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Galvanomagnetic Studies of the Fermi Surface of Zirconium*

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The transverse magnetoresistance has been traced in moderately high-purity samples of zirconium throughout the three symmetry planes in magnetic fields up to 57 kG. The Fermi surface was found to be compensated and no open orbits were observed. In addition, the even component of the sample voltage transverse to both current and magnetic field and the components transverse to the current and parallel to the magnetic field were found to vanish when both the magnetic field and current were along symmetry directions.

I. INTRODUCTION

Lifshitz, Azbel, and Kaganov[1] (LAK) have presented a general theoretical interpretation of the high-field limit of the galvanomagnetic properties of metals. The LAK theory together with extensions by Lifshitz and Pechanskii[2] and Fawcett[3] have been used to relate these properties to the topology of the Fermi surface. Such information has proved to be very useful in distinguishing between competing Fermi-surface models.

Zirconium is a transition metal with the atomic configuration $5s^2 4d^2$ and the hexagonal-close-packed crystal structure at low temperatures. Two band calculations have been performed for Zr. The first by Altmann and Bradley[4] (AB) used the cellular approach and double-zone scheme and supported no open orbits. However, introduction of a spin-orbit energy gap would produce open orbits along [0001].[5] The second by Loucks[6] used the augmented-plane-wave (APW) method and the double-zone scheme. This Fermi surface originally did support open orbits along [0001] through the third and fourth zones. However, in order to qualitatively fit his results to the de Haas–van Alphen (dHvA) data of Thorsen and Joseph (TJ),[7] which indicates that a closed, simply connected sheet of the Fermi surface exists, Loucks rather artificially pinched off the connection between the third and fourth zones creating two closed sheets, and removing the only possibility for open orbits. However, given that a spin-orbit energy gap exists across the hexagonal zone face between these two zones it is not clear that the third-zone sheet could not be be closed while the fourth-zone sheet remained an undulating cylinder. Both models then could support open orbits depending on the size of the spin-orbit interaction and on what other reasonable distortions of the models that could be made.

The purpose of this investigation is to determine the state of compensation of the Zr Fermi surface and the existence and extent of any open orbits. Presently the Fermi surface of Zr is not clearly understood. Determination of the existence or nonexistence of open orbits along [0001] will not constitute conclusive evidence for or against either of the existing models. However, detection of basal-plane open orbits would be cause for the rejection of both models. In any case determination of the topology of the Zr Fermi surface will be of fundamental importance in the development of new models and the determination of the true Fermi surface.

II. FERMI-SURFACE TOPOLOGY AND GALVANOMAGNETIC EFFECTS

The topology of the Zr Fermi surface must reflect the hexagonal symmetry of the lattice. Periodic open orbits may exist along the three symmetry directions. If, however, open orbits extended along ⟨11$\bar{2}$0⟩ or ⟨10$\bar{1}$0⟩, the hexagonal symmetry would imply the existence of a hexagonal network and with it the existence of a two-dimensional zone of aperiodic open orbits. Thus in looking for open orbits in Zr, the Fermi surface should be examined for the existence of an undulating cylinder extending in the [0001] direction and for the existence of a network in the basal plane that supports aperiodic open orbits and may or may not support periodic open orbits. The combination of both cases into a three-dimensional network is also a possibility with the creation of supplementary zones of aperiodic open orbits, and such a network could also be detected with galvanomagnetic measurements.

In discussing the various components of the sample potential, the current I will be taken to be along the x axis and the applied magnetic field H along the z axis. With this arrangement of I perpendicular to H, the component of potential parallel to the current measures the transverse magnetoresistance (TMR) which is always an even function of H. The y component of the sample potential in general contains both odd and even components in H. The odd component has been traditionally referred to as the Hall field (HF) and the even component as the transverse even field (TEF). No particular names have been assigned to the z components.

