The de Haas-Van Alphen Effect

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Phil. Trans. R. Soc. Lond. A 1952 **245**, 1-57
doi: 10.1098/rsta.1952.0016

THE DE HAAS–VAN ALPHEN EFFECT

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(*Communicated by Sir Lawrence Bragg, F.R.S.—Received* 22 *December* 1951)

The magnetic anisotropy of single crystals of various metals has been studied experimentally particularly at liquid-helium temperatures, and an oscillatory variation with field (de Haas-van Alphen effect) has been discovered in gallium, tin, graphite, antimony, aluminium, cadmium, indium, mercury and thallium. Previously the effect has been found only in bismuth and zinc, and recently it has been found by Verkin, Lazarev & Rudenko also in magnesium and beryllium. After a brief statement of Landau's theory of the effect and some recent modifications by Dingle, the experimental technique is described and the results for the individual metals are presented. The effect has been studied most thoroughly for gallium, tin, graphite and antimony, and it has been possible to explain the results in considerable detail on the basis of the theory, though some features such as the modulations of the oscillations cannot be fully explained; the theoretical interpretation of the results for the other metals is less complete, mainly because of experimental difficulties specific to each metal which hindered a complete investigation.

Comparison with the theory shows that the effect can be explained if it is assumed that only a very small number of free electrons (ranging from 10^{-6} to 10^{-3} per atom) are effective and that these electrons have effective masses which are small (usually of order of one-tenth of an electron mass) and depend on the direction of the applied magnetic field. The period, amplitude and temperature-dependence of the oscillations vary considerably from one metal to another, depending on the particular values of these parameters. These 'effective' electrons are presumably those which overflow at certain places in wave-number space from one Brillouin zone into another, or the 'holes' left behind in nearly full zones, and their small effective masses are associated with large curvature of the Fermi surface in these regions. The theory assumes that the relevant parts of the Fermi surface can be represented by ellipsoids, and for some of the metals the form of these ellipsoids can be worked out in detail on the basis of the experimental results. The fact that the de Haas-van Alphen effect has not been found in monovalent metals such as copper, silver and gold up to fields of 15800 G, supports this interpretation, since the Fermi surface in these metals does not cross Brillouin zone boundaries. Although the oscillatory variation of anisotropy was the main object of the investigation, some new data on the steady part of the anisotropy were also obtained, and where a detailed comparison with theory was possible it was found that the free electrons effective in producing the oscillations could account only partly for the observed steady anisotropy.

An important feature of the comparison with theory is that in order to explain both the temperature and field variation of the amplitude of the oscillations consistently it is necessary to add to Landau's formula an exponential 'damping factor' involving a parameter x which has the dimensions of temperature and is usually of order 1° K. The effect of this 'damping' is equivalent to that of raising the temperature by x° K. Dingle has shown that just such a factor is to be expected if broadening of the energy levels due either to collisions or other causes is taken into account. Experiments on the de Haas-van Alphen effect in a series of alloys of tin with mercury and indium support Dingle's interpretation in showing that the parameter x varies approximately linearly with the reciprocal of the collision time (i.e. with the residual resistance), and the slope of the linear relation gives a reasonable value of the collision time. It is clear, however, that collision broadening alone cannot account for the experimental values of x for pure metals, and other causes of level broadening, such as the effect of the electric field of the crystal lattice, must be invoked.

INTRODUCTION

An oscillatory variation of magnetic susceptibility with field strength at low temperatures was first discovered in bismuth by de Haas & van Alphen (1930, 1932) and the effect is usually named after them. Peierls (1933) showed theoretically that such an effect could be expected for a free electron gas, but that in ordinarily practicable experimental conditions in metals it should occur only if there were very few free electrons per atom which were relevant, and, moreover, if the effective mass of these electrons was rather small. Further development of the theory by Blackman (1938) and Landau (1939) enabled more precise comparison with experiment to be made, and later experiments (Shoenberg 1939) showed that the theory could successfully account for many of the finer details of the experimental results if it was assumed that only about 10^{-5} electrons per atom were effective, and that the effective mass was of the order of one-tenth of an electron mass (varying suitably with the direction of the magnetic field in the crystal).

All this work supported the view that rather particular conditions were necessary for the de Haas-van Alphen effect to be observed, and it seemed likely that the right combination of conditions might occur only in bismuth, which was in other respects already known to be rather an anomaly among metals. This point of view, however, became untenable when Marcus (1947) found that zinc also showed a marked de Haas-van Alphen effect. Comparison of the theory with the more detailed experiments of Sydoriak & Robinson (1949) and Mackinnon (1949) showed that the behaviour of zinc could be explained if electronic parameters were assumed of orders of magnitude quite similar to those which had to be assumed to explain the behaviour of bismuth. This discovery suggested that the de Haas-van Alphen effect might occur in reasonably practicable conditions of field and temperature much more generally than had at first been thought, particularly in multivalent metals for which the Fermi surface may, over small regions in phase space, be very distorted where it crosses Brillouin zone boundaries, thus producing, as it were, 'pockets' containing very few electrons or 'holes' of low effective mass.

An exploratory investigation was accordingly initiated early in 1949, in the course of which the magnetic behaviour of as many metals as could be easily crystallized has been studied by the method of measuring the torque on a single crystal in a uniform field. It has turned out that gallium, tin, graphite, cadmium, indium, antimony, aluminium, mercury and thallium all show the de Haas-van Alphen effect, while lead, copper, silver, gold, germanium and tellurium do not show the effect in the most extreme conditions tried (up to 15800 G and down to about 1·1° K). At about the same time a similar series of experiments has been carried on independently by Verkin, Lazarev & Rudenko (1949, 1950*a*, *b*, 1951*a*) who have also found the de Haas-van Alphen effect in tin, cadmium, indium, magnesium, beryllium and antimony. Thus it is indeed true that most of the multivalent metals so far tried do show the effect, while the monovalent metals do not.

Although the present investigation has been largely exploratory it has had also the aim of studying the extent to which the theory applies to actual metals in detail, and of obtaining information where possible about the electronic parameters of the various metals. Some of the metals (gallium, tin, graphite and antimony) have been studied in fair detail, but the others have been studied only to the stage where it became apparent that a much longer investigation would be required for a thorough analysis. Novel features have appeared in nearly every new metal studied, but the general policy has been not to impede the general exploratory character of the research, and to leave for the future any more detailed investigation of features which would have diverted too much effort from the main research.

While the experiments were in progress Dingle (1952 *a*, *b*) suggested some improvements to the theory, and in particular showed that if collisions are taken into account the de Haas-van Alphen effect should be 'damped' to an extent which increases as the collision time is reduced.* Special experiments on tin contaminated by various small quantities of mercury and indium have provided support for this extension of the theory and have yielded a reasonable estimate of the collision time in pure tin.

The results are most easily presented with reference to the theoretical formulae, and so it will be convenient first to summarize the theoretical predictions and to indicate just what features of the de Haas-van Alphen effect can most profitably be studied and what can be learnt from such a study. After this theoretical introduction, the experimental technique will be described, then the results for the individual metals in turn will be presented and discussed, followed by a summary of the results on the steady anisotropy and an account of the work on tin alloys; the final section summarizes the quantitative information derived from this and other investigations on the fundamental electronic parameters characterizing the metals which show the de Haas-van Alphen effect. A number of preliminary notes on this work and on some of Dingle's theoretical results have already appeared (Shoenberg 1949, 1951 *a*, *b*; Dingle & Shoenberg 1950).

THEORETICAL STATEMENT

The original theory of Peierls (1933) and its extension by Blackman (1938) to take into account anisotropic effects gave only implicit relations between the magnetization and the field, and the main advance of Landau's (1939) theory was in expressing these relations in explicit form. Since then, essentially the same results have been obtained by other authors using a variety of mathematical methods (Akhieser 1939; Rumer 1948; Sondheimer & Wilson 1952; Dingle 1952 *a*). In its simplest form Landau's final result for the anisotropy may be expressed as

$$\frac{C}{H^2\sin\psi\cos\psi}=\Sigma\frac{A\Delta m}{\rho}\left\{\frac{\pi^2}{6}\left(\frac{k}{E_0}\right)^{\frac{1}{2}}-\frac{1}{T^{\frac{1}{2}}}\left(\frac{2\pi^2kT}{\beta H}\right)^{\frac{3}{2}}\exp\left[-\frac{2\pi^2kT}{\beta H}\right]\sin\left(\frac{2\pi E_0}{\beta H}-\frac{\pi}{4}\right)\right\}. \qquad (1)$$

Here C is the observed couple per unit mass about an axis perpendicular to the direction of the field H and ψ is the angle between the field and a suitably chosen axis in a plane normal to the axis of measurement of C; thus the left-hand side of (1) is essentially the difference $\Delta\chi$ of the mass susceptibilities in two directions at right angles. On the right-hand side ρ is the density and A is a constant given by

$$A=e^2E_0/\pi^4c^2\hbar(2k)^{\frac{1}{2}}m'^{\frac{3}{2}}; \qquad (2)$$

β is an 'effective' double Bohr magneton defined by

$$\beta=e\hbar/mc, \qquad (3)$$

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* After Dingle's work was complete I learnt that a similar calculation has also been made by Robinson (1950).

where m is a suitable 'effective' electronic mass which is in general dependent on the field direction relative to the crystal axes; Δm is a factor containing the difference between two effective masses and in general it may depend on ψ; m' in (2) is yet another combination of effective masses and E_0 is the degeneracy parameter of the relevant electrons. The precise definitions of m, m' and Δm depend on the geometry of the experiment and also on the symmetry properties of the crystal, and some special cases will be discussed in more detail later.

Equation (1) is based on the assumption that the surfaces of constant energy in phase space can be considered as ellipsoids whose equations are of the form

$$\alpha_{11}p_x^2+\alpha_{22}p_y^2+\alpha_{33}p_z^2+2\alpha_{23}p_yp_z+2\alpha_{31}p_zp_x+2\alpha_{12}p_xp_y=2Em_0, \tag{4}$$

where m_0 is the true electronic mass, and it is these various coefficients α_{ij} which enter into the precise definitions of the effective masses mentioned above. In order to satisfy the requirements of crystal symmetry, either the ellipsoid must itself have the symmetry properties of the crystal, which imposes severe restrictions on the coefficients α_{ij} (for instance, for cubic symmetry evidently $\alpha_{11}=\alpha_{22}=\alpha_{33}$ and $\alpha_{12}=\alpha_{23}=\alpha_{31}=0$), or else several ellipsoids must be introduced, obtained one from the other by the appropriate symmetry operations (for instance, if $\alpha_{11}\neq\alpha_{22}\neq\alpha_{33}$ but $\alpha_{12}=\alpha_{23}=\alpha_{31}=0$, six ellipsoids would be required for cubic symmetry, but if no terms vanish, twenty-four ellipsoids would be required). There may also be several independent systems of ellipsoids involved, each system separately fulfilling the requirements of crystal symmetry. It is because of the possibility of such a multiplicity of ellipsoids that the summation sign is required in equation (1), though in practice often only a single term, or occasionally two, are important, owing to the dominating influence of the exponential term with the highest value of β. It should be noticed that although E_0 has to be the same for all the ellipsoids obtainable from each other by symmetry operations, it need not be the same for any independent system of ellipsoids, since it is measured from the bottom of the relevant zone (or for 'holes', from the top of the relevant zone).

It must now be pointed out that equation (1) is a valid approximation only when $E_0\gg kT\gg\beta H/2\pi^2$. If the latter half of the inequality is not satisfied (which as we shall see does sometimes happen in our experimental conditions), the product of the exponential and the sine in (1) must be replaced by the more general expression

$$\sum_{p=1}^{\infty}\frac{\sin\left(\dfrac{2\pi pE_0}{\beta H}-\dfrac{\pi}{4}\right)(-1)^{p+1}}{2p^{\frac{1}{2}}\sinh\dfrac{2\pi^2kT}{\beta H}}. \tag{5}$$

Arising out of Dingle's recent theoretical work (1952 *a*, *b*)* three further modifications of equation (1) have to be considered:

(1) Landau's original theory took no account of electron spin; this was considered by Akhieser (1939), but only for free electrons. Dingle (1952 *a*) and also Sondheimer & Wilson

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* In the earlier version of this work (Dingle & Shoenberg 1950) it was suggested that if E_0 rather than n (the number or free electrons per atom contributing to the effect) were regarded as constant the formulae became substantially modified. It has since been proved that this conclusion was based on an erroneous argument, and that at low fields ($\beta H\ll E_0$) it does not matter whether E_0 or n is regarded as constant. I have to thank Professor L. Onsager for pointing out this error.

(1952) have shown that in general a factor $\cos(\pi p\beta_0/\beta)$ must be included in each term to take into account the modification of the energy levels due to the spin magnetism. Since for most metals showing the de Haas-van Alphen effect β proves to be several times greater than β_0 (the true double Bohr magneton), this factor does not usually differ appreciably from unity, but occasionally it is just of practical significance (e.g. in gallium).

(2) If collision broadening of the energy levels is taken into account, an extra factor $e^{-h/\tau\beta H}$ must be included in equation (1), or more generally a factor $e^{-ph/\tau\beta H}$ in each term of (5). Here τ is the collision time, and it should be emphasized that this rather simple result with τ independent of H and T is valid only on certain simplifying assumptions. It should be noticed that as far as equation (1) is concerned the influence of the extra factor in reducing the amplitude of the oscillations is exactly the same as if the temperature had been raised by an amount x, where

$$x = h/2\pi^2 k\tau. \tag{6}$$

The introduction of the extra factor $e^{-2\pi^2 kx/\beta H}$ turns out to be very useful not only in the interpretation of the present experiments but also of the earlier results on bismuth and zinc. Indeed, it was pointed out as an empirical fact in the discussion of the bismuth results (Shoenberg 1939) that the field and temperature variations of amplitude could have been made to agree much better with (1) if the temperature had been for some reason about 1° K higher than it was supposed to be.

(3) It is probable that other causes of level broadening exist, for instance the periodic electric field of the lattice, and these will also reduce the amplitude; thus the above theoretical formulae should be regarded as giving only upper limits to the amplitude, and they may not even give the form of the field variation correctly. The theory of such effects has not yet been worked out quantitatively.

We are now in a position to review briefly the information that can be obtained from suitable measurements of the de Haas-van Alphen effect. To avoid confusion the discussion will be limited at present to cases where only one term of (1) is relevant, and discussion of the more complicated behaviour when several terms are present will be postponed until the relevant experimental results have been presented.

For all the metals studied so far, the curve of magnetic anisotropy against $1/H$ has uniform periodicity, and the positions of the maxima and minima are independent of temperature. This is entirely in accord with the prediction of (1), and the period in $1/H$ gives a value of β/E_0. On the basis of the variation of period with the orientation of the field relative to the crystal axes, it is possible to consider the question of what system of ellipsoids is needed to represent the relevant parts of the Fermi surface. However, as we shall see in the detailed discussion of individual metals below, it is probable that the representation by ellipsoids is sometimes inadequate in detail, and a more general theoretical approach may be required before a full interpretation of the data is possible.

As predicted by (1), the amplitude a of the oscillations always grows as the temperature T is lowered, and if $\log a/T$ is plotted against T for given H a straight line is obtained from the slope of which β may be deduced. In this way β may be determined for various orientations, and it is possible to see whether or not it varies in proportion to β/E_0 as found from the period, i.e. whether or not E_0 has the same value for all orientations. At the highest fields and lowest temperatures $2\pi^2 kT/\beta H$ occasionally becomes small enough to make the difference between exponential and sinh (see (5) and (1)) appreciable, and the logarithmic plot ceases to be linear. As will be explained in the detailed discussion later (see p. 15) this situation can be dealt with by a process of successive approximations. Another consequence of a sufficiently small value of $2\pi^2 kT/\beta H$ is the presence of harmonic components, and we shall see that these have in fact been detected experimentally in gallium and graphite.

The next comparison with theory is as regards the field variation of the amplitude of the oscillations; it is appropriate to plot log $aH^{\frac{3}{2}}$ against $1/H$. The slope of the straight line gives $2\pi^2 k(T+x)/\beta$, and, knowing the value of β from the temperature variation, x can be deduced. The value of x may thus be found for any curve of anisotropy against $1/H$ which extends far enough, and important points of interest are to verify that it does indeed have the same value for the same orientation at different temperatures*, and also to see how it varies with orientation and impurity content. On the basis of such results the interpretation of x in terms of equation (6) may be discussed. Further evidence on the validity of the theory comes also from a study of the variation of amplitude at a given field strength with orientation and with impurity content.

The absolute value of the oscillation amplitude is in principle of interest, though in practice the information obtained from it gives, at best, only orders of magnitude. This is partly because (for reasons not completely understood) it was not experimentally a very reproducible feature, and sometimes (e.g. in tin) it differed by as much as a factor 2 between experiments in which conditions were nominally identical, and partly because the theoretically predicted value of the absolute amplitude might be expected to be sensitive to some of the simplifying assumptions of the theory. In particular, as Dingle has pointed out, the influence of the electric field of the lattice is only crudely taken into account by the device of introducing modified effective masses and a modified number of electrons. The absolute value of the amplitude can be used in two rather different ways. If (as for gallium and tin) the scheme of ellipsoids is sufficiently clearly understood and the relevant effective masses have been determined from the periods at various orientations and the temperature variation of amplitude, then it is possible to predict a theoretical value of absolute amplitude and thus, by comparison with the observed value, to obtain evidence on the validity of the theory. For most of the metals studied, however, this procedure cannot be carried through, either because a satisfactory representation of the Fermi surface in terms of ellipsoids has not been found, or because one of the effective masses is so much smaller or so much larger than the others that only a limit to its value can be set. In the latter case (which applies for graphite, antimony, bismuth and zinc) the absolute amplitude can be used to supply an estimate of the extreme effective mass by assuming the theoretical formula is correct. Since this procedure involves the square of the observed amplitude, and since neither theoretical formula is likely to be completely correct, this estimate of the extreme effective mass is useful only in indicating a probable order of magnitude.

The phase of the oscillations can in principle be studied by two methods. First, by direct extrapolation to zero $1/H$ of the linear plot of the values of $1/H$ at which maxima or minima occur against successive integers, and, secondly, from a study of the relative phases of the higher harmonic components in (5). In practice the first method works only if $E_0/\beta H$ can

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* Since the resistivity of most metals is independent of temperature at the low temperatures concerned, τ, and therefore x should also be independent of temperature.

be made small enough for its value to be determined with an uncertainty considerably less than unity, and among the new metals studied this proves to be possible only for graphite and gallium; the second method is possible only if $2\pi^2kT/\beta H$ can be made small enough for the harmonics in (5) to be of appreciable magnitude, and this again proves to be possible only for graphite and gallium. As for bismuth and zinc, it turns out that the phases do not agree well with the theoretical prediction, and it is probable that the phase, like the absolute amplitude, is sensitive to the simplifying assumptions of the theory.

Although the study of the oscillatory part of the anisotropy was the major aim of the investigation many new measurements were also made, incidentally, of the steady part. The definite theoretical value predicted by the first term of equation (1) is rather misleading, since important contributions to the steady part of the anisotropy may come from parts of the Fermi surface which contribute only a negligible oscillatory part, and are therefore ignored in the scheme of ellipsoids deduced from analysis of the oscillatory part. In fact, where a fairly complete scheme of effective masses has been worked out from the oscillations, the steady anisotropy arising from these masses according to (1) proves to be usually considerably different from that observed experimentally.

Experimental details

The first experiments, which were of a preliminary character, were carried out early in 1949 with the apparatus previously used by Mackinnon (1949) in his investigation on zinc, and in this series the de Haas-van Alphen effect was discovered in gallium, tin and graphite (Shoenberg 1949). The apparatus, however, was not very flexible in dealing with the necessary variety of conditions and, moreover, the restrictions of field up to 9500 G (which could be obtained only by overrunning the magnet) and of temperature down to about 1·5° K, imposed several limitations. A new apparatus was accordingly constructed late in 1949 which, though working on the same principle as the earlier one, was arranged for more convenient interchange of suspensions and specimens; the new apparatus was mounted in a larger electromagnet, giving fields up to 15800 G, and the arrangements for pumping the liquid helium were improved so that temperatures of about 1·05° K could be reached.

This apparatus was used for all the subsequent experiments, in the course of which nearly all the early experiments were repeated and extended; since no new principles are involved no further description of the apparatus will be given. One feature of the measuring technique used in both series of experiments should, however, be mentioned. In measuring the deflexion of the spot of light reflected from the mirror attached to the suspension it was found that in general the use of a travelling microscope was too slow, and, moreover, especially when the oscillation period in $1/H$ was short, it was difficult to keep the spot of light continuously in the field of view. The ease and speed of working was greatly improved by reading the deflexions directly on an ordinary galvanometer scale instead of with a travelling microscope, and at the same time increasing the sensitivity of the suspension so that deflexions of a few centimetres instead of a few millimetres were produced. This increase of deflexion, although speeding up the readings, introduced a rather troublesome complication. This was that the specimen twisted by approximately 1° for each 6 cm deflexion; now where the oscillation period in $1/H$ was short (as in gallium and tin) the positions of the oscillations were very sensitive to change of crystal orientation, and the small change of orientation associated with the measuring deflexion could in extreme conditions cause mechanical instability and generally complicate the interpretation of the measurements. This was at first suffered as a necessary evil, but an improvement was brought about by again reducing the sensitivity of the suspension (or the mass of the specimen) so that the deflexion did not exceed a few millimetres, and reading the deflexions with a magnifying eyepiece on a specially prepared microscopic scale marked in 0·1 mm divisions. In this way the twist of the specimen could usually be kept within manageable limits without appreciably reducing the speed of taking readings.

The return to small deflexions was beneficial also in two indirect ways. One was that it also reduced the difficulties caused by eddy current damping; in the early experiments on tin, for instance, measurements were very slow because of the persistence of the eddy currents induced by a change of field. This had the effect that the spot of light came only slowly to its final position, and it was often difficult to prevent the field from drifting slowly while waiting for the eddy currents to die down. Again, any slight wobble of the field (due to generator ripple) caused irregular deflexions which made the assessment of the final position very trying. Increasing the stiffness of the suspension and reducing the linear dimensions of the specimen produced a marked improvement in reducing this eddy-current damping. It may be mentioned too that in this respect conditions of measurement were always found to be easier at higher fields, presumably because of the increasing magneto-resistance effect. The second indirect advantage of working with the smaller deflexions obtained by reducing the specimen size was the greater homogeneity of field over the specimen. In fact the inhomogeneity of the field round the centre of the pole-piece region, although slight, was large enough to cause an appreciable reduction in the amplitude of the de Haas-van Alphen oscillations for large specimens of metals such as tin where the period was very small.

Although accurate determination of the 'zero' position of the light spot was not important, since the amplitude of the oscillations was the main point of interest, it was convenient to determine the zero roughly to avoid measuring the deflexions from too arbitrary a zero (which would have resulted in the final curves of anisotropy against $1/H$ being tilted). In this connexion a difficulty arose with metals which became superconducting at the temperature of measurement, since the small remanent field of the magnet was sufficient to exert large couples on the crystal due to its irregular shape. This difficulty was overcome by finding a 'zero' position in a field of order 1000 G—large enough to destroy superconductivity but too small to produce a serious deflexion.

