High-Field Magnetoresistance of Molybdenum and Tungsten

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The transverse magnetoresistance of high-purity samples of Mo and W was measured in magnetic fields up to 83 kOe. No deviation from the quadratic magnetoresistance characteristic of a compensated metal was observed, which shows that the Fermi surfaces of these metals support less than 10^{-4} open cyclotron orbits per atom for Mo and 10^{-7} per atom for W. The numbers of electrons and holes in W differ by less than 0.07%, which indicates that to this accuracy the number of quasiparticles in a many-body scheme is equal to the number of particles in a one-electron scheme.

1. INTRODUCTION

PREVIOUS measurements of the magnetoresistance of molybdenum and tungsten in fields up to 31.3 kOe indicated that in both metals no open cyclotron orbits occur for any field direction.[1] On the other hand, a model of the band structures of these metals proposed by Lomer[2] contains two sheets of the Fermi surface which touch at a point. This degeneracy might be expected to give rise to an infinitesimal number of open orbits; this number could become finite and produce an appreciable effect on the magnetoresistance at high fields if magnetic breakdown occurs.[3] Consequently, we were prompted to make additional measurements of the magnetoresistance of these metals, using more accurately oriented samples at higher magnetic fields, in order to set an upper limit on the number of open orbits which might exist.

High-purity samples of molybdenum and tungsten were measured in magnetic fields up to 83 kOe. The current and field directions were chosen to optimize the effect of the particular set of open orbits expected for the Lomer model. At 83 kOe the magnetoresistance of the molybdenum sample was $\sim 10^2$, and that of the tungsten sample was $\sim 10^5$. As each sample was rotated, no minima in the magnetoresistance of the form expected for open orbits were observed to an accuracy better than one percent. We show that this means there can be no more than about 10^{-4} open orbits per atom in molybdenum and 10^{-7} open orbits per atom in tungsten associated with magnetic breakdown at the degeneracy of the Lomer model.

2. THE LOMER MODEL

The features of the Lomer model which relate particularly to the occurrence of open orbits are illustrated in Figs. 1 and 2. Figure 1 shows the energy E for the various branches of the energy band structure as a function of the wave-vector k along the ⟨100⟩ axis between the center Γ and the corner H of the Brillouin zone. The Fermi level intersects at the point X the branch Δ_5, which is doubly degenerate along the line ΓH. This results in a single point of contact at X between two energy bands. The form of $E(k)$ for neighboring directions of k shows that the sheet of the Fermi surface in one of these bands is an electron surface centered on Γ and that the other is a hole surface centered on H.

Figure 2 shows an extended section in the (010) plane of the reciprocal lattice. The small pocket of electrons centered on a nonsymmetry point along ΓH and the pocket of holes at N are closed surfaces, which cannot therefore support open orbits. When the field lies in the (100) plane, one might expect, for a vanishingly small field, an infinitesimally narrow band of open orbits in the ⟨100⟩ direction. Such an open orbit would run along the electron surface centered on Γ, through the point of degeneracy X, and along the hole surface centered on H; its projection in the (010) plane when the field makes an angle of $\sim 30°$ to the ⟨001⟩ axis is shown in Fig. 2.

Lomer emphasizes that although the proposed band structure may be incorrect in detail,[4] its main features are expected to survive considerable modification of the potential. In particular, the Fermi level is expected to intersect the doubly-degenerate branch Δ_5. This is,

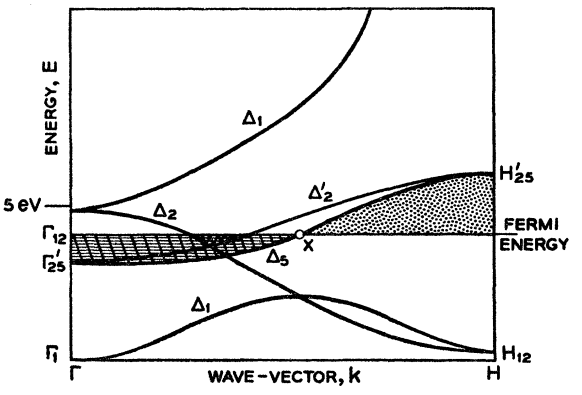

FIG. 1. Lomer model of the band structure of chromium (Ref. 2). The other group VI transition metals are probably similar (Refs. 5, 8).

[1] E. Fawcett, Phys. Rev. **128**, 154 (1962).
[2] W. M. Lomer, Proc. Phys. Soc. (London) **80**, 489 (1962).
[3] M. H. Cohen and L. Falicov, Phys. Rev. Letters **7**, 231 (1961).
[4] For example, Lomer points out (private communication) that the electron pockets along ΓH must touch the electron surface centered on Γ in the {110} and {100} planes, because of symmetry requirements.

