

## Chapter 2: Crystallography

### 2.1:

Scientists are considering using nanoparticles of magnetic materials such as iron-platinum (Fe-Pt) as a medium for ultrahigh density data storage. Arrays of such particles potentially can lead to storage of trillions of bits of data per square inch—a capacity that is 10 to 100 times higher than any current storage devices such as computer hard disks. If these scientists consider iron (Fe) particles that are 3 nm in diameter, what is the number of atoms in one such particle?

### Answer:

The radius of such a Fe nanoparticle is 1.5 nm.

The volume of each iron magnetic nanoparticle =  $(4/3)\pi(1.5 \times 10^{-7} \text{ cm})^3 = 1.4137 \times 10^{-20} \text{ cm}^3$ .

Density of iron =  $7.8 \text{ g/cm}^3$ . Atomic mass of iron is 56 g/mol.

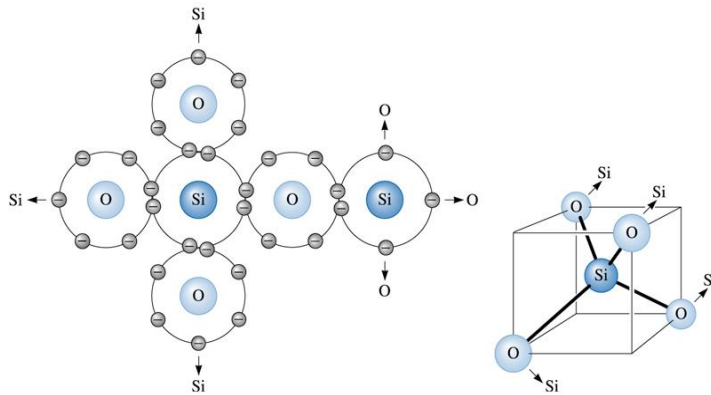
Mass of each iron nanoparticle =  $7.8 \text{ g/cm}^3 \times 1.4137 \times 10^{-20} \text{ cm}^3 = 1.102 \times 10^{-19} \text{ g}$ .

One mole or 56 g of Fe contains  $6.023 \times 10^{23}$  atoms, therefore, the number of atoms in one Fe nanoparticle is 1186.

### 2.2:

Assuming that silica ( $\text{SiO}_2$ ) has 100% covalent bonding, describe how oxygen and silicon atoms in silica ( $\text{SiO}_2$ ) are joined.

### Answer:



Silicon has a valence of four and shares electrons with four oxygen atoms, thus giving a total of eight electrons for each silicon atom. However, oxygen has a valence of six and shares electrons with two silicon atoms, giving oxygen a total of eight electrons (see figure above on the left). The figure above on the right illustrates one of the possible resulting structures: similar to the case of silicon (Si), a tetrahedral structure is observed.

### 2.3:

What is the difference between lattice and basis and between unit cell and primitive cell?

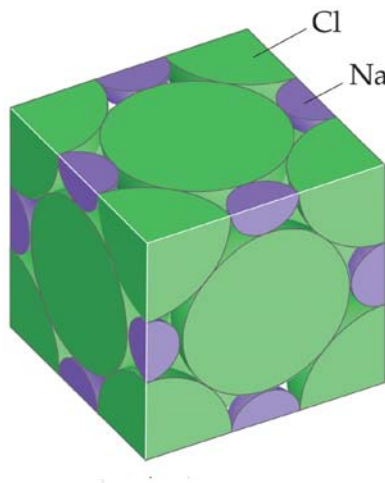
### Answer:

A lattice is a set of points in space with translational symmetry, i.e., each point has an identical environment. A basis is a set of atoms that are arranged around each lattice point to make a structure. A unit cell is a volume of space containing lattice points and associated atoms, which can be repeated to fill space and reproduce the desired structure. The conventional cell may contain any number of lattice points, and has geometry chosen to reflect the symmetry of the structure. The primitive cell, on the other hand, contains strictly one lattice point, and may have a non-intuitive geometry.