The magnet was calibrated by a search coil and fluxmeter with a relative accuracy of much better than 1 % at the highest fields and an absolute accuracy of the order of 1 % at the highest fields. The sensitivities of the various suspensions were determined by timing torsional oscillations with various suitable systems of known moments of inertia attached. No great accuracy was aimed at and, indeed, it is probable that the sensitivity varied slightly according to the degree of bowing of the torsion wire. Some incidental comparisons of absolute values of the steady anisotropy of the same crystal measured with different suspensions or with the same suspension on different occasions, suggest that the overall inaccuracy arising from calibration errors and also from the magnetic properties of the empty suspension (which varied irregularly but were not usually allowed for) did not exceed 5 % (see

specimen	source and impurity	mass (mg)	method of preparation	method of determination of orientation and remarks
Ga 3	JM 3419	254	melted on quartz plate smeared with silicone oil, and when supercooled, crystallized by inoculation with small seed	X-rays confirmed that *c*-axis was along length of seed; *a*- and *b*-axes, at first identified magnetically (without knowing which was which), later identified from X-ray photos; the names of the axes are as given by Bradley (1935)
Ga 4		155		
Ga 5		142		
Sn 3	JM 2356, < 0·004 %	167	crystallized on flat plate and cut at constriction with razor from seed; for Sn 3 see figure 19	etched with conc. HCl, but for some of the alloys 5 % HNO_3 and water added; later X-rayed to check quality
Sn 8		21·0		
Sn 9		19·0		
Sn 4, 5, 7, 12, 15, 16, 17, 18, 19, 20	JM 2356, alloyed with Hg or In; for details see table 13			
G 1	Ceylon (Sir K. S. Krishnan)	5·07	flake as supplied	binary axes identified by triangular patterns; X-ray examination of specimen similar to G 1 showed poor quality; the triangular pattern of G 4 was not clearly visible, so binary axis not identified; G 4 contained more ferromagnetic impurity than G 1
G 4	Trevandrum, Travancore (British Museum 54922)	2·4	separated from large flake by razor and flattened	
Sb 1	JM 2696, < 0·1 %	7·4	chip off rod as supplied	trigonal axis of Sb 1 identified by cleavage plane; ferromagnetic impurity present, probably introduced in chipping; Sb 2 gave good reflexions without etching
Sb 2		29·2	bead slowly cooled in quartz tube in helium atmosphere	
Al 3	JM 1011, < 0·005 %	42·5	as Sb 2	etched with conc. HCl + 5 % HNO_3
Al 5		15·6		
Cd 1	HS 8961, < 0·001 %	510	crystal used by Mackinnon (1949), but dissolved down to reduce size	etched; later shown by X-rays to be a poor crystal
In 1	HS 10874, < 0·02 %	95	thin rod crystallized as Sn, but without seed	etched with conc. HCl, but poor reflexions; later, In 2 X-rayed to check orientation found to be good crystal
In 2	JM 3332	148		
Hg 1	JM 2505	1570	slow cooling of bead in quartz cup on suspension	some indications from magnetic behaviour (see p. 44)
Hg 2		1460		
Hg 3		1180		
Hg 4		208		
Tl 1	JM 2544	200	as Sb 2	etched in $H_2SO_4 + K_2Cr_2O_7$, but poor reflexions; magnetic behaviour indicated appreciably different orientation, so probably not a single crystal
Te 1	JM 3467	760	piece broken off rod as supplied	good reflexions without etching; strong ferromagnetic impurity, probably picked up in breaking
Ge 1	Bell Telephone Laboratory *n*-type, $\rho \sim 0·6$ ohm cm	503	see Teal & Little (1950); cut to size with carborundum saw	good reflexions without etching
Pb 1	HS 8334, < 0·001 %	355	prepared in 1936 by similar method to Sb 2	etched
Cu 2	JM 1554, < 0·002 %	475	as Sb 2	etched with conc. HCl + 5 % HNO_3; slight inclusion of different orientation
Ag 4	HS 8459, < 0·001 %	465	as Sb 2	etched with dilute (20 %) HNO_3
Au 1	Heraeus sponge, < 0·001 %	335	as Sb 2	etched with conc. HCl + 10 % HNO_3

Notes. JM = Johnson Matthey, HS = Hilger spectroscopic purity; the numbers refer to suppliers' reports and total impurity contents when quoted. Reports on recently supplied batches have been more cautious and do not give any definite figures, though probably the material is purer than that of older batches. When etching is mentioned the orientation was determined by the optical etch-pit method; the etching procedures were arrived at empirically and are not necessarily the best; for Pb and Cd the etchant was not recorded.

table 11). The temperatures were determined from the vapour pressure of the helium bath using the 1949 tables (van Dijk & Shoenberg 1949). Here, again, no great accuracy was aimed at, since for comparison with theory an accuracy of 0·01° K is usually quite adequate; on some occasions the arrangements for reading the lowest pressures did not work very reliably, so that errors of as much as 0·05° K were possible at the lowest temperatures.

A list of the specimens used is shown in table 1, which is largely self-explanatory; it is hoped that the brief details about preparation and examination of the crystals may be of practical value, since such 'cookery-book' information is not usually mentioned in the literature.

The crystal was stuck with Durofix cement in the desired orientation on to a small quartz plate, which was then stuck also with Durofix to the flat quartz plate which formed the lower end of the quartz rod suspension; it was in general possible to achieve any desired orientation to within 1 or 2°, though occasionally trouble was experienced from the Durofix shrinking unevenly as it set and pulling the specimen slightly out of its intended orientation. A check on the correctness of the orientation was provided by rotating the magnet and finding the positions where the torque due to the anisotropy just vanished with the specimen at any convenient temperature, e.g. room temperature; this establishes the direction of the projection of the principal axis on the plane of rotation of the magnetic field. This method of finding the direction of the projection becomes inaccurate if the torque acting on the mounting of the specimen is at all comparable to that acting on the crystal, as was indeed sometimes the case, especially with the tin crystals where the steady anisotropy was small. A more precise method is to determine at a suitable temperature the position of the magnet at which the amplitude of the de Haas-van Alphen effect vanishes, since this amplitude is not influenced by the steady magnetic properties of the mounting. The angles ψ quoted in the results were nearly always measured from a zero position determined in this way; where necessary they are corrected for the finite twist of the crystal under the influence of the torque due to the field.

RESULTS ON INDIVIDUAL METALS

Gallium

The preliminary series of measurements (Shoenberg 1949) need not be discussed, for it has since become likely that the specimen used was not in fact a single crystal. In the later series, measurements were made on Ga 4 with each of the *a*-, *b*-, and *c*-axes vertical in turn, at each of a variety of angles between the field and the relevant axis. Measurements on Ga 3 and Ga 5 were made only with the *c*-axis vertical, and established that the results were rather accurately reproducible from one specimen to another as regards the periods of the oscillations and the relative amplitudes for different values of ψ, though the absolute amplitudes were reproducible only to about 20 %. Since two series of measurements on Ga 4 also differed in absolute amplitude by 20 %, it is quite likely that the irreproducibilities arise from small errors of orientation and positioning in the magnet rather than from any differences between the crystals.

A representative selection of curves of anisotropy against $1/H$ for various directions of the field in the *ab*-, *bc*- and *ca*-planes is shown in figures 1, 2 and 3. All the main measurements on gallium were completed before the improvement mentioned on p. 8 of restricting the deflexions to a few millimetres had been introduced, and the appreciable twist of the crystal is responsible for the pronounced asymmetry of some of the curves (e.g. $\psi = 33{\cdot}5^\circ$, figure 1). In its extreme form this effect leads to mechanical instability (see, for example, $\psi = 57{\cdot}6^\circ$, figure 3) which greatly complicates the interpretation of the results. For this reason it was not possible to obtain useful results at the lowest temperatures except for ψ close to 0 or 90°, and most of the measurements at other angles were made only at 4·22° K. In order to obtain in a reasonable time the general picture of the behaviour of gallium, as illustrated by the curves shown, it was necessary to sacrifice a good deal of detail and a little accuracy. The procedure was to observe only the maximum and minimum deflexions and the fields at which they occurred; the extremes of C/H^2 of course occur at slightly different fields from those at which extremes of the deflexions (proportional to C) occur, but where the period is short and the oscillation amplitude relatively large compared with the steady mean deflexion, the difference is slight and in practice could be ignored without serious inaccuracy. In some of the curves, particularly those at lower temperatures, it was evident that there was a good deal of detail in the curves, and it is likely that some subsidiary maxima and minima and points of inflexion were overlooked. A full study of these peculiarities would, however, have been extremely tedious, and, moreover, probably of little value, since some of the peculiarities were 'instrumental' in character, being undoubtedly due to the instability effects associated with the finite twisting of the crystal. Later, a detailed study of one particular curve, in conditions such that the instrumental effect was absent, was in fact made (see p. 17).

The modulations of the envelopes of many of the curves considerably complicate the interpretation; evidently such modulations are caused by the presence of two terms in equation (1) of comparable periods and amplitudes, but a detailed analysis is made difficult by the superimposed exponential factors which are in general slightly different for the two periods. Where the modulation is not too deep (as for $\psi = 10^\circ$, figure 2, or $\psi = 57{\cdot}6^\circ$, figure 3) the mean period over several 'beats' should be the period of the term with largest amplitude, while the period of the subsidiary term should be less or greater than the dominant period according as the period at a 'waist' in the envelope is greater or less than the mean period over several beats. The difference of the reciprocals of two periods (i.e. the frequencies) is of course given by the reciprocal of the beat period (i.e. the beat frequency). In practice, the two separate periods could not always be determined unambiguously, owing to insufficient or insufficiently precise data. In a few instances the two periods are not even comparable, and their relative amplitudes change drastically as the temperature is lowered; the curves then have a complicated appearance (e.g. $\psi = 8{\cdot}8^\circ$, figure 1, or $\psi = 9{\cdot}5^\circ$, figure 3), and a detailed separation into separate periods is not always reliable. At the lowest temperature a new short period was found for $\psi = 10^\circ$ in the bc-plane (figure 2); the step-wise nature of the curve is almost certainly due to the instability associated with large deflexions and is not fundamental. This short period was observed only late in the investigation and may be present in other orientations than the one which was studied in detail. The quantitative information about the periods is summarized in table 2 and figure 7, but it will be convenient to postpone discussion until the other features of the results have been presented.

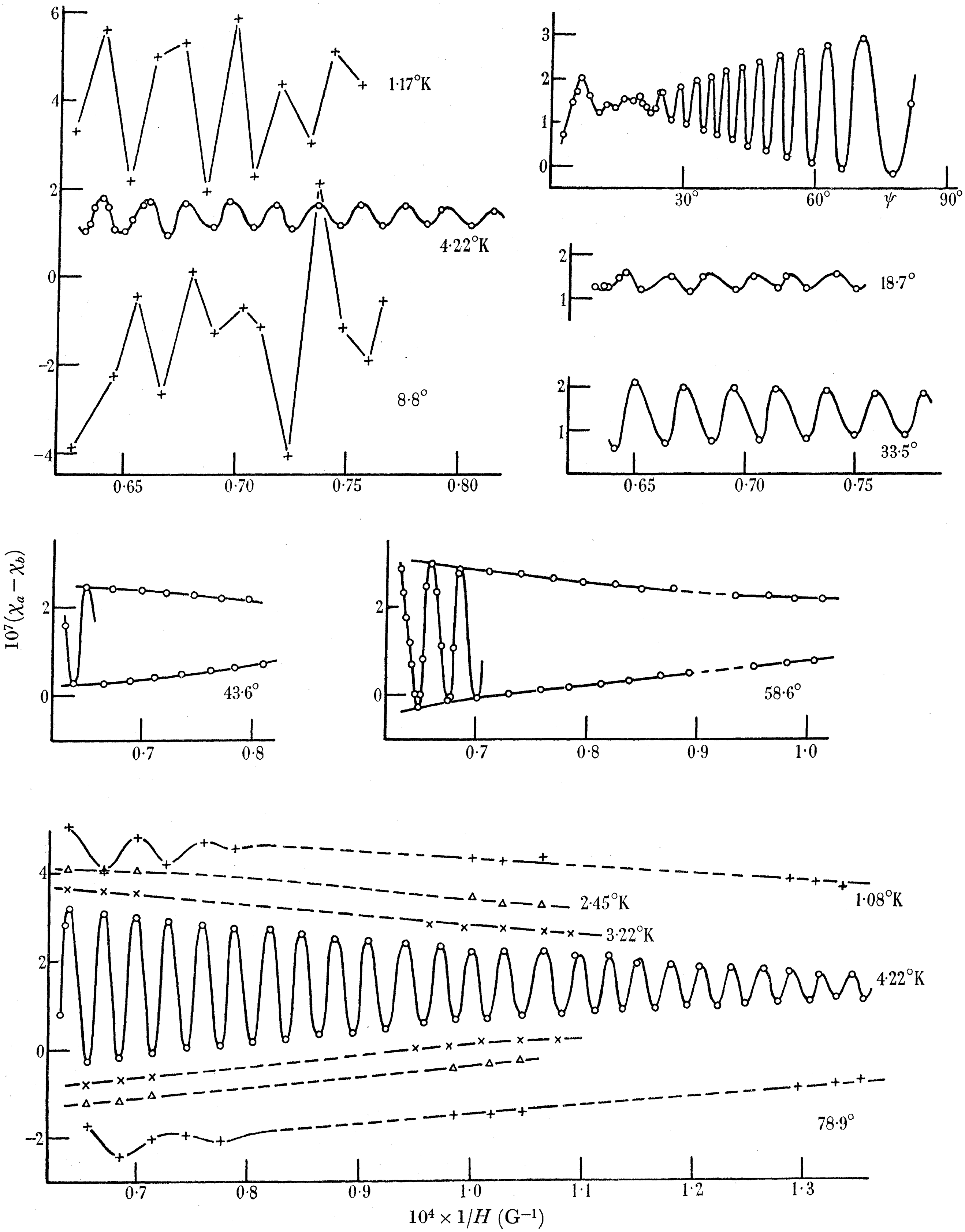

Figure 1. Ga 4, *ab*-plane: variation of anisotropy with $1/H$ at various ψ and (top right) for Ga 5 with ψ at $1/H = 0{\cdot}65\times10^{-4}$; ψ is the angle between the field and the *a*-axis and is indicated for each curve. The temperature is 4·22° K, except where otherwise indicated, and the experimental points are usually maxima and minima. To avoid confusing the diagram only the envelopes are shown for many of the curves.

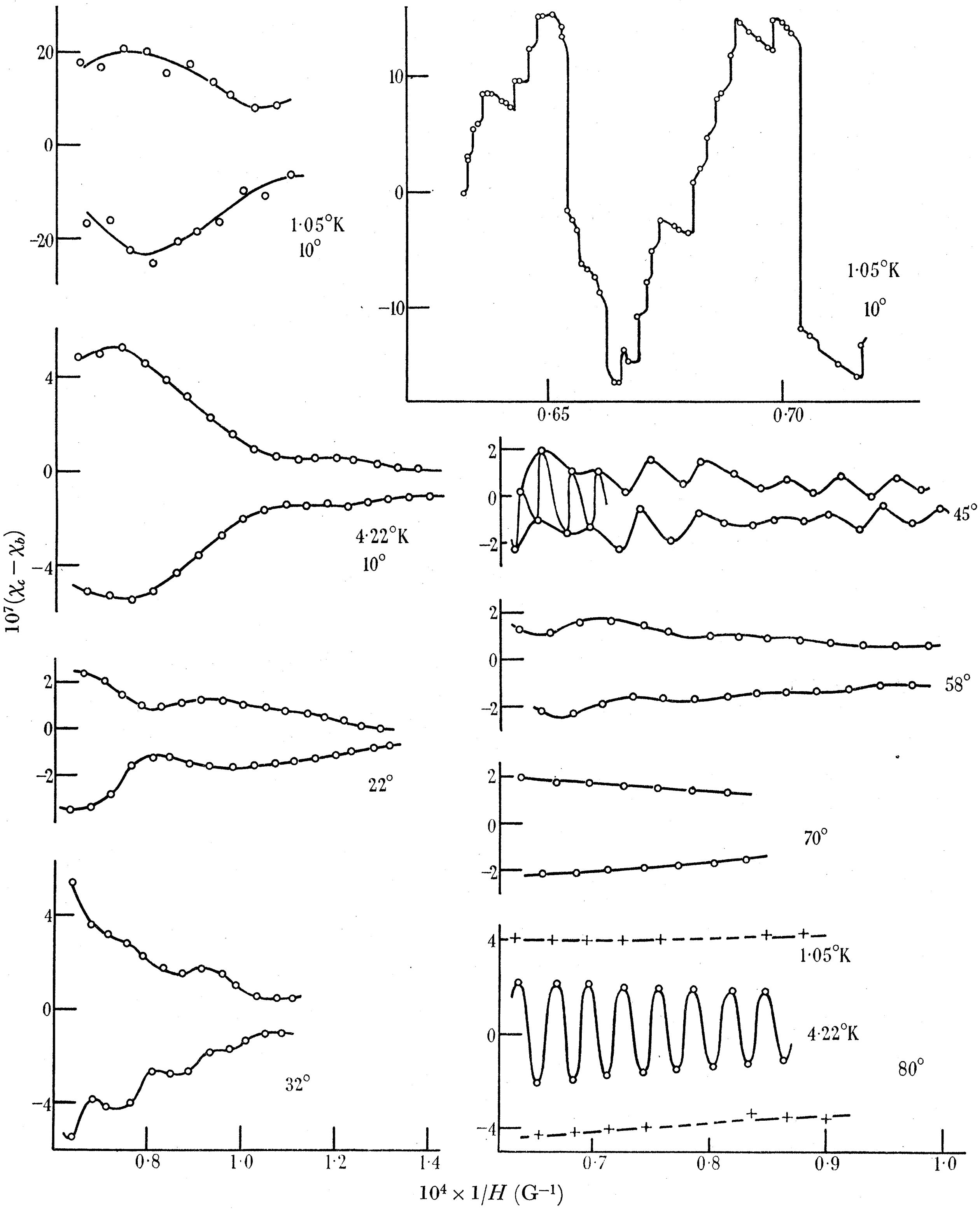

FIGURE 2. Ga 4, *bc*-plane: variation of anisotropy with $1/H$ at various angles ψ between the field and the *c*-axis; the value of ψ is indicated for each curve. The temperature is 4·22° K, except where otherwise indicated, and the experimental points are usually maxima and minima. To avoid confusing the diagram only the envelopes are shown for many of the curves. The right-hand diagram for $\psi = 10°$, 1·05° K shows a detailed survey of two cycles; the finite twist of the crystal caused considerable instability so that the maximum and minimum heights were not very reproducible; the experimental points have been joined up rather schematically bearing in mind discontinuities noted at the time.

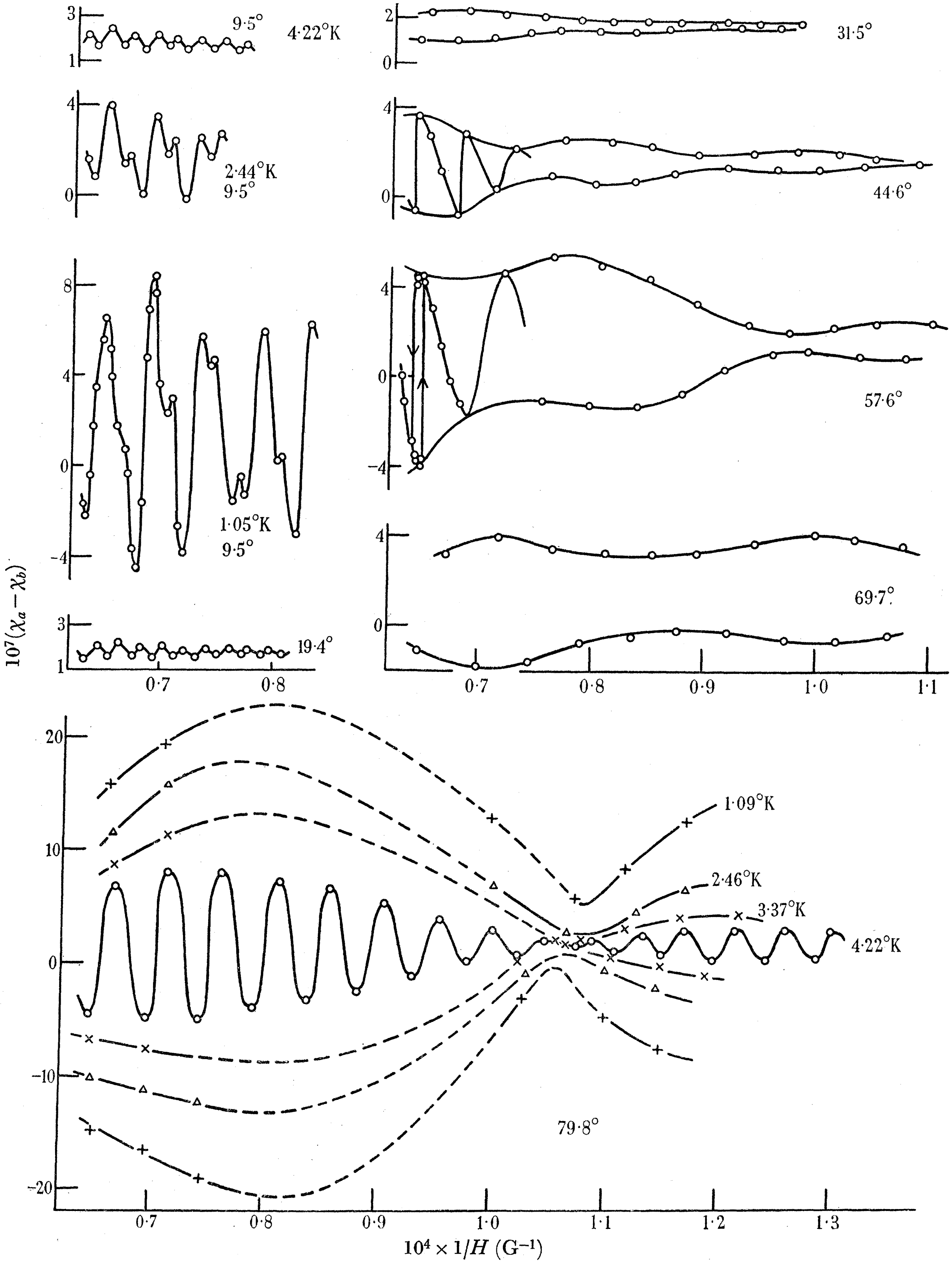

FIGURE 3. Ga 4, *ac*-plane: variation of anisotropy with $1/H$ at various angles ψ between the field and the *a*-axis; the value of ψ is indicated for each curve. The temperature is 4·22° K, except where otherwise indicated, and the experimental points are usually maxima and minima. To avoid confusing the diagram only the envelopes are shown for many of the curves.

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The determination of β from the temperature variation of amplitude is also complicated by the modulations. In principle, the two amplitudes could be separately determined from a study of the depth of the modulations, but because of the exponential factors this could in general be done reliably only if a run of several beats were available, and in practice the data were usually insufficient. Since, however, one of the terms is often fairly dominant, it is probably not too inaccurate a procedure to assume that the temperature variation of some particular feature of the curve is governed entirely by the exponential of the dominant term. For instance, in the curves for $\psi = 9{\cdot}5°$, ac-plane (figure 3), the distance from minimum to maximum at $1/H = 0{\cdot}685 \times 10^{-4}\,\mathrm{G}^{-1}$ is for the lower temperatures determined mainly by the long-period oscillation, and it is only at the two higher temperatures that the shorter period begins to have a dominant influence; this is reflected in the plot of $\log a/T$ against T, which becomes less steep at the higher temperatures. By considering only the two low-temperature points an estimate of β for the long-period term is obtained.

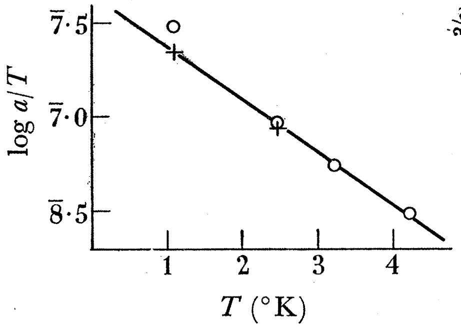

FIGURE 4

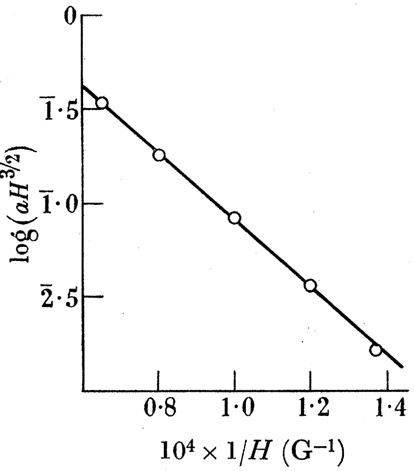

FIGURE 5

FIGURE 4. Variation of $\log_{10} a/T$ with temperature T, for Ga 4, ab-plane, $\psi = 78{\cdot}9°$, $1/H = 0{\cdot}80 \times 10^{-4}$. ○, as observed; +, corrected to allow for difference between exponential and sinh.

FIGURE 5. Variation of $\log_{10}(aH^{\frac{3}{2}})$ with $1/H$ for Ga 4, ab-plane, $\psi = 78{\cdot}9°$ at 4·22° K.

In the analysis of the curves of $\psi = 78{\cdot}9$, ab-plane (figure 1), where only a single period is evident, it became apparent that the difference between the exponential in (1) and the sinh in (5) may be significant. This is illustrated by figure 4, where $\log a/T$ is plotted against T for $1/H = 0{\cdot}8 \times 10^{-4}$, and it can be seen that the point at 1·08° K lies well above the straight line indicated by the other three points. From the slope of the straight line it follows that $2\pi^2kT/\beta H$ for $T = 1{\cdot}08°$ K is about 0·7, and therefore that the ratio of $1/2\sinh 2\pi^2kT/\beta H$ to its approximate form $\mathrm{e}^{-2\pi^2kT/\beta H}$, i.e. $1/(1-\mathrm{e}^{-4\pi^2kT/\beta H})$, is 1/0·75. A better approximation may therefore be obtained by reducing the amplitude a by the factor $(1-\mathrm{e}^{-4\pi^2kT/\beta H})$ (which here is 0·75) before taking logarithms. It can be seen that this 'correction' brings the low-temperature point much closer to the straight line, while affecting the next point only very slightly. This correction for the difference between formulae (5) and (1) proved relevant in nearly all the orientations for which temperature variation of a was studied, and the final estimates of β are collected in table 2. It can be seen by comparison with the appropriate values of β/E_0 deduced from the periods, that several values of E_0 are involved, though the accuracy is not sufficient to decide whether or not those values which are approximately equal are really identical.

