Shubnikov–de Haas Effect in Bismuth*

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The oscillatory component of the transverse magnetoresistance of single crystals of bismuth has been measured at 1.15°K. The magnetic field range was 700 to 23 000 G. Measurements were taken in the three principal planes. The experimental results may be explained on the basis of two sets of carriers. No evidence was found for the third and fourth carriers reported recently. For holes we find $\beta_{11}{}^2=75.4\times10^{+28}(E_F{}^h)^2$ erg^{-2}, $\beta_{11}\beta_{33}=7.25\times10^{+28}$ $(E_F{}^h)^2$ erg^{-2}; for electrons, $\alpha_{11}\alpha_{33}=23.3\times10^{30}(E_F{}^e)^2$ erg^{-2}, and the tilt angle is 4°. Here E_F is the Fermi energy measured in ergs. The effects of spin splitting of hole Landau levels is observed at 70° from the z axis, from which we find $g_3\cong62$ (assuming $g_1\ll g_3$).

I. INTRODUCTION

QUANTUM oscillations have been observed in susceptibility (de Haas–van Alphen effect), magnetoresistance[1–3] (Shubnikov–de Haas effect), specific heat (magnetothermal oscillations), velocity of sound,[4] ultrasonic attenuation, and magnetostriction.[5] For the extraction of the periods of these quantum oscillations, the Shubnikov–de Haas effect is the simplest and most effective method for the semimetals.

Charge neutrality can be satisfied to within experimental error if we assume one hole and three electron ellipsoids or two hole and six electron ellipsoids. Lerner[1] recently found indications of a third and fourth carrier (called heavy holes and electrons by him) in his magnetoresistance measurements. It was the purpose of the present work to verify the existence or nonexistence of these additional carriers.

II. THEORY

Bismuth has rhombohedral crystal structure. We define the x, y, and z axis to be the binary, bisectrix, and trigonal axis of Bi.

The usual model of the band structure of Bi is the Shoenberg-Brandt model. In this model three electron ellipsoids are located symmetrically about the z axis. In addition, a hole ellipsoid lies on the z axis. The form of the principal electron ellipsoid is

$$E_F{}^e=\alpha_{11}P_x{}^2+\alpha_{22}P_y{}^2+\alpha_{33}P_z{}^2+2\alpha_{23}P_yP_z, \qquad (1)$$

and that of the hole ellipsoid is

$$E_F{}^h=\beta_{11}(P_x{}^2+P_y{}^2)+\beta_{33}P_z{}^2. \qquad (2)$$

The two remaining electron ellipsoids are obtained by a $\pm120°$ rotation of the reciprocal effective mass tensor α_{ij} about the z axis.

* Based on work performed under the auxpices of the U. S. Atomic Energy Commission.

[1] L. S. Lerner, Phys. Rev. **130**, 605 (1963); **127**, 1480 (1962).

[2] A comprehensive list of references for these other effects pertaining to the Fermi surface of Bi is given in Ref. 1.

[3] C. G. Grenier, J. M. Reynolds, and J. R. Sybert, Phys. Rev. **132**, 58 (1963).

[4] J. G. Mavroides, B. Lax, K. J. Button, and Y. Shapira, Phys. Rev. Letters **9**, 451 (1962).

[5] B. A. Green and B. S. Chandrasekhar, Phys. Rev. Letters **11**, 331 (1963).

The energy levels of an ellipsoid for an electron on an extremal orbit in a magnetic field, including the effects of spin, are

$$E_n=(n+\tfrac{1}{2})\hbar\omega_c\pm\tfrac{1}{2}g\mu H=(n+\tfrac{1}{2}\pm\Delta)\hbar\omega_c, \qquad (3)$$
$$\Delta=\tfrac{1}{2}g(m^*/m),$$

and where μ is the free electron Bohr magneton. Figure 1 shows a possible energy level diagram. No electron spin splitting was seen in this experiment so our discussions pertain only to holes.

