Temperature-Dependent de Haas-van Alphen Parameters in Zinc

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The magnetic susceptibility of a single crystal of zinc has been investigated from 4.2°K to 300°K in fields up to 25 kilogauss. Traces of the de Haas-van Alphen effect persisted at temperatures as high as 200°K. The period of the characteristic susceptibility oscillations increased with increasing temperature, rising from 6.4×10^{-5} gauss^{-1} at 4.2°K to 12.5×10^{-5} gauss^{-1} at 61.2°K. If present interpretations of the de Haas-van Alphen parameters are valid, temperature dependent effective masses, or chemical potential, or both are implied for the pertinent electrons. A rough calculation indicates that temperature dependences of the right order of magnitude might arise from alteration of the overlap of Brillouin zone boundaries by the Fermi surface as a result of anisotropic thermal expansion of the lattice.

In addition to the main oscillations, terms exhibiting periods of approximately 2×10^{-7} gauss^{-1} were observed at 4.2°K but were not investigated in detail.

INTRODUCTION

THE low temperature periodic dependence of magnetic susceptibility upon magnetic field characteristic of the de Haas-van Alphen effect is of interest not only because it yields values for the effective masses and chemical potential of the pertinent electrons, but perhaps more so because of its correlation with the low temperature magneto-oscillatory behavior of magnetoresistance,[1-3] Hall effect,[4,5] thermoelectric effect,[6] and thermal conductivity.[7] The magnetic susceptibility oscillations were first observed by de Haas and van Alphen[8] in bismuth in 1930 and have since been observed in a total of fifteen metal single crystals. They were observed in zinc by Marcus[9-11] in 1947, and since then the effect in zinc has been studied in the liquid helium and liquid hydrogen temperature ranges by Sydoriak and Robinson,[12] Mackinnon,[13] Verkin, Lazarev, and Rudenko,[14] Verkin,[15] and Donahoe.[16]

Marcus had noted that a field dependence persisted in χ_3, the component of magnetic susceptibility per unit mass parallel to the hexagonal axis of zinc, at temperatures as high as 60°K, and in 1951 McClure and Marcus[17] reported that χ_3 was field dependent up to 85°K. Furthermore, they observed that, "The behavior

of χ_3 at liquid nitrogen temperatures somewhat resembles the de Haas-van Alphen effect with the amplitude of oscillation sharply decreased and the maxima and minima displaced in field strength." The present investigation was undertaken in order to clarify the relation between these field dependences of susceptibility in the low and intermediate temperature ranges. As will be evident from the experimental results of this investigation, both are indeed manifestations of the same phenomenon, for oscillations which are strictly periodic in reciprocal magnetic field, as is characteristic of de Haas-van Alphen oscillations, were observed up to 61.2°K. However, in contrast to the de Haas-van Alphen effect at lower temperatures, the period of oscillation becomes temperature dependent at the higher temperatures, increasing with increasing temperature. Although such a dependence of period upon temperature has not been reported for any of the other fourteen metal single crystals known to exhibit the de Haas-van Alphen effect, it is unlikely that the property is exclusive to zinc alone. In any event, such behavior implies either temperature dependent effective masses, or chemical potential, or both for the pertinent electrons as will be evident from the theory.

According to the usual interpretations of Landau's[18] theory for the de Haas-van Alphen effect, the constant energy surface in momentum space for the pertinent electrons can often be accurately represented by an ellipsoid. Such an ellipsoidal surface may occur where the Fermi surface overlaps a Brillouin zone boundary producing a "pocket" of low effective mass electrons or holes. In the case of zinc, a suitable representation (see reference 12) for our purposes is

$$E_0 = (p_1^2 + p_2^2)/2m_1 + p_3^2/2m_3, \qquad (1)$$

where the subscripts 1, 2, and 3 correspond respectively to digonal axes of type I, digonal axes of type II, and the hexagonal axis. m_1 and m_3 are the effective masses perpendicular and parallel respectively to the hexagonal

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[15] B. I. Verkin, Doklady, Akad. Nauk. S.S.S.R. **81**, 529 (1951).
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[18] L. Landau, see Appendix to D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939).

axis (i.e., isotropy in the basal plane is assumed), and E_0 is the chemical potential measured from the bottom of the relevant zone in the case of electrons (or the top in the case of holes). For this case, Landau's final expression for the anisotropy $\Delta\chi = \chi_3 - \chi_1$, is

$$\Delta\chi = \frac{(m_1-m_3)A}{\rho}\left\{\frac{\pi^2}{6}\left(\frac{k}{E_0}\right)^{\frac{1}{2}} - \frac{1}{T^{\frac{1}{2}}}\left(\frac{2\pi^2 kT}{\beta H}\right)^{\frac{1}{2}}\right.$$
$$\left.\times \sum_{p=1}^{\infty} \frac{(-1)^{p+1}\sin(2\pi p E_0/\beta H + \delta)}{2p^{\frac{3}{2}}\sinh(2\pi^2 pkT/\beta H)}\right\}, \quad (2)$$

provided that $E_0 \gg kT$ and $E_0 \gg \beta H$, which, as will be evident later, is not fulfilled at the highest temperatures or highest fields in this investigation. ρ is the density, $\delta = -\pi/4$, and A is a constant given by

$$A \equiv \frac{e^2 E_0}{\pi^4 c^2 \hbar (2k)^{\frac{1}{2}} m_1 (m_3)^{\frac{1}{2}}}. \quad (3)$$

