# Azbel'-Kaner Cyclotron Resonance in Arsenic*

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Azbel'-Kaner cyclotron resonance has been studied in arsenic at a frequency of 134 GHz. Cyclotron effective masses have been measured for magnetic field directions in the three principal crystallographic planes. The results are in general accord with the Fermi surface deduced from other experiments and from band-structure calculations. An attempt to fit the results to an ellipsoid model and direct comparison with de Haas–van Alphen data indicate considerable deviation of the energy bands at the Fermi surface from quadratic behavior. Estimates of the electron and hole Fermi energies and densities are made using the experimental masses and de Haas–van Alphen periods.

## I. INTRODUCTION

THE band structures of the group-V semimetals arsenic, antimony, and bismuth have long been the subject of intensive experimental and theoretical study.[1] Interest in these materials has been heightened by the observation of a great many striking experimental phenomena which are directly attributable to the unique properties of the mobile charge carriers in the semimetals. All three are compensated metals, i.e., have equal numbers of holes and electrons, but the carrier concentrations are low (the electron or hole concentration is $2.1\times10^{20}$ cm$^{-3}$ in arsenic,[2] $5.5\times10^{19}$ cm$^{-3}$ in antimony,[3] and $2.5$–$3.0\times10^{17}$ cm$^{-3}$ in bismuth[4]), and the carrier effective masses and Fermi energies are small. A consistent detailed picture of their band structures has begun to emerge from the masses of experimental measurements and theoretical calculations made in recent years. Cohen, Falicov, and Golin[5] have shown that the band structures are determined primarily by the $A7$ trigonal crystal structure shared by all three materials, and that the band structures should therefore show marked similarities. This seems to be the case; detailed experiments and theoretical calculations indicate that in all three semimetals there are pieces of Fermi surface containing electrons at the symmetry points $L$ of the Brillouin zone (see Fig. 1) and pieces containing holes near the symmetry points $T$. There is an enormous body of experimental information on bismuth[1,6,7] but as yet no band-structure calculation of sufficient accuracy for reasonable comparison. The theoretical problem in bismuth is extremely difficult because the important energy gaps and Fermi energies are very small and because spin-orbit coupling effects are large. A variety of detailed experiments have been reported for antimony.[3,8] A careful band-structure calculation using the pseudo-

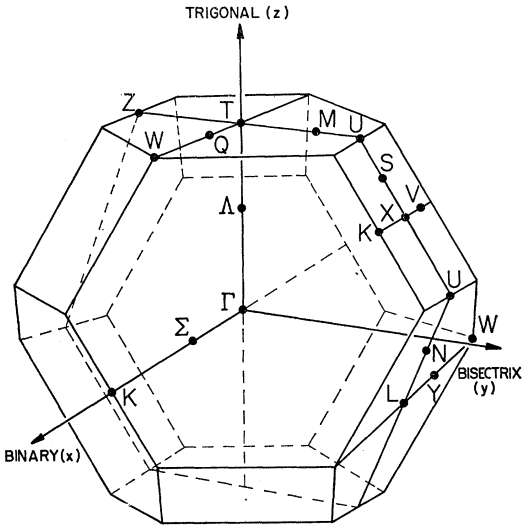


FIG. 1. Brillouin zone and conventional coordinate system for the $A7$ crystal structure. The standard notation is indicated for the symmetry points and lines. $\Gamma T$ is in the direction of the trigonal ($z$) axis. $\Gamma K$ is in the direction of the binary ($x$) axis. A bisectrix ($y$) axis in the mirror plane completes a right-handed coordinate system. Angles in the $yz$ plane are measured from the $z$ axis and are positive toward $\Gamma X$ in the first quadrant of the coordinate system. $\Gamma T$ is at 0°, $\Gamma X$ is at +58°17′, $\Gamma U$ is at +75°27′, and $\Gamma L$ is at +107°10′. (The value 59°17′ for the $\Gamma T$-$\Gamma X$ angle given in Ref. 2 appears to be an error traceable to Ref. 32.) A complete discussion of the symmetry properties of the $A7$ structure is given in Ref. 3.

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[1] See, for example, IBM J. Res. Develop. 8, No. 3 (1964), and the references quoted therein.

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

[3] L. R. Windmiller, Phys. Rev. 149, A472 (1966). Complete references to earlier work on antimony are given in this paper.

[4] See, for example, G. A. Williams and G. E. Smith, IBM J. Res. Develop. 8, 276 (1964). This carrier concentration is so small that it is sensitive to impurities even at the low impurity concentrations found in the purest samples. The numbers quoted by various workers therefore show some scatter.

[5] M. H. Cohen, L. M. Falicov, and S. Golin, IBM J. Res. Develop. 8, 215 (1964).

[6] N. B. Brandt, D. F. Dolgolenko, and N. N. Stupochenko, Zh. Eksperim. i Teor. Fiz. 45, 1319 (1963) [English transl.: Soviet Phys.—JETP 18, 908 (1964)].

[7] V. S. Edelman and M. S. Khaikin, Zh. Eksperim. i Teor. Fiz. 49, 107 (1965) [English transl.: Soviet Phys.—JETP 22, 77 (1966)].

[8] W. R. Datars and J. Vanderkooy, IBM J. Res. Develop. 8, 247 (1964).

potential method has been made by Falicov and Lin[9] and the results are in general agreement with the experiments.

Arsenic has come in for its fair share of attention only relatively recently. The first study of the Fermi surface in arsenic was made by Berlincourt[10] using the de Haas–van Alphen effect. He found two sets of carriers, one with de Haas–van Alphen periods of the order of $10^{-5}$ $G^{-1}$ and the other with periods of the order of $5\times10^{-7}$ $G^{-1}$. The latter periods could be fitted to a set of approximately ellipsoidal pieces of Fermi surface. However, the density of carriers corresponding to the long periods was far too small to provide the expected carrier compensation using these two types of carriers alone. The missing carrier turned up later in experiments by Shapira and Williamson[11] (quantum oscillations in ultrasonic attenuation and de Haas–van Alphen effect) and by Ketterson and Eckstein[12] (geometric resonance and quantum oscillations in ultrasonic attenuation). These new carriers were shown to occupy another set of approximately ellipsoidal pieces of Fermi surface with sizes of the right order of magnitude to give compensation, but the data did not permit establishment of the number of pockets in either set so that compensation could not be demonstrated quantitatively.

