INTERNATIONAL TABLES

FOR

X-RAY CRYSTALLOGRAPHY

Volume I

SYMMETRY GROUPS

Edited by

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CONTENTS

1. HISTORICAL INTRODUCTION

by M. von LAUE

THE science which the *International Tables* are intended to serve is concerned primarily with the atomic theory of crystals, and secondarily with optical theory as applied to the short wavelengths of X-radiation. Moreover, now that we know of electron and neutron diffraction by crystals, it must include quantum mechanical wave theory, which is also, as it happens, of importance in the branch of optics already mentioned. This introduction has to deal, therefore, with the history of these three branches of physics. Let us begin with the most important and the oldest branch, the theory of crystals.

We may take as a beginning the small pamphlet written in the year 1611 by the great astronomer Johannes Kepler, which bears the title *Strena seu de nive sexangula*, or in translation "A New Year's present; on hexagonal snow." It is dedicated to one of his patrons at the court of the Emperor Rudolph II, whose friendship Kepler enjoyed during his stay in Prague. Kepler's astronomical works show that throughout his life he believed that the material world was the creation of a Spirit delighting in harmony and mathematical order. Had he not tried in his youth to deduce the radii of the planetary orbits from the dimensions of certain regular polyhedra, and did not his principal work (1619) bear the title *Harmonice Mundi*? It need not surprise us, therefore, that it was the appearance of these regular and beautifully shaped snowflakes rather than the appearance of the crystals of the mineral world that inspired Kepler with the idea that this regularity might be due to the regular geometrical arrangement of minute and equal brick-like units. Thus he was led to think of close-packed spheres, and, although he did not coin the expression "space-lattice" and although his development of these ideas is not always correct, we can find among his illustrations the first pictures of space-lattices.

Nevertheless Kepler felt uneasy about these speculations. He realised, quite correctly, that his way would lead to an atomic theory; yet the idea of the atom, as handed down from the ancient Greeks, lacked an empirical foundation and therefore has often been the subject of excessively fanciful speculation even until well into the nineteenth century. Hence it was not without reason that the natural scientist in Kepler mistrusted this idea and would not take it seriously. He toyed with the double meaning of the word "nix," which in Latin means snow but in German dialect "nichts" —nothing. And so from beginning to end he repeatedly explained the whole idea away as a mere "nothing."

In these circumstances the little pamphlet, even though it was printed, naturally made no deep impression on his contemporaries, and was gradually forgotten. Crystallography took another direction, that of the description of the external form of crystals, after Niels Stensen had in 1669 pointed out the existence of characteristic angles between crystal faces. By devious ways this led eventually to the Millerian indexing of faces (1839), to the laws of symmetry and to the classification of crystals in 32 classes, which was accomplished in 1830 by Johann Friedrich Christian Hessel and in 1867, independently and rather more simply, by Alex Gadolin.

This consistently phenomenological approach was not abandoned, even though the crystal-optical discoveries made early in the nineteenth century by such men as Baptiste Biot, David Brewster, Augustin Fresnel and Frederick William Herschel had led to the development of the important idea that the same laws of symmetry which were valid for the positions of crystal faces also controlled the physical events inside the crystal. This was first made clear by Franz Neumann in 1833.

Apart from these trends of thought, however, ideas about the internal structure of crystals continued to appear. Thus Christiaan Huygens' fundamental work on the wave theory of optics, *Traité de la lumière*, which was published in 1690, contains among other things a wave-theoretical explanation of birefringence, and ascribes to calcite a structure made up of ellipsoidal particles; the threefold periodicity of this arrangement characterises it as a space-lattice, although Huygens, like Kepler, did not define it as such. It was the cleavage along three planes which led him to this idea. Like Kepler's pamphlet, however, this part of the otherwise famous work was soon forgotten. Independently of Huygens, crystal cleavage in general led Torbern Bergman in 1773 and René Just Haüy in 1782 to suppose that all crystals consist of a kind of masonry of equal, parallelepipedal building bricks. That these "molécules soustractives"

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were often supposed to consist of "molécules intégrantes" of other shapes need not concern us here. A structure of this kind involves a space lattice, and Haüy could therefore easily go on from this idea to deduce the laws governing the geometry of crystal faces, already empirically known. But it would be premature to describe this as an atomic theory of crystals. No wonder! For the scientific theory of atoms had yet to be created, in its own good time, by the great chemists of the eighteenth century. The theorem that a lattice may be divided into unit cells, as we should say today, in an infinite number of different ways would have made no physical sense whatever to Haüy (although he would have admitted, of course, its geometrical correctness), since the shape of the "molécules soustractives" was fixed unambiguously by Nature.

Thus the true beginning of the atomic theory of crystals must be dated from a paper published in the year 1824 by Ludwig August Seeber, physicist in Freiburg, in Gilbert's *Annalen der Physik*, vol. 16, page 229. Seeber, who certainly knew of Haüy's works but probably did not know the part we have quoted from Huygens', was trying to find an explanation of the thermal expansion and the elasticity of solids, of which he quite rightly believed crystals to be the normal type. He found the bricklike structure unsuitable for his purpose, since, he argued, the only view compatible with this picture would be that the single bricks themselves possess these physical properties, which does not solve the problem but only pushes it one step farther back. Seeber, whose outlook was essentially modern, introduced instead the idea of a structure consisting of chemical atoms or molecules (at the time these two concepts were not strictly differentiated), whose mutual distances are determined by the balance of attractive and repulsive forces, thus forming a system of stable equilibrium. External disturbances cause certain changes of position—this is his explanation of elasticity—and possibly also elastic vibrations about the equilibrium positions. Seeber, of course, did not visualise thermal vibration: he explained thermal expansion in terms of the temperature dependence of the attractive and repulsive forces. In order to retain the sound parts of Haüy's postulate, Seeber placed each of his molecules, assumed by him to be spherical, at the midpoint of the cell which would have formed one of Haüy's "molécules soustractives"; he thus arrived at a "parallelepipedal arrangement of the indivisible parts of matter," as he describes it at the end of his paper. In our language such an arrangement implies a primitive translation lattice, and it is not far from this concept to the idea that each unit cell of the space lattice is occupied by several atoms.