#### 2.4:

What are the net number of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in the NaCl unit cell represented below?  
The crystal is an example of which type of cubic lattice?  
Identify the atom positions of the Na and Cl atoms in the NaCl structure.

**Answer:**



There are 4  $\text{Na}^+$  resulting from:  
 $(1/4 \text{ Na}^+/\text{edge})(12 \text{ edges}) = 3 \text{ Na}^+$   
 $(1 \text{ Na}^+/\text{center})(1 \text{ center}) = 1 \text{ Na}^+$   
 There are 4  $\text{Cl}^-$  resulting from:  
 $(1/8 \text{ Cl}^-/\text{corner})(8 \text{ corners}) = 1 \text{ Cl}^-$   
 $(1/2 \text{ Cl}^-/\text{face})(6 \text{ faces}) = 3 \text{ Cl}^-$

NaCl is an example of a face-centered crystalline (FCC) lattice.

Na atoms:  $(000) (1/2 \ 1/2 \ 0) (1/2 \ 0 \ 1/2) (0 \ 1/2 \ 1/2)$   
 Cl atoms:  $(1/2 \ 0 \ 0) (0 \ 1/2 \ 0) (0 \ 0 \ 1/2) (1/2 \ 1/2 \ 1/2)$

#### 2.5:

Consider the plane defined by the three points,  $P_1(2,4,-3)$ ,  $P_2(-1,2,1)$ , and  $P_3(3,0,-2)$ .  
Calculate the points where this plane intersects with the axes and derive the Miller indices associated with this plane.

**Answer:**

$$\mathbf{r} = x \cdot \mathbf{i} + y \cdot \mathbf{j} + z \cdot \mathbf{k}$$

$$\mathbf{r}_1 = 2 \cdot \mathbf{i} + 4 \cdot \mathbf{j} - 3 \cdot \mathbf{k}$$

$$r_2 = -1 \cdot i + 2 \cdot j + 1 \cdot k$$

$$r_3 = 3 \cdot i + 0 \cdot j - 2 \cdot k$$

$$(r-r_1) \cdot [(r_2-r_1) \times (r_3-r_1)] = 0$$

$$\begin{vmatrix} x-2 & y-4 & z+3 \\ -3 & -2 & 4 \\ 1 & -4 & 1 \end{vmatrix} = 2x + y + 2z - 2 = 0$$

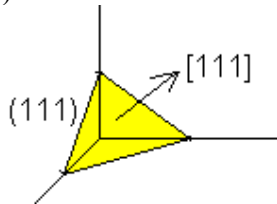
so the plane is  $2x+y+2z = 2$  with intersections with the axes with coordinates  $(1,0,0)$ ,  $(0,2,0)$ ,  $(0,0,1)$  with reciprocals of  $1, 1/2, 1$  and thus miller indices of  $(212)$ .

## 2.6:

Calculate (a) the angle between  $[111]$  and the direction normal to  $(111)$  plane in a simple cubic crystal and (b) the angle between the  $[121]$  direction and the direction normal to  $(113)$  plane in a simple cubic crystal.

### Answer:

(a)



In the above figure, the shaded plane is the  $(111)$  plane. The arrow sketched is along the  $[111]$  direction. From geometry we know that in a cubic system the  $[111]$  direction is normal to the  $(111)$  plane. The angle between the  $[111]$  vector and the vector normal to  $(111)$  plane can be calculated by the dot product of the two vectors. The dot product is:

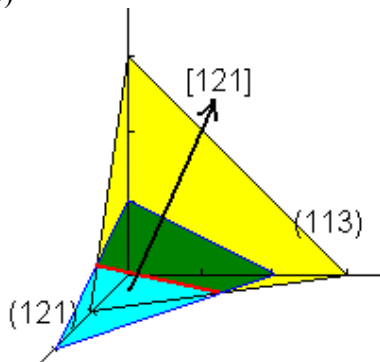
$$\mathbf{A} \cdot \mathbf{B} = AB \cos \theta \text{ or also}$$

$$A_x B_x + A_y B_y + A_z B_z = AB \cos \theta$$

From the above figure and from geometry, we can see that in a cubic system,

$$3 = \sqrt{3} \sqrt{3} \cos \theta \text{ or } \cos \theta = 1 \text{ so that } \theta = 0^\circ.$$

(b)



From the above figure and from geometry:  $\cos \theta = (3 \cdot 2 + 3 \cdot 1 + 2 \cdot 1) / [\sqrt{(3^2 + 3^2 + 1^2)} \cdot \sqrt{(2^2 + 1^2 + 2^2)}] = 0.841$  or  $\theta = 32.73^\circ$ .

