XXVI. A quantitative X-ray Analysis of the Structure of Potassium Dihydrogen Phosphate (KH_2PO_4).

By

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(With 9 figures.)

I. Introduction.

Following upon a preliminary examination of the dihydrogen phosphates of potassium and ammonium by O. Hassel[1]) the structure of KH_2PO_4 has been examined in detail by S. B. Hendricks[2]). Laue, rotation and powder photographs were employed in this last investigation, and, in the case of the rotation photographs, a correction was applied to the intensities of the registered photographic spots to allow for the different degree of absorption of the incident radiation due to the varied orientation of the reflecting planes.

Of the atoms composing the crystal, the potassium and phosphorus atoms are fixed by symmetry whilst the positions of the hydrogen atoms must to some extent remain speculative. The oxygen atoms are in the general position and, being all equivalent, require the evaluation of three parameters only. The structure is therefore a very simple one.

In his treatment of the problem, Hendricks virtually assumes a PO_4 group by supposing the $P—O$ distance to be less than 1.95 Å. His assumption with regard to the relative scattering powers of the constituent elements practically reduces to an assumption that the atoms scatter proportionately to their atomic number.

His conclusions are rather challenging. He insists on the PO_4 group possessing a very definite sphenoidal rather than regular tetrahedral shape and considers the structure as evidence that the shape of the PO_4 group is not independent of the ionic surroundings. He also considers it impossible for an oxygen atom to be equidistant from its two potassium neighbours. Some idea of the general shape and dimensions of the group of four oxygen atoms about each phosphorus atom and

1) Z. Elektrochem. **31**, 523, 1925. 2) Am. J. Sci. **14**, 269, 1927.

of eight oxygens about each potassium atom may be gathered from a study of Fig. 8 in conjunction with Table VI. The bracketed pairs of letters in Table VI refer to distances in Fig. 8.

The present investigation was undertaken for two reasons. First, because of the interest of Hendricks' conclusions with regard to the geometrical configuration in the structure, and second because it was thought that the crystal would offer an interesting example of the use of direct quantitative X-ray analysis. The development of this type of analysis has advanced rapidly during recent years, and now appears to have reached a stage when a more accurate determination of parameters in the more interesting simple structures can be attempted with some confidence. This paper is the first of a proposed series of such attempts.

The following treatment which is based on experimental work with the ionisation spectrometer and some photometric measurements of powder photographs makes no initial assumptions other than the generally accepted formal relations between the intensity of reflexion of X-rays from crystal planes and certain known factors affecting their intensity.

II. Crystallographic Details.

The crystals were kindly prepared for me by Mr. H. E. Buckley. They are referred to by him in a recent paper[1]).

The measurements made on the crystal with the ionisation spectrometer and by the powder method lead to a unit cell and space group in agreement with those given previously by Hassel[2]) and by Hendricks[3]).

The unit cell is body-centred tetragonal with sides $a = b = 7.43$ Å, $c = 6.97$ Å and contains four molecules of KH_2PO_4.

The Space Group is V_d^{12}. For the symmetry elements of this group reference should be made to the usual sources. Some of these elements are indicated in Fig. 1 which may be regarded as a key diagram to the paper showing the way in which a typical atom in the general position (angular coordinates θ_1, θ_2, θ_3[4])) is repeated throughout the unit cell. Hendricks, following Wyckoff, takes the origin of coordinates on the tetragonal axis halfway between the two points where it is intersected by screw axes parallel to (001). For simplicity of comparison we shall adopt the same origin although a displacement to a point $\pm(0\,\frac{1}{4}\,\frac{1}{8})$ possesses advantages.

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1) In press (Z. Krist.). 2) Z. Elektrochem. **31**, 523, 1925.

3) Am. J. Sci. **14**, 269, 1927.

4) $\theta_1 = 2\pi x/a$; $\theta_2 = 2\pi y/b$; $\theta_3 = 2\pi z/c$. In the text these coordinates are expressed in degrees.

There are $4P$, $4K$, $8H$ and $16O$ atoms to be placed in the unit cell. The $4P$ and $4K$ must clearly go to the two sets of fourfold equivalent points, viz.

$$0\,0\,0;\ \tfrac{1}{2}\,0\,\tfrac{1}{4};\ \tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2};\ 0\,\tfrac{1}{2}\,\tfrac{3}{4} \qquad \text{(set 1)}$$

$$\text{and}\ \ 0\,0\,\tfrac{1}{2};\ \tfrac{1}{2}\,0\,\tfrac{3}{4};\ \tfrac{1}{2}\,\tfrac{1}{2}\,0;\ 0\,\tfrac{1}{2}\,\tfrac{1}{4}. \qquad \text{(set 2)}$$

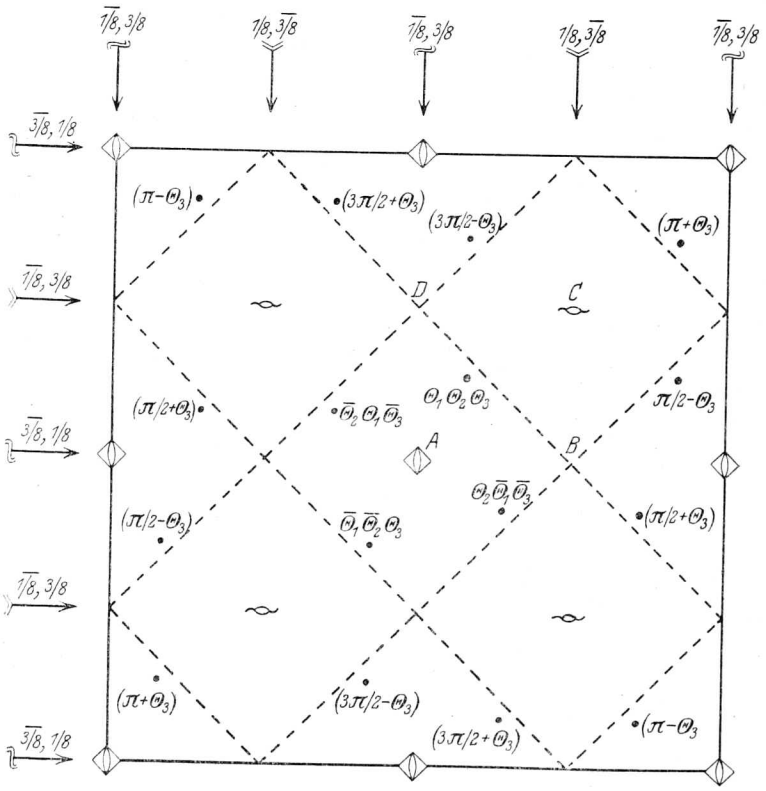


Fig. 1. Projection of symmetry elements on (001). The broken lines represent glide planes; the full lines merely define the unit cell. The θ_1 θ_2 coordinates are not given for each point; they will be clear from the symmetry.

It is immaterial which of these sets we initially adopt for the position of the P and K atoms. We shall with Hendricks place the P atoms in the positions given by set 1 whilst the K atoms must belong to set 2. The hydrogen atoms must be in one of the two sets of eightfold equivalent points; we shall ignore them for the moment. The space group would now permit the $16O$ atoms to belong to one set in the 16 fold equivalent position — the general position — or to two sets of eight-

fold positions. A qualitative consideration of the spectra does not reveal the simplicity to be expected if we suppose the last. We therefore suppose the oxygen atoms to be in the general position.

We begin our problem therefore, neglecting the hydrogen atoms, with the following positional information

P atoms set (1)
K atoms set (2)
O atoms xyz; $y\bar{x}\bar{z}$; $\bar{x}\bar{y}z$; $\bar{y}x\bar{z}$; $(\frac{1}{2}-x), y, (\frac{1}{4}-z)$;
$(\frac{1}{2}-y), \bar{x}, (z+\frac{1}{4})$; $(x+\frac{1}{2}), \bar{y}, (\frac{1}{4}-z)$; $(y+\frac{1}{2}), x, (z+\frac{1}{4})$
and these $+\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

We have to find xyz (or $\theta_1\theta_2\theta_3$).

