Table 4 (*cont.*)

hkl	$\sin\theta$ ($\lambda=1{\cdot}54$ A.)	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*hkl*	$\sin\theta$ ($\lambda=1{\cdot}54$ A.)	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*hkl*	$\sin\theta$ ($\lambda=1{\cdot}54$ A.)	$F_{\text{meas.}}$	$F_{\text{calc.}}$
520	0·403	2·5	+ 2·5	770	0·994	< 1·0	− 1·0	11,1,0	0·698	2·0	− 2·5
530	0·494	1·5	+ 5·0	810	0·516	6·0	− 6·5	11,2,0	0·733	4·0	+ 4·0
540	0·599	< 2·0	− 2·5	820	0·561	3·0	− 3·0	11,3,0	0·786	< 2·0	+ 1·5
550	0·711	3·0	− 6·0	830	0·629	11·0	+ 10·0	11,4,0	0·856	2·0	+ 2·0
560	0·826	< 2·0	− 1·5	840	0·714	10·0	+ 10·0	11,5,0	0·937	< 1·5	+ 0·5
570	0·945	< 1·5	− 1·0	850	0·810	2·0	+ 0·5	12,1,0	0·759	2·5	+ 2·5
610	0·397	15·0	+ 14·0	860	0·914	< 1·5	+ 0·5	12,2,0	0·790	< 2·0	0
620	0·454	16·0	+ 16·0	910	0·575	4·0	− 4·0	12,3,0	0·840	2·5	+ 2·5
630	0·536	2·5	+ 1·0	920	0·616	3·0	+ 3·0	12,4,0	0·956	1·5	− 0·5
640	0·634	7·5	− 7·5	930	0·679	3·0	+ 4·0	12,5,0	0·983	< 1·0	0
650	0·740	7·5	+ 4·0	940	0·759	2·0	+ 2·5	13,1,0	0·821	< 2·0	0
660	0·851	6·0	− 4·5	950	0·850	2·0	− 2·0	13,2,0	0·850	4·0	+ 1·5
670	0·968	1·0	− 1·0	960	0·948	< 1·5	− 2·0	13,3,0	0·897	1·5	− 1·0
710	0·456	15·0	− 9·0	10,1,0	0·637	2·5	+ 1·5	13,4,0	0·958	< 1·0	− 1·0
720	0·507	7·0	− 7·0	10,2,0	0·674	6·0	+ 5·5	14,1,0	0·884	4·5	+ 3·5
730	0·581	3·0	+ 5·0	10,3,0	0·731	< 2·0	− 1·0	14,2,0	0·909	3·0	− 2·0
740	0·672	14·0	+ 5·0	10,4,0	0·805	< 2·0	− 2·0	14,3,0	0·953	< 1·0	+ 0·5
750	0·774	6·5	+ 3·0	10,5,0	0·893	1·5	+ 1·5	15,1,0	0·943	< 1·5	+ 2·0
760	0·881	7·5	+ 4·0	10,6,0	0·987	< 1·0	− 1·0	15,2,0	0·969	1·5	+ 2·0

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The Ambiguity Factor in Implication Theory

By M. J. Buerger

Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

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The *implication* is a transformation of a Harker synthesis that has the property of indicating the possible positions of atoms in the crystal structure. The location of the atoms is subject to a certain ambiguity which can be defined by an ambiguity factor, $m=M/q$. M is a basic ambiguity characteristic of the symmetry axis and arising from group products, while q is a degeneracy factor expressing a particular kind of equivalence of these products. The ambiguity factor can also be determined more easily with the aid of missing spectra. It is shown that M is the modulus of the transformation from the implication cell to the crystal cell, and $1/q$ is the fraction of spectra present. The ambiguity factor of any implication synthesis can, therefore, be easily determined from the symmetry and characteristic missing spectra of the space group.

The ambiguity of an implication can be resolved with the aid of m Patterson line syntheses. The implication synthesis, therefore, provides a theoretical device for untangling the Patterson synthesis. This suggests that there should exist a simple relation between the Fourier coefficients in the implication function and the corresponding coefficients in the Fourier expression of the projected electron density. The details of this relation are dealt with in another paper.

