It is to be observed that the data of Hendricks are substantially confirmed in so far as concerns the coordinates of the halogens and the pair of halogens between which are the benzene rings. There is, however, disagreement in the orientation and shape of the benzene rings, which, according to Hendricks, should be hexagonal strongly deformed rings, almost parallel to the 001 plane.

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An Orthogonal Unit Vector Triplet Associated with a General Lattice*

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It is shown that there exists an orthogonal unit vector system **E** and a symmetric matrix γ (together with its inverse γ^*) such that the four expressions

$$\mathbf{a} = \gamma\mathbf{E};\ \mathbf{E} = \gamma\mathbf{a}^*;\ \mathbf{a}^* = \gamma^*\mathbf{E};\ \mathbf{E} = \gamma^*\mathbf{a}$$

give the transformations between the systems **a**, **a*** and **E**. The γ-matrices are then defined by the matrix equations $\gamma^2 = \mathbf{g}$ and $\gamma^{*2} = \mathbf{g}^*$. The solutions are given explicitly for all two-dimensional nets and for all symmetrical three-dimensional lattices. Methods are suggested for the numerical calculation for the triclinic lattice. Uses for the **E**-systems in crystal calculations are also discussed.

This paper is concerned with normal orthogonal vector triplet systems $\mathbf{E}_i$ which are unique among the infinitely many possible normal orthogonal systems $\mathbf{e}_i$ in the sense that the linear transformation which expresses the triplet $\mathbf{E}_i$ in terms of $\mathbf{a}_i$ is the same as that which expresses the $\mathbf{a}_i^*$ in terms of the $\mathbf{E}_i$.

Although little application has as yet been made of these systems, their theoretical interest seems to merit a presentation of their properties.

Properties of the E-systems

For the axial system $\mathbf{a}_i$, represented in matrix notation by the symbol **a**, the metric tensor has a matrix representation **g** with components

$$g_{ij} = (\mathbf{a}_i\mathbf{a}_j) \qquad (1a)$$

while the determinant of the matrix **g** has the value g. Similarly the reciprocal system $\mathbf{a}_i^*$ is represented by the matrix symbol **a*** and has for reciprocal metric tensor the matrix **g*** with components

$$g_{ij}^* = (\mathbf{a}_i^*\mathbf{a}_j^*)\,, \qquad (1b)$$

with determinant g^*. The matrix **g*** is thus the inverse of **g**, i.e.

$$\mathbf{g}\mathbf{g}^* = \mathbf{1} \qquad (2a)$$

and

$$gg^* = 1\,. \qquad (2b)$$

It is well known (cf. Ewald, 1923, note 1) that

$$\mathbf{a} = \mathbf{g}\mathbf{a}^* \qquad (3a)$$

and also that

$$\mathbf{a}^* = \mathbf{g}^*\mathbf{a}\,. \qquad (3b)$$

We now define a vector system **E** (without further specification of its properties), and a matrix γ with components γ_{ij} such that

$$\mathbf{a} = \gamma\mathbf{E} \qquad (4a)$$

and

$$\mathbf{E} = \gamma\mathbf{a}^*\,. \qquad (4b)$$

If γ^* is the inverse matrix to γ we have

$$\mathbf{a}^* = \gamma^*\mathbf{E} \qquad (5a)$$

and

$$\mathbf{E} = \gamma^*\mathbf{a}\,. \qquad (5b)$$

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Table 1. $\boldsymbol{\gamma}$-*Matrices for plane nets*