This was the earliest application of the scientific atomic theory to a purely physical problem. The kinetic theory of gases, which is usually regarded as the beginning of atomic theory in physics, did not appear until thirty-two years later. Seeber was therefore far ahead of his time, and it was no wonder that his contemporary physicists failed to respond to his ideas, which were forgotten until Sohncke revived them in 1879. But at least one mathematical problem had been raised—the number of geometrically possible space lattices that correspond to the 32 crystal classes and to their symmetry operations. Moritz Ludwig Frankenheim and Auguste Bravais took up this problem, and in 1850 Bravais described the 14 pure translation lattices which have been named after him. Incidentally, his papers also contain the concept of the reciprocal lattice, which was later rediscovered and used in connection with the study of interference effects from crystals. This purely group-theoretical investigation was extended by Leonhard Sohncke in 1879 through the introduction of further symmetry operations, thus arriving at 65 different "space groups." The complete solution of the problem, taking into account *all* possible symmetry operations on a lattice, was given simultaneously in the year 1890 by Evgraph Stepanovitsch Fedorov and by Artur Schoenflies. They derived the 230 space groups which are used in modern structural research.

Investigations pursued by English scientists of the following decade were less systematic and far more hypothetical, but their ideas possessed the advantage that they could be visualised more easily. Inspired by the success of stereochemistry, they devised three-dimensional models of atomic structures based on lattices. Lord Kelvin published a paper on this subject in 1894. Reasoning along these lines was most fully expressed in a series of long papers by W. Barlow in the last decade of the nineteenth century. Barlow took up the idea of close packing, and distinguished for the first time correctly between the cubic and hexagonal forms of packing. He also considered the question of packing of spheres of two or three different sizes and described, for example, the sodium chloride structure, although neither in this nor in any other case did he in these early papers name a substance which might be expected to have one of the proposed structures. This was undoubtedly one of the reasons why the whole of his structure

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theory at first attracted little attention. Moreover, the very reality of atoms was doubted again and again right up to the end of the nineteenth century. Even in the absence of such doubts, and even when collaboration with Pope had given the chemical application of Barlow's theory, there was still no way of bringing the hypothetical structures into relation with experiment. In order to establish structure theory on a firm basis, yet another set of ideas, those of physical optics, had to be brought in.

The diffraction of visible light by gratings, which mostly consisted of lines scratched on glass or metal, had already been described by Grimaldi in the seventeenth century, and again by Joseph Fraunhofer at the beginning of the nineteenth. The relevant theory can be found in the comprehensive treatise by Friedrich Magnus Schwerd: *Die Beugungserscheinungen, aus den Fundamentalgesetzen der Undulationstheorie analytisch entwickelt* (1835). The grating was and still is the most important instrument in spectroscopy. Later physicists engaged in work on optics have often returned to Schwerd's theory. In particular, Lord Rayleigh frequently emphasised that the essential characteristic of a grating is the periodic repetition of its elements and not the nature of those elements. Round about 1910 M. von Laue, in writing an article on wave theory for the *Encyklopädie der mathematischen Wissenschaften*, set himself the task of elaborating, as clearly as possible, this idea of Rayleigh's, and arrived at an equation for the position of the diffraction maxima which could be extended without difficulty to the case of double periodicity as it exists in cross-gratings; in the latter case two such equations had to be formulated.

In the meantime the science of optics had been extended far beyond the limits of the visible spectrum. The farthest extension on the short-wave side had come about in 1895 through Röntgen's discovery of X-rays; soon afterwards (1896) Emil Wiechert and George Gabriel Stokes concluded from the way in which X-rays are produced that they must be short waves consisting of electromagnetic pulses. This was confirmed by the observation of their polarisation, made by C. G. Barkla in 1906. Wilhelm Wien in 1907 estimated their wavelength to be 7×10^{-9} cm. on the basis of their observed photoelectric effect, while A. Sommerfeld in 1912 calculated a value of 4×10^{-9} cm. from their diffraction by a slit. On the other hand, they showed such strong quantum effects that some very eminent physicists held firmly to the corpuscular theory of X-rays.

Both these questions and that of the fine structure of crystals were decided by the researches of W. Friedrich and P. Knipping, which were published in the summer of 1912 in the *Sitzungsberichte der Bayerischen Akademie*. Von Laue's diffraction theory, which had provided the inspiration for these experiments and which had indeed been confirmed by their results, simply consisted of the diffraction conditions for a cross-grating, with the addition of a third condition to take account of the three-dimensional periodicity of a space lattice. Admittedly von Laue had expected, in accordance with the Stokes–Wiechert pulse theory, that many more interference spots would appear on the photographs than were actually observed, and he could only explain their absence by ascribing to the atoms of the crystal a strongly selective scattering power for X-rays: this idea, though it later proved to be mistaken, was not altogether unreasonable in view of the characteristic X-ray emission of the elements which had been found by Barkla. Towards the end of 1913, at the second Solvay Congress, von Laue used the rediscovered reciprocal-lattice theory to extend to the general case of any crystal the geometrical construction for the interference maxima from cubic crystals that had been given by P. P. Ewald. He thus provided the foundation for a simple "geometrical" theory of X-ray diffraction.

Meanwhile the experiments of Friedrich and Knipping, and von Laue's interpretation of them, had become known in England, and had inspired much discussion and further investigation, particularly by W. H. and W. L. Bragg. The story of what happened is here continued by Sir Lawrence Bragg:

"In the summer of 1912 my father showed me von Laue's paper, which had aroused his intense interest because of his work on the exciting of cathode rays by X-rays, which pointed to the projectile-like properties of X-rays, and he discussed with me possible alternative explanations for the effects which von Laue had found. I undertook some experiments at Leeds that summer to see whether we could explain von Laue's spots by the shooting of particles down avenues in the crystal lattice rather than by the diffraction of waves, experiments which were of course abortive.

"On returning to Cambridge in the autumn of 1912 I studied von Laue's photographs very intensively, and was very naturally forced to the conclusion that they must be due to diffraction. I also concluded at the same time that one must modify the explanation of them which von Laue had given.

