

Figure 6.18 The reflection sphere in reciprocal space. The extension of the analysis in Figure 6.17 to a three-dimensional crystal is to draw a sphere with radius $1/n\lambda$. Each reciprocal lattice point that intersects the surface of the sphere (filled points) is a reflection in reciprocal space. The points included in the volume of the sphere of reflections (open points) represent points along the surface of smaller concentric spheres.

2.3 RECIPROCAL VECTORS AND THE RECIPROCAL LATTICE

In terms of the crystal axes $\mathbf{a}_1\mathbf{a}_2\mathbf{a}_3$, we define a set of reciprocal vectors $\mathbf{b}_1\mathbf{b}_2\mathbf{b}_3$:

$$\mathbf{b}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \quad \mathbf{b}_2 = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \quad \mathbf{b}_3 = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}. \quad (2.2)$$

$$\mathbf{a}_i \cdot \mathbf{b}_j = \begin{cases} 1, & i = j, \\ 0, & i \neq j. \end{cases}$$

$$\mathbf{H}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3.$$

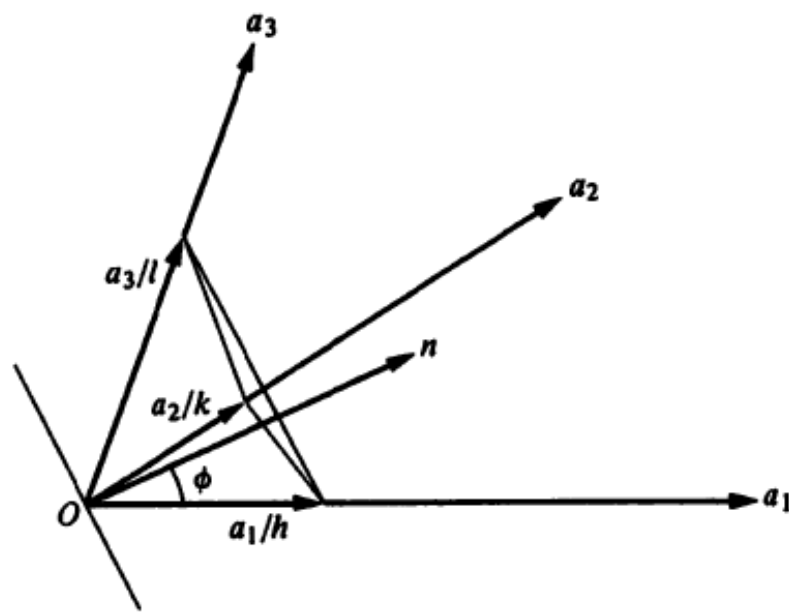


Fig. 2.2 Representation of the crystallographic planes hkl .

From Fig. 2.2 it is evident that $(a_1/h - a_2/k)$ and $(a_2/k - a_3/l)$ are vectors which are parallel to the hkl -planes. But from the relations expressed by Eq. (2.3),

$$\left(\frac{a_1}{h} - \frac{a_2}{k}\right) \cdot \mathbf{H}_{hkl} = \left(\frac{a_1}{h} - \frac{a_2}{k}\right) \cdot (hb_1 + kb_2 + lb_3) = 1 - 1 = 0,$$

$$\left(\frac{a_2}{k} - \frac{a_3}{l}\right) \cdot \mathbf{H}_{hkl} = \left(\frac{a_2}{k} - \frac{a_3}{l}\right) \cdot (hb_1 + kb_2 + lb_3) = 1 - 1 = 0.$$

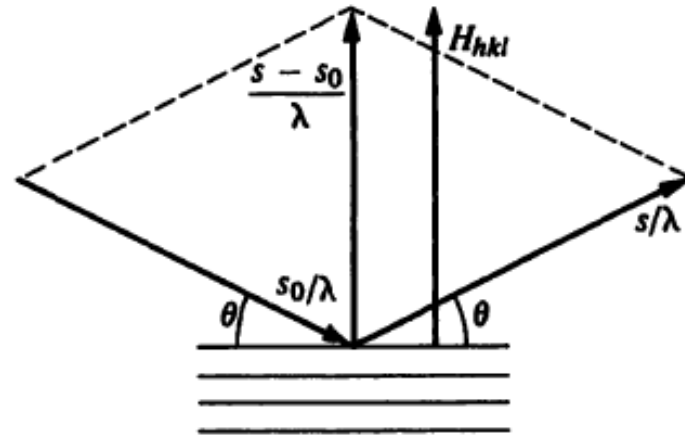


Fig. 2.3 Relations involved in the vector representation of the Bragg law.