III. General Procedure.

1. Experimental Details.

Several good crystals from the same crop were available for analysis. Preliminary tests carried out with the ionisation spectrometer showed that the intensities of reflexion from corresponding natural faces in all the crystals were the same. The two largest crystals were therefore chosen for detailed investigation, one being ultimately used for the examination of planes of the type $(hk0)$, the other for planes of type $(h0l)$.

The general experimental procedure adopted here follows closely that described by Prof. W. L. Bragg and the author in a paper on a technique of structure analysis[1]) and for nomenclature and general information that paper should be consulted.

Using a rocksalt standard for comparison, a set of absolute measurements of the integrated intensity of reflexion of rhodium K_α radiation from the $(h00)$ and $(00l)$ planes of each crystal was first obtained; these measurements were carried out on the ground faces. Two slips from these crystals were then cut; one parallel to (001), the other parallel to (010). The slips had a thickness equal to the reciprocal of the linear absorption coefficient of the material for RhK_α radiation. Using the slip cut parallel to (001) and passing the X-rays through it, a set of absolute intensity measurements for reflexion from all internal planes with the c axis as zone axis — viz. $(hk0)$ planes — was carried out. In a similar way the second slip provided a set of measurements for the $(h0l)$ planes. These experimental observations are sufficient for the evaluation of the parameters of the structure since from them we can deduce the structure amplitudes for the unit cell corresponding to the various planes examined.

1) Z. Krist. **69**, 118, 1928.

2. Reduction of Observations.

Several difficulties are encountered in reducing the experimental observations to values of the corresponding structure amplitudes. These are discussed in the paper quoted above[1]) and will only be referred to here. The general equation expressing the integrated intensity of reflexion (ϱ) of a beam of X-rays (wave length λ) from the extended face of a crystal of the mosaic type is

$$\varrho = \frac{N^2 e^4 \lambda^3}{4 \mu_0 m^2 c^4} \cdot \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot F^2 \tag{1}$$

$$= Q/2\mu_0 \tag{2}$$

where N is the number of unit cells per unit volume, e, m and c refer to an electron, F is the structure amplitude for the plane considered and μ_0 is the linear absorption coefficient of the material.

The corresponding formula for reflexion within a crystal slip is

$$\varrho_{\text{slip}} = Q t e^{-\mu_0 t} \tag{3}$$

where t is the effective thickness of the slip for the plane concerned.

It is customary to use slips of thickness $t_0 = 1/\mu_0$ for which value the intensity is a maximum ($= Q/e\mu_0$). It is also convenient to express all intensities measured through the slip in terms of the intensities which would have been obtained from the corresponding extended faces had they been present or prepared on the large crystal from which the slips were cut. For a variety of reasons the relation between the intensity of reflexion from a crystal plane within the slip and that from the corresponding extended face on the original crystal is sometimes not so simple as the above formulæ suggest. The relation is, however, usually linear, or nearly so, and can be found by a calibration experiment in which reflexions measured for certain extended faces on the original crystal are compared with the corresponding reflexions through the slip. This method is not above criticism, but it has been found in practice to provide the investigator rapidly with a large number of results (dependable within the accuracy usually required) which could not have been obtained from the material available if reflexions from prepared faces had been stipulated.

Supposing now that our observations are all expressed in terms of the intensity of reflexion from an extended face, we cannot immediately apply equation (1) to determine $F(hkl)$ — the object of the experiment — since the crystal will in general exhibit one or both types of extinction. So far no practical method has been suggested by which observations

1) Z. Krist. **69**, 118, 1928.

of the type described above can be corrected for primary extinction, although two methods are in use in the case of secondary extinction. In general, however, the effect of primary extinction in crystals is less serious than that of secondary extinction and we suppose (since both effects are in the same direction) that the correction deduced for secondary extinction accounts to some extent also for the primary extinction which may be present.

Since the result of secondary extinction is effectively to increase the true absorption coefficient μ_0 to μ according to the relation

$$\mu = \mu_0 + g\,Q \tag{4}$$

where g is supposed constant for the crystal, we may correct our experimental values for the intensities of reflexion (ϱ') to the true intensities (ϱ) appropriate to equation (1) by using the relation

$$\varrho = \frac{\varrho'}{1 - 2g\varrho'}\,. \tag{5}$$

We require to evaluate g.

Of the two methods normally employed for this purpose, one is experimental and seeks to find g by determining the effective absorption coefficient μ in (4) for one or more reflexions measured through a crystal slip. The other is based on trial and error and seeks to solve (5). The first method is laborious and, with some crystals, difficult since it depends on a series of observations made on a slip which is gradually ground to a thin flake. The second method depends to some extent on a partial solution of the structure with respect to some direction, and upon a knowledge of the atomic F curves.

In the present experiments a further method of evaluating g has been tried, which, when it can be applied, has much to recommend it; for it is rapid and convenient, and supplies in addition a set of absolute intensities of reflexion from general planes (hkl) not usually measured on the spectrometer. It consists in taking a powder photograph of a portion of the crystal used in the spectrometer experiments, and estimating by photometric measurement, the relative intensities of the various lines[1]). Now, provided the powder be sufficiently fine both primary and secondary extinction will be absent, and the relative intensities of reflexion deduced from the lines on the photograph will represent the relative values which would have been obtained with the spectrometer if both types of extinction had been absent. By comparing therefore a series of planes examined by both powder and ionisation methods

1) With a sufficiently sensitive instrument this experiment is preferably carried out on the ionisation spectrometer.

one can find g from equation (5). At the same time one can use the corrected spectrometer results to calibrate in absolute measure the whole of the powder results. The method of course depends on the reliability of the photometric measurements. This is not the place to discuss at length the many difficulties involved in such measurements. It is perhaps sufficient to say that in the present case, by preliminary tests a method was developed by which — provided certain experimental conditions were realised — a set of relative intensities could be obtained which were, within the limits required for the work, satisfactory. I should like at this stage to express my debt to Dr. A. J. Bradley of this laboratory for carrying out these photometric measurements for me. Table IV is based on his work.

3. Fourier Analysis.

The application of Fourier series to the determination of parameters in crystal structures has been discussed at some length by Prof. W. L. Bragg in a recent paper[1]). In that paper, to which reference should be made, the use of a double Fourier series to represent the projection of the unit cell on some given plane was advocated, and a method by which such a projection could be conveniently carried out was described in detail.

If the projection of the unit cell on the plane chosen possess a centre of symmetry the expression for the electron density at a point in the projection is a simple one if this symmetry centre be chosen as origin; for the difficulty of determining the phase constants in the Fourier series reduces to that of determining the signs of the Fourier coefficients whose magnitudes are dependent on the structure amplitude, $F(hkl)$. Thus for a projection on (001) under these circumstances, the density is given by

$$\varrho_{xz} = \frac{1}{A} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} F(h0l) \cos (2\pi hx/a + 2\pi lz/c) \qquad (6)$$

where A is the area of the projection and

$F(000) = Z$, the total number of electrons in the cell.

The X-ray measurements give us the magnitudes of $F(h0l)$ but not their signs.

In the example of the diopside crystal given in the paper quoted, the signs were known from an earlier analysis of the structure carried out by a "trial and error" process using a set of atomic F curves. Thus the projections by Fourier analysis provided a summary of and final

1) Pr. Roy. Soc. **123**, 537, 1929.

check on the earlier work rather than a direct and independent solution of the crystal structure. To what extent can the method be direct? In the present case of KH_2PO_4, which is of course very simple, an attempt at direct analysis has been made by a method which is virtually one of successive approximation. The success with which the method could be applied to complex crystal structures would depend upon the particular structure. This and related problems will be discussed in detail in a paper shortly to be published by Prof. W. L. Bragg and the author.

General Data.

Linear absorption coefficient (RhK_α radiation) $= 10.7$ (calculated),
$= 10.4$ (observed).

Volume of unit cell $= 385 \times 10^{-24}$ (Å^3)

$$\frac{N^2 e^4 \lambda^3}{4 \mu_0 m^2 e^4} = 2.98 \times 10^{-9}.$$

Extinction coefficient (g of equation 5) $= 9.5 \times 10^3$.

