orientation but wrongly placed with respect to any symmetry elements that may be present in the unit cell. An incorrect structure of this kind may well refine reasonably satisfactorily into a false least-squares minimum; in general, however, it will correspond to unreasonable intermolecular distances. The second way is to try to establish the position of the molecule from the Patterson function calculated with the full set of reflexions. For regularly built structural motifs of known shape and in known orientation, this should not, in general, present severe difficulties.

The main danger is likely to occur from the use of fully automatized procedures for sign or phase determination, combined with automatic peak searches for trial models. These procedures may well lead not to the correct structure but to some pseudo-homometric variant, which may only be recognized as such after considerable expenditure of computer time, if at all.

We are grateful to Dr O. Ermer for helpful discussion.

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The Geometry of X-ray Multiple Diffraction in Crystals

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A derivation of the geometrical distribution of multiply diffracted X-ray beams in single crystals is presented. Included is a brief survey of the geometrical and analytical methods, with some new concepts and constructions, which are useful in the interpretation and prediction of X-ray multiple diffraction phenomena. Applications include the analysis of Kossel patterns, calculation of angles of diffraction, and precision determination of lattice parameters and wavelengths, for which appropriate formulae and procedures are given.

1. Introduction

The phenomena associated with the simultaneous diffraction of an X-ray beam by more than one Bragg plane in a crystal have long been known (Renninger, 1937; Berg, 1926). In most instances their presence constitutes an undesirable complication, as for example in the measurement of diffraction intensities from single crystals, and therefore many workers have attempted to avoid their occurrence (Coppens, 1968; Zocchi & Santoro, 1967). Several authors have found, however, that these effects have a variety of useful applications to the study of single crystals, and for this reason it is necessary to know the directions of singly- and multiply-diffracted X-ray beams in crystals. In the analysis of Kossel patterns (Kossel & Voges, 1935) the points of intersection between diffraction and deficiency conics locate the doubly-diffracted beams and their relationships are used to determine the lattice parameters of the crystal. Of particular value are those cases in which two or more doubly-diffracted beams are separated by a very small angle (Mackay, 1965). The great accuracy of absolute angular measurement possible with very small angles yields the most precise values of the lattice parameters. This principle has been used to measure the lattice parameter of diamond by Lonsdale (1947), and of silicon by Isherwood & Wallace (1966). The effect of arsenic incorporation on the germanium lattice has also been studied (Isherwood & Wallace, 1970). The theoretical basis of this method is the principal subject of the present paper.

Also of considerable interest are cases of systematic triple or multiple diffraction, the occurrence of which is independent of wavelength and is governed only by crystal symmetry. Thus if the symmetry is disturbed by a homogeneous distortion of the lattice, the resulting modifications to the geometry of the doubly-diffracted beams enable the distortion to be measured and analysed. This has been demonstrated by Isherwood (1968) in a study of the surface layers of yttrium iron garnet crystals. The theory of this method will be described in a separate paper.

2. The geometrical interpretation of multiple diffraction

In order to predict the occurrence of multiply-diffracted beams and to calculate their angular relationships to the crystal lattice, a review of the geometry of diffraction is desirable. In this paper consideration is restricted to the description of diffraction in reciprocal space. Although the conditions for multiple diffraction may be derived with equal facility in real space using Huygens's construction, it is the experience of the authors that the Kossel type of construction offers greater advantages in computation. In reciprocal space Bragg's relation is summarized in the statement that the difference between the reflected and incident wave-vectors is equal to the reciprocal-lattice vector of the Bragg plane. This is illustrated in Fig. 1. The incident and reflected beams, KO, OK', are generators of the Bragg cone and terminate on the circle of intersection of the two dispersion spheres of radius $1/\lambda$ drawn about O and G. Allowing λ to vary, K, K' always lie on the Brillouin zone boundary, the plane that mirrors O and G. The parallel plane passing through G at twice the distance from the origin is known as the Kossel plane, and the sphere of radius $2/\lambda$ about O is the limiting sphere. It is convenient to designate the vectors terminating at the intersection points C, C' of the Kossel plane and the limiting sphere as double wave-vectors. The Ewald sphere of radius $1/\lambda$ with centre at K passes through O, G and C.

Simultaneous or double diffraction occurs when the Bragg cones corresponding to two lattice planes intersect and the incident beam is parallel to their common generator. Fig. 2 shows how for a pair of reciprocal-lattice points, G_1 and G_2, the two possible doubly-diffracted incident beams are defined by the points C_{012}, C'_{012} at which the line of intersection of the corresponding pair of Kossel planes intersects the limiting sphere. (In Fig. 2 the beams generated by Bragg reflexion of these two incident beams are indicated by superfixes of the corresponding plane). These two directions coincide at the point S when the Kossel plane intersection is tangent to the sphere. This critical condition defines a maximum wavelength for double diffraction since no solutions are possible if the intersection line lies outside the limiting sphere.

Finally triple diffraction occurs for the three reciprocal-lattice points G_1, G_2, G_3 when the point of intersection of the three Kossel planes, denoted T, lies on the limiting sphere. The Ewald sphere with diameter OT passes through G_1, G_2 and G_3. The condition for triple diffraction requires an exact relationship between the wavelength and lattice parameters of the crystal, which will in general not be satisfied for monochromatic characteristic radiation, except in a rare contingency.

For any three Bragg planes there is thus a single value of λ for triple diffraction, unless they belong to the same zone. The Kossel planes of tautozonal Bragg planes are themselves tautozonal and thus in general only intersect in pairs, so that triple diffraction cannot occur. A special case occurs when, as a result of the symmetry of the lattice, three Kossel planes intersect in a common line. The points of intersection with the limiting sphere define a pair of triply-diffracted incident beams for any wavelength below the critical value. This case is called systematic triple diffraction because its occurrence depends not on the wavelengths or lattice parameters but on the point symmetry group of the crystal.

The point of triple diffraction, T, is effectively the intersection of three Kossel lines of double diffraction corresponding to pairs of reciprocal-lattice points. It follows that if the point T does not lie exactly on the sphere of reflexion but is very close to it, either inside or outside, there will be three points on the sphere very close to each other for which a condition of double dif-

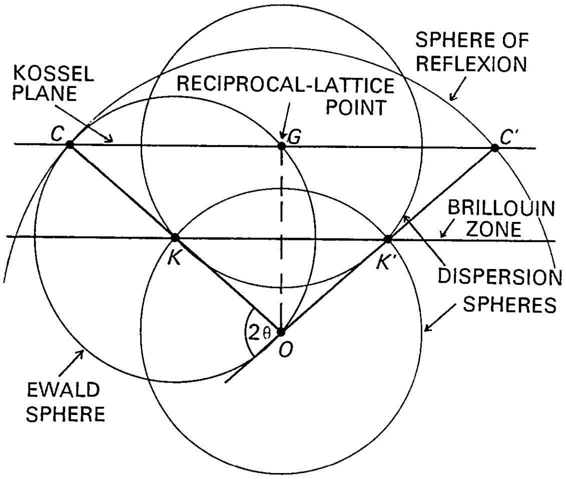

Fig. 1. Bragg reflexion in reciprocal space: ——— double wave-vector, - - - reciprocal-lattice vector.

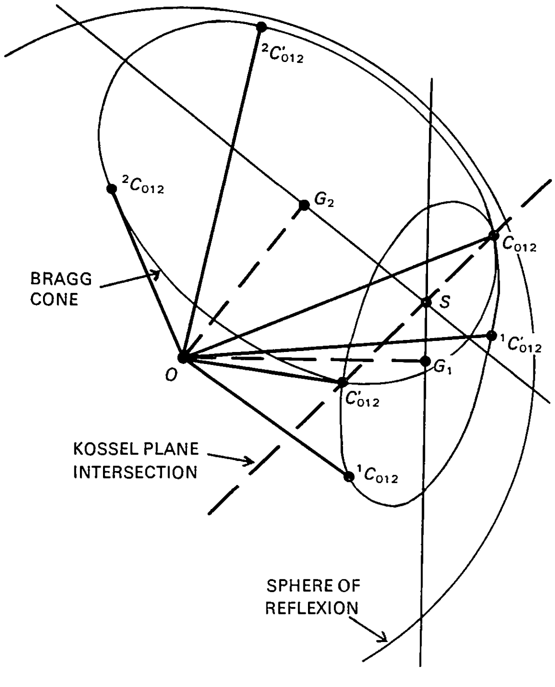

Fig. 2. Double diffraction in reciprocal space.

fraction occurs. This case is illustrated in Fig. 3. The three corresponding doubly-diffracted incident beams will thus be separated by very small angles. Since the values of very small angles can be measured with a great absolute accuracy, this condition of near triple diffraction presents the most favourable conditions for the precise determination of the relationships between the lattice parameters and wavelength. The prediction of the conditions for triple diffraction and the methods of calculating the lattice parameters in cases of near triple diffraction are described in subsequent sections.

