

## Cyclotron Resonance in Silver\*

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Azbel'-Kaner-type cyclotron resonance has been used to examine the Fermi surface of silver. The types of resonances observed from a (110)-surface sample are very like those reported for copper. Resonances originating from orbits about the zone contact regions have been observed over a limited range of angles. Relatively strong signals have been obtained from orbits near the limiting points when the field lies nearly parallel to the [001] direction of the (110) surface. The two orbits reported in copper whose centers lie neither at the center nor the edge of the zone have been observed, and in addition a third orbit of this type has been identified and measured over a large range of angles. Data taken on a (100)-surface specimen (not available in the copper studies) have shown resonances due to both hole and electron orbits; these resonances are consistent with the previous knowledge of the geometry of the Fermi surface. The effect on cyclotron resonance signals of a magnetic field inclined with respect to the specimen surface has been investigated. Apparent shifts in the measured cyclotron mass as large as 50% per degree of field misalignment have been obtained. The similarity of a number of the signals to the peak-reversal phenomena observed in potassium and aluminum is discussed. Certain of the signals in fields inclined at large angles to the surface have yielded a measure of the neck size in excellent agreement with de Haas-van Alphen measurements.

## I. INTRODUCTION

IN order to examine the Fermi surface of silver, Azbel'-Kaner type cyclotron resonance has been used. It is the purpose of this paper to describe the detailed nature of these resonances. The present work closely parallels the re-examination of cyclotron resonance in copper recently reported by Koch, Stradling, and Kip,<sup>1</sup> both in the nature of the experimental work and in the general form of the resulting resonances. The equipment used was the same 68-Gc/sec spectrometer used in the copper study and in the examination of potassium and sodium.<sup>2</sup>

The geometry considered by Azbel' and Kaner<sup>3</sup> requires the magnetic field to lie parallel to the sample surface. In certain of the resonances to be described, the effect of slight misalignment of the field direction with respect to the surface on the position of the resonant field appears to be even more critical than that predicted by Azbel' and Kaner. (Similar behavior was observed for some orbits in copper.) Field misalignment may arise in two ways: either generally, because of incorrect field positioning, or locally, because of surface roughness on the metal samples. In general, the former would be expected to cause shifts in the observed positions of the peaks, while the latter would result in a broadening and a decrease in amplitude of the peaks, perhaps accompanied by a net shift in field position.

In our studies on silver, although tipping of the field direction with respect to the surface had, in some cases, a drastic effect on measured cyclotron masses, it was

generally true that the resonance series could be plotted as a straight line ( $1/H$  versus the subharmonic number) and that all phase shifts (nonzero intercepts of this straight line with the axes) were small and within the uncertainty of our measurements.<sup>4</sup> Our results therefore are described in terms of the cyclotron effective mass. The anisotropy of the cyclotron mass is consistent with Roaf's<sup>5</sup> detailed Fermi-surface model obtained from de Haas-van Alphen and anomalous skin measurements. The results of the present work have been interpreted in terms of Roaf's model wherever possible.

In the following section, a brief description of the experimental aspects of the measurements will be given, stressing mainly the manner in which the metal crystal specimens were prepared. Sections 3 and 4 deal with a description and discussion of the observed resonances as obtained from both (100) and (110) surfaces. The final section deals with the behavior of the signals in a magnetic field inclined with respect to the surface of the specimen.

## II. EXPERIMENTAL ASPECTS

In order to obtain the necessary mean free path for electrons, cyclotron-resonance experiments in metals are carried out on single crystals of high purity at liquid-helium temperatures. In the present work, the silver crystal forms one end wall of a cylindrical cavity designed to resonate at 68 Gc/sec in the  $TE_{111}$  mode. Though the current lines distributed over the end wall are not strictly linear in this mode, it has been estimated that the departure from linearity is only of

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<sup>1</sup> J. F. Koch, R. A. Stradling, and A. F. Kip, *Phys. Rev.* **133**, A240 (1964).

<sup>2</sup> C. C. Grimes and A. F. Kip, *Phys. Rev.* **132**, 1991 (1963).

<sup>3</sup> M. Ya. Azbel' and E. A. Kaner, *J. Phys. Chem. Solids* **6**, 113 (1958).

<sup>4</sup> This behavior under tipped field conditions in silver is somewhat inconsistent with results obtained by Koch *et al.* (see Ref. 1) in copper. In that work non-linear  $1/H$  plots resulted from slight tipping of the field, making statements regarding phase shifts imprecise. The difference in the two cases might be due to differences in the flatness or purity of the specimens.

<sup>5</sup> D. J. Roaf, *Phil. Trans. Roy. Soc. (London)* **A255**, 135 (1962).

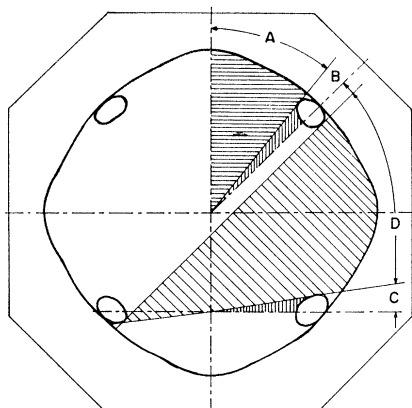


Fig. 1. Projection of the Fermi surface of silver as given by Roaf on the (100) plane. The lines represent the projections of the orbits at the limiting angles, while the shadings indicate the range of angles over which each orbit might be expected to exist. Only one half of the plane projections are shown, to avoid confusion.

the order of 5%.<sup>1</sup> To allow complete freedom in aligning the magnetic-field direction, two degrees of freedom have been provided. The crystal surface lies in a vertical plane; rotation of the horizontal external magnetic field about a vertical axis allows the field direction relative to the crystal surface, to be controlled to within 1 minute of arc. The crystal orientation may be changed with respect to the field direction by rotating the specimen about the symmetry axis of the cavity: The cavity body is split in the choke joint which couples the silver crystal to the cavity, and a gear arrangement allows the specimen to be rotated to any orientation. The reproducibility of such an angular setting is approximately  $\frac{1}{4}^\circ$ .

The spectrometer used to detect changes in the  $Q$  of the cavity is of standard design, except that a three-port circulator has been used in place of a magic tee. A groove in the side wall of the cavity serves to remove the degeneracy of the modes, and the coupling to each mode may be adjusted by means of a shorting plunger located at the bottom termination of the waveguide. The magnetic field is modulated (at 44 cps) so that the observed signal is proportional to the derivative of the power absorption.