Reports of experiments providing information on the band structure and Fermi surface of arsenic have subsequently appeared in profusion. These include studies of the de Haas–van Alphen effect,[2,13–15] Shubnikov-de Haas oscillations in the resistivity and the Hall coefficient,[16–19] magnetothermal oscillations,[18,20] giant quantum oscillations in ultrasonic attenuation,[21,22] the magnetoresistivity tensor,[23] the pressure dependence of the carrier concentration,[24,25] the electronic heat capacity,[26,27] and magnetoreflection studies of interband transitions.[28,29] Theoretical calculations of the arsenic band structure have been made by Golin[30] using the OPW method and by Falicov and Golin[31] and Lin and Falicov[32] using the pseudopotential method. The calculation of Lin and Falicov was adjusted in accord with preliminary de Haas–van Alphen results of Priestley, Windmiller, Ketterson, and Eckstein[2] (hereafter referred to as PWKE). The resulting picture of the Fermi surface and energy band structure near the Fermi energy has guided the interpretation of all subsequent experimental work. The Fermi surface appears to be as follows: There are three roughly ellipsoidal closed centrosymmetric electron pockets centered on the $L$ points (Fig. 1). These are the $\beta$ carriers in the notation used by Lin and Falicov and most subsequent authors. These electron pockets can be crudely pictured as a prolate spheroid with long axis in the $yz$ plane, tilted at $+86°$ from the $z$ axis, and having an axial ratio of about 4.5:1, plus its symmetry partners. There is a single closed centrosymmetric hole surface similar to that shown in Fig. 2, centered on the point $T$. This looks (again, *very* crudely) like six ellipsoids connected by six small necks. The long axes of the "ellipsoids" are tilted about $+37°$ from the $z$ axis and the axial ratio is on the order of 4:1 or 5:1. The de Haas–van Alphen oscillations observed by Berlincourt were all associated with this hole surface. The short-period oscillations came from the ellipsoids (the $\alpha$ carriers) and the long-period oscillations were associated with the necks (the $\gamma$ carriers). The $\beta$ carriers (the electrons) are those first observed by

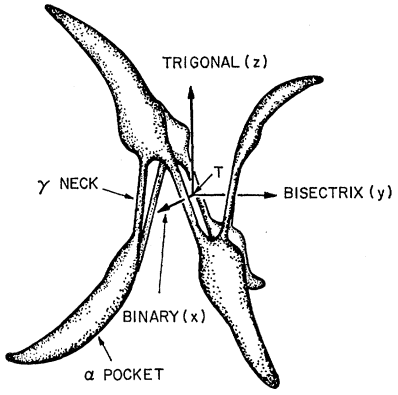


FIG. 2. Fermi surface for holes in arsenic as predicted by the calculation of Lin and Falicov (Ref. 32).

[9] L. M. Falicov and P. J. Lin., Phys. Rev. **141**, 562 (1966).
[10] T. G. Berlincourt, Phys. Rev. **99**, 1716 (1955).
[11] Y. Shapira and S. J. Williamson, Phys. Letters **14**, 73 (1965).
[12] J. B. Ketterson and Y. Eckstein, Phys. Rev. **140**, A1355 (1965).
[13] S. Tanuma, Y. Ishizawa, and S. Ishiguro, J. Phys. Soc. Japan Suppl. **21**, 662 (1966).
[14] J. Vanderkooy and W. R. Datars, Phys. Rev. **156**, 671 (1967).
[15] Y. Ishizawa, J. Phys. Soc. Japan **25**, 160 (1968).
[16] P. R. Baker and A. D. C. Grassie, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966*, edited by M. P. Malkov (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967), Vol. III, p. 280.
[17] J. R .Sybert, H. J. Mackey, and R. E. Miller, Phys. Letters **24A**, 655 (1967).
[18] J. Vanderkooy and W. R. Datars, Can. J. Phys. **46**, 1935 (1968).
[19] C. Miziumski and A. W. Lawson, Phys. Rev. **180**, 749 (1969).
[20] S. Noguchi and S. Tanuma, Phys. Letters **24A**, 710 (1967).
[21] T. Fukase and T. Fukuroi, J. Phys. Soc. Japan **23**, 650 (1967).
[22] T. Fukase, J. Phys. Soc. Japan **26**, 964 (1969).
[23] A. P. Jeavons and G. A. Saunders, Phys. Letters **27A**, 19 (1968).
[24] N. B. Brandt and N. Ya. Minina, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu **7**, 264 (1968) [English transl.: JETP Letters **7**, 205 (1968)].
[25] N. B. Brandt, N. Ya. Minina, and Yu. A. Pospelov, Zh. Eksperim. i Teor. Fiz. **55**, 1656 (1968) [English transl.: Soviet Phys.—JETP **28**, 869 (1969)].
[26] H. V. Culbert, Phys. Rev. **157**, 560 (1967).
[27] W. A. Taylor, D. C. McCollum, B. C. Passenheim, and H. W. White, Phys. Rev. **161**, 652 (1967).
[28] M. Maltz and M. S. Dresselhaus, Phys. Rev. Letters **20**, 919 (1968).
[29] M. Maltz and M. S. Dresselhaus, Phys. Rev. **182**, 741 (1969).
[30] S. Golin, Phys. Rev. **140**, A993 (1965).
[31] L. M. Falicov and S. Golin, Phys. Rev. **137**, A871 (1965).
[32] P. J. Lin and L. M. Falicov, Phys. Rev. **142**, 441 (1966).

Shapira and Williamson and by Ketterson and Eckstein.

By comparing their results with the calculation of Lin and Falicov, PWKE were able to make unambiguous assignments of the number and locations of Fermi-surface pockets and the signs of the carriers. With these assignments, the numbers of holes and electrons were estimated and found to be equal to within about 20% with an estimated uncertainty of the same order. This indicates that the expected compensation can be achieved within the Lin-Falicov model using the carrier parameters observed in the de Haas–van Alphen experiments, but it does not exclude the possibility of additional small pockets of carriers. The magnetoreflection experiments of Maltz and Dresselhaus[28,29] indicate that there may, in fact, be an additional pocket of carriers centered at the $T$ point and associated with a small energy gap at this point. The density of these carriers is too small to affect the conclusions of PWKE about compensation. This small density may account for the fact that they have not been observed in any other experiments. However, the required small energy gap between bands of the required symmetry types is not predicted by Lin and Falicov, so there is some question about the validity of their calculated bands near the $T$ point. Another open question concerns the nature of the intersections between the $\alpha$ pockets and $\gamma$ necks of the hole surface. PWKE observed oscillations which they attributed to orbits near these intersections and interpreted them as indicating a somewhat different topology from the Lin-Falicov model. Recently, however, Miziumski and Lawson[19] have concluded from Shubnikov-de Haas experiments that the intersections are in fact as indicated by Lin and Falicov. Aside from these questions, however, the Lin-Falicov model is in general accord with all of the other experimental information, and continues to serve as a useful basis for interpretation of experimental results.

Observation of Azbel'-Kaner cyclotron resonance (AKCR) in arsenic has been reported by Datars and Vanderkooy.[33] The resonance was studied only in the trigonal ($xy$) plane, and most of the data appeared to come from one type of carrier. We report here experiments in which we have studied AKCR in all three of the principal symmetry planes and have observed resonances due to both holes and electrons. In Sec. II we discuss the experimental details, in Sec. III we present the results, and in Sec. IV we discuss them and compare them with results of other experiments. A preliminary account of our experiments has been presented elsewhere.[34]

[33] W. R. Datars and J. Vanderkooy, J. Phys. Soc. Japan Suppl. 21, 657 (1966).

[34] D. N. Langenberg and C. S. Ih, in *Proceedings of the Tenth International Conference on Low-Temperature Physics, Moscow, 1966*, edited by M. P. Malkov (Proizvodstrenno-Izdatel'skii Kombinat, VINITI, Moscow, 1967), Vol. III, p. 11.