Net	$\boldsymbol{\gamma} = \mathbf{g}^{\frac{1}{2}} = \boldsymbol{\gamma}^{*-1}$		$\boldsymbol{\gamma}^* = \mathbf{g}^{*\frac{1}{2}} = \boldsymbol{\gamma}^{-1}$	
Rhombic				
$a_1 \neq a_2 \quad \alpha_{12} \neq \pi/2$	$A_{11}/(A_{11}+A_{22})^{\frac{1}{2}}$	$g_{12}/(A_{11}+A_{22})$	$A^*_{11}/(A^*_{11}+A^*_{22})^{\frac{1}{2}}$	$g^*_{12}/(A^*_{11}+A^*_{22})^{\frac{1}{2}}$
$A_{11} = g_{11}+\sqrt{g}$	$g_{12}/(A_{11}+A_{22})^{\frac{1}{2}}$	$A_{22}/(A_{11}+A_{22})^{\frac{1}{2}}$	$g^*_{12}/(A^*_{11}+A^*_{22})^{\frac{1}{2}}$	$A^*_{22}/(A^*_{11}+A^*_{22})^{\frac{1}{2}}$
$A_{22} = g_{22}+\sqrt{g}$				
Equilateral				
$a_1 = a_2 = a$	$\frac{a}{\sqrt{2}}(1+s)^{\frac{1}{2}}$	$\frac{ac}{\sqrt{2}.(1+s)^{\frac{1}{2}}}$	$\frac{(1+s)^{\frac{1}{2}}}{\sqrt{2}.as}$	$\frac{-c}{\sqrt{2}.as(1+s)^{\frac{1}{2}}}$
$\alpha_{12} \neq \pi/2$ or $2\pi/3$				
$c = \cos\alpha_{12}$, $s = \sin\alpha_{12}$	$\frac{ac}{\sqrt{2}.(1+s)^{\frac{1}{2}}}$	$\frac{a}{\sqrt{2}}(1+s)^{\frac{1}{2}}$	$\frac{-c}{\sqrt{2}.as(1+s)^{\frac{1}{2}}}$	$\frac{(1+s)^{\frac{1}{2}}}{\sqrt{2}.as}$
Hexagonal				
$a_1 = a_2 = a$	$\frac{a(1+\sqrt{3})}{2\sqrt{2}}$	$\frac{-a}{\sqrt{2}.(1+\sqrt{3})}$	$\frac{(1+\sqrt{3})}{a\sqrt{6}}$	$\frac{\sqrt{2}}{a\sqrt{3}.(1+\sqrt{3})}$
$\alpha_{12} = 2\pi/3$				
	$\frac{-a}{\sqrt{2}.(1+\sqrt{3})}$	$\frac{a(1+\sqrt{3})}{2\sqrt{2}}$	$\frac{\sqrt{2}}{a\sqrt{3}.(1+\sqrt{3})}$	$\frac{(1+\sqrt{3})}{a\sqrt{6}}$
Orthogonal				
$a_1 \neq a_2$	a_1	0	$1/a_1$	0
$\alpha_{12} = \pi/2$	0	a_2	0	$1/a_2$
Square				
$a_1 = a_2 = a$	a	0	$1/a$	0
$\alpha_{12} = \pi/2$	0	a	0	$1/a$

By a combination of equations (3), (4) and (5) it is clear that

$$\boldsymbol{\gamma}^2 = \mathbf{g} \tag{6a}$$

and

$$\boldsymbol{\gamma}^{*2} = \mathbf{g}^* . \tag{6b}$$

The system **E** thus satisfies the transformation condition specified in the first paragraph of this paper and we have shown that the required transformation matrix is a square root of the metric tensor matrix for the axial system. The existence of the triplet **E** thus follows from that of a square root for the matrix **g** and for its inverse **g***. The fact that **E** is normal and orthogonal then depends on the following argument.

Since $\boldsymbol{\gamma}^*$ is the inverse of $\boldsymbol{\gamma}$ we have

$$\gamma_{ij}\gamma^*_{jk} = \delta_{ik} , \tag{7}$$

in which summation is implied by the repeated index j and δ_{ik} is the Kronecker delta. We also have the definition of the reciprocal triplet

$$(\mathbf{a}_i\mathbf{a}^*_j) = \delta_{ij} . \tag{8}$$

We now expand equations (4*b*) and (5*b*) in the forms

$$\mathbf{E}_i = \gamma_{ip}\mathbf{a}^*_p \tag{9a}$$

and

$$\mathbf{E}_j = \gamma^*_{jq}\mathbf{a}_q , \tag{9b}$$

and from these expressions obtain the scalar products

$$(\mathbf{E}_i\mathbf{E}_j) = \gamma_{ip}\gamma^*_{jq}(\mathbf{a}^*_p\mathbf{a}_q) = \gamma_{ip}\gamma^*_{qj}\delta_{pq} = \gamma_{ip}\gamma^*_{pj} = \delta_{ij} . \tag{10}$$

The triplet **E** thus forms a normal orthogonal system, and the matrix $\boldsymbol{\gamma}$ satisfies the required transformation conditions.

