical studies**

Max von Laue
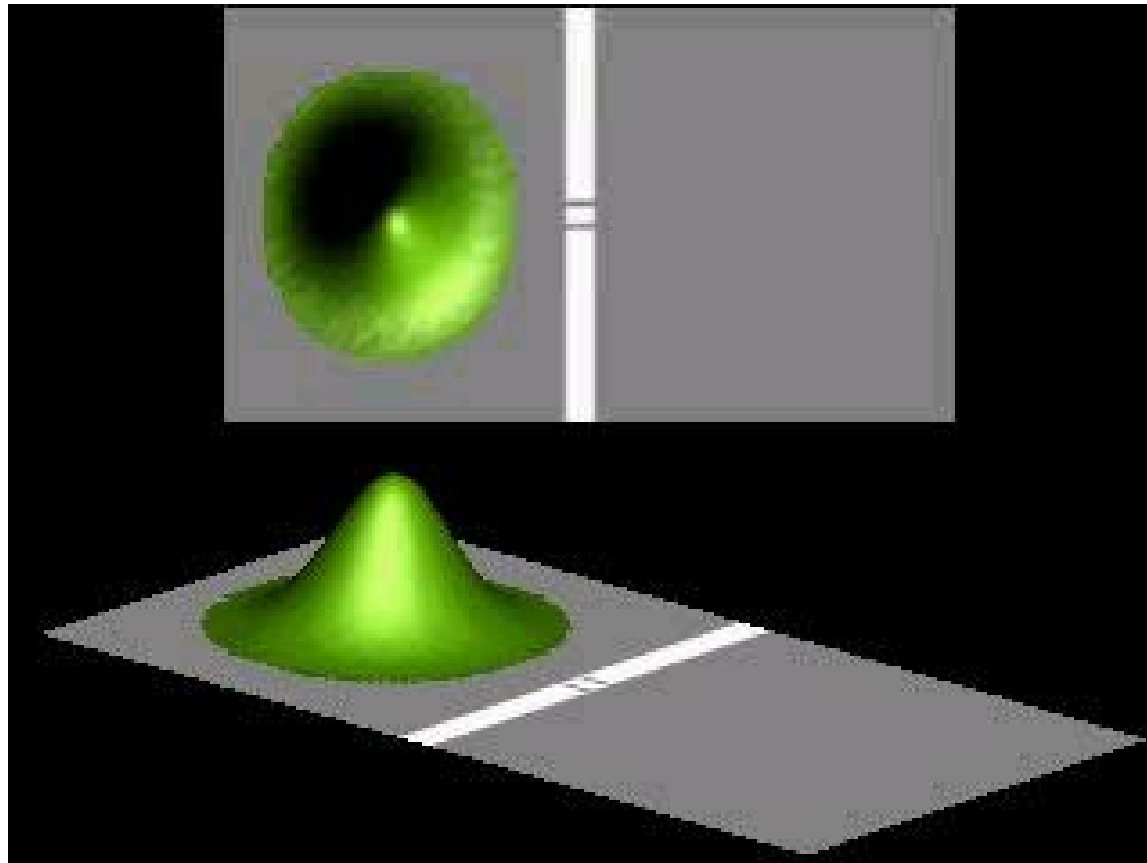**Nobel Prize in Physics, 1914**

Sir William Lawrence Bragg
Nobel Prize in Physics, 1915

Diffraction of Waves

• While we have described the crystal structure of a **VARIETY** of materials

    * We have not explained **HOW** this structure is determined in experiment

        ⇒ One approach we discuss here is crystal **DIFFRACTION**

• Diffraction is a phenomenon exhibited by **WAVES** that impinge on an obstacle

    * Whose size is **COMPARABLE** to the wavelength of the incoming waves

INCOMING WAVE

OBSTACLE

DIFFRACTION PATTERN FORMED ON A SCREEN

MAXIMUM INTENSITY AT THE CENTER!!! DUE TO INTERFERENCE OF WAVES THAT ARE DIFFRACTED BY THE OBSTACLE

Light travels farther to this ring, so that it has gone an additional phase shift of 2π.

We can visualize this in a plane by passing a wave packet through a slit.

