

Temperature and Field Dependence of the de Haas-van Alphen Effect*†

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The functional dependence of the observed de Haas-van Alphen effect in zinc has been compared with the predictions of the free electron theory. The dependence of the period on the magnetic field, and of the amplitude on the temperature appear to be correctly given. However, the predicted dependence of the amplitude on the magnetic field is in disagreement with the experimental results. An empirical formula for the amplitude dependence is given which differs from the free electron formula in that it contains an additional factor of $1/H$. This formula is in good agreement with the experimental results.

INTRODUCTION

THE de Haas-van Alphen effect is an oscillatory component of the diamagnetic susceptibility of certain conductors. It has been observed in some elements such as bismuth,¹ zinc,² and beryllium³ at liquid hydrogen temperatures and in magnetic fields less than ten thousand oersteds. Other elements, such as lead,⁴ only show the effect at temperatures of the order of one degree Kelvin and in magnetic fields of the order of eighty thousand oersteds. In all cases, except possibly lead, the effect is highly anisotropic. This is true even in aluminum⁵ where the lattice has cubic symmetry.

No satisfactory calculation of the diamagnetism of conduction electrons has yet been made. The thermodynamic properties of a free electron gas in a uniform magnetic field may, however, be calculated to any desired accuracy.^{6,7} An oscillatory component of susceptibility is found which possesses many features of the observed de Haas-van Alphen effect. In order to obtain any sort of quantitative agreement, it is necessary to assume values for the electron mass and for the electrochemical potential which are smaller by several orders of magnitude than those expected for a free electron gas having the particle density of a conduction band. The use of these quantities as adjustable parameters is usually justified by an appeal to the results of the Bloch theory.^{8,9}

The dominant functional dependence of this oscillatory term on the absolute temperature T and magnetic

field H is given by

$$\chi(T, H) = AT(1/H)^{\frac{3}{2}} \operatorname{csch}(aT/H) \times \exp(-b/H) \sin\pi[(1/dH) - \frac{1}{4}], \quad (1)$$

where A , a , b , and d are constants which are determined in terms of fundamental atomic constants by the theory.

In the first three mentioned elements, bismuth, zinc, and beryllium, the experimental parameters which characterize the effect are of such a magnitude that almost the whole range of the phenomena from the strong field case in which the power of $1/H$ is dominant, to the weak field case in which the exponential form of the hyperbolic cosecant dominates, may be observed at liquid helium temperatures using an electromagnet capable of producing ten thousand oersteds maximum. The effect in bismuth and beryllium is complicated by geometrical factors which will be explained in the following.

We present here the results of a detailed comparison of the observed de Haas-van Alphen effect, in a zinc single crystal containing 0.03 atomic percent aluminum, with the functional form predicted by the free electron theory. We find that quantitative agreement cannot be obtained without using two free parameters in addition to those permitted by the Bloch theory. These two parameters are the phase of the oscillations and the exponent of the factor $1/H$. An empirical formula will be given which is in satisfactory agreement with experiment.

FREE ELECTRON THEORY

The Landau formula¹⁰ for the oscillatory part of the grand canonical potential $\Omega(T, V, \zeta, H)$ of a free electron gas is

$$\Omega_{\text{osc.}} = \frac{kTV}{4\pi^2} \left(\frac{eH}{\hbar c} \right)^{\frac{3}{2}} \sum_{r=1}^{\infty} \frac{(-1)^r \cos\pi(r\zeta/\beta H - \frac{1}{4})}{r^{\frac{3}{2}} \sinh(r\pi^2 kT/\beta H)}. \quad (2)$$

Here ζ is the electrochemical potential, β is $e\hbar/2mc$, and the other symbols have their usual significance. This formula is valid for arbitrary values of the magnetic field. The error is temperature dependent and is of the order of $\exp(-\zeta/kT)$.

¹⁰ D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939).

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¹ W. J. de Haas and P. M. van Alphen, Proc. Koninkl. Akad. Wetenschap Amsterdam **33**, 680, 1106 (1930).

² J. A. Marcus, Phys. Rev. **71**, 559 (1947).

³ Verkin, Lazarev, and Rudenko, Doklady Akad. Nauk. S.S.S.R. **73**, 59 (1950).

⁴ D. Shoenberg, Nature **170**, 569 (1952).

⁵ D. Shoenberg, Nature **167**, 647 (1951).

⁶ E. H. Sondheimer and A. H. Wilson, Proc. Roy. Soc. (London) **A210**, 173 (1951).

⁷ R. B. Dingle, Proc. Roy. Soc. (London) **A211**, 500, 517 (1952); **212**, 38, 47 (1952).

⁸ H. Jones, Proc. Roy. Soc. (London) **A147**, 396 (1934).

⁹ M. Blackman, Proc. Roy. Soc. (London) **A166**, 1 (1938).

Dingle has shown that if an electron spends a mean time τ in a given quantized state before making a transition to another state under the influence of some perturbation such as impurity scattering, the r th harmonic in the above expression is reduced by the factor $\exp(-r\pi\hbar/\tau\beta H)$.

