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XVII-2. Cyclotron Resonance in Arsenic*

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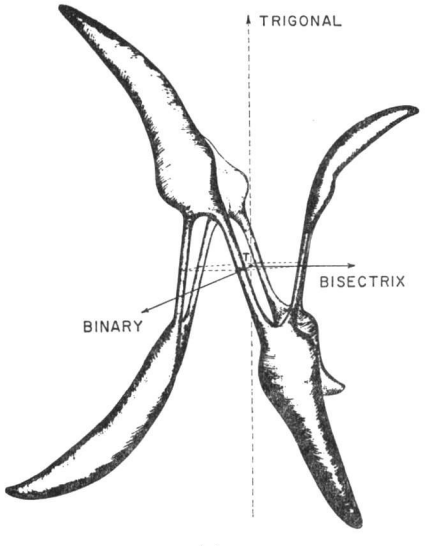
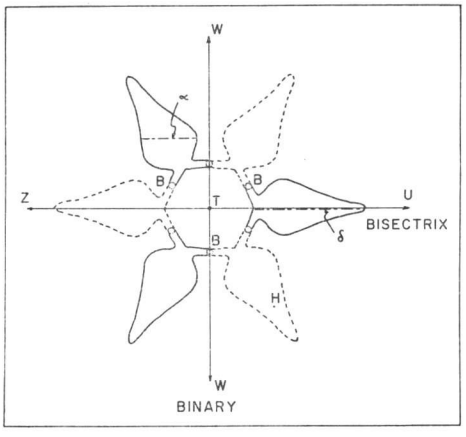
Cyclotron resonance has been studied in the (111) plane of arsenic at 1.4°K using microwave frequencies of 34.5 GHz and 70 GHz. Azbel'-Kaner cyclotron resonance was observed with the magnetic field parallel to the sample surface. Several mass series have been determined and identified for the (111) plane of arsenic. The data are compared with a theoretical model of the Fermi surface of arsenic proposed recently by Lin and Falicov. The topology of the model is supported by this experiment. The effective masses of the model are much smaller than measured effective masses.

§ 1. Introduction

The Fermi surface of the semi-metals Sb, Bi and As have been studied extensively over the past few years.[1] However, it is only recently that a satisfactory understanding of the Fermi surface of Sb has been obtained.[2] Arsenic, which is the last of these semi-metals to be studied in detail, is presently being investigated by several research groups.[3,4] In the first experimental investigation of the band structure of As,[5] carriers of one band were studied and were interpreted using a model of the Fermi surface that consisted of three or six ellipsoids in the Brillouin zone. Each ellipsoid was tilted +36° from the three-fold axis and the three or six ellipsoids were related by the $\bar{3}$m crystal symmetry. More recently, carriers have been observed in two bands.[3,6,7] They were interpreted by Ketterson and Eckstein[7] in terms of tilted ellipsoids in both bands. However, recently Lin and Falicov[8] have proposed a model of the Fermi surface of arsenic which was determined by a pseudopotential band structure calculation. This surface consists of three electron pockets and a single, multiply-connected hole surface. Each electron pocket resembles a distorted ellipsoid. The hole surface is shown in Fig. 1 and consists of six pockets which are connected by six thin necks. Since this model



(a)



(b)

Fig. 1. Fermi surface of arsenic according to Lin and Falicav.
(a) A perspective of the complete view of the hole "crown."
(b) A cross-section and projection of the hole "crown" on the binary bisectrix plane through *T*. The full lines are parallel projection from above and the dashed lines are parallel projection from below.

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deviates considerably from the simpler tilted-ellipsoid scheme, it is of interest to test it experimentally. The present experiment was carried out to obtain cyclotron masses for the binary-bisectrix plane of As and to provide information on the Fermi surface of As.

Arsenic belongs to the rhombohedral crystal system and to the symmetry class $R\bar{3}m$. A system of orthogonal axes is formed by the three-fold axis, the two-fold axis, and a third axis mutually perpendicular to the first two axes. This is called the trigonal-binary-bisectrix system and is used in this paper. The binary-bisectrix plane is a (111) plane in which all necessary information is given in a 30° interval.