β is a double effective Bohr magneton given by

$$\beta = \frac{e\hbar}{cm_1(m_3)^{\frac{1}{2}}}(m_1 \sin^2\phi + m_3 \cos^2\phi)^{\frac{1}{2}}, \quad (4)$$

where ϕ is the angle between the hexagonal axis and the magnetic field. The remaining quantities have their usual meanings. Note that $\Delta\chi$ consists of a field-independent term upon which is superposed a summation of oscillating terms. We will be concerned chiefly with the first term of the summation, for under the conditions of our experiments the harmonics were not in general important. This first term exhibits a period of oscillation β/E_0 in reciprocal field, which, according to the theory, is temperature independent. Hence, the observed dependence of β/E_0 on temperature is not accounted for by the theory but might be included by making β or E_0 or both suitable functions of temperature.

THE EXPERIMENTAL WORK

I. The Torsion Balance and Crystal

The general techniques used for measuring $\Delta\chi$, the difference of susceptibility per unit mass along two perpendicular directions in a metal single crystal, by observation of the vertical couple acting on the crystal placed in a homogeneous horizontal magnetic field, have been described adequately elsewhere.[19] However, it should be mentioned that in the present work the maximum observed couples never exceeded 13 dyne-cm which corresponded to angular deflections of the crystal of less than 0.3°.

The zinc single crystal used in this investigation was kindly donated by Dr. John K. Logan of this Laboratory. It was grown from New Jersey zinc (99.99 percent

purity) and weighed 0.709 gram. All of the measurements were made with the hexagonal or 3 axis and a digonal axis of type I in a horizontal plane such that $\Delta\chi = \chi_3 - \chi_1$.

II. Temperature Attainment and Measurement

Several methods were used to reach and maintain the desired temperatures. In all cases, the crystal was suspended on the lower end of a quartz rod inside a long glass tube containing helium thermal exchange gas. A copper-constantan thermocouple (which was shown to be magnetic field independent) was attached to the outside of this glass tube directly opposite the crystal permitting temperature measurement to an estimated accuracy of $\pm 1°K$ above 28°K. (In the liquid helium range, the temperature was determined from the vapor pressure of the helium bath.) Surrounding the glass tube, but not in direct contact with the thermocouple, was a copper tube (approximately 0.5 mm wall and 13 cm long) to the upper end of which was attached a carbon resistor heater. The copper tube, which helped minimize temperature gradients, was surrounded by necked down portions of two concentric Dewar flasks. Temperatures above 90°K were reached by passing liquid nitrogen cooled helium gas into the inner flask at appropriate flow rates. Temperatures between 59°K and 90°K were attained by pumping on liquid nitrogen and liquid oxygen baths in the inner flask. In checking temperatures using the vapor pressure of the oxygen bath, it was necessary to correct for the dependence of vapor pressure upon field.[20]

In order to cover the range from 4.2°K to 59°K, liquid nitrogen was placed in the outer flask, about 100 cm³ of activated charcoal were added to the large diameter upper portion of the inner flask just making contact with the upper end of the copper tube, and liquid helium was bled into the inner flask until the lowest desired temperature was reached. The activated charcoal constituted a good heat sink because of its large thermal capacity and also permitted cooling via the desorption of helium gas when pumped under reduced pressure. In the absence of pumping, warm up took place at the rate of about 3°K per hour above 20°K. The temperature could be held constant to better than $\frac{1}{2}°K$ during the course of a field sweep (about 20 minutes) by adding heat to the carbon resistor heater for a short time, thus warming the copper tube but not appreciably warming the charcoal because of its poor thermal conductivity. With a little practice, a situation could be realized in which the normal heat leak to the copper tube (after the flow of current to the heater was stopped) was just compensated by the cooling from the charcoal. This method would probably have been applicable throughout the entire temperature range from a bit above 4.2°K to room temperature, but

