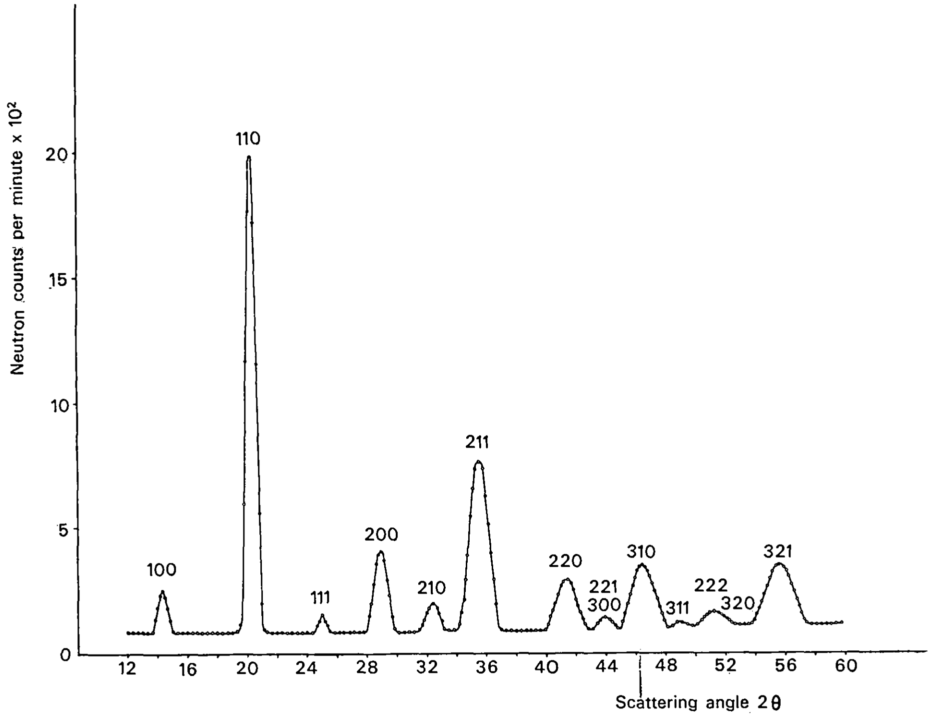

Fig. 1. Neutron diffraction powder diagram of caesium chloride, $\lambda=1\cdot031$ Å.

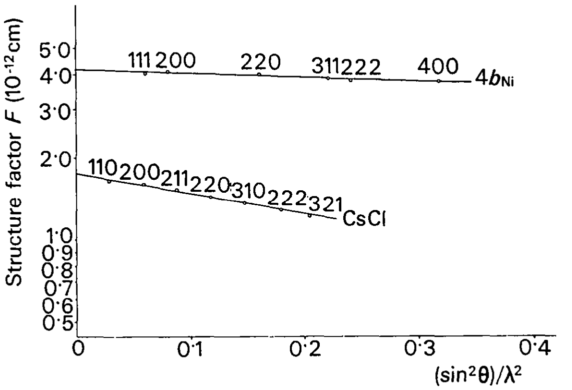

Fig. 2. Structure factors of nickel and caesium chloride as the functions of $(\sin^2\theta)/\lambda^2$.

redetermined $b_{\rm Rb}$ of $0\cdot85\times10^{-12}$ cm by Mueller, Sidhu, Heaton, Hitterman & Knott (1963) is also considerably higher than the previous one of $0\cdot55\times10^{-12}$ cm. It is interesting to note that the redetermined constants both for caesium and rubidium are, therefore, higher by a factor of about 1·5 than the previous ones.

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Transformation of thermal vibration tensors.

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It has been found that the formulae for the transformation of thermal vibration tensors given by Cruickshank (1956*a*, 1961) have to be modified for oblique crystal systems, and thus also the programs based on them. The appropriate formulae will be derived. The mathematical formalism used is also chosen to allow a comparison between the existing methods of determining the principal representation of the vibration tensors, and to derive an explicit formula for their symmetry-equivalent representations. We refer to Cruickshank's papers as CR and CRU respectively. If not stated otherwise, the notation will be as used in CR.