Blackman⁹ has shown that if one assumes a generalized form for the energy relation $2mE = \mathbf{p} \cdot \boldsymbol{\alpha} \cdot \mathbf{p}$, where $\boldsymbol{\alpha}$ is a tensor of rank two whose components in space coordinates are $\alpha_{ij} = (m/\hbar^2)(\partial^2 E/\partial k_i \partial k_j)$, the resulting relations between energy, momenta, coordinates, and field may be reduced to spherical form by the substitutions $p'_i = \alpha_i^{1/2} p_i$; $q'_j = \alpha_j^{-1/2} q_j$, and $H'_k = (\alpha_i \alpha_j)^{1/2} H_k$. The coordinate system has been chosen to diagonalize $\boldsymbol{\alpha}$. To complete the substitution, one must replace V by $V' = (\alpha_1 \alpha_2 \alpha_3)^{-1/2} V$ and H by $H' = (\alpha_1 \alpha_2 H_3^2 + \alpha_2 \alpha_3 H_1^2 + \alpha_3 \alpha_1 H_2^2)^{1/2}$ in Eq. (2) above.

The magnetic moment is then given by

$$\begin{aligned} \mathbf{M} &= -\text{grad}_H \Omega(T, V', \zeta, H') \\ &= \mathfrak{M} \chi(T, V', \zeta, H') \begin{Bmatrix} \alpha_2 \alpha_3 H_1 \\ \alpha_3 \alpha_1 H_2 \\ \alpha_1 \alpha_2 H_3 \end{Bmatrix}, \end{aligned} \quad (3)$$

where \mathfrak{M} is the total mass and χ the susceptibility per unit mass.

The effect of electron spin is to include the factor $2 \cos(r\pi H/H')$ in the r th harmonic in Eq. (2).

The complete expression for χ thus includes harmonic terms which have been omitted from Eq. (1). Once the fundamental has been obtained, it is possible to estimate the magnitude of the error made in neglecting them.

METHOD OF MEASUREMENT

In general, a body with magnetic moment \mathbf{M} in a magnetic field \mathbf{H} experiences a translational force $-(\mathbf{M} \cdot \nabla)\mathbf{H}$ and a torque $\mathbf{M} \times \mathbf{H}$. Either the force or the torque may be used as a measure of the susceptibility of nonferromagnetic bodies. For a measurement of the field independent susceptibility, the body force (Faraday) method is to be preferred, since it is capable of yielding absolute values of the susceptibility. The torsion method is capable of measuring only the susceptibility difference in various directions in anisotropic media. For the measurement of field dependent susceptibility, the torsion method has the distinct advantage that homogeneous magnetic fields may be used. If the susceptibility be strongly dependent on the field, the body force method will reveal only a value of the susceptibility averaged over the different fields along the specimen.

The z component of the torque on a body having a magnetic moment described by Eq. (3) above is

$$C_z = (\mathbf{M} \times \mathbf{H})_z = -\mathfrak{M} H^2 \{ a_{21} a_{22} \alpha_1 \alpha_3 + a_{11} a_{12} \alpha_2 \alpha_3 + a_{31} a_{32} \alpha_1 \alpha_2 \} \chi(T, V', \zeta, H'), \quad (4)$$

where the a_{ij} 's are components of the matrix which

transforms the coordinate system from the space coordinates in which the torque is measured in the z direction and the magnetic field is applied along the x axis to the body coordinate system in which the tensor $\boldsymbol{\alpha}$ is diagonal. H' is now

$$H \{ a_{11}^2 \alpha_2 \alpha_3 + a_{21}^2 \alpha_3 \alpha_1 + a_{31}^2 \alpha_1 \alpha_2 \}^{1/2}.$$

If ϕ be the angle between the magnetic field and the line of nodes of the body system, θ the angle between the z axis and the 3 axis of the body system, and ψ the angle of rotation of the 1 axis of the body system from the line of nodes about the 3 axis, these components are

$$\begin{aligned} a_{11} &= \cos\phi \cos\psi - \cos\theta \sin\phi \sin\psi, \\ a_{12} &= \sin\phi \cos\psi + \cos\theta \cos\phi \sin\psi, \\ a_{21} &= -\cos\phi \sin\psi - \cos\theta \sin\phi \cos\psi, \\ a_{22} &= -\sin\phi \sin\psi + \cos\theta \cos\phi \cos\psi, \\ a_{31} &= \sin\theta \sin\phi, \\ a_{32} &= -\sin\theta \cos\phi. \end{aligned} \quad (5)$$

An hexagonal crystal has sixfold rotational symmetry in the basal plane. Unless one assumes isotropy in the basal plane ($\alpha_1 = \alpha_2$), at least three such tensor distributions arranged so that they go into each other under a rotation through $2\pi/3$ must be chosen. Since this is the simplest nontrivial case, we shall assume it for further computation.

The three distributions will each contribute to the torque. One contribution will be that given above and the other two may be obtained from it by replacing functions of ψ by functions of $\psi \pm 2\pi/3$. In these experiments, we attempted to put the 1 and 3 axes of the crystal in the plane of the magnetic field. Therefore, let $\theta = \frac{1}{2}\pi + \eta$ and $\psi = \xi$ where $\eta, \xi \ll 1$.