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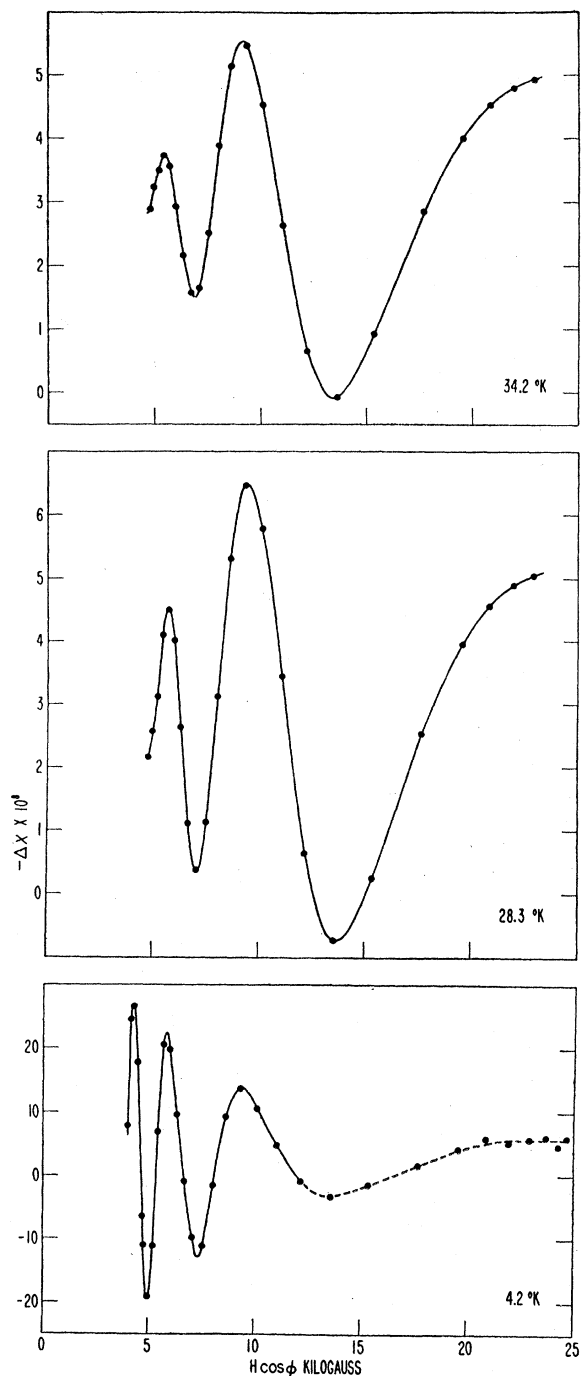[20] A. Van Itterbeck and A. de Bock, Ann. Physik 20, 231 (1945).

FIG. 1. $-\Delta\chi$ in emu g^{-1} as a function of the component of magnetic field parallel to the hexagonal axis of a zinc single crystal for various temperatures.
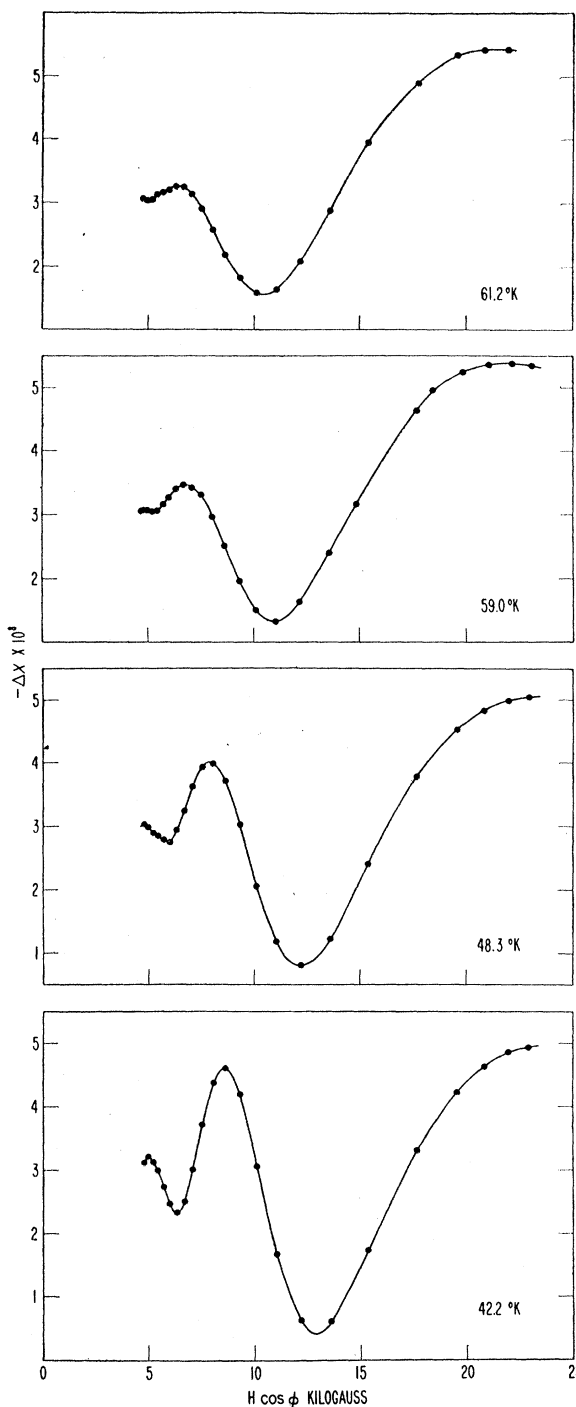

FIG. 2. $-\Delta\chi$ in emu g^{-1} as a function of the component of magnetic field parallel to the hexagonal axis of a zinc single crystal for various temperatures. Note the displacement to lower fields of the last maximum as the temperature is increased.

it was not tried until after the data above 59°K had already been obtained.

