where $\mathcal{G}$ is the exact Green's function, and

$$\langle L|\mathcal{G}|L\rangle_i=\int\frac{\delta(x-R)}{R^2}Y_L(x)\mathcal{G}(\mathbf{x},\mathbf{x}')\times\frac{\delta(x'-R)}{R^2}Y_L(\mathbf{x}')d\mathbf{x}d\mathbf{x}',$$

where the integration is over the surface of the ith sphere and the notation is defined in the text.

Relation (B1) is therefore valid whenever the Green's function is essentially the same on all atomic spheres (such as for s-p type states) and is useful for semiquantitative work whenever one type of atom completely dominates the average, such as occurs for the d-type state in α-brass. It is emphatically not valid near the region where the amplitude of one type of atom has a singularity (see Fig. 5). For near the singularity it may easily be shown that the imaginary part of the corresponding angular-momentum component of Green's function vanishes, yielding a finite $\Delta\rho(E)$, whereas our procedure yields a singularity in $\Delta\rho(E)$.

PHYSICAL REVIEW VOLUME 151, NUMBER 2 11 NOVEMBER 1966

Analysis of the Shubnikov–de Haas Effect in Bismuth*

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(Received 1 June 1966)

The Shubnikov–de Haas effect has been measured in single crystals of high-purity bismuth. Some of the observed oscillations have periods similar to those found by Lerner and attributed by him to heavy-holes and electrons. Some of these periods are shown to be the result of superposition of oscillations due to different parts of the Fermi surface of the two-carrier model of Smith, Baraff, and Rowell, and the others to be the result of frequency modulation due to oscillations in the Fermi energy.

INTRODUCTION

Recent measurements of the Shubnikov–de Haas effect,[1,2] the de Haas–van Alphen effect,[3] and cyclotron resonance[4] have revealed the presence of a group of holes in the band structure of bismuth, in addition to the electrons originally found by Shoenberg.[5] The differences between the estimates of the size and shape of the Fermi surface made by various authors are consistent with the differences in purity of the samples used in their experiments, and in each case a calculation of the electronic component of the low-temperature specific heat based on the band structure leads to a value an order of magnitude smaller than that measured.[6,7] This discrepancy may be explained by postulating another set of charge carriers in bismuth, with greater effective masses than those already observed. Lerner,[8,9] claims to have found Shubnikov–de Haas oscillations which are caused by these heavy carriers, and deduces from them the sizes and shapes of the corresponding pieces of Fermi surface. The measurements described here were made with the object of providing confirmatory evidence for Lerner's suggestions, whose validity has been doubted by several authors. It is found that a straightforward interpretation of our results is consistent with Lerner's observations, but that a more thorough analysis shows that all the results may be explained on the basis of the two-carrier model of the bismuth band structure.

EXPERIMENT

Zone-refined bismuth, purchased from the Consolidated Mining and Smelting Company of Canada Limited, and of a nominal purity of 99.9999% was subjected to further zone refining in Union Carbide grade AUC graphite boats *in vacuo*. Central sections, 15 cm long, cut from three 50-cm-long ingots which had each been passed through a zone-melting furnace at 4 cm/h 21 times, were placed end to end in another boat and repassed 13 times. Single crystals were grown from the central section of the resulting ingot by passing a molten zone along its, starting from a small

* Research supported from grants in aid of research awarded by the National Research Council of Canada and the Ontario Research Foundation. One of us (A.M.F.) acknowledges support by a Garnet W. McKee-Lachlan Gilchrist Scholarship.
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[2] G. E. Smith, G. A. Baraff, and J. M. Rowell, Phys. Rev. **135**, A1118 (1964).
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seed crystal. Natural cleavage planes were used to determine the orientation of these crystals, and specimens, about 5 cm long with a 12-mm-diam semicircular cross section, were cut from them with a Servomet spark-erosion machine.

To minimize strain due to differential thermal expansion on cooling, the sample holder was made of bismuth covered with a layer of varnish to insulate it from the specimen. Beryllium-copper springs served to keep the sample in the holder and to hold point electrical contacts against it, thus avoiding the possibility of contamination with solder.