$$\begin{aligned} H'_0 &= H \{ \alpha_1 \alpha_2 \sin^2\phi + \alpha_2 \alpha_3 \cos^2\phi \}^{1/2}, \\ H'_\pm &= H \{ \alpha_1 \alpha_2 \sin^2\phi + \frac{1}{4}(\alpha_2 \alpha_3 + 3\alpha_3 \alpha_1) \cos^2\phi \\ &\quad \mp \frac{1}{2}\sqrt{3}(\alpha_2 \alpha_3 - \alpha_3 \alpha_1)(\xi \cos^2\phi - \eta \sin\phi \cos\phi) \}^{1/2}, \\ C_z/\mathfrak{M} H^2 &= \{ [\alpha_1 \alpha_2 - \alpha_2 \alpha_3] \chi(H'_0) + [\alpha_1 \alpha_2 - \frac{1}{4}(\alpha_2 \alpha_3 + 3\alpha_3 \alpha_1)] \\ &\quad \cdot [\chi(H'_+) + \chi(H'_-)] \} \sin\phi \cos\phi \\ &\quad + \frac{1}{2}\sqrt{3}[\alpha_3 \alpha_1 - \alpha_2 \alpha_3] [\chi(H'_+) - \chi(H'_-)] \\ &\quad \cdot [\xi \sin\phi \cos\phi - \frac{1}{2}\eta(\cos^2\phi - \sin^2\phi)]. \end{aligned} \quad (6)$$

We can see that small errors in orientation are negligible except where ϕ is close to zero or to $\frac{1}{2}\pi$. For $\phi = \frac{1}{2}\pi$ the torque vanishes regardless of the value of ψ . It is this feature which leads Shoenberg¹¹ to suggest that the vanishing of the de Haas-van Alphen effect be used to determine the position of the 3 axis rather than the vanishing of the couple at room temperature, since any anisotropy in the suspension may shift the angle at which the couple vanishes.

As we shall subsequently show, our experimental value of the product $\alpha_1 \alpha_2$ is so much greater than either $\alpha_2 \alpha_3$ or $\alpha_3 \alpha_1$ that the effect in zinc has a very simple

¹¹ D. Shoenberg, Trans. Roy. Soc. (London) A245, 1 (1952).

dependence on the angle ϕ . It is this feature which makes the analysis of the temperature and field dependence in zinc considerably less difficult than is the case for bismuth or beryllium.

THE TORSION BALANCE¹²

The torsion balance used in these experiments differs from those previously used in that the torsion head is replaced by a wall type galvanometer modified by drilling an extra hole through its base. The quartz rod holding the specimen is cemented to the galvanometer coil. Light reflected from the galvanometer mirror falls on a split photocell. The output of the photocell is amplified and the voltage applied to the galvanometer coil in such a way as to oppose its motion. The current in this feedback loop is thus proportional to the torque acting on the specimen. This scheme has several advantages. One is the very high effective spring constant of the balance so the actual deflections of the specimen are negligible, of order of a few minutes of arc for the largest torques. With this small motion, the effect of eddy currents in the specimen is not noticeable and equilibrium is achieved almost immediately. Another advantage is the possibility of using an ayrton shunt to vary the sensitivity of the balance. The circuit may be used for automatic recording as in the block diagram given in Fig. 1.

PREPARATION OF SPECIMEN

The single-crystal specimen, in the form of a sphere approximately $\frac{5}{16}$ inches in diameter, was grown by the method of Tammann in a graphite mold. The furnace was cooled from about 30°C above the melting point to 20°C below at a rate of about $\frac{1}{2}$ °C per hour. A helium atmosphere was used to protect the melt from oxidation. The crystal was etched with ten percent hydrochloric acid in ethyl alcohol. The strongest etch plane is parallel to the basal plane (001) and three secondary etch planes are parallel to crystal planes of type (010).

To achieve the desired orientation with respect to the specimen holder, the specimen was placed in the holder on the stage of a metallurgical microscope. The vertical illuminator of the microscope was used to

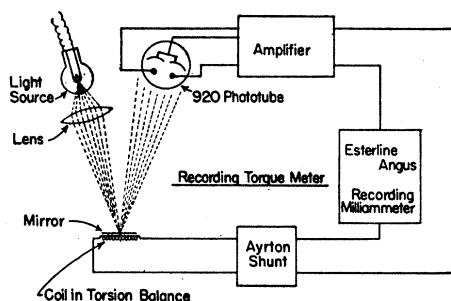


FIG. 1. Block diagram of circuit for recording torsion balance.

¹² The final form of this balance was the result of contributions by W. F. Love and G. T. Croft as well as the authors.

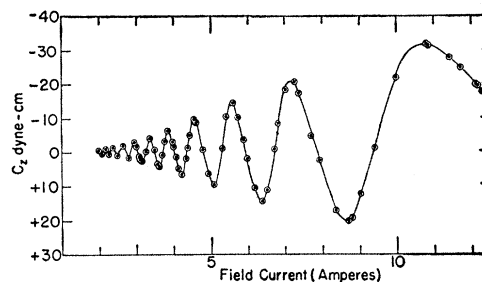


FIG. 2. Typical torque vs magnet field current curve for a zinc crystal at liquid helium temperatures. The angle ϕ between the hexagonal axis of the crystal and the magnetic field is 40°.

provide light having a known direction. The specimen was rotated until one of the secondary etch planes reflected strongly. The specimen was raised slightly without altering its orientation and the holder carefully wet with Duco cement. The specimen was then replaced in the holder and the brilliance of the reflection checked while minor adjustments in orientation could still be made. After the cement had dried, the reflection was again observed. If nothing had changed, the assembly of holder and specimen was cemented to the quartz rod connected to the torsion balance. The error in orientation could hardly be greater than a few degrees of arc.

Measurements at room temperature were made primarily to determine the relative orientation of the crystal axes with respect to the reference scale on the magnet base. The torque at constant field was measured at fifteen-degree intervals through three hundred and sixty degrees of arc. The orientation of the crystal axes with respect to the reference angle ω was determined by the method of least squares.