Introduction

In an earlier contribution (Buerger, 1946) it was pointed out that the Harker function (Harker, 1936) can be generalized so that it can be applied to any level of the Patterson function (Patterson, 1934, 1935) which represents a translation component of a general screw axis. If the screw is assumed parallel to [001], the generalized Harker function has the form

$$P(xyz_1)=\sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty} C_{hk}\cos 2\pi(hx+ky) -C'_{hk}\sin 2\pi(hx+ky), \quad (1)$$

where

$$C_{hk}=\sum_{l=-\infty}^{\infty} |F_{hkl}|^2\cos 2\pi l z_1, \quad (2)$$

$$C'_{hk}=\sum_{l=-\infty}^{\infty} |F_{hkl}|^2\sin 2\pi l z_1, \quad (3)$$

z_1 is the level of the section in Patterson space, and is equal to 0, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, or $\frac{1}{6}$.

Because of the antisymmetrical property of the sine, C' vanishes whenever the symmetry provides that $|F_{hkl}|^2=|F_{hk\bar{l}}|^2$. The condition for this is that the crystal have a plane of symmetry (001) in Patterson space. Since Patterson space is centrosymmetrical, this situation obtains whenever the c axis has even-fold symmetry (by virtue of the relation $C_2.C_s = C_h$). The only crystallographic case of odd-fold symmetry is for $n=3$ (where n is the 'fold' of the axis). For this reason (3) vanishes except in the case of the screw, 3_1. Taking this into account, the expansions of the generalized Harker coefficients C and C' are given in Table 1.

Table 1. *Coefficients of the generalized Harker function*

Level in Patterson space	Symbol	Expansion
0	C_0	$= \sum_l \lvert F_{hkl}\rvert^2$
$\frac{1}{2}$	$C_{\frac{1}{2}}$	$= \sum_{l=2N} \lvert F_{hkl}\rvert^2 - \sum_{l=2N+1} \lvert F_{hkl}\rvert^2$
$\frac{1}{3}$	$C_{\frac{1}{3}}$	$= \sum_{l=3N} \lvert F_{hkl}\rvert^2 - \frac{1}{2} \sum_{l=3N\pm 1} \lvert F_{hkl}\rvert^2$
	$C'_{\frac{1}{3}}$	$= \frac{\sqrt{3}}{2}\left(\sum_{l=3N+1} \lvert F_{hkl}\rvert^2 - \sum_{l=3N-1} \lvert F_{hkl}\rvert^2\right) = 0$
$\frac{1}{4}$	$C_{\frac{1}{4}}$	$= \sum_{l=4N} \lvert F_{hkl}\rvert^2 - \sum_{l=4N+2} \lvert F_{hkl}\rvert^2$
$\frac{1}{6}$	$C_{\frac{1}{6}}$	$= \sum_{l=6N} \lvert F_{hkl}\rvert^2 + \frac{1}{2} \sum_{l=6N\pm 1} \lvert F_{hkl}\rvert^2$ $- \frac{1}{2} \sum_{l=6N\pm 2} \lvert F_{hkl}\rvert^2 - \sum_{l=6N+3} \lvert F_{hkl}\rvert^2$

N is an integer.
All summation limits: $l = -\infty$ to ∞.

It was also shown (Buerger, 1946) that the generalized Harker synthesis could be transformed into another synthesis known as the *implication*, which has properties which are useful in investigating crystal structures. The peaks of the implication correspond to (*a*) locations of the atoms in the crystal; (*b*) alternate locations of the atoms consistent with the data, and known as ambiguities, which are brought about by translation symmetry as well as possible lack of a center of inversion; and (*c*) false locations, known as satellites, which are due to other operations of the space group, each such satellitic peak being geometrically related to (*a*) and (*b*):

Alternative forms of implication synthesis

Perhaps the simplest way of devising an implication synthesis is to prepare the corresponding Harker synthesis and then transform it by a polar co-ordinate transformation. This requires shrinking the scale of the Harker plot by a factor 1/2 sin (π/n) and then rotating it through an angle $\frac{1}{2}(\pi - \alpha)$, where n is the 'fold' of the axis and $\alpha = 2\pi/n$.

