

Highly-angle-resolved ultraviolet photoemission study of a black-phosphorus single crystal

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Angle-resolved photoemission spectra of a black-phosphorus single crystal have been measured with very high angular resolution using He I and Ne I resonance lines. The experimentally determined band structure has been compared with the self-consistent pseudopotential calculations. Some special points and bands with almost no energy dispersion along the interlayer direction have been successfully assigned in the experimentally derived band structure.

Black phosphorus (black P) is the most stable form among the many allotropes of phosphorus and has a layered structure consisting of puckered layers with four atoms per unit cell.¹ It is a *p*-type semiconductor with a narrow gap of about 0.3 eV.^{2,3} Black P shows a reversible structural transformation upon an application of high pressure from orthorhombic form to successively denser rhombohedral and cubic forms,^{4,5} and this structural change is accompanied by the semiconductor-semimetal-metal transition.⁶ Despite these interesting properties, precise experimental studies of black P have been long prohibited by the difficulty in growing a large single crystal: almost all the early experiments have been done with a polycrystal²⁻¹⁰ or a tiny fragment of single crystal.^{11,12} Recent success^{13,14} in growing a large single crystal, however, has made it possible to study the electrical and optical properties in detail. Some preliminary studies¹⁵⁻²⁰ with a large single crystal have been already reported and compared with the preceding theoretical studies.²¹⁻²³ The possibilities of intercalation as in graphite and the alloying with arsenic are now also being examined.

We have already reported an x-ray photoemission spectrum of black-P single crystal¹⁶ and also a preliminary result of an angle-resolved ultraviolet photoemission spectroscopy (ARUPS) with He I resonance line.²⁰ In this Rapid Communication, we present refined results of the ARUPS study on a larger black P single crystal. In the present study, we also used the Ne I resonance line in addition to the He I as an exciting source in order to study or check the effects of the conduction bands, which sometimes give a large disturbance to the observed photoemission spectra.²⁴

Black P single crystal (10-mm-diam × 15-mm length) was prepared with essentially the same method as described before.¹³ The crystallinity and the orientation of the sample were checked by the Laue diffraction pattern. The single crystal was cleaved *in vacuo* (less than 2×10^{-9} Torr) along the basal plane to obtain a clean surface for the photoemission measurements.

The ARUPS spectra were measured with the He I (21.22 eV) and Ne I (16.85 and 16.67 eV) resonance lines as exciting sources. As for the doublet of Ne, the mean value (16.76 eV) was used to analyze the spectra. The total energy resolution of the spectrometer was about 0.1 eV and the angular resolution was less than 1.5°. This high angular

resolution is one of the key points in the present study and accounts for the very rich structures of the observed spectra leading to a precise determination of the band structure. The incidence angle of the photon beam was about 45° to the surface normal of the sample. The relative orientation of the sample to the electron energy analyzer was determined in advance by the Laue pattern and then precisely in the spectrometer by the azimuthal and polar angle dependence of the ARUPS spectra. The measurements were carried out on the two planes with high symmetry: Γ -*T*-*T'*-*Z* and Γ -*X*-*L*-*Z* planes as indicated by shaded areas in Fig. 1. The Fermi level of the sample was referred to that of a silver film deposited onto the sample.

Figure 2 shows the angle-resolved He I photoemission spectra of the Γ -*X*-*L*-*Z* plane. Polar angle referred to the surface normal is denoted on each spectrum. One spectrum was obtained by continuous scanning for about 2 h and the typical peak count was 2000–3000. All the spectra show rich structures and both the intensity and the position of the peaks and shoulders are very sensitive to the change of the polar angle.

