The magnetic properties of bismuth
III. Further measurements on the de Haas-van Alphen effect

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Introduction

As was first shown by de Haas and van Alphen (1932), the susceptibility of bismuth single crystals at low temperatures depends in a peculiar periodic fashion on the magnetic field, and later this effect was studied in greater detail by Shoenberg and Zaki Uddin (1936), especially as regards the influence of temperature and impurities. The general features of the effect were found to agree qualitatively with Peierls' theory (Peierls 1933), but since this theory was for a cubic lattice it could take no account of the directional features of the effect, and no detailed comparison could be made between the theory and the experiments. Since then, however, the theory has been developed by taking into account the actual crystal symmetry of bismuth (Blackman 1938; Landau 1938), and Landau has shown that the theory assumes a relatively simple analytical form at low field strengths, thus making desirable measurements at fields rather lower than those used in the previous experiments.

With the ordinary Faraday method, it is not easy to make accurate susceptibility measurements at field strengths below about 4000 gauss, and this indeed was roughly the lowest field used in the previous work, but an even more serious disadvantage of this method is that it necessarily involves the crystal being in an inhomogeneous field, with the result that the measured susceptibility is always an average over an appreciable range of fields. Thus if the susceptibility varies rapidly with field—as is particularly the case at low fields—the measured susceptibility-field curve is a greatly "smoothed-out" version of the true curve. To avoid these difficulties, we have adopted a different method in the present investigation, namely the measurement of the couple acting on a crystal suspended in a uniform magnetic field; this has the disadvantage that it gives only differences of susceptibilities, but for purposes of comparison with theory this is not serious, and is outweighed by the great ease of measurement of a couple, and by the fact that no inhomogeneity of field is required.

Using this method, we have studied the de Haas-van Alphen effect down to about 1500 gauss, along a variety of directions in the crystal at temperatures from 2·1 to 20° K (mostly at 4·2° K, however), and a detailed comparison with Landau's theory has been made, from which we have been able to deduce approximate values of the effective masses, the chemical potential, and the number of the electrons responsible for the de Haas-van Alphen effect in bismuth.

Experimental technique

(*a*) *Measurement of the couple*

The specimen was suspended from the short beryllium bronze wire w by means of a long quartz rod q, which carried also a mirror m and damping vanes v dipping in oil. Any couple acting on the specimen slightly twisted the wire, thus rotating the mirror and causing a displacement of the image of an illuminated slit, as produced by the lens l and observed by a travelling microscope. The whole suspension hung inside a glass tube filled with helium gas at low pressure, the lower part of this tube being surrounded by liquid hydrogen or helium in a Dewar vessel d_1, itself surrounded by a second Dewar vessel d_2 containing liquid air; the specimen was maintained at the temperature of the surrounding bath by conduction through the gas in the tube. The whole suspension could be easily removed—for the purposes of changing the specimen or its position—by undoing the brass-glass joint at j, which was made vacuum-tight with plasticine.

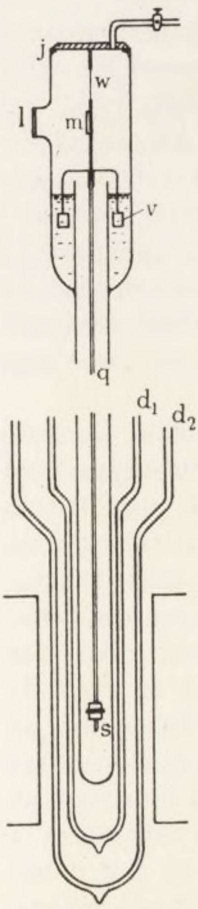

Fig. 1

The actual measurement of the couple was carried out by measuring the displacement of the travelling microscope necessary to bring back the image of the slit on to the cross-wires. The "zero" reading of the microscope, i.e. the position when there was no couple acting, proved to be very constant, but to allow for any slight changes which did occur, zero readings were taken several times during each series of measurements, and interpolated values used for the intervening measurements.

The calibration of the instrument was made by measuring the couple acting on a bismuth crystal of known mass at room temperature, assuming the difference of principal susceptibilities to be $0{\cdot}43 \times 10^{-5}$ per c.c. (Focke 1930), and the calibration showed that a couple of 1 dyne-cm. caused a displacement of 0·06 cm., while the accuracy of measurement of this displacement—limited by slight vibrations, slight changes of the zero, and the breadth of the image—was about 0·002 cm. By using a thinner wire there should be no difficulty in increasing this sensitivity at least ten times, but we did not do this since it would have given deflexions for the largest couples too large to be measured by the travelling microscope (which had a range of only 5 cm.), and it was convenient to carry out all the measurements with a single suspension. In practice the smallest couples to be measured were of order $\frac{1}{2}$ dyne-cm. and the largest of order 50 dyne-cm., so that except for the lowest fields a fairly high accuracy was obtained.

(*b*) *The magnetic field*

The field was provided by an air-cooled electromagnet with a pole-piece gap of 5 cm., and the highest field that could conveniently be obtained was 9500 gauss, for a current of 30 amp. The magnet was calibrated by measuring the couple on a bismuth crystal at room temperature for various currents; since the susceptibilities are constant at room temperature this couple is proportional to the square of the field, and hence, knowing the field for the largest current from an ordinary calibration with search coil and fluxmeter, all the fields for lower currents were determined. The calibration of the lower field strengths was checked also by the search coil and fluxmeter. The magnet was mounted on a turn-table provided with a scale of angles, and the apparatus was mounted on a support independent of the magnet, so that the angle between the field and any fixed direction in the specimen could be varied by rotating the magnet. In determining this angle from the scale on the magnet, a small correction was necessary for the slight turning of the specimen itself under the influence of the couple acting on it; this correction was, however, never greater than 1°, and could usually be neglected.

(*c*) *The crystal*

The crystal* was grown by Kapitza's method of cooling a molten piece of bismuth from one end on a copper plate with a temperature gradient; the material used was Hilger H.S. bismuth no. 10,283, which the previous work had shown to be very pure, and the mass of the crystal was 0·141 g. By means

* Measurements were made also with crystals grown by other methods, which showed that the method of growing the crystal did not affect the results obtained.

of a seed crystal the crystal axes were oriented in a definite way relative to a small rectangular quartz plate, to which the crystal was attached with Durofix after the seed had been removed at a narrow constriction. This orientation was such that the trigonal (z) axis was normal to the plate, while the binary (x) axis was parallel to one edge of the plate. The whole plate was then stuck with Durofix to the quartz rod of the suspension, and we could thus set either the x or the y axis (or any intermediate direction in the xy plane) in the plane of rotation of the magnet, while the z axis was always in this plane (see fig. 2).

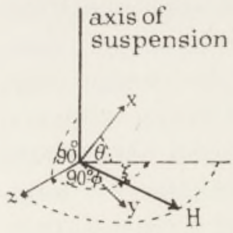

FIG. 2

EXPERIMENTAL RESULTS

The couple C per unit volume acting on a body with magnetization I in a magnetic field H is given by $[IH]$ per unit volume, and with the crystal suspended as described above, this reduces to

$$C = \left(\frac{I_3}{H_3} - \frac{I_2}{H_2}\sin^2\theta - \frac{I_1}{H_1}\cos^2\theta\right) H^2 \cos\phi \sin\phi, \qquad (1)$$

where H_1, H_2, H_3 and I_1, I_2, I_3 are the components of H and I along the x, y, z axes respectively, $90° - \phi$ is the angle between H and the z axis, and θ is the angle between the x axis and the plane of rotation of H (i.e.

$$H_1 = H\cos\theta\cos\phi, \quad H_2 = H\sin\theta\cos\phi, \quad H_3 = H\sin\phi);$$

this geometry is illustrated by the sketch of fig. 2. All our experiments were made with $\theta = 0$ or $90°$, so that

$$\frac{C}{H^2\cos\phi\sin\phi} = \frac{I_3}{H_3} - \frac{I_1}{H_1} \quad \text{or} \quad \frac{I_3}{H_3} - \frac{I_2}{H_2}, \text{ respectively.} \qquad (2)$$

As a preliminary check on the working of the apparatus, measurements were made at room and liquid-air temperatures, when as we know from the previous work, the differences on the right-hand side of (2) are constants equal to each other and to the difference of the principal susceptibilities of bismuth. Thus at constant H, the angle ϕ was varied and $C/H^2\cos\phi\sin\phi$ was plotted against $H\cos\phi$ (the component of H in the xy plane); a very good constancy was obtained, and we confirmed also that the ratio of this constant value at liquid-air temperature to that at room temperature was very close to the ratio of the susceptibility differences at these temperatures as given by the previous work. The positions of the magnet for which $\phi = 0$ and 90° were determined from the magnetic measurements, as the positions for which there was no couple, and we verified that these positions were accurately 90° apart.