III. The Magnet

An Arthur D. Little electromagnet capable of rotation about a vertical axis supplied horizontal magnetic fields up to 25 kilogauss in strength. Pole pieces 5.75 inches in diameter and a gap of 1.75 inches assured field homogeneity to a few gauss over the volume of the crystal. The magnet was calibrated with a nuclear
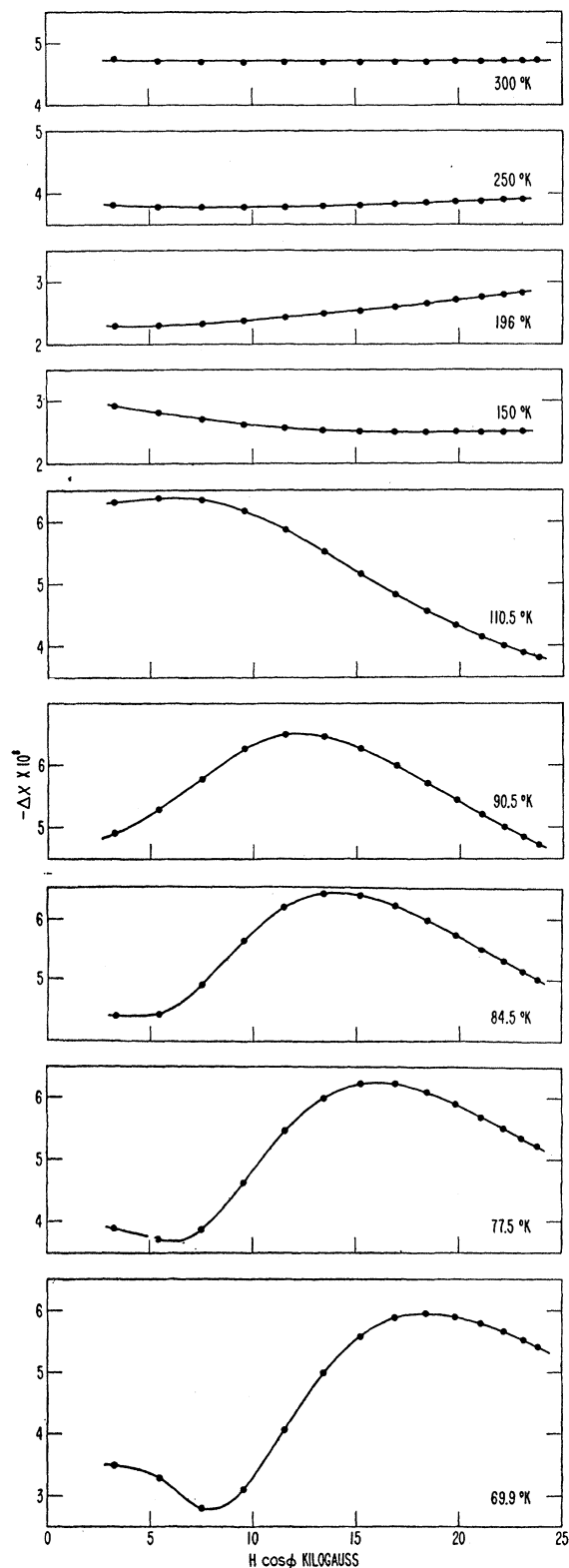
FIG. 3. $-\Delta\chi$ in emu g^{-1} as a function of the component of magnetic field parallel to the hexagonal axis of a zinc single crystal for various temperatures.

fluxmeter to an accuracy of better than 0.02 percent, and time variations of the field were limited to less than 5 gauss during the course of a single measurement.

EXPERIMENTAL RESULTS

The experimental data are presented in Figs. 1, 2, and 3, where $\Delta\chi = \chi_3 - \chi_1$ has been plotted for several temperatures as a function of $H\cos\phi = H_3$, the component of magnetic field along the hexagonal or 3 axis. This mode of presentation is suitable because of the experimental fact that at a given temperature $\Delta\chi$ depends to high accuracy only upon the component of the field along the hexagonal axis. (This verifies, incidentally, that $m_3 \gg m_1$.) The curves from 4.2°K to 61.2°K, inclusive, were obtained by setting the magnetic field at 25 kilogauss, ϕ at 0°, and then taking data at 5° intervals as ϕ was increased from 0° to 45°. Finally, with ϕ fixed at 45°, points were taken as the field was reduced from 25 kilogauss by uniform increments in reciprocal field. For temperatures from 69.9°K to 300°K, the magnetic field was set at 25 kilogauss, and points were taken at 5° intervals from $\phi = 90°$ to $\phi = 0°$ to $\phi = -90°$. Each plotted point represents the average of the points obtained for $+\phi$ and $-\phi$. In order to verify that $\Delta\chi$ depends only upon H_3, this procedure was repeated in a magnetic field of 15 kilogauss at several of the temperatures, and within experimental error the data coincided with the 25 kilogauss data.

The estimated relative error for the curves of Figs. 1, 2, and 3 is about ±1 percent. Although the absolute error may be as much as ±2 percent due to uncertainties in balance calibration, the room temperature value $\Delta\chi = -4.7 \times 10^{-8}$ emu per gram is in good agreement with other determinations.[12,13]

The high field portion (above 12 kilogauss) of the 4.2°K curve is dashed because, in this region, shorter (by a factor of about 300) period oscillations were observed making the data uncertain to within the amplitude of the high-frequency term. The existence of these high-frequency oscillations, as well as anisotropies in the basal plane observed by Verkin, Lazarev, and Rudenko[14] at high fields, indicate that the simple representation for the constant energy surface given by Eq. (1) is not adequate to account for the detailed behavior of zinc even though it is quite satisfactory for the long period oscillations with which this investigation was concerned.