In Fig. 3(b) are plotted the position of the peaks and shoulders in the spectra in Fig. 2 versus the wave vector parallel to the surface calculated using the formula²⁴

$$k_{\parallel} = [2m(h\nu - E_B - e\Phi)]^{1/2} \sin\sigma,$$

where *m* is the mass of an electron, *E_B* the binding energy of the electron, *hν* the energy of the exciting light, *eΦ* the work function of black P (5.3 eV, determined from the cut-

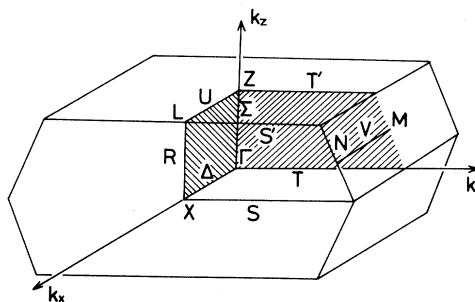


FIG. 1. Brillouin zone of black phosphorus.

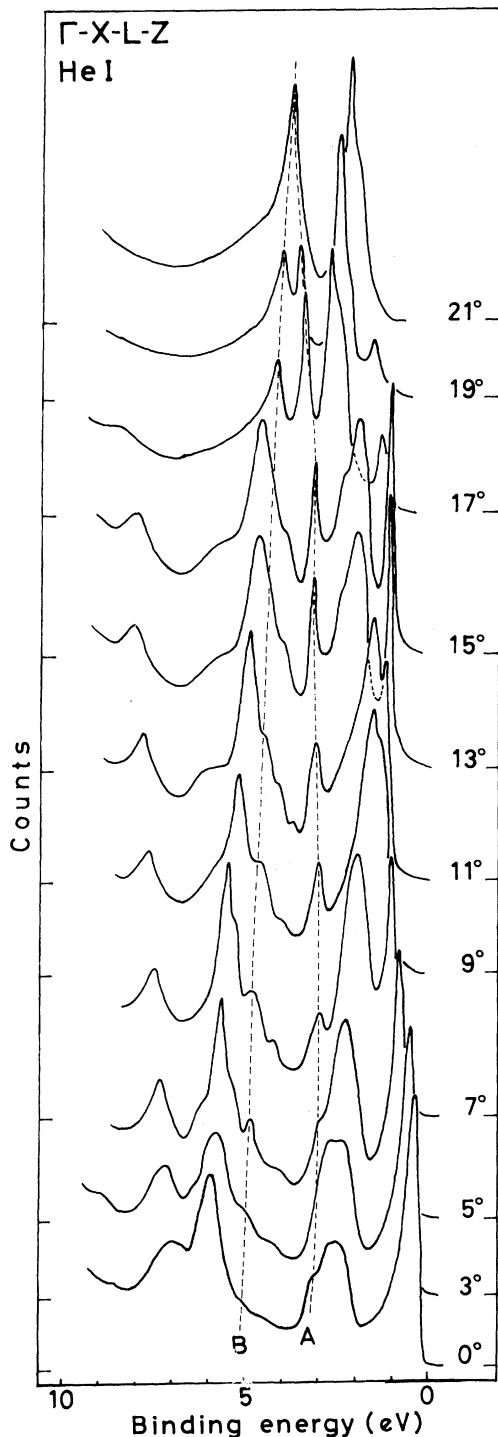


FIG. 2. Angle-resolved He I photoemission spectra of the Γ -X-L-Z plane. Polar angle referred to surface normal is denoted on each spectrum. Bands A and B [see Fig. 3(a)] are indicated by dashed lines.

off of the secondaries of photoemission spectra), and σ the polar angle. In Fig. 3(a) are shown the energy bands along the Γ -X and Z-L directions calculated by Asahina, Shindo, and Morita by the self-consistent pseudopotential (SCP) method.²² The experimental band structure of the Γ -X-L-Z plane determined by the Ne I measurements is also shown