IV. The ($hk0$) reflexions.

Fig. 1 represents a projection of the unit cell on (001). In it are shown certain symmetry elements and the positions of an atom in the general position. The coordinates chosen for this atom (relative to the origin at the centre of the cell) are conveniently those found later for the oxygen atoms. The potassium and phosphorus atoms are on the tetragonal axes at heights given already above.

The expression for the phase factor for reflexions of type ($hk0$) referred to the origin is

$$n(\cos h\theta_1 \cos k\theta_2 + \cos h\theta_2 \cos k\theta_1) \text{ for planes with } h \text{ even} \quad (7)$$

$$\text{and } n(\sin h\theta_1 \sin k\theta_2 - \sin h\theta_2 \sin k\theta_1) \quad ,, \quad ,, \quad ,, \quad h \text{ odd.} \quad (8)$$

where n is half the number of equivalent positions occupied by the atoms considered (e.g. 2 for potassium or phosphorus, 8 for oyygen).

Owing to the special positions of the potassium and phosphorus atoms, the ($hk0$) spectra reduce to two types corresponding to expressions (7) and (8) viz.

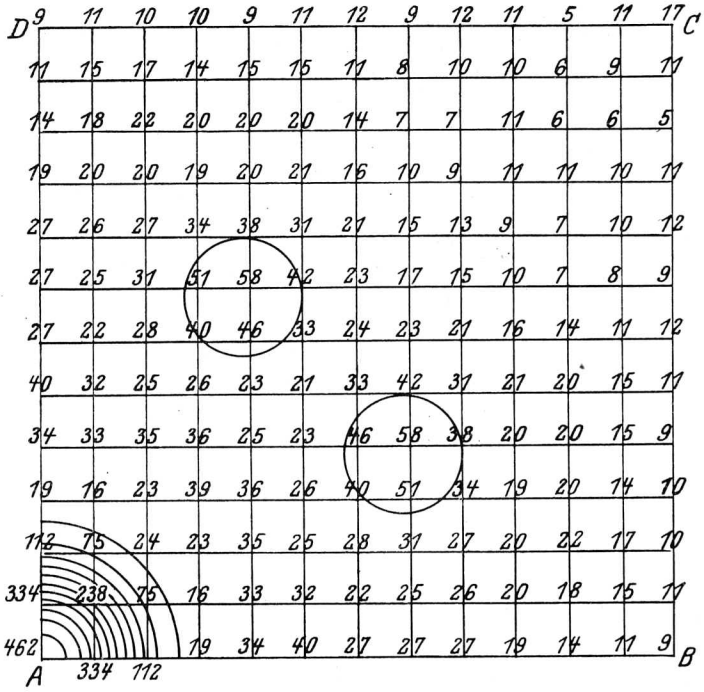
Type I. (h even) Contribution of atoms is potassium + phosphorus + oxygens.

(h odd) Contribution from oxygen atoms only.

The spectra of type II are all weak compared with those of type I which receive a full contribution from potassium and phosphorus. We conclude that the signs of the phase factors (and therefore of the structure amplitudes $F(hk0)$) for type I spectra are governed by the potassium

and phosphorus atoms. It follows that in applying the method of double Fourier analysis to the $(hk0)$ planes we shall know the signs of the Fourier coefficients, $F(hk0)$, for all planes with h even though not with h odd.

We now carry out a preliminary double Fourier analysis using only those terms whose signs we know (type 1). A portion of the resulting



Figs. 2, (a), (b) and (c). Fourier diagrams of projection of a portion (1/16th) of unit cell on (001). The numbers are calculated for intervals of $7\frac{1}{2}^{\circ}$ (i. e. 1/48th of cell edge).

Fig. 2(a). $(hk0)$ planes for which h and k are even. K, P and O atoms contribute.

projection representing $\frac{1}{16}$ of the unit cell is given in Fig. 2(a). It should be compared with the portion $ABCD$ of Fig. 1. Each number represents one tenth of the electron density at the point occupied by the number. Since we have only used a portion of the Fourier terms available, we cannot expect to obtain a true picture of the projected structure. Thus, examining Fig. 2, although we note the true positions of the potassium and phosphorus atoms (superimposed) at (0, 0) there are in addition two small peaks (at approximately 30°,

50° and 50°, 30°) clearly outlining oxygen atoms, which are symmetrical about the line $x = y$. These peaks cannot represent independent atoms however since there are only 16 such atoms in the complete cell. The difficulty is removed when we realise that the positional symmetry of the potassium and phosphorus atoms is higher than that required by V_d^{12} and, since we have only considered terms to which potassium and phosphorus atoms contribute, this higher symmetry is imposed on the

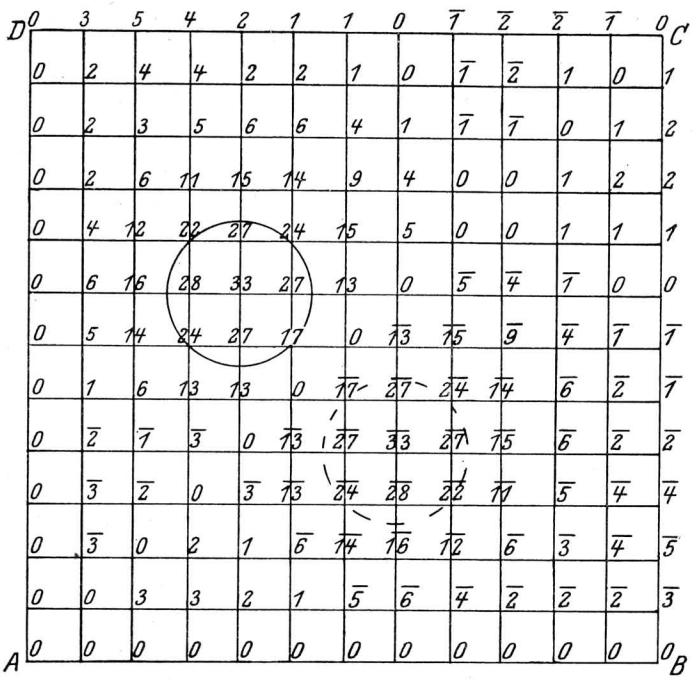


Fig. 2(b). $(hk0)$ planes with h and k each odd. Only O atoms contribute. The contours are here drawn for an electron density of 20 instead of 40 as in all other diagrams.

resulting projection. The positions of either of these two small peaks in Fig. 2 does however give us good preliminary values for the x (or θ_1) and y (or θ_2) coordinates of the oxygen atom. Owing to the symmetrical character of the expressions (7) and (8) it is not possible at this stage to distinguish between θ_1 and θ_2 and we shall arbitrarily adopt the peak giving $\theta_1 = 30°$ and $\theta_2 = 52°$.

