INVESTIGATION OF THE FERMI SURFACE IN BISMUTH BY MEANS OF CYCLOTRON RESONANCE

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Cyclotron resonance studies have been carried out on single crystals of bismuth at frequencies of 8.7-9.8 Gcs and at sample temperatures of 1.5-1.7°K. The exact values of the masses of the carriers in bismuth have been determined for rational crystallographic directions of the magnetic field and for the principal directions relative to the Fermi surface of the electrons. The anisotropy of the effective masses is investigated in three crystallographic planes. The data obtained are more exact and more complete than the results of previous work.

From the cyclotron resonance studies it is shown that the energy spectrum of the electrons is non-quadratic, and the nature of the deviations of the Fermi surface from an ellipsoidal shape is determined. The influence of the polarization of the high-frequency field, the direction of the field, and the orientation of the sample surface on the excitation of the cyclotron resonance of the current carriers in the central section and at the limiting points is studied. The main technical innovation in the present work is the use of a transverse modulation of the magnetic field applied to the sample (the modulation field is not parallel to the steady field). This makes it possible to observe separately effective masses with different anisotropy, and to determine with high accuracy some of the characteristic directions of the Fermi surface.

INTRODUCTION

RECENTLY the energy spectrum of the conduction electrons in bismuth has been intensively studied both theoretically and experimentally. It has been established that the Fermi surface in bismuth consists of three electron and one hole region, whose shape is nearly ellipsoidal (for brevity we shall in the following refer to them as ellipsoids). The data obtained from studies of the oscillations in the magnetic susceptibility and the conductivity\[1-3\], ultrasonic absorption\[4\], cyclotron resonance\[5,6\], cut-off in cyclotron resonance\[7\], hybrid resonance\[8\] agree well with this model. None of these papers showed up deviations of the Fermi surface from the ellipsoidal shape\[1\], although these should be expected on the basis of experimental results on the reflection of light\[9\], the quantum oscillations in strong magnetic fields\[10\], the specific heat\[11,12\], and the behavior of Bi-Te\[13\] and Bi-Sb\[14\] alloys.

The present paper contains the results of a detailed investigation of cyclotron resonance in bismuth, which made it possible to determine accurately the quantitative structure of the energy spectrum of the carriers in bismuth, to detect the deviations of the spectrum from the quadratic form, and to indicate possible deviations of the shape of the Fermi surface from the ellipsoidal.

EXPERIMENT

The measurements were carried out by the method of frequency modulation\[15\] in the frequency range 8.7—9.8 Gcs. The bismuth specimens were single crystals in the shape of a disc of 17.8 mm diameter and 0.2—2 mm thickness. They had the following orientations of their crystallographic axes relative to the normal N to the plane of the disc:

I. Two-fold axis C₂ ≡ N

II. Three-fold axis C₃ ≡ N

III. C₂ ⊥ N, the angle between C₃ and N being...
84°, selected so as to make the major axis of one of the electron ellipsoids parallel to the normal N.

The possible error in the determination of the crystallographic orientation of any sample did not exceed 0.5°.

Samples were studied which either had been used previously [3, 5, 7, 16], or had been prepared by the same technique from bismuth with higher initial purity. The purity of the metal could be judged by the fact that twice as many orders were visible in the cyclotron resonance, and that they were much narrower. Both materials had, according to their specification, impurity concentrations below 10⁻⁵% (resistance ratio ρ₃₀₀°K/ρ₂·⁴°K ≥ 100).

For the experiment the sample was placed in the strip resonator [7, 15]; the high-frequency currents along its surface were flowing in straight lines. The direction of these currents was determined with an accuracy of ~ 1° by finding the direction of the strong magnetic field H (about 10 kG) which gave the best performance of the oscillator. This maximum is due to the fact that the excitation of plasma oscillations is least effective when H // J [18]. During the experiment the sample could be rotated relative to the high-frequency currents by an angle which was measured to within ~ 5°.

The magnetic field was produced either by an electromagnet, or by a system of Helmholtz coils with an earth-field compensator. The strength of the field was measured in the case of the electromagnet by means of a Hall indicator, and in the case of the Helmholtz coils though the exciting current. The absolute calibration was done in both cases by means of a nuclear resonance magnetometer [17]. The magnetic field could be turned in any direction in the plane of the disc, and also inclined to it by ~ 2°. The accurate coincidence of the field direction with that of the plane of the disc was verified to within ± 5° by the modulation signal induced in a flat pick-up coil placed below the specimen. When the cyclotron resonance was very sensitive to the inclination of the field, the effect itself could serve as a check on the alignment.