In the geometry commonly used for Azbel'-Kaner cyclotron resonance,[9] a *dc* magnetic field is applied parallel to a flat, smooth, single-crystal metal surface on to which simultaneously is shone high-frequency microwave radiation. Minima in the real part of the surface impedance are observed when

$$\omega=\frac{neH}{m^*c}\,, \qquad (1)$$

where ω is the angular frequency of the radiation, H is the magnetic field, m^* is the cyclotron effective mass of the orbiting charge carrier, n is an integer, e is the electronic charge in Gaussian units and c is the velocity of light. This resonance occurs when the mean free path of charge carriers is greater than both its radius of curvature in the magnetic field and the microwave skin depth. These conditions are satisfied in pure metals at low temperatures but are not necessarily satisfied in pure semi-metals.[10] In this present experiment conditions for Azbel'-Kaner resonance were satisfied in As, and Azbel'-Kaner cyclotron resonance was observed.

§ 2. Experimental

Single crystals were grown from high-purity arsenic in a quartz tube using a modified Bridgman method by Dr. J. B. Taylor. The resistance ratio $\rho_{300}/\rho_{4.2}$ was approximately 1000. Silicon was one of the chief impurities in the crystal. In an attempt to reduce this impurity, the inside of a quartz tube was coated with carbon before growing one crystal. This crystal gave somewhat better resonance signals. A flat crystal surface was obtained by cleaving a crystal slab approximately 4 mm thick. The cleaved surface was a binary-bisectrix crystal plane. Crystal slabs from five different crystals were used in order to find satisfactory resonance. The best resonance was obtained from a crystal slab which cleaved fortuitously in the growth tube and was annealed for 24 hours before being removed from the tube.

Microwave radiation at frequencies of 34.5 GHz and 70 GHz were used in this experiment. The detection system employed a standard microwave bridge and magnetic field modulation at 108 c/sec in conjunction with a narrow band amplifier, phase sensitive detector and X-Y recorder. The sample cavities at both frequencies operated in a cylindrical TE_{113} mode. The sample formed the end wall of each cavity and was held in place by a phosphor-bronze spring. Each cavity was divided into two halves so that the bottom half and sample could be rotated about the axis of the cavity from above the Dewar. In this way, the crystal orientation was set to an accuracy of 1/2°. The magnetic field was produced by a 12-inch magnet which could be rotated about a vertical axis. The sample and cavity were immersed in liquid helium and experiments were done at 1.4°K.

It was important to align H along the crystal surface accurately and to set it with respect to the polarization of the microwave field. The former was accomplished by adjusting the tilt of the Dewar with micrometer screws in the 70 GHz experiments where the sample surface was horizontal and by rotating the magnet in the 34.5 GHz experiments where the sample surface was vertical. The direction of E_{rf} as the surface was set by a small wire stirrup over the iris of the cavity. All data were taken with H perpendicular to E_{rf}.

Figure 2 shows a recorder trace taken with H along a bisectrix axis. A plot of reciprocal fields of the absorption derivative maxima vs. the integer n is linear and satisfies eq. (1) for

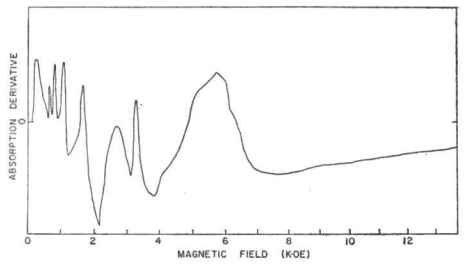

Fig. 2. Cyclotron resonance in As for H parallel to the bisectrix axis with E_{rf} perpendicular to H.

cyclotron effective masses of $0.135\,m_0$ and $0.23\,m_0$ for the bisectrix direction. The plot for the binary axis yields cyclotron effective masses of $0.15\,m_0$, $0.42\,m_0$ and $0.50\,m_0$. The $\omega\tau$ for the resonance is estimated to be 5. The cyclotron masses that are reported were determined from eq. (1) from the periodicity in $1/H$ of each Azbel'-Kaner resonance by using a least squares computer program to find the slope of the $1/H$ vs. n plot.

§ 3. Cyclotron Masses and Orbit Assignment

The cyclotron masses are shown in Fig. 3 for directions of $\boldsymbol{H}$ in the binary-bisectrix crystallographic plane of As. For a given crystallographic direction, the cyclotron masses measured in different samples agree to $\pm 3\%$ and the measurements made at two microwave frequencies of 34.5 GHz and 70 GHz agree to $\pm 4\%$. However, measurements at 70 GHz are more accurate due to the higher resolution. There are also systematic errors due to phase shifts and other effects of cyclotron resonance.[9] Thus, the error of each point in Fig. 3 is approximately 5% except for certain indicated points where the errors are larger for reasons given below. The cyclotron mass plot (Fig. 3) is divided into branches, a, b, c, and d in order to facilitate the description.

