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The de Haas-Van Alphen Effect. III. Experiments at Fields up to 32 kG

J. S. Dhillon and D. Shoenberg

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THE de HAAS–van ALPHEN EFFECT*
III. EXPERIMENTS AT FIELDS UP TO 32 kG

By J. S. DHILLON and D. SHOENBERG, F.R.S.†
National Physical Laboratory of India, New Delhi

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CONTENTS

The periodic field dependence of magnetic anisotropy (de Haas–van Alphen effect) has been studied for bismuth and zinc crystals by the torque method between about 1·5 and 32 kG at 4·19° K and about 1·5° K; in each case the orientation was chosen so that only a single fundamental periodicity was present. Particular attention was paid to the phase and harmonic content of the oscillations and to the form of the field dependence of amplitude. For bismuth good agreement was found with the theoretical formula except that the signs of the fundamental and the odd harmonics had to be reversed. For zinc the field dependence of amplitude at high fields was quite at variance with the theoretical formula and (probably in consequence) the harmonics were much weaker than in bismuth; the phases of the fundamental and the first harmonic were quite different from those of the theoretical formula. A slight field dependence was found for bismuth even at 85° K, similar to the rather more marked one previously found in zinc. Oscillations of very much shorter period than the main ones were observed in zinc at the highest fields and their characteristics were briefly studied. Qualitative observations were made of the very short-period oscillations in a lead crystal, previously only observed by an impulsive method at much higher fields. No oscillations could be detected in copper, silver or gold crystals.

Introduction

As was emphasized in II (Shoenberg 1952), a study of the de Haas–van Alphen effect at higher magnetic fields than hitherto used might help to clarify certain features of the effect. It is at high fields that the harmonic content of the oscillations becomes most pronounced and that the phase of the oscillations can be most precisely determined; the use of higher

* It is convenient to treat this paper as the third of a series, I being Shoenberg (1939) and II Shoenberg (1952). The introduction to the latter gives a general account of the de Haas–van Alphen effect, which will not therefore be repeated here.

† Temporarily acting as U.N.E.S.C.O. expert in low-temperature physics at the National Physical Laboratory of India; now returned to the Royal Society Mond Laboratory, Cambridge.

fields permits also an investigation of the form of the field variation of amplitude over a wider range of fields. Also, at higher fields there is the possibility of discovering higher frequency oscillations whose amplitude is unobservably small at lower fields, or of discovering the de Haas–van Alphen effect in new metals. Much higher fields than those of a conventional electromagnet can be obtained by impulsive methods, and such a method was recently developed particularly for the purpose of looking for new high-frequency oscillations at fields up to 100 kG (Shoenberg 1953); this method is not, however, suitable for studying low-frequency oscillations, and even its suitability for looking for new oscillations is limited by eddy-current effects. It seemed therefore worth while to carry out some measurements with the large electromagnet of the National Physical Laboratory of India, which gives fields up to about 32 kG.

According to theory, the harmonic content of the oscillations should be greatest for $2\pi^2 kT/\beta H$ small (β is the effective double Bohr magneton for the electrons, i.e. $\beta = eh/2\pi mc$ if m is the effective mass), and, moreover, if $2\pi E_0/\beta H$ is small (E_0 is the degeneracy parameter), it is possible to observe oscillations of low order, in which the constant-phase part of the argument of the periodic term in the theoretical formula (see p. 4) becomes more significant compared to the variable part, $2\pi E_0/\beta H$, so that the constant phase can be better determined. This explains why a high field is desirable for an investigation of harmonic content and phase, and it can be seen that a low temperature is also desirable, and that both β and β/E_0 should be as large as possible. Reference to table 14 of II shows that bismuth and zinc are quite outstanding among the metals in this respect. Bismuth has previously been studied only up to 9 kG at 2·1° K (see I), and in the various investigations on zinc (Mackinnon 1949; Sydoriak & Robinson 1949; Verkin 1951) the extreme conditions were 15 kG and 1·9° K.* The conditions of these earlier experiments were, moreover, not ideally suitable for the study of harmonic content, so that new measurements were desirable even apart from the advantages of using higher fields and lower temperatures. The only other metals which approach bismuth and zinc from the present point of view are graphite, beryllium, gallium and aluminium (roughly in order of merit), though even for graphite β and β/E_0 are about four times less than for bismuth and zinc. Graphite and gallium have already been studied for phase and harmonic content up to 15 kG and 1·2 °K (see II), aluminium is awkward because of the presence of strong high-frequency oscillations and beryllium crystals are not easy to prepare; since time was limited, the investigation was therefore confined to bismuth and zinc.

For each metal detailed curves have been obtained showing the variation of anisotropy ($\Delta(I/H)$) with $1/H$ at two temperatures (4·19° K and about 1·5° K), for an orientation chosen in such a way that only a single fundamental periodicity should appear. These curves were first analyzed to give β/E_0, β and the parameter x which controls the field dependence of amplitude, and then with the help of these data the detailed form and phase of the oscillations at high fields were examined to see how far they agreed with theory.

In the course of the investigation some new oscillations of high frequency were discovered in zinc, and the opportunity was also taken to verify the existence of oscillations in

* Details of a new investigation by Berlincourt & Steele (1954), up to 25 kG at 4·2° K and higher temperatures, became available only after our measurements had been completed. This investigation was, however, primarily concerned with other aspects (see p. 19).

lead, previously found only with the impulsive field method. Copper, silver and gold crystals were also examined, but just as in II (up to 15 kG) no de Haas–van Alphen oscillations could be found up to 32 kG even at the lowest temperatures.

Experimental details

As in I and II, the experimental method was to measure the couple acting on a crystal suspended by a long quartz rod from a short torsion wire, and the apparatus was practically identical with that used in II. For ease of observation the deflexions of the image of a slit reflected from a mirror fixed to the quartz rod were read directly on a galvanometer scale and in order to keep the minimum deflexions (at low fields) not much less than 1 mm, the deflexion for the highest fields had to be allowed to be as high as 5 or 10 cm. Since every 7 cm corresponds to a twist of the crystal of 1° and such twists could appreciably modify detailed features of the oscillations (see II, pp. 7, 17) the simple but tedious procedure was adopted of rotating the magnet by just the twist of the crystal, so that the angle between field and crystal axis remained constant. Actually the magnet was rotated only in steps of 0·1° (as read on a vernier) which was considered to be an adequate approximation to exact compensation.

Table 1. The specimens

metal	source	mass (mg)
Bi	JM 5773	116
Zn	JM 5079	129
Pb	JM 5873	350
Cu, Ag, Au	as described in table 1 of II	

Note. JM = Johnson, Matthey and Co Ltd.

The values of deflexion were converted into couples from the approximately determined torsion constants of the various torsion wires used. The magnet was calibrated by a search coil standardized by a mutual inductance in the usual way, and it is unlikely that the calibration errors are much worse than 1 %.* Temperatures were determined in the usual way from the vapour pressure of the helium bath. Towards the end of an experiment the liquid helium enters the narrow 'tail' of the Dewar flask and the vapour has to pass through a narrow annular space before reaching the pumping line; for this reason there is probably an appreciable pressure drop between the manometer and the liquid level, and temperatures in the region of 1·5° K or below as derived from the manometer readings may be too low by as much as 0·1° K. Fortunately, the results are very insensitive to temperature in this region and even such a large uncertainty is not important.

The crystals were grown by slow cooling of a molten bead lying along a temperature gradient; particulars of the crystals are given in table 1. After etching to verify that the crystal was single, a cleavage plane was chipped off the bismuth and zinc crystals, thus revealing the direction of the trigonal axis in bismuth and the hexagonal axis in zinc.† The

* The region of fields below about 5 kG was, however, rather less accurately calibrated and systematic errors of perhaps 3 % may be possible.

† Although this was easy for the bismuth crystal, difficulty was found in cleaving the zinc crystal; successful cleaving was achieved on cooling with liquid air, but the crystal was slightly distorted in the process.

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bismuth crystal was stuck with its cleavage face to a rectangular thin glass plate and the direction of the binary axis located by X-rays with respect to the plate edges. Since the trigonal axis is normal to the glass plate, it is automatically horizontal if the back surface of the plate is stuck to the (vertical) quartz rod, and by varying the angle between the edge of the plate and the rod, the binary axis could be fixed at any angle to the vertical. For the zinc crystal it was important only that the hexagonal axis should be nearly horizontal and since the cleavage plane was not perfect the glass plate was not used but the crystal stuck directly to the quartz rod, with its cleavage plane parallel to the rod as judged by eye.