The theory of the g factor in bismuth has been worked out in detail by Cohen and Blount.[6] We give here only a summary of their results. The hole g factor for H in the x-z or y-z plane is given by $g(\theta)=(g_1{}^2\sin^2\theta$

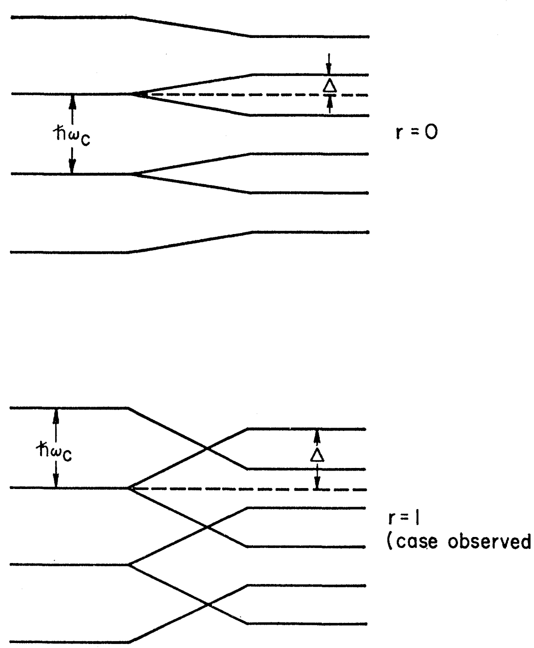

FIG. 1. Energy level of an electron in a magnetic field including spin for the case of $\Delta=(\hbar\omega_c/4)$ (upper diagram) which corresponds to H being 5° from the y axis in the y-z plane. The lower diagram is the case $\Delta=\frac{3}{4}\hbar\omega_c$ corresponding to H being 20° from the y axis in the y-z plane. In both cases one expects to see only the second harmonic.

[6] M. H. Cohen and E. T. Blount, Phil. Mag. **5**, 115 (1960).

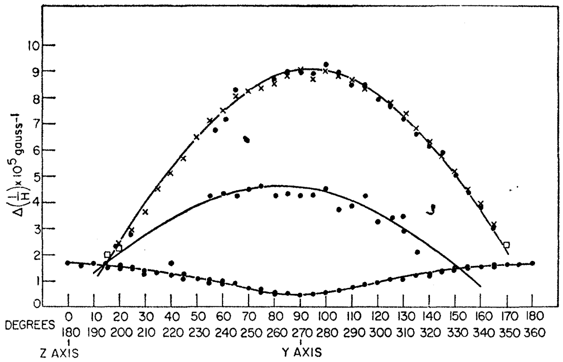

FIG. 2. Observed periods as a function of magnetic field angle for H in the y-z plane and $I\|x$. Crosses are low-field data (700–2000 G), while circles are high-field data. Squares represent periods derived from analysis of beat periods. The two upper curves are for electrons and the lower one is a hole curve. The curves are those derived from least-squares fits.

$+g_3^2\cos^2\theta)^{1/2}$ where θ is measured from the z axis. Since the g factor is now allowed to be different from two, the usual Dingle-Sondheimer-Wilson term, which multiplies all harmonics of the de Haas–van Alphen effect, changes to $\cos(r(m^*/m_s)\pi)$ where m^* is the effective cyclotron mass and m_s is defined as: $m_s=(2m/g)$. In particular, if $g=(m/m^*)(2r+1)$ we expect to see no contribution from the first harmonic. In this case $2\Delta=r+\frac{1}{2}$.

The period of the quantum oscillations is given by the usual Onsager expression

$$\Delta(1/H)=eh/cA, \qquad (4)$$

where A is the extremal cross-sectional area in momentum space of the Fermi surface. This expression may be combined with (1) and (2) to obtain the expressions for the period as a function of angle. The expressions resulting may be found in Ref. 7.

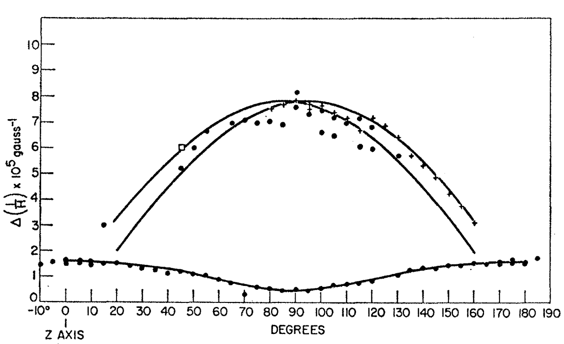

FIG. 3. Observed periods as a function of magnetic field angle for H in the x-z plane and $I\|y$. Crosses are low-field data (700–2000 G), while circles are high-field data. Squares represent periods derived from analysis of beat periods. The two upper curves are for electrons and the lower one is a hole curve. The curves are those derived from least-squares fits.