## II. EXPERIMENTAL DETAILS

The samples used in our experiments were taken from a monocrystal boule provided by Dr. L. R. Weisberg of RCA Laboratories.[35] The measured resistivity ratio was approximately 1000. The crystal was annealed by the method described by Ketterson and Eckstein[12] before samples were cut from it. The crystal was placed in a Pyrex tube filled with fiber glass and the tube was evacuated and closed. The crystal was annealed for 12 h at 375°C and then for 15 min at 425°C. Evaporation of the crystal during annealing was negligible. The crystal was oriented by the Laue back reflection method. Three disks approximately 2.5 mm thick were spark cut with their faces approximately parallel to one of the three principal crystallographic planes. Each sample was then spark planed to within 1° of the desired orientation.

The most troublesome problem encountered in the preparation of samples was, as usual, that of preparing flat, unstrained, polished surfaces. It is possible to obtain a satisfactory surface in the $xy$ plane normal to the trigional axis by cleaving. The sample used by Datars and Vanderkooy[33] was prepared this way. However, this would not work for other planes, so it was necessary to devise a suitable electropolishing technique. We were unable to find a method in the literature. Considerable trial and error led to the following electropolishing solution: 65 g potassium sulfide, 15 g sodium hydroxide (pellet form), 100 g water. The solution was prepared by dissolving first the potassium sulfide, then the sodium hydroxide. The samples were electropolished using a stainless steel cathode at a potential between 1.8 and 3.0 V. The quality of the surfaces obtained seemed to improve with aging of the pure potassium sulfide solution. Since arsenic tarnishes very rapidly in air, the polished samples were stored in vacuum until used and the mounting was done in a nitrogen atmosphere. We estimate that the surfaces obtained in this way were flat to within $\frac{1}{2}°$. This is not as flat as is desirable for an AKCR sample because of the possible influence of "tipping effects." However, for reasons discussed below (Sec. IV), tipping effects are expected to be considerably less important in this experiment than in previous experiments on more typical metals where tipping effects were prominent; in any case, this was the best we could manage.

In order to obtain as high a resolution as possible, the experiments were done at a frequency of 134 GHz. The microwave spectrometer was of the conventional reflection type, with the source frequency stabilized at the sample resonator frequency using a frequency-modulation automatic frequency control. Magnetic field modulation and phase-sensitive detection were used so that the recorded signals were proportional to

[35] L. R. Weisberg and P. R. Celmer, J. Electrochem. Soc. **110**, 56 (1963).

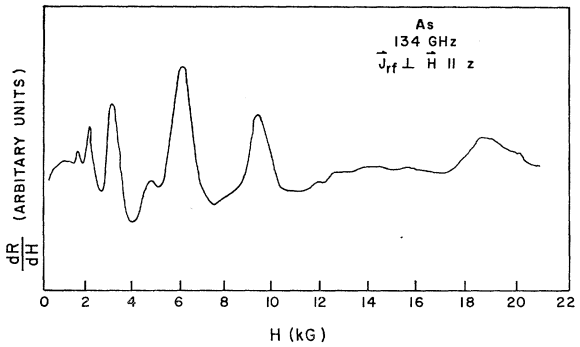


FIG. 3. Resonance observed with $\mathbf{H}\|z$, $\mathbf{J}_{rf}\perp\mathbf{H}$.

the field derivative of the sample surface resistance. The sample resonator was side-wall coupled to the wave guide and a mode splitter and adjustable short-circuit plunger were incoporated to permit control of the current polarization direction and coupling in the manner discussed previously by several authors.[36,37]

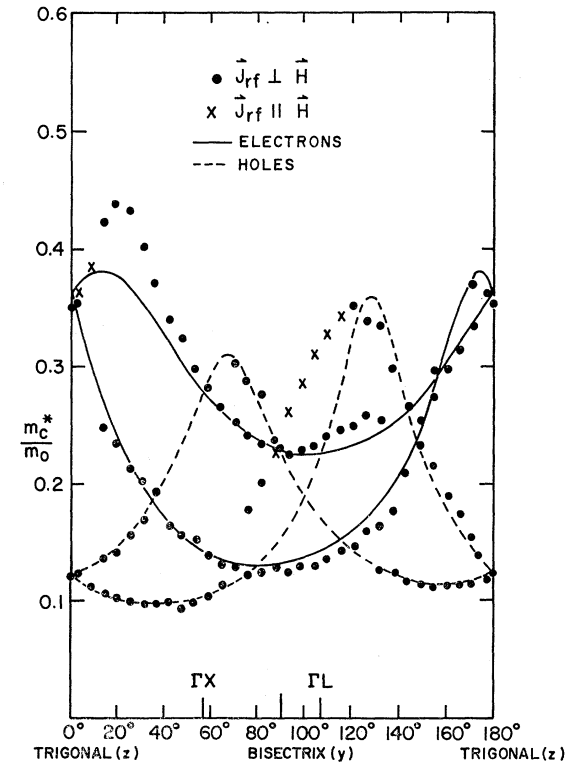


FIG. 4. Cyclotron effective masses in the $yz$ plane. The points are values obtained with $\mathbf{J}_{rf}\perp\mathbf{H}$; the crosses are values obtained with $\mathbf{J}_{rf}\|\mathbf{H}$. In regions where both types of data points were obtained and where they essentially coincide, only $\mathbf{J}_{rf}\perp\mathbf{H}$ points are plotted. The curves are the results of a least-squares fit to an ellipsoid model as discussed in the text.

[36] J. F. Koch, R. A. Stradling, and A. F. Kip, Phys. Rev. **133**, A240 (1964).

[37] D. N. Langenberg and S. M. Marcus, Phys. Rev. **136**, 1383 (1964).

The microwave source was a carcinotron [CO-20, manufactured by Compagnie Générale de Télégraphie sans Fil (CSF)]. This device is voltage-tuned and the output power is a rapidly and irregularly varying function of voltage or frequency. It was therefore necessary to arrange for tuning the sample resonator frequency at liquid-helium temperatures in addition to the usual sample rotation and resonator coupling control. Full details of the apparatus can be found in Ref. 38.

## III. EXPERIMENTAL RESULTS

Resonance was studied in the three principal crystallographic planes. A resonance recording taken with the field parallel to the $z$ axis is shown in Fig. 3. The apparent $\omega\tau$ of most of the resonances observed was of the order of 5. This relatively low $\omega\tau$ coupled with the large number of separate masses (as many as six) observed for some field directions made it almost impossible to derive cyclotron masses by the conventional method of determining the period in $H^{-1}$ of the derivative maxima belong to each series of resonance peaks. Instead, the cyclotron masses were in most cases derived from the magnetic field at which the fundamental derivative peak occurred. This means that there may be errors in the derived masses due to the shift of the fundamental derivative peak at finite $\omega\tau$ relative to its position for infinite $\omega\tau$ and to phase-shift tipping effects, in addition to the usual errors inherent in the frequency and field measurements. According to calculations of Kip, Langenberg, and Moore[39] based on the Azbel'-Kaner theory, for $\omega\tau=5$ a mass derived solely from the position of the fundamental derivative peak will be 6% too high. The error decreases with increasing $\omega\tau$. Koch, Stradling and Kip[36] have shown that the earlier cyclotron mass results of Kip *et al.*[39] for copper contained errors which were probably due to tipping effects, i.e., lack of precise parallelness of magnetic field and sample surface at all points on the surface. In the earlier experiments the sample surface was not extremely flat and there was no provision for checking the effect of a variation of the angle between the field and the sample surface. The errors were typically a few percent and both positive and negative errors occurred.

