

1 Crystal Structures

A *crystal* is a periodic array of atoms. Many elements and quite a few compounds are crystalline at low enough temperatures, and many of the solid materials in our everyday life (like wood, plastics, and glasses) are not crystalline. Nevertheless, texts concerning solid-state physics typically start with the discussion of crystals for a good reason: the treatment of a large number of atoms is immensely simplified if they are arranged into a periodic order.

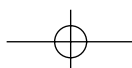
Figure 1.1 shows a few two-dimensional “crystals”.¹⁾ All crystals have *discrete translational symmetry*: If displaced by a properly selected *lattice vector* \mathbf{R} , every atom moves to the position of an identical atom in the crystal. Owing to this translational symmetry, a crystal can be constructed by repeating the *basis* at every *Bravais lattice* point. The basis is the “building block” of the crystal. It may be simple, a spherical atom, or as complex as a DNA molecule. Sometimes we have to use a basis made up of two (or more) atoms, even if there is only one type of atom in the crystal (see the example in Figure 1.2).

The *Bravais lattice*, or *space lattice*, is an infinite array of points determined by the lattice vectors \mathbf{R} , where $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ such that every n_i is an integer. The \mathbf{a} 's are the three *primitive vectors* of the Bravais lattice; in three dimensions they must have a nonzero $\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ product. There are an infinite number of different choices for the primitive vectors of a given lattice. For example, $\mathbf{a}'_1 = \mathbf{a}_1 + \mathbf{a}_2$; $\mathbf{a}'_2 = \mathbf{a}_1 - \mathbf{a}_2$; and $\mathbf{a}'_3 = \mathbf{a}_3$ describe the same lattice. The *lattice spacings* are the lengths of the shortest possible set of primitive vectors.

All three crystals in Figure 1.1 have the same Bravais lattice. Note that not all symmetric arrays of points are Bravais lattices. For example, Figure 1.2 shows a *honeycomb lattice* and a choice for its Bravais lattice and basis.

In addition to translational symmetry, most crystals have other symmetries, including reflection, rotation, or inversion symmetries, or more complicated symmetry operations, like the combination of rotation and translation by a fraction of the lattice vector. In Figure 1.1 the threefold rotational symmetry around the point P is common to all three crystals. The honeycomb lattice (Figure 1.1c) also has a

1) Many textbooks, including [1–4], provide introductions to crystal symmetries. We refer the reader to those books for descriptions of three-dimensional crystals. Here we use two-dimensional examples to illustrate the concepts.



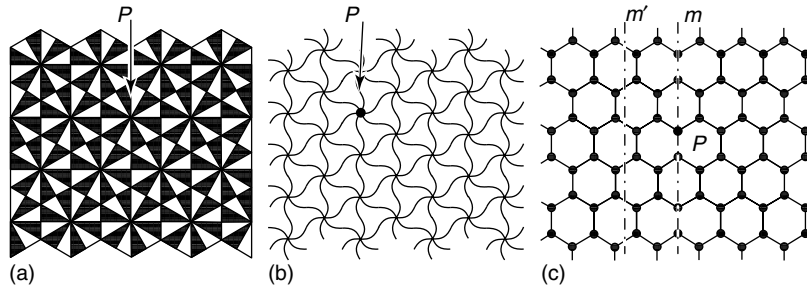


Figure 1.1 Examples of crystals in two dimension. Dots, curved lines, or shaded areas represent various molecules or atomic arrangements.

“mirror line” m , while the other two crystals do not have this symmetry. A less trivial symmetry operation is mirroring the honeycomb lattice with respect to the line m' , and then shifting it parallel to the line, until it overlaps with itself.

The collection of symmetry operations forms a *symmetry group*. The important property that defines a symmetry group is the relationship between the symmetry elements – i.e. what happens if two symmetry operations are applied successively. In the language of group theory, this relationship is described by the multiplication (direct product) table. (An introduction to basic group theory is given by Yu and Cardona [3, pp. 21–43] or Harrison [5, pp. 16–20] or Sólyom [4, Section 5.3.1].) The symmetry group can be represented in many ways (collections of matrices, symmetry operations of a simple geometric object, and so on). As long as the multiplication table is the same, we are dealing with the same group. The crystals in Figure 1.1(a and b) have equivalent symmetry groups, while some of the symmetries of the honeycomb lattice are different.