The sample was mounted with its length vertical in a conventional liquid-helium cryostat, so that it was in a central position between the pole faces of an electromagnet, which could be rotated about a vertical axis with the field kept horizontal. The magnet (Harvey-Wells model L-158) was capable of producing fields up to 19 kG which were calibrated in terms of the current with an accuracy of $\frac{1}{10}\%$ using a Harvey-Wells precision NMR gaussmeter (G-502) and a Rawson rotating coil gaussmeter (type 829S).

Resistance measurements were made by passing a steady current (about 1 mA) through the specimen and measuring the resulting potential difference with a Keithley Model 149 millimicrovoltmeter. The output of this meter was fed into the y input of an x-y recorder, whose x input was fed from a high current resistance in series with the magnet windings, via a low pass filter which reduced noise from the generator.

Most measurements were made at 1.4°K to maximize the Shubnikov–de Haas oscillations, the normal procedure being to set the orientation of the field and then increase the magnet current from zero to its maximum value at a rate slow enough that the resistance recorded at any field was identical with that obtained in the same steady field. Apart from the obvious advantage of simplicity, this method was chosen in preference to a differential technique to avoid distortion of the resistance oscillations by eddy currents and because field values for which resistance minima occur, which can be related directly to the band structure, are more easily obtained from a graph of resistance R rather than dR/dH, plotted against field H, if corrections have to be made for zero errors introduced by the instruments. The method is, however, less sensitive than the differential methods and comparisons of our results and Lerner's suggest little difference due to eddy currents.

RESULTS

Measurements were made on three samples: the first two were oriented with their trigonal (z) axes within three degrees of the vertical, the magnetic field making an angle ψ with the bisectrix (y) axis, and the third with its z axis horizontal, its binary (x) axis inclined at 10° to the vertical and H making an angle θ with the z axis. The resistance ratios $[R(300°\text{K})/R(4.2°\text{K})]$ of these samples were, respectively, >1000, ~150, and ~300. The significance of these numbers is somewhat doubtful because the measurements were made in the earth's magnetic field, which, according to Zitter's[10] results, may be enough to increase the resistance of a very pure sample to several times its zero-field value. An alternative criterion for deciding which samples would be most profitable for detailed study was the sharpness of the peaks obtained in a constant field when the resistance was plotted as a function of angle when the magnet was rotated.[11]

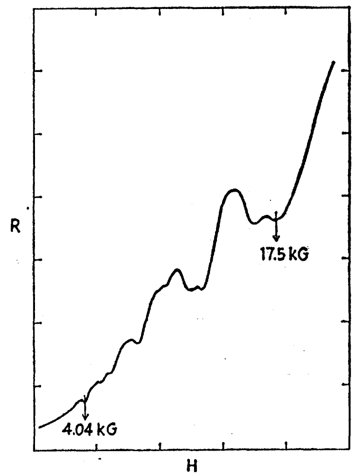

FIG. 1. Recording of R versus H for specimen 1 at $\psi=44°$.

Graphs of R versus H (or magnet current) were obtained from the first two samples for values of ψ ranging between 0 and 120° in 2° intervals, and from the third with θ ranging from $-90°$ to $+90°$ in 2° intervals. A typical example of such a recording is shown in Fig. 1. The positions of the resistance minima could be determined by inspection of the original recordings (which were of larger scale than Fig. 1), with an uncertainty of less than 60 G, representing a possible error in H of about $1\frac{1}{2}\%$ and $\frac{1}{2}\%$ at the lowest and highest fields, respectively. The effect of the background magnetoresistance on the positions of the minima was estimated by fitting to the data of one recording a simple polynomial in H and then subtracting it from the resistance values to leave only the oscillatory part. The minima were found to be shifted randomly from their original positions by less than $\frac{1}{2}\%$ on the average, so that no significant correction could be made and the procedure was not repeated for the rest of the data.

On each graph successive minima were labeled with the natural numbers, starting at the highest fields. Then the value of $1/H$ at which each minimum occurred was plotted against the number assigned to it. In some cases many of the points so obtained lay on a straight

[10] R. N. Zitter, Phys. Rev. **127**, 1471 (1962).

[11] Measurements of this kind are described by A. M. Forrest and A. C. Hollis Hallett, in *Proceedings of the Ninth International Conference on Low Temperature Physics*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), p. 740.

