lines will be similarly affected. Since the pressure coefficients of the different parts of these band structures are well known,[14] quantitative data on wave functions could be found. Similar pressure measurements should also be useful in confirming the indirect character of the band gap in GaP, in investigating the mechanism of red emission in this compound, and in determining the energies of higher minima, which are at present uncertain.[14] Extensions to the 2–6 compounds are certainly possible; it is to be noted that experiments of this sort have already been reported by Langer.[25]

ACKNOWLEDGMENTS

It is a pleasure to acknowledge many conversations on the subject of this investigation with Dr. Marshall I. Nathan of the IBM Corporation who provided us with most of the diodes used in this study. The gift of a diode from Lincoln Laboratory through Dr. R. J. Keyes was also appreciated. We are grateful to Mr. Michael DeMeis for discussions on his recent determination of the pressure coefficient of the refractive index of GaAs. We have also benefitted from discussions with other colleagues too numerous to mention individually. The help of James Inglis, David MacLeod, and Albert Manning in the construction of apparatus is also acknowledged.

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de Haas–van Alphen Effect in Zirconium*

A. C. Thorsen and A. S. Joseph
Atomic International, A Division of North American Aviation, Inc., Canoga Park, California

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The de Haas–van Alphen effect has been observed in single crystals of zirconium in pulsed magnetic fields up to 190 kG. A rotating coil device has been used to study the periods of the oscillations as a function of magnetic field direction in the $(00\cdot1)$, $(10\cdot0)$, and $(1\bar{1}\cdot0)$ planes of the hexagonal crystals. Five separate oscillatory terms have been observed with periods ranging in value from 2.0 to $3.4\times10^{-8}\,\mathrm{G}^{-1}$. The data, in general, do not agree with the Fermi surface predicted by the nearly free electron model.

I. INTRODUCTION

The diamagnetic susceptibility of pure metal single crystals exhibits an oscillatory behavior at low temperatures known as the de Haas–van Alphen (dHvA) effect. These oscillations are periodic in the reciprocal magnetic field and are important in the study of the electronic structure of metals due to their relation to the Fermi surface of the metal. The period P is related to an extremal cross-sectional area of the Fermi surface normal to the magnetic field direction by the relation[1] $P=4\pi^2e/chA=9.546\times10^7/A$, when P is expressed in G^{-1} and A is the extremal area in $\mathbf{k}$ space in units of cm^{-2}. Studies of the dHvA effect have proved to be extremely valuable in mapping the Fermi surface of the noble metals[2] and many other low valence metals (e.g., Mg,[3] Zn,[4] Al,[5] Pb [6]). In contrast, there have been few detailed measurements relating to the Fermi surface of transition metals. We report here on a systematic pulsed-magnetic-field study of the dHvA effect in zirconium.

II. APPARATUS

The pulsed-magnetic-field apparatus used in the present experiments has in principle been described elsewhere.[7] Magnetic fields up to 190 kG are produced impulsively by discharging an 1800-μF capacitor bank charged to 3000 V through a copper wire-wound solenoid cooled to liquid-nitrogen temperature. The field rises approximately sinusoidally to a peak value in 4.44 msec,[8] and 1 msec later the magnet is shorted, allowing the field to decay exponentially with an L/R time constant of 16 msec. To insure field uniformity in the central region, the solenoid is fitted with trimmer coils which maintain field homogeneity to better than one part in 10^4 over a distance of 10 mm. A stainless steel liquid helium Dewar with 1.27-cm outer tail diameter fits into the solenoid and provides a 1.09-cm-diam working space for the rotating coil apparatus. (The rotating coil device has been described in detail in a separate publication.[9]) The detection coil containing the

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[8] In the final measurements on zirconium, the capacitor banks were enlarged to 5400 μF, giving a rise time of ≈7 msec.

sample can be rotated ±60° about an axis perpendicular to the magnetic field and can be positioned accurately to better than 0.5°. Signals from this coil are displayed on an oscilloscope after being filtered and amplified, and are recorded photographically.