In order to gauge the importance of these two sources of error in the present experiments, we made the following checks: With the magnetic field parallel to the $z$ axis, only two series of peaks were observed and it was possible to compare masses derived from plots of $H_n^{-1}$ versus $n$ ($n$ is the order of the subharmonic derivative peak and $H_n$ is the field at which the peak occurred) with masses derived from the position of the

[38] C. S. Ih, Ph.D. thesis, University of Pennsylvania, 1966 (unpublished).

[39] A. F. Kip, D. N. Langenberg, and T. W. Moore, Phys. Rev. **124**, 359 (1961).

fundamental peak only. The masses agreed to within several percent. A prominent feature of the results of Kip *et al.* was the appearance of phase shifts, i.e., anomalous intercepts of $H_n^{-1}$ versus $n$ plots at $n=0$. These phase shifts were strongly correlated with features of the mass anisotropy curves which were later found to be spurious by Koch *et al.* Our results for $\mathbf{H}\|z$ showed no appreciable phase shift for the resonance which we identified as the electron resonance, but some phase shift for the hole resonance. We also checked the effect of tipping the magnetic field out of the sample surface plane for a number of orientations. In no case did we find that the resonance displayed the extreme sensitivity to field tipping which has frequently been reported in other AKCR experiments (see, for example, Refs. 36 and 37). This point is discussed in Sec. IV.

Because of the difficulty of estimating the proper correction to the cyclotron masses determined from the fundamental derivative peaks alone for general orientations, we have chosen to present the results without correction. Taking into account this source of error, the uncertainty about possible tipping effects, and the usual sources of experimental error, we estimate

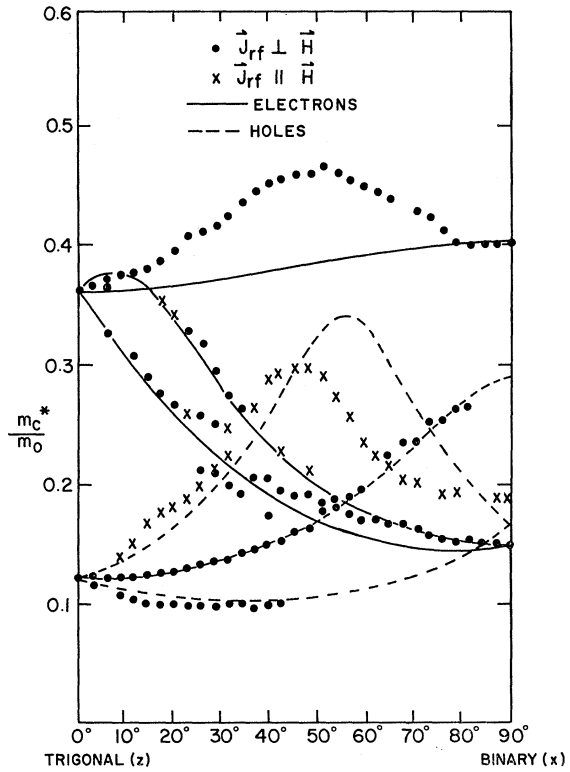


FIG. 5. Cyclotron effective masses in the $xz$ plane. The points are values obtained with $\mathbf{J}_{rf} \perp \mathbf{H}$; the crosses are values obtained with $\mathbf{J}_{rf} \| \mathbf{H}$. In regions where both types of data points were obtained and where they essentially coincide, only $\mathbf{J}_{rf} \perp \mathbf{H}$ points are plotted. The curves are the results of a least-squares fit to an ellipsoid model as discussed in the text.

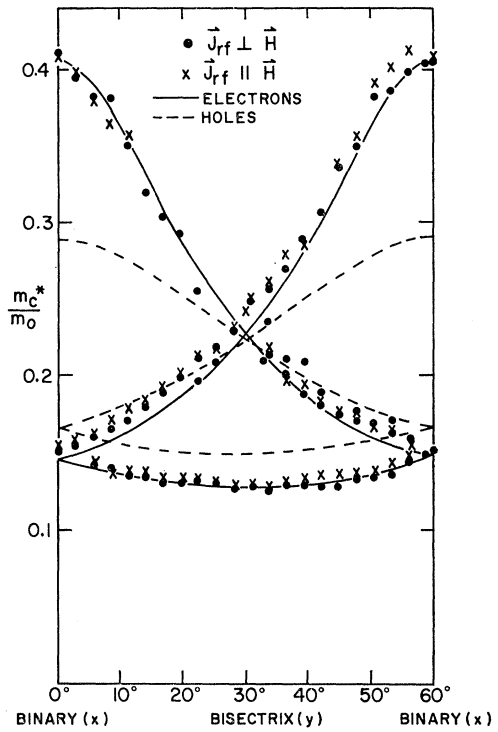


FIG. 6. Cyclotron effective masses in the $xy$ plane. The points are values obtained with $\mathbf{J}_{rf} \perp \mathbf{H}$; the crosses are values obtained with $\mathbf{J}_{rf} \| \mathbf{H}$. In regions where both types of data were obtained and where they essentially coincide, only $\mathbf{J}_{rf} \perp \mathbf{H}$ points are plotted. The curves are the results of a least-squares fit to an ellipsoid model as discussed in the text.

that the cyclotron masses obtained with $\mathbf{H}\|z$ are accurate to a few percent and that the error may be as large as 10% for some orientations. The results are presented as data points in Figs. 4–9. Points obtained with the microwave-frequency current in the sample surface polarized parallel and perpendicular to the dc magnetic field are included.

## IV. INTERPRETATION AND DISCUSSION

There are several alternative ways to view these results. One is based on the observation that the mass anisotropy resembles that of two sets of tilted ellipsoids. This suggests an attempt to fit the observed masses to such a model. The curves plotted in Figs. 4–6 are the result of a computer least-squares fit of the data to two sets of ellipsoids of appropriate symmetry. Each ellipsoid has one principal axis parallel to a binary axis and the other two in a trigonal-bisectrix plane. The parameters of the fitted ellipsoids are given in Tables I and II. It is clear from the figures that there are sizable deviations from ellipsoidal anisotropy for both sets of carriers. The principal effective masses obtained from the ellipsoid fit should therefore not be taken too seriously. The ellipsoid model does, however, provide a basis for identifying the carriers. The pseudopotential