[7] J. B. Ketterson and Y. Eckstein, Phys. Rev. **132**, 1885 (1963).

III. EXPERIMENT

Bismuth (purchased from the Cominco Company) of quoted purity better than 0.999999 was melted in a conical quartz vessel placed in a furnace. The surface of the metal was protected from the atmosphere by a layer of Dow Corning No. 704 diffusion pump oil. The furnace was slowly turned off by a motor-variac combination over an 18-h period. The region near the tip of the cone was maintained colder than the rest of the bulk so as to favor growth starting from that point. A single crystal resulted on the first attempt indicating a fairly high degree of purity.[8]

Three samples approximagely $\frac{1}{8}$ in$\times\frac{1}{8}$ in.$\times\frac{1}{2}$ in. were cut with a Servo-Met Spark Cutter with the long axes parallel to the x, y, and z axis of Bi. The magnet, cryogenics, detection and recording systems were the same as those used in our previous studies on Sb.[7] The measured residual resistance ratio for $I\|y$ was 110.

While taking data the current in the sample was in the region of 10–100 mA, and a series of runs at currents between 0.5–100 mA were made so as to be sure that there was no helium boiling or other phenomena that

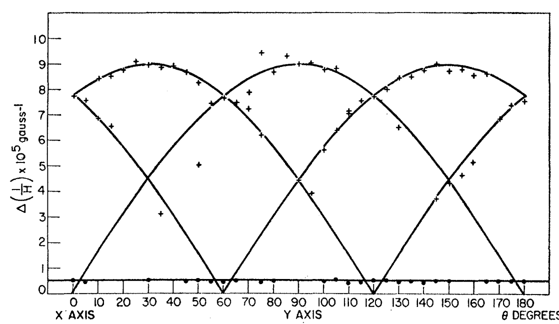

FIG. 4. Observed periods as a function of magnetic field angle for H in the x-y plane and $I\|z$. Crosses are low-field data (700–2000 G), while circles are high-field data. The two upper curves are for electrons and the lower one is a hole curve. The curves are those derived from least-squares fits.

might affect the data. The form of the resulting data was independent of sample current in this range. In particular, the spike-like character of data for $I\|z$ was seen at all currents. Data was taken for H in the x-y, x-z, and y-z planes of Bi and the data is shown in Figs. 2, 3, and 4. Data for holes on an enlarged scale are shown in Figs. 5 and 6. For H in the x-y and y-z planes, the data were taken to 13.8 kG while for H in the x-z plane the data were extended to 25 kG. Data were also taken at low fields (approximately 700–1000 G) because here only one oscillation dominates (that of smaller area) and it is thus easier to analyze long period contributions before the amplitude of shorter periods grows enough to complicate the analysis. Both first and second derivatives of the magnetoresistance were taken as a function of angle, the second derivative

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

being employed to emphasize the shorter hole periods, especially at angles where it is expected to double.

IV. RESULTS AND DISCUSSION

A least-squares fit was made to the data for the principal branches of the electron and hole ellipsoids. From those fits we obtained the following combinations of reciprocal effective mass tensor elements,

$$\begin{aligned} \text{Tilt angle} &= \tfrac{1}{2}\,\text{arc}\,\tan(2\alpha_{23}/\alpha_{22}-\alpha_{33})=4°, \\ \alpha_{11}\alpha_{33} &= 23.3\times10^{30}(E_F{}^e)^2\ \text{erg}^{-2}, \\ \beta_{11}\beta_{33} &= 7.25\times10^{28}(E_F{}^h)^2\ \text{erg}^{-2}, \\ \beta_{11}{}^2 &= 75.4\times10^{28}(E_F{}^h)^2\ \text{erg}^{-2}. \end{aligned} \tag{5}$$

The effects of spin splitting of the hole levels are seen at a few angles. At 70° from the z axis the hole period suddenly decreases by a factor of 2 (see Fig. 7).

