Magnetoresistance of Molybdenum and Tungsten

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The transverse magnetoresistance of pure single crystals of molybdenum and tungsten is measured at 4.2°K in high magnetic fields. The anisotropy of the magnetoresistance is very similar for the two metals, exhibiting a smooth variation with angle by a factor ~2 with no pronounced minima, and the field dependence is approximately quadratic at the highest fields for all field directions. This behavior in the high-field region is characteristic of a compensated metal, whose Fermi surface supports no open cyclotron orbits.

I. INTRODUCTION

THE study of the anisotropy and field dependence of the magnetoresistance of pure single crystals of a metal at low temperature and in high magnetic fields has proved a useful method of determining its electronic structure. This is especially true when open cyclotron orbits on the Fermi surface occur for some field directions, since with appropriate choice of the field and current directions a pronounced effect of such orbits is seen in the behavior of the magnetoresistance.[1] The absence of open orbits, when *a priori* considerations of the topology of the Fermi surface suggest that they might occur, can also be informative.

The predominant character of the field dependence in the high-field limit, in which $\omega_c\bar{\tau}\gg 1$ for all cyclotron orbits, ω_c being the cyclotron frequency and $\bar{\tau}$ the relaxation time averaged over the orbit, is also an important feature of the magnetoresistance.[2] For a compensated metal (i.e., one having equal numbers of electrons and holes, which compensate each other and cancel the linear Hall term of the conductivity tensor), the field dependence is quadratic, whereas for a noncompensated metal the magnetoresistance saturates. Because the capacity of the Brillouin zone is two electrons per atom, one expects compensation for any metal having an even number of conduction electrons (i.e., occupied states in partially-filled zones) per primitive unit cell. But this criterion is not very useful, since the number of conduction electrons is not known in the transition metals, for which the chemical valency is multivalued. It was proposed in earlier publications,[3] in which preliminary measurements of the magnetoresistance of molybdenum, niobium and tantalum were reported, that a more useful criterion for compensation is that the product sZ of the atomic number Z and number s of atoms in the primitive unit cell should be even.

In the present paper more extensive measurements of the anisotropy and field dependence of the magnetoresistance of molybdenum are described, together with similar measurements on more accurately oriented single crystals of tungsten of higher purity than have been reported previously.[4,5] The results show that the anisotropy of the magentoresistance is very similar for the two metals. This indicates that they have similar electronic structures, as one might expect from the fact that both metals occur in Group VI of the periodic table and have body-centered cubic lattices. Both metals exhibit predominantly quadratic field dependence of the magnetoresistance, which confirms at least for these of the transition metals, the validity of the criterion for compensation that sZ should be even. The fact that neither metal exhibits any evidence for the existence of open orbits is compared with the predictions of a free electron model, and shows that this is not a good approximation for the Fermi surfaces of molybdenum and tungsten.

II. EXPERIMENTAL

The preliminary measurements on single crystals of molybdenum were done at the Royal Radar Establishment, Malvern, England.[3] Magnetic fields up to 33 kG were employed, and the anisotropy of the transverse magnetoresistance was recorded continuously as the magnet was rotated about the axis of the sample. The resistance was measured as a function of field for several field directions for each sample. Subsequent measurements on molybdenum and on tungsten were done at the Bell Telephone Laboratories in magnetic fields up to 18 kG. A similar geometry was used in the latter experiments, and also for some samples the axis of crystal symmetry nearest to the sample axis was made the axis of rotation of the magnet in order to search more closely for evidence of open orbits.

All measurements were done at a temperature of 4.2°K, except for some of the preliminary experiments

[1] I. M. Lifshitz, M. Ia. Azbel' and M. K. Kaganov, J. Exptl. Theoret. Phys. (U.S.S.R.) **31**, 63 (1956) [translation: Soviet Phys.—JETP **4**, 41 (1957)]. Definitive studies of the magnetoresistance under these conditions have now been done for the following metals: Au—Yu. P. Gaidukov, J. Exptl. Theoret. Phys. (U.S.S.R.) **37**, 1281 (1959) [translation: Soviet Phys.—JETP **10**, 913 (1960)]. Cu—J. R. Klauder and J. E. Kunzler, *Proceedings of the International Conference on the Fermi Surface* (John Wiley & Sons, Inc., New York, 1960), p. 125. Sn—N. E. Alekseevskii, Yu. P. Gaidukov, I. M. Lifshitz, and V. G. Peschanskii, J. Exptl. Theoret. Phys. (U.S.S.R.) **39**, 1201 (1960) [translation: Soviet Phys.—JETP **12**, 837 (1961)]. Pb—N. E. Alekseevskii and Yu. P. Gaidukov, J. Exptl. Theoret. Phys. (U.S.S.R.) **41**, 354 (1961) [translation: Soviet Phys.—JETP **14**, 256 (1962)]. Ga—W. A. Reed and J. A. Marcus, Phys. Rev. **126**, 1298 (1962).

