Electronic band structure of rhombohedral arsenic studied by highly-angle-resolved ultraviolet photoelectron spectroscopy

H. Tokailin, T. Takahashi, and T. Sagawa

Department of Physics, Tohoku University, Sendai 980, Japan

K. Shindo

College of Humanities and Social Sciences, Iwate University, Morioka 020, Japan

Angle-resolved ultraviolet photoemission spectra of a rhombohedral arsenic single crystal have been measured for the first time in very high angular resolution with the He I resonance line as an exciting source. The experimentally derived band structure has been compared in detail to the self-consistent pseudopotential calculation performed in this study and with four others presented mainly by Falicov and co-workers. The present angle-resolved photoemission measurement directly identified the location of an electron pocket at the L point in the Brillouin zone and a hole pocket near the T point. It has also been elucidated that contrary to the early calculations only one band goes across the Fermi level near the L point, forming the electron pocket. Some special points with high symmetry and/or almost no dispersion along the interlayer direction have been successfully assigned in the experimentally determined band structure.

I. INTRODUCTION

Arsenic is a semimetal with the same $A7$ trigonal crystal structure as the other group-V semimetals, bismuth and antimony,[1] having attracted the considerable attention of many investigators. The interesting and peculiar electronic properties of arsenic are attributed to the special shape of the Fermi surface and its relationship to the band structure. A number of experimental[2-7] and theoretical[8-10] studies have been done to investigate the Fermi surface of arsenic, finally leading to an accurate determination of the surface.[10] However, in contrast to the good understanding of the Fermi surface, little is known about the electronic structure below and above the Fermi level (the valence- and conduction-band structures); a limited number of experiments on the electronic structure (optical reflectivity,[11-15] x-ray photoelectron spectrum,[16,17] angle-integrated ultraviolet photoelectron spectrum[17]) have been reported so far. Furthermore, a discrepancy in the electron pocket at the L point between experiments[6,7] and calculation[10] has still remained unresolved; there are two levels at the L point (L_4 and L_1) just below the Fermi level in the calculation, while no experimental confirmation for this has yet been given.

In this paper, we present results of the first angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) of rhombohedral arsenic. ARUPS is now extensively used for a direct determination of the electronic structures of various materials.[18] We have already performed an ARUPS study of the group-V narrow-gap semiconductor, black phosphorus, with very high angular resolution, and obtained the experimental band structure of black phosphorus with considerable accuracy.[19] The high angular resolution in ARUPS measurements is one of the key points in the present study, enabling us to study the complicated band structure of arsenic, especially near the Fermi level.

In this paper we also present a refined theoretical band structure of rhombohedral arsenic calculated by the self-consistent pseudopotential method. The electronic band structure of rhombohedral arsenic is discussed by comparing the experimental results with the present and four other band calculations reported previously.[8-10,20]

II. EXPERIMENTAL METHOD

A single crystal of rhombohedral arsenic (about $5 \times 10 \times 1$ mm^3) was supplied by The Institute for Solid State Physics of The University of Tokyo. The sample was prepared for the de Haas–van Alphen measurement,[5,21] and its purity is higher than 99.999%. 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 [(111) plane in the rhombohedral system] to obtain a clean surface for the photoemission measurements; rhombohedral arsenic has a layered structure consisting of As$_4$ pyramidal units along the (111) plane.[1]

The ARUPS spectra were measured with the He I (21.22 eV) resonance line as an exciting source. He I light was incident at about 45° onto the surface of the sample (i.e., mixed s and p polarization). The total-energy resolution of the spectrometer was about 0.1 eV and the angular resolution was less than 1.5°. Further details of the spectrometer have been described elsewhere.[22] The relative orientation of the sample to the electron-energy analyzer was determined roughly in advance by the Laue pattern and then precisely in the spectrometer by the azimuthal- and polar-angle dependence of the ARUPS spectra. Measurements were carried out in the three planes with high symmetry in the Brillouin zone: Γ-T-U-L-U-X-U-T-Γ

(abbreviated to Γ-L-X), Γ-T-W-K-T-Γ (Γ-W-K), and Γ-T-U'-X'-U'-L'-U'-T-Γ (Γ-X'-L') (see Fig. 1). The Γ-L-X and Γ-X'-L' planes are fully equivalent to each other through inversion symmetry, but in the ARUPS measurements they are no longer equal because the three-dimensional inversion symmetry breaks at the surface. The Fermi level of the sample was referred to that of a silver film deposited onto the sample. No noticeable effect of oxidization of the sample surface was observed during the measurements.