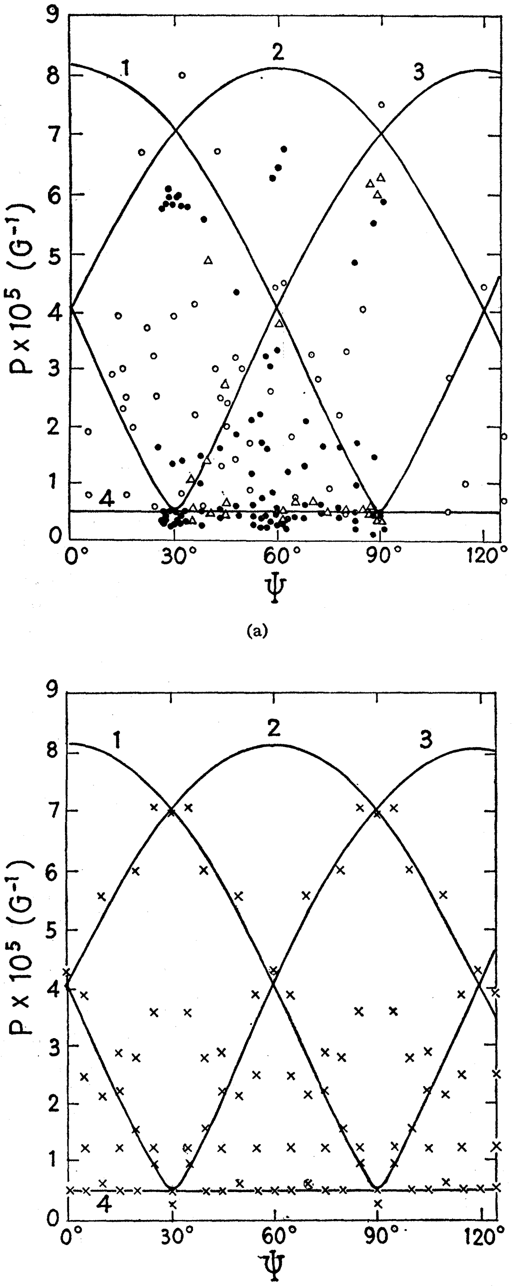

FIG. 2. (a) Observed Shubnikov–de Haas periods for **H** in the x-y plane at an angle ψ with the y axis. O, specimen 1; △, specimen 2; ●, data from Fig. 3 of Ref. 9. (b) Periods due to interference between Shubnikov–de Haas oscillations.

line, but more often the pattern was broken up into various groups each containing several collinear points (see, for example, Fig. 4 shown later). Whenever four or more points were collinear, the slope of the line through them was taken to be the period $P=\Delta(1/H)$, of the Shubnikov–de Haas oscillations. The values thus obtained are plotted against orientation in Fig. 2(a), which includes Lerner's[9] data for this orientation, and in Fig. 3.

DISCUSSION

The data in Figs. 2(a) and 3 are so scattered that any attempt to interpret them without prior knowledge of the band structure of bismuth to serve as a guide could be little better than guesswork. Fortunately, there is no lack of literature on the subject, and we have chosen for a starting point the model used by Smith, Baraff, and Rowell[2] together with their experimental parameters.

The curves in Figs. 2 and 3 represent periods of Shubnikov–de Haas oscillations calculated from these parameters, using the well known result

$$P=\Delta(1/H)=2\pi e/\hbar\mathcal{A}, \qquad (1)$$

where $\mathcal{A}$ is the extremal cross sectional area (in k space) of the Fermi surface in a plane normal to the field, e is the electronic charge (in emu) and $\hbar$ is Planck's constant divided by 2π. Curves 1, 2, and 3 in each case correspond to the three electron ellipsoids disposed symmetrically about the trigonal axis, and curve 4 corresponds to the hole ellipsoid of revolution.

In Fig. 2(a), Lerner's data for periods greater than 1.0×10^{-5} G^{-1} are less scattered than ours but differ widely from the electron curves, and are better described in terms of different effective masses and Fermi energy. The discrepancy in the latter could be due to a difference in purity between the samples of Lerner and of Smith *et al.*, but effective-mass ratios would not be expected to differ significantly between samples as pure as these. Our long-period data, on the other hand, could be described as well by Smith's parameters as by any others.

