$$I>I_1 \quad m^2_{hi}=1$$
$$I_1>I>I_2 \quad m^2_{hi}=I_1/I$$
$$I<I_2 \quad m^2_{hi}=(I_2/I)^{\frac{1}{2}}I_1/I\,.$$

A percentage error was assumed for intensities greater than I_1, taken to be the highest intensity that can be accurately measured from the top intensity film of a Weissenberg multipack. A constant error was assumed for intensities I_2 and I_1, the intensity region of the top film for which further measurement could be obtained from the second film of the multipack. An arbitrary factor $(I_2/I)^{\frac{1}{2}}$ was applied below I_2 to account for difficulty in accurately assessing these reflexions.

The reflexions were punched on cards together with the appropriate values of m^2_{hi} and i. The cards were sorted to put all the cards of the same hkl indices together so that the matrix elements of the equations $\mathbf{AL}=\mathbf{B}$ could be built up for each set of indices without prolonged storage of the individual reflexions. The equations were solved by replacing the first of the N normal equations by the equation $\sum_{j=1}^{N} a_{jj}l_j=0$. The values for the scale constants were punched out on cards and were used in a subsidiary program to obtain final values for F_{hkl} and mF_{hkl}, the standard of F_{hkl}, from the expressions

$$F_{hkl}=\frac{\sum_i m_{hi}^{-2}k_iF_{hi}}{\sum_i m_{hi}^{-2}} \qquad F^{hkl}_2 m^2=\frac{\sum_i m_{hi}^{-2}k_i^2F^2_{hi}}{(\sum_i m_{hi}^{-2})^2}\,.$$

It was found advantageous to recalculate the scale constants omitting those correlations for which $|\log(k_iF_{hi}/k_jF_{hj})|$ exceeded an arbitrary limit as a check on the accuracy of the data measurement and to exclude data containing extinction errors.

The basic difference between the present method and that of Hamilton, Rollett & Sparks is aptly demonstrated by considering the first example given by them.

Example 1. Consider the following set of data

	Layer 1	Layer 2	Layer 3
F^2_1	100	2	
F^2_2		1	2
F^2_3	100	3	

Both methods give $k_2/k_3=2{\cdot}00$ independent of the weights used though the method of Hamilton, Rollett & Sparks gives a value of

$$\frac{k_1}{k_2}=\frac{F^2_{12}+F^2_{32}}{F^2_{11}+F^2_{31}}=\frac{0{\cdot}050}{2{\cdot}000}$$

if all the weights are the same, that is there exists a constant absolute error in the F^2_{hi} values, whereas the present method gives a value of

$$\frac{k_1}{k_2}=\frac{\sqrt{(F^2_{12}\,.\,F^2_{32})}}{\sqrt{(F^2_{11}\,.\,F^2_{31})}}=\frac{0{\cdot}049}{2{\cdot}000}$$

if all the weights are the same, that is there exists a constant percentage error in the F^2_{hi} values. For a constant absolute error in the F^2_{hi} values the present method gives a value of $k_1/k_2=0{\cdot}053/2{\cdot}000$, giving a larger weight to the percentagewise more reliable correlation of F^2_3. It seems more realistic to use the present method of correlation depending on the percentage error of individual correlations, though with a large number of data little difference between the values given by the two methods should result.

References

ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.
SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
HAMILTON, W. C., ROLLETT, J. S. & SPARKS, R. A. (1965). *Acta Cryst.* **18**, 129.

Acta Cryst. (1965). **19**, 684

Refinement of the crystal structure of black phosphorus.

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(*Received* 26 *February* 1965)

Elementary phosphorus occurs in a number of modifications, but so far only the crystal structure of the black, orthorhombic modification has been determined. On the basis of powder diffraction data, Hultgren, Gingrich & Warren (1935) reported the following structure: Space group *Cmca*, $Z=8$, unit-cell dimensions $a=3{\cdot}31$, $b=10{\cdot}50$, $c=4{\cdot}38$ kX; 8P in 8(f) with $y=0{\cdot}098$, $z=0{\cdot}090$.