III. CALCULATION

The band structure is obtained by solving the self-consistent one-electron Schrödinger equation,[23,24]

$$\left[-\frac{\hbar}{2m}\nabla^2 + \sum_i V_{\text{ion}}(\,|\,r-R_i\,|\,) + V_H(r) + V_{\text{xc}}(r) \right]\psi_{nk}(r)$$

$$= E_{nk}\psi_{nk}(r) , \quad (1)$$

where $V_{\text{ion}}(\,|\,r-R_i\,|\,)$ is the Topp-Hopfield-type potential of the As^{5+} ion positioned at R_i, $V_H(r)$ is the Hartree potential given by the Poisson equation, and $V_{\text{xc}}(r)$ is the exchange-correlation potential, for which we applied the Slater exchange approximation, i.e., the self-consistent potential is given by the charge density of the valence electron. In a recent calculation[24] one of the authors has shown that the Slater exchange approximation gives a better band structure in the neighborhood of the T point than the $X\alpha$ approximation.

By expanding ψ_{nk} in terms of plane waves, we can solve the self-consistent equation (1). In the diagonalization of the secular equation at a point k, all reciprocal-lattice vectors G such that $\hbar^2(k+G)^2/2m < 10$ Ry are taken as a basis set which has about 160 plane waves. The charge density has been calculated by means of the five-special-point method.[23-25] Thus, we obtained the self-consistent potential and the band structure.

In the present calculation we used the rhombohedral shear parameter $\epsilon=0.0883$, the relative displacement parameter of sublattices in the [111] direction $u=0.2271$, and the crystal density $r_s=1.907$ at room temperature. The resulting potential was very similar to that of Ref. 23 and the self-consistent potential was also assumed to be
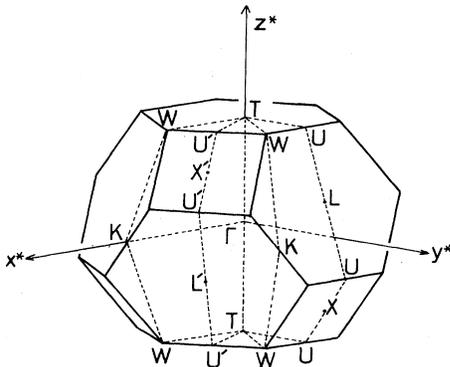

FIG. 1. Brillouin zone of rhombohedral arsenic.

equal to the bare-ion potential for the wave vectors greater than 3.0 a.u.

IV. RESULTS AND DISCUSSION

Figures 2—4 show the polar-angle dependence of the ARUPS spectra measured in the Γ-L-X, Γ-X'-L', and Γ-W-K planes, respectively. 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. As found in Figs. 2—4, ARUPS spectra are full of fine structures and the position and intensity of the peaks are very sensitive to the change of the polar angle. The intensity and polar-angle dependence of the photoemission spectra are quite different between the Γ-L-X (Fig. 2) and Γ-X'-L' (Fig. 3) planes, although, as described in Sec. II, these two planes are fully equivalent in the crystal.

Some notable series of peaks and shoulders in the spectra are indicated by dashed lines labeled with capital letters, A—P. We find a very narrow peak just below the Fermi level at zero polar angle in all three planes. This prominent peak should correspond to the T_1 point close to the hole pocket.[10] The electron pocket is also clearly observed in the spectra; series of peaks B and G just below the Fermi level at polar angles of 18°—34° are supposed to be due to the electron pocket at the L point. The existence of an electron pocket at the L point has been predicted by the band calculations[8-10] and has been obtained experimentally. In the following we discuss in detail the band structure of rhombohedral arsenic by comparing the experimental results with the calculations.

Plotted in Figs. 5(b) and 5(c) are the positions of the peaks and shoulders in the spectra in Figs. 2 and 3, respectively, versus the wave vector parallel to the surface calculated by the formula[26]

$$k_{||} = [2m\,(\hbar\omega - E_B - e\Phi)/\hbar^2]^{1/2}\sin\theta , \quad (2)$$

where m is the mass of an electron, $\hbar\omega$ is the photon energy of the exciting light (He I, 21.22 eV), E_B is the binding energy of a photoemitted electron, $e\Phi$ is the work function of the sample (4.3 eV, determined from the cutoff of the secondaries of photoelectron spectra), and θ is the polar angle. Also shown in Fig. 5 is the theoretical band structure along the T—U, Γ—L, and Γ—X directions calculated by the self-consistent pseudopotential method in this study. The calculated bands along the Γ—L and Γ—X directions are plotted versus the wave vector parallel to the surface in order to directly compare them with the experimental bands. Figure 6 shows the results for the Γ-W-K plane. In Figs. 5(b), 5(c), and 6(b), experimental points are tentatively connected to clarify the correspondence to the notable structures in the photoelectron spectra (series of peaks labeled A—P in Figs. 2—4).