Choice of experimental conditions and results

According to the theory, the field variation of the anisotropy for both bismuth and zinc should be given by an expression of the form

$$\frac{C}{H^2} = \frac{A}{\rho}\sum_{i=1}^{3}\frac{a_i}{T^{\frac{1}{2}}}\left(\frac{2\pi^2 kT}{\beta_i H}\right)^{\frac{3}{2}}\sum_{p=1}^{\infty}(-1)^p \frac{\sin\left(\frac{2\pi p E_0}{\beta_i H}-\frac{\pi}{4}\right)\mathrm{e}^{-2\pi^2 pkx_i/\beta_i H}}{2p^{\frac{1}{2}}\sinh 2\pi^2 pkT/\beta_i H}. \tag{1}$$

Here C is the couple per unit mass, so that $C/H^2\sin\psi\cos\psi$ has the physical meaning of anisotropy of mass susceptibility (ψ being the angle between H and an appropriate axis in the crystal); A is a constant defined in II, ρ is the density, the a_i's are appropriate differences of effective electron masses (the a_i's were denoted in II by $(\Delta m)_i\sin\psi\cos\psi$) and the x_i's are constants having the dimensions of temperature which have to be introduced for reasons explained in II. It will be seen that essentially this expression is the sum of three periodic terms, each having the same functional form, but with different fundamental periods β_i/E_0, and different amplitudes proportional to the a_i, but also functions of β_i and x_i.

Since the main aim of the investigation is to examine the functional form, i.e. the strengths and phases of the various harmonics in (1), it is evidently desirable (and in practice essential) to choose an orientation of the crystal with respect to the field such that only a single a_i appears. Otherwise the complicated interference effects between the various periodic terms make any analysis of harmonic content practically impossible (for illustrations see figure 2). The values of β_i and a_i appropriate to the trigonal symmetry of bismuth are given in II, p. 38, for three simple modes of suspension. Inspection of these formulae shows that it is only for one of these modes, the one with the trigonal axis horizontal and the binary axis vertical, that it is possible to eliminate all but one of the a_i's. For this case the values of the periods $P_i=\beta_i/E_0$ and the relative values of the a_i's are given by

$$\left.\begin{aligned} P_1 &= (1{\cdot}4+68{\cdot}5\sin^2\psi-14{\cdot}0\sin\psi\cos\psi)^{\frac{1}{2}}\times 10^{-5},\\ P_2 = P_3 &= (1{\cdot}4+16{\cdot}1\sin^2\psi+7{\cdot}0\sin\psi\cos\psi)^{\frac{1}{2}}\times 10^{-5},\end{aligned}\right\} \tag{2}$$

$$\left.\begin{aligned} a_1 &= 68{\cdot}5\sin 2\psi-14{\cdot}0\cos 2\psi,\\ a_2 = a_3 &= 16{\cdot}1\sin 2\psi+7{\cdot}0\cos 2\psi,\end{aligned}\right\} \tag{3}$$

where ψ is the angle between the trigonal axis and the field.

The values of the numerical coefficients have been chosen to fit the periods found for various values of ψ in I, and it should be noticed that the expressions for the a_i's (which are in arbitrary units) are just proportional to $\mathrm{d}P_i^2/\mathrm{d}\psi$, so that an a_i vanishes whenever the

corresponding P_i has a maximum or minimum. Graphs of the relations (2) are shown in figure 1 and it can be seen that P_2 and P_3 have a maximum for $\psi = 78°$, so that $a_2 = a_3 = 0$, and we are left with only a single periodic term, fortunately having a period not much below the maximum possible. This evidently is the most suitable orientation for detailed investigation.*

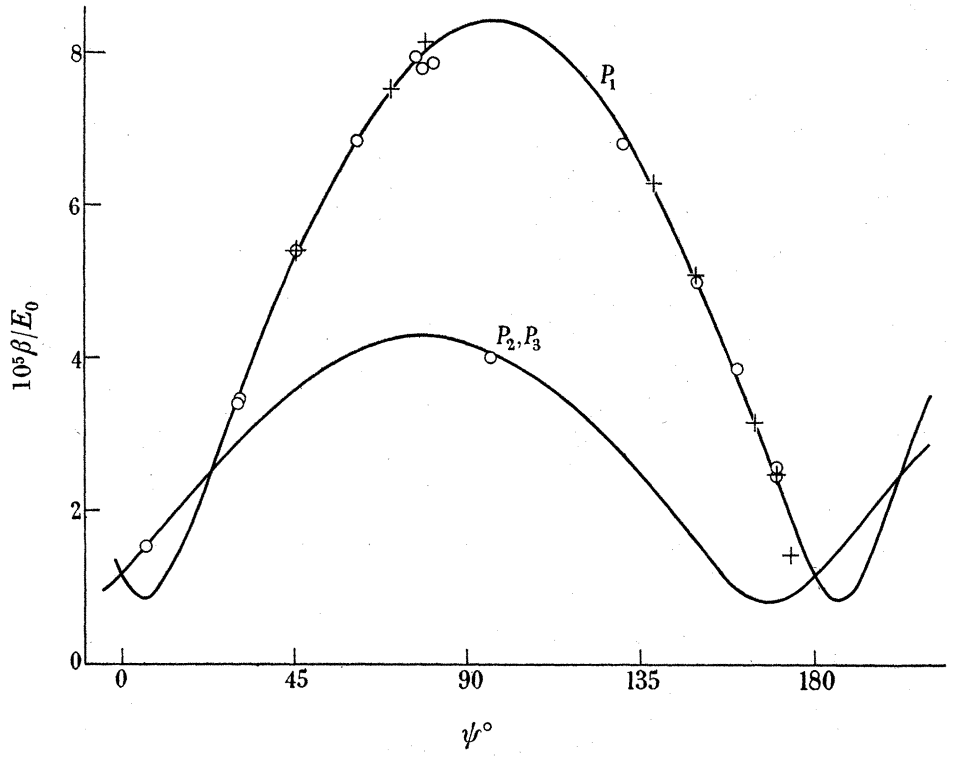

FIGURE 1. Variation of period (β/E_0) with ψ; full curves theoretical (equation (2)): +, data from I; ○, present data.

Since all these considerations are based on the data of I and the exact electronic parameters of bismuth are sensitive to small impurities, it was first necessary to check that the periods of figure 1 could be repeated for the present bismuth crystal. Accordingly, the crystal was suspended with its trigonal axis horizontal and its binary axis vertical and the field variations measured for a series of angles ψ; a few of the curves are shown in figure 2 and the periods are indicated in figure 1. Curves such as *a*, *b* and *f* illustrate incidentally the difficulty of making any detailed analysis when all the *a*'s are comparable.† It can be seen that as far as P_1 is concerned, the agreement with the results of I, and with the theoretical equation (2), is very satisfactory. This presumably indicates that the effect of impurities was negligible both in I and in the present crystal, since it is improbable that crystals from two different batches of metal should have exactly the same impurity contents. The

* Another possibility would be for $\psi = 168°$, which also makes $a_2 = a_3 = 0$, but the corresponding period is much smaller; $\psi = 6°$ and $96°$, where a_1 vanishes, would also seem possible, leaving a_2 and a_3, but apart from the smaller periods, these settings prove to be exceedingly sensitive to small orientational errors which make P_2 slightly different from P_3 (see p. 7).

† There is much less distortion in the analogous curves in I because of the lower fields used there.

