GALVANOMAGNETIC DETERMINATION
OF ENERGY BANDS IN ARSENIC

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GALVANOMAGNETIC DETERMINATION
OF ENERGY BANDS IN ARSENIC

THESIS

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For the Degree of

MASTER OF SCIENCE

By

Kyle Lee Hathcox, B. S. in Physics
Denton, Texas
January, 1968
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CHAPTER I

INTRODUCTION

A study of the transport properties of a substance requires the determination of a set of transport coefficients by experiment. From these coefficients, the elements of the electrical conductivity tensor, thermoelectric tensor, et cetera can be determined. In this experiment, measurements and analyses of galvanomagnetic effects in a single crystal of arsenic were performed. The measurements were made at liquid-helium temperatures in magnetic fields ranging to 25 kilogauss. The experimentally determined coefficients were the isothermal magnetoresistivity, $\rho_{11}$, and the isothermal Hall resistivity, $\rho_{21}$. The magnetoresistance and Hall effect both exhibit quantum oscillations (Shubnikov-de Haas effect) at the higher fields and colder temperatures (7). No attempt was made to analyze these effects. The gross isothermal, electrical conductivities have been analyzed to determine various parameters characterizing the energy bands in arsenic. The gross effects were analyzed on the basis of a modified theory of electrical conductivities by Sondheimer and Wilson (11).

The general problem of galvanomagnetic determination of energy-band structure in metals is quite involved for crystals
with three-fold symmetry. Simultaneous determination of twelve independent resistivity tensor components to second order in magnetic field is necessary for arsenic. Difficulty in obtaining an exact algebraic solution to the twelve independent equations generally leads one to a curve-fitting technique for a reasonable determination of the resistivity components. As an approximation, a modified Sondheimer-Wilson theory was used with the conductivity properties of arsenic written in simple parameters. Additional parameters can be obtained by combining Fermi-surface parameters obtained from quantum-oscillation experiments with a modified Sondheimer-Wilson analysis.

The first detailed investigation of the electronic structure of arsenic was carried out by Berlincourt, using the de Haas-van Alphen effect (1). Recently, the Fermi-surface and energy-band structure of arsenic have been studied by various techniques. The phenomena studied include de Haas-van Alphen effect (6, 10), ultrasonic attenuation (4, 6), de Haas-Shubnikov effect (7), specific heat (2, 9), cyclotron resonance (3), and oscillatory magnetothermal effect (5). Theoretical considerations yield a model for the Fermi surface consistent with that proposed from the most recent de Haas-van Alphen studies (5). Many parameters relating to the Fermi surface have yet to be accurately determined; however, the recently proposed model seems quite reasonable, and is perhaps subject only to small modifications. This experiment will show that the galvanomagnetic data are compatible
with the model, yielding numerical values for several parameters in reasonable agreement with those obtained from quantum oscillation studies. A summary of this work will be published in Physical Review (2).
CHAPTER I BIBLIOGRAPHY


APPARATUS AND EXPERIMENTAL PROCEDURE

Crystal Structure

The crystalline structure of arsenic is rhombohedral (trigonal). The rhombohedral lattice may be thought of as a distorted cube, one which has had opposite corners along a diagonal pulled out along the projections of that diagonal. The edges of the cube are approximately 4.13 angstroms in length, and the angle between the primitive translation vectors in arsenic is 54° 10' (2, 3). Arsenic has two atoms per unit cell which are not located at the lattice sites. Three axes relate symmetry in rhombohedral crystals; these are called binary, bisectrix, and trigonal.

The lattice has three-fold rotational symmetry parallel to the trigonal axis; that is, the lattice when observed parallel to the trigonal axis appears the same after any number of 120° rotations. The plane perpendicular to the trigonal axis is called the basal plane and contains the binary and bisectrix axes. Three binary axes which are 120° apart exhibit two-fold rotational symmetry. Three bisectrix axes, axes which bisect the angles between the binary axes, exhibit false two-fold rotational symmetry. The two-fold symmetry is due to mirror reflection. The bisectrix axis is represented by an arrowhead and bar, —→; the binary by two
arrowheads, ——• and the trigonal by three arrowheads, ——•—•.

For a more complete discussion on crystal structure and symmetry refer to Miller (4).

The Sample

The arsenic crystal used in this experiment was obtained from Semi-Elements, Inc., Saxonburg, Pennsylvania. The sample of high-purity arsenic was in the form of a flat, rectangular plate of dimensions 16.6 mm. x 8.2 mm. x 1.6 mm. Dimensions were measured with a Unitron depthscope. Resistivity ratio was of the order of $\rho^{300}/\rho^{4.2} = 200$. After temperature cycling of the arsenic crystal, repeated measurements of the resistivity ratio gave values in the range $149 < \rho^{300}/\rho^{1.90} < 207$. It is interesting to note that variations of this order in the resistivity ratio are not at all uncommon in bismuth (5). No attempt was made to determine the purity of the sample. Surface scattering was neglected due to the large dimensions of the crystal.

Orientation of the crystalline axes was found by Laue X-ray photographs. A commercially built back-reflection camera and two-dimensional goniometer were used on a Norelco X-ray machine for the photographs. The best pictures were obtained by operating the X-ray machine at 13 kilovolts and 19 milliamperes for 50 minutes. A very clean surface was necessary for good pictures. The surface was cleaned by etching the crystal in one part fuming nitric acid and three parts
perpendicular to the rectangular plate's surfaces, are denoted by $X_1$, $X_2$, $X_3$; see Fig. 1, while the crystalline axes are given with reference to $X$, $Y$, and $Z$ as shown in Fig. 2. The trigonal axis was in the -Z direction and the binary axis in the X direction. With respect to the sample's axes, the trigonal axis was tilted 4° in the $X_1X_3$ plane and 2° in the $X_2X_3$ plane as shown in Fig. 1. For a more detailed discussion see Miller (4).