First, we discuss the results for the Γ-L-X and Γ-X'-L' planes. In Figs. 5(b) and 5(c) we immediately find that the overall features of the experimental bands in the two planes are very similar to each other, although, as shown in Figs. 2 and 3, the intensity of each peak and its dependence on the polar angle are quite different. The observed similarity in the experimental band structure between the
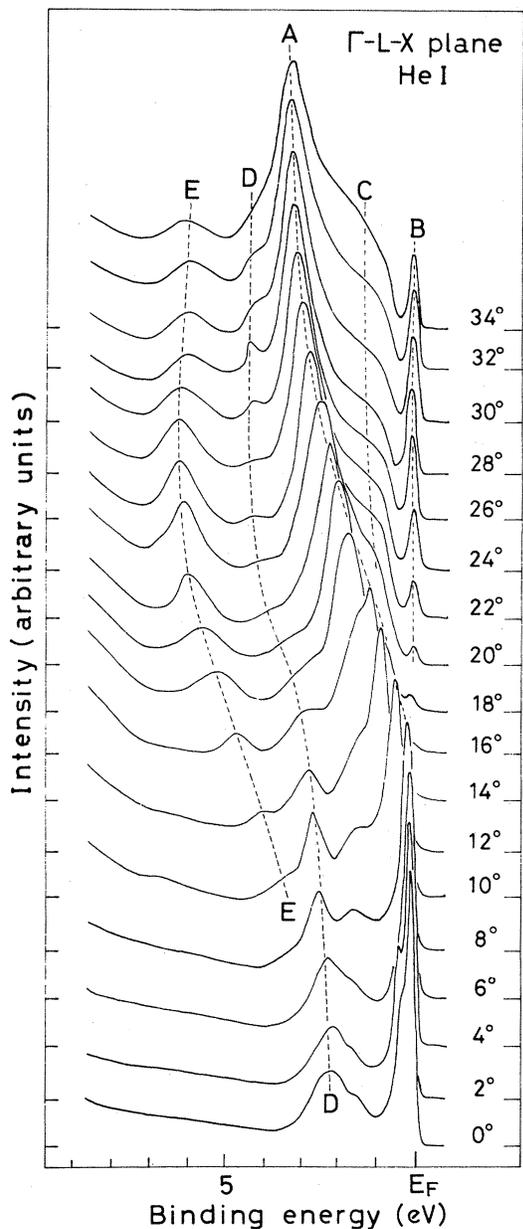
FIG. 2. Angle-resolved He I photoemission spectra in the Γ-L-X plane. Polar angle referred to the surface normal is indicated on each spectrum. Notable series of peaks and shoulders are indicated by dashed lines labeled by capital letters A—E.

FIG. 3. Angle-resolved He I photoemission spectra in the Γ-X'-L' plane. Polar angle referred to the surface normal is indicated on each spectrum. Notable series of peaks and shoulders are indicated by dashed lines labeled by capital letters F—K.