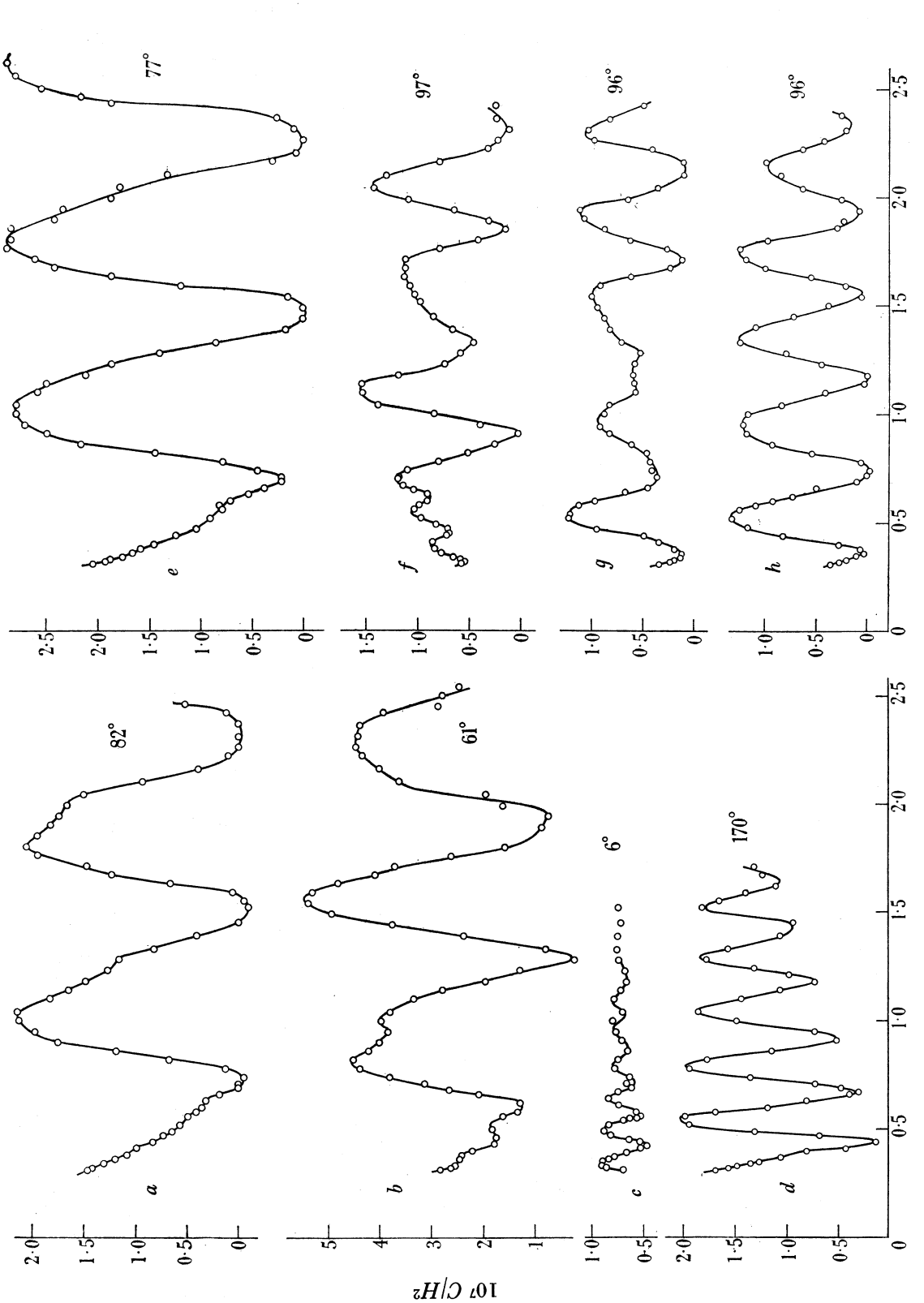

FIGURE 2. Field variation of C/H^2 for bismuth at 4·2° K for various values of ψ (indicated at right); the sign of C is chosen to be that of $I_3/H_3 - I_2/H_2$, and all curves were taken with the stiff suspension. Curves *f*, *g*, *h* illustrate the effect of progressive elimination of orientational errors; curves *a* to *e* were taken with the same degree of error as in *f*, i.e. the binary axis at about 5° off vertical.

agreement with the P_2, P_3 curve at $\psi = 97°$ (where a_1 should be nearly zero) was, however, rather poor in the first series of measurements, and, moreover, a complicated beat pattern is apparent (figure 2*f*); the curve for $\psi = 77°$ (figure 2*e*) also shows slight peculiarities which suggest that the elimination of a_2 and a_3 is not as complete as it should be. These complications proved to be due to orientational errors; a straightforward calculation shows that if the trigonal axis is inclined at a small angle ζ to the horizontal and the binary axis at a small angle ξ to the vertical, P_1 is unchanged to the first order in ζ and ξ, while P_2 and P_3 and also the corresponding amplitudes a_2 and a_3 become appreciably unequal.

Thus it becomes impossible for both the second and third terms to vanish simultaneously, and their residual effects produce the complications of figure 2*e* at high fields; the strong beats of figure 2*f* are due to the inequality of P_2 and P_3 and can be accounted for if $\sqrt{(\xi^2-\zeta^2)}\sim 5°$. Improvement of the orientation eventually produced a simple curve for $\psi = 96°$ (figure 2*h*)* and a less distorted curve for $\psi = 78°$ (figure 3). After the final improvement the detailed curves (figure 3) were taken at $\psi = 78°$, and these will be discussed in the next section. Two different suspensions were used—one to cover the high fields, but giving fair accuracy only above about 10 kG, and the other covering the lower fields, but going only up to 20 kG. Unfortunately, owing to difficulties in locating the origin of ψ quite precisely, errors of order 1° in ψ were not excluded, and it is probable that the curves with the different suspensions, though nominally described as at $\psi = 78°$, are actually taken at slightly different ψ.† This, and the errors of measurement, are probably responsible for slight discrepancies of detail between the curves in the regions of field where they overlap.

Turning now to the question of a suitable orientation for zinc, we find that the situation is much simpler because of the higher symmetry of zinc as compared with bismuth. If the hexagonal axis is horizontal and the binary axis is inclined at angle ξ to the vertical (ξ no longer to be assumed small), the formulae for the P's now become

$$\left.\begin{aligned} P_1 &\propto ((m_1 \sin^2\xi + m_2\cos^2\xi)\sin^2\psi + m_3\cos^2\psi)^{\frac{1}{2}},\\ P_2, P_3 &\propto ((m_1\sin^2(\xi\pm 60°) \pm m_2\cos^2(\xi\pm 60°))\sin^2\psi + m_3\cos^2\psi)^{\frac{1}{2}},\end{aligned}\right\} \qquad (4)$$

(the relative values of the a's are as before given by $\mathrm{d}P^2/\mathrm{d}\psi$). Now, as Mackinnon (1949) has shown, m_3 is much larger than m_1 or m_2, so for ψ small, P_1, P_2 and P_3 should be nearly identical and proportional to $m_3^{\frac{1}{2}}\cos\psi$. Thus any reasonably small angle ψ should achieve the object of producing effectively a single periodic term (i.e. $P_1 = P_2 = P_3$). Since the amplitude is reduced as ψ gets smaller, ψ cannot conveniently be chosen too small and the readings were in fact taken for $\psi\sim 20°$; the angle ξ should be irrelevant for this setting and the crystal was suspended merely with its hexagonal axis horizontal, but with its binary axis arbitrarily oriented. Later it was found by X-rays that the angle ξ between the binary axis [10$\bar{1}$0] and the vertical was 5°.

* Owing to an accidental error this had to be done in two stages and the curve for $\psi = 96°$ after the first improvement still shows beats (figure 2*g*), from which P_2 and P_3 could be estimated as $4{\cdot}4\times 10^{-5}$ and $3{\cdot}7\times 10^{-5}$, which requires $\sqrt{(\xi^2-\zeta^2)}\sim 3°$; X-rays indicated that ξ was indeed about $4\pm 1{\cdot}5°$, in very satisfactory agreement, since ζ was probably not greater than 1°.

† After the measurements were complete it was realized from more detailed consideration of the results that ψ may have been as high as 80° for the thin suspension curves. The scale of ordinates for these curves has been adjusted to make the amplitude of C/H^2 approximately the same as for the thick suspension curves in the region where comparison is possible.