At liquid hydrogen and helium temperatures—when the susceptibility is no longer independent of the field—we found that the couple was always zero for $\phi = 90^\circ$, but for $\phi = 0$ the couple was zero only in the case $\theta = 0$ (i.e. the x axis parallel to the field). If the crystal was hung so that θ differed from 0, even very slightly, the couple varied in a periodic fashion with field for $\phi = 0$, becoming successively positive and negative and increasing in magnitude as H was increased. As can be seen from eqn. (1), the couple for $\phi = 0$ is just

$$C = I_3 H,$$

and so the fact that it does not vanish means that there is a non-vanishing component of magnetization along the trigonal axis even when the field is perpendicular to the trigonal axis, and the observed periodic variation is due to the field dependence of this component. It can easily be seen from considerations of crystal symmetry that no such component can occur for the particular case of the field along the x axis, and this indeed is what was found experimentally. A very slight error in the setting of the crystal however, such as to make $\theta = 3^\circ$ say, is sufficient to produce a large effect; the reason for this will become apparent when we consider the theory.

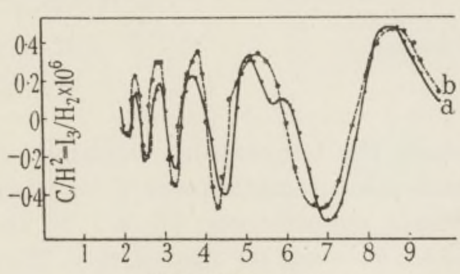

FIG. 3. $\theta = 90^\circ$, $\phi = 0$, $4{\cdot}2^\circ$ K (two independent settings).

In fig. 3 we show the variation of C/H^2 ($= I_3/H_2$) with H, for the case $\phi = 0$, $\theta = 90^\circ$, and in this case also, the detailed form of the curves is very sensitive to slight changes in θ. This is illustrated by the differences between the two curves shown, which were for two independent series of measurements in between which the crystal was removed from the suspension and reset; the difference in θ could hardly have been greater than 2°.

The main measurements at low temperatures were of the field variation of the couple for different values of ϕ and for θ either 0 or 90°; these results may be most simply represented as curves of $C/H^2 \cos\phi \sin\phi$ against H. Since, as we shall see later, the theory is not able to describe all the details of the curves, but only their general features, we present all the reliable experimental curves to enable comparison with any future theoretical

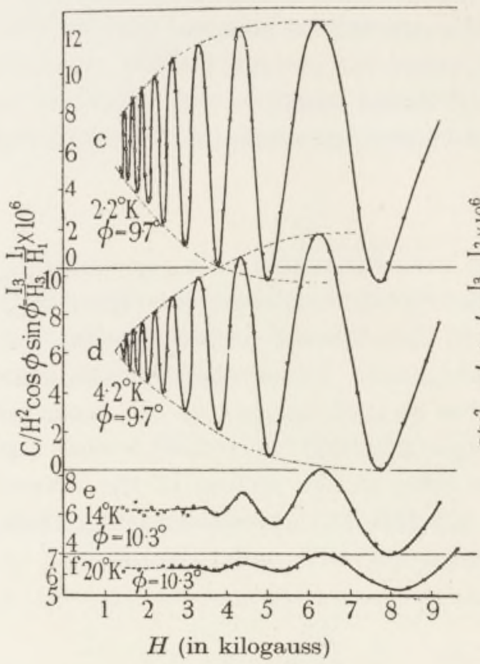

FIG. 4. $\theta = 0$.

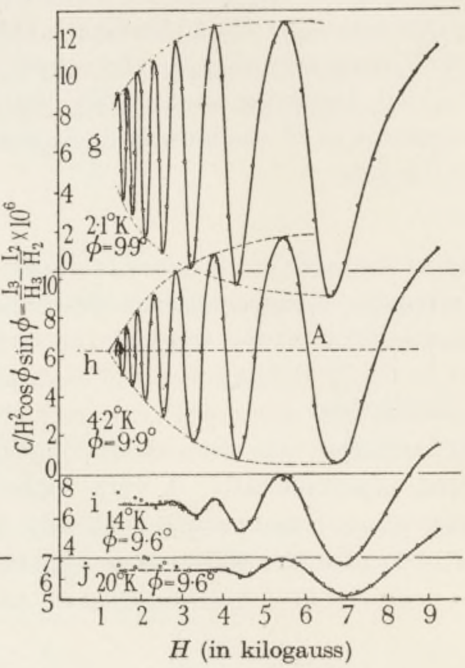

FIG. 5. $\theta = 90°$.

developments. To study the temperature variation of the de Haas-van Alphen effect, we made measurements (mostly for one particular value of ϕ, about 10°) at different temperatures: 2·1, 4·2, 14 and 20° K; these are shown in figs. 4 and 5 for $\theta = 0$ and 90° respectively. The effect of varying ϕ was studied systematically only at 4·2° K, and the results are shown in figs. 6 and 7, which are for $\theta = 0$ and 90° respectively. We should point out that in the case $\theta = 0$, positive and negative values of ϕ are entirely equivalent, while in the case $\theta = 90°$ they are not; this is in agreement with the requirements of crystal symmetry, and is also taken account of by the detailed theory, as can be seen from the formulae given below.

Finally, we should draw attention to one feature of many of the curves which is due purely to experimental errors and should not be considered as significant. This is that at low fields the susceptibility difference sometimes

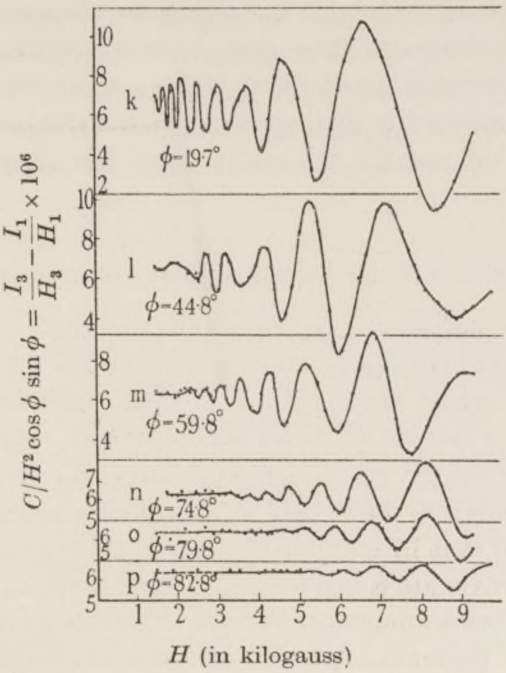

FIG. 6. $\theta = 0$, 4·2° K.