The silver samples were prepared from 99.9999% grade silver supplied by Consolidated Mining Company of Canada. This figure does not include an estimation of gaseous impurities. The solubility of oxygen in silver is quite high,<sup>6</sup> the oxygen probably entering the lattice interstitially.<sup>7</sup> Fortunately, the diffusion rate of oxygen in silver is enormous<sup>7</sup> in the neighborhood of the melting point, so that most of it may be removed rather easily by vacuum annealing. It is therefore necessary that all melting and annealing of the silver take place in a relatively good vacuum. The mean free path of electrons

in the samples used was probably limited by the metallic impurities rather than by the residual oxygen content.

Single-crystal boules were cast in sooted Vycor boats under a vacuum limited by the vapor pressure of silver. The crystals were oriented using Laue back-reflection x-ray techniques, and the desired surface was cut using a Servomet spark cutter. The surface was lapped chemically using concentrated nitric acid as the reagent and finely woven Teflon cloth stretched over glass as the lapping surface. A few minutes of electropolishing then produced a sufficiently flat and strain-free surface for cyclotron resonance studies. Surface strains were examined using the divergent beam x-ray technique described by Koch<sup>8</sup>; sample purity was monitored by measuring the ratio of electrical resistivity at room and liquid helium temperatures using the eddy current decay method of Bean *et al.*<sup>9</sup>; and surface flatness was estimated using reflected light. A more complete discussion of the techniques of sample treatment and surface evaluation has been given by Howard.<sup>10</sup>

### III. (100) SURFACE

In this section we shall discuss the results of measurements taken with the magnetic field as nearly parallel to a (100) surface as allowed by the imperfect flatness of the specimen. The surface of this crystal was somewhat less flat than desirable, the average deviation from a plane surface being perhaps as large as 15 minutes of arc. The resistivity ratio ( $\rho_{300^\circ\text{K}}/\rho_{4^\circ\text{K}}$ ) was about 2300. Divergent beam x-ray studies showed the crystal structure to be less perfect than in the specimen used for the (110) surface, to be discussed below.

Figure 1 shows the angular ranges over which the four types of resonances might be expected to appear. Using the convention of previous papers, these are (A) *belly*; (B) *dog's bone*; (C) *four-cornered rosette*; and (D) *noncentral* orbits. All four of these types of orbits have been identified and the experimentally determined cyclotron masses are shown in Fig. 2.

#### Belly Orbits

Of the two harmonic series observed with the magnetic field along the [001] direction in the (100) surface, the one of lower cyclotron mass (A) is identified as a belly orbit, for which  $k_H=0$  ( $k_H$  being the component of the wave vector  $k$  in the direction of the applied field). The cyclotron mass ratio obtained along the symmetry direction is  $m^*/m_0=0.93\pm 0.01$ . The orbit identification follows from two characteristics: First, the signal appears strongest when the rf currents are oriented perpendicular to the field, and becomes very weak for

<sup>8</sup> J. F. Koch, Doctoral dissertation, University of California, Berkeley, 1962 (unpublished).

<sup>9</sup> C. P. Bean, R. W. deBlois, and L. B. Nesbitt, *J. Appl. Phys.* **30**, 1976 (1959).

<sup>10</sup> D. G. Howard, Doctoral dissertation, University of California, Berkeley, 1963 (unpublished).

<sup>6</sup> E. W. R. Steacie and F. M. G. Johnson, *Proc. Roy. Soc. (London)* **A112**, 542 (1926).

<sup>7</sup> Eifenauer and Müller, *Z. Metallk.* **53**, 321 (1962).

the parallel orientation, indicating that the principle component of motion of the resonating carriers lies perpendicular to the field. Second, the anisotropy of the cyclotron mass is in good agreement with that to be expected for the belly orbit based on the Roaf model of the Fermi surface.

One requirement for the observability of orbits is that the mass as a function of  $k_H$  (the component of  $k$  parallel to the field) be an extremum, so as to give a large number of electrons possessing very nearly identical cyclotron masses. Orbits for which  $k_H=0$  always possess such a mass extremum, by symmetry. However, these are not the only extrema present for a Fermi surface as complicated as that of silver.

The fact that signals from the belly orbits are strongest when the rf currents are normal to the magnetic field indicates that the electrons are traveling very nearly normal to the field while they traverse the skin layer. In the present orientation, the orbits with  $k_H$  very nearly zero are the ones whose electrons are traveling nearly normal to the field, and therefore their contribution dominates the observed signals. However, the observed cyclotron mass may differ slightly from the extremum effective mass value due to the contributions from neighboring orbits (for which  $k_H \neq 0$ ) which may possess slightly different effective masses. These neighboring orbits are less effective in the case of a rough surface than for a perfectly flat surface. The electrons in orbits having nonzero  $k_H$  have net drift velocity parallel to the magnetic field, and since parts of a rough surface possess tangents nonparallel to the field, the helical path of these electrons will carry them to regions where they no longer return to the surface layer.

Because of the presence of the necks in the Fermi surface, additional stationary orbits will exist for a field along the [001] direction, and these might be expected to contribute to the observed signals. For orbits of increasing values of  $k_H$ , the net drift velocity must reach a maximum, and then decrease and change sign owing to the increasingly negative contribution of the parts of the orbit nearest necks. The orbit just tangent to a neck will have electrons traveling parallel to the magnetic field at the point of tangency; the time to complete an orbit will become infinite and the cyclotron mass of such an orbit will also be infinite. If the cyclotron mass of the  $k_H=0$  orbit corresponded to a maximum, then minima in the mass would exist at some value of  $k_H \neq 0$ . One would expect, should the minima in the mass be near the stationary orbit, that another signal should be observed. The lack of this additional resonance signal is taken to mean one of two things: that the cyclotron mass of the  $k_H=0$  orbit is a minimum and therefore the only extremum, or that the signals from the  $k_H \neq 0$  minima are masked by the observed signals, either because their cyclotron mass is not sufficiently different or because the mass is changing

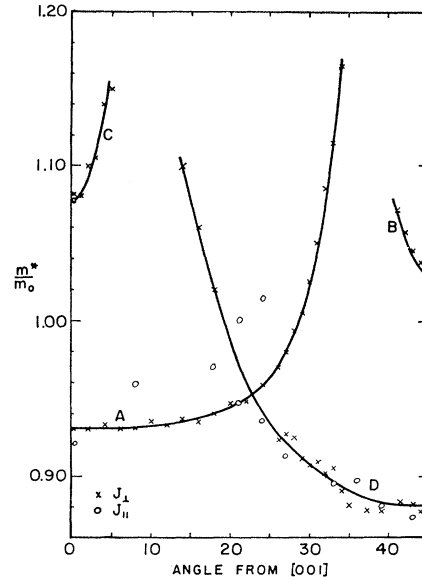


FIG. 2. Experimentally determined mass versus field direction for resonances observed in the (100) surface.

too rapidly with  $k_H$  to give sufficient intensity to the resonances.