A similar case is observed when the intersection of a pair of Kossel planes is not quite tangential to the limiting sphere but lies just inside it. Then the two doubly-diffracted incident beams defined by C_{012}, C'_{012} are again separated by a very small angle. These cases have been of particular interest in the analysis of Kossel patterns where they give rise to lens-shaped figures (Heise, 1962).

It may be shown that the two reflected beams O^1K_{12}, O^2K_{12} generated by the incident doubly-diffracted beam $K_{12}O$ are themselves simultaneously diffracted beams. Let the symbol $\mathbf{k}$ represent the vector $\overrightarrow{OK}$. Then the incident beam may be represented by the vector $\bar{\mathbf{k}}_{12}$, and the two reflected beams by the vectors ${}^1\mathbf{k}_{12}$, ${}^2\mathbf{k}_{12}$. Bragg's relation is satisfied for both reflexions in the expressions ${}^1\mathbf{k}_{12}-\bar{\mathbf{k}}_{12}=\mathbf{g}_1, {}^2\mathbf{k}_{12}-\bar{\mathbf{k}}_{12}=\mathbf{g}_2$. A third diffraction condition is obtained by subtraction, yielding ${}^1\mathbf{k}_{12}-{}^2\mathbf{k}_{12}=\mathbf{h}$, where $\mathbf{h}$ is the reciprocal-lattice vector $\mathbf{g}_1-\mathbf{g}_2$. Thus the beam ${}^1\mathbf{k}_{12}$ is diffracted simultaneously by the planes represented by $\bar{\mathbf{g}}_1$ and $\bar{\mathbf{h}}$, while ${}^2\mathbf{k}_{12}$ is diffracted simultaneously by both $\bar{\mathbf{g}}_2$ and $\mathbf{h}$. Furthermore each simultaneously diffracted beam as well as the incident beam may also be regarded as a consecutively diffracted beam. For instance $\bar{\mathbf{k}}_{12}$ is the beam reflected by $\bar{\mathbf{g}}_2$ and incident on $\mathbf{g}_1$, or the beam reflected by $\bar{\mathbf{g}}_1$ and incident on $\mathbf{g}_2$, and so on.

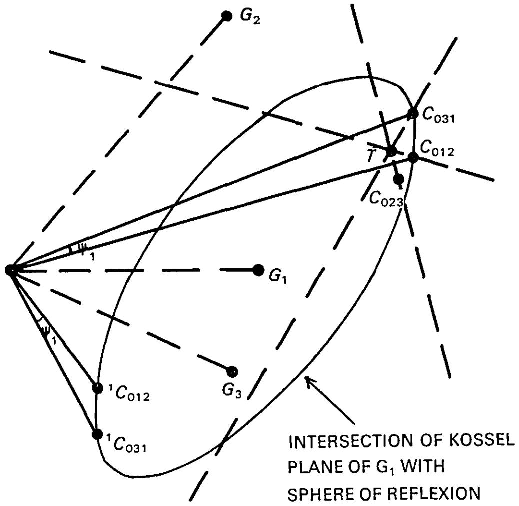

Fig. 3. The condition of near triple diffraction: ——— double wave-vector, – – – Kossel plane intersection.

It is convenient therefore to devise an alternative system of notation which expresses the symmetry of the beams and the reciprocal-lattice vectors involved in double diffraction. A notation of this type has also been used, for example by Ewald & Héno (1968) in their exposition of the dynamical theory of double diffraction. Let us use Roman numerals to denote the beams as follows:

$$\begin{aligned}\mathbf{k}_{\mathrm{I}} &= {}^2\mathbf{k}_{12}\\ \mathbf{k}_{\mathrm{II}} &= {}^1\mathbf{k}_{12}\\ \mathbf{k}_{\mathrm{III}} &= \bar{\mathbf{k}}_{12}\,.\end{aligned}\tag{1}$$

Now let us define three reciprocal-lattice vectors as follows using Bragg's relation.

$$\begin{aligned}\mathbf{g}_{\mathrm{I}} &= \mathbf{k}_{\mathrm{III}}-\mathbf{k}_{\mathrm{II}}\\ \mathbf{g}_{\mathrm{II}} &= \mathbf{k}_{\mathrm{I}}-\mathbf{k}_{\mathrm{III}}\\ \mathbf{g}_{\mathrm{III}} &= \mathbf{k}_{\mathrm{II}}-\mathbf{k}_{\mathrm{I}}\,.\end{aligned}\tag{2}$$

It is clear that $\mathbf{g}_{\mathrm{I}}=\bar{\mathbf{g}}_1$, $\mathbf{g}_{\mathrm{II}}=\mathbf{g}_2$, $\mathbf{g}_{\mathrm{III}}=\mathbf{h}$. $\mathbf{k}_{\mathrm{I}}$ is the beam reflected by $\mathbf{g}_{\mathrm{II}}$ and incident on $\mathbf{g}_{\mathrm{III}}$, $\mathbf{k}_{\mathrm{II}}$ is consecutively diffracted by $\mathbf{g}_{\mathrm{III}}$ and $\mathbf{g}_{\mathrm{I}}$, and $\mathbf{k}_{\mathrm{III}}$ by $\mathbf{g}_{\mathrm{I}}$ and $\mathbf{g}_{\mathrm{II}}$. Since $\mathbf{h}=\mathbf{g}_1-\mathbf{g}_2$, $\mathbf{g}_{\mathrm{I}}+\mathbf{g}_{\mathrm{II}}+\mathbf{g}_{\mathrm{III}}=0$, so that the three vectors form a triangle. This is illustrated in Fig. 4 circumscribed by a section of the Ewald sphere. The corresponding doubly-diffracted wave-vectors are shown.

3. The dynamics of double diffraction

Although doubly- and multiply-diffracted beams can be identified in Kossel patterns by the intersections of diffraction on deficiency conics generated by a point source, they may be more specifically indicated by the intensity contrast effects which distinguish them from singly-diffracted beams. Both positive and negative contrast effects may be observed, for which the doubly-diffracted beam has a greater or lesser intensity than the singly-diffracted background. These effects may be regarded as being caused by the redistribution of energy between the diffracted beams due to the coupling of Bragg reflexions. A strong positive contrast occurs in a relatively weak Bragg reflexion when a strong reflexion is simultaneously excited, provided that the intermediate or difference reflexion is also strong. There is a corresponding decrease in intensity in the coupled reflexion. Renninger (1937) and others have shown that certain systematically absent reflexions may be excited by coupling to a strong reflexion. Renninger used the term 'Umweganregung' to describe the generation of a forbidden reflexion by consecutive diffraction by two Bragg planes. An example of negative contrast is the 'Aufhellung' effect, first observed by Berg (1926). There is a decrease in diffracted intensity when the incident beam simultaneously satisfies the diffraction conditions for two Bragg reflexions of equivalent strength.

In transmission through thick crystals singly-diffracted beams suffer less than the normal absorption due to the Bormann effect. For certain combinations of reflexions the doubly-diffracted beams suffer a further decrease in absorption and a strong positive contrast is observed. This so-called 'double Bormann' effect has been observed in beams simultaneously reflected by the 111 and $11\bar{1}$ planes of germanium by Bormann & Hartwig (1965).

The detailed theory of the intensity contrast associated with multiply-diffracted beams is at present little understood. Although Renninger used a kinematical description, most theoretical studies have been based on the dynamical theory of diffraction due to Ewald (1937) and von Laue (1931), but the solution of the equations for the constant frequency (or dispersion) surfaces presents formidable difficulties. Solutions for special cases have been given by Saccocio & Zajac (1965), Dalisa, Zajac & Chiu (1968), Joko & Fukuhara (1967), and Ewald & Héno (1968), while a more complete solution has been given by Penning (1968) for the case of centrosymmetric crystals.

When making measurements using doubly-diffracted beams, the most favourable conditions are provided by beams subject to the Renninger effect which have the greatest contrast and visibility. It is useful to select these conditions in advance. Renninger reflexions are not to be found in crystals where the atoms lie on a Bravais lattice, and the presence of a glide plane or screw axis in the space group is necessary. For certain lattices, such as diamond, the reciprocal-lattice vectors of the forbidden or very weak reflexions form a superlattice. These reflexions may be excited by coupling to any reflexion whose reciprocal-lattice vector is not a translation vector of this superlattice, to ensure that the intermediate reflexion is not also forbidden. For example in the diamond lattice the forbidden reflexions are those for which $(h+k+l)=2(2n+1)$, and they may only be excited simultaneously with reflexions for which h,k,l are all odd.

4. Calculation of the diffraction conditions

In all the calculations that follow, the Kossel plane method has been used. Most of the results may be obtained with equal facility using the Huygens wavefront construction in real space. Methods of solving Kossel patterns based on the use of spherical trigonometry are given by Heise (1962) and others.