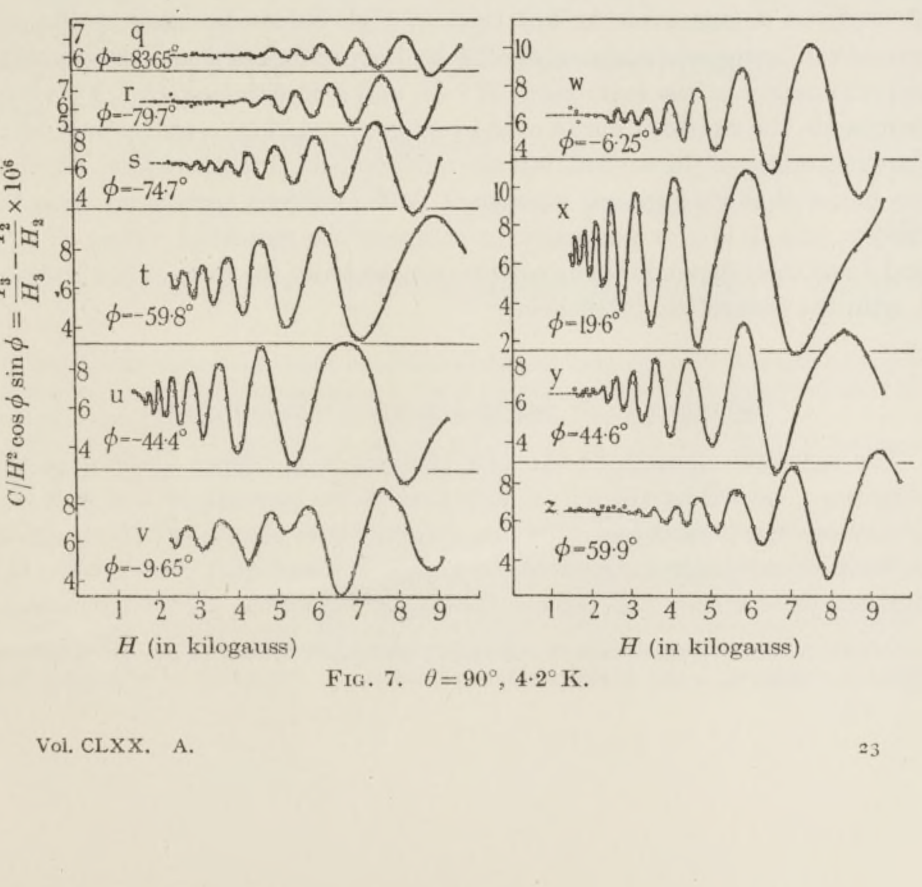

FIG. 7. $\theta = 90°$, 4·2° K.

appears to become not constant, but either to increase or decrease slowly with field. Rough estimates show that errors in the determination of the field and of the deflexion (particularly if the zero varies slightly) are quite adequate to account for any such apparent systematic trend in the susceptibility difference, and also for the scattering of the experimental points at low fields.

Preliminary discussion of the curves

All the curves consist of a periodic variation about a constant value, which represents the susceptibility difference at low fields, and is, within our experimental errors, the same for all cases, and independent of temperature between 2 and 20° K. If we disregard such "distorted" curves as a, b, k and v, it can be seen that roughly the curves for different orientations at the same temperature differ only as regards the scales of the ordinates and abscissae, and that by suitable changes of these scales they can all be brought into approximate coincidence. As regards the curves for the same orientation at different temperatures these evidently have the same "scale of periodicity", i.e. the maxima and minima occur at the same field strengths, but they cannot be brought into coincidence by a mere change of scale of the ordinates, since the amplitude of the periodic variation depends more strongly on temperature at low than at high fields. In other words, the curves can be represented analytically by the product of a periodic junction, approximately of the form $\sin(\alpha/H-\delta)$, and a function $\gamma f(H/\alpha, T)$, which represents the envelope curve of the periodic variation; α and γ depend on the orientation of the crystal, but are independent of temperature. We shall see below that this general statement is in excellent agreement with the theory, and it is now necessary to compare the empirical values of α, γ and δ and their dependence on orientation, and also the form of the function f, with the theoretical predictions.

Statement of the theoretical predictions

The essential advance of the new theories is in taking account of the anisotropy caused by the actual structure of the bismuth lattice, and this introduces four parameters m_1, m_2, m_3 and m_4* (they should strictly speaking be written as tensor components m_{11}, m_{22}, m_{33} and m_{23}), which have the dimensions of masses and replace the single "effective" electronic mass of

* Blackman uses parameters α, which are related to these m's by the equation $m_0/\alpha=m$, where m_0 is the ordinary electronic mass.

Peierls' original theory; they may be thought of roughly as the effective electronic masses in different directions in the crystal. Just as before, the theory also involves the parameter E_0, the chemical potential of the electrons (the energy of the highest occupied state), and it turns out that a marked field dependence of susceptibility can be expected at low temperatures, if some of the effective masses and E_0 are abnormally low. In Blackman's work the results are given in implicit form, i.e. both the susceptibility and the field are given as complicated functions of the above parameters, and the susceptibility field curves are then deduced by graphical computation choosing particular values of the parameters which give the best agreement with the previous experimental data. Landau showed that for sufficiently low fields and temperatures (fortunately just covering the range of the present experiments) Blackman's results can be reduced to give an explicit formula for the susceptibility as a function of field;* we shall therefore refer only to Landau's formulae in the comparison with the present experiments, and then finally compare our final estimates of the parameters with Blackman's estimates.

The explicit formulae for the susceptibility give† in the case $\theta = 0$

$$\frac{I_3}{H_3} - \frac{I_1}{H_1} = (m_1 - m_3) f(\beta_1 H) + \left[\frac{m_1 + 3m_2}{4} - m_3 - m_4 \frac{\sqrt{3}}{2} (\tan\phi - \cot\phi)\right] f(\beta_2 H)$$
$$+ \left[\frac{m_1 + 3m_2}{4} - m_3 + m_4 \frac{\sqrt{3}}{2} (\tan\phi - \cot\phi)\right] f(\beta_3 H), \qquad (3)$$

where

$$\left.\begin{aligned} \beta_1 &= \lambda \cos\phi (m_1 + m_3 \tan^2\phi)^{\frac{1}{2}}, \\ \beta_2 &= \lambda \cos\phi \left(\frac{m_1 + 3m_2}{4} + m_3 \tan^2\phi - \sqrt{3} m_4 \tan\phi\right)^{\frac{1}{2}}, \\ \beta_3 &= \lambda \cos\phi \left(\frac{m_1 + 3m_2}{4} + m_3 \tan^2\phi + \sqrt{3} m_4 \tan\phi\right)^{\frac{1}{2}}, \end{aligned}\right\} \qquad (4)$$

* We should emphasize that the advance of these formulae on Blackman's results is a matter entirely of mathematics, no new physical assumptions being required in the derivation. The method of derivation is described in the appendix.

† The formulae are valid for $E_0 \gg kT \gg \beta H/2\pi^2$. If $E_0 > \beta H$, and $E_0 \gg kT$, but nothing is known of the relative sizes of βH and kT (8) is replaced by

$$f(\beta H) = A \left[\frac{\pi^2}{6}\left(\frac{k}{E_0}\right)^{\frac{1}{2}} + \frac{1}{2\sqrt{\tau}}\left(\frac{\beta H}{2\pi^2 kT}\right)^{-\frac{3}{2}} \sum_{p=1}^{\infty} \left\{\frac{\sin\left(\frac{2\pi p E_0}{\beta H} - \frac{\pi}{4}\right)(-1)^p}{\sqrt{p}\sinh 2\pi^2 pkT/\beta H}\right\}\right], \qquad (8a)$$

of which (8) is a special case. Similarly it is easy to deduce a suitable approximation for *very* low temperatures ($kT \ll \beta H/2\pi^2$). Landau's general formula (8*a*) is derived in the appendix (eqn. (A 11)).

while for $\theta = 90°$

$$\frac{I_3}{H_3} - \frac{I_2}{H_2} = [m_2 - m_3 + m_4(\tan\phi - \cot\phi)]f(\beta_1' H) + 2\left[\frac{3m_1 + m_2}{4} - m_3 - \frac{m_4}{2}(\tan\phi - \cot\phi)\right]f(\beta_2' H), \quad (5)$$

where

$$\left.\begin{aligned} \beta_1' &= \lambda\cos\phi\,(m_2 + m_3\tan^2\phi + 2m_4\tan\phi)^{\frac{1}{2}}, \\ \beta_2' &= \lambda\cos\phi\left(\frac{3m_1 + m_2}{4} + m_3\tan^2\phi - m_4\tan\phi\right)^{\frac{1}{2}}, \end{aligned}\right\} \quad (6)$$