INCOMING *WAVE*

OBSTACLE

DIFFRACTION PATTERN
FORMED ON A SCREEN
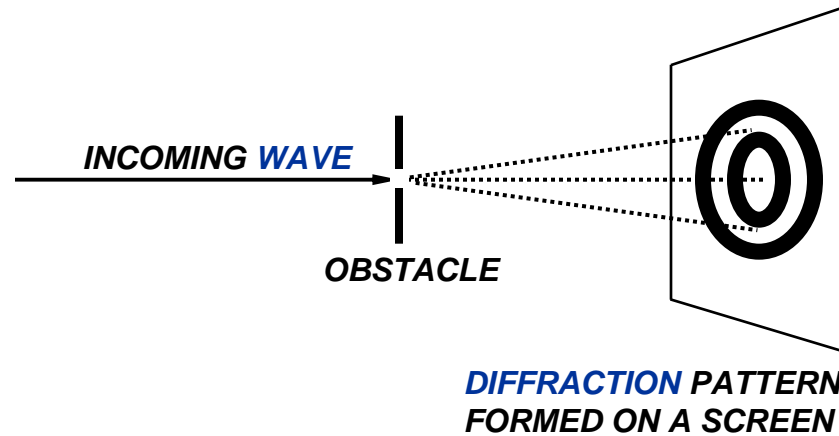
Light varies as a wave $e^{i\mathbf{k}\bullet\mathbf{r}}$

Light that is "diffracted" around the edge of the hole
has interference between waves from the center and
that reflected off the edge of the hole.

$$e^{i\mathbf{k}\bullet\mathbf{r}} + e^{i\mathbf{k}\bullet\mathbf{r}'} \sim \cos\left(\mathbf{k}\bullet(\mathbf{r}-\mathbf{r}')\right)$$

The importance for the crystal is that we scatter off each atom independently, and the wave interfere. We can sense this from a 2-slit experiment.
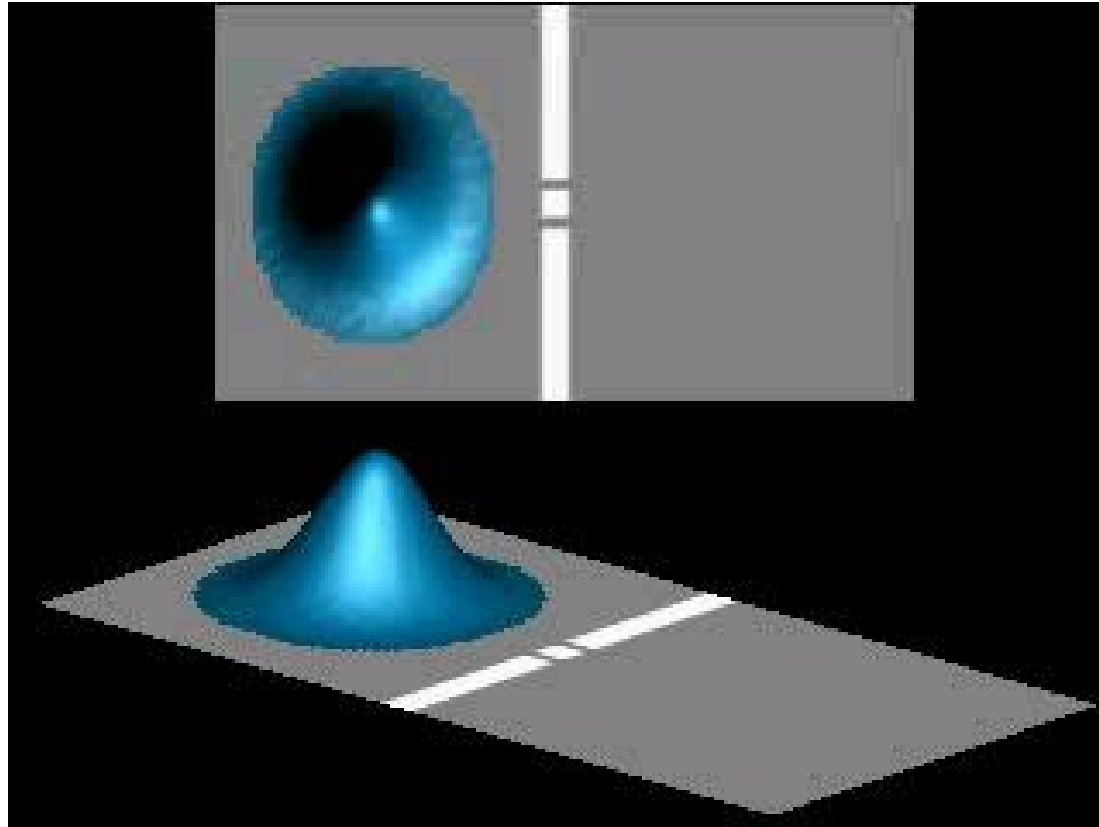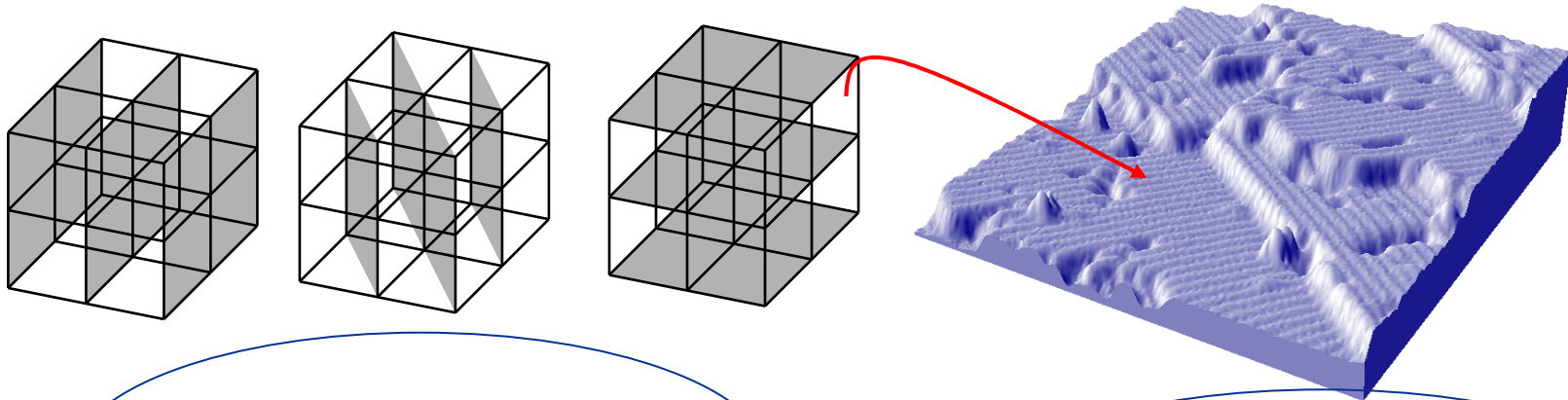
Crystal Diffraction