[2] E. Fawcett, Phys. Rev. Letters **6**, 534 (1961).

[3] E. Fawcett, Phys. Rev. Letters **7**, 370 (1961); Bull. Am. Phys. Soc. **7**, 231 (1962).

[4] E. Justi and H. Scheffers, Physik Z. **37**, 700 (1936).

[5] J. De Nobel, Physica **23**, 349 (1957).

TABLE I. Characteristics of samples.

Sample	Orientation[a]	r[b]	Source[c]
Mo 51	4° to [110]	{3760 3880	Bell Telephone Laboratories
Mo 1	4° to [001]	1570	{Metals Research,
Mo 2	14° to [110]	3640	Cambridge, England}
Mo 228	5° to [11$\bar{2}$]	820	{J. A. Belk, Armaments
Mo 227	8° to [001]	990	R. and D. Establishment, England}
W 4	7° to [110]	{5000 5520	H. W. Schadler, General Electric Company
W 75	5° to [001]	7910	Westinghouse Lamp Division

[a] Square brackets are used to indicate the axis of crystal symmetry nearest the sample axis, and in the figures angular brackets indicate the symmetry axis nearest to a field direction.
[b] r is defined in the text; two values for the same sample refer to different experiments with the potential contacts in different positions.
[c] All the samples were prepared by electron-beam zone-melting, and their diameters were about 5 mm, with the exception of W 4 which was nearer 3 mm. Each sample was about 50 mm long and the separation of indium-soldered potential contacts was about 30 mm.

when the temperature was near 2°K. Because of the high Debye temperature for both metals, scattering of electrons by lattice vibrations is already negligible at 4.2°K even in the samples with the least impurity scattering. The increase in the magnetoresistance at 18 kG on lowering the temperature to 2°K was found to be only 1.6% for the purest sample of either metal (W 75 in Table I).

The orientations, resistance ratios, and sources of the samples are listed in Table I. The resistance ratio between room temperature and 4.2°K was the measured quantity, and the ratio r of the resistivities at the Debye temperature θ_D and at 4.2°K was calculated from this by the use of White and Woods'[6] data. They give the ratio of the resistivities at θ_D and at 295°K; for molybdenum ($\theta_D=380$°K) this ratio is 1.374 and for tungsten ($\theta_D=315$°K), 1.092.

The resistance of the purest samples in zero field at 4.2°K was only of the order of 10 m$\mu\Omega$, and could be measured with an accuracy of about 5%. The accuracies of r and of the absolute values of the magnetoresistance ratio are limited accordingly, but the relative accuracy for the latter at high fields is better than 1%.

III. RESULTS

In Figs. 1(a) and 2(a), the anisotropy of the magnetoresistance as the magnetic field is rotated about the sample axis is shown for the two samples of molybdenum with axes at 4° to the symmetry axes [110] and [001], which are shown in stereographic projection on the polar diagrams. When the field is near the equivalent symmetry axes the resistance goes through minima, but the field dependence here and at the maxima, plotted in Figs. 1(b) and 2(b), shows no sign of saturation. Indeed the variation of the fractional change in resistance, $\Delta\rho_H/\rho_0$, with field H, is quite linear in the logarithmic plots as H is reduced by a factor of 2 to 3 from its highest value. But the exponent m in the