**2.7:**

A signal  $x(t)$  has a Fourier transform  $X(f)$ . Express the Fourier transforms of  $x_1$  in terms of  $X(f)$  the function  $x_1(t) = x(3-t)$

**Answer:**

$$\begin{aligned}
 X(f) &= \int_{-\infty}^{+\infty} x(t) \cdot e^{-2\pi i f t} dt \\
 X_1(f) &= \int_{-\infty}^{+\infty} x_1(t) \cdot e^{-2\pi i f t} dt \\
 &= \int_{-\infty}^{+\infty} x(3-t) \cdot e^{-2\pi i f t} dt \xrightarrow{r=3-t} \int_{-\infty}^{+\infty} x(r) \cdot e^{-2\pi i f (3-r)} d(3-r) \\
 &= \int_{-\infty}^{+\infty} x(r) \cdot e^{-6\pi i f} e^{-2\pi i (-f)r} d(-r) \\
 &= -e^{-6\pi i f} \cdot \int_{-\infty}^{+\infty} x(t) e^{-2\pi i (-f)t} dt \\
 &= -e^{-6\pi i f} \cdot X(-f)
 \end{aligned}$$

**2.8:**

In an x-ray set-up with a crystal-to-detector distance of 100 mm (D), you find that the highest resolution reflection is at  $x = 20$  mm,  $y = 15$  mm, relative to the direct beam position. The wavelength  $\lambda = 1.54$  Å. What is the Bragg angle of this reflection? What is the d-spacing of the crystal? If the detector is circular and has a radius of 100 mm, and you would like to collect data so that the highest resolution reflection is at the detector edge, would you move the detector closer to or further away from the crystal?

**Answer:**

$x = 20$  mm,  $y = 15$  mm, so  $r = 25$  mm  
 $\phi = \arctan(r/D) = \arctan(25/100) = 14.04^\circ$   
 Bragg angle  $\theta = \phi/2 = 7.02^\circ$

$\theta$  is the Bragg angle from Bragg's law.

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

$$d = \lambda / 2 \sin \theta = 1.54 \text{ Å} / 2 \sin \theta = 6.3 \text{ Å}$$

The highest resolution reflection is at  $r = 25$  mm. The detector radius is 100 mm. It's far from the edge. Therefore, to make sure that the highest resolution data is at the detector edge, move the detector to a larger distance from the crystal. Using the equations above, the exact distance can be calculated.

**2.9:**

Describe the difference between a reciprocal lattice and a real one.

**Answer:**

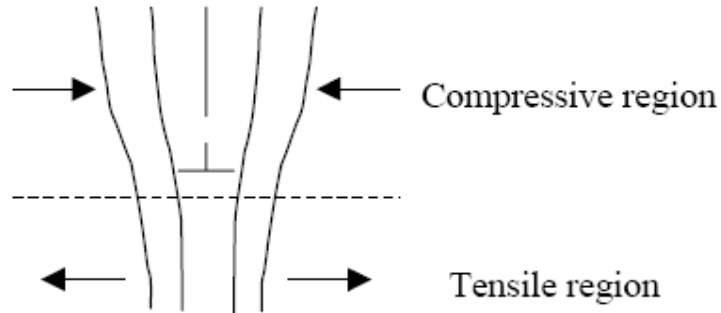
A real lattice represents the location of real objects (atoms) and has dimensions **m**. The reciprocal lattice indicates the positions of abstract points (magnitude and direction of momentum) and comes with dimensions of **m<sup>-1</sup>**.