In this investigation, the TMR was observed throughout the three symmetry planes. The y and z voltages were measured only with both I and H lying along symmetry directions. Under these symmetry conditions the TEF must vanish identically as well as the z voltage.[8] Thus, under the experimental conditions, the only observable quantities should be the TMR and HF. The asymptotic high-field dependences of these quantities predicted by the LAK theory are summarized in Table I. Thus the state of compensation of a metal and the existence and extent of open orbits on the Fermi surface can be determined from studies of the galvanomagnetic effects.

In real metals, open-orbit directions are fairly isolated. Therefore, the field dependence of the TMR for general field directions will indicate the state of compensation. An even-valent metal is expected to have equal numbers of electrons and holes and be compensated. An odd-valent metal is expected to be uncompensated. Each Zr atom contributes two highly mobile s electrons and two less-mobile d electrons to the conduction process. It seems most likely that Zr is even valent. It would not be very reasonable to treat each d electron as only partially contributing to the conduction band because of its low mobility thereby making Zr non-even-integer valent.

Determination of the field dependence of the TMR for all field directions would clearly indicate the extent of any sheets of the Fermi surface that support open orbits. If periodic open orbits exist, they must exist for the entire range of field directions lying throughout the symmetry plane normal to the open orbit direction. If aperiodic open orbits exist, they must exist for a finite solid-angle range, and some part of this solid-angle range must be in one of the symmetry planes. In looking for the existence of open orbits in Zr, then, it is sufficient to examine the TMR for field directions lying throughout the three symmetry planes.

TABLE I. Asymptotic high-field dependence of the galvanomagnetic properties of metals with field and current located along symmetry directions.

Orbit type and compensation	TMR	HF
Closed and uncompensated	H^0	H
Closed and compensated	H^2	H
Open orbit along current	H^2	H
Open orbit perpendicular to current	H^0	H
Open orbits in two directions	H^0	$1/H$

Studies of the field dependence of the HF will not yield much information since it is proportional to H in every case except the least likely one of simultaneous open orbits in more than one direction.

III. EXPERIMENTAL ARRANGEMENT

The high-purity crystals of Zr used in this investigation were obtained from Oak Ridge National Laboratory[9] in the form of an annealed electron-beam-zone-refined rod. One small section of this rod (6-mm diam, 6 mm long) had an average residual resistance ratio[10] (RRR) of 600. The three samples used in a dHvA investigation[11] and two of the samples used in this investigation were cut from this section. The third sample used in this investigation was cut from a different section of the rod with a RRR $\simeq$ 300. The crystals were oriented to better than $\frac{1}{4}°$ by back-reflection Laue techniques, and the samples were cut with an acid-erosion string saw.[12] This cutting technique was used since it proved to be much faster than spark erosion, and there was no danger of straining the samples in the cutting process.

The three samples cut for this investigation had dimensions of approximately $0.6 \times 1.2 \times 6$ mm. The crystal orientation and nominal RRR of each sample is shown in Table II. Three pairs of 0.12-mm-diam copper wire leads were welded to each sample with a Hughes model MCW/IL spot welder. The configuration of the leads is shown in Fig. 1. One pair of leads, marked I, was used to introduce a current along the length of the sample. Another pair, marked V_L, was used to measure the voltage developed in the direction of the current. The V_L leads were placed no closer than 1 mm to the nearest current lead to insure that the current was spread out evenly over the breadth of the sample before it reached the voltage lead. The third pair, marked V_T, was used to measure the voltage perpendicular to the current. The leads were aligned by eye using a microscope to be parallel

TABLE II. Crystal orientation and residual resistance ratio (RRR) of the samples.

Sample	RRR	Symmetry axis parallel to length of sample	Symmetry axis parallel to placement of transverse leads
1	600	[0001]	$\langle 11\bar{2}0 \rangle$
2	600	$\langle 11\bar{2}0 \rangle$	$\langle 10\bar{1}0 \rangle$
3	300	$\langle 10\bar{1}0 \rangle$	[0001]

or perpendicular to the sample length.