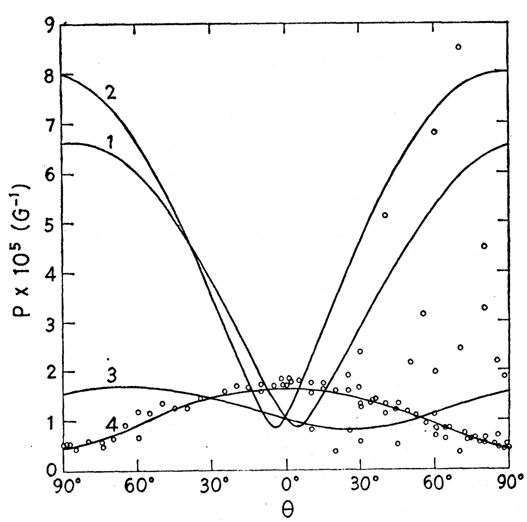

FIG. 3. Observed Shubnikov–de Haas periods for H in a plane containing the z axis (specimen 3). z axis is at $\theta=0°$.

For periods less than $1.0\times10^{-5}\,G^{-1}$ our data are similar to Lerner's, some of which he accounts for in terms of a light-hole ellipsoid and a group of heavy holes associated with a piece of Fermi surface in the shape of a "trefoiloid." The light-hole periods are supposed to lie on or near a horizontal line at $0.41\times10^{-5}\,G^{-1}$ [curve 4 in Fig. 2(a) is at $0.49\times10^{-5}\,G^{-1}$] and the heavy-hole periods on a curve with maxima of about $0.8\times10^{-5}\,G^{-1}$ at $\psi=0$, 60°, etc., and minima of about $0.48\times10^{-5}\,G^{-1}$ at $\psi=30°$, 90°, etc. To conserve charge neutrality it is necessary to postulate another group of electrons, which are assumed by Lerner to be associated with a spherical piece of Fermi surface and to give rise to oscillations with a period of about $1.2\times10^{-5}\,G^{-1}$, three of which appear in Fig. 2(a) at $\psi=52\frac{1}{2}°$, 63°, and 68°, and a few more when the field is in the y-z plane.

Lerner's suggestions might be supported on the evidence of the similarity of the two sets of short-period data, were it not for the scatter of the rest of our results, which casts doubt on the validity of the interpretation of the experiment. This doubt has led us to seek alternative explanations of the oscillations attributed by Lerner to heavy carriers, as well as others which he dismissed as being spurious, and to account for most of our long-period data. The following sections describe two different effects which account for the confused appearance of Fig. 2(a).

INTERFERENCE BETWEEN OSCILLATIONS

Under ideal conditions at 0°K the Landau levels for electrons in a magnetic field are very sharply defined. As the field is increased, the energy of a Landau level increases, and when its minimum value becomes equal to the Fermi energy, it is suddenly depopulated. The relaxation time for electron scattering, which depends on $f(E)[1-f(E)]$, where $f(E)$ is the Fermi function, is temporarily increased at this field value, giving rise to a sharp dip in the transverse magnetoresistance. In practice, the Landau levels are not so sharply defined and the temperature is finite, so that the resistance dip is spread over a range of field values which are such as to keep the difference between the minimum energy of the level and the Fermi energy within about $k(T+x)$. (k is Boltzmann's constant, T is the temperature and x is the Dingle temperature.) If this difference is small compared with the separation of the Landau levels the Shubnikov–de Haas effect will appear as a series of fairly sharp dips superposed on the normal magnetoresistance of the metal.

When several sets of Landau levels exist, several sets of resistance dips will occur as the field is varied. The separation between some of them may be so small that they will merge into each other. An order-of-magnitude criterion for the resolution of two dips may be set up: If the energies of the corresponding Landau levels at the same field value differ by more than a few times $k(T+x)$ then the resistance dips should be distinguishable.

Consider first two sets of Shubnikov–de Haas oscillations, each periodic in $1/H$, but with slightly different periods. These will "interfere" to form a pattern with regions in which the resistance dips are in phase, and combine to give a periodicity similar to that of the components, and out-of-phase regions giving an apparent period of approximately half that of the components. This is somewhat different from the beating which occurs when two sinusoidal oscillations are superposed. Many of the observed periods in Fig. 2(a) occur at approximately half the value indicated by the calculated curves, and may therefore be explained in this way. In general, however, there are four different sets of oscillations at any orientation (if we ignore Lerner's heavy carriers), and the interference effects will be much more complicated. A quantitative estimade of these was made by calculating the $1/H$ values at which resistance dips would be expected for the four sets of carriers in a particular orientation, combining together those which would not be resolved, and plotting the resulting values against the natural numbers.