**2.10:**

Edge dislocations may be used to getter impurities in semiconductors. In an edge dislocation, there are always two regions, a compressive region, where the layer is inserted, and a tensile region (see figure below). Which of these two regions will best accommodate (via elastic interactions) *substitutional* atoms whose radius is larger than that of the host atoms?

**Answer:**

The substitutional atom will be attracted to the tensile region because a larger atom will tend to “open up” the structure and the tensile stress will facilitate this.

**2.11:**

Show that the reciprocal lattice of a face-centered cubic (FCC) lattice is a body-centered cubic (BCC) lattice or conversely that the reciprocal lattice of a BCC lattice is an FCC lattice.

**Answer:**

(1) For an FCC,

$$\left\{ \begin{array}{l} \bar{a}_1 = \frac{a}{2}(\hat{y} + \hat{z}) \\ \bar{a}_2 = \frac{a}{2}(\hat{x} + \hat{z}) \\ \bar{a}_3 = \frac{a}{2}(\hat{x} + \hat{y}) \end{array} \right.$$

$$\begin{aligned}
\bar{b}_1 &= 2\pi \frac{\bar{a}_2 \times \bar{a}_3}{\bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3)} \\
\bar{a}_2 \times \bar{a}_3 &= \left(\frac{a}{2}\right)^2 (\hat{x} + \hat{z}) \times (\hat{x} + \hat{y}) \\
&= \left(\frac{a}{2}\right)^2 (\hat{x} \times \hat{x} + \hat{x} \times \hat{y} + \hat{z} \times \hat{x} + \hat{z} \times \hat{y}) \\
&= \left(\frac{a}{2}\right)^2 (\hat{y} - \hat{x} + 0 + \hat{z}) \\
&= \left(\frac{a}{2}\right)^2 (-\hat{x} + \hat{y} + \hat{z}) \\
\bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3) &= \frac{a}{2} (\hat{y} + \hat{z}) \cdot \left(\frac{a}{2}\right)^2 (-\hat{x} + \hat{y} + \hat{z}) \\
&= 2 \cdot \left(\frac{a}{2}\right)^3 \\
\bar{b}_1 &= 2\pi \frac{(a/2)^2 \cdot (-\hat{x} + \hat{y} + \hat{z})}{2 \cdot (a/2)^3} = \frac{2\pi}{a} (-\hat{x} + \hat{y} + \hat{z})
\end{aligned}$$

Similarly, we can also calculate that:

$$\begin{aligned}
\bar{b}_2 &= \frac{2\pi}{a} (\hat{x} - \hat{y} + \hat{z}) \\
\bar{b}_3 &= \frac{2\pi}{a} (\hat{x} + \hat{y} - \hat{z})
\end{aligned}$$

These are unit vectors for a BCC.

(2) For a BCC,

$$\begin{cases} \bar{a}_1 = \frac{a}{2} (-\hat{x} + \hat{y} + \hat{z}) \\ \bar{a}_2 = \frac{a}{2} (\hat{x} - \hat{y} + \hat{z}) \\ \bar{a}_3 = \frac{a}{2} (\hat{x} + \hat{y} - \hat{z}) \end{cases}$$

$$\begin{aligned}
\bar{b}_1 &= 2\pi \frac{\bar{a}_2 \times \bar{a}_3}{\bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3)} \\
\bar{a}_2 \times \bar{a}_3 &= \left(\frac{a}{2}\right)^2 (\hat{x} - \hat{y} + \hat{z}) \times (\hat{x} + \hat{y} - \hat{z}) \\
&= \left(\frac{a}{2}\right)^2 (\hat{x} \times \hat{y} - \hat{x} \times \hat{z} - \hat{y} \times \hat{x} + \hat{y} \times \hat{z} + \hat{z} \times \hat{x} + \hat{z} \times \hat{y}) \\
&= \left(\frac{a}{2}\right)^2 (\hat{x} + \hat{y} + \hat{z} - \hat{x} - \hat{y} + \hat{z}) \\
&= \left(\frac{a}{2}\right)^2 (\hat{y} + \hat{z}) \cdot 2 \\
\bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3) &= \frac{a}{2} (-\hat{x} + \hat{y} + \hat{z}) \cdot 2 \left(\frac{a}{2}\right)^2 (\hat{y} + \hat{z}) \\
&= \left(\frac{a}{2}\right)^3 \cdot 2 \cdot 2 = 4 \left(\frac{a}{2}\right)^3 \\
\bar{b}_1 &= 2\pi \frac{(a/2)^2 \cdot (\hat{y} + \hat{z}) \cdot 2}{4 \cdot (a/2)^3} = \frac{2\pi}{a} (\hat{y} + \hat{z})
\end{aligned}$$