A scale drawing of the sample holder used in this investigation is shown in Fig. 2. The sample [k in Fig. 2(b)] was placed in a cavity in the sample mounting piece (j). The sample was held in place with two flat-tipped phosphor-bronze-spring clips, one at each end of the sample, and the welded current leads were soldered to the spring-clip bases. The clips then paralleled the current leads and helped spread the current out over the breadth of the sample. The four voltage leads were soldered to tabs attached to the sample mounting piece. The sample was then x rayed for a final check of its orientation. If a sample had a misorientation of more than $\frac{1}{2}°$, it was remounted. The sample was also x rayed in the mounting piece after each run to insure that it had maintained its orientation. The sample mounting piece was then placed in the tilt wheel (l). Heavier copper leads were soldered to the tabs and clips and led to the top of the sample holder. The tilt wheel and sample were rotated in the magnetic field of a superconducting solenoid by translation of the rack (m) which was connected to a corresponding rack at the top of the Dewar [g in Fig. 2(a)]. Sample rotation was accomplished either by hand or with a speed-controlled motor. The angle of rotation was read either from a multi-turn dial (a) or from the voltage across a potentiometer (b) geared into the drive shaft. The uncertainty in the angle of rotation was never more than 0.2°.[13] All the lower tail pieces were machined from rods cast from Hysol Epoxy No. CP3-4287. This material machines very easily and does not distort at low temperatures. The sample-holder rotation was as smooth at liquid-helium tempera-

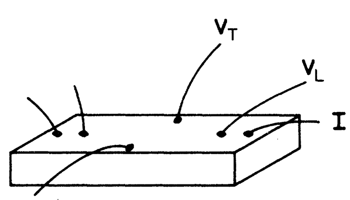

FIG. 1. Placement of welded leads on sample. This drawing is not to scale.

