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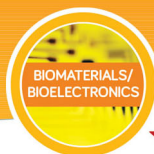
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## The Atomic Distribution in Red and Black Phosphorus and the Crystal Structure of Black Phosphorus

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No satisfactory crystal structure determination has been made of any of the forms of phosphorus. Five samples of black phosphorus gave identical powder patterns different from those reported by Linck and Jung, whose rhombohedral structure gives improbable interatomic distances and coordination. A sample which had been prepared at room temperature and 35,000 atmospheres gave the diffuse rings of an "amorphous" x-ray pattern. Another sample, prepared at 300°C and 8000 atmospheres, is a new form of phosphorus, having the same density as black. Atomic distribution curves of crystalline and "amorphous" black and red phosphorus were obtained by the method of Fourier analysis. All four gave practically

the same curve, showing three neighbors at 2.28 Å and about twelve at 3.6 Å. With the aid of the atomic distribution curves and the fact that certain lines showed a preferred orientation, it was possible to determine the structure of black phosphorus. It consists of double layers; the cell is side-centered orthorhombic with  $a=3.31\text{Å}$ ,  $b=4.38\text{Å}$  and  $c=10.50\text{Å}$ . There are eight atoms in the cell, giving a calculated density of 2.69 compared with 2.70 observed. The space group is  $V_h^{18}-Bmab$ . The black phosphorus structure allows a closer packing than the arsenic structure, where the atomic environment is similar, and so is favored by the high pressure.

### INTRODUCTION

PHOSPHORUS crystallizes in a number of allotropic forms, three of which are easily distinguished because of their widely differing physical and chemical properties. These three forms are the red, white and black varieties. Their peculiar conditions of formation and transformation make their study of interest in the theory of the dynamics of crystalline changes. The data on phosphorus are confusing and incomplete.<sup>1</sup> None of the crystal structures have been satisfactorily worked out by x-ray methods; the various investigators do not even agree on the positions of the lines in the powder patterns.

### PROPERTIES OF THE ALLOTROPIC FORMS OF PHOSPHORUS

When heated, all three forms sublime to a vapor composed of  $P_4$  molecules, which yields white phosphorus when condensed. However, at lower temperatures (100°C in a vacuum), the vapor of red phosphorus condenses to give red phosphorus; but the vapor density is so low that no molecular weight determination has been made. White phosphorus is easily changed to

red by the action of heat, light or x-rays. Under a pressure of 12,000 atmospheres and at a temperature of 200°C, it changes to black phosphorus.<sup>2</sup> Red phosphorus does not change under these conditions.<sup>†</sup> Black phosphorus changes to red when heated to 550°C. All of these changes are irreversible.

The physical differences between these forms are striking as shown in Table I.

TABLE I. *Physical properties of the forms of phosphorus.*

COLOR	DENSITY	M.P.	B.P.	INFLAMMABILITY	SOLUBILITY
White	1.83	44.1	280	Very high	Soluble in number of organic solvents with mol. wt. $P_4$
Red	2.34	590	725	High	Insoluble
Black	2.70	—	—	Low	Insoluble

These facts seem to indicate that white phosphorus is composed of more or less loosely bound  $P_4$  molecules which readily break up to form the more stable structures of red and black phosphorus, which consist of larger molecules or else are continuous, nonmolecular structures.

White phosphorus can be obtained in beautiful, transparent crystals of the cubic system by crystallization from solution or by slow sublima-

\* National Research Fellow.

<sup>1</sup> For a discussion of physical and chemical properties of phosphorus see Ephraim. *Anorganische Chemie*, Steinkopff, Dresden and Leipzig, 1934, pp. 87-92.

<sup>2</sup> P. W. Bridgman, *J. Am. Chem. Soc.* **36**, 1344 (1914).

<sup>†</sup> Professor Bridgman has recently succeeded in changing red phosphorus to black by the application of a shearing stress at very high pressures.

tion. Jung<sup>3</sup> reports that x-ray analysis is impossible since the x-rays transform the white to the red form. However, Natta and Passerini<sup>4</sup> announced that by cooling the sample to  $-35^{\circ}\text{C}$  and by using iron radiation, they were able to obtain 22 lines of a cubic pattern with  $a=7.17\text{\AA}$ . But they failed to publish their data or the crystal structure.