Similarly, we can also calculate that

$$\begin{aligned}
\bar{b}_2 &= \frac{2\pi}{a} (\hat{x} + \hat{z}) \\
\bar{b}_3 &= \frac{2\pi}{a} (\hat{x} + \hat{y})
\end{aligned}$$

These are unit vectors for an FCC lattice.

### 2.12:

An electron moves with speed  $u = 0.7c$ . Calculate its total energy and its kinetic energy in eV.

#### Answer:

The rest energy of an electron is 0.511 MeV.

The total energy  $E = mc^2 / \sqrt{1 - u^2/c^2} = 0.716$  MeV

The kinetic energy  $K = E - mc^2 = 0.205$  MeV

### 2.13:

Calculate the number of atoms in a 100  $\mu\text{m}$  long Ag line (1  $\mu\text{m}$  wide and 1  $\mu\text{m}$  high). If using STM we put one atom down per second, how long will it take to finish this Ag line?

#### Answer:

The crystal structure of Ag is face-center cubic (FCC). In an FCC crystal structure the unit cell contains  $6 \cdot \frac{1}{2} + 8 \cdot \frac{1}{8} = 4$  atoms.

Next we need to calculate the volume of a unit cell of Ag in the solid state. From the figure below, we know that:

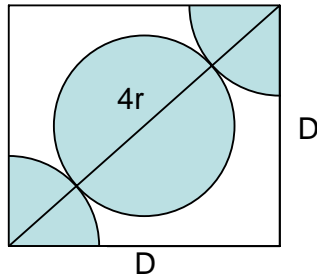
$$(4r)^2 = D^2 + D^2 = 2D^2$$

So that:

$$D = \sqrt{8r^2}$$

The atomic radius  $r$  of Ag is  $1.75 \cdot 10^{-10}$  m so we can calculate the value of  $D$  as  $4.95 \cdot 10^{-10}$  m.

Therefore, the volume of the unit cell of Ag is  $(4.95 \cdot 10^{-10})^3 = 121.23 \cdot 10^{-30} \text{ m}^3$ .

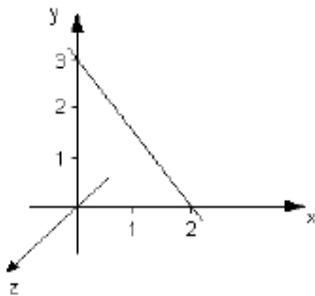


The volume of the Ag line ( $100 \cdot 10^{-6}$  m long,  $1 \cdot 10^{-6}$  wide and  $1 \cdot 10^{-6}$  high) is  $10^{-16} \text{ m}^3$ . So the total number of the atoms in the Ag line is:  $(10^{-16}/121.23 \cdot 10^{-30}) \cdot 4 = 3.3 \cdot 10^{12}$  atoms. As we are depositing 1 atom per second, to finish the line it will take  $3.3 \cdot 10^{12}$  seconds.

The above calculation assumes single crystalline Ag. In reality one usually deals with polycrystalline Ag. So a better calculation would also include the density of the Ag polycrystalline material. The latter would take into account all the Ag line defects.

## 2.14:

What is the Miller index for the plane shown below?



**Answer:**

(320)

## 2.15:

What is the number of nearest neighbors for the following crystal lattices:

- (a) simple cubic (SC)
- (b) face-centered cubic (FCC)
- (c) body-centered cubic (BCC)

**Answer:**



- (a) (6)
- (b) (12)
- (c) (8)

**2.16:**

Calculate the angle  $\theta$  of reflection for an x-ray experiment with  $\lambda = 1.54 \text{ \AA}$ , for a cubic crystal with a lattice parameter of  $a = 5 \text{ \AA}$ .