In the course of recent studies of the polymorphism of phosphorus, it was found that the black modification can be prepared in a well-crystallized condition from solutions of phosphorus in liquid bismuth. The crystals, obtained as a residue after dissolving the bismuth matrix with 1:1 nitric acid, were generally needle shaped with the needle axis coincident with the crystallographic a axis. Full details of the preparation of black phosphorus from liquid bismuth will be reported elsewhere. It may, however, be mentioned here that the sample used in the present investigation contained only 0·055 at.% Bi as determined by chemical analysis. Some of this bismuth may possibly be dissolved in the black phosphorus crystals, but there are strong reasons for believing that most of this residual bismuth is present only as a mechanical impurity left by incomplete dissolution in nitric acid.

Preliminary X-ray investigations of the black phosphorus product indicated that the structure proposed by Hultgren *et al.* is substantially correct. Since this structure determination is not very accurate by present standards, a refinement of the structure by single-crystal methods was thought to be worth while.

Accurate unit-cell dimensions were determined by powder diffraction methods. Powder patterns were recorded at room temperature (22°C) both in a Guinier–Hägg camera using strictly monochromatized Cr $K\alpha_1$ radiation and silicon ($a=5{\cdot}43054$ Å) as internal calibration standard, and in a Philips Debye–Scherrer camera with Cr K radiation. The dimensions obtained from measurements of the Guinier films are $a=3{\cdot}3138$, $b=10{\cdot}477_6$, $c=4{\cdot}3759$ Å, while those from measurements of the Debye-Scherrer films are $a=3{\cdot}3136$, $b=10{\cdot}477_8$, $c=4{\cdot}3766$ Å (Nelson-Riley extrapolation from lines with $54°<\theta<85°$). These results yield the following values for the unit-cell dimensions of black phosphorus: $a = 3{\cdot}3136$, $b = 10{\cdot}478$, $c = 4{\cdot}3763$ Å; with an estimated accuracy of 0·0005 Å for a and c and 0·001 Å for b.

For the single-crystal work, a needle-shaped crystal with a nearly cylindrical cross-section of less than 0·1 mm was used. Intensities were recorded in a Weissenberg camera employing zirconium-filtered Mo K radiation and the multiple-film technique with thin iron foils interleaved between successive films. The intensities were estimated visually by comparison with an intensity scale calibrated by timed exposures of one reflexion from the phosphorus crystal. A total of 89 $0kl$ and 56 $1kl$ reflexions were observed and their intensities were estimated and used in the structure determination without applying any corrections for absorption or extinction. The absorption correction is practically negligible for the crystal concerned. After the final refinement, the agreement between observed and calculated structure factors was found to be as good for the strong low-angle reflexions as for the remaining reflexions, indicating that extinction effects have a very small influence.

After some preliminary Fourier work, the structure was refined by the least-squares method, employing the program ORFLS, written by Busing, Martin & Levy (1962) for the IBM 7090 computer. Only the observed reflexions were included, and the weights assigned to the structure factor values were proportional to $1/|F|^2$. Atomic scattering factors for phosphorus were interpolated from the values given in *International Tables for X-ray Crystallography* (1962). The parameters refined were two scale factors, one for each of the layer lines ($0kl$) and ($1kl$), one isotropic temperature factor and two positional parameters (y and z).

The final structure data obtained are as follows:

Space group $Cmca$; $Z = 8$;

8P in 8(f): $y = 0{\cdot}10168$, $\sigma(y) = 0{\cdot}00009$;
$z = 0{\cdot}08056$, $\sigma(z) = 0{\cdot}00028$;
$B = 0{\cdot}798$ Å^2, $\sigma(B) = 0{\cdot}020$ Å^2.

The final R value for the 145 observed reflexions was 0·056. A list of observed and calculated structure factors can be obtained on request from the Institute of Chemistry, Uppsala, Sweden.