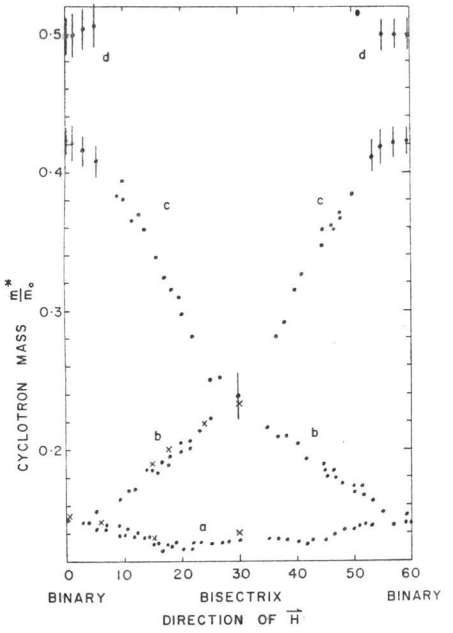

Fig. 3. Cyclotron effective masses in As as a function of the direction of $\boldsymbol{H}$ in the (111) plane.
× measured at 34.5 GHz
● measured at 70 GHz.

Branch a runs from 0.13 to $0.15\,m_0$, b from 0.15 to $0.23\,m_0$, c from 0.23 to $0.42\,m_0$ and branch d is between $0.48\,m_0$ and $0.53\,m_0$.

Cyclotron masses on branches a, b and c are assigned to electron orbits on the warped ellipsoids in the conduction band. This assignment is made because each of the three warped ellipsoids should support a cyclotron orbit for a given magnetic field direction and these branches have three masses for a magnetic field direction except at the symmetry axes where degeneracy exists. Furthermore, the shape of the mass plot of these branches is similar to that expected for three ellipsoids.

Identification of hole orbits in the valence band is difficult since its Fermi surface is probably a complicated crown. Branch d is surely due to a hole orbit and is assigned to the orbit δ shown in Fig. 1. It is about a hole pocket and goes between the connecting arms to that pocket. It occurs for an angular range of $\pm 5°$ from the binary axis. This branch does not decrease as $\boldsymbol{H}$ moves away from the binary axis. The uncertainty in the values of masses of branch d is due to the large line width of its resonance. Other hole orbits should also exist, *i.e.* α with $\boldsymbol{H}$ along a binary direction shown in Fig. 1. Resonances from these orbits were not evident. The reason why they were absent is very puzzling and requires further investigation.

§ 4. Discussion

The electron cyclotron effective masses are compared with those for a tilted-ellipsoidal model of the electron Fermi surface in Fig. 4. Parameters for this model were determined from a theoretical fit to electron periods of the de Haas-van Alphen effect and from the temperature dependence of the amplitude of the de Haas-van Alphen oscillations[11] rather than from the cyclotron resonance data. The mass tensor components along the principal axes of an ellipsoid in this model are $m_1'/m_0=0.135$, $m_2'/m_0=1.52$, $m_3'/m_0=0.127$. The 2′ principal axis is tilted $+86°$ [12] from the trigonal axis and the 1′ axis is along the binary direction. The electron Fermi energy is $(30.1\pm 2.0)\times 10^{-14}$ ergs. The error in E_f is due to experimental uncertainties and to the use of the ellipsoidal approximation for its determination. It can be seen that there is close agreement in Fig. 4 between the predicted and experimental curves. The flat region of branch a for directions of $\boldsymbol{H}$ between 15° and

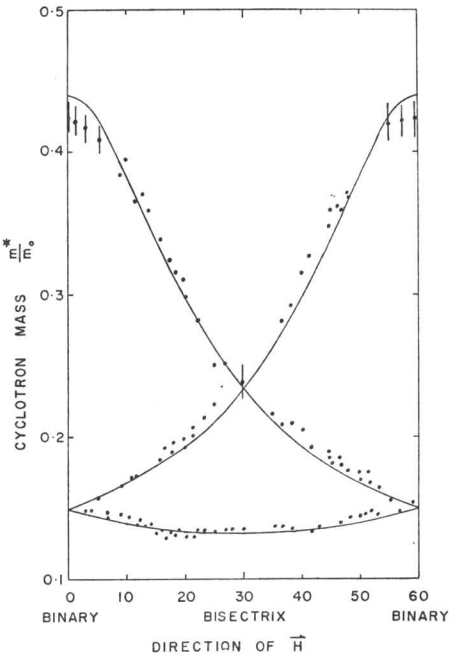

Fig. 4. Comparison of electron masses to that predicted by a tilted-ellipsoidal model of the Fermi surface.