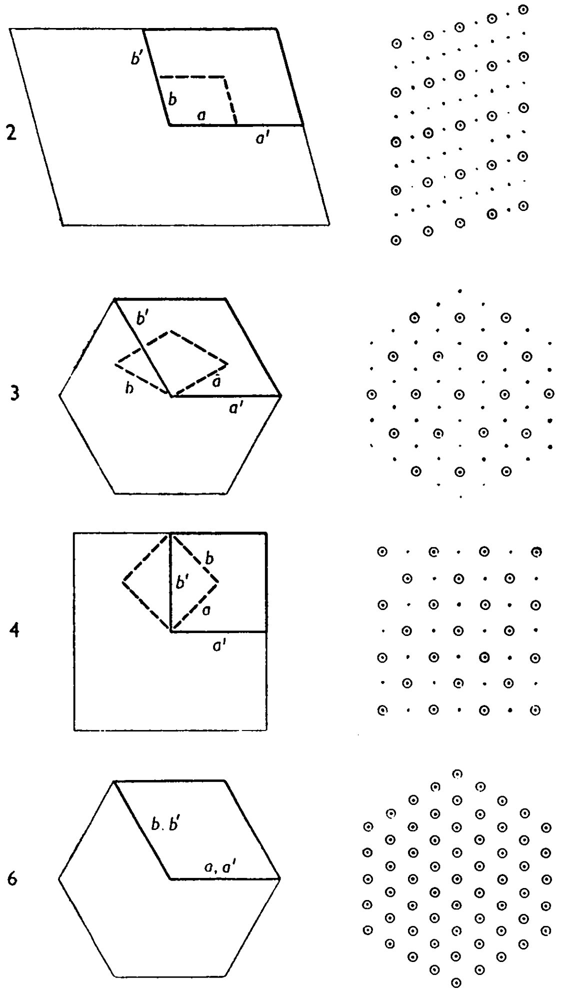

Fig. 1. Lattice transformation giving transformation of generalized Harker synthesis into implication synthesis. Crystal cell, full lines; implication cell, broken lines.

Table 2. *Crystal elements expressed in terms of implication elements*

n	Axial transformation	Index transformation
2	$a' = 2a$ $b' = 2b$	$h' = 2h$ $k' = 2k$
3	$a' = a - b$ $b' = a + 2b$	$h' = h - k$ $k' = h + 2k$
4	$a' = a - b$ $b' = a + b$	$h' = h - k$ $k' = h + k$
6	$a' = a$ $b' = b$	$h' = h$ $k' = k$

The polar co-ordinate transformation involved in transforming a generalized Harker synthesis into an implication synthesis can also be provided by an appropriate lattice transformation, shown on the left of Fig. 1. The transformation can be defined by expressing the crystal axes in terms of the implication axes. The specific transformations for the various values of n are shown in Table 2. With the aid of these transformations, the implication function can be computed directly in terms of crystal indices, and plotted directly in co-ordinates referred to the crystal axes. The implication function, I_n, then has the following form, the values of h' and k' being provided by Table 2 for the appropriate value of n for the symmetry (the strategy of the selection of n when the symmetry permits a choice is discussed in the earlier paper (Buerger, 1946)):

$$I_n(xyz_1) = \sum_{h'=-\infty}^{\infty} \sum_{k'=-\infty}^{\infty} Q_{h'k'} \cos 2\pi(h'x+k'y), \quad (5)$$

where
$$Q_{h'k'} = \sum_{l=-\infty}^{\infty} |F_{h'k'l}|^2 \cos 2\pi l z_1. \quad (6)$$

The expansion of Q is given in Table 3.

Table 3. *Coefficients of the implication function*

Level in Patterson space	Symbol		Expansion
0	Q_0	=	$\sum_l \|F_{h'k'l}\|^2$
$\frac{1}{2}$	$Q_{\frac{1}{2}}$	=	$\sum_{l=2N} \|F_{h'k'l}\|^2 - \sum_{l=2N+1} \|F_{h'k'l}\|^2$
$\frac{1}{3}$	$Q_{\frac{1}{3}}$	=	$\sum_{l=3N} \|F_{h'k'l}\|^2 - \frac{1}{2} \sum_{l=3N\pm1} \|F_{h'k'l}\|^2$
$\frac{1}{4}$	$Q_{\frac{1}{4}}$	=	$\sum_{l=4N} \|F_{h'k'l}\|^2 - \sum_{l=4N+2} \|F_{h'k'l}\|^2$
$\frac{1}{6}$	$Q_{\frac{1}{6}}$	=	$\sum_{l=6N} \|F_{h'k'l}\|^2 + \frac{1}{2} \sum_{l=6N\pm1} \|F_{h'k'l}\|^2$
			$-\frac{1}{2} \sum_{l=6N\pm2} \|F_{h'k'l}\|^2 - \sum_{l=6N+3} \|F_{h'k'l}\|^2$

N is an integer.
All summation limits $l = -\infty$ to ∞.
h' and k' provided by Table 2.

