

film surface area. Formation of a lead oxide layer at the interface could also greatly reduce the effective heat flow from the film. These factors might help to explain the relatively slow relaxation times observed for the Pb-Bi films. Broom and Simpson also mention film non-uniformities as a possible significant factor in their results.

The observed thermal relaxation times of the In-Sn films on sapphire single crystals provide strong evidence that the blackbody-radiation model is valid for certain films when the substrate has a long phonon mean free path so that phonon back-scattering can be neglected. Also, this data indicates that phonon reflection at the boundary as predicted by the acoustic-mismatch theory does not play a significant role in decreasing the rate of thermal flow across the boundary. It would thus appear that the acoustic-mismatch model may overestimate the size of the interfacial surface resistance in some cases of contact between a metal and an insulator. The data for

indium-tin films on quartz indicates a rate of heat flow somewhat less than that predicted by the blackbody model. However, in this case, the predictions of the two models do not differ greatly. Also, since the phonon mean free path in quartz is not as long as that in sapphire,<sup>7</sup> phonon back-scattering may in part influence this result. Finally, since our measured thermal relaxation times are in every instance faster than those which are indicated by previous measurements, it appears that our experimental results may more closely approximate those expected for an ideal interface.

### ACKNOWLEDGMENTS

We wish to thank H. Foster for his help with the film evaporations. We have also had helpful conversations with Dr. W. B. Pennebaker, Dr. R. E. Jones, and Dr. D. A. Neeper. R. F. Rutz kindly supplied the GaAs injection lasers used.

## Fermi Surface of Arsenic\*

P. J. LIN† AND L. M. FALICOV‡§

*Department of Physics and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois*

(Received 23 September 1965)

The Fermi surface of arsenic has been determined by means of a pseudopotential band-structure calculation. Recent experiments on the de Haas-van Alphen effect permit a more accurate determination of the pseudopotential parameters. The surface consists of three electron pieces located at the point  $L$  in the Brillouin zone and the holes are distributed in a multiply connected surface around  $T$ . The hole surface can be thought of as being formed by six pockets joined by thin cylinders. Good agreement with experiment is found throughout.

### 1. INTRODUCTION

THE pseudopotential approach for calculating the band structure of solids has been proved particularly successful in the case of the group-V semimetals.<sup>1-3</sup> In addition, several new experiments concerning the electronic properties of As, Sb, and Bi have been published recently<sup>4,5</sup> or are now under way.<sup>6,7</sup>

\* Work supported in part by the National Science Foundation and the U. S. Office of Naval Research.

† Present address: Department of Physics, University of California, Berkeley, California.

‡ Alfred P. Sloan Research Fellow.

§ Present address: Cavendish Laboratory, Cambridge, England.

<sup>1</sup> L. M. Falicov and S. Golin, *Phys. Rev.* **137**, A871 (1965); (referred to as I).

<sup>2</sup> S. Golin, *Phys. Rev.* **140**, A993 (1965).

<sup>3</sup> L. M. Falicov and P. J. Lin, *Phys. Rev.* (to be published) (referred to as II).

<sup>4</sup> See, for instance, the *Proceedings of the Topical Conference on Semimetals, New York, 1964* [IBM J. Res. Develop. **8**, 215 (1964)], and the many references quoted there.

<sup>5</sup> Y. Shapira and S. J. Williamson, *Phys. Letters* **14**, 73 (1965).

<sup>6</sup> J. Vanderkooy (private communication and to be published).

These two facts considered together have, for the first time, allowed a quantitative determination of the electronic structure of the semimetals, in particular Sb<sup>3</sup> and, as reported here, As.

In this paper we describe a calculation of the Fermi surface of As, which has been obtained by determining the pseudopotential parameters as was done previously for Sb<sup>3</sup> and readjusting slightly the Fermi energy so as to satisfy a few experimental observations. Complete analysis of the surface has been carried out and good agreement with all available experimental data has been found throughout.

Until recently the only experimental data reported in the literature were those of Berlincourt.<sup>8</sup> The information there included was accurately and exhaustively analyzed, but it was not complete since no compensation of electrons and holes was found, i.e.,

<sup>7</sup> M. G. Priestley, L. R. Windmiller, J. Ketterson, and Y. Eckstein (private communication and to be published).

<sup>8</sup> T. G. Berlincourt, *Phys. Rev.* **99**, 1716 (1955).