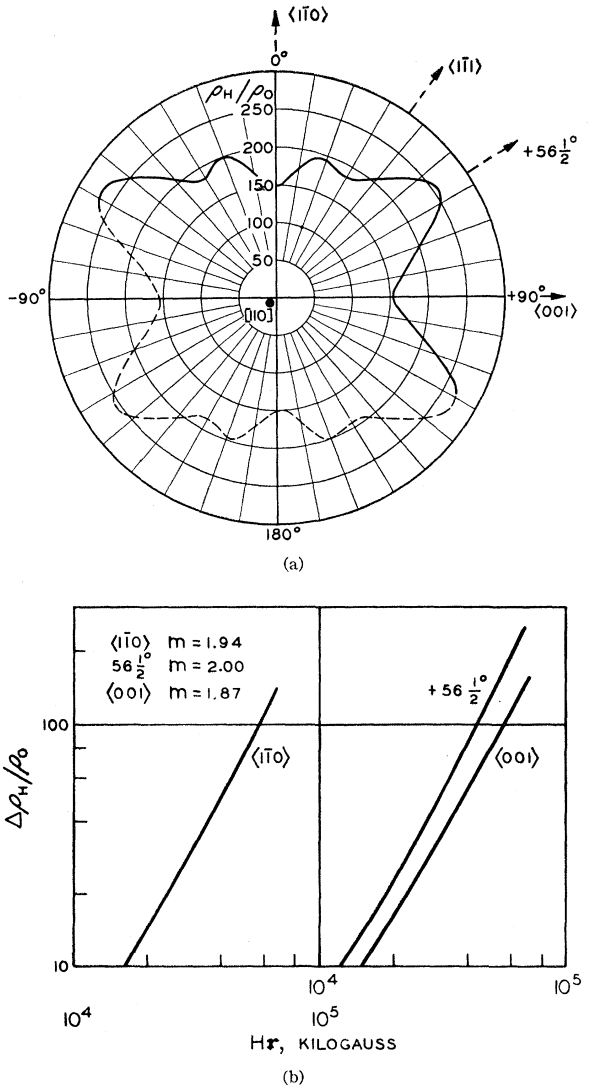
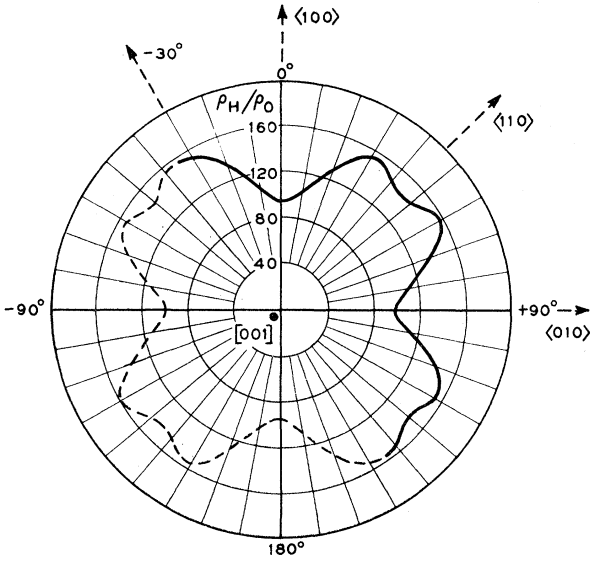
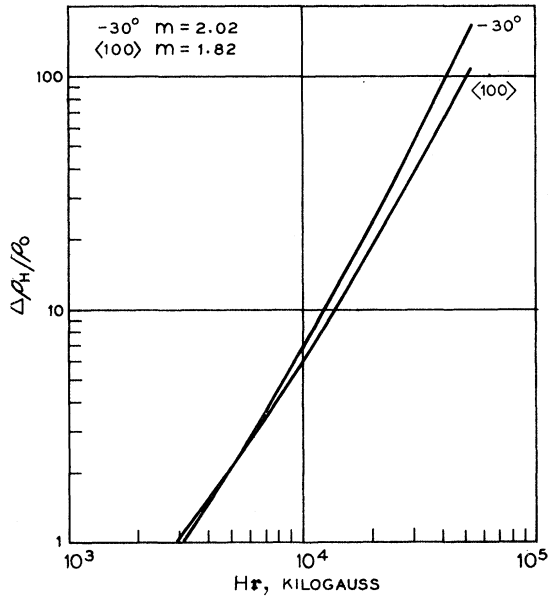


FIG. 1. Magnetoresistance of molybdenum. (a) Anisotropy of the magnetoresistance as the magnetic field $H=18.0$ kG is rotated about the axis of sample Mo 51. (b) Field dependence of the magnetoresistance.

[6] G. K. White and S. B. Woods, Phil. Trans. Roy. Soc. (London) **A251**, 35 (1959)



(a)



(b)

FIG. 2. Magnetoresistance of molybdenum. (a) Anisotropy of the magnetoresistance as the magnetic field $H=31.3$ kG is rotated about the axis of sample Mo 1. (b) Field dependence of the magnetoresistance.

expression,

$$\Delta\rho_H/\rho_0=CH^m,$$

is smaller at the minima than at the maxima, where the field dependence is exactly quadratic to within the experimental accuracy for m of about 2%.

When the sample axis makes an angle of 14° to [110], the polar diagram of the magnetoresistance shown in Fig. 3 has lost the symmetrical form of Fig. 1(a), but the field dependence is still nearly quadratic both at the minimum and at the maximum. For the sample with its axis near [11$\bar{2}$] (Fig. 4), the field dependence is again nearly quadratic at the shallow minima.

The immediate conclusion, which may be drawn from the approximately quadratic variation of the magnetoresistance at high fields for the field directions illustrated in Figs. 1 to 4, is that molybdenum is a compensated metal having equal numbers of electrons and holes. The exponent m varies from 1.82 to 2.02, both these extreme values being observed for different field directions with the same sample (Fig. 2). The lower values of m probably correspond to some few cyclotron orbits with unusually high effective masses or short relaxation times, for which the high-field limit is still not achieved at the highest fields.