Calculation of the matrix $\boldsymbol{\gamma}$

The n^2 components of the matrix $\boldsymbol{\gamma}$ in n dimensions must satisfy the n^2 equations

$$\gamma_{ik}\gamma_{kj} = g_{ij} . \tag{11}$$

Since the matrix **g** is symmetric, and it can be shown that $\boldsymbol{\gamma}$, its square root, is also symmetric, only $\frac{1}{2}n(n+1)$ of the equations (11) are independent. In two dimensions and for simple cases in three dimensions these equations are easily soluble.

The forms which the matrix $\boldsymbol{\gamma}$ takes for the various two-dimensional nets are exhibited in Table 1 from which it appears that an explicit solution of the problem can be found for the general plane net. In three dimensions explicit solutions can be found for all cells except the triclinic, and the latter must also be taken to include the primitive cells of the orthorhombic and monoclinic centered lattices. The explicit results for three dimensions are shown in Table 2.

Examination of the tables indicates that for the orthogonal nets and lattices the directions of the vectors $\mathbf{E}_i$ are the same as the coinciding directions of the vectors $\mathbf{a}_i$ and $\mathbf{a}^*_i$. The unit length of $\mathbf{E}_i$ is clearly the geometric mean of the lengths a_i and $1/a_i$ of the base and reciprocal vectors respectively. In the

Table 2. $\boldsymbol{\gamma}$-*Matrices for space lattices*

Lattice	$\boldsymbol{\gamma} = \mathbf{g}^{\frac{1}{2}} = \boldsymbol{\gamma}^{*-1}$	$\boldsymbol{\gamma}^* = \mathbf{g}^* = \boldsymbol{\gamma}^{-1}$
Monoclinic		
$\alpha_{12} = \alpha_{23} = \pi/2$	$\begin{matrix} A_{11}(A_{33}+A_{11})^{\frac{1}{2}} & 0 & g_{31}/(A_{33}+A_{11})^{\frac{1}{2}} \\ 0 & a_2 & 0 \\ g_{31}/(A_{33}+A_{11})^{\frac{1}{2}} & 0 & A_{33}/(A_{33}+A_{11})^{\frac{1}{2}} \end{matrix}$	$\begin{matrix} A^*_{11}/(A^*_{33}+A^*_{11})^{\frac{1}{2}} & 0 & g^*_{31}(A^*_{33}+A^*_{11})^{\frac{1}{2}} \\ 0 & a^*_2 & 0 \\ g^*_{31}/(A^*_{33}+A^*_{11})^{\frac{1}{2}} & 0 & A^*_{33}/(A^*_{33}+A^*_{11})^{\frac{1}{2}} \end{matrix}$
$A_{11} = g_{11}+\gamma/(gg^*_{22})$		
$A_{33} = g_{33}+\gamma/(gg^*_{22})$		
Hexagonal		
$a_1 = a_2$, $\alpha_{12} = 2\pi/3$	$\begin{matrix} \frac{a_1(1+\gamma 3)}{2\gamma 2} & \frac{-a_1}{\gamma 2.(1+\gamma 3)} & 0 \\ \frac{-a_1}{\gamma 2.(1+\gamma 3)} & \frac{a_1(1+\gamma 3)}{2\gamma 2} & 0 \\ 0 & 0 & a_3 \end{matrix}$	$\begin{matrix} \frac{(1+\gamma 3)}{a_1\gamma 6} & \frac{\gamma 2}{a_1\gamma 3.(1+\gamma 3)} & 0 \\ \frac{\gamma 2}{a_1\gamma 3.(1+\gamma 3)} & \frac{(1+\gamma 3)}{a_1\gamma 6} & 0 \\ 0 & 0 & 1/a_3 \end{matrix}$
$\alpha_{23} = \alpha_{31} = \pi/2$		
Rhombohedral		
$a_1 = a_2 = a_3 = a$	$\begin{matrix} a(A+2B)/3 & a(A-B)/3 & a(A-B)/3 \\ a(A-B)/3 & a(A+2B)/3 & a(A-B)/3 \\ a(A-B)/3 & a(A-B)/3 & a(A+2B)/3 \end{matrix}$	$\begin{matrix} (2A+B)/3aAB & -(A-B)/3aAB & -(A-B)/3aAB \\ -(A-B)/3aAB & (2A+B)/3aAB & -(A-B)/3aAB \\ -(A-B)/3aAB & -(A-B)/3aAB & (aA+B)/3aAB \end{matrix}$
$\alpha_{12} = \alpha_{23} = \alpha_{31} = \alpha$		
$\cos\alpha = c$		
$A = \gamma(1+2c)$ $B = \gamma(1-c)$		
Orthogonal		
$\alpha_{12} = \alpha_{23} = \alpha_{31} = \pi/2$	$\begin{matrix} a_1 & 0 & 0 \\ 0 & a_2 & 0 \\ 0 & 0 & a_3 \end{matrix}$	$\begin{matrix} 1/a_1 & 0 & 0 \\ 0 & 1/a_2 & 0 \\ 0 & 0 & 1/a_3 \end{matrix}$