TABLE 2. SUMMARY OF DATA ON GALLIUM

ψ	(β/E_0) $\times 10^7$	beat period $\times 10^7$	β $\times 10^{20}$	E_0 $\times 10^{14}$	x (°K)	a $\times 10^8$	$a_{\text{theor.}}$ $\times 10^8$
Ga 4 *ab*-plane, 8 February 1950 (ψ from *a*)							
8·8	19·8, 11·9	27·0	20·1, ~9·7	10·2, ~8·2		4·0	
18·7	19·2, 11·3					1·9	
33·5	21·8					7·2	
43·6	24·6					11·3	
58·6	27·3				0·5	14·4	16·7
68·8	28·9						
78·6	29·8					19·1	
Ga 4 *ab*-plane, 15 Februry 1950 (specimen remounted)							
8·6	20·1, 11·5	27·4	13·1	11·4		3·4	
18·5	20·0					1·6	
26·6	20·7				1·3	4·0	5·7
43·7	24·6					10·2	
57·0	27·3					14·4	
78·9	29·8		33·8	11·3	0·8, 1·1	17·4	(17·4)
Ga 5 *ab*-plane, 17 February 1950							
8·5	19·9					3·3	
37·5	23·1				1·3	6·8	7·9
49·5	25·9				1·0	10·8	10·8
79·0	30·2					16·0	
Ga 3 *ab*-plane, 24 February 1950							
~0·5	42·0, 11	200					
8·0	20·0, 11·3	27·5				4·6	
78·3	30·2					19·1	
Ga 4 *ac*-plane, 10 February 1950 (ψ from *a*)							
9·5	20·3, 46·6		12·2	2·6		3·5	
19·4	19·1					2·6	
31·5	32·3, 29·2 or 36·2	300				6·4	
44·6	40·7, 32·8	170				20, 6	
57·6	43·2, 50·2	270				37, 9	
69·7	45·7, 54·6	280				34, 5	
79·8	45·3, 49·8	500	27·5	6·1		37, 37	
84·8	51·3, 47·4	600				53, 53	
Ga 4 *bc*-plane, 22 February 1950 (ψ from *c*)							
10	45·3, 50·2, 2·7	460	26·1	5·8	0·8	49, 13	
22	42·3, 52·3	400				21, 8	
32	39·6, 55	140				47, 6	
45	22·8, 42 or 15·7	50				14, 9	
58	26·8, 34·5 or 21·9	120				22, 4	
70	29·2					20·4	
80	30·2		31·6	10·5	0·1, 0·8	20·4	

Notes. The first figure under β/E_0 is the dominant period, usually as measured at 4·2° K, and the accuracy is usually better than 2 %; the second, either a subsidiary period deduced from the beats or a new period appearing at low temperatures. Where two entries appear in the x column, the first is for 4·22° K and the second for a low temperature. a is the amplitude of the dominant frequency at 4·22° K and $1/H = 0{\cdot}65 \times 10^{-4}$; when beats occur this estimate is very rough, and the second figure is an even rougher estimate of the amplitude of the subsidiary frequency. The entries under $a_{\text{theor.}}$ are calculated, assuming a for $\psi = 78{\cdot}9°$ to be $17{\cdot}4 \times 10^{-8}$, using the appropriate value of x, and assuming E_0 is the same for all the curves concerned, i.e. β proportional to period.

Only a few of the curves are either simple enough or extend far enough to make any analysis of the field variation of amplitude reliable. The most extensive and simplest curve is that for $\psi = 78{\cdot}9^\circ$ in the *ab*-plane at $4{\cdot}22^\circ$ K (figure 1), and the analysis of its field variation is illustrated in figure 5, where $\log aH^{\frac{3}{2}}$ is plotted against $1/H$ (no correction for the difference between (5) and (1) is necessary because of the relatively high temperature). It can be seen that the points lie fairly well on a straight line, but this must not be regarded as proving that the index of the power of H in (1) is really $\frac{3}{2}$, since the form of the plot is insensitive to the exact value of the index. From the slope of the plot a value of $2\pi^2k(T+x)/\beta$ is obtained, and comparison with the slope $2\pi^2k/\beta H$ of the appropriate logarithmic plot of temperature variation gives x as $0{\cdot}80^\circ$ K. A similar analysis for the envelope at $1{\cdot}08^\circ$ K, this time making the appropriate correction for the difference between (5) and (1), and ignoring the high-field region where the points fluctuate, gives $x = 1{\cdot}07^\circ$ K. Since x appears as the difference of two not very different quantities the accuracy of determination is not high, and these two estimates of x may be regarded as reasonably consistent. The values of x found from the various curves which could be usefully analyzed are collected in table 2.

It is now possible to discuss the relative amplitudes for a given field and temperature at the different orientations for which x has been determined. If the theory is taken literally, the product $a\beta^{\frac{3}{2}}/\mathrm{e}^{2\pi^2k(T+x)}$ should not vary as the orientation (and hence also β and x) varies, provided the same ellipsoid is concerned; thus theoretical values of a can be calculated at different orientations based on the value of a at one particular orientation. This has been done for some of the curves for ψ between $26{\cdot}6$ and $78{\cdot}9^\circ$ in the *ab*-plane, and as can be seen from table 2, the theoretically predicted amplitudes fall less rapidly than the observed ones as ψ is reduced from $78{\cdot}9^\circ$ (where the theoretical value has been adjusted to agree with observation). However, as mentioned in the introduction, it is probably just in such matters as comparison of amplitudes that the theory is least likely to be adequate.

When $2\pi^2kT/\beta H$ is sufficiently small, formula (5) differs appreciably from (1) not only in predicting modified amplitudes, but also in predicting the presence of harmonic components. As can be seen from (5) the predicted ratio r_p of the amplitude of the pth harmonic to that of the fundamental is given by

$$r_p = \frac{1}{p^{\frac{1}{2}}}\frac{\cos \pi p\beta_0/\beta}{\cos \pi\beta_0/\beta}\frac{\sinh 2\pi^2kT/\beta H}{\sinh 2\pi^2pkT/\beta H}\exp\left[-\frac{2\pi^2(p-1)\,kx}{\beta H}\right], \tag{7}$$

if the Landau formula is modified to take account of electron spin (see p. 4) and collision broadening. Detailed measurement of a single cycle for $\psi = 78{\cdot}9^\circ$ in the *ab*-plane at $1{\cdot}08^\circ$ K did in fact suggest the presence of harmonics, but since the envelope curve showed beats in this region (figure 1) and the finite twist of the crystal could have also contributed a second harmonic of strength comparable to that observed, it was decided to repeat the measurements under more favourable conditions before making any analysis. The repetition was made with Ga 5, using a stiffer suspension and at $\psi = 84{\cdot}3^\circ$ in the *ab*-plane, where the beats were much less pronounced; under these conditions the instrumental effect could be shown to be very small. Measurements were made at several temperatures and some of the curves are shown in figure 6 and summarized in table 3, in which the values of r_2, r_3 and r_4 found by Fourier analysis of the experimental curves are compared with the values predicted by (7); the relative phases of the harmonic components will be considered later (see p. 21). The facts that the third and fourth harmonic amplitudes are appreciably different in the two cycles analyzed at the low temperatures, and that they occur at all with appreciable amplitudes at 4·22° K, may be ascribed partly to the residual influence of the beats, and partly

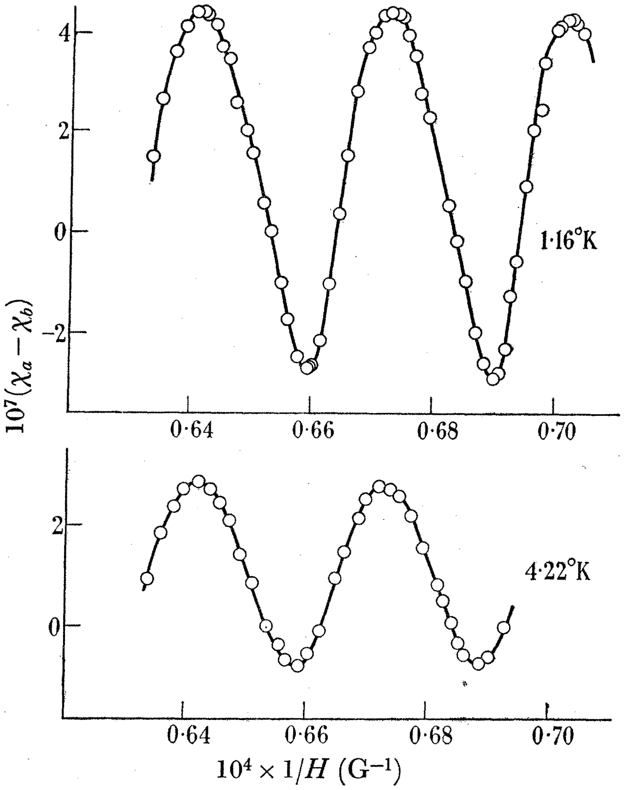

FIGURE 6. Ga 5: detailed plot of variation of anisotropy with $1/H$ for *ab*-plane, $\psi = 84{\cdot}3°$ at 4·22° K and 1·16° K.

TABLE 3. STRENGTHS AND PHASES OF HARMONIC COMPONENTS

	phases in degrees											
	$\phi_1 = 45°$			$\phi_1 = 90°$			observed			theoretical		
T (°K)	ϕ_2	ϕ_3	ϕ_4	ϕ_2	ϕ_3	ϕ_4	r_2	r_3	r_4	r_2	r_3	r_4
1·16:												
1st cycle	55	25	103	145	160	−77	0·19	0·05	0·019	0·21	0·06	0·017
2nd cycle	48	35	73	138	170	−107	0·20	0·08	0·024			
1·29:												
1st cycle	52	35	222	142	170	42	0·17	0·05	0·012	0·20	0·05	0·015
2nd cycle	49	53	99	139	188	−81	0·19	0·08	0·005			
4·22	40	60	2	130	195	182	0·07	0·025	0·017	0·058	0·004	2×10^{-4}

Notes. The entries under 'theoretical' are the values of r calculated for $1/H = 0{\cdot}65\times10^{-4}$ from (7). The values of x required in the calculation were determined specially in the same experiment and found to be $x = 0{\cdot}50°$ K at 4·22° K and $x = 0{\cdot}62°$ K at 1·29° K; the 1·29° K value was used at 1·16° K. The values of the factor $\cos(\pi p\beta_0/\beta)/\cos(\pi\beta_0/\beta)$ were 0·96, 0·88 and 0·78 for $p=2, 3, 4$ respectively. In analyzing the experimental curves a small correction was applied to take account of the instrumental effect (finite twist of crystal); this hardly affected the values of r but changed ϕ_2 by a few degrees.

to inaccuracies of measurement; bearing this in mind the agreement with theory can be considered as satisfactory. It should be noticed that in the various logarithmic plots discussed earlier the possible presence of harmonics was ignored; this is in fact fairly justified, since even with $r = 0{\cdot}2$, the peak to peak amplitude of the experimental curve differs by only a few per cent from that of the fundamental, and the difference of the logarithms is very small. It is, however, possible that some slight residual departures from linear plots may be due to this neglect.

We may now consider the question of the representation of the Fermi surface by ellipsoids. The simplest assumption consistent with the orthorhombic symmetry of gallium is a single ellipsoid with α_{11}, α_{22} and α_{33} all different and the other α's all zero; the theoretical formulae can then be defined more precisely as follows. If the c-axis is vertical, the symbols in equation (1) become

$$\left.\begin{aligned} \beta &= e\hbar(m_1\cos^2\psi + m_2\sin^2\psi)^{\frac{1}{2}}/c(m_1m_2m_3)^{\frac{1}{2}}, \\ \Delta m &= m_1 - m_2 \quad \text{(to give } \chi_a - \chi_b \text{ in equation (1))}, \\ m' &= (m_1m_2m_3)^{\frac{1}{3}}, \end{aligned}\right\} \tag{8}$$

where

$$m_1 = m_0/\alpha_{11}, \quad m_2 = m_0/\alpha_{22}, \quad m_3 = m_0/\alpha_{33}. \tag{9}$$

For the a- or b-axis vertical the suffixes must be commuted in an obvious way.

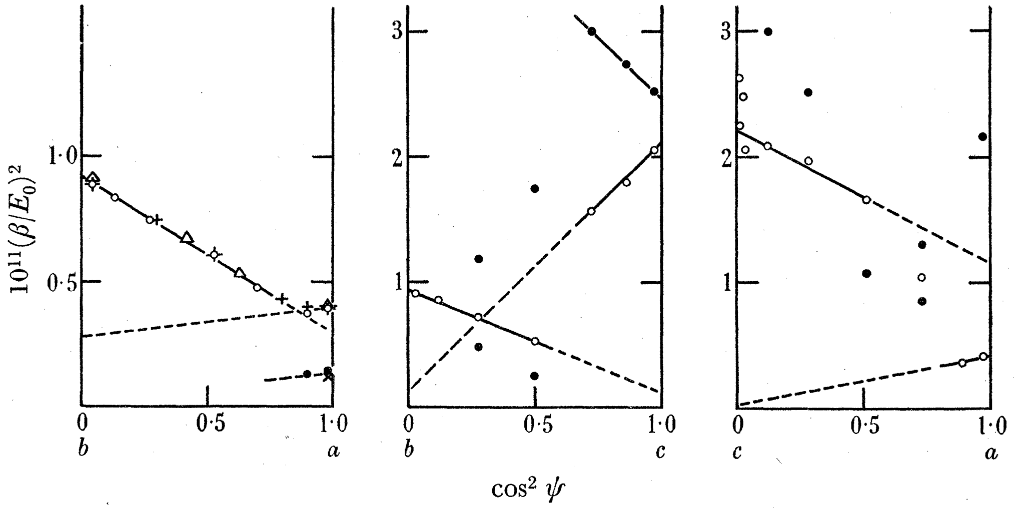

FIGURE 7. Gallium: variation of square of period $(\beta/E_0)^2$ with $\cos^2\psi$. The various points in the left-hand diagram have the following meanings: ○, Ga 4, 8 February 1950; ●, Ga 4, 8 February 1950, subsidiary periods; +, Ga 4, 15 February 1950; ×, Ga 4, 15 February 1950, subsidiary period; △, Ga 5. In the other diagrams ○ means a main period and ● a subsidiary one; where two subsidiary periods are shown these are alternatives; for the two orientations nearest the c-axis in the right-hand diagram it was not clear which was the main period and which the subsidiary, so both are marked with open circles.

It is evident from the multiplicity of periods that such a single ellipsoid is too simple a representation, but before going further it is useful to compare the variation of period (i.e. of β/E_0) with ψ, with the prediction of (8). The appropriate procedure is to plot $(\beta/E_0)^2$ against $\cos^2\psi$, as has been done in figure 7, where it can be seen that in the ab-plane at least, a straight line is indeed obtained over a fair range of ψ. In the other two planes also, many of the experimental points can be connected by straight lines within the experimental accuracy, as indicated, though the points referring to the subsidiary components which cause the beats do not seem to fall on a linear plot. Departure from a linear plot suggests non-vanishing cross-terms in the ellipsoid representation, and crystal symmetry would then automatically require the ellipsoids to be in pairs, leading to pairs of values of β of the type

$$\beta \propto (m_1 \cos^2 \psi + m_2 \sin^2 \psi \pm m_6 \cos \psi \sin \psi)^{\frac{1}{2}}.$$

No scheme of this kind, however, can fit the facts in detail, since it would involve two periods which become exactly equal for $\psi = 0$ or $\frac{1}{2}\pi$, while extrapolation suggests that the two periods for the field nearly along the *c*-axis will not in fact become equal for the field exactly along the *c*-axis. It should be noticed too that the experimentally determined value of E_0 for the field along the *c*-axis and for the field along the *a*- or *b*-axes are quite different (see table 2), so it is probable that the ellipsoids involved are unrelated by symmetry. The departure of the points from the main straight line of figure 5 as the field turns nearly into the *a*-axis is greater than can be ascribed to experimental error, and even though the E_0 values close to the *a*- and *b*-axes are approximately equal, here too it is probable that independent ellipsoids are involved. It is worth pointing out that the variation of amplitude with ψ serves as a useful guide in relating particular periods to particular ellipsoids. Thus in the *ab*-plane it is plausible to suppose that as ψ passes through the range of 20 to 30° the effects of one ellipsoid fade out and the effects of the other take over. The whole situation is further complicated by the various new periods which show up only at the lowest temperatures, and it is evident that considerable effort, with measurements at much closer intervals of ψ, will be necessary before anything like a full description will be possible.

Although in view of these difficulties any detailed discussion of the absolute values of the amplitudes (see table 2) would be unprofitable, it is of interest to consider how big the amplitude should be for the field close to the *b*-axis if only the single ellipsoid relevant in this region is taken into account. From the periods, if we extrapolate as in figure 7, we have that the mass ratios are $m_1 : m_2 : m_3 = 3{\cdot}75 : 11{\cdot}6 : 1$, and from the absolute value of β extrapolated to the *b*-axis ($3{\cdot}4 \times 10^{-19}$) we obtain $(m_1 m_3)^{\frac{1}{2}}/m_0$ as $0{\cdot}054$, where m_0 is the ordinary electron mass; we thus find

$$m_1/m_0 = 0{\cdot}104, \quad m_2/m_0 = 0{\cdot}32 \quad \text{and} \quad m_3/m_0 = 0{\cdot}028.$$

Knowing the value of x, all the data are available for calculating the amplitude according to the theoretical formula, and it turns out that for $\psi = 78{\cdot}9°$ in the *ab*-plane, $T = 4{\cdot}22°\,\mathrm{K}$ and $1/H = 0{\cdot}65 \times 10^{-4}$, the amplitude should be 7×10^{-8}. The fact that the experimental value, 17×10^{-8}, is higher than that predicted theoretically is puzzling, since, as was mentioned on p. 5, if the theoretical formula has to be modified to take proper account of the disturbing influence of the lattice this modification would probably reduce rather than increase the theoretically predicted values. It is, however, not impossible that the discrepancy between the observed and predicted amplitudes is due to an over-simplified description of the Fermi surface rather than any failing of the theoretical formula.

A similar analysis can also be made for the ellipsoid mainly responsible for the de Haas-van Alphen effect near the *c*-axis. If the subsidiary periods are ignored, we find (though the extrapolations here are less reliable than for the *b*-axis) $m_1 : m_2 : m_3 = 0{\cdot}52 : 0{\cdot}055 : 1$, and from the absolute value of β along the *c*-axis, we have $(m_1 m_2)^{\frac{1}{2}}/m_0 = 0{\cdot}067$, so that

$$m_1/m_0 = 0{\cdot}2, \quad m_2/m_0 = 0{\cdot}02 \quad \text{and} \quad m_3/m_0 = 0{\cdot}4.$$

We then find that the theoretically predicted amplitude for $\psi = 10°$ in the bc-plane at $T = 4{\cdot}22°$ K and $1/H = 0{\cdot}65\times10^{-4}$ is 4×10^{-8}, while the observed value is about 50×10^{-8}. Thus the discrepancy is in the same sense as near the b-axis. For the a-axis the data is insufficient to provide more than rough upper limits of the effective masses; figure 7 suggests (but only very roughly) that $m_2/m_1 = 0{\cdot}7$ and $m_3/m_1 < 0{\cdot}25$; the appropriate value of β (also rough) gives $(m_2m_3)^{\frac{1}{2}}/m_0 = 0{\cdot}09$, and we find

$$m_1/m_0 > 0{\cdot}2, \quad m_2/m_0 > 0{\cdot}15 \quad \text{and} \quad m_3/m_0 < 0{\cdot}05.$$

This information is too rough to make any calculation of amplitude worth while, especially since x could not be reliably determined because of the various frequencies present.

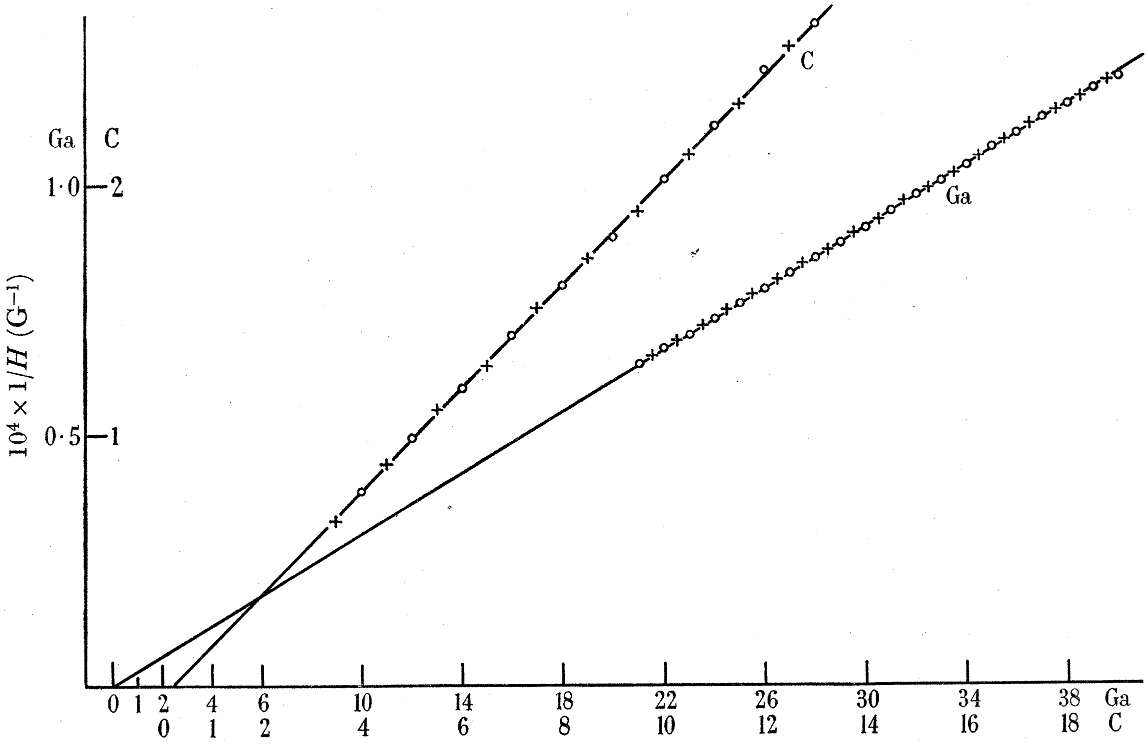

FIGURE 8. Plot of values of $1/H$ for maxima (○) and minima (+) of oscillations in gallium and graphite against successive half-integers (even multiples for the maxima); thus each integer on the scale of abscissae represents 2π in phase.

We shall now conclude our discussion of the gallium results by considering the phase of the oscillations; this can be done with confidence only for curves which show no marked beats, i.e. only for curves in which the field is directed nearly along the b-axis. The curve of anisotropy against $1/H$ for $\psi = 84{\cdot}3°$ in the ab-plane can be described by the expression

$$\frac{I_1}{H_1}-\frac{I_2}{H_2} = a\{r_0-\sin(\theta-\phi_1)+r_2\sin(2\theta-\phi_2)-r_3\sin(3\theta-\phi_3)+r_4\sin(4\theta-\phi_4)\}, \qquad (10)$$

where θ stands for $2\pi E_0/\beta H$ and the r's are the ratios introduced on p. 17. According to the theory a should be proportional to m_2-m_1 and therefore positive, and all the ϕ's should be equal to 45°. In the harmonic analysis of the curves of figure 6 the precise origin of θ is unknown, so only relative values of the phases can be estimated, i.e. the values of ϕ_2, ϕ_3 and

ϕ_4 depend on the choice of a value for ϕ_1. In table 3 the values of the ϕ's derived from harmonic analysis of the various curves and based on the alternative assumptions $\phi_1 = 45$ and 90° are shown (the latter is indicated by the considerations discussed below). It can be seen that the values of ϕ_4 show little consistency and so cannot be regarded with any confidence; the values of ϕ_2 and ϕ_3 are reasonably consistent and point in favour of the assumption $\phi_1 = 45°$.

An independent estimate of the phase can be made by attempting to fix the origin of θ precisely. The positions of the maxima and minima of a curve at 4·22° K, such as that for $\psi = 78{\cdot}9°$ in figure 1, depend almost entirely on the fundamental term in (10), and as can be seen from figure 8 a plot of the values of $1/H$ at which the maxima and minima occur against successive half-integers (even multiples for maxima) gives a good straight line (the slight departure beyond $1/H = 1{\cdot}1 \times 10^{-4}$ can be ascribed to slight calibration errors). The intercept of this straight line on the axis of abscissae (i.e. $\frac{1}{4} - \phi_1/2\pi$) comes at 0·0 which would imply $\phi_1 = 90°$, but the extrapolation is considerable, and an error of 45°, partly from random and partly from systematic causes, cannot be regarded as impossible; it may be mentioned, however, that analysis of the less extended data for Ga 5 at $\psi = 84{\cdot}3°$ (from the experiment in which the harmonics were studied) also points to $\phi_1 = 90°$. If ϕ_1 were really 90° the values of ϕ_2 and ϕ_3 would become quite different from each other and from ϕ_1 (see table 3), which would be entirely contradictory to the theory, but since the determination of ϕ_1 is not very precise, and since it is also possible that the harmonic analysis on which the other ϕ's are based is falsified by the residual effects of beats, the evidence against the theory is not conclusive.

Tin

The de Haas-van Alphen effect in tin was discovered in the preliminary series of measurements in May 1949 (Shoenberg 1949), but since these early measurements have been entirely superseded by the more systematic and accurate experiments with the new apparatus they will not be discussed further. Most of the measurements were made with the crystal suspended with its tetragonal axis horizontal and a binary axis* vertical, but one series was made also with a binary axis set 45° off vertical and in another series the tetragonal axis was vertical. Some representative curves illustrating the salient features of the results are shown in figure 9.