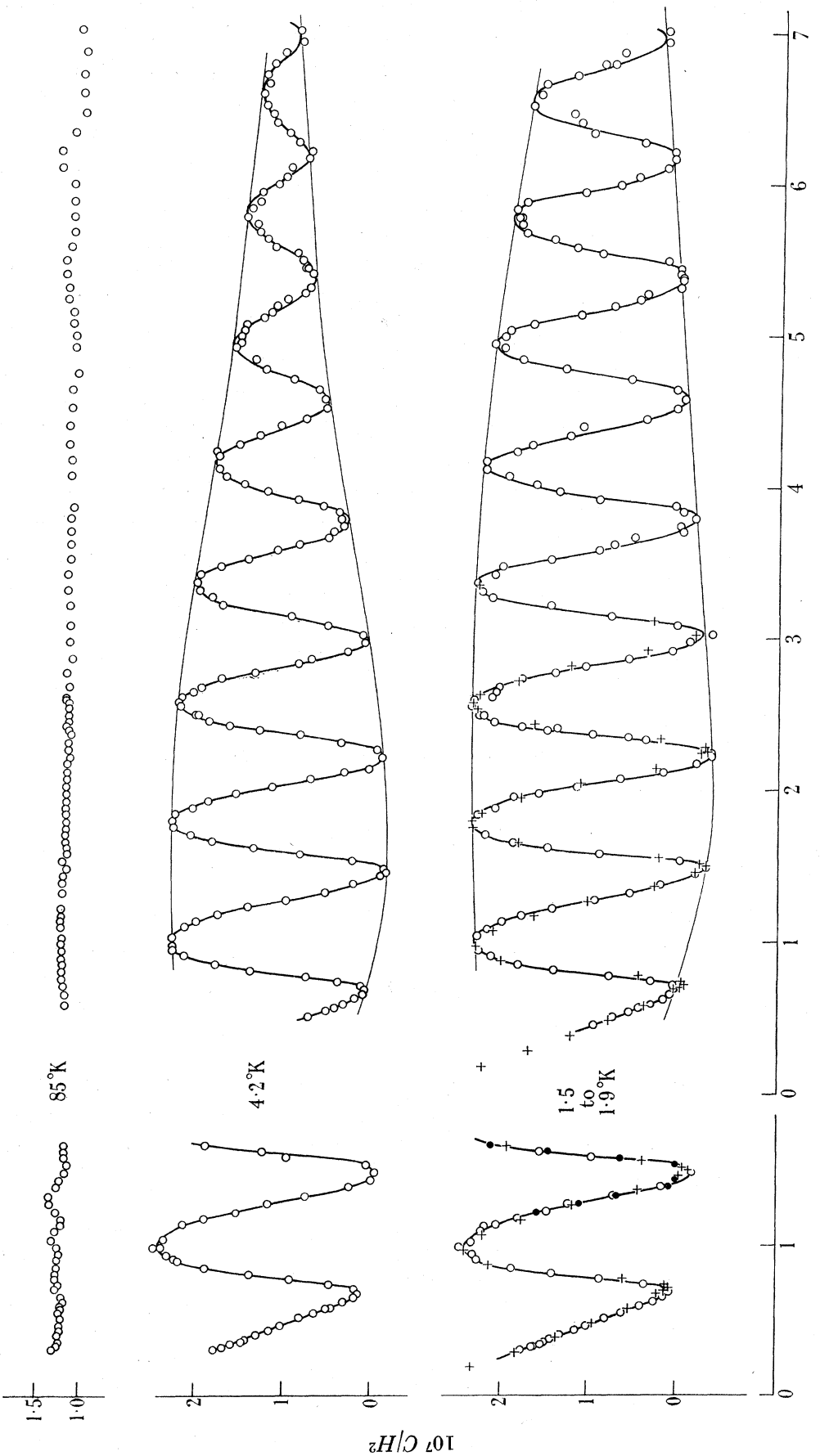

FIGURE 3. Field variation of C/H^2 for bismuth for $\psi \doteqdot 78°$; the left-hand curves were taken with the stiff suspension and the right-hand ones with the thin. In the bottom curve T was between 1·87 and 1·88° K from $10^4/H = 7$ to 1·2 and then fell to about 1·5° K at and below 0·7; in the bottom left curve T was between 1·4 and 1·5° K for the open points and 1·9° K for the black points. The points marked + are theoretical, but the curves are drawn taking only the experimental points into account.

Detailed curves were taken for 303, about 85, 4·19° K, and a low temperature, for each of two suspensions in order to cover a wide range of fields. One series of measurements was also taken for $\psi \sim 10°$ at 4·2° K with the stiffer suspension only. The results for $\psi \sim 20°$ are

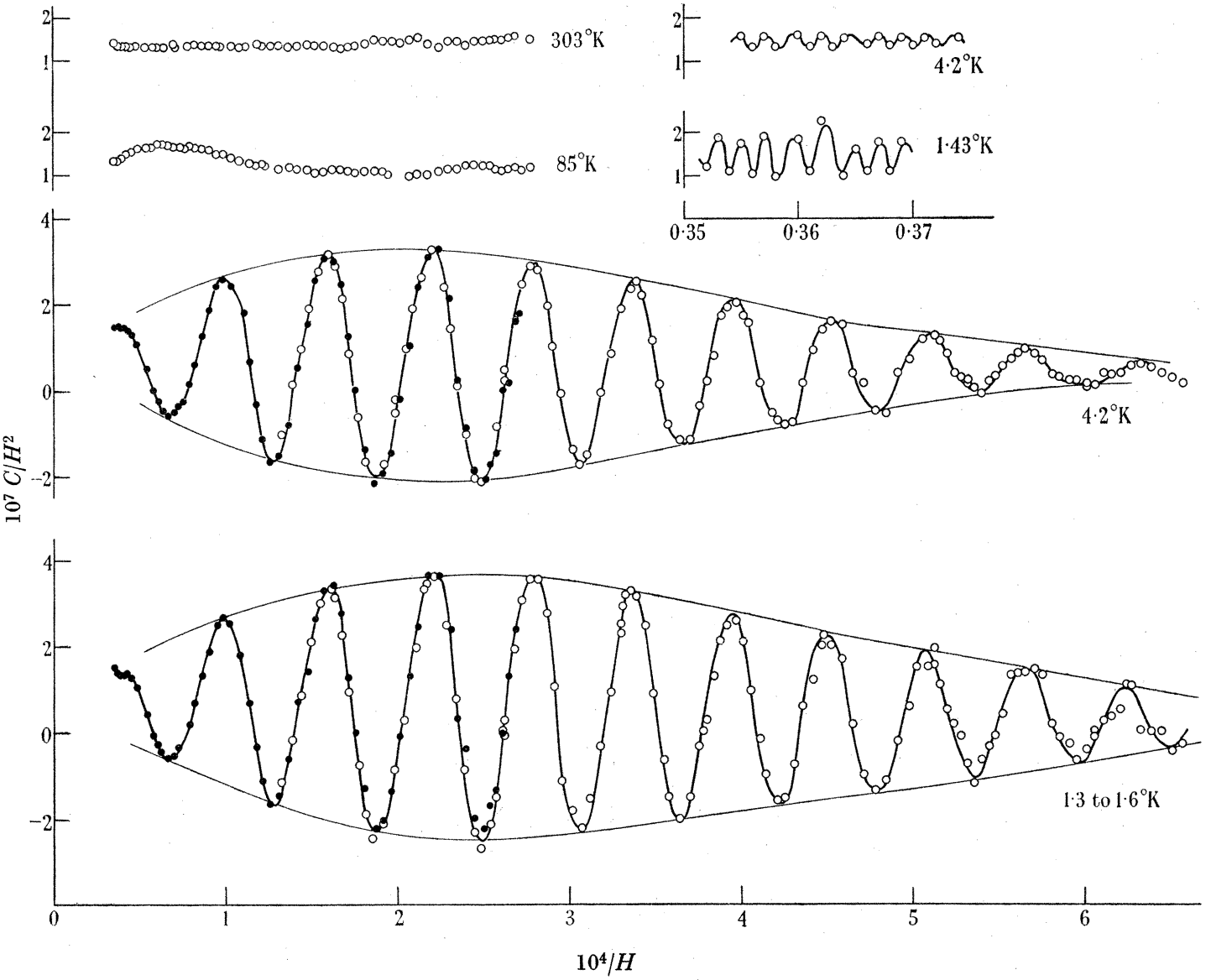

FIGURE 4. Field variation of C/H^2 for zinc, $\psi \sim 20°$; the sign of C is chosen to be that of $I_1/H_1 - I_3/H_3$. The upper curves and the black points in the lower curves refer to the stiff suspension, the other points on the lower two curves to the thin suspension. In the lowest curve T was 1·63° K from $10^4/H = 6$ to 3, and then fell to 1·34° K at and below 2·3 (open points); for the black points T was 1·6° K down to $10^4/H = 2{\cdot}3$ and then fell to 1·45° K below about 2. The inset at top right shows the rapid oscillations on a more open $1/H$ scale; only maxima and minima were observed.

shown in figure 4 and will be discussed in the next section. At high fields, new oscillations of much higher frequency were found, but it is convenient to discuss these later (see p. 18); in figure 4 the high field points are averages between the maxima and minima of these fast oscillations, but the averaging was rough so that there is rather more scatter in this region than at lower fields, where the fast oscillations have become imperceptible.

Detailed discussion of results

(*a*) *Bismuth*

Before discussing the detailed form of the oscillations we must first derive the numerical values of the parameters involved, namely, β/E_0, β and x. From a plot of the values of $1/H$ for maxima and minima against successive half-integers (figure 5), β/E_0 is obtained as the slope of the straight line obtained. Actually for low $1/H$, owing to the harmonics, the minima points lie slightly above and the maxima points slightly below the line, while for higher $1/H$ the accuracy becomes poorer and, moreover, the field calibration is probably not quite so

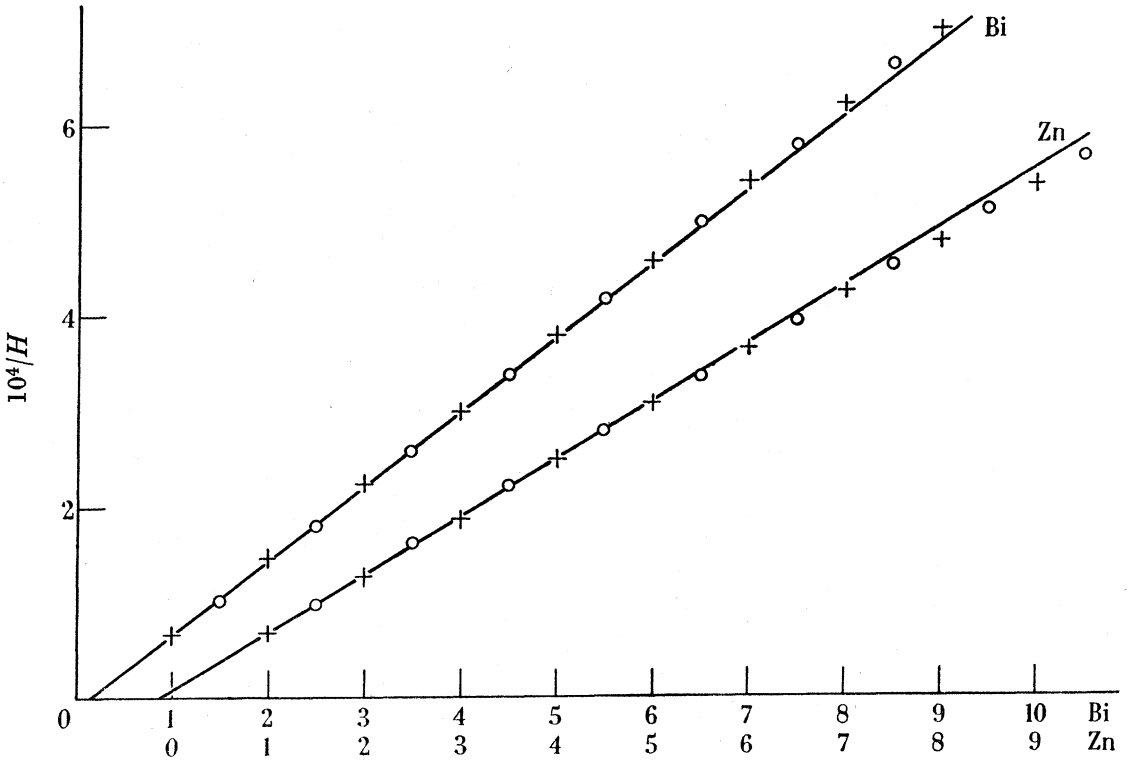

Figure 5. Values of $10^4/H$ for maxima and minima plotted against successive half-integers for bismuth and zinc: ○, maxima; +, minima.

