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The Electrical Properties of Black Phosphorus*

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The electrical conductivity of black phosphorus has been measured as a function of temperature and pressure up to 350°C and 8000 kg/cm^2. The Hall constant of the same material has been measured as a function of temperature at atmospheric pressure. At low temperatures p-type impurity conduction is observed; at high temperatures the phosphorus is an intrinsic semiconductor with a gap width of 0.33 ev. The mobilities at 27°C are 350 cm^2/volt sec and 220 cm^2/volt sec for the holes and electrons, respectively. Application of hydrostatic pressure decreases the gap at a rate $VdW/dV=8.3$ ev. The results are also interpreted in terms of a two-dimensional semiconductor model.

INTRODUCTION

PHOSPHORUS is an element of the fifth group of the periodic table which exists in a number of allotropic modifications. The most stable form,[1] black phosphorus, can be prepared only under high hydrostatic pressure, and was discovered by Bridgman[2] in 1914. Bridgman has measured the density[2] (2.69 gm/cm^3) and the compressibility[3] of black phosphorus, and its electrical resistivity as a function of pressure over a limited range of temperature.[2,4] These measurements have shown that this type of phosphorus is a semiconductor, and that it apparently becomes more metallic with increasing hydrostatic pressure, the temperature coefficient of resistivity between 30°C and 75°C reversing sign at 12 000 kg/cm^2.

The crystal structure of black phosphorus has been determined,[5] the lattice is orthorhombic with eight atoms per unit cell and lattice parameters $a=3.31$A, $b=4.38$A, $c=10.50$A. The atoms are arranged in puckered layers; in a layer each atom is joined by covalent bonds to three neighbors at the same distance as the interatomic distance observed in the P_4 molecule, while the layers are held together at a distance about 50 percent greater by van der Waals forces.[6]

In view of the limited number of elementary semiconductors and the unusual structure of black phosphorus, further measurements of the electrical properties of this material have been made in order to provide a better understanding of the electronic processes involved. The following quantities have been measured: 1. Electrical conductivity from −195°C to 350°C; 2. Hall coefficient from −195°C to 350°C; 3. Electrical conductivity at pressures up to 8000 kg/cm^2 in the temperature range 27°C to 350°C; 4. Magnetoresistance coefficients at −195°C and −80°C; 5. Infrared absorption from 2μ to 30μ.

PREPARATION OF SAMPLES

The black phosphorus was prepared from white phosphorus by the method described by Bridgman.[2] Hydrostatic pressure of 13 000 kg/cm^2 is applied to the white phosphorus in high-pressure apparatus of a type which has been described elsewhere.[7] The vessel containing the phosphorus is heated to 200°C; after several minutes at this temperature the transition to black phosphorus takes place abruptly, accompanied by a marked change in volume (0.18 cm^3/gm). After cooling of the high-pressure bomb the ingot of black phosphorus was washed in carbon disulfide to remove any untransformed white phosphorus. As a result of the large volume change and the violent nature of the transition, the ingot was polycrystalline and contained numerous cracks. Metallographic polishing of a sample disclosed grains of roughly 0.1-mm diameter. Dow-Corning silicone oil and hexane have both been used as pressure transmitting fluids in the preparation of black phosphorus. Small silica inclusions were found in the cracks in the material made in silicone oil; electrically both materials were the same. When black phosphorus is melted or vaporized, P_4 molecules are formed which crystallize into white or red phosphorus; thus it does not appear possible to prepare single crystal samples.

For the electrical measurements, pieces of phosphorus were sawed from the ingot and machined to rectangular shapes. The samples were cut as long and narrow as was consistent with the cracks in the ingot and the fragility of the material; cross-sectional dimensions of the samples veried from 0.1 to 0.2 cm and lengths from 0.5 to 1 cm. After machining, the samples were washed in acetone, and nickel electrode surfaces were electroplated onto the ends.

ELECTRICAL MEASUREMENTS

Sample holders for the electrical measurements were machined from lavite. The samples were held in place by forces transmitted through the electrodes. A copper plate was mounted beneath the samples, and separated

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[1] R. B. Jacobs, J. Chem. Phys. 5, 945 (1937).

[2] P. W. Bridgman, J. Am. Chem. Soc. 36, 1344 (1914).

[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 62, 207 (1927).