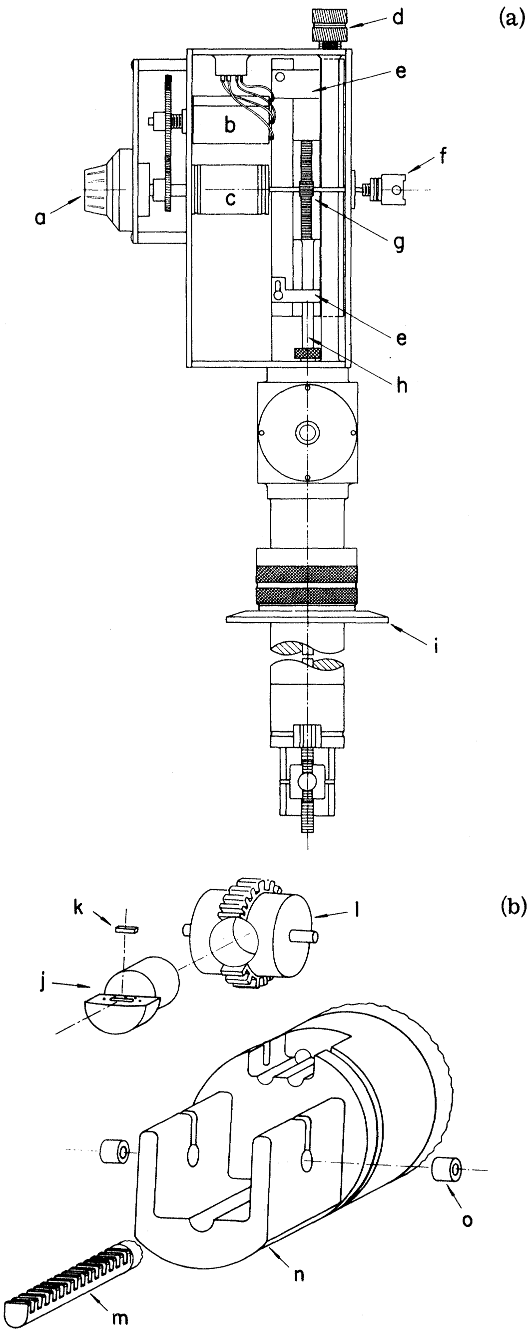

FIG. 2. (a) Scale drawing of sample holder: a, multi-turn dial used to read sample orientation; b, 10-turn potentiometer producing voltage proportional to sample orientation; c, spur-gear speed increaser; d, O-ring sealed port for transfer tube; e, stops for limits of sample rotation; f, coupling to speed-controlled motor; g, rack and pinion; h, stainless-steel tube connecting racks at upper and lower ends of sample holder; i, flange attaching sample holder to Dewar. (b) Expanded and exploded view of lower section of sample holder: j, sample mounting piece; k, sample; l, tilt wheel; m, rack to rotate tilt wheel; n, yolk; o, bushings. The rack and tilt-wheel teeth are more even than shown in the drawing.

ture as it was at room temperature.

A block diagram of the experimental setup is shown in Fig. 3. The standard Dewar system is not shown. The magnetic field was produced by a Westinghouse 57-kG superconducting solenoid. The magnet was powered by a Harrison model LTV 620A programmable power supply. The magnetic field was swept linearly to full field in a time interval of 10 min. The field was monitored by passing the magnet current through a 2-mΩ manganin resistor and reading the voltage drop with a digital voltmeter. The voltmeter readings were calibrated with the nuclear magnetic resonance of Al^{27}. At a finite sweep rate part of the power supply current passed through the persistent-mode-switch in parallel with the solenoid. Corrections to the voltmeter readings were calculated from a knowledge of the persistent-mode-switch resistance, solenoid inductance, and sweep rate.

The sample holder was placed in a separate Dewar inserted into the core of the solenoid. The helium in this Dewar was pumped to 1.2°K. The currents used were approximately 125 mA and were stable to 100 μA. The voltage leads were soldered directly to the input of a Keithley model 148 breaker-type nanovoltmeter with Cd-Sn low-thermal solder.[14] The signal was recorded on a strip-chart recorder. The detected signals at maximum field ranged from 10 μV to 100 nV.

IV. RESULTS

The three samples used in this investigation allowed measurement of the TMR with the field along each symmetry axis and with the current along both of the other two axes. The largest uncertainty in sample orientation was rotation of the sample mounting piece in the tilt wheel, and the single rotation axis could not correct for this. All misalignment uncertainties considered, it was estimated that the TMR field sweeps were made within 1° of

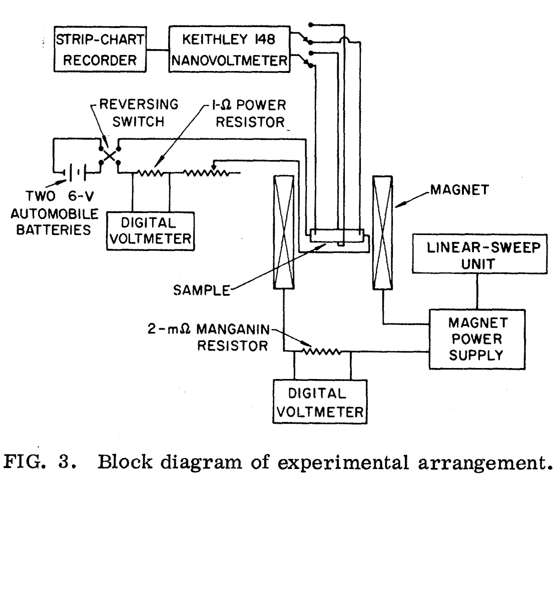

FIG. 3. Block diagram of experimental arrangement.

the symmetry axes. All six sets of data showed that the TMR increases as H^2 in the high-field limit. The data were always taken with the current in both the forward and reversed directions to eliminate rectifying junction effects although none were found. The data were also taken with the field in the forward and reversed directions, and the two sets of data were added and subtracted to give the odd and even components in field of the TMR. No odd component was ever observed. One set of data, taken with sample 1 with the field along $\langle 11\bar{2}0\rangle$ and the current along [0001], is shown in Fig. 4. In the usual manner, the change in resistance from the zero-field value divided by the zero-field value[15] has been plotted against field direction. For purposes of discussion in Sec. V, a corresponding plot of the data taken with sample 3 with the field along $\langle 11\bar{2}0\rangle$ and the current along $\langle 10\bar{1}0\rangle$ is shown in Fig. 5. The straight lines in both figures are least-squares fits through the eight high-field points.