Powder data recorded in a Guinier–Hägg camera using Cr $K\alpha_1$ radiation are given in Table 1. A closer inspection of observed intensities and calculated pF^2 values in this table reveals notable discrepancies; compare *e.g.* the adjacent reflexions indexed as 002 and 131. This effect can be ascribed to preferred orientation, introduced during the preparation of the powder specimen. Comparable effects were observed in the powder patterns obtained by the Debye–Scherrer method. The occurrence of this effect may have some significance in connexion with the earlier structure determination by Hultgren *et al.*, which was based on an estimation of powder diffraction intensities. Small errors introduced by preferred orientation may, to some extent, explain the differences between the results of the present and the earlier structure determinations.

The main atomic arrangement in black phosphorus is well known and no detailed description is necessary. The structure is composed of puckered layers parallel with the (010) plane. A part of one layer is illustrated in Fig. 1.

The phosphorus atoms have three close neighbours within the same layer with the following bond distances and angles (as denoted in Fig. 2):

$d_1 = 2{\cdot}244$ Å, $\sigma = 0{\cdot}002$ Å
$d_2 = 2{\cdot}224$ Å, $\sigma = 0{\cdot}002$ Å
$v_1 = 96{\cdot}34°$, $\sigma = 0{\cdot}09°$
$v_2 = 102{\cdot}09°$, $\sigma = 0{\cdot}04°$

In addition, each phosphorus atom has eight neighbours (within 4 Å) in the same layer at the distances 3·314 (2), 3·334 (2) and 3·475 (4) Å, and four more neighbours in the adjacent layer at 3·592 (2) and 3·801 (2) Å. There are, accordingly, no contacts shorter than 3·59 Å between successive layers.

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *A Fortran Crystallographic Least-Squares Program.* ORNL-TM-305, Oak Ridge, Tennessee.

HULTGREN, R., GINGRICH, N. S. & WARREN, B. E. (1935). *J. Chem. Phys.* **3**, 351.

International Tables for X-ray Crystallography (1962). Vol. III. p. 202. Birmingham: Kynoch Press.

Table 1. *Powder diffraction data for black phosphorus*
(Guinier–Hägg camera, Cr $K\alpha_1$ radiation)

hkl	$\sin^2\theta_o$	$\sin^2\theta_c$	$p\|F\|^2\times10^{-2}$	I_0	d
020	0·04779	0·04775	18·6	w+	5·239 Å
021	0·11620	0·11620	72·8	m	3·359
040	0·19103	0·19101	93·6	m−	2·619
111	0·19971	0·19973	259·9	st+	2·561
041	0·25949	0·25946	16·5	w−	2·247
002	0·27374	0·27377	31·3	w+	2·188
131	0·29529	0·29524	37·6	w	2·107
022	—	0·32153	4·8	–	2·019
112	0·40509	0·40506	91·6	st	1·799
060	0·42979	0·42978	51·3	w	1·746
042	0·46483	0·46479	32·2	w−	1·679
200	0·47740	0·47740	81·3	st	1·657
151	0·48623	0·48625	245·3	st	1·642

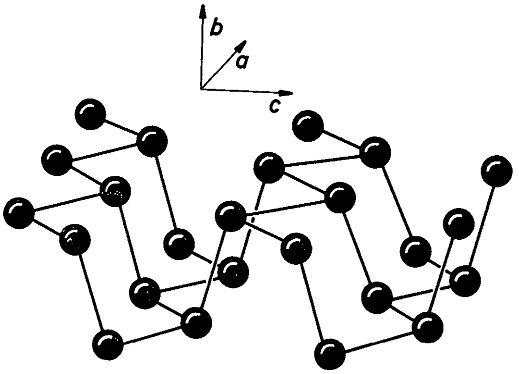

Fig. 1. A part of an infinite puckered layer of phosphorus atoms parallel with the (010) plane in the structure of black phosphorus.

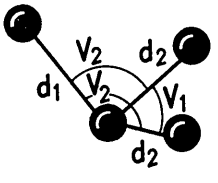

Fig. 2. Representation of bond distances and bond angles in the structure of black phosphorus (see text).