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

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

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

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(*Received* 22 *July* 1948)

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

Density determinations on these barium phosphate samples, also carried out by Mr Evans, gave values $\rho = 5{\cdot}18\text{–}5{\cdot}27$ g.cm.$^{-3}$

A sample of a strontium phosphate precipitate gave an X-ray diffraction pattern analogous to that of $Ba_3(PO_4)_2$. This observation was regarded as satisfactory proof of the formula $Sr_3(PO_4)_2$.

None of the chemical preparations contained single crystals sufficiently large to be isolated. Microscopic examination under high magnification showed the samples to consist of very tiny flakes too small to permit any measurement of optical properties. Attempts to prepare larger crystals were unsuccessful. As a consequence only powder diffraction patterns could be obtained. These were taken with Cu K radiation filtered through nickel foil. Powder diffraction photographs were taken of both the barium and the strontium compound, using cameras of 9 and 19 cm. diameter. In the case of the barium compound the diffraction pattern was also recorded with the Norelco Spectrometer. Because of the flaky character of the crystallites it was necessary to take great care to minimize preferential orientation in the powder specimens.

Interpretation of the diffraction patterns

A partial list of the observed diffraction lines is given in Table 1. The measurements from the original photographs extend to $\sin^2\theta = 0{\cdot}985$. Thus less than half of the actually observed diffraction lines are included in Table 1.

Table 1. *Data from powder photographs*

$H_1H_2H_3$	$Ba_3(PO_4)_2$ Int.	$Ba_3(PO_4)_2$ $\sin^2\theta$	$Sr_3(PO_4)_2$ Int.	$Sr_3(PO_4)_2$ $\sin^2\theta$
100	*w*−*	0·0266	*vw*	0·0290
110	*vvw*	0·0307		
211	*w*+	0·0473	*w*	0·0518
221	*vs*	0·0594	*s*	0·0663
$10\bar{1}$	*vs*	0·0764	*s*	0·0835
$11\bar{1}$	*vw*	0·1034	*vvw*	0·1113
200	*vw*	0·1069	*w*	0·1170
333	*m*	0·1100	*m*	0·1249
220 321	*w*	0·1241	*w*	0·1354
			vw	0·1386
311	*ms*	0·1356	*s*	0·1489
433	*s*−	0·1608	*m*	0·1810
331	*vw*	0·1682		
$20\bar{1}$	*vw*	0·1790		
432	*m*	0·1859	*m*	0·2069
310	*vw*+	0·1994	*vw*	0·2158
320	*s*−	0·2115	*s*	0·2311
$2\bar{1}\bar{1}$	*wm*	0·2284	*m*	0·2482
442	*w*	0·2364	*w*	0·2636
421	*vvw*	0·2438		
554	*wm*	0·2898	*ms*	0·3298
$20\bar{2}$	*m*	0·3038		
532	*m*	0·3121	*ms*	0·3450
522, 441	*w*	0·3374	*vw*−	0·3711
422, $32\bar{1}$	*vvw*	0·3512	Trace	0·3794
410	*w*	0·3622	*m*	0·3952
644	*w*	0·3659	*vw*−	0·4089
654	*ms*	0·3792	*m*+	0·4263
531	*w*	0·4128	*w*+	0·4528

* *s* = strong, *m* = medium, *w* = weak, *vw* = very weak.

The observed sine squares correspond to a rhombohedral translation lattice. Measurements in the back-reflection region led to the following unit-cell dimensions:

	a	α
$Ba_3(PO_4)_2$	7·696 ± 0·002 kX.	42° 35′ ± 2′
$Sr_3(PO_4)_2$	7·280 ± 0·002 kX.	43° 21′ ± 2′

The unit cell contains one molecule, the calculated densities being $\rho = 5{\cdot}25$ g.cm.$^{-3}$ for $Ba_3(PO_4)_2$ and $\rho = 4{\cdot}53$ g.cm.$^{-3}$ for $Sr_3(PO_4)_2$.

The observed intensities are to a first approximation dependent only upon the value of ΣH_i. Thus a reflection appears with strong intensity when $\Sigma H_i = 0$, 5, 9, 10, 14, 15, 19, 20, while a reflection is absent or very faint if $\Sigma H_i = 2$, 3, 8, 11, 12, 13, 16, 17, 21 or 22.

These facts require barium (or strontium) atoms to be in positions: 1 Ba_I (or Sr_I) in (0, 0, 0), 2 Ba_{II} (or 2 Sr_{II}) in $\pm(u_1, u_1, u_1)$ with $u_1 = 0{\cdot}20\text{–}0{\cdot}21$.

Since there are two phosphate groups per unit cell, and since the PO_4 group is known to have tetrahedral shape, the two phosphorus atoms and two of the eight oxygen atoms must lie on three-fold axes. The size of the PO_4 group is accurately known and corresponds to P–O = 1·56 A. (West, 1930).

The shape and size of the PO_4 groups being known, their positions in the structure are characterized by only two degrees of freedom. The two parameters represent the translation of the group along the three-fold axis and the rotation of the group about this axis. These two parameters were varied until the best possible agreement between observed and calculated intensities was obtained.