When all possible symmetry operations are taken into account, we talk about *crystallographic space groups*. Any given three-dimensional crystal belongs to one of the 230 possible crystallographic space groups. (Two-dimensional crystals are much simpler; there are only 17 inequivalent “crystallographic plane groups”.) The symmetries are often identified by the name of a representative material, like “sodium chloride structure”, “diamond structure”, “wurzite (or zinblende, zinc sulfide) structure”, and so on. More sophisticated group theoretical notations are used by crystallographers (Ashcroft and Mermin [2, pp. 122–126]; Sólyom [4, Section 5.4.2]). For a complex structure, the identification of the symmetry group may be a rather nontrivial task.

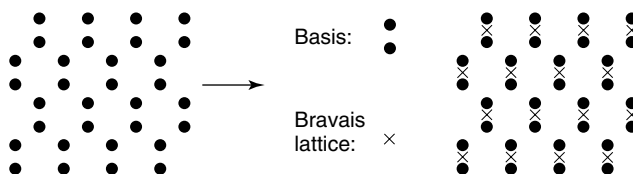


Figure 1.2 Example of a regular array of points that is not a Bravais lattice (honeycomb lattice).

A subset of symmetry operations that leaves at least one point invariant makes up the *crystallographic point group*. There are 32 different crystallographic point groups in three dimensions and 10 in two dimensions. Considering the examples in Figure 1.1, the rotations around P and the mirror line m are point group symmetries, but the combination of mirroring around m' and the subsequent shift is *not* a point group operation.

Sorting out the symmetries of the Bravais lattices is much simpler. There are 14 different space groups for three-dimensional Bravais lattices, including the *simple cubic (sc)*, *face-centered cubic (fcc)*, *body-centered cubic (bcc)*, *simple tetragonal*, *centered tetragonal (ct)*, and others. Figure 1.3 shows all possible Bravais lattices in two dimensions. It is important to emphasize that the symmetries of the Bravais lattice are intimately related to the symmetries of the original lattice. For example, the threefold rotational symmetry of the honeycomb lattice results in the requirement that its Bravais lattice must have threefold rotational invariance (which leaves the hexagonal lattice as the only choice, see Figure 1.2).

Finally, when the point group symmetries of the Bravais lattices are considered, the choices are further limited, and in three dimensions only seven distinct groups are left. These define the seven *crystal systems*: cubic, tetragonal, orthorhombic, monoclinic, triclinic, trigonal, and hexagonal. (In two dimensions there are four crystal systems. The rectangular and centered rectangular Bravais lattices shown in Figure 1.3 make up the “rectangular” system.)

The *primitive unit cell* or *primitive cell* is a volume that fills space completely, without overlap, if shifted by each of the lattice vectors. The primitive unit cell contains exactly one Bravais lattice point and the atoms in it can be used as the basis to construct the crystal. The volume made up by the primitive vectors is a possible primitive unit cell, but there are many other possibilities. More often than not, the primitive unit cell is less symmetric than the Bravais lattice.

The *unit cell* is a volume that fills up space with an integer multiplicity, if shifted by each of the lattice vectors. It contains an integer number of lattice points. Sometimes it is more convenient than the primitive unit cell (as shown in Figure 1.4).

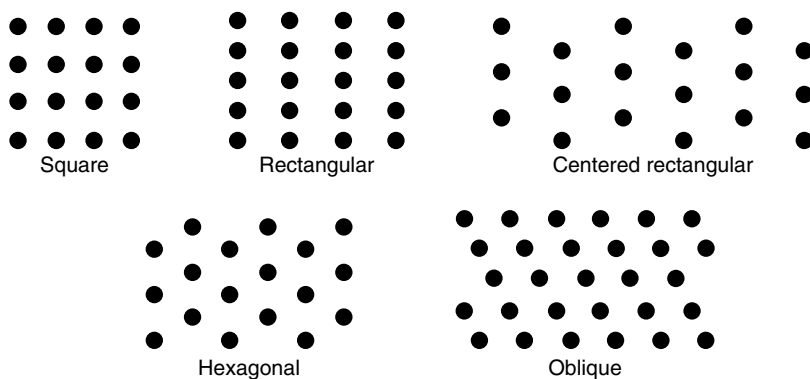


Figure 1.3 Two-dimensional Bravais lattices.