We now use these approximate perliminary coordinates to determine the signs of $F(hk0)$ for the crystal planes with h odd. The oxygen

atoms alone contribute to the reflexions from these planes. The results of a Fourier analysis of these spectra alone are contained in Fig. 2(b). Comparing this diagram with Fig. 2(a) we find, of course, no peak corresponding to the potassium and phosphorus atoms, and we note that instead of the two small peaks of Fig. 2(a) we have in Fig. 2(b) one small peak and a symmetrically placed hollow (negative terms)

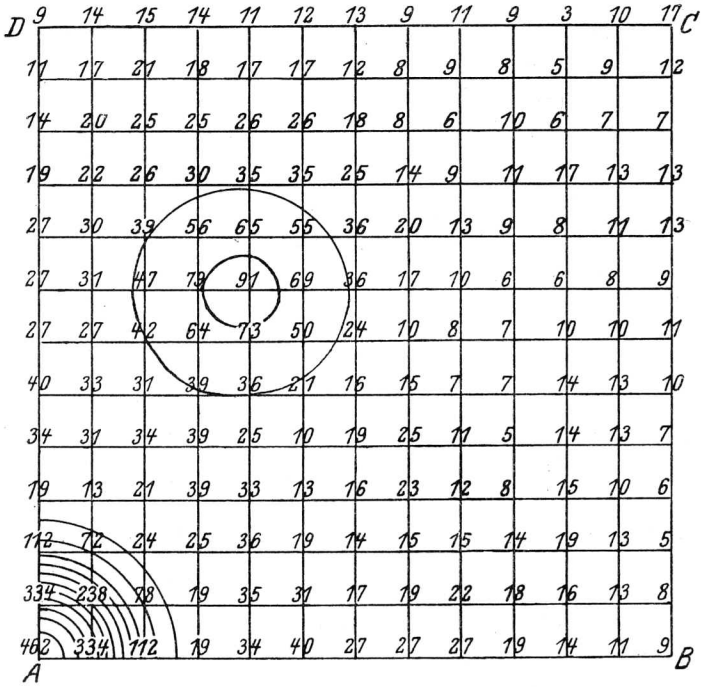


Fig. 2(c). Complete diagram using all reflexions $(hk0)$.

which is an inversion of the peak. Combining Figs. 2(a) and 2(b) we derive Fig. 2(c) which represents the full information obtainable by double Fourier analysis of all the $(hk0)$ spectra. We see that one of the small peaks of Fig. 2 has vanished whilst the other small peak has correspondingly increased, the diagram now having the symmetry indicated in Fig. 1. Fig. 3 represents the complete projection of the cell obtained by the operation of the symmetry elements on Fig. 2(c). It should be compared with the key diagram Fig. 1. From Fig. 2(c) we estimate $\theta_1 = 29^\circ$, $\theta_2 = 52^\circ$.

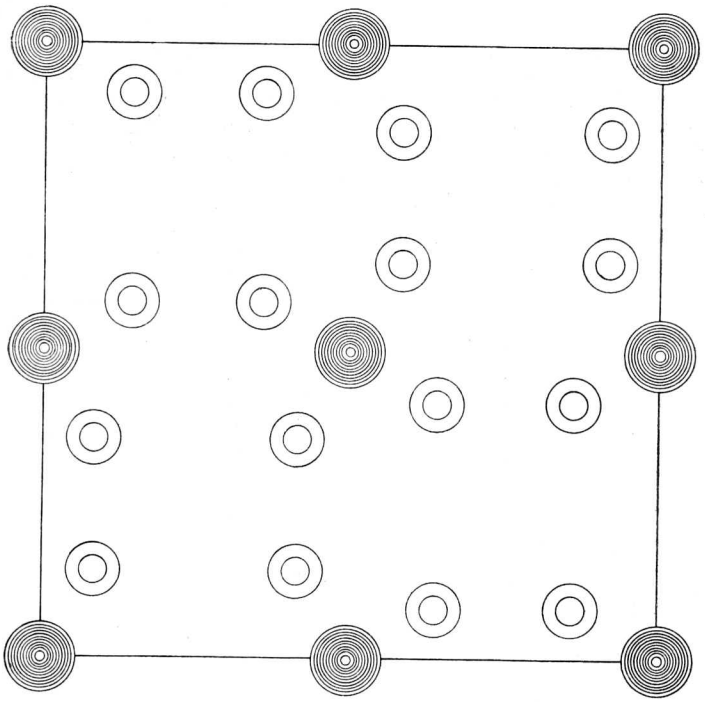


Fig. 3. Complete Fourier projection of atoms in unit cell on (001). The contours are drawn for the same intervals as in Fig. 2. These contours are so nearly circular that circles have been drawn in this diagram (for detailed form see Fig. 2).

Deduction of Atomic *F* curves.

Although we have now obtained the information required, viz. the values of the parameters θ_1 and θ_2, we may go further and use these values to deduce a set of atomic F curves appropriate for use with our crystal. Thus, considering reflexions of type II above, which are due to oxygen atoms only, we can at once find the value of $F(hk0)$ per oxygen atom corresponding to each plane $(hk0)$, and, therefore, to some value of the glancing angle. In this way we obtain the lower full line curve of Fig. 4 and the numbers of column 5 of Table I(a). Furnished with this curve for oxygen, we may in a similar manner consider reflexions of type I, to which potassium and phosphorus atoms also contribute, and deduce an atomic F curve for potassium + phosphorus (the upper full line curve of Fig. 4); we cannot deduce from the $(hk0)$ spectra separate curves for potassium and phosphorus. *These curves apply without correction to our particular crystal and can be used in the anaylsis of other reflexions.*

Table I(a).

Theoretical and experimental F values for oxygen.

Column lettered (a) refers to F values for the atom at rest. Column lettered (b) refers to F values for the atom at room temperature and have been obtained from the numbers in the (a) column by using a temperature factor found for KCl[1]. Column lettered (c) is similar to the (b) column except that the temperature factor used was an approximate one obtained experimentally for KH_2PO_4. In the last column are given the observed F values.

sin θ	(a)	(b)	(c)	Observed
0	8.0	8.0	8.0	
0.1	6.6	6.4	6.5	6.0
0.2	3.6	3.0	3.3	3.0
0.3	2.3	1.50	1.80	1.65
0.4	1.75	0.90	1.20	1.10
0.5	1.50	0.50	0.80	0.70
0.6	1.35	0.25	0.55	

Table I(b).

Theoretical and experimental F values for potassium and, approximately, for phosphorus. The lettered columns have the same meaning as in Table I(a).

sin θ	a			b			c			Observed		
	K	P	$(K+P)$	K	P	$(K+P)$	K	P	$(K+P)$	K	P	$(K+P)$
0.1	14.6	9.7	24.3	13.7	9.1	22.8	14.1	9.5	23.6	11.8	8.2	20.0
.2	10.3	6.8	17.1	8.6	5.4	14.0	9.2	6.2	15.4	8.0	5.0	13.0
.3	7.9	5.3	13.2	5.3	3.3	8.6	6.3	4.3	10.6	5.3	3.7	9.0
.4	6.7	4.5	11.2	3.3	2.2	5.5	4.7	3.1	7.8	3.8	2.6	6.4
.5	5.8	3.8	9.6	1.9	1.2	3.1	3.3	2.1	5.4	2.4	1.6	4.0
.6	4.9	3.2	8.1	1.0	0.7	1.7	2.1	1.4	3.5	1.2	0.8	2.0

It is however of interest to compare these curves with those available from other sources. For example, in a recent paper[2] R. W. James and G. W. Brindley have given a theoretical curve for potassium (at rest) (see Column 2, Table I(b)). This curve was found to be in quite good agreement with an experimental curve for potassium deduced from a study of a crystal of KCl, provided due allowance was made for the considerable heat motion present in crystals of KCl. A theoretical F curve for phosphorus is not yet available, but we can obtain a reasonably approximate one from the potassium curve (Column 3, Table I(b)). We are thus able to compute a (potassium + phosphorus) curve. For a theoretical F curve for oxygen (Column 2, Table I(b)), I am indebted

1) Pr. Roy. Soc. **121**, 155, 1928. 2) Pr. Roy. Soc. **121**, 155, 1928.

to Mr. R. W. James who based his calculations on data supplied by Prof. Hartree. These curves refer to atoms at rest, and when compared with those of Fig. 4 are found to be definitely higher, especially