Transformation in oblique crystal systems

CR equation (1.6) for the 'smearing function' $t(\mathrm{X})$ and CR equation (1.7) for its transform $q(\mathrm{S})$ are only valid for orthogonal crystal systems. In oblique systems the components of **X** in Å and the components of **S** in Å^{-1} are no longer co- and contravariant components of the same representation of a given vector. Therefore these components cannot define the same representation of a given tensor. Specifically, the symbol $\mathbf{U}^{-1}$ in CR(1.6) no longer represents the inverse matrix of the matrix **U** in CR(1.7). For, if we define

$$\mathbf{X}_C = \mathbf{A}\mathbf{X}_S \qquad (1)$$

as coordinate transformation in crystal space,

$$\mathbf{S}_R = \mathbf{D}\overline{\mathbf{A}}^{-1}\mathbf{S}_S \qquad (2)$$

is the corresponding transformation in reciprocal space. $\overline{\mathbf{A}}^{-1}$ is the transposed inverse matrix of **A**; the subscripts *C*, *R* and *S* denote directions of oblique crystal axes, oblique reciprocal axes, and standard orthogonal axes (not their lengths). The subscripts *C* and *R* will be used in such a way that quantities, to which either subscript can be attached, will become equal in orthogonal systems. **D** is a diagonal matrix with the elements $a_i a_i^*$, $i = 1,2,3$; a_i and a_i^* are the length of the oblique unit cell and oblique reciprocal cell axes respectively. [Thus **D** is the same matrix as defined in CRU (4·6).] **D** in (2) has been omitted in the Appendix of CR. In order to find the appropriate tensor transformation and the related equations, the set of basic equations CR(1·6) and (1.7) has to be modified for oblique systems.

The electron density distribution is a scalar quantity and is thus invariant w.r.t. coordinate transformations. Hence, with the coordinate transformation (1), the multivariate Gaussian distribution function $t(\mathbf{X}_S)$, as given by CR(1·6), is transformed so that the tensor $\mathbf{U}_S$ is transformed according to

$$\mathbf{U}_C = \mathbf{A}\mathbf{U}_S\overline{\mathbf{A}} \qquad (3)$$

(see *e.g.* Linnik, 1961). The type of distribution function remains unchanged, although $\det \mathbf{U}_C \neq \det \mathbf{U}_S$. The transform $q(\mathbf{S}_R)$ of $t(\mathbf{X}_C)$ also represents a physical property; hence $q(\mathbf{S})$ has to remain constant when **S** is transformed. With (2) and (3) we obtain

$$\begin{aligned}\overline{\mathbf{S}}_R\mathbf{U}_R\mathbf{S}_R &= \overline{\mathbf{S}}_S\mathbf{U}_S\mathbf{S}_S \\ &= \overline{\mathbf{S}}_R\mathbf{D}^{-1}\mathbf{A}\mathbf{A}^{-1}\mathbf{U}_C\overline{\mathbf{A}}^{-1}\overline{\mathbf{A}}\mathbf{D}^{-1}\mathbf{S}_R \\ &= \overline{\mathbf{S}}_R\mathbf{D}^{-1}\mathbf{U}_C\mathbf{D}^{-1}\mathbf{S}_R\,.\end{aligned}$$

($\overline{\mathbf{S}}$ represents a 1×3-row matrix.) Hence

$$\mathbf{U}_R = \mathbf{D}^{-1}\mathbf{U}_C\mathbf{D}^{-1}\,. \qquad (4)$$

(4) shows that the tensor components represented by $\mathbf{U}_C$ and $\mathbf{U}_R$ are in general not equal. **D** is a unit matrix and $\mathbf{U}_R = \mathbf{U}_C$ only for orthogonal systems. With (4) CR(2.2) becomes

$$(b_{ik})_R = 2\pi^2 a_i^{-1} a_k^{-1} (U_{ik})_C\,, \qquad (5)$$

counting 9 elements for $\mathbf{b}_R$. Thus a_i^* in CR(2.2) has to be replaced by a_i^{-1}.