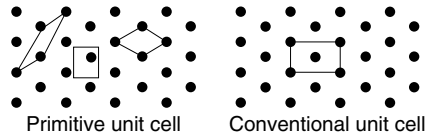


Figure 1.4 Some choices of primitive unit cells and the conventional unit cell for a centered rectangular lattice.

The *Wigner–Seitz cell* (WS cell) is a volume made up of space that is closer to a given lattice point than to any other point. There is a practical recipe for the construction of this cell: Select a lattice point, draw the lines connecting it to its neighbors (nearest and next-nearest is usually sufficient), and draw the perpendicular bisecting planes to these lines. The smallest volume enclosed within these planes is the WS cell. The WS cell is a primitive unit cell that preserves the symmetries of the Bravais lattice.

Imagine that a crystal is made of spheres with their diameters being equal to the nearest-neighbor distance. The *filling factor* is the volume fraction of the spheres relative to the total volume. The *coordination number* is the number of nearest neighbors to any sphere.

When waves are scattered from a periodic array, the constructive interference is often described by the *Bragg condition*: $n\lambda = 2d \sin \theta$, where λ is the wavelength, d is the spacing between subsequent lattice planes (that is, planes containing a high density of lattice points), and θ is the angle between the incident beam and the lattice planes. The scattered beam will have the same angle with respect to the planes as the incident beam, so the total scattering angle is 2θ .

Instead of wavelength, the concept of the *wave vector* is often used to characterize a plane wave. The wave vector \mathbf{k} points in the direction of the propagation of the wave, and the magnitude of the vector is $|\mathbf{k}| = 2\pi/\lambda$. The condition for constructive interference can be expressed in terms of wave vectors as $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{d} = 2\pi n$, where n is an integer, \mathbf{k} and \mathbf{k}' are the incident and scattered wave vectors, and \mathbf{d} is the vector pointing from one scattering center to another.

The *reciprocal lattice* is a very useful tool to handle the diffraction of waves; it is generally used to describe all things of “wavy nature” (like electrons and lattice vibrations). Definitions of the reciprocal lattice are as follows:

- The collection of all wave vectors that yield plane waves with a period of the Bravais lattice (*note*: any \mathbf{R} vector is a possible period of the Bravais lattice).
- A collection of vectors \mathbf{G} satisfying $\mathbf{G} \cdot \mathbf{R} = 2\pi n$ or $e^{i\mathbf{G} \cdot \mathbf{R}} = 1$.
- There is also a practical definition in three dimensions:

$$\mathbf{g}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V} \quad (1.1)$$

and cyclic permutations of 1, 2, 3, where $V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ is the volume of the unit cell.

The volume of the primitive unit cell in the reciprocal lattice is $(2\pi)^3/V$. The crystal system of the reciprocal lattice is the same as the direct lattice (for example, cubic remains cubic), but the Bravais lattice may be different (e.g. *fcc* becomes *bcc*). The *Brillouin zone* is the WS cell in the reciprocal lattice.

Using the reciprocal lattice, the condition for constructive interference becomes quite simple: If the difference between the incident (\mathbf{k}) and scattered (\mathbf{k}') wave vectors is equal to a reciprocal lattice vector, the diffracted intensity may be nonzero. This is the *Laue condition*. With $\mathbf{K} = \mathbf{k}' - \mathbf{k}$, this leads to the simple equation $\mathbf{K} = \mathbf{G}$ or $\mathbf{K} \cdot \mathbf{G} = 1/2|\mathbf{G}|^2$. The *Ewald construction* is a geometric representation of these equations.

