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ELECTRONIC STRUCTURE OF BLACK PHOSPHORUS

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The band structure of black phosphorus was calculated by using the self-consistent pseudopotential method. The resulting band structure was used to discuss the electronic properties of black phosphorus. We also calculated the crystal energies for a variety of crystal structures of phosphorus as a function of crystal density and explained theoretically the sequence of pressure-induced structural transformations of black phosphorus.

I. Introduction

Phosphorus is an element of the fifth group of the periodic table which exists in a number of allotropic modifications and shows an interesting sequence of structural transformations under pressures such as semiconductor-semimetal-metal [1]. The most stable form at zero pressure, black phosphorus (abbreviated as BP hereafter), is a narrow gap semiconductor [2] with a layer structure consisting of puckered layers [3].

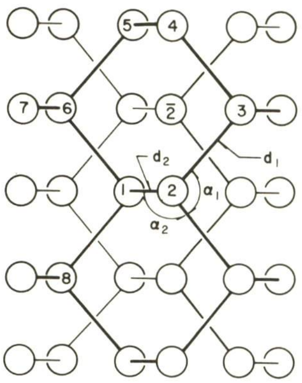

Fig.1 The projection of two adjacent puckered layers on the xy plane

The projection of two successive layers on the xy-plane is shown in Fig.1. The crystal structural parameters are shown in Table 1. A primitive cell of BP contains four atoms in positions $\pm(ua, 0, vc)$ and $\pm((u+1/2)a, b/2, -vc)$. The first Brillouin zone of BP is shown in Fig.2.

The first of the two aims of the present paper is to calculate the energy bands of BP and apply them to discussion of the electronic properties of BP. The second is to calculate the crystal energies of a variety of crystal structure types of phosphorus as a function of crystal density in order to investigate the sequence of pressure-induced structural transformations.

II. The Band Structure of Black Phosphorus

Our method to calculate the band structure is based on the use of the bare ion potential of the Appelbaum-Hamann type [4]

Table 1 Crystal structure parameters of black phosphorus at room temperature [3]

a	4.376Å	Lattice constants in orthorhombic system
b	3.314Å	
c	10.478Å	
d_1	2.224Å	Bond lengths
d_2	2.244Å	
α_1	96.34°	Bond angles
α_2	102.09°	
u	0.08056	Crystal structural parameters
v	0.10168	

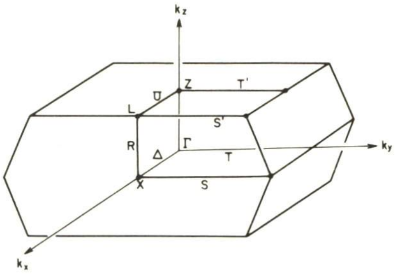

Fig.2 Brillouin zone of black phosphorus

$$\Omega_0^{-1}\left\{-\frac{8\pi Z}{g^2}+\left(\frac{\pi}{\alpha_1}\right)^{3/2}\nu_1+\left(\frac{\pi}{\alpha_1}\right)^{3/2}\left(\frac{3}{2\alpha_1}-\frac{g^2}{4\alpha_1^2}\nu_2\right)\right\}\exp(-g^2/4\alpha_1)$$

where the parameters α_1, ν_1 and ν_2 are determined by fitting the potential to the spectroscopic terms of P^{4+} ion. We have used two sets of these parameters, namely, (A) $\alpha_1=1.0$, $\nu_1=22.86$ and $\nu_2=-13.638$; (B) $\alpha_1=1.0$, $\nu_1=12.497$ and $\nu_2=-6.443$.

The core potential is then self-consistently screened by the valence electrons according to the Xα method. The resulting energy bands for the set (A) with $\alpha=0.7$ for the exchange correlation parameter are shown in Fig.3. For the core potential (B), we have to use $\alpha=1.25$ in order to get the energy gap of about 0.3 eV. In calculation we have used about 230 waves.

A primitive cell of BP contains 20 valence electrons which occupy up to the second lowest Z_2^+ level at Z. Thus a semiconducting direct energy gap appears at Z in accordance with the result in the tight binding approach [5].