more general systems the notion of geometric mean is given a wider meaning, as indicated in Fig. 1 in which it is seen that the **E**-system lies between the **a** and **a*** systems for the rhombic net in position and in dimensions.

While most of the results of Tables 1 and 2 were obtained by solution of special cases of the equations (11), theoretical discussion is facilitated by reference to more general theory, and it is only in terms of this more general theory that it is at all convenient to deal with the case of the general triclinic lattice.

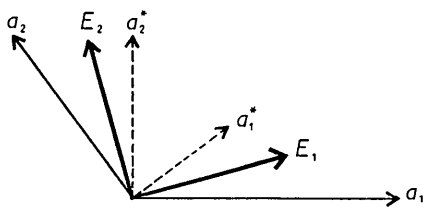

Fig. 1. **E**-system for a plane lattice. The **a**-system is indicated by light full lines, the reciprocal system **a*** by dashed lines, and the orthonormal **E**-system by heavy full lines.

The calculation of the 2^n roots an $(n \times n)$ matrix is discussed in many places (e.g. Wedderburn, 1934; Frazer, Duncan & Collar, 1950). The matrix $\mathbf{g}$ can be transformed to diagonal form by the similarity transformation

$$\mathbf{ugu}^{-1} = \Lambda\,, \tag{12}$$

in which $\mathbf{u}$ is an orthogonal matrix and the matrix Λ is of the form ($n = 3$):

$$\Lambda = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}. \tag{13}$$

In this matrix, the λ_i are the roots of the characteristic equation

$$\Delta(\lambda) = |\lambda\mathbf{1} - \mathbf{g}| = \begin{vmatrix} \lambda - g_{11} & -g_{12} & -g_{13} \\ -g_{21} & \lambda - g_{22} & -g_{23} \\ -g_{31} & -g_{32} & \lambda - g_{33} \end{vmatrix} = 0 \tag{14}$$

of the matrix $\mathbf{g}$. In two dimensions, equation (14) can be solved explicitly as a quadratic and in three dimensions, for all the cases of Table 2, this equation is factorable. In the general triclinic case it must be solved by numerical methods as a cubic equation. It may be shown from the properties of the matrix $\mathbf{g}$ that equation (14) has three real positive roots, the components of the matrix Λ.

The transformation matrix $\mathbf{u}$ is calculated from the matrix equation

$$\mathbf{ug} = \Lambda\mathbf{u} \tag{15}$$

obtained from (12) by post-multiplication by $\mathbf{u}$. In component form (15) is expressed in the nine equations

$$\left.\begin{matrix} u_{i1}(g_{11}-\lambda_i)+u_{i2}g_{21} & +u_{i3}g_{31} & = 0\,, \\ u_{i1}g_{12} & +u_{i2}(g_{22}-\lambda_i)+u_{i3}g_{32} & = 0\,, \\ u_{i1}g_{13} & +u_{i2}g_{23} & +u_{i3}(g_{33}-\lambda_i) = 0\,, \end{matrix}\right\} \tag{16}$$

and in addition there are three equations

$$u_{i1}^2+u_{i2}^2+u_{i3}^2 = 1\,. \tag{17}$$

The condition (14) on the coefficients of the equations (16) indicates that at least one non-trivial solution

exists and that in case of multiple roots for (14), infinitely many such solutions may exist. From the solutions of (16) and (17) we need choose only one for the transformation (12).