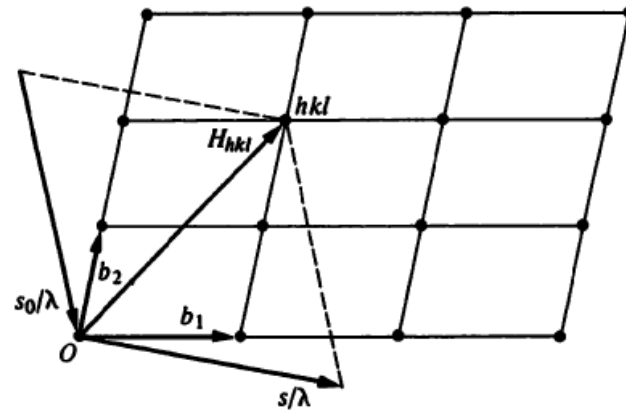


Fig. 2.4 Reciprocal lattice representation of the satisfying of the Bragg law for a set of planes hkl . The diffraction vector $(s - s_0)/\lambda$ must terminate on the point hkl of the reciprocal lattice.

In a crystal whose Bravais lattice is face-centered, for every atom with fractional coordinates $x_n y_n z_n$, there must be three identical atoms with coordinates $x_n + \frac{1}{2}, y_n + \frac{1}{2}, z_n$; $x_n + \frac{1}{2}, y_n, z_n + \frac{1}{2}$; and $x_n, y_n + \frac{1}{2}, z_n + \frac{1}{2}$. If the cell contains n atoms, there are $n/4$ groups of four, all four atoms in each group having the same scattering factor. The structure factor can be expressed as a sum over such groups of 4 atoms:

$$F_{hkl} = \sum_{n/4} f_n \left\{ e^{2\pi i(hx_n + ky_n + lz_n)} + e^{2\pi i(h[x_n + 1/2] + k[y_n + 1/2] + lz_n)} \right. \\ \left. + e^{2\pi i(h[x_n + 1/2] + ky_n + l[z_n + 1/2])} + e^{2\pi i(hx_n + k[y_n + 1/2] + l[z_n + 1/2])} \right\}.$$

This can be written in the simpler form

$$F_{hkl} = [1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}] \sum_{n/4} f_n e^{2\pi i(hx_n + ky_n + lz_n)}. \quad (3.11)$$

This can be written in the simpler form

$$F_{hkl} = [1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}] \sum_{n/4} f_n e^{2\pi i(hx_n + ky_n + lz_n)}. \quad (3.11)$$

If m is an integer, $e^{\pi im} = (-1)^m$, and hence the first factor takes the value 4 if hkl are unmixed (all odd or all even) and the value zero if hkl are mixed:

$$hkl \text{ unmixed: } F_{hkl} = 4 \sum_{n/4} f_n e^{2\pi i(hx_n + ky_n + lz_n)}, \quad (3.12)$$

$$hkl \text{ mixed: } F_{hkl} = 0.$$

Regardless of the atomic coordinates $x_n y_n z_n$, $F_{hkl} = 0$ for all reflections with mixed hkl . Hence the face-centered Bravais lattice is recognized by the fact that all reflections with mixed indices are missing.