In reciprocal space the basic equations are those defining the Kossel planes. Let $\mathbf{c}_i$ be a double wave-vector terminating on the Kossel plane generated by the reciprocal-lattice vector $\mathbf{g}_i$, shown in Fig. 1. Then we have, following Mackay (1965),

$$\mathbf{c}_i \cdot \mathbf{g}_i = |\mathbf{g}_i|^2 = G_i \, . \tag{3}$$

The index zero is given to any vector lying on the sphere of reflexion which is defined by

$$|\mathbf{c}_0|^2 = 4/\lambda^2 \tag{4}$$

The suffixes carried by the vector $\mathbf{c}$ indicate the equations which they satisfy. In reciprocal space the principal elements occurring in the equations are the quadratic forms and scalar products of the reciprocal-lattice vectors, which are denoted by

$$G_i = |g|^2$$
$$E_{ij} = \mathbf{g}_i \cdot \mathbf{g}_j$$

It is often convenient however to replace the elements E by the quadratic forms of the difference vectors

$$H_{ij} = |\mathbf{h}_{ij}|^2 = |\mathbf{g}_i - \mathbf{g}_j|^2$$

so that the only quantities appearing in the formulae are the moduli of the reciprocal-lattice vectors. Since these are the same quantities that are directly measured in the Debye–Scherrer photograph, using equations like

$$(G_i, H_i) = 2(1 - \cos 2\theta_i)/\lambda^2$$

a direct comparison between the powder pattern and Kossel pattern is possible. In each case the two formulae are quoted, one containing elements G and E, the other G and H. A full summary of the symbols and notation used in the calculations is given in the Appendix together with some basic definitions and equations.

The formulae to be calculated are perfectly general and can therefore be applied to all classes of crystal. When a single characteristic wavelength is used it is often convenient to normalize the equations with respect to the wavelength so that the elements G, E and H are multiplied by λ^2. In the case of cubic crystals all the formulae naturally take on simpler forms. It is then most convenient to normalize the equations with respect to the lattice parameter, so that $|\mathbf{c}|^2$ is multiplied by a^2, and G, E and H are simply quadratic functions of the Miller indices, h, k and l.

4·1. *The condition for double diffraction*

The condition for double diffraction by the two Bragg planes whose reciprocal-lattice vectors are $\mathbf{g}_1$, $\mathbf{g}_2$ may be expressed by the following equations

$$\left.\begin{array}{l} \mathbf{c}_{12} \cdot \mathbf{g}_1 = G_1 \\ \mathbf{c}_{12} \cdot \mathbf{g}_2 = G_2 \end{array}\right\} \tag{5}$$

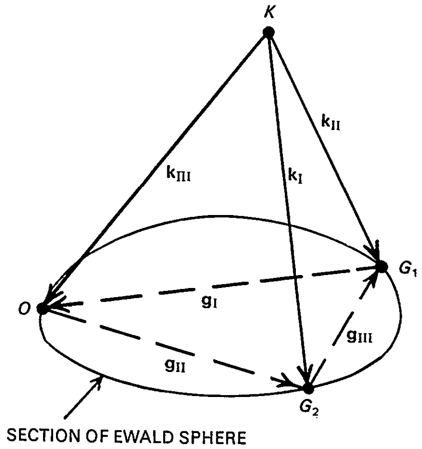

Fig. 4. Vector diagram for double diffraction: ——— wave-vector, – – – reciprocal-lattice vector.

where $\mathbf{c}_{12}$ is twice the doubly-diffracted wave-vector. Let us consider first the case of critical double diffraction which occurs for the smallest value of $\mathbf{c}_{12}$ which is denoted $\mathbf{s}$. $\mathbf{s}$ is coplanar with $\mathbf{g}_1$ and $\mathbf{g}_2$ and may be written

$$\mathbf{s}=\mu_1\mathbf{g}_1+\mu_2\mathbf{g}_2\,. \tag{6}$$

Substituting in equation (5) we obtain the following expressions for μ_1, μ_2

$$\left.\begin{aligned} U\mu_1&=G_2(G_1-E)\\ U\mu_2&=G_1(G_2-E)\end{aligned}\right\} \tag{7}$$

where E denotes the scalar product $\mathbf{g}_1\,.\,\mathbf{g}_2$, and

$$U=|\mathbf{g}_1\times\mathbf{g}_2|^2=G_1G_2-E^2\,.$$

X-rays of wavelength λ are diffracted if

$$|\mathbf{s}|^2=4/\lambda^2\,.$$

After simplification the following expression is obtained for $|\mathbf{s}_0|^2$:

$$U|\mathbf{s}_0|^2=G_1G_2(G_1+G_2-2E); \tag{8}$$

therefore

$$\frac{1}{\lambda^2}=\frac{G_1G_2(G_1+G_2-2E)}{4(G_1G_2-E^2)}\,. \tag{9}$$

When this critical condition is not satisfied the doubly-diffracted beam corresponds to a point on the line $\mathbf{c}_{12}$ determined by λ. $\mathbf{c}_{12}$, which is the intersection line of the two Kossel planes, may be expressed as follows

$$\mathbf{c}_{12}=\mathbf{s}+\mu_3(\mathbf{g}_1\times\mathbf{g}_2)\,. \tag{10}$$

The intersection with the sphere of reflexion is denoted $\mathbf{c}_{012}$ and is given by

$$|\mathbf{c}_{012}|^2=|\mathbf{s}|^2+\mu_3^2U=4/\lambda^2 \tag{11}$$

since $\mathbf{s}\,.\,(\mathbf{g}_1\times\mathbf{g}_2)=0$. Therefore

$$\mathbf{c}_{012}=\mathbf{s}\pm(4/\lambda^2-|\mathbf{s}|^2)^{1/2}(\mathbf{g}_1\times\mathbf{g}_2)U^{-1/2}\,. \tag{12}$$

The direction cosines of the doubly-diffracted beam are found by resolving equation (12) into its components.

There are two doubly-diffracted beams defined by each pair of Bragg planes and these correspond to the two signs before the square root in equation (12). The angle between this pair of beams, ψ, is calculated as follows. Let $\mathbf{b}_0$ be the difference vector between the two solutions $\mathbf{c}_{012}$, $\mathbf{c}'_{012}$. Then using the cosine formula

$$|\mathbf{b}_0|^2=2|\mathbf{c}_0|^2(1-\cos\psi) \tag{13}$$

$\mathbf{b}_0$ is also calculated from equation (12) which yields

$$|\mathbf{b}_0|^2=4(|\mathbf{c}_0|^2-|\mathbf{s}|^2)\,. \tag{14}$$

Eliminating $|\mathbf{b}_0|$, we obtain a relation between $|\mathbf{c}_0|$ and ψ

$$2|\mathbf{c}_0|^2(1+\cos\psi)=|\mathbf{s}|^2\,. \tag{15}$$

Substituting for $|\mathbf{s}|$ and $|\mathbf{c}_0|$ we have

$$\frac{1}{\lambda^2}=\frac{G_1G_2(G_1+G_2-2E)}{4(G_1G_2-E^2)2(1+\cos\psi)}\,. \tag{16}$$

This is the same as equation (9) except for a factor $2(1+\cos\psi)$ which may also be written $4\cos^2\psi/2$. In the Kossel pattern ψ is the angle between the intersections of two conics forming a lens-shaped figure which is most commonly used in analysing such patterns (Heise, 1962). The trigonometric form of equation (16) is obtained by writing

$$|\mathbf{g}_1-\mathbf{g}_2|^2=G_1+G_2-2E$$

and

$$G_1G_2\sin^2\varphi=U$$

and taking square roots this yields

$$\frac{1}{\lambda}=\frac{|\mathbf{g}_1-\mathbf{g}_2|}{4\sin\varphi\cos\psi/2}\,. \tag{17}$$

If we replace E by $H=(G_1+G_2-2E)$, equation (16) becomes

$$\frac{1}{\lambda^2}=\frac{G_1G_2H}{4U2(1+\cos\psi)} \tag{18}$$

where

$$\begin{aligned}4U&=4G_1G_2-(G_1+G_2-H)^2\\ &=(G_1+G_2+H)^2-2(G_1^2+G_2^2+H^2)\,.\end{aligned} \tag{19}$$

It is clear that both U and $|\mathbf{c}_0|^2$ are perfectly symmetrical in the three quadratic forms G_1, G_2, and H, which we may replace by those corresponding to the triad of vectors defined in equation (2). Then we may write

$$\frac{1}{\lambda^2}=\frac{G_{\mathrm{I}}G_{\mathrm{II}}G_{\mathrm{III}}}{[(G_{\mathrm{I}}+G_{\mathrm{II}}+G_{\mathrm{III}})^2-2(G_{\mathrm{I}}^2+G_{\mathrm{II}}^2+G_{\mathrm{III}}^2)]\,2(1+\cos\psi)} \tag{20}$$

This form of equation reflects the symmetry of the double diffraction process and the equivalence of double-diffraction conditions applied to each of the beams.