Field-rotation patterns of the TMR were made in the three symmetry planes at approximately 55.8 kG. In the vicinity of the symmetry axes, the sample was rotated at the rate of 1°/min. In the intermediate-field directions, the sample was rotated more rapidly at 3°/min. The sample and the lead wires necessarily formed a loop that rotated in the magnetic field. At the faster rotation rate, the pickup from this loop imposed a gently sloping background of about 5% of the signal on the rotation patterns. This background was not enough to mask in any way the detection of a change in asymptotic behavior and thus the detection of open orbits. The background was removed by retaking the data point by point with the the points spaced about 3° apart. The results are shown in Figs. 6(a), 6(b), and 6(c). There is no indication of a shift from one type of asymptotic behavior to another.

For a particular sample the transverse leads measured the y voltage with the field along one symmetry axis and the z voltage with the field along the other in the plane of sample rotation. In each of the three cases, the y voltage contained odd and even components in field. In this configuration the even component, the TEF, should vanish. However, the transverse probes could not be perfectly placed across such a narrow sample, and the probe misalignment introduced a measurable amount of TMR which could not be separated from the TEF. The magnitude of the even component was what would be expected from probe misalignment.[16] The odd component of one orientation with the field along [0001] and the current along $\langle 11\bar{2}0\rangle$ is shown in Fig. 7. The straight line is again a least-squares fit through the eight high-field points. The other two data sets show the same linear field dependence.

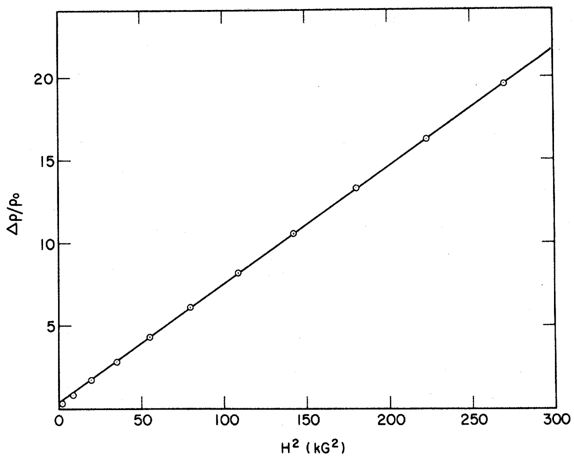

FIG. 4. Transverse magnetoresistance vs H^2 for I along [0001] and H along ⟨11$\bar{2}$0⟩, sample 1. The straight line is a least squares fit through the eight high-field points for this and successive figures.

In two cases, the transverse leads gave only an even component when aligned along the field. When the corresponding even component of the y voltage was scaled by the change in TMR between the two axes and subtracted from the z component, the z component was reduced entirely into the noise level. This indicates that for these two cases the z component was due entirely to probe misalignment and that both the z component and the TEF vanished. In the third case with the field along [0001] and the current along ⟨10$\bar{1}$0⟩, there was a small odd component and a barely detectable residual even component in the z voltage, but these amounts were observed to dip sharply in the vicinity of the axis. It appears then that the residual z voltage would