*Red phosphorus* in its commercial form gives diffuse rings in its x-ray pattern and is supposed to be amorphous. After suitable heat treatment it gives a normal line pattern. Red phosphorus is usually considered to be either a finely divided form of violet phosphorus or a solution of white in violet because of similarity in physical properties. Frost,<sup>5</sup> however, has shown by x-ray evidence that they have different crystalline forms. He concluded from his powder patterns that both structures had a low symmetry. *Violet phosphorus* can be obtained in small, transparent, monoclinic crystals by crystallization from molten lead. Olshausen<sup>6</sup> and Jung<sup>3</sup> report patterns which do not agree with either of the patterns of Frost, nor do they agree with one another. Olshausen used red phosphorus and Jung, violet.

*Black phosphorus* resembles graphite when pulverized. Linck and Jung<sup>7</sup> assign it a rhombohedral cell on the basis of their x-ray pictures. However, the coordination of atoms in their cell (one nearest neighbor at  $2.46\text{\AA}$  and six at  $3.01\text{\AA}$ ) does not agree with the accepted atomic radius of  $1.10\text{\AA}$ , nor does it give the three or five nearest neighbors to be expected from a covalent structure.

#### EXPERIMENTAL WORK

We were fortunate in securing seven samples of black phosphorus from Professor Bridgman at Harvard. Five of these were prepared at the usual temperature of  $200^{\circ}\text{C}$  and pressures of 12,000 atmospheres or more. These samples varied in age from a few months to twenty years. All gave identical powder patterns which

were not the same as those reported by Linck and Jung.<sup>7</sup> Heat treatments of 100 hours at  $450^{\circ}\text{C}$  and two hours at  $550^{\circ}\text{C}$  failed to change the patterns in any way except to make the lines somewhat sharper. Linck and Jung had used samples from the same source and the physical properties they describe are the same as those we observed. We are at a loss to account for the discrepancy in the patterns.

The other two samples had been made under different conditions. One was made at room temperature and 35,000 atmospheres.<sup>8</sup> Its physical properties were similar to those of the other samples except that it had a density of 2.6 instead of 2.7. Its powder pattern showed diffuse rings instead of sharp lines. The other had been made by Dr. F. Birch at  $300^{\circ}\text{C}$  and 8000 atmospheres and gave a powder entirely different in appearance from the other samples. It had a deep red color and no flakiness. Its x-ray pattern was different from any of the other forms of phosphorus. It is a new form of phosphorus which we have not found time to investigate further.

Samples of commercial, "amorphous" red phosphorus were obtained from the stock room and showed diffuse rings on the powder pattern. We also obtained a sample of red phosphorus from Professor Bridgman which had withstood a pressure of 12,000 atmospheres without change, and prepared other samples by heating black phosphorus to  $550^{\circ}\text{C}$  in a sealed quartz tube. All of the samples except, of course, commercial red phosphorus, gave the same set of x-ray lines which checked that of Frost<sup>5</sup> for red phosphorus.

We have applied the method of Fourier analysis to the x-ray powder patterns of black and red phosphorus. This method, which was developed by Zernike and Prins<sup>9</sup> and by Debye and Menke,<sup>10</sup> yields information about the distances between atoms, but nothing about their arrangement in the crystalline lattice. It has been used as an aid in crystal structure determinations by Warren and Gingrich<sup>11</sup> and by Warren.<sup>12</sup>

<sup>3</sup> Jung, *Centralblatt f. Min. u. Geol.* 1926, 107-114.

<sup>4</sup> Natta and Passerini, *Nature* 125, 707 (1930).

<sup>5</sup> Frost, *J. Russ. Phys. Chem. Soc.* 62, 2235 (1930).

<sup>6</sup> Olshausen, *Zeits. f. Krist.* 61, 463 (1925).

<sup>7</sup> Linck and Jung, *Zeits. f. anorg. Chemie* 147, 288 (1925).

<sup>8</sup> P. W. Bridgman, *Phys. Rev.* 45, 844 (1934).

<sup>9</sup> Zernike and Prins, *Zeits. f. Physik* 41, 184 (1927).

<sup>10</sup> Debye and Menke, *Erg. d. Techn. Röntgenkunde* 11.

<sup>11</sup> Warren and Gingrich, *Phys. Rev.* 46, 368 (1934).

<sup>12</sup> Warren, *J. Chem. Phys.* 2, 551 (1934).