4·2. *The condition for triple diffraction*

The double wave-vector, $\mathbf{c}_{123}$, corresponding to triple diffraction by the three Bragg planes $\mathbf{g}_1$, $\mathbf{g}_2$, $\mathbf{g}_3$ is denoted $\mathbf{t}$ and is defined by three equations of the form (3)

$$\left.\begin{aligned}\mathbf{t}\,.\,\mathbf{g}_1&=G_1\\ \mathbf{t}\,.\,\mathbf{g}_2&=G_2\\ \mathbf{t}\,.\,\mathbf{g}_3&=G_3\end{aligned}\right\}. \tag{21}$$

It may be readily proved that $\mathbf{t}$ is then given by the equation

$$W\mathbf{t}=G_1(\mathbf{g}_2\times\mathbf{g}_3)+G_2(\mathbf{g}_3\times\mathbf{g}_1)+G_3(\mathbf{g}_1\times\mathbf{g}_2) \tag{22}$$

where

$$W=\mathbf{g}_1\,.\,(\mathbf{g}_2\times\mathbf{g}_3)\,.$$

The direction and magnitude of the vector $\mathbf{t}$ may be found by resolving equation (22) into its components.

In the case of cubic crystals we may normalize with respect to the lattice parameter and obtain the following expressions:

$$\left.\begin{aligned} Wt_x &= \begin{vmatrix} G_1 & k_1 & l_1 \\ G_2 & k_2 & l_2 \\ G_3 & k_3 & l_3 \end{vmatrix} \\ Wt_y &= \begin{vmatrix} h_1 & G_1 & l_1 \\ h_2 & G_2 & l_2 \\ h_3 & G_3 & l_3 \end{vmatrix} \\ Wt_z &= \begin{vmatrix} h_1 & k_1 & G_1 \\ h_2 & k_2 & G_2 \\ h_3 & k_3 & G_3 \end{vmatrix} \end{aligned}\right\} \qquad (23)$$

where

$$W = \begin{vmatrix} h_1 & k_1 & l_1 \\ h_2 & k_2 & l_2 \\ h_3 & k_3 & l_3 \end{vmatrix} \qquad (24)$$

The triple diffraction condition is then expressed by

$$|\mathbf{c}_0|^2 = \left(\frac{2a}{\lambda}\right)^2 = |\mathbf{t}|^2 = t_x^2 + t_y^2 + t_z^2 . \qquad (25)$$

A more general formula for $|\mathbf{t}|^2$ may be obtained by squaring equation (22). $W^2|\mathbf{t}|^2$ is conveniently denoted Δ. Then expanding the scalar products we have

$$\begin{aligned} \Delta = W^2|\mathbf{t}|^2 &= G_1^2(G_2G_3 - E_1^2) + G_2^2(G_3G_1 - E_2^2) \\ &+ G_3^2(G_1G_2 - E_3^2) + 2G_2G_3(E_2E_3 - G_1E_1) \\ &+ 2G_3G_1(E_3E_1 - G_2E_2) + 2G_1G_2(E_1E_2 - G_3E_3) \qquad (26) \end{aligned}$$

where

$E_1 = \mathbf{g}_2 \cdot \mathbf{g}_3$, *etc.*

Rearranging the terms yields

$$\begin{aligned} \Delta &= G_1G_2G_3[(G_1+G_2+G_3) - 2(E_1+E_2+E_3)] \\ &- (G_1^2E_1^2 + G_2^2E_2^2 + G_3^2E_3^2) + 2(G_2E_2G_3E_3 \\ &+ G_3E_3G_1E_1 + G_1E_1G_2E_2) . \qquad (27) \end{aligned}$$

The last two terms are better written in the form

$$(G_1E_1 + G_2E_2 + G_3E_3)^2 - 2(G_1^2E_1^2 + G_2^2E_2^2 + G_3^2E_3^2) .$$

Alternatively we may use another abbreviation and write

$$M_1 = (G_2E_2 + G_3E_3 - G_1E_1),\ etc.$$

Then the last two terms reduce to $M_2M_3 + M_3M_1 + M_1M_2$.

The calculation of W, the volume of the reciprocal cell, will not be repeated here, but the result is as follows.

$$W^2 = G_1G_2G_3 + 2E_1E_2E_3 - (G_1E_1^2 + G_2E_2^2 + G_3E_3^2). \qquad (28)$$

The condition for triple diffraction is

$$4/\lambda^2 = |\mathbf{t}|^2 = \Delta/W^2 . \qquad (29)$$

An alternative formula for $|\mathbf{t}|^2$ may be derived by replacing the scalar products, E_i, throughout by the quantities, H_i, which are defined by the relations $H_1 = G_2 + G_3 - 2E_1$, *etc.* The calculations will not be reproduced here, but they result in the following expressions, if we make use of the abbreviations,

$$N_1 = G_2H_2 + G_3H_3 - G_1H_1$$

etc. Then

$$4\Delta = N_2N_3 + N_3N_1 + N_1N_2 \qquad (30)$$

$$\begin{aligned} 4W^2 &= (G_1+H_1)N_1 + (G_2+H_2)N_2 + (G_3+H_3)N_3 \\ &- G_2G_3H_1 - G_3G_1H_2 - G_1G_2H_3 - H_1H_2H_3. \qquad (31) \end{aligned}$$

In the case of cubic crystals it is, however, usually more convenient to leave W in its determinantal form, equation (24).

4·3. *Calculation of angles between doubly-diffracted beams*

When the sphere of reflexion does not coincide with a point of triple diffraction, the triply-diffracted beam is replaced by three doubly-diffracted beams, each shared by a pair of Bragg reflexions, and designated $\mathbf{c}_{023}$, $\mathbf{c}_{031}$, $\mathbf{c}_{012}$. These are shown in Fig. 3. The difference vectors $\mathbf{b}_{01}$, $\mathbf{b}_{02}$, $\mathbf{b}_{03}$ are defined by the relations $\mathbf{b}_{01} = \mathbf{c}_{031} - \mathbf{c}_{012}$, *etc.* The angles between pairs of doubly-diffracted beams are similarly defined ψ_1, ψ_2, ψ_3, and given by the cosine formula:

$$\left.\begin{aligned} |\mathbf{b}_{01}|^2 &= 2|\mathbf{c}_0|^2(1 - \cos\psi_1) \\ |\mathbf{b}_{02}|^2 &= 2|\mathbf{c}_0|^2(1 - \cos\psi_2) \\ |\mathbf{b}_{03}|^2 &= 2|\mathbf{c}_0|^2(1 - \cos\psi_3) \end{aligned}\right\} . \qquad (33)$$

It is convenient to measure from the triple intersection $\mathbf{t}$, rather than the critical points $\mathbf{s}_{ij}$. Thus, if ν_i are variable parameters,

$$\left.\begin{aligned} \mathbf{c}_{23} &= \mathbf{t} + \nu_1(\mathbf{g}_2 \times \mathbf{g}_3) \\ \mathbf{c}_{31} &= \mathbf{t} + \nu_2(\mathbf{g}_3 \times \mathbf{g}_1) \\ \mathbf{c}_{12} &= \mathbf{t} + \nu_3(\mathbf{g}_1 \times \mathbf{g}_2) \end{aligned}\right\} . \qquad (34)$$

Finally, the double wave-vectors must satisfy the condition

$$|\mathbf{c}_0|^2 = |\mathbf{c}_{023}|^2 = |\mathbf{c}_{031}|^2 = |\mathbf{c}_{012}|^2 = 4/\lambda^2 . \qquad (35)$$

These equations are sufficient in principle to establish relationships between the angles, ψ_i, and the wavelength and lattice parameters. However, although the ψ_i may be calculated directly from a knowledge of the latter, there is, in general, no analytical solution of the equation for λ in terms of the ψ_i.

There is, however, a special case in which the equations are exactly soluble. This occurs when the following identities are observed

$$\left.\begin{aligned} G_2 &= G_3 \\ E_2 &= E_3 \\ H_2 &= H_3 \end{aligned}\right\} \qquad (36)$$

from which it follows that

$$\begin{gathered} |\mathbf{b}_{02}|^2 = |\mathbf{b}_{03}|^2 \\ \psi_2 = \psi_3 \\ \nu_2 = \nu_3 \end{gathered}$$

These relationships are automatically satisfied when there is a plane of Laue symmetry containing $\mathbf{g}_1$ and in which $\mathbf{g}_2$ and $\mathbf{g}_3$ are mirror images. From equation (33) we have

$$\begin{aligned}|\mathbf{b}_{01}|^2 &= |\mathbf{c}_{031}-\mathbf{c}_{012}|^2\\ &= \nu_2^2[(\mathbf{g}_3\times\mathbf{g}_1)-(\mathbf{g}_1\times\mathbf{g}_2)]^2\\ &= \nu_2^2[2G_1(G_2+E_1)-4E_2^2]\\ &= 2|\mathbf{c}_0|^2(1-\cos\psi_1)\,. \qquad (37)\end{aligned}$$