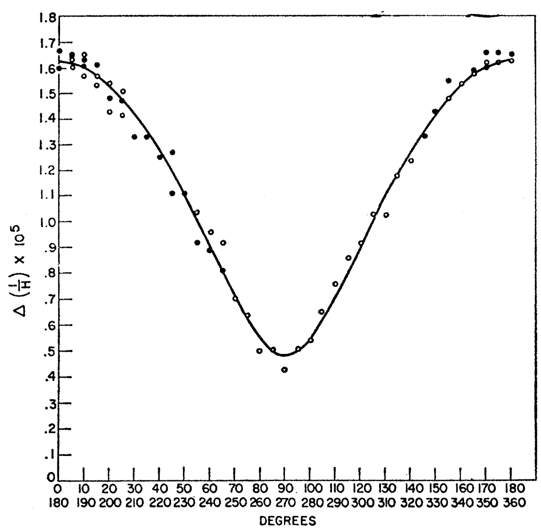

FIG. 5. Observed hole periods as a function of magnetic field angle for H in the y-z plane and $I\|x$. The curve is the result of a least-squares fit.

This is just the angle at which Smith[9] and Vuilliman[10] have shown that the hole levels are split into equally spaced levels and one would expect the first harmonic to disappear and the second to appear (Fig. 1).

The analysis of the data is complicated by several factors. First there is the usual problem of separating out the contributions from the various sheets of the Fermi surface. Ordinarily this is done by the analysis of the beat periods.[7] This was not practicable in bismuth because (1) the total number of oscillations was small (at most fifteen) and (2) periods from the various sheets tended to be dominant for only a few oscillations, and therefore the periods could not be determined with as high an accuracy as desirable. The problem was, of course, simplier along an axis of high symmetry (x and z axis) because there distinct electron ellipsoids have the same period. There is a second problem which also appears in the data of Lerner. As the magnetic field is increased, the electron oscillations for electron ellipsoids having small area change from approximately growing sine waves periodic on $(1/H)$ to sharp spikes [also periodic in $(1/H)$]. Thus each maximum from each sheet of these electron ellipsoids contributes a spike at high fields. If one were to plot the maxima and minima of each of these spikes, one might wrongly conclude that there was a rather fast period dominating the magnetoresistance and thus conclude that there is yet another carrier in Bi. At a few angles we analyzed the data carefully and were able to assign each of the peaks to a given ellipsoid. In general, it was simpler to analyze low or high field than it was to treat the intermediate field region.

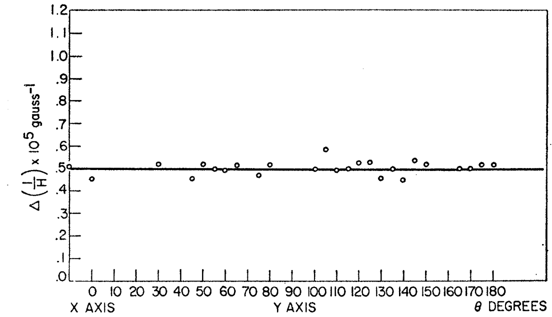

FIG. 6. Observed hole periods as a function of magnetic field angle for H in the x-y plane. The curve is the result of a least-squares fit.

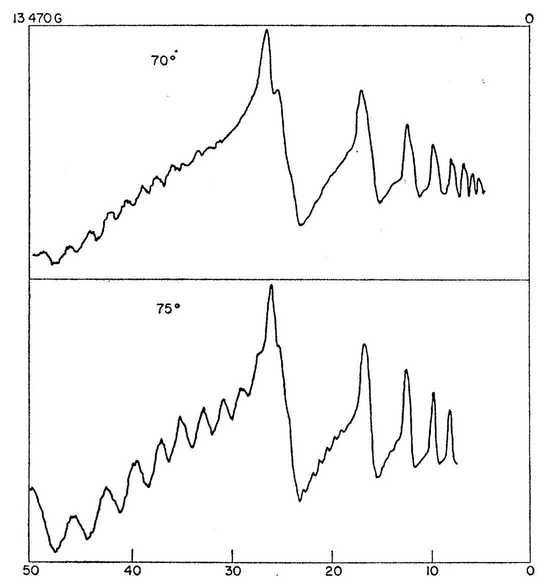

FIG. 7. Experimental curves for $I\|y$ H at 70° and 75° from the z axis. Note how the second harmonic appears abruptly for a change of only 5° in magnetic field angle. In addition, note the spikey character of the electron peaks.

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[9] G. E. Smith, G. A. Baraff, and J. M. Rowell, Phys. Rev. **135**, A1118 (1964).

[10] J. Vuilliman, IBM J. Res. Develop. (to be published).