(3) and (5) can also be derived in a different manner. We start from Levy's (1956) equation (4), which we list as

$$(b_{ik})_R = 2\pi^2 \sum_{r=1}^{3} \varrho_{ri}\varrho_{rk}\,. \qquad (6)$$

The elements ϱ_{ri} are defined by Levy's equation (3). Then $\varrho_{ri}\, a_i$ is the *i*th component of the *r*th r.m.s. principal vibration amplitude in Å, where $i = 1,2,3$ denote the crystal axes. Hence

$$(U_{ik})_C = a_i a_k \sum_{r=1}^{3} \varrho_{ri}\varrho_{rk}\,. \qquad (7)$$

We combine (6) and (7), and obtain (5). Now (3) is derived as follows: Let

$$\mathbf{x}_C = \mathbf{F}\mathbf{x}_S \qquad (8)$$

correspond to (1) with the components of **x** in lattice units. Then **A** and **F** are related by

$$\mathbf{A} = \mathbf{N}_C\mathbf{F}\mathbf{N}_s^{-1}\,, \qquad (9)$$

where $\mathbf{N}_C$ and $\mathbf{N}_S$ are diagonal matrices with the elements a_i, $i = 1,2,3$. The transformation of the Miller indices is contragredient to (8). Hence **b** is transformed according to

$$\mathbf{b}_R = \mathbf{F}\mathbf{b}_S\overline{\mathbf{F}}\,. \qquad (10)$$

Now, if (5) is applied to $\mathbf{b}_S$, (10) results in

$$\mathbf{b}_R = 2\pi^2\mathbf{F}\mathbf{N}_s^{-1}\mathbf{U}_S\mathbf{N}_s^{-1}\overline{\mathbf{F}}\,. \qquad (11)$$

We equate (5) and (11), and obtain

$$\mathbf{N}_c^{-1}\mathbf{U}_C\mathbf{N}_c^{-1} = \mathbf{F}\mathbf{N}_s^{-1}\mathbf{U}_S\mathbf{N}_s^{-1}\overline{\mathbf{F}} \qquad (12)$$

which, with the use of (9), gives the desired tensor transformation (3).

We shall now take a different point of view: We accept CR(2.2) as valid – then by definition the components of **U** are given by $\mathbf{U}_R$ – and look for the respective tensor transformation. We combine (3) and (4), solve for $\mathbf{U}_S$, use $\mathbf{B} = \mathbf{A}^{-1}$, and obtain

$$\mathbf{U}_S = (\mathbf{B}\mathbf{D})\mathbf{U}_R(\overline{\mathbf{B}\mathbf{D}})\,. \qquad (13)$$

(13) may also be derived from CR(2.2) in a manner similar to deriving (3) from (5). CR(2.2) and (13) are a set of equations equivalent to the set (5) and (3); either one can be used. CR(2.2) and (3), which correspond to CR(1.7) and to CR(1.6) and which are the basis for computation in CR, form an incorrect set.

Now CRU's revised formula (4.5) for the tensor transformation may be discussed, which we list for reference as

$$\mathbf{U}_S = (\mathbf{D}\mathbf{B})\mathbf{U}_C(\overline{\mathbf{D}\mathbf{B}})\,. \qquad (14)$$

A comparison with (13) shows that the representation $\mathbf{U}_C$ has to be replaced by the representation $\mathbf{U}_R$, but with the use of CR(2.2) – or CRU(2.11) – the representation $\mathbf{U}_R$ is calculated by definition. Still the position of **D** makes equation (14) incorrect.