Von Laue had remarked that one did not get all the spots one would expect from a simple cubic lattice, but only a selection of the whole range. He ascribed this to the existence in the X-radiation of five characteristic wavelengths chosen so that they approximately satisfied the diffraction conditions for the spots which actually appeared in the photographs. I, on the other hand, concluded that von Laue's spots were due to the diffraction of 'white' X-radiation, representing a continuous band of wavelengths over a certain range. I was led to this first by noting the changing shape of the Laue spots when the distance from the photographic plate to the crystal was altered. This in turn led me to consider the diffraction effect as a reflection of X-ray pulses by the lattice planes of the crystal. I pointed out that this was equivalent to the selection from the continuous spectrum of a wavelength determined by the lattice spacing of the crystal. I tested this by reflecting the X-rays from a mica plate set at a series of angles, getting in every case a spot in the reflected position and so showing, as I believed, that all wavelengths were represented over a certain range in the X-rays. The problem then remained to explain why only certain spots appeared in the Laue photographs, and I ascribed this to the fact that the essential underlying lattice of the crystal was face-centred and not simple cubic. I communicated these results to the Cambridge Philosophical Society in November 1912. The 'Bragg equation' appeared in this paper (p. 46) in the form $\lambda = 2d \cos \theta$, but in later papers θ was defined as the glancing angle and not the angle of incidence.

"Professor Pope at Cambridge was very interested in these results, because the close-packed lattices which he and Barlow had devised for atoms which they believed to be of equal size were face-centred cubic. He procured crystals of potassium chloride and sodium chloride for me, and I took their Laue photographs. I showed that these could be explained by an arrangement of alternate scattering centres in two interleaved face-centred lattices, the NaCl structure in fact, and that these centres must be equal in scattering power in KCl but different in scattering power in NaCl.

"This work was done at Cambridge before I collaborated with my father. We worked along divergent lines at first, which came together later. My father was very interested in my explanation of the diffraction effect as a reflection, and he set up at Leeds the first X-ray spectrometer. He was primarily interested in the nature of X-rays. He checked that the reflected rays were really X-rays,

a point on which he wished to satisfy himself because of his speculations about the corpuscular nature of X-rays. He found as I did that there appeared to be a continuous spectrum, but his spectrum also showed some peaks superimposed upon this continuous range, and by improving the apparatus he soon narrowed these down so much that it was clear that they were monochromatic components characteristic of the target. Incidentally I think it is not often realised how much work he did on characteristic X-rays before Moseley made his brilliant generalisations. My father constructed tubes with about a dozen different anti-cathodes and identified Barkla's K and L radiation, showing that the K contained two peaks and the L three peaks. He related the wavelengths to the atomic weights of the metals in each anti-cathode (the idea of atomic number had not yet come to the fore) by a simple law. In fact he gave the first hint of Moseley's relations, and it was his work which inspired Moseley to his broader generalisations.

"My father then examined with his spectrometer crystals of KCl and NaCl such as I had used for my Laue photographs, and found the reflections of the characteristic peaks from the (100), (111) and (110) faces. It was clear at once that the spectrometer was a far more powerful way of investigating crystal structure than the Laue photographs, which I had used. It was only at this stage that we joined forces. In particular, I had been trying to analyse the diamond structure by Laue methods without success, but my father mounted it on the spectrometer and the structure became immediately obvious. We wrote a paper on the diamond structure together, but the results which gave the clue to it were obtained by him. I was able, however, to work along with him with the spectrometer in the summer of 1913, and so to work out the structures of zincblende, fluorspar, pyrites and some of the carbonates, which showed how powerful the spectrometer could be. My father was at first principally interested in X-ray spectra and X-ray absorption edges, but crystal structures also fascinated him, and from that point on we both mainly devoted ourselves to crystal structure analysis."

These experiments, together with those of Friedrich and Knipping, not only confirmed von Laue's diffraction theory but gave a direct proof of the existence of the space-lattice, and provided a simple expression (the Bragg law) for the relationship between the wavelength of the X-rays used and the lattice spacings of the crystal. The ionisation

curves obtained by means of the Bragg spectrometer showed clearly that the "mirror-image reflection" postulated by Bragg is selective and is conditioned by multiple interference. The Bragg equation was first published in its usual form in a paper by W. H. and W. L. Bragg in the *Proceedings of the Royal Society*, vol. 88, page 428 (1913). Soon afterwards von Laue [*Physikalische Zeitschrift*, **14,** 421 (1913)] was able to show that this equation was only another way of expressing the results of the geometrical space-lattice theory.

Ionisation spectrometer measurements also revealed another reason for the absence of many of the interference spots at first expected by von Laue. The pulse theory of X-rays predicted much too wide an extension of their spectrum in the short-wave direction. In fact, as W. Duane and F. L. Hunt established in 1915, this spectrum ends abruptly at the short-wavelength limit given by the now well-known quantum rule.

Still further credit is due, however, to W. H. and W. L. Bragg. X-ray diffraction patterns had made it possible to compare the wavelengths of X-rays with the three lattice constants, whose axial ratios were already known. Absolute measurements, however, remained impossible without a knowledge of the absolute value of the lattice constant of at least one substance. It was necessary for this purpose to know the number of atoms in the unit cell, and this was impossible without a knowledge of the structure. The Braggs' measurements, however, had shown that sodium chloride really did possess one of the hypothetical structures postulated by Barlow. Thus it was possible to obtain the absolute value of the lattice constant of this salt; this in turn provided an absolute measure of the wavelengths of X-rays, and hence the absolute lattice constants of all other crystals investigated. Rarely has the value of hypothesis in research been so strikingly demonstrated.

This brings us to the end of the historical introduction as far as X-rays are concerned, since all that has followed is merged into present-day practice. Yet the space lattice has had another most important part to play in physics.

In 1924 L. de Broglie put forward in his *Thèses* the basic idea of wave mechanics. In the summer of 1925 Walter Elsasser, in a letter to the editor of *Naturwissenschaften*, pointed out that the de Broglie waves of electrons must cause space-lattice interference effects, and that experiments by Davisson and Kunzman on the reflection of electrons from a platinum sheet had actually shown maxima of the expected kind. When in 1926 E. Schrödinger published his communications on *Quantisierung als Eigenwertproblem*, C. J. Davisson and L. H. Germer began systematically to look for these effects. In March 1927 they were able to publish a note in *Nature* to say that their efforts, made on a single crystal of nickel, had been crowned with success. In May of the same year G. P. Thomson and A. Reid announced that an electron beam of several thousand volts had, on passing through a celluloid film, produced Debye–Scherrer rings, and G. P. Thomson found the same effect even more clearly with metal foils. Thus Elsasser's prediction was confirmed and the plainest of all proofs had been given of the connection of a wave with the movement of a corpuscle.