- **Diffraction in crystals arises from the presence of natural crystal PLANES which will reflect the waves**

  * The three dimensional arrangement of atoms in crystals can be imagined

  ⇒ **As defining a series of PARALLEL planes**

  ⇒ **These planes may be chosen in a NUMBER of different ways**

THREE POSSIBLE (OF MANY) CHOICES OF CRYSTAL PLANES FOR A SIMPLE CUBIC LATTICE

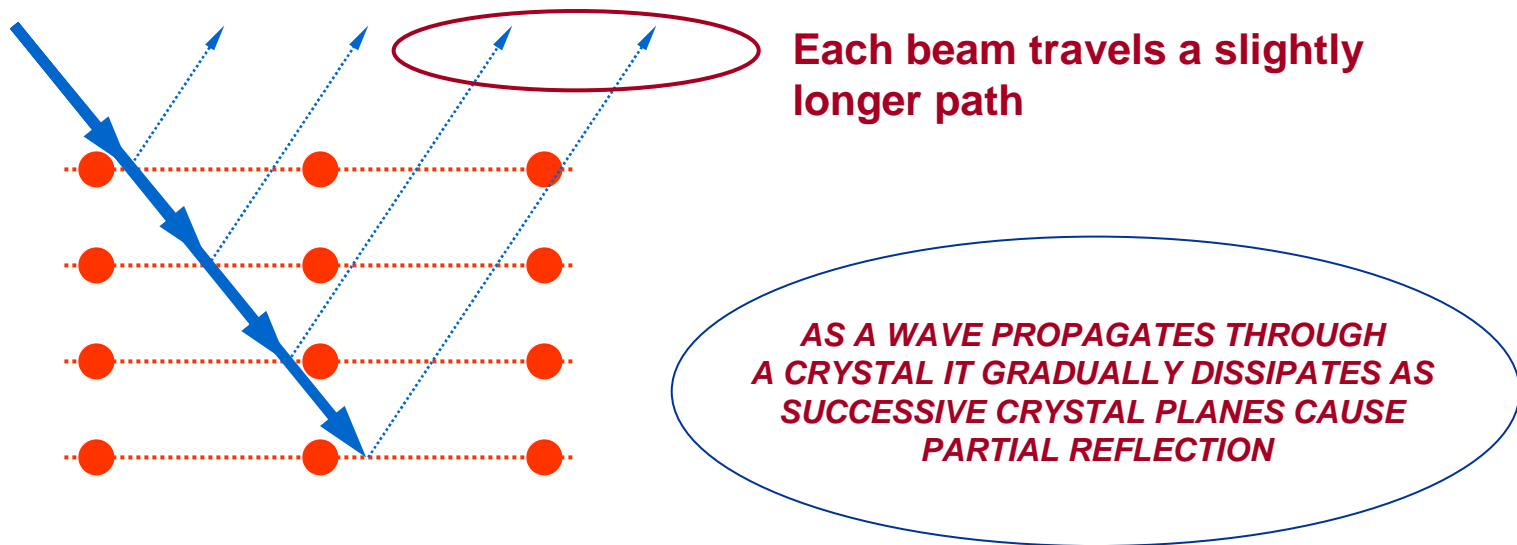*ATOMIC LEVEL IMAGE OF CRYSTAL PLANES AT SILICON SURFACE*

Crystal Diffraction

• When waves strike a **SINGLE** crystal plane a **FRACTION** of the beam is **REFLECTED**

 * This fraction is typically **MUCH LESS** than one percent

 * The **REMAINDER** of the beam travels on through the crystal

  ⇒ And a small fraction is once again reflected at the **NEXT** plane

  ⇒ This continues as the wave passes through the crystal

Each beam travels a slightly longer path

AS A WAVE PROPAGATES THROUGH A CRYSTAL IT GRADUALLY DISSIPATES AS SUCCESSIVE CRYSTAL PLANES CAUSE PARTIAL REFLECTION