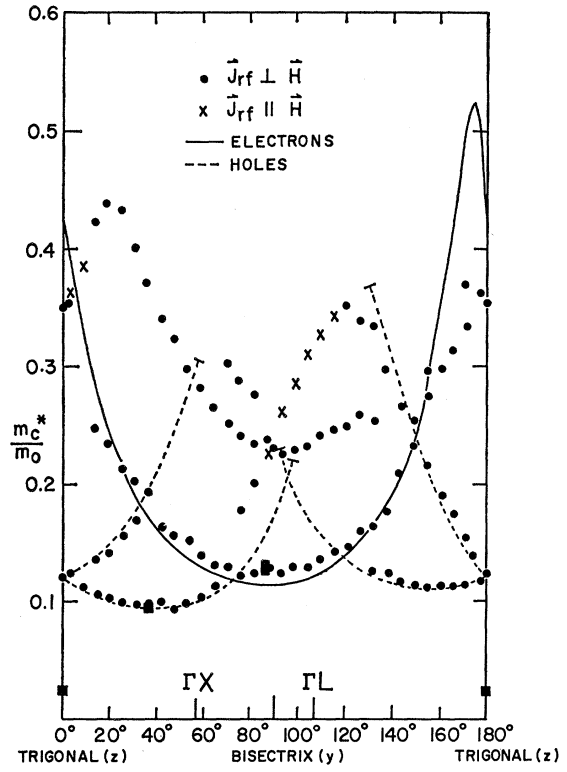


FIG. 7. Comparison of cyclotron effective masses (points) in the *yz* plane with de Haas–van Alphen frequencies (curves) measured by Priestley *et al.* (Ref. 2). The scale factors chosen correspond to a Fermi energy of 0.210 eV for the electrons and 0.178 eV for the holes. The solid rectangles are masses measured by Priestley *et al.*; the heights of the rectangles correspond to the quoted error.

calculation of Lin and Falicov[32] predicts for the electron surfaces a tilt angle of $\sim+80°$ and for the ellipsoid-like parts of the hole surface (Fig. 2) a tilt angle of $\sim+44°$. A comparison of our ellipsoid-model tilt angles with these theoretical angles provides clear evidence for the carrier identification made in Tables I and II and Figs. 4–6.

The large deviations of the electron masses from the ellipsoid curves on the highest mass branches between 10° and 50° in the *yz* plane (Fig. 4) and over the whole range of angles in the *xz* plane (Fig. 5) are strikingly similar to those observed in antimony.[8] (The reader is reminded that later work has shown that the electron-hole assignment in this paper should be reversed.) We have investigated whether this type of deviation might be obtained from an ellipsoidal-nonparabolic or a non-ellipsoidal-nonparabolic model of the electron energy bands, but we have been unsuccessful. It is perhaps premature to speculate on the kind of warping of the electron surfaces which would produce such deviations, but it is clear that the electron surfaces in both arsenic and antimony must be distorted in very much the same way and by about the same amount.

Our data in the *xy* plane appear to be due to only one type of carrier. The *xz* and *yz* plane data led us to conclude that these were the electrons. The data in this plane were therefore used in the least-squares fitting of the electron surfaces; the hole surfaces were fitted using only *xz* and *yz* plane data. Datars and Vanderkooy[33] also observed only one type of carrier in this plane (with an exception we note below) and also assigned these as electrons. There is close agreement between their data and ours. It is not clear why the holes were not observed. The higher mass branches indicated by the hole-ellipsoid curves in this plane near the binary axis would not be expected actually to exist because of the necks which connect the hole pockets, but there is no clear reason why the lowest mass branch should not have been detectable. If the difference between the lowest hole and electron masses is really as large as the ellipsoid curves suggest, we should have been just able to resolve them. If it is not, it is quite possible that the lower mass resonances we observed were really an unresolved mixture of electron and hole resonances. In this connection it is worth noting that the apparent $\omega\tau$ of the resonances observed in the *xy* plane seemed to

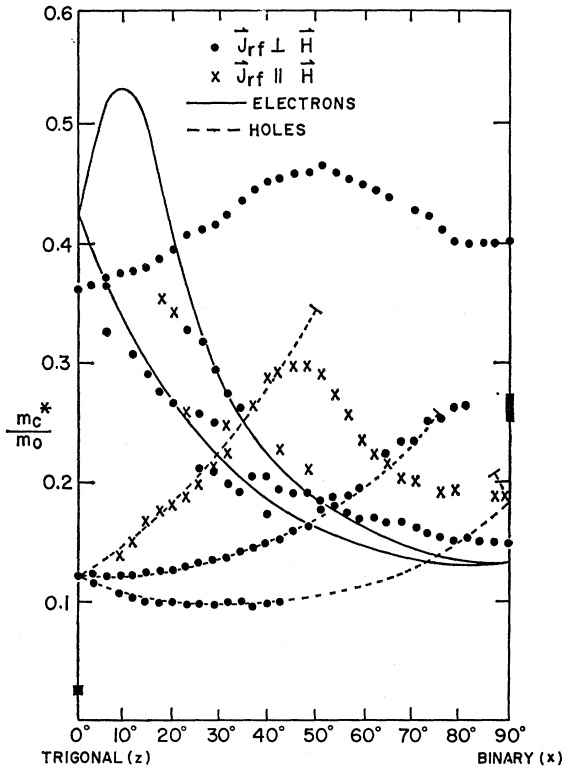


FIG. 8. Comparison of cyclotron effective masses (points) in the *xz* plane with de Haas–van Alphen frequencies (curves) measured by Priestley *et al.* (Ref. 2). The scale factors chosen correspond to a Fermi energy of 0.210 eV for the electrons and 0.178 eV for the holes. The solid rectangles are masses measured by Priestley *et al.*; the heights of the rectangles correspond to the quoted error.

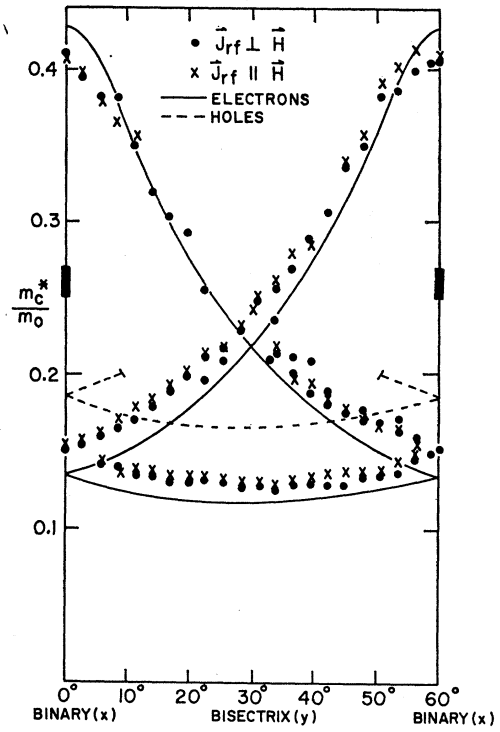


FIG. 9. Comparison of cyclotron effective masses (points) in the $xy$ plane with de Haas–van Alphen frequencies (curves) measured by Priestley *et al.* (Ref. 2). The scale factors chosen correspond to a Fermi energy of 0.210 eV for the electrons and 0.178 eV for the holes. The solid rectangles are masses measured by Priestley *et al.*; the heights of the rectangles correspond to the quoted error.

be lower than in the other two planes, although this could simply be due to a difference in quality between samples rather than to broadening due to superposition of two resonances. One should also note that these low mass resonances were observable with $\mathbf{J}_{rf} \| \mathbf{H}$ at all angles in the $xy$ plane, a fact which suggests extremal mass orbits with planes tilted away from normal to the field direction rather more than might be expected for central orbits on the electron surfaces, or extremal mass orbits with nonzero average velocities parallel to the magnetic field. It is quite plausible that the latter might occur on the noncentrosymmetric hole pockets.