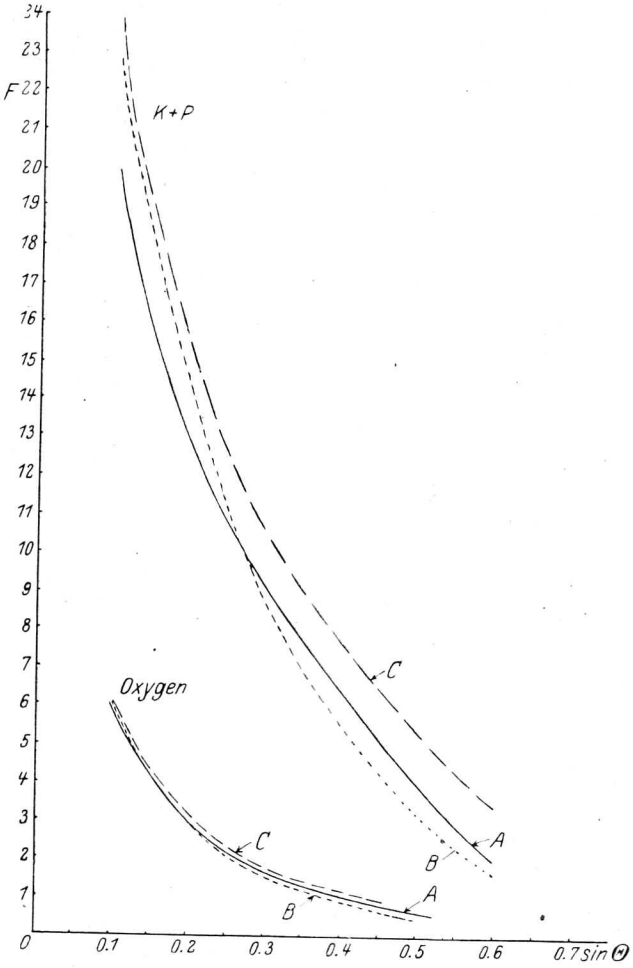


Fig. 4. F curves for O and $(K+P)$ atoms.

A curves are the F curves found directly by experiment. — C curves are theoretical F curves for the atoms at rest reduced to room temperature by means of an approximate factor found by experiment. — B curves are the theoretical curves reduced to room temperature by means of the factor found for KCl.

for large values of $\sin\theta$, where θ is the glancing angle of incidence. The discrepancies are mainly attributable to the possible under correction for extinction and to the effect of heat motion.

The correction for extinction, as explained above, was based on a photometric examination of the intensities of the lines on a powder diagram and it is quite possible that the intensities of the strongest lines was underestimated — underestimation would certainly be the direction of error in the experiments. There is also the possibility that the powder was not sufficiently fine to remove all traces of extinction. In this last connection, reference may be made to a determination of the atomic F curve for carbon by A. H. Armstrong[1]) using a powder method with diamond. Great pains were taken by her to obtain a very fine powder, and the differences between her results and those obtained in an earlier investigation by Ponte[2]) are ascribed primarily to the state of division of the diamond particles.

In order to get some idea of the importance of heat motion in the phosphate crystal, a set of measurements at the temperature of liquid air was carried out reflecting from the (010) face of a large crystal. I am indebted to Mr. R. W. James, whose work on the temperature effect in crystals is well known, for the loan of his apparatus for this purpose. Although the results were only preliminary in character — a more detailed investigation may be carried out later — they indicated that the heat motion at room temparatures was very considerable. For example, the intensity of the (0100) reflexion was increased some four times when the temperature of the crystal was lowered from room temperature to that of liquid air. With the help of certain assumptions, an approximate value for the temperature factor was obtained which, when applied to the above mentioned theoretical F curves for the atoms at rest, gave the curves (broken lines) of Fig. 4. If however we suppose the temperature factor for the phosphate crystal to be as great as that for crystals of KCl, we obtain the remaining two curves (dotted) of Fig. 4. Our experimental curves (full lines) will clearly be comparable with curves which could be drawn from theoretical curves if we adopt a temperature factor somewhat less than that for KCl and greater than that deduced from the preliminary temperature experiments, and if we suppose the extinction to be slightly greater than that actually adopted from the powder results.

The agreement may be taken as a further demonstration that it is practicable to employ a universal set of atomic F curves in investigating any crystal provided one can apply a satisfactory correction for temperature. This correction which need not be very accurate for normal structure determination might be found directly by experiment or pos-

1) Phys. Rev. **34**, 1115, 1929. 2) Phil. Mag. **3**, 195, 1927; **4**, 232, 1927.

sibly inferred from certain physical properties of the crystal. Of course, whenever one can, as in the present case, derive directly from a portion

Table II.

Indices	$\sin\theta$	Observed Intensity ϱ' (face)	F(observed) corrected for extinction	F(calcul.)
(200)	0.083	45.0	90	105
(220)	.117	29.6	54	59
(310)	.131	8.5	22	22
(400)	.165	9.0	24	20
(420)	.185	15.7	40	45
(510)	.211	5.0	20	20
(440)	.234	19.2	52	57
(530)	.241	5.1	22	22
(600)	.248	12.1	40	38
(620)	.262	16.6	49	50
(710)	.292	0.3(5)	5	5
(640)	.298	10.9	39	43
(730)	.315	0.12	3	3
(800)	.331	6.1	32	32
(820)	.341	7.1	33	35
(660)	.351	2.2	18	17
(750)	.355	0.12	3	3
(840)	.370	5.3	30	30
(910)	.374	0.60	9	11
(930)	.392	0.70	10	11
(860)	.413	2.2	20	18
(1000)	.414	2.4	21	20
(1020)	.422	2.1	20	19
(950)	.426	0.03	3	3
(1040)	.445	2.50	22	22
(880)	.468	1.20	16	15
(1060)	.482	2.5	24	24
(1200)	.496	1.8	20	18
(1220)	.503	0.80	14	15
(1240)	.523	0.40	10	10
(1080)	.530	1.10	16	16
(1260)	.554	0.70	14	14
(1400)	.579	0.80	14	14
(10100)	.584	0.20	8	7
(1420)	.585	0.60	12	11
(1280)	.596	0.40	11	10

of the available experimental data a set of F curves appropriate to the crystal, it is better do so.

In Table II are collected the results for the $(hk0)$ planes. The absolute intensities of reflexion deduced for an extended face and uncorrected for extinction are given in column 3 whilst in column 4 are given the corresponding values of F $(hk0)$ corrected for extinction (taking $2g = 1.9 \times 10^4$ in expression 5). Column 5 contains the values of F calculated from the structure adopted using the full line atomic F curves of Fig. 4. Since these curves were deduced from a portion of the $(hk0)$ spectra we may expect good agreement. It is thus the uniformity of agreement in this Table which is to be taken as evidence of the correctness of the structure.

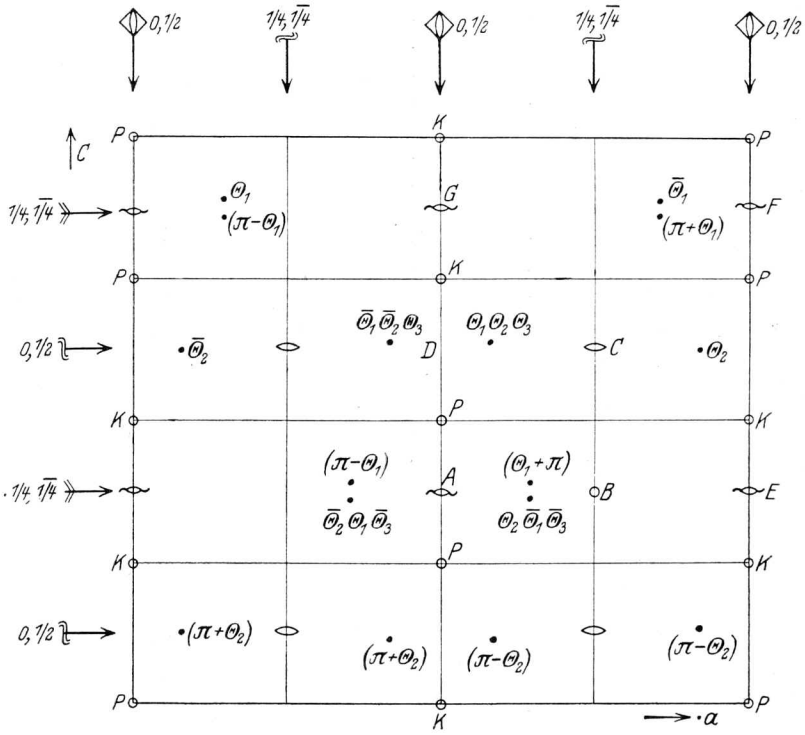


Fig. 5. Projection on (010) of some symmetry elements. The full lines are merely introduced to indicate the unit cell or to serve as convenient reference lines. The coordinates of the atom in the general position (oxygen) are referred to the true origin at the centre of the cell, although the origin adopted for the Fourier analysis is at A. The positions of the P and K atoms are shown.

