Magnetic Susceptibility of Zinc at Liquid Helium Temperatures

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The de Haas-van Alphen effect in zinc has been investigated at 4.2°K by measuring the couple on a zinc crystal in a uniform magnetic field. The data obtained give the dependence of the susceptibility both on field strength and on orientation of the crystal relative to the direction of the field. The susceptibility is found to be isotropic in the main cleavage plane. The experimental results are compared to the theory of Blackman and Landau, with which their main features are in qualitative agreement.

Detailed examination, however, indicates discrepancies in (a) the phase of the periodicity, and (b) the shape and amplitude of the envelope of the oscillations, in that the theoretical envelope as interpreted from the data at low fields decreases too slowly at high fields. From the comparison we estimate that the electrons responsible for the effect have a chemical potential $E_0=0.02$ electron volts, a transverse effective mass $m_1=0.01m_0$ (where m_0 is the free electron mass), and a ratio of transverse mass to longitudinal mass $m_1/m_3=0.01$. From these values, the specific heat of these electrons is estimated to be 0.1 percent of the measured electronic heat, and their number to be 2×10^{-6} per atom. Comparison of these results to the work of Marcus on zinc and Shoenberg on bismuth has also been made.

INTRODUCTION

IN 1930 de Haas and van Alphen[1] found that at very low temperatures the diamagnetic susceptibility of a bismuth single crystal depends on the field at which the measurement is made. With increasing field the susceptibility rose and fell periodically with ever increasing amplitude. They made further measurements in 1932[2] and in 1936 Shoenberg and Uddin[3] studied the effect in still greater detail, especially in regard to the influence of temperature and impurities. Definitive measurements on bismuth were made by Shoenberg[4] in 1939. The effect was observed for a variety of crystal orientations and for temperatures ranging from 20°K to 2.1°K but principally at 4.2°K.

In bismuth it is found that susceptibility is independent of the field only when the field is along the trigonal axis, 3. Along a binary axis, 2, and along axis 1, perpendicular to 3 and 2, the susceptibility depends on the field, the periodicity being different for each of these axes.

An attempt to discover the effect in a single crystal of antimony[5] was not successful, but low temperature magnetic measurements on many other metals[2] are not conclusive since the measurements were made with polycrystals.

In 1947 the effect was discovered by J. A. Marcus[6] of this Laboratory in zinc. He investigated the range of temperatures down to 14°K and found that for zinc it is the susceptibility in the direction of the hexagonal axis, χ_3, which is dependent on the magnetic field. He was able to observe the periodic field dependence at temperatures as high as 64°K, provided there was a component of the field in the 3-direction.

In a direction perpendicular to the hexagonal axis, the susceptibility was found to be field independent, having the constant value $\chi_1=-0.15\times10^{-6}$ for all fields and for temperatures from 100°K down to the minimum he observed, at 14°K. In this paper we have extended the measurements on zinc into the liquid helium region and also to a wider range of magnetic field. Shoenberg found many features of his results in remarkable agreement with the theory developed by the successive contributions of Peierls,[7] Blackman,[8] and Landau.[9] Our results for zinc bear a similar relation to these theories. Like Shoenberg, we find certain discrepancies. The simpler symmetry of zinc facilitates comparison of theory and experiment.

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[1] W. J. de Haas and P. M. van Alphen, Comm. Phys. Lab. Leiden, Nos. 208d, 212a (1930).

[2] See Reference 1, Nos. 220d, 225b (1932).

[3] D. Shoenberg and Z. M. Uddin Proc. Roy. Soc. A156, 687, 701 (1936).

[4] D. Shoenberg, Proc. Roy. Soc. A170, 341 (1939).

[5] D. Shoenberg and M. Z. Uddin, Proc. Camb. Phil. Soc. 32, 499 (1936).

[6] J. A. Marcus, thesis, Yale University (1947); Phys. Rev. 71, 559 (1947).

[7] R. Peierls, Zeits. f. Physik 80, 763 (1933).

[8] M. Blackman, Proc. Roy. Soc. A116, 1 (1938).

[9] L. Landau, by private communication to Shoenberg. See reference 4.

EXPERIMENTAL PART

For the accurate measurement of field dependent susceptibilities the body force (Faraday) method is unsatisfactory because of the necessary gradient of the magnetic field. We shall see that at liquid helium temperatures a 5 percent change in field may cause a shift from a peak of positive susceptibility to a peak of negative susceptibility. Now with a crystal of zinc such as we have used, having dimensions of the order of 6 mm, the electromagnet and Foex pole pieces available here for use in a body force measurement and used by Marcus provide a field which increases by 5 percent from the top of the specimen to the bottom. With this apparatus we would evidently observe only a greatly smoothed out version of the effect.

Although it would be possible to reduce the gradient by use of other pole pieces, this could be done only at a considerable sacrifice of sensitivity.

I. Principle of the Torsion Method

We have, therefore, following Shoenberg,[4] used a torsion method. The turning couple $\mathbf{C}$ acting on a body with magnetization $\mathbf{I}$ and mass m is given by

$$\mathbf{C}=m\mathbf{I}\times\mathbf{H}, \tag{1}$$

i.e.,

$$\frac{\mathbf{C}}{m}=(I_2H_3-I_3H_2)\mathbf{i}+(I_3H_1-I_1H_3)\mathbf{j}+(I_1H_2-I_2H_1)\mathbf{k}. \tag{2}$$

In the present investigation we are dealing with an hexagonal close-packed structure and shall take the 3 axis along the hexagonal axis [000.1]. The other two crystal axes then lie in the principal or cleavage plane [000.1]. The two-crystal orientations we have used are depicted in Fig. 1. In Fig. 1(a) the hexagonal axis is horizontal (its elevation, $\beta=0$) while in Fig. 1(b) it is vertical. We shall be principally concerned with arrangement (*a*).

The horizontal magnetic field may be set at any angle ϕ to the hexagonal axis. The 2 axis and 1 axis are in the cleavage plane, which is vertical in Fig. 1(a). Equation (2) is then

$$C=(\chi_3-\chi_2\cos^2\theta-\chi_1\sin^2\theta)mH^2\sin\phi\cos\phi, \tag{3}$$

where θ is the elevation of the 2 axis, which is in the hexagonal plane.

The corresponding equation applying to the case of vertical hexagonal axis ($\beta=90°$) is

$$C'=(\chi_1-\chi_2)mH^2\sin\phi'\cos\phi', \tag{4}$$

where ϕ' is the angle between H and the 2 axis. It is well known that at room temperatures there is no magnetic anisotropy in the cleavage plane; i.e., $\chi_1=\chi_2$. Hence, the measurement corresponding to Fig. 1(a) gives us the differential susceptibility $(\chi_3-\chi_1)$ directly since then Eq. (3) reduces to

$$C=(\chi_3-\chi_1)mH^2\sin\phi\cos\phi, \tag{5}$$

if $\chi_1=\chi_2$. It is necessary, however, to verify that $\chi_1=\chi_2$ at liquid helium temperatures.