Electrical probes were soldered to the crystal using 30/70 Diveo lead-tin solder and Ruby flux. The flux was applied to the soldering gun and wires only, not to the crystal. The probes were 1/4" pieces of #24 copper wire tinned about 1/16" on the tips. The surface of the crystal must be very clean when soldering to arsenic. The previously mentioned etching solution and abrasive powder on cotton swabs were used to clean the surface. The surface must be cleaned after every single attempt to solder to the crystal. A 25-watt gun was used to tin a solder spot on the crystal, then a 100-watt gun was used to solder the probe to the spot. The Hall probes were fastened across the long dimension of the crystal, thus having an 8.2-millimeter separation. The magnetoresistance probes were attached on top of the large flat plate with an 8.0-millimeter separation, see Fig. 2. The current probes were soldered to the end plates of the crystal with a separation of 16.6 millimeters. Leads of #32 copper wire were twisted in pairs to reduce magnetically
Fig. 1--Crystal Axis in Relation to Sample Axis
Fig. 2--Crystal Dimensions and Orientation with Respect to $\mathbf{R}$
induced voltages and placed in a grounded, shielded braid to prevent electrostatic noise. The leads were then soldered to the crystal probes with low thermal solder.

Experimental Equipment

The current for the crystal was obtained from a 6-volt wet-cell, car battery. This was found to give a steady current to within 1% over the period of an experimental run. The current was monitored by measuring the voltage drop with a Leeds and Northrup millivolt potentiometer across a 1 ohm, 0.005% precision resistor in series with the crystal. The current was varied by use of a Leeds and Northrup resistance box in series with the crystal. The entire current supply was enclosed in an aluminum box which was grounded to reduce noise. The current was varied from 10 milliamperes to 200 milliamperes. The current source is shown in Fig. 3a.

The circuit used in this experiment, shown in Fig. 4, includes a Honeywell Rubicon thermal-free potentiometer (Model 2798), Keithley (Model 147) Nanovolt Null detector, voltage divider, and Beckman (Model 1005) recorder. The output of the null detector was too large to connect directly to the Beckman recorder so use of a voltage divider, shown in Fig. 3b, was required. The input leads to the null detector were obtained from Magnetic Shield Division of Perfection Mica Company, Chicago, Illinois. The leads consisted of inter-8 weave cable inside shielding braids of Co-Netic foil. Low thermal solder was used to attach connectors
Fig. 3b—Voltage Divider

Fig. 3a—Current Source
Fig. 4--Data-Measuring Circuit
at each end of the cable. This cable was found to reduce magnetic pick-up appreciably. All leads and equipment were carefully shielded electrically and grounded to reduce noise. Connections to the instruments were wrapped in cotton to avoid thermal EMF's. The Honeywell potentiometer was magnetically shielded with Co-Netic foil obtained from Perfection Mica Company. The noise of the total system was less than 10 nanovolts and a voltage change of $10^{-8}$ volt was detectable.

The crystal was supported in a liquid-helium bath inside the inner Dewar of a double-Dewar system by means of a crystal holder, shown in Fig. 5, constructed in the Physics Department machine shop. The crystal was mounted on the crystal holder with the trigonal axis perpendicular to the holder's base with Duco cement. The crystal holder was optically aligned by the use of mirrors such that the trigonal axis was parallel to the magnetic field. The inner Dewar was surrounded by a second Dewar containing liquid nitrogen; Alsup (1) has shown a picture of such an apparatus. In order to obtain a temperature less than 4.2°K, a vacuum was pumped above the liquid helium with a Kinney large-capacity vacuum pump. The pressure above the liquid helium was maintained by adjustment of a large ball valve and a small needle valve connected in parallel. The pressure above the liquid helium was measured by a mercury manometer and an oil manometer connected in parallel. The pressure was converted to temperature by the use of the "1958 He$^4$ Scale of Temperatures."
Fig. 5 -- Crystal Holder

STAINLESS STEEL

TUBING

BRASS
The magnetic field for this experiment was obtained by a Pacific Electric Motor Company electromagnet capable of fields from 0 to 24500 gauss through 6" pole faces with a 1.75" air gap. The power for the magnet was supplied by a Varian Associates Fieldial power supply. This power supply was field regulated and was capable of sweeping the field linearly in time between pre-set limits. The pre-set time was found to be approximately 2% in error due to time needed to end a sweep and return to the minimum field. This correction was taken into account in the data analysis. The field calibration was checked by a Bell (Model 240) differential gaussmeter.


CHAPTER III

THEORY

Modified Sondheimer-Wilson Theory

The isothermal transport effects are represented in kinetic theory by the expression

$$J = \hat{\sigma} \cdot E^*$$  \hspace{1cm} (1)

where $J$ is the electric current density, $\hat{\sigma}$ is the conductivity tensor, and $E^*$ is the electric field. The notation is for the special case of isothermal conditions, derived from more general transport equations discussed in earlier publications (1, 2). The experimentally determined coefficients of magnetoresistivity $\rho_{11} = E^* x / J x$ and Hall-resistivity $\rho_{21} = E^* y / J x$, measured with current in the binary direction and magnetic field along the trigonal direction, are related to elements of the conductivity tensor by

$$\sigma_{11} = \rho_{11} / (\rho_{11}^2 + \rho_{12}^2)$$

$$\sigma_{12} = \rho_{21} / (\rho_{11}^2 + \rho_{21}^2).$$  \hspace{1cm} (2)

The element $\sigma_{11}$ is the magnetoconductivity and $\sigma_{12}$ is the Hall conductivity.