λ is a constant given by

$$\lambda = e\hbar/c[m_1(m_2 m_3 - m_4^2)]^{\frac{1}{2}}, \quad (7)$$

and f is the function

$$f(\beta H) = A\left[\frac{\pi^2}{6}\left(\frac{k}{E_0}\right)^{\frac{1}{2}} - \frac{1}{\sqrt{T}}\left(\frac{\beta H}{2\pi^2 kT}\right)^{-\frac{3}{2}} e^{-2\pi^2 kT/\beta H}\sin\left(\frac{2\pi E_0}{\beta H} - \frac{\pi}{4}\right)\right], \quad (8)$$

while A is a constant given by

$$A = \frac{\sqrt{2}\, e^2 E_0}{2\pi^4 c^2 \hbar \sqrt{k}\,[m_1(m_2 m_3 - m_4^2)]^{\frac{1}{2}}}. \quad (9)$$

It will be seen that in agreement with experiment, f consists of a constant term added to a periodic term; it is convenient to postpone discussion of the constant term until later (p. 358), and for the present we discuss only the periodic variation.

An important feature of the periodic term of f is that it becomes negligible for sufficiently small values of $\beta H/2\pi^2 kT$ (for values less than about 0·1), i.e. for sufficiently low fields or high temperatures. Thus roughly speaking only the term which is a function of the highest β need be considered in eqns. (3) and (5), if we limit ourselves to sufficiently low fields; this is of course not always true, for it takes no account of the coefficients of the f's in these equations, but we shall use it as a preliminary guide to the interpretation of the experimental curves, and then consider the exceptions after we know the relative values of the m's (i.e. of the coefficients, see p. 353).

Evaluation of the theoretical parameters

By a comparison of the experimental with the theoretical curves it is possible to deduce the values of all the parameters entering into the theoretical formulae. First, by considering the scale of the periodicity of the experimental curves, we can obtain values of the parameter β/E_0, and from its variation with orientation (i.e. with θ and ϕ) the ratios m_3/m_2 and m_4/m_2 and the value of $\lambda\sqrt{(m_2)}/E_0$ can be deduced. Next, by considering the envelopes of the experimental curves, the absolute value of β can be determined for each curve, and hence the value of $\lambda\sqrt{m_2}$. From the absolute value of the breadth of the envelope curve for some given field strength, the parameter Am_2 (see eqn. (9)) can be found. It will be convenient to introduce the following notation for the various quantities thus determined from analysis of the experimental curves:

$$P = Am_2, \tag{10}$$

$$Q = \lambda\sqrt{(m_2)}/2\pi^2 k, \tag{11}$$

$$R = \lambda\sqrt{(m_2)}/2E_0. \tag{12}$$

From the values of P, Q, R, m_3/m_2 and m_4/m_3 and the definitions of λ and A (eqns. (7) and (9)), we shall finally determine the values of E_0 and all the m's.

This procedure will now be discussed in detail, and it will be possible to see how far the theoretical formulae fit the experiments. Later (p. 359), it is shown how the theory explains some features of various experimental curves which are not used in the evaluation of the parameters, and also how the theory explains the great sensitivity of the results to small errors in the setting of the crystal.

(*a*) *The phase and scale of the periodicity*

We have already pointed out that the periodic variation is in most cases as $-\sin(\alpha/H-\delta)$ (we put in a minus sign to facilitate comparison with eqn. (8)), taken with a steadily varying amplitude. This periodic term should vanish whenever $\alpha/H-\delta = r\pi$ (r is an integer), and so if we plot the reciprocals of the fields at which the susceptibility difference has the constant value characteristic of very low fields, e.g. the fields at which fig. 5*h* meets the dotted horizontal line, against a suitable series of integers 0, 1, 2, etc., we should obtain a straight line whose slope gives π/α, i.e. $\beta/2E_0$ according to the theory, and whose intercept on the axis of abscissae gives $-\delta/\pi$. As can be seen from fig. 8, this procedure does indeed yield quite good straight lines, but the phase δ comes out to be $-\pi$ (with a possible error of order 25 %) instead of $\pi/4$, the theoretical value;* it may be noticed that δ

* In assigning the values of r we have taken into account the results of de Haas and van Alphen (1932) at high fields, which suggest that the point A of fig. 5 corresponds to $r=5$. In any case it is clear that A must correspond to an *odd* value of r, since the slope of the curve is negative at A, and $-\sin 1/x$ has a negative slope for $1/x = r\pi$, only if r is odd. We have of course taken into account the signs of the coefficients in the theoretical formulae in this comparison with the theory.

is approximately the same for all the curves. This discrepancy of phase must be attributed to some inadequacy of the theory; roughly speaking it is as if the experimental curve agreed within the limits of experimental error with the theoretical curve turned upside down.

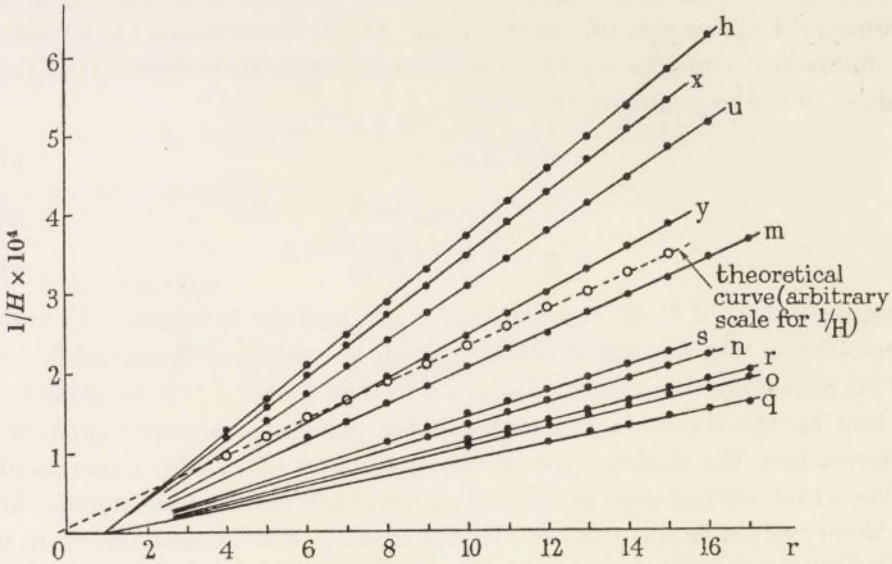

FIG. 8

The slopes of the straight lines of fig. 8 give the values of $\beta/2E_0$ for different orientations, and in Table I we give the values of B, where

$$B = \beta^2/4E_0^2 \cos^2\phi \tag{13}$$

for the various cases (only curves in which there is no serious distortion of the envelope have been considered). From these results we can now examine how far the theory predicts the dependence of B on the orientation, and also estimate the relative values of the m's. From eqns. (4) and (6) it can be seen that if $m_1 < m_2$ the largest value of B (i.e. the largest β) will in general be proportional to

$$\frac{m_1 + 3m_2}{4} + m_3 \tan^2\phi \pm \sqrt{3}\, m_4 \tan\phi$$

for $\theta = 0$, and to

$$(m_2 + m_3 \tan^2\phi + 2m_4 \tan\phi)$$

for $\theta = 90°$ (it can easily be seen that the assumption $m_1 > m_2$ leads to a contradiction). Thus by plotting B against $\tan\phi$ and extrapolating to $\phi = 0$ we obtain the ratio $\frac{1}{4}(m_1 + 3m_2) : m_2 = 0{\cdot}76 \pm 0{\cdot}02$, which shows that

m_1/m_2 must be very small, probably less than 0·10. Since we cannot estimate m_1/m_2 accurately, and m_1 occurs only in the combination $\frac{1}{4}(m_1+3m_2)$ in most cases, we shall simply neglect it in these calculations—later on we shall be able to estimate m_1 by a different method.