For the calculation in oblique crystal systems it is important to know the variance properties of the tensor components represented by $\mathbf{U}_R$ and $\mathbf{U}_C$ w.r.t. the relevant systems of base vectors. By definition of $\mathbf{U}_R$ and from (7) we see immediately that $\mathbf{U}_R$ is doubly covariant to the system of the unit base vectors $\mathbf{e}_i^*$ being parallel to the reciprocal axes, and that $\mathbf{U}_C$ is doubly contravariant to the system of the unit base vectors $\mathbf{e}_i$ being parallel to the crystal axes. From (4) we see that $\mathbf{U}_R$ is doubly contravariant to the base vectors $a_i a_i^* \mathbf{e}_i$. (Note that by CRU(4.6) $a_i a_i^*$ does only depend on the angles between the base vectors.) The variance properties may also be understood from the following relation between the metric tensors **h** ($h_{ik} = \mathbf{e}_i \,.\, \mathbf{e}_k$) and h^* ($\mathbf{h}_{ik}^* = \mathbf{e}_i^* \,.\, \mathbf{e}_k^*$) of the unit base vectors

$$\mathbf{h}^* = \mathbf{D}^{-1}\mathbf{h}^{-1}\mathbf{D}^{-1}$$

which parallels (4), and may be derived from the corresponding relation $\mathbf{g}^* = \mathbf{g}^{-1}$ for the metric tensors of the crystal. Hence for the calculation of the mean square vibration amplitude in the direction of a given unit vector **l**, as indicated by CR(1.5), $\mathbf{U}_R$ and the contravariant components of **l** w.r.t. the unit base vectors $\mathbf{e}_i^*$ have to be used. If, on the other hand, $\mathbf{U}_C$ is evaluated, the covariant components of **l** w.r.t. the unit base vectors $\mathbf{e}_i$ must be used.

Consider a monoclinic crystal with $\beta=60°$: If CR(2.2) is used and subsequently (3), the elements 11, 33, 13 of $\mathbf{U}_C$ as needed in (3) will be too small by a factor of 0·78, the elements 12 and 23 by a factor of 0·89, while the element 22 is correctly evaluated. If **DB** in (13) is used instead of **BD**, only the elements 12, 21, 23 and 32 of **BD** become false [except they are all zero as in CRU(4.1)]. The errors introduced are difficult to estimate but are probably of the same order of magnitude.

In Cruickshank's method (1956*b*) the atomic tensors $\mathbf{U}^{\text{obs}}$ are used as data for the least-squares determination of the rigid-body tensors **T** and $\boldsymbol{\omega}$. If the $\mathbf{U}^{\text{obs}}$ have been obtained with an incorrect transformation in oblique systems, the actual values of **T** and $\boldsymbol{\omega}$ will also be incorrect. Nevertheless the agreement $\mathbf{U}^{\text{obs}}$ *versus* $\mathbf{U}^{\text{calc}}$ may still be good. This is suggested by the fact that the transformation $\mathbf{U}_C \rightarrow \mathbf{U}_S$ (or $\mathbf{U}_R \rightarrow \mathbf{U}_S$) is influenced by the errors in the same manner for each atom. However, it cannot be shown rigorously that the differences $\mathbf{U}^{\text{obs}}-\mathbf{U}^{\text{calc}}$ remain completely unaffected by the errors.

It is possible that the errors discussed explain the inconsistencies reported by Lonsdale & Milledge (1961). These authors point out that the atomic principal vibration tensors – obtained from a numerically correct eigenvalue calculation – deviate in a systematic fashion from the atomic vibration tensors – obtained from the rigid-body tensors referred to the 'natural' molecular axes. Lonsdale & Milledge also state that the deviations are less pronounced in orthogonal crystal systems. They give other – physical – explanations for these effects, which, of course, may still be valid.