The most striking novelties in tin as compared with the metals previously studied are the very short period of the oscillations, which accentuates some of the experimental difficulties met with in gallium, and the peculiar modulation of the oscillations. A good deal of time was spent investigating the nature of this modulation, but no satisfactory interpretation has been found. The two features of the modulation which are difficult to understand are (*a*) the alternating cusp-shaped and flat maxima and minima and (*b*) the fact that the envelope of the minima is displaced from the mirror image of the envelope of the maxima by half a period of the modulating cycle. At first it was thought that these features might be associated with the finite twist of the crystal, which effectively makes ψ slightly different for the maxima and the minima of the oscillations. This difference, however, is least for the smallest values of ψ, and since it is just then that the features (*a*) and (*b*) are most clearly pronounced, and, moreover, since the features were just as pronounced in two specimens with

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* The binary axis referred to here is the one along which the spacing is 5·82 Å.

deflexions (i.e. twists of the crystal) differing by a factor of about 3, it is unlikely that they are associated with the finite twist of the crystal. It should be noticed that although the depth of the modulations varies considerably as between specimens (cf. curves for Sn 8 and Sn 9) the periods of the modulations for several specimens are rather accurately reproducible, confirming that the modulations have some fundamental origin rather than one associated with an instrumental feature or with slight errors in angles. If it were not for the shape of the modulations, a simple explanation of the fact that the envelopes of the maxima and minima are not mirror images of each other would be that the modulations are caused by the presence of a periodic term with the low frequency of the modulation itself, rather than a frequency close to that of the fundamental, but the fact that the distance between the upper and the lower envelope curves itself varies periodically, and other considerations discussed below make this explanation improbable.

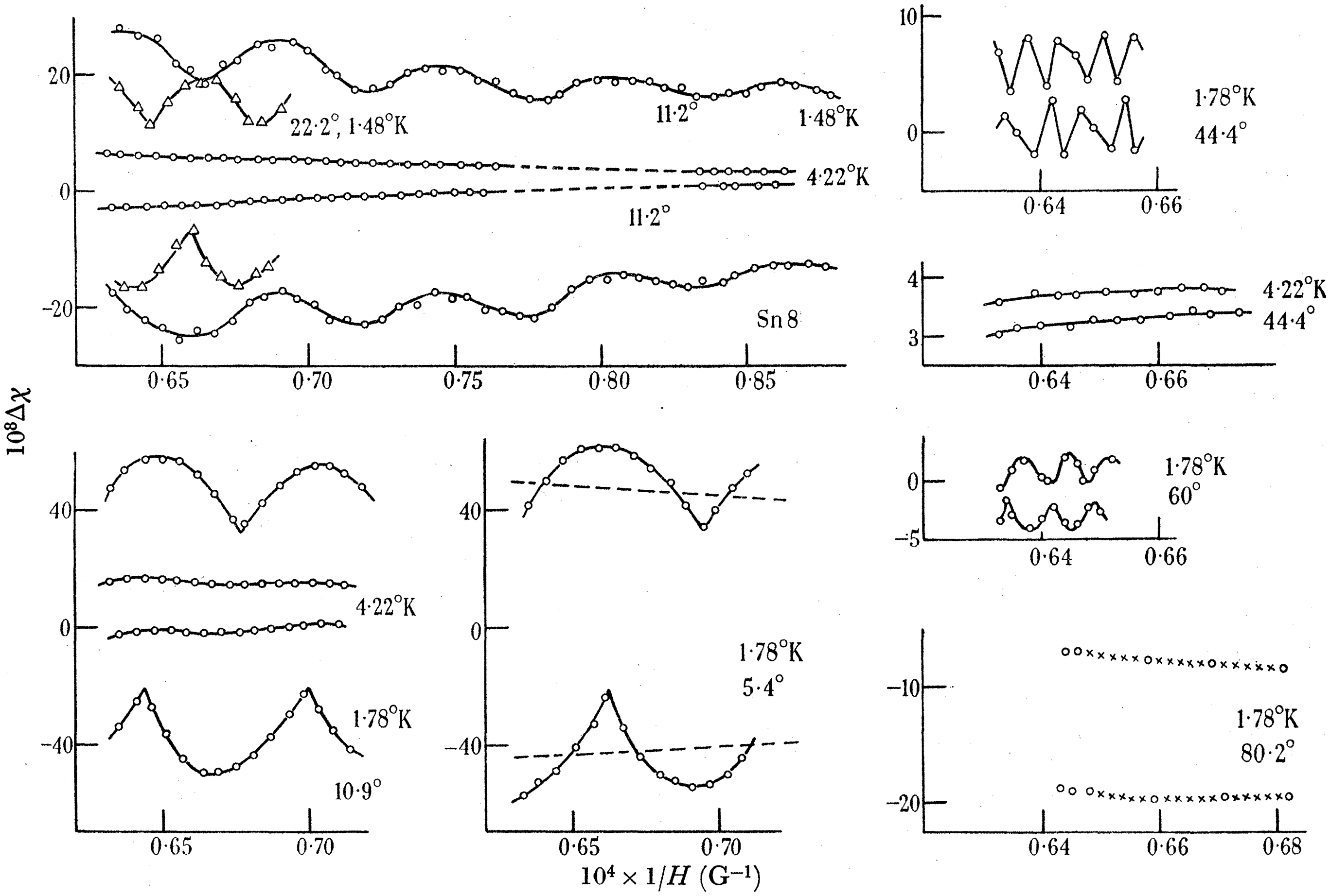

FIGURE 9. Tin: variation of anisotropy with $1/H$ at various angles ψ between the field and the tetragonal axis; the binary axis was vertical except for $\psi = 60°$, when it was at 45° to the vertical; the values of ψ and the temperature are indicated for each curve. Except for the top left-hand diagram which is for Sn 8, all the curves are for Sn 9; the points are maxima and minima of the oscillations and only the envelope curves are shown. For $\psi = 80{\cdot}2°$ only the maxima and minima indicated by ○ were actually measured, while those marked × were interpolated from a count of how many had been passed through; this procedure permitted a rapid determination of the very short period. The broken curves for $\psi = 5{\cdot}4°$ indicate schematically the method of 'smoothing' the modulations.

The variation of the fundamental period with orientation is summarized in table 4 and figure 10. Since tin is tetragonal, the simplest representation would be by a single ellipsoid with $m_1 = m_2$; this would cause the square of the period to vary as

$$m_3 \cos^2 \psi + m_1 \sin^2 \psi, \tag{11}$$

which is in satisfactory agreement with the observed behaviour for small values of ψ, if it is supposed that $m_1 \ll m_3$. The behaviour for large values of ψ is, however, more complicated, and it is clear that quite other terms than (11) are required to describe it, and, moreover, terms which will depend on the direction of the field relative to the binary as well as the tetragonal axis. This is not only because the periods for large ψ are modified when the binary axis is set 45° off vertical, but also because they are sometimes appreciably affected even by the accidental changes of a degree or so in orientation associated with a remounting of the crystal in nominally the same orientation. In order to study further the importance of the binary axis orientation, an experiment was made in which the tetragonal axis was vertical; unfortunately, the observed couples were small and became too small to measure except for the direction of the field fairly close to a binary axis. Owing to the smallness of the effects and the extreme shortness of the period, the period could be estimated only roughly and no significant results on its directional dependence were obtained. It was, however, possible to plot the variation of amplitude with angle (figure 11), and it can be seen that although the pattern has something like the required tetragonal symmetry, the heights of the various peaks are quite different at positions where the symmetry requires them to be identical. This is probably another illustration of the great sensitivity to angular errors, but may also be partly due to imperfections in the crystal.*

Attempts to analyze the dependence of the periods of the modulation on ψ did not prove fruitful. Thus, if the modulation is regarded as caused by the beating of two neighbouring frequencies, the subsidiary periods at various orientations can be estimated, but do not fit in any obvious way into the scheme of figure 10, while if it is treated as due to a periodic term with the same period as the modulation itself, the square of this period does not give a linear plot against $\cos^2 \psi$.

The temperature variation of the amplitude (ignoring the modulations by drawing a smoothed envelope as for $\psi = 5{\cdot}4°$ in figure 9) gives the values of β shown in table 4, and it is interesting to note that these values are, within experimental accuracy, proportional to the periods, so that E_0 is approximately the same throughout, even for the presumably independent ellipsoids necessary to describe the behaviour for the field nearly perpendicular to the tetragonal axis. The value of E_0 is about 31×10^{-14} erg, corresponding to a degeneracy temperature T_0 of 2250° K. It may be mentioned that the values of $2\pi^2 kT/\beta H$ were never large enough to make the difference between the exponential in (1) and the sinh in (5) important, and the corrections discussed for gallium were therefore very small here. If the depth of the modulation is treated as an independent periodic term, a value of β (which is denoted by β' in table 4) may be estimated from its temperature-dependence, and it is perhaps significant that the value of β' is within experimental error proportional to the

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* Since the crystal was not carefully centred in this experiment, and it is possible that the axis of rotation of the magnet does not pass exactly through the region of most homogeneous field, it is possible that a reduction of amplitude occurs owing to field inhomogeneity (see p. 28), and that this reduction varies with rotation of the magnet.

fundamental period, but not to the modulation period. This provides further evidence against regarding the modulations as due to an independent long-period term, and suggests rather that the modulation is associated in some direct way with the fundamental periodic term.

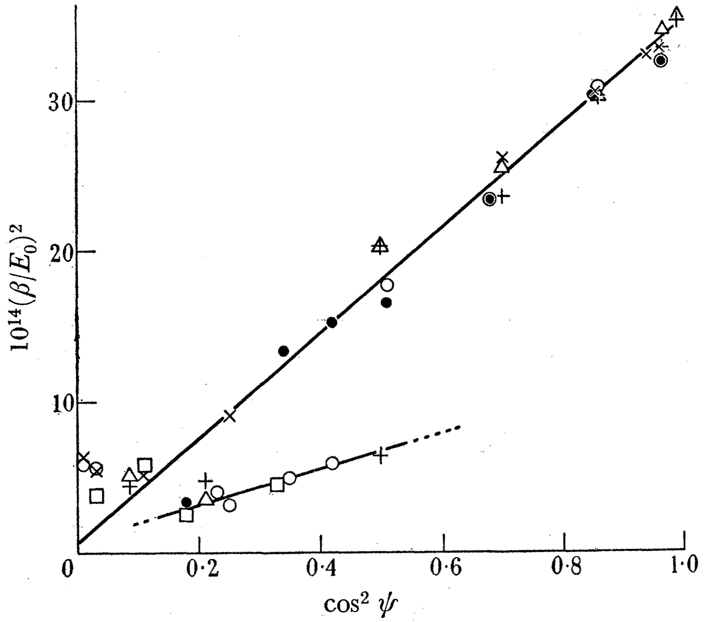

FIGURE 10. Tin: variation of square of period $(\beta/E_0)^2$ with $\cos^2\psi$. ○, Sn 9, 1 November 1950; □, Sn 9, 22 November 1950; ●, Sn 9, 3 November 1950 (binary axis at 45° to vertical); +, Sn 4; ×, Sn 8; △, Sn 3. For Sn 4 at $\psi = 45°$, two points are shown, since the dominant period changed as the temperature was lowered; except for this case no subsidiary periods are shown.

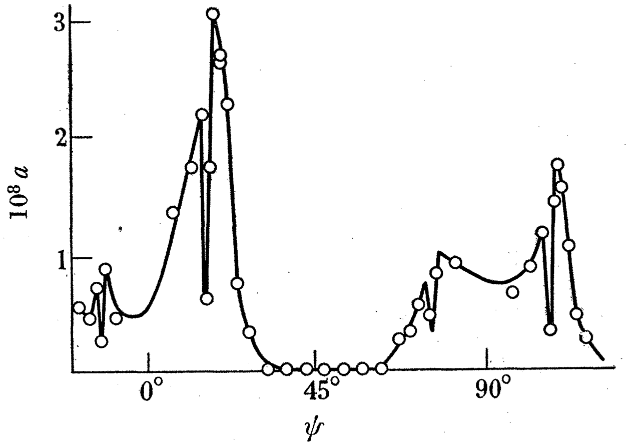

FIGURE 11. Tin: variation of amplitude (a) with the angle ψ between the field and a binary axis, in the tetragonal plane. The position at which $\psi = 0$ could not be very precisely determined.

Analysis of the field variation of amplitude led, as with gallium, to linear plots of log $aH^{\frac{3}{2}}$ against $1/H$, from which the values of x shown in table 4 were estimated; it can be seen that these values are fairly consistent both as between different temperatures and as between different specimens, though as with gallium there seems to be a tendency for the values at 4·22° K to be systematically smaller than those at a low temperature. The significance of

TABLE 4. SUMMARY OF DATA ON TIN

ψ	β/E_0 $\times 10^7$	beat period $\times 10^7$	β $\times 10^{20}$	β' $\times 10^{20}$	E_0 $\times 10^{14}$	x (°K)	a $\times 10^8$	a' $\times 10^8$
Sn 3, 28 July 1950, $T = 4{\cdot}22$°K, 1·50°K								
6	5·97	64					12·1	4·6
11	5·89	55	16·6	11·2	28·2	~0·6	2·1	0·2
						~1·6	14·2	4·2
22	5·50	44	16·3	12·1	29·7		2·0	0·2
		37					14·6	3·6
33	5·05	24					1·3	0·1
45	4·5						0·14	
63	1·88	7·8					0·7	0·2
73	2·25						0·1	
Sn 3, 16 August 1950, $T = 4{\cdot}22$°K, 1·4°K—remounted and 4 mm low in magnet								
11	5·82	51	16·7	12·5	28·7	~1·0	3·6	0·4
		52				~1·4	24·5	7·2
22	5·45	35					2·3	0·4
Sn 4, 2 August 1950, $T = 4{\cdot}22$°K, 1·50°K								
−11							4·4	
6	5·86	61					24·5	5·5
11	5·78		18·3		31·7	0·8	4·4	
						1·2	23·3	
22	5·50	38					3·1	0·2
33	4·86	22	15·2	10·9	31·3		1·4	0·2
45	4·50, 2·50*	irregular*	~12·3				0·15	
63	2·17						0·6	
73	2·12						0·5	
Sn 8, 18 October 1950, $T = 4{\cdot}22$°K, 1·48°K								
11·2	5·79		18·0	11·7	31·1	1·05	4·1	0·2
		57·7				1·03	22·9	3·5
14·2	5·74						4·0	
22·2	5·53	36					14·0	4·5
33·2	5·10	~23					5·3	1·6
60·2	~3						0·2	
70·2	~2·25						0·2	
80·2	~2·3						0·9	
85·2	~2·5						1·1	
Sn 9, 1 November 1950, $T = 4{\cdot}22$°K, 1·78°K								
2·4		>45					49	>15
5·4		64					46	15
10·9	5·71	55	18·2	12·5	31·9		9·1	0·9
		55					43	12
22·4	5·54	36·5	17·4	11·5	31·4		5·4	0·5
		36·5					28	9
34·4	4·82	22	15·8	9·4	32·8		1·7	0·1
		22·5					11·3	2·7
44·4	4·20		13·0		31·0		0·24	
		5·9					3·0	2
49·4	~2·4		9·1		38		0·08	
							4·0	
54·4	2·21	6·2					3·0	0·9
59·4	1·75	5·5					1·1	0·3
62·4	~2·0						0·4	
80·1	2·36						0·9	
85·1	2·43						0·9	

* Based on a curve taken at 2·55°K.

TABLE 4 (*cont.*)

ψ	β/E_0 $\times 10^7$	beat period $\times 10^7$	β $\times 10^{20}$	β' $\times 10^{20}$	E_0 $\times 10^{14}$	x (°K)	a $\times 10^8$		a' $\times 10^8$	
Sn 9, 22 November 1950, $T = 4{\cdot}22$°K, $1{\cdot}78$°K (displaced sideways by 1 or 2 mm, probably by different amounts at the two temperatures)										
−10·8							11·1			
2·4		70						54		21
10·9							~10		?	
								~50		?
11·2	~5·8						9·8		0·8	
22·6	~5·3						6·1		?	
34·6	~5·0						1·9		?	
45·2	~2·75	~ 8·5						2·8		0·8
50·2	~2·4							1·0		?
55·2	2·11	~ 7						0·5		0·2
60·2	2·72							0·2		
65·2	1·50							0·2		
70·2	2·40							1·2		
80·2	1·95							5·8		
84·7	~2·5							5·3		
Sn 9, 3 November 1950, $T = 4{\cdot}22$°K, $1{\cdot}78$°K (binary axis 45° to vertical)										
−11							~7			
2·5								44		?
5·5		65						38		11·4
11	5·70		18·4		32·3		7·0			
		54·5						32		5·9
22·5	5·50		17·2		31·3		3·0			
		28						15·8		1·8
34·5	4·86		~16·7	10·4	34		1·2		0·2	
		21						6·9		4·4
44·5	4·06						0·3			
49·5	3·9		11·1		28		0·2			
		8						5·0		1·2
54·5	3·65							3·6		?
60	~2·0	7						2·1		0·9
65	1·83	9						0·6		0·3
75								<0·03		
85								<0·1		
Sn 9, 7 March 1951, $T = 1{\cdot}78$°K, $1{\cdot}07$°K (tetragonal axis vertical; ψ measured from a binary axis)										
20	2·25		6·6		29·4		2·7			
								11·2		
22	2·25						2·3			
24	2·13						0·7			
27	2·13						0·3			

Notes. a and a' are the amplitudes of the main oscillations and the modulation respectively, defined as half the swing from maximum to minimum; the figures at the left always refer to the higher temperature and those at the right to the lower temperature mentioned in the title of the series. Data at intermediate temperatures have been omitted. Where no entry appears under a' opposite an entry under a, no appreciable modulation was observed; a question mark indicates that modulation was present but that there were insufficient data to estimate a'. The main period (β/E_0) is usually determined to better than 1 % accuracy; where the accuracy is poor owing to insufficient range of field this is indicated by the ~ sign. Independent estimates of the beat periods at two temperatures are shown to indicate the order of consistency. The estimates of β when strong modulations are present (e.g. Sn 4, $\psi = 45°$) are sometimes rough. For the last series (tetragonal axis vertical) only those values of a are given for which the period was accurately measured; other values of a are shown in figure 11.

these values will be discussed later in connexion with the results on the variation of x with purity.

As can be seen from table 4 the absolute amplitudes of the oscillations varied in an irreproducible fashion, not only as between different specimens but even between different series of measurements on the same specimen on different occasions. A good deal of effort was spent in studying this irreproducibility, and though it did not prove possible to eliminate it, the following causes were shown to be relevant:

(*a*) Since the period is very short, the finite size of the crystal coupled with the slight inhomogeneity of the field might be expected to reduce the amplitude of the oscillations. We may assume that near the centre of the magnet, the field varies as

$$H = H_0(1-\tfrac{1}{2}cz^2),$$

where z is the distance from the centre measured in some particular direction. If the specimen is idealized to a thin cylinder with its axis in this direction, and its ends at $z = z_1$ and $z = z_2$, it is easily shown that the amplitude should be reduced by a factor f given by

$$f = \frac{1}{(v_1-v_2)}\left\{\left(\int_{v_1}^{v_2}\cos\frac{\pi v^2}{2}\,dv\right)^2+\left(\int_{v_1}^{v_2}\sin\frac{\pi v^2}{2}\,dv\right)^2\right\}^{\frac{1}{2}},$$

where $v = (2E_0c/\beta H)^{\frac{1}{2}}z$. It can be seen that f is just the ratio of the chord to the arc of a Cornu spiral, and thus differs appreciably from unity only when values of v comparable with unity are involved. The inhomogeneity parameter c was found by observing with a microscope the position of a steel ball sliding in a vertical glass tube and loaded by non-magnetic (phosphor bronze) balls; the value found was about 0·018 cm^{-2}, in good agreement with an independent estimate based on observing the variation with specimen position of the magnet current at which a particular feature of the de Haas-van Alphen effect in tin occurred. Putting in typical numerical values, $1/H = 0{\cdot}65\times10^{-4}$, $2E_0/\beta H = 225$ (for $\psi \sim 10^\circ$), we find that $v = 2z$, so for a specimen 1 cm long symmetrically placed, f differs from unity by less than $\frac{1}{2}$ %, while if it is displaced to bring one end to the magnetic centre, $f = 0{\cdot}9$. For a field two-thirds as big, and for a period one-third of that assumed (as for values of ψ near 90°), v becomes about $4z$, and for the displaced specimen $f = 0{\cdot}3$. These figures show that in most of the measurements, where care was taken to place the specimen centrally and the length was usually only 2 or 3 mm, this effect could be safely ignored, but in some of the early specimens which were as long as 1 cm, and not so carefully placed, a reduction by 10 % or so might have been possible. It should be noticed that in this discussion only a single direction (in fact the vertical) has been considered; it is possible, however, that in spite of the small thickness of the specimens (1 or 2 mm) in the horizontal direction, an appreciable reduction might occur due to horizontal inhomogeneity, because of the difficulty of accurate horizontal centring and since c for the horizontal direction parallel to the field should be about twice as large as for directions perpendicular to the field.

(*b*) In the course of an experiment (Sn 3, 16 August 1950) to see if the reduction of amplitude just discussed could be made appreciable by deliberately putting the centre of the specimen farther from the centre of the magnet, it was observed that the amplitude at first increased with increasing distance from the centre before finally decreasing; the maximum amplitude was nearly twice as large as at the centre. It is probable that this increase is due to the force acting on the crystal in the inhomogeneous field away from the centre which, acting on the slightly bowed suspension wire, causes it to twist slightly. This sensitivity of the suspension to a force as well as a couple may have caused part of the irreproducibilities, since it was difficult to be certain that the specimen was always sufficiently central.

(*c*) Probably the main cause of irreproducibility arises from imperfections in the specimen itself. Laue X-ray photographs gave rather smeary or streaky spots, especially if the specimen was displaced without rotation during the exposure, and the size of the spots suggests that the directions of the crystal axes vary by a degree or so through the specimen. This is not improbable, since the crystals are very soft and may easily have got slightly bent during handling and in the setting of the Durofix cement. Since for $\psi = 10^\circ$ a change of only about 3° in ψ is sufficient to cover a full cycle of oscillation, any such variation of orientation through the specimen could cause serious reductions of amplitude. The possibility is also not excluded that the specimen is damaged in cooling, owing to differential thermal contraction of the Durofix and the tin, or in between experiments if the crystal is remounted.

(*d*) Finally, it should be mentioned again that in mounting the crystal, errors of up to 2 or 3° were possible in setting the axes in the desired orientations. For large values of ψ, as has already been pointed out, the amplitude is very sensitive to the exact orientation of the binary axis, so such angular errors must be considered as another contributory cause to the irreproducibility.

It should be noticed that causes (*a*) and (*c*) predict a reduction of amplitude which should be the more severe the lower the field strength, and so we should expect to find that x, which is a measure of the variation of amplitude with field, should appear to be larger for specimens where the absolute amplitude is smaller. Since the measured value of x depends only on the logarithms of the amplitudes, and the field was rarely reduced to less than two-thirds of its highest value, no great effect is to be expected, but it is perhaps significant that in one of the early specimens (Sn 3) the amplitude at $\psi = 11^\circ$ was only about half of that obtained with Sn 8, and the value of x was about 1·6° K compared with about 1·0° K for Sn 8.

As for gallium, we may attempt to predict the absolute amplitude theoretically assuming a single ellipsoid representation, which seems adequate to account for the periods at small ψ. For this purpose we assume $m_1 = m_2$ in view of the tetragonal symmetry of tin and put $m_3/m_1 = 20$ (though this estimate is very rough in view of the scatter of points in figure 10); it turns out that the predicted amplitude of $\Delta\chi$ at 4·22° K and for $1/H = 0{\cdot}65 \times 10^{-4}$ is $6{\cdot}5 \times 10^{-7}$, which is greater than the highest observed value, $8{\cdot}5 \times 10^{-8}$. The predicted value is proportional to the square root of the assumed value of (m_3/m_1), so it can be seen that a very considerable error would be necessary to bring it down to the highest observed value.

In conclusion, the present results may be compared with those of Verkin *et al.* (1949, 1950 *a*, *b*), who discovered the effect in tin independently in June 1949, but have published only two detailed curves. One of these, which is of $\Delta\chi$ against ψ for a fixed field strength, appears to be wrongly labelled, since from its symmetry it is evident that ψ should be zero at the point for ψ marked as about -22°; this error suggests that the orientation of the tetragonal axis was wrongly determined. Possibly the determination was based on the weak steady anisotropy, which in the author's experience is an unreliable criterion, since it is so small that it is easily upset by the weak magnetic anisotropy of the mounting; in the present experiments the point where $\psi = 0$ was always determined by the vanishing of the de Haas-van Alphen effect. In view of this angular error, the interpretation of their only other curve (stated to be for $\psi = 24^\circ$) is a little uncertain. The period in $1/H$ can be estimated from this curve as about $5{\cdot}6 \times 10^{-7}$. This agrees quite well with the value of $5{\cdot}5 \times 10^{-7}$ at $\psi = 22{\cdot}4^\circ$, obtained in the present experiments, which suggests that the zero correction of 22° is not required here; possibly the orientation was independently and differently estimated in the two experiments to which the curves refer. Assuming that ψ is indeed 24°, their value of the absolute amplitude of $\Delta\chi$ is about $2{\cdot}7 \times 10^{-8}$ for $T = 4{\cdot}22^\circ$ K and $1/H = 0{\cdot}71 \times 10^{-4}$, which, in view of the irreproducibilities discussed above, can be considered as being in good agreement with 4×10^{-8}, the largest absolute value obtained in the present experiments for $\psi = 22{\cdot}4^\circ$ at the same field and temperature.

