Magnetic Susceptibility of Zinc at Liquid Hydrogen Temperatures*

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The magnetic susceptibility of zinc has been investigated down to liquid hydrogen temperatures in fields ranging from 3 to 10.5 kilogauss. Measurements were made on single and polycrystalline specimens by the Faraday method. At 20°K, the susceptibility parallel to the hexagonal axis shows a marked field dependence similar to that found by de Haas and van Alphen for the susceptibility of bismuth perpendicular to the trigonal axis. Maxima were observed at 4.1, 5.6, and 9.8 kilogauss; minima at 4.8 and 7.1 kilogauss. The amplitude of the oscillations decreases with temperature increase but some field dependence persists to 64°K. The susceptibility in a plane perpendicular to the hexagonal axis remains isotropic down to the lowest temperature investigated (14°K) and is independent of the field. Oscillations in susceptibility characteristic of the de Haas-van Alphen effect were not observed in measurements on a polycrystal.

The results are compared with those for bismuth, and it is noted that the observation of the de Haas-van Alphen effect in zinc supports the view that this effect is closely related to the anomalous field dependence of resistance which has been previously observed for both metals at low temperatures.

INTRODUCTION

IN 1930, de Haas and van Alphen[1] observed that at liquid hydrogen temperatures, the diamagnetic susceptibility of bismuth single crystals becomes a complicated periodic function of the magnetic field. This has come to be known as the de Haas-van Alphen effect. The effect is confined to a plane perpendicular to the trigonal axis and is such that the susceptibility which is isotropic at high temperatures, becomes anisotropic at temperatures for which the field dependence occurs. Subsequently de Haas and van Alphen[2] investigated several additional metals and found no field dependence of susceptibility. Since the latter measurements were made on polycrystalline specimens, the results cannot be regarded as conclusive.

Shoenberg and Uddin[3,4] studied the effect in greater detail for pure bismuth and bismuth alloys. In every case, the result of alloying was to reduce the magnitude of the field dependence. They concluded that such dependence must be limited to an extremely narrow range of bismuth-like electronic structures and was therefore unlikely to occur in other pure metals. In this connection, they[5] also investigated antimony at 4°K and found the susceptibility to be independent of the field.

In the first attempt to formulate a theory of the de Haas-van Alphen effect, Peierls[6] considered the quantization of essentially free electrons in a magnetic field and showed that all metals should exhibit the effect under conditions such that $\mu H > kT$. However, for fields and temperatures attainable in the laboratory (~ 1°K, $\sim 10^4$ gauss), $\mu H \ngtr kT$ unless the effective mass of some of the conduction electrons is abnormally small. As this is just the condition for large normal diamagnetism, Peierls concluded that the effect would only be observable in metals exhibiting large diamagnetism.

Blackman[7] and Landau[8] extended Peierls' theory by considering the particular electronic structure of bismuth. Fair quantitative agreement with experimental data was obtained by assuming that the electrons responsible for the fluctuations in susceptibility were only 1 percent of those contributing to the large diamagnetism at higher temperatures and therefore large diamagnetism is not an essential condition for the occurrence of the de Haas-van Alphen effect. As to predicting additional occurrences of the effect, the theory is inadequate since it depends on a more detailed account of the particular electronic structures of other metals than is presently available.

That the de Haas-van Alphen effect might be observed in zinc was suggested by an experiment performed in 1939 by Lazarev *et al.*[9] who found an anomalous field dependence of resistance for zinc single crystals. Schubnikov and de Haas[10] had discovered that in addition to a field dependence of susceptibility, bismuth also exhibited a peculiar field dependence of resistance at low temperatures consisting in maxima and minima superimposed on the normal increase in resistance with increase in magnetic field. The theory which Davydov and Pomeranchuk[11] developed to account for this phenomenon, indicates that the re-

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1 W. J. de Haas and P. M. van Alphen, Comm. Phys. Lab. Leiden, Nos. 208d, 212a (1930).
2 W. J. de Haas and P. M. van Alphen, Comm. Phys. Lab. Leiden, No. 225b (1933).
3 D. Shoenberg and Z. M. Uddin, Proc. Roy. Soc. **A156**, 687, 701 (1936).
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10 L. Schubnikov and W. J. de Haas, Comm. Phys. Lab. Leiden, Nos. 207a, 207d (1930).
11 B. Davydov and I. Pomeranchuk, J. Phys. (U.S.S.R.) **2**, 147 (1940).