The samples of zirconium used for the present work were spark cut from a rectangular bar [$\rho(300°\mathrm{K})/\rho(4.2°\mathrm{K})\approx 150$] containing large single crystal grains of the hcp phase. The crystals were grown by H. Shimizu of this laboratory by vacuum annealing close to the transition temperature (≈867°C) between the high-temperature β (bcc) and low-temperature α (hcp) phases. A total of four cylindrical samples were used (≈0.76-mm diam×≈5-mm long) whose rod axes were along the [10·0], [1$\bar{1}$·0], [00·1], and [10·1] directions. The samples were glued in a Micarta holder, oriented by x-ray back-reflection techniques, and inserted into the detection coil. Each sample was mounted so that (1) the symmetry axis of the sample was colinear with the axis of the detection coil and the magnetic field direction, and (2) upon rotation of the sample and detection coil the magnetic field remained in a symmetry plane of the crystal. The resulting error in orienting the appropriate symmetry direction along the magnetic field is estimated to be ±3°.

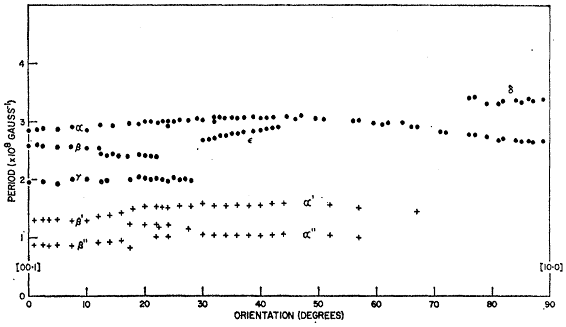


FIG. 1. Angular variation of the de Haas–van Alphen periods in zirconium in the (1$\bar{1}$·0) plane. Data were taken at a temperature of ≈1.1°K. Crosses (+) denote periods which we ascribe to harmonics.

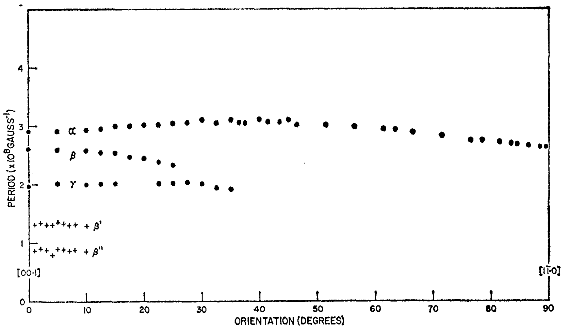


FIG. 2. Angular variation of the de Haas–van Alphen periods in zirconium in the (10·0) plane. Data were taken at a temperature of ≈1.1°K. Crosses (+) denote periods which we ascribe to harmonics.

III. RESULTS

The results of measurements of the dHvA periods in the (1$\bar{1}$·0), (10·0), and (00·1) planes of the zirconium crystals are shown in Figs. 1–3. Only one set of dHvA oscillations (labeled α) could be followed over all angles, and can thus be associated with a closed piece of the Fermi surface. The amplitude of these oscillations is quite strong and is dominant over the other oscillations except near the [00·1] direction. The total variation of this period is slightly less than 20% suggesting that the corresponding segment of Fermi surface is similar to a distorted sphere. The oscillations corresponding to the period labeled β, although dominant along the c axis, decrease rapidly in amplitude and are unresolvable at angles greater than 22°–24° from the c axis. The period decreases approximately as the cosine of the angle between the field direction and the c axis, which might result from a nearly cylindrical segment of the Fermi surface. The γ oscillations, which appear as weak beats superimposed on the α and β oscillations, similarly disappear as the angle between the magnetic field and the c axis increases. In the range over which it is observed, this period is constant within the limits of experimental error, and hence can be associated with a piece of the Fermi surface having a spherical curvature. Near the [10·0] direction the oscillations δ are seen beating with the α oscillations. Although these oscillations are relatively strong along the symmetry direction, their amplitude diminishes and virtually disappears at angles greater than 15° from the [10·0] direction. Another set of oscillations, labeled ϵ, were detected between 30° and 43° from the c axis in the (1$\bar{1}$·0) plane. Along the c axis two shorter period oscillations, which we shall call β' and β'' were observed

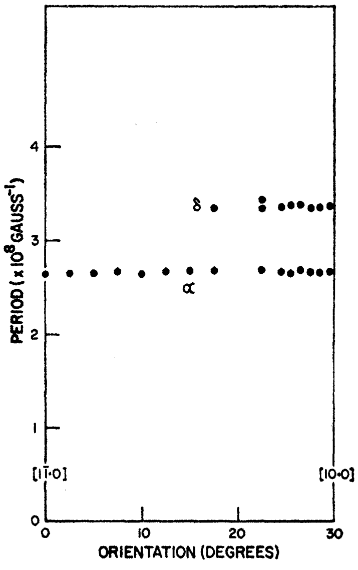


FIG. 3. Angular variation of the de Haas–van Alphen periods in zirconium in the (00·1) plane. Data were taken at a temperature of ≈1.1°K.

