Crystal Structures Adopted by Black Phosphorus at High Pressures

Abstract. *Black phosphorus undergoes two reversible structural transitions at high pressures. The first is to a structure of the type arsenic A7. This structure is transformed to a simple cubic structure at higher pressures. The reversibility between the A7 and simple cubic structures at 111 kilobars indicates that the transition obtainable at this pressure provides a good calibration point by which high-pressure x-ray data may be united with volumetric or resistance measurements, or both.*

Black phosphorus has held a unique position in high-pressure research since it was first made by Bridgman (*1*) at high pressure, and it is in a sense the first truly "high-pressure" product to have been recovered at atmospheric pressure. Its semi-conducting properties have been given by Keyes (*2*). Bridgman (*3*) found a transition in black phosphorus at about 50 kb which Keyes suggested was a transition to the metallic state. Hence it was decided to investigate this substance by high-pressure x-ray diffraction techniques described elsewhere (*4*).

The black phosphorus was semiconductor grade manufactured by Raytheon Company (*5*). Initial zero-pressure patterns were those of the complicated orthorhombic structure determined by Hultgren *et al.* (*6*). On application of pressure, the first diffraction pattern given in Table 1 was obtained. This was readily indexed as hexagonal (rhombohedral) $a = 3.377$ Å, $c = 8.806$ Å with intensities appropriate to the A7 (arsenic) type of structure. Although the high background in the pattern precluded any accurate determination of the parameter u for this structure, a value near 0.22 to 0.21 is not in severe disagreement with the observed pattern. The calculated density of this phase is $\rho = 3.56$. The smallest rhombohedral cell (r) is given by $a_r = 3.524$ Å, $\alpha = 57.25°$, with $Z = 2$.

Table 1. The A7 phase of black phosphorus (arsenic type); W, weak; M, medium; S, strong; VW, very weak.

hk·1	Calc. (Å)	Obs. (Å)
00·3	2.935	2.894 W
10·1	2.775	2.728 W
01·2	2.436	2.428 S+
01·4	1.759	1.744 S
11·0	1.689	1.692 S
01·5	1.509	1.511 W
00·6	1.468	1.462 W
11·3	1.463	
20·2	1.388	1.398 M
02·4	1.218	1.223 M
10·7	1.155	1.151 W
20·5	1.125	1.119 VW
11·6	1.108	1.108 M
21·1	1.096	
12·2	1.072	1.078 M
01·8	1.030	1.031 VW
21·4	0.9878	0.9887 W
00·9	0.9784	
30·0	0.9748	
02·7	0.9536	0.9562 W
12·5	0.9362	0.9382 W
30·3	0.9250	
11·9	0.8465	0.8487 W
22·0	0.8443	
21·7	0.8303	
03·6	0.8120	0.8133 VW
31·2	0.7977	0.8004 VW
12·8	0.7799	0.7825 W
31·4	0.7611	0.7642 W

On further increase of pressure, the arsenic-type pattern disappeared and was replaced by a simple cubic pattern (Table 2) with $a = 2.377$ Å and $\rho = 3.83$. When the pressure was decreased, the simple cubic pattern was replaced by the arsenic-type pattern. Pictures taken at atmospheric pressure after the sample had been exposed to a pressure cycle showed only the orthorhombic form, but the lines in the picture were grossly broadened, indicating that only quite small coherent domains existed in the material.

Bridgman reported only one transition in black phosphorus in a study in which the pressure was raised to 100,000 kg/cm^2; he was not able to determine the pressure of that transition more precisely than to state that it occurred at about 50,000 kg/cm^2 as the pressure was increased and that the reverse transition occurred at less than 25,000 kg/cm^2 as the pressure was decreased. Although my apparatus is not ideal for determining pressures of transition, some information was obtained by using a mixture of NaCl and black phosphorus. Bridgman's (*7*) volumetric data for NaCl served as an internal pressure gage by which pressure could be measured by the displacement of the diffraction lines of NaCl. The lowest pressure at which patterns of the arsenic structure were taken was 83 kb. A second pattern, still A7, was taken at 102 kb. This determination is certainly no better than Bridgman's. However, the transition of A7 to simple cubic was determined, with better precision, to occur at least by 124 kb on the "NaCl scale."