TABLE I. Values of susceptibility for zinc at room temperature.

	$-\chi_{\parallel}\times10^6$	$-\chi_{\perp}\times10^6$	$\bar{\chi}\times10^6$	$\chi_{\parallel}/\chi_{\perp}$
McLennan, Ruedy, and Cohen[a]	0.190	0.145	0.160	1.31
Rao[b]	0.202	0.149	0.167	1.36
Endo[c]	polycrystal		0.126	
de Haas and van Alphen[d]	polycrystal		0.143	
Specimen *A*	0.169	0.124	0.139	1.36
Specimen *B*	0.169	0.124	0.139	1.36
Specimen *C*	polycrystal		0.141	

[a] McLennan, Ruedy, and Cohen, Proc. Roy. Soc. **A121**, 9 (1928).
[b] S. R. Rao, Proc. Ind. Acad. Sci. **4**, 186 (1936).
[c] H. Endo, Sci. Tohoku Imp. Univ. **14**, 479 (1925).
[d] See reference 2.

sistance fluctuations should be accompanied by a marked de Haas-van Alphen effect.

Lazarev's[9] experiment showed a similar field dependence of resistance for zinc single crystals. In the case of zinc however, it occurs for only one orientation of the crystal with respect to the magnetic field and is not observable for deviations of as little as 5 percent from the one orientation. This indicated that the de Haas-van Alphen effect might be observable in zinc single crystals although it was not found in previous measurements[2] on polycrystals. Accordingly, a preliminary investigation of zinc single crystals was made at liquid hydrogen temperatures. Initial results were reported in an earlier communication.[12] The present paper gives a more extensive account of this research.

EXPERIMENTAL PROCEDURE

Single crystals of zinc were grown using metal from two different sources. Specimen *A* was prepared from Eimer and Amend chemical purity zinc shot with total impurities given as less than 0.01 percent and iron impurities as 0.003 percent. Specimen *B* was prepared from Johnson, Matthey & Company "H. S." brand zinc rods for which spectrographic analysis indicated total impurities of less than 0.0001 percent. Crystal *A* was grown by allowing a bead of the molten metal, sealed under a vacuum in a Pyrex tube, to cool slowly in an electric furnace. Crystal *B* was grown by the Bridgman[13] method whereby a Pyrex tube containing a polycrystalline rod of the metal and sealed under a vacuum, was slowly lowered out of an electric furnace. Orientation was determined by cleavage. A polycrystal, specimen *C*, was prepared from the higher purity material by rapid quenching from the melting point. The mass of the specimens ranged from 0.5 to 0.7 g and the maximum dimension of the largest crystal was 0.6 cm.

Susceptibilities were determined by the Faraday method in which the force on a small specimen in an inhomogeneous field is given by $F=\chi m H_x(\partial H_x/\partial z)$, where χ is the susceptibility per unit mass, m the mass of the specimen, H_x the horizontal magnetic field and $\partial H_x/\partial z$ the gradient of the field in the vertical direction. The field varied by about 10 percent over the volume of the specimen. It was found that this amount of variation did not appreciably effect the results for the range of fields used (3 to 10 kilogauss). Absolute values of susceptibility were determined in terms of a polycrystalline bismuth standard of the same dimensions as the specimen. The susceptibility of the bismuth standard was known to be $(-1.31\pm0.01)\times10^{-6}$.

To minimize the error of placement in changing specimens, specially designed pole pieces were used similar to those employed by Foex and Forrer.[14] With these poles, the force varied by less than ±1 percent for a ±0.3 cm displacement of the specimen. As the position of the specimen could easily be reproduced to 0.005 cm, the error from this source was negligible.