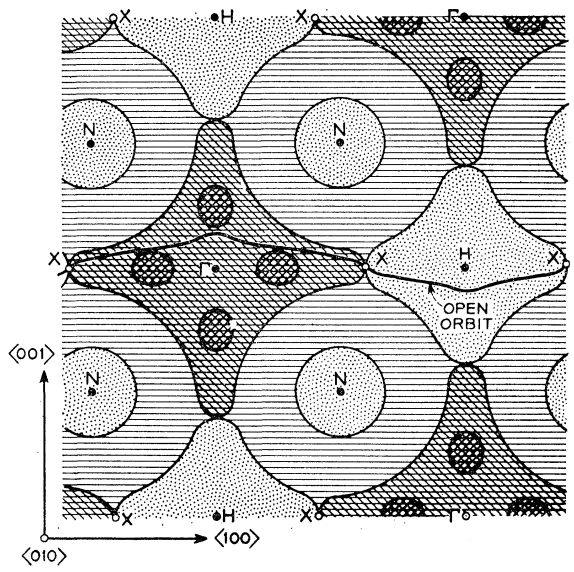

FIG. 2. An extended section of the (010) plane in reciprocal space. Each direction of hatching indicates the occupied states in a separate zone, and corresponds to the hatching in Fig. 1. The hole regions are shown by dots.

in fact, the case for the band structures calculated for several other bcc transition metals (viz., V,[5] Cr,[5,6] Fe[5,7]), if the Fermi level is adjusted to a value appropriate to six electrons per atom, as well as for molybdenum and tungsten themselves.[8]

However, Blount[9] points out that one expects the number of open orbits associated with the point of contact of the two energy bands to be very small. This is because the matrix element expressing the probability of transitions from the electron to the hole surface is identically zero when the magnetic field is exactly perpendicular to the {100} and {110} planes of reflection symmetry, while for intermediate field directions in the (100) plane the transition probability is likely to be very small. The effect of magnetic breakdown is difficult to estimate without a detailed knowledge of the band structure near the point of contact.

3. EXPERIMENTAL

Samples of high-purity molybdenum and tungsten, supplied by Sell of the Westinghouse Lamp Division, were prepared in the form of rectangular blocks. The long axis, which defines the current direction, was made parallel to the ⟨001⟩ axis to an accuracy of $\frac{1}{4}°$. The ratios of the resistivities at room temperature and at 4.2°K were measured, and to assist comparison with the previous measurements[1] each ratio was converted to the ratio $\mathfrak{R}$ of the resistivities at the Debye temperature and 4.2°K. For the tungsten sample, $\mathfrak{R}=14\,600$, and for the molybdenum sample, $\mathfrak{R}=1140$. In the previous measurements,[1] the best samples of similar orientation had comparable values of $\mathfrak{R}$ ($\mathfrak{R}=7910$ for tungsten sample W4, and $\mathfrak{R}=1570$ for molybdenum sample Mo 1). But the sample axes were at angles of ~4° from the ⟨001⟩ axis, and they were measured only in fields up to 31.3 kOe.

The magnetoresistance of each sample at the temperature 4.2°K in a field of 83 kOe was measured as it was rotated in the manner illustrated in Fig. 3. The axis of rotation was in the (001) plane, making a small angle $\psi(<8°)$ with the ⟨100⟩ axis. The plane of rotation could be tilted to an angle φ with the magnetic field, φ ranging from +8° to −8°. In Fig. 3 the axis of rotation is taken to be at an angle $\psi=6°$ from the ⟨100⟩ axis, and the locus of the field direction is shown for $\varphi=0°$, 4°, 8°. When the tilt angle $\varphi=0°$, the field is perpendicular to the ⟨100⟩ axis only at an angle $\theta=0°$, making the field parallel to the current direction J (the longitudinal orientation). As φ is increased, the field intersects the (100) plane at increasing values of θ, and when $\varphi=4°$ the intersection corresponding to $\psi=6°$ would be at the point P in Fig. 3, for which $\theta=42°$. When $\varphi=8°$, the field is never perpendicular to the ⟨100⟩ axis.