Admittedly the geometrical theory of space-lattice interference does not apply so well to electrons as it does to X-rays, especially not to low-energy electrons. But it has enjoyed further triumphs in the diffraction of neutrons, observed first by D. P. Mitchell and P. M. Powers, then since 1946 by W. H. Zinn, E. Fermi, C. Shull and other American physicists using the cyclotron or the uranium pile as a source. Here a new possibility has to be taken into account: the atomic structure factor, which is characteristic for the scattering of single atoms, may be negative as well as positive. This branch of research is, however, still in its infancy. It appears to be capable of great development.

2. CRYSTAL LATTICES

2.1. The One- and Two-dimensional Lattices

There is only one one-dimensional lattice. This consists of a single row of equally spaced points, the lattice being completely specified by one vector. The lattice symbol is p

The general two-dimensional lattice is an infinite array of points which obey the lattice condition that every point should have the same environment in the same orientation. The unit cell of this lattice is a general parallelogram which can be outlined in several different ways. It is conventional in drawing the unit cell to take the origin at the top left corner; the positive direction of the y-axis points horizontally to the right, and the positive direction of the x-axis points down the page, either straight down or to the left.

Specialisation of the two vectors needed to specify the lattice gives rise to four other lattices, described in Table 2.1.1. Small italic letters are used in the nomenclature for the two-dimensional lattices in order to distinguish their symbols from those of the three-dimensional lattices, for which capital italic letters are used. The symbol p is used when the conventionally chosen unit cell is "primitive," i.e. has points at the corners only. The symbol c is used when the conventional choice of unit cell produces a centring point. There is only one centred two-dimensional lattice, and it would be easy to select a primitive unit cell in this also, but only if the conventional rule for the choice of unit cell were disregarded. This conventionally chosen unit cell is related to the symmetry elements of the lattice, and this relation is discussed in section 2.3; but here the rules are given in terms of the vectors chosen as axes.

TABLE 2.1.1

The 5 Two-dimensional Lattices

Shape of unit cell	Lattice symbol	Conventional rule for choice of axes	Nature of axes and angles[1]	Name of corresponding system
General parallelogram (rhomboid)	p	None	$a \neq b$ $\gamma \neq 90°$	Oblique
Rectangle	p c	Two shortest, mutually perpendicular vectors	$a \neq b$ $\gamma = 90°$	Rectangular
Square	p	Two shortest, mutually perpendicular vectors	$a = b$ $\gamma = 90°$	Square
60° angle rhombus	p	Two shortest vectors at 120° to each other	$a = b$ $\gamma = 120°$	Hexagonal

[1] The symbol $\neq$ implies non-equality by reason of symmetry; accidental equality may, of course, occur.

It is not necessary to add to the lattice symbol p a mark to distinguish one primitive lattice from the other three primitive ones, because this is done by the rest of the space-group symbol which follows the lattice symbol (see section 4.1).

It should be noted that the four different shapes of unit cell given in the above table can be referred to four "systems" of co-ordinate axes analogous to the systems in three dimensions.

2.2. The 14 Three-dimensional Bravais Lattices

A one-dimensional lattice may be called a "row." An evenly spaced array of rows forms a two-dimensional lattice, that is, a "net." An evenly spaced array of nets forms a three-dimensional lattice, which is an infinite array of points such that each point has the same environment in the same orientation. A "unit cell" may be defined in an infinite number of ways, and it will be characterised by three vectors, not in one plane, which are the edges of a parallelepiped.

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The Bravais lattices may be taken as arrangements of points in real space, the repeat distance between the points in any direction being proportional, in any particular case, to the corresponding repeat distance in the real crystal under study. Consequently the magnitude of the vectors of the Bravais lattice may be expressed in Å units and the lattices drawn to an appropriate scale. The general symbols for the unit-cell vectors are **a**, **b**, **c** and for their magnitudes a, b, c; while the co-ordinate axes, or directions of the sides of the unit cell, are referred to in general as the x-, y- and z-axes. The interaxial angles $y \wedge z$, $z \wedge x$, $x \wedge y$ are denoted by α, β, γ.

When one or more of the vectors is specialised in a non-trivial way the lattice possesses symmetry (other than identity symmetry). In such cases it is much more convenient to select the unit-cell vectors in such a way that they are closely related to the symmetry elements of the lattice, even though the unit cell may not then be primitive (i.e. with one lattice point only). This sometimes results in the conventional choice of a unit cell centred in various ways.

TABLE 2.2.1 **The 14 Bravais Lattices and Conventional Unit Cells**

System	Number of lattices in system	Lattice symbols		Nature of unit-cell axes and angles[1]	Lengths and angles to be specified	Symmetry of lattice[2]
Triclinic	1	P		$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	a, b, c α, β, γ	$\bar{1}$
Monoclinic[3]	2	1st setting	$\begin{cases} P \\ B \end{cases}$	$a \neq b \neq c$ $\alpha = \beta = 90° \neq \gamma$	a, b, c γ	$2/m$
		2nd setting	$\begin{cases} P \\ C \end{cases}$	$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$	a, b, c β	
Orthorhombic	4	P C[4] I F		$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	a, b, c	mmm
Tetragonal	2	P[5] I		$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	a, c	$4/mmm$
Cubic	3	P I F		$a = b = c$ $\alpha = \beta = \gamma = 90°$	a	$m3m$
Trigonal	1	R[6]		$a = b = c$ $\alpha = \beta = \gamma$ $< 120°, \neq 90°$	a α	$\bar{3}m$
Hexagonal	1	P[7]		$a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$	a, c	$6/mmm$