ANALYSIS AND EVALUATION OF PARAMETERS

I. Period, Phase, and Mean of the Oscillations

In order to obtain values for the period β/E_0 of the oscillations of χ_3 in reciprocal field, the mean of the oscillations was first ascertained for each temperature. Then, values of reciprocal field at which the observed curve crossed the mean were plotted against even integers. In general, good straight lines were obtained,

from the slopes of which β/E_0 could be calculated. When values of reciprocal field at which maxima and minima occurred were plotted against odd integers, they fell on the same lines, but since fewer uncertainties arise in the determination of crossover points they were more heavily weighted. β/E_0 is plotted as a function of temperature in Fig. 4 where the probable error is indicated by the size of the points. The 4.2°K value is in good agreement with other determinations.[12,13,16] That the upward trend of β/E_0 continues to considerably higher temperatures than 60°K is suggested by the continued displacement of the highest-field maximum in $-\Delta\chi$ toward lower fields.

The phase δ of the oscillations is also of interest and may be obtained from the intercept on the integer axis of the plots of crossover points *versus* integers used in the determination of β/E_0. (It should be pointed out that the sign of the oscillating term follows that of

Fig. 5. The dependence upon temperature of the phase δ of the de Haas-van Alphen (magnetic susceptibility) oscillations in zinc. The theoretical value is $\delta = -\pi/4$.
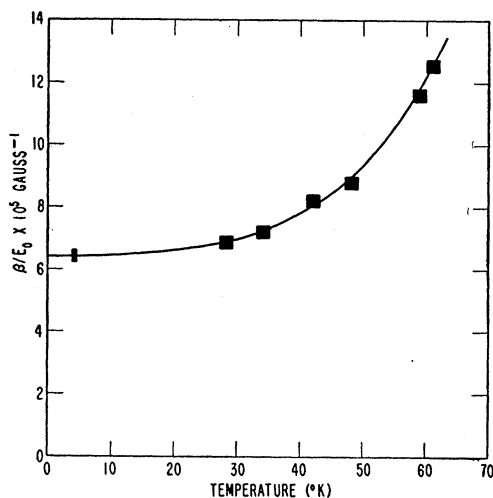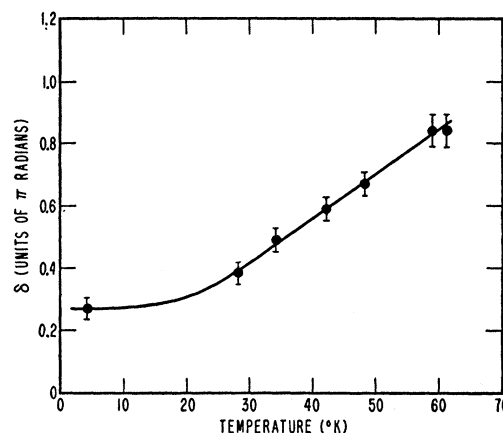

Fig. 4. The dependence upon temperature of the period β/E_0 of the de Haas-van Alphen (magnetic susceptibility) oscillations in zinc parallel to the hexagonal axis.

$+\sin(2\pi E_0/\beta H+\delta)$ since $m_3 > m_1$.) δ has been plotted as a function of temperature in Fig. 5, and we note that, like the period, it increases with increasing temperature. Furthermore, it differs considerably from the theoretical value $-\pi/4$.

The dependence of the mean of the oscillations (i.e., $\lim_{H\to 0}\Delta\chi$) upon temperature is illustrated in Fig. 6. While there is some evidence for a kink between 20°K and 60°K, this might arise from uncertainties in determining the actual mean. The maximum in $-\Delta\chi$ at roughly 110°K is perhaps noteworthy because, below this temperature, Marcus[9,11] observed that χ_1 (the field-independent susceptibility perpendicular to the hexagonal axis) was temperature-independent while above it χ_1 increased strictly linearly at least to 380°K. Very recently, Elcock[21] has considered the theoretical

temperature variation of the field-independent diamagnetic susceptibility of orbital electrons in metals. In his model, electron transfer across the Brillouin zone boundary arises from departure of the Fermi function from a true step function as the temperature is increased above absolute zero. This might account at least in part for the observed effects in zinc, but incomplete knowledge of the energy surface prohibits rigorous interpretation in terms of this theory.

