

University of Calcutta

Semester 5

PHYSICS

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CRYSTAL STRUCTURE

ASSIGNMENTS

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MILLER INDICES

1.6. CRYSTAL PLANES AND MILLER INDICES

The position and orientation of a crystal plane within the crystal may be determined by any three noncollinear points in the plane. If each of the points lies on a crystal axis, the position and the orientation of the plane may be obtained by specifying the locations of the points along the axes in terms of the lattice constants or the basis vectors. For example, if the atoms contained in the plane have coordinates $(4, 0, 0)$, $(0, 1, 0)$ and $(0, 0, 2)$ relative to the axis vectors from some origin, the location of the plane within

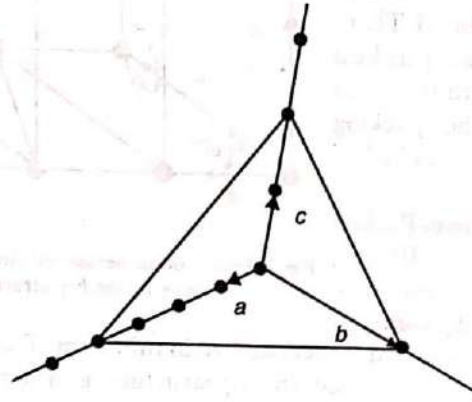


Fig. 1.5: Determination of Miller indices.

the crystal may be specified by the three numbers 4, 1, 2. However, for structure analysis it is more convenient to specify the orientation of a plane by *Miller indices*, defined as follows (Fig. 1.5).

- (i) Take any atom in the crystal and form coordinate axes with this atom as origin in the directions of the basis vectors.
- (ii) Determine the intercepts of the plane on the axes. Express these intercepts as multiples of the basis vectors along the axes.
- (iii) Find the reciprocals of these numbers and reduce them to the smallest three integers h, k, l having the same ratio. Then the Miller indices of the plane are given by (hkl) .

Consider the plane as shown in Fig. 1.5. The intercepts of the plane on the axes as multiples of the basis vectors a, b and c are 4, 1 and 2, respectively. The reciprocals of these intercepts are $\frac{1}{4}$, 1 and $\frac{1}{2}$. The Miller indices are obtained by reducing them to three smallest integers having the same ratio. This is done by multiplying each of the reciprocals by 4 resulting in 1, 4, 2. Therefore the Miller indices are (142) .

X-RAY DIFFRACTION

X-ray diffraction, a phenomenon in which the atoms of a **crystal**, by virtue of their uniform spacing, cause an interference pattern of the waves present in an incident beam of X rays. The atomic planes of the crystal act on the X rays in exactly the same manner as does a uniformly ruled grating on a beam of light. *See also* **Bragg law**; **Laue diffraction pattern**.

X-ray diffraction is a powerful nondestructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. XRD peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the atomic positions within the lattice planes. Consequently, the XRD pattern is the fingerprint of periodic atomic arrangements in a given material. An online search of a standard database for X-ray powder diffraction patterns enables quick phase identification for a large variety of crystalline samples [442].

2.2. REASONS FOR USING X-RAY

The choice of X-ray for producing diffraction effects in crystals arises from the following reasons :

(i) X-rays can be produced either by the deceleration of electrons in metal targets or by exciting the core electrons in the atoms of the target inelastically. The first method produces a broad continuous spectrum whereas sharp lines are obtained in the second method.

(ii) Longer-wavelength radiation (e.g., light) gives rise to the familiar effects of optical refraction and reflection and so cannot be used to explore the structure of crystals on an atomic scale.

(iii) Radiation of wavelength shorter than X-rays, on the other hand, is diffracted through inconveniently small angles.

(iv) The wavelength corresponding to each line of X-radiation can be determined with very high precision.

(v) The wavelength of X-rays is comparable to the interatomic distances in actual crystals.

The discovery of the X-ray diffraction effect for single crystal samples by von Laue in 1912 paved the way for determining the crystal structure by using X-ray diffraction as a technique. According to von Laue, the atoms of a single crystal specimen diffract an incident parallel monochromatic X-ray beam and produce a series of diffracted beams, the directions and intensities of which depend upon the lattice structure and the chemical composition of the crystal.