On decreasing pressure, the pattern was still simple cubic at 120 kb, and the A7 structure reappeared on a pattern taken at 93 kb. No effort was made to fix the transition pressure more closely than these bounds (111 ± 9 kb) since the apparatus could not be controlled more closely. The pattern shown in Table 2 corresponds to about 120 kb. It is interesting to note that these transition pressures are slightly beyond Bridgman's exploration (*3*) to 100,000 kg/cm^2, and thus a mild confirmation is provided by his finding of only the lower transition in his range.

Table 2. Simple cubic phase of black phosphorus.

h,k,l	d (Å)	a (Å)
100	2.369	2.369 S+
110	1.681	2.377 S
111	1.372	2.376 M
200	1.191	2.381 M
210	1.064	2.379 M+
211	0.9698	2.376 M
220	0.8410	2.379 W
221	0.7945	2.384 W
310	0.7514	2.376 W
311	0.7145	2.370 W
222		
320	0.6608	2.383 VVW
321	0.6367	2.382 VW

A comparison of the arsenic-type and orthorhombic structures has been given by Hultgren *et al.* (*6*) and will not be repeated. In the A7 structure (u equal to 0.215) a phosphorus atom has three neighbors at 2.13 ± 0.03 Å, a second set of three at 3.27 ± 0.03 Å, and six at 3.377 Å; the latter figure is independent of u and hence more accurate. The three nearest neighbors are appropriate for local covalent bonding, and electrically A7 phosphorus will probably prove to be as poor a metal as arsenic, antimony, and bismuth. The transition of orthorhombic phosphorus to the arsenic-type structure that occurs under pressure was predicted by Parthé (*8*), contrary to an earlier assertion by Hultgren *et al.* (*6*). In addition, Parthé predicted a density of 3.5 for A7-type phosphorous, a value in excellent agreement with my value of 3.56 (at about 100 kb). In the transformation to simple cubic structure, the interatomic distance becomes 2.378 Å; this is an increase of 12 percent, corresponding presumably to the distance in a more normal metal.

The simple-cubic type of structure may be regarded as a special case of A7 with $\alpha = 60°$ and $u = 1/4$. Hence the transition of one to the other is exceedingly simple; it is a minor displacement of the "body-center" atom and an adjustment of an angle through only 3 degrees. This undoubtedly explains the easy reversibility and suggests that this transition when fixed by the measurement of pressure in more suitable apparatus may serve as a very valuable calibration point since the volume change is large and the change in resistance should be easily detectable. Phosphorus has the added advantage that its absorption is low and hence it may be added to samples for x-ray study without impairing the quality of the picture.

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References and Notes

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5. I thank Dr. Douglas Warschauer for the black phosphorus. Supported by the National Science Foundation grant G19744 and a grant from the Petroleum Research Fund of the American Chemical Society.
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20 February 1963

Antigenic Determinants in Fragments of Gamma Globulin from Rabbit Serum

Abstract. *Peptic digestion of fraction III from papain-digested rabbit serum γ-globulin produces a variety of smaller fragments. Some are too large to pass through a dialysis bag, and these retain the capacity to precipitate with antiserum to rabbit γ-globulin. Others pass through the bag and fail to precipitate with antibody, but they can inhibit the precipitation of antibody with fraction III. This indicates that antigenic determinants of the γ-globulin molecule are carried in these fragments.*

Rabbit γ-globulin, when digested by crystalline papain, is split into three fragments; each comprises roughly one-third of the parent molecule (*1*). One of these pieces (fraction III) carries a number of properties characteristic of γ-globulin including most of the antigenic determinants (*1*), the ability to fix complement (*2*), reactivity with sera from rheumatoid arthritis patients (*3*), and the capacity to be recognized as γ-globulin by homologous cells (*4*).

Pepsin also splits rabbit γ-globulin into smaller units (*5*), but apparently produces rapid degradation of the portion of the molecule corresponding to fraction III. Therefore, smaller fragments of fraction III possessing these activities might be obtained by controlled treatment with pepsin.

