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The Fermi Surface of Antimony: Radio-Frequency Size Effect.

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THE FERMI SURFACE OF ANTIMONY:

RADIO-FREQUENCY SIZE EFFECT

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in

The Department of Physics and Astronomy

by

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ABSTRACT

Radio-frequency size effect measurements have been performed on high-purity, single crystal, antimony plates approximately 0.15 to 0.36 mm thick. Extremal calipers of the Fermi surface which were obtained from the data were fit in an internally consistent manner to a Fermi surface model consisting of three electron pockets and three sets of doubly degenerate hole pockets. The tilt angles and shapes of the pockets basically confirm the general features of the Fermi surface model arising from a previous pseudopotential calculation. The sizes of the pockets, however, differ somewhat from the pseudopotential model. Comparisons between the present data and previous de Haas-van Alphen and ultrasonic geometric resonance measurements are made. Details of the pseudopotential calculation are given in an appendix along with the results arising from a slight change in the Fermi energy. A further appendix investigates an attempt to measure the temperature dependence of the cyclotron effective mass in Sb.

I. INTRODUCTION

In the last two decades rapid progress has been made in developing experimental techniques for obtaining information about the electronic structure of metals. The results of the investigations show that there is a constant energy surface, the Fermi surface, which at $T = 0^{\circ}\text{K}$ separates the occupied from the unoccupied electron states in k -space. From all of the experimental methods that have been tried four techniques have evolved which give the most direct information about the size and shape of the Fermi surface of metals.

Of these four techniques, perhaps the most widely used has been the de Haas-van Alphen effect. In observing the de Haas-van Alphen effect one measures the influence of quantized electronic states in a magnetic field on the magnetic susceptibility of a metal or upon the various transport properties (de Haas-Shubnikov effect, for example) as these states pass through the Fermi level with increasing magnetic field. Values of the extremal areas of the various sheets of the Fermi surface are deduced from the periodic variation of these properties as the magnetic field is increased. The method suffers from the difficulty of trying to separate the many different periods that may be observed and from the fact that only the area and not the shape of a particular section of the Fermi surface can be obtained. An advantage of the technique, however, is that it does not require as long a mean free path of the carriers as do the other methods.

The rate of change of area with respect to energy evaluated at the Fermi energy can be obtained through cyclotron resonance measurements. Once both the area and its derivative with respect to energy are known, in principle, the Fermi surface can be constructed. In practice this is a very difficult procedure requiring the fitting of data to assumed models. The cyclotron resonance experiments also suffer from the rather stringent conditions placed on the preparation of samples and from the fact that the frequency of scattering of the carriers must be much less than the frequency of the applied radiation in order to observe the resonance.

A much more direct method of determining the size and shape of the Fermi surface is to caliper it across its extremal dimensions. Two techniques are available for doing this. The first of these to be investigated was the oscillatory change in the attenuation of ultrasound propagating in a sample subjected to an increasing magnetic field applied perpendicular to the direction of the sound wave propagation. The oscillatory change occurs when diameters of extremal orbits of carriers on the Fermi surface become equal to multiples of the ultrasound wavelength. Observation of this geometric resonance is possible when the mean free path of the carriers is long compared to the acoustic wavelength and the gross acoustic attenuation is small so that the small oscillatory changes are not masked. As in both the de Haas-van Alphen effect and cyclotron resonance the information that is available from the geometric resonance data depends upon

ones ability to separate many periodic oscillations superimposed upon one another.

The remaining technique for determining extremal dimensions of the Fermi surface is the radio-frequency size effect (RFSE). The RFSE consists of measuring the rf surface impedance (R) of a thin, single crystal plate as a function of magnetic field applied in the plane of the plate. Discontinuities in the surface impedance are exhibited when the strength of the magnetic field is such that extremal electronic orbits on the Fermi surface exactly span the sample thickness. The magnetic field strength at which this occurs is directly proportional to an extremal dimension of the Fermi surface. The technique is limited, however, to very pure metals in which the mean free path can be made several times the thickness of the samples. The application of this technique to antimony is the subject of most of the remainder of this paper.

The Fermi surface (FS) of antimony has been studied by each of the above mentioned methods. In addition, galvanomagnetic measurements have been made by Freedman and Juretschke,¹ and Epstein and Juretschke² in an attempt to determine the band structure of Sb. Their analysis leads to a multivalleyed band structure the energy surfaces of which are represented by ellipsoids tilted with respect to crystal axes. Several ultrasonic attenuation measurements have been made. Those by Eckstein³ yielded minimum calipers in all three orientations but the sign of the carriers responsible was unclear. Ericksson, Beckman, and Hornfeldt⁴ repeated the measurements using a higher frequency.

The results yield maximum and minimum calipers in only two orientations. Ketterson⁵ observed de Haas-van Alphen (dHvA) oscillations in the ultrasonic attenuation. Korolyuk and Matsakov⁶ used even higher frequencies in their geometric resonance experiment and obtained periods from which calipers can be computed in all three orientations. The de Haas-Shubnikov effect has been observed by Rao et al.,⁷ and Lerner and Eastman.⁸ Cyclotron resonance measurements have been performed by Datars and Vanderkooy.⁹ Several dHvA measurements¹⁰⁻¹³ have been made on Sb the latest very extensive ones being by Windmiller.¹³

The interpretation of these experiments was confusing and often in conflict until an energy band calculation by Falicov and Lin (FL)¹⁴ was performed. In this calculation FL showed that (a) there are three electron pockets and six hole pockets and (b) the electron pockets are located at the L point in the Brillouin zone (BZ) while the hole pockets are in the mirror plane near the T point in the BZ (Fig. 1). While this calculation resolved the situation concerning the sign of the carriers, number of pockets of each, and their location in the BZ, it did not have sufficient accuracy to predict the detailed shapes of these pieces of the FS. The data which are reported here give the details of the dimensions of the FS from which a refinement of the band structure calculation can be performed.

In the sections which follow, first a discussion of the facts concerning the FS of antimony is given together with the results of the band structure calculation of FL followed by a

Fig. 1

general discussion of the RFSE and the details of the present experiment. The last two sections present the data and its interpretation. Appendix I contains a listing of the calipers obtained for each of the three directions investigated. In Appendix II a full discussion of the pseudopotential calculation performed by FL as well as the results of this calculation as modified by the RFSE data is given. Appendix III contains the results of measurements made of the temperature dependence of the cyclotron effective mass in an effort to learn something of the electron-phonon interactions in Sb.

II. THEORY

A. Crystal Structure and Fermi Surface of Antimony

Antimony is a group-V semimetal (atomic number 51) which has the A7 (arsenic) crystal structure. The unit cell (which is also a primitive cell) is rhombohedral and contains two atoms.