(1) The symbol $\neq$ implies non-equality by reason of symmetry; accidental equality may, of course, occur.
(2) For explanation of the symmetry symbols see section 3.1.
(3) The side-centred monoclinic lattice is conventionally taken as B in the 1st setting (z-axis unique) and as C in the 2nd setting (y-axis unique). It would be an equally correct description to take A in either case, but this would not distinguish which setting had been chosen. (See Preface to Volume I for the reason for listing alternative settings in the monoclinic system.)
(4) When referring to lattices alone, it is conventional to call the side-centred orthorhombic lattice C. In the space groups of the point group $mm2$, the "z-axis unique" convention requires that the side-centred lattice shall sometimes be called C, and sometimes A (or B).
(5) The tetragonal lattices P and I may also be described as C and F, but only if the $\mathbf{a}, \mathbf{b}$ vectors chosen are not the shortest ones perpendicular to $\mathbf{c}$.
(6) The R-lattice is here described on rhombohedral axes, but it may also be referred to hexagonal axes. Where it is necessary to distinguish these the symbols R_{obv} or R_{rev} (see p. 20) are used for the description on rhombohedral axes and R_{hex} for that on hexagonal axes.
(7) In the 1935 *Tables* the symbol C was used to denote the hexagonal lattice. The reasons for this, although valid, do not outweigh the confusion caused. The lattice is, in fact, primitive and is therefore called P. It is common to both the trigonal and hexagonal systems (see pp. 10, 11).

The different types of lattice are as follows:

A, B or C	Centred on one pair of opposite faces of the unit cell [A (100), B (010), C (001)] as well as having points at the corners.
F	All faces centred, in addition to points at the corners.
I	Body centred, in addition to points at the corners.
P	Primitive (points only at the corners); except rhombohedral.
R	Primitive rhombohedral.

The relationships between the magnitudes of the axes and the interaxial angles in the conventional unit cell are given in Table 2.2.1. But it must be emphasised that in every lattice it is possible to choose a primitive unit cell, although this is not always convenient. Such a primitive unit cell (the vectors of which are known as a ''primitive triplet'') may be found from the analysis of diffraction data and may have to be 'reduced' to the corresponding conventional unit cell (see section 5.1). It should be noted that in choosing the primitive unit cell various alternatives are possible, although sometimes one of these might be obviously more convenient than another. The relationships of axes and angles in *some* of these non-conventional unit cells corresponding to conventional but non-primitive unit cells are shown in Table 2.2.2. These are listed as (1), (2), (3), etc. It will be noticed that although symmetry is *ignored* in choosing these primitive cells, it is always, if present, *revealed* by axis or angle relationships.

The 14 Bravais lattices can be referred to seven different co-ordinate systems on the basis of the specialisation of their vectors. These systems are discussed in section 2.3. In each of the systems, with the exception of the trigonal, the shape of the unit cell (see column 4, Table 2.2.1) of the lattice is characteristic of the system. In the trigonal system two kinds of primitive unit cell are possible; and it is found in practice that some trigonal crystals have a structure based on the hexagonal lattice while others have a structure based on the rhombohedral lattice.

TABLE 2.2.2

Relationships between Axes and Angles in some Primitive Unit Cells and in the Conventional Non-primitive Unit Cells to which they Correspond

NOTE. See section 5.1 for systematic reduction of the general primitive unit cell to the corresponding conventional Bravais lattice unit cell, and for the complete list of 24 possible ''reduced cells'' defined there.
The symbol $\neq$ implies non-equality by reason of symmetry; accidental equality may, of course, occur.

Conventional unit cell (symmetry considered)	Primitive unit cell (symmetry ignored)
Triclinic $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$ (including all non-primitive unit cells)	*Triclinic* $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$ α, β, γ not satisfying any of the restrictive conditions given below, except in an accidental way.
Monoclinic 1st setting (z-axis unique) Lattice A or B $a \neq b \neq c$; $\alpha = \beta = 90° \neq \gamma$ 2nd setting (y-axis unique) Lattice A or C $a \neq b \neq c$; $\alpha = \gamma = 90° \neq \beta$ 1st or 2nd setting Lattice I or F	*Monoclinic* (1) $a \neq b \neq c$ $\alpha = 90° \neq \beta \neq \gamma$ $\quad \beta = \cos^{-1} \dfrac{c}{2a}; \quad \gamma \neq \cos^{-1} \dfrac{b}{2a}$ (2) $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$ $\quad \alpha \neq \cos^{-1} \dfrac{b^2 + c^2 - a^2}{2bc}$ $\qquad\qquad\qquad \beta = \cos^{-1} \dfrac{c^2 + a^2 - b^2}{2ca}$ $\qquad\qquad\qquad \gamma = \cos^{-1} \dfrac{a^2 + b^2 - c^2}{2ab}$ (3) $a = b \neq c$ $\alpha = \beta \neq \gamma \neq 90°$ $\quad \alpha \neq \cos^{-1} \dfrac{c}{2a} \neq \cos^{-1} \left[\dfrac{a}{2c}(1 + \cos \gamma) \right]$ etc.

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TABLE 2.2.2 *(continued)*

Relationships between Axes and Angles in some Primitive Unit Cells and in the Conventional Non-primitive Unit Cells to which they Correspond

NOTE. See section 5.1 for systematic reduction of the general primitive unit cell to the corresponding conventional Bravais lattice unit cell, and for the complete list of 24 possible "reduced cells" defined there.
The symbol $\neq$ implies non-equality by reason of symmetry; accidental equality may, of course, occur.