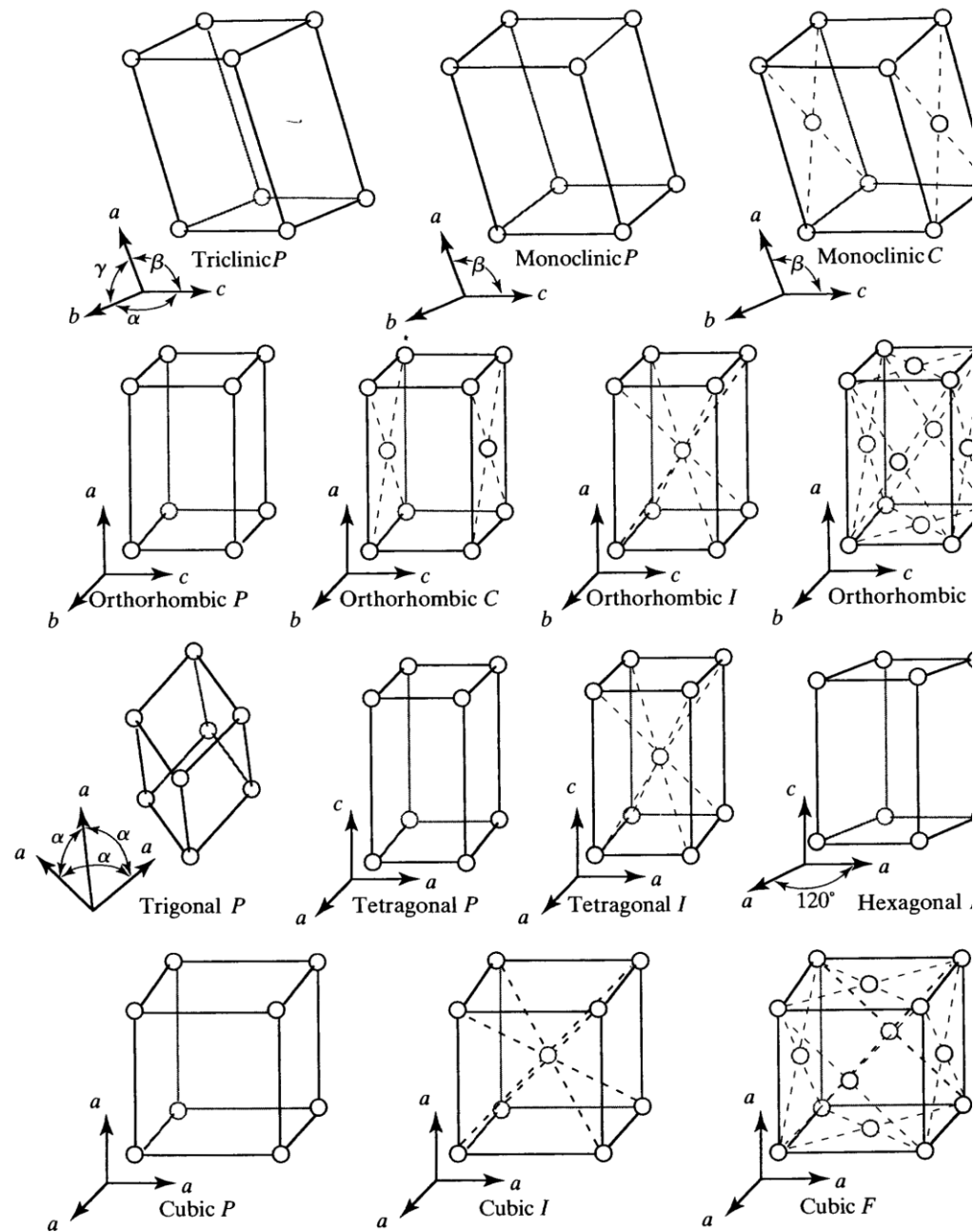


Figure 6.5 The 14 Bravais lattices in crystallography. [Adapted from G. H. Stout and L. H. Jensen (1989), *X-Ray Structure Determination, a Practical Guide*, 2d ed., John Wiley & Sons, New York, p. 50.]

Rhombohedral, $a = b = c$, $\alpha = \beta = \gamma$:

$$\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + lh)(\cos^2 \alpha - \cos \alpha)}{a^2(1 + 2 \cos^3 \alpha - 3 \cos^2 \alpha)}. \quad (2.9)$$

Hexagonal, $a = b$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}. \quad (2.10)$$

Monoclinic, $\alpha = \gamma = 90^\circ$:

$$\frac{1}{d_{hkl}^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right). \quad (2.11)$$

Orthorhombic, $\alpha = \beta = \gamma = 90^\circ$:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}. \quad (2.12)$$

Tetragonal, $a = b$, $\alpha = \beta = \gamma = 90^\circ$:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}. \quad (2.13)$$

Cubic, $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}. \quad (2.14)$$

TABLE 6.3 RELATIONSHIP BETWEEN UNIT CELL PARAMETERS IN REAL SPACE AND RECIPROCAL SPACE

Lattice type	Real Space	Reciprocal Space
Orthorhombic and higher symmetry	a	$a^* = \frac{1}{a}$
	b	$b^* = \frac{1}{b}$
	c	$c^* = \frac{1}{c}$
	$\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$	$\alpha^* = 90^\circ$ $\beta^* = 90^\circ$ $\gamma^* = 90^\circ$
	V	$V^* = \frac{1}{V} = a^*b^*c^*$
Monoclinic	a	$a^* = \frac{1}{a \sin \beta}$
	b	$b^* = \frac{1}{b}$
	c	$c^* = \frac{1}{c \sin \beta}$
	$\alpha = 90^\circ$ $\beta \neq 90^\circ$ $\gamma = 90^\circ$	$\alpha^* = 90^\circ$ $\beta^* = 180^\circ - \beta$ $\gamma^* = 90^\circ$
	V	$V^* = \frac{1}{V} = a^*b^*c^* \sin \beta^*$
Triclinic	a	$a^* = \frac{bc \sin \alpha}{V}$
	b	$b^* = \frac{ac \sin \beta}{V}$
	c	$c^* = \frac{ab \sin \gamma}{V}$
	$\alpha \neq 90^\circ$	$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma}$
	$\beta \neq 90^\circ$	$\cos \beta^* = \frac{\cos \alpha \cos \gamma - \cos \beta}{\sin \alpha \sin \gamma}$
	$\gamma \neq 90^\circ$	$\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta}$
	V	$V^* = a^*b^*c^* \sqrt{1 - \cos^2 \alpha^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \cos \beta^* \cos \gamma^*}$

[From G. H. Stout and L. H. Jensen (1989), *X-Ray Structure Determination, a Practical Guide*, 2d ed., John Wiley & Sons, New York, p. 37.]

