The unit cell contains 4 $BaZrS_3$ units based on the density of 4·23 g.cm.$^{-3}$ reported by Hahn & Mutschke for their preparation. The systematic absences are ($hk0$) for $h+k$ odd and ($0kl$) for l odd. Thus, the space group is either D_{2h}^{16}–$Pnmc$ or C_{2v}^{9}–$Pnc2_1$. The reflections marked with an ǂ in Table 8 can be indexed on the basis of a tetragonal cell with $a \cong \frac{1}{2}\sqrt{(2)}a_t \cong \frac{1}{2}\sqrt{(2)}c_t$ and $c=\frac{1}{2}b_t$, where the subscript t refers to the true unit cell dimensions. These reflections correspond very nearly in position and intensity to those expected for an ideal perovskite structure. Thus, barium zirconium sulfide must have a distorted perovskite structure probably similar to that of $CaTiO_3$ (Kay & Bailey, 1957) or $GdFeO_3$ (Geller, 1956). The difference in structure between the barium zirconium sulfide obtained in this study and that reported by Hahn & Mutschke may again be due to a sulfur deficiency resulting from the present method of synthesis.

Attempts to obtain a high temperature modification of $BaZrS_3$ were unsuccessful. Only mixtures of BaS, ZrS_2 and the $BaZrS_3$ phase described above were obtained when the reaction was carried out above 1200 °C.

Strontium and calcium zirconium sulfides were prepared from the corresponding ternary oxides at 1000–1200 °C. Below 1000 °C. mixtures of binary oxides and sulfides together with small amounts of ternary oxide and sulfide phases were obtained. Usually, complete reaction was achieved in 24 hours as shown by the analyses in Table 7 and the constancy of the X-ray patterns on longer reaction. The powder patterns are given in Table 8. It was possible to index the patterns on the basis of orthorhombic unit cells with the following dimensions:

	a	b	c
$SrZrS_3$	13·49 Å	9·79 Å	14·23 Å
$CaZrS_3$	13·07	9·58	14·05

The unit cells contain 16 molecules based on measured densities of 3·85 g.cm.$^{-3}$ for $SrZrS_3$ and 3·33 g.cm.$^{-3}$ for $CaZrS_3$. The space groups of these compounds could not be determined because the large unit cell dimensions do not permit unambiguous indexing. However, the similarity of the powder patterns to that of barium zirconium sulfide indicates that $SrZrS_3$ and $CaZrS_3$ have highly distorted multiple-cell perovskite structures.

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A Rapid Method of Obtaining the Third Set of Coordinates in a Crystal Structure Analysis

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When two of the coordinates of the atoms in the unit cell of a centrosymmetric crystal have been obtained by finding the projection of the electron density down one of the principal axes, the coordinates in the third direction are sometimes difficult to obtain without a tedious trial-and-error process. The following paper gives a simple method of determining the signs of the larger structure factors for a second projection and hence obtaining the third set of coordinates. The method appears to be useful as long as the number of atoms in the unit cell is no more than fifty to sixty.

Theory

In a centrosymmetric crystal, any structure factor has the form

$$F(h, k, l) = 2 \sum_{j=1}^{N/2} f_j(h, k, l) \cos 2\pi(hx_j + ky_j + lz_j)\ . \quad (1)$$

In two dimensions and more suitable form, it becomes

$$F(h, k, 0) = 2 \sum_{j=1}^{N/2} f_j(h, k, 0)\,(\cos 2\pi hx_j \cos 2\pi ky_j - \sin 2\pi hx_j \sin 2\pi ky_j)\ . \quad (2)$$

If the x_j coordinates are as yet undetermined but the y_j coordinates are known, $|F(h, k, 0)|$ and the factors $f_j(h, k, 0) \cos 2\pi ky_j$ and $f_j(h, k, 0) \sin 2\pi ky_j$ are known quantities. A series of simultaneous equations is obtained by keeping h constant and varying k, which, if the signs of the structure factors were known, could theoretically be solved for each $\cos 2\pi hx_j$ and $\sin 2\pi hx_j$. As it is, the signs of a large number of the structure factors may be obtained by suitably combining two or more of the equations so as to reduce the coefficients of the terms on the right-hand side of the resultant equation to as small values as possible.