As a precaution against the presence of ferromagnetic impurity, either in the specimen or on the suspension, the torque was also measured as a function of field at constant angle. The computed values of the susceptibility difference were plotted as a function of reciprocal field (Honda plot). If a significant amount of ferromagnetic impurity be present, the susceptibility difference will depart from constancy, and if the impurity can be assumed saturated, the slope of the Honda plot gives the magnetic moment and the intercept at infinite field gives the true susceptibility difference. Those specimens which showed ferromagnetic contamination were discarded.

MEASUREMENTS AT LIQUID HELIUM TEMPERATURES

A typical result of measurements at liquid helium temperature is shown in Fig. 2. The zinc-aluminum crystal weighted 1.6377 grams. There are more points at the low field end of the graph than could conveniently be shown. The especial virtue of the torsion balance used is that it permits one to measure these small torques with the same relative ease and accuracy

TABLE I. Reciprocal field at crossover points, in $10^4(\text{oersted})^{-1}$.

Integer n	Pure zinc				Zinc-aluminum				
	ω ϕ	ω ϕ	ω ϕ	ω ϕ	ω ϕ	ω ϕ	ω ϕ	ω ϕ	ω ϕ
4									
5									
6	1.157	1.032	1.170		1.193	1.057			1.188
7	1.408	1.250	1.803		1.513	1.357			1.505
8	1.648	1.463	2.120	1.197	1.829	1.627			1.834
9	1.884	1.676	2.446	1.619	2.154	1.905	1.088		2.149
10	2.142	1.892	2.765	1.832	2.493	2.193	1.263		2.478
11	2.392	2.111	3.087	2.042	2.815	2.482	1.427		2.809
12	2.646	2.329	3.416	2.266	3.142	2.778	1.584		3.132
13	2.900	2.558	3.737	2.476	3.457	3.066	1.747		3.454
14	3.157	2.788	4.062	2.698	3.809	3.358	1.912		3.789
15	3.412		4.391	2.913	4.133	3.644	2.078	1.098	
16	3.666		4.717	3.108	4.478	3.961	2.249	1.193	
17	3.924		5.053	3.336			2.412	1.290	
18	4.176			3.573			2.583	1.378	
19	4.448			3.760			2.750	1.467	
20	4.697			4.008				1.522	
21				4.229				1.643	
22				4.447				1.728	
23				4.667				1.817	
24				4.896				1.892	
25				5.104				1.997	
				5.328				2.087	

as the large torques at high fields. The magnetic field at the highest point shown (field current 12.19 amperes) is 9570 oersteds.

PERIOD AND PHASE OF THE OSCILLATIONS

After the results of observation have been transformed, that is, the magnetic field current converted to field strength, and the torques weighted by the factor H^{-2} , the next and most straightforward step is to determine the period and phase of the oscillations. A large-scale plot is made with abscissa proportional to H^{-1} and ordinate proportional to $C_z H^{-2}$. The contribution of the field independent susceptibility difference is taken as the mean of the oscillations. The values of the reciprocal field at which the graph crosses this mean value are tabulated. The crossover points should satisfy the relation

$$(1/H)_{\text{crossover}} = d(n + \delta), \quad (7)$$

where n is an integer and δ is the phase in multiples of π radians. [See Eq. (1).]

The n corresponding to the first observed crossover may be assigned arbitrarily, but has been taken even

TABLE II. Period and phase of oscillations.

$T^\circ\text{K}$	ω	ϕ	$d \times 10^6 (\text{oersted})^{-1}$	$\delta (\text{radian}/\pi)$
Pure zinc				
4.2°	349°	45°	2.534 ± 0.007	0.512 ± 0.037
4.2°	82.8°	41.2°	2.186 ± 0.003	0.308 ± 0.019
Zinc-aluminum				
4.2°	15°	70°13'	3.233 ± 0.007	0.422 ± 0.020
4.2°	45°	40°13'	2.177 ± 0.006	0.589 ± 0.040
4.2°	105°	75°	3.282 ± 0.011	0.408 ± 0.028
4.2°	240°	60°	2.888 ± 0.012	0.366 ± 0.042
4.2°	30°	30°	1.655 ± 0.005	0.414 ± 0.033
4.2°	15°	15°	0.888 ± 0.005	0.538 ± 0.104
4.2°	255°	75°	3.251 ± 0.006	0.366 ± 0.014
14.1°	345°	40°	2.186 ± 0.009	0.424 ± 0.041
18.0°	345°	40°	2.189 ± 0.015	0.477 ± 0.059
20.4°	345°	40°	2.201 ± 0.027	0.494 ± 0.109

or odd to conform to the sign convention of the free electron theory.

Table I gives the values of these crossover points measured at various angles ϕ between the 1 axis of the crystal and the magnetic field. Results for two specimens are tabulated, one pure zinc and the other zinc-aluminum. The results for zinc-aluminum are also shown graphically in Fig. 3.

The results of the calculations of the period and phase are given in Table II. The precision indices are the standard, or root mean square deviations which were computed according to formula given for example in Worthington and Geffner.¹³

We have included in this table the results of measurements of the period and phase at liquid hydrogen temperatures. Within the experimental error, these are the same as at 4.2°K.

