UNIVERSITY of EXETER

Direct Lattice	**Simple Cubic**		**Body-Centred Cubic**	**Face-Centred Cubic**
Reciprocal Lattice (cube lattice parameter)	Simple Cubic ($2\pi/a$)		Face-Centred Cubic ($4\pi/a$)	Body-Centred Cubic ($4\pi/a$)
Planes, spacing	(100)	a	No	No
	(110)	$a/\sqrt{2}$	Yes	No
	(111)	$a/\sqrt{3}$	No	Yes
	(200)	a/2	Yes	Yes
	(210)	$a/\sqrt{5}$	No	No
	(211)	$a/\sqrt{6}$	Yes	No
	(220)	$a/\sqrt{8}$	Yes	Yes
	(221)	a/3	No	No
	(300)	a/3	No	No
	(310)	$a/\sqrt{10}$	Yes	No
	(311)	$a/\sqrt{11}$	No	Yes
	(222)	$a/\sqrt{12}$	Yes	Yes
	(320)	$a/\sqrt{13}$	No	No
	(321)	$a/\sqrt{14}$	Yes	No
	(400)	$a/\sqrt{16}$	Yes	Yes
Rule:	All h, k, l		Sum (h + k + l) even	h, k, l all odd or all even
Ratio of sines of Bragg angles	$1:\sqrt{2}:\sqrt{3}:2:\sqrt{5}:\sqrt{6}:\sqrt{8}$:...		$1:\sqrt{2}:\sqrt{3}:2:\sqrt{5}:\sqrt{6}:\sqrt{7}:\sqrt{8}$:...	$1:2/\sqrt{3}:\sqrt{8}/\sqrt{3}$:...

APPENDIX 6

QUADRATIC FORMS OF MILLER INDICES

Cubic					Hexagonal	
	hkl					
$h^2 + k^2 + l^2$	Simple	Face-centered	Body-centered	Diamond	$h^2 + hk + k^2$	*hk*
1	100				1	10
2	110	. . .	110		2	
3	111	111	. . .	111	3	11
4	200	200	200		4	20
5	210				5	
6	211	. . .	211		6	
7					7	21
8	220	220	220	220	8	
9	300, 221				9	30
10	310	. . .	310		10	
11	311	311	. . .	311	11	
12	222	222	222		12	22
13	320				13	31
14	321	. . .	321		14	
15					15	
16	400	400	400	400	16	40
17	410, 322				17	
18	411, 330	. . .	411, 330		18	
19	331	331	. . .	331	19	32
20	420	420	420		20	
21	421				21	41
22	332	. . .	332		22	
23					23	
24	422	422	422	422	24	
25	500, 430				25	50
26	510, 431	. . .	510, 431		26	
27	511, 333	511, 333	. . .	511, 333	27	33
28					28	42
29	520, 432				29	
30	521	. . .	521		30	
31					31	51
32	440	440	440	440	32	
33	522, 441				33	
34	530, 433	. . .	530, 433		34	
35	531	531	. . .	531	35	
36	600, 442	600, 442	600, 442		36	60
37	610				37	43
38	611, 532	. . .	611, 532		38	
39					39	52
40	620	620	620	620	40	
41	621, 540, 443				41	
42	541	. . .	541		42	
43	533	533	. . .	533	43	61
44	622	622	622		44	
45	630, 542				45	
46	631	. . .	631		46	
47					47	
48	444	444	444	444	48	44
49	700, 632				49	70, 53

(*cont.*)

10-3 Indexing patterns of cubic crystals. A cubic crystal gives diffraction lines whose $\sin^2\theta$ values satisfy the following equation, obtained by combining the Bragg law with the plane-spacing equation for the cubic system:

$$\frac{\sin^2\theta}{(h^2+k^2+l^2)} = \frac{\sin^2\theta}{s} = \frac{\lambda^2}{4a^2}. \tag{10-2}$$

Since the sum $s = (h^2 + k^2 + l^2)$ is always integral and $\lambda^2/4a^2$ is a constant for any one pattern, the problem of indexing the pattern of a cubic substance is one of finding a set of integers s which will yield a constant quotient when divided one by one into the observed $\sin^2\theta$ values. (Certain integers, such as 7, 15, 23, 28, 31, etc., are impossible because they cannot be formed by the sum of three squared integers.) Once the proper integers s are found, the indices hkl of each line can be written down by inspection or from the tabulation in Appendix 6.