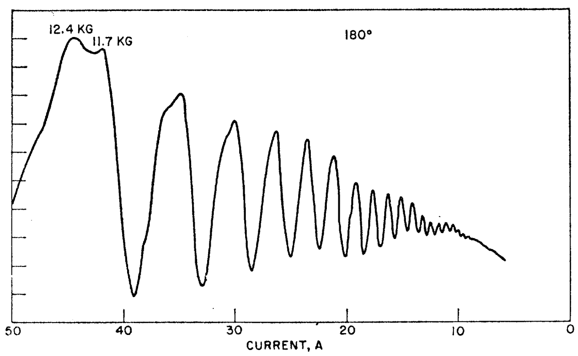

FIG. 8. Experimental curve for $I\|x$ and $H\|z$. A splitting is clearly observed at 12 kG.

In his recent pulsed field measurements, Vuilliman[10] has reported that the hole levels are split into equally spaced levels near 70° and 85° from the z axis. Using the spin masses given by Smith[9] one finds essentially the same angles. From the angle where the period doubles one can find an estimate of g_3 assuming g_1 to be small. The condition for equally spaced levels is

$$\frac{(g_1^2 \sin^2\theta_D + g_3^2 \cos^2\theta_D)^{1/2}}{(\beta_{11}^2 \cos^2\theta_D + \beta_{11}\beta_{33} \sin^2\theta_D)^{1/2}} = 2r+1\,, \tag{6}$$

where θ_D is an angle at which the first harmonic disappears.

Using our values of β_{ij}, $\theta_D = 70°$ and $r=1$, we find $g_3 = 34.2\times10^{14}\ E_F{}^h\ \mathrm{erg}^{-1}$. Using Brandt's[11] $E_F{}^h = 1.8\times10^{-14}$ ergs, we find $g_3 = 62$. This agrees with the findings of Vuilliman and Smith. Our ratio β_{11}/β_{33} agrees well with published values.[3,9,11]

For angles near $H\|z$ the maxima are split (see Fig. 8). It is found that this splitting is too large to be interpreted as hole spin splitting. It is possible that we see a period half of the hole period and this is the electron period. This interpretation gives

$$\alpha_{11}\alpha_{22} = 0.09\times10^{28} E_F{}^2\ \mathrm{erg}^{-2}. \tag{7}$$

This value is in agreement with the value quoted by Brandt; however, Brandt obtained his value by extrapolation. From the value of $\alpha_{11}\alpha_{22}$ given here one finds $(\alpha_{33}/\alpha_{22}) = 122$ compared with 60 quoted by Smith.

It should be pointed out that the "singularities" observed by Brandt, Dolgolenko, and Stupochenko[11] and the "interference effect" reported by Suzuki and Kikuchi,[12] which appear at approximately 5° and 20° from the binary axis, are the results of spin splitting of the hole levels as described perviously here.

We would like to emphasize that the least-squares fits of the electron data invariably come out to be hyperbolic and the period is imaginary for areas of large cross section, showing the Fermi surface to be slightly nonellipsoidal. It can be seen that the variation of the data as a function of angle is quite smooth.

It should be said that accurate geometric-resonance measurements of a few of the electron periods would allow an independent measurement of α_{ij} which would not necessitate the use of the high fields used by Smith, and its associated reliance on a particular model. Such a study was carried out by Reneker[13] but was of a preliminary nature. An attempt is now being made to observe accurate geometric resonances in Bi.

Finally, it should be pointed out that since bismuth contains so few carriers (10^{-5}/atoms) one has to be cautious about comparing the results of one experiment to another. Ratios of values of α_{ij} are more likely to show close agreement. As an example, the principal electron period of Lerner and of Brandt differs from ours for $H\|y$. Brandt finds the period to be 7.9×10^{-5}, Lerner in his second paper finds $6.3\times10^{-5}\ \mathrm{G}^{-1}$, while we get $8.9\times10^{-5}\ \mathrm{G}^{-1}$. The differences between these values are outside the experimental error and are caused by the change in the Fermi level due to carriers contributed by impurities.

[11] N. B. Brandt, D. F. Dolgolenko, and N. N. Stupochenko, Zh. Eksperim. i Teor. Fiz. **45**, 1319 (1963) [English transl.: Soviet Phys.—JETP **18**, 908 (1964)].

[12] M. Suzuki and S. Kikuchi, J. Phys. Soc. Japan **19**, 134 (1964).

[13] D. H. Reneker, Phys. Rev. **115**, 303 (1959).