The phase of the oscillations is markedly different from that predicted by the free electron theory. There is considerable scatter in the values obtained at various angles. The average value is about 0.4π radian as compared with -0.25π radian predicted by the free elec-

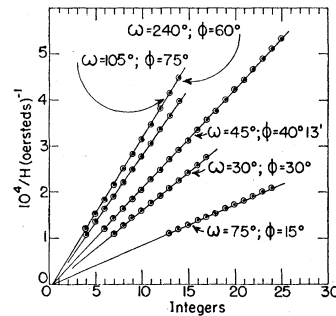


FIG. 3. Crossover points of oscillations vs integers for various orientations of magnetic field with respect to the crystal axes.

tron theory. This value is in agreement with the results of Mackinnon¹⁴ with pure zinc, but not with those of Sydoriac and Robinson¹⁵ who reported a phase of zero.

The square of the quantity d which we have given for various angles in Table II has been shown to be a linear function of $\sin^2\phi$. We assume that the values of d^2 are known more accurately than those of $\sin^2\phi$. Moreover, errors in ϕ and not in $\sin^2\phi$ are assumed equiprobable. For this reason, we assign a weighting factor w proportional to $(\sin\phi \cos\phi)^{-2}$. Because the standard deviation of d also differs from angle to angle, we make the weight w proportional to $(d\sigma_d)^{-2}$ as well. The weights so assigned are listed in the column headed w in Table III. They have been normalized such that $\sum w = 9$, the number of observations. Figure 4 shows the graph of $\sin^2\phi$ against d^2 .

From the intercept at $d^2=0$ in principle, one could

¹³ A. G. Worthington and J. Geffner, *Treatment of Experimental Data* (John Wiley and Sons, Inc., New York, 1943), p. 249.

¹⁴ L. Mackinnon, Proc. Phys. Soc. (London) **B62**, 170 (1949).

¹⁵ G. Sydoriac and J. E. Robinson, Phys. Rev. **75**, 118 (1949).

determine the ratio $\alpha_3/\alpha_1 - \alpha_3$. The parameters are such that our value for this ratio is $-10^{-3} \pm 10^{-2}$. The negative sign is hardly significant in view of the uncertainty, but it is at least consistent with the known positive Hall coefficient of zinc. From the intercept at $\sin^2\phi = 1$, the effective temperature $(\alpha_1\alpha_2)^{1/2}T_0$ may be computed. The value obtained is $1.98 \pm 0.01^\circ\text{K}$ which agrees within the stated error with the value published by Mackinnon of $1.96 \pm 0.02^\circ\text{K}$ for pure zinc. In this expression T_0 is the degeneracy temperature ζ/k of the electrons responsible for the effect.

The calculated errors in angle from the fitted curve are also listed in Table III. There are no errors in excess of the expected accuracy in orientation of the crystals.

TEMPERATURE DEPENDENCE OF THE AMPLITUDE

In this section, and in the following, whenever we refer to the magnitude of an extremum it is understood that the correction for the contribution of the field independent susceptibility has been made. At con-

TABLE III. Quantities used to compute $(\alpha_1\alpha_2)^{1/2}T_0$.

ω	ϕ	$d^2 \times 10^{10}$ (oersted) ⁻²	$\sin^2\phi$	w	$\Delta\phi$
Pure zinc					
349°	45°	6.419	0.5000	0.009	-3°27'
82.8°	41.2°	4.778	0.4339	0.557	+0°59'
Zinc-aluminum					
255°	75°	10.57	0.9330	0.982	+1°12'
105°	75°	10.77	0.9330	0.327	-0°47'
15°	70°13'	10.45	0.8854	0.533	-2°32'
240°	60°	8.341	0.7500	0.098	+1°27'
45°	40°13'	4.739	0.4169	0.448	+0°12'
30°	30°	2.739	0.2500	1.069	+0°44'
15°	15°	0.7886	0.0670	4.977	-0°13'

stant field and angle, the amplitude of an extremum $|C_z|_{\text{ext}}$ should obey the equation [see Eqs. (1) and (6)]:

$$|C_z|_{\text{ext}} = A'T \text{csch}(a'T).$$

Dividing through by T and taking logarithms of both sides gives

$$\log(|C_z|_{\text{ext}}/T) = \log A' - \log \sinh(a'T), \quad (8)$$

which for large enough values of the argument of the hyperbolic function becomes the equation of a straight line. Such a plot for the extremum at H equal 5800 oersteds, ϕ equal 40° of arc, for temperatures between 1.5 and 4.2°K is given in Fig. 5. The pronounced positive curvature of the graph shows that the asymptotic formula for the logarithm of the hyperbolic function cannot be used. The graph is a plot of $-\log \sinh(0.3T)$ with the constant chosen so that the curve passes through the point at T equal 3°K.

The temperature range available through the use of liquid helium is not great enough to obtain much more than order of magnitude accuracy for the parameters involved. Consequently, the measurements were re-

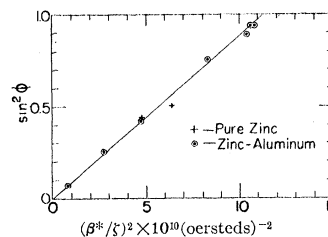


FIG. 4. $\sin^2\phi$ plotted against the square of the period of the oscillations. A linear relation is predicted by the theory.

peated at liquid hydrogen temperatures. Values were obtained at 20.4° at 18.0°, and at 14.1°K. All the points are shown in Fig. 6.