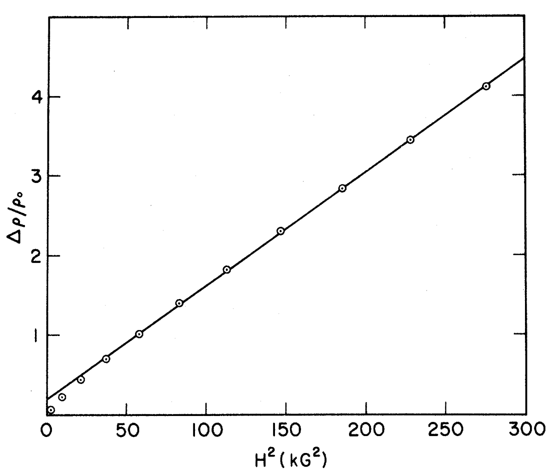

FIG. 5. Transverse magnetoresistance vs H^2 for I along ⟨10$\bar{1}$0⟩ and H along ⟨11$\bar{2}$0⟩, sample 3.

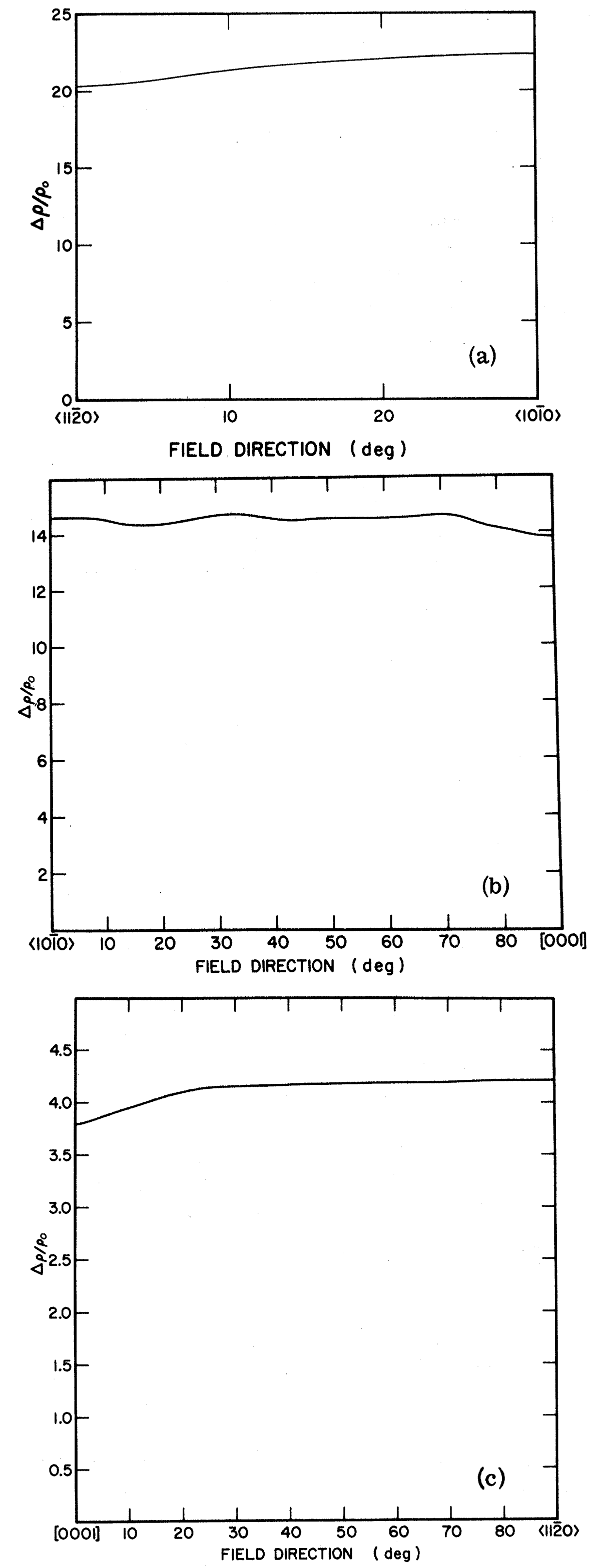

FIG. 6. Field rotation patterns of the transverse magnetoresistance: (a) sample 1 with I along [0001]; (b) sample 2 with I along ⟨11$\bar{2}$0⟩; (c) sample 3 with I along ⟨10$\bar{1}$0⟩.