A further conclusion from these experimental results, which is justified in the following discussion, is that there are no open orbits on the Fermi surface of molybdenum. The transverse magnetoresistance for a compensated metal should saturate at high fields only for a field direction which gives rise on a multiply-connected sheet of the Fermi surface to a band of open orbits whose net direction in momentum space is perpendicular to the current direction.[1,2] A comprehensive and rigorous treatment of the conditions under which open orbits may occur for a Fermi surface, subject only to the symmetry properties of the metal, has not been given. But a consideration of some of the possible shapes of a multiply-connected sheet of the Fermi surface for a body-centered cubic metal, and a knowledge of the observed magnetoresistance and its interpretation for

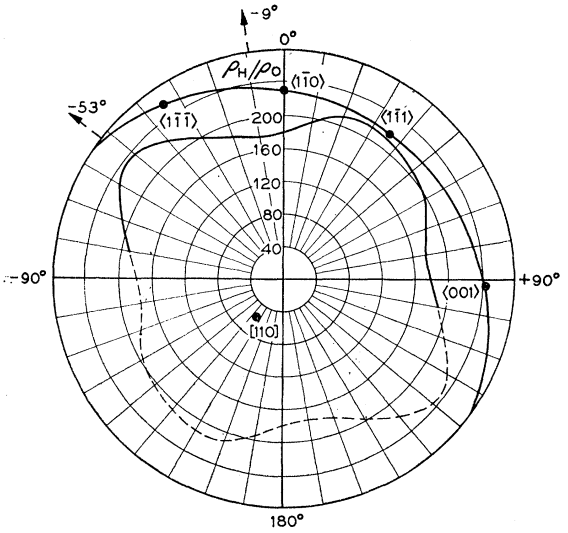


FIG. 3. Magnetoresistance of molybdenum. The anisotropy of the magnetoresistance is shown as the magnetic field $H=18.0$ kG is rotated about the axis of sample Mo 2. The plane (110) and the symmetry axes lying in it are shown in stereographic projection. For the field-dependence curves, the exponent $m=1.90$ for H at $-53°$, and $m=1.85$ for H at $-9°$.

other metals,[1] shows that two types of open orbit may occur: type A for a one-dimensional set of field directions perpendicular to a symmetry axis, and type B for a two-dimensional region centered on a symmetry axis.[7]

The absence of narrow minima with a saturating magnetoresistance in Figs. 1–4, when the field passes through directions perpendicular to the symmetry axes ⟨100⟩, ⟨110⟩, and ⟨111⟩ and when the current is nearly perpendicular to the corresponding axis, shows that no type-A open orbits exist. Also at some point in one or another of these figures the field is within 3° from each of these symmetry axes, and when nearest to the axis any band of type-B open orbits would have a net direction perpendicular to the current. Although the resistance goes through minima when the field is near these symmetry axes, the absence of saturation which one would expect for a minimum due to type-B open orbits shows that none exist.

The upper limit for the radius of any region of field directions producing type-B open orbits was shown to be less than 1° by a more precise experimental arrangement. The symmetry axes [110] and [001] at 4° to the sample axes of Mo 51 and Mo 1, respectively, were made the axes of rotation of the field to an accuracy better than 1°. The anisotropy and field-dependence of the magnetoresistance was found to be essentially unchanged from the form shown in Figs. 1 and 2.

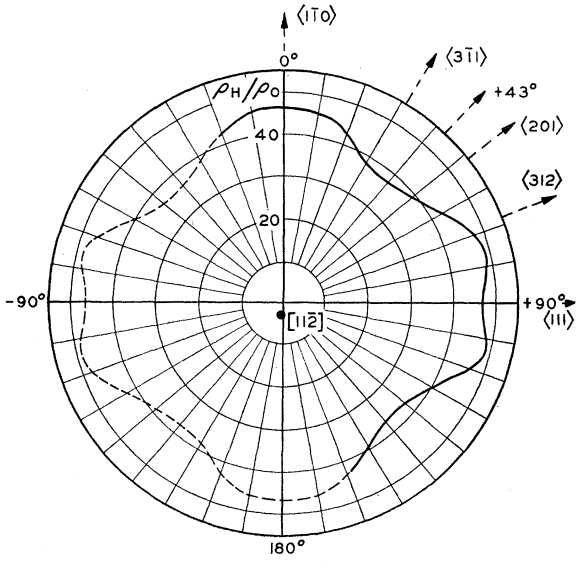


FIG. 4. Magnetoresistance of molybdenum. The anisotropy of the magnetoresistance is shown as the magnetic field $H=31.2$ kG is rotated about the axis of sample Mo 228. For the field-dependence curves, the exponent $m=1.87$ for H at +43°, and $m=1.89$ for H at ⟨111⟩.

[7] Illustrations of these two types of open orbits for a simple cubic lattice are given by R. G. Chambers, *Proceedings of the International Conference on the Fermi Surface* (John Wiley & Sons, Inc., New York, 1960), p. 100. The existence of type-B open orbits was first pointed out by Lifshitz, Azbel', and Kaganov (reference 1).