The short-period oscillations observed at the lowest temperature and highest fields and at $\phi = 8.5°$ exhibited a dominant period of 2.1×10^{-7} gauss^{-1} and a beat period of roughly 15×10^{-7} gauss^{-1}. These oscillations may be associated in some way with those observed by Verkin, Lazarev, and Rudenko[14] in the anisotropy of the basal plane of zinc, but an investigation of this feature was not pursued.
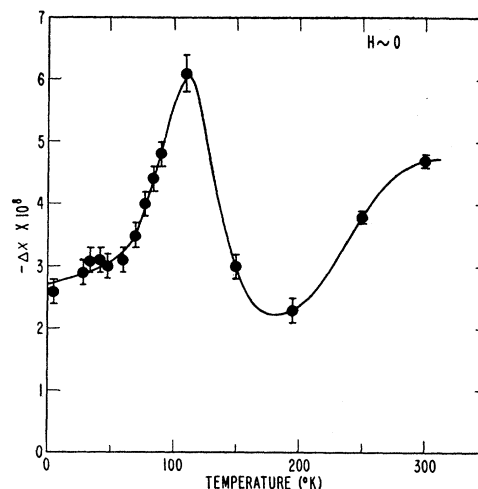

Fig. 6. The dependence upon temperature of the mean of the susceptibility oscillations in zinc. $-\Delta\chi$ is in emu g^{-1}.
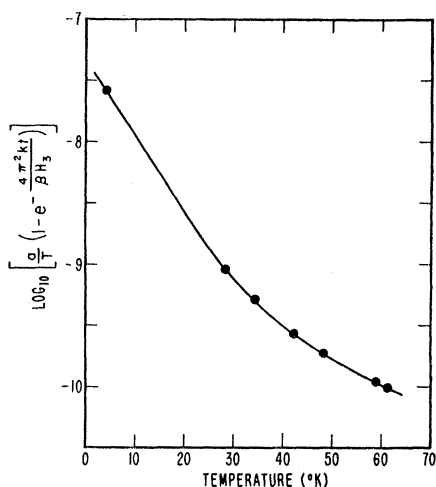
[21] E. W. Elcock, Proc. Roy. Soc. (London) A222, 239 (1954).

FIG. 7. The temperature dependence of the amplitude a of the susceptibility oscillations in zinc is illustrated. A value for β at $4.2°K$ can be derived from the slope of the linear portion.

II. Chemical Potential and Effective Mass

Provided Eq. (2) is valid, a plot of $\log_e\{aT^{-1} \times[1-\exp(-4\pi^2kT/\beta H_3)]\}$ (where a is the amplitude of the oscillations) against T for fixed H_3 should yield a straight line of slope $-2\pi^2k/\beta H_3$ (where β is referred to $\phi=0$). Thus a first approximation to β may be obtained from the slope of a plot of $\log_e(a/T)$ against T. This value of β may then be used in a plot of $\log_e\{aT^{-1}[1-\exp(-4\pi^2kT/\beta H_3)]\}$ against T, the slope of which yields a second approximation to β. This process may be repeated until a value for β of the desired accuracy is obtained.

Despite the fact that β/E_0 is temperature-dependent and hence Eq. (2) is not strictly valid, a value for β was calculated on the above basis using values of a at $4.207°K$ and $28.3°K$ for $H_3=7350$ gauss. A value of $\beta=2.65\times10^{-18}$ erg gauss^{-1} was obtained such that $m_1=7.0\times10^{-3}m_0$ (where m_0 is the free electron mass), and since at $4.2°K$ $\beta/E_0=6.4\times10^{-5}$ gauss^{-1}, $E_0=4.1 \times10^{-14}$ erg at the same temperature. Such a calculation is not without some justification inasmuch as Donahoe[16] found the temperature dependence in Eq. (2) obeyed quite accurately for zinc between $1.5°K$ and $20°K$ and obtained $E_0=4.0\times10^{-14}$ erg in what is probably the most accurate determination for zinc, whereas a recalculation of Mackinnon's[12] data between $2°K$ and $20°K$ yielded $E_0=4.1\times10^{-14}$ erg.

It was not possible to obtain reliable values of β at higher temperatures from the temperature dependence of a because of the failure of Eq. (2) to account for the temperature dependence of β/E_0. Nevertheless, Fig. 7 is included in order to facilitate analysis in terms of possible future theoretical developments. The linearity of this plot between $4.2°K$ and $28.3°K$ despite the lack of experimental points is favored by the agreement between the above independent determinations of E_0. It should be mentioned that, even if the

uncertainties in β were as great as a factor of two at the higher temperatures, the plot is a valid one since at $28.3°K$ $1\gg\exp(-4\pi^2kT/\beta H_3)$ for $H_3=7350$ gauss.

III. The Field-Dependence of Amplitude

In principle, one could calculate β at any given temperature from the field-dependence of amplitude. Such a calculation would then yield the temperature-dependences of β and hence m_1 and E_0. Unfortunately, attempts to fit the observed field-dependence to the theoretical dependence,

$$aH_3^{3/2} \propto \frac{1}{\sinh(2\pi^2kT/\beta H_3)}, \qquad (5)$$

from Eq. (2) revealed a wide divergence between experiment and theory. Consequently, in an attempt to ascertain an empirical relation for the field dependence of amplitude, the following forms were tried