two planes may be attributed to the photoelectron momentum broadening in the direction normal to the surface.[27] If such momentum broadening does not take place in the photoexciting process (i.e., if the strict momentum conservation stands in the direction normal to the surface as well as parallel to the surface), the photoelectrons emitted from the Γ-L-X and Γ-X'-L' planes with the same kinetic energy and the same polar angle (i.e., the same wave vector parallel to the surface) should have different initial states, because the points on the two planes defined by the
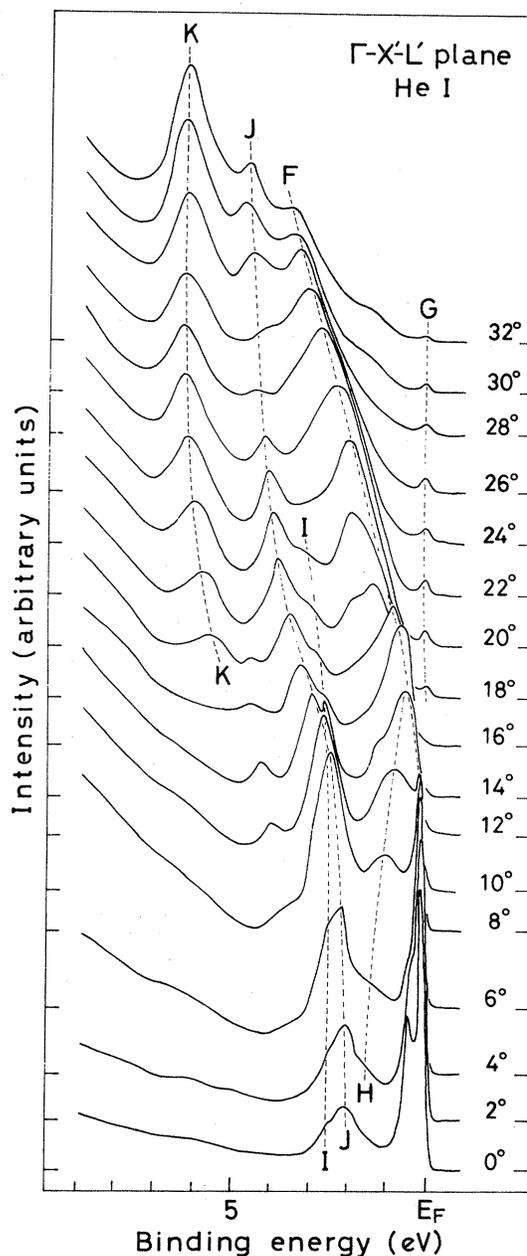
two components of wave vectors (parallel and normal to the surface) are not equivalent to each other in the Brillouin zone except for some special cases (for example, on the Γ—T line). Thus, the disappearance of the momentum broadening should make the experimental band structures of the two planes quite different from each other. However, as stated above, the obtained band structures are very similar to each other. This is certainly due to the electron momentum broadening. The photoexcited electrons have a small ambiguity in the initial states along the
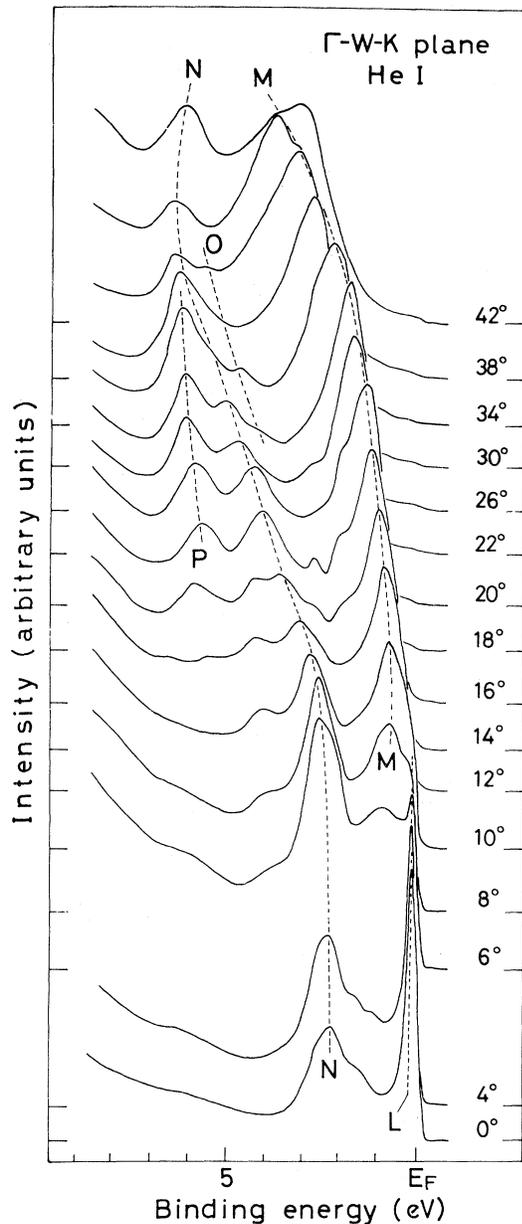
FIG. 4. Angle-resolved He I photoemission spectra in the Γ-W-K plane. Polar angle referred to the surface normal is indicated on each spectrum. Notable series of peaks and shoulders are indicated by dashed lines labeled by capital letters $L-P$.

FIG. 5. Theoretical and experimental band structures in the Γ-L-X and Γ-X'-L' planes. (a) Self-consistent pseudopotential calculation (SCP) along the $T-U$ (solid line), Γ$-L$ (dashed line), and Γ$-X$ (dashed-dotted line) directions. The calculated bands along the Γ$-L$ and Γ$-X$ directions are plotted versus the wave vector parallel to the surface (i.e., $T-U$ direction). Small letters indicate stationary points with high symmetry. (b) and (c) The experimental band structures in the Γ-L-X and Γ-X'-L' planes, respectively. Solid and open circles represent prominent peaks and shoulders or small peaks, respectively. Capital letters show a correspondence to the notable series of peaks and shoulders in Figs. 2 and 3.