The temperature of the specimen was kept during the experiment at 1.5–1.7°K. A temperature increase to 4.2°K resulted in a broadening of the peaks and a reduction in their amplitude, corresponding to a reduction of the relaxation time by a factor 1.5–2, differing between different groups of carriers and different sections of the Fermi surface. The position of the lines was not affected by the change in temperature to the accuracy of the experiment.

DETERMINATION OF THE PERIODS OF CYCLOTRON RESONANCES

The value of the effective mass is calculated from the formula [18]

\[ \mu = m^* / m_e = e / m_e c \omega \Delta H^{-1}, \]

where \( \Delta H^{-1} \) is the period of cyclotron resonances, which can be found from the experimental records of the kind shown in Fig. 1. The shape of the resonances evidently changes as a function of the field,
and one has to give some thought to the question how $\Delta H^{-1}$ should be defined.

From estimates of the variation of the amplitude of the cyclotron oscillations with their order (using the record of experiments in which only the resonances from a single group of carriers were observed) one finds that the magnitude of the parameter $\omega T$ varies for different groups of carriers and different field directions between 5 and 20. In these circumstances only the peaks of the first few orders have the characteristic resonance shape. With increasing order the resonances are less completely resolved and their shape becomes more and more sinusoidal. However, according to Azbel' and Kaner[18] the surface resistance of a metal follows, when $\Omega \tau < 1$ ($\Omega = eH/m^*c$ is the cyclotron frequency) the law

$$Z \sim \exp [2\pi\Omega^{-1}(i\omega - \tau^{-1})]$$

and therefore a measurement of the period of oscillation of $Z$ yields also in this case a determination of the effective mass of the carriers. Comparison of the results of measurements on samples of different purity, in which the relaxation times differed by about a factor 2, confirmed that this procedure was justified.

There is one other experimental fact which favors the use of resonances of as high an order as possible. This is the fact that the first-order resonance lies in a region of fields for which plasma oscillations are excited in bismuth, and therefore this resonance is partly suppressed, and its form distorted[19], as can be seen on Fig. 1.

Similar phenomena can occur for some resonances in the region of weaker fields, where plasma oscillations can also be excited[20]. A distortion of the shape of a resonance may evidently cause an error in the determination of its position.

It should be noted that for the first-order resonances of electrons with a small effective mass the field is of the order $H_1 \approx 30$ Oe, and the measurement of the field of the electromagnet by means of the Hall indicator becomes very inaccurate for the higher orders. In order to reduce the relative error in determining the anisotropy of the masses, the periods were determined earlier[15] only from the first one or two orders in the cyclotron resonance, both for large and for small masses. The present work uses samples of substantially better quality, and employs Helmholtz coils, and therefore allows the measurements to be extended to much weaker fields. Hence all visible resonances were used in the absolute determination of effective masses. It was found that the absolute values given in[15] for certain masses were too high.

**OBSERVED VALUES OF EFFECTIVE MASSES**

The anisotropy of the masses for all crystallographic planes studied is shown in the diagrams of Figs. 2—5. The values of the effective masses for fields parallel to the principal crystallographic directions, and to the principal axes of the electron ellipsoid of the Fermi surface, are given in the table.

The anisotropy of the effective masses agrees with a model of the Fermi surface which consists of three electron ellipsoids whose major axes are

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FIG. 2. Polar diagram of the variation of the effective electron masses $\mu$ with the direction of the magnetic field: A. Field acting on a single crystal of bismuth in the base plane (orientation II). B. Field in the plane orthogonal to the $C_4$ axis. The straight lines through the experimental points correspond to a system of three ellipsoids inclined to the base plane by $6^\circ20'$. Subscripts on $\alpha$ and $\delta$ are the conventional numbers of the ellipsoids making up the Fermi surface for electrons. Wherever the experimental error exceeds the size of the point, it has been indicated.
at right angles to the $C_2$ axis, and inclined to the base plane by an angle of $6^\circ 20' \pm 15'$, as well as one hole ellipsoid with its major axis parallel to the $C_3$ axis.