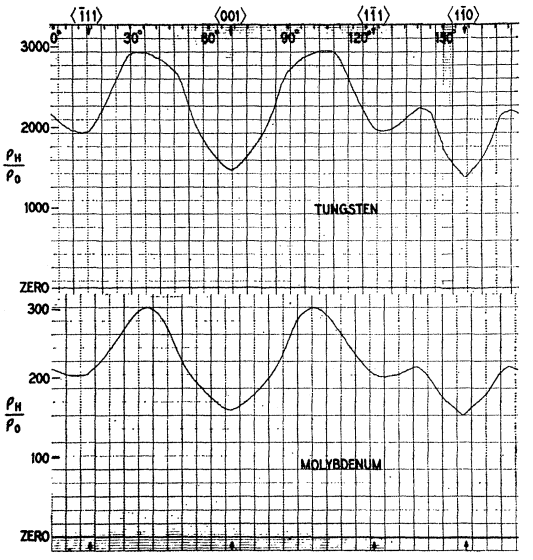
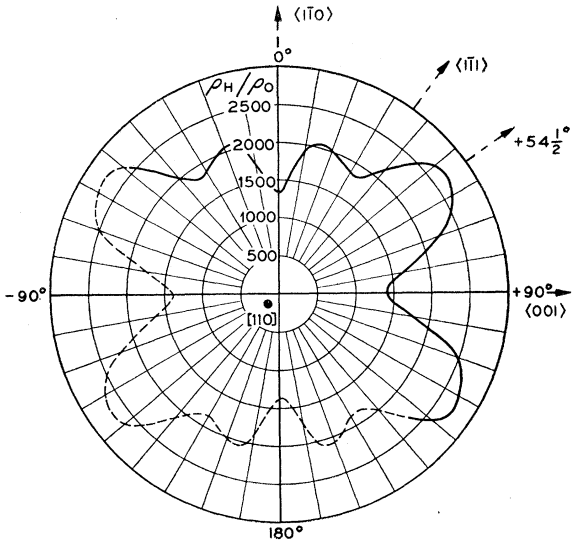


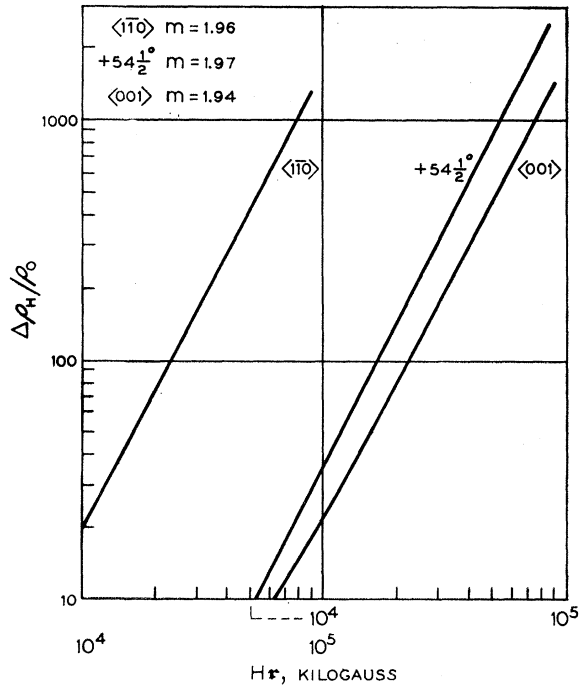
FIG. 5. Magnetoresistance of molybdenum and tungsten. The recorder traces show the anisotropy of the magnetoresistance in the magnetic field $H=18.0$ kG rotated about a direction within 1° from the symmetry axis [110] for samples Mo 51 and W 4. The trace for tungsten has been cut and transposed so that corresponding symmetry axes for the two samples lie in the same vertical line.

The recorder trace for sample Mo 51 in this experiment is shown in Fig. 5, together with that of the tungsten sample W 4 of similar orientation and measured also with its [110] axis as axis of rotation of the field. The juxtaposition of the two traces illustrates the close similarity of the anisotropy of the magnetoresistance for the two metals. The anisotropy of the magnetoresistance for the same sample of tungsten when its axis is made the axis of rotation of the field is shown in Fig. 6(a), which is seen to be essentially the same as the curve for sample W 4 in Fig. 5. The field dependence plotted in Fig. 6(b) is nearly quadratic at the highest fields both at the two minima and the maximum.

A sample of tungsten with its axis near the symmetry axis [001] exhibits an anisotropy, illustrated in Fig. 7, which is also very similar to that of the corresponding sample of molybdenum [Fig. 2(a)]. The resolution of detail in the curve for this very pure tungsten sample is high, and clearly defined breaks in the slope occur at angles of 13° and 26° to ⟨100⟩ on both sides of the minimum there, which are indicated in Fig. 7 by continuous and broken arrows, respectively. A similar break occurs at 18° from the ⟨100⟩ minimum for molybdenum, but this detail is lost in the polar diagram of Fig. 2(a). These effects presumably correspond to some features of the shape of the Fermi surface producing a change in the character of a band of cyclotron orbits at each of these angles.