Evaluation of the Parameter θ_3 — $(h0l)$ spectra.

Fig. 5 represents the projection of the unit cell on (010). The origin chosen earlier and coinciding with the position of a phosphorus atom

is at the centre of the projection. As for Fig. 1, an atom in the general position (with its equivalent positions) is shown. The atomic pattern presented by the potassium, phosphorus and oxygen atoms in this projection is seen to possess an effective symmetry centre at the point A $(0, \frac{1}{8})$. We shall accordingly choose this as our origin when considering the $(h0l)$ reflexions in order that in the subsequent double Fourier analysis of these reflexions we shall need only to know the magnitudes and signs of the Fourier coefficients, $F(h0l)$.

The phase factor for an atom in the general position is

$$n[\cos h\theta_1 \cos(l\pi/4 + l\theta_3) + \cos h\theta_2 \cos(l\pi/4 - l\theta_3)] \qquad (9)$$

subject to the condition $(h + l)$ even, n being the same as in (7), where θ_1, θ_2, θ_3 are *coordinates referred to the earlier origin.* Considering now the special positions of the potassium and phosphorus atoms we see from (9) that the spectra are of three types to which the contributions are:

Type I (l a multiple of 4) $K + P \pm$ oxygen terms.

Type II (l odd) $K - P \pm$ oxygen terms.

Type III (l even and not a multiple of 4) oxygen terms only.

As in the case of the $(hk0)$ spectra, and for the same reason, the $(h0l)$ spectra of type I are very strong compared with those of types II and III, and we may conclude that the signs of $F(h0l)$ are in this type determined by the potassium and phosphorus terms. We may also reasonably expect the scattering power of potassium to be somewhat greater than that of phosphorus when considering spectra of type II. Actually the difference was taken to be that between columns 11 and 12 of Table I(b) although the final results suggest that the differences adopted should be somewhat smaller. Spectra of types I and III do not help us to distinguish between θ_1 and θ_2; for this we must rely on spectra of type II.

Two methods of evaluating θ_3 are now open to us; (a) "trial and error" and (b) double Fourier analysis.

(a) Method of trial and error.

We have available the work on the $(hk0)$ planes and the values of $F(h0l)$.

Consider the $(00l)$ spectra. These are quartered by the space group requirements and only three (004), (008), and (0012) are available for examination; these will nevertheless serve to give an approximate value for θ_3. Thus, using $F(004)$, $F(008)$, $F(0012)$ the full line curves of Fig. 4 and expression (9) we find that θ_3 must be about $\pm 50°$ (or its complement $\pm 40°$). The values are confirmed by an examination of $(h0l)$ spectra of type III.

Table III.

Indices	$\sin\theta$	Observed Intensity ϱ' (face)	F(observed) corrected for extinction	F(calc.)
(101)	0.0604	14.2	21	21
(202)	.1208	12.4	29	31
(301)	.1316	18.9	38	41
(103)	.1385	14.0	30	35
(004)	.1770	1.20	8	7
(303)	.1812	4.5	19	18
(402)	.1874	1.8	9	11
(204)	.1949	20.0	46	46
(501)	.2111	0.35	7	8
(105)	.2242	0.3	7	8
(404)	.2416	23·0	59	64
(503)	.2449	0	0	0
(305)	.2534	2.2	15	12
(602)	.2631	6.8	28	28
(206)	.2770	1.00	10	11
(701)	.2930	1.80	14	12
(505)	.3020	0	0	1
(604)	.3041	9.3	37	39
(107)	.3112	0.20	4	5
(406)	.3120	0.15	4	5
(703)	.3180	2.00	16	14
(307)	.3326	1.10	12	12
(802)	.3422	0.90	11	12
(008)	.3540	10.8	39	41
(208)	.3622	3.6	25	29
(606)	.3624	1.60	15	14
(705)	.3637	1.50	15	15
(507)	.3714	0	0	3
(804)	.3748	5.5	30	29
(901)	.3748	0	0	0
(408)	.3998	2.4	20	19
(309)	.4155	0.40	9	9
(1002)	.4222	0.50	10	10
(707)	.4228	trace	<3	4
(806)	.4269	0.25	7	9
(608)	.4321	1.42	18	20
(1004)	.4584	1.0	15	15
(808)	.4832	1.20	16	17
(1006)	.4899	0.20	6	7
(1202)	.5037	trace	<3	4
(1204)	.5296	0.25	8	9
(0012)	.5300	0.25	8	8
(1008)	.5417	0.21	7	8
(4012)	.5540	0.39	9	10

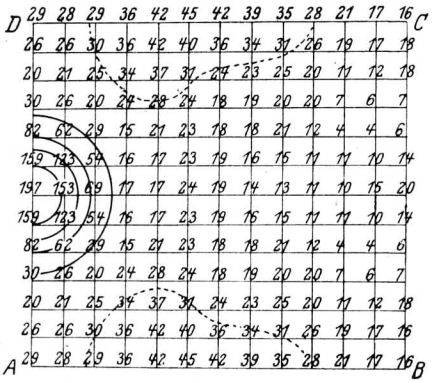


Fig. 6(a). Fourier diagram using only a portion of the $(h\,0\,l)$ spectra.

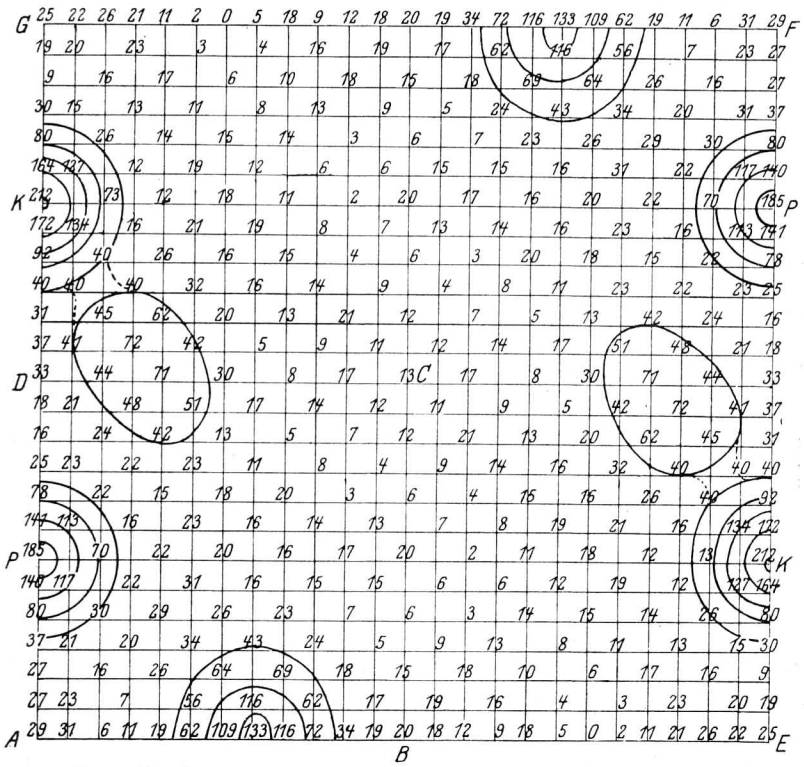


Fig. 6(b). Fourier diagram using complete set of $(h\,0\,l)$ spectra.

Fig. 6. Fourier projections of portion of unit cell on (0 1 0). These two figures 6(a) and 6(b) should be studied in conjunction with the key diagram Fig. 5. Corresponding portions on Fig. 5, Fig. 6(a) and 6(b) are similarly lettered. Note how the false high symmetry of Fig. 6(a) due to a partial Fourier analysis is corrected in Fig. 6(b).

