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Cyclotron Resonance and the Fermi Surface of Antimony*

Abstract: A new series of cyclotron resonance experiments has been made on antimony which gave extended information on electron and hole cyclotron masses. Experiments were carried out with the magnetic field in the principal crystal planes of antimony at 1.5°K and with 35 Gc/sec microwave radiation. The magnetic field of cyclotron resonance in certain regions was dependent upon the angle of tip of the magnetic field with respect to the metal surface. These effects were minimized by accurate alignment of the magnetic field along the sample surface. The carriers of two bands were observed. The cyclotron mass of one band, assumed to be the conduction band, was consistent with a tilted-ellipsoidal model for the energy surfaces. The cyclotron mass along the 1′ principal electron ellipsoid axis was measured from data in the binary-trigonal plane to be 0.215 m_0. The conduction band ellipsoids were found to have a tilt angle of 36° and mass tensor components: $m_{11} = 0.068\ m_0$, $m_{22} = 0.63\ m_0$, $m_{33} = 0.34\ m_0$, $|m_{23}| = 0.41\ m_0$. The data indicated three sets of warped ellipsoids for the valence band. The warped ellipsoids were found to have a tilt angle of 4° and mass tensor components: $m_{11} = 0.093\ m_0$, $m_{22} = 1.14\ m_0$, $m_{33} = 0.093\ m_0$, and $|m_{23}| = 0.082\ m_0$. The cyclotron masses of holes and the measurement of cyclotron resonance at limiting points of the Fermi surface indicated that the hole surfaces probably are deformed from an ellipsoid.

I. Introduction

Detailed studies of the de Haas - van Alphen effect,[1,2,3] Shubnikov - de Haas effect,[4,5] galvanomagnetic effects,[6] cyclotron resonance,[7] ultrasonic attenuation,[8] and infrared absorption[9] have yielded valuable information about the band structure of antimony. It is known that carriers occupy at least two bands. The recent oscillatory experiments[2,4] indicated that, in each of two bands, there were three or six sets of ellipsoidal energy surfaces at the Fermi energy, arranged in accordance with the rhombohedral symmetry of the crystal. Carriers from two bands were detected also in the previous cyclotron resonance experiment.[7] However, the results indicated that one band consisted of sets of tilted ellipsoids of the Shoenberg form and the second band had non-ellipsoidal energy surfaces of shape that was still to be determined. The present work was undertaken to consider the relationship of the band for which an ellipsoidal model was not adequate to the band observed recently[2,4] in the oscillatory experiments. It was considered likely that carriers in the same two bands were observed in all experiments and that the different experiments observed details of different parts of the Fermi surface. The results of this work show that carriers in two bands only have been observed and reveal considerable information about these bands.

At the present, there is little direct evidence to aid in the assignment of the sign of the carriers occupying each band. However, most previous work, including cyclotron resonance, has assumed the Shoenberg scheme of tilted ellipsoids to be in the conduction band. The model used by Saito[2] has been assumed for the valence band. In each model one set of ellipsoids is tilted to the triad axis with a principal axis along the dyad axis; two other sets of ellipsoids, called nonprincipal ellipsoids, are obtained by rotation of $\pm 2\pi/3$ about the triad axis; the three remaining sets of ellipsoids are obtained by inversion. The principal axes 1′, 2′, 3′ of the principal set of ellipsoids and the binary, bisectrix, trigonal axes are described in Figure 1.

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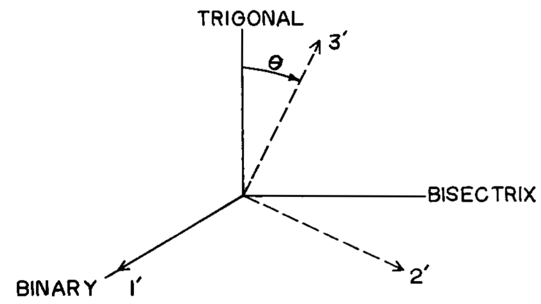

Figure 1 **Axes (1′, 2′, 3′) of the tilted-ellipsoidal model and the binary, bisectrix, trigonal crystal axes.**

(The 1′ axis is parallel to the binary axis.) The chief difference between the ellipsoids used for each band is the angle of tilt of the ellipsoids to the trigonal crystal axis. Previous experiments have given the tilt angle of the electron ellipsoids ranging from 35° to 38° and that of the hole ellipsoids from 0° to 4°. In this work, it will be assumed that the hole Fermi surface is tilted by several degrees and that the electron Fermi surface is tilted approximately 36°. These assumptions are the ones used in this analysis to identify masses with the carriers of each band.