(a)



(b)

FIG. 6. Magnetoresistance of tungsten. (a) Anisotropy of magnetoresistance as the magnetic field $H=18.0$ kG is rotated about the axis of sample W 4. (b) Field dependence of the magnetoresistance.

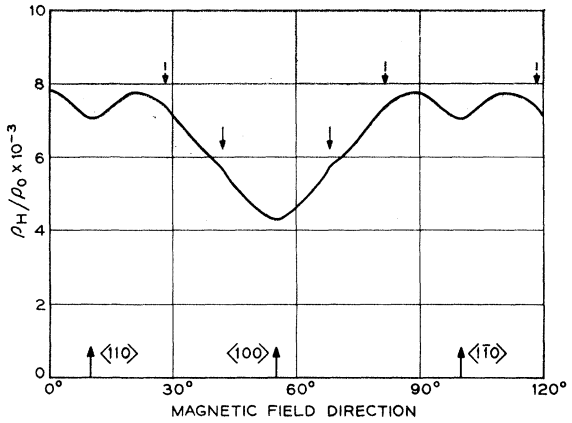


FIG. 7. Magnetoresistance of tungsten. The anisotropy of the magnetoresistance is shown as the magnetic field $H=18.0$ kG is rotated about a direction within 1° from the symmetry axis [001] of sample W 75. The sample axis at 5° to [001] is in the (1$\bar{1}$0) plane. The field-dependence curves at ⟨110⟩ and ⟨100⟩ are shown in Fig. 9, and for both field directions the exponent $m=2.03$.

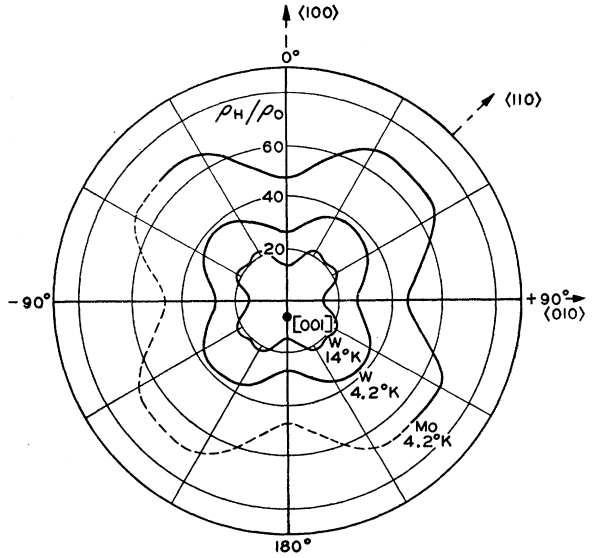


FIG. 8. Magnetoresistance of molybdenum and tungsten samples having axes near the symmetry axis [001]. The anisotropy of the magnetoresistance for sample Mo 227 is measured in a magnetic field $H=18.0$ kG, and its [001] axis is shown in stereographic projection on the polar diagram. The tungsten sample was measured at two temperatures at 18.6 kG by Justi and Scheffers (reference 4).

For this sample of tungsten the curve for the anisotropy of the magnetoresistance was retraced with a deviation of not more than 2% when the field was reduced by a factor $\sqrt{2}$ from its maximum value, 18.0 kG, and the amplifier gain was increased by a factor of 2, showing that the field-dependence is quadratic to this accuracy for all field directions.[8] Evidently, tungsten, like molybdenum, exhibits behavior characteristic of a compensated metal, with no open orbits on its Fermi surface.

[8] A more accurate measurement of the field dependence for the field directions ⟨110⟩ and ⟨100⟩ gives a value 2.03 of the exponent m for both. This exceeds 2.00 by an amount slightly greater than the experimental accuracy, which is better than 1% in this case because of the large range of linearity of the curves in the logarithmic plot shown in Fig. 9.