The A7 structure can be obtained from a simple-cubic structure with one atom at each lattice site by applying two independent distortions: a shear and an internal displacement of the atoms. The shear is along a body diagonal and transforms the unit cube into a rhombohedron. This diagonal retains its three-fold symmetry and becomes the trigonal axis of the A7 structure. To visualize the second distortion, it is convenient to think of the simple-rhombohedral lattice as being composed of two interpenetrating face-centered-rhombohedral lattices. Each point of either lattice is in the center of the cell of the other lattice. Then the A7 structure is obtained by shifting one of these lattices toward the other along the trigonal axis. This results in a face-centered-rhombohedral structure in which two atoms are associated with each lattice point.

Two parameters are needed to specify these distortions:

a) The parameter u is used to characterize the internal displacement. If $2\mathbf{t}$ is the smaller vector in the trigonal direction separating the two interpenetrating lattices, and $\mathbf{d}$ is the trigonal body-diagonal of one of the lattices, then

$$\underline{t} = u\underline{d}; \quad u \leq 1/4$$

The value $u = 1/4$ corresponds to a simple-rhombohedral structure or to a simple cubic structure in the absence of shear.

b) The angle α between the primitive translations of the A7 structure determines the shear, 60° being the value corresponding to the face-centered or simple-cubic structures.

Table 1 contains a list of all the relevant crystal structure parameters of Sb at 4.2°K . Figure 2 shows the BZ of Sb and the rhombohedron of twice the volume from which it is obtained. The rhombohedron is the BZ in the absence of internal displacement, i.e., $u = 0.25$. The axes labeled x, y, z are the cubic axes in the absence of shear and it is convenient to keep them as an orthogonal system of coordinates. The three primitive translation vectors of the Sb lattice can then be expressed by $\underline{a}_1 = a_0(\epsilon, 1, 1)$, $\underline{a}_2 = a_0(1, \epsilon, 1)$, $\underline{a}_3 = a_0(1, 1, \epsilon)$ where () indicate rectangular coordinates.

Values of $|\underline{a}_i|$, a_0 , and ϵ are given in Table 1. The parameter ϵ is related to the shear angle α by

$$\cos \alpha = (1+2\epsilon)/(2+\epsilon^2)$$

$$\epsilon = [1 - (1 + \cos \alpha - 2 \cos^2 \alpha)^{\frac{1}{2}}] / \cos \alpha$$

α is the angle between any two $\underline{a}_i$.

The three reciprocal lattice vectors defined by

$$\underline{g}_i \cdot \underline{a}_j = 2\pi \delta_{ij} \text{ are given by}$$

TABLE I. Crystal Structure Parameters of Sb at 4.2°K

a	4.3007 Å	} Lattice constants in hexagonal system
c	11.222 Å	
A_1	2.902 Å	Nearest neighbor distance
A_2	3.343 Å	Next nearest neighbor distance
$ a_i $	4.489 Å = 8.486 a.u.	Primitive lattice parameter
a_o	5.998 a.u.	
α	57°14'	Rhombohedral angle
ϵ	0.0416	
Ω_o	404.7 a.u.	Volume of primitive cell
$(2\pi)^3/\Omega_o$	0.6130 a.u.	Volume of the Brillouin zone
u	0.2336	Internal displacement parameter
g_o	0.5353 a.u.	
$ g_i $	0.9402 a.u.	Length of primitive reciprocal lattice vectors
E_F	0.4060 hartree	Free-electron Fermi energy
k_F	0.9011 a.u.	Free-electron Fermi momentum

Fig. 2

$$\underline{g}_1 = g_0(-(1+\epsilon), 1, 1),$$

$$\underline{g}_2 = g_0(1, -(1+\epsilon), 1),$$

$$\underline{g}_3 = g_0(1, 1, -(1+\epsilon)),$$

where g_0 is listed in Table 1. A general reciprocal lattice vector is indicated by

$$(h, k, \ell) = h\underline{g}_1 + k\underline{g}_2 + \ell\underline{g}_3,$$

where h, k, ℓ are integers; similarly, points in the BZ or in reciprocal space in general are denoted by

$$(a, b, c) = a\underline{g}_1 + b\underline{g}_2 + c\underline{g}_3.$$

The band structure and FS of semi metallic Sb were determined by means of a pseudopotential approach by Falicov and Lin.¹⁴ This approach was used by the author to obtain a detailed picture of the FS of Sb in the binary or mirror plane. The result of this calculation is shown in Fig. 3. There are three electron pockets situated at the L point and six hole pockets near the point T in the BZ. While this calculation agrees well with the present experiment for type, number, and tilt angle of the FS pockets the size and detailed shape of these pockets do not agree. A detailed description of the pseudopotential method used is presented in Appendix II together with the results obtained by modifying the value of the Fermi energy used.

Fig. 3

B. The Radio-Frequency Size Effect

In the presence of an applied magnetic field, $\underline{H}$, the carriers in a metal move in reciprocal space on the FS in planes perpendicular to the direction of $\underline{H}$. The projections of the real space orbits that result from this motion onto a plane perpendicular to $\underline{H}$ have the same shape as the orbits in reciprocal space but are rotated 90° about $\underline{H}$. Classically, the equation of motion for a charge q at position $\underline{r}$, velocity $\underline{v}$, in a constant external field $\underline{H}$ is

$$d\underline{p}/dt = q/c \underline{v} \times \underline{H} . \quad (1)$$

If $\underline{p}$ is expressed semiclassically in terms of the wave vector, $\underline{k}$, of the charge carriers, equation (1) becomes

$$\hbar d\underline{k}/dt = q/c \underline{v} \times \underline{H} . \quad (2)$$

The integration of equation (2) with respect to time yields

$$\hbar \underline{k} = q/c \underline{r} \times \underline{H} . \quad (3)$$

Thus if a real space dimension of an electron orbit is given at a known magnetic field, the corresponding orbit dimension in reciprocal space can be determined.

The determination of these FS dimensions using the RFSE has been described in detail earlier.^{15,16} If a thin, flat, single crystal of metal is placed in a coil carrying a radio frequency current of angular frequency ω , then there is induced in the metal an antisymmetric electromagnetic field near the

surfaces which extends into the metal a distance, δ , known as the skin depth. If the frequency ω is high enough such that the sample thickness, d , is much larger than the skin depth, and yet low enough that it is much smaller than the cyclotron frequency of the carriers, then the antisymmetric electric field experienced by the carriers is almost static. In the RFSE experiment a magnetic field is applied parallel to the surface of the sample and the rf surface impedance (R) is measured as a function of this field. Discontinuities in the surface impedance are exhibited when the strength of the magnetic field is such that extremal electronic orbits on the FS exactly span the sample thickness. The extremal FS dimensions are then obtained from equation (3) using the relation $k_c = 0.015194 Hd$, where H is the value of the applied field in gauss at the point where the extremal orbits just span the sample, d is the sample thickness in millimeters, and k_c is the FS extremal dimension in $\text{\AA}^{-1}$.

