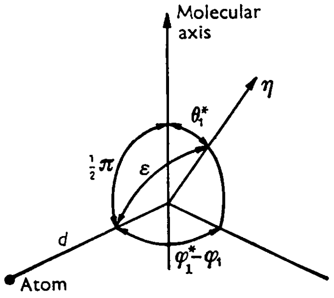

Fig. 2.

which, using (5), gives

$$G(\boldsymbol{\eta}) = \mu . (\pi/2z^*)^{\frac{1}{2}} \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left\{ (2n+1)(-i)^n J_{n+\frac{1}{2}}(z^*) \times \frac{(n-m)!}{(n+m)!} P_n^m (\cos \tfrac{1}{2}\pi) P_n^m (\cos \theta_1^*) \exp [im(\varphi_1^*-\varphi_1)] \right\} .$$

This is an expansion of $G(\boldsymbol{\eta})$ in spherical harmonics. Now

$$P_{2n+1}(0) = 0 ,$$

$$P_{2n}(0) = (-)^n . (2n)!/2^{2n}(n!)^2 .$$

Hence

$$G^0_{2n+1}(r^*) = 0,$$

$$G^0_{2n}(r^*) = \mu \cdot \frac{(4n+1)(2n)!}{2^{2n} . (n!)^2} \cdot (\pi/2z^*)^{\frac{1}{2}} . J_{2n+\frac{1}{2}}(z^*) .$$

Therefore, the contribution this atom makes to the average intensity per molecule from the whole assemblage is

$$I_i(r^*,\theta^*) = \sum_{n=0}^{\infty} \frac{(2n)!}{2^{2n}(n!)^2} D_{2n}\mu_i(d_ir^*)^{-\frac{1}{2}} J_{2n+\frac{1}{2}}(2\pi d_ir^*) P_{2n} (\cos \theta^*) .$$

Here subscripts i have been added to all quantities referring to the particular atom considered. The average intensity per molecule is therefore

$$I(r^*,\theta^*) = \sum_i I_i(r^*,\theta^*) ,$$

where the summation is taken over all atoms in the Patterson fold of the real molecule.

Two things about this summation should be noted. First, since d_i always occurs together with r^* as the product r^*d, a change in the value of d leaves the form of $I(r^*, \theta^*)$ unchanged and the effect can be regarded as a change in the scale of r^*. A similar remark is true of the previous example. Secondly, the contribution of the large atom at the origin of the Patterson fold is large, positive and constant, and will therefore prevent $I(r^*, \theta^*)$ from becoming negative, as it would do otherwise.

The method of this paper is to express $G(\boldsymbol{\eta})$ etc. as spherical harmonic expansions. This is the mathematical form most suited for averaging a function over various orientations about a fixed point. In this paper the function so averaged is $G(\boldsymbol{\eta})$. This choice is dictated by the physics of the problem. The averaging process can be applied equally well to $F(\boldsymbol{\eta})$, the Fourier transform of the molecular density, to give a mean structure factor (Zachariasen, 1945, p. 223) though in certain problems difficulties may arise from phase factors.

The author is indebted to Prof. P. P. Ewald, who suggested this problem, for advice and encouragement and to The Queen's University of Belfast for the award of a Senior Studentship.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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A graphical method for applying Harker–Kasper inequalities to structure determination.

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For a centro-symmetrical structure, the inequalities of Harker & Kasper (1948) permit us to determine the signs of structure factors or to deduce relations among them. One important inequality generally applicable to a centro-symmetrical structure is

$$(U_H \pm U_{H'})^2 \leq (1 \pm U_{H+H'})(1 \pm U_{H-H'}) , \qquad (1)$$

where U_H is the unitary structure factor for the reflexion $H = hkl$. Since the computational application of (1) involves multiplication, it is rather tedious to deal with such a great number of combinations of U_H's appearing in (1) as is necessary in an actual procedure of sign determination. In view of this fact, a graphical method is devised which requires no computation and is convenient to use.

Putting

$$|U_H|+|U_{H'}| = k, \quad 1 \pm |U_{H+H'}| = X, \quad 1 \pm |U_{H-H'}| = Y;$$

it follows from (1) that the allowed values of X and Y must satisfy the inequality

$$k^2 \leq XY , \qquad (2)$$

which requires that the values of X and Y satisfying it must lie on the positive side of a rectangular hyperbola $xy-k^2 = 0$. In Fig. 1 we draw this rectangular hyperbola and take four points A, B, C and D so that their co-ordinates, referred to the point O' ($x = 1$, $y = 1$) as origin, are respectively four possible combinations of $\pm|U_{H+H'}|$, $\pm|U_{H-H'}|$. Here we may arbitrarily assume that $|U_{H+H'}| > |U_{H-H'}|$. Then, among the four points, only those lying on the positive side of the hyperbola can be allowed, and from this, without any computation, we can readily find a relation among the signs of U_H, $U_{H'}$, $U_{H+H'}$ and $U_{H-H'}$. This is the principle of the graphical method.