$$I_p = I_e F^2 \frac{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot N_1 \mathbf{a}_1}{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_1} \frac{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot N_2 \mathbf{a}_2}{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_2} \times \frac{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot N_3 \mathbf{a}_3}{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_3}, \quad (3.6)$$

where

$$I_e = I_0 \frac{e^4}{m^2 c^4 R^2} \left(\frac{1 + \cos^2 2\theta}{2} \right)$$

$$I = I_e \sum_i f_i e^{(2\pi i/\lambda)(s-s_0)\cdot(R_i+\delta_i)} \sum_{i'} f_{i'}^* e^{-(2\pi i/\lambda)(s-s_0)\cdot(R_{i'}+\delta_{i'})}.$$

$$I = I_e F_T^2 \frac{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot N_1 \mathbf{a}_1}{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_1} \frac{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot N_2 \mathbf{a}_2}{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_2} \times \frac{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot N_3 \mathbf{a}_3}{\sin^2(\pi/\lambda)(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_3}, \quad (3.23)$$

where

$$F_T = \sum_n f_n e^{-M_n} e^{2\pi i(hx_n + ky_n + lz_n)}. \quad (3.24)$$

If the three Laue equations were exactly satisfied, Eq. (3.23) would predict a maximum intensity:

$$(I_p)_{\max} = I_e F_T^2 N_1^2 N_2^2 N_3^2.$$

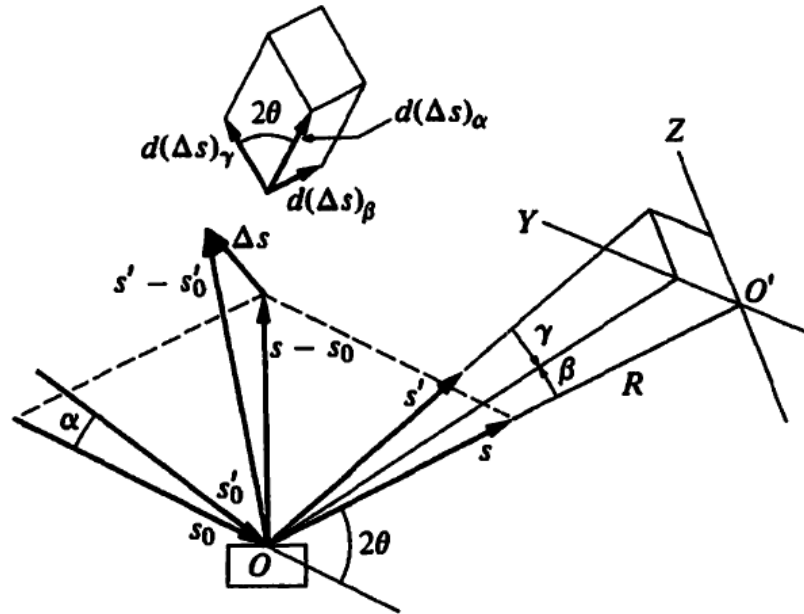


Fig. 4.1 The geometry involved in calculating the integrated intensity from a small single crystal which is rotated at constant angular velocity ω about an axis normal to the paper.

$$\mathbf{H}_{hkl} = hb_1 + kb_2 + lb_3.$$

$$\sin^2 \frac{\pi}{\lambda} \Delta \mathbf{S} \cdot N_1 \mathbf{a}_1 = \sin^2 \pi (p_1 \mathbf{b}_1 + p_2 \mathbf{b}_2 + p_3 \mathbf{b}_3) \cdot N_1 \mathbf{a}_1 = \sin^2 \pi N_1 p_1.$$

The total diffracted energy given by Eq. (4.1) can now be expressed by

$$E = I_e \frac{R^2}{\omega} F_T^2 \iiint \frac{\sin^2 \pi N_1 p_1}{\sin^2 \pi p_1} \frac{\sin^2 \pi N_2 p_2}{\sin^2 \pi p_2} \frac{\sin^2 \pi N_3 p_3}{\sin^2 \pi p_3} d\alpha d\beta d\gamma. \quad (4.4)$$

$$E = I_e \frac{R^2 F_T^2}{\omega \sin 2\theta} \iiint \frac{\sin^2 \pi N_1 p_1}{\sin^2 \pi p_1} \frac{\sin^2 \pi N_2 p_2}{\sin^2 \pi p_2} \frac{\sin^2 \pi N_3 p_3}{\sin^2 \pi p_3} dV. \quad (4.5)$$

$$E = I_e \frac{R^2 \lambda^3 F_T^2}{\omega v_a \sin 2\theta} \int_{-\infty}^{+\infty} \frac{\sin^2 \pi N_1 p_1}{(\pi p_1)^2} dp_1 \int_{-\infty}^{+\infty} \frac{\sin^2 \pi N_2 p_2}{(\pi p_2)^2} dp_2 \times \int_{-\infty}^{+\infty} \frac{\sin^2 \pi N_3 p_3}{(\pi p_3)^2} dp_3.$$

$$|d(\Delta\mathbf{S})_\alpha| = d\alpha, \quad |d(\Delta\mathbf{S})_\beta| = d\beta, \quad |d(\Delta\mathbf{S})_\gamma| = d\gamma$$

are shown by Fig. 4.1. As a result of these three changes, the terminal point of the vector $\Delta\mathbf{S}$ traces out a volume element in reciprocal space:

$$dV = d(\Delta\mathbf{S})_\beta \cdot d(\Delta\mathbf{S})_\gamma \times d(\Delta\mathbf{S})_\alpha = \sin 2\theta \, d\alpha \, d\beta \, d\gamma.$$

$$E = I_e \frac{R^2 F_T^2}{\omega \sin 2\theta} \iiint \frac{\sin^2 \pi N_1 p_1}{\sin^2 \pi p_1} \frac{\sin^2 \pi N_2 p_2}{\sin^2 \pi p_2} \frac{\sin^2 \pi N_3 p_3}{\sin^2 \pi p_3} dV. \quad (4.5)$$

$$E = I_e \frac{R^2 \lambda^3 F_T^2}{\omega v_\alpha \sin 2\theta} \int_{-\infty}^{+\infty} \frac{\sin^2 \pi N_1 p_1}{(\pi p_1)^2} dp_1 \int_{-\infty}^{+\infty} \frac{\sin^2 \pi N_2 p_2}{(\pi p_2)^2} dp_2 \times \int_{-\infty}^{+\infty} \frac{\sin^2 \pi N_3 p_3}{(\pi p_3)^2} dp_3.$$

$$E = \frac{I_0}{\omega} \left(\frac{e^4}{m^2 c^4} \right) \frac{\lambda^3 \delta V F_T^2}{v_a^2} \left(\frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \right). \quad (4.6)$$

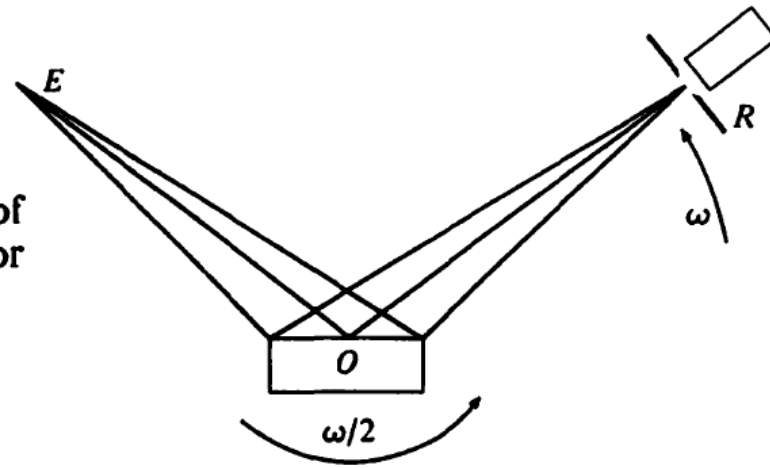
The factor $(1 + \cos^2 2\theta)/2 \sin 2\theta$ is the Lorentz-polarization factor for a single crystal in an unpolarized primary beam. Notice that the total diffracted energy E depends only upon the volume δV of the crystal. The restriction which we made when we assumed the crystal to have the shape of a parallelepipedon was a real restriction as long as we talked about intensity. As soon as we change to the experimentally observable quantity "total energy" or "integrated intensity," the restriction vanishes. A small single crystal, which

THE POWDER METHOD

The ideal powder sample consists of an enormous number of very tiny crystals of size 10^{-3} cm or smaller with completely random orientation.

The $\text{CuK}\alpha_1\alpha_2$ doublet ($\lambda = 1.542$ Å) with a Ni filter ($\lambda_K = 1.488$ Å) is probably used more than any other source. A wavelength of radiation which is just shorter than an absorption edge wavelength in the sample is always to be avoided, since these conditions lead to a high absorption coefficient and strong fluorescence radiation. For example, $\text{CuK}\alpha$ ($\lambda = 1.542$ Å) would never be used with a sample of iron ($\lambda_K = 1.743$ Å).

Fig. 5.5 Schematic representation of the counter diffractometer as used for recording powder patterns.