III. EXPERIMENTAL PROCEDURE

A zone-refined bar of Sb (quoted purity: 99.9999%) was obtained from Cominco Products, Incorporated. The Sb bar contained crystals of sufficient size that further crystal growth was unnecessary. After orienting the selected crystals, thin slabs were cut out by spark erosion. A table was also planed by spark erosion insuring that the planing wheel and table were parallel. The sample was then cemented to the table with conducting silver paint, care being taken that no paint ran between the sample and table. After planing, the sample was removed and the table was replaned to assure that the sides of the sample would be parallel. The sample was cemented in place once more and the remaining side planed until the sample was of the desired thickness. The slabs were then spark cut to the desired dimensions. After removal from the table the samples were lapped on a flat glass plate in a solution containing equal parts of acetic, hydrofluoric, and nitric acids and water to remove the surface strain caused by the thinning process.

The finished samples were checked by Laue back reflection X-ray to assure that the final orientation was within $\pm 0.5^\circ$ of the desired direction. The final sample thicknesses were typically between 0.15 and 0.36 mm. Samples this thin were used in order to make the small calipers obtained occur at reasonable field values. A single, pre-formed tank coil was used throughout the experiment. The coil was made by winding forty gauge copper

wire around a dummy sample of mica. The windings were banded together using Duco household cement and the mica removed after the cement had hardened. The coil was then matched with the actual sample dimensions to insure that the thin Sb plates would not be strained due to the shrinkage of the windings during the cooling process. The slab dimensions were measured by using a traveling microscope to find the area of the face of the plate. Then the mass of the sample was divided by the density and the area to determine the thickness d . The value of d at 1.2°K was then calculated by compensating for the thermal contraction of Sb along its respective crystallographic axes.³¹

The experimental apparatus represented schematically in Fig. 4 has been described previously by Steenhaut and Goodrich.¹⁶ This apparatus allows both the first and second derivatives of the real part of the surface impedance to be recorded. The tank coil is the inductive element in a modified version of a high level marginal oscillator which provides the bilateral antisymmetric excitation for the sample. The present measurements were all taken at an rf frequency of 9 MHz., which optimized the sensitivity of the marginal oscillator for the tank coil used, in magnetic fields ranging between 20 and 200 G. The electronic system and sample thickness measuring techniques give an overall reproducibility to the caliper values of $0.006 \text{ \AA}^{-1}$ determined by comparing the caliper values obtained on different samples.

Fig. 4

IV. EXPERIMENTAL RESULTS

Data were obtained for field rotations in three planes. Samples were used having the normal, $\underline{n}$, to the face of the slab parallel to the binary and bisectrix axes and to an axis rotated 7° from the trigonal axis toward the bisectrix axis away from IX. The last orientation was chosen because thin samples with $\underline{n} \parallel$ trigonal axes failed to produce RFSE signals. A probable reason for the inability to detect signals in this orientation is that the thin plates may "peel" during the cool-down process due to the close orientation to the easily cleaved bisectrix, binary plane. Also, an axis 7° from the trigonal towards the bisectrix axis was chosen because of the geometry of the electron pockets determined from data taken in the other two orientations. The resulting FS calipers for $\underline{n}$ along the binary, bisectrix, and 7° from the trigonal axes are shown in Figs. 5, 6, and 7, respectively. The calipers which could be definitely assigned as being due to the addition of two orbits are not shown on this figure. Signals attributable to the addition of as many as five orbits were seen.

The RFSE line shapes observed in Sb display the same general characteristics observed earlier in Cd,¹⁵ Zn,¹⁶ and Tl.¹⁷ The signal-to-noise ratio in samples with $\underline{n}$ directed 7° off the trigonal axis was higher than that observed in the above three metals. Signals observed from samples having $\underline{n}$ parallel to the other two symmetry axes also exhibited high signal-to-noise ratios.

Fig. 5

Fig. 6

Fig. 7

The signal strength decreased rapidly with angle as the turning points of the pockets were approached. Since at these points the electrons spend very little time in the skin depth, their effect on the change in surface impedance is small. Signal strengths decreased slowly with increasing temperature with signals associated with the minimal calipers for H parallel to the electron pocket axis clearly visible at 4.2°K .

All of the caliper values reported here were calculated by choosing the point in field of maximum slope preceding the first major peak in the RFSE line shape obtained on a plot of the derivative of the real part of the surface impedance with respect to magnetic field (dR/dH). This point corresponds to the first peak in the second derivative curve (d^2R/dH^2). This has been shown to be a reliable point on the line shape from which to compute the caliper value in past RFSE experiments devoted to FS determinations.¹⁵⁻¹⁷ In angular regions where several caliper series are present and the RFSE lines overlap, a slightly different procedure was used to determine the caliper point on each line. It was observed that the difference in field values between peaks (ΔH) on the second derivative curves was a constant for a given line. In Fig. 8 a recorder tracing of d^2R/dH^2 versus H taken with H applied 20° from the bisectrix direction in an $\underline{n}$ 7° off the trigonal axis sample is shown. The line shapes associated with series M, O, P, Q and S are shown in this plot. It is seen that ΔH is a constant for each line and the caliper point can be determined by extrapolating to the first peak in the line shape.

Fig. 8

This procedure was applied even when the first peak in the second derivative was visible. In these latter cases the agreement between the extrapolated position of the first peak and the measured position agreed to within the measuring accuracy. The experimental error in the determination of the calipers by this method is $\pm 0.006 \text{ \AA}^{-1}$. This accuracy was checked by comparing the caliper values obtained from different samples for the same orbit and by comparing the determination of points on the FS obtained from different sample orientations. These independent determinations always agreed to within the quoted accuracy. This point on the line has also been shown to be the caliper point for cylindrical Fermi surfaces in a recent calculation of line shapes by Juras.¹⁸ Further support for the choice of this point on the line as the caliper point has recently been given by Boudreau and Goodrich¹⁹ from line shape studies on Cd.

During the course of the experiment it was discovered that the RFSE line shape in Sb depended on the frequency of the marginal oscillator. A frequency dependence of such magnitude has not been reported before and may be peculiar to semi-metals. The low carrier concentration ($\sim 10^{19} / \text{cm}^3$) in Sb causes the skin depth, δ , at rf frequencies to be at least a factor of ten larger than in normal metals with the result that the condition for RFSE that $\delta/d \ll 1$ is not well satisfied. An extensive study of this frequency dependence using oscillators tunable over a wide frequency range should add a great deal of information to the

field of RFSE line shapes. To insure that the caliper point used was consistent a constant frequency of 9 MHz was used throughout the experiment.

V. DATA ANALYSIS AND CALIPER ASSIGNMENT

In the following discussion the term caliper will be defined as a vector quantity in k space which is in the direction of $\pm \underline{n} \times \underline{l}$ and has a magnitude equal to the length of the line segment formed by projecting an extremal orbit (in k space) onto a plane perpendicular to $\underline{n}$. Since RFSE always obtains values of extremal (maximum or minimum length) calipers, the term caliper will be taken to mean an extremal caliper throughout the remainder of this paper.