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BRAGG'S LAW

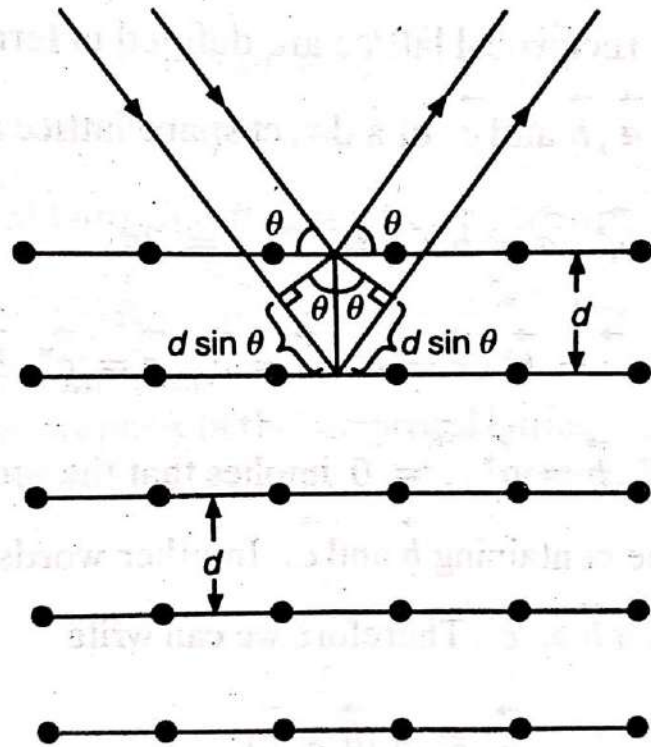


Fig. 2.1. Bragg reflection from a particular family of crystal planes.

W.L. Bragg for the first time formulated a relationship for the diffraction condition of X-rays incident on a crystalline material on the basis of a simple model. He assumed that the monochromatic X-rays are reflected from successive parallel planes of atoms in the crystal specularly, *i.e.* the angle of incidence equals the angle of reflection. The strong diffracted beams are obtained when the reflections from the parallel planes of atoms interfere constructively, as shown in Fig. 2.1. In his model, Bragg further assumed that the scattering is elastic so that the wavelength is not changed on reflection.

Figure 2.1 shows a particular family of crystal planes of ions, spaced at a distance d apart. Consider that a plane wavefront is incident at a glancing angle θ . The incident radiation is reflected specularly by the planes of the crystal. The path difference between the incident and the reflected rays from adjacent planes is $2d \sin \theta$. Constructive interference of the X-radiation from the successive planes will occur when this path difference is equal to an integral number of wavelength λ . That is,

$$2d \sin \theta = n\lambda, \quad \dots(2.3)$$

where n is an integer. This is *Bragg's law of diffraction*. Equation (2.3) states that X-ray diffraction in terms of inphase reflections from successive planes of atoms of a crystal will occur for a beam of monochromatic X-rays incident at an angle θ on a crystal having interplaner spacing d . For an incident angle other than θ the beam will not be diffracted. This means that the lattice planes do not act like ordinary mirrors. Also, Bragg reflec-

IMPORTANT POINTS

1. Bragg's reflection occurs only for wavelength less than equals to $2d$
2. Bragg's law is a consequence of the periodic nature of the space lattice, it does not refer to the orientation or basis of lattice atom.

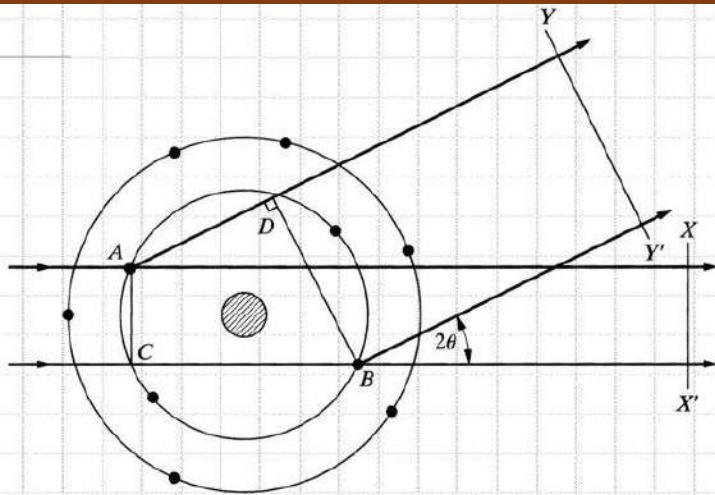
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CRYSTAL STRUCTURE ANALYSIS