TABLE I

Curve	$\tan\phi$	$B = \beta^2/4E_0^2\cos^2\phi$ Obs. $\times 10^9$	Calc. $\times 10^9$
		$\theta=0°$	
m	1·72	1·96	1·96
n	3·68	3·02	2·94
o	5·56	4·37	4·16
p	7·92	6·62	6·00
		$\theta=90°$	
q	−8·99	7·70	7·81
r	−5·50	4·72	4·79
s	−3·66	3·59	3·54
t	−1·72	2·56	2·49
u	−0·98	2·25	2·16
h	0·18	1·71	1·71
x	0·36	1·60	1·64
y	0·99	1·44	1·45

We are thus left with only the two ratios m_3/m_2 and m_4/m_2 to determine, and find that the best agreement is obtained by taking

$$m_3/m_2 = 0{\cdot}020 \quad \text{and} \quad m_4/m_2 = -0{\cdot}100, \tag{14}$$

while the value of $\sqrt{B}$ for $\theta=90°$, $\phi=0°$, i.e. $\lambda\sqrt{(m_2)}/2E_0$ is given by

$$R = \sqrt{(m_2)}/2E_0 = 4{\cdot}2\times10^{-5}. \tag{15}$$

As can be seen from Table I, the values of B calculated, using these estimates, agree fairly well with the experimental values, showing that the theory does fairly correctly predict the dependence of the scale of periodicity on the crystal orientation.* We estimate that m_3/m_2 is within 25 %, m_4/m_2 within 10 % and R within 5 % of the true values.

* If the figures for $\theta=0$ and $\theta=90°$ are analysed separately, we obtain for the former case $m_3/m_2=0{\cdot}026$ and $m_4/m_2=-0{\cdot}088$, and for the latter $m_3/m_2=0{\cdot}017$, $m_4/m_2=-0{\cdot}105$. The discrepancy is however not greater than could be caused by errors in the estimates of B and in the measurement of the angle ϕ (particularly when ϕ is close to $\pi/2$).

(b) *Shape of the envelope and temperature dependence*

The next step in the comparison of the curves with theory is to compare the shape of their envelopes with the theoretically predicted shape; from this comparison we can deduce absolute values of the β's, and at the same time see how accurately the theory describes the temperature variation of the effect. From eqn. (8) we have that if $F(H)$ is the envelope of the theoretical curve

$$\log F + \tfrac{3}{2}\log H - \log T = -\frac{2\pi^2 kT}{\beta H} + \text{constant}. \qquad (16)$$

Thus, if we plot the left-hand side of (16) against T/H, we should obtain a straight line (the same for all temperatures), whose slope is $-2\pi^2 k/\beta$. Carrying out this procedure for the curves g, h, i, j, in which as can be shown from the values of the mass ratios, only the term with the largest β need be considered, owing to the small size of the coefficient of the other term in eqn. (5), we obtain the graphs shown in fig. 9. We see first of all that the

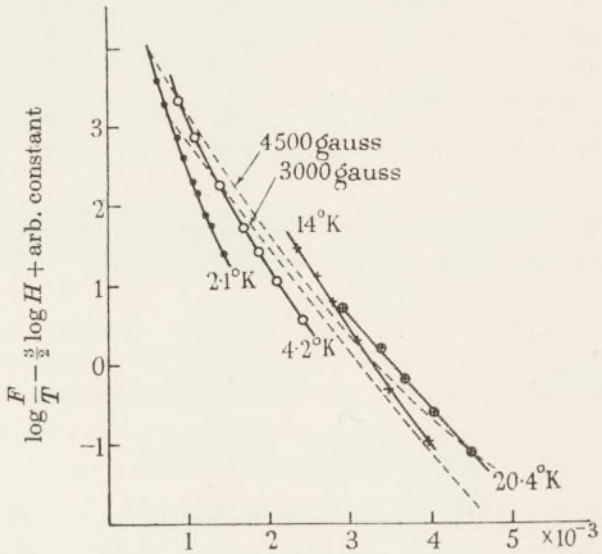

Fig. 9

theory does not predict correctly the temperature variation, since the points for different temperatures do not lie on a single line; the discrepancy is as if the amplitude of the periodic field dependence did not fall off fast enough with increase of temperature, and this suggested that perhaps the temperature of the specimen was higher than that of the surrounding bath—if in all cases it was about 1° K higher than assumed, the discrepancy would be greatly reduced. To investigate this suggestion, we made a special experiment, in which, instead of the bismuth crystal, a thin lead foil (Hilger, H.S., no. 8334) was suspended in identical conditions; from measurement of the couple acting on this specimen we could deduce the critical field for destroying superconductivity, and hence the temperature of the specimen itself. The critical field came out as 530 ± 15 gauss, when the temperature of the bath was $4 \cdot 2°$ K, and so the temperature of the specimen must have been less than $4 \cdot 4°$ K, and we see that the discrepancy described above cannot be attributed to an error in the temperature measurement.

From fig. 9 we see also that except for high values of H/T, the graphs are not quite linear, while detailed considerations which take into account the range of validity of the theoretical formulae suggest that they should be practically linear over the whole experimental range. We plotted also similar graphs for some of the other curves where we had reason to believe that there was only a single β concerned, and found that whenever the ratio $\beta H/T$ was small, i.e. whenever the periodicity became marked only at relatively high fields, the graphs were fairly good straight lines (all these graphs were, however, only for a single temperature—$4 \cdot 2°$ K, so that the question of the temperature variation was not studied), so it seems that the function f has the theoretically predicted form (as regards its field dependence) for sufficiently low values of $\beta H/T$. For each such graph we determined the slope (when the graph was not exactly linear, we took the slope for low values of H/T), and hence obtained estimates of the value of $\beta/2\pi^2 k$. Knowing the relative values of the β's from the previous considerations of the scale of the periodicity, we reduced these estimates to values of $\beta_1'/2\pi^2 k$ for $\theta = 90°$, $\phi = 0$, i.e. to values of $\lambda\sqrt{(m_2)}/2\pi^2 k = Q$ (see eqn. (11)). These estimates of Q from the various curves chosen for analysis are shown in Table II, and it will be seen that although they are all of the same order of magnitude, the largest and smallest differ by a factor of about 2.* Finally we should mention that the β's, and hence Q, can also be estimated from the temperature variation alone; thus if, instead of taking the slopes of the separate graphs of fig. 9, we join together points corresponding to the same fields but different temperatures, we obtain a series of lines (two of these are shown in fig. 9 by the broken lines) whose slopes should also give $-2\pi^2 k/\beta$. As is evident from fig. 9, this gives a lower slope and hence a higher value of Q (about 50 % higher than the highest estimate quoted in Table II). In view

* Another but less accurate method of estimating Q which gives quite similar results is to estimate the field strength at which the periodicity ceases (by extrapolating the envelope curve to low fields), and comparing this with the theoretical value of $\beta H/2\pi^2 kT$ at which the periodicity should become inappreciable.

of the discrepancies between theory and experiment it is difficult to say which of the estimates of Q has the most significance and we shall provisionally take for each curve the particular Q value indicated by the analysis of that curve taken alone; this is in fact the only method which allows us to proceed to the next step of the calculation—the determination of the constant A of eqn. (8) from our experimental curves.

TABLE II

Curve	$P \times 10^5$*	$Q \times 10^4$†	(m_2/m_0)	$(m_1/m_0) \times 10^4$	$(m_1/m_2) \times 10^4$	E_0/k° K.
c	1·58	4·7	9·3	23	2	107
d	1·81	7·2	2·2	41	19	173
e	2·45	7·9	2·7	27	10	190
g	1·32	4·3	9·0	28	3	104
h	1·65	6·1	3·4	36	11	147
i	2·37	7·1	4·0	24	6	171
r	1·00	5·2	2·5	71	28	125
w	1·79	4·3	16·9	15	1	104
x	1·78	5·8	5·0	28	6	140
Mean	1·75	5·8	4·9	29	6	140

* See eqn. (10). † See eqn. (11).