Since the electron pockets are centered at the L point in the BZ they must exhibit inversion symmetry through the L point. Calipers arising from the electrons then could be plotted with their midpoint at L for the $\underline{n} \parallel$ binary data. That is, all of the calipers for the electrons in this orientations are due to central orbits. On the other hand the hole pockets are located at a general point in a mirror plane and do not exhibit inversion symmetry. Therefore, the assignment of calipers to these pockets cannot be done unambiguously. In order to be consistent, we have assigned all of the calipers of the hole pockets as if they arose from central orbits. As will be seen in what follows this leads only to a small error in the dimension obtained.

The extremal areas for some of the outlines obtained from the data were computed. Both polar planimeter measurements and direct computation of the areas using Simpson's rule were made in each case and were found to agree with each other to better than 1%.

A. Bisectrix Plane

In the bisectrix plane calipers were assigned to the two electron pockets which when projected onto the bisectrix plane cross at the binary axis and to two rather distorted hole pockets also crossing at the binary axis. Figure 9 is a plot of the caliper points in this plane. Caliper series K was assigned to the curved side of one electron pocket while series J formed the curved side of the other one. Series F was then assigned to the flat side of the electron pocket bounded by series K while series L formed the flat side of the pocket bounded by series J. The projections of these electron pockets have their axes 8.3° on either side of the binary axis and have a length of $0.518\text{\AA}^{-1}$ and a width perpendicular to this axis of $0.075\text{\AA}^{-1}$. As will be discussed later, the curvature of these electron pockets with respect to the binary axis aided in assigning calipers in the binary plane.

The signals produced by these electrons were very strong. Line shapes were observed over most of the angular region resulting from the addition of up to five orbits. These strong harmonic series crossed over other weaker series prematurely terminating them or masking them altogether. The intensity of the RFSE peaks is, to a large extent, dependent upon the geometry of the orbit. That is, extremal orbits that spend proportionately longer time in the skin depth of the sample, and whose trajectories are parallel to the surface while in the skin depth, have a greater effect on the surface impedance than do

FIG. 9

extremal orbits calipered at more pointed segments of the FS. An example of the result of these effects is the termination of series F 15° before the turning point of the electron pocket. As the FS gets rapidly more pointed in this region, one of the orbit addition series associated with series J crosses over and masks the weakened line. The third electron pocket which should have been seen in an almost end-on fashion in this orientation was entirely masked by the harmonic series occurring in the region. A probable explanation for the lack of strong signals from this type of orbit is that the carriers are almost parallel to the surface during most of their trajectory in the sample. That is, the carriers simultaneously produce changes in the impedance as if the orbits were exactly spanning the sample, spanning the sample at one, two, etc. skin depths. This would produce a cancelling effect in the RFSE line shape resulting in very weak signals. The observed shape and the symmetry requirements for the electron pockets suggest that the central polar plots of the caliper series result in a very representative cross section for these pieces of the FS.

Only two caliper series were observed in this orientation which could be assigned to hole pockets of the FS. Series G was observed over a 120° angular region before being hidden by the stronger electron signals of series K and L and the harmonic signals of series F. Series G was assigned to one side of a hole pocket having an axis of minimum caliper 48.3° on one side of the trigonal axis. Series H was assigned to one side of

another hole pocket having an axis of minimum caliper 48.3° on the other side of the trigonal axis. This pocket's orientation was such that series H could be followed for only 60° before series L and K on one side and series F and J on the other side interfered. The third hole pocket expected in this orientation was not seen. The two observed series associated with the hole pockets yield a fairly complete outline of the shape of these pieces of the FS. The shape and value of the turning points of these hole pockets were deduced from caliper values in the trigonal plane.

B. Binary Plane

Figure 10 shows a plot of the caliper points in the binary plane. At least parts of all four pockets expected in this orientation were seen. Series A was assigned to the relatively flat side of the in-plane electron pocket while series D was assigned to the curved side. The maximum length of this pocket is $0.594 \text{ \AA}^{-1}$ with its width being $0.080 \text{ \AA}^{-1}$. The axis of the electron pocket lies 7° off the bisectrix axis towards the trigonal axis. The dHVA area of this pocket was computed directly from the measured calipers and is compared with the area of Windmiller¹³ in Table II. The 6.2% difference in the two values is not too surprising since the claimed measuring accuracy of $0.006 \text{ \AA}^{-1}$ becomes quite significant in the regions of very small caliper values. It was originally thought that the actual caliper peak in the d^2R/dH^2 curves was being consistently washed out. Assuming this, new caliper values were assigned by extrapolating back another ΔH . This procedure led to internal

Fig. 10

TABLE II. Comparison of dHVA areas. Extremal areas in $\text{\AA}^{-2}$.

Field Direction	Type Pocket	Present Data	Windmiller ^a
Binary	Electron	0.0364	0.0343
7° from trigonal			
toward bisectrix	Electron	0.0425	0.0413
Binary	Hole	0.0214	0.0205
31° from trigonal			
cowards bisectrix	Hole	0.0204	0.0188

^aSee Ref. 13.

inconsistencies as well as to a dHvA area 5.5% too small. Attempts were then made to determine a constant scaling factor for the caliper values which would leave all the pockets internally consistent and yield closer agreement with the dHvA data. This procedure also failed to satisfy both requirements. Since the original caliper values at least provided complete internal agreement from one orientation to another, these values have been used.

Series I was assigned to one side of the electron pocket not lying in the binary plane. Other caliper points for this pocket were completely hidden by the much stronger in-plane electron series as well as the hole series in this orientation. The axis of this electron pocket projects onto the binary plane 13.5° from the bisectrix axis on the side opposite the main electron pocket. Series C and B are assigned to the in-plane hole pocket. The axis of minimum caliper lies 52.5° off the trigonal axis towards the bisectrix axis. This is in excellent agreement with the dHvA observed minimum area axis of 53.0° from trigonal. These caliper series, as mentioned previously, were plotted as if they were arising from central orbits. The dHvA area calculated from these calipers is also compared with that of Windmiller in Table II. The percent difference is comparable to that of the electron pocket. Thus, the use of central calipers for this pocket has only a small effect. Series E was assigned to the out of plane hole pocket. This series could be followed for only 40° before being lost in the much stronger series A, D,

and C. The axis of minimum caliper projects onto this plane at an angle of 33° from the trigonal axis on the side opposite the main hole pocket which agrees with that value obtained by projecting the in-plane axis 60° out of this plane. The shapes of the hole pockets near the turning points were drawn in using caliper values obtained in the trigonal sample.

The calipers assigned in the bisectrix plane and binary plane give a model which shows good internal consistency. The extremal dimension of the main electron pocket in the binary plane is $0.594 \text{ \AA}^{-1}$. When projected back onto the bisectrix plane its value of $0.514 \text{ \AA}^{-1}$ is in excellent agreement with the measured dimension of $0.518 \text{ \AA}^{-1}$. The shape and axes direction of the holes are consistent in these two planes also.