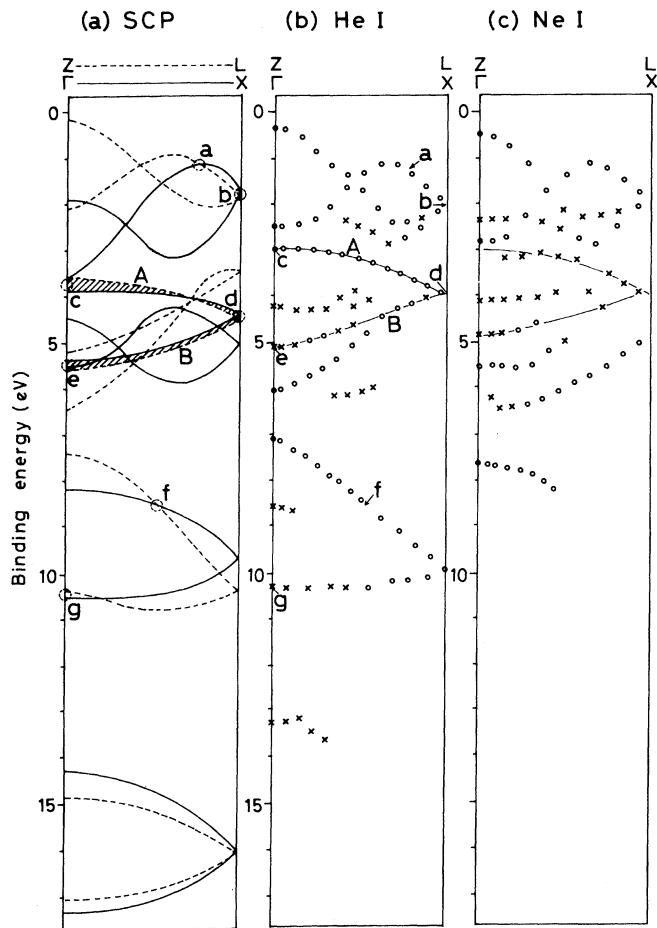


FIG. 3. Theoretical and experimental band structures of the Γ -X-L-Z plane. (a) Calculated bands along the Γ -X (solid line) and Z-L (broken line) directions. Small (*a-g*) and large (*A, B*) alphabets indicate special points and bands with almost no dispersion along the interlayer direction. (b) The experimental band structure determined from the He I photoemission measurements. Circles and crosses represent prominent peaks and shoulders or small peaks, respectively. Some points and crosses are tentatively connected to clear the correspondence between the calculation and the experiments. Points corresponding to the special points *a-g* are also indicated by the same symbols. (c) The experimental band structure derived from the Ne I measurements.

in Fig. 3(c). Figure 4 shows the results for the Γ -T'-T'-Z plane.

The overall feature of the band structure is in good agreement between the experiments and the calculations, although a slight displacement is observed for some bands. The experimental band structures determined by the He I and Ne I measurements are, as a whole, similar to each other, but are certainly different in detail. This indicates that the effect of the conduction-band structure is small but undoubtedly exists, affecting the observed spectra through the interlayer energy dispersion of the valence band.²⁴ Therefore, in the course of analyzing the experimental results, we must take into account the effect of the energy dispersion along the interlayer direction. In order to avoid this ambiguity, we have picked out some special points and bands in the calculations which have almost no interlayer dispersion.