Principal representations

Two ways of determining the principal presentations of the vibration tensors have been established. In the first approach (Rollett & Davies, 1955; CRU) the tensors are first transformed to orthogonal axes, $\mathbf{U}_R \rightarrow \mathbf{U}_S$, and then the eigenvalues $\boldsymbol{\Lambda}$ and the eigenvectors, as columns of **T**, are determined so that

$$\mathbf{U}_S=\mathbf{T}\boldsymbol{\Lambda}\mathbf{T}^{-1}\,, \tag{15}$$

$\mathbf{T}^{-1}=\overline{\mathbf{T}}$. In the second approach (Waser, 1955; Busing & Levy, 1958) $\boldsymbol{\Lambda}$ is determined directly from **b** and the metric tensor **g** of the crystal system, so that $2\pi^2\boldsymbol{\Lambda}$ is the principal representation of **gb**. The two approaches may now be related and their computational aspects considered.

We show that in both approaches the same lengths of the principal axes are obtained: With (8) **g** is transformed according to

$$\mathbf{g}_C=\overline{\mathbf{F}}^{-1}\mathbf{g}_S\mathbf{F}^{-1}\,,$$

and with (10) we obtain†

$$\mathbf{g}_C\mathbf{b}_R=\overline{\mathbf{F}}^{-1}\mathbf{g}_S\mathbf{b}_S\overline{\mathbf{F}}\,.$$

By definition $\mathbf{g}_S=\mathbf{N}_S\mathbf{N}_S$, and $2\pi^2\mathbf{U}_S=\mathbf{N}_S\mathbf{b}_S\mathbf{N}_S$. Hence $\mathbf{g}_C\mathbf{b}_R$ and $2\pi^2\mathbf{U}_S$ have the same eigenvalues. It cannot be shown generally that in both approaches the same orientation of the principal axes is obtained. For Waser's equation $\mathbf{e}_r=\sum\limits_i(q_i^r/q^r)\mathbf{b}_i$ requires that some actual vector in reciprocal space is used. Thus we can only compare the computational effort. **A**, as defined by (1), must always be set up in terms of three orienting angles. Then **T** can be interpreted in terms of three Eulerian angles. If H_{ri} are the elements of Waser's transformation, **T** is obtained by

$$\mathbf{T}=\mathbf{A}^{-1}\mathbf{N}_C\mathbf{H}^{-1}\,.$$

Also note that $\mathbf{U}_S$ is symmetric and $\mathbf{g}_C\mathbf{b}_R$ is not. [Symmetry may be gained, however, by once determining $\boldsymbol{\gamma}$, so that $\boldsymbol{\gamma}\boldsymbol{\gamma}=\mathbf{g}_C$, and by using $\boldsymbol{\gamma}\mathbf{b}_R\boldsymbol{\gamma}$ instead of $\mathbf{g}_C\mathbf{b}_R$ (Johnson, 1965)]. Thus we conclude that the use of (1), (3) – or (13) – and (15) is the more straightforward computational procedure.

Symmetry transformations

We shall now apply the formal results already obtained to symmetry transformations of the vibration tensors. Vibrating atoms related by a symmetry operation have an equivalent electron-density distribution .Thus this distribution and its transform are invariant with respect to symmetry operations. Hence **b** is also a tensor with respect to symmetry. With the coordinate transformation

$$\mathbf{x}'=\mathbf{G}\mathbf{x} \tag{16}$$

(the components of **x** are in lattice units) the tensor transformation

$$\mathbf{b}'=\mathbf{G}\mathbf{b}\overline{\mathbf{G}} \tag{17}$$

holds. (17) follows from (16) as (3) from (1), or as (10) from (8). This is the shortest derivation of the symmetry-equivalent representations of **b** when compared with the derivations given by Trueblood (1956) and Levy (1956)‡. (17) is an explicit formula whereas Trueblood and Levy only outline a path of solution. (17) is also suited to generate, with a logical program in a computer, the symmetry-equivalent representations of **b** for all crystal classes (space groups). If **G** represents an inversion centre, then $\mathbf{b}'=\mathbf{b}$ as it should be.