and followed toward the [10·0] axis. Their orientation dependence near the *c* axis and their magnitude suggest they are the second and third harmonics of the β oscillations. In the region from 10°–18° from the *c* axis, where the α oscillations become dominant over β, the short periods are somewhat difficult to resolve and appear to become the second and third harmonics of the α oscillations (labeled α' and α'' in Fig. 1).

The temperature dependence of the amplitude of the α oscillations was examined near the [11·0] direction from which we find[7] an effective mass of $m^* = 1.2m_0$. Similar measurements were not made at other orientations due to beating effects which made effective mass measurements extremely unreliable.

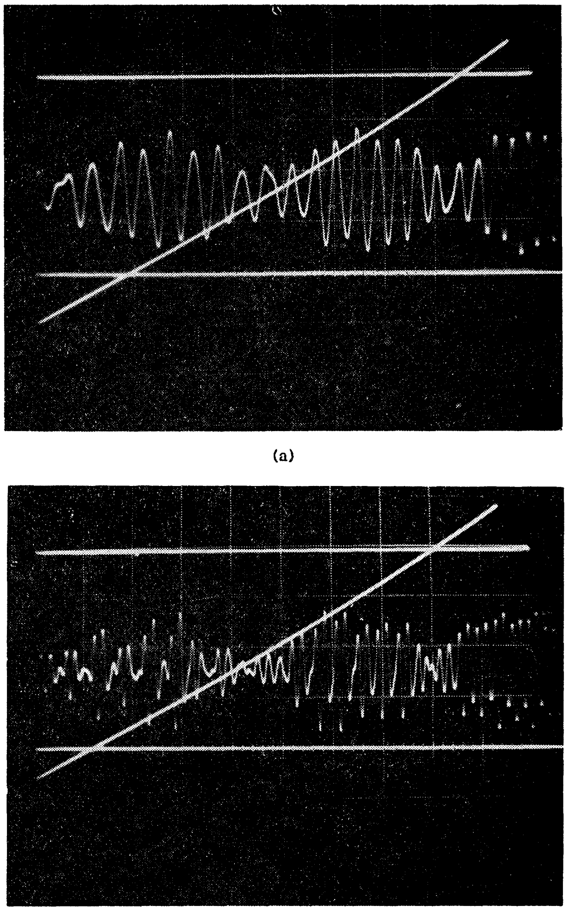
IV. DISCUSSION

It is interesting to note that all of the oscillations found have periods of the same order of magnitude. Attempts to observe both shorter and longer period oscillations were unsuccessful. A separate sample was cut and studied in steady fields up to 40 kG by the torsion balance method[4] but no dHvA oscillations were observed with the field in the basal plane of the crystal. Negative results were also obtained as the field was rotated (in an undetermined plane) from the *c* axis to the basal plane.

Although data were taken with the magnetic field increasing and decreasing, all data plotted in Figs. 1–3, except those points labeled with crosses, were taken as the field was increasing. The discontinuity in the slope of the magnetic-field pulse (due to the electronic shorting which occurs shortly after the field maximum) generally made it more convenient to take data while the field was increasing. The effects of eddy currents induced in the sample and the metal helium Dewar tend to make the measured periods smaller than the true value in an increasing field and larger in a decreasing field. In all of our measurements the two determinations agreed within 3% and most often the difference was only 1–2%. We have calculated the effects of eddy currents in the zirconium samples and in the stainless steel helium Dewar and find under typical conditions that the period would be ≈1% high or low depending on whether the period was measured in a decreasing or increasing field.

In most cases the periods of the separate oscillating terms could be determined from their beat patterns. However, in one region around 25° from the *c* axis in the (1$\bar{1}$·0) plane there is some question about the experimental curves. In this region (from 22°–29°) the α oscillations are dominant and beating strongly with γ. There is a suggestion in the data of the existence of other oscillating terms, which are probably the β and ϵ terms, but they are not strong enough to allow reliable period determinations. It is possible, therefore, that the β curve continues to decrease with angle from the *c* axis, or alternatively, that the β and ϵ curves join together around 25°.