C. 7° Off Trigonal Plane

For the sample with $\underline{n}$ 7° from the trigonal axis towards the bisectrix axis, signals were observed which could be attributed to three electron and three sets of doubly degenerate hole pockets. The calipers are shown plotted in Fig. 11. Series N and S were assigned to the electron pocket lying in the plane of the sample. This pocket has an extremal length of $0.594 \text{ \AA}^{-1}$ in excellent agreement with the lengths found in the other planes. The caliper points on one side of the axis when folded over lie along the caliper points on the other side showing the symmetry of the pocket. The dHvA area computed for this pocket is 3% larger than that measured by Windmiller. Series P and R were assigned to the two electron pockets not lying in the plane of

Fig. 11

the sample.

Series M was assigned to the hole pocket which projects onto this plane along the axis of the main electron pocket. Projecting the extremal length of this hole back onto the binary plane perpendicular to the minimum caliper direction yields $0.350 \text{ \AA}^{-1}$ and is shown in Fig. 10. The shape near the turning point in the binary plane is not known but a continuation of the measured curvature in the turning point region has been drawn in. Since this hole pocket is ellipsoidal in the 7° off trigonal plane, a rough estimate can be made of its area $= \pi ab$. This area of $0.0204 \text{ \AA}^{-2}$ is 8.5% larger than that measured by Windmiller. Series Q and O were then assigned to the other two hole pockets observed in this orientation.

VI. CONCLUSION

The shape and size of the FS proposed here shows excellent internal agreement in caliper values and tilt angles. The tilt angles measured in this experiment agree with those measured by Windmiller. The dHVA areas computed from the data are consistently larger than those measured by Windmiller. The uncertainty in the measured caliper values is $0.006 \text{ \AA}^{-1}$ as determined by the reproducibility from sample to sample and the internal agreement shown between orientations. This uncertainty inherent in the RFSE experiment introduces a very small percentage error in measurements on the fairly large Fermi surfaces of metals but the error becomes as large as 8% for the small calipers of the FS encountered in Sb. In addition, the low carrier concentration in Sb ($\sim 10^{19}/\text{cm}^3$) causes the skin depth, δ , at rf frequencies to be at least a factor of ten larger than in normal metals. This could cause a shift in the observed RFSE lines because the condition for the RFSE that $\delta/d \ll 1$ is not well satisfied.

In general, good agreement between this experiment and the pseudo-potential calculation of FL is exhibited for type, number, and tilt angle of the FS pockets. In order to make direct comparisons of the present data to the model obtained by FL, the pseudopotential and Fermi energy used by FL was used to recalculate the FS at approximately 40 points on the electron surface and 40 points on the hole surface. Eighty-nine plane waves were

used in the expansion and the accuracy of the present calculation was checked at symmetry points in the BZ and found to agree with the values quoted by FL to three significant figures. Table III is a comparison of extremal caliper values for the FS of Sb between this experiment and others and the results of FL. The discrepancy in caliper values between the experiments and the calculations of FL is not surprising since a slight shift in the Fermi energy changes the dimensions of the calculated FS drastically. Appendix II contains a full discussion of the pseudopotential of FL. The large dependence on the value of the Fermi energy used is also shown. Table IV is a comparison of the tilt angles obtained by Windmiller and FL with those measured in this experiment.

Appendix III contains the results of measurements made of the temperature dependence of the cyclotron effective mass in Sb. This experiment was performed in an attempt to measure the mass enhancement due to electron-phonon interactions in Sb. The results indicate, however, that the change in the effective mass is less than 0.05% between 2.2° and 8°K as compared with a 2.2% change in zinc from 4.2° to 10.6°K and a 5.7% change in lead from 1.5° to 6.5°K .

TABLE III. Comparison of maximum and minimum caliper values.

<u>n</u>	Type Carrier	Eckstein ^a	Minimum and Maximum Caliper ($\text{\AA}^{-1}$)						This Experiment ^e		FL ^f	
			KW ^b		KM ^c		EBH ^d					
Trigonal	Holes				(0.075)	(0.305)			0.092	0.302		
		0.086					0.095	0.458				
	Electrons				(0.092)	(0.568)			0.105	0.594		
Binary	Holes				0.091	0.341	0.083		0.084	(0.350)	0.069	0.413
		0.067									(0.068)	(0.486)
	Electrons		0.083	0.499	0.085	0.596	0.076	0.489	0.080	0.594	0.061	0.398
Bisectrix	Holes				(0.085)				0.080	(0.301)		
		0.081										
	Electrons				(0.085)				0.075	0.518		

^aSee Ref. 3. No assignment to electrons or holes was made by this author.

^bSee Ref. 20. These results were obtained by inversion of dHvA data for a non-ellipsoidal FS.

^cSee Ref. 6. Bracketed values taken from graphs ($\pm 10\%$). Other numbers are the quoted values.

^dSee Ref. 4. No assignment to electrons or holes was made by these authors.

^eBracketed calipers are obtained by projection from data from the other orientations. The trigonal orientation is data from the n || to 7° from the trigonal toward the bisectrix away from IX. All values are ± 0.006 .

^fSee Ref. 14. Bracketed values obtained from the present calculation and unbracketed were measured from the graphs of FL.

TABLE IV. Comparison of tilt angles in binary plane.

Axis angle for minimum area from trigonal axis towards
bisectrix axis.

Pocket	FL ^a	Windmiller ^b	Present Experiment ^c
Holes	41.0°	53.0 ± 0.1	52.5 ± 0.5
Electrons	83.0°	84.0 ± 0.3	83.0 ± 0.5

^aSee Ref. 14.

^bSee Ref. 13.

^cField direction for minimum caliper.

APPENDIX I

Experimental Calipers for Sb

TABLE V. RFSE caliper values and directions obtained on Sb samples with $\underline{n}$ parallel to the bisectrix axis. $d = 0.2451$ mm.

Angle	F	G	H	J	K	L
0°						
5						
10	.094					
15	.089					
20	.084					
25	.083					
30	.080					
35	.079	.146				
40	.076	.135				
45	.075	.127				
50	.075	.120				
52.5 Trigonal						
55	.075	.116				
60	.075	.107				
65	.075	.100				
70	.077					
75	.079					
80	.083					
85	.089					
90	.096					

Angle	F	G	H	J	K	L
95	.106	.080		.101		
100	.121	.080		.108		
105	.136	.081		.116		
110	.154	.083		.130		
115	.172	.086		.146		
120	.222	.089		.165		
122.5	.242					
125	.285	.095		.190		
130	.441	.103	.201	.235		
132.5						
133.5				.257		
135		.110	.172	.278	.519	
137.5				.296		
138					.463	
139				.308	.445	
140		.122	.144	.340	.429	
142.5 Binary				.369	.369	
145		.139	.128	.426	.340	
148				.478	.316	
149				.500		
150		.164	.115	.517	.279	
152.5					.258	.469
154						.426
155		.190	.105		.235	.383
157.5						.356

Angle	F	G	H	J	K	L
160			.098		.196	.283
165			.093		.166	.215
170			.088		.147	.173
175			.086		.131	.155
180			.084		.119	.136
185			.083		.110	.120
190			.083		.104	.104
195					.091	.091
200					.084	.084

TABLE VI. RFSE caliper values and directions obtained on Sb samples
with $\underline{n}$ parallel to the binary axis. $d = 0.1552$ mm.