We now show that (17) also holds for the transformation of the tensors **U** referred to crystal axes. With (17) we have

$$\mathbf{N}\mathbf{b}'\mathbf{N}/2\pi^2=\mathbf{U}'=\mathbf{N}\mathbf{G}\mathbf{N}^{-1}\mathbf{U}\mathbf{N}^{-1}\overline{\mathbf{G}}\mathbf{N}\,. \tag{18}$$

In the monoclinic and orthorhombic crystal classes **G** is diagonal. In all other classes the permuted coordinates refer to cell edges of the same length. Hence for all possible combinations of rotation axes $\mathbf{N}\mathbf{G}\mathbf{N}^{-1}=\mathbf{G}$. Thus from (18)

$$\mathbf{U}'=\mathbf{G}\mathbf{U}\overline{\mathbf{G}} \tag{19}$$

follows, which parallels (17). By the same reasoning, and with the use of $(\mathbf{N}^*)^{-1}$ instead of **N**, or with (4) and (19), it follows that (19) also holds for the tensors **U** referred to

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† For the tensors **b** and **g** the subscripts *C* and *R* are only used to indicate the fact that the cell is oblique. Although the metric tensor of the reciprocal cell $\mathbf{g}^*$ is covariant to its base vectors, *R* cannot be used to indicate this tensor. For $\mathbf{g}^*\neq\mathbf{g}$ in an orthogonal system. Correspondingly, $\mathbf{b}^{-1}$ being covariant to the base vectors of the crystal cell cannot be denoted by $\mathbf{b}_C$. On the other hand, $\mathbf{h}^*=\mathbf{h}$ in an orthogonal system, and the subscript *R* could have been used instead of the asterisk. The same holds, of course, for the unit base vectors $\mathbf{e}_i^*$. The reverse, however, does not hold for the tensor components represented by $\mathbf{U}_R$ and $\mathbf{U}_C$ w.r.t. their unit base vectors. For we would obtain $\mathbf{U}_C\neq\mathbf{U}$ (without an asterisk) because $\mathbf{U}_C^{-1}=\mathbf{U}$, with **U** being covariant to the unit base vectors $\mathbf{e}_i$. ($\mathbf{U}_R=\mathbf{U}^*$ would be all right.)

‡ Equation (17) has also been obtained by Wells (1965), although his derivation is incorrect for the general case. For, in the trigonal and hexagonal crystal system, **b** and **b′** do not have the same eigenvalues, as in these systems **G** is a non-orthogonal matrix (with the elements +1, 0, −1). Thus Wells's equations (2·10) and (2·11*a*) are incorrect, but the errors compensate each other to yield finally the correct result (2·11*c*).

reciprocal axes. Hence for special positions the restrictions which are valid for the components of **b** are equally valid for the components of **U** referred to either crystal or reciprocal axes. .

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On the refinement of thermal rigid-body vibration tensors.

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Cruickshank (1956) – here referred to as CK – was the first to propose a procedure for the refinement of rigid-body vibration tensors. These are obtained in a least-squares procedure, in which the vibration tensors of the individual atoms are used as data. These tensors in turn have been obtained from a normal refinement with diffraction data. Recently Pawley (1964) – here referred to as PA – described a least-squares method for refining rigid-body tensors by making direct use of diffraction data. The question arises whether or not the two approaches yield the same results. It turns out that this is true only under certain conditions, which will be determined in this paper. This provides a theoretical foundation for the setting of weights in CK's determination of rigid-body tensors.