Given detailed de Haas–van Alphen data there is another useful way to view our results. If the energy is a quadratic function of wave vector, the Fermi surface is ellipsoidal, cylindrical, or hyperboloidal, and the cyclotron mass $m_c^*$ and de Haas–van Alphen period $P$ for a given direction of magnetic field are related by

$$m_c^*/m_0 = (e\hbar/m_0 c E_F)P^{-1} = (e\hbar/m_0 c E_F)F, \quad (1)$$

where $m_0$ is the free-electron mass, $E_F$ is the Fermi energy, and $F = P^{-1}$ is the de Haas–van Alphen frequency. This relation holds only if the energy-wave vector dependence is quadratic. It fails, for example, in the simple two-band model[40] where the energy $E$ is given by

$$E(1+E/E_g) = \tfrac{1}{2}\hbar^2(k_1^2/m_1 + k_2^2/m_2 + k_3^2/m_3), \quad (2)$$

where $E_g$ is the energy gap between two interacting bands. In this model, the constant energy surfaces are still ellipsoidal, but the wave vector dependence of the

TABLE I. Summary and comparison of arsenic electron data.

| | Azbel'-Kaner cyclotron resonance | | | | |
|---|---|---|---|---|---|
| | Present experiments | Other experiments[a] | de Haas–van Alphen effect[b] | Ultrasonic attenuation[c] | Theory[d] |
| Experimental cyclotron masses, field parallel to crystal axes (units of $m_0$) | $x$: 0.404<br>0.150<br>$y$: 0.232<br>0.130<br>$z$: 0.361 | $x$: 0.42<br>0.15<br>$y$: 0.23<br>0.135 | 0.130[e]<br>(field in direction giving minimum Fermi-surface cross section) | | |
| Effective masses in ellipsoid principal axis system[f] (units of $m_0$) | $m_1=0.121$<br>$m_2=0.138$<br>$m_3=1.18$ | | $m_1=0.163$<br>$m_2=0.105$<br>$m_3=2.11$ | | $m_1=0.11$<br>$m_2=0.038$<br>$m_3=0.94$ |
| Effective masses of principal ellipsoid in crystal axis system[f] (units of $m_0$) | $m_{xx}=0.121$<br>$m_{yy}=0.608$<br>$m_{zz}=0.155$<br>$m_{yz}=1.408$ | | | $m_{xx}=0.120$<br>$m_{yy}=1.09$<br>$m_{zz}=0.071$<br>$m_{yz}=0.662$ | |
| Tilt angle | $+83.6°\pm2°$ [f] | | $+86.4°\pm0.1°$ [g] | $+84°$ | $\sim+80°$ |
| Fermi energy (eV) | 0.210[h] | | 0.190[f] | | 0.367 |
| Density per pocket ($cm^{-3}$) | $6.20\times10^{19}$ [f] | | $7.07\times10^{19}$ [f] | | |

[a] Datars and Vanderkooy (Ref. 33).
[b] Priestley *et al.* (Ref. 2).
[c] Ketterson and Eckstein (Ref. 12).
[d] Lin and Falicov (Ref. 32).
[e] This may be compared with our $(m_1 m_2)^{1/2} = 0.129$.
[f] Derived using ellipsoid model.
[g] Angle of minimum Fermi-surface cross section.
[h] Estimated using comparison with de Haas–van Alphen period anisotropy.

[40] B. Lax, J. G. Mavroides, H. J. Zeiger, and R. J. Keyls, Phys. Rev. Letters 5, 241 (1960).

TABLE II. Summary and comparison of arsenic hole data.

| | Azbel'-Kaner cyclotron resonance | | de Haas–van Alphen effect[b] | Ultrasonic attenuation[c] | Theory[d] |
|---|---|---|---|---|---|
| | Present experiments | Other experiments[a] | | | |
| Experimental cyclotron masses, field parallel to crystal axes (units of $m_0$) | $x$:<br>$y$: 0.24<br>$z$: 0.122 | | 0.098[e]<br>(field in direction giving minimum Fermi-surface cross section) | | |
| Effective masses in ellipsoid principal axis system[f] (units of $m_0$) | $m_1=0.122$<br>$m_2=0.0805$<br>$m_3=1.04$ | | | $m_1=0.125$<br>$m_2=0.059$ | |
| Tilt angle | +38° [f] | | 37.25°±0.1° [g] | +36° | ∼+44° |
| Fermi energy (eV) | 0.178 [h] | | 0.177 [f] | | 0.362 |
| Density per pocket ($cm^{-3}$) | $3.46\times10^{19}$ [f] | | $3.9\times10^{19}$ [f] | | |

[a] Datars and Vanderkooy (Ref. 33).
[b] Priestley *et al.* (Ref. 2).
[c] Ketterson and Eckstein (Ref. 12).
[d] Lin and Falicov (Ref. 32).
[e] This may be compared with our $(m_1m_2)^{1/2}=0.099$.
[f] Derived using ellipsoid model.
[g] Angle of minimum Fermi-surface cross section.
[h] Estimated using comparison with de Haas–van Alphen period anisotropy.

energy is nonquadratic. This suggests that a rational way to compare measured cyclotron masses and de Haas–van Alphen periods for approximately ellipsoidal surfaces is to plot the cyclotron masses and de Haas–van Alphen frequencies together, choosing a normalizing factor for one or the other in such a way as to bring the two sets of data as nearly into coincidence as possible. This should provide a convenient way to judge the general correlation of the two types of data as well as a measure of the deviation from quadratic behavior, even in a situation where the two sets of data separately may look nearly ellipsoidal. If the deviations are not too large, one might expect that the normalizing factor which gives the best over-all fit would yield a value for the Fermi energy at least as reliable as one obtained by inserting a small number of measured parameters into a parabolic energy model.

In Figs. 7–9, we have replotted our cyclotron mass data together with curves obtained by inverting PWKE's de Haas–van Alphen periods and multiplying by a constant factor. We have also indicated the four cyclotron masses measured by PWKE as solid rectangles with heights representing their quoted errors. In the two cases where we measured the same masses (minimum electron and hole masses in the $yz$ plane) the agreement is good. An over-all comparison of the two sets of data indicates considerable deviation from a quadratic ellipsoidal model for both carriers. There is appreciably less anisotropy in the electron cyclotron masses than in the electron de Haas–van Alphen periods. Unfortunately, PWKE were unable to observe the de Haas–van Alphen oscillations corresponding to the high-mass electron branches in the $xz$ and $yz$ planes, so that the question of whether the de Haas–van Alphen periods show the same large deviations from the ellipsoid model as do our cyclotron masses on these branches remains unanswered. Band-structure calculations[32] indicate energy gaps at $L$ of the same order of magnitude as the electron Fermi energies estimated by us (see below) and by PWKE, so the nonquadratic behavior of the electrons is not surprising.