The proper integers s can be determined by means of the C and D scales of an ordinary slide rule, which permit simultaneous division of one set of numbers by another, if the quotient is constant. Pencil marks corresponding to the $\sin^2\theta$ values of the first five or six lines on the pattern are placed on the D scale. A single setting of the C scale is then sought which will bring a set of integers on the C scale into coincidence with all the pencil marks on the D scale. Because of the systematic errors mentioned earlier, these coincidences are never exact, but they are usually close enough to permit selection of the proper integer, particularly if the C scale is shifted slightly from line to line to compensate for the systematic errors in $\sin^2\theta$. If a set of integers satisfying Eq. (10-2) cannot be found, then the substance involved does not belong to the cubic system, and other possibilities (tetragonal, hexagonal, etc.) must be explored.

The following example will illustrate the steps involved in indexing the pattern of a cubic substance and finding its lattice parameter. In this particular example, Cu $K\alpha$ radiation was used and eight diffraction lines were observed. Their $\sin^2\theta$ values are listed in the second column of Table 10-1. By means of a slide rule, the integers s listed in the third column were found to produce the reasonably constant quotients listed in the fourth column, when divided into the observed $\sin^2\theta$ values. The fifth column lists the lattice parameter calculated from each line position, and the sixth column gives the Miller indices of each line. The systematic error in $\sin^2\theta$ shows up as a gradual decrease in the value of $\lambda^2/4a^2$, and a gradual increase in the value of a, as θ increases. We shall find in Chap. 11 that the systematic error decreases as θ increases; therefore we can select the value of a for the highest-angle line, namely, 3.62A, as being the most accurate of those listed. Our analysis of line positions therefore leads to

TABLE 10–1

1	2	3	4	5	6
Line	$\sin^2\theta$	$s = (h^2 + k^2 + l^2)$	$\frac{\lambda^2}{4a^2}$	a(A)	hkl
1	0.140	3	0.0466	3.57	111
2	0.185	4	0.0463	3.58	200
3	0.369	8	0.0462	3.59	220
4	0.503	11	0.0457	3.61	311
5	0.548	12	0.0456	3.61	222
6	0.726	16	0.0454	3.62	400
7	0.861	19	0.0453	3.62	331
8	0.905	20	0.0453	3.62	420

the conclusion that the substance involved, copper in this case, is cubic in structure with a lattice parameter of 3.62A.

We can also determine the Bravais lattice of the specimen by observing which lines are present and which absent. Examination of the sixth column of Table 10–1 shows that all lines which have mixed odd and even indices, such as 100, 110, etc., are absent from the pattern. Reference to the rules relating Bravais lattices to observed and absent reflections, given in Table 4–1, shows that the Bravais lattice of this specimen is face-centered. We now have certain information about the arrangement of atoms within the unit cell, and it should be noted that we have had to make use of observed line intensities in order to obtain this information. In this particular case, the observation consisted simply in noting which lines had zero intensity.

Each of the four common cubic lattice types is recognizable by a characteristic sequence of diffraction lines, and these in turn may be described by their sequential s values:

Simple cubic: 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16, ...
Body-centered cubic: 2, 4, 6, 8, 10, 12, 14, 16, ...
Face-centered cubic: 3, 4, 8, 11, 12, 16, ...
Diamond cubic: 3, 8, 11, 16, ...

The same information is tabulated in Appendix 6 and shown graphically in Fig. 10–2, in the form of calculated diffraction patterns. The calculations are made for Cu $K\alpha$ radiation and a lattice parameter a of 3.50A. The positions of all the diffraction lines which would be formed under these conditions are indicated as they would appear on a film or chart of the length shown. (For comparative purposes, the pattern of a hexagonal close-packed structure is also illustrated, since this structure is frequently