[4] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 70, 71 (1935).

[5] Hultgren, Gingrich, and Warren, J. Chem. Phys. 3, 351 (1935).

[6] L. Pauling and M. Simonetta, J. Chem. Phys. 20, 29 (1952).

[7] P. W. Bridgman, *Physics of High Pressure* (G. Bell and Sons, London, 1939), Chap. 2.

from them by a thin sheet of mica, to reduce thermal gradients. The electrodes were made of Nichrome wire and ribbon. During the measurements above room temperature the samples were in an atmosphere of helium. Between room temperature and −80° the samples were immersed in acetone. Below the latter temperature, data were taken by cooling the sample in liquid nitrogen and taking data while the sample and holder were gradually warming up.

The Hall constant and conductivity were measured in a sample holder designed for use with a large electromagnet. With a 4-inch gap between the pole faces, which was large enough to contain the furnace used for the high-temperature measurements and the Dewar flask for the low-temperature measurements, fields up to 5600 gauss were obtainable. At this field strength the field was uniform within one percent over a region $1\frac{1}{2}$ inches in diameter. The field strength as a function of magnet current was determined with a G.E. fluxmeter, and the magnet current was read with a Sensitive Research Instrument Corporation DC Polyranger, appropriately shunted. The current corresponding to maximum field, at which most readings were taken, was 40 amperes, and the meter could be read with an accuracy of 0.2 ampere. An electronic current controller regulated the current, and no fluctuation could be detected in the time necessary to take data at a single temperature (about 10 minutes).

The conductivity was measured by the direct current potential probe method. Thermocouple emf, potential drop in the sample, potential across a standard resistor in series with the sample, and Hall emf were measured with a Leeds and Northrup Type K potentiometer. The directions of the sample current and the magnetic field could be reversed, and in order to eliminate thermal emf's conductivity measurements were made for both directions of current, and Hall voltage measurements for all combinations of directions of current and magnetic field.

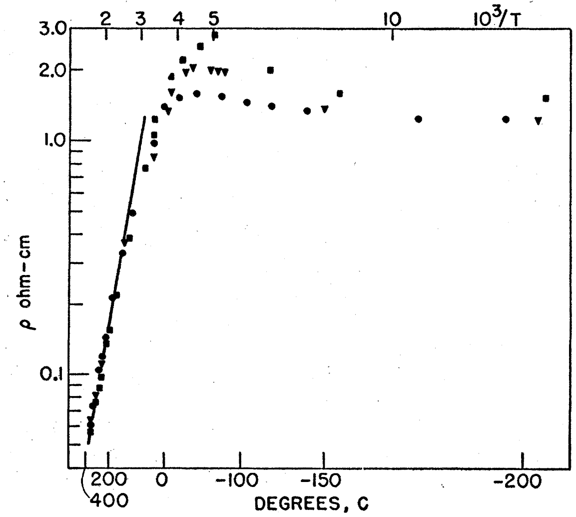

FIG. 1. The resistivity of three different specimens of phosphorus as a function of the reciprocal of the temperature in °K.

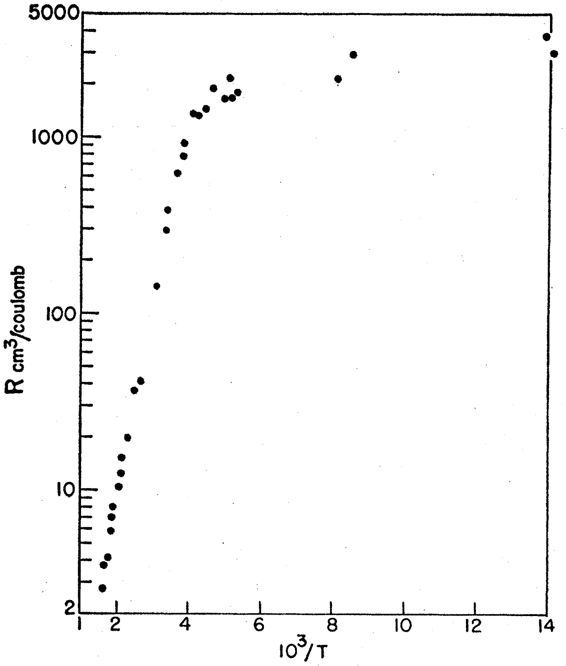

FIG. 2. The Hall constants of several samples as a function of the reciprocal of the temperature.