**Answer:**

From  $2d \sin\theta = n\lambda$ , the (100) reflection with  $d = 5 \text{ \AA}$  and  $n = 1$  occurs at  $\theta = 8.86^\circ$ ; for  $n = 2$ ,  $\theta = 17.93^\circ$ ; for  $n = 3$ ,  $\theta = 27.52^\circ$ ; for  $n = 4$ ,  $\theta = 38.02^\circ$ ; for  $n = 5$ ,  $\theta = 50.35^\circ$ ; for  $n = 6$ ,  $\theta = 67.52^\circ$ ; no reflection for  $n \geq 7$ . The (200) reflection with  $d = 2.5 \text{ \AA}$  for  $n = 1$  is at  $\theta = 17.93^\circ$ ; for  $n = 2$ ,  $\theta = 38.02^\circ$ ; for  $n = 3$ ,  $\theta = 67.52^\circ$ ; no reflection for  $n \geq 4$ .

**2.17:**

X-rays with wavelength  $1.54 \text{ \AA}$  are “reflected” from the (110) planes of a cubic crystal with unit cell  $a = 6 \text{ \AA}$ . Calculate the Bragg angle,  $\theta$ , for all orders of reflection,  $n$ .

**Answer:**

Using the d-spacing equation

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{1+1+0}{6^2} = 0.056 \text{ we calculate for the lattice spacing}$$

$d = 4.24 \text{ \AA}$  and combining this result with Bragg’s law,

$$\theta = \sin^{-1}\left(\frac{n\lambda}{2d}\right)$$

it can be found that:

$$n = 1: \theta = 10.46^\circ = (110)$$

$$n = 2: \theta = 21.30^\circ = (220)$$

$$n = 3: \theta = 33.01^\circ = (330)$$

$$n = 4: \theta = 46.59^\circ = (440)$$

$$n = 5: \theta = 65.23^\circ = (550)$$

**2.18:**

What is the closest packed crystal? Simple cubic (SC), body-centered cubic (BCC), or face-centered cubic (FCC)?

**Answer:**

FCC is more closely packed than SC or BCC structures. You can see why FCC is more closely packed than BCC or SC structures by noting that SC has 8 atoms at the corners of a cube but only the corners are contributing to the unit cell one-eighth each. For a BCC, 1 whole atom is in the center and 8 at the corners contributing one-eighth each again for a total of 2 in the unit cell. The FCC has 8 at the corners (1/8 each) and 6 at each face (contributing 1/2 each) for a total of 4 atoms in the unit cell. More atoms per cube = more closely packed.

**2.19:**

Is five-fold symmetry ever found in crystal lattices? Why or why not?

**Answer:**

No, because there is no way to pack a five-fold symmetric unit cell into a lattice such that all the volume of the crystal occupied; that is, it would leave gaps.

**2.20:**

Calculate the number of atoms in 100 g of silver.

**Answer:**

$$\text{The number of silver atoms is} = \frac{(100 \text{ g})(6.023 \times 10^{23} \text{ atoms/mol})}{(107.868 \text{ g/mol})} = 5.58 \times 10^{23}$$

**2.21:**

The derivation of Bragg's law results in  $n\lambda = 2d\sin\theta$ . What does  $n$  represent and why is it usually omitted? Can you give an example to show why  $n$  is not needed?

**Answer:**

$n$  represents the number of wavelengths between x-rays reflected from different planes. It is not needed, but higher order reflections are accounted for in the Miller indices. For example, a (200) reflection in a simple cubic crystal is actually a second order diffraction ( $n = 2$ ) between (100) planes.

**2.22:**

Calculate the packing factor in a FCC lattice

**Answer:**

Assume the lattice parameter is  $a$  if  $R$  is the radius of an atom. Since the atoms touch each other on the face of the cube.

$$(a^2 + a^2)^{1/2} = R + 2R + R$$

$$a = 2^{1/2} R$$

$$\text{Packing fraction} = \text{Volume of atoms} / \text{Total Volume of unit cell} = (4/3\pi R^3 * 4) / a^3 = 0.74.$$

This means that 74% of the lattice space is occupied by atoms.