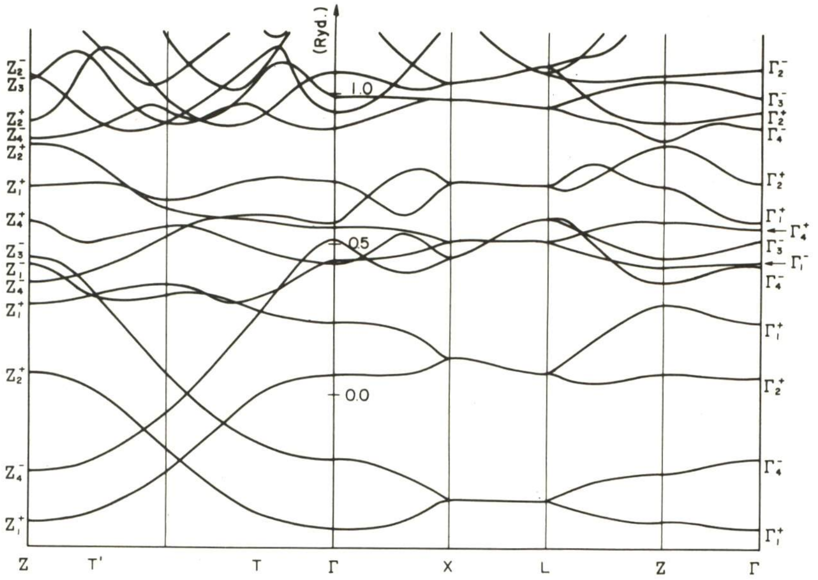

Fig.3 Energy bands of black phosphorus

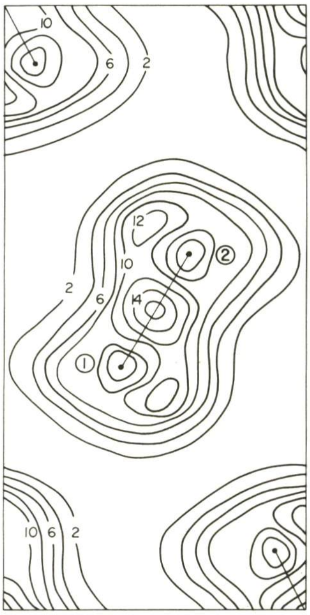

Fig.4 Valence-electron charge density in the plane containing the atoms 1 and 2 and perpendicular to the plane of Fig.1

Table 2 Calculated effective masses

	$(\frac{m^*}{m_o})_x$	$(\frac{m^*}{m_o})_y$	$(\frac{m^*}{m_o})_z$	average
hole	0.17	0.71	0.59	0.34
electron	0.16	0.81	0.24	0.26

The self-consistent charge density shown in Fig.4 indicates that the main bindings in the puckered layer are covalent bonds due to 3p orbitals of P and those between puckered layers are van der Waals' interactions.

The effective masses of carriers are calculated as shown in Table 2. It is somewhat surprising that in spite of the layered structure the effective masses in the z-direction are even smaller than those in the in-plane y-direction. This result suggests that the anisotropic property of the electrical conductivity of BP will not be two-dimensional as might be expected from its layered structure, although it has not yet been observed.

We have also calculated the decreasing rate of the energy gap by hydrostatic pressure. The lattice constants under pressures are taken from experiment [6]. The pressure dependence of the energy gap is calculated to be $(dE_g/dP)_{cal}=2.35\times10^{-2}$eV/kbar. The experimental value is given by $(dV/VdP)\times(VdE_g/dV)=30.2\times10^{-4}(\text{kbar})^{-1}$[6]$\times8.3$ eV[2]$=2.51\times10^{-2}$ eV$\times$ $(\text{kbar})^{-1}$. Thus $(dE_g/dp)_{cal}$ is in good agreement with $(dE_g/dP)_{exp}$.

III. Structural Stability of Black Phosphorus

BP transforms to a semimetallic form with "arsenic" A7 structure at about 80 kbar. At 110 kbar it transforms to a primitive sc metal. We have calculated the crystal energy of a variety of crystal structure types of phosphorus as a function of crystal density using the structural expansion method in the third order approximation with respect to the pseudopotential. In calculation we have used the set (B) as the bare pseudopotential. The results are shown in Fig.5.

In the figure the point (b) represents the energy of the A7 structure at 83 kbar estimated from the energy of BP at 1 bar (the point (a) with -2.649 ryd/ele and $\Omega/\Omega_{A7}=1.311$) and the compressibility data [6]. The atomic energy shown in the figure (-2.5988 ryd/ele) is the ionization energy from P to P^{5+} divided by five (the number of valence electrons).

The curve of the A7 was obtained by calculating the minimum energy for change of the structural parameters at each crystal density. But the curve of the BP was obtained by fixing the structural parameters at the observed values at 1 bar. The point (c) is the minimum energy of the BP for change of the structural parameters at $\Omega/\Omega_{A7}=1.311$.

The results are summarized: (1) Under high pressures the sc is most stable in accordance with experiment. (2) The diamond (A4) structure is always higher in energy than the A7 and BP. (3) The stable structure at zero pressure is not the BP but the A7 in contrast with observation.

The conclusion (2) differs from Schiferl's results [7] in which the second order approximation was used instead of the third order and the A4 becomes lower in energy than the A7 and BP in some range of Ω/Ω_{A7}.

The cause of (3) is attributed to the following fact. In general the third order approximation of the structural expansion method is successfully applicable to metallic and semimetallic phases such as the SC and A7, but is insufficient for semiconducting phases such as the BP having energy gaps on the whole Jones zone surface [8]. In order to overcome this shortcoming, we have to go beyond the third order approximation or to use the self-consistent pseudopotential method to calculate the energy of BP.

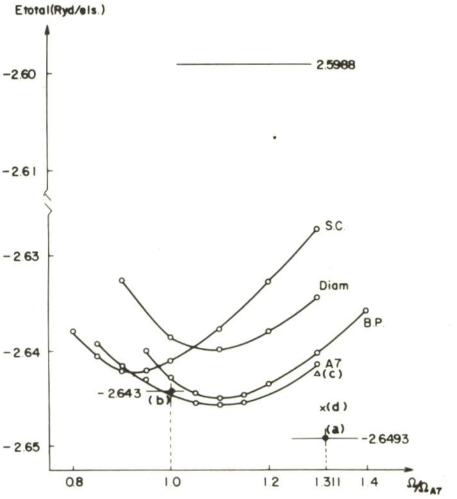

Fig.5 Crystal energies in rydbergs per electron for a variety of crystal structure types as a function of reduced volume (atomic volume divided by the atomic volume of the A7 at 80k bar): For the points (a) to (d), see the text

We have performed the latter calculation for the BP at zero pressure using the potential (B) and $\alpha=2/3$. The result is shown as the point (d) in Fig.5. Though more calculations are needed to get a final and quantitative conclusion, we can say that the sequence of pressure-induced structural transformations of BP is explained theoretically.

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