Conventional unit cell (symmetry considered)	Primitive unit cell (symmetry ignored)
Orthorhombic	*Orthorhombic*
Lattice A or B or C	(1) $a \neq b \neq c$; $\alpha = \beta = 90°$; $\gamma = \cos^{-1} \dfrac{a}{2b}$
$a \neq b \neq c$	(2) $a = b \neq c$; $\alpha = \beta = 90° \neq \gamma \neq 120°$
$\alpha = \beta = \gamma = 90°$	etc.
Lattice I	(1) $a \neq b \neq c$; $4a^2 \neq 2b^2 + c^2$
$a \neq b \neq c$	$\alpha = 90°$; $\beta = \cos^{-1} \dfrac{c}{2a}$; $\gamma = \cos^{-1} \dfrac{b}{2a}$
$\alpha = \beta = \gamma = 90°$	(2) $a = b \neq c$; $\alpha = \beta \neq \gamma \neq 90°$; $\alpha = \cos^{-1} \dfrac{c}{2a}$
	(3) $a = b = c$; $\alpha \neq \beta \neq \gamma$; $1 + \cos \alpha = \cos \beta + \cos \gamma$
	etc.
Lattice F	(1) $a \neq b \neq c$; $\alpha = \cos^{-1} \dfrac{b^2 - c^2 - a^2}{2bc}$
$a \neq b \neq c$	$\beta = \cos^{-1} \dfrac{c^2 - a^2 - b^2}{2ca}$
$\alpha = \beta = \gamma = 90°$	$\gamma = \cos^{-1} \dfrac{a^2 - b^2 - c^2}{2ab}$.
	(2) $a = b \neq c$; $\alpha = \beta \neq \gamma$; $\alpha = \cos^{-1} \left[\dfrac{a}{2c}(1 - \cos \gamma) \right]$
	etc.
Tetragonal	*Tetragonal*
Lattice I or F	(1) $a \neq b \neq c$; $4a^2 = 2b^2 + c^2$
$a = b \neq c$	$\alpha = 90°$; $\beta = \cos^{-1} \dfrac{c}{2a}$; $\gamma = \cos^{-1} \dfrac{b}{2a}$
$\alpha = \beta = \gamma = 90°$	(2) $a = b \neq c$; $\alpha = \beta = \cos^{-1} \dfrac{a}{2c}$; $\gamma = 90°$
	(3) $a = b = c$; $\alpha = \beta \neq \gamma$
	etc.
Cubic	*Cubic*
$a = b = c$; $\alpha = \beta = \gamma = 90°$	
Lattice I	(1) $a = b = c$; $\alpha = \beta = \gamma = \cos^{-1}(-\tfrac{1}{3}) = 109° 28'$; etc.
Lattice F	(1) $a = b = c$; $\alpha = \beta = \gamma = \cos^{-1} \tfrac{1}{2} = 60°$; etc.

Note on Nomenclature

If any point of the lattice is taken as origin, the vectors corresponding to any other lattice point may be expressed as $u\mathbf{a}$, $v\mathbf{b}$, $w\mathbf{c}$, where u, v, and w are integers. The co-ordinates of the lattice point are then said to be u, v, w (no brackets).

The direction joining the origin to the points u, v, w; $2u$, $2v$, $2w$; . . . defines a row of points $[u\ v\ w]$ (square brackets); the same symbol stands for any line parallel to the given direction, since the lattice is infinite and the origin may be taken at any point. $[u\ v\ w]$ is the symbol for a single zone axis; a form of zone axes (directions related by symmetry) is denoted by the use of angular brackets $\langle u\ v\ w \rangle$.

Any position whatever in space may be given co-ordinates in terms of a lattice point taken as origin and the edges of the unit cell as axes. If the vectors corresponding to the required position are $(u+x)\mathbf{a}$, $(v+y)\mathbf{b}$, $(w+z)\mathbf{c}$, where u, v, w are integers and x, y, z are all less than unity, then the co-ordinates of the position are said to be x, y, z (no brackets).

The lattice may be intersected by sets of equally spaced parallel planes, in an infinite number of ways. If the plane in any set nearest to, but not passing through, the origin, intersects the unit-cell vectors at $\mathbf{a}/h$, $\mathbf{b}/k$, $\mathbf{c}/l$, then the set of planes is said to have the indices $(h\ k\ l)$ (in parentheses). The same symbol stands for the indices of a single crystal face parallel to the set of planes. A form of faces (or sets of planes, related by symmetry) is denoted by the use of braces $\{h\ k\ l\}$.

In the hexagonal lattice the equilateral nature of the nets perpendicular to the unique axis is often emphasised by the use of indices $(h\ k\ i\ l)$, where the three indices h, k and i refer to the directions x-, y- and u-, all at $120°$ to each other. In this case the relationship holds that $i = -(h+k)$.

2.3. Crystal Axes and Systems

The morphological study of crystals of different symmetry showed that they could be referred to seven different sets of crystallographic axes of reference, each set possessing characteristic symmetry. A more fundamental division, however, was that into 32 crystal classes, on the basis of point-group symmetry (see section 3). The grouping of the 32 point groups into the seven systems is shown in Table 2.3.1.

The 14 Bravais lattices may also be referred to the same seven systems (see Table 2.2.1) because the sets of axes of reference are simply the edges of the unit cells of the Bravais lattices.

The seven systems were originally taken as follows: Triclinic, Monoclinic, Orthorhombic, Tetragonal, Rhombohedral, Hexagonal and Cubic (or Isometric).

It had long been known, of course, that crystals belonging to the "Rhombohedral" system could be described equally well on hexagonal (Miller–Bravais) axes as on rhombohedral (Miller) axes. The later development of space-group theory, and then of X-ray diffraction methods of crystal structure investigation, showed that there was a complication in the case of crystals with 3-fold symmetry but lacking a symmetry plane normal to the 3-fold axis. The 230 space groups (see section 4) are obtained by adding the point-group symmetry, with possible translations, to appropriate lattices. Five point groups possess 3-fold symmetry but no perpendicular symmetry plane. A given crystal belonging to any one of the five crystal classes so defined might, it was discovered, have a space group based either on a primitive hexagonal lattice or on a primitive rhombohedral lattice. This is the basis of the use of alternative hexagonal or rhombohedral axes of reference for crystals belonging to these five classes (as in Tables 2.2.1 and 2.3.1). Consequently it is not possible to make an altogether satisfactory grouping of crystal classes into systems. The five classes mentioned above can be grouped as the Trigonal system; alternatively they can be grouped as a subdivision of the Hexagonal system. It is not satisfactory to call them Rhombohedral.