In the expression for the magnetic force given above, χ is the susceptibility in the direction of the field. For a single crystal, the magnetization does not generally coincide with the direction of the applied field. If as is usually the case, the magnetization is a linear vector function of the field, then for crystals with the hexagonal symmetry of zinc, the measured value of susceptibility is related to the principal susceptibilities $\chi_{\parallel}$ (in the direction of the hexagonal axis) and $\chi_{\perp}$ (at right angles to the hexagonal axis) by the expression

$$\chi=(\chi_{\parallel}\sin^2\phi+\chi_{\perp}\cos^2\phi)\cos^2\theta+\chi_{\perp}\sin^2\theta, \qquad (1)$$

where ϕ is the angle between the hexagonal axis and the vertical z direction and θ is the angle between the

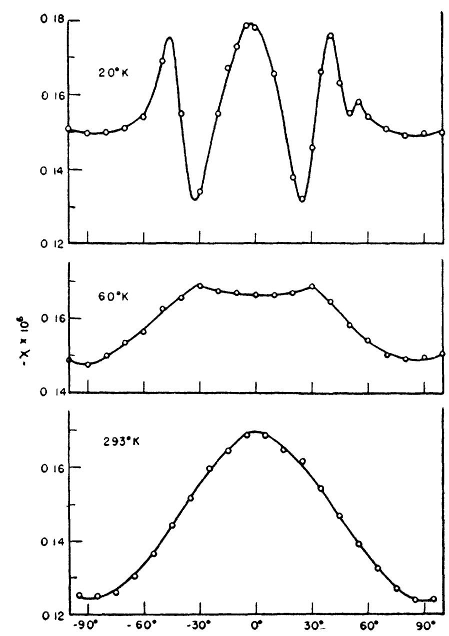

FIG. 1. Variation of the susceptibility of a zinc single crystal with angular orientation for $\phi=90°$ and $H=8.25$ kilogauss at 293°K, 60°K, and 20°K.

[12] J. A. Marcus, Phys. Rev. **71**, 559 (1947).
[13] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **60**, 305 (1925).
[14] G. Foex and R. Forrer, J. de Phys. **7**, 180 (1926).

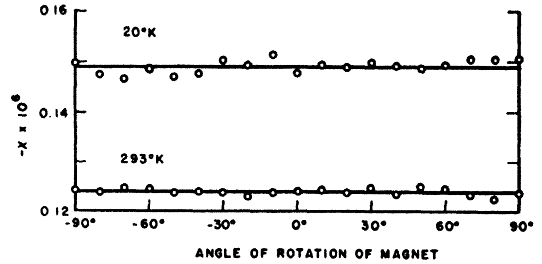

FIG. 2. Variation of the susceptibility of a zinc single crystal with angular orientation for $\phi=0°$ and $H=8.25$ kilogauss at 293°K and 20°K.

field and the projection of the hexagonal axis on the horizontal $x-y$ plane.

The present measurements were made with $\phi=90°$ or 0° so that

$$\chi=\chi_{\parallel}\cos^2\theta+\chi_{\perp}\sin^2\theta, \quad (2)$$

or

$$\chi=\chi_{\perp}, \quad (3)$$

respectively. For either mode of suspension, rotation of the magnet permitted variation of θ through 360°. Where $\phi=90°$, χ varies sinusoidally with θ and the principal susceptibilities were determined from the maxima and minima which occur at $\theta=0°$ and 90°, respectively.

Where the susceptibility is field dependent, the magnetization is not a linear vector function of the field and Eq. (1) is not valid. Therefore, if χ is measured as a function of θ in a constant field, any field dependence of χ will be apparent as deviations from (2) and (3), providing a convenient method for detecting the de Haas-van Alphen effect. Following this procedure in the initial measurements, only $\chi_{\parallel}$ was found to be field dependent. The field dependence of $\chi_{\parallel}$ was then studied by varying the field for the fixed orientation $\phi=90°$ and $\theta=0°$.