reliable (this probably is responsible for the apparent slight change of slope). Our best estimate* is

$$\beta/E_0 = 7{\cdot}8 \times 10^{-5}.$$

To obtain β we must compare the amplitudes of the oscillations at two temperatures. To a first approximation we may ignore the harmonics for this purpose, since the amplitude of the fundamental proves to be not very different from that of the sum of the fundamental and harmonics, and we are in any case concerned only with ratios. According to (1) the ratio of the amplitudes of the fundamentals at low temperatures T_1 and T_2 should be

$$\frac{T_2 \sinh(2\pi^2 k T_1/\beta H)}{T_1 \sinh(2\pi^2 k T_2/\beta H)},$$

* It will be noticed that this estimate falls slightly below the graph of figure 1. The other points on the graph were based only on the low $1/H$ readings, which tend to indicate systematically higher values of β/E_0. Thus it is possible that the agreement with the values from I may not be quite as perfect as figure 1 suggests.

and the procedure adopted was one of trial and error, to find a value of β which made the theoretical values of the ratio agree as well as possible with the experimental values at various values of $1/H$. The best value was found to be

$$\beta = 2{\cdot}20 \times 10^{-18},$$

and as can be seen from table 2, the agreement is quite good except at high $1/H$, where the experimental accuracy is poor;* this value is unlikely to be in error by more than $0{\cdot}05 \times 10^{-18}$. We may note that this gives

$$E_0 = 2{\cdot}83 \times 10^{-14} \quad \text{and} \quad E_0/k = 205^\circ\,\text{K},$$

in fair agreement with the less accurate estimates in II based on a re-evaluation of the data in I.

TABLE 2. TEMPERATURE VARIATION OF AMPLITUDE FOR BISMUTH

		w_2/w_1	
$10^4 \times 1/H$	T_2 (°K)	expt.	theor.
1·0	1·45	1·02	1·04
1·0	1·80	1·07	1·04
1·5	1·88	1·09	1·08
2·0	1·88	1·14	1·15
2·5	1·88	1·23	1·24
3·0	1·88	1·35	1·35
4·0	1·87	1·68	1·64
5·0	1·87	2·34	2·09
6·0	1·87	2·88	2·76
7·0	1·87	3·76	3·50

Notes. w_2 and w_1 are the amplitudes at T_2 and 4·19°K respectively; the experimental error in w_2/w_1 may be as high as 15 % at the highest $1/H$, but is unlikely to exceed 2 or 3 % below $1/H = 2{\cdot}5 \times 10^{-4}$. All the readings except the first are taken from the thin suspension curve. The theoretical entries are calculated assuming $\beta = 2{\cdot}2 \times 10^{-18}$.

The value of x may now be obtained from the field variation of amplitude of the graphs of figure 3. It is again assumed that the amplitude may be taken as that of the fundamental, though here the assumption is probably less reliable, and discrepancies are to be expected for low $1/H$.† The procedure is to plot $\log_{10}\{(T^{-1}H^{\frac{3}{2}}w)\sinh(2\pi^2kT/\beta H)\}$ against $1/H$, where w is the experimental amplitude, and to derive x from the slope, which should be $-2\pi^2kx/\beta$. As can be seen from figure 6, the plot is indeed reasonably linear over most of the range, though, owing to the theoretical uncertainty at low $1/H$ and the poor experimental accuracy at high $1/H$, the slope can be determined only roughly. The best estimate is

$$x = 1{\cdot}5^\circ\,\text{K},$$

* It is probable that there was a systematic error of a psychological nature in reading deflexions; when the slit image was just beyond a millimetre division on the scale, the tendency was to underestimate the deflexion until it got to nearly the half-way mark, and when it was approaching the next division the tendency was to overestimate. The effect of this error can be seen in the spurious oscillations at 85° K for high $1/H$ in figure 3, and detailed examination of the data shows that it is in the right sense to account for the discrepancies of table 2 at high $1/H$.

† From a comparison of the amplitudes of the synthetic curve (see below) and the fundamental alone it was later found that the error is rather more appreciable than was at first thought, the correction being about 9 % at $1/H = 10^{-4}$ and decreasing to 5 % at $1/H = 2{\cdot}5 \times 10^{-4}$. If allowance is made for this, the estimate of x is reduced to about 1·3° K; this reduction would not seriously modify the subsequent calculations.

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and this is unlikely to be wrong by more than $\pm 0{\cdot}2^\circ$ K. It should be noted that, so far, the theoretical predictions of (1) regarding the temperature and field variation of the oscillation amplitude have been very reasonably confirmed; we shall see, however, that for zinc the field variation is in flagrant disagreement with (1) although the temperature variation still agrees well.

We are now ready to discuss the more detailed features of the oscillations. According to (1), the form of the oscillations can be written as

$$a(-\sin(\theta-\phi_1)+r_2\sin(2\theta-\phi_2)-r_3\sin(3\theta-\phi_3)+\ldots), \tag{5}$$

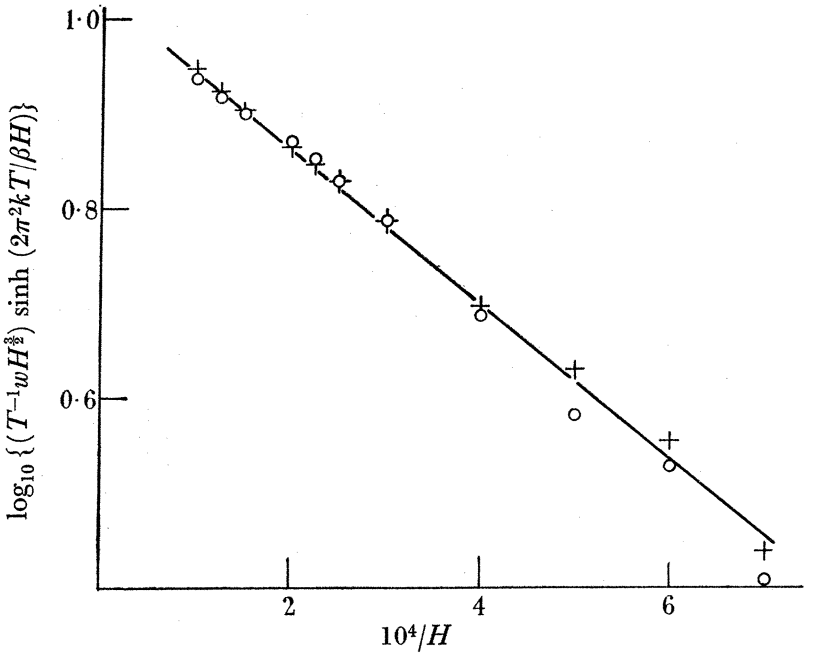

FIGURE 6. Plot of $\log_{10}\{(T^{-1}wH^{\frac{3}{2}})\sinh(2\pi^2kT/\beta H)\}$ against $10^4/H$ for bismuth: ○, 4·19° K; +, about 1·88° K (see legend to figure 3); w is the width of the envelope curve of figure 3 expressed in arbitrary units.

where $\theta = 2\pi E_0/\beta H$, a is positive, and all the ϕ's should be equal to 45°. An estimate of the experimental value of ϕ_1 can be made from the intercept of the straight line of figure 5 on the axis of abscissae; this intercept comes at 0·15 ($\pm 0{\cdot}05$), so

$$\phi_1/2\pi+\tfrac{1}{4} = -0{\cdot}15 \quad \text{or} \quad \phi_1 = -145^\circ \pm 20^\circ,$$

which agrees within the estimated limits of error with the value $-180\pm 45^\circ$ found in I, but based on a more considerable extrapolation. Both estimates of course entirely contradict the theoretical prediction $\phi_1 = 45^\circ$.