direction normal to the surface owing to the momentum broadening. This results in that the stationary parts with a high density of states along the dispersion normal to the surface (usually high-symmetry points) are most likely to appear as distinct peaks in the photoemission spectra. This is a main reason why the experimental band structures in the Γ-L-X and Γ-X'-L' planes are very similar to each other, whereas the intensity and polar-angle dependence of the photoemission spectra of the two planes are apparently different.
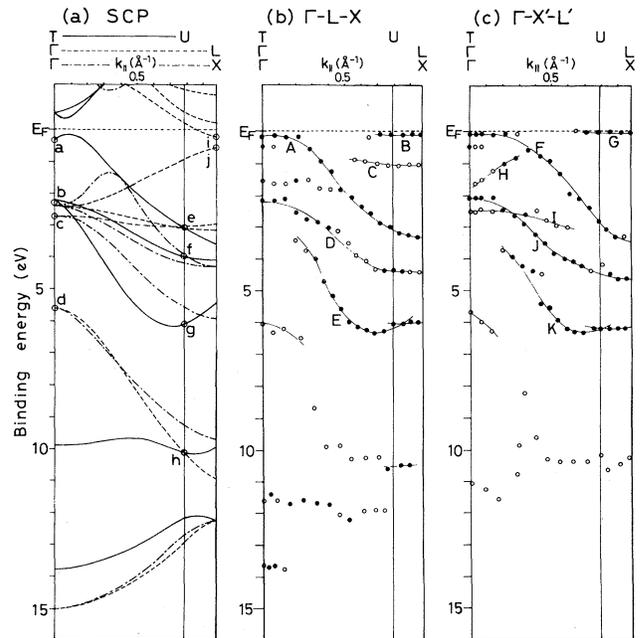
The photoexciting process in the angle-resolved photoemission has been intensively discussed theoretically and experimentally by many researchers,[18,27−29] and at present it is seen that the degree of the electron momentum broadening normal to the surface depends on the material (band structure, etc.) and the experimental condition (photon energy, takeoff angle, etc.). The occurrence of the electron momentum broadening normal to the surface in the present case of arsenic has also been confirmed by the comparison of the ARUPS spectra excited with different sources, namely He I (21.22 eV), Ne I (16.85 and 16.67 eV), and Ar I (11.83 and 11.62 eV); in all three different photoexciting measurements, the electron pocket which strongly localizes at the L point in the Brillouin zone appears as distinct peaks in the spectra (spectra not shown), notwithstanding that the wave vector normal to the surface of the photoelectron is considerably different among the three cases. Therefore, the observed similarity of the overall features of the experimentally derived band structures between the Γ-L-X and Γ-X'-L' planes, which are equivalent in the crystal but no longer equal in the photoemission process, is due to a considerable electron momentum broadening normal to the surface. In the pioneering
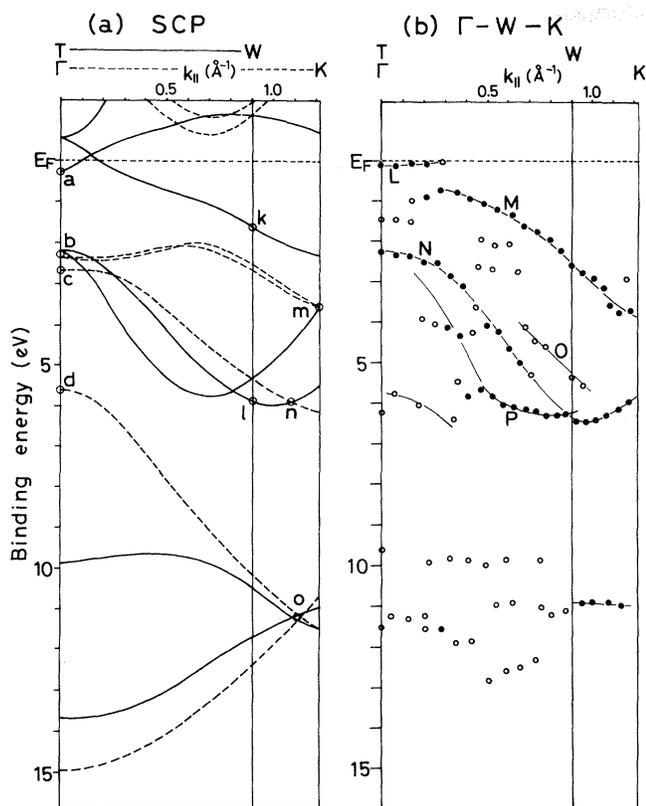
FIG. 6. Theoretical and experimental band structures in the Γ-W-K plane. (a) Self-consistent pseudopotential calculation along the T—W (solid line) and Γ—K (dashed line) directions. Small letters indicate stationary points with high symmetry and/or almost no dispersion along the interlayer, [111] direction. (b) The experimental band structure in the Γ-W-K plane. Solid and open circles represent prominent peaks and shoulders or small peaks, respectively. Capital letters show a correspondence to the notable series of peaks and shoulders in Fig. 4.

work of the ARUPS study by Smith and Traum on tantalum diselenide,[30] a situation and result similar to those in the present case are found: They carried out the ARUPS measurements for two planes in the Brillouin zone (the Γ-A-L-M and Γ-A-L'-M' planes in Ref. 30) which are fully equivalent to each other on the perimeter but not in the interior, and they reported that peaks in the spectra occur at almost the same binding energies in the two planes while the intensity ratios among the peaks are considerably different.

An alternative explanation may be presented for the appearance of the band G in the ARUPS measurements in the Γ-X'-L' plane if the momentum broadening is not as large as described above; the band G may be due to a surface umklapp transition of the band B because (1) a reciprocal-lattice vector of the surface Brillouin zone of the (111) surface of rhombohedral arsenic is just a projection of the $\overrightarrow{LL}$' plane onto the surface if no surface reconstruction takes place, and (2) the intensity of the band G is considerably smaller than that of the band B. Nevertheless, the close resemblance of overall features of the experimental bands of the two planes and the observation of the

electron pocket in the three different (He I, Ne I, and Ar I) photoemission measurements favor the relatively large electron momentum broadening normal to the surface as the most plausible reason for the appearance of the band G.