[web]

Crystal Diffraction

• **Waves REFLECTED from the crystal planes INTERFERE with each other**

     * **In a manner that depends on the SPACING (*d*) of the crystal planes**

     * **The interference also depends on the WAVELENGTH (λ) of the waves**

        $\Rightarrow$ **And the ANGLE (θ) at which they are incident on the crystal**

     * **Consider the case of waves reflected from TWO successive crystal planes**
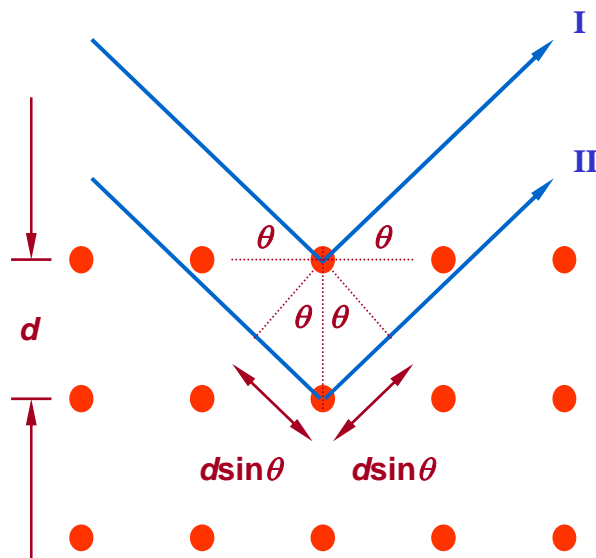
• *BY THE TIME IT LEAVES THE CRYSTAL BEAM II HAS TRAVELED LONGER DISTANCE THAN BEAM I*

• *A PATH DIFFERENCE HAS THEREFORE DEVELOPED BETWEEN BEAM II AND BEAM I*

• *A SIMPLE GEOMETRIC ANALYSIS MAY BE USED TO COMPUTE THIS PATH DIFFERENCE ΔL*

$$\frac{\Delta L}{2} = d \sin\theta \quad \therefore \quad \Delta L = 2d \sin\theta$$
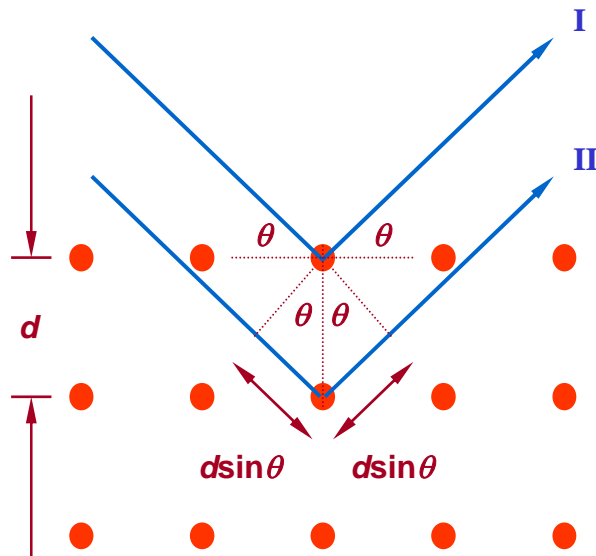
Crystal Diffraction

Here we are interested in the interference of waves reflected from MANY crystal planes