Section II deals briefly with the experimental technique and the experimental method. The cyclotron masses for the binary-trigonal plane, binary-bisectrix plane, and bisectrix-trigonal plane are presented in Section III. The discussion and conclusions follow in Sections IV and V, respectively.

II. Experimental method

Single-crystal antimony was oriented using optical techniques[7] and crystal surfaces were cut to within 2° with a Servomet spark cutter and then electropolished. The antimony sample formed the end wall of a cylindrical, resonant, microwave, copper cavity operating in TE_{111} mode. A good electrical contact between the sample and cavity was formed with low-melting point solder. A reflection bridge microwave spectrometer operating at approximately 34 Gc/sec and magnetic field modulation in conjunction with an amplifier and phase sensitive detector were used to observe the derivative of the surface resistance, dR/dH, as a function of magnetic field. Magnetic fields up to 18.8 kOe were supplied by a 12-inch electromagnet. The sample was immersed in liquid helium and the temperature of the bath was reduced to 1.5° by pumping.

The data were taken on an X-Y recorder with its X-axis driven by a Hall probe. The magnetic field was calibrated by nuclear magnetic resonance above 2000 gauss and by a Bell Incremental Fluxmeter below 2000 gauss. Measurements were taken every few degrees of crystal orientation. The effects of tilting the magnetic field relative to the sample surface were studied by rotating the magnetic field about a vertical axis with the sample surface in a vertical plane. Other effects due to the direction of polarization of the microwave electric field E_{rf} were studied with the sample surface in a horizontal plane. However, cyclotron masses were measured with $\mathbf{H} \perp \mathbf{E}_{rf}$.

In the phenomenon of cyclotron resonance,[10] there are minima in the surface resistance close to $H = \omega m^* c/en$ where n is an integer, m^* is the cyclotron mass and ω is the applied frequency. According to Azbel' and Kaner,[11] the cyclotron mass may be determined from the positions of dR/dH maxima of the fundamental resonance or from the periodicity in reciprocal magnetic field. The latter method is better because corrections for the phase shift that occur for finite $\omega\tau$ are small.[12] However, in this experiment not sufficient subharmonics were visible to use this condition. The following procedure was used to reduce the data: Magnetic fields of dR/dH maxima were measured. For each orientation, cyclotron resonance of each carrier was determined by grouping its fundamental and subharmonic resonances. The cyclotron mass was calculated from the magnetic field H_0 of the fundamental resonance[12] from the relation

$$m^* = eH_0/\omega c. \tag{1}$$

If any dependence on the inclination angle of the magnetic field to the sample surface was noted, the mass was measured as a function of this angle to determine the value for the field accurately in the plane of the surface. For each sample surface, plots of m^* vs orientation were made. Four surfaces for each of the binary-trigonal plane and the binary-bisectrix plane were used. All of the carriers in a given plane were observed in a single surface. The results are not a composite of data taken on several surfaces where one carrier was observed in one surface and another in a different surface. The experimental error of mass values was due mostly to the width of resonances and to small misorientations of crystal surfaces.

III. Experimental results

Results for the binary-trigonal plane are shown in Figure 2. We measured cyclotron masses every few degrees of magnetic field direction in this plane. If the energy surfaces in the valence band are tilted by a few degrees,[4] one should observe closely related anisotropy in the masses of holes on the two sets of non-principal energy surfaces. For the binary-trigonal plane, these two sets of masses would coincide for surfaces with no tilt. We can