Graphite

In tin and gallium the oscillations of anisotropy were immediately apparent as oscillations in the deflexion, but in graphite the steady anisotropy is so large, and the period of the oscillations so long, that even though the amplitude is large, the deflexion in general does not itself show maxima and minima, and the oscillations become apparent only after division by the square of the field. This made the measurements somewhat tedious, since it was necessary to take a great many readings at suitable intervals of $1/H$ and only later to find out the form of the curve, instead of directly observing the maxima and minima as was possible in gallium and tin. Measurements were made with the hexagonal axis of the crystal horizontal, and since it was established in the early experiments that the form of the curves was not appreciably affected by twisting the crystal through 8° in the hexagonal plane, most of the more detailed measurements were made with a binary axis vertical (except for G 4, for which the direction of the binary axis was not determined). Representative curves for two crystals from different sources are shown in figure 12, and it can be seen that the positions of the oscillations and modulations are fairly well reproduced from one crystal to the other, and that the amplitudes are also fairly similar. The modulation effects, which become particularly marked at the lowest temperatures, considerably complicate the quantitative discussion of the results, but as we shall see later, a reasonably consistent interpretation may be obtained by supposing that the observed curves contain a fundamental term and a term of frequency almost exactly four-thirds that of the fundamental, as well as harmonics of these which become marked only at low temperatures. The four-thirds frequency component fades out more rapidly with rise of temperature than does the fundamental and probably arises from an independent ellipsoid; it is not clear whether the simple numerical relation between the frequencies has any fundamental significance or is merely accidental.

The fundamental period can be found accurately only for fairly low values of ψ, since the oscillations die out too rapidly above $\psi = 40^\circ$ to make any accurate determination possible. Within experimental error, however, the observed maxima and minima occur always at

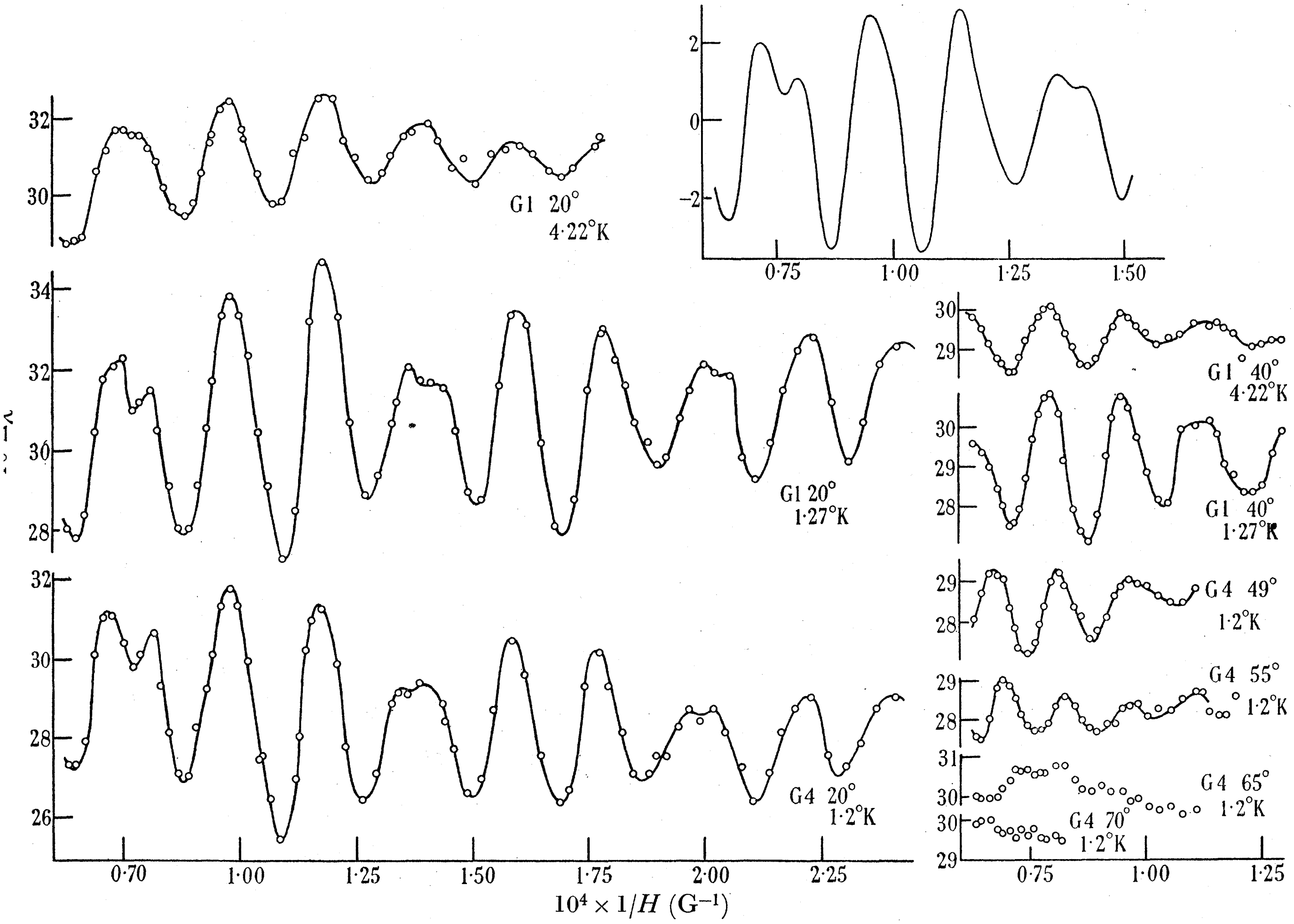

FIGURE 12. Graphite: variation of anisotropy with $1/H$ at various angles ψ between the field and the hexagonal axis. The data for G1 have not been corrected for slight ferromagnetism, but are corrected for the slight changes of ψ with deflexion. The data for G4 (which showed a stronger ferromagnetic effect) have been corrected by dividing them by the corresponding deflexions at 80° K and adjusting the scale of ordinates to make the mean value of $\Delta\chi$ agree approximately with that for G1; it can be seen that this method of correction is not quite successful in producing a mean value of $\Delta\chi$ which is independent of $1/H$. The top right-hand diagram is a theoretical curve constructed as explained in the text and scaled to be comparable with the low-temperature curves for G1 and G4 at $\psi = 20°$.

the same values of $1/(H\cos\psi)$ as ψ is varied*, so it can be assumed that the period is almost exactly proportional to $\cos\psi$. This means that if we assume the energy surface in phase space to be represented by two independent ellipsoids† each having $m_1 = m_2$ in accordance with the hexagonal symmetry of graphite, then in both ellipsoids m_1/m_3 is less than about 10^{-2}; we shall see later that probably the ratio is even smaller. The fundamental period extrapolated to $\psi = 0$ immediately gives for the 'dominant' ellipsoid

$$\beta/E_0 = 2{\cdot}20\times10^{-5}, \quad \text{where} \quad \beta = e\hbar/cm_1$$

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[*] There is, however, some slight indication that the values of $1/(H\cos\psi)$ become slightly low (by 1 or 2 % perhaps) at the highest values of ψ.

[†] The possibility that the second frequency was due to the presence of an appreciable amount of the rhombohedral modification of graphite was ruled out by the X-ray evidence, which showed that there was certainly less than 5 % of the modification present.

and for the 'subsidiary' ellipsoid we then have, since the subsidiary period is three-quarters of the fundamental,

$$\beta'/E'_0 = 1{\cdot}65 \times 10^{-5}, \quad \text{where} \quad \beta' = e\hbar/cm'_1.$$

The values of β and β' can be estimated from the temperature variation of the amplitude, though, owing to the simultaneous presence of several frequencies, this cannot be done very accurately. For $\psi = 20°$ the amplitudes of the two main frequencies (i.e. smoothing over the irregularities due to the harmonics) were roughly estimated at 1·27 and 2·50° K from the depth of the modulations, and after making due allowance for the correction due to the difference between (5) and (1) on the same lines as for gallium (this correction is quite considerable here), values of $\beta = 4{\cdot}7 \times 10^{-19}$ and $\beta' = 2{\cdot}5 \times 10^{-19}$ were obtained. A rather more accurate procedure for obtaining β was to study the temperature variation of each 'feature' of the curve separately; thus, defining a as the difference between each minimum in turn and the mean of the two adjoining maxima, and plotting $\log a/T$ against T after correcting a suitably, a number of slightly differing values of β could be found, whose average is probably a fairly reliable estimate of the value of β characteristic of the fundamental. In this way β for $\psi = 20°$ was found to be $4{\cdot}83 \times 10^{-19}$, and this estimate is probably within 2 or 3 % of the true value. A similar (though less thorough) analysis for $\psi = 40°$ gave a value of β 1·32 times as high, which is reasonably consistent with the ratio 1·23 of cos 20° to cos 40°. Dividing the $\psi = 20°$ values of β and β' by cos 20°, we have that for $\psi = 0$

$$\beta = 5{\cdot}13 \times 10^{-19} \quad \text{and} \quad \beta' \sim 2{\cdot}6 \times 10^{-19},$$

or, since $\beta_0 = e\hbar/cm_0 = 1{\cdot}85 \times 10^{-20}$,

$$m_1/m_0 = 3{\cdot}6 \times 10^{-2} \quad \text{and} \quad m'_1/m_0 \sim 7 \times 10^{-2}.$$

The corresponding values of E_0 and E'_0 are

$$E_0 = 2{\cdot}33 \times 10^{-14}\,\text{erg} \quad \text{and} \quad E'_0 \sim 1{\cdot}6 \times 10^{-14}\,\text{erg},$$

i.e. $T_0 = 169°$ K and $T'_0 \sim 120°$ K.

The decay of amplitude with field can be analyzed in a way similar to that just described for the temperature variation; $\log aH^{\frac{3}{2}}$ is plotted against $1/H$, where a is the difference between a minimum and the mean of the adjoining maxima, and though the points scatter a good deal, the lines joining the points from 'corresponding' features (e.g. all the shallow minima) are fairly parallel, and a rough average slope may be estimated. The values of a must, of course, be corrected as before for the difference between (5) and (1). From the slopes, the value of x for $\psi = 20°$ at 1·27° K was found to be 1·5° K. Owing to the rapid fading away of the oscillations at 2·5 and 4·22° K the estimates of x were very rough at these temperatures but agreed with that at 1·27° K to within about 0·5° K, which can be regarded as within the uncertainty of the procedure. For $\psi = 40°$ at 4·22° K (where the beats are not pronounced) a rough value of $x = 2{\cdot}5°$ K was obtained.

Examination of the amplitudes for different values of ψ suggested that up to about $\psi = 50°$, the reduction in amplitude for increasing ψ can be roughly accounted for by supposing that x increases as $\sec^2\psi$. Thus if $x = x_0 \sec^2\psi$ we have

$$\log a = -2\pi k x_0 \sec^2\psi/\beta H \cos\psi + \text{terms independent of } \psi,$$

where a is the amplitude of a particular feature, which for different ψ occurs at the same value of $H\cos\psi$, and x_0 refers to $\psi = 0$; a logarithmic plot of a against $\sec^2\psi$ should therefore give a straight line of slope $2\pi kx_0/\beta H\cos\psi$. The logarithmic plots are indeed roughly linear (except that the point for $\psi = 57°$ comes rather high) and the slopes are roughly proportional to $1/(H\cos\psi)$, and we find $x_0 = 1{\cdot}7°$ K with an uncertainty of about 30 %, which is not too different from the value derived from the field variation for $\psi = 20°$ after division by $\sec^2 20°$ ($x_0 = 1{\cdot}3°$ K). We shall refer later (p. 53) to the possible significance of the rough empirical relation $x = x_0\sec^2\psi$.

In discussing the absolute amplitudes of the oscillations we cannot follow the procedure adopted in gallium and tin, since for graphite only an upper limit can be set to the ratio m_1/m_3. We can, however, assume the validity of the theoretical formula and the corresponding value of (m_3/m_1) is then found to be about 5500 (i.e. $m_3/m_0 \sim 200$). It should be noted, however, that these figures are very rough, since they involve the square of the absolute amplitude which cannot be very accurately determined and the value of x assumed is rather rough too; moreover, if the theoretical formula has to be reduced by some factor as a result of taking into account the influence of the lattice field in a more fundamental way, the estimate of m_3/m_1 would be increased. Finally, it is worth mentioning that an even rougher estimate may be made of the ratio m_3'/m_1', where the dashes refer to the subsidiary ellipsoid which is responsible for the beats; making a rough estimate that the absolute amplitude of the subsidiary term at 4·22° K is about 15 % of the fundamental, and guessing arbitrarily that x for the subsidiary term is the same as for the fundamental, we find $m_3'/m_1' \sim 10^4$ (i.e. $m_3'/m_0 \sim 700$). Actually there is some evidence (see below) that x may be rather smaller for the subsidiary term than for the fundamental, and if we put $x = 0$, we find $m_3'/m_1' \sim 350$ (i.e. $m_3'/m_0 \sim 25$).

We come now to the question of the phase of the oscillations and the harmonic analysis of the experimental curves. This is more difficult than for gallium, first because of the presence of the independent (four-thirds) frequency, and secondly because the amplitude varies more strongly over one full cycle than it does for gallium. Owing to the difficulty of reliably 'idealizing' a cycle to eliminate the amplitude modulation it was decided to try synthesis rather than analysis, and after some trial and error it was found that the expression

$$\frac{I_1}{H_1} - \frac{I_3}{I_3} = a\{r_0 - \sin(\theta-\phi) - 0{\cdot}4\sin(\tfrac{4}{3}\theta + 100° - \tfrac{4}{3}\phi) + 0{\cdot}4\sin(2\theta + 30° - 2\phi)\} \qquad (12)$$

could be used as the basis of a representation of the low-temperature curves at $\psi = 20°$ in figure 12; here a is positive, θ, as in (10), stands for $2\pi E_0/\beta H$ and ϕ is for the moment arbitrary. To obtain a still closer representation, the amplitudes of the three periodic terms in (12) were varied in accordance with the appropriate values of the relevant parameters; it was found that to avoid too rapid decay of the four-thirds frequency term the parameter x had to be taken as 0·3° K, a value much lower than the 1·5° K found for the main frequency.* The final result is shown in figure 12, and it can be seen that it does give a fair representation

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* The calculation of the modulation was in fact somewhat simplified by assuming that the amplitudes of the successive terms in (12) fell linearly from their initial values at $1/H = 0{\cdot}65\times10^{-4}$ to final values at about $1/H = 1{\cdot}3\times10^{-4}$ of 0·72, 0·72 and 0·32 of the initial values. The use of a linear rather than exponential interpolation is not likely to cause any serious distortion.

of the experimental curves. It is quite likely that a still better fit might be obtained by considering higher harmonics and harmonics of the four-thirds frequency, but the data are hardly accurate enough (not consistent enough between G 1 and G 4) to make this profitable. The relative phases chosen in (12) are probably not wrong by more than 30°, since it was found that if they were varied by more, one or other of the experimental features began to be seriously distorted. It can be seen at once that it is impossible to choose ϕ to make all the phase angles equal, but if ϕ is chosen as 30°, the arguments of the various terms become $(\theta-30^\circ)$, $(\frac{4}{3}\theta+60^\circ)$, $(2\theta-30^\circ)$, so that at least the phases of the main term and its harmonic agree.

Just as for gallium we can now obtain an independent estimate of ϕ from extrapolation of the plot of the values of $1/H$ for which maxima and minima occur against successive half-integers. Here the extrapolation required is not so great since E_0/β is smaller than for gallium, but the plot (figure 8) is not quite such a good straight line owing to the beats; the effect of the beats in throwing the points off a straight line is particularly serious at the highest fields, and a systematic error may well occur in determining the intercept. The intercept of the best straight line indicates $\phi = 0$, but $\phi = 30^\circ$ (as indicated by the harmonic analysis) cannot be regarded as inconsistent with the data. We thus see that the main frequency and its harmonic have phases nearly, but not quite, in accordance with the theoretical prediction (45°), while the subsidiary frequency has a very different phase. It may be noticed that it is only because of the presence of the four-thirds frequency that the harmonic is able to make its presence so apparent in the 'double-hump' feature. A puzzling feature of (12) is the large strength ($r_2 = 0{\cdot}4$) of the harmonic, for according to (7) r_2 should be only 0·18. The experimental determination of r_2 is of course only rough, but it seems hardly possible to reproduce the double hump adequately unless $r_2 > 0{\cdot}3$. Perhaps the discrepancy should be taken to indicate that the extra factor $\mathrm{e}^{-2\pi^2 pkx/\beta H}$ introduced to reconcile the temperature and field variations of amplitude has not quite the correct form.

Antimony

In the preliminary experiments the de Haas-van Alphen effect was missed because of its small amplitude, but with the higher fields of the larger magnet and improved measuring technique, the effect was later observed (February 1951) on the same crystal. This crystal (Sb 1) contained a considerable ferromagnetic impurity and all the detailed measurements were carried out on a second crystal (Sb 2) which had no appreciable contamination. Since the first results promised to fit nearly into a three-ellipsoid scheme, analogous to that used for bismuth, it was thought worth while to make a rather detailed survey, in order to see how well the scheme worked. Measurements were taken for closely spaced values of ψ for the crystal suspended with (*a*) a binary axis vertical and trigonal axis horizontal, (*b*) a binary axis and the trigonal axis horizontal and (*c*) the trigonal axis vertical.* Only a few typical curves of the many actually measured, are shown in figure 13; the salient features of the others are indicated in table 5 and figures 14 and 15. It should be noticed

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* For suspension (*a*) ψ and $180-\psi$ are not equivalent; the sense of ψ has been chosen so that ψ increases from zero as the field turns away from the trigonal axis [0001] into the acute-angled sector between [0001] and $[10\bar{1}1]$. It should be noticed that ψ and $180+\psi$ are always equivalent, i.e. reversal of the field has no effect.

that C/H^2 is plotted rather than $C/(H^2 \sin\psi \cos\psi)$, which would, of course, become infinite for $\psi = 90°$, where C does not vanish; the non-vanishing of C for $\psi = 90°$ has already been discussed and explained for bismuth (Shoenberg 1939), and the explanation will be self-evident from the formulae below. Owing presumably to slight errors in mounting the crystal in the desired orientation, it was also possible to observe a small oscillating couple for $\psi = 0°$. It can be seen that even at 1·5° K the oscillations are not very marked, and for some orientations the steady anisotropy was so large in comparison that, as in graphite, the oscillations were not immediately apparent, and a series of closely spaced measurements had to be taken which revealed the oscillations only when divided by H^2.

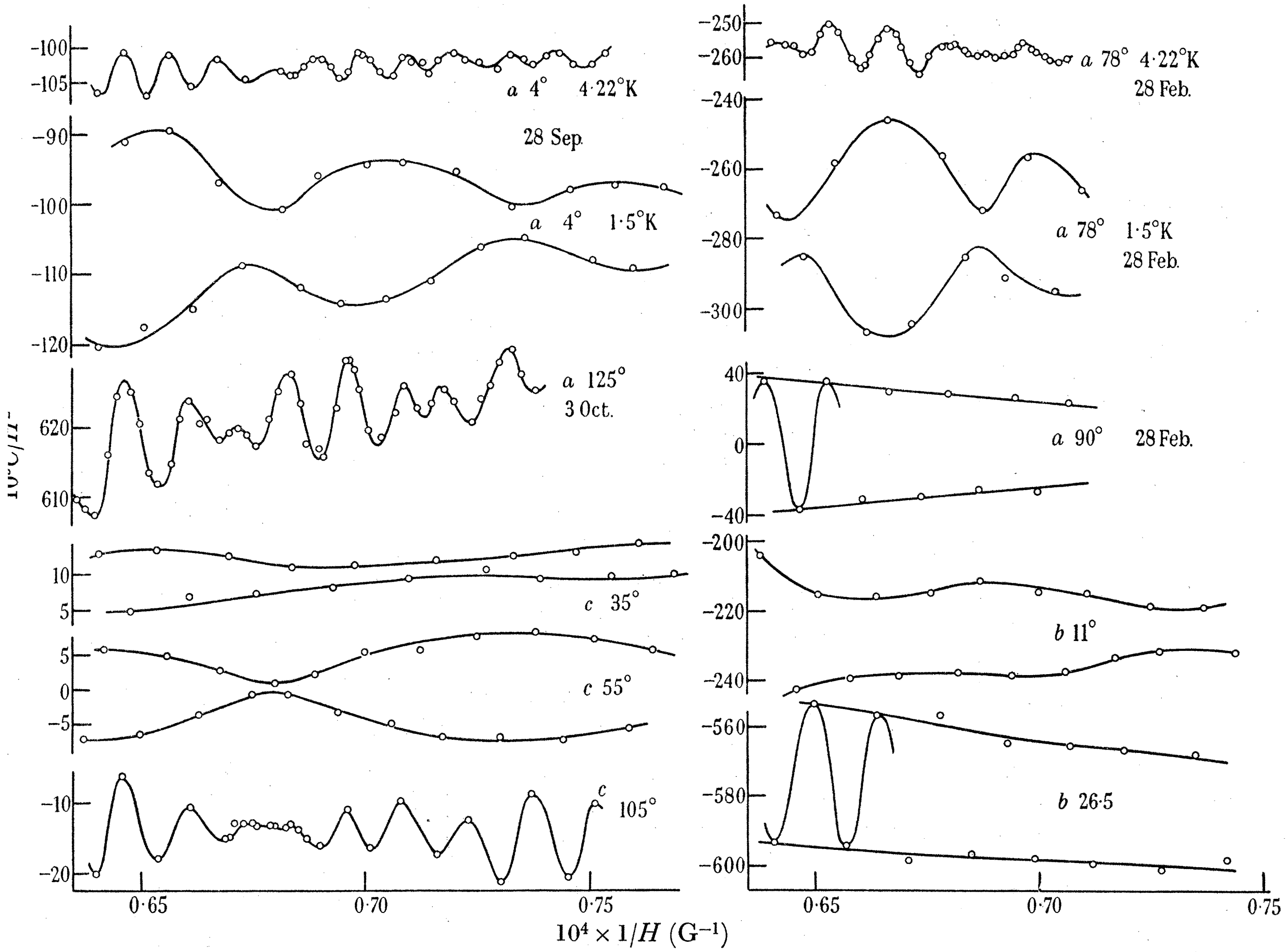

FIGURE 13. Antimony: variation of C/H^2 with $1/H$ at various angles ψ for (*a*) trigonal axis horizontal, binary axis vertical, (*b*) trigonal axis horizontal, binary axis horizontal, (*c*) trigonal axis vertical; except for the two top curves the temperature is 1·5° K. The magnetic anisotropy of the empty mounting was in some instances comparable to that of the specimen, so the zero level in the *c*-mounting, for instance, is not reliable, and in some curves (e.g. *a*, $\psi = 125°$ and *b*, $\psi = 26{\cdot}5°$), the mean level of the oscillations is field-dependent on account of slight ferromagnetic impurities. The signs of the ordinates are such that $C/H^2 \sin\psi \cos\psi$ gives $\chi_3 - \chi_1$.