Although the torsion method gives us only a difference of susceptibilities, $(\chi_3-\chi_1)$, this does not introduce any difficulty in the application of the theory, particularly since only χ_3 is field dependent while χ_1 has the constant value of -0.15×10^{-6} for all fields. In addition to the fact that a constant field is used, other advantages of this method over the body force method are that torsion apparatus is inherently more stable than a microbalance. Finally, we shall see that ferromagnetic impurities can be readily detected by noting the effect of rotating the field relative to the crystal at room temperature. The apparatus described below makes it possible to measure $(\chi_3-\chi_1)$ at fields down to 1 kilogauss in a field which varies less than 0.1 percent over the 0.6 cm specimen.

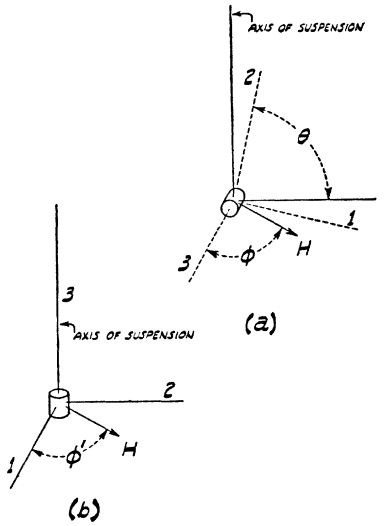

FIG. 1. Crystal orientations used in the experiment.

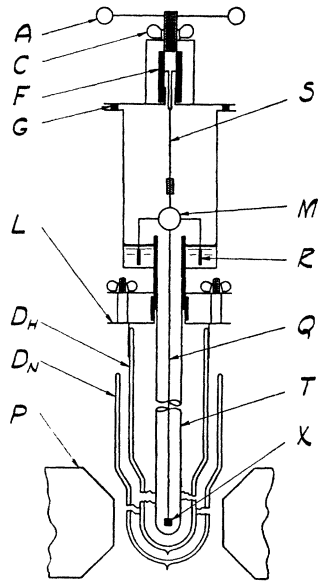

FIG. 2. Schematic diagram of the torsion balance.

II. Apparatus

A schematic diagram of the torsion balance and cryostat are shown in Fig. 2. A single torsion wire has been used in the present investigation.

A mirror M, damping ring, R, dipping in Octoil, and a rigid glass or quartz suspension S are attached to the lower end of the torsion wire. The specimen X is attached to the rigid suspension by means of Duco cement.

A vertical slit illuminated by a 60-watt half-silvered G. E. candlebulb and a traveling microscope were used to observe the deflection of the mirror, the image being focused by a 1-meter focal length lens (not shown) attached over a hole in the balance case.

A critical element in the design is the glass tube T. Since it is necessary to leave the balance mounted while filling the flask with helium in another room, T must have a minimum heat capacity in order to minimize the loss of liquid on assembly. A wall thickness of 0.015″ with a $\frac{1}{2}$″ O.D. was found to be satisfactory.

The specimen and surrounding Dewars are placed between the 10.2-cm diameter flat poles of an electromagnet, the gap being 5.1 cm. With this spacing the field is uniform in the region of the center to the extent that a 0.5-cm displacement toward either pole raises the field about 0.05 percent, while moving parallel to the pole face lowers the field about 0.15 percent. In all our measurements the sample was aligned on the axis of rotation of the magnet to within 0.5 mm.

A maximum field of about 8.5 kilogauss is attainable with our magnet when the coils are in parallel with a 220-volt battery but the necessary maximum current of 25 amperes can be maintained for only a few minutes as the magnet warms up and the batteries polarize.

Mechanical devices for adjusting the suspension are indicated by letters on the left-hand side of Fig. 1. A is an arm by which the zero setting of the mirror can be adjusted and C is a wing nut for controlling its elevation. These operations can be performed in the course of an experiment without breaking the vacuum, the seal being a flexible rubber tube F. Neoprene gasket G seals this suspension adjustment device to the body of the balance. In the front of the balance is a rectangular hole (not shown) covered by the galvanometer lens previously mentioned.

When the superstructure is lifted off, everything comes out of the balance, including the oil tub (not shown). Sealed to the helium flask is the lid L. Three bolts solidly fixed to the lid make possible a rapid attachment and reproducible alignment of the filled helium flask. This is important because of the close tolerances allowed in the region of the pole pieces. When alignment is not good the Dewar may touch the bottom of tube T, displacing it sidewards to the point where it touches the crystal. The nitrogen flask is attached in a somewhat similar fashion to the lid L but with its top end open to the atmosphere.

Choice of the torsion wire presented a problem which was not immediately apparent. At liquid helium temperatures eddy currents in the zinc crystal are very large and persistent. In consequence, if the magnet is rotated while the field is on, the specimen follows the motion of the magnet almost in step. The torsion wire is then subjected to a twist far greater than ever occurs during room temperature measurements, the result being a semipermanent set which lasts an hour or so. That is, there occurs a sudden change in the zero field reading θ_0 of the traveling microscope followed by a very gradual return toward the initial zero reading. In one experiment with a 0.003-in. diameter Nichrome wire this change in zero reading was greater than the effect being

looked for, and it was necessary to reduce the magnet current to zero before each change in the magnet position—a time consuming operation, since the magnet must then be remagnetized at maximum current for each reading. The necessity for remagnetization will be explained later in the section on magnet calibration.

To reduce this semipermanent set a ribbon suspension, S, was finally used. A 0.0063-in. diameter Nichrome wire flattened to 0.0013″×0.016″ is free of the trouble for twists up to 20 degrees. Nichrome and phosphor bronze are found to be suitable materials when flattened. Tungsten is very poor. A strip of platinum rolled from round wire is also poor. A piece of gold galvanometer strip was found to be less satisfactory than nichrome. Quartz is by far the best material of those tested but is not entirely satisfactory because of its fragility.

The torsion wire was calibrated by timing 100 oscillations of a brass bar attached to the bottom end. The torsion constants, expressed in dyne-cm per cm deflection of the slit image were found to be 0.1524 for the round wire used for the first four helium runs and 0.360 for the flat strip used thereafter. These numbers correspond to an optical arm (slit to mirror to microscope) of 193.4 cm.

The oil used for damping is a frequent source of trouble and might better be replaced by electromagnetic damping. On one occasion a sticky coagulant formed in the oil, caused perhaps by the presence of impurities such as dust or particles of sealing wax. The effect was to cause the zero reading to depend on the direction of the prior deflection. For a time the phenomenon was confused with mechanical hysteresis in the suspension, but on changing the oil the trouble disappeared.

The most persistently annoying aspect of oil damping is the necessity of careful and prolonged outgassing before beginning measurements, particularly when these are made at very low temperatures. On one occasion when the temperature of the helium bath was being reduced, a sudden onset of outgassing caused the image to dart off scale at regular intervals. The reduction in temperature was also reducing the pressure inside the balance case to some extent, thus creating a condition more favorable for outgassing. Direct observation of the oil through the lens window verified that outgassing was taking place.

Several pump oils and manometer oils were tested and all except Octoil were found to be completely unsatisfactory, in that outgassing persisted for a very long time after an exposure to the atmosphere. Attempts to speed up outgassing by application of heat were found to be unsatisfactory because of the danger of cracking the oil.