45° indicates a departure of the Fermi surface from an ellipsoid since the ellipsoidal model predicts a minimum at the bisectrix direction. Further departures from this model are expected and may be observed when cyclotron resonance data on other crystal planes become available.

Several comparisons make it seem reasonable to have the low hole masses of the same magnitude as the low electron masses although the former were not measured in their experiment. The shapes of the plots of the de Haas-van Alphen period vs. direction of H in the binary-bisectrix plane are similar for electron and hole orbits with low masses.[6] The magnitude of these electron and hole periods differ by about 10%. If the hole Fermi energy were 28.4×10^{-14} ergs and the electron Fermi energy, 30.1×10^{-14} ergs then, using the ellipsoidal approximation, the low cyclotron masses of electrons and holes as determined from the periods would coincide for the binary-bisectrix plane. These Fermi energy values agree with those obtained in the de Haas-van Alphen experiment. The second comparison is obtained by comparing cyclotron masses of As and Sb for which band structures are quite similar except for the necks in the hole surface. The cyclotron resonance of the low-mass electrons and holes in Sb for H in the binary-bisectrix plane are resolved only in samples with high $\omega\tau$.[13] The low masses of electrons and holes for this plane in Sb differ at most by 10%.

The only direct evidence from this experiment of the multiply-connected hole surface proposed by Lin and Falicov[8] is branch d in Fig. 4. This corresponds to the δ orbit which is cut off by the connecting necks when H is 5° from the binary direction (see Fig. 1). Further evidence that supports this model is provided by a detailed study of the long periods of the de Haas-van Alphen effect.[11] The long periods arise from the six necks that are hyperbolic in shape and that are tilted from the trigonal axis by $\pm10°$.

Lin and Falicov predict an electron Fermi energy, *i.e.*, the energy between the Fermi level and the bottom of the L_4 band, to be 43.2×10^{-14} ergs. This value is 44% larger than our value of 30.1×10^{-14} ergs. Several factors that were neglected in the band structure calculation may tend to raise the L_4 band and reduce the electron Fermi energy. These factors may be the same as those invoked by Lin and Falicov to raise the L_1 band above the Fermi level. A comparison of theoretical and experimental values of the electron Fermi surface is interesting. There is reasonable agreement between theoretical and experimental values of cross-sectional areas. However, the cyclotron effective masses of the theory differ considerably from those measured in this experiment. In particular, the electron effective mass along the binary axis is $0.19\,m_0$ from theory and $0.42\,m_0$ from this experiment. The explanation of this discrepancy could be that the theoretical Fermi energy was fixed to fit a minimum area rather than to fit cyclotron masses.

Acknowledgement

The authors would like to thank Dr. J. B. Taylor for the arsenic crystals.

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COMMENT BY THE AUTHORS

Recently additional information on the Fermi surface of arsenic has become available from the de Haas-van Alphen experiment of Priestley *et al.*[4]. They observed an extremal orbit which they called the δ orbit, with a cyclotron mass of $0.26\,m_0$ for $\bar{H}$ parallel to the binary axis. It is worthwhile pointing out that the δ-orbit observed by Priestley *et al.* is different from the δ-orbit with a cyclotron mass of $0.50\,m_0$ which is described in the present paper. Both orbits are predicted by Lin and Falicov's model of the Fermi surface. Also, the existence of the two-hole orbits with cyclotron masses of $0.26\,m_0$ and $0.50\,m_0$ for the binary direction is consistent with our data. The fundamental and first subharmonic of the orbit with cyclotron mass $0.26\,m_0$ would coincide with the first and third subharmonics, respectively, of the orbit with cyclotron mass $0.50\,m_0$.

DISCUSSION

Lerner, L. S.: Can you describe the preparation of the arsenic samples?

Datars, W. R.: The crystals were prepared by Dr. J. B. Taylor of the National Research Council. They were grown using a modified Bridgman technique in a thick-walled quartz tube.

Tanuma, S.: How did you determine the carrier sign of the thin cylinder surface?

Datars, W. R.: The sign of the carriers detected by cyclotron resonance was determined by comparison with de Haas-van Alphen data. The short periods of these data were assigned to electron or hole orbits by comparing the tilt angle of the pockets in each band with that predicted by Lin and Falicov.