The monotonic parts of $\sigma_{11}$ and $\sigma_{12}$ are analyzed in terms of a modified Sondheimer-Wilson theory (9). Here, one
assumes a quasi-continuum of states in "parabolic" bands
with sharp Fermi distribution functions and isotropic relaxation times independent of energy. The resulting expressions are

\[ \sigma_{11} = e\Sigma a_{i} n_{i} H_{i} L_{i} \]

\[ \sigma_{12} = e\Sigma(\pm)n_{i} L_{i} H_{i} \]  \hspace{1cm} (3)

where the summation extends over all bands. The (+) sign is for holes and (-) for electrons. In the above Eq. (3),

\[ H_{i} = (\alpha_{1}\alpha_{2})^{-1/2}c/e\tau_{i} \]

is a quantity inversely proportional to the mobility at zero field and is called the saturation field; \( \alpha_{1} \) and \( \alpha_{2} \) are elements of the inverse effective-mass tensor, \( \tau_{i} \) is the relaxation time, \( n_{i} \) is the carrier concentration, and \( L_{i} \) is the Lorentz factor:

\[ L_{i} = (H_{i}^{2} + H_{2}^{2})^{-1}. \]

The factor \( a_{i} \) is introduced to correct for non-circular orbits of the carriers; \( a_{i} = 1 \) for circular orbits, while for the tilted ellipsoids applicable to the problem at hand, it is most simply expressed in terms of the reciprocal effective-mass tensor elements:

\[ a_{i} = 1/2[\left(\alpha_{1}/\alpha_{2}\right)^{1/2} + \left(\alpha_{2}/\alpha_{1}\right)^{1/2}] \]  \hspace{1cm} (4)

Equation (3) is expected to be a good approximation for low fields. It will be seen that the expressions are quite
applicable over the entire range of 25 kilogauss covered in this experiment. In the analysis which follows, experimental data for the magnetic-field dependence of $\sigma_{12}$ and $\sigma_{11}$ will be fitted to Eqs. (3). The data are fitted by a least-squares technique (5), varying the parameters $H_i$, $a_i n_i$, and $n_i$. In this manner it is possible to obtain numerical values for the partial mobilities $\mu_i = 1/H_i$, carrier concentrations, and eccentricities of the Fermi ellipsoids (given the angle of tilt obtained from quantum-oscillation experiments).

Model for the Arsenic Fermi Surface

A reasonably detailed model of the Fermi surface has been suggested theoretically by the pseudopotential band-structure calculation of Lin and Falicov (4) and experimentally by the de Haas-van Alphen studies of Priestly et al. (6). The proposed model is quite similar to the multiple-ellipsoid surface observed by various investigators in Sb. (7, 10). For purposes of analysis in terms of a small number of simple parameters the model is taken in the multi-ellipsoid approximation.

Specifically, the electron Fermi surface consists of three ellipsoids with major axis lying within 6° of the basal plane (x-y plane). The primary ellipsoid has one principal axis tilted a few degrees from the basal plane toward the trigonal axis.
This principal ellipsoid is represented by the expression

\[ 2m_0\zeta^\beta = \beta_1 p_x^2 + \beta_2 p_y^2 + \beta_3 p_z^2 + 2\beta_4 p_y p_z. \]

The remaining two non-principal ellipsoids are obtained by 120° and 240° rotation about the trigonal axis and are given by

\[ 2m_0\zeta^\alpha = \frac{1}{4}(\beta_1 + 3\beta_2) p_x^2 + \frac{1}{4}(3\beta_1 + \beta_2) p_y^2 + \beta_3 p_z^2 \]
\[ \pm \frac{3}{2}(\beta_1 - \beta_2) p_x p_y \pm \beta_4 p_y p_z. \]

With this notation, the \( \beta_i \) are elements of the tensor, \( \hat{\beta} = m_0 \hat{m}^{-1} \) where \( \hat{m}^{-1} \) is the inverse effective mass tensor; \( \hat{\beta} \) has the form

\[
\hat{\beta} = \begin{pmatrix}
\beta_1 & 0 & 0 \\
0 & \beta_2 & \beta_4 \\
0 & \beta_4 & \beta_3
\end{pmatrix}
\]

The Fermi surface for holes is described in exactly the same manner simply by replacing \( \zeta^\zeta \) for \( \zeta^\beta \). De Haas-van Alphen results indicate a multiply-connected 6-ellipsoid surface for the holes. In that which follows the six ellipsoid model is used and the connecting surface is either neglected or accounted for (in a rough manner) by considering it to be an additional parabolic band of carriers.
Values for the elements of the inverse effective-mass tensors $\hat{\alpha}$ and $\hat{\beta}$ have been inferred from results of quantum-oscillation studies (3, 6, 8). These values are given in Table I along with the anisotropy factor $a_i$. 
CHAPTER III BIBLIOGRAPHY


CHAPTER IV

RESULTS AND CONCLUSION

Band Fit to $\sigma_{11}$

Results of the 3-band fit for the magnetoconductivity $\sigma_{11}$ as a function of magnetic field are shown in Figs. 6, 7. Table II gives the values of parameters obtained from the least-squares fit to the data.