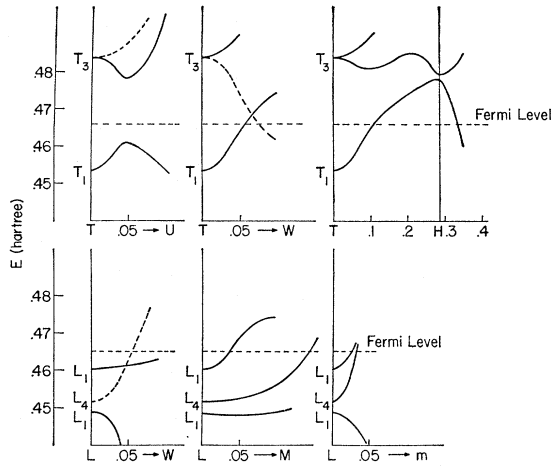


FIG. 1. The band structure of arsenic in the neighborhood of the points  $T$  (holes) and  $L$  (electrons). Energy and  $k$  vectors are in atomic units (a.u.).

some piece or pieces of the Fermi surface were missing. Berlincourt reported the existence of a set of three (or six) "ellipsoids" with a tilt angle of about  $36^\circ$  and very anisotropic effective mass. There was, in addition, a second set of long-period de Haas-van Alphen oscillations, tentatively assigned to the "hole pocket"; this was much smaller in volume than each of the "ellipsoids."

Recently Shapira and Williamson<sup>5</sup> reported the existence of a second set of "ellipsoids," with a smaller tilt angle ( $4.6^\circ$  or equivalently  $85.4^\circ$  for the minimum area) and with a volume which is apparently slightly larger (within 10%) than each of Berlincourt's pockets; these were found to depart from ellipsoids. Vanderkooy<sup>6</sup> and Priestley *et al.*<sup>7</sup> have also found the two sets of "ellipsoids" in addition to Berlincourt's long periods. Priestley *et al.*<sup>7</sup> have further shown that the Berlincourt carriers deviate considerably from ellipsoids and are probably multiply connected; the long periods, on the other hand, arise from three or six small necks tilted away from the trigonal axis by about  $10^\circ$ .

The situation, except for the existence of the long periods, strongly resembles that in antimony.<sup>9</sup> In the case of Sb the assignment of carriers was unequivocal,<sup>3</sup> with six large-tilt pockets corresponding to the holes and three small-tilt pockets to the electrons. The electrons were located at  $L$ , corresponding to an  $L_4$  level<sup>10</sup> in the sixth band. The holes were located on the mirror planes  $\sigma$  at a point designated as  $H$ . The similarity of the de Haas-van Alphen effect in Sb and As thus points out to a similarity in the structure, the ordering of levels at  $L$  corresponding to  $L_1 < L_4 < L_1$  for the 5th to 7th bands at  $L$  and  $T_1 < T_3 < T_2'$  or  $T_1 < T_2' < T_3$  for the 5th to 8th bands at  $T$ .

In Sec. 2 we describe briefly the details of the calculations of the band structure and the results in the

neighborhood of  $L$  and  $T$ . In Sec. 3 we determine the Fermi surface and compare it with experiment.

## 2. THE BAND STRUCTURE

The band structure was calculated in the same way as described in I and II. The form factor or atomic pseudopotential was determined as in II, i.e., by adding to the form factor<sup>11</sup> of Ge one-half of the antisymmetric form factor<sup>12</sup> of GaAs and renormalizing according to the volumes of the unit cells:

$$U^{\text{As}}(K) = [U^{\text{Ge}}(K) + (1/2)U^{\text{A}}(K)](\Omega_{\text{GaAs}}/\Omega_{\text{As}}). \quad (2.1)$$

The resulting function was then expressed as

$$U(K) = A_1(K^2 - A_2)[\exp A_3(K^2 - A_4) + 1]^{-1}, \quad (2.2)$$

where the parameters  $A$  took the values

$$\begin{aligned} A_1 &= 0.0874, & A_3 &= 2.53, \\ A_2 &= 2.68, & A_4 &= 3.4. \end{aligned} \quad (2.3)$$

It should be noted that these parameters differ appreciably from those used in I, especially  $A_1$ . One point which is worth mentioning is that the crystal parameters used in the calculation are those reported in I, which correspond to room temperature. No measurements are available at helium temperature, and it is believed (as it occurs<sup>13</sup> in Sb) that they should change with temperature; the rhombohedral angle  $\alpha$  in particular, which is  $54^\circ 10'$  at room temperature, should increase, making the crystal "more cubic."