The periods of the oscillations for the various orientations are collected together in table 5 and illustrated graphically in figure 14. They fit rather well into the same kind of

TABLE 5. SUMMARY OF DATA ON ANTIMONY

ψ	$\beta/E_0\times10^7$		$a=\lvert C/H^2\rvert\times10^9$		ψ	$\beta/E_0\times10^7$		$a=\lvert C/H^2\rvert\times10^9$	
Binary axis vertical, ψ from trigonal axis (see footnote on p. 34)									
28 February 1951					28 September 1951 (remounted)				
2	9·9	10·9	22	16	0	10·2	10·7	8	8
5	11·0	9·2	25	10	4	10·9	9·1	9	5
11	11·3	7·5	18	5	89	13·8		5·1	at 4·22° K
31	12·8		7		93	14·5		6·1	
51	12·4		1·4	1·0	(175)	11·0		11	6
66			2·4	1·9					
78	11·6	9·2	18	14					
86	12·9		24	8					
90	13·4		35						
3 October 1951 (remounted)					10 October 1951 (not disturbed since 3 October)				
0	10·1		7	3	69·5	10·9	8·8	7	4
5	11·1	9·3	7	3	(119·5)	16·5	13·2	16	8
10	11·4		8	2·1	(125·5)	16·4		7	2·9
15	11·9		3·7	0·5	(129·5)	17·0		6	1·6
25	12·2		4·2	1·0	(134·5)	16·4		16	
40	12·3		2·9	1·6	144·5	16·3		29	
50	12·2		5·4	1·4	(144·5)	16·0		27	
60	11·5	10·1	6	3	(154·5)	15·0		34	
65	11·4	9·9	4·0	2·4	(164·5)	13·3		21	
73	10·1	13·7	4·5	1·9	(169·5)	12·5		19	
85	12·9	8·6	10	4	(174·5)	11·4	10·0	11	3·5
97	15·1		19						
105	16·1	11·8	26	1·6					
115	16·6	13·9	18	6					
125	12·1	16·2	6	4					
Binary axis horizontal, ψ from trigonal axis					Trigonal axis vertical, ψ from a binary axis				
12 October 1951					17 October 1951				
1	10·1		5·6	2·4	5	12·4	13·9	3·5	2·1
11	12·6		12	1·3	15	14·3		4·3	1·1
26·5	14·4		20		25	14·7		1·9	
41	15·1		10		35	15·1	13·4	2·7	1·8
70·5	14·6		16		45	14·6		5·1	2·9
81	13·5		10		55	12·2	13·7	4·5	3·5
86	12·8		7	4	65	12·6		5·4	2·6
91	12·4		9	2·6	75	14·1		4·8	1·6
111·5	14·8		13	4	85	14·0		1·4	0·5
155·5	13·8		14		95	15·3	13·9	2·7	1·1
171	11·4		10		105	15·0	11·2	4·2	3·0
176	10·5		3·7	2·9	115	12·7	11·8 or 13·6	7·2	5·6
					125	14·1	10·8	6·1	3·7
					135	14·7		4·0	2·4
					(135)	14·9	12·8	4·3	2·4
					145	15·1	14·0	1·9	1·3
					(145)	15·1		1·3	1·3
					(155)	14·1		1·4	1·4
					(165)	14·6	11·0	4·3	2·4
					(175)	13·3	12·0	4·5	3·2

Notes. The second figure under β/E_0 refers to the period of the subsidiary oscillation where beats are observed; often the beats are too vague to make any estimate possible, and even where an estimate is made it may be very rough owing to insufficient range of observation. The values of a, which is half of the 'peak to peak' distance of C/H^2, refer to 1·5° K and $1/H=0{\cdot}65\times10^{-4}$; here again the second figure is a rough estimate of the amplitude of the subsidiary oscillation. The two figures are given by $\frac{1}{2}(a_{\text{max.}}\pm a_{\text{min.}})$, and since the inaccuracies are often comparable with the depth of the modulations, the existence of a subsidiary oscillation must not be taken as certain even if a figure is given for its amplitude.

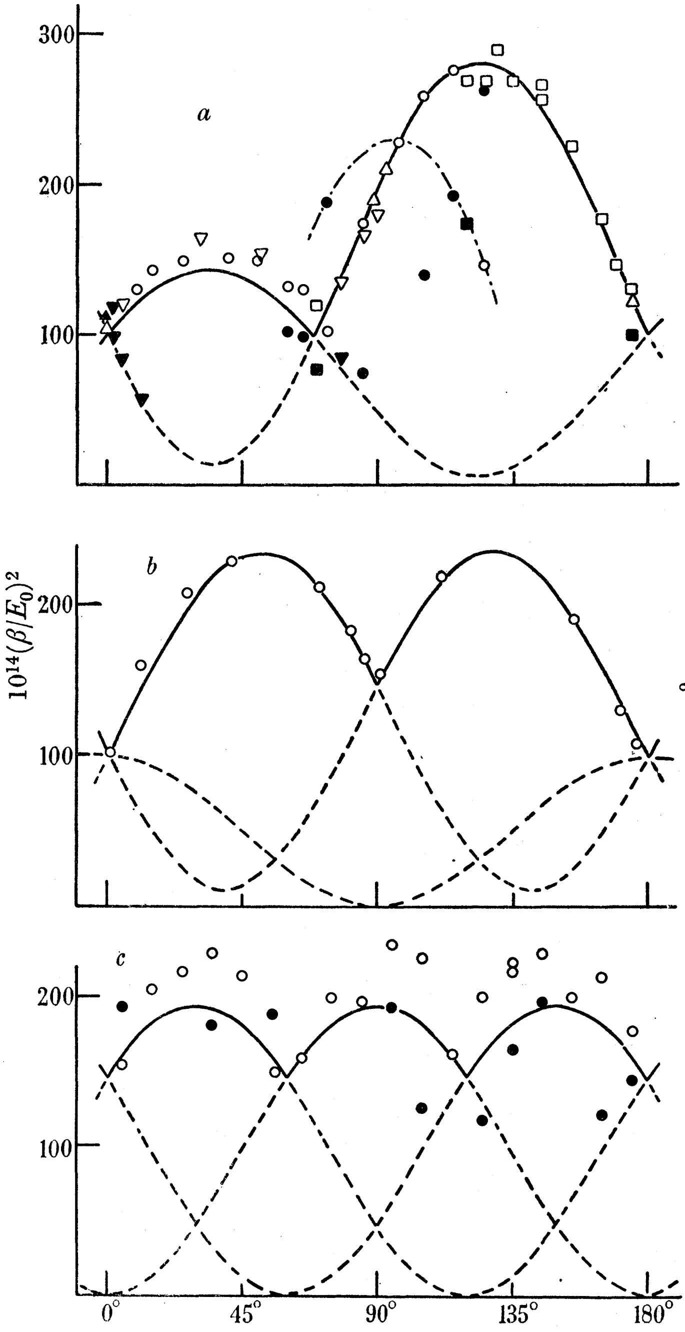

FIGURE 14

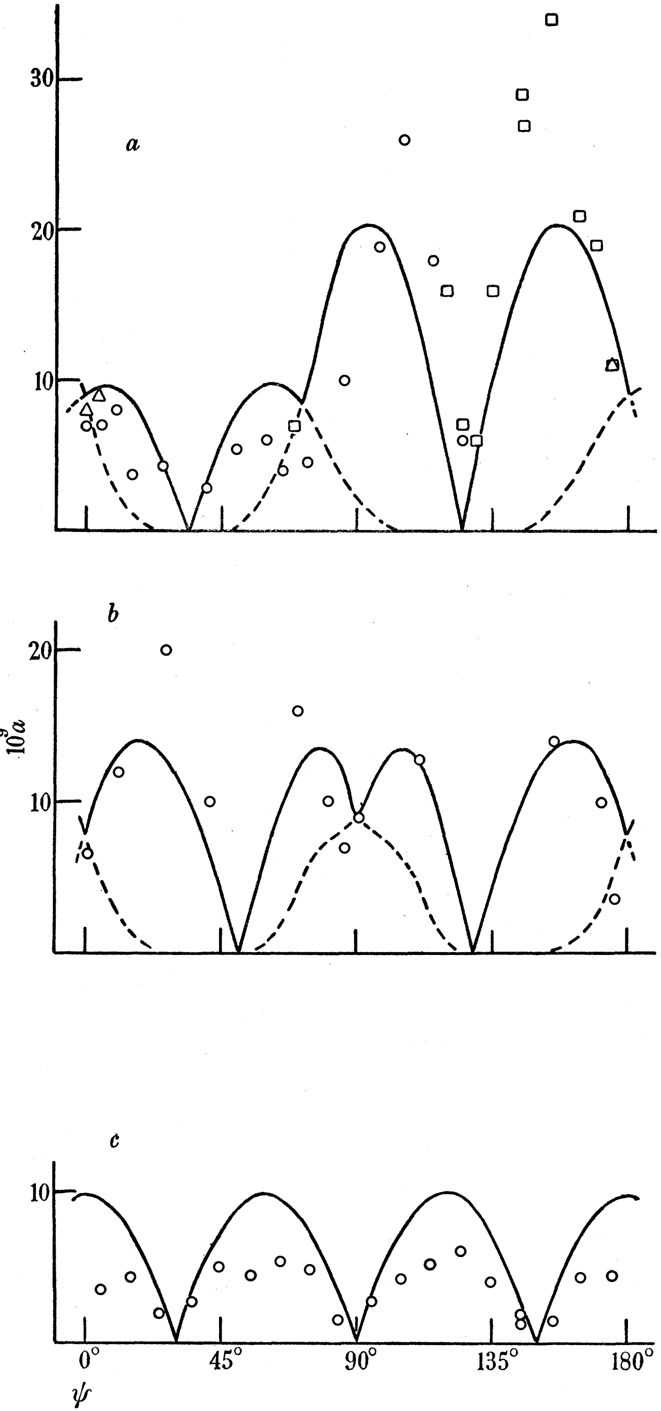

FIGURE 15

FIGURE 14. Antimony: variation of square of period $(\beta/E_0)^2$ with ψ for the three modes of suspension indicated in figure 13. The curves are theoretical, broken in the region where the period should be subsidiary; the chain curve is schematic, joining up some of the unexplained observed points. The points filled in black refer to subsidiary periods, and the various styles of points in (*a*) refer to the different runs: ▽, 28 February 1951; △, 28 September 1951; ○, 3 October 1951; □, 10 October 1951.

FIGURE 15. Antimony: variation of amplitude a $(=|C/H^2|)$ at 1·5°K and $1/H = 0{\cdot}65 \times 10^{-4}$ with ψ for the three modes of suspension indicated in figure 13. The curves are theoretical, broken in the region where the amplitude arising from one particular ellipsoid is no longer dominant. To avoid confusion the curve for the third ellipsoid in *b*, which has small amplitude throughout, and all the subsidiary curves in *c* are omitted. The various points in *a* refer to the various runs, using the same notation as in figure 14; the points for the run of 28 February 1951 have been omitted, since, although the relative amplitudes are roughly the same as in the other runs, the absolute amplitudes are about twice as high. The experimentally observed subsidiary amplitudes are not shown.

scheme of ellipsoids that was used to interpret the bismuth results, and it is possible to demonstrate the fit even better here than for bismuth. According to the scheme, the relevant parts of the energy surface in phase space may be represented by three ellipsoids,

$$\alpha_1 p_x^2 + \alpha_2 p_y^2 + \alpha_3 p_z^2 + 2\alpha_4 p_y p_z = 2Em_0, \tag{13}$$

and the two ellipsoids derived from this one by rotations of ±120° about the p_z axis, where

$$\alpha_1 = \frac{m_0}{m_1}, \quad \alpha_2 = \frac{m_0 m_3}{m_2 m_3 - m_4^2}, \quad \alpha_3 = \frac{m_0 m_2}{m_2 m_3 - m_4^2}, \quad \alpha_4 = \frac{m_0 m_4}{m_2 m_3 - m_4^2}.$$

As explained in the paper on bismuth,* this leads to three periodic terms in equation (1), which for the three modes of suspension investigated have the following values of β and Δm:

(*a*) Trigonal axis horizontal, binary axis (x) vertical:

$$\left.\begin{aligned} \beta_1 &= \lambda(m_3 \cos^2\psi + m_2 \sin^2\psi + 2m_4 \sin\psi \cos\psi)^{\frac{1}{2}}, \\ \beta_2 = \beta_3 &= \lambda\left(m_3 \cos^2\psi + \frac{3m_1 + m_2}{4}\sin^2\psi - m_4 \sin\psi \cos\psi\right)^{\frac{1}{2}}, \end{aligned}\right\} \tag{14}$$

$$\left.\begin{aligned} (\Delta m)_1 \sin\psi \cos\psi &= \tfrac{1}{2}(m_2 - m_3)\sin 2\psi + m_4 \cos 2\psi, \\ (\Delta m)_2 \sin\psi \cos\psi = (\Delta m)_3 \sin\psi \cos\psi &= \frac{1}{2}\left(\frac{3m_1 + m_2}{4} - m_3\right)\sin 2\psi - \tfrac{1}{2}m_4 \cos 2\psi. \end{aligned}\right\} \tag{15}$$

(*b*) Trigonal axis horizontal, binary axis horizontal:

$$\left.\begin{aligned} \beta_1 &= \lambda(m_3 \cos^2\psi + m_1 \sin^2\psi)^{\frac{1}{2}}, \\ \beta_2, \beta_3 &= \lambda\left(m_3 \cos^2\psi + \frac{m_1 + 3m_2}{4}\sin^2\psi \pm \sqrt{3}m_4 \sin\psi \cos\psi\right)^{\frac{1}{2}}, \end{aligned}\right\} \tag{16}$$

$$\left.\begin{aligned} (\Delta m)_1 \sin\psi \cos\psi &= \tfrac{1}{2}(m_1 - m_3)\sin 2\psi, \\ (\Delta m)_2 \sin\psi \cos\psi,\ (\Delta m)_3 \sin\psi \cos\psi &= \frac{1}{2}\left(\frac{m_1 + 3m_2}{4} - m_3\right)\sin 2\psi \pm m_4 \frac{\sqrt{3}}{2}\cos 2\psi. \end{aligned}\right\} \tag{17}$$

(*c*) Trigonal axis vertical (ψ = angle from a binary axis):

$$\left.\begin{aligned} \beta_1 &= \lambda(m_1 \cos^2\psi + m_2 \sin^2\psi)^{\frac{1}{2}}, \\ \beta_2, \beta_3 &= \lambda\left(\frac{m_1 + 3m_2}{4}\cos^2\psi + \frac{m_2 + 3m_1}{4}\sin^2\psi \pm (m_2 - m_1)\frac{\sqrt{3}}{2}\sin\psi \cos\psi\right)^{\frac{1}{2}}, \end{aligned}\right\} \tag{18}$$

$$\left.\begin{aligned} (\Delta m)_1 \sin\psi \cos\psi &= \tfrac{1}{2}(m_1 - m_2)\sin 2\psi, \\ (\Delta m)_2 \sin\psi \cos\psi,\ (\Delta m)_3 \sin\psi \cos\psi &= \tfrac{1}{2}(m_2 - m_1)\left(\tfrac{1}{2}\sin 2\psi \pm \frac{\sqrt{3}}{2}\cos 2\psi\right). \end{aligned}\right\} \tag{19}$$

In all these expressions λ is given by

$$\lambda = e\hbar/c\{m_1(m_2 m_3 - m_4^2)\}^{\frac{1}{2}}, \tag{20}$$

and the m' of equation (2) is given by

$$m' = \{m_1(m_2 m_3 - m_4^2)\}^{\frac{1}{3}}. \tag{21}$$

If then for any mode of suspension the square of the period (i.e. $(\beta/E_0)^2$) is plotted against ψ we should expect to find plots of the form $A\sin 2\psi + B\cos 2\psi$ representing the appropriate terms. As can be seen from figure 14, this is indeed the case. The dominant term is usually

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* All the formulae quoted below are taken from this paper, but it is convenient to repeat them here, especially in view of slight changes in notation.

the one with the highest β out of β_1, β_2 or β_3, so each diagram consists of two or three branches, but where two branches meet, beats occur since the terms are then comparable. In a few cases it has been possible to determine the subsidiary period from the beat frequency, and it can be seen that often it lies within experimental error on the continuation of the neighbouring branch. The curves drawn in figure 14 are calculated from equations (14), (16) and (18), assuming

$$m_1/m_3 = 0, \quad m_2/m_3 = 1{\cdot}94, \quad m_4/m_3 = -1{\cdot}26, \quad (\beta/E_0)_{\psi=0} = 1{\cdot}00\times 10^{-6}, \tag{22}$$

and it can be seen that they fit the experimental points closely except on the left-hand branch of (*a*) and on (*c*). Detailed consideration of the influence of small angular errors in mounting the crystal shows that such errors could be particularly effective in modifying the theoretical formula for the left-hand branch of (*a*), but that it is unlikely that they could account for the discrepancy in (*c*). A possible clue to the discrepancy in (*c*) is the presence in (*a*) of subsidiary periods at quite unexpected places; these are indicated schematically by the chain curve in (*a*). It is possible that these unexplained subsidiary periods which occur for the field fairly close to the position at which it is perpendicular both to the trigonal axis and a binary axis are showing up as the dominant periods in the region of maximum period in (*c*), which also occurs for the field perpendicular to both the trigonal axis and a binary axis. In this region, as can be seen from (19), the amplitude of the 'legitimate' period becomes small (see also figure 15*c*), and so it is not unreasonable to find a subsidiary effect becoming dominant.

Comparatively few curves were taken at any temperature other than 1·5° K, but from the few curves taken at 4·2° K a sufficiently good estimate can be made of the temperature variation and hence of the absolute values of β and of E_0. With an accuracy of order 5 % we find that $E_0 = 18\times 10^{-14}$ erg ($T_0 = 1300°$ K), and the absolute value of the ratio β_0/β for $\psi = 0$ is given by

$$\frac{\beta_0}{\beta} = \frac{(m_1 m_3)^{\frac{1}{2}}}{m_0}\frac{(m_2 m_3 - m_4^2)^{\frac{1}{2}}}{m_3} = 0{\cdot}10.$$

The value of $(m_2 m_3 - m_4^2)^{\frac{1}{2}}/m_3$ is already known to be 0·6 from the ratios given in (22), so we obtain

$$(m_1 m_3)^{\frac{1}{2}}/m_0 = 0{\cdot}17.$$

Just as for bismuth and graphite, the ratio m_1/m_3 cannot be found without appeal to absolute amplitudes, since it is too small to show up appreciably in (22). The first step as usual is to find the value of x for some suitable orientation; this is difficult except for curves with no beats, and analysis of the curves near $\psi = 90°$ for mounting (*a*) gives $x = 3{\cdot}3 \pm 0{\cdot}5°$ K. We then find from the absolute amplitude of the curve for $\psi = 93°$ (28 September 1951) that $m_1/m_3 \sim 0{\cdot}4$. The situation is rather similar to that in tin and graphite; the theoretical formula for the amplitude gives a more consistent interpretation if multiplied by a factor less than unity (in this case about $\frac{1}{2}$).* On the basis of this discussion it is probable that m_1 is only just too small to show up in the period measurements, and we may guess that $m_1/m_3 \sim 0{\cdot}1$; on this basis the final scheme of masses comes out to be

$$m_1/m_0 = 0{\cdot}05, \quad m_2/m_0 = 1{\cdot}00, \quad m_3/m_0 = 0{\cdot}52, \quad m_4/m_0 = -0{\cdot}65.$$

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* It is of course possible that it is the experimental value which is at fault in being reduced by some of the factors discussed on pp. 28, 29, and, indeed, in the run of 28 February 1951 the amplitudes were about double those observed in the later runs.

The relative amplitudes agree qualitatively with the theory, as can be seen from figure 15, where the experimental amplitudes are shown together with the theoretical relative values calculated on the assumption that x does not change with orientation. The experimental values are rather rough when beats occur (e.g. a, $\psi = 125°$; c, $\psi = 105°$ in figure 13), and, moreover, were not always reproducible from one experiment to another to better than a factor 2, and exact agreement with theory would in any case be unlikely, first because the assumption of a constant x is probably unjustified and secondly because, as in gallium and tin, it is improbable that the theoretical formulae as they stand should completely account for the variation of amplitude with orientation. The satisfactory feature of the qualitative agreement is that the experimental values of a become small at just the orientations where the relevant Δm's of (15), (17) and (19) vanish, thus confirming in an independent way that our choice of mass ratios is sound.

Finally, the present results may be compared briefly with the single curve recently published by Verkin *et al.* (1951 *a*) for $\psi = 53°$ and a binary axis vertical at 2·04° K. The period of this curve agrees well with the period interpolated from our data, and the amplitude is of the order of magnitude to be expected on the basis of our data, so the agreement can be considered as satisfactory. Their qualitative account of the behaviour at other angles ψ is also in general agreement with our own observations.

Aluminium

Aluminium is the first metal of cubic symmetry in which the de Haas-van Alphen effect has been observed. A selection of representative curves for the crystal suspended with a cube axis vertical is shown in figure 16, and it can be seen that the effect varies in a complicated way with ψ, the angle between the field and a tetrad axis. In terms of any reasonably simple representation by ellipsoids—as in the metals already discussed—the features of this effect should vary only slowly as the field direction moves away from an axis of symmetry, since the period, for instance, is usually predominantly determined by $\cos^2\psi$. In aluminium, however, it can be seen that the curve for $\psi = -4{\cdot}8°$ is drastically different from that for $-0{\cdot}8°$. This very rapid variation of the behaviour with angle is even more strikingly brought out in the bottom left-hand curve where the variation of couple with ψ for a fixed field is shown; it can be seen that the region over which the couple increases proportionally to $\sin\psi\cos\psi$ (i.e. to ψ for the small angles concerned) is only about 1° wide, and it was found that where the couple becomes small (e.g. for $\psi = 2{\cdot}5°$) it is not merely that the couple happens to be small for the particular field chosen, but that it is small at all fields. It is rather as if the whole effect were modulated by a factor which passed through zero and changed sign every few degrees. This complicated behaviour made the precise magnetic determination of the orientation of the tetrad axis rather difficult, since the de Haas-van Alphen amplitude vanished for several directions of the field within the possible uncertainty of the direction of the tetrad axis as determined by the optical method. In each series of measurements it was in fact necessary to measure a rotation curve such as that of figure 16 and choose the origin of ψ in such a way that the curve for negative ψ was the image of the curve for positive ψ after reflexion in both the axes of ordinates and abscissae.

Within the small region where the couple increases linearly with ψ the curves of C/H^2 against $1/H$ have the usual sinusoidal form, but at larger angles complicated modulations

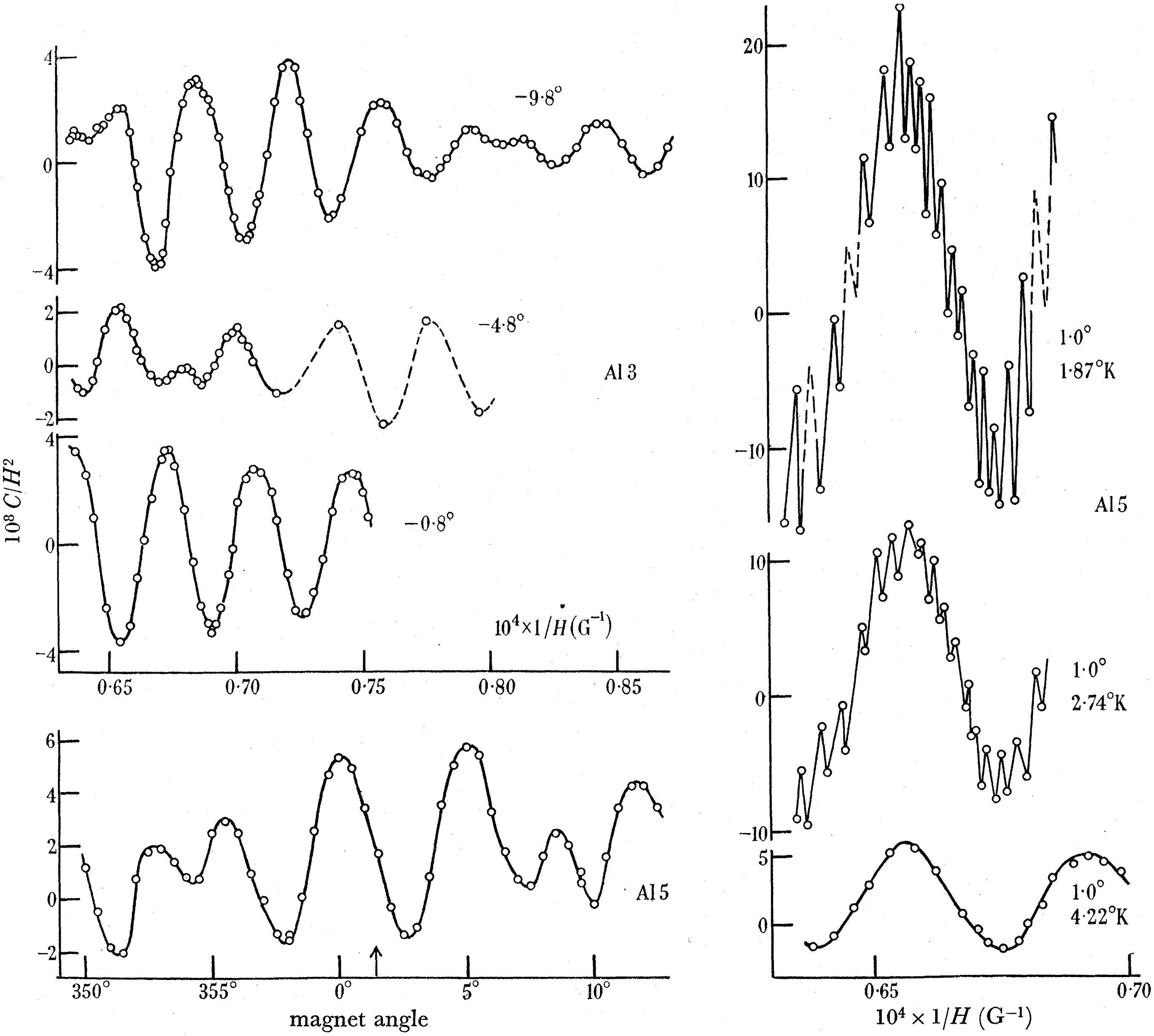

FIGURE 16. Aluminium: variation of C/H^2 with $1/H$, at 4·22° K except where indicated. The bottom left-hand diagram shows the variation of C/H^2 with the angle of rotation of the magnet for $1/H = 0{\cdot}67 \times 10^4$; from the symmetry of this curve the origin of ψ (i.e. the position of the magnet for which the field lies along a tetrad axis) is determined, as marked by the arrow. The sign of ψ has been chosen arbitrarily but consistently; thus it should be noticed that the curves for $\psi = -0{\cdot}8°$ and $\psi = 1{\cdot}0°$ may be brought into approximate coincidence by changing the sign of C/H^2 in one of them. The details of the high-frequency ripple at low temperatures could not be very accurately established and are indicated only schematically, though the experimental points are intended to be maxima and minima. The mean level of the oscillations, which, since aluminium has no steady anisotropy, should always be zero, is actually only approximately zero because of the magnetic anisotropy of the mounting, which produces a value of C/H^2 dependent on both H and ψ.

appear, and the oscillations over the limited range of $1/H$ which would be used in practice cannot be readily analyzed into periodic terms. It is not impossible that an interpretation in terms of many ellipsoids may ultimately prove possible, but a considerably more detailed investigation will be required. Before discussing some of the quantitative aspects of the curves a qualitative feature must be pointed out. This is the presence of a high-frequency ripple which is prominent at low temperatures (see the right-hand curves of figure 16), but can be just noticed if specially looked for even at 4·2° K; a similar feature has already been pointed out in gallium (see p. 11). This ripple increases the difficulties (already considerable because of eddy current effects) of obtaining significant experimental results, since the experimental points must be taken at very close intervals to give a reliable curve.