The values of $n_1$ and $n_2$, for the $\alpha$-holes and the $\beta$-electrons respectively, have been calculated using the $a_i$ from Table I. Note that the values of carrier concentrations deduced in this manner are in general agreement with values reported by others (1, 3). The conductivity is governed almost entirely by the first two bands, $\alpha$-holes and $\beta$-electrons respectively. The contribution of the third band is almost insignificant, as verified by a two-band fit to the same experimental data. The temperature dependence of the $H_i$ is not in the expected direction. The small variation in the $H_i$ values is extremely dependent upon the relative weight given experimental points in the least-squares curve fit. Here the experimental points have been taken equally spaced in $H$ on a logarithmic scale, with equal weight assigned to the points. A different weighting of the points does give the expected increase of the $H_i$'s with temperature. However, due to the
Fig. 6--Three-band Curve Fit to $\sigma_{11}$ Data at 1.19°K
Fig. 7--Three-band Curve Fit to $\sigma_{11}$ Data at 4.2°K
### TABLE I

**Inverse Effective-Mass Tensor Elements and Anisotropy Factors for the α and β-Carriers (Tilted Ellipsoids).**

<table>
<thead>
<tr>
<th>α</th>
<th>((m_1))_1</th>
<th>((m_2))_2</th>
<th>((m_3))_3</th>
<th>((m_4))_4</th>
<th>(a_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.72</td>
<td>9.12</td>
<td>5.48</td>
<td>6.53</td>
<td>1.004</td>
<td></td>
</tr>
<tr>
<td>(\hat{\beta})</td>
<td>6.10</td>
<td>0.56</td>
<td>10.13</td>
<td>1.07</td>
<td>1.685</td>
</tr>
</tbody>
</table>

### TABLE II

**Energy-Band Parameters Determined from \(\sigma_{11}\) Curves. Three-Band Fit.**

<table>
<thead>
<tr>
<th></th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T=1.19°K</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H_1(G))</td>
<td>579</td>
<td>1595</td>
<td>8803</td>
</tr>
<tr>
<td>(a_1n_1(10^{20}/\text{cm}^3))</td>
<td>2.46</td>
<td>2.93</td>
<td>0.241</td>
</tr>
<tr>
<td>(n_1(10^{20}/\text{cm}^3))</td>
<td>2.45</td>
<td>1.74</td>
<td>---</td>
</tr>
<tr>
<td><strong>T=4.2°K</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(H_1(G))</td>
<td>523</td>
<td>1437</td>
<td>8397</td>
</tr>
<tr>
<td>(a_1n_1(10^{20}/\text{cm}^3))</td>
<td>1.52</td>
<td>3.36</td>
<td>0.238</td>
</tr>
<tr>
<td>(n_1(10^{20}/\text{cm}^3))</td>
<td>1.51</td>
<td>1.99</td>
<td>---</td>
</tr>
</tbody>
</table>
sensitivity of the $H_i$'s to the weighting of the experimental points, and the small variation of $H_i$ from 1.19° to 4.2°K, it is not reasonable to attempt an analysis of the temperature dependence by this technique. Note, however, that from the values of the elements of $\alpha$ and $\beta$ given in Table I, and assuming approximately equal relaxation times for the $\alpha$-holes and $\beta$-electrons, one expects a ratio $H_2/H_1 \approx 4.2$. Values of $H_2/H_1$ ranging from 3 to 4 are obtained, in rough agreement with the expected value. Relaxation times calculated from the data of Tables I and II give $\tau \approx 10^{-10}$ sec. in the liquid-helium range of temperatures.

**Band Fit to $\sigma_{12}$ Data**

Experimental data for the Hall isothermal conductivity are given in Table III and displayed in Fig. 8. Again, there are two predominant bands, identified by their algebraic sign as $\alpha$-holes and $\beta$-electrons, the carriers of highest mobility (lowest $H_i$ value) being the $\alpha$-holes. Saturati on field values are essentially the same as in the $\sigma_{11}$ data, but the carrier concentrations are a factor of 3 smaller than expected from magnetoconductivity results alone. Inclusion of a third band has little effect upon the results, and must be considered quite insignificant in the conduction process. At 1.19°K the third band appears as holes of high mobility, whereas the 4.2°K data give the third band as low mobility electrons. In either case the carrier concentration and contribution of the band to the total conductivity are
Fig. 8--Three-band Curve Fit to $\sigma_{12}$ Data at 4.2°K
### TABLE III
ENERGY-BAND PARAMETERS DETERMINED FROM $\sigma_{12}$ CURVES

<table>
<thead>
<tr>
<th></th>
<th>Two-band fit</th>
<th>Three-band fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T=1.19^\circ K$</td>
<td>(1) (2)</td>
<td>(1) (2) (3)</td>
</tr>
<tr>
<td>$H_i(G)$</td>
<td>--- ---</td>
<td>69 418 2462</td>
</tr>
<tr>
<td>$n_i(10^{20}/cm^3)$</td>
<td>--- ---</td>
<td>0.009 0.578 -0.483</td>
</tr>
<tr>
<td>$T=4.2^\circ K$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_i(G)$</td>
<td>464 2172</td>
<td>472 2060 1093</td>
</tr>
<tr>
<td>$n_i(10^{20}/cm^3)$</td>
<td>0.538 -0.533</td>
<td>0.554 -0.541 -0.013</td>
</tr>
</tbody>
</table>