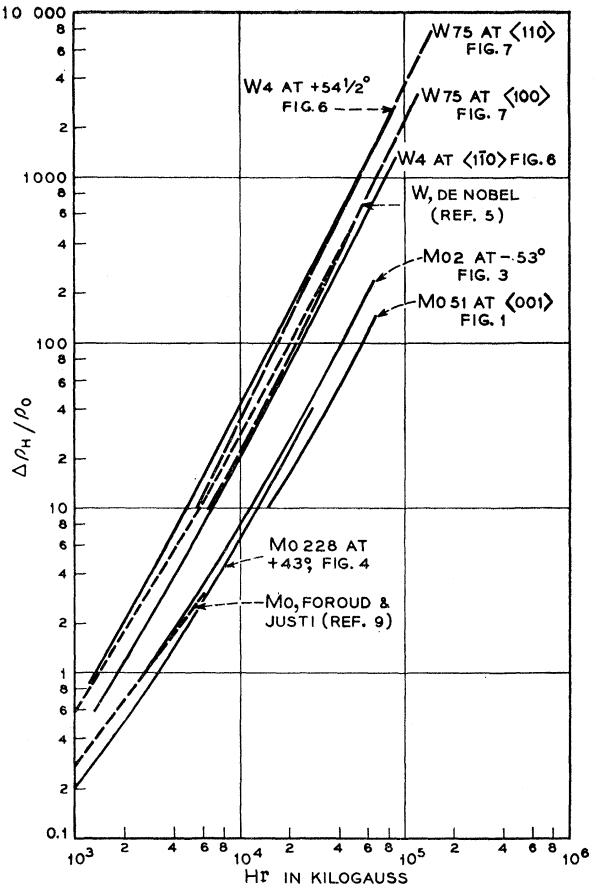


FIG. 9. Field dependence of the magnetoresistance for molybdenum and tungsten.

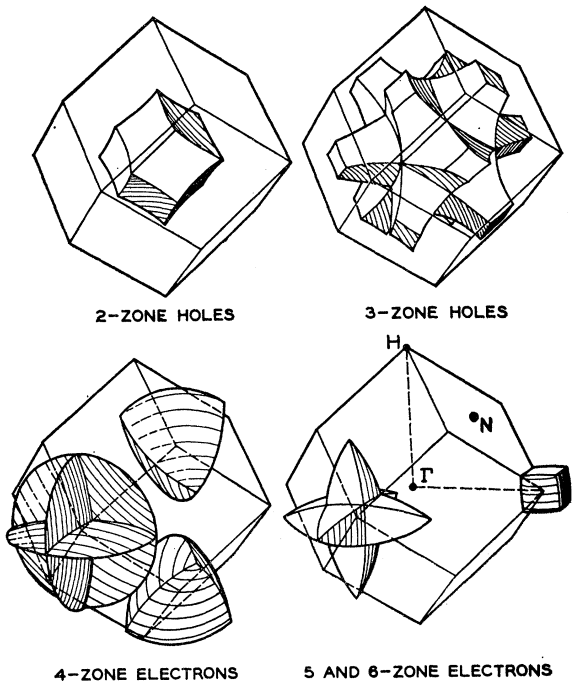


FIG. 10. Free electron model in the reduced zone scheme for a Fermi sphere containing six electrons per atom in the body-centered cubic structure.

In Fig. 8 are shown some of the results of Justi and Scheffers[4] for the anisotropy of the magnetoresistance of tungsten, compared with measurements for one of the molybdenum samples of a similar orientation. Figure 9 is a Kohler diagram showing in comparison with previously published results[5,9] the full range of the measured field dependence for both the tungsten samples, and representative curves for the molybdenum samples. For the same reduced field the magnetoresistance of tungsten is about a factor 3 greater than that of molybdenum at low fields, and about a factor 6 greater in the quadratic region at high fields.

IV. DISCUSSION

The fact that the field dependence of the transverse magnetoresistance at all orientations for both molybdenum and tungsten is approximately quadratic at the highest fields, and achieves values between two and four orders of magnitude greater than the resistance at zero field, is conclusive evidence that both metals are compensated and are in the high-field region, where $\omega_c\bar{\tau}>1$ for most, if not all, cyclotron orbits. By contrast, the metals for which sZ is odd and which have been measured to high enough values of the reduced field all show, for field directions producing no open orbits, saturation of the magnetoresistance, the fractional change in the resistance $\Delta\rho_H/\rho_0$ at the highest fields being asymptotic to values less than about 10. The compensation shows that there must be an even number per atom of occupied states in partially-filled Brillouin zones. Each zone has a capacity of two electrons per atom so that the number of holes in partially filled inner zones is then equal to the number of electrons overlapping into outer zones.

The success of the free electron model in providing a rough description of the electronic structure for several nontransition metals[10] suggests, as a starting approximation to the Fermi surface of a metal in Group VI of the periodic table, a sphere containing six electrons per atom. The resultant surfaces in a reduced zone scheme are shown in Fig. 10. Of particular interest is the multiply connected hole surface in the third zone, which would support broad bands of type-B open orbits for field directions near the symmetry axes ⟨100⟩, ⟨110⟩, and ⟨111⟩, and type-A open orbits for field directions in the (110) plane. These would give rise to a saturating magnetoresistance and a corresponding minimum when the field moves through each of these directions and the current is perpendicular to the direction of the corre-

[9] A. Foroud and E. Justi, Physik Z. **40**, 501 (1939).