The forces, which ranged from 0.2 to 5 dynes, were measured by means of a Sucksmith[15] ring balance constructed by S. H. Browne[16] for measurements at liquid nitrogen temperatures. The only modification required was a more sensitive ring since Browne's had been designed for the measurement of considerably larger forces. With a ring 9 cm in diameter formed from a strip of phosphor bronze 0.20 cm wide and 0.010 cm thick, the sensitivity was 1 dyne per mm deflection of the optical image. The position of the image could be read to 0.001 mm but mechanical vibrations and a slow drift in the zero position due to thermal effects limited the accuracy of the force measurements to ± 0.01 dyne under average working conditions.

The specimen was suspended from the balance ring by a quartz fiber 0.01 cm in diameter. No correction was made for the magnetic force due to the suspension alone as it was less than 1 percent of the total force.

To eliminate the large magnetic effect of oxygen at low temperatures, the balance was evacuated and then filled with helium gas at a pressure of about 30 cm of mercury to provide thermal equilibrium between the specimen and the surrounding bath.

The low temperatures were obtained by using liquid hydrogen and nitrogen and were determined from the vapor pressures.

RESULTS AND DISCUSSION

Principal susceptibilities of the specimens used, measured at room temperature, are given in Table I along with the determinations of other investigators. For single crystals, the mean values of susceptibility, $\bar{\chi}$, were calculated from $\bar{\chi}=\frac{1}{3}(\chi_{\parallel}+2\chi_{\perp})$. The estimated error in our absolute values is less than 4 percent and similar estimates are given by the other investigators. Such large discrepancies between the individual values characterize most of the available data concerned with magnetic properties of metals and has usually been attributed to the presence of impurities. However, the anisotropy given by $\chi_{\parallel}/\chi_{\perp}$ (which is independent of the calibration errors) varies by less than 4 percent and it seems unlikely that impurities present in sufficient amounts to account for the large discrepancies in the individual values of $\chi_{\parallel}$ and $\chi_{\perp}$ should have so little effect on the ratio.

Since the data on both single crystals employed in the present investigation were in substantial agreement, the specimens will not be distinguished in stating the results.

Figure 1 shows the variation of χ with θ for $\phi=90°$ and $H=8.25$ kilogauss at the temperatures 293°K, 60°K, and 20°K. At 293°K, the variation is sinusoidal

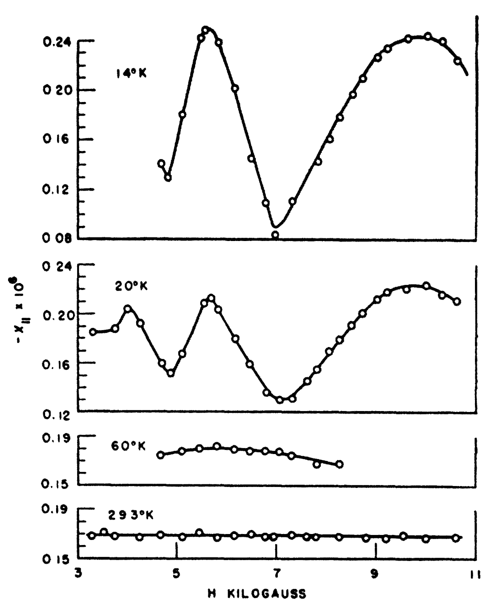

FIG. 3. Variation of $\chi_{\parallel}$ with magnetic field at 293°K, 60°K, 20°K, and 14°K.

[15] W. Sucksmith, Phil. Mag. 8, 158 (1929).
[16] S. H. Browne and C. T. Lane, Phys. Rev. 60, 899 (1941).

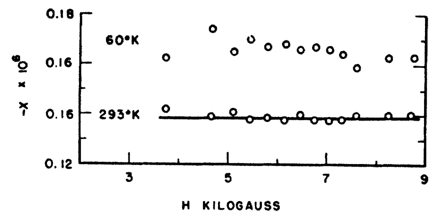

FIG. 4. Variation of the susceptibility of a zinc polycrystal with magnetic field at 293°K and 20°K.

as expected from Eq. (2); at 60°K some departure from Eq. (2) is apparent and at 20°K the effect is pronounced, indicating a marked field dependence of susceptibility. Additional rotation curves at liquid nitrogen temperatures showed that above 64°K, the deviation from Eq. (2) was less than the experimental error.