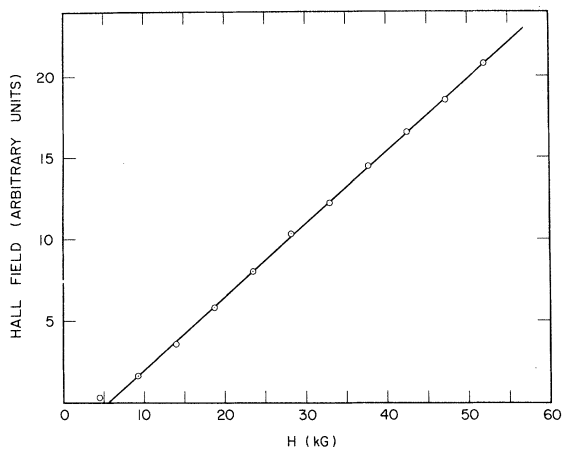

FIG. 7. Hall field with I along $\langle 11\bar{2}0\rangle$ and H along [0001]. In subtracting the two data sets with the magnetic field in opposite directions to obtain the odd component, it was not possible to insure that a constant offset or zero shift was not included. No particular significance then should be attached to the positive H intercept of the least-squares-fitted line.

have vanished if the field had been precisely aligned along [0001] and that the symmetry predictions of Ref. 8 are correct.

V. DISCUSSION OF RESULTS

The normals to open orbit directions in Zr are expected to be fairly isolated.[17] If an undulating cylinder extended along [0001], open orbits would exist on it only for field directions lying in the basal plane. Similarly, if a hexagonal network that would support periodic open orbits existed, these open orbits would be limited to field directions lying in the planes normal to the open-orbit directions. Aperiodic open orbits would be limited to field directions lying in finite solid angular ranges around the symmetry axes.

The TMR increases quadratically in the high-field limit throughout all three symmetry planes. Since open orbits along the current directions cannot exist for all these field directions, the Fermi surface of Zr must be compensated.

Sample 1 was used to trace the TMR in the basal plane. However, with this sample the current was along [0001], and if open orbits existed along [0001], the TMR would still be asymptotically quadratic. However, with samples 2 and 3, rotations were made throughout the $\langle 11\bar{2}0\rangle$ and $\langle 10\bar{1}0\rangle$ planes, respectively. Since in both cases the TMR did not saturate as the field passed through the basal plane, it can be concluded that no substantial number of carriers take part in open orbit conduction along [0001]. From Fig. 5 it was estimated that the maximum $\omega\tau$ value reached with samples 1 and 2 was about 20, and from Fig. 6 that with sample 3 about 10. It cannot be definitely concluded then that all sheets of the Fermi surface are completely closed in the [0001] direction. However, if an undulating cylinder or three-dimensional grid does exist, it must be very narrowly necked to severely limit the number of carriers that can take part in open orbit conduction along [0001].

If basal plane periodic open orbits exist on a hexagonal network, they should have been observed with sample 1. In addition, they should have been observed with samples 2 and/or 3. With these samples the current would have been perpendicular to the open-orbit direction, and the field would have been required to pass through the symmetry plane normal to the open-orbit direction even if slight sample misalignment had occurred.

As well, a hexagonal network may support aperiodic open orbits. The field directions producing these orbits would be limited to solid angular ranges around [0001] and, if it is a three dimensional network, conceivably around $\langle 11\bar{2}0\rangle$ and $\langle 10\bar{1}0\rangle$. In the rotation patterns the field passed well within a degree of the symmetry axes. Therefore, if a hexagonal network exists it must be extremely narrowly necked so that the solid-angle ranges of open orbits extend less than one degree from the symmetry axes.