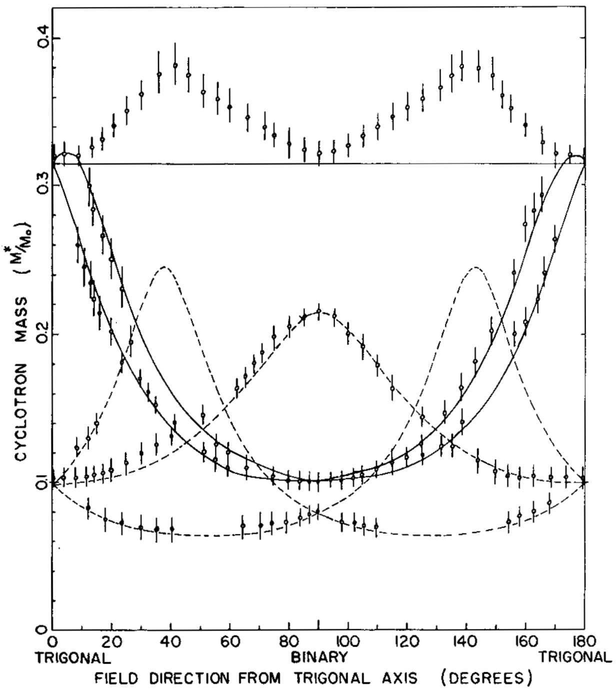

Figure 2 **Cyclotron mass versus magnetic field direction in the binary-trigonal plane of antimony.** *The solid and dashed curves are for holes and electrons, respectively, and are a plot of Equation (2) for the binary-trigonal plane using mass tensor components given in Table 1.*

identify a closely related anisotropy of two sets of masses which are therefore assigned to holes. These two sets of masses coincide in the trigonal direction at a value of $(0.32 \pm 0.01)m_0$. Since all hole masses are expected to coincide for a trigonally-directed magnetic field due to symmetry, the heaviest mass for each direction is also that of holes. These carriers are on the set of surfaces whose axis $1'$ is parallel to the binary axis. For these carriers, the resonance peak was dependent upon the angle of tip of the magnetic field to the sample surface. For magnetic field directions between 25° and 65° from the trigonal axis, the increase of the resonance magnetic field over that for an aligned field was approximately 10% per degree of tip and resonances broadened when the angle of tip exceeded about 3°. Similar effects due to magnetic field tipping have been observed recently in copper by Koch et al.[13] As a result of our study of field tipping effects, the magnetic field was aligned accurately along the surface for the measurement of cyclotron masses of holes on the principal surface in the valence band. The masses of Shoenberg carriers on the principal ellipsoids, which are those ellipsoids with the $1'$ axis along the binary direction, would be symmetric in the binary-trigonal plane with a maximum in the binary direction. One set of masses in Figure 2 has this symmetry. Therefore, the cyclotron mass along the $1'$ axis of Shoenberg ellipsoids is $(0.215 \pm 0.005)m_0$. The smallest masses in the binary-trigonal plane are assigned to electrons on the sets of non-principal Shoenberg ellipsoids.

The solid and dashed curves in Figure 2 represent the theoretical cyclotron masses for holes and electrons, respectively. They were determined using ellipsoidal models for both sets of carriers and the mass tensor components from the data. The cyclotron masses of the holes on the principal surface do not follow the corresponding theoretical curve and are the non-ellipsoidal carriers which have been measured by cyclotron resonance previously.[7]

The cyclotron masses observed in the binary-bisectrix plane are shown in Figure 3. In this plane, the angular dependence of mass of electrons and holes is very similar so that identification of carriers depends upon the analysis of data in the binary-trigonal plane. In the binary direction, we know from Figure 2 that the masses of electrons and holes for the principal surfaces are 0.215 m_0 and 0.32 m_0, respectively, and for the nonprincipal surfaces 0.080 m_0 and 0.097 m_0, respectively. Use of these masses

Figure 3 **Cyclotron mass versus magnetic field direction in the binary-bisectrix plane of antimony.** *The solid and dashed curves are for holes and electrons, respectively, and are a plot of Equation (2) for the binary-bisectrix plane using mass tensor components given in Table 1.*