Figure 4 shows the expected anisotropy of the magnetoresistance of molybdenum and tungsten for this experimental geometry when there are no open orbits,

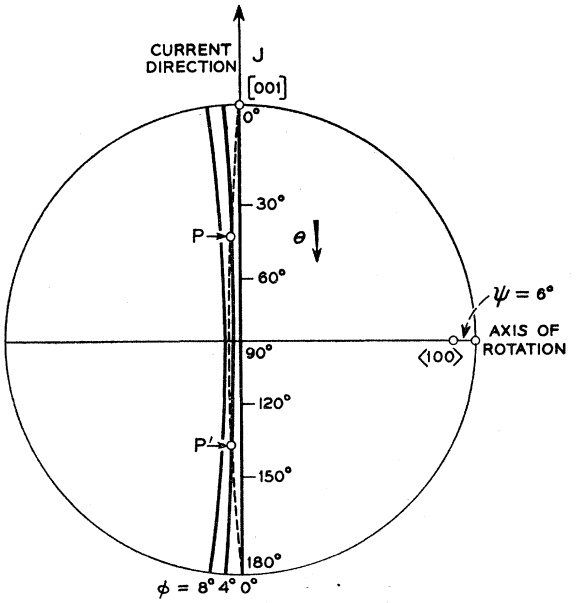

FIG. 3. Stereogram showing the locus of the field direction **H** relative to the crystal axes as the sample is rotated (angle θ) about an axis at angle $\psi=6°$ from the ⟨100⟩ axis in successive tilt planes (angle φ). The continuous line indicates the locus of **H** for $\varphi=0$, 4, 8°; the dashed line indicates the (100) plane; P, P' are the points at which **H** intersects the (100) plane for $\varphi=4°$.

[5] L. F. Mattheiss, MIT Solid-State and Molecular Theory Group Quarterly Progress Report 48, 5 (1963).
[6] M. Asdente and J. Friedel, Phys. Rev. 124, 384 (1961).
[7] J. H. Wood, MIT Solid-State and Molecular Theory Group Quarterly Progress Report 33, 20 (1959).
[8] L. F. Mattheiss (private communication).
[9] E. I. Blount (private communication).

and the effect on the anisotropy of a hypothetical band of open orbits along the ⟨100⟩ axis. If there are no open orbits the variation of the magnetoresistance with the rotation angle θ is expected to be of the form (see Sec. 4),

$$\rho_H(\theta)/\rho_0 = A\cos^2\theta + (H/H_0)^2 f(\theta)\sin^2\theta. \quad (1)$$

The longitudinal magnetoresistance ($\theta=0°$) saturates at a value $A \gtrsim 1$ for all metals.[10] The transverse magnetoresistance ($\theta=90°$) is quadratic with the field, since both molybdenum and tungsten are compensated.[1] The term $(H/H_0)^2$ is much greater than unity since the applied field H is 83 kOe, while H_0 is the field at which the magnetoresistance is of the order unity, i.e., $\langle\langle\omega_c\tau\rangle\rangle \sim 1$. Here ω_c is the cyclotron frequency and τ the relaxation time, the double average being taken over the cyclotron orbits on the various sheets of the Fermi surface and over *all* field directions. For the molybdenum sample, $\mathfrak{R}=1140$ give $H_0\sim 3$ kOe, while for tungsten sample, $\mathfrak{R}=14\,600$ give $H_0\sim 0.1$ kOe (see Fig. 9 of Ref. 1).

The term $f(\theta)$ in Eq. (1) expresses the anisotropy of $\langle\omega_c\tau\rangle$, the average being taken over the set of cyclotron orbits for the *single* field direction θ. $f(\theta)$ reflects the anisotropy of the transverse magnetoresistance, which is known to be a slowly varying function of θ for both molybdenum and tungsten.[1] A comparison of the observed transverse magnetoresistance for $\mathbf{J}\|\langle 001\rangle$, $\mathbf{H}\|\langle 100\rangle$ (Figs. 4 and 7 of Ref. 1), corresponding to $\theta=0°$, 90°, with its value for $\mathbf{J}\|\langle 110\rangle$, $\mathbf{H}\|\langle 1\bar{1}0\rangle$ (Fig. 5 of Ref. 1), corresponding to $\theta=45°$, indicates that $f(\theta)$ probably varies less than 20% between $\theta=0°$ and 90° for both molybdenum and tungsten.

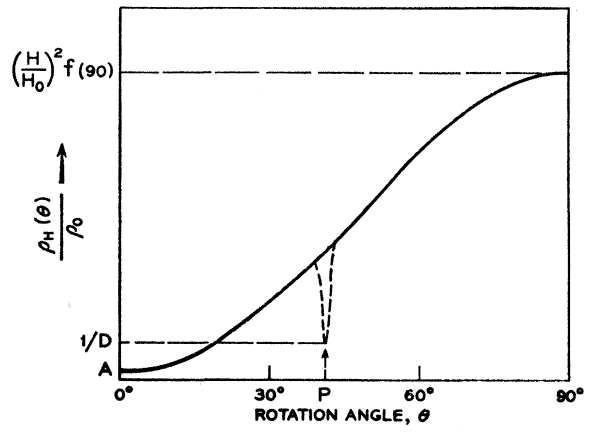

FIG. 4. Schematic diagram of the expected anisotropy of the magnetoresistance. The continuous line indicates the anisotropy when there are no open orbits, given by Eq. (1). The dashed line shows the minimum associated with the saturation of the magnetoresistance due to a hypothetical band of open orbits along the ⟨100⟩ axis when the field direction is at P in the (100) plane (see Fig. 3).