TABLE 2.3.1

Crystallographic Axial and Angular Relationships, and Characteristic Symmetry of the Crystal Systems

Point groups[1]	System	Axial and angular relationships[2]	Axial ratios and angles to be specified for each substance	Characteristic symmetry
$1, \bar{1}$	Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$	$a : b : c$ α, β, γ	1-fold (identity or inversion) symmetry only.
$2, m, 2/m$	Monoclinic[3]	1st setting $a \neq b \neq c$ $\alpha = \beta = 90° \neq \gamma$ 2nd setting $a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$	$a : b : c$ γ $a : b : c$ β	2-fold axis (rotation or inversion) in one direction only, this being taken as the z-axis in the first setting and as the y-axis in the second setting.
$222, mm2,$ mmm	Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	$a : b : c$	2-fold axes (rotation or inversion) in three mutually perpendicular directions.
$4, \bar{4}, 4/m,$ $422, 4mm,$ $\bar{4}2m, 4/mmm$	Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	$c : a$	4-fold axis (rotation or inversion) along the z-axis.
$23, m3,$ $432, \bar{4}3m,$ $m3m$	Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90°$	None	Four 3-fold axes each inclined at 54° 44′ to the crystallographic axes.
$3, \bar{3},$ $32, 3m, \bar{3}m$	Trigonal (may be taken as subdivision of hexagonal)	(Rhombohedral axes) $a = b = c$ $\alpha = \beta = \gamma < 120° \neq 90°$ (Hexagonal axes)[4] $a = b \neq c$ $\alpha = \beta = 90°, \gamma = 120°$	α $c : a$	3-fold axis (rotation or inversion) along [111] using rhombohedral axes, or along the z-direction using hexagonal axes.
$6, \bar{6}, 6/m,$ $622, 6mm,$ $\bar{6}m2, 6/mmm$	Hexagonal	$a = b \neq c$ [4] $\alpha = \beta = 90°$ $\gamma = 120°$	$c : a$	6-fold axis (rotation or inversion) along the z-axis.

[1] For explanation of point-group symbols see section 3.1.
[2] The sign $\neq$ implies non-equality by reason of symmetry; accidental equality may, of course, occur.
[3] See Preface to Volume I for explanation of alternative settings.
[4] In drawing the hexagonal axes, it is customary to take three axes, x-, y- and u-, at 120° to each other, and normal to the z-axis.

2.4. The Reciprocal Lattice

To each direct (or real-space) lattice there is a corresponding lattice in "reciprocal" space, which has the same symmetry and can therefore be referred to the same type of co-ordinate axes of reference (system). Rows of points (zone axes) in the direct lattice are normal to nets (planes) of points in the reciprocal lattice, and vice versa. The repeat distance between successive points along a row in reciprocal space is inversely proportional to the interplanar spacing between nets of points in real space normal to the row of points in question, and vice versa. It should be noticed that the interplanar spacing is the perpendicular distance between successive planes (nets) of lattice points, and is not, in general, an actual distance between points, but that it reciprocates into a distance between points.

The lattice reciprocal to a given primitive direct lattice may be obtained by taking any point as origin and from it drawing normals to all sets of direct-lattice planes (hkl), $(h, k,$ and l integral, but not necessarily prime to each other). Points are then placed along these normals at distances K/d_{hkl} from the origin, where K is a constant and d_{hkl} is the interplanar spacing of the planes (hkl). The array of points thus obtained forms a lattice as defined in section 2.2. Each reciprocal lattice point is denoted by the symbol hkl (without brackets) of the set of direct-lattice planes to which it is thus related, and h, k, l (always integral) are the co-ordinates of the lattice point in reciprocal space (Fig. 2.4.1, p. 14).

In applying reciprocal lattice methods in X-ray diffraction problems it is common to take the constant $K=\lambda$ (the wavelength used); in this case the distance of the reciprocal lattice point hkl from the origin, λ/d_{hkl}, is given in dimensionless units. Alternatively, K may be taken as unity. In all representations of the reciprocal lattice it is therefore necessary to give the value of K and also the scale on which the lattice is drawn. Scales such as 5 or 10 cm. to 1 unit (dimensionless, or $Å^{-1}$) are convenient in practice.

Table 2.4.1 gives the relationships between the unit-cell axes and angles in real space and in reciprocal space, for primitive unit cells only. The unit cell in the reciprocal lattice which corresponds to a primitive unit cell chosen in the direct lattice may be constructed as follows. Any lattice point is taken as origin and from this point normals are drawn to the axial planes (100), (010), (001) of the primitive direct-lattice unit cell. Along each of these normals a point is placed at distances from the origin respectively $a^*=K/d_{100}$, $b^*=K/d_{010}$, $c^*=K/d_{001}$. The three vectors, $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$, defined in this way are the edges or axes of the reciprocal-lattice unit cell (also primitive) which corresponds to the primitive direct-lattice unit cell originally chosen. The repetition of this unit cell produces the lattice which is reciprocal to the original direct lattice. The reversal of this procedure will give the direct lattice corresponding to the reciprocal lattice. Since a primitive unit cell can be outlined (in an infinite number of ways) in any direct lattice, the above procedure can always be used to find the direct lattice from the reciprocal lattice and vice versa. Use may be made here of Table 2.2.2.

If, however, the direct lattice is such that the conventional choice of unit cell is non-primitive, then the above procedure must not be applied without modification to the *conventional* unit cell in order to obtain the reciprocal lattice. The necessary modification required is shown in Table 2.4.2. It will be seen in this table that if the conventional unit cell in the direct lattice is non-primitive, then that in the reciprocal lattice will also be non-primitive, although not necessarily of the same kind.

Fig. 2.4.2 (p. 14) shows, two-dimensionally, the relationship between direct and reciprocal-lattice cells when both are primitive, and Fig. 2.4.3 shows the relationship (again two-dimensionally) in the case where the net is centred, the actual values of the direct unit-cell vectors $\mathbf{a}$ and $\mathbf{b}$ being the same in the two figures. The conventional unit cell in the reciprocal lattice is now centred also, and the lengths of its sides are $2a^*$, $2b^*$, its area being four times that of the primitive cell shown in Fig. 2.4.2.

TABLE 2.4.1

Relation between Axes and Angles of Direct-lattice and Reciprocal-lattice Primitive Unit Cells for the Various Systems

Symbols	
a, b, c	Lengths of edges of direct-lattice unit cell.
α, β, γ	Inter-axial angles of direct-lattice unit cell.
a^*, b^*, c^*	Lengths of edges of reciprocal-lattice unit cell.
$\alpha^*, \beta^*, \gamma^*$	Inter-axial angles of reciprocal-lattice unit cell.
K	Reciprocal constant.
$V; V^*$	Volume of direct-lattice unit cell; of reciprocal-lattice unit cell.

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TABLE 2.4.1 (continued)

For symbols see previous page.