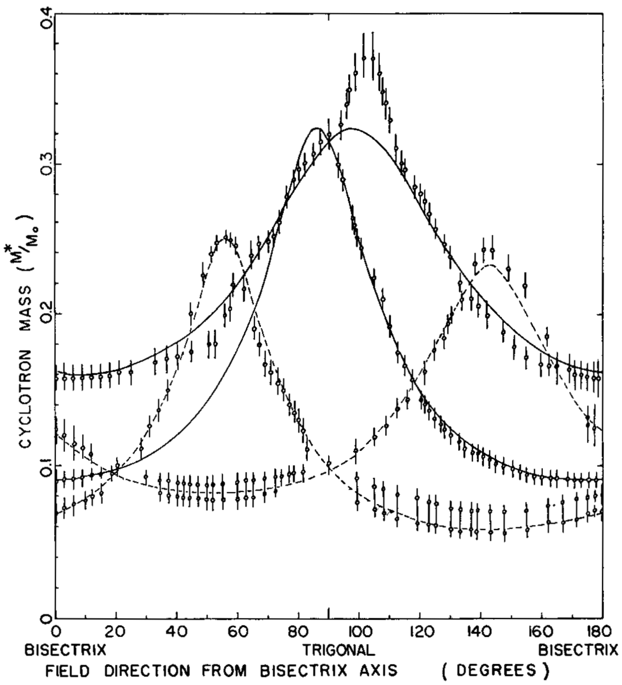

Figure 4 **Cyclotron mass versus magnetic field direction in the bisectrix-trigonal plane of antimony.** *The solid and dashed curves are for holes and electrons, respectively, and are a plot of Equation (2) for the bisectrix-trigonal plane using mass tensor components given in Table 1.*

leads to the identification shown in Figure 3: the masses of electrons and holes are close to the dashed and solid curves, respectively, which were calculated using an ellipsoidal model for each band.

Data for the bisectrix-trigonal plane were particularly necessary because the (2′, 3′) axes of the principal sets of energy surfaces in both bands lie in this plane. For the Shoenberg model, the masses $m^*_{2'}$, $m^*_{3'}$, and the ellipsoid tilt angle were measured previously[7] to be 0.055 m_0, $0.25m_0$, and 36°, respectively. When we assumed that resonance of holes was observed also in the bisectrix-trigonal plane and that their Fermi surface was tilted by only several degrees, we measured $m^*_{2'}$ and $m^*_{3'}$ for the valence band as 0.090 m_0 and 0.325 m_0, respectively. The data for the bisectrix-trigonal plane were obtained on two surfaces in the former experiment.[7] The cyclotron masses for the bisectrix-trigonal plane are shown in Figure 4.[14] Theoretical curves using the ellipsoidal model for electrons and holes are shown by the dashed and solid lines, respectively.

IV. Analysis and discussion

The cyclotron mass of ellipsoidal carriers for a magnetic field direction specified by the direction cosines $\lambda_{1'}$, $\lambda_{2'}$, $\lambda_{3'}$ is given by

$$m^* = \left[\frac{m_{1'}m_{2'}m_{3'}}{m_{1'}\lambda_{1'}^{\,2} + m_{2'}\lambda_{2'}^{\,2} + m_{3'}\lambda_{3'}^{\,2}}\right]^{1/2}. \qquad (2)$$

Masses $m_{1'}$, $m_{2'}$, $m_{3'}$ are the mass components along the principal axes of an ellipsoid in units of m_0, the free electron mass. A direct solution for the mass components was obtained in the following way from the cyclotron masses along the principal axes, $m^*_{1'}$, $m^*_{2'}$, $m^*_{3'}$. A computer calculation of Equation (2) for the three planes that were studied was compared with the experimental masses that were observed. In the case of electrons, this fit for all the planes was made by going through the above procedure for closely-spaced values of $m^*_{2'}$ and for values of the tilt angle of ellipsoids between 34° and 36°; this procedure was used because the accuracy of the measurement of $m^*_{2'}$ was reduced by neighbouring resonances.[7] The best fit was obtained using a value of $m^*_{2'} = 0.058$ and a tilt angle of 36° along with the observed values $m^*_{1'} = 0.215$, $m^*_{3'} = 0.25$. For the valence band, the observed values $m^*_{1'} = 0.315$, $m^*_{2'} = 0.090$, $m^*_{3'} = 0.325$ were used to determine the mass components and a computer calculation was run for closely spaced values of the ellipsoid tilt angle. The best fit was obtained for a 4° tilt angle. The mass components that were determined for the electrons and holes are given in Table 1. The theoretical curves for those values shown in Figures 2, 3, and 4 were calculated using the values in Table 1 with Equation (2).

The observed masses do support the ellipsoidal model of the Fermi surface for the conduction band to within the accuracy of this experiment. However, there are several reasons for concern. In the binary-trigonal plane, there were no resonances for mass greater than $0.2m_0$ that could be attributed to the electrons for directions of magnetic field 30°–50° and 130°–150° from the trigonal direction. Although our model predicts a mass in this region, a careful search did not reveal the presence of any reso-

Table 1 **Mass tensor components of electrons and holes of antimony in units of the free electron mass for the principal axes (1′, 2′, 3′) and for the binary, bisectrix, trigonal axes.**