The fact that the relations between matrix functions are preserved under similarity transformations enables us to write

$$\mathbf{u}\mathbf{g}^{\frac{1}{2}}\mathbf{u}^{-1} = \mathbf{u}\boldsymbol{\gamma}\mathbf{u}^{-1} = \Lambda^{\frac{1}{2}}, \tag{18}$$

in which $\Lambda^{\frac{1}{2}}$ is of course

$$\Lambda^{\frac{1}{2}} = \begin{pmatrix} \lambda_1^{\frac{1}{2}} & 0 & 0 \\ 0 & \lambda_2^{\frac{1}{2}} & 0 \\ 0 & 0 & \lambda_3^{\frac{1}{2}} \end{pmatrix}. \tag{19}$$

Equation (18) can be written

$$\mathbf{g}^{\frac{1}{2}} = \boldsymbol{\gamma} = \mathbf{u}^{-1}\Lambda^{\frac{1}{2}}\mathbf{u}, \tag{20}$$

which is the solution to our problem. There are clearly 2^n values for the matrix $\Lambda^{\frac{1}{2}}$ and hence 2^n values for the matrix $\boldsymbol{\gamma}$ since it can be shown that a change in the order of naming the roots λ_i does not affect the result, nor does any ambiguity in the choice of $\mathbf{u}$ from among the solutions to (16) and (17).

Each of the 2^n values of $\boldsymbol{\gamma}$ can be used to define an **E**-system via equations (4) and (5). We have, however, selected only one of these systems as of crystallographic interest and that is the system for which all roots in the diagonal of the matrix (19) are taken as positive to correspond to the positive values of the terms of the matrix (13). In this way we insure that the matrix $\boldsymbol{\gamma}$ shall correspond to a homogeneous strain, as does the matrix $\mathbf{g}$. For any other choice of signs* in (19), the $\boldsymbol{\gamma}$-matrix will involve strain combined with an inversion, reflection, or rotation. The latter part of the operation is then removed by a second application leaving the operation $\boldsymbol{\gamma}^2$ as a pure strain once more.

Yet another method for the calculation of $\boldsymbol{\gamma}$ is contained in an application of Sylvester's theorem (cf. Frazer, Duncan & Collar, 1950, § 3·9–3·10). We define the matrix

$$\mathbf{f}(\lambda) = \lambda\mathbf{1} - \mathbf{g}, \tag{21}$$

where $\mathbf{g}$ is any matrix. Then $\mathbf{f}(\lambda_i)$ is matrix obtained from $\mathbf{f}(\lambda)$ by substituting in it one of the roots of equation (14). $\mathbf{F}(\lambda_i)$ is the adjoint of the matrix $\mathbf{f}(\lambda_i)$, i.e. the transposed matrix of the cofactors of the components of $\mathbf{f}(\lambda_i)$. Sylvester's theorem then states that a function $P(\mathbf{g})$ of the matrix $\mathbf{g}$ is given by

$$P(\mathbf{g}) = \sum_i P(\lambda_i)\mathbf{Z}_0(\lambda_i) \tag{22}$$

in which the characteristic roots λ_i are distinct* and the matrices $\mathbf{Z}_0(\lambda_i)$ are given by

$$\mathbf{Z}_0(\lambda_i) = \mathbf{F}(\lambda_i)/\Delta'(\lambda_i) \tag{22a}$$

in which

$$\Delta'(\lambda_i) = [d\Delta(\lambda)/d\lambda]_{\lambda=\lambda_i}. \tag{22b}$$

Thus

$$\boldsymbol{\gamma} = \mathbf{g}^{\frac{1}{2}} = \sum_i \lambda_i^{\frac{1}{2}}\mathbf{Z}_0(\lambda_i) \tag{23}$$

is an alternative form for the solution to our problem. From this expression we see clearly that there are 2^n roots and that the result is independent of the order of naming of the roots and is also independent of the choice of $\mathbf{u}$ in (20) since $\mathbf{u}$ does not appear explicitly in (23).