The band structure resulting from the diagonalization of a  $90 \times 90$  secular equation is very similar in over-all features to that shown in I. Details close to  $L$  and  $T$  are shown in Fig. 1. It is seen that both at  $L$  and  $T$  the expected ordering of levels occurs. The maximum of the fifth band occurs at the points  $H$  in the mirror planes. The coordinates of one of these points are

$$\begin{aligned} H &= [0.2043, 0.3758, 0.2043] \\ &= g_0\{0.3595, 0.0027, 0.3595\} \end{aligned} \quad (2.4)$$

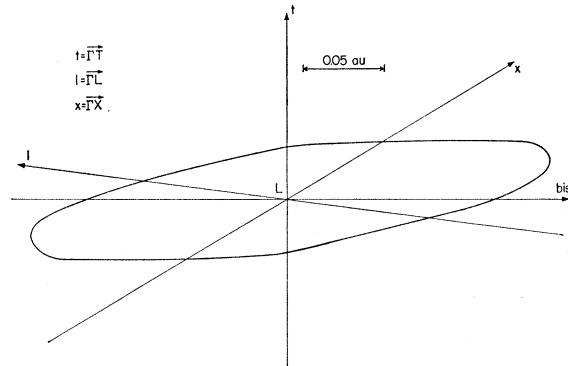


FIG. 2. Cross section of one electron piece with the trigonal-bisectrix plane passing through  $L$ .

<sup>9</sup> L. R. Windmiller and M. G. Priestley, Solid State Commun. **3**, 199 (1965).

<sup>10</sup> For the notations for symmetry points and lines, as well as the group-theoretical representations, we follow Refs. 1 and 3.

<sup>11</sup> D. Brust, Phys. Rev. **134**, A1337 (1964).

<sup>12</sup> M. L. Cohen (private communication and to be published).

<sup>13</sup> C. S. Barrett, P. Cucka, and K. Haefner, Acta Cryst. **16**, 451 (1963).

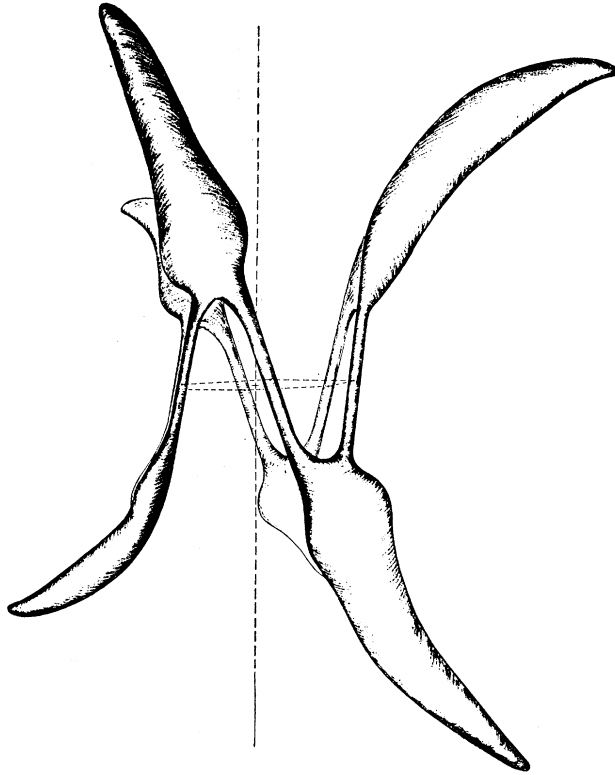


FIG. 3. A perspective of the complete view of the hole "crown."

in the trigonal and rectangular systems, respectively; both coordinate systems and the value of  $g_0$  are given in I. It is also observed that along the  $TW$  line a point of accidental degeneracy (removed by spin-orbit coupling) exists. One of the six equivalent cross-over points  $B$  has the coordinates

$$\begin{aligned} B &= [0.4617, 0.5, 0.5383] \\ &= g_0\{0.5397, 0.4600, 0.3803\} \end{aligned} \quad (2.5)$$

in the trigonal and rectangular systems, respectively. Holes are expected to appear in the neighborhood of both  $H$  and  $B$ .