The correspondence between our results and those of PWKE for the holes is, if anything, better than for the electrons. The PWKE data match our hole data at least as well as our ellipsoid fit, *where the PWKE data exist*. Therein lies a problem. The bars which terminate hole curves in Figs. 7 and 8 mark angles at which PWKE found that the amplitude of the de Haas–van Alphen oscillations decreased sharply to zero, indicating the disappearance of the corresponding extremal orbit. They interpreted this as a consequence of the necks of the hole surface; the necks prohibit simple extremal orbits around the hole pockets for some field orientations. However, our data continues past the cutoff points in both planes. A striking example is the highest-mass hole branch in the $xz$ plane (Fig. 8). This begins to deviate from the PWKE curve at 40° and continues on past PWKE's cutoff at 50°, all the way to the $x$ axis. Since there seems to be no reason to doubt PWKE's interpretation of the cutoffs, we conclude that the observed hole resonances in these regions correspond to noncentral or limiting point orbits. For a true quadratic ellipsoidal surface, where the cyclotron mass is the same for all orbits, the elimination of a group of orbits would not affect the measured mass but would simply reduce somewhat the amplitude of the resonance. For the actual hole surface in arsenic it is reasonable to suppose that the cutting off of the extremal area orbits (which need not necessarily be extremal mass orbits, since the individual hole pockets are not centrosymmetric) may simply change the weighting of the orbits to favor the limiting point. If the limiting-point mass is not very different from the central-orbit mass, the change may take place rather

smoothly, at least smoothly enough so that nothing very anomalous can be discerned with an $\omega\tau$ of only 5. Rather severe tipping effects usually accompany observation of a limiting-point resonance.[36] We did not observe prominent tipping effects. Possible reasons other than lack of sample flatness are discussed below.

The scale factors used to plot the curves shown in Figs. 7–9 yield Fermi-energy estimates of 0.210 eV for the electrons and 0.178 eV for the holes. These may be compared with the values derived by PWKE in a quadratic ellipsoidal approximation using measured or extrapolated de Haas–van Alphen periods and their minimum cyclotron masses shown on Fig. 7. Their values are 0.190 eV for the electrons and 0.177 eV for the holes. Our estimate for the electrons could be brought into almost exact coincidence with that of PWKE by shifting the curves upward to match the smallest-mass electron branches in the $yz$ and $xy$ planes at the expense of the already rather bad fit at the higher masses.

These Fermi energies may be combined with the principal masses obtained from the ellipsoid fit to estimate the number of carriers in the electron and hole ellipsoids using a formula valid for quadratic bands,

$$n=(8\pi/3h^3)(2E_F)^{3/2}(m_1m_2m_3)^{1/2}. \tag{3}$$

The results are $n_e=6.20\times10^{19}$ cm$^{-3}$ and $n_h=3.46\times10^{19}$ cm$^{-3}$. The ratio $n_e/n_h=1.8$, the same ratio found by PWKE. This supports their conclusion that there are twice as many hole pockets as electron pockets, in fact six hole pockets and three electron pockets. Our total electron or hole density, taken as three times the electron density per pocket, is $1.86\times10^{20}$ cm$^{-3}$, about 12% less than PWKE's value of $2.12\times10^{20}$ cm$^{-3}$.

The numerical results of the present experiments are listed and compared with results from some other experiments and with theory in Tables I and II.

We failed to observe several other types of orbits reported by other workers. The first is the $\gamma$ orbit on the small necks which connect the hole pockets. PWKE measured a cyclotron mass of $0.028m_0$ for this orbit with magnetic field parallel to the $z$ axis, and a similar value was obtained by Maltz and Dresselhaus[29] from a magnetoreflection experiment. We searched particularly diligently for a resonance associated with this orbit but were unable to find one, probably because the rather small number of carriers on these orbits yielded a signal too small to be detected. A second type of orbit, the $\delta$ orbit, was first observed by PWKE over a narrow angular range near the $x$ axis. They assigned this orbit as a skew orbit associated with the junction of the $\gamma$ necks and the $\alpha$ pockets. Miziumski and Lawson[19] observed the same oscillations but attributed them to orbits about an $\alpha$ pocket passing between the two $\gamma$ necks and lying on either side of the mirror plane. They also observed another set of oscillations, the $\epsilon$ oscillations, and assigned these to an orbit parallel to the $\delta$ orbits but in the mirror plane. PWKE measured a cyclotron mass of $0.26m_0$ for the $\delta$ orbits (Figs. 8 and 9). Datars and Vanderkooy[33] observed an AKCR over a narrow range of angles near the $x$ axis with a cyclotron mass of $0.5m_0$. They suggested that this mass might be associated with the $\epsilon$ orbit. (They actually labeled it $\delta$.) We were unable to identify resonances associated with any of these orbits. (At our operating frequency, the fundamental resonance of a $0.5m_0$ mass would have been just beyond our maximum magnetic field, and the subharmonics might easily have been too weak to identify. We can therefore neither confirm nor deny the existence of this resonance.) However, we note the following: If we combine the Fermi energy which we have derived for the hole pockets with the observed $x$-axis de Haas–van Alphen periods of the $\delta$ and $\epsilon$ oscillations using Eq. (1), we find cyclotron masses of $0.24m_0$ and $0.21m_0$, respectively. These are quite close to PWKE's measured value of $0.26m_0$ for the $\delta$ oscillations. We also note that our $xz$-plane data contains a hole mass branch which reaches a value of $0.26m_0$ at 80° before becoming unobservable near the $x$ axis. If the $\alpha$ pockets did not have necks attached, the central orbits on this branch would exist over the entire range of angles and near the $x$ axis would in fact be the $\epsilon$ orbits. The $\delta$ orbits of Miziumski and Lawson would be noncentral orbits with rather similar masses. We believe these facts lend some support to the identification of the $\delta$ orbits made by Miziumski and Lawson and weigh against Datars and Vanderkooy's assignment of their $0.5m_0$ mass to the $\epsilon$ orbit. Our inability to observe resonances associated with this cyclotron mass branch near the $x$ axis in either the $xz$ or $xy$ planes is presumably attributable to a relatively small number of carriers on the $\delta$ and $\epsilon$ orbits.

We come now to a consideration of the apparent absence of pronounced tipping effects in the present experiments. These have been discussed by many authors; a detailed theoretical analysis of the phenomenon has been given by Smith.[41] The detailed nature of the tipping effects is controlled by the relative sizes of three lengths, the skin depth $\delta$, the mean free path $l$, and the radius of an extremal cyclotron orbit $r$. We are interested here primarily in the small tip angle regime defined by $l\sin\alpha\cong l\alpha\lesssim\delta$, where $\alpha$ is the tip angle. For this range of tip angles, all the carriers continue to orbit through the skin depth throughout the period between scatterings, and the tipping effects can be qualitatively discussed in terms of a simple Doppler-shift picture.[36]

We require an estimate of the skin depth. We have estimated the skin depth in arsenic by the following procedure: In the anomalous skin effect (ASE) regime the zero magnetic field surface impedance is given (in

[41] D. A. Smith, Proc. Roy. Soc. (London) **A297**, 205 (1967).