The electron surface. The ratios of the axes of an electron ellipsoid, calculated from the ratios of the masses for its central sections, are 1:1.40:14.8. On the other hand, data obtained from observing the cut-off in the cyclotron resonance\cite{7} and the de Haas-van Alphen effect give the ratios of the axes as 1:1.46:15. The difference between these sets of numbers does not exceed the experimental error, and it follows that the deviations of the electron energy spectrum from the quadratic form are small.

Since the major axis of the ellipsoid is about 15 times the minor one, the central part of the ellipsoid is almost a cylinder. For a cylindrical Fermi surface \( \mu(\varphi) = \mu_0 / \cos \varphi \sin \varphi \) (where \( \mu_0 \) is the mass for \( H || O \), \( \varphi_0 \) the angle between \( N \) and \( O \), and \( \varphi \) is the angle in the plane of the specimen counting from the minimum \( \mu \)) the experimental points in the polar diagram for \( \mu \) lie on a straight line. (Fig. 2, masses \( \alpha_1 \), \( \alpha_2 \), \( \alpha_3 \)). The angle between the straight lines \( \alpha_1 \) and \( \alpha_2,3 \) in Fig. 2B was used to determine the angle between the electron ellipsoid and the base plane, which was quoted above.

Such studies of the anisotropy of the effective masses of the electrons in the central section of the ellipsoids by experiments with \( J \perp H \), and measurements of the surface resistance for \( J \parallel H \), which show cyclotron resonances from the electrons at the ends of the ellipsoid made it possible to notice the deviations from the quadratic law. Figure 3 shows that the points for the effective masses \( \alpha_2,3 \) do not lie on the ellipse constructed by using the extremal values of the

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**Table:**

<table>
<thead>
<tr>
<th>Orientation</th>
<th>( \mu (H \perp J) )</th>
<th>( n )</th>
<th>Figure, mass</th>
<th>( \mu (H \parallel J) )</th>
<th>( n )</th>
<th>Figure, mass</th>
<th>Carrier type</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H \parallel C_2 )</td>
<td>0.120±0.003</td>
<td>5</td>
<td>4, ( \alpha_1 ), 5, ( \alpha_1 )</td>
<td>0.137±0.003</td>
<td>4</td>
<td>4, ( \gamma_1 )</td>
<td>n</td>
</tr>
<tr>
<td></td>
<td>0.0003±0.0001</td>
<td>20</td>
<td>2,4, ( \alpha_1 )</td>
<td>0.0003±0.0001</td>
<td>20</td>
<td>2,4, ( \alpha_2 )</td>
<td>p</td>
</tr>
<tr>
<td></td>
<td>0.203±0.004</td>
<td>4</td>
<td></td>
<td>0.210±0.004</td>
<td>4</td>
<td>5, ( \gamma_1 )</td>
<td>p</td>
</tr>
<tr>
<td>( H \parallel C_1 )</td>
<td>0.0081±0.0001</td>
<td>20</td>
<td>2,4, ( \alpha_2 ), 2B, ( \alpha_2 )</td>
<td>0.0169±0.0005</td>
<td>2</td>
<td>2B, ( \delta_3 )</td>
<td>n</td>
</tr>
<tr>
<td></td>
<td>0.203±0.004</td>
<td>4</td>
<td>5B, ( \eta )</td>
<td>0.210±0.004</td>
<td>4</td>
<td>5B, ( \eta )</td>
<td>p</td>
</tr>
<tr>
<td>( H \parallel C_3 )</td>
<td>0.0062±0.0001</td>
<td>20</td>
<td>5B, ( \eta_1 (5,4,n) )</td>
<td>0.064±0.003</td>
<td>2</td>
<td>5B, ( \eta_1 (5,4,n) )</td>
<td>p</td>
</tr>
<tr>
<td>( H \perp C_2 )</td>
<td>0.088±0.002</td>
<td>5</td>
<td>3, ( \alpha_2,3 )</td>
<td>0.117±0.004</td>
<td>3</td>
<td>3, ( \beta_2,3 )</td>
<td>n</td>
</tr>
</tbody>
</table>

Legend: \( n \) is the order of the cyclotron resonance, i.e., the number of periods over which averages were taken in calculating the effective mass. In the last column \( n \) indicates electron carriers and \( p \) holes.

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**Fig. 3.** Polar diagram of the variation of the effective mass \( \mu \) for electrons with the direction of a magnetic field acting on a single crystal of bismuth in the plane orthogonal to the \( C_3 \) axis (orientation I). The full lines are ellipses constructed from the extremal values of the masses; the dashed and dashed lines indicate the directions of the extremal masses for \( \alpha_2,3 \) and \( \beta_2,3 \), respectively.* \( \times H \parallel J \), \( \circ H \perp J \); \( N \parallel C_3 \).