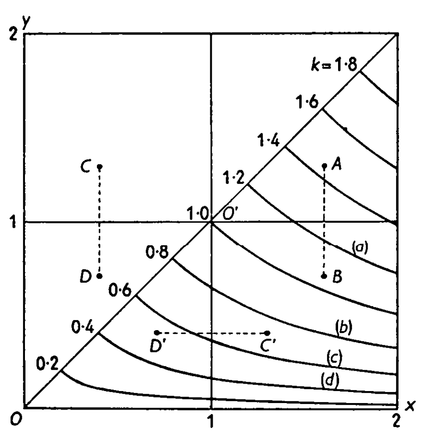

Fig. 1. Chart for the graphical method. For the sake of mere illustration hyperbolas are drawn at intervals of 0·2 for varying values of k. Four cases (a), (b), (c) and (d) are distinguished by varying the value of k, $|U_{H+H'}|$ and $|U_{H-H'}|$ being held constant.

Since a rectangular hyperbola is symmetrical with respect to the straight line $x = y$ (OO' in Fig. 1), only one half of the diagram, say the portion bounded by the x axis and the line OO', will suffice in practice, and the points C and D can then be taken at the respective symmetrical points C' and D'.

A chart was constructed consisting of rectangular hyperbolas drawn for varying values of k from 0·2 to 1·8 at intervals of 0·02, which proved to be sufficient for practical purposes.

According to the relative magnitudes of k, $|U_{H+H'}|$ and $|U_{H-H'}|$, four cases can arise and are shown in Fig. 1 as cases (a), (b), (c) and (d). Let S_H be the sign of U_H. Then, remembering that $S_{H+H'}$ is the sign of the larger one between $|U_{H+H'}|$ and $|U_{H-H'}|$, it can easily be shown that the conclusion drawn for each case is as follows:

Case (a): $S_{H+H'} = S_{H-H'} = S_H S_{H'}$.
Case (b): $S_{H+H'} = S_H S_{H'}$, $S_{H-H'}$ undetermined.
Case (c): $S_{H+H'}$ and $S_{H-H'}$ cannot be equal to $-S_H S_{H'}$ at the same time.
Case (d): no conclusion.

In U_H or $U_{H'}$ is zero, only case (c) or (d) is possible, and for case (c) the point A is not allowed. The conclusion for case (c) is therefore $S_{H+H'} = -S_{H-H'}$.

So far only the value of $k = |U_H|+|U_{H'}|$ has been considered. Now, putting

$$k' = \big||U_H|-|U_{H'}|\big| ,$$

it is readily seen that for the values of k' only either of two cases corresponding to the above (c) and (d) is allowed, which we designate as (c') and (d'). Moreover, the allowed combinations of the former four cases with these two are only those listed in Table 1, where the conclusion drawn for each combination is also given.

Table 1. *Possible cases and conclusions for the use of the inequality* (1)

$|U_{H+H'}| > |U_{H-H'}|$ is assumed.

Case	Conclusion	Grison's classification
(a) (d')	$S_{H+H'}=S_{H-H'}=S_H S_{H'}$	$E > B > D > F$
(b) (c')	$S_{H+H'}=S_H S_{H'}$, $S_{H+H'}=-S_{H-H'}$	$E > C > F > D$
(b) (d')	$S_{H+H'}=S_H S_{H'}$, $S_{H-H'}$ undetermined	$E > C > D > F$
(c) (c')	$S_{H+H'}=-S_{H-H'}$	$E > F > D$
(c) (d')	$S_{H+H'}=S_{H-H'}=-S_H S_{H'}$ not allowed	$E > D > F$
(d) (d')	None	

During the preparation of this manuscript the paper of Grison (1951) appeared, in which a similar table for using the inequality (1) has been given. In Table 1 his classification of the various cases is added in terms of his notation for comparison.

The results of sign determination are obtained in the form, for example, $S_{H+H'}=S_H S_{H'}$. Without the knowledge of the relation between S_H and $S_{H'}$, $S_{H+H'}$ cannot be uniquely determined. If we choose, as is possible in many cases, the pairs of U_H and $U_{H'}$ of which the relations between the signs are fixed by space-group symmetry, $S_{H+H'}$ can be determined as either $+1$ or -1. Further, even if the relations between S_H and $S_{H'}$ are unknown, the results are expressed by introducing parameters $a, b, c, \ldots,$ and some of these parameters can be determined in due course in the manner shown by Gillis (1948). In this connexion it should be remarked that a definite number of arbitrary parameters must be involved in the final results according to the number of possible ways of choosing the origin, and to these parameters we can arbitrarily assign $+1$ or -1. This point must be taken into account before proceeding to sign determination.