[10] W. A. Harrison, Phys. Rev. **118**, 1190 (1960).

sponding open orbits. The absence of such minima in the experimental data when the field is as close as one degree to these axes, or passes through this plane, and the current is near the appropriate direction, shows that for molybdenum and tungsten the free electron model is not a good approximation to the Fermi surface.[11] The reduced zone schemes for Fermi spheres containing four and two electrons per atom in a body-centered cubic lattice have been given by Harrison.[10] They support open orbits in the second and first zones, respectively, so that apart from any theoretical objections to these models they also can be rejected on the basis of the experimental data.

Lomer[12] has recently shown how the band structure calculations for body-centered cubic iron may be adapted to discuss a Group VI transition metal of the same structure. The resultant Fermi surface is quite different from the free electron picture and consists of a pocket of holes in the third zone centered on H (see Fig. 10), which are degenerate at a point on the ΓH axis with a pocket of electrons centered on Γ. This degeneracy would permit an infinitesimally narrow band of open orbits when the field is exactly along a $\langle 100 \rangle$ axis, which would probably not be detectable experimentally. There are also smaller pockets of holes centered on N and of electrons centered on some point along ΓH. The total volumes of the electron and hole regions are equal, and the behavior of the magnetoresistance at high fields for this model would be consistent with the experimental results.

A two-band model may be used to estimate roughly the average mobility. For equal numbers of electrons and holes with isotropic effective masses, m_1, m_2, and relaxation times, τ_1, τ_2, the expression for the fractional change in the transverse magnetoresistance is[13]

$$\Delta\rho_H/\rho_0 = (eH/c)^2(\tau_1/m_1)(\tau_2/m_2) = (\omega_c\tau)_1(\omega_c\tau)_2.$$

Substituting average values of the magnetoresistance at the highest fields from Fig. 9, and scaling the relaxation times inversely as the resistivity in zero field, one obtains for the average mobility, $(e/c)(\tau_1\tau_2/m_1m_2)^{1/2}$, at the Debye temperature, the values 20 cm^2/V-sec for molybdenum and 50 cm^2/V-sec for tungsten.

Values of this parameter of the same order of magnitude are obtained for the other compensated metals, Zn,[14] Cd,[14] Sn,[1] Pb,[1] and Ga,[1] which is simply another way of saying that in a Kohler diagram the curves showing the field dependence of the magnetoresistance for all these metals differ by less than a factor 10 in the reduced field. The somewhat surprising conclusion follows that the mobility in the hole band, which one might have expected to be low because of the high effective mass implied by the fairly large electronic specific heats and small Fermi surface areas[8] of molybdenum and tungsten, is in fact roughly equal to that in the electron band and comparable to that of a non-transition metal. The alternative explanation, that the mobility in the electron band is unusually high and that in the hole band low, can be dismissed as being inconsistent with the experimental data, since any such large disparity would result in a region of saturation of the magnetoresistance at intermediate fields followed by quadratic variation due to compensation at higher fields. Presumably, the explanation is that the mean free paths in the two bands are roughly equal, and any effect on the mobility of the high mass in the hole band is canceled out by the effect of the correspondingly low Fermi velocity.

The anisotropy of the magnetoresistance for a compensated metal in the high-field region in the absence of open orbits depends upon the variation with the field direction of all the terms of the conductivity tensor. Each term may vary in a complicated fashion, since it depends on the effective masses and relaxation times in the corresponding cyclotron orbits over the whole Fermi surface. The problem of extracting this detailed information unambiguously from the observed anisotropy is quite intractable without the assistance of other methods of studying the Fermi surface of these metals, such as cyclotron resonance,[15] the de Haas-van Alphen effect,[16] or the oscillatory magnetoacoustic effect.[17] For the present, it must suffice to remark that the shape of the Fermi surface, and the variation over it of the relaxation time, must be very similar for molybdenum and tungsten to result in such close parallelism in the anisotropy of their magnetoresistance.

ACKNOWLEDGMENTS

The author is indebted to J. E. Kunzler for his generous provision of experimental facilities, to P. H. Schmidt for orienting the samples, and to E. Buehler for supplying a high-purity molybdenum crystal.

[11] Further evidence of the inadequacy of the free electron model to describe the Fermi surfaces of molybdenum and tungsten is provided by measurements of the surface conductance of polycrystalline samples of these metals under anomalous skin effect conditions [E. Fawcett and D. Griffiths (to be published)]. The resultant values of the Fermi surface area are only about 10% of the area of the free electron sphere containing six electrons per atom.

[12] W. M. Lomer (to be published).

[13] See, for example, A. H. Wilson, *The Theory of Metals* (University Press, Cambridge, England, 1953), 2nd ed, p. 216.

[14] C. A. Renton, *Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960* (University of Toronto Press, Toronto, 1960), p. 153.

[15] E. Fawcett and W. M. Walsh, Jr. Phys. Rev. Letters 8, 476 (1962).

[16] R. F. Girvan and A. V. Gold (private communication).

[17] J. A. Rayne and H. Sell, Phys. Rev. Letters 8, 199 (1962).