* This depends on the path difference we have just computed

⇒ For waves reflected from successive PAIRS of planes

* If this path difference is equal to an INTEGER number of wavelengths

* Then the NET interference of the reflected waves is CONSTRUCTIVE

$$\Delta L = 2d\sin\theta = n\lambda, \quad n = 1, 2, 3, \ldots$$

WHEN THE PATH DIFFERENCE BETWEEN SUCCESSIVELY REFLECTED WAVES IS EQUAL TO AN IRRATIONAL NUMBER OF WAVELENGTHS THEN BEAMS I & II WILL BE OUT OF PHASE WITH EACH OTHER

I

II

θ θ

θ θ

d

$d\sin\theta$ $d\sin\theta$

Hence, at those angles for which

$$\Delta L = 2d \sin \theta = n\lambda, \quad n = 1, 2, 3, \ldots$$

we will get a "spot" of bright intensity. Photographic film, or a photodetector can be used to sense this intensity.

If we take *d* ~ 0.3 nm, as for crystals, then we need to use light with

$$\lambda < 2d \sim 0.6 nm$$

$$f = \frac{c'}{\lambda} = \frac{3 \times 10^8 \, m/s / \sqrt{16}}{0.6 \times 10^{-9}} \sim 1.3 \times 10^{17}$$

These are *X*-rays. Even shorter wavelengths can be achieved with high energy electrons (in a TEM for example).
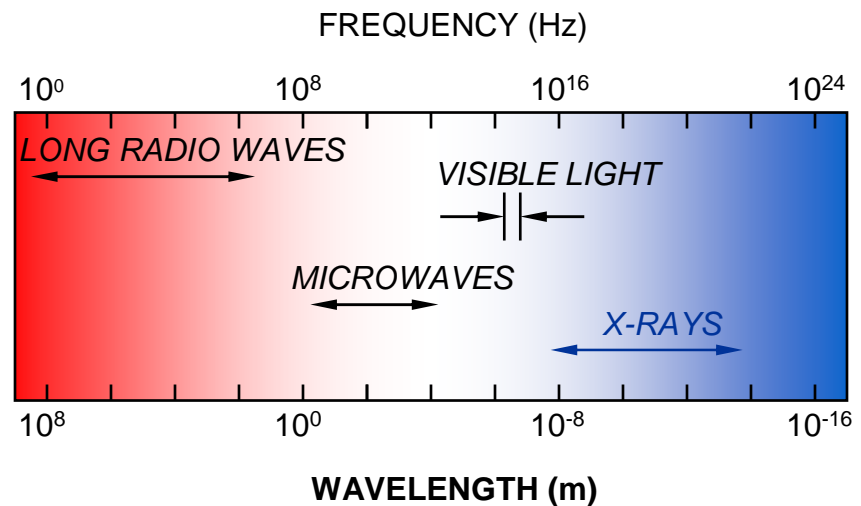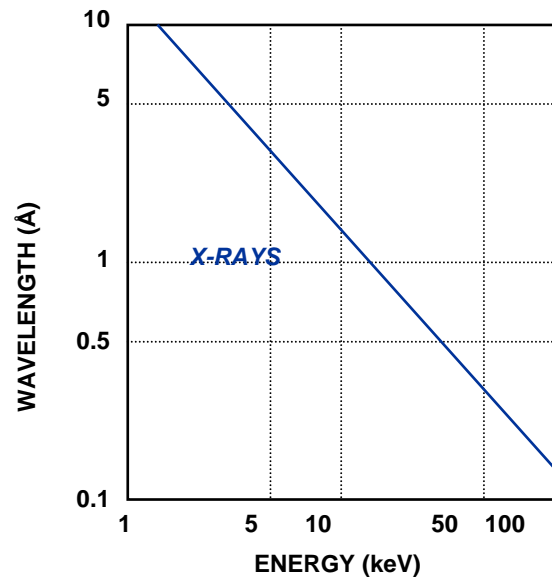
X-Ray Diffraction

• **The Bragg condition allows DIFFRACTION to be used as a PROBE of crystal structure**

      * Crystal diffraction studies are typically performed using X-RAY sources

            ⇒ X-rays are HIGH ENERGY electromagnetic waves

            ⇒ With characteristic wavelengths in the ÅNGSTROM range

            ⇒ This is COMPARABLE to the spacing of typical crystal planes
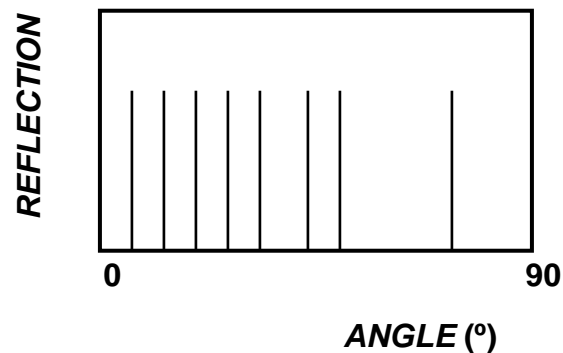
X-Ray Diffraction