We have so far confined ourselves to the inequality (1). It is noted, however, that the same graphical method can be used in applying other inequalities which are of the type (2) or a special case of it.

The graphical method was used to determine the signs of $F(hk0)$'s and $F(0kl)$'s of tetragonal ethylenediamine sulphate. Using the above-mentioned chart, together with the inequality (1), the signs of 21 out of 31 $F(hk0)$'s and those of 38 out of 57 $F(0kl)$'s could easily be determined, and it was possible to make at once Fourier projections on (001) and (100). Details of the structure determination will be published later.

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The habit plane of the zirconium transformation.

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In connection with a recent investigation by Bowles (1951) concerning the habit plane of the β–α lithium transformation, we have carried out an analogous investigation of the habit plane of the zirconium transformation. These transformations have the same crystallographic character, both with regard to lattice type (body-centred cubic to close-packed hexagonal) and orientation relationship ($\{110\}_\beta || \{0001\}_\alpha$; $[111]_\beta || [11\bar{2}0]_\alpha$).

For lithium Bowles found the habit plane to be approximately {144} of the cubic lattice. As the mechanism proposed by Burgers & Jacobs (1934) for zirconium involves as the principal shear a shear parallel to a {211} plane of the cubic lattice, the habit plane found for lithium cannot be directly understood on the basis of this mechanism. Therefore, as Bowles suggests, the possibility must be envisaged that the Burgers mechanism proposed for zirconium must be revised.

For our measurements we employed the original material used by Burgers & Jacobs when determining the orientation relationship between the two lattices in the zirconium transformation, namely, two crystals prepared by de Boer and Fast by thermal decomposition of ZrJ_4 on a core wire at a temperature above the transition point (±862° C.). Prepared in this way, these two 'crystals' were cubic single crystals (cubic in the parent phase); they had the form of rods of about 1 cm. length and 1 mm. thickness, one with a six-sided and one with a four-sided cross-section. On grounds, given in Burgers's paper, it was assumed that the lengths of these rods were originally parallel to a [111] direction and a [001] direction respectively, whereas the side-faces of both rods were parallel to {110} planes.

Several faces of both rods, which in their present state at room temperature consist of aggregates of definitely oriented hexagonal crystallites, were etched with etchant No. 3 (Roborson, 1949) and the directions of the relief effects observed on the surfaces were measured. The accuracy of these measurements lies within 2°. Fig. 1 shows an example of an etched surface.

By plotting in stereographic projection the zones that were normal to each of the traces and determining their common point of intersection in a way analogous to that followed by Bowles, we found in the case of the six-sided rod that the habit plane was either {569} or {145}. The ambiguity between these two possibilities arises from the fact that, for a particular {110} boundary face, it is not known which of the two [111] directions in this plane coincides with the axis of the rod. Dependant on this choice the chosen plane can be considered as 'right' or 'left'.

This ambiguity does not present itself with the four-sided rod, as the length in this case is the only [001] direction in a {110} plane. We therefore hoped to solve the alternative with the aid of this rod, but unfortunately, for reasons unknown, we did not succeed with this rod in obtaining such well defined traces as with the six-sided one.

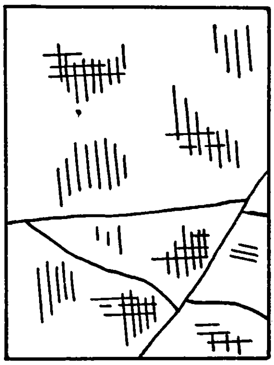

Fig. 1. Traces of habit plane on a {110} plane of a transformed single crystal of cubic zirconium, obtained with Roberson's etching reagent No. 3. Schematic drawing from actual photograph (magnification 50×).

In an effort to solve this alternative we took the traces on *adjacent* boundary faces of the six-sided rod in pairs, considering each pair as the intersection of the habit plane with the two adjacent surfaces, and determined the poles of the planes of intersection for each of the two above-mentioned possibilities. For the possibility that gave {569} for the habit plane according to the method described above, the poles corresponding to the planes of intersection, while exhibiting a weak spreading, had —in stereographic projection—a 'centre of gravity' very close to {569}. For the other possibility not only was the spreading large, but also the point {145} lay outside the region enclosed by the poles. However, we do not want to stress this point too much.

We may conclude that our measurements agree with those of Bowles in so far as both point to a habit plane for the transformation of a cubic body-centred into a close-packed hexagonal lattice with rather complicated