For it is clear that

$$\begin{aligned} F(h, k, 0) \pm F(h, k', 0) \leq 2 \sum_{j=1}^{N/2} &|f_j(h, k, 0) \\ \times \cos 2\pi ky_j \pm f_j(h, k', 0) \cos 2\pi k'y_j| + 2 \sum_{j=1}^{N/2} &|f_j(h, k, 0) \\ \times \sin 2\pi ky_j \pm f_j(h, k', 0) \sin 2\pi k'y_j| & \qquad (3) \end{aligned}$$

the right-hand side of equation (3) being the maximum possible value of the right-hand side of the equation obtained by adding or subtracting the relevant equations from the set given by equation (2). If $|F(h, k, 0)| + |F(h, k', 0)|$ is greater than the right-hand side of equation (3), then the two structure factors have the same or opposite sign, depending on whether the minus or plus sign is applicable throughout the equation. Judicious combination of the equations (multiplied by factors if necessary) should yield the relative signs of the majority of the structure factors from the set with h constant and almost certainly all those with the largest unitary factors.

The process may be repeated using different values of h, and sets of signs, for sets of structure factors with constant h, will be obtained. Certain signs may be attached arbitrarily in the usual manner, these merely fixing the origin, so that the signs of certain sets will be known absolutely. The others will only have signs consistent within the set, and it remains to correlate signs between sets. This is most easily done by using Zachariasen's relation (Zachariasen, 1952)

$$S(h+h') = S(\overline{S(h)S(h')})\,, \qquad (4)$$

$S(h)$ denoting the sign of $F(h, k, l)$, on the larger unitary structure factors. This yields relationships between the signs of the structure factors from different sets and allows the correlation to be made.

The totality of signs obtained permits an electron-density map to be calculated and this map should show clearly the positions of the atoms. If the signs of any one set cannot be correlated with the rest, because Zachariasen's relation does not yield unambiguous results for that set, two electron-density maps can be drawn using the two possible totalities of signs, the correct map being easily distinguishable.

Use of the method

In the determination of the structure of α-methyl tetronic acid, $C_5H_6O_3$ (MacDonald & Alleyne, in preparation), the third set of coordinates was obtained by the above method. The space group is $P2_1/c$, the cell dimensions being

$$a = 4{\cdot}00,\ b = 21{\cdot}57,\ c = 6{\cdot}30\ \text{Å};\ \beta = 107°\,36'.$$

The y and z coordinates were obtained by a combination of probability relations and Fourier-transform techniques but these methods yielded no result when applied to the second projection. It was found that, even with the expected chemical structure and the y coordinates known, there were several possible trial structures which gave reasonable initial agreement between the observed and calculated structure factors. The above method was therefore applied to give a rapid choice between the various alternatives.

As an illustration of the application of the method, the working out of the signs of $F(2, k, 0)$ for k odd is given. For space group $P2_1/c$ and k odd,

$$F(h, k, 0) = -4 \sum_{j=1}^{N/4} f_j(h, k, 0) \sin 2\pi hx_j \sin 2\pi ky_j \qquad (5)$$

and with the known values of $f_j(h, k, 0) \sin 2\pi ky_j$ and multiplying up to get rid of fractions, we get the following set of simultaneous equations with variation of k, $F(2, 13, 0)$ and $F(2, 17, 0)$ being zero

$$\begin{array}{rrl} k=1 & 51A = & 36a+42b+63c+80d+48e+72f+18g+48h \\ 3 & 68B = & 54a+42b-30c-56d+6e+8f+42g+80h \\ 5 & 87C = & -12a-42b-12c+16d-60e-72f+60g+16h \\ 7 & 101D = & -60a-42b+48c+32d+42e+56f+54g-64h \\ 9 & 114E = & -12a+42b-60c-64d+24e+24f+36g-64h \\ 11 & 94F = & 54a+42b+42c+80d-60e-80f+6g+16h \\ 15 & 216G = & -36a-48b-42c+40d+42e+56f-54g+40h \\ 19 & 169H = & 12a+48b-48c-40d+6e+56f-48g-80h \\ 21 & 114I = & 60a-36b+12c+72d+48e+48f-24g-8h \\ 23 & 110J = & 12a-48b+30c-80d-48e-80f+6g+72h \end{array} \qquad (6)$$

where $a = \sin 4\pi x_1$, $b = \sin 4\pi x_2$ etc. and $A, B, C, \ldots$ have the values either $+1$ or -1.