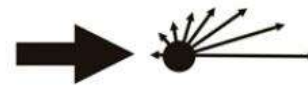
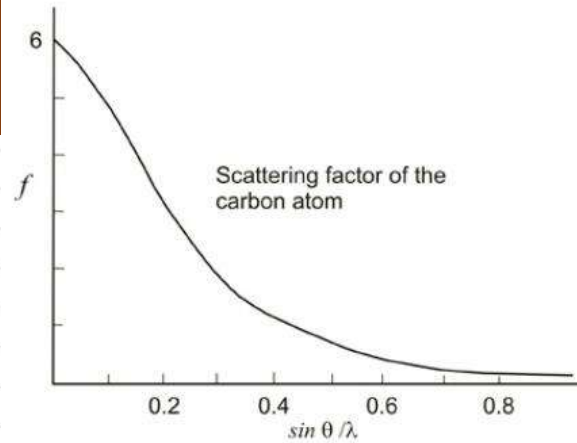
A crystal with its strictly periodic atomic structure represents a natural, very symmetrical three-dimensional diffraction grating for wavelengths of the order of the interatomic distances. Crystal structure analysis is thus based on the theories of symmetry (space groups) on the one hand and of interaction of radiation with solids (diffraction) on the other. The diffraction techniques, with the help of extensive computer calculations, lead to the atomic arrangements of crystalline materials. Depending on the problem. X-rays, electrons, or neutrons are used, which provide the electron-density, electrostatic potential density and nuclear density (also magnetic spin density) distribution, respectively, in a crystal.

ATOMIC FACTOR



Atomic Scattering Factor

$$f = \frac{\text{amplitude of the waves scattered by an atom}}{\text{amplitude of the waves scattered by one electron}}$$



The **atomic scattering factor** is independent of the position of the atom in the unit cell. It depends only on the type of atom and the direction of scattering, so that it reaches a maximum in the same direction of the incident X-rays, and decreases as a function of the angle of departure. The variation of the scattering factor of the carbon atom is shown in the left drawing. At the angular value corresponding to $(\sin \theta) / \lambda = 0$, the magnitude of the atomic scattering factor is always equal to the total number of electrons in the atom, but decreases strongly as the angular value increases.

ATOMIC STRUCTURE

The scattering power for X-rays is not the same for atoms of different sorts. Besides, since the size of the atoms is comparable to the X-ray wave-lengths, the angular distribution of scattered amplitude is not the same for the atom as for the point scatterer which was considered so far. The wavelets issuing from various parts of the electron cloud of the atoms arrive with phase differences in the direction of observation and this makes the total amplitude received a function of the angle of scattering and of the size and distribution of the electron density in the atom. This function differs from the simple amplitude which, according to a classical calculation by J. J. Thomson, a single electron would give if it were substituted for the atom; the ratio of the actual amplitude to this fictitious one is called the '*atomic factor*' f . Like all quantities that depend on phase differences caused by differences of optical path, f depends only on the order of diffraction, that is, on the vector \mathbf{h} if we have to do with a crystal, or on the continuously variable position vector in Fourier space, $\boldsymbol{\eta}$, if we consider a single atom instead of a periodic array of such. The definitions are

$$\boldsymbol{\eta} = \eta_1 \mathbf{b}_1 + \eta_2 \mathbf{b}_2 + \eta_3 \mathbf{b}_3$$

$$\boldsymbol{\eta}_h = \mathbf{h} = h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3. \quad (3)$$

GEOMETRICAL FACTOR

When we have monatomic crystals with an n - atom basis, the basis atoms act as a set of identical scattering points at positions $\mathbf{d}_1, \dots, \mathbf{d}_n$ in the primitive cell. The rays which are scattered from these basis atoms interfere with one another. The extent to which the rays interfere is related to the intensity of radiation at a given Bragg peak.

GEOMETRICAL FACTOR

Since the order of diffraction (h_1, h_2, h_3) indicates the differences of optical path for wavelets scattered by an atom and its neighbours along the directions of the axes \mathbf{a}_i , an atom in the cell which is removed only by fractions of \mathbf{a}_i sends out a wavelet whose path length is compounded of the corresponding fractions of h_1, h_2 , and h_3 , respectively. That is, for the atom of sort s in (1) the path difference, measured in wave-lengths, will be

$$h_1x_1^s + h_2x_2^s + h_3x_3^s = \varphi^s(\mathbf{h}) \quad (\text{as in } \varphi^s(h^s)). \quad (4)$$

For reasons which need not be explained here the path difference of φ wave-lengths against some standard wave is described mathematically by the exponential function \exp with an imaginary argument, namely by $\exp(-j\varphi)$, where $j = 2\pi\sqrt{-1}$. Using this symbolism we can now write down the factor by which the amplitude diffracted into an order \mathbf{h} ($= h_1, h_2, h_3$) will be modified through the superposition of the fields generated by each sort of atom separately. Owing to the definition of the atomic factors f^s , this factor F , which is called the '*structure amplitude*', compares the amplitude of the diffracted wave received from the crystal in any direction to that amplitude which would be obtained if the atoms were all replaced by single electron scatterers. The formal expression of F is

$$F(\mathbf{h}) = \sum_s f^s(\mathbf{h}) \exp(-j\varphi^s(\mathbf{h})), \quad (5)$$

the summation extended over all atoms in the cell (the base), be they chemically alike or not.