• **APPLICATION**

     * **A beam of X-rays with a wavelength of 1 Å is directed at a sample whose crystal planes have a spacing of 4 Å. How many diffraction peaks can be observed as the sample orientation is rotated with respect to the beam?**
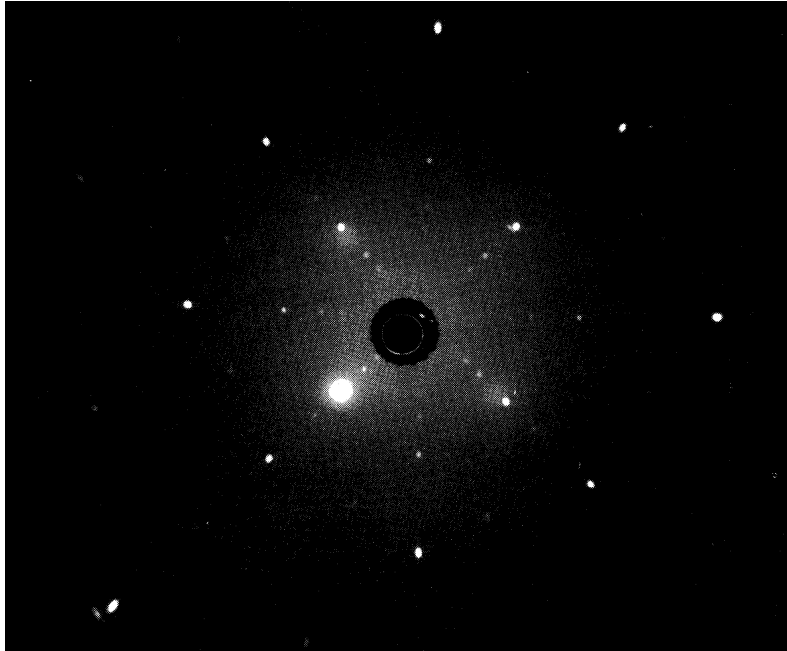
$$n\lambda = 2d\sin\theta \quad \therefore \quad \sin\theta = \left[n\frac{\lambda}{2d} \right] = \left[n\frac{1\times10^{-10}}{2\times4\times10^{-10}} \right] = \left[\frac{n}{8} \right]$$