III. Specimens

The zinc crystal used in this investigation was made by J. A. Marcus, by the Bridgman method[10] of slowly lowering a glass tube containing the molten and outgassed metal through a temperature gradient. The crystal has a weight of 0.6058 g. The metal is "Hilger Spectroscopic," 99.99 percent pure.

IV. Cryogenic Technique

In preparation for a liquid helium run the suspension is carefully aligned on the magnet axis of rotation and the balance is evacuated. Helium gas is admitted to a pressure of 1 mm of mercury to provide thermal contact to the specimen.

Following the procedure in use in this laboratory for some time in connection with Pyrex Dewar flasks[11] the interspace of D_H is evacuated and refilled with 1 mm Hg of air before each run. The air is for the purpose of rapid cooling of the inner wall and contents of the flask down to the temperature of the liquid nitrogen flask D_N. When liquid helium is admitted to D_H, this air freezes and the interspace is then at high vacuum, providing excellent thermal insulation.

While the helium flask is being filled in an adjoining room, the tube T surrounding the specimen is cooled with liquid nitrogen. When all is ready, this nitrogen Dewar is replaced as rapidly as possible by the filled helium flask. By this procedure we gain the advantage of avoiding movement of the specimen after alignment. When properly done the volume of liquid helium evaporated is less than the volume displaced by the tube, with the result that the liquid level is higher after assembly than before.

[10] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. 60, 305 (1925).

[11] C. T. Lane and H. A. Fairbank, Rev. Sci. Inst. 18, 522 (1947).

However, the transfer time is quite critical. In a side experiment done with liquid nitrogen it was estimated that the tube warmed up from 77°K to about 145°K during a 10-second exposure to the atmosphere. It was observed that for exposures of slightly more than 10 seconds ice became visible on the surface of the precooled tube. It appears plausible that ice formation is an important factor in the rapid warming up of the tube. If so, the success of the transfer operation should depend critically on the humidity as well as on the transfer time.

Large variations were, in fact, noted in the volume of liquid helium lost in actual practice. Removal of the precooling flask and insertion of D_H actually takes about 10 seconds. The volume of liquid helium lost was as little as 4 cc on one occasion and as much as 40 cc on another, the average loss for seven experiments being 20 cc. Thus the latent heat of the evaporating liquid averaged 60 joules and was as little as 12 joules on one occasion. It is also interesting to note that the heat removed from tube T on immersion is considerably greater than 12 joules, indicating that the heat exchange between the escaping vapor and the tube is the principal factor in cooling down the tube.

V. Magnet Calibration

Because of hysteresis of the magnet, it is essential that the same procedure be followed during a calibration run and in all subsequent measurements. The invariable procedure was adopted of approaching a desired magnet current from above—from the maximum current attainable. If approached from below, the field may differ by as much as 0.1 kilogauss.

To make this procedure possible, a suitable array of rheostats and resistors for adjusting the magnet current were carefully chosen. They meet the requirement that continuous reduction of current is possible without back tracking.

It suffices to calibrate the field at a single value of magnet current by the ordinary method employing a ballistic galvanometer, together with an observation of the couple acting on the crystal at room temperature at the same magnet current. Since it is well known that diamagnetic susceptibilities are independent of field at ordinary temperatures, other fields can now be measured simply by measuring the couple (proportional to the deflection, $\Delta\theta$, of the mirror) at other values of magnet current.

In measurements on feebly magnetic substances it is important to be sure that ferromagnetic impurities are not present in significant amounts and to apply appropriate corrections for unavoidably small amounts of such impurities. Hence, a well-known method of Honda's[12] is frequently used to correct body force measurements for the effects of such impurities. When the observed susceptibility is plotted as a function of reciprocal field, the result is a straight line whose slope is proportional to the impurity and which intersects the axis at the true diamagnetic susceptibility. It is easy to show that this method is applicable to the torsion measurements as well. The couple acting on a specimen with a ferromagnetic impurity of moment $\mathbf{M}$ is

$$C=k\Delta\theta=\Delta\chi mH^2\sin\phi\cos\phi+MH\sin\phi', \quad (6)$$

where ϕ' is the angle between $\mathbf{M}$ and $\mathbf{H}$ and k the torsion constant. Dividing by $mH^2\sin\phi\cos\phi$ we have what we may call the "observed differential susceptibility,"

$$\Delta\chi_{\text{obs}}=\Delta\chi+\left(\frac{M\sin\phi'}{m\sin\phi\cos\phi}\right)\frac{1}{H}. \quad (7)$$

Since any ordinary ferromagnetic impurity will be saturated in fields of the order of a few hundred gauss, M will be a constant in fields covering the usable range of our balance. In this case, a "Honda plot" of the observed differential susceptibility as a function of $1/H$ would be a straight line whose intercept at infinite field would give the true differential susceptibility of the diamagnetic material.

If, however, the ferromagnetic impurity is localized somewhere high up on the suspension where the field is far less than H or if it is extremely "hard" magnetically, M will depend on H and the Honda plot cannot then be used to correct for the impurity.

Inspection of Eq. (6) suggests another procedure which is in some respects superior. It will be evident that a 360° rotation of the field causes the diamagnetic term to go through 2 cycles while the ferromagnetic term goes through only one. It

[12] K. Honda, Ann. d. Physik **32**, 1048 (1910).

is therefore possible to separate out the diamagnetic term. Thus, by averaging the balance deflections ($\Delta\theta$) at any pair of angles ϕ and $\phi+180$ it is seen that the impurity term is eliminated. Knowing the field at which this data was taken one can then make a correction for the impurity at any other value or orientation of the field, provided it can be assumed that the impurity is saturated. The advantage of this procedure over a Honda plot is that the latter is applicable only to the particular crystal orientation at which the data was taken. Furthermore, the Honda plot requires a complete field calibration by the cumbersome and not very precise search coil procedure.

Figure 3 shows the results of an analysis of this type. Since the data shown in (*a*) is for the case of crystal axis nearly vertical the amplitude of the diamagnetic term is quite small and the over-all angle characteristic is badly distorted by the effect of the suspension, shown in (*b*). No analysis of the data on the "suspension alone" is needed, since it is obviously ferromagnetic. When its effect is subtracted from (*a*) and this is analyzed*** for components, it is seen that there may be a slight ferromagnetic impurity in the crystal itself, but its amplitude is scarcely greater than the experimental errors in the points. Thus we see the crystal is substantially free from impurity, although the effect of the suspension itself is not negligible. Even when the crystal is oriented for maximum couple the suspension can cause an error of 1.5 percent in the susceptibility. The other features of Fig. 3 will be discussed later.

*** We assume three possible contributions to the deflection of the crystal alone:

(1) a one-cycle term resulting from ferromagnetic impurity,
(2) a two-cycle term, present if the hexagonal axis is not accurately vertical,
(3) a three-cycle term, present if $\chi_1 \neq \chi_2$.