Ambiguities from a group-theory viewpoint

In the earlier contribution, the properties of the implication function were developed almost entirely from a point of view of group theory. Expressed in this form, the nature of the ambiguity factor involved has the following significance, and its magnitude can be found in the following way.

For space groups which can be developed from generating operations consisting of the operations of a symmetry axis plus perpendicular translations only, $M-1$ other similar (but, in general, not necessarily equivalent) sets of axes arise in the group as group products of the rotations and translations. M has the following values:

n	2	3	4	6
M	4	3	2	1

Unless other operations are present in the group, there are M sets of non-equivalent axes. In more complicated space groups, however, other group operations may require certain sets of these M axes to become equivalent. If this occurs in such a way that the axes of the set project on a perpendicular plane as if they were translation-equivalent, then clusters of atoms about one axis appear, in projection, to be translation-equivalent to the clusters about the other axes. Of course, in such cases, the duplication of atoms by the implication ceases to be an ambiguity, and the ambiguity factor is reduced by a factor $1/q$, where q is the number of axes of the set that are equivalent by translation in projection. Now, only two kinds of operations can bring axes into such projected translation-equivalence, namely, (1) a pure translation which is a submultiple of a cell translation (i.e. a 'centering' translation of a non-primitive cell); and (2) a glide component of a glide plane perpendicular to the axes.

As a consequence of these considerations, the net ambiguity of an implication may be a submultiple of M. Indeed, if the M axes are collected together in sets of q axes, the net ambiguity of the implication is $m = M/q$. Here q is the number of axes made actually equivalent by a 'centering' translation, or equivalent in projection by a perpendicular glide.

Examples of these cases are shown in Table 4.

Ambiguities from a Fourier point of view

The matter of ambiguities can be looked at from a different point of view which is, of course, equivalent to the group theoretical approach, but which has certain practical advantages over it. When a Harker function is computed, F^2's corresponding to all available hk combinations are utilized. The Harker function consequently gives complete information about interatomic vectors between atoms related by the symmetry operation corresponding to the Patterson level in question.

When, however, the Harker function is used in transformed form as an implication, the situation is different. In this application, it is used in connection with a crystal cell which has M' times the area of the implication cell (see the left side of Fig. 1 and also Buerger (1946, Fig. 5)). Therefore, the same implication cell is required to cover by repetition M' equal parts of the crystal cell area, which are not necessarily equivalent.

It is now easy to show that the crystal cell requires M' times as many Fourier coefficients to define its

Table 4. *Ambiguity of implications*

Space groups	Basic ambiguity factor M	Degeneracy coefficient q	Net ambiguity factor $m = M/q$	Absent spectra	Fraction of $hk0$ spectra absent	Fraction of $hk0$ spectra present $1/q$	Fraction of $h0l$ spectra present $1/q$
$P2$	4	1	4	None	0	1	.
$C2$	4	2	2	hkl when $h+k=2n+1$	$\frac{1}{2}$	$\frac{1}{2}$	.
$C3$	3	1	3	None	0	1	.
$R3$	3	3	1	hkl when $h-k+l=3n\pm1$	$\frac{2}{3}$	$\frac{1}{3}$	.
$P4$	2	1	2	None	0	1	.
$I4$	2	2	1	hkl when $h+k+l=2n+1$	$\frac{1}{2}$	$\frac{1}{2}$	.
$P2_1$	4	1	4	$0k0$ when $k=2n+1$	.	.	1
$P2_1/n$	4	2	2	$h0l$ when $h+l=2n+1$	.	.	$\frac{1}{2}$

structure as can be provided by transformation from the coefficients of the implication. Each Fourier coefficient is represented by a point of the reciprocal lattice. The reciprocal lattice of the crystal can be easily found. It is represented on the right of Fig. 1 by dots. The reciprocal lattice of the implication cell can also be found. For example, it can be determined by inspection from the geometrical relation between implication cell and crystal cell shown on the left of Fig. 1. Alternatively, it can be found in relation to the reciprocal lattice of the crystal by systematically taking all implication indices and transforming them into crystal indices with the aid of Table 2. By either method, the reciprocal lattice shown by rings on the right of Fig. 1 results. It is evident that the ringed points, in general, correspond to only a fraction of the total number of points. This fraction, f, is the ratio of the two reciprocal cell areas. Now let

A_c^* = the area of the crystal reciprocal cell,
A_i^* = the area of the implication reciprocal cell,
A_c = the area of the crystal cell,
A_i = the area of the implication cell.