n =	θ
1	7.2º
2	14.5º
3	22.0º
4	30.0º
5	38.7º
6	48.6º
7	61.0º
8	90º

But $\sin\theta \leq 1$ $\therefore$ *Maximum Allowed Value of* n *is* 8 &

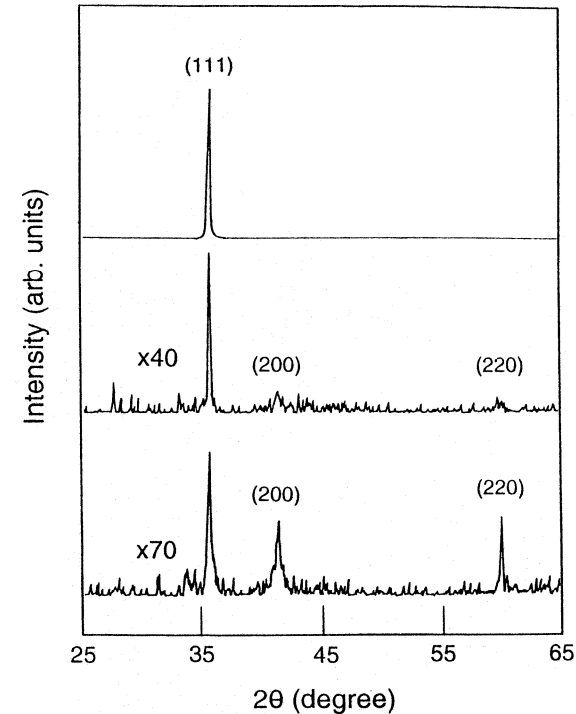*EIGHT Diffraction Peaks are Observed*

Crystal Diffraction

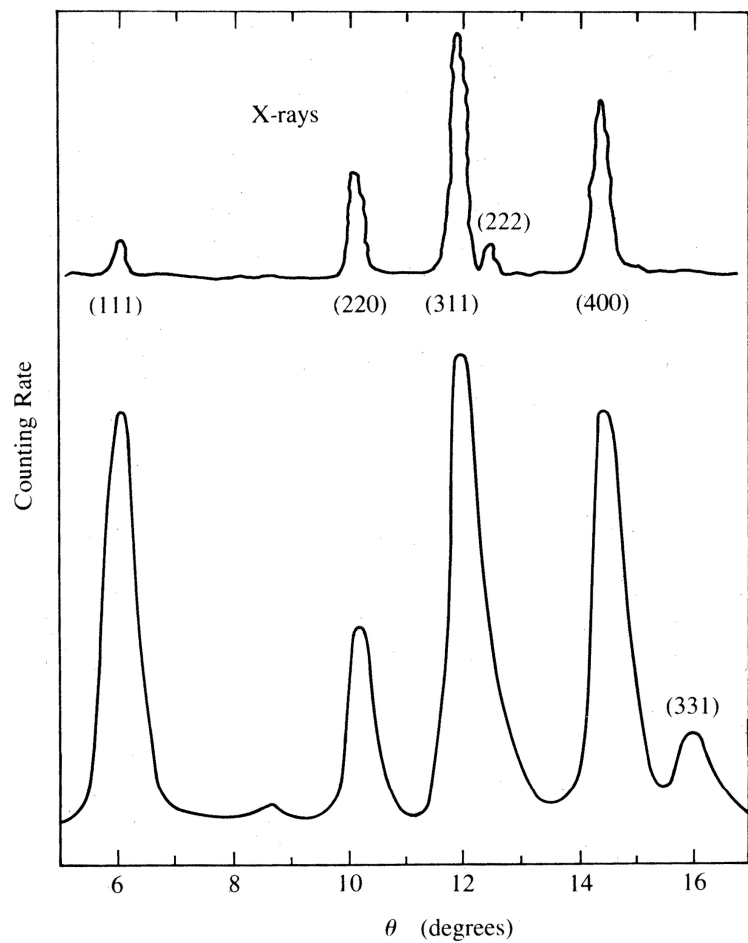## There are two major methods of measuring the diffraction.

Von Laue scattering measures all the scattered beams, recording them on photo-sensitive film.
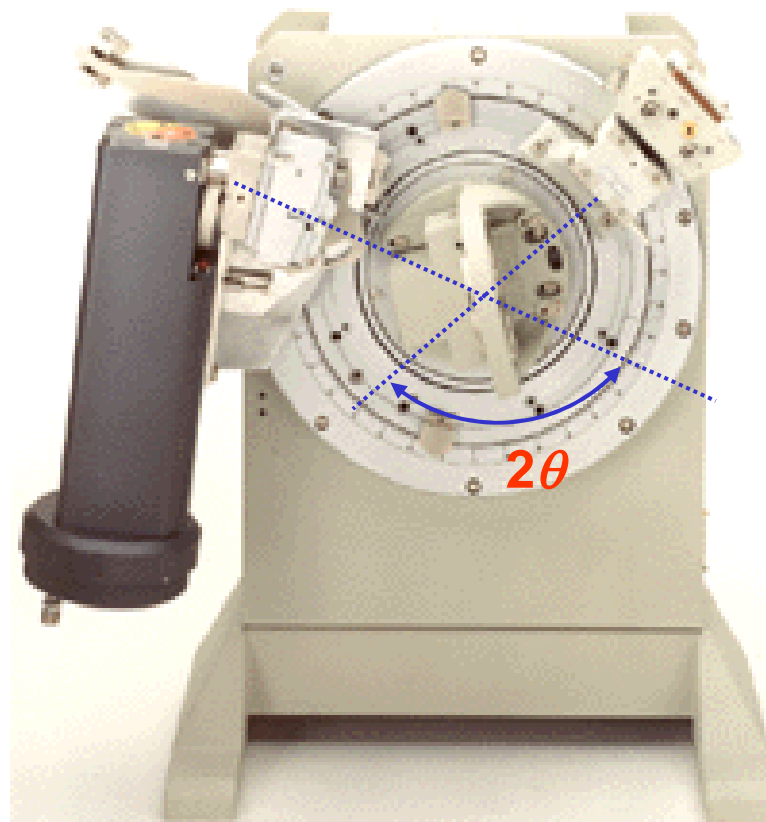
Bragg scattering measures the signal when both the incoming and outgoing (scattered) waves make an angle of θ with respect to the surface normal.

X-rays are used in both cases! This is because we need to have light with a wavelength comparable to the lattice spacing.