As the magnetic field is rotated away from the [001] direction, as shown in Fig. 1, the mass infinities caused by the necks gradually reduce the allowed region of the belly orbits, until at about  $37^\circ$  such orbits can no longer exist. Hence a rapidly increasing mass, accompanied by a steadily decreasing signal amplitude, might be expected as the angle approaches this value. The actual signals have been followed experimentally to  $34^\circ$ , and are indeed observed to have a rapidly increasing mass near this angle, as shown in Fig. 2.

The other mass series observed, (C), as shown in Fig. 2, gives a cyclotron mass ratio of  $1.08 \pm 0.01$  at the symmetry axis. This is a somewhat weaker signal which is little affected by the direction of the rf current relative to the magnetic field. It has been identified as arising from four-cornered rosette orbits, and will be discussed below.

#### Noncentral Orbits

With the field along the [011] direction ( $45^\circ$  from the [001] direction) two other series have been observed. The higher mass signal (B), with a cyclotron mass ratio of  $1.03 \pm 0.01$  measured along the axis, is identified as arising from the dog's bone orbit, to be described below. This is the weaker of the two series and is enhanced when the rf current is normal to the applied field. The stronger series, (D) which gives a cyclotron mass ratio of  $0.88 \pm 0.01$  near the axis, is not much affected by changing the rf current from normal to parallel to the field direction.

These latter signals, attributed to belly orbits which are noncentral (that is, for which  $k_H \neq 0$ ), have been

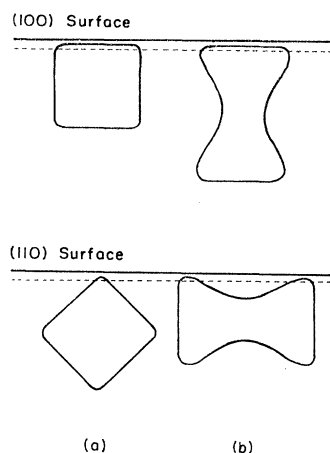


FIG. 3. The approximate cross section of (a) the four-cornered rosette and (b) the dog's bone orbits, showing the relative orientations of each with respect to the (100) and (110) surface in real space.

observed with the rf current both parallel and perpendicular to the magnetic field direction over about a  $20^\circ$  interval, as is shown in Fig. 2. At angles smaller than about  $26^\circ$  from the  $[001]$  direction, the signals observed with the rf current normal to the magnetic field become inseparable from those of the belly orbits, the resultant trace showing somewhat broadened peaks. A few peaks believed to belong to this second series have been resolved between  $14^\circ$  and  $18^\circ$ , though their amplitude is extremely small compared to the dominant belly orbit signals.

The fact that these signals could be observed more or less equally with either parallel or perpendicular rf polarization is in good qualitative agreement with our identification of the signals as due to noncentral belly orbits, since these orbits would have appreciable components of velocity in the field direction. The anisotropy of the cyclotron mass and its disappearance at minimum angles somewhat greater than  $10^\circ$  from the  $\langle 001 \rangle$  axis further corroborates our identification. At the latter angle, the plane in  $k$  space of the orbits under discussion would be tangent to two necks and the orbits would therefore possess an infinite mass, giving rise to no signal.

#### Hole Orbits

Two hole orbits have also been observed in the (100) plane, the *four-cornered rosette* (C) near the  $\langle 001 \rangle$  axis and the *dog's bone* (B) near the  $\langle 011 \rangle$  axis. The shape of these orbits is shown in Fig. 3. In each, the mass increases rather rapidly with angle away from the symmetry axis. (See Fig. 2.) This behavior is to be expected, since there are once again mass infinities at the limiting angles caused by the perturbation of the velocity direction in the neck regions.

It is, at first thought, difficult to see why the masses of these orbits should be larger than the belly mass. The path length of the central dog's bone orbit is very nearly the same as that of the belly orbit; in fact, as a glance at the (110) projection in Fig. 4 will show, it

differs only in the neck regions. Also like the belly, it has no component of velocity parallel to the field. The larger mass must therefore come from smaller velocities at some points on the dog's bone orbit. The necks are believed to have velocities smaller by perhaps as much as a factor of two, as will be discussed in Sec. 4. It is possible that the mass increase due to the necks is sufficient to explain the observed mass of the dog's bone orbit.

The four-cornered rosette has a still larger cyclotron mass, despite the fact that the projection of this orbit is considerably smaller than the other orbits whose resonances have been observed in this surface. However, the rosette orbit is not planar, the side portions being alternately directed upward and downward at  $45^\circ$  to the projection plane. The actual length of the orbit is greater than that of the projection by very nearly a factor of  $\sqrt{2}$ . Since the electrons are not moving normal to the magnetic field while traversing the skin, they would be expected to be observable with the rf current directed parallel to the field as well as with it normal to the field. The relatively strong resonances observed with the rf current parallel to the field are therefore easily explained.

A final point regarding the hole orbits should be mentioned. Since each is centered about a major symmetry axis that is also contained in the (110) surface, one might expect to find, among the resonances for the latter surface, signals resulting from hole orbits. Signals attributable to these hole orbits have in fact been found in the (110) surface, but they are extremely weak. The lower amplitude is thought to be due to the relative geometry of the orbits with respect to the different surfaces. As may be seen from Fig. 3, large portions of each orbit lie within the skin layer of the (100) surface, while for the (110) surface the orbits enter the skin only while traversing the necks. The smaller radius of curvature in the latter case results in the conduction