**Fig. 4.** Effective electron mass \( \mu \) vs. field direction, in the base plane of the bismuth single crystal (orientation II). The full curve corresponds to an ellipse based on the extremal mass values.
masses in that plane. One can draw through the experimental points a curve which possesses a single symmetry element, namely a center in the coordinate origin (in agreement with the symmetry of the crystal structure). This fact was convincingly confirmed by measurements of $\alpha_{2,3}$ using transverse field modulation. This made it possible to locate with an accuracy of $\pm 10'$ the dash-dotted line in Fig. 3, which indicates the direction of extremal $\alpha_{0,3}$; this is just the direction chosen as the direction of the major axis of the ellipse constructed in Fig. 3.

The study of the effective masses for the electrons at the limiting points, $\beta_{1,2,3}$ and $\gamma$ showed that for some directions these masses are greater than the masses $\alpha_{1,2,3}$ of the electrons in the central section (cf. Figs. 3—5). The direction of the magnetic field for which the masses $\beta_{2,3}$ are greatest lies in the plane orthogonal to the $C_2$ axis, and is about $0.5^\circ$ closer to the $C_3$ axis than the corresponding direction for $\alpha_{2,3}$ (cf. the dashed line in Fig. 3). For a sample with orientation I, and in a field close to the bisector axis $C_1$, one can clearly see the resonance $\delta_{2,3}$ for the limiting point. (In the first two orders one sees resonances which are clearly resolved from the $\delta_{2,3}$ resonances belonging to the central section, and in the places where one expects the third and fourth orders from $\delta_{2,3}$ the periodic structure of the $\alpha_{2,3}$ resonances is strongly disturbed. The anisotropy of the masses $\delta_{2,3}$ is shown in Fig. 2B.

The nature of the deviations of the experimental points for $\alpha_{2,3}$, $\beta_{2,3}$ and $\beta_1$ from the ellipses shown in Fig. 3, and the differences between the effective masses $\alpha$ in the central section and the masses $\beta$, $\gamma$, $\delta$ for the limiting points suggests that the electron Fermi surface looks like an ellipsoid which has been pushed out in a region $A$ near the ends of the major axis, which has an opening angle of about $6^\circ$ (Fig. 6). For a fixed ratio of axes such a deformation of the electron energy surface will result in a reduced Gaussian curvature $K$ in the regions $B$ and $\Delta$ of the Fermi surface, and therefore to an increase in the effective mass of the electrons at the limiting points $\beta$ and $\delta$, according to the formula $m^* = (\nu_F \sqrt{K})^{-1}$ ([18] (\nu_F$ is the limiting velocity). On the other hand the masses $\alpha$ in the central section should not undergo any substantial changes.

One should, however, point out that the above...
model of the electron Fermi surface, although the simplest, is by no means the only one that could give agreement with experiment. Thus, for example, according to Fal’kovskii and Razina[217], its central section at right angles to the \( \text{C}_2 \) axis could be hyperbolic for small values of the momentum. In that case the elliptic limiting points are displaced from the central section of the electron ellipsoid, and the dependence of the curvature of the Fermi surface on momentum becomes more complicated than that suggested above.

Incidentally, the parameters of the spectrum given in[21] cannot yet be taken as final, as some of them disagree with experiment. For example, the greatest effective electron mass for \( \text{H} \perp \text{C}_2 \) as calculated in[21] is twice the measured value (\( \alpha_p \), Fig. 5). A full comparison of the calculated parameters and their experimental values is given in[21].

The hole surface. For the holes one did not obtain as clear a proof of the deviations from the quadratic law as for the electrons. The table shows those values of the effective masses for holes whose existence is at present established. The curves 5 and 6 of[5], which have been attributed to cyclotron resonances in the hole surface, must apparently be related to hybrid resonances and dielectric anomalies[8].

The experimental points for all planes which were studied lie well on ellipses (\( \eta \), Fig. 5), which turn out to be sections of an ellipsoid of rotation with axes in the ratio 3.2 ± 0.1. Within the limits of error this ratio agrees with the ratio of the areas of sections, measured by means of the de Haas—van Alphen effect[2,3]. The effective masses of the holes in the central section and the limiting points in the basic plane are isotropic to about 1%, which shows that the hole Fermi surface must have axial symmetry. The difference in the mass of the holes between the central section and the limiting points for fields in the base plane never exceeds twice the error of measurement and cannot at present be taken as significant.