Numerical example

To illustrate the method for calculating $\boldsymbol{\gamma}$ and hence $\mathbf{E}$ for a general triclinic crystal, the results of the calculation for copper sulphate pentahydrate are given. The lattice constants (Beevers & Lipson, 1934) are

$$a(a_1) = 6{\cdot}12 \text{ Å};\ b(a_2) = 10{\cdot}7 \text{ Å};\ c(a_3) = 5{\cdot}97 \text{ Å};$$
$$\alpha(\alpha_{23}) = 82°\ 16';\ \beta(\alpha_{31}) = 107°\ 26';\ \gamma(\alpha_{12}) = 102°\ 40';$$
$$V = 363 \text{ Å}^3.$$

The matrix $\mathbf{g}$ and its adjoint $\mathbf{G}$ then take the forms†

$$\mathbf{g} \equiv \begin{pmatrix} 37{\cdot}4544 & -14{\cdot}3451 & -10{\cdot}9643 \\ -14{\cdot}3451 & 114{\cdot}4900 & 8{\cdot}5917 \\ -10{\cdot}9643 & 8{\cdot}5917 & 35{\cdot}6409 \end{pmatrix} (\text{Å}^2)$$

and

$$\mathbf{G} \equiv \begin{pmatrix} 4006{\cdot}71 & 417{\cdot}39 & 1131{\cdot}98 \\ 417{\cdot}39 & 1214{\cdot}69 & -164{\cdot}42 \\ 1131{\cdot}98 & -164{\cdot}42 & 4082{\cdot}11 \end{pmatrix} (\text{Å}^4).$$

From these one calculates the coefficients of the equation (14), i.e.

$$\Delta(\lambda) = \lambda^3 - \lambda^2 \operatorname{tr}\mathbf{g} + \lambda \operatorname{tr}\mathbf{G} - g = 0$$

in which tr $\mathbf{g}$ stands for the trace (i.e. the sum of the leading diagonal terms) of the matrix $\mathbf{g}$. The numerical values of these quantities are: tr $\mathbf{g}$ = 187·5853 Å^2; tr $\mathbf{G}$ = 9303·51 Å^4; and g = 131,666 Å^6. As a check, one computes $g^{\frac{1}{2}} = 362{\cdot}85 \approx 363$ Å^3 for the cell volume. The solution of the characteristic equation by Horner's method and factoring then leads to λ_1 = 25·3958 Å^2; λ_2 = 43·7882 Å^2; λ_3 = 118·4014 Å^2 and hence to $\sqrt{\lambda_1}$ = 5·0394 Å; $\sqrt{\lambda_2}$ = 6·6172 Å; $\sqrt{\lambda_3}$ = 10·8812 Å. Substitution of the λ_i values in (21) then leads to values of the three matrices $\mathbf{f}(\lambda_i)$ and of their three adjoints $\mathbf{F}(\lambda_i)$ which are not given here to save printing. The values for the quantities (22b) are then computed as $\Delta'(\lambda_1)$ = 1710·59 Å^2; $\Delta'(\lambda_2)$ = −1372·32 Å^2; $\Delta'(\lambda_3)$ = 6939,46 Å^2. The quantities $\sqrt{\lambda_i}/\Delta'(\lambda_i)$ are then

* It was thought for a long time by the author that the 2^n possible **E**-systems corresponded merely to the 2^n ways of choosing base vectors from an axial cross in n dimensions. While this is true in special cases, it is not true in general. This can be seen most easily in the case of the rhombic net (Table 1). A second solution is obtained by replacing $\sqrt{g}$ by $-\sqrt{g}$ in the solution given. The third and fourth solutions are obtained from the first two by inversion. It is then clear that in general the relation between the first two solutions is not merely a simple interchange of axes.

* If the roots λ_i are not distinct, a special form of Sylvester's theorem must be used (Frazer *et al.*, 1950, § 3·10).