According to Smith *et al.*,[2] there is a resistance dip whenever

$$E_F(1+E_F/E_G)=\{(n+\tfrac{1}{2})m_0/m_c\pm g/4\}e\hbar H/m_0 \quad (2)$$

for electrons, and

$$E_0-E_F=\{(n+\tfrac{1}{2})m_0/M_c\pm g/4\}e\hbar H/m_0 \quad (3)$$

for holes, where E_F is the Fermi energy, E_G is the band gap for the electrons, E_0 is the band overlap for the holes, m_0 is the free-electron mass, m_c and M_c are the electron and hole cyclotron masses, g is the spin-splitting factor, and n is the number of the Landau level.

The cyclotron masses are defined for electrons by

$$m_c=[\det\mathbf{m}^*/\mathbf{h}\cdot\mathbf{m}^*\cdot\mathbf{h}]^{1/2}, \quad (4)$$

where $\mathbf{h}$ is a unit vector in the direction of the magnetic field and $\mathbf{m}^*=m_0\alpha^{-1}$ is the effective-mass tensor which is used in defining the electron energy in the absence of a field by

$$2m_0E(1+E/E_G)/\hbar^2=\mathbf{k}\cdot\alpha\cdot\mathbf{k}, \quad (5)$$

where $\mathbf{k}$ is the electron wave vector. For one of the electron ellipsoids $\mathbf{m}^*$ has the form

$$\mathbf{m}^*=\begin{bmatrix} m_{11} & 0 & 0 \\ 0 & m_{22} & m_{23} \\ 0 & m_{23} & m_{33}\end{bmatrix}, \quad (6)$$

where the subscripts 1, 2, and 3 refer to the x, y, and z axes, respectively, and for the other two ellipsoids $\mathbf{m}^*$ is the same tensor rotated by ±120° about the z axis.

For the holes the cyclotron mass is similarly defined

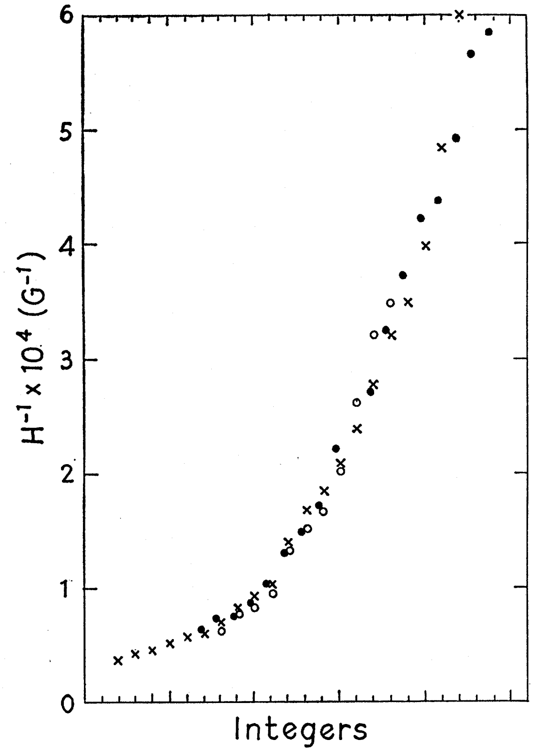

FIG. 4. ×, calculated $1/H$ values for successive resistance dips for **H** in the x-y plane at $\psi=5°$; ○, observed $1/H$ values for specimen 1; ●, $1/H$ values from Lerner [Fig. 6(b), Ref. 8].

in terms of an effective mass

$$\mathbf{M}^*=\begin{bmatrix} M_1 & 0 & 0 \\ 0 & M_1 & 0 \\ 0 & 0 & M_3 \end{bmatrix}. \tag{7}$$

The spin-splitting factor is given by

$$g=2m_0[\mathbf{h}\cdot\mathbf{m}_s\cdot\mathbf{h}/\det\mathbf{m}_s]^{1/2}, \tag{8}$$

where $\mathbf{m}_s$ is a spin-mass tensor similar in form to the effective mass tensor, and its components for both holes and electrons have been determined experimentally by Smith *et al.*[2]

The variation of E_F with H has been calculated by Smith *et al.*, to satisfy the condition that the total carrier density in the metal be field-independent. They find that at fields below 15 kG, E_F remains within about 1% of its zero-field value of 27.6 meV, which we have therefore used in our calculations. The effect of the variation of E_F on our results is described in the next section.