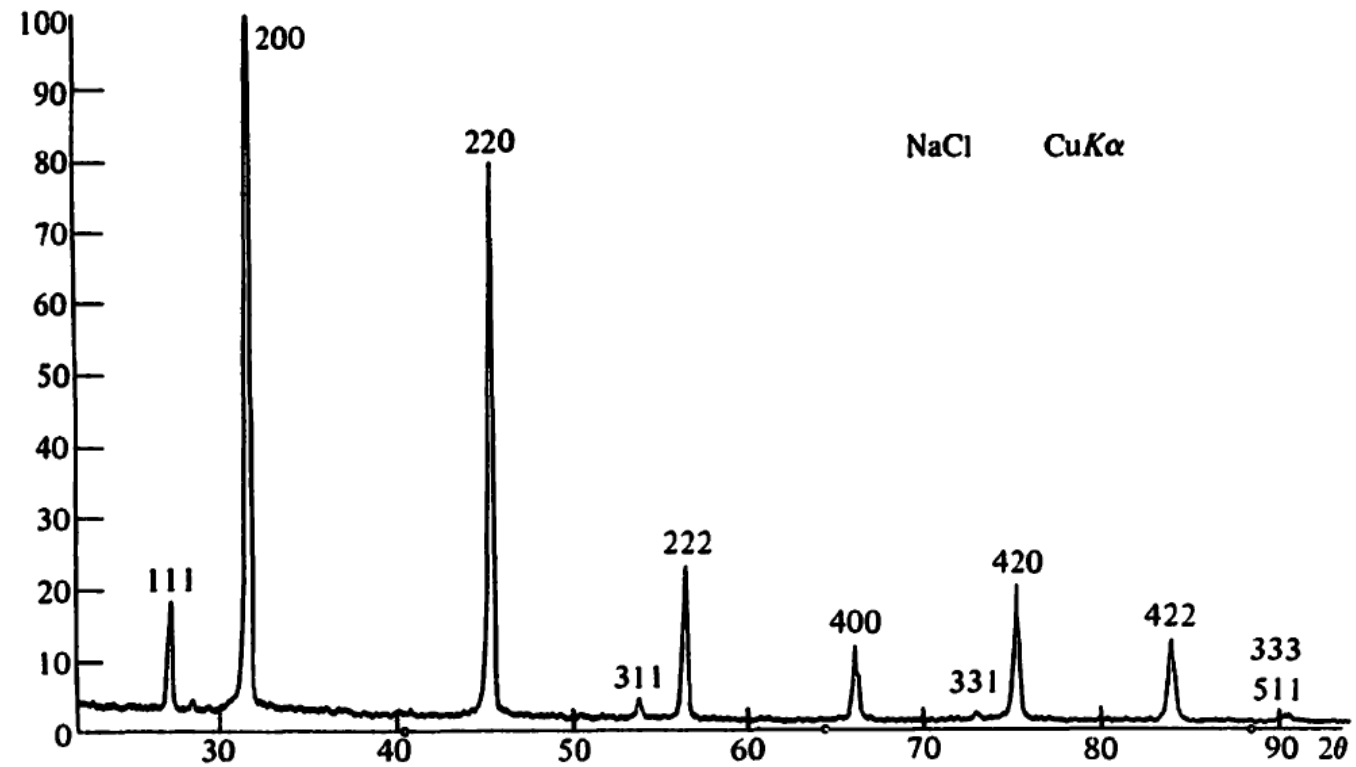


Fig. 5.6 Diffractometer recording of the powder pattern of NaCl using Ni filtered CuK α radiation.

The 2θ -values for the different reflections are read directly from the chart recording and tabulated in column 1. The corresponding values of $1/d^2 = 4 \sin^2 \theta / \lambda^2$ are computed and recorded in column 2. Rock salt is a cubic crystal, but even when the crystal system is unknown, we would start out by trying to index the pattern in terms of a cubic lattice. If it is not cubic, this will quickly turn out to be impossible, and we would then fall back on the various schemes for handling systems of lower symmetry.

From Eq. (2.14) for a cubic crystal,

$$\frac{4 \sin^2 \theta}{\lambda^2} = \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}; \quad (5.7)$$

For a face-centered cubic lattice, we have seen that for every atom with coordinates xyz there must be three identical atoms at coordinates $x + \frac{1}{2}, y + \frac{1}{2}, z$; $x + \frac{1}{2}, y, z + \frac{1}{2}$; and $x, y + \frac{1}{2}, z + \frac{1}{2}$. Hence if we choose as origin the position of one of the Cl, the coordinates of the four Cl atoms will be $0\ 0\ 0, \frac{1}{2}\ \frac{1}{2}\ 0, \frac{1}{2}\ 0\ \frac{1}{2}, 0\ \frac{1}{2}\ \frac{1}{2}$. If we place one of the Na at xyz , the positions of the other three Na are fixed at $x + \frac{1}{2}, y + \frac{1}{2}, z$; $x + \frac{1}{2}, y, z + \frac{1}{2}$; and $x, y + \frac{1}{2}, z + \frac{1}{2}$. But there are only 3 unoccupied sets of xyz -values which will allow cubic symmetry in a crystal with the 4 Cl already placed. These three possible sets of Na positions are $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$; $\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$; and $\frac{3}{4}\ \frac{3}{4}\ \frac{3}{4}$. Since the third can be obtained from the second by rotating the crystal 90° , we need consider only the first two sets.

We next consider the evaluation of the structure factor for two common structures having the face-centered cubic Bravais lattice. In rock salt, the cubic cell contains 4 Na and 4 Cl at the following positions:

$$\begin{array}{ccc}
 & 0 & 0 & 0 & & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\
 \text{Cl} & \frac{1}{2} & \frac{1}{2} & 0 & \text{Na} & 0 & 0 & \frac{1}{2} \\
 & \frac{1}{2} & 0 & \frac{1}{2} & & 0 & \frac{1}{2} & 0 \\
 & 0 & \frac{1}{2} & \frac{1}{2} & & \frac{1}{2} & 0 & 0
 \end{array}$$

To evaluate the structure factor using Eq. (3.12), we can choose any one of the positions in each group of 4 atoms. Using 0 0 0 for Cl and $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ for Na, the structure factor is given by

$$\begin{array}{ll}
 hkl \text{ mixed:} & F_{hkl} = 0 \\
 hkl \text{ unmixed:} & F_{hkl} = 4[f_{\text{Cl}} + f_{\text{Na}}e^{\pi i(h+k+l)}].
 \end{array}$$