Angle	A	B	C	D	E	I
0	.118	.086				
5	.115	.085				
10	.108	.085				
20		.084				
30	.084					
35	.083					
40	.081					
50	.080	.100				
56.5 Trigonal						
60	.080	.112				
70	.082	.135				
80	.091					
90	.102	.200				
95		.220				
100	.120	.246			.095	
105		.269			.094	
110	.152	.295			.094	
115					.095	
120	.208				.097	
125	.267				.098	
130	.371		.280		.101	
131	.404		.233			
132	.434		.225			

Angle	A	B	C	D	E	I
133	.466					
134	.505					
135	.540		.209		.103	
138.5	.594					
140			.175		.109	
145			.147	.461		
146.5 Bisectrix						
150			.132	.348		
155			.120	.291		
160			.110	.229		
165			.104	.197		
170			.097	.169		
175			.094	.142		.240
180			.090	.128		.177
185			.089	.120		.148
190			.087	.108		.127
195			.086			.114
200			.085			.106

Angle	M	N	O	P	Q	R	S
95	.175	.209	.090	.101	.151	.174	
100	.199	.243	.090	.101	.139	.162	
105	.227	.300	.090	.102	.130	.148	
110	.257	.373	.091	.103	.122	.139	
115	.292	.472	.094	.107	.113	.130	
116		.503					
117		.536					
118.5		.562					
120		.583			.101	.124	
121.5 Bisectrix							
125	.282			.124	.097	.116	
130	.253			.132	.094	.110	
135	.218		.122	.141	.092	.103	
140	.187		.130	.151	.090	.101	.270
145	.166		.139	.166	.089	.099	.226
150	.150		.150	.180	.088	.098	.197
155	.138			.206	.088	.098	.174
160	.126			.237	.089	.101	.155
165	.118			.286	.090	.103	.146
170					.091		.134
175	.105				.094		.127
180	.100						.118
185	.097					.120	.114
190	.095					.128	.110
195	.092					.134	.107

APPENDIX II

Pseudopotential Calculation

In order to analyze the data from a RFSE experiment it is necessary to have some workable model from which to start. The pseudopotential calculation of Falicov and Lin¹⁴ was used to calculate approximately forty points on the hole and electron FS pockets in the binary plane. A brief description of the calculation of FL follows.

The cancellation of potential and kinetic energies in the neighborhood of the atomic cores in the lattice result in an effective potential, the pseudopotential V_p , much weaker than the true potential. Its matrix elements between two plane-waves can be accurately approximated by

$$\langle \underline{k} | V_p | \underline{k}' \rangle = S(\underline{G}) U(|\underline{G}|) \delta_{\underline{k}-\underline{k}'-\underline{G}},$$

where $\underline{G}$ is a reciprocal lattice vector, $S(\underline{G})$ is the structure factor and $U(|\underline{G}|)$ is the Fourier transform $U(K)$ of an atomic pseudopotential or form factor taken at $K = |\underline{G}|$. If $\underline{G}$ is expressed for Sb in terms of the three fundamental reciprocal lattice vectors $\underline{g}_1$, $\underline{g}_2$, and $\underline{g}_3$ by

$$\underline{G} = (h, k, l) = h\underline{g}_1 + k\underline{g}_2 + l\underline{g}_3,$$

then

$$S(\underline{G}) = \cos(2\pi u(h+k+l)),$$

where u is given in Table 1.

In order to determine $U(K)$ FL added to the pseudopotential of grey Sn one half of the contribution of the antisymmetric pseudopotential of InSb. The final result is approximated by an expression of the form

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

where, for $U(K)$ and K in atomic units

$$\begin{aligned} A_1 &= 0.0782 & A_3 &= 3.260 \\ A_2 &= 2.367 & A_4 &= 2.803 \end{aligned}$$

The actual mechanics involved in the calculation are described below. The one electron Schroedinger equation for a perfect crystal can be rewritten in terms of the pseudopotential as

$$\left(\frac{p^2}{2m} + V_p \right) \varphi_{nk}(\underline{r}) = E_n(\underline{k}) \varphi_{nk}(\underline{r}) .$$

The solution of this equation was accomplished by expanding φ_{nk} in a series of symmetrized combinations of plane waves, calculating the matrix elements of the Hamiltonian, and solving the corresponding secular equation

$$|H_{pm}(\underline{k}) - E_{nk} \delta_{pm}| = 0$$

where

$$H_{pm}(\underline{k}) = \frac{1}{2} |\underline{k} - \underline{G}_{mi}|^2 \delta_{pm} + \sum a_{mi}^* a_{pj} \\ \times \cos [(\underline{G}_{mi} - \underline{G}_{pj}) \cdot \underline{r}] U(\underline{G}_{mi} - \underline{G}_{pj}).$$

The coefficients a_{mi} of the symmetrized combinations of plane waves were obtained by ordering the kinetic energies and using the eighty-nine coefficients producing the lowest kinetic energies. This number was chosen because it was shown by FL to be the smallest size usable at a general point in the BZ which gave convergence to the eigenvalues to a reasonable accuracy. The 89 plane wave set was checked to assure that it included all of the members of a degenerate plane wave set. The solution of the secular equation was found numerically by diagonalizing the resulting 89 x 89 matrix and solving for the fifth and sixth eigenvalues for the holes and electrons respectively. The pockets resulting from this calculation are shown in a binary plane view in Fig. 3. The computer program is shown on the following pages.

The results of the pseudopotential calculation presented here depend greatly on the value of Fermi energy used. The value used by FL was 0.445 hartree. In order to determine the degree that this value contributed to the discrepancies between the theoretical FS and that determined by the present experiment the following calculations were carried out.

The experimental caliper values for the binary plane electron pocket were fed into the pseudopotential program in place of the interpolation scheme used to calculate the calipers. For each

caliper value the resulting matrix was diagonalized and the sixth eigenvalue calculated. The results are shown in Table VIII.

The average value of these eigenvalues was 0.4468 hartrees.

Using this new value as the Fermi energy, the resulting hole pocket calipers were calculated and are shown plotted in the binary plane in Fig. 12. The shape of the new hole pocket is the same as before but the size is much smaller, particularly the smaller dimension. No attempt has been made to adjust the four pseudopotential parameters to obtain a better fit with the experimental data.

TABLE VIII. Binary experimental electron calipers and resulting Fermi energies.