The asymptotic form of the logarithm of the hyperbolic sine may be used in the liquid hydrogen temperature range. In an effort to get a good value for the parameters of the curve the logarithm of the hyperbolic sine was rewritten as

$$\log \sinh a'T = -\log 2 + \log[1 - \exp(-2a'T)] + \log \exp(a'T).$$

The quantity $\log[1 - \exp(-2a'T)]$ was calculated for each point using the value of the constant a' equal to 0.26 estimated from the slope in the asymptotic region. This quantity was then used to linearize the curve and the slope taken. This procedure yielded a new value of the constant a' equal to 0.264. An iteration of this procedure resulted in a new value of the constant, but negligibly different from the old. The curve drawn in Fig. 5 is computed from the fitted parameters.

FIELD DEPENDENCE OF THE AMPLITUDE

By reasoning similar to that used for the temperature dependence, we expect that at constant temperature

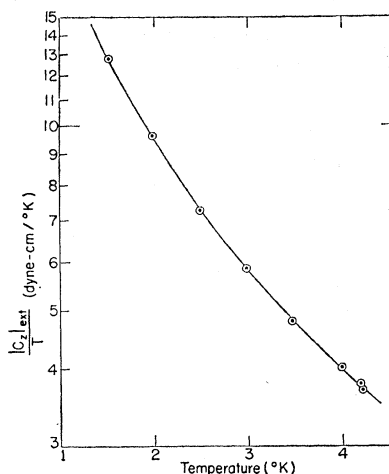


FIG. 5. The logarithm of the amplitude at constant field minus the logarithm of the temperature plotted against temperature from 1.5 to 4.2°K. Positive curvature is expected of the logarithm of a hyperbolic sine for small values of the argument.

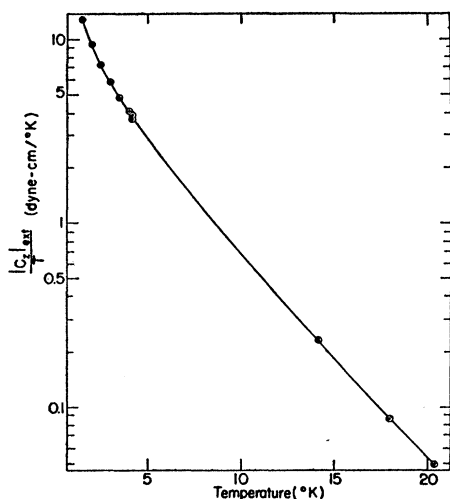


FIG. 6. Log(amplitude) minus log(temperature) vs temperature from 1.5 to 20.4°K. At hydrogen temperatures, the argument of the hyperbolic sine is large so that it may be approximated by the exponential function.

and angle the equation,

$$\log \left\{ \frac{|C_z|_{\text{ext}} \left(\frac{\sin \phi}{H} \right)^{\frac{1}{2}}}{\mathfrak{M} \cos \phi} \right\} = \log A'' - \log \sinh(a''/H \sin \phi) - \log \exp(b''/H \sin \phi), \quad (9)$$

will be satisfied by the values $|C_z|_{\text{ext}}$ marking the envelope of the oscillations, and that the graph will approach a straight line at large values of the reciprocal field.

Forewarned by the results of the temperature measurement, we shall expect that considerable curvature will be shown at small values of the reciprocal field if the temperature be in the liquid helium range.

The actual results are shown in Fig. 7. The angle ϕ is again 40° of arc. The temperature is the normal boiling point of liquid helium (4.2°K).

The plotted points do indeed show a pronounced

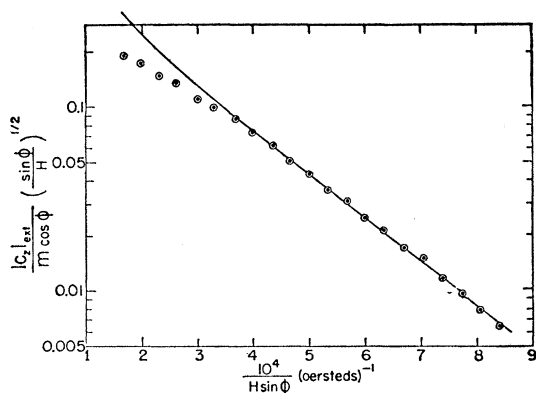


FIG. 7. Log(amplitude) minus $\frac{1}{2} \log H$ vs H^{-1} . The solid curve is the theoretical relation. The experimental points show negative curvature at high fields where theory predicts positive curvature.

curvature, and exactly in the expected region, but the curvature has the wrong sign.

This negative curvature may be found in the results of Shoenberg¹⁰ for the amplitude dependence of the de Haas-van Alphen effect in bismuth and in those of Sydoriac and Robinson¹⁵ and of Mackinnon¹⁴ with zinc. They tended to place more confidence in the high field points than in the low field points and, in consequence, drew straight lines through the points taken at high fields (small values of the reciprocal field) and observed that the amplitude falls off more rapidly at low fields than the theory predicts.

EMPIRICAL RELATION FOR FIELD DEPENDENCE

If one wishes to preserve the theoretical form of the temperature dependence, and we see no reason to abandon it, the left-hand side of Eq. (9) must be altered. We have found that the addition of $\log(H \sin \phi)$

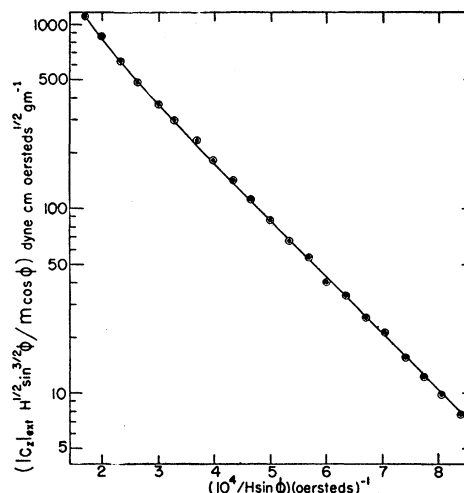


FIG. 8. Log(amplitude) plus $\frac{1}{2} \log H$ vs H^{-1} . The empirical equation is a good fit to the experimental points.

is sufficient to give to the graph of the experimental points the correct sign and magnitude of the curvature. Figure 8 shows a log plot of the quantity $(|C_z|_{\text{ext}} H^{\frac{1}{2}} \sin^3 \phi) / (\mathfrak{M} \cos \phi)$ as a function of $(H \sin \phi)^{-1}$.