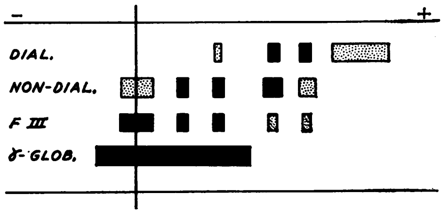

Fig. 1. Electrophoretic patterns in starch gel of dialysate (*DIAL*), nondialyzable fraction (*NON-DIAL*), fraction III (*FIII*), and rabbit γ-globulin (*γ-GLOB*). The solid areas indicate heavy protein concentrations; the speckled areas indicate lower concentrations.

The γ-globulin, prepared from rabbit serum by precipitation with sodium sulfate (*6*), was digested by crystalline papain and fractionated (*1*). Fraction III was digested by 3 percent crystalline pepsin at room temperature, *p*H 4.0, in a dialysis bag under air pressure (2 lb/in.^{2}) within a vessel containing water at *p*H 4.0. The dialysate was changed twice daily over a period of 4 days; by that time the volume within the bag had been greatly reduced and a crystalline precipitate had formed. Both the dialysate and the nondialyzable material were adjusted to *p*H 7.5, and the dialysate was lyophilized.

Starch-gel electrophoresis (*7*) in borate buffer, 0.2*M*, *p*H 8.4, of dialysate, nondialyzable material, rabbit γ-globulin, and fraction III revealed four peaks each for fraction III (F III) and for the nondialyzable material (Fig. 1). These differed quantitatively in that fraction III contains few of the faster moving components, and a large portion of it remained at the origin. The dialysate was composed exclusively of faster moving fractions, much of which appeared as a diffuse smear near the anode end of the gel.

The four components of the nondialyzable fraction were isolated by preparative starch-gel electrophoresis. They were eluted from the starch by electrodialysis. Each was examined in a Spinco model E ultracentrifuge; the sedimentation constant, S_{20}, values ranged from 2.3 to 3.2 as compared to 3.5 for fraction III. Ultracentrifugation of the dialysate gave a slow diffuse boundary that closely resembled a salt boundary.

The nondialyzable fraction gave four precipitin bands in reaction with a goat antiserum to the γ-globulin of rabbit serum, when studied by the Ouchterlony gel-diffusion technique (*8, 9*) (Fig. 2). The specificity of this antiserum was characterized by quantitative precipitin and gel-diffusion tests (*10*). Fraction III gave a single precipitin band, while the dialysate produced no discernible reaction. When the components of the nondialyzable fraction were tested individually, each showed a single precipitin line which gave reactions of identity with bands produced by the others. This suggests that these fragments all carried the same antigenic determinants. The presence of multiple bands in diffusion tests of the whole nondialyzable fraction may have been the result of differences in relative concentration of the components.

Immunoelectrophoresis in agar (*11*) of the nondialyzable material at *p*H 8.6 produced five precipitin lines when developed with the goat antiserum while fraction III itself gave a single band (Fig. 3). Each of the four components of the nondialyzable fraction gave a single band with a characteristic electrophoretic mobility.

The dialysate was chromatographed

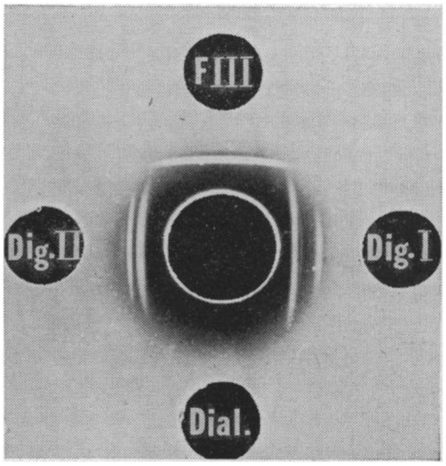

Fig. 2. Gel diffusion patterns of fragments of rabbit γ-globulin reacted against anti-rabbit γ-globulin. Goat antiserum is in central well. Fraction III (*FIII*), nondialyzable fractions of two independent digestions (*Dig. I* and *Dig. II*), and the dialysate from one of the digestions (*Dial.*) are in the peripheral wells.