CRYSTAL STRUCTURE ANALYSIS

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<https://youtu.be/SlrGYHPOqDg>

WORK OUT PROBLEMS

5. Sodium chloride (NaCl) crystal has a cubic structure. If the molecular weight of NaCl is 58.46 and its density is 2.17 gm per cm^3 , find the distance between two adjacent atoms in the NaCl crystal.

(cf. Burd. U. 1995)

Ans. Mass of a NaCl molecule, $M = \frac{\text{Molecular weight in gm.}}{\text{Avogadro number}}$
 $= \frac{58.46}{6.02 \times 10^{23}} \text{ gm} = 9.7 \times 10^{-23} \text{ gm}.$

No. of NaCl molecules per unit volume = $\frac{\text{density}}{M}$
 $= \frac{2.17}{9.7 \times 10^{-23}} = 2.237 \times 10^{22} \text{ molecules per cm}^3.$

Since NaCl is diatomic, no. of atoms per unit volume will be $2 \times 2.237 \times 10^{22} = 4.47 \times 10^{22} \text{ atoms/cm}^3.$

If a be the distance between two adjacent atoms, the volume a^3 will contain one atom due to the cubic structure. Therefore the number of atoms per unit volume will be $1/a^3$.

Hence, $\frac{1}{a^3} = 4.47 \times 10^{22}$

or, $a^3 = 2.237 \times 10^{-23} \text{ cm}^3$

or, $a = 2.82 \text{ \AA}.$

6. Cs metal (atomic weight 130) has a cubic unit cell of side 6 Å. If the density of Cs is 2g/cm³, determine whether the unit cell is simple, face-centered, or body-centered.

Ans. Let x be the number of Cs atoms in cubic unit cell of side a . Then the number of atoms per unit volume is x/a^3 . If N is Avogadro's number and A is the atomic weight, then the mass of one atom is A/N gm. So, the density

is $\rho = \frac{x}{a^3} \cdot \frac{A}{N} \text{ g/cm}^3$, or $x = \frac{\rho a^3 N}{A} = \frac{2 \times 6^3 \times 10^{-24} \times 6.02 \times 10^{23}}{130} = 2$

So, the unit cell is body-centered.

WORK OUT PROBLEMS

1. The first order (100) reflection angle is 18° for a cubic crystal using X-rays of wavelength 1.54 \AA . Determine the distance between the (100) planes and the (111) planes of the crystal.

Ans. In this case, Bragg's law gives $2d \sin \theta = \lambda$, where d is the separation between the (100) planes. $d = \frac{\lambda}{2 \sin \theta} = \frac{1.54}{2 \sin 18^\circ} =$

$$\frac{1.54}{0.618} = 2.49 \text{ \AA}.$$

The separation (d) between the (100) planes gives the cube edge length of the unit cell, *i.e.* a . The distance between the (111) planes is

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{2.49}{\sqrt{3}} = 1.44 \text{ \AA}$$

2. The wavelength of the K_α line of Ag is 0.563 \AA . The radiation from the Ag target is analysed with a Bragg spectrometer using a calcite crystal (a simple cube of lattice constant 3.02945 \AA). Determine the angle of reflection for the first order. What is the highest order for which this line may be observed? (C.U. 1990)

Ans. For the first order ($n = 1$), Bragg's law gives $2d \sin \theta = \lambda$. Here $d = 3.02945 \text{ \AA}$ and $\lambda = 0.563 \text{ \AA}$.

Hence $\sin \theta = \lambda / (2d) = 0.563 / 6.0589 = 0.0929$. Therefore the angle of reflection is $\theta = \sin^{-1} 0.0929 = 5.33^\circ$.

For the n th order reflection, we have $2d \sin \theta = n \lambda$. As n increases θ increases. For the highest value of θ , *i.e.* 90° , we have $n = 2d / \lambda \approx 6.0589 / 0.563 = 10.8$. The highest value of n is the integer below 10.8, *i.e.*, 10.