### TABLE IV
ENERGY-BAND PARAMETERS OBTAINED FROM A SIMULTANEOUS FIT FOR $\sigma_{11}$ AND $\sigma_{12}$ AT 4.2$^\circ K$

<table>
<thead>
<tr>
<th></th>
<th>Two-band fit</th>
<th>Three-band fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1) (2)</td>
<td>(1) (2) (3)</td>
</tr>
<tr>
<td>$H_i(G)$</td>
<td>521 1880</td>
<td>537 1502 6750</td>
</tr>
<tr>
<td>$a_in_i(10^{20}/cm^3)$</td>
<td>2.01 3.12</td>
<td>1.73 3.11 0.26</td>
</tr>
<tr>
<td>$n_i(10^{20}/cm^3)$</td>
<td>0.650 -0.644</td>
<td>0.738 -0.675 -0.061</td>
</tr>
<tr>
<td>$a_i$</td>
<td>3.09 4.84</td>
<td>2.34 4.60 4.26</td>
</tr>
</tbody>
</table>
quite small and could be considered as resulting simply from small experimental inaccuracies in the resistivity data.

Two-Band Simultaneous Fit of $\sigma_{11}$ and $\sigma_{12}$

It has been observed in the preceding discussion that the two major energy bands account for almost all of the $\sigma_{11}$ and $\sigma_{12}$ effects. In terms of the simplified theory (with isotropic relaxation time) the saturation fields $H_i$ for a given band of carriers appearing in the $\sigma_{12}$ and $\sigma_{11}$ curves should be identical. With this in mind, a simultaneous fit to the $\sigma_{12}$ and $\sigma_{11}$ curves has been made, requiring that each curve-fitting have the same value for $H_i$ and also for $H_z$. No restriction has been placed upon the numerator factors involving carrier concentrations. Figs. 9, 10 show the results of the 2-band simultaneous fit at $4.2^\circ K$. Table IV lists the energy-band parameters obtained from the curve fitting and corresponding to the Fig. 6. Upon inspection of Tables IV and V, one again observes features which are characteristic of the individual curve fittings: the expected increase in the $H_i$ with increasing temperature is not established, but the ratio $H_2/H_1=4$. The $\sigma_{11}$ data for $n_ia_i$ are of the same order as those obtained from the individual fit, and independently determined values for $a_i$, yield values for carrier concentrations in close agreement with quantum-oscillation experiments. The $n_i$ as determined from the Hall conductivity are very close to the values
Fig. 9--Simultaneous Two-band Curve Fit to $\sigma_{11}$ Data at 4.2°K
Fig. 10--Simultaneous Two-band Curve Fit to $\sigma_{12}$ Data at 4.2°K
TABLE V
ENERGY-BAND PARAMETERS OBTAINED FROM A SIMULTANEOUS
FIT FOR $\sigma_{11}$ AND $\sigma_{12}$ AT 1.19°K

<table>
<thead>
<tr>
<th></th>
<th>Two-band fit</th>
<th>Three-band fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
<td>(2)</td>
</tr>
<tr>
<td>$H_i(G)$</td>
<td>470</td>
<td>1916</td>
</tr>
<tr>
<td>$a_i n_i (10^{20}/cm^3)$</td>
<td>2.26</td>
<td>3.32</td>
</tr>
<tr>
<td>$n_i (10^{20}/cm^3)$</td>
<td>0.631</td>
<td>-0.621</td>
</tr>
<tr>
<td>$a_i$</td>
<td>3.58</td>
<td>5.31</td>
</tr>
</tbody>
</table>
obtained from the individual $\sigma_{12}$ curve fit. The $a_i$ are approximately three times larger than those given in Table I.

Three-Band Simultaneous Fit

Inclusion of a third band gives, as in the case of the individual curve-fittings, a closer fit to the experimental data. However, one can see from Table V that the computer search routine has found it necessary to split the $\alpha$-band developed in the two-band fit into two separate bands in order to work with a three-band model. Taken at face value the numerical results are anomalous with respect to the results of all the other curve-fits. But if one coalesces the two $\alpha$-bands into one whose parameters are here designated by primes, the following approximate values are obtained:

$$H_1' = \frac{(H_1 + H_2)}{2} = 516$$
$$a_1n_1' = (a_1n_1 + a_2n_2) = 3.57$$
$$n_1' = (n_1 + n_2) = 0.548$$
$$a_1' = \frac{(a_1'n_1')}{n_1'} = 6.51$$

Comparison of these rough values to the results of the two-band fit indicates that the formation of two $\alpha$-bands at low fields is indeed just due to a splitting of the $\alpha$-band of the two-band fit in an attempt to minimize the total error. The weight of the total evidence supports the view that the actual presence of a third band of carriers cannot be resolved due to the experimental inaccuracies inherent in the measurement of the small, but critical, low-field data.
Fig. 11--Reconstructed $\rho_{11}$ From $\sigma_{11}$ and $\sigma_{12}$ Data at 4.2°K
Fig. 12—Reconstructed $\rho_{21}$ from $\sigma_{11}$ and $\sigma_{12}$ data at 4.2°K
Resistivities

Reconstructions of the $\rho_{21}$ and $\rho_{11}$ from the $\sigma_{12}$ and $\sigma_{11}$ curve fits of Figs. 6, 7 are shown in Figs. 11, 12. The curve, reconstructed from inverting the $\sigma$-tensor and using the established energy-band parameters, is seen to follow the experimental points quite closely for all ranges of magnetic field. (It is interesting to note that the Sondheimer-Wilson theory has no magnetic field dependence in $\rho_{11}$ for a single band.)