The *Miller indices*, h , k , and l , are obtained from the “coordinates” of a reciprocal lattice vector $\mathbf{G} = h\mathbf{g}_1 + k\mathbf{g}_2 + l\mathbf{g}_3$. By definition, the Miller indices are integers. For a simple cubic lattice, these numbers are real coordinates in a Cartesian coordinate system.

There is an interesting relationship between Miller indices and lattice planes. For any plane there is an infinite number of other parallel lattice planes, separated by a distance d . It is easy to see that the ratio $x : y : z$ is the same for all parallel planes, where x , y , and z are the intercepts of a given plane with the coordinate axis defined by the primitive vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$.

Sometimes the need arises to classify these planes. There is a convenient mapping between a given class of lattice planes and a lattice vector in reciprocal space: For any family of lattice planes separated by a distance d , there is a reciprocal vector with length $|\mathbf{G}| = 2\pi/d$, and this vector is perpendicular to the lattice planes. One can show (nontrivially) that $h : k : l = (1/x) : (1/y) : (1/z)$.

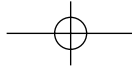
The Laue condition is based solely on the Bravais lattice, so the positions of the diffraction peaks are independent of the atomic basis. However, the intensities of the peaks are strongly influenced by the basis. The *structure factor*, $S(\mathbf{G})$, and the *form factor*, f_α , tell us how the intensities of the peaks depend on the atoms making up the crystals. These quantities are calculated as a sum (or integral) within the unit cell; therefore, they may be totally different for two different crystals, even if the crystals have the same Bravais lattice. In the simplest approximation, the scattering depends on the atomic charge distribution $\rho_\alpha(\mathbf{r})$, and the intensity is proportional to the absolute value squared of

$$S(\mathbf{G}) = \sum_{\alpha} f_{\alpha} e^{-i\mathbf{G} \cdot \mathbf{r}_{\alpha}} \quad (1.2)$$

and

$$f_{\alpha}(\mathbf{G}) = \frac{1}{e} \int \rho_{\alpha}(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} d^3\mathbf{r} \quad (1.3)$$

where e is the electron charge, the sum is over the atoms in the unit cell, and the integration is over the volume of an atom. Similar formulae work for electron and neutron scattering, except that the form factor integral is different depending on the microscopic interaction at play. Even for X rays, the calculation of the form factor as an integral over the charge density works only for the simplest cases. For



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a realistic calculation of scattered radiation intensities, one has to include factors representing the directional dependence of the scattering by a single point charge, the absorption of the radiation, and other effects. For powder samples this process is called *Rietveld analysis*. The expression becomes much more complicated, for example, if there is a match between the energy of atomic transitions and the X-ray quanta.

When the atomic positions are time dependent (for example, if lattice waves are excited in the crystal), the crystal scatters radiation at a frequency different from the incident frequency. In this case, energy is either absorbed or emitted by the crystal. The process can be described by the *dynamic structure factor*, which depends also on the frequency difference ω between the incident and scattered radiation: $S = S(\mathbf{k}, \omega)$. The general expression

$$S(\mathbf{k}, \omega) = \frac{1}{N} \int \frac{dt}{s\pi} e^{i\omega t} \langle \rho(\mathbf{k}, 0) \rho(-\mathbf{k}, t) \rangle \quad (1.4)$$

relates the structure factor to $\langle \rho(\mathbf{k}, 0) \rho(-\mathbf{k}, t) \rangle$, the density–density correlation function. (Here N is the number of primitive unit cells and $\rho(\mathbf{k}, t)$ is the charge density at time t .) This formula is equally useful when dynamics of the system are described by quantum mechanics (and the $\langle \rangle$ expectation value is that of the density operators) or at finite temperature [when the (classical) atoms have thermal motion]. For a static array of classical atoms, the quantity $\int d\omega S(\mathbf{G}, \omega) = S(\mathbf{G})$ is identical to the structure factor defined in Equation 1.2.