	Electrons	*Holes*
$m_{1'}$	0.068	0.093
$m_{2'}$	0.92	1.14
$m_{3'}$	0.050	0.088
tilt angle	36°	4°
m_{11}	0.068	0.093
m_{22}	0.63	1.14
m_{33}	0.34	0.093
$\lvert m_{23}\rvert$	0.41	0.082

nance. However, all other portions of the electron curves in Figures 2, 3 and 4 are supported by cyclotron masses so that the present model of the electron Fermi surface appears to be satisfactory and resonances in the above region were probably attenuated in some way. Another area of concern is the explanation of the low masses in the bisectrix-trigonal plane. The small masses, which were originally attributed to holes,[7] are slightly larger than the smallest electron masses that were observed. However, if the former set of masses is evidence of carriers in a third band, they should be evident in other planes. Since there is no evidence in other planes in this experiment, we shall identify the low masses in the bisectrix-trigonal plane with Shoenberg carriers. Two sets of low masses reported previously could have been measured from a resonance which was split by the magnetic field tipping effect which has been discussed recently by Grimes and Kip.[15] The uncertainty in the low masses which this effect would introduce is shown in Figure 4.

There were three resonances of holes for magnetic field directions in the binary-bisectrix and binary-trigonal planes. This is direct evidence that there are three or six sets of energy surfaces in the valence band. Some orbits in this valence band have been observed by both the de Haas - van Alphen effect[3,4] and cyclotron resonance. These orbits are fitted to an ellipsoidal model satisfactorily. However, this model is not completely satisfactory for several reasons. The cyclotron mass of the principal surface with the magnetic field in the binary-trigonal plane differs from the theoretical curve by as much as 20%. The cyclotron mass of the nonprincipal ellipsoids near the trigonal direction in the bisectrix-trigonal plane is larger than that predicted by the ellipsoidal model.

Further evidence of the non-ellipsoidal shape of this energy surface is supplied by the limiting-point cyclotron resonance observed previously.[7] In this resonance, carriers at points on the Fermi surface where the electron velocity is parallel to the magnetic field contribute to the resonance.[10] Since the cyclotron mass at an elliptic limiting point equals $1/v_0K^{\frac{1}{2}}$, where v_0 is the Fermi velocity and K is the Gaussian curvature at the limiting point,[10] it can differ from the mass of the central section for a non-ellipsoidal surface. The masses at limiting points for the magnetic field in the binary-bisectrix plane are shown in Figure 5. The limiting point cyclotron resonance consisted of both a fundamental and subharmonics. It was identified as such because the resonance became unobservable when the magnetic field was more than 20° from the direction of the microwave electric field or when it was more than 1° from the sample surface. Both properties are necessary for cyclotron resonance at limiting points. The limiting point cyclotron resonance observed when the magnetic field was along the binary axis was shifted about 15% to lower magnetic fields, when the field was tipped $\frac{1}{2}$° to

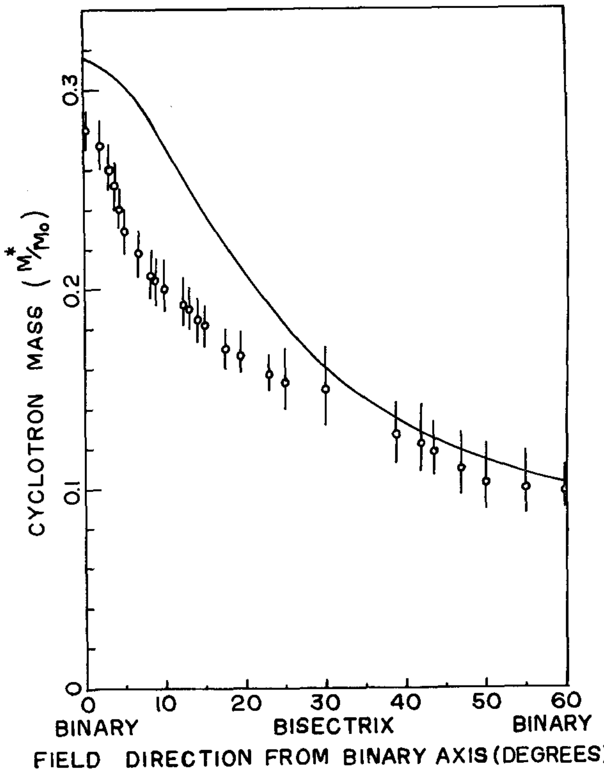

Figure 5 **Cyclotron mass at limiting points of the Fermi surface of holes versus magnetic field direction in the binary-bisectrix plane.** *The solid curve is a plot of Equation (2) for holes and for the binary-bisectrix plane using mass tensor components given in Table 1.*