From the period (which was accurately reproduced as between the two crystals Al 3 and Al 5 for $|\psi| \sim 1°$), we obtain $\beta/E_0 = 3{\cdot}6 \times 10^{-6}$, while the period of the ripple (assuming this is associated with independent values of β and E_0 distinguished by dashes) is $\beta'/E_0' = 2{\cdot}7 \times 10^{-7}$, and it may be noted that the ripple period increases slightly with ψ up to about $3{\cdot}5 \times 10^{-7}$ at $\psi = 20°$ (the accuracy is not sufficient to make any detailed analysis profitable). The usual procedure for determining β from the temperature variation gives $\beta = 2{\cdot}2 \times 10^{-19}$, so that the effective mass m involved, for the field close to a cube axis, is given by

$$\frac{m}{m_0} = \frac{\beta_0}{\beta} = 0{\cdot}082, \quad \text{and} \quad E_0 = 6{\cdot}1 \times 10^{-14}\,\text{erg}, \quad T_0 = 440°\,\text{K}.$$

For the ripples a similar, though rather rougher, analysis gives $\beta' \sim 1{\cdot}2 \times 10^{-19}$, so that

$$\frac{m'}{m_0} = \frac{\beta_0}{\beta'} \sim 0{\cdot}15, \quad E_0' \sim 45 \times 10^{-14}\,\text{erg}, \quad T_0 \sim 3200°\,\text{K}.$$

No useful analysis can be made at present of the field variation since, owing to the difficulties of measurement, none of the curves has been extended to low enough fields, and discussion of the absolute amplitudes is likewise unprofitable in the absence of any guiding scheme. It is, however, worthy of comment that the absolute amplitudes of $\Delta\chi$ (i.e. of $C/H^2 \sin\psi \cos\psi$), for small ψ at least, are high compared with those for most of the other metals studied. It should also be mentioned that in one series of measurements where the tetrad axis was deliberately set 3° off vertical, the amplitudes both of the main oscillations and the ripples were considerably reduced (by about 40 %).

Cadmium and indium

The de Haas-van Alphen effect in cadmium and indium was discovered in December 1949 when the new apparatus was first installed, but since it was evident that a full investigation would be very difficult because of the extremely short periods and low amplitudes, only rough preliminary measurements were made. Soon afterwards it was learnt that (apparently a month or two earlier) Verkin *et al.* (1950*a*) had also found the effect in cadmium and indium, and to avoid duplication no further experiments were made on these metals; a fuller account of the Russian work (Verkin *et al.* 1950*b*) has since appeared.

In cadmium the effect was observable only at the lowest temperatures (below about 1·5° K) and only for small values of ψ (below 35°). The period was extremely short, only $1{\cdot}94 \times 10^{-7}$ for $\psi = 10°$; for higher ψ there was evidence that the period decreased slightly, but the range of ψ over which accurate data could be obtained was too small to make any useful analysis possible. From the temperature variation of the amplitude between 1·55 and 1·15° K the effective β could be estimated as

$$\beta = 4{\cdot}5 \times 10^{-20}, \quad \text{so that} \quad \frac{m}{m_0} = \frac{\beta_0}{\beta} = 0{\cdot}4.$$

Combining this result with the value of β/E_0 from the period, we have also

$$E_0 = 23 \times 10^{-14}\,\text{erg}, \quad T_0 = 1700^\circ\,\text{K}.$$

The amplitudes of the oscillations of $\Delta\chi$ (defined as half peak-to-peak) were very small, as indicated in table 6. Verkin *et al.* (1950*b*) mention only one curve, for $\psi = 7^\circ$, at 1·84° K; their period agrees very well with that given here, but their amplitude is very much greater—about 20 times according to a rough extrapolation to the present conditions. We have seen in the discussion on tin that there may be several causes for a reduction in amplitude, owing to unsuitable experimental conditions, particularly when, as here, the period is very short; an X-ray examination showed that the crystal was far from perfect (the Laue spots were very smeary), and, moreover, the crystal was about 5 mm in its linear dimensions, so the smearing effect of field inhomogeneity may have been appreciable, especially as no special precautions were taken to mount the crystal exactly centrally.

TABLE 6. SUMMARY OF DATA ON CADMIUM

		$a \times 10^9$	
ψ	$\beta/E_0 \times 10^7$	1·15° K	1·55° K
10	1·94	8·7	2·5
20	1·90	7·1	
25		1·6	
35		0·8	

Note. 2 December 1949; the absolute values of a are not reliable to better than 10 % owing to an instrumental fault; they refer to $1/H = 0{\cdot}65 \times 10^{-4}$.

The character of the effect in indium was similar to that in cadmium, except that the effect appeared to be most marked perpendicular to the tetragonal axis and to become unobservable for angles ψ less than about 60°. The scanty data taken (table 7) show that the period varies roughly as $\sin\psi$, and that for $\psi = 90^\circ$ the period would be $2{\cdot}25(\pm 0{\cdot}05) \times 10^{-7}$. From the temperature variation of amplitude, the value of the effective β was deduced as

$$\beta = 5{\cdot}9 \times 10^{-20}, \quad \text{so that} \quad \frac{m}{m_0} = \frac{\beta_0}{\beta} = 0{\cdot}3,$$

and from the period we find

$$E_0 = 29 \times 10^{-14}\,\text{erg}, \quad T_0 = 2100^\circ\,\text{K}.$$

The amplitudes were again rather small and, as can be seen from table 7, do not always have the same values for $\pm\psi$ as crystal symmetry would demand; this is probably because the amplitudes are very sensitive to the exact orientation of the crystal. The amplitudes were in fact considerably modified when the tetragonal axis and a binary axis* were set more nearly horizontal and vertical respectively after the first experiment in which they were 15 and 12° off these directions respectively. Verkin *et al.* find the effect for small rather than large

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* The binary axis referred to here and in table 7 is the one along which the spacing is 3·26 Å.

values of ψ, but since their periods for $\psi = 8{\cdot}5$ and $18{\cdot}5°$ agree well with the periods obtained in this work for the complementary angles, it is likely that either in the present work or in theirs the tetragonal axis has been wrongly identified. This interpretation is confirmed by the fact that opposite signs are found for the steady anisotropy (see table 11), and since the present sign is confirmed by Verhaeghe, Vandermeerssche & Le Compte (1950) it is probable that the mistake is not in the present work. As with cadmium the Russian results indicate a much larger amplitude than in the present work (something like 5 or 10 times); this discrepancy is probably due more to the large size (about 1 cm length) of the present specimen than to the quality of the crystal, since the Laue spots were considerably better than in cadmium.

Table 7. Summary of data on indium

		$a \times 10^9$				
ψ	$\beta/E_0 \times 10^7$	1·1° K	1·15° K	1·25° K	1·3° K	1·8° K
6 December 1949; tetragonal axis 15° off horizontal, binary axis 12° off vertical, ψ measured from projection of tetragonal axis on horizontal plane. The sign of ψ is arbitrary.						
67·5	2·00	6·4				
74		11				
78·5	2·19	23				
84·7		32				
−79·5		12				
9 December 1949; orientation modified to bring tetragonal axis horizontal and binary axis vertical, but uncertain how well this was achieved.						
61·5	no accurate determinations			8·2		
71·7			11·4		9·0	2·4
78·4				9·6		
82·2			9·2		7·8	
−72·7					5·4	
−82·1					16	

Note. Same remarks apply as to table 6.

Mercury

Mercury presents obvious experimental difficulties since there is no simple way of obtaining any particular desired orientation, and, moreover, a crystal cannot be easily preserved from one experiment to another. The procedure adopted was to freeze the mercury slowly by putting liquid air in the outer Dewar vessel of the apparatus, the inner Dewar being 'soft', and then to observe the anisotropy at 80° K. The largest possible anisotropy occurs if the trigonal axis is horizontal, and in the experiments with the old apparatus where several freezings were made, a highest value of $C/H^2 \sin\psi \cos\psi = 0{\cdot}095 \times 10^{-7}$ was found (see table 11), which therefore represents a lower limit to the value of $|\chi_{\parallel} - \chi_{\perp}|$; at that time no de Haas-van Alphen effect was found, partly because of the limitations of the equipment and partly because the right technique of observation had not yet been developed. In the more recent experiments (Shoenberg 1951 *b*) several freezings were tried, but in none of them was a value of $C/H^2 \sin\psi \cos\psi$ found as high as the earlier value; it would seem therefore either that the specimen was not a single crystal or that the trigonal axis was inclined to the horizontal. If the latter hypothesis is assumed (the absence of beats in the de Haas-van Alphen effect is evidence against the former), it can be concluded that in the two experiments in which the de Haas-van Alphen effect was studied the inclinations to the horizontal were 55 and 30°. As the magnet is rotated, one of the two mutually perpendicular directions of the field for which the couple at 80° K vanishes gives the direction of the projection of the trigonal axis on the horizontal plane, though which of the two cannot be decided in this way; ψ was measured from one of these directions chosen arbitrarily.

For none of the orientations studied did the de Haas-van Alphen effect show any beats, and the amplitude of the oscillations of the couple did not vanish for either $\psi = 0$ or $90°$, which is not surprising in view of the arbitrariness of the orientation. In the absence of any knowledge of the direction of the binary axes, nothing quantitative can be deduced from the variation of the period with ψ without guesswork, so the experimental data are summarized in table 8 merely to give a general idea of the observed features, and only the information for the particular orientation $\psi = 28°$, which was more thoroughly studied, is discussed quantitatively; the curves for this orientation are shown in figure 17. From the period we have $\beta/E_0 = 1{\cdot}33 \times 10^{-6}$, while from the temperature variation we find

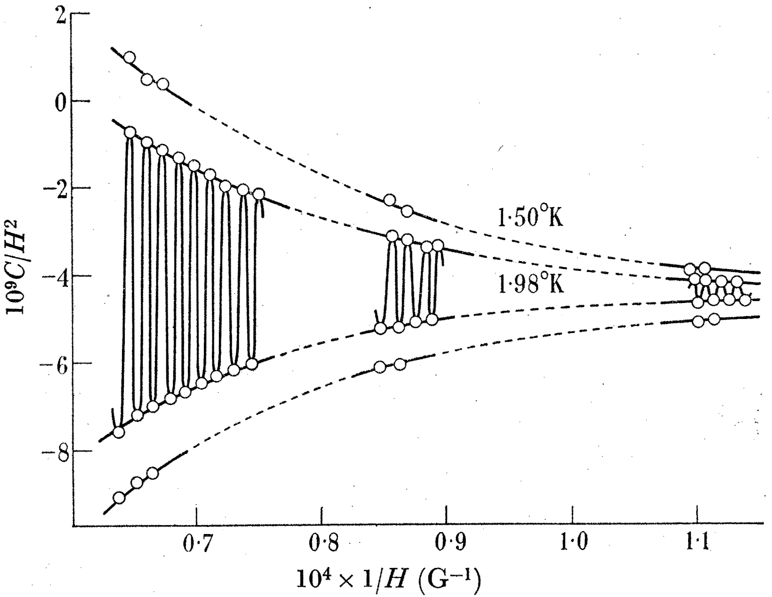

FIGURE 17. Mercury: variation of C/H^2 with $1/H$ for $\psi = 28°$. Since the definition of ψ is somewhat arbitrary, the sign of C/H^2 is also arbitrary. Only the envelope of the oscillations is indicated at the lower temperature.

$$\beta = 1{\cdot}21 \times 10^{-19}, \quad \text{so that} \quad \frac{m}{m_0} = \frac{\beta_0}{\beta} = 0{\cdot}15$$

and
$$E_0 = 9{\cdot}1 \times 10^{-14}\,\text{erg}, \quad T_0 = 660°\,\text{K}.$$

As is indicated in table 8, very similar estimates of E_0 were obtained also from the temperature variation of amplitude at several other orientations. From the field variation at 1·98° K we find $x = 1{\cdot}62°$ K, while at 1·50° K $x = 1{\cdot}47°$ K. Although the difference is hardly outside experimental uncertainties, it is just possible that x increases with temperature on account of the rise of electrical resistance of mercury with temperature (for all the other metals studied the electrical resistance is, apart from superconductivity, entirely constant in the liquid helium range).

TABLE 8. SUMMARY OF DATA ON MERCURY

13 July 1951; trigonal axis estimated (but not reliably) to be at 56° to horizontal: angles ψ from one of the zero positions of the steady anisotropy (determined to within only a few degrees).

ψ	5	15	30	45	52	60	65	90	100
$\beta/E_0 \times 10^7$	9·5	9·0	12·3	13·0	13·3		13·0	11	12·5
$a \times 10^9$ at 1·95° K	0·4	0·3	1·2	1·6	1·0	0·3	0·8	1·0	0·6

18 July 1951; recrystallized since 13 July; trigonal axis estimated (but not reliably) to be at 30° to horizontal, angles ψ measured from one of the zero positions of the steady anisotropy, more precisely than on 13 July.

ψ	−12	−15	−1	3	13	28	38	43	45	48	58	73	83	90
$\beta/E_0 \times 10^7$	10·5	10·5	9·7	10·2	11·5	13·3	14	13·8	12	13·7		12·2	11·0	10·0
$a \times 10^9$:														
1·15° K	0·8	1·1			6·1	5·7				1·3			4·6	
1·5° K			2·5	2·5		4·8				0·8			2·6	
1·97° K			1·35	1·2	2·9	3·2	1·5	0·5	0·1	0·6	2·1	2·4	1·35	0·6
$\beta \times 10^{20}$			9·2	8·3	11·3	12·1				12·0			8·8	
$E_0 \times 10^{14}$			9·5	8·1	9·8	9·1				8·8			8·0	

Note. All values of a refer to $1/H = 0{\cdot}65 \times 10^{-4}$ and refer to $|C/H^2|$; the lowest temperature is only rough (it was near 1·12° K for $\psi = 28°$, and 1·17° K for $\psi = 83°$). The values of β are not very accurate, since where three points were available the log plots were not quite linear; thus the values of E_0 can be considered as agreeing within experimental error.

Thallium

The specimen used was probably not a single crystal, but since several attempts to produce a good single crystal were unsuccessful, and it is unlikely that any further experiments will be made for some time, it is worth while summarizing the results obtained on this specimen (mentioned in Shoenberg 1951 *b*), though their significance can be only qualitative. As can be seen from table 9, in which ψ refers to the angle between the field and one of the positions at which the couple vanishes at high temperatures, the amplitudes were very small, and, indeed, the long-period oscillations for low values of ψ were discovered only after the results had been plotted graphically; some of the results are illustrated in figure 18. The amplitudes were very small and became inappreciable above 1·5° K, so that only a very rough determination of β was possible; for $\psi = 78°$,

TABLE 9. SUMMARY OF DATA ON THALLIUM

ψ	$\beta/E_0 \times 10^7$	$a \times 10^9$
18	38	0·8
28	46	1·9
38	36·5	1·9
73	4·86	0·8
78	4·7	0·8
88		< 0·5

Note. 25 July 1951; ψ measured from what was thought to be the hexagonal axis, but probably was an arbitrary direction; absolute values of $a(=|\Delta\chi|)$ rather rough: all refer to about 1·15° K and $1/H = 0{\cdot}65 \times 10^{-4}$.

$$\beta = 5{\cdot}1 \times 10^{-20}, \quad \text{so that} \quad m/m_0 = \beta_0/\beta = 0{\cdot}35,$$

and from the period we have

$$E_0 = 11 \times 10^{-14}\,\text{erg}, \quad T_0 = 800°\,\text{K}.$$

Metals not showing the de Haas-van Alphen effect

A number of other metals was investigated for which no de Haas-van Alphen effect was found, and the results are summarized in table 10. For cubic metals of course no anisotropy is possible as long as the magnetization varies linearly with field, so that a de Haas-van Alphen effect must always show up directly as an oscillating couple, and not merely as an oscillation in the value of the couple divided by H^2. An upper limit to the amplitude of any possible oscillations is therefore easily assessed in terms of the steadiness of the zero deflexion (actually there is a slight deflexion due to the slight anisotropy of the mounting, arising from small ferromagnetic inclusions). For tellurium, the only non-cubic crystal studied which has not shown the effect, the upper limit given in table 10 refers to oscillations of period sufficiently short to show up directly as oscillations of the couple; long-period oscillations of small amplitude, such as were observed in thallium for small ψ, might have been missed. In any case the tellurium specimen was probably not a very good single crystal, so the negative result should not be regarded as conclusive.

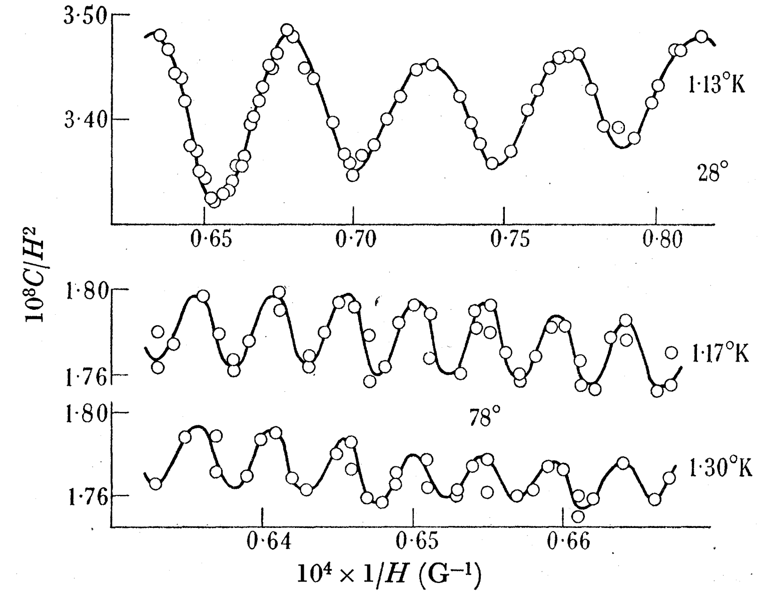

FIGURE 18. Thallium: variation of C/H^2 with $1/H$ for $\psi = 28°$ and $78°$.

TABLE 10. NEGATIVE RESULTS

metal	orientation	T (°K)	upper limit to $\lvert\Delta\chi\rvert$ for $1/H = 0{\cdot}65 \times 10^{-4}$
Pb	{110} plane horizontal	1·1	2×10^{-10}
Te	hexagonal axis horizontal	1·3	3×10^{-11}
Ge	{110} plane nearly horizontal	1·3	5×10^{-11}
Cu	{100} plane horizontal	1·3	2×10^{-10}
Ag	{100} plane horizontal	1·3	2×10^{-10}
Au	{100} plane horizontal	1·3	1×10^{-10}

It should be noticed that in going from the preliminary experimental conditions in which fields of only 9500 G were available, to the better set-up with fields up to 15800 G, several metals (antimony, cadmium, indium, mercury, thallium) which appeared at first to give negative results have proved to have in fact a quite marked de Haas-van Alphen effect. From a purely empirical point of view this suggests that a further increase of field to, say, 30000 G might well show up the effect in some of the metals listed in table 10 as giving negative results. According to the theory for an ideally free electron gas, an effect should show up appreciably only at very much higher fields, of the order of 100000 G, and the period would then be of the order of 50 G, so very special experimental conditions would be necessary to observe it. Since we should expect that this 'ideal' theory would apply at least qualitatively to metals such as copper, in which the Fermi surface does not cross any Brillouin zone boundaries, it would in fact be surprising from a theoretical point of view if any appreciable de Haas-van Alphen effect were observed with such metals at fields much less than 50000 G.

The steady anisotropy

The steady anisotropy of most of the specimens was measured at room temperature (say 290° K), at 80 and at 4·2° K, and the data obtained are summarized in table 11 and compared with some other determinations where they exist. Except for mercury, no correction has been applied for any couple due to the empty mounting which is, of course, irrelevant for the oscillating part of the anisotropy; this couple, probably due to ferromagnetic contaminations, was usually appreciable but varied from one experiment to another, so that neglect of it leads to an error which has not always the same magnitude. It is unlikely that this error ever exceeded $0{\cdot}1\times10^{-7}$ in $\Delta\chi$, and in mercury, since it was comparable to $\Delta\chi$ itself, it was eliminated by careful study of the magnetic properties of the empty mounting; for tin the steady anisotropy of the crystal appeared to be small compared with that of the empty mounting, so only an upper limit is quoted. Bearing in mind the experimental inaccuracies, and the possible sensitivity of the susceptibility to impurities (e.g. note the appreciably different temperature dependence of $\Delta\chi$ in In 1 and In 2), the present results agree fairly well with previous determinations where they exist. The exceptions are: (*a*) indium, where there is a difference of sign, which suggests a mistaken identification of the tetragonal axis either in both the present work and that of Verhaeghe *et al.* (1950) or in that of Verkin *et al.* (1950) (see p. 44); (*b*) thallium, providing further evidence that our specimen was not a single crystal; and (*c*) tellurium, where a large ferromagnetic correction had to be applied and it is moreover not impossible that the specimen was not a single crystal.

Where the data permit, an estimate has been made of how big the steady anisotropy should be on the basis of the theoretical formula and the experimental values of the amplitude of the oscillatory part. As far as the contribution of any one ellipsoid is concerned, the ratio of the oscillatory to the steady part should be

$$\frac{6}{\pi^{\frac{3}{2}}}\left(\frac{2\pi^2kT}{\beta H}\right)\left(\frac{2\pi E_0}{\beta H}\right)^{\frac{1}{2}}\exp\left[-\frac{2\pi^2k(T+x)}{\beta H}\right]. \tag{23}$$

The results listed in table 12 show that (23) leads to estimates which are sometimes of nearly the right order of magnitude. To some extent the discrepancies may be attributed to the unreliability both of the experimental values of absolute amplitude and of the theoretical formula; however, in spite of these uncertainties, it is probable that the main cause of the discrepancies is the one suggested by Blackman (1938), that parts of the Fermi surface which do not contribute appreciably to the de Haas-van Alphen effect may contribute appreciably to the steady susceptibility. Such additional contributions may either increase the calculated steady anisotropy (as presumably in bismuth, zinc, antimony and graphite) or decrease it by making the two principal susceptibilities more nearly equal (as presumably in the *bc*-plane of gallium, and in tin and mercury). The marked temperature-dependence of the steady anisotropy of antimony, mercury and gallium far below room temperature supports this point of view. No such dependence would be expected so far below the degeneracy temperature T_0, which, as found from the de Haas-van Alphen effect, appears to be 1300° K for antimony, 650° K for mercury and 740° K for the relevant ellipsoid in gallium, so it is improbable that the observed temperature-dependence can be associated with the same electrons as cause the de Haas-van Alphen effect. For graphite, Ganguli & Krishnan (1941) conclude from analysis of the temperature variation of the steady anisotropy that

TABLE 11. VALUES OF STEADY ANISOTROPY $\Delta\chi\times 10^7$

specimen	room temperature	80° K	4·2° K	other estimates (room temperature except where stated)
Ga 3* *a*−*b*	3·50	2·17		
Ga 3 *a*−*b*	3·44			
Ga 5 *a*−*b*	3·40	2·11	∼1·39	
Ga 4 *a*−*b*	3·45	2·14	∼1·45	
Ga 4 *a*−*c*	1·25	0·99	∼1·54	
Ga 4 *c*−*b*	2·21, 2·29	1·19, 1·22	∼0	
Sn (all specimens)	<0·1	<0·1	<0·1	−0·06 (*m*), −0·03 (*a*)
G 1*	−201	−285		−211 −288 (90° K) (*b*)
G 1	−205→−190	−291	∼−300	
G 4	−227→−194	−325		
Sb 2	−9·7	−12·8	−13·2	−8·7 −11·7 (90° K) (*j*) −12·1 (4·2° K)
Cd 1*	−0·99	−2·60	−5·35 −5·38 at 1·4° K	−1·01 (*d*), −0·60 (*h*), −1·11 (*k*), −1·58 (*m*) −1·0 −6·0 (4·2° K) (*c*), −1·01 −5·49 (14° K) (*e*),
Cd 1			−6·8	
In 1*	−1·0	−3·05	−3·9	1·07 3·45 (78° K) (*m*), −0·60 (*l*) 4·45 (2° K)
In 2*	−0·86	−2·99	−3·87	
In 2	−0·96		−4·22	
Hg 1*	−0·06 (at melting point)	0·073	0·14	0·089 (80° K) (*n*)
Hg 2*		0·095	0·17	
Hg 3*		0·038		
Hg 4 (10 July 1951)		0·060		
Hg 4 (13 July 1951)		0·028	0·06	
Hg 4 (18 July 1951)		0·058	0·109	
Tl 1	∼0·6	0·82	0·88	−2·47 (*i*), −2·56 (*g*), −1 (*k*)
Te 1*	∼0·05	0·032	0·025	0·33 (*f*)
Te 1	∼0·08		0·04	

Notes. $\Delta\chi$ means $\chi_{\parallel}-\chi_{\perp}$ for crystals with only two principal susceptibilities and is as indicated for Ga. For mercury the sign of $\Delta\chi$ is unknown in this work though it is clear that it reverses between 80° K and the melting point. * denotes the preliminary series of experiments in which the suspensions were not very accurately calibrated. In general relative values at different temperatures are more accurate than absolute values; the absolute accuracy is illustrated by the consistency for Ga 4 ($c-b$) of the two determinations with different suspensions. Except for the Hg data of July 1951 no allowance has been made for the magnetic behaviour of the empty mounting. For G 1 and G 4 the effect of allowing for a field variation of $\Delta\chi$ due to ferromagnetic contamination (i.e. extrapolating to zero $1/H$) is indicated by the arrows. A considerable correction of this kind has been applied in the second measurement of Te 1. The second measurements of Cd 1 and In 2 are unreliable to better than 10 or 20 % owing to an instrumental fault.