1.1

Problem: Symmetries

In Figure 1.5, two “crystals” (a and b) and a polygon (c) are shown. Identify the point group symmetry operations of the three objects (assume that the crystals are of infinite size). Show that the point groups of the two crystals are different, and that one of them has the equivalent point group as the polygon.

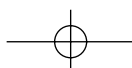
1.2

Problem: Rotations

A group is represented by three matrices:

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad A = \begin{bmatrix} \alpha & \beta \\ -\beta & \alpha \end{bmatrix} \quad B = \begin{bmatrix} \alpha & -\beta \\ \beta & \alpha \end{bmatrix} \quad (1.5)$$

where $\alpha = \sin 30^\circ$ and $\beta = \cos 30^\circ$. Determine the multiplication table for this group. What is an example of a (two-dimensional) crystal with these point group symmetries?



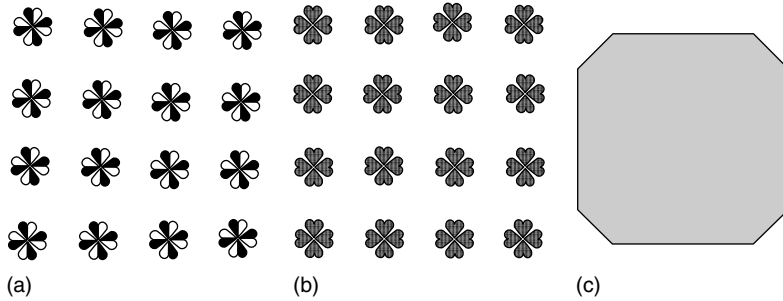


Figure 1.5 Two-dimensional objects with fourfold rotational symmetry.

1.3

Problem: Copper Oxide Layers

The common building blocks for most high temperature (high T_c) superconductors are copper oxide layers, as depicted in Figure 1.6(a). Assume the distance between copper atoms (filled circles) is a . For simplicity let us also assume that in the third dimension these CuO_2 layers are simply stacked with spacing c , and there are no other atoms in the crystal. In first approximation the layers have a fourfold symmetry; the crystal is tetragonal.

- (a) Sketch the Bravais lattice and indicate a possible set of primitive vectors for this crystal. What is the unit cell, and what is the basis?
- (b) In LaCuO_4 one discovers, at closer inspection, that the CuO_2 lattice is actually not flat, but that the oxygen atoms are moved a small amount out of the

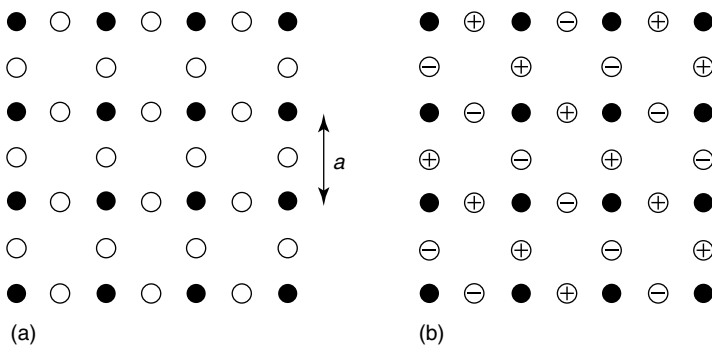


Figure 1.6 (a) CuO_2 lattice; (b) Distorted CuO_2 lattice.

plane (“up” or “down”) in an alternating fashion (in Figure 1.6(b), \oplus means up and \ominus means down).²⁾ What is the primitive cell and lattice spacing for this crystal? What is the reciprocal lattice? Describe (qualitatively) what happens in the X-ray diffraction pattern as the distortion is decreased gradually to zero.

1.4

Problem: Graphite

Graphene is a single layer of carbon atoms in a honeycomb lattice with a nearest-neighbor distance of 0.142 nm. How many atoms are in the primitive unit cell? Describe the unit vectors. How many atoms are in the primitive unit cell of graphite?