For each of seven equally spaced orientations in the x-y plane, $1/H$ values were calculated from Eqs. (2) and (3) for all four groups of carriers, and arranged in one list in ascending order. Those which were separated by less than a fraction r were merged. The value of r was determined empirically, but an order of magnitude can be obtained for it by assuming the width of a resistance dip corresponds to the Landau level being within ΔE of the Fermi energy. Then, from Eq. (2),

$$\frac{\Delta H}{H}=\frac{\Delta E}{E_F}\frac{E_G+2E_F}{E_G+E_F}, \tag{9}$$

so putting $\Delta E\sim k(T+x)$ and taking Dhillon and Shoenberg's[12] value $x\sim1.3°\text{K}$ we have

$$|\Delta(1/H)/(1/H)|=\Delta H/H\sim1\tfrac{1}{2}\% \tag{10}$$

at 1.4°K, so that for two resistance dips to be resolved r should be about 3%. This value takes no account of detailed line shapes, differences in Shubnikov–de Haas amplitude, or experimental sensitivity. It is also necessary to allow for the fact that the amplitude of the oscillations decreases with decreasing field. In the absence of any quantitative calculation it was assumed that the oscillations would be unobservable if the period was less than r/H, so that when $1/H>(1/r)\Delta(1/H)$ for a set of carriers, no more $1/H$ values were included in the list. The remaining $1/H$ values were plotted against natural numbers and the result for $\psi=5°$ with $r=5\%$ is shown in Fig. 4, together with experimental values for this orientation. (Note that Lerner's points occur at $n-\frac{1}{4}$ because they represent minima in dR/dH.) There is quite a sharp bend in the experimental data at $1/H\sim10\times10^{-5}$ and r was chosen so that the bend in the calculated points was close to this. Similar comparison of calculated and experimental data for other orientations gave values of r varying between 3% and 5% and in one case (at $\psi=30°$) it was necessary to put

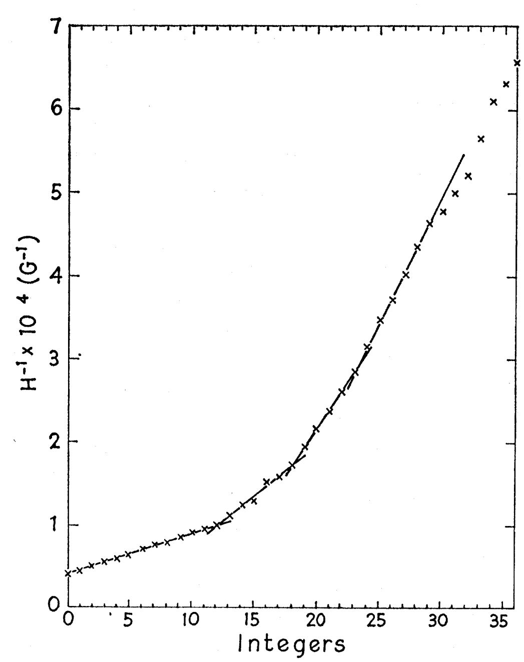

FIG. 5. Calculated $1/H$ values for successive resistance dips for **H** in the x-y plane at $\psi=15°$.

[12] J. S. Dhillon and D. Shoenberg, Phil. Trans. Roy. Soc. London A248, 1 (1955).

$r=5\%$ for electrons and $r=4\%$ for holes. What is surprising is not that the values of r vary, but that the variation should be so small when so many simplifying assumptions have been made.

Figure 5 shows another graph of calculated $1/H$ values against integers. There are several groups of four or more collinear points. It was found that in most orientations the choice of r had very little effect on the slopes of these linear portions, but merely altered the positions at which they occurred. Values of the slopes of all the linear portions for each orientation are plotted in Fig. 2(b). Some of the points fall on or close to the curves, and others at approximately half the height of the curves, illustrating our earlier qualitative discussion. The scatter of the calculated points is not unlike that of the experimental points in Fig. 2(a), although quantitative agreement between them is no better than would be expected in view of the simple nature of the calculations. It is not unreasonable to suggest, therefore, that many of the periods, especially those greater than 1.0×10^{-5} G, in Fig. 2(a), as well as a few observed by Eckstein and Ketterson,[1] are due to interference between oscillations whose periods should be represented by the curves. It is also evident that deviations between these periods and the correct curve might give the impression that curves calculated from different parameters would fit the observed periods better, and suggest departures from ellipsoidal form of the electron Fermi surface.