The occurrence of the momentum broadening normal to the surface makes it simple to compare the experimental bands with the theoretical ones. We picked out some special points in the calculated band which directly correspond to the experimental points. They are indicated in Figs. 5(a) and 6(a) by small letters (a—o); all the points except for n and o are stationary points with high symmetry; points b, m, n, and o are almost dispersionless along the interlayer (i.e., normal to the surface) direction and should appear as prominent and sharp peaks in the photoelectron spectra.[29] In this paper the discussion is limited to the low-binding-energy region (from 0 to about 10 eV, mainly of 4p origin) because the uncertainty of a peak position, and further of the existence of a peak itself, remarkably increases in the high-binding-energy region owing to a large background due to inelastically scattered electrons.

Shown in Table I is a comparison of the binding energy of the special points between the experimental and the present and some previous calculations.[8–10,20] The agreement of the present and another (Lin and Falicov[10]) calculation with experiment is excellent except for points j and k. As shown in Fig. 2, the peaks (or shoulders) of the band C which reaches the point j at the zone boundary [see Fig. 5(a)] are very broad, but even when the broadness of the peaks is taken into account, the point j in the two calculations is somewhat closer to the Fermi level than in the experiment. The point k [Fig. 6(a) and Table I] appears in the experiment [Fig. 6(b), on the band M] at relatively large binding energy compared with the calculations. This may be due to an overlapping from other structures in the photoemission spectra; the lower two bands just below the point k [dashed lines from the points b to m in Fig. 6(a)] may overlap the point k and shift the observed position of k downward in the photoemission spectra. However, it is more plausible that the experimental value (2.5 eV) assigned to the point k should correspond to the lower two bands which are very close to each other, because the experimental band M [Fig. 6(b)] reaches the point m at the zone boundary (see Fig. 6). If the latter is the case, the corresponding theoretical value of the binding energy is 2.5 and 2.8 eV in the present and the Lin-Falicov calculations, respectively. Thus, the agreement of the calculations with the experiment becomes very good. Therefore, it is supposed that the band M in the Γ-W-K plane traces the T—W line as long as the wave vector parallel to the surface ($k_{\parallel}$) is small and then transfers to the Γ—K line before the $k_{\parallel}$ reaches the W point.

In spite of the general agreement of the calculation by Lin and Falicov[10] with experiment, there is one obvious disadvantage in their calculation—it is in the electron pocket at the L point. In the calculation, two bands intersect the Fermi level near the L point, leaving two occupied levels at the L point (L_1 and L_4) with an energy interval of 0.2—0.3 eV just below the Fermi level.

TABLE I. Comparison of binding energy (in eV) of special points with high symmetry and/or almost no dispersion along the interlayer, [111] direction in the band structure of rhombohedral arsenic.

Point	Symmetry	Experiment			Present	Calculations			
		Γ-L-X	Γ-X'-L'	Γ-W-K		Lin and Falicov (Ref. 10)	Golin[a] (Ref. 9)	Falicov and Golin[b] (Ref. 8)	Bullett (Ref. 20)
a	T_1	0.2	0.1	0.1	0.3	0.1	0.1	-0.5^e	0.0
b	T'_3, Γ_3	2.2	2.1	2.3	2.3	2.2	1.5	1.7	2.1
c	Γ_1	d	2.5	d	2.7	3.1	2.7	2.7	2.2
d	Γ'_2	6.1	5.7	5.8	5.6	5.8	4.0	4.9	5.5
e	U_1	3.1	2.9		3.1	3.3	3.1	3.1	2.3
f	U_2	4.4	4.5		4.2	4.2	3.8	3.8	4.0
g	U_1	6.1	6.2		6.1	6.6	6.8	6.7	5.5
h	U_1	10.5	10.4		10.1	10.4	9.5	9.6	10.5
i	L_4^c	0.1	0.1		0.2	0.3	0.4	0.1	-1.1^e
j	L_1^c	1.1	d		0.6	0.5	0.5	0.3	0.4
k	W_2			2.5	1.6	1.8	1.0	1.3	1.4
l	W_2			6.3	5.9	6.3	6.5	6.4	5.5
m	K_1, K_2			3.7	3.6	3.9	3.8	3.9	2.8,3.3
n				6.2	5.9	6.2	6.6	6.5	5.6
o				10.9	11.2	11.4	10.5	10.8	12.2

[a]Without spin.

[b]P1 potential without spin.

[c]Order of the two levels is reversed in Ref. 9. The L_4 level is replaced by another L_1 level in Ref. 8.