## ATOMIC DISTRIBUTION CURVES

Assuming that each phosphorus atom has the same environment, the density of atoms at a distance  $r$  from a given atom can be obtained from the following formula:<sup>11</sup>

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + (2r/\pi) \int_0^\infty i(s) \sin(rs) ds,$$

where  $s = 4\pi \sin \theta / \lambda$ ,

$\rho_0$  = average density of sample in atoms per unit volume,

$\rho(r)$  = average density of atoms at a distance  $r$  from a given atom,

$i(s) = (I/N - f^2)/f^2$ ,

$I$  = experimental intensity corrected for absorption, incoherent radiation and polarization, including polarization due to the monochromatizing crystal,

$f^2$  = intensity of independent scattering per atom,

$N$  = number of scattering atoms.

Consequently  $4\pi r^2 \rho(r) dr$  represents the number of atoms between  $r$  and  $r + dr$ .

The analysis was carried out in the usual way<sup>11, 12</sup> except for the determination of the constant  $N$ , which was evaluated from the following formula:\*

$$N = \int_0^{10} I ds / \int_0^{10} f^2 ds.$$

Molybdenum  $K\alpha$  radiation was used, monochromatized by a sodium chloride crystal. The camera had a radius of 47 mm and the exposures

\* At large angles the experimental error in the determination of intensity is high, partly due to the small intensities involved and partly due to the large uncertain correction for incoherent intensity. Hence the assumption that  $I = Nf^2$  at some arbitrary large angle may give a result which is far from correct. A better way is to choose  $N$  so that the deviations of the experimental curve from independent scattering more or less balance one another at large angles. A method which depends only a little on the inaccurate measurements at large angles is the following. From the formula:<sup>11</sup>

$$I = Nf^2 \{ 1 + \int_0^\infty 4\pi r^2 [\rho(r) - \rho_0] (\sin(sr)/sr) dr \}$$

we easily obtain

$$\begin{aligned} \int_0^S I ds - N \int_0^S f^2 ds \\ = 4\pi N \int_0^\infty \int_0^S f^2 \sin(sr) r [\rho(r) - \rho_0] ds dr = K. \end{aligned}$$

It can be shown that if  $S$  is chosen large enough, the value of  $K$  is small compared with that of the other two integrals, so it is justifiable to assume  $K$  to be zero as a first approximation. We found after doing this that its actual value was about eight percent of the other integrals, hence a second approximation was unnecessary. The error in the first approximation can be estimated in advance by integrating  $K$  over the region where  $\rho(r)$  is known to be zero. In the case of phosphorus this estimate was 11 percent.

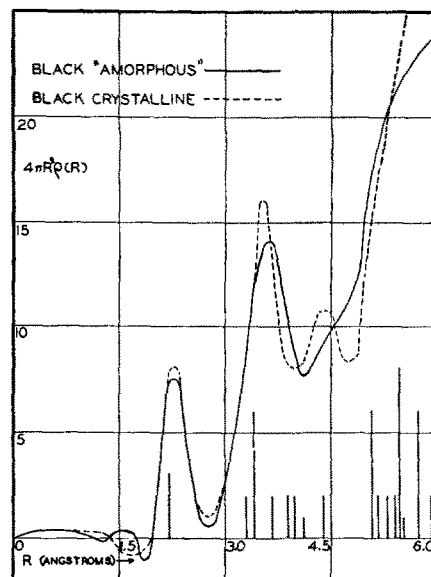


FIG. 1. Atomic distribution in black phosphorus. The solid vertical lines indicate the distribution in the crystal structure found for black phosphorus.

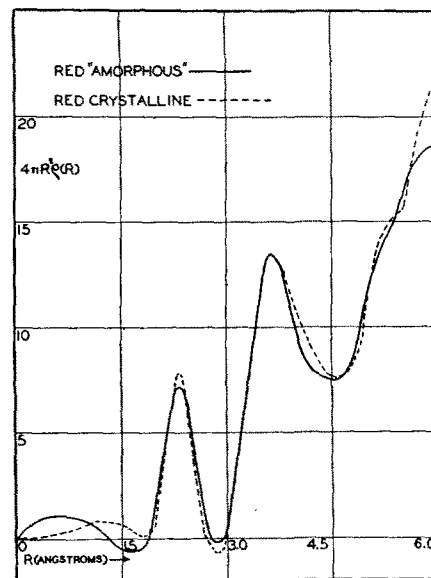


FIG. 2. Atomic distribution in red phosphorus.

required several days. It was found that errors due to stray radiation or to incorrect determination of  $N$  had a considerable effect on the values of density determined, but that the positions of the peaks remained remarkably constant.