In the calculation of $\nu_2(=\nu_3)$ it is necessary to derive expressions for $W^2|t|^2=\varDelta$, W^2, and the product $W\mathbf{t}\,.\,(\mathbf{g}_1\times\mathbf{g}_2)$ which will be abbreviated with the symbol $\Omega_3\,(=\Omega_2)$. From equation (26) above we obtain

$$\begin{aligned}\varDelta = W^2|\mathbf{t}|^2 &= G_2(G_2-E_1)[G_1(G_2+E_1)+2G_2(G_2-2E_2)]\\ &= G_1(G_2-E_1)[2G_2(G_1+G_2-2E_2)-G_1(G_2-E_1)] \qquad (38)\end{aligned}$$

and from equation (28)

$$W^2=(G_2-E_1)[G_1(G_2+E_1)-2E_2^2]\,, \qquad (39)$$

from which the following condition for exact triple diffraction may be derived.

$$\frac{4}{\lambda^2}=|\mathbf{t}|^2=\frac{G_1[2G_2(G_1+G_2-E_2)-G_1(G_2-E_1)]}{G_1(G_2+E_1)-2E_2^2}\,. \qquad (40)$$

Using equation (22) Ω_3 may be expressed

$$\Omega_3=W\mathbf{t}\,.\,(\mathbf{g}_1\times\mathbf{g}_2)=G_1(G_2-E_1)\,(G_2-E_2)\,. \qquad (41)$$

Finally, from equations (37) and (39) we may write

$$(G_2-E_1)|\mathbf{c}_0|^2 2(1-\cos\psi_1)=2W^2\nu_3^2\,. \qquad (42)$$

Now, if we square equation (34) and multiply by W^2 the following equation is obtained;

$$W^2|\mathbf{c}_0|^2=\varDelta+2W\nu_3\Omega_3+(W\nu_3)^2U_3 \qquad (43)$$

where

$$U_3=(G_1G_2-E_3^2)\,.$$

It is useful at this stage to abbreviate the expression $2(1-\cos\psi_1)$ by the symbol Ψ_1^2. Then eliminating ν_3,

$$\begin{aligned}W^2|\mathbf{c}_0|^2=\varDelta&+[2(G_2-E_1)]^{1/2}\Omega_3|\mathbf{c}_0|\Psi_1\\ &+\tfrac{1}{2}(G_2-E_1)\,(G_1G_2-E_2^2)|\mathbf{c}_0\,|^2\Psi_1^2\,. \qquad (44)\end{aligned}$$

If we substitute the expressions derived above, this equation is divisible by (G_2-E_1) and may be written in the form

$$\boldsymbol{P}c_0=\boldsymbol{S}+\boldsymbol{R}|\mathbf{c}_0|\Psi_1+\boldsymbol{Q}|\mathbf{c}_0|^2\Psi_1^2\,. \qquad (45)$$

where

$$\boldsymbol{P}=G_1(G_2+E_1)-2E_2^2 \qquad (46)$$

$$\boldsymbol{Q}=\tfrac{1}{2}(G_1G_2-E_2^2) \qquad (47)$$

$$\boldsymbol{R}=G_1(G_2-E_2)[2(G_2-E_1)]^{1/2} \qquad (48)$$

$$\boldsymbol{S}=G_1[2G_2(G_1+G_2-2E_2)-G_1(G_2-E_1)]\,. \qquad (49)$$

Equation (45) is quadratic in $|\mathbf{c}_0|=2/\lambda$ and Ψ_1, and has the following general solution for $2/\lambda$:

$$\left(\frac{2}{\lambda}\right)=\frac{\boldsymbol{R}\Psi_1\pm[(\boldsymbol{R}^2-4\boldsymbol{QS})\Psi_1^2+4\boldsymbol{PS}]^{1/2}}{2(\boldsymbol{P}-\boldsymbol{Q}\Psi_1^2)}\,. \qquad (50)$$

Although this equation is valid for all values of Ψ_1, it is the case of small Ψ_1 that is of the greatest interest in determining lattice parameters. Thus it is useful to obtain an approximate formula for $2/\lambda$ valid in the neighbourhood of a triple diffraction condition. Let us assume that terms in Ψ_1^3 and above are negligible. Then we may expand Ψ_1 as follows.

$$\Psi_1=2\sin\psi_1/2\simeq\psi_1 \qquad (51)$$

and equation (50) becomes

$$\left(\frac{1}{\lambda}\right)=\frac{1}{2}\left(\frac{\boldsymbol{S}}{\boldsymbol{P}}\right)^{1/2}\left[1+\left(\frac{\boldsymbol{R}^2+4\boldsymbol{QS}}{8\boldsymbol{PS}}\right)\psi_1^2\right]+\frac{\boldsymbol{R}}{4\boldsymbol{P}}\psi_1\,. \qquad (52)$$

Equivalent expressions for $\boldsymbol{P}$, $\boldsymbol{Q}$, $\boldsymbol{R}$, $\boldsymbol{S}$ may be obtained if E_1, E_2 are replaced by $H_1=2(G_2-E_1)$, and $H_2=G_1+G_2-2E_2$. Then we have

$$2\boldsymbol{P}=4G_2H_2-G_1H_1-(G_2+H_2-G_1)^2 \qquad (53)$$

$$2\boldsymbol{Q}=4G_2H_2-(G_2+H_2-G_1)^2 \qquad (54)$$

$$2\boldsymbol{R}=H_1^{1/2}G_1(G_2+H_2-G_1) \qquad (55)$$

$$2\boldsymbol{S}=G_1(4G_2H_2-G_1H_1)\,. \qquad (56)$$

Again the terms have been arranged to demonstrate the symmetry between G_2 and H_2. The exact triple diffraction condition, equation (40), becomes

$$\frac{4}{\lambda^2}=\frac{G_1(4G_2H_2-G_1H_1)}{4G_2H_2-G_1H_1-(G_2+H_2-G_1)^2}\,. \qquad (57)$$

It is interesting to note that if $H_1=0$, *i.e.* if $\mathbf{g}_2=\mathbf{g}_3$, equation (57) becomes identical to the equation for the critical double diffraction case (9), and equation (52) is equivalent to equation (16).

Putting $H_2=G_{\mathrm{III}}$ and dropping the suffix from H_1 we may write equation (40) in its symmetrical form.

$$\frac{4}{\lambda^2}=\frac{4G_{\mathrm{I}}G_{\mathrm{II}}G_{\mathrm{III}}-G_{\mathrm{I}}H}{(G_{\mathrm{I}}+G_{\mathrm{II}}+G_{\mathrm{III}})^2-2(G_{\mathrm{I}}^2+G_{\mathrm{II}}^2+G_{\mathrm{III}}^2)-G_{\mathrm{I}}H}\,. \qquad (58)$$

Although in the general case, when there is no symmetry relationship, it is not possible to deduce an exact expression for the wavelength and lattice parameters in terms of the angular separation ψ, it is possible to derive a formula linear in ψ, which is a good approximation provided that ψ is sufficiently small that terms in ψ^2 and higher may be neglected. This condition is satisfied in the case of near triple diffraction which is of particular interest. Fig. 5 shows how when the difference between $|\mathbf{c}_0|$ and $|\mathbf{t}|$ is small, a small tetrahedron is formed by the three Kossel planes and the sphere of reflexion, which in this region may be approximated by a plane surface normal to the direction OT. Since the ψ_i are small and $|\mathbf{c}_0|\simeq|\mathbf{t}|$ equation (33) may be written

$$\left.\begin{aligned}|\mathbf{b}_{01}|&=\psi_1|\mathbf{t}|\\ |\mathbf{b}_{02}|&=\psi_2|\mathbf{t}|\\ |\mathbf{b}_{03}|&=\psi_3|\mathbf{t}|\end{aligned}\right\}\,. \qquad (59)$$

A simple method of calculating $|\mathbf{b}_{01}|$ follows. Let us construct a tetrahedron similar to $TC_{012}\,C_{023}\,C_{031}$ by projecting the Kossel plane intersections until they intersect a plane normal to OT, but passing through the origin, at points C_{t12} C_{t23} C_{t31}, as shown in Fig. 5. The two tetrahedra are related by a scale factor $|\mathbf{t}|/(|\mathbf{c}_0|-|\mathbf{t}|)$, so we may write

$$\frac{|\mathbf{b}_{01}|}{|\mathbf{b}_{t1}|}=\frac{\psi_1|\mathbf{t}|}{|\mathbf{b}_{t1}|}=\frac{2/\lambda-|\mathbf{t}|}{|\mathbf{t}|} \tag{60}$$

so that

$$\frac{2}{\lambda}=|\mathbf{t}|+|\mathbf{t}|^2\psi_1/|\mathbf{b}_{t1}| \tag{61}$$

where

$$|\mathbf{b}_{t1}|^2=|\mathbf{c}_{t31}-\mathbf{c}^2_{t12}|^2=|\mathbf{c}_{t31}|^2+|\mathbf{c}_{t12}|^2-2\mathbf{c}_{t31}\,.\,\mathbf{c}_{t12}\,. \tag{62}$$

Similar equations apply to ψ_2, ψ_3.