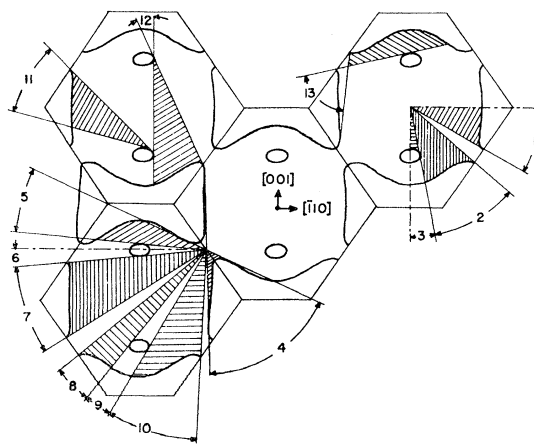
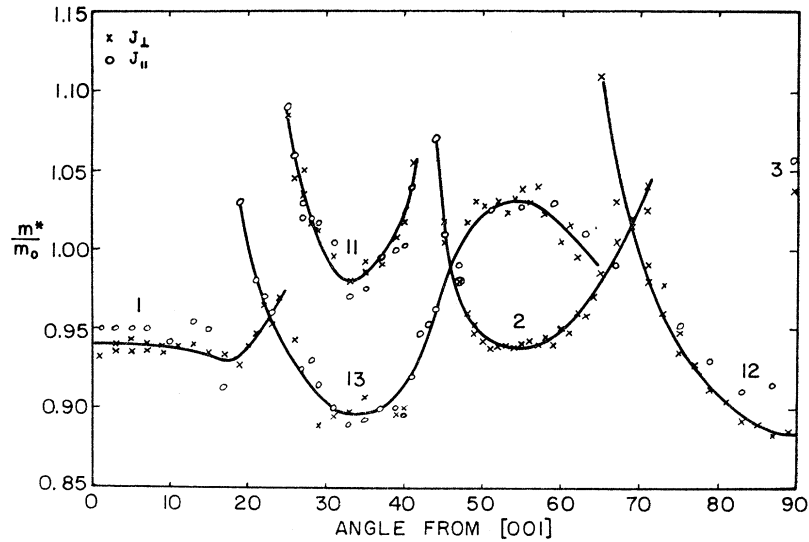


FIG. 4. Projection of the Fermi surface of silver on the (110) plane. Symbols are as in Fig. 1.

FIG. 5. Experimentally determined masses near the free-electron mass versus field direction for resonances observed in the (110) surface.



electrons spending a relatively shorter period of time exposed to the rf currents in the skin, so that they are correspondingly less effective in absorbing energy. Azbel<sup>7</sup> and Kaner<sup>8</sup> have included this effect in their general surface-impedance integral by incorporating the Gaussian curvature as a weighting factor.

#### IV. (110) SURFACE

The major experimental effort of this investigation was devoted to a study of the (110) surface. The crystal used possessed a resistivity ratio of about 2300, as did the other crystal. However, the uniform nature of the Laue spots obtained from the x-ray analysis indicates that the lattice was not appreciably strained. The resolution of an optical image reflected in the surface of this sample corresponds to a mean deviation from a planar surface of not more than 5 minutes of arc over the region in which the rf fields are appreciable, indicating that this sample possessed a surface more nearly planar than did the (100) surface.

A much more imposing array of resonances were found in the (110) surface than in the (100) crystal. The angular regions over which some of the possible orbits might be expected to appear are shown schematically in Fig. 4. The experimental data yielding cyclotron masses near that of the free electron value are shown in Fig. 5, while those of nearly twice this mass are shown in Fig. 6. There are, in addition, light masses observed in a number of orientations, corresponding to *neck* and *limiting point* orbits.

##### Neck Orbits

Orbits around the necks in silver have yielded very weak resonance signals. Fundamentals (that is, derivative maxima for which  $\omega_{rf} = \omega_c$ ) have not been resolved, because subharmonics of series with larger masses

usually occur at nearly the same field. In fact, many of the subharmonics of the neck series are obscured by subharmonics of series of larger mass.

Useful signals from neck orbits were obtainable only between 40° and 70° from the [001] direction. For most angles in this region it was possible to resolve a few subharmonics of the neck series at low fields, where the subharmonics of higher mass series have dropped to a sufficiently small amplitude. A mass ratio of  $0.27 \pm 0.03$  has been obtained from these low-field subharmonics. Within the accuracy of the data, no anisotropy in the mass was detectable over the rather narrow range of angles available. The position of the higher field subharmonics could be approximately located for a number of directions, making it possible to establish the order of the low field peaks. It should be emphasized, however, that the signal intensities were considerably smaller than those observed for the neck orbits in copper,<sup>1</sup> and that the mass obtained is subject to considerable error.

Shoenberg<sup>11</sup> has determined only two masses in silver, by measuring the temperature variation of the amplitude of the de Haas-van Alphen effect. One, presumably corresponding to a belly orbit, was taken 13° from the <001> axis in a plane 5° from the (110); the mass ratio obtained was  $m^*/m_0 = 0.63 \pm 0.03$  for a temperature range 1.1 to 2.8°K. This is surprisingly low compared to our minimum value of 0.93. The other mass is that of the neck orbit, taken along a [111] direction, and is reported as  $0.35 \pm 0.01$  in the range 1.2 to 2.1°K, somewhat larger than our result quoted above. These de Haas-van Alphen masses were obtained from pulsed-field measurements, where eddy-current heating may cause serious errors in the determination of effective mass, since these measurements depend upon the variation of signal amplitude with temperature. More

<sup>11</sup> D. Shoenberg, Phil. Trans. Roy. Soc. (London) A255, 85 (1962).

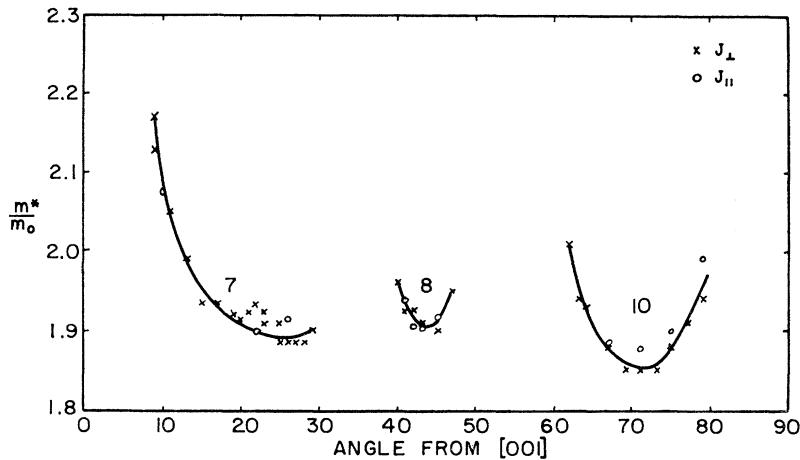


FIG. 6. Experimentally determined mass versus field direction for the two-zone extended orbits observed in the (110) surface.

recent measurements of this type taken in a steady field<sup>12</sup> have yielded a value of  $m^*/m_0 = 0.39 \pm 0.02$ . The reasons for the differences between these and our measured cyclotron mass are not understood.