For n atoms in the molecule assumed to be rigid, CK equation (2·3) may be written in matrix notation as

$$\mathbf{U}=\mathbf{R}\mathbf{T}\,, \tag{1}$$

where **U** represents the $6n$ components of the n atomic tensors, **T** the 12 components of CK's molecular tensors **T** and **ω**. **R** is a $6n\times 12$-matrix with the coefficients of CK (2·3). If the increments ε_U and ε_T of **U** and **T** are substituted in (1), then CK's normal equations (2·5) may be written as

$$\overline{\mathbf{R}}\mathbf{P}\mathbf{R}\varepsilon_T=\overline{\mathbf{R}}\mathbf{P}\varepsilon_U{}^{\mathrm{obs}}\,. \tag{2}$$

P is a $6n\times 6n$ weighting matrix, $\overline{\mathbf{R}}$ the transpose of **R**. Let

$$\mathbf{M}\varepsilon_U{}^{\mathrm{obs}}=\mathbf{N} \tag{3}$$

be the normal equations for determining $\varepsilon_U{}^{\mathrm{obs}}$, then PA's approach can be shown to have the normal equations

$$\overline{\mathbf{R}}\mathbf{M}\mathbf{R}\varepsilon_T=\overline{\mathbf{R}}\mathbf{N}\,. \tag{4}$$

If we now introduce $\varepsilon_U{}^{\mathrm{obs}}=\mathbf{M}^{-1}\mathbf{N}$ in (2), comparison of (2) and (4) shows that these equations are equivalent only if $\mathbf{P}=\mathbf{M}$. Thus CK's and PA's approaches are equivalent, if **M** of the last cycle of structure-factor refinement is chosen to be the weighting matrix. **M** is proportional to the inverse of the covariance matrix of the thermal parameters of the individual atoms, which in turn is obtained from the covariance matrix of the intensity data. Hence the use of **M** as weighting matrix is in accordance with the Gaussian law of setting weights.

The use of **M** as weighting matrix greatly increases the amount of computation necessary in CK's determination of rigid-body tensors. Furthermore, **M** is usually not available, because structure-factor refinement is usually carried out with respect to atomic vibration tensors, which are referred to the reciprocal axes of the crystal system rather than to the molecular axes. Thus we shall now derive a simple but sufficient approximation **Q** which may be used instead of **M** in all practical work.

At first we assume that the Cartesian coordinate system of the molecule coincides in direction with the (orthogonal) crystal system. The results obtained with this assumption will be generalized below. The elements of **M** are

$$M^r_{st}=\Sigma w\,\frac{\partial|F|}{\partial U^r_s}\,\frac{\partial|F|}{\partial U^r_t}\,, \tag{5}$$

w being the weights of the experimental data, F the structure factor. r denotes the atom, $s,\ t=1\ldots6$ the independent components of $\mathbf{U}^r$. We now use unitary form factors $\hat{f}$ for all atoms, given by $f_r=\hat{f}Z_r$, where Z_r is the number of electrons in the rth atom. Let G_r be the geometrical structure-factor term, and $V_s=S_iS_k$ with subscript $s=s(i,k)$ for the elements of $\mathbf{U}^r$ in the sequence 11, 22, 33, 12, 13, 23, and let S_i be the ith component in reciprocal space (in Å^{-1}) of the reflexion considered, then

$$M^r_{st}\simeq 4\pi^4Z_r^2\Sigma w\hat{f}^2\exp\left(-2\overline{\mathbf{h}}\boldsymbol{\beta}_r\mathbf{h}\right)G_r^2V_sV_t\,. \tag{6}$$

h is a 3×1-column matrix of the Miller indices, $\boldsymbol{\beta}_r$ the anisotropic parameter matrix. If one of the indices s or t is >3, a factor of 2 enters on the right-hand side of (6) owing to the symmetry of $\mathbf{U}^r$. For $s>3$, $t>3$ the factor is 4. These factors will be introduced into the final result. We now assume that the data have been obtained with equal quality in each spherical shell of the reciprocal space and that their number is infinite in a finite region. Furthermore, the temperature factor is assumed to be isotropic. Also some mean value G^2_{sh} of G^2_r, assumed to be the same for each atom, is constant for integration over the shell. (These approximations have also been used by Scheringer (1965) to derive an approximate matrix for positional parameters.) With these approximations the factors $4\pi^4$, w, $\hat{f}^2$, $\exp(-2\overline{\mathbf{h}}\boldsymbol{\beta}_r\mathbf{h})$ and