[d]Not observed.

[e]In the unoccupied states.

Nevertheless, as found in Figs. 2, 3, and 5, only one band (band B or G) appears just below the Fermi level at the L point in the ARUPS spectra. Therefore, contrary to the refined calculation by Lin and Falicov,[10] it is almost certain that only one band intersects the Fermi level near the L point, forming an electron pocket. The two bands, however, might be very close to each other, combining into one peak in the photoelectron spectra. This possibility is diminished by the present self-consistent pseudopotential calculation [Fig. 5(a)]: Only one band intersects the Fermi level near the L point in the present calculation, in sharp contrast to the previous calculations.[9,10] The location of the two levels just below the Fermi level at the L point has likewise been given no experimental confirmation by the de Haas—van Alphen studies of rhombohedral arsenic.[6,7] This point was also noted by Lin and Falicov in their paper[10] and they ignored the L_1 level in constructing the Fermi surface.

The self-consistent orthogonalized-plane-wave (OPW) calculation by Golin[9] does not show good agreement with experiment: The binding energy of points a, b, g, and h differs by 0.6—2.1 eV between the OPW calculation and the experiment. Moreover, this calculation has the same fault as that of the pseudopotential calculation by Lin and Falicov[10] in the region of the electron pocket at the L point.

As found in Table I, the first band calculation of rhombohedral arsenic by Falicov and Golin[8] is in a fair agreement with the present experiment. However, it has a great discrepancy at the T points; point a with T_1 symmetry is located above the Fermi level (i.e., in the unoccupied states), while in the ARUPS spectrum of zero polar angle a very sharp peak appears just below the Fermi level which should correspond to emission from the T_1 level (see Figs. 2—4). In the relatively recent calculation by Bullett[20] using a tight-binding approach, fair agreement is found for some points in the band structure (for example, b, d, and h), but not for the others (e, i, and m). The largest and detrimental disadvantage of Bullett's calculation is at the L point. The point i with L_4 symmetry is more than 1 eV above the Fermi level in the calculation; there is no electron pocket at the L point, which is apparently inconsistent with the present ARUPS and the previous experiments.[6,7]

Finally, we must comment on a strange peak appearing in the ARUPS spectra. It is the second peak at about 0.4 eV in the spectrum of zero polar angle in the Γ-X'-L' plane (Fig. 3). It is also observed in the Γ-L-X plane (Fig. 2), but not clearly in the Γ-W-K plane (Fig. 4). We cannot find any bands or levels in the calculations directly corresponding to this peak. If the T_3 level, which is just above the T_1 level (point a) and in the unoccupied states, would go down and into the occupied states, it might account for the strange peak. If this is the case, the Fermi surface for holes[10] must need considerable modification. An alternative origin for the peak may lie in the energy dispersion along the Γ—T direction: If there is a stationary part in the band from T_1 to Γ_1, it would give a peak at 0—2 eV in the normal-emission spectrum. However,

since we do not find such a stationary part in any of the calculations, we cannot attribute the appearance of the strange peak to the band structure along the Γ—T direction. A surface umklapp process cannot serve as a favorable origin of the peak either, because a point on the Γ—T line is transferred by a surface reciprocal-lattice vector to another point also on the Γ—T line of the next Brillouin zone. We examined the possibility that the peak may be due to a surface state, but obtained no affirmative results; the peak did not disappear even after a 10^6-L (1 L=1 langmuir=10^{-6} Torr sec) oxygen exposure. The possibility of impurities or adsorbates is denied by the fact that the intensity of the peak shows the strong polar-angle dependence. The strange peak may be a satellite peak of the first sharp peak (corresponding to the point a) produced through a shake-up process of an electron from the point a to the upper unoccupied level with T_3 symmetry just above the point a, because the energy separation of the two levels (0.346 eV determined by the magnetoreflection study[12]) corresponds well with the observed energy splitting (about 0.4 eV) between the strange and first main peaks. Nevertheless, the shake-up process cannot explain the angular dependence of the intensity of the strange peak. Thus, the origin of this strange peak remains a problem to be solved.

V. CONCLUSION

We have performed the first angle-resolved ultraviolet photoelectron spectroscopy for single-crystal rhombohedral arsenic in very high angular resolution. We found a close similarity in the overall features of the experimental band structure between the two planes in the Brillouin zone which are equivalent to each other in the crystal but no longer equal in the photoemission process. This indicates that a considerable electron momentum broadening normal to the surface takes place in the photoemission process of rhombohedral arsenic. The present ARUPS measurement directly identified the location of an electron pocket at the L point and a hole pocket near the T point. The experimental results were compared in detail with the band calculation performed in this study using the self-consistent pseudopotential method as well as with four other sets of results reported previously.[8—10,20] The comparison has elucidated that, contrary to the early calculations,[8—10] only one band intersects the Fermi level from the unoccupied states near the L point to form an electron pocket.