1.5

Problem: Structure of A_xC_{60}

Fleming and coworkers describe the structure of various alkaline metal- C_{60} compounds in Fleming *et al.* [5a]. Read the paper and answer the following questions:

- In Figure 2a of the paper, an *fcc* structure of A_3C_{60} is indicated. In the usual representation of the *fcc* structure, the C_{60} molecules would be placed on the corners, e.g. at positions $(1, 0, 0)$, $(0, 1, 0) \dots (1, 1, 1)$, and the face centers $(1/2, 1/2, 0)$, $(1/2, 1/2, 1) \dots (0, 1/2, 1/2)$ of a unit cube. The figure certainly does not look like a cube. What is a possible choice for the “conventional” (x, y, z) coordinates of the C_{60} molecule in the middle of Figure 2a from this paper?
- Assume you perform a powder X-ray diffraction measurement on an Rb-doped C_{60} material with $\lambda = 0.9 \text{ \AA}$ X-rays. You want to compare your results with Fleming’s to see what stoichiometry your compound is. What are the positions (2θ , in degrees) of the first five diffraction peaks for the three observed structures (doping = 3, 4, and 6 in Table 2 of the paper)?

1.6

Problem: *hcp* and *fcc* Structures

α -Co has an hexagonal close-packed (*hcp*) structure with lattice spacings of $a = 2.51 \text{ \AA}$ and $c = 4.07 \text{ \AA}$. (Descriptions of the *hcp* structure are given by Harrison [5, pp. 2–4], Ashcroft and Mermin [2, pp. 76–79], Ibach and Lüth [7, p. 23], and Kittel [1, pp. 23–24].) β -Co is *fcc*, with a cubic lattice spacing of 3.55 \AA . What is the difference in density between the two forms?

- $LaCuO_4$ is an antiferromagnetic insulator. High-temperature superconductivity was discovered in a closely related compound, $La_{1-x}Ba_xCuO_4$. See [6].

1.7

Problem: *hcp* and *bcc* Structures

Sodium transforms from *bcc* to *hcp* at about $T = 23$ K. Assuming that the density remains fixed, and the c/a ratio is ideal, calculate the *hcp* lattice spacing a given that the cubic lattice spacing $a' = 4.23$ Å in the cubic phase.

1.8

Problem: Structure Factor of A_xC_{60}

Experiments show that the $(2, 0, 0)$ X-ray diffraction peak of the *fcc* C_{60} solid (lattice spacing: $a = 14.11$ Å) is very weak. Assume that the charge distribution of a fullerene ball is represented by a surface charge on the surface of a sphere of radius 3.5 Å. Calculate the form factor of the C_{60} molecule in this approximation. Show that the form factor of the $(2, 0, 0)$ peak is indeed much less than that of the $(1, 1, 1)$ peak!

1.9

Problem: Neutron Diffraction Device

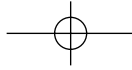
A collimated beam of neutrons of all energies is incident on a powder of cubic, monoatomic crystallites. What will happen to the neutron beam and what will the energies of the collimated neutrons exiting the powder be? How can this be used experimentally?

1.10

Problem: Linear Array of Emitters: Finite Size Effects

Consider a linear array of N identical radiation sources, placed at positions $x_n = na$. Each source emits radiation at frequency ω , wavenumber k , and amplitude A , and the sources are coherent with zero phase difference. We detect the radiation with intensity I_{detector} (defined as the time-averaged amplitude square) with a detector positioned along the line of the array, far away from the sources.

Assume $N \gg 1$, but finite. The $I(k)$ function will exhibit peaks of finite width. What are the main peak positions? What will the $I(k)$ function look like in the neighborhood of a main peak? What is the intensity of the detected radiation at the peak position? Estimate the width of this peak. How will the integrated intensity (integrated over k) depend on N ?



1.11

Problem: Linear Array of Emitters: Superlattice

Consider a linear array of N identical radiation sources, placed at positions $x_n = na$. Each source emits radiation at frequency ω , wavenumber k , and amplitude A and the sources are coherent with zero phase difference. We detect the radiation with intensity I_{detector} (defined as the time-averaged amplitude square) with a detector positioned along the line of the array, far away from the sources.