The plane through the origin is defined by the following equations

$$\mathbf{c}_{t23}\,.\,\mathbf{t}=\mathbf{c}_{t31}\,.\,\mathbf{t}=\mathbf{c}_{t12}\,.\,\mathbf{t}=0\,. \tag{63}$$

Combined with the equations for the Kossel planes (21) this yields the following expressions

$$\left.\begin{aligned}\mathbf{t}\,.\,(\mathbf{g}_2\times\mathbf{g}_3)\mathbf{c}_{t23}&=G_2(\mathbf{g}_3\times\mathbf{t})-G_3(\mathbf{g}_2\times\mathbf{t})\\ \mathbf{t}\,.\,(\mathbf{g}_3\times\mathbf{g}_1)\mathbf{c}_{t31}&=G_3(\mathbf{g}_1\times\mathbf{t})-G_1(\mathbf{g}_3\times\mathbf{t})\\ \mathbf{t}\,.\,(\mathbf{g}_1\times\mathbf{g}_2)\mathbf{c}_{t12}&=G_1(\mathbf{g}_2\times\mathbf{t})-G_2(\mathbf{g}_1\times\mathbf{t})\end{aligned}\right\}. \tag{64}$$

Before substituting for $\mathbf{t}$ from equation (22) it is necessary to multiply both sides of these equations by W. The denominators of $\mathbf{c}_{tij}$ may now be denoted Ω_i, and are given by the following expressions

$$\left.\begin{aligned}\Omega_1&=W\mathbf{t}\,.\,(\mathbf{g}_2\times\mathbf{g}_3)=G_2G_3(G_1-E_2-E_3)+E_1M_1\\ \Omega_2&=W\mathbf{t}\,.\,(\mathbf{g}_3\times\mathbf{g}_1)=G_3G_1(G_2-E_3-E_1)+E_2M_2\\ \Omega_3&=W\mathbf{t}\,.\,(\mathbf{g}_1\times\mathbf{g}_2)=G_1G_2(G_3-E_1-E_2)+E_3M_3\end{aligned}\right\}. \tag{65}$$

We may then write for $|\mathbf{b}_{t1}|$

$$|\mathbf{b}_{t1}|^2=\frac{|\Omega_2\mathbf{c}_{t31}|^2}{\Omega_2^2}+\frac{|\Omega_3\mathbf{c}_{t12}|^2}{\Omega_3^2}-\frac{2\Omega_2\mathbf{c}_{t31}\,.\,\Omega_3\mathbf{c}_{t12}}{\Omega_2\Omega_3}\,. \tag{66}$$

The numerators may be expanded using equation (65) above and the basic equations for $\mathbf{t}$, equation (21). This yields the following expressions

$$|\Omega_2\mathbf{c}_{t31}|^2=W^2|\mathbf{t}|^2G_3G_1(G_3+G_1-2E_2)=\Delta\Theta_2 \tag{67}$$

$$|\Omega_3\mathbf{c}_{t12}|^2=W^2|\mathbf{t}|^2G_1G_2(G_1+G_2-2E_3)=\Delta\Theta_3 \tag{68}$$

$$-2\Omega_2\mathbf{c}_{t31}\,.\,\Omega_3\mathbf{c}_{t12}=W^2|\mathbf{t}|2G_1(G_2G_3-M_1)=\Delta\Phi_1\,. \tag{69}$$

We now have the following expression for $1/\lambda$

$$\begin{aligned}\frac{1}{\lambda}&=\tfrac{1}{2}|\mathbf{t}|+\frac{|\mathbf{t}|^2}{2\Delta^{1/2}}\psi_1\left(\frac{\Theta_2}{\Omega_2^2}+\frac{\Theta_3}{\Omega_3^2}+\frac{\Phi_1}{\Omega_2\Omega_3}\right)^{-1/2}\\ &=\frac{\Delta^{1/2}}{2W}\left[1+\frac{\psi_1}{W}\left(\frac{\Theta_2}{\Omega_2^2}+\frac{\Theta_3}{\Omega_3^2}+\frac{\Phi_1}{\Omega_2\Omega_3}\right)^{-1/2}\right].\end{aligned} \tag{70}$$

Equivalent expressions for the quantities Θ_i, Φ_i, and Ω_i may be derived by replacing the E_i by H_i. The results are as follows:

$$\Theta_2=G_3G_1H_2 \tag{71}$$

$$\Theta_3=G_1G_2H_3 \tag{72}$$

$$\Phi_1=G_1N_1 \tag{73}$$

$$4\Omega_2=G_1N_1+H_2N_2+G_3N_3-2\Theta_2 \tag{74}$$

$$4\Omega_3=G_1N_1+G_2N_2+H_3N_3-2\Theta_3\,. \tag{75}$$

Using these symbols we may also abbreviate the expression for $4W^2$ given in equation (31)

$$\begin{aligned}4W^2=&(G_1+H_1)N_1+(G_2+H_2)N_2+(G_3+H_3)N_3\\ &-(\Theta_1+\Theta_2+\Theta_3)-H_1H_2H_3\,.\end{aligned} \tag{76}$$

5. Some geometrical constructions for triple diffraction

Since close proximity to a condition of triple diffraction results in very favourable circumstances for precise lattice parameter measurement, it is important to be able to predict these conditions in advance of experiment. Instead of the laborious exploration of the Kossel patterns obtained with a variety of wavelengths, the aim is to select the radiation and orientation of the crystal required. In the case of cubic crystals it would be most desirable to derive a selection rule governing the normalized triple diffraction vectors, $\mathbf{t}$, and their quadratic forms, $|\mathbf{t}|^2$. Making use of the choice of radiation, those values of $\lambda^2|\mathbf{t}|^2/4$ lying close to the suspected value of a^2 would then be considered.

Restrictions on values of $|\mathbf{t}|^2$ corresponding to particular crystal lattices and specific intensity contrast effects, such as the Renninger effect, would be provided by additional selection rules, incorporating those given in § 3. The analytical derivation of such rules based on equations (23), (27) and (28) has, however, not been attempted.

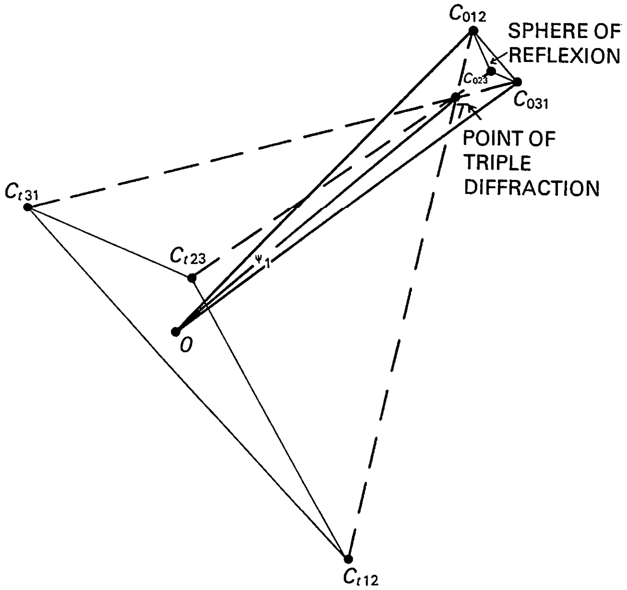

Fig. 5. Kossel plane construction in a near triple diffraction condition.

As an alternative, geometrical methods of predicting triple diffraction have been used. Since three-dimensional constructions are not practicable, it is necessary to restrict consideration to wave-vectors lying in a single plane of real or reciprocal space, although this contains only a fraction of the total number of triple diffraction conditions that are possible. In the reciprocal space representation we choose a plane passing through the origin and draw the lines of intersection with this plane of all the Kossel planes and the sphere of reflexion. There is a condition of triple diffraction where three lines meet, and those intersections are favoured which are close to the circle of reflexion of radius $2a/\lambda$.

The most useful choice of intersection plane is one of the planes of crystallographic symmetry, because being a principal lattice plane it contains a high proportion of triple points. Also as every Kossel plane is duplicated by a plane of Laue symmetry, an intersection of only two lines on the diagram corresponds to an intersection of four Kossel planes. By exception, Kossel planes perpendicular to the intersection plane,