The neck-orbit mass, as determined by either the de Haas-van Alphen or cyclotron resonance methods, is rather larger than would have been expected on the simplest criteria involving the known geometry of the Fermi surface. The neck radius determined experimentally by Shoenberg<sup>11</sup> is  $0.137 k_F$ ; if a constant velocity over the entire Fermi surface is assumed, this radius would lead to an extremal mass of about  $0.15 m_0$ , as compared to our measured cyclotron mass of  $0.27 m_0$ . Even though the measured cyclotron mass may not be accurately the extremal mass (because of contributions to cyclotron resonance from the larger mass nonextremal neighboring orbits) still it is not reasonable to attribute much of the discrepancy to the effect of neighboring orbits. It is more probable that the Fermi velocity is smaller in the zone contact regions than it is elsewhere on the surface. Such a decreased velocity would raise the value expected for the extremal mass; it would also be consistent with the large cyclotron mass values observed for the hole orbits, as mentioned in the preceding section.

Our observations of neck orbits in silver are rather different from those found in copper,<sup>1</sup> but the differences are not surprising in view of the contrast between neck geometries according to Roaf's model.<sup>5</sup> Thus both the lower intensity and narrower angular regions over which neck orbits were observable in silver, compared to copper, can be explained on the basis that the neck area in silver is smaller than in copper. The smaller area would imply fewer extremal orbits and in addition, a more rapid variation of mass with  $k_H$ . Thus at angles away from the  $[111]$  symmetry direction interference between orbits of different mass would be expected to be more serious than for the longer cylinder of the copper neck, with consequent reduction of signal intensity.

<sup>12</sup> A. S. Joseph and A. C. Thorsen, Phys. Rev. Letters 13, 9 (1964).

### Limiting-Point Resonances

As in the case of tin and copper,<sup>1</sup> a limiting-point<sup>13</sup> resonance series has been seen. In silver, as in copper, these resonances occur with the field near the  $[100]$  direction in the (110) surface. As expected, this series was observed only when the rf currents were directed parallel to the magnetic field, in the direction of the carrier motion in the specimen surface. The amplitude of the limiting point signals in silver was greater than in the copper experiments, presumably because of the improved flatness of the surface of the silver crystal. We were able to follow the signals through about  $\frac{1}{3}^\circ$  of field tipping with respect to the surface. Over this angle the measured cyclotron mass was found to vary linearly at the rate of 50% per degree. The maximum tip angle for which signals were seen is in good agreement with expectations based on the criterion that the signal will disappear when the angle of tip is so great that carriers will spiral so far into the metal in one cyclotron period that they will appear only once within the skin depth. This criterion leads to a critical angle given by  $\theta = \omega_c \delta / 2\pi V_F$ , where  $\delta$  is the rf skin depth,  $\omega_c$  is the cyclotron angular frequency, and  $V_F$  is the Fermi velocity. Reasonable estimates of the quantities involved lead to a critical angle of some 20 minutes of arc, in good agreement with our results.

With the field in the plane of the surface, the signals could be followed through an angle of about  $15^\circ$  on each side of the  $\langle 001 \rangle$  axis; over this range the mass does not vary detectably. The value obtained was  $m^*/m_0 = 0.42 \pm 0.01$ ; this is somewhat smaller than would be expected from the relatively small distortions from a spherical Fermi surface, along the  $\langle 100 \rangle$  axes given by Roaf.<sup>5</sup>

<sup>13</sup> A limiting point is a point on the Fermi surface whose normal is parallel to the applied field direction. Orbits of carriers near a limiting point are helical, with a large fraction of their total velocity directed along the helix, parallel to the field. Resonance signals can be expected if a sufficiently large area of the Fermi surface can be represented by a portion of an ellipsoid, giving large enough population of carriers with similar mass.

It would be expected that the limiting-point resonance should have been observable in the (100) surface specimen. Our failure to observe the resonance in that crystal was probably due to the greater roughness of that surface, as mentioned previously. Thus, from the resonance data itself, we estimate that the residual roughness of that surface was not significantly better than the 15 minutes of arc previously estimated by other means. By the same criterion, the (110) surface would appear to be flat to about 3 minutes of arc, since this much change in field inclination was found to cause a detectable change in the resonances.

#### Masses Near $m_0$ in (110) Surface

Five series of masses with values very near the free-electron mass have been identified. Of these, the series (1) (Figs. 4, 5) near the (001) axis is the same belly series (A) that was observed in the (100) surface, except that a different portion of the orbit lies in the skin depth. The cyclotron mass ratio measured with the field along the (001) axis is  $0.94 \pm 0.01$ , in good agreement with the value of the cyclotron mass obtained from the other surface. Series (2) also arises from a similar set of orbits, distributed symmetrically about a central section. Along the  $[\bar{1}11]$  direction a mass ratio of  $0.94 \pm 0.01$  was measured for this series also. The remaining three series have been assigned to non-central groups of orbits. Series 12, found with the field near the  $\langle 110 \rangle$  axis, is identical to the noncentral series (D) observed in the (100) plane, with a measured mass ratio of  $0.885 \pm 0.005$ , agreeing well with the value obtained from the (100) surface crystal. Series (11) is a very similar series, but with a different combination of necks limiting the range of orbits. A minimum mass ratio of  $0.98 \pm 0.01$  has been measured along the  $[\bar{1}12]$  direction. Since all four of these series have essentially the same variation of mass with angles as the series (A) and (D) in the preceding section, and all four have been observed in copper,<sup>1</sup> no further discussion of them need be given. The fifth series (13) has not been observed in copper and will therefore be considered in detail.

We have found that only one set of signals appears near the  $\langle 111 \rangle$  axis when the rf current is applied parallel to the magnetic field. These signals are thought to arise from the noncentral series of orbits (13) shown in Fig. 4, with the observed mass anisotropy given in Fig. 5. The signals observed have been associated with the orbits shown on the basis of the mass anisotropy found and because they were seen with the rf current parallel to the applied field. This identifies them as non-central orbits and thus distinguishes them from the central series (2) orbits which are seen only with the rf current normal to the field. The resonances of series (13) disappear rapidly as the magnetic field is inclined slightly to the surface. The signals were at first thought to arise from hole orbits passing through six necks—the

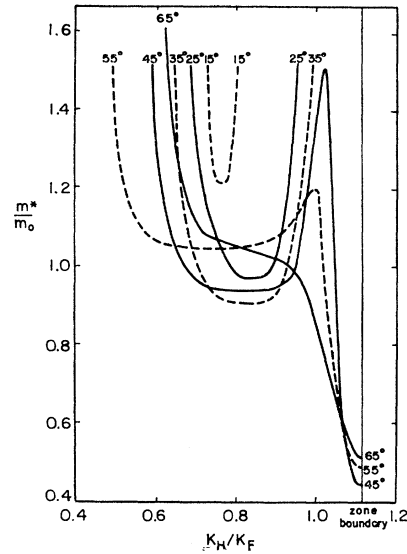


FIG. 7. A sketch of the probable mass as a function of  $k_H$ , obtained from the Roaf model, for orbits contributing to the type (13) mass series. The angles give the field direction relative to the (001) axis.

six-cornered rosette series (9). However, the signals of series (13) exist over a larger angular region than is allowed by the Roaf model for the six-cornered rosette.