Calipers ($\text{\AA}^{-1}$)	Fermi Energy (hartrees)
0.118	0.4455
0.115	0.4460
0.108	0.4461
0.084	0.4460
0.083	0.4461
0.081	0.4461
0.080	0.4462
0.080	0.4462
0.082	0.4461
0.091	0.4464
0.102	0.4464
0.120	0.4465
0.152	0.4466
0.208	0.4465
0.267	0.4468
0.371	0.4473
0.404	0.4475
0.434	0.4476
0.466	0.4476
0.505	0.4478
0.540	0.4479
0.594	0.4478
0.348	0.4473

Calipers ($\text{\AA}^{-1}$)	Fermi Energy (hartrees)
0.291	0.4476
0.229	0.4470
0.197	0.4471
0.169	0.4470
0.142	0.4467
0.128	0.4467
0.120	0.4469
0.108	0.4468

Fig. 12

PSEUDOPOTENTIAL PROGRAM (FORTRAN IV)

```

INPUT PARAMETERS, TRANSFORMATIONS, PLANE WAVES

DIMENSION RR(10),EE(10),X(3),P(3),HI(10)

COMMON A(3,101),TRG(3,3),GAMMA(3),G(3)

REAL*8 EV(89)

DATA KBANDS/5/, FE/0.4468/, NP/3/, RNG/0.2/

READ(5,900) A

900 FORMAT(5(4X,3F4.1))

READ(5,910) ((TRG(I,J),J=1,3),I=1,3),GAMMA

READ(5,910) RP,AL,AU,DA

910 FORMAT(9F8.0)

WRITE(6,915)(( TRG(I,J),J=1,3),I=1,3),GAMMA,RP,AL,AU,DA

915 FORMAT(1H1,45X'THE FERMI SURFACE IN ANTIMONY'///,
* ' TRANSFORMATION MATRIX'10X,3F20.4/32X,3F20.4/32X,3F20.4//,
* ' ORIGIN WITH RESPECT TO GAMMA' 3X,3F20.4//,
* ' RP,AL,AU,DA='4F10.2//)

CHOOSE AN ANGLE AND AN ESTIMATE OF THE FERMI SURFACE RADIUS

RP=RP*0.26458

99 ANG=AL*1.74533E-2

CA=COS(ANG)

SA=SIN(ANG)

CHOOSE A RANGE ABOUT THE RADIUS

RL=RP*(1.-RNG)

RU=RP*(1.+RNG)

```

```

DR=(RU-RL)/FLOAT(NP-1)
DO 100 IP=1,NP
R=R1+DR*FLOAT(IP-1)
X(1)=CA*R
X(2)=SA*R
X(3)=0.0

TRANSFORM COORDINATE SYSTEM FIND BAND ENERGY FOR EACH RADIUS
CALL CALLER(M,KBAND,X,EV,TIME)
RR(IP)=R
EE(IP)=EV(KBAND)
WRITE(6,920) X,R,EV(KBAND),M,TIME
920 FORMAT(' XYZ='3F10.5,10X'R='F10.5,' AU',10X'EV='F10.6,
* 15X'M='13,5X'TIME='F6.2,' SEC')
100 CONTINUE

ORDER THE RADII WITH RESPECT TO THEIR ENERGIES
CALL ORDER(NP,FE,EE,RR,HI)

INTERPOLATE TO FIND THE FERMI SURFACE
F12=(RR(1)-RR(2))/(EE(1)-EE(2))
F23=(RR(2)-RR(3))/(EE(2)-EE(3))
F123=(F12-F23)/(EE(1)-EE(3))
R=RR(1)+(FE-EE(1))*(F12+(FE-EE(2))*F123)
RP=R
R=R/0.26458
X(1)=CA*R
X(2)=SA*R
X(3)=0.0

```

```

WRITE(6,940) X,R,AL
940 FORMAT(/ 1X,132('*')// ' FERMI SURFACE   XYZ='3F10.5,10X'R='F10.5,
*   ' ANG',9X'ANGLE='F6.2,//1X,132('*')//)
AL=AL+DA
IF(AL.LE.AU) GO TO 99
STOP
END

```

```

THIS SUBROUTINE TRANSFORMS COORDINATE SYSTEM
SUBROUTINE CALLER(M,KBAND,X,EV,TIME)
DIMENSION HI(101),X(3),GG(3)
REAL*8 H(89,89),AH(89,89),EV(89),AA(89),B(89),BS(89),WR(89),
*WI(89),QR(89),QI(89),ENORM
DATA AH/7921*0.0/,ENORM/0.098036/,N,LH/101,89/
COMMON A(3,101),TRG(3,3),GAMMA(3),G(3)
GG(1)=TRG(1,1)*X(1)+TRG(1,2)*X(2)+TRG(1,3)*X(3)+GAMMA(1)
GG(2)=TRG(2,1)*X(1)+TRG(2,2)*X(2)+TRG(2,3)*X(3)+GAMMA(2)
GG(3)=TRG(3,1)*X(1)+TRG(3,2)*X(2)+TRG(3,3)*X(3)+GAMMA(3)
CALL CLOCK(ITA)
SET UP MATRIX
CALL TRGMAT(N,M,A,GG,HI,H,LH)
DIAGONALIZE MATRIX
CALL HVTD(M,LH,H,AH,AA,B,BS,WR,WI,QR,QI)
CALL HVVL(M,EV,AA,BS,QR,QI,KBAND)
CALL CLOCK(ITB)
TIME=FLOAT(ITB-ITA)*0.01

```

```

DO 20 I=1,KBAND
20 EV(I)=EV(I)+ENORM

```

```

RETURN

```

```

END

```

```

THIS SUBROUTINE SETS UP THE MATRIX

```

```

SUBROUTINE TRGMAT(N,M,A,G,HI,H,LH)

```

```

REAL*8 H(LH,LH)

```

```

REAL*4 A(3,N),HI(N),G(3)

```

```

DATA GZ/.1433/,EP/1.0416/,U/1.4678/,TDT/0.001/,

```

```

*      A1,A2,A3,A4/0.0782,2.367,3.260,2.803/

```

```

M=89

```

```

      CALCULATE ENERGIES

```

```

DO 10 I=1,N

```

```

AX=A(1,I)+G(1)

```

```

AY=A(2,I)+G(2)

```

```

AZ=A(3,I)+G(3)

```

```

10 HI(I)=GZ*((AY+AZ-AX*EP)**2+(AX+AZ-AY*EP)**2+(AX+AY-AZ*EP)**2)

```

```

      ORDER THE ENERGIES

```

```

NI=N-1

```

```

DO 41 IR=1,NI

```

```

IPASS=0

```

```

NR=N-IR

```

```

DO 40 I=1,NR

```

```

IF(HI(I+1)-HI(I))20,40,40

```

```

20 IPASS=1

```

```

      HK=HI(I+1)
      HI(I+1)=HI(I)
      HI(I)=HK
      DO 30 J=1,3
      HK=A(J,I+1)
      A(J,I+1)=A(J,I)
30  A(J,I)=HK
40  CONTINUE
      IF(IPASS)50,50,41
41  CONTINUE

      DETERMINE THE BASIS SET

50  HK=HI(M+1)-HI(M)
      IF(HK.GT.TDT) GO TO 60
      M=M-1
      IF(M) 51,51,50
51  WRITE(6,1051) G,(I,(A(L,I),L=1,3),I=1,N)
1051 FORMAT(//' ERROR, TOTAL DEGENERACY,  G=',3F10.4/,
*          4(4X'I'2X'A1'4X'A2'4X'A3'6X'HI')/(4(I5,3F6.2,F10.6)))
      RETURN

      CALCULATE LOCAL PSEUDOPOTENTIAL

60  DO 100 I=1,M
      H(I,I)=HI(I)
      IF(M-I)100,100,90
90  NI=I+1
      DO 100 J=NI,M
      H(I,J)=0.0D0