Then $$f=A_i^*/A_c^*=A_c/A_i=M', \qquad (7)$$

where M' is the modulus of the transformation from implication to crystal cell.

Conversely, if only a fraction, f, of the Fourier coefficients of the crystal are used for an electron-density projection, a cell $1/M'$th of the true area appears, or, every atom appears in the corresponding location in the M' subcells of the true crystal cell. Thus M' is identical with the ambiguity factor M. Consequently, if only a (systematically distributed) fraction, f, of the Fourier coefficients of a crystal is used in forming its electron-density function, the function locates the atoms with an ambiguity M, i.e. the crystal structure and $M-1$ ghosts appear as the synthesis.

The discussion so far assumes that the crystal does not have, in projection, submultiple translations, as mentioned in the last section. If it does, every such operation produces missing spectra. If the translation is $1/q$th of the true cell edge, then $1/q$th of the $hk0$ spectra remain and are not extinguished. When the remaining fraction of the spectra is normally missing, then this missing set in the implication ceases to correspond to an ambiguity. The net ambiguity, m, is then M/q.

The determination of ambiguity from extinctions can be summarized as follows: for a particular n of the symmetry axis there is a basic ambiguity, M. The net ambiguity, m, is found by taking the product $M.1/q$, where $1/q$ is the fraction of the spectra remaining in the reciprocal-lattice plane parallel to the implication, and not extinguished. Table 4 shows examples of the determination of ambiguity by missing spectra in comparison with the group method.

In concluding this section, the practical utility of the extinction method of determining ambiguity should be stressed. The determination of ambiguities by group theoretical methods requires a knowledge of group theory, and is somewhat tedious. However, the ambiguity factor for any space group projected normal to any axis can be very easily determined by the simple expedient of looking up the extinctions in the zone of the desired axis. The fraction of the spectra not extinguished is then $1/q$. Study of the examples in Table 4 will make the method clear.

Solution of implication ambiguities

Ambiguities in the locations of specific pairs of atoms can be removed with the aid of linear Patterson syntheses, provided only that the atoms show up as peaks on the implication. The theoretical basis for this removal of ambiguity is illustrated in Fig. 2. Suppose the implication indicates that atom A has one of the m locations $x_1y_1, x_2y_2, \ldots, x_my_m$, while atom B has one of the m locations $X_1Y_1, X_2Y_2, \ldots, X_mY_m$. Now, the ambiguity factor has no meaning with regard to any one equivalent set of atoms, but only with regard to combinations of equivalent sets of atoms (Buerger, 1946, p. 582, Fig. 4). The total number of combinations is m, and thus m represents the ambiguity of a *pair* of atoms. For this reason, the origin may be arbitrarily chosen in the neighbourhood of a particular set of A atoms, say in the neighbourhood of the set represented by the coordinates x_1y_1. The representative A atom is now at $x_1y_1z_1$. Possible B atoms exist at $X_1Y_1Z_1$, $X_2Y_2Z_2, \ldots, X_mY_mZ_m$. Atom B is at only one of these m locations. Consequently if the m Patterson line syntheses, $P(X_1-x_1, Y_1-y_1, z)$, $P(X_2-x_1, Y_2-y_1, z), \ldots$, $P(X_m-x_1, Y_m-y_1, z)$, are computed, a peak of height $P_{AB}=(\rho_A\rho_B)_{\mathrm{Av}}$ must appear on one of them (Buerger, 1946, p. 595). The value of XY for which this peak occurs is the correct set of coordinates for B. This procedure removes the ambiguity for this particular combination of AB atoms.

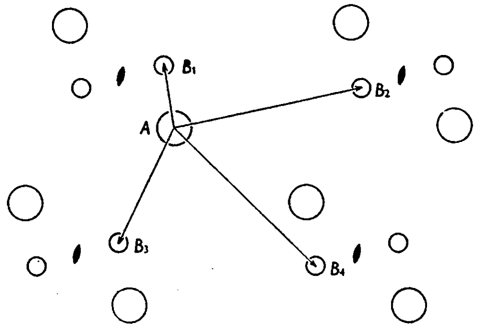

Fig. 2. Theoretical basis for the removal of ambiguities in the location of pairs of atoms with the aid of linear Patterson syntheses.