At  $L$  one discrepancy appears: two levels  $L_4$  and  $L_1$  (sixth and seventh bands) are below the Fermi energy. This is not what is found experimentally; the  $L_1$  level should have an energy at least 0.005 hartree higher than

TABLE I. Electron Fermi surface. All areas are in atomic units.<sup>a</sup>

	Theory	Experiment
Area normal to the binary	0.016	0.020 <sup>b</sup>
Area normal to the trigonal	0.018	0.020 <sup>c</sup>
Minimum area for $H$ in the trigonal-bisectrix plane	0.0055 <sup>d</sup>	0.0055 <sup>c</sup>
Tilt angle for maximum area	$-8^\circ$	$\sim -9^\circ$ <sup>b</sup>
Tilt angle for minimum area	$\sim +80^\circ$	$+85.7^\circ \pm 0.5^\circ$ <sup>b</sup>
Effective mass along the binary axis	0.11	
Principal effective masses in binary-bisectrix plane	0.038	
	0.94	

<sup>a</sup> Angles follow the convention of Ref. 14.

<sup>b</sup> From Ref. 7.

<sup>c</sup> From Refs. 5-7.

<sup>d</sup> Fermi energy fixed so as to fit this area.

actually found. This energy is quite small and certainly within the errors of our calculation (and the pseudopotential method in general); however, it is disturbing to realize that all the other features of the calculation seem to agree with experiment to better than 0.002 hartree. Two factors which have been neglected contribute to raise  $L_1$ :

(a) Spin-orbit interaction exists between the two  $L_1$  levels but not between  $L_1$  and  $L_4$ . This tends to separate the two  $L_1$  levels while leaving  $L_4$  unchanged.

(b) An increase of the rhombohedral angle  $\alpha$  as the temperature decreases will tend to increase the energy of the levels at  $L$  with respect to those at  $T$ . It is also possible that an error in the coefficients (2.3) of the form factors or even some more fundamental assumptions like the momentum independence of the pseudopotential can be responsible for this discrepancy. It is, however, difficult to understand that if this is the case, such good agreement can be obtained for the  $L_4$  electrons and the holes. We have chosen to ignore the  $L_1$  level and consider in the neighborhood of  $L$  only the sheet of surface originating for  $L_4$ .

### 3. THE FERMI SURFACE

#### Electrons

The electron piece originating from the sixth  $L_4$  level at  $L$  can be fairly well approximated by an ellipsoid, although slight departures can be observed. The Fermi energy has been placed 0.0135 hartree above  $L_4$  so as to fit the maximum area for magnetic fields in the trigonal-bisectrix plane. A section of the electron pocket is shown in Fig. 2. Details of the surface are given in Table I. It should be mentioned that the tilt angle<sup>14</sup> is very sensitive to changes in the pseudo-

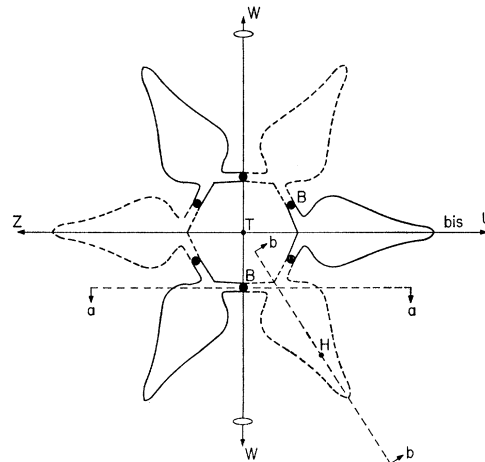


FIG. 4. A cross section and projection of the hole "crown" on the binary-bisectrix plane through  $T$ . The shaded circles are the section with the  $TW$  plane; the full lines are parallel projection from above and the dashed lines are parallel projections from below. Sections  $a-a$  and  $b-b$  correspond to Figs. 5 and 6, respectively.

<sup>14</sup> Tilt angles are measured in the sense of rotation from  $\Gamma T(0^\circ)$  to  $\Gamma X(59^\circ 17')$ .  $\Gamma L$  corresponds to  $-72^\circ 50'$  or equivalently  $+107^\circ 10'$ .

TABLE II. The hole Fermi surface. All areas are in atomic units.<sup>a</sup>

	Theory	Experiment
Cross section of the cylinders	$6.9 \times 10^{-5b}$	$6.9 \times 10^{-5e}$
Tilt angle of the cylinders	$-11^\circ$	$\sim -11^\circ d$
Area of pockets normal to the binary	$\sim 9.6 \times 10^{-3}$	
Tilt angle of minimum area	$\sim +44^\circ$	$+36.4^\circ \pm 0.5^\circ d$

<sup>a</sup> Angles follow the convention of Ref. 14.  
<sup>b</sup> Fermi surface fixed so as to fix this area.