To illustrate the agreement more fully, we show in Fig. 9 a plot of the same set of points as are shown in Fig. 8 except that the ordinates have been corrected by the factor $[1 - \exp(-2a''/H \sin \phi)]$, where the constant a'' has been computed from the parameters determined from the temperature dependence. The graph has become a straight line.

Since the phase of the oscillations is close to $\pi/2$ the series is almost a cosine series. Thus, the second and all even harmonics tend to alternately increase and decrease the magnitude of successive extrema. The fact that this is not observed in the high field points of Figs. 8 and 9 may be due to this effect being partially compensated by a small H^2 term in the monotonic susceptibility.

COMPARISON OF COMPUTED CURVES WITH ORIGINAL DATA

We have combined the results of the measurement of the phase and period for this particular angle from Table II and have computed the solid curve shown in Fig. 10, taking the amplitude from the logarithmic plot of Fig. 8. The envelope taken from Fig. 7 is lightly dashed. Against this background, we display the points computed from those shown in Fig. 1 as torque *versus* magnet field current.

If we had elected to obtain the 3/2 power parameters from the high-field measurements, the lightly dashed envelop would diverge at the low-field end, becoming too large by a factor of two.

The assumed 5/2 power dependence fits very nicely, both at high fields where the power is dominant and at low fields where the exponential dominates. The points

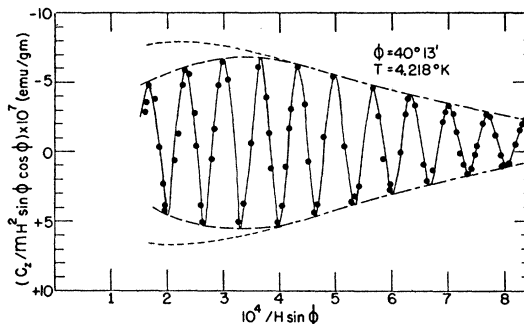


FIG. 10. Field-dependent susceptibility of zinc as a function of H^{-1} . The solid curve is computed from the empirical parameters. The lightly dashed curve indicates where the envelope should be if the amplitude dependence of the free electron theory were correct. These points were calculated from the experimental points shown in Fig. 2.

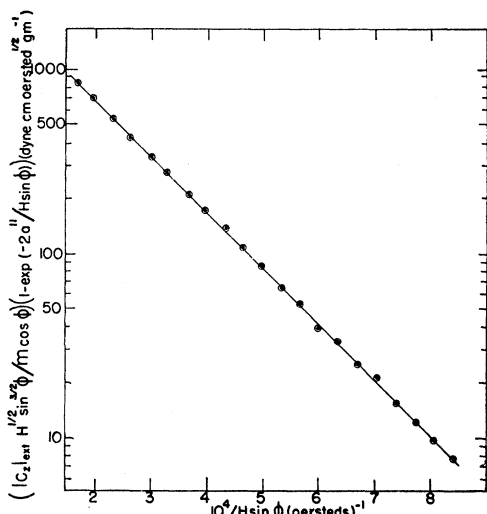


FIG. 9. Log(amplitude) plus $\frac{1}{2} \log H$ plus a correction factor calculated from the temperature dependence plotted against H^{-1} .

at highest field are beginning to deviate from sinusoidal behavior. This can be attributed to the influence of the higher harmonics in the series. The second harmonic is estimated to be about 15 percent of the fundamental for these points.

FIELD DEPENDENCE AT OTHER ORIENTATIONS

Figures 11 and 12 show the field dependence of the amplitude at other angles in the same manner as in Figs. 7 and 8. The curvature has the wrong sign at every angle if the 3/2 power dependence of the susceptibility be assumed. The separation of the curves is a measure of the scatter in the amplitude. The slopes of the curves differ slightly. Some of these discrepancies are no doubt due to errors in determining ϕ . Functions of this angle appear in both ordinate and abscissa.

We have rectified the curves based on the assumption of a 5/2 power dependence of the susceptibility on the

reciprocal field using the constant a'' computed from the temperature dependence. The values of the slopes and intercepts for the various orientations are listed in Table IV.

The best we can say for the intercept is that within the possible error of 30 percent it is independent of the angle ϕ . This constant A has a value of approximately $330 \text{ dyne-cm (oersteds)}^{1/2}$ per gram per degree Kelvin. In the absence of a reliable theory to relate this quantity to fundamental constants, we can proceed no further.