Over at least part of the region of the Fermi surface from which series (13) is thought to arise there is a continuous monotonic variation of mass with  $k_H$  from the neck orbit at the zone boundary to the mass infinities introduced by certain of the necks. However, at angles less than about  $60^\circ$  from the (001), the variation ceases to be monotonic, with a maximum appearing in the mass due to the "shoulder" near the neck. The new mass minimum thus introduced is believed to be responsible for the mass series (13). Figure 7 shows a sketch, based on the geometry of the Roaf model, of a possible variation of mass with  $k_H$  for a number of different orientations of the field. The mass maximum is probably very narrow, and any resonances arising from it are undoubtedly too weak to be observed. Rapid mass variations near the maximum would tend to weaken the resulting signals still further.

Several aspects of this mass series are worthy of mention: (a) This is the only orbit observed in silver for which there exists no stationary orbit; the velocity is at every point directed so that its component along the field direction always has the same sign. (b) The behavior near the (001) axis should be that of an increasing mass as the field direction approaches the (001) axis, since the necks are limiting the orbits; such an increase is indeed observed. (c) Near  $55^\circ$ , where the inner limits shift from one neck to another, the band would be expected to be broadest. The signals of this region would be expected to have the least sensitivity to inclination of the magnetic field since here  $k_H$  is at a minimum and

the drift velocity of the inner orbits would be expected to be relatively small. The signals do seem slightly less sensitive to tip of the field in this region; perhaps the weak signals Koch, Stradling, and Kip report for copper<sup>1</sup> in this orientation could be due to this  $k_H \neq 0$  orbit instead of the six-cornered rosette as they have suggested. Their rougher surface could be responsible for obscuring the remainder of this orbit.

### Extended Orbits

Another very important group of orbits is the one whose orbits undergo two or more Bragg reflections in each cycle of motion in a magnetic field. In an extended zone picture, these orbits are shown as passing through one or more zone boundaries and are therefore often referred to as *extended orbits*. One class of these orbits have a length very nearly equal to an integral multiple of the length of the belly orbit, and therefore would be expected to exhibit a cyclotron mass very near an integral multiple of the belly mass.

In silver, three orbits of this type have been identified, and these each possess a cyclotron mass very nearly double the belly mass, as shown in Fig. 6. Peaks corresponding to orbits passing through more zones may be present, but it has not been possible to obtain any consistent mass measurements on them. The multizone orbits would be expected to exist over more limited angles in silver than in copper because of the smaller neck diameter. At the same time, the intensity of such orbits might be expected to be smaller, both because there are fewer electrons in each group and because the  $\omega_c \tau$  of the silver sample was lower than that of the copper sample.<sup>2</sup>

The masses of the two-zone orbits are much as expected; with two exceptions they correspond directly to those reported for copper.<sup>1</sup> These exceptions are: (a) Mass series (5) has not been observed in silver. The reason is undoubtedly the same as was invoked to explain the failure to observe the neck mass in the parallel mode of rf polarization, namely, that the mass is changing so rapidly as a function of  $k_H$  that the signals are greatly reduced by the destructive interference of mass spread. (b) Mass series (7) does not increase as the limit at  $31\frac{1}{2}^\circ$  is approached. It is interesting to note that actually very little increase is found in the same type of orbit in copper. From Fig. 4 it may be seen that the distortion in this orbit caused by the neck is localized very near the cutoff point, thus making the change so abrupt that it probably cannot be detected. The belly-mass series (1), limited by the same necks, also shows little increase in mass as the limiting angle of  $27\frac{1}{2}^\circ$  is approached.

## V. EFFECTS OF INCLINED FIELDS

As in the earlier studies of copper,<sup>1</sup> we have investigated in some detail the effects of inclining the magnetic

field direction with respect to the sample surface. As in copper, the resulting signals vary in nature from those which are only slightly affected in field position and amplitude by increasingly nonparallel field alignment to cases where large shifts are observed. Still other signals show a splitting of absorption derivative peaks into two components as the field is inclined. A qualitative understanding of these effects is possible, though certain details remain somewhat obscure. In view of the similarity to effects observed in copper, we shall compare and contrast our findings with the previously reported results found in copper.

In the work we are reporting on silver, it has been possible to characterize the shifting of derivative peak maxima in terms of variation of the cyclotron mass. This is possible because, within the experimental uncertainty, the peak positions plotted in units of  $1/H$  against subharmonic number have given straight lines passing through the origin. This contrasts with the work on copper and tin,<sup>1</sup> where in many cases results with inclined fields gave nonlinear plots and evidence of appreciable phase shifts (failure of the extrapolated lines to go through the origin). The reason for the contrast between our experience with silver and the findings for copper and tin is not well understood.

### Signals Varying Little upon Field Inclination

As is to be expected, signals from stationary orbits (those with no net drift velocity parallel to the field) are least affected by field inclination. For example, the dog's bone and four-cornered rosette orbits in the (100) surface appear to be only mildly affected by field inclination. These masses vary with inclination angle at the same rate as with field angle in the surface. However, both series of signals are rapidly reduced in amplitude with increasing field inclination, so that the angular region over which data may be taken is rather small. Signals from the four-cornered rosette have been followed to an angle of inclination of  $3^\circ$ , which is sufficiently far to determine that the rate of increase with field inclination is slightly greater than 1% per degree, in good agreement with the in-surface data given in Fig. 2.

The type (2) stationary orbit seen with the field direction in the vicinity of the  $\langle 111 \rangle$  axis of the (110) surface is also little affected as the field is inclined. This group of orbits is about a central section and is limited to small values of  $k_H$  by the necks. The signals exhibit no measurable change in either amplitude or cyclotron mass through the first  $5^\circ$ ; in the next  $10^\circ$  the mass increases and the amplitude decreases gradually. At  $15^\circ$ , the cyclotron mass ratio has reached 1.05 (compare with the in-surface data shown in Fig. 6). The mass variation observed upon inclination of the field is very similar to the angular variation in the surface, the differences probably being due to the different crystallographic plane containing the range of field directions.