Another contradiction becomes apparent as soon as we consider the harmonics. This is that if we build up the curve of (5), choosing suitable values of a, r_2, r_3, etc., as functions of $1/H$ (based on equation (1)) and putting all the ϕ's equal to -145° (or any value between 125 and 165°), there is an obvious qualitative discrepancy with the experimental curves, namely, that each maximum comes to the right of the midway point between the neighbouring minima, instead of to the left, as in the experimental curves. In order to see how the theoretically predicted phases should be corrected, a Fourier analysis was made of an

'idealized' form of the experimental curve in which the ordinates were 'stretched' to make the amplitude independent of $1/H$. Although this procedure is necessarily rough, it gave quite reasonable estimates of the relative strengths of the first two harmonics, while their phases suggested the guess that the required theoretical modification might be merely to remove the factor $(-1)^p$ from (1). This is equivalent to changing (5) to

$$a(\sin(\theta-\phi)+r_2\sin(2\theta-\phi)+r_3\sin(3\theta-\phi)+\ldots). \tag{6}$$

The phase of the fundamental now agrees reasonably with experiment if we choose $\phi = 45°$, and, moreover, the qualitative discrepancy about the sense of the asymmetry of the positions of maxima and minima is removed.

To try out this guess, (6) was calculated as a function of θ (i.e. of $1/H$), including terms up to r_4, for several trial values of ϕ between 0 and 45°. Values of a and the r's as functions of $1/H$ were obtained by rather tedious computation based on (1) and the numerical values of β and x given above. The resulting curves, although qualitatively resembling the experimental curve, could not fit every detail simultaneously. Thus none of the curves could reproduce the marked difference at low $1/H$ between the very flat top half of the envelope and the rather rounder bottom half. Moreover, when ϕ was taken as high as 45°, the first few maxima and minima came nearly at the right places (except that the positions of the maxima were not quite sufficiently asymmetrical), but the descent to each minimum (for increasing $1/H$) was too rounded as compared with the experimental curve. For ϕ as low as 0°, on the other hand, the descents became almost linear—in fact rather too linear for the second and third descents—but the maxima were far too much displaced to the left. In fact, it looked as if what was required was a variable phase ranging from about 0° near the first minimum to about 45° at the second maximum. Fortunately, a theoretical justification for such a variable phase was realized just as hope was being abandoned of getting a completely satisfactory synthesis on the basis of the guess (6).

In fact equation (1), on which all the calculations have been based so far, is not quite exact. It is derived by differentiating the free energy with respect to H, but omitting the terms arising from the slowly varying modulation of the periodic term. These terms are indeed ordinarily small, but become quite significant when $\beta H/E_0$ is large; thus each sine term in (1) should be replaced by

$$\sin\left(\frac{2\pi pE_0}{\beta H}-\frac{\pi}{4}\right)+\cos\left(\frac{2\pi pE_0}{\beta H}-\frac{\pi}{4}\right)\left\{\frac{\pi kT}{E_0\tanh 2\pi^2pkT/\beta H}+\frac{3\beta H}{4\pi pE_0}+\frac{\pi kx}{E_0}\right\}, \tag{7}$$

as has been pointed out by Dingle (1952*a*, *b*).* The presence of the cosine term, which becomes equal to the sine term for $p = 1$ at $1/H = 0{\cdot}3\times10^{-4}$, provides just the sort of variable phase required (though its effect is of course weaker for each successive harmonic).

Taking (7) into account, a careful synthesis was made assuming $\phi = 45°$ and including harmonics up to the sixth, and the result, as can be seen from figure 3, comes surprisingly

* The last term in (7), which is not mentioned explicitly by Dingle when he introduces the parameter x, comes from differentiation of the factor $e^{-2\pi^2px/\beta}$ in the free energy, and is, in fact, just appreciable. It should be noticed that for $2\pi^2pkT/\beta H$ small the first term is nearly equal to $\beta H/2\pi pE_0$, so that the first two terms add up to $5\beta H/4\pi pE_0$; this helps to simplify numerical computation. It should be noticed also that (1) as modified by (7) predicts that C/H^2 should become infinite as $H^{\frac{1}{2}}$ for $H\to\infty$; this is because the expansion on which our discussion is based breaks down for $\beta H/2E_0>1$. In fact, however, as can be seen from figure 3, the experimental results are described quite well by the formula even up to $\beta H/2E_0 = 1{\cdot}3$.

close to the experimental curve. Since, as was pointed out on p. 7, there are slight discrepancies between the experimental curves with the thick and thin suspensions, there is some arbitrariness in choosing the scale and origin of ordinates of the theoretical synthetic curve. The curve for the thick suspension has been fitted so that the first minimum and maximum appear at the correct ordinates, while that for the thin suspension has been fitted to make the envelope coincide at about $1/H = 1{\cdot}6 \times 10^{-4}$. Although the first fit appears to be rather better, it must not be forgotten that it covers a much more restricted range of $1/H$. As already mentioned, the discrepancies between the two experimental curves probably indicate that the crystal orientation was not quite identically preserved between the experiments, and the better fit with theory suggests that the orientation was perhaps nearer the ideal one with the stiff suspension (see also the footnote on p. 7). It is perhaps significant that the slight discrepancies between the thin suspension curve and the theoretical curve suggest that the experimental curve contains too little first harmonic, and this might indeed be the case if it was slightly misoriented, since, as can be seen from figure 1, the periods of the other two terms, which no longer have zero amplitudes away from the ideal orientation, are approximately half of the period with which we are concerned and would therefore roughly simulate the effect of first harmonic.

That the choice of $\phi = 45°$ cannot be very far wrong was indicated by a trial synthesis assuming $\phi = 35°$; this put the first two maxima appreciably too far to the left, and so did not give quite such a good fit as $\phi = 45°$. It was verified, too, that the role of the higher harmonics is by no means unimportant, for if the third and higher harmonics are omitted from the calculation the agreement with the experimental curve is much worse; even if the third harmonic is included, but higher ones omitted, the curve to the left of the first minimum is appreciably distorted. We must also mention another possible cause of discrepancy between the formula and the experimental curves. This is that the formula is really only valid if $\beta H/2E_0$ is not too large; the 'steady' part of the susceptibility or anisotropy (not included in (1)) is in fact not quite steady, but for $\beta H/2E_0 < 1$ and $kT \ll E_0$ varies as

$$1 + \frac{7}{120}\left(\frac{\beta H}{2E_0}\right)^2 + \frac{31}{896}\left(\frac{\beta H}{2E_0}\right)^4 + \ldots \qquad (8)$$

(Dingle 1952*a*), and so contributes an appreciable field variation for $\beta H/E_0 > 1$ (i.e. $1/H < 0{\cdot}8 \times 10^{-4}$), which would tend to raise the theoretical curve to an increasing extent as $1/H$ becomes smaller. This, in fact, might help to improve the fit with the thin suspension curve, but there is little point in attempting to make this improvement quantitatively, since it is well known that the formula for the steady diamagnetism does not give good agreement with experiment if the parameters from the de Haas–van Alphen effect are used, and, moreover, the slight discrepancy between the two experimental curves makes it uncertain just how much improvement is required anyway.

Bearing in mind the various experimental and theoretical uncertainties, it may be said with some confidence that the full theoretical formula gives a good detailed description of the experimental curve provided only that the factor $(-1)^p$ is omitted. It is interesting that the omission of the factor $(-1)^p$ is predicted theoretically for an ideal free-electron gas (Akhieser 1939), if the electron-spin paramagnetism is taken into account. For anomalously small effective electron masses, however, as in bismuth, the effect of electron spin should be

much less drastic, being limited to the addition of a factor $\cos(\pi p\beta_0/\beta)$ to each term in (1) (Dingle 1952*a*; Sondheimer & Wilson 1951), where β_0 is the true double Bohr magneton (note that for free electrons $\beta = \beta_0$ and this factor is just $(-1)^p$). For bismuth, this factor is almost unity except for very high harmonics, since $\beta_0/\beta = 4{\cdot}2 \times 10^{-3}$ (thus even for $p = 6$ the factor is 0·997), and it is for this reason that we did not include it in (1).

(*b*) *Zinc*

The plot of values of $1/H$ for maxima and minima is shown in figure 5. The slight curvature downwards at high $1/H$ can probably be ascribed to field calibration errors.* The slope obtained from the lower points gives

$$\beta/E_0 = 6{\cdot}10 \times 10^{-5}.$$

TABLE 3. TEMPERATURE VARIATION OF AMPLITUDE FOR ZINC

		w_2/w_1	
$10^4/H$	T_2 (°K)	expt.	theor.
0·7	1·60	1·03	1·02
1·0	1·60	1·03	1·03
1·5	1·60	1·06	1·06
1·5	1·34	1·09	1·06
2·0	1·60	1·10	1·12
2·0	1·34	1·14	1·13
2·5	1·60	1·16	1·18
2·5	1·42	1·21	1·19
3·0	1·63	1·28	1·26
4·0	1·63	1·45	1·50
5·0	1·63	1·86	1·83
6·0	1·63	2·70	2·37

Notes. w_2 and w_1 are as defined in table 2. Where two readings are given for any value of $1/H$, the first refers to the thick and the second to the thin suspension curve. The theoretical entries are calculated assuming $\beta = 2{\cdot}55 \times 10^{-18}$.