† Note that several extra figures are carried throughout to avoid rounding errors (cf. Scarborough, 1950, chap. 1 and also Frazer *et al.*, 1950, chap. 4).

computed and used as multipliers for the matrices $\mathbf{F}(\lambda_i)$ in computing the expression (23). If positive signs for the roots are used we obtain

$$\gamma \equiv \begin{pmatrix} 5{\cdot}9969 & -0{\cdot}8366 & -0{\cdot}8894 \\ -0{\cdot}8836 & 10{\cdot}6565 & 0{\cdot}4744 \\ -0{\cdot}8894 & 0{\cdot}4744 & 5{\cdot}8842 \end{pmatrix}.$$

From this the adjoint $\mathbf{\Gamma}$ can be calculated, the determinant γ and hence the matrix

$$\gamma^* \equiv \begin{pmatrix} 0{\cdot}17220 & 0{\cdot}01240 & 0{\cdot}02503 \\ 0{\cdot}01240 & 0{\cdot}09507 & -0{\cdot}00579 \\ 0{\cdot}02503 & -0{\cdot}00579 & 0{\cdot}01622 \end{pmatrix},$$

which completes the solution to the problem.

Discussion

The existence of the **E**-systems was first recognized in the course of the consideration of orthogonal systems suitable for use with triclinic and monoclinic crystals in the discussion of bond lengths and bond angles. It was realized if coordinate vectors only were under discussion, one matrix and its inverse were needed for transformation between the base lattice and the **e**-system. If, in addition, indices and direction vectors were needed, a second matrix and its inverse would be needed to provide the transformation between the reciprocal lattice and the **e**-system. Thus a total of four transformation matrices is required for work in terms of a general **e**-system while only two matrices γ and γ^* are needed if an **E**-system is used.

For those cases in which the γ-matrices can be written explicitly in terms of the lattice constants (e.g. Tables 1 and 2) the **E**-systems may prove to be very useful. In the orthogonal lattices the choice of the **E**-systems is obvious. In other systems a number of possible **e**-systems are available and it may be that the choice of the **E**-system will prove to be advantageous.

It is unfortunate that, for the triclinic system in which the use of an **E**-system would undoubtedly be the most profitable, the calculation of the γ-matrices is the most difficult. It is expected, however, that if the **E**-systems prove to be of value, the technique of the calculation of the γ-matrices can be improved considerably.

The existence of the **E**-systems introduces an interesting speculation. The problem of the diffraction analysis of structures depends on the interaction of data which belong in crystal space, such as atomicity, positivity, closest approach etc., with data, such as diffraction amplitude, phase, which belong in reciprocal space. The transformation of data from one space to the other always results in considerable increase in complication, as is indicated by the nature of the many ingenious methods of direct structural analysis which are now under consideration. The existence of an **E**-system 'midway' between the **a**-system and the **a***-system suggests the possibility of a function space occupying a similar position between crystal space and transform space. There seems to be little indication of the nature of the functional transformation needed, but the γ-matrix suggests a coordinate transformation which would provide a geometric basis for such a functional space.

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The Crystal Structure of Phosgene, $COCl_2$

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The crystal structure of phosgene is tetragonal C_{4h}^6–$I4_1/a$ with 16 phosgene molecules in a unit cell of dimensions $a = b = 15{\cdot}82$, $c = 5{\cdot}72$ Å. At $-160°$ C., the crystal is completely ordered, and the residual entropy of 1·63 e.u. remains unexplained. Parameters, referred to a center of symmetry as origin, are for Cl_1, (0·0394, −0·1417, 0·150); for Cl_2, (0·1038, −0·0528, −0·250); for O, (0·1982, −0·1306, 0·039); and for C, (0·1295, −0·1126, −0·004). Molecular dimensions are $C–Cl_1 = 1{\cdot}74 \pm 0{\cdot}02$ Å, $C–Cl_2 = 1{\cdot}74 \pm 0{\cdot}02$ Å, $C=O = 1{\cdot}15 \pm 0{\cdot}02$ Å, and $Cl_1–C–Cl_2 = 111{\cdot}0 \pm 1.5°$.

Introduction

As a result of a careful calorimetric study in which the spectroscopic assignment (Thompson, 1941; Stevenson & Beach, 1938*a*, *b*, *c*) and molecular geometry (Brockway, Beach & Pauling, 1935) were employed, Giauque & Jones (1948) have attributed a residual entropy of 1·63 e.u. to phosgene. The purpose of the