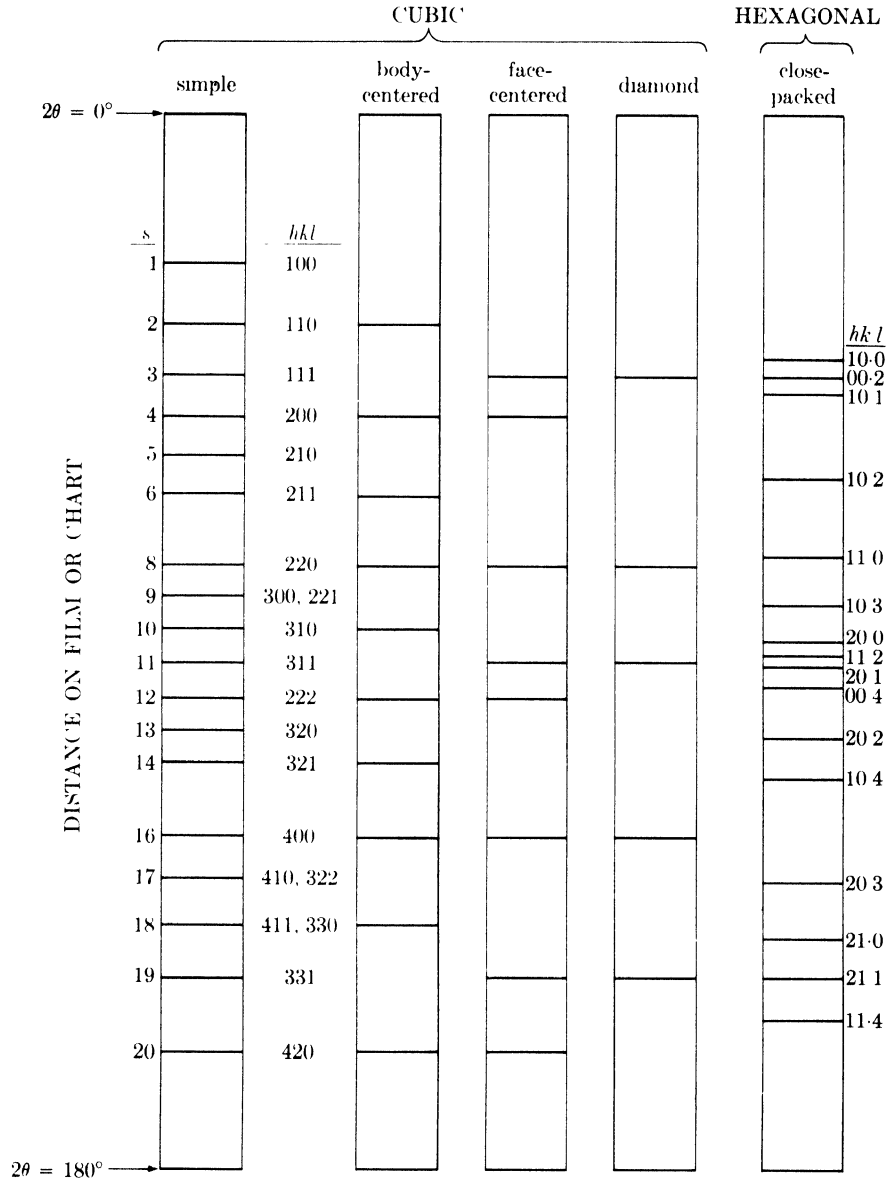

FIG. 10-2. Calculated diffraction patterns for various lattices. $s = h^2 + k^2 + l^2$.

encountered among metals and alloys. The line positions are calculated for Cu $K\alpha$ radiation, $a = 2.50$A, and $c/a = 1.633$, which corresponds to the close packing of spheres.)

Powder patterns of cubic substances can usually be distinguished at a glance from those of noncubic substances, since the latter patterns nor-

mally contain many more lines. In addition, the Bravais lattice can usually be identified by inspection: there is an almost regular sequence of lines in simple cubic and body-centered cubic patterns, but the former contains almost twice as many lines, while a face-centered cubic pattern is characterized by a pair of lines, followed by a single line, followed by a pair, another single line, etc.

The problem of indexing a cubic pattern is of course very much simplified if the substance involved is *known* to be cubic and if the lattice parameter is also known. The simplest procedure then is to calculate the value of $(\lambda^2/4a^2)$ and divide this value into the observed $\sin^2\theta$ values to obtain the value of s for each line.

There is one difficulty that may arise in the interpretation of cubic powder patterns, and that is due to a possible ambiguity between simple cubic and body-centered cubic patterns. There is a regular sequence of lines in both patterns up to the sixth line; the sequence then continues regularly in body-centered cubic patterns, but is interrupted in simple cubic patterns since $s = 7$ is impossible. Therefore, if λ is so large, or a so small, that six lines or less appear on the pattern, the two Bravais lattices are indistinguishable. For example, suppose that the substance involved is actually body-centered cubic but the investigator mistakenly indexes it as simple cubic, assigning the value $s = 1$ to the first line, $s = 2$ to the second line, etc. He thus obtains a value of $\lambda^2/4a^2$ twice as large as the true one, and a value of a which is $1/\sqrt{2}$ times the true one. This sort of difficulty can be avoided simply by choosing a wavelength short enough to produce at least seven lines on the pattern.

10–4 Indexing patterns of noncubic crystals (graphical methods). The problem of indexing powder patterns becomes more difficult as the number of unknown parameters increases. There is only one unknown parameter for cubic crystals, the cell edge a, but noncubic crystals have two or more, and special graphical and analytical techniques have had to be devised in order to index the patterns of such crystals.

The **tetragonal** system will be considered first. The plane-spacing equation for this system involves two unknown parameters, a and c:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}. \tag{10–3}$$

This may be rewritten in the form

$$\frac{1}{d^2} = \frac{1}{a^2}\left[(h^2 + k^2) + \frac{l^2}{(c/a)^2}\right],$$