Gaussian units) by[42]

$$Z=(\sqrt{3}\pi\omega/c^2\sum)(1-\sqrt{3}i). \quad (4)$$

A complex skin depth can be defined by

$$\delta=c^2Z/4\pi\omega. \quad (5)$$

We chose as our representative skin-depth parameter the real part of this $\delta$. In general, the surface impedance is anisotropic and $\sum$ depends on the relative orientations of fields, sample surface, and crystallographic axes. However, a single isotropic value of $\sum$ averaged over all crystallographic orientations is given by

$$\sum{}^3=e^2\omega S_k/4\pi\hbar c^2, \quad (6)$$

where $S_k$ is the total surface area of the Fermi surface in wave-vector space. Two estimates of the Fermi surface area were made. In the first we used a quadratic ellipsoid model with the principal masses obtained from the ellipsoid fit to our data and the Fermi energies obtained by fitting PWKE's periods to our masses. In the second we used an ellipsoid model with principal cross-sectional areas obtained from PWKE's periods. The results differed by about 10%; the mean value was $S_k=1.4\times10^{16}$ cm$^{-2}$. At 134 GHz, the estimated skin depth is thus $7\times10^{-6}$ cm, nearly three times the value obtained for copper by the same procedure using an extrapolation of the anomalous surface resistance measured at lower frequencies.[43]

Before proceeding to discuss tipping effects, we would like to comment briefly on the conditions of the present experiment *vis a vis* the extreme anomalous relaxation (EAR) region. True AKCR is observed in the ASE region where cyclotron orbit radii are large compared with the skin depth. The EAR region is defined by the conditions $\omega\delta/v_F\gg1$, $\omega\tau\gg1$, and these imply that cyclotron orbit radii at resonance are comparable with or smaller than the skin depth. Cyclotron resonance in the EAR region has been studied theoretically by several authors.[44,45] The results indicate that in certain circumstances something very like AKCR should be observable. The threshold of the EAR region lies at very high frequencies for typical metals, but it is not inappropriate to inquire where it is with respect to 134 GHz in the semimetal arsenic. One way to check this point is to compare the surface resistance in the ASE and EAR regions. The considerations of the previous paragraph yield for arsenic a surface resistance in the ASE region, $R_{\rm ASE}=3.2\times10^{-21}\nu^{2/3}$ in Gaussian units, where $\nu$ is the frequency in Hz. In the EAR region Holstein[46] has shown that if the scattering of the electrons from the sample surface is diffuse (as is likely in arsenic), the surface resistance for a spherical Fermi surface is given by

$$R_{\rm EAR}=3\pi v_F/4c^2. \quad (7)$$

Using a mean value of $v_F=6\times10^7$ cm sec$^{-1}$ derived by combining our effective masses and PWKE's de Haas–van Alphen periods we find $R_{\rm EAR}=1.6\times10^{-13}$. These results are plotted in Fig. 10 together with a plausible transition curve. While it is clear that the present experiment was done safely within the ASE region, the threshold to the EAR region lies not far away. This conclusion is corroborated by a comparison of typical cyclotron orbit dimensions with our estimated skin depth. If we define an average extremal orbit radius by $\pi r^2=A_r$, where $A_r$ is the orbit area in real space, then at resonance, $\omega_c=\omega$,

$$r=(1/m_c{}^*\omega)(2eh/cP)^{1/2}. \quad (8)$$

A typical value for the present experiments is $5\times10^{-5}$ cm, only a factor of 7 larger than the skin depth.

Returning now to the tipping effects, we can estimate a value of mean free path from our average $\omega\tau=5$ and $v_F=6\times10^7$ cm sec$^{-1}$: $l=3.6\times10^{-4}$ cm. Then $\delta/l=2\times10^{-2}$, nearly two orders of magnitude larger than in, for example, the copper experiments of Koch *et al.*[36] The small-angle tipping region extends to an angle of more than a degree in our case and to about a minute in theirs. They give a formula for the Doppler shift of the resonances in the small-angle region,

$$\Delta H/H\sim v_D\alpha/\omega\delta, \quad (9)$$

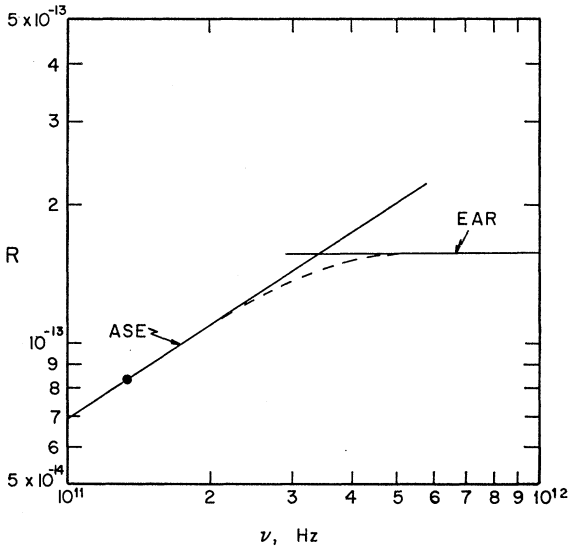


FIG. 10. Surface resistance of arsenic (in Gaussian units) as a function of frequency, showing the transition from the anomalous skin effect (ASE) region to the extreme anomalous relaxation (EAR) region. The curves in the two regions were calculated from experimental data as discussed in the text. The point represents the operating point in the present experiments.

[42] See, for example, A. B. Pippard, *The Dynamics of Conduction Electrons* (Gordon and Breach Publishers, Inc., New York, 1965).
[43] R. G. Chambers, Proc. Roy. Soc. (London) **A215**, 481 (1952).
[44] M. C. Jones and E. H. Sondheimer, Proc. Roy. Soc. (London) **A278**, 256 (1964).
[45] J. P. D'Haenens and D. L. Carter, Phys. Rev. **140**, A1992 (1965).
[46] T. Holstein, Phys. Rev. **88**, 1427 (1952).

where $v_D$ is the average drift velocity parallel to the magnetic field. Putting $v_D=v_F$, we find 0.2 for the fractional shift at 1° tip for a limiting-point orbit. For a continuous distribution of drift velocities, $-v_F<v_D<v_F$, around a central orbit on an approximately ellipsoidal Fermi surface where $v_D=0$, the expected tipping behavior is simply a general broadening and reduction in amplitude over several degrees of tip, with no appreciable shift in the apparent position of the line. This is consistent with our observations. With a much flatter surface on a better sample at lower frequencies it might be possible to observe more interesting tipping effects. We can only conclude that in the present experiments it is reasonable to expect no marked tipping effects and that the measured masses are probably not seriously affected by tipping effects.

## V. SUMMARY

The anisotropy of the cyclotron effective mass in arsenic has been studied in the three principal crystallographic planes using Azbel'-Kaner cyclotron resonance. The results are in general accord with the Fermi surface deduced from other experiments and from band-structure calculations. An attempt to fit the results to a simple ellipsoid model and direct comparison with available de Haas–van Alphen data show that there is considerable deviation of the energy bands at the Fermi surface from quadratic ellipsoidal behavior. The electron masses, in general, show significantly less anisotropy than the extremal cross-section areas of the electron Fermi surface. Particularly large deviations of the electron masses from an ellipsoidal model were observed in some directions; similar deviations have been observed in antimony. No corresponding de Haas–van Alphen data is available for comparison. The experimental masses are generally about 40% larger than calculated theoretical masses. Comparison with de Haas–van Alphen data yields estimates of Fermi energies and carrier concentrations which agree fairly well with estimates obtained solely from de Haas–van Alphen data and support the conclusion that there are twice as many hole pockets as electron pockets. Some of the hole masses observed appear to be due to noncentral, perhaps limiting point, orbits. Several special orbits reported by other workers, including the neck orbits, were not observed. No marked field tipping effects were observed, probably because the experimental frequency was high, the mean free path was relatively short, the skin depth was large, and the samples were not ideally flat.

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