Conclusions

The data and analysis of the preceding section lead to the following conclusions concerning the electron energy-band structure of arsenic:

The carriers with highest mobility are holes and correspond to the large-tilt-ellipsoid portion of the Fermi surface, first observed by Berlincourt (1) and labeled as $\alpha$-carriers. This assignment is in agreement with the theoretical consideration of Lin and Falicov (4).

The carriers of lower mobility (large $H_1$) are electrons, again in agreement with theory and quantum oscillation experiments. Concentration of these electrons ($\beta$-carriers) is substantially the same as for the $\alpha$-holes.

A third band of carriers with concentration an order of magnitude less than the $\alpha$- and $\beta$-carriers is possible, but not strongly indicated by the experimental data. (It is of interest to note that when a four-band fit was attempted for
the conductivity data, two of bands coalesced into a single band, thereby reducing the results to a 3-band fit.

Using established values for elements of the reciprocal effective-mass tensor, the $\sigma_{11}$ data give values of carrier concentration which are in quite good agreement with results of quantum-oscillation experiments. However, the self-consistent results of $\sigma_{11}$ and $\sigma_{12}$ curve fitting give values of $n_i$ a factor of three smaller than those expected from $\sigma_{11}$ data alone. Correspondingly, experimentally determined anisotropy factors $a_i$ are about three times larger than expected, which would be difficult to reconcile with the almost irrefutable measurements of periods in quantum-oscillation phenomena.

Saturation field ratios $H_2/H_1$ are quite close to expected values calculated using inverse effective-mass tensor elements by assuming approximately equal relaxation times for the $\alpha$-holes and the $\beta$-electrons. (Relaxation time is of the order of 10-10 sec.)

The Sondheimer-Wilson curve fittings show major parabolic bands quite clearly, but obviously are not applicable to the problem of determining further detailed parameters of energy bands of relatively low carrier concentration. The Sondheimer-Wilson technique, applied to arsenic, gives values of carrier concentration of the same order but somewhat lower than values of $n_i$ obtained from quantum-oscillation experiments. (The same techniques, applied to the semi-metals
bismuth and antimony, give values of $n_i$ in much closer agreement to quantum-oscillation results (2, 5).
CHAPTER IV BIBLIOGRAPHY


6. The simultaneous curve fitting was performed on the CDC 660 at Los Alamos Scientific Laboratory. A slightly different weighting of the experimental points was used here in order to effect a reduction in the average per cent error of the curve fitting.
APPENDIX A

The effective mass tensor for an ellipsoidal energy surface whose major axis is parallel to a coordinate axis, principal axis system, can be written

\[
\hat{\mathbf{m}} = \begin{pmatrix}
m_{11} & 0 & 0 \\
0 & m_{22} & 0 \\
0 & 0 & m_{33}
\end{pmatrix}
\]

(1)

In the case where the ellipsoid is tilted out of the basal plane (from xy plane toward z axis), the mass tensor becomes

\[
\hat{\mathbf{m}}^* = \hat{\mathbf{S}}^{-1}_\theta \hat{\mathbf{m}} \hat{\mathbf{S}}_\theta
\]

(2)

where

\[
\hat{\mathbf{S}}_\theta = \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \theta & \sin \theta \\
0 & -\sin \theta & \cos \theta
\end{pmatrix}
\]

(A)

\[
\hat{\mathbf{S}}^{-1}_\theta = \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \theta & -\sin \theta \\
0 & \sin \theta & \cos \theta
\end{pmatrix}
\]

(B)

\(\theta\) being the tilt angle.
Upon carrying out the above, one finds

\[
\mathbf{m}^* = \begin{pmatrix}
  m_{11}^* & 0 & 0 \\
  0 & m_{22}^* & m_{23}^* \\
  0 & m_{32}^* & m_{33}^*
\end{pmatrix},
\]

where

\[
\begin{align*}
m_{11}^* & = m_1, \\
m_{22}^* & = m_2 \cos^2 \theta + m_3 \sin^2 \theta, \\
m_{33}^* & = m_2 \sin^2 \theta + m_3 \cos^2 \theta, \\
m_{12}^* & = (m_2 - m_3) \sin \theta \cos \theta, \\
m_{13}^* & = m_{23} = m_{32}.
\end{align*}
\]

Many times equations are written in a more simple form by defining a reciprocal effective-mass tensor,

\[
\mathbf{\alpha}^* = \mathbf{m}^{-1},
\]

where

\[
\mathbf{m}^{-1} = \frac{1}{\text{det } \mathbf{m}} \begin{pmatrix} \text{cofactor at each } \mathbf{m} \text{ element} \end{pmatrix},
\]

and it follows that

\[
\mathbf{\alpha}^* = \begin{pmatrix}
  \alpha_{11}^* & 0 & 0 \\
  0 & \alpha_{22}^* & \alpha_{23}^* \\
  0 & \alpha_{32}^* & \alpha_{33}^*
\end{pmatrix},
\]

where

\[
\begin{align*}
\alpha_{11}^* & = 1/m_{11}^*, \\
\alpha_{12}^* & = m_{23}^*/(m_{22}^* m_{33}^* - m_{23}^*), \\
\alpha_{13}^* & = m_{32}^*/(m_{33}^* m_{32}^* - m_{23}^*), \\
\alpha_{22}^* & = m_{22}^*/(m_{22}^* m_{22}^* - m_{12}^*), \\
\alpha_{33}^* & = m_{33}^*/(m_{33}^* m_{33}^* - m_{13}^*).
\end{align*}
\]
Also, the principal-axis effective mass is sometimes needed in terms of the tilted effective masses. Performing similarity transformations on (3) we obtain

\[ \hat{m} = S^\top \hat{m} S^{-1} \]  