We now consider spectra of type II in order to differentiate between the signs of θ_3 when θ_1 and θ_2 are chosen. By examining reflexions of type $(h0l)$ we find that for $\theta_1 = 29^\circ$ and $\theta_2 = 52^\circ$, θ_3 must be $+50^\circ$ (or $+40^\circ$). Finally by an examination of reflexions $(10l)$ we find θ_3 must be $+50^\circ$. The results of a test of all the $(h0l)$ spectra are given in Table III. The excellent agreement supports both the structure chosen and the atomic F curves obtained from the study of the $(hk0)$ spectra. Since the experiments were not originally designed for a careful examination of the atomic F curves, stress is not laid on the fact that the spectra of type II suggest that the difference between the $F(K)$ and $F(P)$ curves should be less than that adopted from Table I. The interpretation of this would be that the PO_4 group is not to be regarded as a pure ionic group in which a phosphorus ion (charge $+5$) is surrounded by four oxygen atoms (each of charge -2) but rather as one is inclined to regard the SiO_4 group in the silicates.

(b) Double Fourier Analysis of $(h0l)$ Spectra.

It is more difficult to evaluate the parameter by direct Fourier analysis than it was to find θ_1 and θ_2 because the $(h0l)$ spectra belong to three types as explained above whereas the $(hk0)$ spectra belonged only to two types. Of these three types we can only be certain of the signs of $F(h0l)$ for spectra of type I to which a full contribution is made by the potassium and phosphorus atoms. We try therefore an analysis using only these spectra [viz $(h0l)$ reflexions for which l is a multiple of 4] and obtain Fig. 6(a) which represents $\frac{1}{16}$th of the unit cell and corresponds to the portion $ABCD$ of Fig. 5.

The symmetry of the two figures is not however the same, for, as in the case of the partial analysis of the $(hk0)$ spectra which gave Fig. 2(a), the symmetry of Fig. 6(a) is higher than the true symmetry given by Fig. 5. Thus the peak in Fig. 6(a) with the highest value, 197, represents not one phosphorus atom as in Fig. 5 but $\frac{1}{2}(K+P)$ and instead of two oxygen atoms we have four halves distributed in two pairs (overlapping because of nearness) in the regions of higher numbers (of order 40) near the top and bottom of Fig. 6(a). In spite of this false symmetry it is however clear that the value of θ_3 for the oxygen atoms is between 45° and 60° (or their complements 45° and 30°) and probably nearer 45° than 60° (or 30°). If with this information we now examine the remaining $(h0l)$ spectra viz. of Type II and III, we can in practically all the cases decide the signs of $F(h0l)$. The very few cases where the sign is at all doubtful are those in which the spectra are very weak, the values of $F(h0l)$ therefore very small and,

consequently, of no importance in a Fourier analysis. The result of a complete analysis of the $(h0l)$ spectra using the new information is given in Fig. 6(b) which is to be compared with the portion *AEFG* of Fig. 5. We now note that the symmetry of Fig. 6(b) is identical with that of Fig. 5. The highest peak (212) in Fig. 6(b) represents the potassium atom, the next highest (185) represents phosphorus, the peak of height 72 represents a solitary oxygen atom whilst the region with a highest point 133 represents two oxygen atoms partially over-

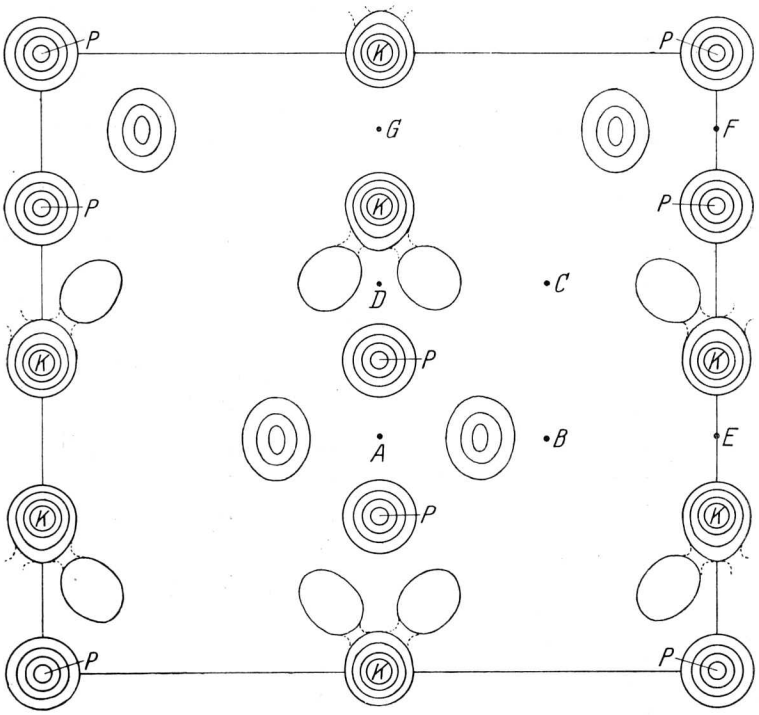


Fig. 7. Complete Fourier diagram of projection of unit cell on (010). Contour intervals are as in Fig 3. This diagram should be compared with Fig. 5.

lapping. From the isolated oxygen atom we find $\theta_3 = 50^\circ$ and check the earlier found value $\theta_1 = 29^\circ$, whilst from the overlapping oxygen atoms we find $\theta_2 = 52^\circ$ as found from Fig. 2(c). Fig. 7 represents the Fourier diagram for the complete cell (cf. Fig. 5) obtained by the operations of the symmetry elements on Fig. 6(b).

Except for the positions of the *H* atoms (discussed below) we have now completed the analysis of this simple structure which involved the determination of the three parameters θ_1, θ_2, θ_3, of the oxygen atom. In Table IV

we give the results of a comparison between the F values calculated from the structure and those deduced by a photometric examination of the powder photographs using certain corresponding reflexions obtained with the ionisation spectrometer as standard intensities. The agreement is very satisfactory when one considers the practical difficulties of photometric measurement. Ideally of course, where a sufficiently sensitive apparatus is available, the powder itself should be examined with the ionisation spectrometer.

Table IV.

Results obtained from Photometric Examination of Powder Photograph (see text).

Indices	$\sin\theta$	F observ.	F calc.	Indices	$\sin\theta$	F observ.	F calc.
(101)	0.060	16	21	(224), (150), (341), (501)	0.212	68	61
(200)	.083	86	105				
(121)	.102	19	23				
(112)	.106	78	82				
(220)	.117	60	59	(143)	.215	9	10
(202)	.121	26	31	(134)	.220	12	15
(130), (301)	.132	46	45	(105)	.224	14	9
(103)	.139	29	35	(251), (152)	.227	53	47
(321)	.155	34	36	(440)	.234	66	57
(132)	.157	67	70	(125)	.239	15	18
(123)	.161	19	17	(350), (404)	.241	73	68
(400)	.165	23	20				
(141), (004)	.176	16	18	(343), (503)	.245	15	16
(303)	.181	15	18	(600)	.248	40	33
(240), (402)	.186	53	48	(305)	.253	? absent	10
(204), (332)	.195	83	76	(161), (244), (352)	.255	77	68
(233)	.200	21	20	(253)	.259	13	14
(242)	.204	19	13	(260)	.261	56	50
				(602)	.263	32	28

In the foregoing analysis we have shown it possible to derive the parameters in a crystal of KH_2PO_4 by two methods, one of which depends wholly on a double Fourier analysis carried out in successive stages, whilst the other makes a partial use of Fourier analysis to determine certain parameters and atomic F curves and then virtually proceeds with this information to solve a set of equations to find the remaining parameter. The extent to which these methods are applicable

without modification to complex structures must depend on the structures e. g. whether some of the parameters of the heavier atoms are fixed by symmetry considerations. In any case, however, it should not often be necessary to use a laborious trial and error method throughout to determine completely the structure. By the aid of certain reasonable assumptions and a qualitative examination of the experimental data a complex structure may often be partially solved. This partial solution may well be sufficient to determine the signs of a considerable portion of the F values for the reflexions from planes in some important zone. The subsequent use of the method of double Fourier analysis (if necessary in successive stages as shown above) will then be best likely to lead rapidly to a complete solution. Care is of course necessary at each stage to ensure that the investigator is not misled by the false higher symmetry imposed on the projections by the incomplete character of the Fourier series used.