For rock salt, the structure factor takes the three forms:

$$\begin{array}{ll}
 hkl \text{ all even:} & F_{hkl} = 4(f_{\text{Cl}} + f_{\text{Na}}), \\
 hkl \text{ all odd:} & F_{hkl} = 4(f_{\text{Cl}} - f_{\text{Na}}), \\
 hkl \text{ mixed:} & F_{hkl} = 0.
 \end{array} \tag{3.14}$$

Table 5.1
POWDER DIFFRACTOMETER PATTERN OF NaCl ($\lambda = 1.542 \text{ \AA}$)

1	2	3	4	5	6	7	8	9	10	11	12	13	14
2θ	$\frac{4 \sin^2\theta}{\lambda^2}$	$h^2 + k^2 + l^2$	hkl	$a(\text{\AA})$	$\frac{\sin \theta}{\lambda}$	f_{Cl}	f_{Na}	F^2	m	(LP)	$\frac{F^2 m(\text{LP})}{1000}$	A , arb. unit	Col. 12 corrected
27.3	0.0940	3	111	5.65	0.154	13.50	8.90	338	8	33.5	91	116	102
31.7	0.1255	4	200	5.65	0.177	12.70	8.70	7330	6	24.0	1057	1260	1160
45.5	0.2516	8	220	5.64	0.251	10.50	7.65	5280	12	10.9	690	694	697
53.9	0.3455	11	311	5.64	0.294	9.60	7.00	107	24	7.4	19	23	18
56.5	0.3768	12	222	5.64	0.307	9.35	6.75	4150	8	6.6	219	200	201
66.3	0.503	16	400	5.64	0.354	8.65	6.10	3490	6	4.7	98	92	82
73.2	0.598	19	331	5.64	0.386	8.30	5.65	112	24	3.8	10	13	8
75.4	0.629	20	420	5.64	0.396	8.20	5.50	3010	24	3.60	260	198	195
84.1	0.755	24	422	5.64	0.434	7.85	5.05	2660	24	3.05	195	136	136
90.6	0.849	27	{511 333}	5.64	0.461	7.60	4.75	130	{24 8}	2.80	12	10	8

$$2M = 2B \frac{\sin^2 \theta}{\lambda^2}$$

$$\ln \left(\frac{1000 A}{F^2 m \text{LP}} \right) = \ln K - 2B \frac{\sin^2 \theta}{\lambda^2}.$$

A theoretical expression for the Debye factor $2M = 2B \sin^2 \theta / \lambda^2$ is developed in Chapter 11. For a cubic element

$$2B = \frac{12h^2 T}{mk\Theta^2} \left\{ \Phi(x) + \frac{x}{4} \right\}, \quad (5.9)$$

A theoretical expression for the Debye factor $2M = 2B \sin^2 \theta / \lambda^2$ is developed in Chapter 11. For a cubic element

$$2B = \frac{12h^2T}{mk\Theta^2} \left\{ \Phi(x) + \frac{x}{4} \right\}, \quad (5.9)$$

where h is Planck's constant, T is the absolute temperature, m is the mass of the atom, k is the Boltzmann constant, Θ is the Debye characteristic temperature of the substance, $x = \Theta/T$, and $\{\Phi(x) + x/4\}$ is a tabulated function which is approximately unity for $T > \Theta$. Approximating NaCl as an element with average atom mass, $m = (23.0 + 35.5)/(2 \times 0.602 \times 10^{24})$ and using $h = 6.62 \times 10^{-27}$, $T = 300^\circ\text{K}$, $k = 1.38 \times 10^{-16}$, $\Theta = 281^\circ\text{K}$, and $\{\Phi(x) + x/4\} = 1.02$, we obtain $2B = 3.02 \text{ \AA}^2$. The value $2B = 2.94 \text{ \AA}^2$ which we obtained from the logarithmic plot is in satisfactory agreement.

$$F_{hkl} = [1 + e^{\pi i(h+k+l)}] \sum_{n/2} f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

To evaluate the structure factor using Eq. (3.12), we can choose any one of the positions in each group of 4 atoms. Using 0 0 0 for Cl and $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ for Na, the structure factor is given by

$$hkl \text{ mixed: } F_{hkl} = 0$$

$$hkl \text{ unmixed: } F_{hkl} = 4[f_{\text{Cl}} + f_{\text{Na}}e^{\pi i(h+k+l)}].$$

For rock salt, the structure factor takes the three forms:

$$hkl \text{ all even: } F_{hkl} = 4(f_{\text{Cl}} + f_{\text{Na}}),$$

$$hkl \text{ all odd: } F_{hkl} = 4(f_{\text{Cl}} - f_{\text{Na}}),$$

$$hkl \text{ mixed: } F_{hkl} = 0.$$

(3.14)