**ON THE EXCITATION OF CYCLOTRON RESONANCE IN CENTRAL SECTIONS AND IN LIMITING POINTS**

The amplitude of the cyclotron resonance in the central section is a maximum when the electron velocity in the skin of the metal is parallel to the high-frequency currents. Usually this is the case when \( \text{H} \perp \text{J} \). However, for a cylindrical Fermi surface the plane of the electron orbit is perpendicular to the axis \( \text{O} \) of the cylinder, whatever the direction of \( \text{E} \), and the resonance amplitude will be greatest when \( \text{J} \perp \text{O} \), and vanish when \( \text{J} \parallel \text{O} \), regardless of the angle between \( \text{H} \) and \( \text{J} \). This statement is in agreement with the observations of the cyclotron resonance on the central sections of the Fermi surface for bismuth, and this provides further evidence of the almost cylindrical shape of the central parts of the Fermi surface (region \( \text{E} \) of Fig. 6).

Figure 5A shows that the curve \( \alpha_1 \) fits equally well the experimental points obtained for \( \text{H} \perp \text{J} \) as those for \( \text{H} \parallel \text{J} \). This would seem to be evidence that the effective mass of the electrons in the central section and at the limiting points is the same. On the other hand, the measurements with samples of orientations I and II show different effective masses \( \alpha, \beta, \) and \( \gamma \) (Figs. 3 and 4). Furthermore, the sample with orientation III (Fig. 5A) shows also masses \( \beta_1 \) and \( \beta_2 \) for the limiting points on ellipsoids 2 and 3, which differ from the mass \( \alpha_1 \) for the central section, if corrected for the change in the orientation ellipsoid.

The coincidence of the experimental points with the curve can be explained in the following way. For a nearly quadratic spectrum there may exist a sufficient number of electrons which possess exactly the same mass as the electrons in the central section, but which have an appreciable velocity component parallel to the field. Such electrons will give a contribution to the surface resistance for \( \text{H} \parallel \text{J} \).

At the same time the cyclotron resonance for the limiting point is not observed, for the following reasons. The electron orbits for the electrons in the central section of ellipsoid 1 have the form of a very elongated ellipse (with axis ratios 1:15:1:10) with its major axis parallel to the surface of the sample (orientation III). For a field corresponding to first-order resonance the diameter of the central orbit in the direction of the normal of the sample, is about \( 2 \times 10^{-4} \) cm, which is comparable to the penetration depth of \( (0.5-1) \times 10^{-4} \) cm[22]. Since the dimensions of the orbits of electrons near the limiting points must be much smaller,
they evidently move, in this case, in a practically uniform high-frequency field, which excludes the possibility of exciting cyclotron resonances. In all those cases in which one observes a cyclotron resonance for the limiting points (orientation I and II, ellipsoids 2 and 3, orientation III) the major axis of the electron orbit lies at an angle to the sample surface (30°–90°). Therefore the electrons penetrate to a depth which exceeds the minimum dimension of the orbit by an order of magnitude.

The effective masses of the holes which are observed in experiments with $H \perp J$ and $H \parallel J$ are practically the same for any direction of the field $H$. It is not impossible that this can be explained by the above reasoning; here one has to take into account the fact that the ratio of the axes of an elliptic hole orbit equals 3.2, and therefore a change in the orientation of the surface of the sample may not have as drastic an effect as in the case of the electron orbits. This causes some uncertainty in the allocation of the cyclotron resonances of holes to the central section and the limiting points according to their appearance in experiments with different directions of the high-frequency currents. Nevertheless we regard the procedure as justified by the fact that the resonances with $H \parallel J$ are sensitive to an inclination of the magnetic field (they are weakened noticeably by an inclination of about 10° to the plane of the specimen) and that the observed energy spectrum for the holes does not deviate from the quadratic shape to the accuracy of the measurement (the measured points lie on an ellipse).

In connection with what is said above, it should be noted that the absence of any difference between the observed cyclotron resonances for $H \perp J$ and $H \parallel J$ at a frequency of 34.5 Gcs in the work of Yi-Han Kao [6] appears completely understandable if one takes into account that the higher frequency (compared to the present work) leads to a correspondingly higher resonance field and to reduced dimensions of the orbits.

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