The results of the analysis are shown in Figs. 1 and 2. The four samples analyzed; crystalline and "amorphous" black phosphorus and crystalline and commercial red phosphorus gave nearly the same distribution curves. The supposedly amorphous samples each show four bands at the positions where the crystalline samples have their strongest lines. Probably they are simply extremely fine crystals. The area under the first peak is 3.3, indicating three neighbors at about 2.28Å. The second peak is at 3.6Å and has an area indicating about twelve atoms at that distance. The red phosphorus distribution curves show peaks slightly farther out than those of black.

#### THE CRYSTAL STRUCTURE OF BLACK PHOSPHORUS

The interplanar spacings of black phosphorus were accurately determined from powder patterns made with filtered iron radiation from a Hadding tube. In one case iron and in another sodium chloride was mixed with the sample as a standardizing substance. The results usually varied from one another less than 0.005Å. Supplementary photographs from a copper tube checked the intensities and approximate positions of the lines, and also yielded a few more faint lines. The camera used had a radius of 47 mm.

The interplanar spacings found will not fit a cubic, tetragonal or hexagonal lattice. Ordinarily, it is hopeless to try to solve a structure of lower symmetry from powder photographs alone. Fortunately, the results of the Fourier analysis, together with the fact that one of the lines and its two higher orders showed preferred orientation, made it possible to determine the structure. The physical properties of the powder and the preferred orientation of the lines indicated a layer structure with the layers 5.25Å apart.

The second order of the line showing preferred orientation is stronger than the first, while the third is weaker. A rough calculation shows that each layer must be double with a spacing of about 2.1Å between halves. In satisfying this

condition and the distribution determined from the Fourier analysis, we are led to an orthorhombic cell of which we know the approximate dimensions. Trial shows that the  $c$  axis must be double the layer spacing and more accurate values for the  $a$  and  $b$  axes are determined from the first few lines. It soon becomes evident that the true lattice is side-centered orthorhombic with the following dimensions:

$$a = 3.31\text{Å}; b = 4.38\text{Å}; c = 10.50\text{Å}.$$

The unit cell contains eight atoms, which gives a calculated density of 2.69, compared with the observed value, 2.70. The space group is

$$V_h^{18} - Bmab$$

with the eight atoms in the following positions:

$$\begin{aligned} &0uv; \frac{1}{2}, \frac{1}{2} - u, v; \frac{1}{2}, u, \frac{1}{2} + v; 0, \frac{1}{2} - u, \frac{1}{2} + v; \\ &0\bar{u}\bar{v}; \frac{1}{2}, \frac{1}{2} + u, \bar{v}; \frac{1}{2}, \bar{u}, \frac{1}{2} - v; 0, \frac{1}{2} + u, \frac{1}{2} - v. \end{aligned}$$

The best agreement of intensities is obtained for  $u = 0.090$  and  $v = 0.098$ .

Calculated and observed interplanar spacings and intensities of the first 42 possible lines of this space group are shown in Table II. The

TABLE II. Calculated and observed interplanar spacings and intensities for black phosphorus.

$hkl$	$d_{calc.}$	$d_{obs.}$	$I_{calc.}$	$I_{obs.}$	$hkl$	$d_{calc.}$	$d_{obs.}$	$I_{calc.}$	$I_{obs.}$
002	5.25	5.24	180	3	214	1.334	1.33*	53	$\frac{1}{2}$
012	3.36	3.36	396	7	131	1.325	—	5	0
004	2.62	2.62	283	5	220	1.320	—	42	0
111	2.56	2.56	837	9	008	1.313	—	5	0
014	2.25	2.25	75	$1\frac{1}{2}$	117	1.304	1.30*	52	$\frac{1}{2}$
020	2.19	2.19	57	1	222	1.280	—	10	0
113	2.11	2.11	60	1	034	1.276	1.27*	89	$\frac{1}{2}$
022	2.02	—	10	0	018	1.257	1.249	64	1
121	1.80	1.80	214	2	133	1.248	—	0	0
006	1.75	1.75	136	$1\frac{1}{2}$	206	1.203	1.200	176	2
024	1.68	—	37	0	224	1.180	1.18*	54	$\frac{1}{2}$
200	1.655	1.640	165	7	216	1.160	1.156	40	4
115	1.644	—	460	—	127	1.159	—	354	$\frac{1}{2}$
016	1.625	—	25	0	135	1.127	—	8	0
123	1.619	1.618	472	6	028	1.126	—	2	0
202	1.579	—	33	0	036	1.121	—	75	0
212	1.485	1.483	137	2	040	1.095	—	63	0
032	1.407	1.400	218	4	232	1.072	1.067	580	4
204	1.400	—	149	—	042	1.072	—	15	$\frac{1}{2}$
125	1.378	—	1	0	119	1.067	1.062	264	5
026	1.367	1.364	32	$\frac{1}{2}$	311	1.065	—	320	$\frac{1}{2}$