The structure arrived at in this manner has the symmetry $R\bar{3}m$ with the following atomic positions:

1 Ba_I or 1 Sr_I	in (0,0,0),
2 Ba_{II} or 2 Sr_{II}	in $\pm(u_1, u_1, u_1)$,
2 P	in $\pm(u_2, u_2, u_2)$,
2 O_I	in $\pm(u_3, u_3, u_3)$,
6 O_{II}	in $\pm(x, x, z)\ (x, z, x)\ (z, x, x)$.

Table 2. *Observed and calculated intensities for* $Ba_3(PO_4)_2$

$H_1H_2H_3$	Intensity Calc.	Intensity Obs.
111	3·2	—
100	15·0	15
110	2·4	—
211	19·6	22
222	1·2	—
221	69	89
$10\bar{1}$	60	65
210	0	—
322	0·8	4
$11\bar{1}$	3·9	5
200	5·0	11
333	10·4	22
332	0·8	—
220	12·7	21
321	4·6	
311	28·0	37
433	14·1	28
331	1·7	—
$20\bar{1}$	3·1	6
$21\bar{1}$	0·5	—
432	15·6	19
422	0	—
443	0·1	—
310	4·7	7
444	0	—
320	19·7	24
$2\bar{1}\bar{1}$	11·1	12
442	6·1	9
300, $22\bar{1}$	0·1	—
421	0·5	—
544	0	—
431	0·2	—
533	0·2	—
411, 330	0·8	—
543	0·2	—
554	5·2	10
$20\bar{2}$	10·3	14
532	10·8	16

The parameter values are:

	u_1	u_2	u_3	x	z
$Ba_3(PO_4)_2$	0·208 ± 0·004	0·412 ± 0·008	0·337	0·285	0·742
$Sr_3(PO_4)_2$	0·208 ± 0·004	0·412 ± 0·008	0·333	0·279	0·753

Table 2 lists calculated and observed intensities for $Ba_3(PO_4)_2$. The former were obtained using the formula

$$I \propto |F|^2 p \frac{1+\cos^2 2\theta}{\sin^2\theta \cos\theta},$$

where p is the permutation factor. The observed intensities were measured using the Norelco Spectrometer.

Discussion of the structure

The tetrahedral configuration of four oxygen atoms (one O_I and three O_{II}) about phosphorus with

$$P\text{–}O_I = P\text{–}O_{II} = 1{\cdot}56 \text{ A.}$$

was assumed. The configuration of oxygen atoms about barium and strontium atoms is as follows:

Ba_I–6 O_I = 3·23 A., Ba_I–6 O_{II} = 2·80 A.,
Ba_{II}–1 O_I = 2·71 A., Ba_{II}–3 O_{II} = 2·80 A.,
Ba_{II}–6 O_{II} = 2·83 A.;
Sr_I–6 O_I = 3·10 A., Sr_I–6 O_{II} = 2·63 A.,
Sr_{II}–1 O_I = 2·48 A., Sr_{II}–3 O_{II} = 2·62 A.,
Sr_{II}–6 O_{II} = 2·72 A.

Thus barium or strontium atoms of the first kind show co-ordination number twelve, barium and strontium atoms of the second kind co-ordination number ten. The total strength of the bonds ending on O_I is 1·95 and on O_{II} 2·02.

The observed mean interionic distances and those calculated from ionic radii (Zachariasen, 1931) agree reasonably well as shown below:

	Observed	Calculated
Ba_I–O	3·01 A.	2·96 A.
Ba_{II}–O	2·81	2·90
Ba–O mean	2·88	2·92
Sr_I–O	2·86	2·78
Sr_{II}–O	2·67	2·72
Sr–O mean	2·73	2·74

In view of the close crystal chemical similarity of lead to strontium and barium it was attempted to prepare the isostructural lead compound. These efforts were unsuccessful.

The writer wishes to thank Miss Anne Plettinger for having taken the X-ray diffraction patterns, and Mr H. B. Evans for having made the chemical preparations, the chemical analyses and the direct density determinations.

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Acta Cryst. (1948). **1**, 265

Crystal Chemical Studies of the 5*f*-Series of Elements. I. New Structure Types

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(*Received* 14 *August* 1948)

The paper gives brief descriptions of new structure types observed for simple compounds of the 5*f*-series of elements and of related elements.

Introduction

In the course of the last five years the writer has determined the crystal structures of a number of compounds of thorium, of uranium, of the transuranic elements, and of the rare elements actinium and protactinium. The work was started in the Manhattan Project and has been continued in the Argonne National Laboratory after the war.

The crystal-structure studies of compounds of the new and rare elements were undertaken for the main purpose of determining the chemical identity of the various micro-preparations, so that the basic chemistry of these elements could be deduced at a time when only microgram amounts were available. In most instances it became necessary to carry out at least a partial crystal-structure determination before the chemical identity of the substance could be ascertained.

This is the first of a series of articles bearing the general title 'Crystal Chemical Studies of the 5*f*-Series of Elements' in which the results of these investigations will be reported. Most of the articles will describe the crystal-structure determination of groups of compounds or of individual compounds. Other articles in the series will contain general discussions of the crystal chemistry of the 5*f*-series of elements. A few of the articles will, like the present one, summarize crystal-structure results which have been obtained.

All the structures described in this article were deduced from X-ray diffraction patterns of crystal powders. Only in two instances, $PuCl_3$ and Na_3UF_7,