The resultant crystal deflection is then

$$\theta(\phi) = a\sin(\phi+\alpha) + b\sin(2\phi+\beta) + c\sin(3\phi+\gamma),$$

where ϕ is the azimuth, and α, β, γ are phase constants. Averaging deflections for pairs of angles ϕ and $(\phi+\pi)$,

$$\tfrac{1}{2}\{\theta(\phi)+\theta(\phi+\pi)\} = b\sin(2\phi+\beta).$$

The two-cycle term is then subtracted from $\theta(\phi)$, yielding a table of values for

$$\theta'(\phi) = a\sin(\phi+\alpha) + c\sin(3\phi+\gamma).$$

Further trigonometric manipulation gives

$$\tfrac{1}{3}\{\theta'(\phi)+\theta'(\phi+\tfrac{2}{3}\pi)-\theta'[\phi+(\pi/3)]\} = c\sin(3\phi+\gamma).$$

Subtracting the three-cycle term from $\theta'(\phi)$ then leaves the one-cycle term, and completes the analysis.

Several glass and quartz suspensions of various diameters were tested in the balance, but all displayed a significant magnetic anisotropy, although this did not always have a strictly ferromagnetic angle characteristic as in Fig. 3(b). Although the anisotropy was found to decrease with the diameter of the rod, only a limited reduction in diameter was permissible because of the rigidity requirement. The anisotropy was unaffected by cleaning the suspension or by subjecting it to temperatures high enough to soften the glass or quartz.

We are now prepared to discuss the actual magnet calibration in further detail. Several measured values of H in the range from 4.2 to 6.5 kilogauss were compared to previously observed deflections (at the same magnet current) of the standard crystal, zinc A, used in these measurements and the ratio $\Delta\theta/H^2 = (0.978\pm0.010)\times10^{-6}$ was obtained. The small spread in the points would appear to indicate that very little impurity was present. Actually, however, analysis of several angle characteristics revealed an impurity which had the effect of reducing $\Delta\theta$ by nearly 1 percent over the entire range of fields at which the calibration was made.

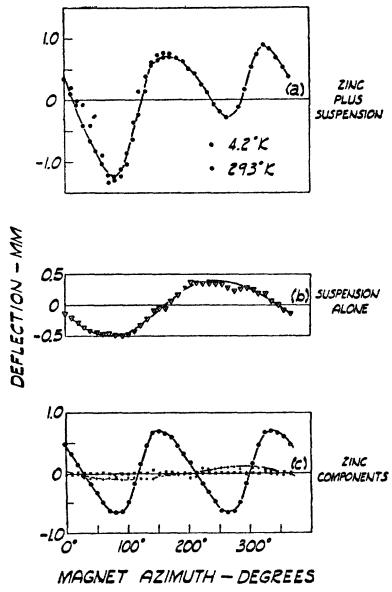

FIG. 3. Angle characteristic with hexagonal axis vertical. By comparison, at the field strength of 5500 gauss at which these measurements were made, the maximum deflection with hexagonal axis horizontal is 29 mm.

TABLE I. Room temperature values of $\chi_3-\chi_1$ for zinc.

Author	$(\chi_3-\chi_1)\times10^6$
Present work	−0.0476
Marcus[a]	−0.045
McLennan, Ruedy, and Cohen[b]	−0.045
Rao[c]	−0.053

[a] See reference 6.
[b] J. C. McLennan, R. Ruedy, and E. Cohen, Proc. Roy. Soc. **A121**, 9 (1928).
[c] S. R. Rao, Proc. Ind. Acad. Sci. **4**, 186 (1936).

VI. Experimental Results

The room temperature value of the differential susceptibility $\Delta\chi=\chi_3-\chi_1$ as measured by us, together with the results of previous investigators on zinc, is given in Table I. It should be noted that the other three determinations cited were all separated measurements of χ_3 and χ_1 and hence ours is inherently the more accurate.

In deriving Eq. (5) we have assumed that $\chi_1=\chi_2$ at 4.2°K as well as at room temperature. Figure 3 shows that this is indeed the case, there being no difference between the data at 293° and 4.2°K. In this connection it should be pointed out that, for the orientation at which the data in Fig. 3 were taken, namely, that shown in Fig. 1(b), we should expect a 3-cycle component in C if $\chi_1\neq\chi_2$. For the orientation corresponding to Fig. 1(a) we should have, as has already been mentioned, a 2-cycle term. Added to both of these would be a 1-cycle term if ferromagnetic impurities were present. The results of a complete analysis on the crystal itself are shown in Fig. 3(c), for the orientation corresponding to Fig. 1(b). The prominent two-cycle term is interpreted as an indication that the hexagonal axis was not accurately vertical.

The slight impurity component has been previously mentioned. It is evident that no three-cycle term (designated by × marks) is present. Hence, $\chi_1=\chi_2$ at 4.2°K.

A. Field Dependence at 4.2°K

Figure 4 shows the de Haas-van Alphen effect at 4.2°K, $\phi=45°$. We have obtained the scale on the right for χ_3 by adding Marcus' value $\chi_1=-0.150\times10^{-6}$ to our observed values of $(\chi_3-\chi_1)$ assuming the value of χ_1 to be constant down to 4.2°K. We see on this scale that a number of the peaks are actually paramagnetic. Although this is not at variance with the theory, it has not been previously observed, either in bismuth or in zinc.†

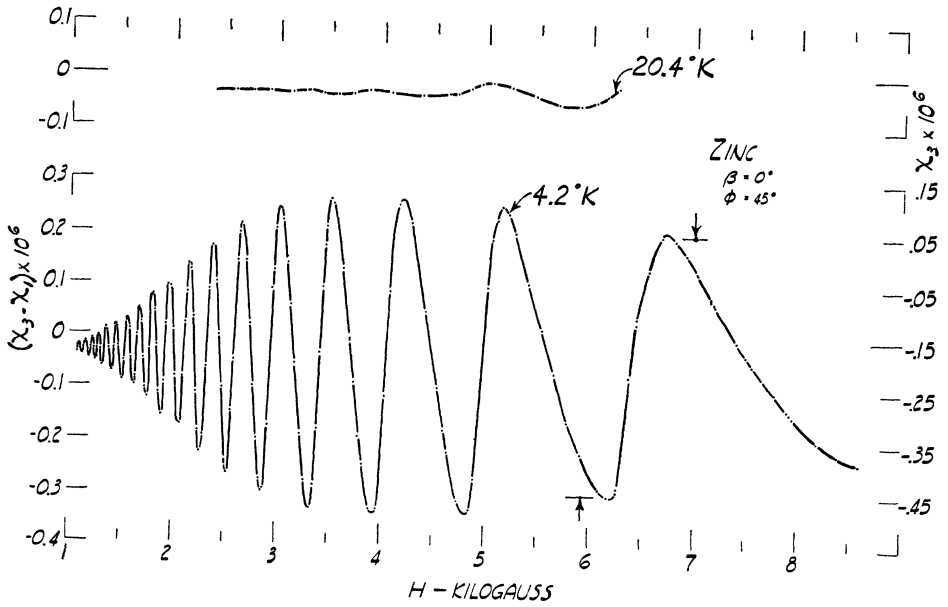

FIG. 4. Variation of differential mass susceptibility with field at 20.4°K and 4.2°K.

† In bismuth it is χ_3 which is field independent, having the value $\chi_3=-1.2\times10^{-6}$. Hence Shoenberg's value of χ_1 ranges from -2.4×10^{-6} to -1.1×10^{-6}, never reaching a positive value.