For a more accurate treatment it is necessary to allow for different values of $M(\text{Cl})$ and $M(\text{Na})$:

$$\frac{A(\text{meas})}{m(\text{LP})} = K^2 \{ f_{\text{Cl}} e^{-M(\text{Cl})} \pm f_{\text{Na}} e^{-M(\text{Na})} \}^2.$$

With the abbreviation $Q^2 = A(\text{meas})/m(\text{LP})$, we have two cases:

$$hkl \text{ all even: } Q(\text{even}) = K[f_{\text{Cl}} e^{-M(\text{Cl})} + f_{\text{Na}} e^{-M(\text{Na})}],$$

$$hkl \text{ all odd } Q(\text{odd}) = K[f_{\text{Cl}} e^{-M(\text{Cl})} - f_{\text{Na}} e^{-M(\text{Na})}].$$

Table 5.2
INTERPRETATION OF NaCl PATTERN IN TERMS OF
ZINC BLENDE STRUCTURE

<i>hkl</i>	<i>f_{Cl}</i>	<i>f_{Na}</i>	<i>F</i> ²	<i>m</i>	(LP)	$\frac{F^2 m(\text{LP})}{1000}$	<i>A</i> arb. units
111	13.50	8.90	4180	8	33.5	1120	116
200	12.70	8.70	256	6	24.0	37	1260
220	10.50	7.65	5270	12	10.9	690	694

By plotting the measured values of Q against $\sin \theta/\lambda$, we can treat $Q(\text{even})$ and $Q(\text{odd})$ as continuous functions of $\sin \theta/\lambda$. From the sums and differences, we obtain

$$\begin{aligned} \ln \left[\frac{Q(\text{even}) + Q(\text{odd})}{2f(\text{Cl})} \right] &= \ln K - B(\text{Cl}) \left(\frac{\sin \theta}{\lambda} \right)^2, \\ \ln \left[\frac{Q(\text{even}) - Q(\text{odd})}{2f(\text{Na})} \right] &= \ln K - B(\text{Na}) \left(\frac{\sin \theta}{\lambda} \right)^2. \end{aligned} \tag{5.10}$$

Table 5.2
INTERPRETATION OF NaCl PATTERN IN TERMS OF
ZINC BLENDE STRUCTURE

<i>hkl</i>	f_{Cl}	f_{Na}	F^2	m	(LP)	$\frac{F^2 m(\text{LP})}{1000}$	A arb. units
111	13.50	8.90	4180	8	33.5	1120	116
200	12.70	8.70	256	6	24.0	37	1260
220	10.50	7.65	5270	12	10.9	690	694

By plotting the measured values of Q against $\sin \theta/\lambda$, we can treat $Q(\text{even})$ and $Q(\text{odd})$ as continuous functions of $\sin \theta/\lambda$. From the sums and differences, we obtain

$$\ln \left[\frac{Q(\text{even}) + Q(\text{odd})}{2f(\text{Cl})} \right] = \ln K - B(\text{Cl}) \left(\frac{\sin \theta}{\lambda} \right)^2,$$

$$\ln \left[\frac{Q(\text{even}) - Q(\text{odd})}{2f(\text{Na})} \right] = \ln K - B(\text{Na}) \left(\frac{\sin \theta}{\lambda} \right)^2. \quad (5.10)$$

From plots of the left-hand side of Eq. (5.10) against $(\sin \theta/\lambda)^2$, the slopes give directly the values of $B(\text{Cl})$ and $B(\text{Na})$.

5.5 ANALYSIS OF ORTHORHOMBIC POWDER PATTERNS

Following the cubic, tetragonal, and hexagonal systems, the next in order of increasing difficulty is the orthorhombic system. For orthorhombic crystals there are three axes, a , b , c , and graphical methods are not practical. A numerical method described by Lipson⁴ can, however, be used. We start with the spacing formula:

$$\frac{1}{d^2(hkl)} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}.$$

For all pairs of reflections with the same h and k but different l ,

$$\frac{1}{d^2(hkl_1)} - \frac{1}{d^2(hkl_2)} = (l_1^2 - l_2^2)(1/c^2) = (1, 3, 4, 5, 8, \dots)(1/c^2).$$

Similarly for pairs of reflections with the same k and l but different h there will be differences $(h_1^2 - h_2^2)(1/a^2)$, and for pairs of reflections with the same l and h but different k there will be differences $(k_1^2 - k_2^2)(1/b^2)$.

We now tabulate the differences of all pairs of experimental $1/d^2$ values and plot the frequency of occurrence. Differences which occur several times are likely to include the numbers $(1, 3, 4, 5, 8, \dots)(1/a^2)$ or $(1, 3, 4, 5, 8, \dots)(1/b^2)$ or $(1, 3, 4, 5, 8, \dots)(1/c^2)$. With a little trial and error consideration, it is often possible to obtain the axes from these occurrences. Since spurious multiple occurrences are to be expected, it is very important to have extremely accurate $(1/d^2)$ -values. The method works best for simple orthorhombic lattices; for centered lattices, the number of coincidences is reduced.