(*c*) *Absolute values of the breadth of the envelope curve*

In order to determine the value of the constant A (see eqn. (9)), we have to compare the absolute amplitudes of the various curves with those predicted theoretically. This we have done by taking for each curve the value of Q indicated by Table II, and for a number of field strengths comparing the breadth of the theoretical envelope curve (for the appropriate value of H) with the breadth of the experimental envelope. In this calculation the slight modifications of the theoretical formulae for higher fields have been taken into account. In this way we obtained for each curve a series of values of A, multiplied by the appropriate coefficient in eqns. (3) or (5), which were roughly constant (except when the graphs analogous to fig. 9 were not linear), and we arbitrarily took the arithmetic mean of each such series as the value obtained from the curve concerned. The values obtained in this way were then reduced to values of $Am_2 = P$ (see eqn. (10)), with the help of the mass ratios (eqn. 14), and we thus found the values of P shown in Table II. As in the case of Q, the P values show a considerable variation—again by a factor of about 2; this lack of constancy is rather greater than can be attributed to errors in the determination, and shows that the theory does not predict the variation of amplitude with orientation quite correctly.

(*d*) *Evaluation of the masses of* E_0

Although the theory does not fit in detail with the experimental data it is evident that it does give a good qualitative account and so the values of P, Q and R determined by fitting the theory as well as possible to the experimental data are probably at least of the right order of magnitude. From them and the mass ratios (eqn. 14) we can easily determine the fundamental parameters entering into the theory, i.e. E_0 and the m's. Thus combining eqns. (7), (9), (10), (11), (12), (14) and (15), we have

$$\left.\begin{aligned} E_0/k &= \pi^4 Q/R = 9\cdot 7Q/R = 2\cdot 4\times 10^5 Q\,^\circ\mathrm{K},\\ \frac{m_2}{m_0} &= \left[\frac{\hbar^4 c^2}{2e^2k^3m_0}\right]\frac{P^2R^2}{Q^4} = 1\cdot 02\times 10^6\frac{P^2R^2}{Q^4} = 1\cdot 8\times 10^{-3}\frac{P^2}{Q^4},\\ \frac{m_1}{m_0} &= \left[\frac{ke^4}{2\pi^4c^2\hbar^2m_0}\right]\frac{Q^2}{P^2R^2S} = 4\cdot 61\times 10^{-17}\frac{Q^2}{P^2R^2S} = 2\cdot 6\times 10^{-6}\frac{Q^2}{P^2},\end{aligned}\right\} \qquad (17)$$

where
$$S = \frac{m_3}{m_2} - \left(\frac{m_4}{m_2}\right)^2 = 0\cdot 01 \quad \text{(see eqn. (14))}, \qquad (18)$$

and m_0 is the ordinary electronic mass. The values of E_0/k, m_1, and m_2 obtained from eqn. (17) are collected together in Table II, and it will be seen that only a rough idea of the order of magnitude of the masses can be obtained; this is of course because the estimates of the masses involve squares and even fourth powers of the experimental quantities P and Q. The estimates of m_1/m_2 show an even greater variation, since they involve Q^6 and P^4, but we may notice that this ratio is certainly small, in agreement with the considerations of p. 352 from the scale of the periodicity, which suggested that $m_1/m_2 < 0\cdot 10$;* to obtain some sort of mean values of the fundamental parameters we arbitrarily take for P and Q the arithmetic means of the values in Table II and apply eqn. (17). We thus obtain

$$E_0/k = 140^\circ\,\mathrm{K}, \quad \left.\begin{aligned} m_2/m_0 &= 4\cdot 9, & m_1/m_2 &= 6\times 10^{-4},\\ m_3/m_2 &= 0\cdot 02, & m_4/m_2 &= -0\cdot 100,\end{aligned}\right\} \qquad (19)$$

Taking into account the spread of the values in Table II, we estimate that E_0/k is probably within 30 % of the true value, m_1 and m_2 may be wrong by a factor of about 3, while as we have already said, m_4/m_2 is probably within 10 % and m_3/m_2 within 25 % of the true values.

* If we had taken the higher value of Q suggested by the temperature variation alone (see p. 355) we should obtain $m_1/m_2 \sim 10^{-2}$, in better agreement with Blackman's estimate.

From these figures we can at once obtain the number of "free" electrons per atom producing the de Haas-van Alphen effect. This is given by

$$n = \frac{(2E_0)^{\frac{3}{2}} \sqrt{\{m_1(m_2 m_3 - m_4^2)\}}}{\pi^2 \hbar^3} \frac{V}{N},$$

where V is the atomic volume and N is Avogadro's number, and substituting numerical values we find

$$n = 1{\cdot}7 \times 10^{-6} \text{ electrons per atom.} \tag{20}$$

For many theoretical calculations it is important to know the electronic masses referred to the principal axes of the mass tensor ellipsoid: these are

$$m_1' = m_1, \quad m_2' = \frac{m_2 + m_3}{2} + \sqrt{\left\{\left(\frac{m_2 - m_3}{2}\right)^2 + m_4^2\right\}},$$

$$m_3' = \frac{m_2 + m_3}{2} - \sqrt{\left\{\left(\frac{m_2 - m_3}{2}\right)^2 + m_4^2\right\}},$$

and so we find the values

$$m_1' = 0{\cdot}003 m_0, \quad m_2' = 5{\cdot}0 m_0, \quad m_3' = 0{\cdot}048 m_0. \tag{21}$$

We may at this point compare our estimates with those of Blackman; this comparison is rather complicated by the fact that Blackman has assumed $m_4 = 0$, whereas our considerations of the scale of periodicity show that this assumption is inadmissible.* From the details of Blackman's paper it can be seen that this will not affect his estimate of the ratio m_1/m_2, but will alter the absolute values of the masses and m_3/m_2 in a complicated way. He finds $m_2 = m_0$, $m_1/m_2 = 0{\cdot}1$, $m_3/m_2 = 10^{-3}$ and $E_0/k = 220°$ K. The discrepancies between these values and our own estimates are rather larger than our estimated possible errors, probably because of the scantiness of the previous data used by Blackman; the two sets of values do not, however, differ seriously as regards order of magnitude.

The constant susceptibility at low fields

We shall now return to the question of the constant term in eqn. (8), i.e. compare the theoretical value of the field independent susceptibilities with

* Actually m_4 can be found only from measurements, such as the present ones, in which ϕ differs from 0 or 90°.

the experimental values. Thus, according to the theory, the principal susceptibilities at low temperatures and very low fields are given by

$$\kappa_1 = \frac{I_1}{H_1} = -\frac{A(m_1+m_2)}{2}\frac{\pi^2}{2}\left(\frac{k}{E_0}\right)^{\frac{1}{2}}, \quad \kappa_3 = \frac{I_3}{H_3} = -Am_3\frac{\pi^2}{2}\left(\frac{k}{E_0}\right)^{\frac{1}{2}}, \qquad (22)$$

and substitution of the numerical values (note that $Am_2 = P$, tabulated in Table II) gives

$$\kappa_1 = -0{\cdot}18\times 10^{-5}, \quad \kappa_3 = -0{\cdot}007\times 10^{-5}.$$

We estimate that these may be wrong by about 40 %, but it is clear that in any case they are less than the experimental values $\kappa_1 = -1{\cdot}8\times 10^{-5}$, $\kappa_3 = -1{\cdot}2\times 10^{-5}$, while their ratio 25 : 1 is very much greater than the experimental ratio 1·5 : 1.