It is also worthy of note that the amplitude is decreasing at high fields, in agreement with theoretical expectations. Shoenberg was unable to reach fields sufficiently high to produce this effect in bismuth, while the earlier observations of de Haas and van Alphen at fields up to 35 kilogauss are not conclusive because of the necessary field inhomogeneity in their set-up.

Finally, it should be pointed out that the prominent asymmetry of the peaks at the higher fields is an artifact which is due to the circumstance that the large couples obtained at high fields displace the crystal to a new position. As a result of the sharpness of the angle characteristic, to which we shall presently refer, the susceptibility is markedly different in the new orientation and peaks of susceptibility are therefore displaced.

The displacement of two of the peaks at high field was determined at the conclusion of the experiment whose results are shown in Fig. 4. In each case the crystal was purposely displaced to the extent that it would actually be at $\phi=45°$ when maximally deflected. The true locations of the two highest peaks for $\phi=45°$ were thus found to be 6.98 and 5.97 kilogauss with minor changes in amplitude. The theory actually predicts symmetrical peaks when the abscissa is in units of reciprocal field strength. On this basis, if we consider the peaks to originate at the value of the mean susceptibility, extremes of susceptibility would be expected at 6.90 and 5.95 kilogauss, in substantial agreement with the above experimental observation.

B. Angle Characteristic at 4.2°K

With a constant field of 2360 gauss, which by coincidence corresponds to one of the peaks in the field dependence, the angle characteristic shown in Fig. 5 was obtained. Because of the persistent eddy currents present at this low temperature, to which reference has already been made, the specimen approaches its equilibrium position very slowly and at some particular orientations two or three minutes are required to reach equilibrium, in comparison to the normal time of about 4 seconds.

Since the couple is very small near $\phi=0$ and near 90°, some parts of the curve have been omitted or shown by dashes—but there was no evidence of oscillations in these regions.

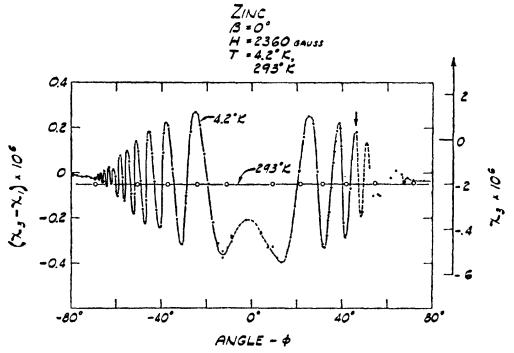

FIG. 5. Variation of differential mass susceptibility with angular orientation at constant magnetic field.

Referring to the χ_3 scale shown in the figure we note that there are several paramagnetic peaks, while most are diamagnetic. Thus there are some directions of field relative to crystal axes in which the crystal appears to be paramagnetic while it is diamagnetic in intervening regions. An angular variation from para- to diamagnetic susceptibility is not unprecedented and has been observed at room temperature by Browne and Lane[13] in dilute solutions of tin in antimony.

C. Cadmium and Thallium

A crystal was briefly tested at temperatures down to 1.65°K, but no field dependence of susceptibility was observed. The magnetic anisotropy was found to be much greater than at room temperature by a factor of 5 at 2.0°K and a factor of 6 at 1.65°K. Unfortunately, the direction of the crystal axes was not known so only a lower limit to $(\chi_3-\chi_1)$ can be given, being -0.111×10^{-6} at room temperature. Our lower limit is slightly greater than the result of McLennan, Ruedy, and Cohen†† (-0.101×10^{-6}), and almost twice that of Rao and Subramaniam[14] (-0.060×10^{-6}).

It is well known that impurities or strain in a single crystal tend to reduce its magnetic anisotropy, and it is evident from the large spread in observed susceptibilities that extraordinary precautions are necessary. While our result with cadmium is in the favorable direction, this was not the case with a single crystal of thallium whose anisotropy was only 40 percent of that of

[13] S. H. Browne and C. T. Lane, Phys. Rev. **60**, 895 (1941).

[14] S. R. Rao and K. C. Subramaniam, Phil. Mag. **21** 609 (1936).

†† See Table I, reference b.

that obtained by Rao and Sriraman[15] ($\chi_3-\chi_1 = -0.247\times10^{-6}$).

Various attempts to etch the crystal were not successful, but it was clear both from magnetic measurements and from superposition of Laue photographs taken of opposite ends that the specimen was really a single crystal. Neither at 4.2° nor at 1.25°K did it exhibit a field dependence††† in susceptibility. Possibly it was badly strained, or the metal, which was "Hilger Spectroscopic," may have been contaminated in the handling. Since Shoenberg has shown that as little as 0.01 percent impurity in bismuth is sufficient to eliminate the field dependence completely, a negative result should not be considered as conclusive unless the purity of the specimen is verified after completion of the experiment.

THEORETICAL PART

I. Introductory

Analysis of the data will be based on Landau's formulation[9] of the theory. Landau's extension of the theory was purely mathematical; the physics was brought to its present stage of development by Blackman.[8] It is essentially a free electron theory, and attributes the effect to a small fraction of the valence electrons which is contained in one or more Brillouin zones. The majority of the valence electrons are assumed to populate other zones, which do not contribute to the oscillating part of the susceptibility, but serve as reservoirs of electrons. These other electrons are then presumed to contribute to the total susceptibility in the more usual manner: e.g., through spin paramagnetism and ordinary Landau diamagnetism.

In outline, Blackman's argument runs as follows. For metals exhibiting the de Haas-van Alphen effect, there exist one or more Brillouin zones in which only the very lowest electronic states are filled. The energies of the electrons occupying these states (hereinafter called the d.H.-v.A. electrons) can then be expressed as a quadratic function of their momenta, and in that sense they may be considered free. Under the influence of a magnetic field, the d.H.-v.A. electrons execute Larmor precession about the lines of force, and their motion in a plane perpendicular to the field is quantized. This quantization gives rise to the spectacular oscillating susceptibility. Motion parallel to the field is not quantized; this permits continuous variation of the susceptibility with field strength. It is assumed that the d.H.-v.A. electrons supply only a negligible portion of the total electronic specific heat, so that their chemical potential E_0 is sensibly constant. Furthermore, they have a highly anisotropic effective mass, from which arises the anisotropy of the effect. It turns out that if E_0 and the effective mass in at least one direction are abnormally small, the theory predicts an appreciable field dependence of the susceptibility at low temperatures.

In the case of bismuth,[8] it was necessary to assume that three zones of trigonal symmetry contribute to the effect. Further, Shoenberg[4] found it necessary to assume that the tensor giving the effective mass in these zones was skewed with respect to the crystal axes, and to use four components of the tensor to fit the data. In zinc, however, the data may be accounted for in terms of a single zone having the full symmetry of the hexagonal crystal. In consequence, Landau's explicit expression for the couple reduces for zinc to a form much simpler than for bismuth. The greater part of this analysis will be a detailed comparison of the periodicity and envelope of the observed oscillations to the predictions of the theory. The principal experimental parameters to be determined are the components of the effective mass tensor and E_0. From these parameters can be calculated the specific heat of the d.H.-v.A. electrons, and this compared to the measured electronic heat. Finally, the present work will be compared to previous work on zinc, and to results for bismuth insofar as is possible.