$$aH_3^{3/2} \propto \exp(-2\pi^2kT/\beta H_3) \qquad (6)$$

$$aH_3^{5/2} \propto \frac{1}{\sinh(2\pi^2kT/\beta H_3)} \qquad (7)$$

$$aH_3^{5/2} \propto \exp(-2\pi^2kT/\beta H_3). \qquad (8)$$

The best empirical fit by far to the data [ignoring the harmonics which according to Eq. (2) should be important only at $4.2°K$] is given by Eq. (8). The accuracy of this fit is illustrated by the linearity of the plots of $\log_{10}(aH_3^{5/2})$ versus H_3^{-1} appearing in Fig. 8. Donahoe[16] favored a field-dependence of the form given by Eq. (7) for fields below about 6 kilogauss. Actually, Eqs. (7)
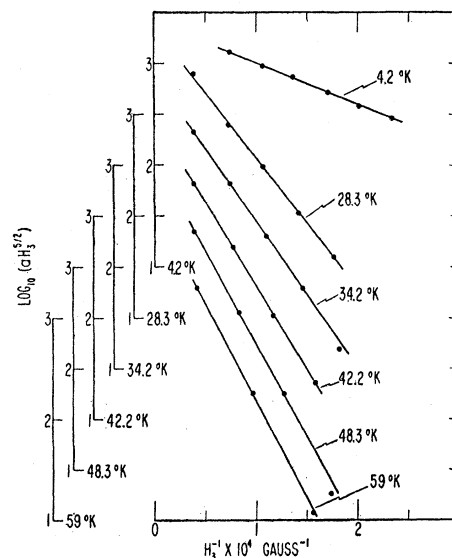

FIG. 8. The magnetic field dependence of the amplitude a of the susceptibility oscillations in zinc is illustrated. The linearity is indicative of the accuracy of the empirical relation given in Eq. (8).

and (8) are equivalent for all of our data except that for 4.2°K. Taking the harmonics in Eq. (2) into account for the 4.2°K data could conceivably favor Eq. (7), but uncertainties in the phase δ prohibit any conclusive analysis.

In any event, an attempt was made to ascertain in a qualitative way the temperature-dependence of β from the field-dependence of amplitude. Inspection of Eq. (8) reveals the fact that values for β can be deduced from the slopes of such plots as appear in Fig. 8. Equivalent plots for the field-dependences given by Eqs. (5), (6), and (7) yield linear portions at low fields, from the slope of which other values for β can be deduced. Before continuing, it is necessary to point out that according to an addition to the theory by Dingle,[22] collision broadening of the electronic energy levels should reduce the amplitude of the oscillations by a factor $\exp(-2\pi^2 kx/\beta H_3)$ where x is an effective temperature related to the collision time. Consequently, in calculating values for β by the scheme described above, the 4.2°K values of β were adjusted to the value obtained from the temperature dependence of amplitude by appropriate adjustment of x. Then, using this value of x, β was calculated at the higher temperatures. Although the assumption that x is temperature-independent is probably unwarranted, a rather violent temperature-dependence of x would be required to alter the calculated values of β appreciably at temperatures above 28.3°K. In all cases, the calculated values for β were within 30 percent of each other at a given temperature, and, in all cases, β increased by a factor of 1.5 to 2 in going from 4.2°K to 59°K. On this basis, it would appear that β does indeed increase (and m_1 therefore decrease) with increasing temperature and that E_0 is at least no more temperature-dependent than β. However, such speculation must be regarded with caution in view of the inadequacies of the theory which was derived in the approximations $E_0 \gg kT$ and $E_0 \gg \beta H$. Actually, at 60°K and 15 kilogauss, $E_0 \cong \beta H_3 \cong 5kT$, so differences between theory and experiment are not unexpected.

CONCLUDING REMARKS

This investigation has yielded the following information:

1. Traces of the de Haas-van Alphen effect persist in zinc at temperatures up to 200°K.

2. The period β/E_0 of the oscillations of χ_3 in zinc increases with increasing temperature from liquid helium temperatures to well above 60°K. This accounts in part for the persistence of the effect at high temperatures since in general the larger β/E_0 the stronger the de Haas-van Alphen effect.

3. The phase δ increases with increasing temperature.

4. It appears that β increases (and therefore m_1 decreases) with increasing temperature, although the

evidence is not conclusive because of discrepancies between theory and experiment.

5. Over the ranges of temperature and field of this investigation, the dependence of the amplitude a of the de Haas-van Alphen oscillations in zinc upon field is better represented by Eq. (8) than the theoretical dependence, Eq. (5).

6. In addition to the long-period term with which this investigation was primarily concerned, very short-period oscillations observable only at high fields and low temperatures exist in the de Haas-van Alpen effect in zinc.

The observed dependence of the de Haas-van Alphen parameters upon temperature might very well arise in part at least from alteration of the overlap of the pertinent Brillouin zone by the Fermi surface brought about by thermal expansion of the crystal. Despite the possibility that the de Haas-van Alphen parameters could be somewhat artificial (as pointed out by Adams[23]), some idea of the orders of magnitude involved was obtained as follows. Using the thermal expansion coefficients for a single crystal of zinc as measured by Grüneisen and Goens,[24] the proportionate change $\Delta n/n$ in the number n of electrons per cm³ for an increase of temperature from 40°K to 60°K was found. Since the Fermi energy ζ is proportional to $n^{2/3}$, the proportionate change $\Delta\zeta/\zeta$ in the Fermi energy was found to be

$$\Delta\zeta/\zeta \cong -6\times 10^{-4}.$$

The ratio of the overlap energy $E_0 = 4.1\times 10^{-14}$ erg $= 0.026$ electron volt at 4.2°K to the Fermi energy $\zeta = 11$ electron volts from soft x-ray measurements on zinc[25] is