A similar discrepancy is obtained, also using Blackman's estimates, and Blackman infers that the constant susceptibility is largely due to other free electrons which do not produce any marked de Haas-van Alphen effect in themselves. It is possible that the discrepancies between theory and experiment as regards the details of the de Haas-van Alphen effect, are connected with some interaction between these other "free" electrons and those reponsible for the field dependence.

Further evidence for the theoretical formulae

(*a*) *Discussion of some particular curves*

From the values of the mass ratios we can immediately obtain the relative values of the coefficients of the f's in eqns. (3) and (5), and so discuss the curves in which more than one term of eqns. (3) or (5) has to be taken into account (the "distorted" curves), or in which, owing to the particular values of the coefficients, the significant term is not the one with the highest β.

If we add together two periodic functions of comparable periods and amplitudes, we can expect to obtain a distorted curve, and in particular if the periods and amplitudes are only slightly different, "interference" effects will be produced. This is in very good agreement with the experimental results, as can be seen for instance in the curves a, b, k, l, m, v, y in each of which two comparable β's are concerned, and the coefficients of the corresponding f's are also comparable. For the case $\theta = 0$, $\phi = 19{\cdot}7^\circ$ (curve k), $\beta_2/\beta_3 = 1{\cdot}18$, while the ratio of the corresponding coefficients in eqn. (3) is 0·55, and as can be seen a characteristic interference curve is obtained. For $\theta = 0$, $\phi = 9{\cdot}7^\circ$ (curve d) the β values are very nearly equal, but the coefficient of the term in the smaller β is about five times larger than that in the larger β, and the scale of the periodicity does indeed correspond to the smaller and not the larger β. Another and even more striking example of a case where it is the smaller β which is relevant, is for $\theta = 90^\circ$, $\phi = -6{\cdot}25^\circ$ (curve w); here the larger β is about twice the smaller one, but the coefficient of the corresponding term in eqn. (5) is only about 0·06 of that of the term in the smaller β—the result of this is to double the scale of the periodicity as compared with curve h ($\theta = 90^\circ$, $\phi = 9{\cdot}9^\circ$), in which the β's are much the same, but the larger coefficient corresponds to the larger β.

Although the theory always predicts accurately in which cases distortions can be expected, it does not predict the details of the distortions correctly; thus if by graphical construction we plot the curves predicted by eqns. (3) or (5), the distortions appear at the field strengths observed experimentally, but are either too exaggerated or not marked enough as compared with the experimental curves.

(b) *Influence of slight errors in crystal setting*

It is convenient at this point to discuss the effects produced by small errors in the setting of the crystal, and to show how they can account for the features mentioned on p. 345. There are two possible errors in setting, which if they are small enough can be treated independently. First, there may be an error in the setting of θ, and it can be shown that the most important effect of this is for $\phi = 0$; thus in the case $\theta = 0$, the last two terms of eqn. (3) are equal but of opposite sign so that there is no couple, but if $\theta = \xi$, β_2 and β_3 become slightly different and so we have a couple varying as the difference of two periodic terms of equal amplitudes but slightly different periods. This means that there will be a couple whose field variation will be determined by the differential coefficient of the function f, and this was verified in a special experiment in which θ was deliberately made 5°. The sensitivity of the curve for $\theta = 90^\circ$, $\phi = 0$ to slight errors in θ can also be explained in a similar way, the last term of eqn. (5) breaking up into two terms which are functions of slightly different β's. Errors in θ affect also the values of the coefficients in eqns. (3) and (5), but this influence is not in general of importance. The second type of error is in the perpendicularity of the trigonal axis to the axis of rotation of the magnet; if there is an error ζ in this perpendicularity, it is easy to show that it modifies the β's as follows. For the case $\theta = 0$, the β's are modified as if m_4 were changed to $m_4 + \frac{1}{2}\zeta m_2$, and m_3, to $m_3 + \zeta m_4$, and since both m_2/m_4 and m_4/m_3 are large, even quite small values of ζ are sufficient to modify the mass ratios deduced from the scale of periodicity of the curves for $\theta = 0$.* For $\theta = 90^\circ$, on the other hand, the error ζ has no appreciable effect on the first term of eqn. (5), and since this is usually the predominant term, the mass ratios deduced from the curves for $\theta = 90^\circ$ should be independent of any possible error ζ; for this reason in the estimates (eqn. (14)), of the mass ratios we have given more weight to the estimates deduced from the $\theta = 90^\circ$ curves.

(c) *Bearing of the results on the previous experiments*

In the earlier experiments (Shoenberg and Zaki Uddin 1936) the susceptibilities I_1/H_1, I_2/H_2 and I_3/H_3 were separately investigated with the field respectively along the x, y and z axes and we shall briefly point out how the theory and the present estimates explain some features of the earlier results.

According to the theory we have (neglecting m_1)

$$\left.\begin{aligned} I_1/H_1 &= -\tfrac{3}{2} m_2 f(\lambda(\tfrac{3}{4} m_2)^{\frac{1}{2}} H), \\ I_2/H_2 &= -m_2 f(\lambda m_2^{\frac{1}{2}} H) - \tfrac{1}{2} m_2 f(\tfrac{1}{2}\lambda m_2^{\frac{1}{2}} H), \\ I_3/H_3 &= -3 m_3 f(\lambda m_3^{\frac{1}{2}} H). \end{aligned}\right\} \qquad (23)$$

The small value of m_3/m_2 immediately explains why no field dependence was found for I_3/H_3, for it is evident from eqn. (23) that such a dependence will become marked only at fields about 6 times higher than in the case of I_1/H_1 (since $(4m_3/3m_2)^{\frac{1}{2}} \sim \frac{1}{6}$), and moreover, when such a field dependence does occur, its amplitude should be only about 4 % of that for I_1/H_1. In other words to obtain the curve for I_3/H_3 from that for I_1/H_1 the scale of abscissae must be expanded by a factor of about 6 and the scale of ordinates contracted about 25 times, and this means that the effect can be observed only at fields rather greater than used in the previous experiments, or else at very much lower temperature ($\sim \frac{1}{2}^\circ$ K) for the range of fields used, and that in any case the effect will not be marked.

Equations (23) also explain why "distortions" appear in the I_2/H_2 curve (Shoenberg and Zaki Uddin 1936) but not in the I_1/H_1 curve, for it will be seen that the expression for the latter contains only a single f term, while the former contains 2 terms with comparable β's.

* Probably the error ζ is responsible for the irreproducibility of the $\theta = 0$ curves if the crystal is removed and reset. Thus in another series of measurements (not reproduced here) B values were obtained for $\theta = 0$ rather different from those in Table I, and the discrepancy could be roughly explained by assuming an error $\zeta \sim 3^\circ$ in this other series. An error ζ, however, is not able to account for the discrepancy mentioned in the footnote on p. 355, since the assumption of such an error would make the discrepancy only worse.

This work was carried out in the Institute for Physical Problems of the Academy of Sciences of the U.S.S.R. It is a pleasure to acknowledge the hospitality of the Institute and to thank the Director, Professor P. Kapitza, for his interest in this research, and Professor L. Landau for informing me of his theoretical work, and much valuable discussion. I should like also to thank the staff of the cryogenic laboratory for the regular supply of liquid helium required for these experiments.

Summary

The investigation of the field dependence of the susceptibility of bismuth (de Haas-van Alphen effect) has been extended down to lower fields (1500 gauss) at helium and hydrogen temperatures, by measuring the couple on a bismuth crystal in uniform magnetic fields. The results are compared with Landau's theory, with which they are in good qualitative agreement.