The Structure — Geometrical Considerations.

Table V.

Atomic coordinates.

Atom	New			According to Hendricks		
K	0°	0°	180°	0°	0°	180°
P	0°	0°	0°	0°	0°	0°
O	29°	52°	50°	(16°—27°) chosen 22°	43°—49° chosen 47°	52°—59° chosen 56°
H	90°	52°	45°			

In Table V are given the parameters determined in the present investigation (left hand side of table). For comparison we have collected in the same table (right hand side) the ranges and chosen values for the corresponding parameters as given by Hendricks. We note that the suggested new values are just outside (and in different directions) the ranges suggested by Hendricks.

Position of Hydrogen Atoms

There are eight hydrogen atoms in the unit cell, and the only positions available for them are the eightfold equivalent sets (in Wyckoff's notation):

$$(c)\ \pm[0\,0\,u],\ \pm[\tfrac{1}{2}\,0\,(\tfrac{1}{4}-u)],\ \text{and these} + \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}.$$

$$(d)\ [\tfrac{1}{4}\,u\,\tfrac{1}{8}],\ [u\,\tfrac{3}{4}\,\tfrac{7}{8}],\ [\tfrac{3}{4}\,\bar{u}\,\tfrac{1}{8}],\ [\bar{u}\,\tfrac{1}{4}\,\tfrac{7}{8}]\ \text{and these} + \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}.$$

Of these two sets we choose the second (*d*) because the first set (*c*) would involve placing the hydrogen atoms in improbable positions next to the potassium atoms. We have therefore to suggest a value for u in (*d*). A consideration of the directions of the interatomic forces in the structure as the hydrogen atom is given various values of u strongly suggests for u a value of 0.145 (i. e. angular coordinates $\theta_2 = 52^\circ$). The hydrogen atom in this position has a coordination of two and is situated at the point bisecting the line joining the two nearest oxygen atoms ($O—O$ distance = 2.54 Å) of adjacent PO_4 groups.

Table VI.

Interatomic distances based on Table V. See also Fig. 8 to which letters in square brackets refer.

New		Ranges according to Hendricks
$P - O = 1.56$ Å	$[P - A, B, C, D]$	$= 1.40 - 1.62$ Å
$O - O = 2.46$	$[A - B$ or $C - D]$	$= 1.92 - 2.20$
$O - O' = 2.60$	$\begin{bmatrix} A - C, D \\ B - D, E \end{bmatrix}$	$= 2.62 - 2.81$
$K - O = 2.79$	$[K - A, B, J, L]$	$= 2.52 - 2.71$
$K - O' = 2.81$	$[K - E, G, H, F]$	$= 2.80 - 2.97$

Shortest distance between two oxygen atoms of adjacent PO_4 groups

$= 2.54$ Å $\qquad = 2.62 - 2.99$ Å

The hydrogen atom is midway between these two atoms.

In Table VI are given two lists of interatomic distances based on the two sets of parameters of Table V. The structure may be regarded as consisting of HO_2, PO_4, and KO_8 groups interconnected so as to satisfy the valency relations. Each hydrogen atom is equidistant from its two oxygen neighbours, each phosphorus atom equidistant from its four surrounding oxygen atoms, and each potassium equidistant from its eight surrounding oxygen atoms. The general shapes of the two last groups will be clear from Fig. 8 studied in conjunction with the interatomic distances of Table VI remembering that the left hand side refers to the results of the present investigation whilst on the right hand side are collected the corresponding data according to Hendricks. The group of eight oxygen atoms about the potassium atom may perhaps best be regarded as consisting of two sets of four atoms arranged in tetrahedral fashion with a common centre of gravity and digonal axis, one set (*ABHJ* of Fig. 8) resulting in a regular tetrahedron which

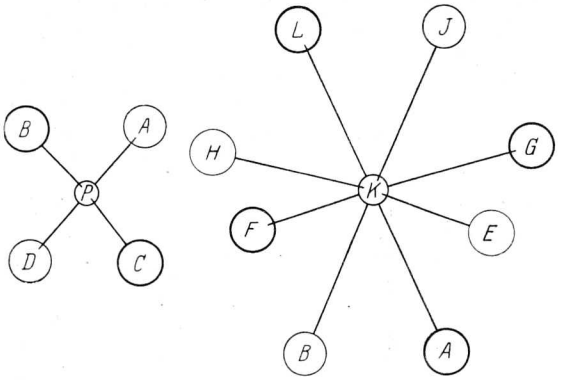


Fig. 8. Groups of four oxygen atoms about a phosphorus atom, and of eiight oxygen atoms about a potassium atom. The letters correspond to those used n Table VI in which interatomic distances are given.

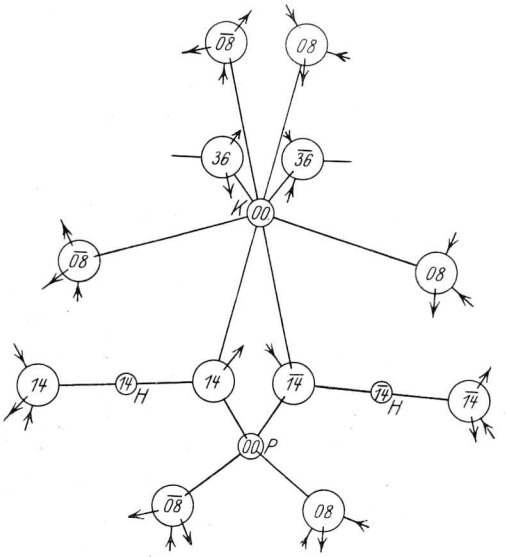


Fig. 9. Projection of portion of unit cell on (010) showing way in which the groups of Fig. 8 and the hydrogen atoms are interconnected. Numbers indicate heights (in decimal fractions of the cell edge) above (positive) and below (negative) the K and P atoms at 00. The lines represent valency bonds starting from the oxygen atoms (large circles). Their sense of direction relative to the reader is indicated by arrows. The letters in this diagram are chemical symbols.

has been extended along this common digonal axis (the alternating tetragonal axis of the cell) whilst the other set ($FEGH$) resembles a similar regular tetrahedron compressed along this axis.

The way in which the groups, HO_2, PO_4 and KO_8 are interconnected throughout the crystal will perhaps be clear from Fig. 9 which represents a portion of the structure projected on (010).

The new results show that the PO_4 group is not seriously distorted and that the potassium atom is equidistantly surrounded by eight oxygen atoms. Moreover the interatomic distances for oxygen are of the order generally observed in other crystals. It may even be doubted whether the small distortion of the PO_4 group deduced in the present experiments is real, for it is possible by a slight alteration of the parameters viz. from 29°, 52°, 50° to 30°, 54°, 47° (rather on the verge of experimental error) to obtain a configuration in which the PO_4 group is definitely regular ($O—O$ distance = 2.55 Å) whilst the potassium atom is still equidistantly surrounded by eight oxygen atoms ($K—O$ distance = 2.82 Å).

In conclusion, I wish to express my best thanks to Professor W. L. Bragg F. R. S. for his interest and advice throughout the course of the work.

Summary.

A quantitative X-ray study of the crystal structure of Potassium Dihydrogen Phosphate, KH_2PO_4, has been carried out. The treatment is based on experimental work with the ionisation spectrometer and on certain photometric measurements of powder photographs. The parameters are determined directly by the application in successive stages of the method of double Fourier analysis. Experimental atomic F curves for potassium, phosphorus and oygen are deduced and these are compared with the corresponding theoretical curves, allowance being made for the considerable heat motion present in the crystal. An additional method (applicable particularly to crystals of high symmetry) of determining the extinction coefficient in single crystals is described.

The structure deduced agrees with that proposed by S. B. Hendricks except that the shape of the PO_4 group is now found to be sensibly regular (tetrahedral) and the potassium atom is equidistant from its eight neighbouring oxygen atoms. Probable positions for the hydrogen atoms are also suggested.

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