Central orbits limited by necks, similar to the type (2) orbits, are responsible for a number of large angle resonance series, which may be seen with fields inclined as much as  $80^\circ$  from the sample surface. Similar large angle resonances have been reported for copper.<sup>1</sup> These signals are particularly useful in establishing accurate experimental estimates of the diameter of the Fermi surface necks, as has been noted in the case of copper.

Large-angle resonances have been observed in the (110) plane normal to the (110) sample surface. Between  $24^\circ$  and  $27^\circ$  from the (001) axis the signals are quite strong, with the cyclotron mass ratio increasing with angle from a value near 0.90 to a value near 1.04; these signals die out at about  $27\frac{1}{4}^\circ$ . Strong signals also appear beyond  $43\frac{1}{4}^\circ$  of inclination, then decrease in amplitude until little can be seen beyond  $48^\circ$ . Some signals which appear to belong to a mass ratio near 2 are also seen over a narrow range of angles in the latter interval. From the angular position for the disappearance of signals on each side of the neck, we determine that the total angle which the neck may subtend is not over  $16^\circ$ .

The strong signal region near  $27^\circ$  of inclination has been observed on each side of the (110) surface, and by comparing the signals the position of the symmetry plane can be found. This plane is found to differ from the surface by about  $1^\circ$ ; the difference is consistent with the slight misorientation of the sample as determined by back-reflection x rays.

Another pair of strong signal regions has been found in the (001) plane normal to the (110) sample surface. Signals with a cyclotron mass ratio of about 1.2 appear at about  $9\frac{1}{2}^\circ$  of inclination from the  $\langle 110 \rangle$  axis, then decrease rapidly in mass and in amplitude until they fade away about  $2^\circ$  later at a mass ratio of about 1.0. This signal region is also symmetric about the crystallographic plane instead of the surface. An identical set of signals has been observed between  $78^\circ$  and  $80\frac{1}{2}^\circ$  of inclination from the symmetry plane, yielding the same values for the mass ratio. These regions are crystallographically equivalent, and correspond directly to the increasing mass portion of the belly orbit (A) seen in the (100) surface. The resulting width,  $19^\circ$ , can be compared to the neck diameter using a scale factor ( $\cos 35.3^\circ$ ). The value then obtained is  $15.5^\circ$ , as compared to  $16^\circ$  for the previous case. The value obtained by Shoenberg<sup>11</sup> and used by Roaf<sup>5</sup> is about  $14.5^\circ$ , in excellent agreement with the angles measured above.

Each of the types of orbits described above are limited to rather small values of  $k_H$ . The net drift velocity in each case is undoubtedly quite small, and therefore no appreciable Doppler shifting due to velocity components parallel to the field (see below) would be expected to occur. The resonances all seem to depend upon crystal orientation, and are not affected by the exact location of the surface.

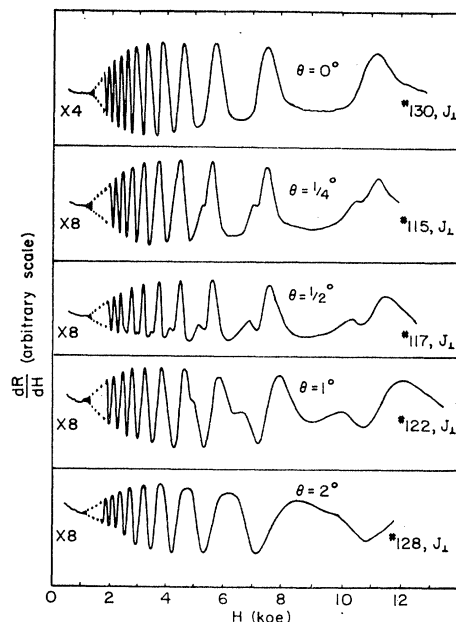


FIG. 8. Experimental traces of the belly-orbit resonances for several angles of tip from the (001) axis of the (110) surface.

#### Signals with Large Mass Shifts

The extreme sensitivity of the limiting point resonance to inclined fields has already been mentioned. Since the observed cyclotron mass of this orbit does not change with orientation as long as the field remains parallel to the surface, the observed shift must be completely due to a change in the geometry of the problem. Koch, Stradling, and Kip<sup>1</sup> have suggested that the electrons actually experience a frequency that has been Doppler-shifted.

In an inclined field, carriers moving with a net velocity along the field will appear at different depths each time they enter the skin. Since both the amplitude and phase of the rf fields vary with depth into the metal, such carriers will be resonant to a Doppler-shifted frequency. An expression has been given for the normal skin-effect region by Miller and Haering,<sup>14</sup> which can be written in the form

$$\Delta m^*/m^* = v_D \theta / \omega \delta,$$

where  $\delta$  is the skin depth,  $\omega$  the experimental frequency, and  $v_D$  the net drift velocity. If we use the Fermi velocity of a free electron,  $v_F = 1.4 \times 10^8$  cm/sec, for the drift velocity, and assume a skin depth of the order of  $10^{-5}$  cm, we obtain a value for  $\Delta m^*/m^*$  of about 55% per degree of arc. This is not very different from the 50% per degree which we have measured for the limiting point resonances. Moreover, the experimental variation is observed to be linear in  $\theta$ , as the above equation predicts.

<sup>14</sup> P. B. Miller and R. R. Haering, Phys. Rev. **128**, 126 (1962).

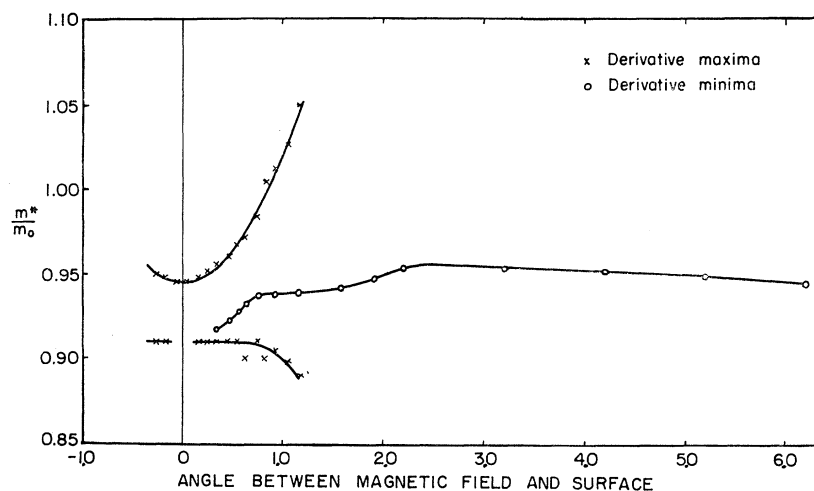


FIG. 9. Variation of the measured mass for small angles of field inclination from the  $\langle 001 \rangle$  axis of the  $\langle 110 \rangle$  surface. Results for both maxima and minima in the derivative of the surface impedance are shown.