<sup>c</sup> From Ref. 6.

<sup>d</sup> From Ref. 7.

potential parameters and the agreement with experiment in this case should be considered very good. It is also important to notice that  $L_1$  gives rise to a pocket with completely different values of the tilt angle, and changes of the pseudopotential cannot modify it appreciably.

### Holes

The holes are located in a single multiply connected piece which resembles a "crown" with  $\bar{3}m$  symmetry. It consists essentially of six pockets around the points  $H$  [given by (2.4) and the six points related to it by symmetry]. These pockets are nonellipsoidal, and the

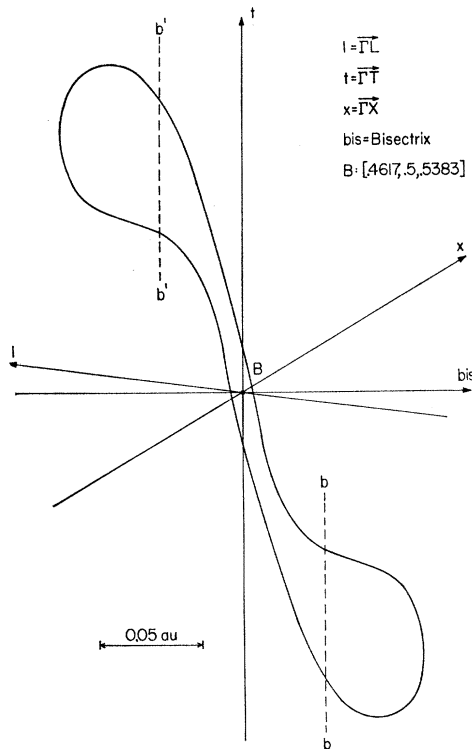


FIG. 5. Cross section of the hole "crown" with the trigonal-bisectrix plane through the point  $B$ . Section  $b-b$  at  $60^\circ$  corresponds to Fig. 6.

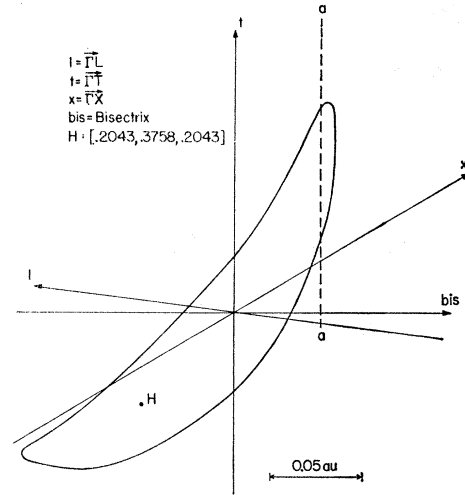


FIG. 6. Cross section of the hole "crown" with the trigonal-bisectrix plane through  $H$ . Section  $a-a$  at  $60^\circ$  corresponds to Fig. 5.

volume of each one is approximately half of the volume of the electron "ellipsoids." They are similar to the hole pockets in Sb and correspond to the "ellipsoids" found originally by Berlincourt.<sup>8</sup> The six pockets are linked by six very small cylindrical pieces with twofold symmetry centered around  $B$  [Eq. (2.5) and points related to it by symmetry]. These cylinders are tilted about  $11^\circ$  from the trigonal axis. The over-all shape of the hole "crown" is depicted in Fig. 3. Three important cross sections and projections are shown in Figs. 4, 5, and 6. Details of the surface are given in Table II. The Fermi energy has been fixed so as to give agreement for the cross-sectional area of the cylinders, i.e., to agree with the long-period oscillations. This yields a value which is 0.0133 hartree above  $T_1$ , this is, in turn, 0.0017 hartree higher than the value chosen for the electrons. The agreement is, therefore, very good, and spin-orbit corrections should improve it.

### ACKNOWLEDGMENTS

The authors would like to thank J. Vanderkooy, Professor M. G. Priestley, and L. R. Windmiller for communicating their results prior to publication and for several stimulating discussions. They are also indebted to Miss M. Puebla for her pictorial representation of the hole "crown" (Fig. 3).

They are grateful to the National Science Foundation and the U. S. Office of Naval Research for direct financial support of this work. In addition, the research benefited from partial support by the National Aeronautics and Space Administration and general support of the Institute for the Study of Metals by Advanced Research Projects Agency and the National Science Foundation.