```

```

H(J,I)=0.000
AX=A(1,J)-A(1,I)
AY=A(2,J)-A(2,I)
AZ=A(3,J)-A(3,I)
STF=COS(U*(AX+AY+AZ))
IF(ABS(STF).LT. 1.0E-4) GO TO 100
HK=(AY+AZ-AX*EP)**2 + (AX+AZ-AY*EP)**2 + (AX+AY-AX*EP)**2
HK=HK*GZ*2.0
H(I,J)=STF*A1*(HK-A2)/(EXP(A3*(HK-A4))+1.0)
H(J,I)=H(I,J)
100 CONTINUE
RETURN
END

```

```

THIS SUBROUTINE ORDERS RADII WITH RESPECT TO THEIR ENERGIES
SUBROUTINE ORDER(N,XO,X,F,W)
DIMENSION X(1),F(1),W(1)
IF(N.LE.L) RETURN
DO 10 I=1,N
10 W(I)=ABS(X(I)-XO)
DO 20 I=2,N
L=I-1
M=L
DO 15 J=I,N
IF(W(L).GT.W(J)) L=J
15 CONTINUE

```

```
IF(L,EQ,M) GO TO 20  
EXCH=W(M)  
W(M)=W(L)  
W(L)=EXCH  
EXCH=X(M)  
X(M)=X(L)  
X(L)=EXCH  
EXCH=F(M)  
F(M)=F(L)  
F(L)=EXCH  
20 CONTINUE  
RETURN  
END
```

APPENDIX III

Temperature Dependence of the Cyclotron Effective Mass in Sb.

The effective mass seen in a cyclotron resonance experiment can be written approximately as²¹

$$m_{CR} = m_{BS} \left(1 + \frac{\delta m}{m}_{el-ph} + \frac{\delta m}{m}_{el-el} \right)$$

where

$$m_{BS} = \left\langle \frac{1}{k_F} \frac{dE_{BS}}{dk} \right|_{E=0} \rangle^{-1}$$

is the band structure cyclotron mass where the average is taken around the appropriate cyclotron orbit. The second and third terms of the equation are a measure of the mass deviation due to electron-phonon and electron-electron interactions respectively. This appendix reports an attempt to measure the first of these effective mass deviations in order to learn something of the electron-phonon interactions in Sb.

Over the past few years, calculations of the electron-phonon interactions in metals have shown that the electron cyclotron effective mass should change when the electron is excited above the Fermi energy.²²⁻²⁴ This mass increase can be effected by two methods. First, in a cyclotron resonance measurement an increase in the rf frequency at which the

resonance is measured should cause an increase in the mass due to the increased energy imparted to the electron system at resonance. Second, the electron-phonon interactions can excite electrons above the Fermi level resulting in a temperature dependent change in the measured effective mass. The frequency dependent effect has been observed in lead and mercury²⁵ and the temperature dependent effect has been observed in zinc²⁶ and lead.²⁷ The present investigation was undertaken to determine the temperature dependence of the cyclotron effective mass in antimony.

The experiments reported here were performed with a standard field modulation 35 GHz microwave spectrometer with the antimony sample forming the end wall of a rectangular cavity resonating in the TE_{103} mode. The dc magnetic field was directed along the trigonal axis in the plane of a sample having its binary axis normal to the surface. The cavity assembly was isolated from the liquid helium bath by enclosing it in a vacuum tight can with a low pressure helium exchange gas maintaining thermal contact between the sample and the helium bath. The temperature of the sample was regulated by varying the current in a heater wrapped around the resonant cavity. The temperature of the sample was measured and controlled by a calibrated carbon resistor thermometer which formed one arm of a bridge circuit controlling the heater current. This arrangement held the sample to within $\pm 0.001^\circ K$ during the measurements.

The Azbel-Kaner subharmonic series were measured as a function of angle of the applied field, H , with respect to the crystallo-

graphic axis until only two subharmonic series were observed. The dc magnetic field was then swept over a 1000 gauss range and the effective mass of the light carriers was calculated using the periodicity in inverse field $\Delta(1/H)$ of the thirteen subharmonics that were observed in the derivative of the surface impedance with respect to field, dR/dH . A least squares fit to a straight line was performed on a plot of the $1/H$ values of the subharmonics versus the subharmonic number, n . The slope of this line was then used to determine the effective mass, m^* , by the formula $m^* = e/[\omega_{rf} c \Delta(1/H)]$ where e is the electronic charge, ω_{rf} is the cyclotron frequency, and c is the speed of light. This procedure gave an effective mass of 0.1000 ± 0.0011 for the holes at 2.24°K . Although the dc magnetic field could be measured at any given point with about 0.1% accuracy, the actual field value of a subharmonic peak could be located only to within about 0.5% due to the width of a peak. The change in mass between 2.2 and 8°K was less than the 2% scatter in the mass values obtained in this manner.

In order to measure the temperature dependence of m^* the position of the fundamental peak was monitored over the temperature range investigated. An NMR calibration point was placed on the recording of dR/dH versus H at two points separated by approximately 20 G on either side of the peak in dR/dH . The entire field sweep covering the fundamental resonance was 100 G. Although the absolute value of the mass, as determined by $m^* = eH/\omega_{rf} c$, is not as accurate as that found by the subharmonic method, changes in the

mass value could be more accurately determined. The change in mass as a function of temperature relative to the mass value at 2.24°K is shown by the open circles in Fig. 13. The relative change from $T = 2.24^{\circ}\text{K}$ to 7.50°K is 0.3%.

Moore²⁸ has shown that finite $\omega_{\text{rf}}\tau$, where τ is the relaxation time, causes an error in the measured cyclotron effective mass and that this error is a function of the relaxation time, τ . The $\omega_{\text{rf}}\tau$ values for several temperatures were calculated using Chambers' formula:²⁹ $\omega\tau = 1.55 H/\Delta H$. The line width of the resonance, ΔH , is the field difference between the maximum and the minimum value of dR/dH on the resonance curve. The relative change of effective mass values due only to this $\omega_{\text{rf}}\tau$ correction is plotted as closed circles in Fig. 13. These measured correction values show that the observed effective mass change can be accounted for by the change in $\omega_{\text{rf}}\tau$.

In both zinc and lead the effective mass of the carriers is found to increase proportional to T^2 between 1.5 and 11°K . The increase in zinc is 2.2% from 4.2°K to 10.6°K and in lead it is 5.7% from 1.5°K to 6.5°K . However, the present results indicate that the change in the effective mass in antimony is less than 0.05% between 2.2 and 8°K .

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Fig. 13

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