**2.23:**

What is the rule for determining the *slip direction* in a close-packed material?

**Answer:**

Close-packed directions have the smallest Burgers vector and therefore correspond to the direction of slip.

**2.24:**

What causes work hardening?

**Answer:**

Tangling and storage of dislocations

**2.25:**

How can we determine the direction cosine between two vectors?

**Answer:**

Use the dot product.

**2.26:**

How can we identify the direction of slip in a crystal (Burgers vector)?

**Answer:**

Close-packed direction

**2.27**

Why do very thin metal wires/whiskers exhibit very high strengths?

**Answer:**

Small enough fibers (whiskers) can be dislocation free.

**2.28:**

Why does the strength of glass fibers increase as the diameter goes down?

**Answer:**

The maximum flaw (crack) size is limited by the fiber size.

**2.29:**

Find the angle between the planes 110 and 100 in a simple cubic crystal.

**Answer:**

$$\cos\theta = (a_1 a_2 + b_1 b_2 + c_1 c_2) / [(a_1^2 + b_1^2 + c_1^2)^{1/2} (a_2^2 + b_2^2 + c_2^2)^{1/2}] = 1/2^{1/2} \text{ Therefore, } \theta = 45^\circ.$$

**2.30:**

Could you use x-ray diffraction to determine the coefficient of thermal expansion (i.e., change in length of a material due to change in temperature)?

**Answer:**

If we have a high temperature diffractometer, we could measure the lattice parameter as a function of temperature. Change in lattice parameters is directly related to the change in macroscopic dimensions.

**2.31:**

Diamond and graphite are examples of which type of crystalline solids: molecular, covalent network, ionic, or metallic?

**Answer:**

Diamond and graphite are both forms of carbon and consist of a network of covalent bonds (hence covalent network).

**2.32:**

What value does the atomic scattering factor  $f$  approach as  $2\theta$  approaches 0?

**Answer:**

$f$  approaches the number of electrons in the atom ( $Z$ ) as  $2\theta$  approaches 0.  $f$  is the intensity of the atom relative to the scattering of one electron. At  $2\theta = 0$ ,  $f$  would be equal to the number of electrons, but for other angles, the x-rays from the different electrons are slightly out of phase, so the intensity decreases.

### 2.33:

How does light affect the color of a crystal?

#### Answer:

The color of any compound (whether or not it is a crystal) depends on how its atoms or its molecules absorb light. Normally white light is considered to have all wavelengths (colors) of light in it. If you pass a white light through a colored compound some of the light is absorbed (we don't see the color which is absorbed, but we see the complementary color of the light) as it is reflected off the compounds surface. Here is a table of colors and their complements:

Color	Complement	Wavelength (of color <i>nm</i> )
violet	green-yellow	400-424
blue	yellow	424-491
green	red	491-570
yellow	blue	570-585
orange	green-blue	585-647
red	green	647-700

So if you have a crystal which absorbs red light, it will appear green. Conversely, if the crystal absorbs green light, it will appear red.

## Chapter 3: Quantum Mechanics and the Band Theory of Solids

### 3.1:

What is the physical meaning of a wave function? In what limit and in what sense does a wave function approach the classical limit?

#### Answer:

The wave function  $\Psi(x,t)$  being complex does not have any direct physical meaning. However, its absolute value squared ( $|\Psi(x,t)|^2$ ) is interpreted as a probability density function. In other words,  $|\Psi(x,t)|^2 dx$  represents the probability of finding the particle, described by  $\Psi(x,t)$ , in the interval  $(x, x+dx)$  at time  $t$ . The classical limit of a quantum system is obtained in the limit of large quantum numbers. The absolute of the wave function squared oscillates then very fast and its value averaged over all these oscillations approaches the classical system description.

### 3.2:

What are allowed and forbidden regions in classical mechanics? What is the general behavior of a wave function in quantum mechanical allowed and forbidden regions? What is a turning point?