$$E_0/\zeta \cong 2\times 10^{-3}.$$

Therefore $E_0 \sim 3|\Delta\zeta|$. Furthermore, in the same temperature interval, 40°K to 60°K, the proportionate changes in the Brillouin zone dimensions l_3 and l_1 parallel and perpendicular respectively to the hexagonal axis are

$$\Delta l_3/l_3 \cong -10^{-3},$$
$$\Delta l_1/l_1 \cong 4\times 10^{-5}.$$

Hence, if the overlap takes place in the perpendicular or 1-direction (which is most likely since $m_3 \gg m_1$) where the zone boundary is almost unchanged as the temperature is increased, the overlap energy E_0 could be altered by an amount of the order of $\Delta\zeta$, which as we have seen is comparable with E_0 itself. This would also change the number of overlapping electrons and possibly their effective masses. Of course this is not the only mechanism capable of giving rise to the transfer of electrons

[22] R. B. Dingle and D. Shoenberg, Nature **166**, 652 (1950).

[23] E. N. Adams II, Phys. Rev. **89**, 633 (1953).
[24] E. Grüneisen and E. Goens, Z. Physik **29**, 141 (1924).
[25] See A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1954), second edition, p. 94.

across the zone boundary, and it is quite likely that the mechanism discussed by Elcock[21] is also operative as well as others. Nevertheless, on the above model one might predict observable temperature-dependent de Haas-van Alphen parameters in other crystals having very anisotropic thermal expansion coefficients, low

Debye characteristic temperatures, and small overlap energies, but the scarcity of data on low-temperature thermal expansion coefficients precludes any concrete conclusions along this line.

We are indebted to the members of the Cryogenics Branch for many stimulating discussions.

Specific Heats of Metals Below One Degree Absolute*

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The heat capacities of a number of metals have been measured in the region below $1°K$, using the technique of adiabatic demagnetization. Copper, silver, platinum, palladium, tungsten, molybdenum, and sodium have been investigated. Apart from sodium, all exhibit a linear dependence of electronic specific heat on temperature. The values of γ are in agreement with those obtained in the liquid helium region, except in the case of tungsten, which gives $\gamma = 3.5 \pm 0.2 \times 10^{-4}$ cal/mole deg^2 in contrast to the previous value $\gamma = 1.8 \pm 0.7 \times 10^{-4}$ cal/mole deg^2 reported in the literature. Sodium exhibits an anomalous peak in its specific heat curve. A low-temperature, martensitic-type transformation is advanced as a likely cause of this behavior.

In the course of the experiments, an independent measurement of the heat capacity of copper potassium sulfate has been made. The relation $C = A/T^2$ appears to be obeyed, the value of the specific heat constant A being $5.8 \pm 0.2 \times 10^{-4} R$ deg^2/mole.

INTRODUCTION

ACCORDING to the simple one-electron approximation,[1] the electronic specific heat of a normal metal is given by an expression

$$C = \frac{\pi^2}{3} k^2 T \left(\frac{dN}{dE} \right)_{E=E_0} = \gamma T, \tag{1}$$

where $(dN/dE)_{E=E_0}$ is the density of states at the top of the Fermi distribution. Experimental data in the liquid helium region seem to be in agreement with this prediction. The resulting values of γ are explained in terms of the variation of the density of states at the Fermi surface. Thus, in the case of the noble metals, where the d shell is completely full, the density of states corresponds roughly to that of a free electron gas with one electron per atom. Again, in the transition metals like platinum, with incomplete d shells and narrow d bands, the density of states is much higher, corresponding to the large values observed experimentally.

Equation (1) is based on the explicit assumption that the energy levels of a solid can be described correctly by a self-consistent field approximation. In particular, it is assumed that the total wave function can be

represented by a simple product of one-electron wave functions, which are solutions of a Schrödinger equation for a periodic, self-consistent potential. Such a wave function cannot be correct since it does not give any recognition to the fact that the electrons in a metal, which interact strongly, tend to keep as far apart as possible. Thus the resulting energies must be too high. Admittedly, it is still possible that their differences may still give correctly the energy level spacings, but this would have to be established. It is thus a matter of conjecture as to whether Eq. (1) really does describe the behavior of an actual metal.

Now it is known that in the case of atomic systems, the Hartree-Fock approximation, which uses antisymmetrized wave functions, is more satisfactory than the Hartree approximation. Thus it gives lower energies and, furthermore, it produces a correct qualitative description of the spectroscopic terms actually observed in atoms. It might therefore be expected (although this expectation proves to be incorrect) that a similar situation exists in metals.

Here, the application of the Hartree-Fock approximation leads to an additional energy known as the exchange energy. For free electrons this exchange term is given by an equation

$$E_{\text{ex}} = -\frac{e^2 k_0}{\pi} \left(1 + \frac{k_0^2 - k^2}{2k k_0} \ln \frac{k + k_0}{|k - k_0|} \right), \tag{2}$$

where k_0 is the value of the wave number corresponding to the surface of the Fermi distribution. It will be seen

[1] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 15–159.