Of course, since the Fermi surface has inversion symmetry, there will always be an identical array of carriers moving in each direction, so that an additional mass shifted toward lower fields would be predicted also. The reason that one velocity direction should be favored over the other is not clearly understood. It should be pointed out, however, that the carriers moving in each direction are not equivalent. Those electrons with a net drift away from the surface can carry information about the rf field deeper into the metal than it can extend in the absence of a magnetic field; those electrons with a net drift toward the surface simply run into it and are scattered. A more detailed analysis of the penetration of the field is necessary to clarify this question.

The noncentral series (13) responds to inclined fields in a manner very similar to the limiting point resonance. In the region near the  $\langle 111 \rangle$  axis, the signal maxima have been observed to move toward higher field with increasing field inclination, apparently without splitting, at about 48% per degree of arc. These signals lie just above those of the belly series in field position, making it difficult to detect any branch moving toward lower fields. The signals have been followed through about 30 minutes of arc, over which the shift in mass appears to be linear with angle. The rate of change, on the basis of the Doppler-shift equations would suggest that the net drift velocity of these electrons is not very different from the Fermi velocity, which on the basis of the position of this orbit on the Fermi surface is reasonable.

#### Signals Exhibiting Peak Splittings

The signals near the  $\langle 100 \rangle$  and  $\langle 110 \rangle$  axes of each surface show still another behavior upon field inclination: they split into two components. Effects in the  $\langle 100 \rangle$  surface are not clearly defined, both because of the rougher surface of that sample, and because of the presence of additional signals from the hole orbits. The

clearest data have been taken near the  $\langle 001 \rangle$  axis of the  $\langle 110 \rangle$  surface, and it is the behavior of signals in this region which will be examined mostly closely.

Figure 8 shows the resonances obtained at several angles of field inclination near the  $\langle 001 \rangle$  axis. The behavior may be summarized as follows: In the surface a single mass series is observed. The peaks move slowly to higher fields as the magnetic field is inclined out of the surface; at the same time, small shoulders separate themselves from the main series, roughly maintaining their field position as the other series appears to move away. All the peaks broaden as the field is inclined farther, while the derivative minima which have appeared between the sets of peaks grow deeper and deeper. By the time the field is  $2^\circ$  from the surface, only these minima remain, and the resultant trace looks almost exactly like that of the series in the surface, both in peak position and in line shape, except that the curve is inverted and the former maxima are now the derivative minima. Figure 9 is a plot of the masses obtained using both derivative maxima and derivative minima. The minima are found to be quite periodic and to plot with zero phase shift from  $\frac{1}{4}^\circ$ , where they appear, to  $6^\circ$ , beyond which the signals become very weak.

The behavior of this set of signals to slightly inclined magnetic fields is suggestive of the peak reversal phenomena observed in potassium and sodium by Grimes and Kip,<sup>2</sup> and discussed at length in terms of current sheets and interacting carriers by Spong and Kip.<sup>15</sup>

The behavior of the signals near the  $\langle 110 \rangle$  axis of the  $\langle 110 \rangle$  surface to inclined fields is similar in nature to that of the  $\langle 001 \rangle$  axis, except that the changes occur more rapidly. The peaks again split, with the one of higher mass shifting upward and the one of lower mass appearing as a shoulder which does not change its position appreciably. The signals begin to weaken, however, after the first  $\frac{1}{2}^\circ$ , before the minima have be-

<sup>15</sup> F. W. Spong and A. F. Kip, Phys. Rev. **137**, A431 (1965).

come deep enough to give the curve the inverted appearance as occurred near the  $\langle 001 \rangle$  axis.

### Light Mass

One of the most curious aspects of the study of the effects of inclined fields near the  $\langle \bar{1}10 \rangle$  axis of the (110) surface is the appearance, at about  $1^\circ$  of inclination, of a series of peaks corresponding to a mass ratio near 0.26. This series has been followed to about  $7^\circ$  from the surface and there is little variation in the observed mass over this interval. Peaks corresponding to subharmonics 2 through 7 can be resolved from the components of the other series, and they are quite periodic with no phase shift. No section of the present model of the Fermi surface for silver seems capable of explaining such a light mass in this direction. Inclined-field studies in silver have been conducted only in the major symmetry planes normal to the surface, so that the region of solid angle over which this resonance may exist is not known. The recent studies in copper<sup>1</sup> did not include an investigation of the angles over which this light mass has been seen.

## VI. CONCLUSION

Cyclotron-resonance studies have been carried out at 68 Gc/sec on two single crystals of silver. Care has been taken to produce surfaces of improved flatness in order to hold the effects of inclined fields to a minimum. The general structure of the results agrees well with the detailed model of the Fermi surface of silver obtained by Roaf<sup>5</sup> from the data of the de Haas-van Alphen and anomalous skin measurements. It is hoped that the present data will allow an exact calculation of the Fermi

velocity distribution to be carried out. On qualitative grounds, it has been proposed from the size of neck- and hole-orbit masses that the velocity in the region of the necks must be smaller than elsewhere, perhaps by as much as a factor of two. The neck diameter used by Roaf agrees well with the present observations; however, from the mass of the limiting point resonances, it appears that "caps" along the [100] directions should be slightly more pronounced.

The resonances for the (110) surface of silver closely parallel those obtained for copper,<sup>1</sup> except that the masses are in general about 30% smaller. Signals from the neck have been observed over a limited range. A noncentral orbit, not reported for copper, has been identified, and the resonances arising from it have been measured over an interval of  $44^\circ$ . In addition, cyclotron masses have been obtained from a (100) surface sample. These include belly, noncentral, and hole-orbit resonances; the hole-orbit resonances have been measured over narrow ranges of angles near the symmetry axes.

The behavior of a number of the resonance series in a field inclined with respect to the sample surface has been investigated. Apparent shifts as large as 50% per degree of inclination have been obtained. The similarity of a number of the signals to the peak-reversal phenomena observed in potassium and aluminum has been discussed.

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