The conductivity at high pressures was measured by the same method in an apparatus of the type described by Bridgman[7] and modified for high temperatures by Kurnick.[8]

RESULTS AND DISCUSSION

The results of the resistivity measurements on several samples are shown in Fig. 1. At high temperatures the resistivity varies as

$$\rho = Ae^{W/2kT}, \tag{1}$$

with $W = 0.33$ ev and $A = 0.0030$ ohm cm. T is the absolute temperature, k is the Boltzmann constant, and A is a constant independent of temperature.

In Fig. 2 the Hall constant, R, is plotted as a function of temperature. The sign of the Hall voltage indicates that the charge carriers are positive. The direction of the thermoelectric effect confirmed this conclusion. The Hall constant was found to be independent of magnetic field up to 5600 gauss.

The logarithm of the product $(8/3\pi)R\sigma$ is plotted against the logarithm of the temperature in Fig. 3. Over most of the temperature range the points are well represented by the two lines of slope $-\frac{3}{2}$.

These results can be interpreted in terms of the conventional theory of an isotropic semiconductor.[9,10] At

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[8] S. Kurnick, J. Chem. Phys. **20**, 218 (1952).

[9] G. L. Pearson and J. Bardeen, Phys. Rev. **75**, 865 (1949).

[10] W. Shockley, *Electrons and Holes in Semiconductors* (D. van Nostrand Company, Inc., New York, 1950).

low temperatures the conductivity is entirely due to holes. The concentration of holes, calculated from the Hall constant by the formula $p=3\pi/8Re$ is about 2×10^{-15} cm^{-3}. The mobility of the holes, found from $\mu_p=(8/3\pi)R\sigma$, is represented by the upper line in Fig. 3, the equation of which is $\mu_p=1.86\times10^6T^{-\frac{3}{2}}$ cm^2 sec^{-1} volt^{-1}. This temperature dependence is in agreement with theoretical expectation for scattering by lattice vibrations.[10] The low value of the mobility for the point at -200°C is probably due to the effect of impurity scattering.

At high temperatures (above 150°C) the conductivity is essentially intrinsic, holes and electrons being present in equal numbers. The energy gap between the conduction and valence bands, derived from the conductivity as mentioned above, is 0.33 ev. This picture explains the shape of the $R\sigma$ curve; the contribution to the Hall coefficient of the electrons which appears at high temperature is of opposite sign to that of the holes and decreases the measured Hall voltage.

The mobility of the electrons can be derived from the data by extrapolating the $T^{-\frac{3}{2}}$ line which describes the mobility of the holes in the impurity region to higher temperatures, and using the values for μ_p thus obtained in the expressions for conductivity and Hall constant when both types of carriers are present. These expressions are:

$$\sigma=(n\mu_n+p\mu_p)e, \tag{2}$$

$$R=\frac{3\pi}{8e}\frac{p-nb^2}{(p+nb)^2}, \tag{3}$$

where n and p are the concentrations and μ_n and μ_p the mobilities of the electrons and holes, respectively, and $b=\mu_n/\mu_p$. In the intrinsic range $n=p$ and these formulas reduce to

$$\sigma=pe(\mu_n+\mu_p), \tag{4}$$

$$R=\frac{3\pi}{8e}\frac{1}{p}\frac{1-b}{1+b}, \tag{5}$$

$$R\sigma=\tfrac{3}{8}\pi(\mu_p-\mu_n). \tag{6}$$

Values for μ_n in the intrinsic range were calculated from the formula:

$$\mu_n=\mu_p-(8/3\pi)R\sigma, \tag{7}$$

and are plotted in Fig. 3. These mobilities can be represented by $\mu_n=1.19\times10^6T^{-\frac{3}{2}}$. Thus $b=0.64$.