We identify the constant b'' with the scattering factor $\pi \hbar / \tau \beta^*$.¹⁶ From the table, it can be seen that this factor is roughly constant as ϕ ranges from 75° to 40° of arc. It reaches a maximum at ϕ equal to 30° of arc and is slightly smaller at ϕ equal to 15° of arc. Croft, Love,

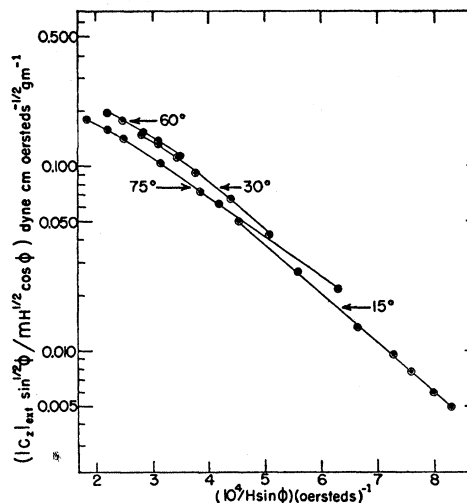


FIG. 11. Log(amplitude) minus $\frac{1}{2} \log H$ vs H^{-1} shown for other orientations of the crystal with respect to the field. The negative curvature at high fields is contrary to the predictions of the free electron theory.

¹⁶ β^* is an effective Bohr magneton defined such that $\beta^* H = \beta H'$.

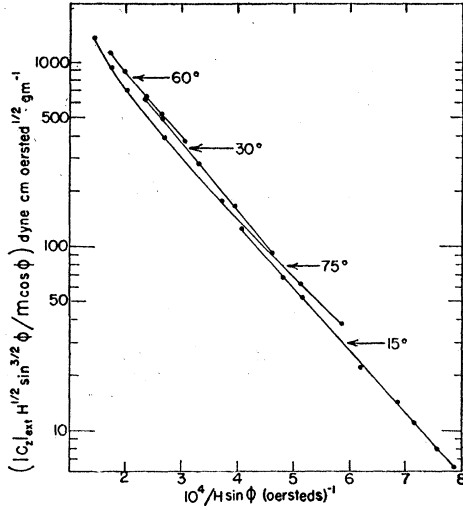


FIG. 12. Log(amplitude) plus $\frac{1}{2} \log H$ vs H^{-1} for various orientations of the crystal with respect to the magnetic field.

and Nix¹⁷ observed similar variation with angle in tin-antimony alloys. The custom is to report this parameter as an effective temperature X which is $b''T/a''$. This effective temperature is also given in Table IV.

ELECTRONIC PARAMETERS

From the measurements of the angle variation of the period of the oscillations, the parameter $(\alpha_1\alpha_2)^{1/2}T_0 = 1.98^\circ\text{K}$ was obtained. On the assumption that the parameter a' appearing in the temperature dependence relation can be identified with the constants given by the free electron theory, we compute the value of $(\alpha_1\alpha_2)^{1/2}$ to be 148. This leads directly to a value of 292°K for the degeneracy temperature T_0 .

SUMMARY

The predictions of the free electron theory with regard to the periodicity of the de Haas-van Alphen effect and its variation with angle have been verified.

Our chief interest has been in the functional form of the temperature and field dependence of the envelope of the oscillations. It had previously been reported¹⁴ that the variation with field was nearly correctly predicted, while the variation with temperature was not. We find, to the contrary, that the temperature variation

¹⁷ Croft, Love, and Nix, following paper, Phys. Rev. **95**, 1403 (1954).

could be fitted quite well to the predicted functional relation. Even with very generous allowance for experimental error, we have been unable to account for the observed field dependence on the basis of the predictions of the free electron theory. We propose an empirical modification of the formula for the oscillatory susceptibility which we have shown to be consistent with our experimental results.

$$\chi(T, H) = AT(1/H)^{5/2} \text{csch}(aT/H) \times \exp(-b/H) \sin\pi[(1/dH) + \delta]. \quad (10)$$

It should be mentioned that a term having this functional dependence has been calculated for the contribution of the surface states of a finite volume of free electron gas.^{18,19} However, it appears improbable that this surface term could be used to justify the empirical formula above since, for the field strengths employed in this investigation, it is smaller than the

TABLE IV. Slopes and intercepts of rectified 5/2 power plots. The constants a'' and b'' are given in units of $10^{-4}(\text{oersted})^{-1}$.

$T = 4.2^\circ\text{K}$							
ω	ϕ	$\log A''$	a''	b''	X ($^\circ\text{K}$)	$\log A$	No. of points
105°	75°	3.069	0.420	0.294	2.97°	2.444	8
255°	75°	3.101	0.417	0.333	3.34°	2.477	8
15°	70°13'	3.094	0.420	0.249	2.52°	2.468	12
240°	60°	3.145	0.417	0.270	2.70°	2.521	5
45°	40°13'	3.145	0.420	0.282	2.85°	2.520	21
30°	30°	3.250	0.417	0.378	3.79°	2.626	6
15°	15°	3.133	0.420	0.354	3.58°	2.508	8
$T = 14.1^\circ\text{K}$							
345°	40°	3.665	1.404	0.304	3.05°	2.516	9
$T = 18.0^\circ\text{K}$							
345°	40°	3.814	1.792	0.297	2.98°	2.559	7
$T = 20.4^\circ\text{K}$							
345°	40°	3.708	2.033	0.137	1.29°	2.406	5

volume term by many orders of magnitude except if the electrons be confined to volumes whose linear dimensions are of the order of a few lattice spacings.

ACKNOWLEDGMENTS

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¹⁸ M. C. Steele, Phys. Rev. **88**, 451 (1952).

¹⁹ R. B. Dingle, Proc. Roy. Soc. (London) **A219**, 463 (1953).