The shorter period terms (α', $\beta'\alpha''$, and β'') which we associated with second and third harmonics display some interesting features which might be mentioned. First of all, the amplitudes of these oscillations are quite strong, being ≈30% and ≈8%, respectively, of the fundamental near the *c* axis. Comparatively strong harmonics might result from a reduction in the fundamental amplitude due to specimen imperfections, eddy currents, and field inhomogeneities as pointed out by Shoenberg.[2] The theoretical formula of Lifshitz and Kosevich[10] permits an estimate of the relative strengths of the harmonics if one knows the effective mass of the pertinent carriers and the Dingle scattering factor x.



(a)

(b)

FIG. 4. The de Haas–van Alphen effect in zirconium at 34° from the *c* axis in the (1$\bar{1}$·0) plane. The diagonal trace represents the magnetic field variation in a sweep time of 1.0 msec. The horizontal traces are field calibrations, the lower and upper lines corresponding to fields of 144.0 and 154.3 kG, respectively. (a) High-frequency oscillations filtered, showing the long beats produced by the addition of the α and ϵ terms. (b) Low-frequency oscillations filtered, showing harmonics and modulation effect discussed in text.

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The theoretical amplitudes obtained in this way agree qualitatively with those measured if one chooses $m^*/m_0 \approx 0.8$ and $x \approx 1°\mathrm{K}$. These values, though arbitrary, are not unreasonable for a period $\approx 3\times10^8$ G^{-1} and a sample with a comparatively low resistivity ratio.

Beating effects in the dominant harmonic indicate the existence of a third harmonic, since beats occur every second oscillation. An example of these short beats is shown in Fig. 4(b). This beat pattern occurs over almost the whole range of angles that the harmonics were studied.

Another beating effect, which is characterized by a longer beat length, appears to be an amplitude modulation due to the fundamental. In Fig. 4(a) the fundamental oscillations are pictured at an angle of 34° from the *c* axis. The long beats are due to the ϵ oscillations beating with the α oscillations. Higher frequencies than those pictured have been filtered. In Fig. 4(b) a similar picture was taken at the same orientation with the same sweep time and magnetic field variation. In this picture, however, the fundamental frequencies were filtered and only the high-frequency harmonics were allowed to pass. In this case the same long beat occurs, the beat waists occurring at the same time and field values, with the exception that there are twice the number of oscillations per beat. Although it might be possible to interpret this beat as due to another period oscillation, we believe it is rather a reduction in amplitude due to the fundamental passing through a beat waist. This feature was prominent over the region where the α and ϵ oscillations were beating and would disappear when the fundamental no longer exhibited beats.

In an attempt to explain the dHvA data in terms of a model of the Fermi surface we have examined those surfaces predicted by the nearly-free-electron model.[6,11] Since the number of free electrons per atom may not be a well-defined quantity for a transition metal, we have initially assumed the valence to be a parameter which might have an integer or noninteger value up to 4. Examination of these surfaces for valences of 2.0, 2.5, 2.7, 3.0, 3.5, and 4.0 using a single-zone scheme[12] and the double-zone surfaces of Harrison[11] reveal no theoretical model which can explain the observed data. A somewhat severe modification of the Fermi surface predicted by the model using a single-zone scheme with four electrons per atom can possibly account for the dominant features of our results. In Fig. 5(a) we have sketched the Fermi surface predicted by this model, and in Fig. 5(b) the fourth band hole and sixth band electron surfaces are shown modified to explain the α, β, and γ oscillations. The sixth band pocket of electrons shown in the figure predicts a dHvA oscillation whose period is very close to that found experimentally. The periods given by this surface are 2.46, ≈ 2.9, and 2.2×10^{-8} G^{-1} for the [00·1], [10·0], and [1$\bar{1}$·0] directions, respectively, compared to the experimental values of 2.85, 2.67, and 2.65×10^{-8} G^{-1}. The fourth band hole surface has been modified to a semicylindrically shaped surface which contains a spherical bulge in the basal plane. Although such a surface would explain the orientation dependence of the experimental curves β and γ, it would not explain the rapid disappearance of the oscillations around 25° from the *c* axis. The nearly-free-electron model does not explain the oscillations ϵ or δ, and alternatively does predict many orbits that are not observed. It is possible that higher purity samples would show such periods. However, on the basis of existing data, it appears that a more meaningful interpretation of the Fermi surface in zirconium will require theoretical developments beyond that inherent in the nearly-free-electron model.