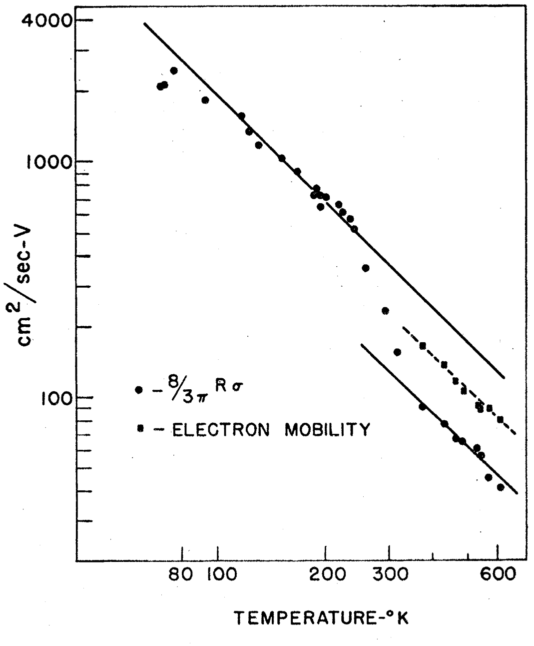

FIG. 3. The product $(8/3\pi)R\sigma$, which is equal to the mobility of the holes at low temperatures, and the mobilities of the electrons as calculated from Eq. (7). The lines drawn through the points have slope $-\frac{3}{2}$.

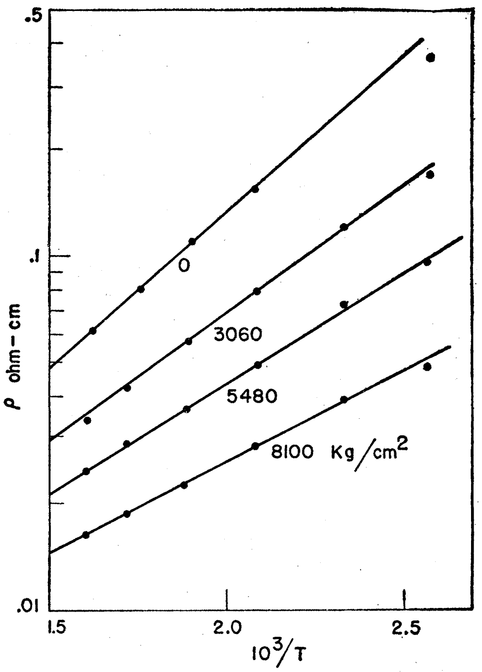

FIG. 4. Temperature dependence of the resistivity in the intrinsic range at various pressures.

The magneto-resistance coefficient was measured at -195°C and -80°C. This coefficient is the constant f in the expression $\rho=\rho_0(1+fH^2)$ for resistivity as a function of transverse magnetic field. In the simple theory applied above, f has the value $0.378\mu_p{}^2$.[11] A calculation of μ_p from this data gives values 2.8 times those calculated from the Hall constant. This coefficient, however, is particularly sensitive to the details of the shape of the energy surfaces.

The conductivity as measured in the high-pressure apparatus is shown in Fig. 4. Values for the energy gap were derived from the slopes of the lines in the

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[11] A. H. Wilson, *The Theory of Metals* (Cambridge Univeristy Press, Cambridge, 1936).

intrinsic region. These energies are plotted as a function of volume in Fig. 5, using the compressibility measured by Bridgman[3] to relate the pressure to the volume. Extrapolation of the lines of Fig. 4 to $1/T=0$ gives values for the term A of Eq. (1) at the pressures indicated. These values of A are independent of pressure within the accuracy of the extrapolation, about 25 percent. This indicates that there is no strong dependence of the mobility on pressure.

An interpretation of data of this type in terms of a simplified model of a semiconductor has been developed by Bardeen and Shockley.[12] The energy gap, regarded as a function of the volume of the crystal, may be written, to first-order terms as

$$W=W_0+E_1\Delta, \tag{8}$$

where E_1 is a constant, W_0 is the gap extrapolated to zero temperature and pressure, and $\Delta=(V-V_0)/V$ is the volume dilation. This Δ depends on both temperature and pressure, and, assuming a constant volume coefficient of thermal expansion, α, is $\Delta=\alpha T+\Delta_p$, Δ_p being the fractional change in volume due to applied pressure. Thus W becomes

$$W=W_0+E_1\alpha T+E_1\Delta_p. \tag{9}$$

If this expression is substituted into the exponential term in the conductivity $e^{-W/2kT}$, it is seen that the temperature-dependent part of W becomes part of the constant factor in the conductivity, and that the energy derived from the graph of conductivity *vs* $1/T$ is $(W_0+E_1\Delta_p)$. Thus W_0 has the value 0.33 ev derived from the atmospheric pressure measurements above, and E_1 is the slope of the line representing energy gap against volume in Fig. 5. This value for E_1 is 8.3 ev.