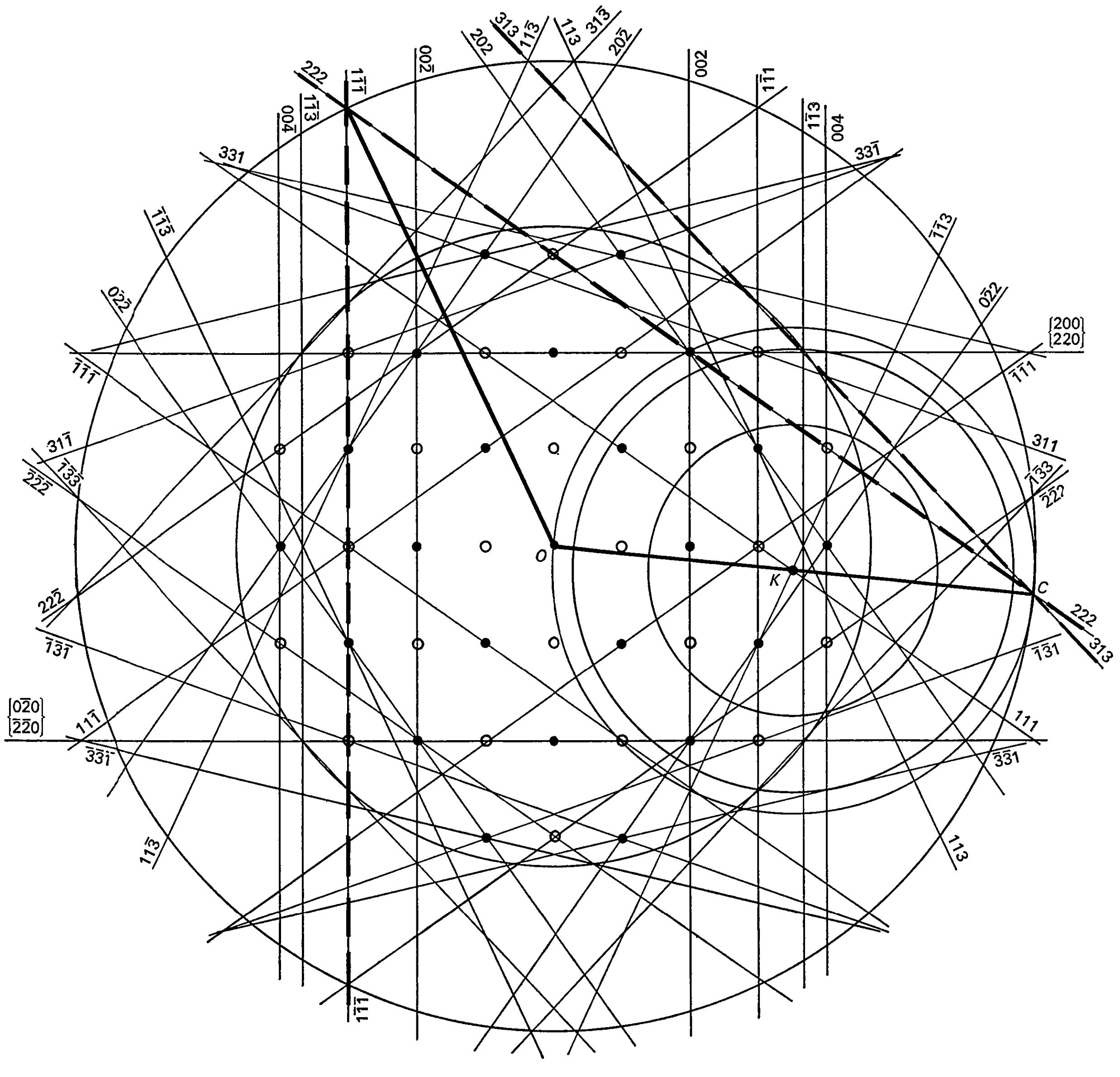

Fig.6. Intersection with the $1\bar{1}0$ plane of Kossel planes in the face-centred cubic lattice. The circles concentric at O represent spheres of reflexion for Cu $K\alpha_1$ radiation of diamond ($|\mathbf{c}_0|=4{\cdot}63$) and silicon ($|\mathbf{c}_0|=7{\cdot}05$). The circles concentric at K are intersections of the Ewald sphere for silicon with the layer planes: ● Reciprocal-lattice points in even layer planes, ○ Reciprocal-lattice points in odd layer planes.

with reciprocal lattice points in the zero layer, are not mirrored in that plane. Thus if one intersection is of this type only triple diffraction occurs. The two doubly-diffracted beams formed in the Kossel plane are themselves related by the plane of symmetry, in which case it is possible to derive an exact formula for the lattice parameter in terms of their separation ψ as shown in § 4·3. For this reason intersections of this type are of particular interest, especially when the zero layer reflexion has a zero structure factor. In cubic crystals there are two types of symmetry plane $\{001\}$ and $\{1\bar{1}0\}$, and the Kossel plane intersections are given by the equations:

$$h\xi + k\eta = G = (h^2+k^2+l^2) \tag{77}$$

for the (001) plane,

$$l\xi + \frac{1}{\sqrt{2}}(h+k)\eta = G = (h^2+k^2+l^2) \tag{78}$$

for the $(1\bar{1}0)$ plane, and the circle of reflexion is defined by

$$\xi^2 + \eta^2 = (2a/\lambda)^2 . \tag{79}$$

ξ and η are normalized Cartesian coordinates based on the unit $1/a$. An example of this type of construction is shown in Fig. 6 in which the plane of intersection is $(1\bar{1}0)$, and the Kossel planes of the face-centred cubic lattice are depicted. In Fig. 6 the spheres of reflexion of Cu $K\alpha_1$ radiation by silicon and diamond are shown. As an example the triply-diffracted rays corresponding to the intersections of Kossel planes $222/1\bar{1}\bar{1}/\bar{1}1\bar{1}$, and 222/313/133 are shown to illustrate the conditions used by the authors to obtain a precise value of the lattice parameter of silicon (Isherwood & Wallace, 1966). [$\bar{1}1\bar{1}$ and 133 are mirror images in $1\bar{1}0$ of $1\bar{1}\bar{1}$ and 313].

It is often useful to combine the Kossel plane and Ewald sphere constructions. For example, suppose that a pair of symmetry-related non-zero layer reflexions has been selected with CO the incident beam. Then the Ewald sphere intersects the diagram in a circle of radius a/λ whose centre is at K, and triple diffraction with a zero layer reflexion occurs if this circle passes through a reciprocal-lattice point. Conversely suppose that the zero layer reflexion has been selected. The intersections of the Ewald sphere with each layer of vertical height ζ are concentric circles of radius ϱ, where $\varrho^2 = (a/\lambda)^2 - \zeta^2$, and centre at K when projected on to the zero layer. Triple diffraction occurs when one of the circles passes through a (projected) reciprocal-lattice point. This is illustrated in Fig. 6.

Two other methods of construction have been used to predict the directions of doubly-diffracted beams. When the crystal and the radiation have already been selected so that the value of a/λ is known, the intersections of the Bragg cones with the sphere of reflexion may be represented by circles on a stereographic projection. The intersections of the circles correspond to the positions of the doubly-diffracted beams. This construction has been used to interpret Kossel patterns and divergent beam patterns (Lonsdale, 1947). An alternative construction has been used by Cole, Chambers & Dunn (1962) and Kottwitz (1968). Suppose that a single reflexion, G_1, is first selected, a forbidden reflexion for example. Then it is useful to plot curves of the ratio a/λ against the azimuthal angle, α, for each of the doubly-diffracted beams simultaneously reflected by the other Bragg planes. α is thus the angle of rotation of the crystal about OG_1 necessary to bring the doubly-diffracted beam into the plane of incidence.

6. Corrections for refraction

Since diffraction occurs within the crystal, the value of λ used in all the diffraction conditions given in § 4 should differ from the value *in vacuo*, λ_c. The dynamical theory of diffraction allows a small finite range of wave-vectors to participate in single or multiple diffraction with slightly different wavelengths, governed by the dispersion surfaces. In calculations it is appropriate to choose a representative value of λ. In the absence of diffraction the wavelength in the crystal is related to that *in vacuo* by the formula

$$\frac{\lambda}{\lambda_c} = 1 + \left(\frac{e^2\lambda^2}{8\pi^2\,\varepsilon_0 mc^2}\right)\varrho \tag{80}$$

where ϱ is the mean electron density. If the effect of absorption may be neglected, this value may be taken as the average, provided that the dispersion surfaces are centrosymmetric about the intersection point, K, of dispersion spheres of radius $1/\lambda$. This condition is obeyed for single diffraction, but for double diffraction only in the case of the Renninger effect, as shown by Ewald & Héno (1968). Under conditions when the single or double Bormann effect occurs the beams which are the least absorbed are those for which the

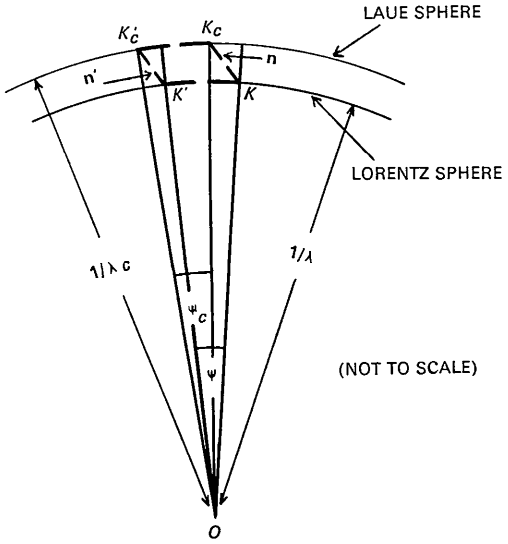

Fig. 7. The refraction correction for beams separated by a small angle ψ.

refractive index is nearest unity. The appropriate average wavelength must be derived using the dynamical theory and lies between λ_c and the value given by equation (80).