X-Ray Diffraction
"Double-angle diffractometer"

- In one type of diffraction experiment a beam of X-rays is **DIRECTED** at a sample, which is then **ROTATED** in a suitable apparatus

⇒ The intensity of the reflected beam is then monitored

AL
ETER

SCHEMATIC OF APPARATUS

X-Ray Diffraction

X-rays

(222)

(111)   (220)   (311)   (400)

(331)

Counting Rate

θ (degrees)

TYPICAL
SPECTRUM

2θ

X-Ray Diffraction

The von Laue approach gets all the diffracted beams at one time.

Film

X-rays

Collimators

Crystal

Diffracted beams of X-rays
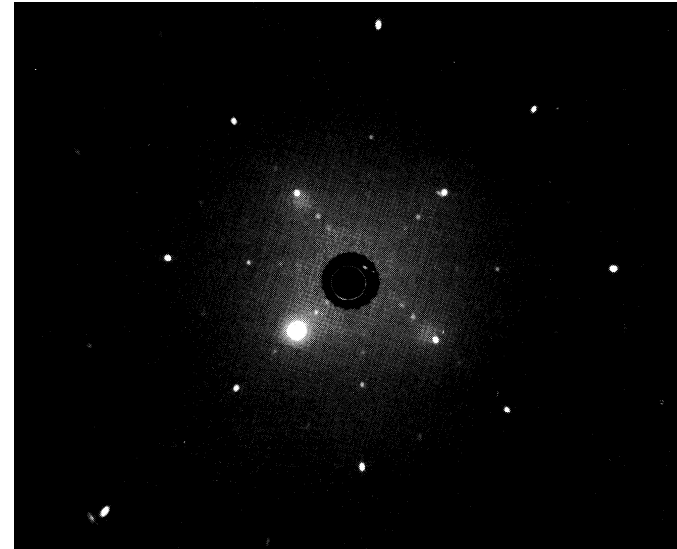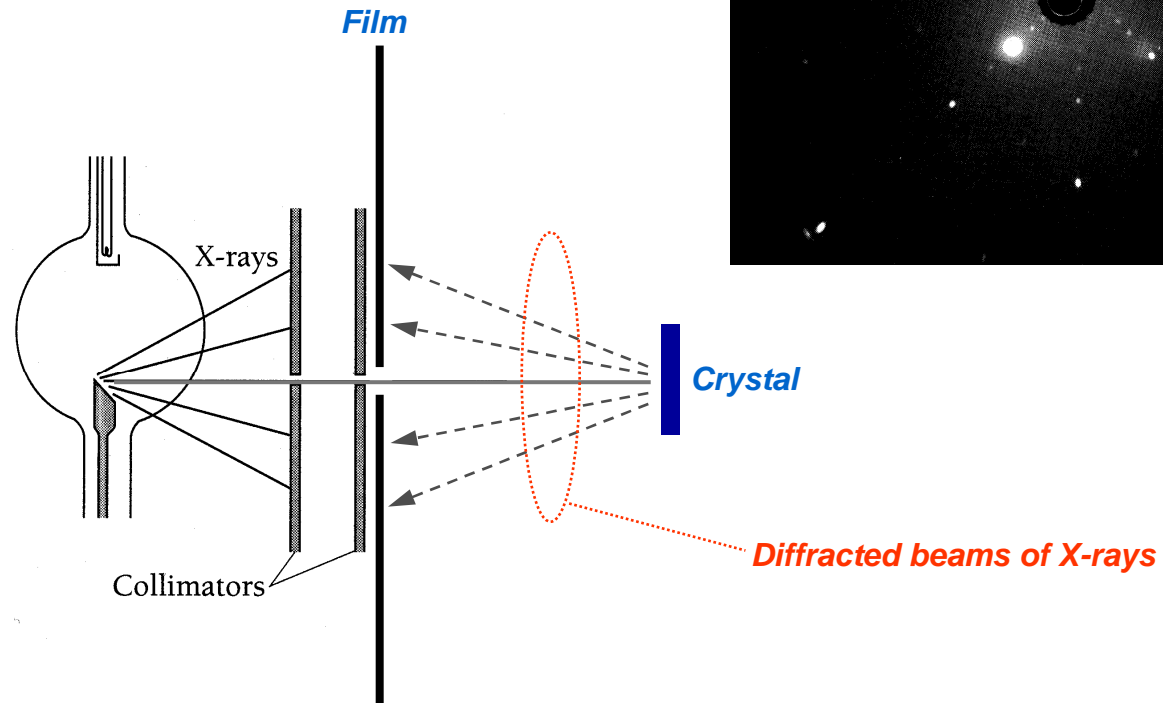
X-Ray Diffraction

Laue diffraction pattern for Si. The crystal is oriented with a (100) surface. Note the square pattern indicative of the cubic nature of the crystal.