Introduce a static modulation to the position of the sources, described by $x_n = na + u_n$, where $u_n = u_0 \cos(qan)$ with $q < 2\pi/a$ and $u_0 \ll a$. In qualitative terms, what will we see in $I(k)$ as u_0 approaches zero? Discuss the peaks between $k = 2\pi/a$ and $k = 4\pi/a$ in greater detail: Calculate the first correction to the magnitude of the main peaks, and the magnitude of the strongest side peaks. (Note: Assume $N \rightarrow \infty$. The calculation of intensity becomes simplified if you concentrate on terms of order N^2 .)

1.12

Problem: Powder Diffraction of hcp and fcc Crystals

Cobalt has two forms: (see Problem 1.6): α -Co, with *hcp* structure (lattice spacing of $a = 2.51 \text{ \AA}$) and β -Co, with *fcc* structure (lattice spacing of $a_{\text{cubic}} = 3.55 \text{ \AA}$). Assume that the *hcp* structure has an ideal c/a ratio. Calculate and compare the position of the first five X-ray powder diffraction peaks. The quantity $K = 4\pi/\lambda \sin \theta$ can be used to characterize the peak positions (here λ is the wavelength of the X-ray radiation and 2θ is the scattering angle).

1.13

Problem: Momentum Resolution

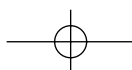
A neutron source provides a monochromatic beam neutrons, with wavelength of $\lambda = 2.502 \pm 0.002 \text{ \AA}$. The divergence of the beam is $\delta\phi = 40 \text{ arcsec}$. There is a collimator on the detector side, providing the same angular resolution. The sample has sc structure of approximate lattice spacing $a = 3.55 \text{ \AA}$.

Describe the experimental geometry for the most accurate measurement of the lattice spacing. What are the angles of the incident and diffracted beam relative to the crystal planes? Make a sketch of this geometry.

1.14

Problem: Finite Size Effects

Consider a finite size, sc crystal of $N_x \times N_y \times N_z$ atoms, with lattice spacing a .



- (a) For $k_x = k_y = 0$, plot the k_z -dependence of the intensity of the scattered X-rays (defined as $|\mathbf{E}|^2$, where \mathbf{E} is the amplitude of the scattered radiation) around the $(0,0,1)$ point in reciprocal space. Show that there is a peak at $(0,0,1)$ and that the peak width is finite. How is the width related to the size of the crystal (N_z)? How does the height of the peak depend on N_z ? How does the integrated intensity behave as a function of N_z ? Assume $N_z \gg 1$.
- (b) What happens to the line width and the peak height if we have a collection of small crystallites, which are all oriented parallel to each other, but their positions are random?

1.15**Problem: Random Displacement**

Consider an “imperfect” crystal, where the n th atom is displaced from its ideal position, \mathbf{R}_n , by a random vector \mathbf{S}_n . We will look at the diffraction peak at around the reciprocal lattice vector \mathbf{G} . Assume that the displacement at site n is $|\mathbf{S}_n| \ll a$, where a is the average lattice spacing. Show that the diffraction peak intensity will change little for small \mathbf{G} , but will disappear at larger \mathbf{G} . What is the shape of the envelope (peak height versus $G = |\mathbf{G}|$)?

1.16**Problem: Vacancies**

Vacancies are missing atoms in an otherwise near-perfect crystal. Since they create disorder and increase the entropy, vacancies are always present at nonzero temperatures. How will the X-ray diffraction of a crystal change due to a small amount of vacancies?

1.17**Problem: Integrated Scattering Intensity**

Assume that in a scattering experiment the amplitude of scattered radiation is

$$A = A_0 \sum_n e^{i\mathbf{K}\mathbf{R}_n} \quad (1.6)$$

where \mathbf{K} is the scattering wave vector and \mathbf{R}_n is the position of atom n . The intensity is given by $I = |A|^2$. Show that the integrated intensity,

$$I_{\text{tot}} = \frac{\int d^3\mathbf{K} I}{\int d^3\mathbf{K}} \quad (1.7)$$

is independent of the atomic positions!