The mobilities of the charge carriers are related to the shifts in energy of the band edges with volume dilation:[12]

$$\mu T^{3/2}=\frac{(8\pi)^{\frac{1}{2}}eh^4C}{3m^{5/2}k^{3/2}E_1^{\,2}}, \tag{10}$$

where C is the elastic constant for longitudinal sound waves, m is the effective mass of the charge carriers, and k is the Boltzmann constant. There is one such equation for the holes, with E_{1c} referring to the bottom of the conduction band and E_{1v} to the top of the valence band. The constant $E_1=E_{1c}+E_{1v}$. In this way a value for E_1 can be obtained from the mobilities.

The only elastic constant known for black phosphorus is the compressibility (2.9×10^{-12} dyne^{-1} cm^2). By comparison of this with elastic constants for other materials, a value of the elastic constant for longitudinal waves was estimated to be 0.6×10^{12} dyne/cm^2. Using the free electron mass for m and the mobilities given above, the calculated values for $|E_{1c}|$ and $|E_{1v}|$ are 4.2 ev and 3.4 ev, respectively. The signs of these constants are not determined by the mobility formula; good agreement with the value of E_1 found from the pressure experiment is obtained by assuming that the bands shift in opposite directions and taking $E_1=+4.2+3.4=7.6$ ev.

The temperature dependence of the energy gap is given by the coefficient $(E_1\alpha)$ in the above equation. In order to calculate this term, the thermal expansion, α, was measured by determining the changes in the lattice parameters between room temperature and 434°C. Powder patterns were taken with a Unicam 19-cm diameter high-temperature camera at 24°C, 272°C, and 434°C. Values for the changes in lattice constants were derived from the changes in position of about ten lines by a least-squares fitting of the data. The values of the linear coefficients are: *a* direction, 22×10^{-6} deg^{-1}; *b* direction, 39×10^{-6} deg^{-1}; *c* direction, 38×10^{-6} deg^{-1}. This gives 99×10^{-6} deg^{-1} for the volume coefficient. Because of the broadening of the lines at high temperatures these values are accurate to only about 10 percent; however, this is sufficient for the present purpose. The rate of temperature variation of the energy gap $E_1\alpha$ is 8×10^{-4} ev/deg. The temperature variation of the energy gap can also be estimated from the data by comparing the number of carriers in the intrinsic range as calculated from Eq. (5) with the number derived from theory.[9,13] This gives $dW/dT=2.3\times10^{-4}$ ev/deg.

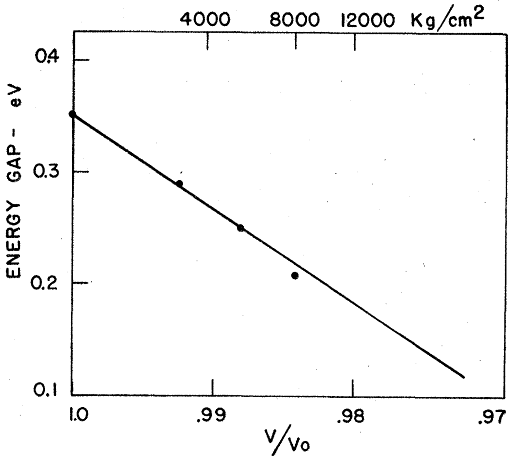

FIG. 5. Dependence of the activation energies derived from Fig. 4 on the dilation.

Although the picture just presented reproduces satisfactorily most of the observed electrical properties, because of the structural anisotropy and the polycrystallinity of the samples, the derived parameters must be considered as properties averaged over spatial direction. In fact, a comparison of the measured characteristics of the phosphorus with the theory of a two-dimensional semiconductor is also interesting. A statistical mechanical analysis of an electron gas

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[12] J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

[13] V. A. Johnson and H. Y. Fan, Phys. Rev. **79**, 899 (1950).

constrained to move in a plane, with application of the Boltzmann equation to determine the transport properties, was carried out. Naturally the observed electrical characteristics depend on the orientation of the planes relative to the electric and magnetic fields, and for comparison with the properties of a polycrystalline aggregate the properties of the planar semiconductor were simply averaged over all possible directions of the planes. The relationships between the averaged electrical properties of such a polycrystalline aggregate differ from those of an isotropic conductor because of the altered distribution of the energy states of the electrons in the two-dimensional case and differences in the effect of the averaging process on the various electrical parameters. The mobility in the two-dimensional case may be characterized by a quantity v, the mobility of a charge carrier in a plane under the influence of an electric field parallel to the plane. The significant points of difference are as follows.