(9)

and from this

\[ M = \begin{pmatrix} m_{11} & 0 & 0 \\ 0 & m_{22} & m_{23} \\ 0 & m_{32} & m_{33} \end{pmatrix} \]

(10)

where

\[ m_{11} = m_{11}^*, \]
\[ m_{22} = m_{22}^* \cos^2 \theta + m_{23}^* \sin^2 \theta + 2 m_{23}^* \sin \theta \cos \theta, \]
\[ m_{33} = m_{33}^* \sin^2 \theta + m_{23}^* \cos^2 \theta - 2 m_{23}^* \sin \theta \cos \theta, \]
\[ m_4 = (m_{33}^* - m_{22}^*) \sin \theta \cos \theta + m_{23}^* (2 \cos^2 \theta - 1). \]

(11)

Notice in all cases that the (2, 3) and (3, 2) components are the same. These are often written as a fourth component, \( \sigma_4 \) or \( m_4 \). From these equations, one can obtain any relation needed between the principal-axis effective mass, the tilted-axis effective mass, and the reciprocal effective mass.
APPENDIX B

Sondheimer-Wilson Theory

Assume that Boltzmann's equation is valid for $\frac{\hbar}{e!} \ll \frac{mc}{eU}$ or $\omega^* r \ll 1$, since quantization becomes important for $\frac{\hbar}{e!} \ll \frac{mc}{eU}$, and let $e \cdot \mathbf{E} \cdot \mathbf{F} + \mathbf{F} \cdot \mathbf{F} = -\frac{e - f}{r}$ (1)

Assume that $f = f_0 + f_1$, where $f_0$ = equilibrium distribution function, and consider the individual terms of eq. (1).

(a) $\mathbf{E} \cdot \nabla f = \mathbf{E} \cdot \nabla f_0 + \mathbf{E} \cdot \nabla f_1$

(b) $(\mathbf{U} \times \mathbf{H}) \cdot \nabla f = (\mathbf{U} \times \mathbf{H}) \cdot (\nabla f_0 + \nabla f_1)$ (2)

In eq. 2(a) neglect the second term since it leads to a non-linear term and would violate Ohm's law, and assume that $f_1 = -\phi \frac{\delta f_0}{\delta E}$ and that $f_1$ not a function of $r$; then

$\mathbf{f} = f_0 - \phi \frac{\delta f_0}{\delta E}$ (3)

Substitution in (1) gives

$-\frac{\phi}{r} \frac{\delta f_0}{\delta E} = e \mathbf{E} \cdot \nabla f_0 - \mathbf{V} \cdot \nabla f_0 + \frac{e}{c} (\mathbf{U} \times \mathbf{H}) \cdot \nabla \phi (f_0 - \phi \frac{\delta f_0}{\delta E})$ (4)

Next, consider in the first right-hand term of (4) $\mathbf{V} f_0 = \mathbf{V} \frac{\delta f_0}{\delta E}$. But $E(p) = \frac{p^2}{2m}$, and $\mathbf{V} \phi (x) = \mathbf{v}$; hence

$\mathbf{V} f_0 = \frac{\delta f_0}{\delta E} \mathbf{v}$ (5)
Now, \( f = \frac{1}{1 + e^{\frac{E - f}{kT}}} = \frac{1}{1 + e^{-\beta E}} \),

where \( f \) = Fermi energy.

Next, in the second right-hand term of (4)

\[
\vec{\nabla}_r f = \frac{\delta f_o}{\delta T} \vec{v}_T + \frac{\delta f_o}{\delta E} \frac{\partial}{\partial T} \vec{v}_T .
\]  

(6)

But

\[
\frac{\delta f_o}{\delta E} = \frac{\delta f_o}{\delta \mu} \frac{\partial \mu}{\partial E} = \frac{\delta f_o}{\delta \mu} \frac{1}{kT} ,
\]

\[
\frac{\delta f_o}{\delta T} = \frac{\delta f_o}{\delta \mu} \frac{\partial \mu}{\partial T} = - \frac{e^{-\beta E}}{kT} \frac{\delta f_o}{\delta \mu} ,
\]

\[
\frac{\delta f_o}{\delta \mu} = \frac{\delta f_o}{\delta E} \frac{\partial}{\partial \mu} = kT \frac{\delta f_o}{\delta E} ,
\]

\[
\frac{\delta f_o}{\delta \beta} = - \frac{\delta f_o}{\delta E} ;
\]

therefore in (5)

\[
\vec{\nabla}_r f_o = - \left( \frac{E - f}{T} \right) \frac{\delta f_o}{\delta E} \vec{v}_T - \frac{\delta f_o}{\delta T} \frac{\partial}{\partial E} \vec{v}_T .
\]

but in the present case (isothermal) \( \vec{v}_T = 0 \), thus

\[
\vec{\nabla}_r f_o = 0 .
\]

(7)