ACKNOWLEDGMENTS

[1]A. F. Wells, *Structural Inorganic Chemistry*, 4th ed. (Clarendon, Oxford, 1975), p. 701.

[2]T. G. Berlincourt, Phys. Rev. **99**, 1716 (1955).

[3]Y. Shapira and S. J. Williamson, Phys. Lett. **14**, 73 (1965).

[4]J. B. Ketterson and Y. Eckstein, Phys. Rev. **140**, A1355 (1965).

[5]S. Tanuma, Y. Ishizawa, and S. Ishiguro, in *Proceedings of the International Conference on Physics of Semiconductors, Kyoto, 1966* (Physical Society of Japan, Tokyo, 1966), p. 662.

[6]M. G. Priestley, L. R. Windmiller, J. B. Ketterson, and Y. Eckstein, Phys. Rev. **154**, 671 (1967).

[7]J. Vanderkooy and W. R. Datars, Phys. Rev. **156**, 671 (1967).

[8]L. M. Falicov and S. Golin, Phys. Rev. **137**, A871 (1965).

[9]S. Golin, Phys. Rev. **140**, A993 (1965).

[10]P. J. Lin and L. M. Falicov, Phys. Rev. **142**, 441 (1966). Since the entire band structure is not given in this paper, we performed the pseudopotential calculations with the same parameters as used by Lin and Falicov. The binding energies of special points given in Table I are from our calculations.

[11]M. Cardona and D. L. Greenaway, Phys. Rev. **133**, A1685 (1964).

[12]M. Maltz and M. S. Dresselhaus, Phys. Rev. Lett. **20**, 919 (1968).

[13]M. Maltz and M. S. Dresselhaus, Phys. Rev. **182**, 741 (1969).

[14]L. Smith and A. L. Jain, Opt. Commun. **5**, 413 (1972).

[15]C. Raisin, G. Leveque, and J. Robin, Solid State Commun. **14**, 723 (1974).

[16]L. Ley, R. A. Pollak, S. P. Kowalczyk, R. McFeely, and D. A. Shirley, Phys. Rev. B **8**, 641 (1973).

[17]T. Takahashi, Y. Harada, and H. Hamanaka, Phys. Rev. B **24**, 3663 (1981).

[18]See, for example, L. Ley, M. Cardona, and R. A. Pollak, *Photoemission in Semiconductors*, in *Photoemission in Solids II: Case Studies*, edited by L. Ley and M. Cardona (Springer, Berlin, 1979), p. 80.

[19]T. Takahashi, H. Tokailin, S. Suzuki, and T. Sagawa, Phys. Rev. B **29**, 1105 (1984).

[20]D. W. Bullett, Solid State Commun. **17**, 965 (1975).

[21]S. Tanuma, S. Minomura, O. Shinomura, G. Fujii, and W. R. Tatars, in *Proceedings of the 12th International Conference on Low Temperature Physics, Kyoto, 1970*, edited by E. Kanda (Keigaku, Tokyo, 1971), p. 597.

[22]S. Suzuki, K. Furusawa, M. Terasawa, M. Yoshida, and T. Sagawa, Sci. Rep. Tohoku Univ. **1**, 16 (1980).

[23]K. Shindo, J. Phys. Soc. Jpn. **45**, 699 (1978).

[24]K. Shindo, J. Phys. Soc. Jpn. **47**, 547 (1979).

[25]D. J. Chadi and M. L. Cohen, Phys. Rev. B **8**, 5747 (1973).

[26]N. V. Smith, *Angular Dependent Photoemission*, in *Photoemission in Solids I*, edited by M. Cardona and L. Ley (Springer, Berlin, 1978), p. 237.

[27]P. J. Feibelman and D. E. Eastman, Phys. Rev. B **10**, 4932 (1974).

[28]See, for example, L. Ilver and P. O. Nilsson, Solid State Commun. **18**, 677 (1976); G. V. Hansson and S. A. Flodström, Phys. Rev. B **17**, 473 (1978); J. Stöhr, P. S. Wehner, R. S. Williams, G. Apai, and D. A. Shirley, *ibid.* **17**, 587 (1978); T. Grandke, L. Ley, and M. Cardona, *ibid.* **18**, 3847 (1978); J. A. Knapp, F. J. Himpsel, and D. E. Eastman, *ibid.* **19**, 4952 (1979); Y. Petroff, *Optical Properties of Semiconductors Above Band Edge*, in *Optical Properties of Solids (Handbook on Semiconductors 2)*, edited by M. Balkanski (North-Holland, Amsterdam, 1981), p. 1.

[29]T. C. Chiang, J. A. Knapp, M. Aono, and D. E. Eastman, Phys. Rev. B **21**, 3513 (1981).

[30]N. V. Smith and M. M. Traum, Phys. Rev. B **11**, 2087 (1975).