Detailed examination shows, however, that there are discrepancies as regards (*a*) the phase of the periodic variation, (*b*) as regards the details of the envelope curve of the periodic variation and the dependence of its amplitude on the crystal orientation, and (*c*) the temperature variation of the effect, which was not as rapid as predicted by the theory. From the comparison, we obtained the following estimates of the fundamental parameters of the electronic structure: for the "effective" electronic masses,

$$m_2 = 4{\cdot}9m_0, \quad m_1/m_2 = 6\times 10^{-4}, \quad m_3/m_2 = 0{\cdot}02, \quad \text{and} \quad m_4/m_2 = -0{\cdot}10$$

(m_0 is the ordinary electronic mass), and for the degeneracy temperature: $E_0/k = 140°$ K. From these data the number of electrons responsible for the effect is deduced as $1{\cdot}7\times 10^{-6}$ per atom. These results are compared with Blackman's estimates, with which they are in rough agreement as regards order of magnitude, and their bearing on the previous experimental results is also discussed.

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Appendix*

The following is a brief account of the derivation of Landau's formula. To obtain the formula for the isotropic case, we start from eqns. (17) and (18) of Blackman (1938), which in our notation† become:

$$\frac{F}{V} = -\int_{-\infty}^{\infty} \frac{Z(E,H)\,e^{-(E-E_0)/kT}\,dE}{(1+e^{-(E-E_0)/kT})} + \frac{NE_0}{V}, \tag{A 1}$$

$$Z(E,H) = \frac{\beta H \sqrt{(2m^3)}}{\pi^2\hbar^3} \sum_l (E-(l+\tfrac{1}{2})\beta H)^{\frac{1}{2}}. \tag{A 2}$$

We assume E_0 constant, in accordance with Blackman's method (p. 12) (for the weak fields of our experiments the condition $N =$ const. gives practically the same result as $E_0 =$ const.). Introducing the abbreviations

$$\frac{E}{\beta H} = \epsilon, \quad \frac{kT}{\beta H} = \theta, \quad \frac{(2m)^{\frac{3}{2}}}{3\pi^2\hbar^3} = \alpha, \tag{A 3}$$

and integrating by parts, we have

$$\frac{F-NE_0}{V} = \alpha(\beta H)^{\frac{5}{2}} \int_{-\infty}^{\infty} \phi(\epsilon) \frac{d}{d\epsilon} g\left(\frac{\epsilon-\epsilon_0}{\theta}\right) d\epsilon, \tag{A 4}$$

where

$$\phi(\epsilon) = \sum_l (\epsilon - l - \tfrac{1}{2})^{\frac{3}{2}}, \tag{A 5}$$

the summation being over all positive integers l which make the radicand positive, and where

$$g(x) = 1/(1+e^x). \tag{A 6}$$

Using Poisson's summation formula, we have

$$\phi(\epsilon) = \sum_{p=-\infty}^{\infty} (-1)^p \int_0^{\epsilon} (\epsilon - x)^{\frac{3}{2}}\, e^{2\pi i p x}\, dx. \tag{A 7}$$

The term in $p = 0$ can be immediately evaluated; for $p \neq 0$, integrating twice by parts, the integral can be expressed in terms of Fresnel's integrals for the argument $2\pi p\epsilon$. It can be seen, however, from (A 4) that the value of ϕ need be known only in the neighbourhood of $\epsilon \doteq \epsilon_0$, since the derivative of $g((\epsilon-\epsilon_0)/\theta)$ is appreciable only there, provided $E_0 \gg kT$. Since ϵ_0 is a large

* My best thanks are due to Professor R. Peierls for putting this appendix in a form suitable for publication.

† For the isotropic case, $m_1 = m_2 = m_3 = m$, and $m_4 = 0$, so the β's defined in eqns. (4) and (6) of the text all become equal to $\beta = e\hbar/mc$.

number, provided $E_0 \gg \beta H$, the Fresnel integrals may be replaced by their values for infinite argument. This transforms (A 7) into

$$\begin{aligned}\phi(\epsilon) &= \tfrac{2}{5}\epsilon_0^{\frac{5}{2}} + \sum_{p=1}^{\infty}(-1)^p \frac{3}{4\pi^2 p^2}\epsilon^{\frac{1}{2}} - \sum_{p=1}^{\infty}(-1)^p \frac{3}{8\pi^2\sqrt{2}\,p^{\frac{3}{2}}}\cos\left(2\pi p\epsilon - \frac{\pi}{4}\right)\\ &= \tfrac{2}{5}\epsilon_0^{\frac{5}{2}} - \tfrac{1}{16}\epsilon^{\frac{1}{2}} - \sum_{p=1}^{\infty}(-1)^p \frac{\cos\left(2\pi p\epsilon - \frac{\pi}{4}\right)}{8\pi^2\sqrt{2}\,p^{\frac{3}{2}}}. \qquad \text{(A 8)}\end{aligned}$$

Inserting this into (A 4), we notice that the first two terms of (A 8) vary very slowly in the range for which $dg((\epsilon-\epsilon_0)/\theta)/d\epsilon$ is appreciable, and we may therefore use their values at ϵ_0. The last term, however, varies rapidly. Hence

$$\begin{aligned}\frac{F-NE_0}{V} = -\alpha(\beta H)^{\frac{5}{2}}\Bigg\{&\tfrac{2}{5}\epsilon_0^{\frac{5}{2}} - \tfrac{1}{16}\epsilon_0^{\frac{1}{2}}\\ &+ \sum_{p=1}^{\infty}\frac{(-1)^p\,3}{8\pi^2\sqrt{2}\,p^{\frac{3}{2}}}\mathscr{R}\left[e^{(2\pi p\epsilon - \frac{1}{4}\pi)i}\int_{-\infty}^{\infty} e^{2\pi i p(\epsilon-\epsilon_0)}\frac{d}{d\epsilon}g\left(\frac{\epsilon-\epsilon_0}{\theta}\right)d\epsilon\right]\Bigg\}, \qquad \text{(A 9)}\end{aligned}$$

where $\mathscr{R}$ stands for "the real part of".

The integral in (A 9) can be evaluated, and gives

$$\int_{-\infty}^{\infty} e^{2\pi i p\epsilon}\frac{d}{d\epsilon}g\left(\frac{\epsilon}{\theta}\right)d\epsilon = -\frac{2\pi^2 p\theta}{\sinh 2\pi^2 p\theta}. \qquad \text{(A 10)}$$

So, substituting for α, ϵ_0, and θ from (A 3), and omitting the term which does not depend on H, we have

$$\frac{F}{V} = \frac{(2m)^{\frac{3}{2}}}{3\pi^2\hbar^3}\left\{\tfrac{1}{16}(\beta^2 H^2 E_0^{\frac{1}{2}}) + \sum_{p=1}^{\infty}(-1)^p \frac{3kT(\beta H)^{\frac{3}{2}}}{4\sqrt{2}\,p^{\frac{3}{2}}}\frac{\cos\left(2\pi p\epsilon_0 - \frac{\pi}{4}\right)}{\sinh 2\pi^2 p\theta}\right\},$$

and hence the susceptibility, $\dfrac{I}{H} = -\dfrac{I}{H}\dfrac{\partial}{\partial H}\left(\dfrac{F}{V}\right)$, is given by

$$\begin{aligned}\frac{I}{H} &= \frac{\sqrt{2}\,m^{\frac{3}{2}}\beta^2 E_0^{\frac{1}{2}}}{12\pi^2\hbar^3} + \frac{m^{\frac{3}{2}}kTE_0(\beta H)^{\frac{1}{2}}}{\pi\hbar^3 H^2}\sum_{p=1}^{\infty}(-1)^p \frac{\sin\left(\frac{2\pi p E_0}{\beta H} - \frac{\pi}{4}\right)}{\sqrt{p}\sinh(2\pi^2 pkT/\beta H)}\\ &= mA'f(\beta H), \qquad \text{(A 11)}\end{aligned}$$

where f is the function defined by eqn. ($8a$) of the text, and A' is

$$A' = \frac{\sqrt{2}\,e^2 E_0}{2\pi^4 c^2\hbar\sqrt{k}\,m^{\frac{3}{2}}}. \qquad \text{(A 12)}$$

The transformation to the non-isotropic case is carried out just as in § 1 of Blackman's paper, except that the coefficient m_4 is taken into account, and the formulae quoted in the text (eqns. (3)–(9)) are obtained.