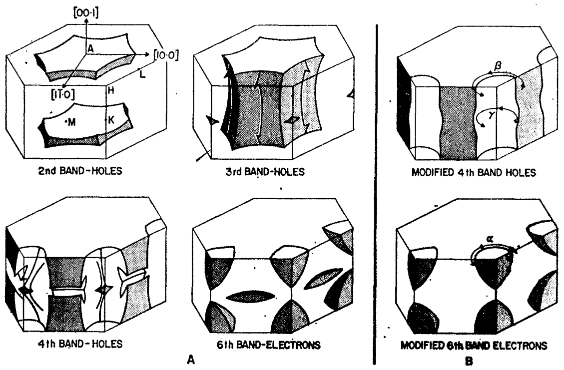

FIG. 5. (a) Sketches of the nearly-free-electron model of the Fermi surface predicted for a valence four metal using the single zone scheme. All zones are centered on Γ. The first band is completely filled. (b) A modification of the fourth and sixth band surfaces to account for the experimental dHvA oscillations.

ACKNOWLEDGMENTS

The authors wish to thank Dr. T. G. Berlincourt and Dr. R. E. Behringer for many helpful discussions during the course of this work.

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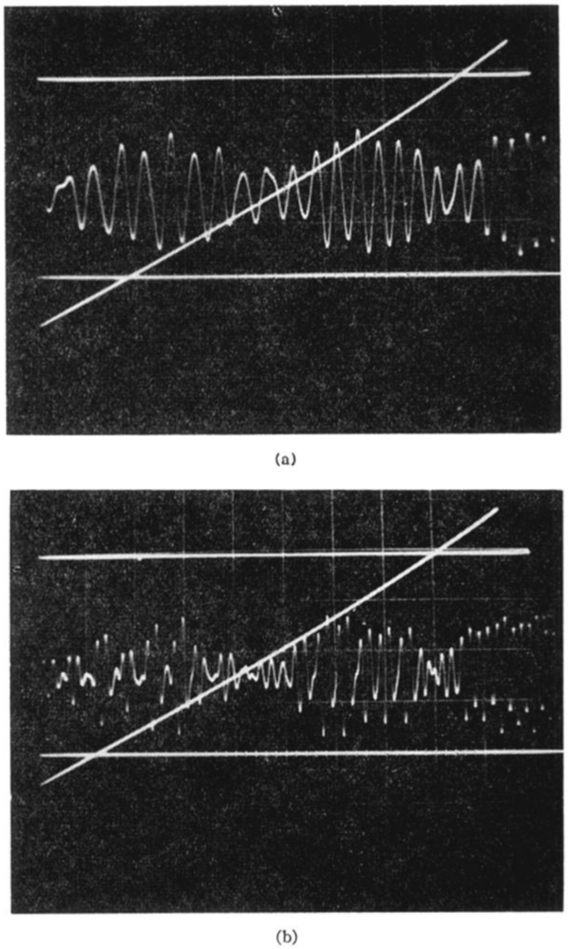
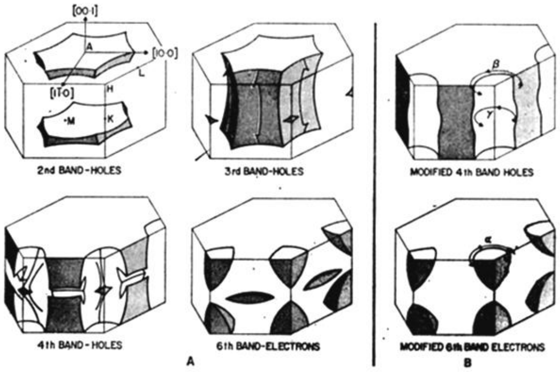


(a)

(b)

FIG. 4. The de Haas–van Alphen effect in zirconium at 34° from the c axis in the $(1\bar{1}\cdot 0)$ plane. The diagonal trace represents the magnetic field variation in a sweep time of 1.0 msec. The horizontal traces are field calibrations, the lower and upper lines corresponding to fields of 144.0 and 154.3 kG, respectively. (a) High-frequency oscillations filtered, showing the long beats produced by the addition of the α and ϵ terms. (b) Low-frequency oscillations filtered, showing harmonics and modulation effect discussed in text.



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