No open orbits were detected along [0001]. The field dependence of the TMR indicates that the asympotic, quadratic field dependence was reached at 6–9 kG with the three samples used in this investigation. It seems unlikely that the spin-orbit energy gap could be so small as to be completely broken down at these fields, and the results, therefore, appear to contradict the AB model. If Loucks is taken at his word, his Fermi surface supports no open orbits, and these results are not at variance with his model. However, the way in which the doubly degenerate band was pulled below the Fermi level at the A point was not made clear by Loucks, and the degeneracy would be expected to be removed by the spin-orbit interaction. It seems entirely possible that the third-band sheet of Loucks's model could become closed while the fourth-band sheet remained open, and such a situation would not affect the comparison of the Loucks model with TJ's data. Since it is not clear whether or not this model should support open orbits along [0001], a statement of support or nonsupport cannot be made for this model. It is clear, however, that within the reasonable experimental uncertainties of this investigation that no open orbits exist on the Zr Fermi surface.

The rather smooth character of the TMR rotation patterns indicates that the Zr Fermi surface is rather rounded and does not have pointed sections giving the electrons large velocity components in particular directions. However, if the Fermi surface consisted of a large number of sheets this smoothness could result simply from averaging.

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[5]References 4, 6, and 7 all used a four-integer system of Miller indices in which the reciprocal-lattice vectors were used as the basis vectors. The present investigations use the now standard system where the real-space lattice vectors are used as basis vectors. Thus the reciprocal-lattice-vector direction is given as $\langle 10\bar{1}0\rangle$. In discussing trajectories, the direction in reciprocal or k space is always given.

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[7]A. C. Thorsen and A. S. Joseph, Phys. Rev. 131, 2078 (1963).

[8]C. G. Grenier (private communication).

[9]The author would like to thank R. G. Goodrich and J. M. Reynolds for their help in obtaining this material.

[10]This is the ratio of the sample resistivity at room temperature, ~313 °K, to that at 4.2 °K.

[11]P. M. Everett, following paper, Phys. Rev. B 6, 3559 (1972).

[12]The cutting solution used consisted of 13% concentrated nitric acid and 2% hydrofluoric acid in water.

[13]The angle of rotation was calibrated at room temperature by reflection of a focused light beam off a mirror attached to the tilt wheel. Very small and negligible unevenness in the teeth were observed. The reading at which the tilt wheel was aligned along the length of the sample holder, i.e., along the field, could not be determined in this way since differential thermal contraction would rotate the tilt wheel on cool down. However, this sample holder was also used in the investigation of Ref. 11, and the dHvA rotation patterns very accurately determined this dial reading.

[14]This solder has a work function very near that of copper thereby reducing thermoelectric effects to an acceptable level.

[15]Presentation of the data in this way makes the results independent of sample geometry.

[16]This even component was less than 1% of the TMR.

[17]The unusual case of a plane Fermi surface where open orbits exist for all field directions except the singular direction normal to the plane is not considered.

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de Haas-van Alphen Studies in Zirconium*

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The de Haas–van Alphen effect has been studied in Zr in fields up to 57 kG. The five previously reported frequency branches have been observed as well as two new ones. The symmetry-axis frequency values have been determined with an uncertainty on the order of 0.1%, and the angular dependence of all the branches has been firmly established. It seems unlikely that any Fermi-surface model presently available can account for these results. All but one of the cyclotron masses associated with these oscillations have been measured at the symmetry axes. Except in one case these mass values are greater than the free-electron mass.

I. INTRODUCTION

The first study of the Zr Fermi surface was the de Haas–van Alphen (dHvA) investigation of Thorsen and Joseph[1] (TJ). They used the pulsed-field technique up to 190 kG and established the existence of five dHvA frequency branches. Since it was not clear to what degree and in what manner the d electrons contributed to the conduction process, they considered the nearly-free-electron model for fractional valence ranging from two through four and found that they could not fit their data to any reasonable distortion of it. Recently, Schirber,[2] as part of a study of the pressure dependence of the