Referring to the simultaneous equations for simplicity by the values of k that they represent, (21) subtracted from (15) yields

$$216G - 114I = -96a - 12b - 54c - 32d - 6e + 8f - 30g + 48h\,. \qquad (7)$$

We can affix one sign arbitrarily and we choose G to be $+1$. The maximum possible value of the right hand side of the equation is 286 and it is thus obvious that I must be $+1$. Similarly simultaneous equations

(9) + (11) + (15) show that $E = F = -1$; (19)—(9) shows that $H = -1$; (19) + (23) shows that $J = +1$; (19) + (5) yields $C = +1$; (3) + (15) − (19) gives $B = -1$; (15) − (19) − $\frac{1}{2}$ × (1) gives $A = +1$; (15) − (19) − (7) gives $D = +1$. In fact the signs of all the structure factors in this set are determined with ease.

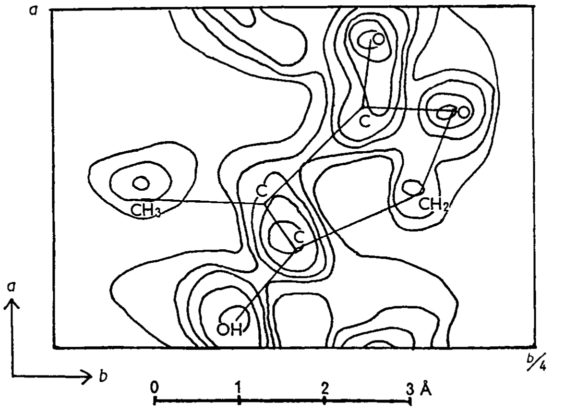

Fig. 1. Projection of the electron density of α-methyl tetronic acid on (001) using signs of structure factors obtained by the method explained. Contours are at arbitrary intervals. The correct position of the molecule is shown by straight lines.

The same technique applied to $h = 1, 3, 4$, k odd, and $h = 1, 2, 3, 4$, k even, yielded similar sets of signs. The signs for $h = 0$ were already known from the first projection and, indeed, of the 87 non-zero structure factors in this zone, 64 were determined. Zachariasen's method, applied in the normal manner to the larger unitary structure factors, correlated the signs of all sets to the known signs of the $F(h, 0, 0)$s and the arbitrarily fixed signs $F(2, 15, 0)$ and $F(1, 21, 0)$. Fig. 1 shows the electron-density map obtained using these results. The correct position of the molecule is indicated by full lines and it will be seen how good the agreement is.

Discussion of the method

Since the values of the structure factors are subject to experimental error, any temperature factor present is not known in the initial stages, and the values of $f_j(h, k, 0) \sin 2\pi k y_j$ etc. are rounded off for ease of working, a few of the signs determined by this method will be incorrect. They will, however, only be a few and the method appears to be one which yields a very good initial structure which requires little refining.

The method will obviously become more cumbersome to use, and have a smaller chance of successfully giving the signs of a large number of structure factors, the greater the number of atoms in the asymmetric unit. However, the more complicated the molecule, the more difficult it is to find two alternative positions for it in the second projection. It is, in fact, for the smaller molecule that a number of alternative positions arises and a rapid method of choice is most desirable.

The following reasoning shows that the method is only likely to work for crystals with a unit cell containing no more than fifty to sixty atoms. For if $U(h, k, l)$ denotes a unitary structure factor defined in the usual way, then equation (2) may be written as

$$U(h, k, 0) = 2 \sum_{j=1}^{N/2} n_j \cos 2\pi(hx_j + ky_j) \qquad (8)$$

where n_j is the fraction of the total number of electrons in the unit cell possessed by the jth atom. $|U(h,k,0)|$ is distributed according to a Gaussian law with mean approximately $N^{\frac{1}{2}}$ (Hughes, 1949). The average value of

$$2 \sum_{j=1}^{N/2} n_j \, |\cos 2\pi(hx_j + ky_j)|$$

is $\frac{1}{2}$. There is little chance that combinations of equations will yield a reasonable number of signs unless about 10% of the $|U(h, k, 0)|$ values are greater than half the expected value of the sum of the moduli of the terms on the right hand side of equation (8). This means that $1.7N^{-\frac{1}{2}}$ must be greater than $\frac{1}{4}$ or $N < 46$. This criterion for success is a little on the harsh side and $50 < N < 60$ is probably more realistic. It is assumed that the atoms present are not markedly different from one another. The presence of one or more heavy atoms will alter the situation considerably.

An attempt to use the method to obtain signs in the second projections of a series of known structures of increasing numbers of atoms per unit cell showed reasonable agreement with the above argument. Signs were readily obtainable for $N \leq 48$, less readily obtainable but still in useful quantity up to $N = 60$, and hardly obtainable at all for more complex structures.

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