1. Because some grains are oriented so as to make only small contributions to the conductivity or Hall constant, the mobility calculated from $\mu=(8/3\pi)R\sigma$ is less than v by a factor 4.2. The mobilities shown in Fig. 3 must be multiplied by this factor to obtain the corresponding v's.

2. Because of the changed velocity distribution, the magnetoresistance coefficient for a magnetic field perpendicular to the planes is larger for a two-dimensional semiconductor; the decrease due to the averaging process almost exactly cancels this effect, so that the mobility calculated from the magnetoresistance coefficient in the usual way is equal to $0.99v$. This means that this mobility should be 4.1 times as large as that calculated from the Hall constant, which coincides qualitatively with the observation noted above of an anomalously large magnetoresistance effect.

3. The intrinsic conductivity varies with temperature as $T^{-\frac{1}{2}}\exp(-W/2kT)$. The two types of temperature dependence cannot be distinguished experimentally; in the two-dimensional case W comes out 0.02 ev higher.

4. The temperature dependence of the energy gap required to account for the density of charge carriers in the intrinsic range is $dW/dT=9\times10^{-4}$ ev/deg, in better agreement with that calculated from the thermal expansion and E_1.

Extrapolation of the line of Fig. 5 reperesenting the variation of energy gap with volume indicates that the bands will begin to overlap when the volume has been decreased by 4 percent, which corresponds to a pressure somewhat over 20 000 kg/cm^2. Bridgman[14] has observed a transition from black phosphorus to a denser form in the pressure range 25–50 000 kg/cm^2; the possibility that these two phenomena are related was considered. An attempt was made to produce the high-pressure phase at pressures around 50 000 kg/cm^2 with a shearing apparatus described by Bridgman,[15] and to quench this phase in liquid nitrogen and determine its structure by x-ray diffraction methods.[16] Only lines attributable to black phosphorus could be found in powder patterns of the quenched samples.

For certain simple types of dependence of electron energy on wave number, an infrared absorption edge should occur at quantum energies corresponding to the thermal excitation energy, i.e., at a wavelength $\lambda=hc/W$. For $W=0.33$ ev, $\lambda=3.8$ microns; if the temperature dependence of energy gap $dW/dT=8\times10^{-4}$ ev/deg is accepted, at room temperature $W=0.57$ ev and $\lambda=2.2$ microns. The material was found to be transparent to wavelengths from 2 to 30 microns.

CONCLUSIONS

1. The black phosphorus studied is a semiconductor with an energy gap of 0.33 ev; the resistivity above 200°C is $\rho=0.0030\exp(0.33/2kT)$. At low temperatures p-type impurity semiconduction is observed.

2. The mobility of holes in this material is $1.9\times10^6 T^{-\frac{3}{2}}$ cm^2/volt sec, and that of the electrons is $1.2\times10^6 T^{-\frac{3}{2}}$ cm^2/volt sec. It appears that over most of the temperature range the mobility is limited by scattering by lattice vibrations.

3. At room temperature the values of the electrical properties for an intrinsic sample are: $\rho=1.5$ ohm cm, $\mu_p=350$ cm^2/volt sec, $\mu_n=220$ cm^2/volt sec. These values and the band separation are very similar to the corresponding properties of tellurium.

4. The energy gap decreases with decreasing volume of the crystal at a rate $VdW/dV=8.3$ ev.

5. It should be noted that the structure of black phosphorus is highly anisotropic and that the electrical properties may vary strongly with crystalline direction; certain data are more consistent with a model of a polycrystalline two-dimensional semiconductor than with the common, three-dimensional, isotropic model.

ACKNOWLEDGMENTS

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[14] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 55 (1948).

[15] P. W. Bridgman, Phys. Rev. **48**, 825 (1935).

[16] The apparatus for quenching high pressure phases with liquid nitrogen was developed by I. S. Jacobs.