References: (*a*) Hoge (1935). (*b*) Krishnan & Ganguli (1939), Ganguli & Krishnan (1941). (*c*) Mackinnon (1949). (*d*) McLennan, Ruedy & Cohen (1928). (*e*) Marcus (1949). (*f*) Rao & Govindarajan (1939). (*g*) Rao & Narayanaswami (1938). (*h*) Rao & Sriraman (1938). (*i*) Rao & Subramaniam (1936). (*j*) Shoenberg & Uddin (1936). (*k*) Sydoriak & Robinson (1949). (*l*) Verhaeghe, Vandermeerssche & Le Compte (1950). (*m*) Verkin, Lazarev & Rudenko (1950*b*). (*n*) Vogt (1934).

T_0 is 550° K, while the de Haas-van Alphen effect indicates only 170 and 115° K for the two relevant ellipsoids; here again, then, it is probable that different groups of electrons are relevant in the steady and the oscillatory effects.

TABLE 12. COMPARISON OF CALCULATED AND OBSERVED STEADY ANISOTROPY

specimen	ψ	T (°K)	$1/H \times 10^4$	theoretical ratio of oscillatory amplitude to steady anisotropy	contribution to steady anisotropy $\Delta\chi \times 10^7$	observed value of $\Delta\chi \times 10^7$ (table 11)
Ga 4 *ab*	78·9	4·22	0·65	1·8	1·0	1·4
bc	80	4·22	0·65	2·0	1·0	0
Sn 8	11·2	4·22	0·65	0·6	0·7	< 0·1
G 1	20	1·27	1·1	0·73 0·4 to 2·3	34 4 to 26	290
Sb 2 (binary axis horizontal)	26·5	1·5	0·65	0·7	0·7	13·2
Hg 4 (18 July 1951)	28	1·98	0·65	0·3	0·27	0·06

Note. For G 1 the lower figures refer to the subsidiary ellipsoid: the limits correspond to the alternative assumptions $x = 1{\cdot}5$ and $x = 0$.

Experiments on tin alloys and the interpretation of x

If the collision time τ of equation (6) has the same order of magnitude as the collision time which enters into the well-known formula for electrical resistivity:

$$\rho = mc^2/ne^2\tau, \tag{24}$$

we should expect x to vary in direct proportion to ρ if slight impurities are added to a pure metal, provided the other parameters such as β and E_0 are not appreciably affected. A series of experiments on the de Haas-van Alphen effect was accordingly carried out on alloys of tin with small admixtures of mercury and indium. For each alloy crystal, curves of anisotropy as a function of $1/H$ were taken at 4·22° K and a low temperature—usually about 1·5° K—and from a comparison of the field and temperature variations, values of x were obtained. It was found that neither the period (i.e. β/E_0) nor β itself, as deduced from the temperature variation, showed any appreciable systematic variation with the degree of contamination, so the conditions for a crucial test of equation (6) were satisfied. In the final estimations of x, however, the more accurately determined value of β for pure tin was used, rather than the values which could be estimated for the individual alloys, since the amplitudes at 4·22° K for the most contaminated specimens were very small, and only rough estimates of β could be obtained. Most of the alloys showed (though to a lesser extent) the modulations characteristic of pure tin and, as for pure tin, 'smoothing' was adopted to estimate the field variation.

In the preliminary experiments it was hoped to use the data of Hulm (1950) on the variation of resistivity with mercury concentration, but it early became apparent that it was quite impossible to assume that the mercury concentration in the crystals was at all the same as that put into the original alloy from which the crystal was grown; thus if x was plotted against nominal concentration, not only were the points badly scattered, but they did not even indicate any monotonic behaviour. It was thought likely that mercury had been lost to a varying extent by the different specimens, and this was in fact later confirmed by direct chemical analysis of some of the crystals. To overcome the difficulty, new crystals were grown taken from the middle portion of a long wire of the alloy arranged as shown in figure 19, so that the remaining portions on either side could be used for resistance measurements. In this way for each new crystal a reliable value of R/R_0 was obtained, where R is the residual resistance, measured at 4·22° K, and R_0 the resistance measured at room temperature. For the most contaminated alloys it was found that the transition to superconductivity (normally occurring at 3·73° K) was so smeared out that the resistance at 4·22° K was already less than the residual resistance, owing to incipient superconductivity; this was dealt with by applying a magnetic field large enough to restore a value of the resistance which was field- and temperature-independent and therefore assumed to be the residual resistance. In view of the difficulties of working with mercury alloys it was decided to try also some indium alloys, and these in fact proved much simpler to work with, since R/R_0 varied linearly with the nominal concentration.

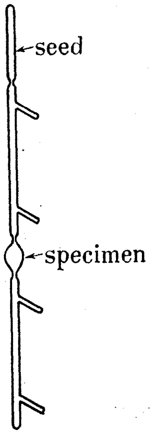

FIGURE 19. Method of preparing tin alloy crystal: after crystallization from the seed, the specimen was cut away at the two constrictions, leaving single-crystal wires of the same orientation on either side, provided with potential leads for resistance measurements.

The final results are shown in table 13 and figures 20 and 21. It can be seen that, apart from the single point for Sn 5, the values of x for both the mercury and the indium alloys fall roughly on a single straight line, if plotted against R/R_0. The linearity of the plot supports Dingle's theory that x is to be ascribed to collision broadening, and it is very satisfactory that the value of τ_0, the collision time at room temperature, deduced from the slope, $h/2\pi^2k\tau_0$ comes out to be $1{\cdot}5\times10^{-14}$ s, which compares well with the order of magnitude estimate 10^{-14} s, which can be deduced from the work of Pippard (1947) and Chambers (1950) if a plausible estimate of the electron velocities is made, or from the resistivity using equation (24) and assuming one electron of normal mass per atom.

The point which falls particularly badly off the plots of figures 20 and 21 is probably due to an imperfect crystal. To investigate this, Laue X-ray photographs were taken of most of the specimens (with the X-ray beam falling on several different areas of each crystal), and it did indeed turn out that Sn 5 consisted of two distinct crystals, each with its tetragonal axis horizontal but inclined at several degrees to each other. Thus the observed curves could very well have been smeared out, producing not only an abnormally low amplitude but also a high value of x. The scatter of the other points, particularly in figure 21, may also be due to varying degrees of imperfection (as discussed on p. 29), but though several of the crystals did give rather streaky Laue spots, indicating distortion, it did not prove possible to correlate the distortion with the absolute amplitudes or the x values in full detail.

In figure 21 the absolute amplitudes are plotted logarithmically against R/R_0, and though, on account of the irreproducibility of absolute amplitudes already discussed on p. 28, the scatter of the points is even worse than in figure 20, it can be seen that a straight line of slope $-h/\beta H\tau_0\log_e 10$ does not fit too badly, if τ_0 is given the value found from figure 20. There is some indication that the points for the indium alloys lie systematically below those for the mercury alloys, but it is not clear whether this has any fundamental significance or is merely accidental.

Although the changes of x with impurity are in good qualitative agreement with the view that x changes linearly with $1/\tau$, the fact that the linear plot of figure 20 does not pass through the origin shows that part of x must be due to some other cause than collision broadening, for if x was due to collision broadening alone it should vanish with R/R_0. The residual value of x—about 1° K—must be due to other causes and Dingle has suggested that it might be associated with a broadening of the energy levels caused by the lattice electric field; no quantitative development of this suggestion has yet been made.

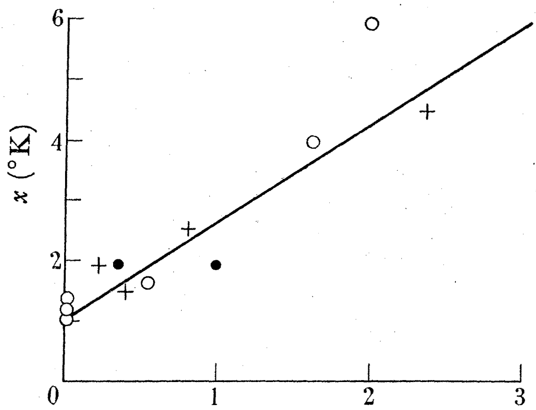

FIGURE 20

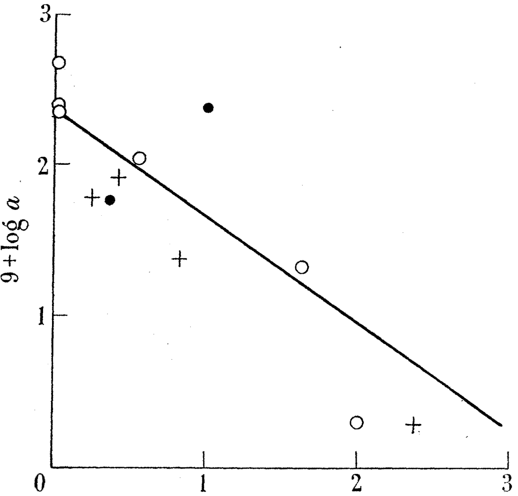

FIGURE 21

FIGURE 20. Variation of x with R/R_0 for the tin alloys: ○, alloys with mercury; ●, alloys with mercury, but R/R_0 determined by interpolation based on chemical analysis; +, alloys with indium. The slope of the straight line gives $h/2\pi^2k\tau_0$, where τ_0 is the collision time at room temperature.

FIGURE 21. Variation of $\log_{10} a$ (a at $1/H = 0{\cdot}65 \times 10^{-4}$ and $T = 1{\cdot}5$°K) with R/R_0 for the tin alloys; notation as in figure 20. The straight line is drawn with slope $-h/2{\cdot}3\beta H\tau_0$, assuming the value of τ_0 deduced from figure 20.

TABLE 13. VALUES OF AMPLITUDE AND x FOR TIN ALLOYS

	composition						
specimen	% Hg	% In	$R/R_0 \times 10^2$	ψ	$a \times 10^8$	$9+\log_{10} a$	x (°K)
Sn 3	pure		0·02	11	25	2·40	1·4
Sn 8	pure		(0·02)	11·2	23	2·36	1·0
Sn 9	pure		(0·02)	10·9	48	2·68	
Sn 4	< 0·04		(∼0·02)	11	25	2·40	1·2
Sn 12	(0·61) 0·07		(0·36)	10	5·9	1·77	1·9
Sn 15	(0·61) 0·08		0·55	10	11·3	2·05	1·6
Sn 7	(0·3) 0·19		(1·0)	12·5	24	2·38	1·9
Sn 16	(1·87) 0·37		1·63	11	2·1	1·32	4·0
Sn 5	(0·75) 0·34		2·0	10	0·2	0·30	5·9
Sn 17		0·05	0·24	10	6·2	1·79	1·9
Sn 18		0·08	0·41	10·3	8·2	1·91	1·5
Sn 19		0·20	0·82	9·6	2·4	1·38	2·5
Sn 20		0·53	2·37	11·4	0·19	0·28	4·5

Note. For the Hg alloys the compositions in brackets are the nominal ones; the second figure gives the composition as determined by chemical analysis. For the indium alloys only the nominal concentration (probably close to the truth) is given. The values of R/R_0 in brackets were not determined directly, but obtained by interpolation of the relation between R/R_0 and concentration. The values of a have been adjusted to give amplitudes (as defined in table 4) at 1·5°K; most of them were in fact measured close to this temperature but Sn 9 was measured at 1·78°K and Sn 18 at 1·15°K.

For the other metals for which x was determined (gallium, mercury, antimony and graphite) the determination was made only for the pure metals, and for gallium and mercury as well as tin it is fairly clear that x is too large to be accounted for by collision broadening alone. Thus the values of x for pure tin, gallium and mercury are all about 1° K, which according to equation (6) would imply a collision time of about 2×10^{-12} s, while the resistivities at low temperatures* indicate collision times of order 10^{-10} s if equation (24) is used and one electron of normal mass per atom is assumed. This assumption may well be unreliable (though it does appear to be right for tin), and moreover, the collision time that enters into Dingle's theory is rather differently defined from that which enters into the resistivity, but it is unlikely that a discrepancy of a factor of order 50 in the collision time can be accounted for in this way. For antimony there are no suitable data on low-temperature resistivity so no comparison can be made. For graphite a value $\rho\sim4\times10^{-6}$ ohm cm at 4·2° K was obtained in the hexagonal plane of specimens similar to G 1 and G 4 (Goodman, private communication; Kinchin, private communication). This would give $\tau = 0{\cdot}7\times10^{-14}$ s if the assumption of one electron of normal mass per atom is again made, but for graphite this assumption may be seriously wrong, since probably much less than one electron per atom is effective in conductivity, and the effective mass too may be anomalous. Thus for graphite it is quite conceivable that the collision time deduced from the value of x may prove to be of the same order of magnitude as the resistive collision time, and so collision broadening alone may be adequate to account for the observed value of x. It may also be possible to associate the variation of x approximately as $\sec^2\psi$ with the corresponding variation of resistivity in a graphite crystal, but this is only speculative.

Finally, it should be pointed out that our analysis of the field variation has been based on a rather limited range of fields, and the particular theoretical form of field variation assumed cannot be regarded as proved experimentally. Indeed, the introduction of the exponential factor $e^{-2\pi^2kx/\beta H}$ depends on special assumptions about the nature of the level broadening, which may prove to be too simple. Since the value of x determined from the data depends crucially on the theoretical formula used, it is not impossible that in some modified theory the values of x for the pure metals might become much smaller, so that appeal to other causes of level broadening might become unnecessary.

CONCLUDING DISCUSSION

A summary of the values of the effective masses and degeneracy temperatures deduced for the various metals is presented in table 14. Included also in this table are the results for bismuth and zinc recalculated to take account of the energy-level broadening parameter x; it may be mentioned that introduction of the parameter helps considerably to remove the discrepancies which were previously present. Also analyzed are the few curves given by Verkin *et al.* (1950 *b*) for magnesium and beryllium, though for magnesium, since a curve is given at only a single temperature, only β/E_0 can be deduced.

The number of electrons per atom has been calculated from the formula

$$n = \Sigma\frac{8\pi}{3}\left(\frac{2m'E_0}{h^2}\right)^{\frac{3}{2}}\frac{V}{N}, \tag{25}$$

---

* Resistivity data for specimens of purity comparable to those used in the present experiments may be found for tin and mercury in Andrew (1948) and for gallium in Olsen-Bär & Powell (1951).

TABLE 14. SUMMARY OF RESULTS

metal	effective masses m_1/m_0	m_2/m_0	m_3/m_0	m_4/m_0	typical values of $\beta/E_0\times10^7$	$E_0\times10^{14}$ (erg)	E_0/k (°K)	n per atom
Cubic								
Al	0·08				36	6	430	
	0·15				2·7	45	3200	
Tretragonal								
Sn	0·10		~ 2		2 to 6	31	2250	$1{\cdot}5\times10^{-3}$
In	0·3				2	29	2100	
Orthorhombic								
Ga (*a*)	$>0{\cdot}2$	$>0{\cdot}15$	$<0{\cdot}05$		20	10	430	$>0{\cdot}3\times10^{-4}$
(*b*)	0·1	0·3	0·03		30	11	740	$0{\cdot}4\times10^{-4}$
(*c*)	0·2	0·02	0·4		50	6	800	$0{\cdot}7\times10^{-4}$
							total	$>1{\cdot}4\times10^{-4}$
Hexagonal								
C (*a*)	$3{\cdot}6\times10^{-2}$		~ 200		220	2·3	170	$3{\cdot}4\times10^{-5}$
(*b*)	7×10^{-2}		25 to 700		165	1·6	115	$1{\cdot}4$ to 7×10^{-5}
Zn	$5{\cdot}3\times10^{-3}$		0·2		700	4·9	350	$0{\cdot}9\times10^{-6}$
Cd	0·4				2	23	1650	
Tl	0·35				5 to 50	11	800	
Be	0·03				70	8·4	600	
Mg					19			
Rhombohedral								
Bi	$2{\cdot}4\times10^{-3}$	2·5	0·05	$-0{\cdot}25$	200 to 800	2·9	210	$1{\cdot}5\times10^{-5}$
Sb	0·05	1·00	0·52	$-0{\cdot}65$	10 to 16	18	1300	$1{\cdot}1\times10^{-3}$
Hg	0·15				10 to 14	9	650	

Notes. The figures have been somewhat rounded off in the table to avoid giving more significant figures than is justified; where only one effective mass is given (and no entry appears under n) only a partial analysis has been possible and the field direction for which this mass has been obtained is mentioned below. Al: m and β/E_0 are for H along a tetrad axis; the two figures refer to the main and subsidiary oscillations. Sn: m_3/m_0 is a very rough estimate; it is probable that other ellipsoids are present. In: m and β/E_0 are for H nearly along a binary axis; thus if only a single ellipsoid is assumed, $m=(m_1m_3)^{\frac{1}{2}}$. Ga: the figures refer to the three main ellipsoids which are separately important when H is along the a, b or c axes respectively. The masses for c are rough and those for a are little more than guesses; they are given merely to indicate probable orders of magnitude. As explained in the text there are certainly other ellipsoids present. C: (*a*) and (*b*) refer to the two independent ellipsoids; in each case m_3 is deduced from the absolute amplitude assuming the truth of Landau's formula. For (*b*) the procedure is very rough since x can only be guessed; the limits given are for $x=0$ and $x=1{\cdot}5$ (which is the value for (*a*)) and it is probable that $x<1{\cdot}5$. Zn: Mackinnon's (1949) data have been re-evaluated assuming only a single ellipsoid and taking into account the x factor ($x=5{\cdot}5$°K); m_3 is calculated from the absolute amplitude as for C. Cd: m and β/E_0 are for H along the hexagonal axis; if a single ellipsoid is assumed $m=m_1$. Tl: direction of H relative to crystal unknown. Be and Mg: Verkin, Lazarev & Rudenko's (1950*b*) data have been analyzed as far as possible; in both cases H was perpendicular to a binary axis and the angle to the hexagonal axis was 44° for Be and 74° for Mg. For both metals the effect is most marked perpendicular to the hexagonal axis and fades out as ψ is reduced. Bi: Shoenberg's (1939) data has been re-evaluated taking into account the x factor ($x=1{\cdot}5$°K for $\theta=0$ and $x=2{\cdot}2$°K for $\theta=90°$): it should be noticed that a numerical slip occurs in equation (20) of Shoenberg (1939) which should read $n=1{\cdot}7\times10^{-5}$; the modification of taking x into account does not therefore change n much. Sb: as regards the effective masses, only the relative values of m_2, m_3 and m_4 are at all reliable; the periods indicate $m_1/m_3<0{\cdot}2$; while application of Landau's formula to the observed absolute amplitude indicates $m_1/m_3=0{\cdot}4$. Since however this estimate is inversely proportional to the observed amplitude, and this may well be too low on account of non-ideal experimental conditions, the estimate could easily be too high; it might also be too high on account of inadequacy of the theoretical formula. A reasonable guess is $m_1/m_3=0{\cdot}1$ and this leads to the values given in the table; m_1/m_0 is directly proportional to, and the other figures inversely proportional to the square root of the assumed value of (m_1/m_3). Hg: direction of H relative to the crystal axes not reliably known.

where m' is as introduced in equation (2) (see also equations (9) and (21)), V is the atomic volume, N Avogadro's number and the summation is over all the relevant ellipsoids. It can be seen that n is always small and there are several lines of evidence which confirm that it is in fact only part of the free electrons which effectively contribute to the de Haas-van Alphen effect. The evidence from the steady susceptibility has already been discussed, and other evidence comes from the anomalous skin effect (Pippard 1947; Chambers 1950) which suggests that for tin n is of order one electron of normal mass per atom, from the Hall effect, which, except for bismuth and antimony, indicates that for most metals the numbers of electrons and 'holes' are not very much less than one per atom, and from the electronic specific heat. The electronic specific heat per atom is given by

$$c = \frac{\pi^2}{2} nk \frac{T}{T_0}, \tag{26}$$

provided $T \ll T_0$ (T_0 is E_0/k); if n and T_0 have values such as shown in table 14, c comes out of order at least 100 times smaller than if n is taken as one electron of normal mass per atom (this gives $T_0 \sim 10^4$ to 10^5° K), while the experimental values of c usually agree in order of magnitude with this latter assumption. The detailed values of the effective masses and E_0 may prove useful in developing the theory of the electronic structure of the various metals, but will not be discussed here.

The experiments have established that Landau's theoretical formula as modified to take account of level broadening gives a very good general description of the de Haas-van Alphen effect, particularly as regards the analytical form of the oscillations, and even as regards fine details such as the existence of harmonics. The formula is based on the assumption of ellipsoidal energy surfaces in phase space, and though sometimes, as in bismuth and antimony, it is possible to predict in considerable detail on this basis how the effect varies with the orientation of the field relative to the crystal, for some metals such as gallium, aluminium and tin the assumption does not appear adequate, and a more general formulation may be needed. The phase of the oscillations does not appear to be the same in the four metals (gallium, graphite, bismuth and zinc) for which any evidence is available. In gallium and for the main periodic term in graphite the phase angle is nearly in agreement with the prediction of Landau's formula but for the subsidiary periodic term in graphite, and for bismuth and zinc the phase is not correctly predicted. It is not, however, impossible that more refined measurements and proper allowance for the effect of the harmonics in bismuth and zinc (not considered in the original analyses) may modify this conclusion.

Nearly all the questions touched on in this discussion could be settled more definitely if higher magnetic fields were available, and it is in this direction that further research could most profitably be pursued. Thus, at sufficiently high fields other periodic terms might show up, arising from those of the free electrons not causing any appreciable de Haas-van Alphen effect at lower fields; the harmonic terms would show up more strongly at higher fields which would enable the phase question to be studied more precisely, and with a greater range of fields it should be possible to decide more definitely the form of the field dependence. Another important question which might be settled by going to higher fields is the one discussed on p. 48, of whether the 'good' metals such as copper, silver and gold have any appreciable de Haas-van Alphen effect in fields appreciably less than 10^5 G. Experiments at very high fields, i.e. 10^5 G or so, by special methods would of course be particularly valuable in providing a check on the theory of the de Haas-van Alphen effect for such 'good' metals, where the electric field of the lattice might be expected to influence the free electron gas theory least.

My greatest single debt of gratitude is to Mr E. Laurmann, whose willing assistance in preparing the crystals and determining their orientations, in the preparation and conduct of the experiments and finally in the preparation of the diagrams for this paper has been invaluable. My thanks are due also to the following for much valuable help and advice: to Dr R. B. Dingle, Dr E. H. Sondheimer, and Professor L. Onsager for theoretical discussions and advance information about their theoretical work; to Dr A. B. Pippard and Dr F. C. Powell for advice about the analysis of periodic curves, to Dr R. G. Chambers for assistance with resistance measurements and discussions on the theory of metals, to my wife for help with some of the experiments, to Dr J. V. Smith and Dr K. Robinson for advice about X-ray analysis matters, to Professor K. Lonsdale and Dr H. J. Grenville Wells of University College, London, and Dr G. E. Bacon of A.E.R.E., Harwell, for X-ray examination of some graphite crystals and Mr A. Fullick of University College, London, for detailed identification of the axes of the gallium crystals, to Dr N. P. Allen of the National Physical Laboratory for arranging the chemical analysis of the tin-mercury alloys, to Professor Sir K. S. Krishnan and Dr F. M. Bannister for providing the graphite crystals and to Dr J. Bardeen, of Bell Telephone Laboratories, for providing a germanium crystal.

Note added in proof 25 *April* 1952. Since the manuscript was completed, I have learnt of a recent note by Verkin, Lazarev & Rudenko (1951 *b*) reporting their discovery of the de Haas-van Alphen effect in mercury, and of a paper by Zilbermann (1951) giving some theoretical discussion of the de Haas-van Alphen effect.

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