II. Theoretical Predictions

Since the susceptibility is isotropic in the main cleavage plane, we may assume there to be only two different effective masses: m_1 perpendicular and m_3 parallel to the hexagonal axis. The simplest assumption is then that the d.H.-v.A. electrons in zinc are contained in a single zone of

[15] S. R. Rao and S. Sriraman, Proc. Roy. Soc. A166, 325 (1938).

††† Since thallium is superconducting at this temperature, the measurements were, of course, made in fields greater than the critical threshold.

hexagonal symmetry and have an ellipsoidal energy surface:

$$E=\frac{1}{2m_1}(p_1^2+p_2^2)+\frac{1}{2m_3}p_3^2. \tag{8}$$

Landau's formula then gives, for not too strong fields,

$$\chi_3-\chi_1=(m_1-m_3)f(\beta H), \tag{9}$$

where

$$f(\beta H)=A\left\{\frac{\pi^2}{6}\left(\frac{k}{E_0}\right)^{\frac{1}{2}}-\frac{1}{(T)^{\frac{1}{2}}}\left(\frac{2\pi^2kT}{\beta H}\right)^{\frac{1}{2}}\times\exp\left(-\frac{2\pi^2kT}{\beta H}\right)\sin\left(\frac{2\pi E_0}{\beta H}-\frac{\pi}{4}\right)\right\}, \tag{10}$$

$$\left.\begin{aligned}A&=\frac{\sqrt{2}e^2E_0}{2\pi^4c^2\hbar(k)^{\frac{1}{2}}m_1(m_3)^{\frac{1}{2}}},\\ \beta&=\frac{e\hbar}{cm_1(m_3)^{\frac{1}{2}}}(m_1\sin^2\phi+m_3\cos^2\phi)^{\frac{1}{2}}.\end{aligned}\right\} \tag{11}$$

The principal susceptibilities are given by

$$\left.\begin{aligned}\chi_1&=-m_1f(\beta_1H),\quad \beta_1=\frac{e\hbar}{c(m_1m_3)^{\frac{1}{2}}},\\ \chi_3&=-m_3f(\beta_3H),\quad \beta_3=e\hbar/cm_1.\end{aligned}\right\} \tag{12}$$

Since the amplitude of the envelope varies with the numeric $2\pi^2kT/\beta H$, the fields for which χ_1 and χ_3 have maximum envelope amplitude are in the ratio

$$H_1/H_3=\beta_3/\beta_1=(m_3/m_1)^{\frac{1}{2}}.$$

The observations of Marcus showed no oscillations in χ_1 for fields up to 8.25 kilogauss. Since the oscillations in χ_3 have appreciable amplitude for fields as low as one kilogauss, m_1/m_3 must be very small. Therefore, in discussing the field dependence we may write

$$\beta=(e\hbar/cm_1)\cos\phi.$$

If m_1/m_3 is sufficiently small, the approximation will also be valid in discussing the angle dependence except at very high angles. Equation (9) is then symmetrical in H and $\cos\phi$, and the field and angle characteristics may be analyzed by nearly equivalent procedures. Moreover, it should be possible to bring the two characteristics into coincidence by treating each as dependent on $H\cdot\cos\phi$ rather than on H or $\cos\phi$.

III. Evaluation of Experimental Parameters

In calculating the parameters we need be concerned only with the oscillating term in the susceptibility; consideration of the constant term which obtains at low fields will be postponed. From the periodicity of the experimental curves we can determine β/E_0. From examining the envelope we determine β and m_3A. In addition, the ratio m_1/m_3 can be estimated roughly from the periodicity of the angle characteristic. Wherever possible, calculations will be made independently for the angle and field dependences.

A. Periodicity of the Oscillations

1. Field dependence.—Inspection of (10) shows that the oscillations should vanish whenever

$$\frac{2\pi E_0}{\beta H}-\frac{\pi}{4}=r\pi\quad r=0,\,1,\,2,\,3\cdots \tag{13}$$

We take the points where the curve crosses the line of average susceptibility to be those which satisfy Eq. (13). Plotting the reciprocals of the fields‡ at these points against integers should give a straight line of slope

$$b_h=\frac{\beta}{2E_0}$$

whose intercept on the axis of integers gives the phase constant. The choice of integers is somewhat arbitrary, but in any event r must be an even integer at the last crossover.‡‡ A good straight line is indeed obtained (Fig. 6), giving a slope $b_h=0.0223$ kilogauss^{-1}, but the phase turns out to be 0 instead of $-\pi/4$. The discrepancy is similar to that found by Shoenberg for bismuth.

2. Angle dependence.—We first write (13) in

‡ Corrections have been made in the field dependence calculations for a small ferromagnetic impurity which evidently occurred high on the suspension. The correction amounted to lowering the observed field strength by less than 2 percent at the lowest fields, and was negligible above 4 kilogauss.

‡‡ Since $m_3>m_1$, the sign of the oscillating term follows that of $+\sin[(2\pi E_0/\beta H)-(\pi/4)]$. The slope at the last crossover is negative, and the slope of $\sin(1/x)$ is negative at $r=1/x$ only if r is even. This is exactly opposite to the situation for bismuth.

TABLE II.

	$e\hbar/2cm_1E_0$
Angle dependence, negative ϕ	0.0340
Angle dependence, positive ϕ	0.0331
Field dependence, run 1	0.0324
Field dependence, run 2	0.0316

the form

$$\frac{1}{t\cdot\cos\phi}-\text{constant}=\frac{ehH}{2cm_1E_0}r, \qquad (13a)$$

where

$$t=\left(\frac{m_1}{m_3}\tan^2\phi+1\right)^{\frac{1}{2}}.$$

Plotting $1/\cos\phi$¶ against integers for the crossovers of the angle characteristic should give a line which is straight at low angles but which curves upward at high angles because of the factor t. In Fig. 7 are plotted the values of $1/\cos\phi$, and $1/t\cdot\cos\phi$ for various assumed values of m_1/m_3, the data being taken from the oscillations for $\phi<0$. It can be seen that m_1/m_3 must be of the order of magnitude 1/100, since larger values lead to a downward curvature at high angles. Although the deviations at high angles from the straight line fitted to low angle points are small, they are appreciably larger than could be accounted for by experimental error in measuring ϕ. The integers were chosen by identifying the maximum at 45.6 degrees on the angle characteristic with that at 2.38 kilogauss in the field characteristic. We obtain the value 0.0802 for the slope $b_\phi=e\hbar H/2cm_1E_0$. A similar calculation for positive angles yields $b_\phi=0.0781$.

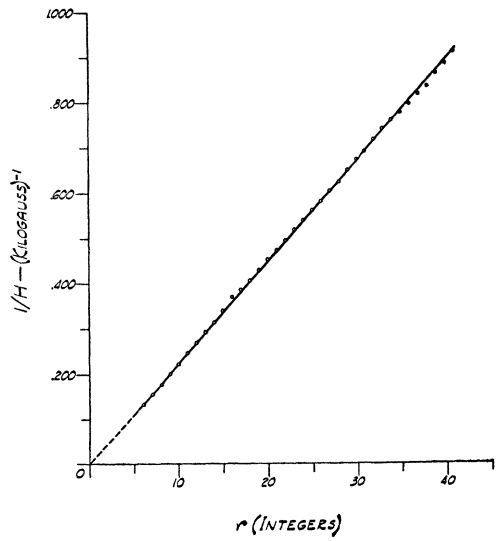

FIG. 6. Periodicity of the field dependence.