Triclinic

$$a^* = \frac{Kbc \sin \alpha}{V}; \quad b^* = \frac{Kca \sin \beta}{V}; \quad c^* = \frac{Kab \sin \gamma}{V}$$

where $V = abc\{1 + 2 \cos \alpha \cos \beta \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma\}^{\frac{1}{2}}$

$$= 2 \, abc\{\sin s. \sin (s-\alpha). \sin (s-\beta). \sin (s-\gamma)\}^{\frac{1}{2}}; \quad V^* = \frac{1}{V}$$

$$2s = \alpha + \beta + \gamma$$

$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma}; \quad \cos \beta^* = \frac{\cos \gamma \cos \alpha - \cos \beta}{\sin \gamma \sin \alpha}; \quad \cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta}$$

Monoclinic

1st setting $\quad a^* = \frac{K}{a \sin \gamma}; \quad b^* = \frac{K}{b \sin \gamma}; \quad c^* = \frac{K}{c}; \quad \alpha^* = \beta^* = 90°; \quad \gamma^* = 180° - \gamma$

2nd setting $\quad a^* = \frac{K}{a \sin \beta}; \quad b^* = \frac{K}{b}; \quad c^* = \frac{K}{c \sin \beta}; \quad \alpha^* = \gamma^* = 90°; \quad \beta^* = 180° - \beta$

Orthorhombic	Tetragonal	Cubic
$a^* = \frac{K}{a}; \quad b^* = \frac{K}{b}; \quad c^* = \frac{K}{c}$	$a^* = b^* = \frac{K}{a}; \quad c^* = \frac{K}{c}$	$a^* = b^* = c^* = \frac{K}{a}$
$\alpha^* = \beta^* = \gamma^* = 90°$	$\alpha^* = \beta^* = \gamma^* = 90°$	$\alpha^* = \beta^* = \gamma^* = 90°$

Hexagonal	Rhombohedral
$a^* = b^* = \frac{2K}{a\sqrt{3}}; \quad c^* = \frac{K}{c}$	$a^* = b^* = c^* = \frac{K.a^2 \sin \alpha}{V}$ where $V = a^3[1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha]^{\frac{1}{2}}$
$\alpha^* = \beta^* = 90°; \quad \gamma^* = 60°$	$\cos \alpha^* = \cos \beta^* = \cos \gamma^* = \frac{\cos^2 \alpha - \cos \alpha}{\sin^2 \alpha} = - \frac{\cos \alpha}{(1 - \cos \alpha)}$

TABLE 2.4.2

Modification of Table 2.4.1 required to include Non-primitive Unit Cells

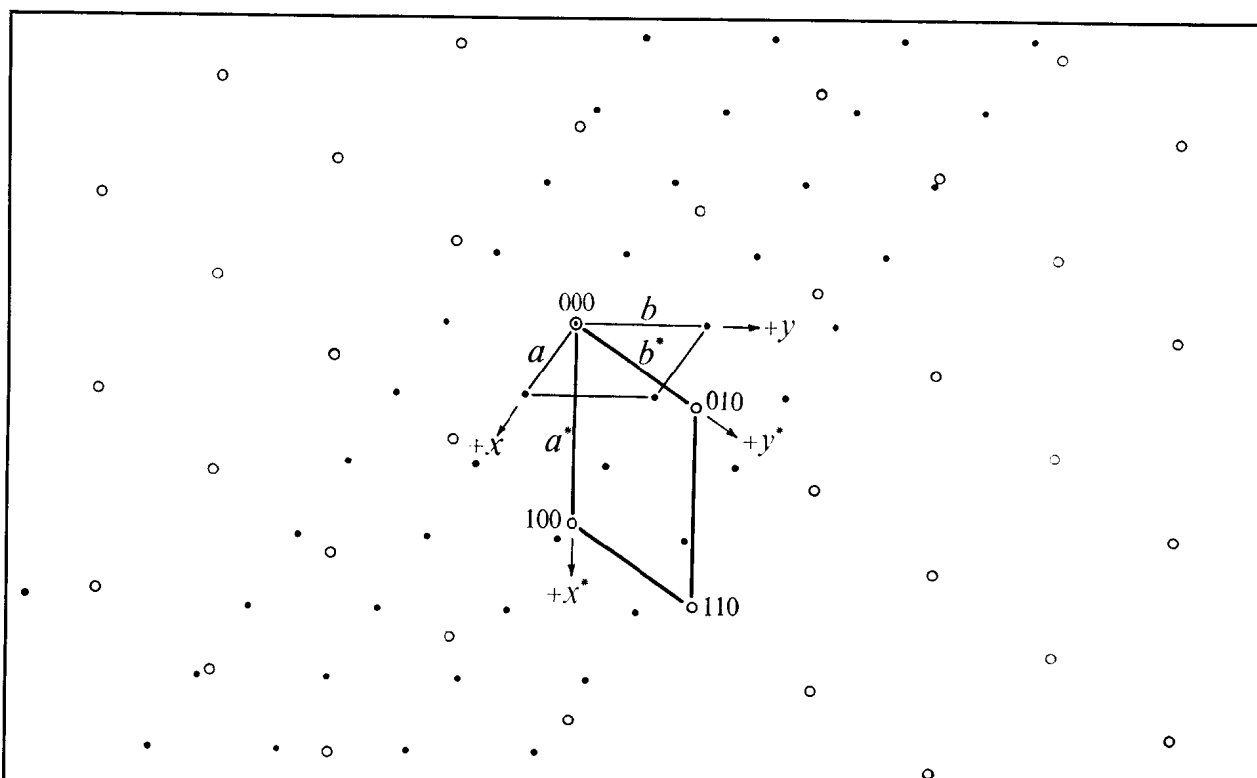| Direct lattice		Reciprocal lattice		
Unit cell edges	Type	Type	Unit cell edges	Volume
a, b, c	P and R	P and R	a^*, b^*, c^*	V^*
	A	A	$a^*, 2b^*, 2c^*$	$4V^*$
	B	B	$2a^*, b^*, 2c^*$	$4V^*$
	C	C	$2a^*, 2b^*, c^*$	$4V^*$
	I	F	$2a^*, 2b^*, 2c^*$	$8V^*$
	F	I	$2a^*, 2b^*, 2c^*$	$8V^*$

Fig. 2.4.1.
Oblique direct lattice and the reciprocal lattice.

Fig. 2.4.2.
Primitive rectangular direct lattice and
the reciprocal lattice.

Fig. 2.4.3.
Centred rectangular direct lattice and the
reciprocal lattice.

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