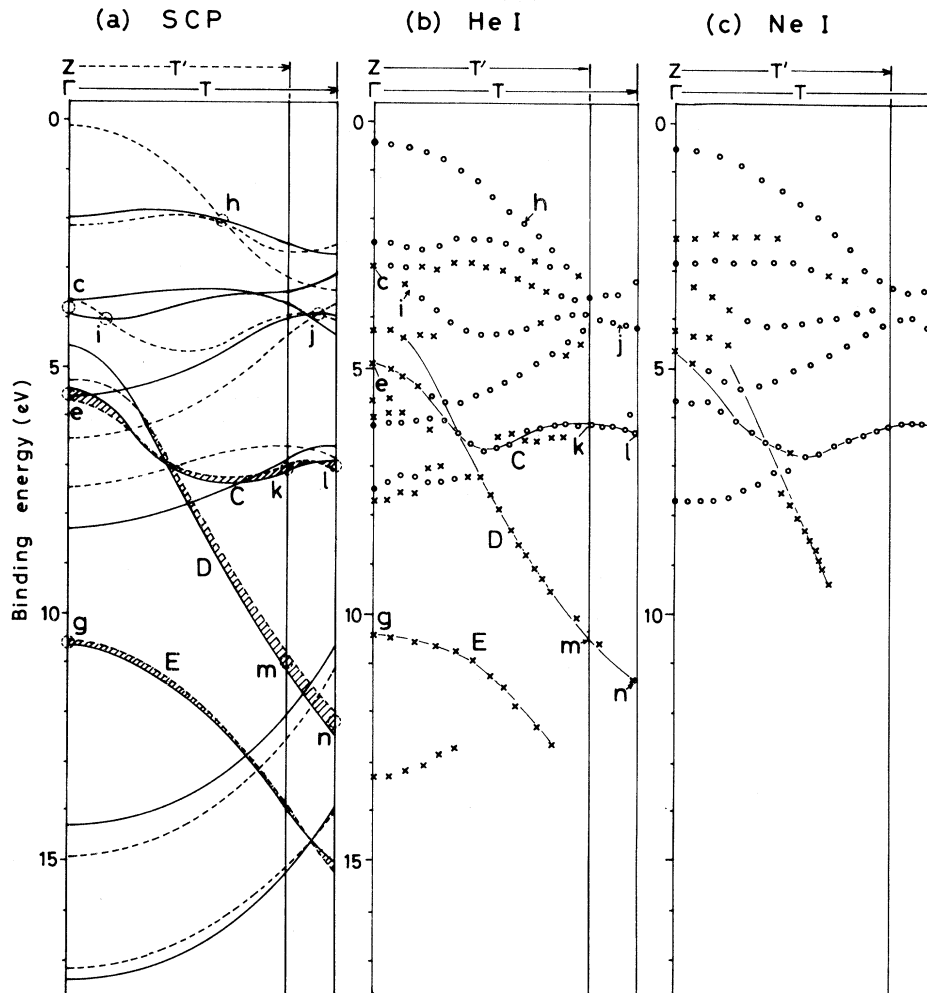


FIG. 4. Theoretical and experimental band structure of the Γ - T - T' - Z plane. (a) Calculated bands along the Γ - T (solid line) and Z - T' (broken line) directions. (b) and (c) The experimental band structures determined from the He I and Ne I measurements, respectively. For details, see text and the caption to Fig. 3.

These points and bands are indicated in Figs. 3(a) and 4(a) by small (a - n) and large (A - E) alphabets, respectively. They can be directly compared with the experimental results, if the calculation is not far from the real one. These points and bands are also relatively easily distinguished in the ARUPS spectra because the electronic states with almost no interlayer dispersion should form a sharp peak in the photoemission spectra:²⁵ for example, the first very narrow peak with about 0.2 eV full width at half maximum in the spectrum of 13° polar angle in Fig. 2 corresponds to the point very close to the special point a in Fig. 3(a), and a series of narrow peaks at 3-4 eV in the spectra of 7° - 19° (Fig. 2) corresponds to band A in Fig. 3(a). As for band B , which should be almost dispersionless along the interlayer direction, however, the observed bands are not so narrow or prominent as those of band A except for the spectra of the polar angle of 5° and 7° (Fig. 2). This may be that band B is covered with the other bands or that band B might not be so dispersionless as the calculation predicts.

Bands A and B , and points c , d , and e in the calculation, are located at the larger binding energy by about 0.5 eV compared with the experimental results. On the other hand, points a and b in the calculation have slightly shifted

(about 0.2 eV) toward the smaller binding energy with respect to the experiments. This means that the calculation overestimates the bandwidth of the $3p$ region (0 to about 6.5 eV) by about 0.7 eV. This observation is consistent with the previous x-ray photoemission spectroscopy measurement.¹⁶ In the higher-binding-energy region (points f and g), the agreement is fairly good.

As for the Γ - T - T' - Z plane (Fig. 4), the overestimation of the $3p$ bandwidth is also recognized: points c , i , e , k , and l and band C in the calculation appear at the higher-binding-energy while point h at the similar binding energy compared with the experiments. Band D , which is very steep and has both the $3p$ and the $3s$ characters,²² is observed at the binding energy about 1 eV lower than the calculation. Band E shows a fairly good agreement.

A quantitative and detailed comparison of the experiments with the calculations, which will give a basis for choosing better parameters for more precise and realistic band calculations, will be described elsewhere.

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