According to (5) this should be $\cos\psi$ times the period for $\psi = 0$ (i.e. for H along the hexagonal axis), and since ψ was approximately 20°, we find $\beta_{\|}/E_0 = 6{\cdot}49 \times 10^{-5}$. From a similar analysis of a curve taken at $\psi = 10°$, we get $6{\cdot}43 \times 10^{-5}$ in quite good agreement. Our values of $10^5\beta/E_0$ may be compared with 6·88 (Mackinnon 1949), 6·32 to 6·80 (Sydoriak & Robinson 1949), 6·40 (Berlincourt & Steele 1954) and 5·32 (deduced from curves at $\psi = 20°$ and 30° given by Verkin (1951)). The discrepancies (except with Verkin's result) are not more than can be reasonably ascribed to experimental errors, and possibly to differences in impurity content.

The value of β was deduced in the same way as for bismuth and as table 3 shows, the value

$$\beta = 2{\cdot}55 \times 10^{-18}$$

gives quite reasonable agreement between the theoretical and experimental ratios of amplitude at the low temperature and 4·19° K. This corresponds to $\beta_{\|} = 2{\cdot}71 \times 10^{-18}$. The value of E_0 deduced from β/E_0 and β is

$$E_0 = 4{\cdot}18 \times 10^{-14} \quad \text{and} \quad E_0/k = 302° \text{ K}.$$

* The zinc experiments were done with different pole pieces, and so a different calibration is involved from that used in the bismuth experiments. It must be assumed that the calibration errors were in opposite senses in the two cases, in order to explain the opposite curvatures of the plots for bismuth and zinc.

Berlincourt & Steele (1954) give $E_0 = 4{\cdot}1 \times 10^{-14}$ and quote a value of $4{\cdot}0 \times 10^{-14}$ found by Donahoe & Nix (1954); the re-evaluation of Mackinnon's results mentioned in table 14 of II gave $E_0 = 4{\cdot}9 \times 10^{-14}$·, but the re-evaluation was rather rough, so the difference is not necessarily significant.

To deduce x, we plot as before $\log_{10}\{(T^{-1}H^{\frac{3}{2}}w)\sinh(2\pi^2kT/\beta H)\}$ against $1/H$, and as can be seen from figure 7, there is a striking departure from the theoretically predicted straight line. For high $1/H$, the plot does indeed appear to be asymptotically approaching linearity, and a rough estimate of the slope of the asymptote gives

$$x = 4{\cdot}9^\circ\,\mathrm{K},$$

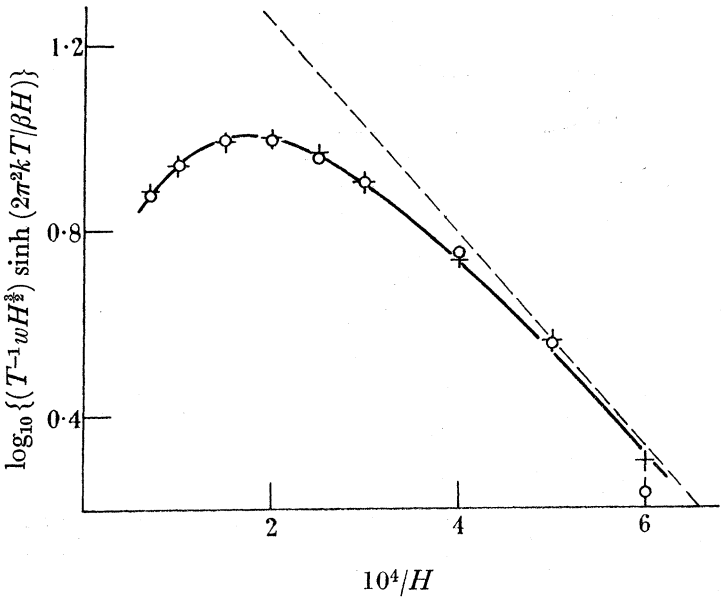

FIGURE 7. Plot of $\log_{10}\{(T^{-1}wH^{\frac{3}{2}})\sinh(2\pi^2kT/\beta H)\}$ against $10^4/H$ for zinc: ○, 4·19° K; +, about 1·60° K (see legend to figure 4); w is the width of the envelope curve of figure 4 expressed in arbitrary units.

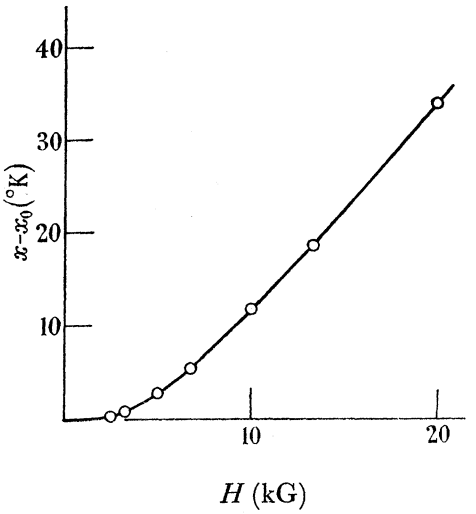

FIGURE 8. Field variation of $x-x_0$ deduced from figure 7.

in reasonable agreement with the estimate 5·5° K given in II from the re-evaluation of Mackinnon's data. The strong curvature of the plot at lower $1/H$, however, suggests that the introduction of a constant parameter x into (1) is not justified for zinc (though hitherto it has satisfactorily described the field variation of all other metals studied). In terms of the original experimental curve this discrepancy means that the width of the envelope curve narrows much too rapidly as $1/H$ is reduced; this can also be seen qualitatively in the earlier experimental results on zinc, particularly those of Verkin, and in the recent work of Berlincourt & Steele (1954), who point out as an empirical fact that if $H^{\frac{5}{2}}$ is substituted for $H^{\frac{3}{2}}$ the plot of figure 7 becomes linear.

One speculative possibility of interpreting the discrepancy is to suppose that (1) is still correct, but that x should be regarded as a function of H, constant at low fields and increasing gradually at high fields. The ordinates of figure 7 would then represent $C-2\pi^2kx/\beta H$, where C is a constant, and $C-2\pi^2kx_0/\beta H$ would describe the asymptotic straight line which the

curve approaches at high $1/H$. The distance of the curve from the asymptote for any value of $1/H$ should then give $2\pi^2 k(x-x_0)/\beta H$. From such an analysis it would appear that x varies with H as indicated in figure 8; since, however, the results, especially at lower fields, depend critically on how the asymptote is drawn, the curve can be taken only as a rough indication of the general trend.

The very high value of x at high fields might then be responsible for the obvious lack of strong harmonics in the anisotropy curve for zinc. Thus, assuming the values of x indicated on figure 8, the ratio r_2 of the first harmonic to the fundamental should be only about 0·06 for $1/H = 10^{-4}$, should rise slightly to about 0·07 for $1/H = 2\times10^{-4}$, and then fall off again. These values may be compared with $r_2 \sim 0{\cdot}3$ for bismuth, so it is not surprising that the zinc curves look almost simple harmonic. Before considering in more detail the actual harmonic content, we must first discuss the phase of the oscillations.

The phase of the fundamental can be found from the intercept of figure 5, which gives (see equation (5))

$$\phi_1 = -49^\circ \pm 10^\circ$$

(exactly the same phase is obtained also from the results for $\psi = 10^\circ$). Berlincourt & Steele (1954) find $\phi_1 = -49 \pm 6^\circ$, and the re-evaluation of Mackinnon's results for $\psi = 15^\circ$ gives ϕ_1 as between -50° and -80°, but the extrapolation required is greater than in figure 5, so the discrepancy cannot be regarded as significant (Mackinnon himself gives 90°, but the omission of the minus sign must be a slip). Actually the phase determination requires a slight correction in the light of (7), for it is the phase of the sine term alone with which we are concerned, while what is observed is the resultant phase of (7). Each point on figure 5 should therefore be shifted slightly to the left by an amount which increases as $1/H$ decreases and the intercept is thereby slightly, but appreciably, changed. In calculating the shift we must remember that (7) assumes x to be independent of H; it is easily shown that if x is regarded as a function of H it should be replaced in (7) by $x - H\mathrm{d}x/\mathrm{d}H$, which can be estimated at each field from figure 8. We find that the bottom point in figure 5 is shifted by about 17° (0·05 on the scale of abscissae) while for $1/H = 1{\cdot}90\times10^{-4}$ the shift is only about 5° (0·014). This changes our estimate of ϕ_1 to about -30°.