This resolution of the ambiguity fails if any two x and y differences are the same, for example, if

$$(X_p-x_1,\ Y_p-y_1)=(X_r-x_1,\ Y_r-y_1).$$

Such fortuitous circumstances correspond with a Patterson cyclotomic ambiguity (Patterson, 1944), and cannot be resolved.

With the exception of Patterson cyclotomic ambiguities, the possibility of resolving implication ambiguities implies in principle that the three-dimensional Patterson function contains (and can be untangled to provide) a complete solution of the projection of the crystal structure for any case involving symmetry other than 1-fold symmetry.

(An alternative, but less elegant, way of solving the implication ambiguity is to compute the two-dimensional Patterson function

$$P(xy)=\sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}|F_{hk0}|^2\cos 2\pi(hx+ky). \qquad (8)$$

Unlike the Harker or implication synthesis, this synthesis contains peaks due to unsymmetrical interactions. Among these there is a peak due to interaction AB. Thus, if A of the implication, Fig. 2, is set at the origin of $P(xy)$, the latter contains a peak at one of the four positions B_1, B_2, B_3, or B_4. The value of XY for which the peak (of appropriate height) is found is the correct set of co-ordinates for B.)

An invitation to phase determination

In cases uncomplicated by satellites and ambiguities (for example, for space group $C6_1$), the implication function and the Fourier function representing the electron density projected on a plane normal to the symmetry axis have peaks at the same places. They differ only in the exaggeration of the peaks. Furthermore, these Fourier functions have the same form. The general electron density function is

$$\rho(xy)=\sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty}A_{hk0}\cos 2\pi(hx+ky) + B_{hk0}\sin 2\pi(hx+ky),$$

while the implication general function is

$$I_n(xyz_1)=\sum_{h'=-\infty}^{\infty}\sum_{k'=-\infty}^{\infty}Q_{h'k'}\cos 2\pi(h'x+k'y).$$

It is, therefore, obvious (and indeed has been obvious since the discovery of the implication function) that the Fourier coefficients of the implication function must bear a simple relation to those of the electron-density projection function. In favorable cases this relation should be capable of giving information about the phases of the F's of the electron-density function. It therefore offers a possible alternative approach to the problem of phase determination which has been provided by the Harker-Kasper (1947) inequalities. The relations between F's and F^2's suggested by implication theory is discussed in another paper (Buerger, 1948). The ambiguities discussed in this paper pervade all such phase determination.

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The Crystal Structure of the Normal Orthophosphates of Barium and Strontium

By W. H. Zachariasen

Argonne National Laboratory and the Department of Physics, University of Chicago, Illinois, U.S.A.

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The compounds $Ba_3(PO_4)_2$ and $Sr_3(PO_4)_2$ are rhombohedral and isostructural. The unit cell contains one molecule. The dimensions of the unit rhombohedron and the calculated densities are:

	a	α	ρ
$Ba_3(PO_4)_2$	7·696 ± 0·002 kX.	42° 35′ ± 2′	5·25 g.cm.$^{-3}$
$Sr_3(PO_4)_2$	7·280 ± 0·002 kX.	43° 21′ ± 2′	4·53 g.cm.$^{-3}$

The space group is $R\bar{3}m$ and the atomic positions are: 1 Ba in (0, 0, 0), 2 Ba in $\pm(u_1, u_1, u_1)$, 2 P in $\pm(u_2, u_2, u_2)$, 2 O in $\pm(u_3, u_3, u_3)$, 6 O in $\pm(x, x, z)$ (x, z, x) (z, x, x); with parameter values $u_1=0·208$, $u_2=0·412$, $u_3=0·337$, $x=0·285$ and $z=0·742$.

Introduction

The phosphates, the crystal structures of which are discussed in this paper, were prepared by Mr H. B. Evans by slow precipitation. The X-ray diffraction patterns showed that many of the precipitates contained other phases, such as $BaHPO_4$, $SrHPO_4$ or $Sr_5(OH)(PO_4)_3$.

Two samples of barium phosphate, which according to the X-ray patterns contained only one phase, were chemically analyzed by Mr Evans with the following results:

	I	II	Theoretical for $Ba_3(PO_4)_2$
% Ba	68·2	67·0	68·4
% P	10·0	11·0	10·3