Substitution of (5) and (6) or (7) into (4) gives

\[
- \frac{\Phi}{r} \frac{\delta f_o}{\delta E} = e \vec{E} \cdot \vec{v} \frac{\delta f_o}{\delta E} + \frac{e}{c} (\vec{U} \times \hat{A}) \cdot \vec{v} (f_o - \Phi \frac{\delta f_o}{\delta E}) ,
\]

but

\[
\vec{\nabla}_r f_o = \vec{U} \frac{\delta f_o}{\delta E}
\]

and in the last term \( (\vec{U} \times \hat{A} \cdot \vec{v}) = 0 \), thus

\[
- \frac{\Phi}{r} \frac{\delta f_o}{\delta E} = e \vec{E} \cdot \vec{v} \frac{\delta f_o}{\delta E} - \frac{e}{c} (\vec{U} \times \hat{A}) \cdot \vec{v} \Phi \frac{\delta f_o}{\delta E} .
\]

(8)

Next, let \( \Phi = \vec{p} \cdot \vec{c} \),

then

\[
\vec{\nabla}_r \Phi = \vec{c} (\vec{E}) + (\vec{p} \cdot \vec{c}) \vec{v} .
\]
Also take \( \overline{F} = c \overline{E} \);

then (8) becomes

\[
- \frac{\overline{F} \cdot \overline{c}}{r} \frac{\partial \overline{A}}{\partial E} = \overline{F} \cdot \overline{c} \frac{\partial \overline{A}}{\partial E} - \frac{c}{c} \left( \overline{u} \times \overline{A} \right) \cdot \frac{\partial \overline{c}}{\partial E} \left[ \overline{c} + \left( \overline{c} \cdot \frac{\partial \overline{c}}{\partial E} \right) \overline{c} \right].
\]

Notice that \( \left( \overline{u} \times \overline{A} \right) = 0 \)

and that \( \frac{\partial \overline{c}}{\partial E} \) can be divided out, giving

\[
- \frac{\overline{F} \cdot \overline{c}}{r} = \overline{F} \cdot \overline{u} - \frac{c}{c} \left( \overline{u} \times \overline{c} \right) \cdot \overline{u}. \tag{9}
\]

Take

\[
\overline{H} = (0, 0, H),
\]

\[
\overline{c} = (c_1, c_2, c_3),
\]

\[
\tau = \begin{bmatrix}
\tau_1 & 0 & 0 \\
0 & \tau_2 & 0 \\
0 & 0 & \tau_3
\end{bmatrix},
\]

\[
\overline{p} = \overline{\tau} \overline{u}.
\]

It follows that

\[
- \frac{\overline{F} \cdot \overline{c}}{r} = - \frac{\overline{\tau} \cdot \overline{c} \cdot \overline{u}}{r} = - \overline{\tau} \cdot \overline{u} \cdot \overline{c},
\]

where

\[
\overline{\tau}^{-1} = \overline{\tau}^{-1} \overline{\tau}^{-1};
\]

then substitution in (9) gives

\[
- \overline{\tau}^{-1} \overline{c} = \overline{F} - \frac{c}{c} \left( \overline{H} \times \overline{c} \right). \tag{10}
\]

Let us consider the left-hand side of (10)

\[
- \overline{\tau}^{-1} \overline{c} = \overline{\tau}^{-1} \overline{\tau}^{-1} \overline{c} = \begin{bmatrix}
- \frac{c_1}{\tau_1 + \delta_1} \\
- \frac{c_2 d_{33} + c_3 \delta_4}{\tau_2 (d_{22} d_{33} - d_{44})} \\
\frac{c_2 d_{44} - c_3 d_{33}}{\tau_3 (d_{22} d_{33} - d_{44})}
\end{bmatrix},
\]
Set each component in (10) on the right side equal to the components in (11):

\[
\begin{align*}
(A) \quad & \quad - \frac{c_1}{T_1 \nu} = F_1 + \frac{e}{c} C_2 H \\
(B) \quad & \quad - \frac{c_3 d_{12} + C_3 d_4}{T_2 (d_{12} d_{13} - d_4^2)} = F_2 - \frac{e}{c} C_1 H \\
(C) \quad & \quad - \frac{C_3 d_{12} + C_2 d_4}{T_3 (d_{12} d_{23} - d_4^2)} = F_3 
\end{align*}
\tag{12}
\]

Assume no z component of the electric field, i.e., \( F_3 = 0 \).

Consider 12(c) if \( F_3 = 0 \),

\[
C_3 \alpha z = C_2 d_4 
\tag{13}
\]

Substitute (13) in 12 (A) and 12 (B) and solve for \( C_2 \),

\[
C_2 = \frac{-F_1 - \frac{c H}{e c^2} - F_2 \frac{c^2}{T d_{12} e^2}}{\left[ H^2 + \frac{c^2}{e^2 T d_{12} d_{23}} \right]} 
\tag{14}
\]

Let

\[
H_i = \frac{c^2}{e^2 T d_{12} d_{12}} \quad \text{and} \quad L = (H^2 + 4)^{-1}
\]

then (14) becomes

\[
C_2 = \left[ -F_1 - \frac{c H}{e c^2} + F_2 \frac{c^2}{T d_{12} e^2} \right] L 
\tag{15}
\]

Notice that 12 (A) looks like 12 (B) if \( e \rightarrow -e \), subscript 1 \( \rightarrow \) 2

\[
C_1 = \left[ -F_2 \frac{c H}{e c^2} + F_1 \frac{c^2}{T d_{12} e^2} \right] L 
\]

\[\text{47}\]
Now our values of $C$ are known, and thus we know $\phi$, which in turn gives us $f$. Therefore our $f$ in Boltzmann's equation is known and can be used in deriving such quantities as current density.
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