the sample surface. Limiting point cyclotron resonance has been observed recently by Koch et al.[13] in copper. Their resonance for the magnetic field along the [001] axis also shifted to lower fields upon tipping the field. When the magnetic field was parallel to the binary direction, cyclotron resonance from the limiting point was observed without the normal resonance for a mass of 0.32 m_0. Since limiting point resonance is expected to occur without the normal resonance of the same surface when the magnetic field lies along a symmetry axis of the Fermi surface,[10] and since the mass 0.32 m_0 has been identified with holes in this experiment, the limiting point cyclotron resonance is attributed to holes. The limiting point cyclotron resonance indicates that the Fermi surface segment may be warped near the 1′ axis. The cyclotron masses observed with the magnetic field in the (1′3′) plane reach a maximum value with the field 40° from the 1′ axis. This may result from warping of cross sections in planes perpendicular to the 2′ axis. The non-elliptic orbits on the nonprincipal energy surfaces observed with the magnetic field near the trigonal axis are approximately 30° from the (1′3′) plane. The warped surface could change the cyclotron mass of these orbits also. Detailed calculations of cyclotron mass using the Cohen non-ellipsoidal model[16] for the bismuth type structure have been made. However, Cohen's models do not appear to be tenable.

A significant part of the present experiment has been the identification and measurement of masses of the principal surfaces of both bands, with the magnetic field in the binary-trigonal plane. The cyclotron mass along the 1′ axis was determined to be 0.215 m_0 for the electron ellipsoid and 0.32 m_0 for the hole ellipsoid. These masses for this direction were assigned to electrons and holes by conconsidering the symmetry of the cyclotron mass about the binary axis. Previous values of the masses or periods for this direction were not determined so directly, and the assignment of periods or masses to electrons and holes is in opposition to those of the present work. The results of a de Haas - Shubnikov experiment[17] became available during the writing of this paper. The values of Rao et al.[17] for cyclotron masses of electrons and holes for the magnetic field along the binary direction are not in agreement with those of the present experiment. However, their mass values for the magnetic field 11° from the bisectrix axis in the bisectrix-trigonal plane are in agreement, to within 5%.

V. Conclusions

Cyclotron resonance in antimony has the form predicted by Azbel' and Kaner when the magnetic field is aligned parallel to the sample surface. Cyclotron resonances from certain regions of the Fermi surface of antimony are affected by a small inclination of the magnetic field to the sample surface. Cyclotron resonance at limiting points of the Fermi surface was observed when the magnetic field was parallel to the microwave electric field.

It has been shown that cyclotron resonance in antimony arises from two bands of carriers. The simplest model of the Fermi surface of antimony supported by the data has three or six sets of ellipsoids tilted 36° from the trigonal direction in the conduction band and three or six ellipsoids tilted a few degrees from the trigonal direction in the valence band. There is the possibility that the Fermi surface may be more complicated than this model. Values of the mass tensor parameters of the ellipsoids of each band were determined from measured cyclotron masses. It was indicated that the ellipsoids in the valence band may be warped slightly. However, the resonances that indicated this warping could have been affected also by a very slight inclination of the magnetic field to the sample surface.

Acknowledgments

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Discussion

M. H. Cohen: Bloomfield, at Chicago, has recently worked out a detailed theory of cyclotron resonance in tipped magnetic fields. He finds, and this is substantiated by the experiments of Kip and his coworkers, that for the usual Azbel'-Kaner resonance to dominate it is necessary for the surface to be flat to within 0.1°, with a comparable requirement on field orientation. By the time tippings (or waviness) of order 1° to 2° occur, the contribution of the Azbel'-Kaner type of resonance to the surface impedance is negligible. Instead, contributions come from near the elliptic limiting point and an orbit near the central section. The former set up field sheets parallel to the surface and the latter undergo geometric resonances between these field sheets. Thus, grossly separated parts of the Fermi surface contribute comparably. It is possible that some of the complexities of the observed data are associated with these tilted-field effects. It is certainly of great importance to try to get surfaces flat to well within a degree.

W. R. Datars: The magnetic field was aligned parallel to the surface to within ½ degree for the measurement of cyclotron masses. However, we are concerned about the effects of tipping the magnetic field to the sample surface. The possibility does exist that cyclotron masses observed to indicate that the Fermi surface of the valence band is warped were affected by roughness of the sample surface.