The points at $P\sim1.2\times10^{-5}$ G^{-1} near the bisectrix axes shown in Fig. 2(b) are of special interest. These are very close to three of Lerner's experimental points in the x-y plane, mentioned earlier, and to another near the y axis in the y-z plane[13] and suggest that they are due to interference rather than to the proposed group of heavy electrons. Lerner's other evidence for heavy electrons consists of a few more periods in the y-z plane, all of which seem too close to light-electron or light-hole periods to be distinguished from them.

The points at $P=0.24\times10^{-5}$ G^{-1}, $\psi=30°$ and 90° in Fig. 2(b) are due to spin splitting of the electronic Landau levels associated with curves 3 and 1, respectively. When $g=m_0/m_c$ the spacing of the spin-split levels is exactly half that of the unsplit levels, and this occurs when H is at an angle of 1.4° with the binary axes. There is, however, a small range of angles around this value where g is so close to m_0/m_c that deviations of corresponding $1/H$ values from a straight line graph would be comparable with experimental error, and a "harmonic" of the Shubnikov–de Haas frequency would be deduced. It appears that several of the periods of $\sim0.24\times10^{-5}$ G^{-1} near the binary axes in Fig. 2(a) originate in this way. It should be noted that the spin splitting observed by Lerner[9] in this orientation was in the Landau levels of the electrons represented by the intersecting curves. Smith's[2] parameters give $g=2.13m_0/m_c$ for these, while Lerner finds $g=1.86m_0/m_c$, but the latter's determination is not unambiguous and $g=2.14$ m_0/m_c would fit his results equally well.

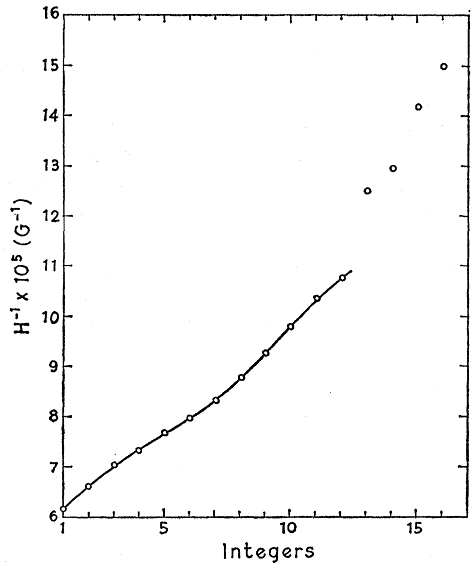

FIG. 6. Observed $1/H$ values for successive resistance dips specimen 2, with **H** in the x-y plane at $\psi=35°$ showing frequency modulation.

Interference between hole and electron oscillations does, in some cases, affect the period of the former, but not enough, apparently, to cause the considerable scatter about curve 4 in Fig. 2(a). However, the assumption made in our calculations, that the Fermi energy is constant, is not valid at the higher fields at which most of the short-period oscillations were observed. This is considered in detail in the next section.

In Fig. 3 the long-period data is just as scattered as in Fig. 2(a), but most of the shorter periods can be associated with the hole oscillations, associated with curve 4. Most of the scatter of these periods is caused by fluctuations in the Fermi energy. There are, however, a few points where $P\sim0.5\times10^{-5}$ G^{-1} between $\theta=20°$ and 45° which are probably "harmonics" of the electron oscillations represented by curve 3. For these electrons $g=m_0/m_c$ at $\theta=30.5°$ but it is within 20% of this value from $\theta=22°$ to $\theta=44°$. Spin splitting of the hole levels should produce harmonics at $\theta=\pm85.5°$, where $g=m_0/m_c$, and at $\pm67.5°$ where $g=3m_0/m_c$. The period of 0.4×10^{-5} G^{-1} at $\theta=70°$ is probably a harmonic (Eckstein and Ketterson[1] also observe a harmonic when the field is 70° from the z axis), but harmonics at $\pm85.5°$ would probably be too short in period to be observed in this experiment. The other points well below curves 3 and 4 could be caused by interference between electron and hold oscillations. There is no evidence for heavy carriers in Fig. 3.