\* Measured with less accuracy from copper radiation.

agreement is excellent in nearly all cases. The few small deviations are due to preferred orientation, which cannot always be allowed for, tending to make planes near (00 $\bar{L}$ ) stronger and other planes weaker. Allowance for the temperature factor would make the calculated intensity for planes of smaller  $d$ , smaller. After the unit cell is once

discovered, the determination is rigorous. The atomic distribution is shown in Fig. 1 for the crystal as well as that determined by Fourier analysis. The agreement is very good, except that the Fourier analysis gives slightly too large distances.

#### DISCUSSION OF RESULTS

The unit cell of black phosphorus consists of two double layers, one of which is shown in Fig. 3. Each atom is bonded to three nearest neighbors at 2.18Å, in agreement with the accepted atomic radius of 1.10Å, and with the coordination to be expected from covalent bonding of phosphorus. Two of the bonds are in the plane of the layer, at  $99^\circ$  from one another; the third is between layer halves at  $103^\circ 30'$  from both, making the average bond angle  $102^\circ$ . This agrees with the tendency of bond angles to be nearer tetrahedral for the lighter elements of the periodic group. Thus for the fifth period the trend is: P  $102^\circ$ , As  $97^\circ$ , Sb  $96^\circ$  and Bi  $94^\circ$ . The atomic environment is quite similar to that in the arsenic structure, which is assumed by the other members of the group, except nitrogen. The difference consists in the fact that in the latter structure all bonds are between halves of the double layer, while in the former only one-third of the bonds are.

The question arises as to why phosphorus does not assume the arsenic structure. A good reason is that the black phosphorus structure is closer packed than the arsenic structure and so is favored by the high pressure under which black phosphorus is formed. If phosphorus assumed the arsenic structure, retaining the bond distances and angles of black phosphorus and also the closest distance of approach between atoms in different layers, it would have a density of only 2.44 instead of 2.69. Arsenic at high pressures might be expected to take the black phosphorus structure since, by doing so, its density would be increased from 5.73 to 6.43.

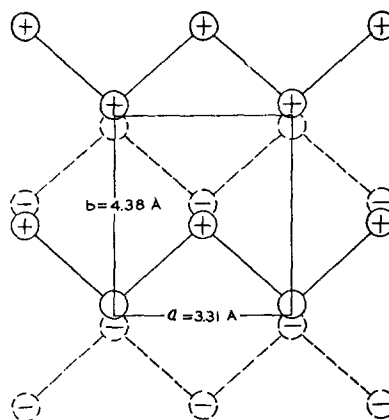


FIG. 3. A double layer of the black phosphorus structure. "+" and "-" indicate that the atom is, respectively, 0.098 c above or 0.098 c below the plane of the paper.

The fact that it has not been observed is not a conclusive argument against its possibility, since, as we saw, black phosphorus forms only under special conditions.

In this connection it should be pointed out that arsenic is a good deal more metallic than black phosphorus, having a specific resistance of  $35 \times 10^{-6}$  ohm cm compared with 0.711 ohm cm for the latter.<sup>2</sup> The decisively covalent character of phosphorus is nicely shown by the fact that the distance between bonded atoms is only 2.18Å compared with 3.68Å as the closest approach between atoms in different layers. In arsenic the bonds are less sharply differentiated; three nearest neighbors are at 2.51Å, with three more atoms at 3.15Å.

The Fourier analysis furnishes a valuable clue to the structure of red phosphorus. We know that each atom forms three covalent bonds in the normal manner. The fact that the second peak is at practically the same position as in black phosphorus suggests that the bond angles are nearly the same.