Variation of χ with θ for $\phi=0°$ and $H=8.25$ kilogauss at 293°K and 20°K is shown in Fig. 2. At both temperatures the susceptibility is isotropic in the basal plane (the greater spread at 20°K being due to an increase in vibration due to boiling of liquid hydrogen). The latter result together with the rotation curves for $\phi=90°$ indicate that the field dependence is confined to $\chi_{\parallel}$. This was confirmed by measurements of $\chi_{\parallel}$ and $\chi_{\perp}$ in fields ranging from 3 to 10.5 kilogauss.

The field dependence of $\chi_{\parallel}$ at 293°K, 60°K, 20°K, and 14°K is plotted in Fig. 3. While at 293°K, $\chi_{\parallel}$ is independent of the field, the curve at 20°K shows the marked oscillations characteristic of the de Haas-van Alphen effect. At 20°K and 14°K, the positions of the maxima and minima occur at approximately the same field strengths; the amplitude on the other hand is considerably increased with decrease in temperature. Thus, between the minimum at 7.1 kilogauss and the maximum at 9.8 kilogauss, the difference in susceptibility of 0.09×10^{-6} at 20°K increases to 0.162×10^{-6} at 14°K. If the increase in amplitude with temperature decrease continues at the same rate, then in the neighborhood of 4°K, the minima should be paramagnetic. At 60°K, $\chi_{\parallel}$ is still field dependent though the oscillations have smoothed out to the extent that the de Haas-van Alphen effect is no longer obvious.

The complicated form of the rotation curve at 20°K (Fig. 1) suggested that the effect might average out for a polycrystal. The results of measurements on a polycrystalline specimen are shown in Fig. 4. The specimen may not have been a true polycrystal since the average grain size was about 0.5 mm. However, the rotation curve at room temperature showed only a small deviation from the straight line. Comparison of the field dependence curve at 20°K with the corresponding curve for a single crystal (Fig. 3) shows that the de Haas-van Alphen effect is hardly apparent in measurements made on a polycrystal, accounting for de Haas and van Alphen's[2] failure to observe it in their previous measurements.

It is interesting to compare the above results with those for bismuth. In bismuth the effect is somewhat more complicated as the susceptibility is independent of the field only when the field is parallel to the trigonal axis. The field dependence occurs in a plane perpendicular to the trigonal axis, the periodicity being different in directions parallel and perpendicular to a binary axis. In both metals, the oscillations take place about a mean diamagnetic value, the spacing and amplitude increasing with increasing field. The amplitude is greater for bismuth than zinc but in zinc the oscillations constitute a greater fractional change in the mean value of susceptibility and as aforementioned, it seems likely that some of the minima may become paramagnetic at about 4°K. Bismuth remains diamagnetic to 2°K and Blackman[7] concluded that only a small fraction of the electrons responsible for the large mean value of diamagnetism contribute to the de Haas-van Alphen effect. No such conclusion can be drawn in the case of zinc as the mean diamagnetism is less than that of free zinc ions (-0.23×10^{-6}) and the net effect of the electrons must be paramagnetic.

For both metals, the magnitude of the oscillations decreases with temperature increase. In zinc, some field dependence is observed at temperatures as high as 64°K while for bismuth, no field dependence is observed above 35°K.

The observation of the de Haas-van Alphen effect in zinc single crystals, together with the previous discovery by Lazarev[9] of an anomalous field dependence of resistance support the contention of Davydov and Pomeranchuk[11] that the two effects are closely related. This is further borne out by the failure to observe either of these effects in cadmium despite its zinc-like electronic structure: Lazarev[9] found no resistance anomaly for cadmium; in the course of the present investigation the susceptibility of cadmium was measured at 14°K but no field dependence was observed.

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