¶ No corrections for impurities have been made in plotting these graphs.

3. Comparison of angle and field dependence.—To compare the periodicity of the angle and field dependence we plotted $1/H\cdot\cos\phi$ against integers for each set of crossovers. The slope of each line obtained is $e\hbar/2cm_1E_0$; the results are given in Table II. (We have included the preliminary measurements of the field dependence in this comparison, indicated as run 1.) The angle and first field characteristics were taken without removing the crystal from the suspension, but the crystal was removed and reset before the second and more complete field dependence was obtained. In addition, the angle characteristic is not quite the same for negative and positive ϕ. Since the field characteristics were taken at $\phi=+45°$, the closer agreement between the values of $e\hbar/2m_1E_0$ given by the angle periodicity for $\phi>0$ and by the first field run is to be expected. The difference between the periodicities of the two field runs could be accounted for by a difference in orientation of 1 degree in resetting the crystal. Within the limits of experimental uncertainty, therefore, the angle and field dependent periodicities are in extremely good agreement. Their linearity suggests strongly that the spacing of the Larmor energy levels is accurately proportional to field.

B. Shape and Absolute Breadth of the Envelope

1. Field dependence.—If we let F be the absolute magnitude of the envelope, Eq. (9) gives

$$\log F+\tfrac{3}{2}\log H=-d_1\frac{1}{H}+\log d_1^{\frac{1}{2}}d_2, \qquad (14)$$

where we have set

$$d_1=\frac{2\pi^2kT}{\beta}, \quad d_2=\frac{m_3A}{(T)^{\frac{1}{2}}}.$$

Plotting the left member of (8) against $1/H$ should then give a straight line of slope $-d_1$, d_2 being determined by the intercept on the axis of

abscissae. The constants d_1 and d_2, together with b_h, are then sufficient to determine the effective masses and E_0. We have

$$\left.\begin{aligned} m_1 &= wd_1\cos\phi \\ (m_3)^{\frac{1}{2}} &= vd_1^{\frac{1}{2}}d_2b_h\cos\phi \\ E_0 &= u/(d_1b_h) \end{aligned}\right\}, \tag{15}$$

where

$$\left.\begin{aligned} u &= \pi^2kT = 5.74\times10^{-15} \\ v &= \frac{ch^2}{\pi^2e(2kT)^{\frac{1}{2}}} = 3.52\times10^{-12} \\ w &= \frac{eh}{4\pi^3ckT} = 1.47\times10^{-33} \end{aligned}\right\}. \tag{16}$$

Following this procedure for the more complete field characteristic, we get the curve of Fig. 8. A straight line is not obtained; the observed amplitude of the envelope falls off more rapidly with increasing field than the theory predicts. The curve is most nearly linear at low fields (high $1/H$), and a straight line was fitted to the low field points in order to determine d_1 and d_2. The best fit gives $d_1=9.61\times10^3$ and $d_2=1.51\times10^{-5}$, and leads finally to

$$\begin{aligned} &m_1=0.011m_0, \\ &m_3=6.5m_0, \\ &E_0=0.017 \text{ electron volts}, \end{aligned}$$

where m_0 is the free electron mass. Because of the scattering of the data at low fields, several different straight lines were drawn through the low end of the curve in Fig. 8 to investigate the effect of the fit on the calculated values of the experimental parameters. As could be expected from Eqs. (15), the values of m_1 and E_0 are relatively insensitive to the fit. All possible fits give $m_1=0.01m_0$, and E_0 does not change order of magnitude. The value of m_3 varies from $2m_0$ to $10m_0$. This large sensitivity to the fit makes it impossible to get an accurate estimate of the value of m_3.

Shoenberg also found a discrepancy in the envelope for bismuth, but one which is opposite to that for zinc. He plotted $\log F/T+\frac{3}{2}\log H$ *versus* T/H at constant temperature, obtaining curves for several different temperatures. All plots showed a slight upward curvature at high fields, whereas our curvature at high fields is downward. The departure of the experimental points in Fig. 8 from the straight line fitted at low

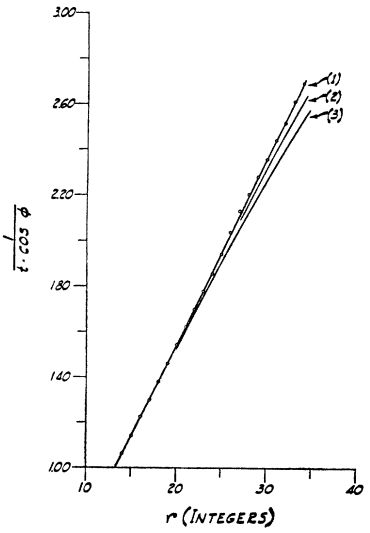

FIG. 7. Periodicity of the angle dependence. (1) $m_1/m_3=0$, (2) $m_1/m_3=1/100$, (3) $m_1/m_3=1/50$.

fields indicates that at the observed envelope maximum the theoretical amplitude is too high by a factor of at least two.

2. Angle dependence.—The envelope of the angle characteristic may be analyzed by the same procedure used for the field characteristic, Eq. (14) being replaced by

$$\log F+\tfrac{3}{2}\log(t\cdot\cos\phi) = -d_3(1/t\cdot\cos\phi) + \log d_3^{\frac{1}{2}}d_2, \tag{14a}$$

where

$$d_3=4\pi^3ckTm_1/ehH.$$

Since we cannot estimate m_1/m_3 accurately, the values of $t\cdot\cos\phi$ for high angles were chosen from consideration of the periodicity of the maxima and minima of the angle dependence. The experi-

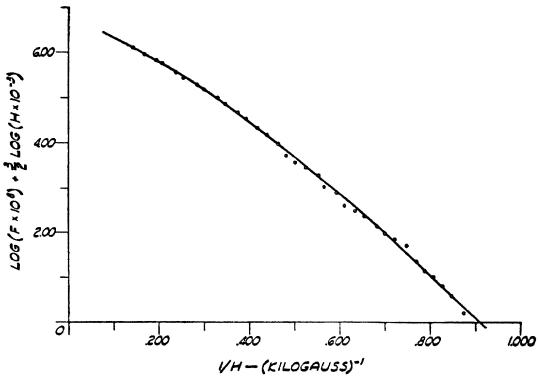

FIG. 8. Variation of envelope with field.

mental parameters are then given by

$$\begin{aligned} m_1 &= wd_3H, \\ (m_3)^{\frac{1}{2}} &= vd_3^2d_2b_\phi H, \\ E_0 &= u/d_3b_\phi. \end{aligned} \tag{15a}$$

As for the field dependence, a straight line is not obtained, and the curve is most nearly linear for low angles (Fig. 9). Fitting a straight line to the low angle points yields $d_3=4.69$, $d_2=5.48\times10^{-6}$ and

$$\begin{aligned} m_1 &= 0.018m_0, \\ m_3 &= 7.1m_0, \\ E_0 &= 0.008 \text{ electron volts.} \end{aligned}$$

The discrepancy is the same as before, and can be considered for either characteristic as failure of the theoretical envelope to decrease rapidly enough with increasing $H_3=H\cos\phi$. Because of the greater number of oscillations observed in the field dependence and the greater scattering of experimental points at high angles in the angle dependence, the values of the parameters calculated from the field characteristic are more accurate, and will be used in further calculations.