The authors have found angular deviations and changes in intensity in the weak 222 reflexion of silicon and germanium, in the neighbourhood of Renninger reflexions, which do not appear to be accounted for by the existing dynamical theory of diffraction. Until these are explained the theoretical refraction correction for Renninger reflexions should be treated with reserve.

A second consequence of refraction is that all the angles between beams measured *in vacuo* are subject to a small correction given by Snell's law. We shall consider here only the effect on the small angle ψ which has been used to derive accurate lattice parameters. Fig. 7 shows a pair of doubly-diffracted wave-vectors (incident or reflected), separated by the angle ψ, drawn from one of the reciprocal-lattice points to its sphere of dispersion of radius $1/\lambda$. Outside the crystal the wave-vectors must lie on the sphere of radius $1/\lambda_c$. To satisfy the boundary conditions at the surface, the wave-vectors on either side must differ only by a vector parallel to the surface normal. In Fig. 7 $\mathbf{n}$, $\mathbf{n}'$ are normal to a surface of arbitrary orientation. It is clear that if ψ is small, $\Delta\mathbf{k}_c \simeq \Delta\mathbf{k}$. Thus if ψ_c is the angle measured *in vacuo*

$$\psi_c = \frac{\Delta\mathbf{k}_c}{\mathbf{k}} = \frac{\lambda_c}{\lambda}\psi \,. \tag{81}$$

Since the difference between λ and λ_c is far smaller than the experimental error, for all practical purposes we may write $\psi_c = \psi$. Thus whereas the individual beams may suffer significant deviations due to refraction, the angle ψ does not. This approximation no longer applies when the surface normal approaches the direction $\Delta\mathbf{k}$.

Thus it is clear that when the lattice parameter is measured by the method described above the only correction for refraction that is necessary is to replace λ_c by λ using the formula given in equation (80).

7. Discussion

The methods outlined above provide a useful alternative to Kossel patterns for the precise measurement of lattice parameters. The conditions for obtaining pairs of doubly-diffracted beams with a small separation ψ can be predicted in advance for radiation of any wavelength and formulae for determining the lattice parameters have been derived. The lattice parameters of cubic crystals require only a single experimental measurement of ψ, while for crystals of lower symmetry the number of independent measurements necessary is equal to the number of lattice parameters. Procedures for crystals of lower than cubic symmetry have yet to be evolved. The same procedure may also be used to determine the wavelength of a radiation when the lattice parameters of the crystal are already accurately known.

APPENDIX

In this Appendix is given a list of the symbols and notation which have been used in this paper, together with some basic definitions. The conventional symbols are used for the lattice parameters and the wavelength.

Vectors are denoted by small letters thus, $\mathbf{a}$, and their terminations in the diagrams are indicated by the corresponding capital, A. The same letter is also used to denote the square of the modulus of a vector, $A = |\mathbf{a}|^2$, and capital letters are used to denote scalar products of vectors. Angles are denoted by small Greek letters.

The suffixes have the following meanings. Arabic numerals indicate reciprocal-lattice vectors, while Roman numerals indicate beams. Each Bragg reflexion condition satisfied transfers the corresponding suffix to the diffracted beams (and superfix to the reflected beam). The index zero refers to a beam of the characteristic wavelength, λ. Thus a point in reciprocal space carries three suffixes, a line two, and a plane one. Elements which are functions of more than one vector may combine the suffixes of their components, but are usually given simpler indices where possible.

List of symbols and notation

Vectors		Definitions
Reciprocal lattice vector	$\mathbf{g}$	$\mathbf{g} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$
Difference vector	$\mathbf{h}$	$\mathbf{h}_{ij} = \mathbf{g}_i - \mathbf{g}_j$
Wave-vector	$\mathbf{k}$	
Double wave-vector	$\mathbf{c}$	$\mathbf{c} = 2\mathbf{k}$
Point on sphere of reflexion	$\mathbf{c}_0$	$\lvert\mathbf{c}_0\rvert^2 = 4/\lambda^2$
Difference vector	$\mathbf{b}$	$\mathbf{b}_{ij} = \mathbf{c}_i - \mathbf{c}_j$
Point of critical double diffraction	$\mathbf{s}$	
Point of potential triple diffraction	$\mathbf{t}$	$\mathbf{t} = \mathbf{c}_{123}$
Normal to surface	$\mathbf{n}$	

Quadratic forms

$$G_i = |\mathbf{g}_i|^2$$
$$E_{ij} = \mathbf{g}_i \,.\, \mathbf{g}_j$$
$$H_{ij} = |\mathbf{h}_{ij}|^2 = G_i + G_j - 2E_{ij}$$
$$U_{ij} = |\mathbf{g}_i \times \mathbf{g}_j|^2 = G_iG_j - E^2{}_{ij}$$

Functions of three reciprocal-lattice vectors

$$W = \mathbf{g}_1 \,.\, (\mathbf{g}_2 \times \mathbf{g}_3) = \begin{vmatrix} h_1 & k_1 & l_1 \\ h_2 & k_2 & l_2 \\ h_3 & k_3 & l_3 \end{vmatrix} \mathbf{a}^* \,.\, (\mathbf{b}^* \times \mathbf{c}^*)$$

$$W^* = \mathbf{d}_1 \,.\, (\mathbf{d}_2 \times \mathbf{d}_3) = \mathbf{g}_1 \,.\, (\mathbf{g}_2 \times \mathbf{g}_3)/G_1G_2G_3$$

The following definitions are subject to the operation of cyclic permutation of the indices 1, 2, 3 symbolized $\circlearrowright$. $\sum\limits_{123}$ indicates the cyclic sum.

$$\circlearrowright M_1 = G_2E_2 + G_3E_3 - G_1E_1$$
$$\circlearrowright N_1 = G_2H_2 + G_3H_3 - G_1H_1$$
$$\circlearrowright \Theta_1 = G_2G_3(G_2 + G_3 - 2E_1) = G_2G_3H_1$$
$$\circlearrowright \Phi_1 = 2G_1(G_2G_3 - M_1) = G_1N_1$$

$$\begin{aligned}
\circlearrowright\ \Omega_1 &= G_2G_3(G_1-E_2-E_3)+E_1M_1\\
\circlearrowright\ 4\Omega_1 &= H_1N_1+G_2N_2+G_3N_3-2\Theta_1\\
\circlearrowright\ W^2 &= G_1G_2G_3+2E_1E_2E_3-\sum_{123}G_1E_1^2\\
4W^2 &= \sum_{123}[(G_1+H_1)N_1-\Theta_1]-H_1H_2H_3\\
\Delta &= G_1G_2G_3\sum_{123}(G_1-2E_1)+\sum_{123}M_2M_3\\
4\Delta &= \sum_{123}N_2N_3
\end{aligned}$$

Angles

Angles between planes	φ
Bragg angle	θ
Angles between wave-vectors	ψ
$\Psi=2\sin\psi/2$	

Physical parameters

Wavelength in space	λ_c
Wavelength in crystal	λ

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Tensor Analysis of the Harmonic Vibrations of Atoms in Crystals

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It is shown how the tensor algebra of general affine systems gives a useful and natural representation of the harmonic vibration tensor **U**. Formulae given by Cruickshank for the 'smearing function' $t(\mathbf{x})$ and its Fourier transform $q(\mathbf{h})$ are proved to be generally valid, provided the upper and lower suffix notation is used for the vector and tensor components. It is also shown how representing the tensor **U** in a system whose basis vectors are unit vectors and parallel to the crystal axes has many advantages. Finally a simple formalism for the determination of metric quatities of **U**, introducing its mixed components U^i_j, is suggested.

Introduction

The purpose of the present note is to treat the problem of describing the thermal motion of atoms as one of tensor analysis in affine systems.

Assuming an anisotropic harmonic potential field, the thermal motion of atoms in crystals is normally described for every atom in terms of the well-known symmetric tensor **U** (Cruickshank, 1956). The crystallographic system in which this tensor is defined is an affine system (*i.e.* a system whose axes and interaxial angles are in general $\mathbf{a}_1\neq\mathbf{a}_2\neq\mathbf{a}_3$, $\gamma_1\neq\gamma_2\neq\gamma_3$, $\gamma_i\neq\pi/2$).

The problem of describing the thermal motion of atoms has therefore a more logical and natural formulation if for any general affine system $\mathbf{a}^i$ we introduce its own reciprocal system $\mathbf{a}^i$ defined by $\mathbf{a}_i\,.\,\mathbf{a}^j=\delta^j_i$, and use these dual bases throughout the vector and tensor analysis of the thermal motion.

Three main conclusions are reached:

i) Cruickshank's (1956) original formulae (1·6) and (1·7) for the 'smearing function' $t(\mathbf{x})$ and its Fourier transform $q(\mathbf{h})$ are valid in any non-orthogonal crystal system provided contravariant components of **U** and covariant components of **l**, with respect to crystal axes, are used in formula (1·5) of the same paper;

ii) it is useful to refer the tensor **U** to a coordinate system whose basis vectors are unit vectors parallel to the crystal axes, in order to give an expression