FLUCTUATIONS IN THE FERMI ENERGY

The calculations of Smith *et al.*[2] show that at fields above 15 kG, the Fermi energy undergoes considerable

[13] See Fig. 3 of Ref. 9.

fluctuations which are roughly periodic in $1/H$ with the same period as the long electron oscillations. The period of the short oscillations is proportional to $[E_F(1+E_F/E_G)]^{-1}$ for electrons and to $[E_0-E_F]^{-1}$ for holes, and will therefore fluctuate with the Fermi energy. In fields below 20 kG the period of the hole oscillations with H along the y axis will vary between 0.36 and 0.72×10^{-5} G^{-1},[14] and a similar variation of the period of de Haas–van Alphen oscillations has been observed with H 8° from the y axis by Brandt and Lyubutina.[15] (These authors could not observe de Haas–van Alphen oscillations due to holes with H along the y axis because the contribution to the torque from the holes vanishes in this orientation.) The range of hole periods corresponds quite closely with the short periods observed in this work and by Lerner near the bisectrix axis. Ideally the modulation of the hole periods should be apparent when $1/H$ values are plotted against integers, and an example of this is shown in Fig. 6. More often, however, the pattern is distorted by interference and the modulation is not obvious. The slopes of linear portions of such graphs defined by only a few points may take almost any value between the maximum and the minimum of the modulated period. It thus appears that most of the data in the range 0.35 to 0.7×10^{-5} G^{-1} in Fig. 2(a) are from modulated-hole oscillations, and that the curve drawn by Lerner through some of these points, on which he bases his heavy holes, is quite fortuitous. Frequency modulation also accounts for the scatter of the hole periods in Fig. 3.

CONCLUSION

Although this work has produced no new information about the band structure of bismuth, it provides alternative explanations for the observations which led to the proposal of two new sets of carriers, and demonstrates that extreme caution must be used in the interpretation of Shubnikov–de Haas oscillations. It is interesting to compare our experimental results with those of Lerner, who measured dR/dH, and of Eckstein and Ketterson,[1] who measured dR/dH and d^2R/dH^2. They find far fewer spurious periods due to interference. This may be partly because the differential methods are more sensitive than ours, enabling long-period measurements to be made at lower fields where short-period oscillations are too small to cause interference, and partly because differentiation emphasizes the interference so that it may be allowed for in the analysis of the data. It is apparent that a much more satisfactory method of analysis is that adopted by Smith *et al.*,[2] in which they try to assign a quantum number to each resistance dip. It is doubtful, however, whether this method could be used conveniently at fields below 20 kG, where the quantum numbers become large and much more difficult to fit by trial and error.

Finally, we should emphasize that while our results are consistent with the band-structure model of Smith *et al.*, which involves no heavy carriers, there is still no good explanation of the high specific heat of bismuth. According to these band-structure parameters the electronic component of the low-temperature specific heat of bismuth is given by γT, where $\gamma=2.50$ erg cm^{-3}°K^{-2}, which is much lower than the measured values. The value of γ is, however, dependent on the carrier concentration in the metal, but we have to assume 3.3×10^{-4} excess electrons or 5.3×10^{-4} excess holes per atom to raise γ to Phillips[7] value of 9.8 erg cm^{-3}°K^{-2}, or 1.9 $\times10^{-3}$ excess electrons or 2.2×10^{-3} excess holes per atom to raise it to the value of 31 erg cm^{-3} °K^{-2} obtained by Kalinkina and Strelkov.[6] The purities of the samples of these authors do not justify such an assumption. If we assume that there are six electron and two hole ellipsoids in the band structure we can double our estimated value of γ, but this would be inconsistent with Zitter's[10] low-field galvanomagnetic measurements. It is possible, therefore, that the high specific heat of bismuth might be due in part to other groups of charge carriers, but no direct evidence for these has yet been found.

ACKNOWLEDGMENTS

We are grateful to Dr. A. C. Hollis Hallett and Dr. G. M. Graham for many helpful discussions.

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[14] See Fig. 5 of Ref. 2.

[15] N. B. Brandt and L. G. Lyubutina, Zh. Eksperim. i Teor. Fiz. **47**, 1711 (1964) [English transl.: Soviet Phys.—JETP **20**, 1150 (1965)].