IV. Specific Heat

From Eq. (8), the number of electronic states of energy less than E in a crystal volume V is

$$(8\pi V/3h^3)m_1(m_3)^{\frac{1}{2}}(2E)^{\frac{3}{2}}.$$

The number of electrons per atom which are responsible for the effect is then

$$n(E_0)=\frac{8\pi V}{3h^3}m_1(m_3)^{\frac{1}{2}}(2E_0)^{\frac{3}{2}}. \tag{17}$$

Using the values of m_1 and E_0 calculated in section III, and taking $m_1/m_3=0.01$,

$$n=2\times10^{-6} \text{ per atom.}$$

As for bismuth, the number is very small. The electronic specific heat is then

$$C_e=aT=\frac{8\pi^3k^2}{3h^3}Vm_1(2m_3E_0)^{\frac{1}{2}}T. \tag{18}$$

Using the same values of the parameters as above gives for the linear coefficient of T, $a=1\times10^{-7}$ cal. mole^{-1} deg.$^{-2}$. The value given by Burton,[16] obtained from threshold field measurements, is $a=1.6\times10^{-4}$ cal. mole^{-1} deg.$^{-2}$. Allowing for the largest possible values of the parameters consistent with any kind of a fit to the data, the d.H.-v.A. electrons can account for only about 0.1 percent of the measured electronic heat, so that Blackman's assumption is indeed valid for zinc. Such a check was not possible in the case of bismuth, where no measurements of the electronic heat exist.

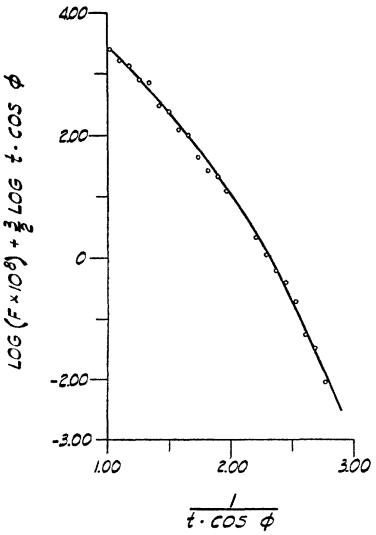

FIG. 9. Variation of envelope with angular orientation.

V. Low Field Constant Susceptibility

From Eq. (12), the principal susceptibilities at very low fields are

$$\kappa_1=-m_1A\frac{\pi^2}{6}(k/E_0)^{\frac{1}{2}}, \quad \kappa_3=-m_3A\frac{\pi^2}{6}(k/E_0)^{\frac{1}{2}}. \tag{19}$$

In terms of the constants employed in fitting the data,

$$\begin{aligned} \kappa_3 &= -(\pi/6)d_2(d_1b_h)^{\frac{1}{2}}, \\ \kappa_1 &= -(\pi/6)(m_1/m_3)d_2(d_1b_h)^{\frac{1}{2}}. \end{aligned}$$

Substitution of the numerical values gives (using $m_1:m_3=1:100$)

$$\kappa_3=-4\times10^{-6}, \quad \kappa_1=-0.04\times10^{-6}.$$

Although considerable uncertainty attaches to these values because of the discrepancy in the envelope, in any case the calculated value of $-\kappa_1$

[16] Burton, Grayson Smith, and Wilhelm, *Phenomena at the Temperature of Liquid Helium* (Reinhold Publishing Corporation, New York, 1940), p. 348.

is less than the observed $+0.15\times10^{-6}$, and that of $-\kappa_3$ larger than the observed $+0.18\times10^{-6}$. In the case of bismuth, both calculated values were smaller than the experimental, and Blackman inferred that the major part of the constant diamagnetic susceptibility was due to other "free" electrons which do not contribute appreciably to the de Haas-van Alphen effect. Such an explanation cannot suffice for zinc. At all temperatures down to 4.2 degrees, the total susceptibility of crystalline zinc is less than that of the free ions.[17] If the ion core susceptibility then be assumed independent of the crystal structure, it follows that the valence electrons most probably have a net paramagnetic effect. In view of the highly anomalous temperature dependence of χ_3 found by Marcus,[6] more cannot be said at this time.

VI. Comparison with Previous Work

An extensive comparison of the results of the present work with the data obtained by Marcus is not possible, but a rough comparison of the periodicity can be made. In Table III are given the fields at which extremes and crossovers of the oscillations were found by Marcus at 14°K and 20°K, together with the components of field along the hexagonal axis for which the present work indicates the same extremes and crossovers occur at 4.2°K. All measurements were made on the same crystal. (Values in braces were obtained by extrapolation of the periodicity from low fields.) The argument of the periodic term of $f(\beta H)$ is not a function of temperature, so that the extremes and crossovers theoretically should occur at the same H_3 at all temperatures. The rough agreement shown in Table III is fairly good, considering the difference in experimental method. Although the data at the higher temperatures are too meager to permit accurate calculation of $\beta/2E_0$, it is certainly of the same order of magnitude at all three temperatures. (A crude estimate gives a spread of about 50 percent of the value at 4.2°K.) The paucity of data at 14° and 20°K and the bizarre temperature dependence[6] of χ_3 prohibit comment on the envelope.

TABLE III.

r	Extremes of the oscillations 4.2°K	14°K	20°K
7	4.21		4.13
6	4.88		4.85
5	(5.74)	5.62	5.64
4	(7.07)	6.74	7.15
3	(9.19)	9.85	9.83
	Cross-overs of the oscillations		
7	4.52		4.45
6	5.32	5.02	5.16
5	(6.27)	6.31	6.21
4	(7.91)	8.12	8.20

VII. Validity of the Theoretical Formulae

It is, of course, important to ascertain whether or not the discrepancies reported in the preceding sections can have their origin in the mathematical approximations made by Landau in deriving (10). One of us has undertaken an investigation of the validity of these approximations for zinc at the temperatures and fields employed in obtaining the data. While the analysis is not yet completed, we have satisfied ourselves that the mathematics alone cannot account for the discrepancies.

ACKNOWLEDGMENTS

The experimental problem was suggested to one of us (S.G.S.) by Professor C. T. Lane, and I wish to thank him for his interest in the progress of the work. The participation of Mr. T. R. McGuire in all of the low temperature measurements and of Mrs. S. M. Sydoriak on numerous occasions is also gratefully acknowledged. The theoretical problem was suggested to J.E.R. by Professor Lars Onsager, and I wish to thank him for his guidance and continued interest.

The experimental part was submitted by S.G.S. to the faculty of the Yale Graduate School in partial fulfillment of requirements for the degree of Doctor of Philosophy.

[17] The value -0.235×10^{-6} for free ion susceptibility is given by Mott and Jones, *Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 211.