Turning now to the harmonic content of the anisotropy curve, it is possible to make a Fourier analysis of the region around $1/H = 2{\cdot}5\times10^{-4}$ where the overall amplitude is fairly constant. To check the accuracy of the analysis two full periods were analyzed independently (*a*) from $2{\cdot}05$ to $2{\cdot}65\times10^{-4}$ and (*b*) from $2{\cdot}2$ to $2{\cdot}8\times10^{-4}$. Choosing the origin of θ in such a way that the phase of the fundamental agrees with the considerations above, but ignoring the slight phase shift (of order 4° for the fundamental and 2° for the first harmonic) indicated by (7) in this region of $1/H$, we find

$$(a) \quad -\sin(\theta+30^\circ) - 0{\cdot}060\sin(2\theta+53^\circ) - 0{\cdot}016\sin(3\theta-81^\circ),$$

$$(b) \quad -\sin(\theta+30^\circ) - 0{\cdot}036\sin(2\theta-11^\circ) + 0{\cdot}014\sin(3\theta-99^\circ).$$

The discrepancies between (*a*) and (*b*) indicate that because of the feebleness of the harmonics, the analysis is very sensitive to the exact manner of drawing the curve through the experimental points and probably also to computational errors. The estimate of the strength of the first harmonic agrees in order of magnitude with the theoretical estimate

$r_2 \sim 0{\cdot}06$ based on our interpretation of a field-dependent x, but the phase is very uncertain. The result could be regarded as consistent with the omission of the $(-1)^p$ factor as for bismuth, and the assumption $\phi = 150°$ in (6), but this is very speculative. It is evident that the experimental curve is not sufficiently precisely determined to give any useful information about the third harmonic except that it is very small; the theoretical value of r_3 on the basis of a field-dependent x should be about 0·005.

Discussion

The present results on bismuth and zinc, taken together with those already obtained with graphite and gallium, confirm the conclusion provisionally made in II that the theory in its present form does not in general correctly predict the phases of the fundamental and harmonics, and that each metal shows an individual behaviour. Using the notation of equation (5) the situation may be summarized as follows:

gallium: if ϕ_1 is assumed to be 45°, ϕ_2 and ϕ_3 are also roughly 45°, though the plot of maxima and minima suggests that ϕ_1 is actually closer to 90°, which would make ϕ_2 about 135° and ϕ_3 about 170°;

graphite: here two independent terms are superimposed; for the main one, if ϕ_1 is taken as 30°, ϕ_2 is also 30°, while for the subsidiary ϕ_1 becomes $-60°$ (no information on ϕ_2 for the subsidiary); the plot of maxima and minima suggests ϕ_1 for the main term is actually closer to 0°, which would make ϕ_2 $-30°$, and ϕ_1 for the subsidiary $-100°$;

bismuth: this is the only metal where the evidence is nearly unambiguous; the results are consistent with $\phi_1 = -135°$, $\phi_2 = 45°$, $\phi_3 = -135°$, etc., though probably the results would be equally consistent with different phases for harmonics beyond the third; thus the phases in bismuth are consistent with the theoretical formula if the factor $(-1)^p$ is omitted;

zinc: $\phi_1 = -30°$, ϕ_2 may be anywhere between 130 and 190°.

For all the metals the strengths of the harmonics are reasonably in accord with theoretical prediction, except in graphite, where the first harmonic appears to be rather too strong. The experimental estimation of the harmonic strengths is, however, in all cases rather rough.

As Dingle (1952*a*) has pointed out, the theory in its present form does not take proper account of the effect of the periodic electric field of the lattice, and he has suggested that this might modify the theoretical phase relations and also the detailed form of the field dependence of amplitude. This suggestion has not, however, yet been worked out, and it is hoped that the present results will stimulate a re-examination of the theory.

Miscellaneous results at high fields

(*a*) *The high-frequency oscillations in zinc*

As already mentioned, short-period oscillations were observed at high fields and they are illustrated in the inset to figure 4; Berlincourt & Steele (1954) also mention having observed such short-period oscillations. Although there is some suggestion of beats, this cannot be

regarded as definite, since the current could not be held steady enough to get accurate maximum and minimum deflexions. The period also could not be measured with great accuracy, since usually not more than eight or ten periods could be definitely identified (at smaller fields the field varies more rapidly with current, and the amplitude also falls off rapidly). The variation of period with ψ is shown in figure 9; for angles outside this range it was difficult to follow the oscillations, though for $\psi = -49°$ there was evidence of yet another periodicity with $\beta/E_0 \sim 17 \times 10^{-7}$. The complicated nature of the variation with ψ is probably partly due to the arbitrary orientation of the crystal (see p. 7), but it is possible that here, as in cadmium (Berlincourt 1954), the variation is not describable in terms of any reasonable scheme of ellipsoids.

For $\psi = 20°$, the amplitude was estimated at 1·45° K as well as at 4·19° K, and from the amplitude ratio it follows that $\beta \sim 4{\cdot}5 \times 10^{-20}$. Since $\beta/E_0 = 2{\cdot}3 \times 10^{-7}$, we have

$$E_0 \sim 20 \times 10^{-14} \quad \text{or} \quad E_0/k \sim 1400° \text{ K}.$$

These results are similar in order of magnitude to those for cadmium.

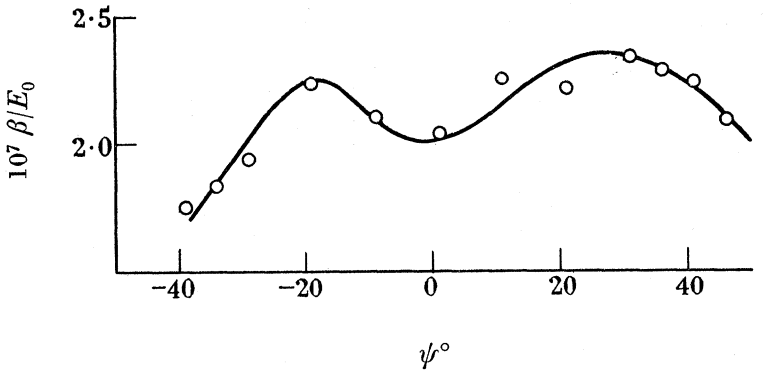

FIGURE 9. Variation of short period of oscillations in zinc with ψ.

(*b*) *Field dependence of anisotropy of zinc and bismuth at* 85° K

The 85° K curve of figure 4 confirms the result found by McClure & Marcus (1951) and studied in much greater detail by Berlincourt & Steele (1954) that the deHaas–van Alphen effect persists up to quite high temperatures, but with a period which increases at temperatures above about 20° K. This change of period with temperature is probably closely associated with the peculiar temperature dependence of the steady susceptibility (Marcus 1947, 1949; McClure & Marcus 1951), and a discussion of possible mechanisms has been given by Berlincourt & Steele.

A careful examination of the bismuth data suggests that both these effects occur there too. Thus the 85° K curve for bismuth (figure 3) shows a just appreciable field dependence of susceptibility at high fields with a maximum amplitude of something like 2 or 3 % of that at liquid-helium temperature. The effect is too slight to permit any definite estimate of the period, but it might well be appreciably greater than at the lower temperatures; a calculation of the amplitude to be expected at 85° K predicts less than one-tenth of the observed effect at $1/H = 10^{-4}$ if β is assumed constant, but this estimate would be increased if β increased appreciably with rise of temperature. Again there is some evidence that the

steady part of the anisotropy as a function of temperature passes through a flat maximum between 85° K and liquid-helium temperatures, though the magnitude of this effect is much less marked than the corresponding one in zinc.

(*c*) *Lead*

The de Haas–van Alphen effect in lead was discovered by the impulsive high field method and β/E_0 was found to be about 4×10^{-8} and not very sensitive to crystal orientation (Shoenberg 1953). It seemed worth while to check that the effect could be observed in a steady field, and the oscillations were in fact found with a just appreciable amplitude at temperatures below 1·5° K for a lead crystal of arbitrary orientation. The difficulty of field stability was even more serious here than in (*a*) above, so that detailed study of orientational effects was hardly practicable. It was found, however, that the period had just the expected magnitude, and the order of magnitude of the amplitude too was reasonably consistent with extrapolation of the impulsive field results (for $T = 1{\cdot}34°$ K and $1/H = 0{\cdot}31 \times 10^{-4}$, the maximum amplitude $|C/H^2|$ was approximately $1{\cdot}7 \times 10^{-10}$).

(*d*) *Copper, silver and gold*

Although eddy-current effects caused serious difficulties (the crystal responded strongly to any change or rotation of the field, and the ensuing deflexion then fell off only very slowly), it was established that there was no appreciable de Haas–van Alphen effect in any of these metals. Very roughly the limits given in table 10 of II can be extended by the statement that for all three metals $|C/H^2| < 5 \times 10^{-11}$ at 1·4° K and $1/H = 0{\cdot}31 \times 10^{-14}$. This is not surprising in view of the fact that no effect was found at 10^5 G by the impulsive method, but it was thought worth while making the check, since the negative results in the impulsive method may well prove to be due to the masking effects of eddy currents.

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