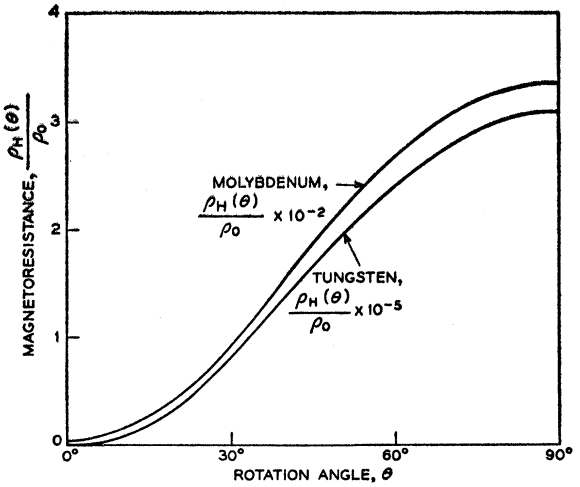

FIG. 5. Anisotropy of the magnetoresistance of molybdenum and tungsten in a field of 83 kOe at temperature 4.2°K for the experimental geometry of Fig. 3. The deviations from the simple curves, $f(90)\sin^2\theta$, due to anisotropy of $f(\theta)$ are 12 and 8% of the magnetoresistance at $\theta=45°$ for molybdenum and tungsten, respectively.

The expected anisotropy of the magnetoresistance expressed by Eq. (1) is shown schematically by the continuous line in Fig. 4. We show in Sec. 4 that, when a band of open orbits exists covering a fraction D of the total area of the Fermi surface, the transverse magnetoresistance saturates at a value $\sim 1/D$. The dashed line in Fig. 4 shows, for the case $\varphi=4°$ of Fig. 3, the sharp minimum at P which one would expect to be caused by a band of open orbits along the ⟨100⟩ axis due to the saturation of the magnetoresistance.

The observed anisotropy of the magnetoresistance as the tungsten sample was rotated in a plane at tilt angle $\varphi=0°$ is shown in Fig. 5. The axis of rotation was nominally the ⟨100⟩ axis (i.e., $\psi=0°$), but it was oriented with an accuracy of only about 5°. However, the rotation of the sample for various values of φ must in some cases have taken the field direction through the (100) plane, as illustrated in Fig. 3. For all values of φ tried the anisotropy was always essentially identical to that for $\varphi=0°$. In no case did it exhibit a narrow minimum as deep as one percent of the total magnetoresistance which could be attributed to open orbits. We conclude that to this accuracy there is no observable effect of open orbits along the ⟨100⟩ axis in tungsten.

The corresponding curve for molybdenum shown in Fig. 5 is also essentially independent of φ. Again, to about the same accuracy there is no observable effect of open orbits along the ⟨100⟩ axis. The magnetoresistance of the molybdenum sample for $\theta=90°$ is about a factor 10^3 smaller than that of the tungsten sample. This is consistent with the value of $\mathfrak{R}$ being a factor 10 smaller, the quadratic dependence of the magneto-

[10] A. B. Pippard, *Les Houches Lectures on Low Temperature Physics*, edited by C. DeWitt (Gordon and Breach, New York, 1962), p. 99.

resistance on $H\mathfrak{R}$, and the fact that for the same value of $H\mathfrak{R}$, molybdenum has a lower magnetoresistance by about a factor 10 than tungsten (see Fig. 9 or Ref. 1). The field dependence of the magnetoresistance for both the molybdenum and tungsten sample was measured at the orientation $\theta=90°$ and found to be quadratic above about 10 kOe to an accuracy better than one percent.

4. DISCUSSION

A rough estimate of the upper limit on the number of open orbits per atom in molybdenum and tungsten can be obtained as follows from the absence of observable effects in the magnetoresistance. It is of some interest to estimate at the same time the effect of a small deviation from exact compensation.

The parameter D defined in Sec. 3 may loosely be described as the number of open orbits per atom, since the total area of the Fermi surface corresponds to a number of carriers per atom of order unity. The parameter, $N=(|n_e-n_h|)/(n_e+n_h)$, n_e and n_h being the number per unit cell of electrons and holes, respectively, is a measure of the deviation from exact compensation ($n_e=n_h$). If the magnetic field is along the z axis and the direction of the open orbits in reciprocal space is along the x axis, the conductivity tensor in the high-field limit, when the parameter $\gamma=1/\langle\langle\omega_c\tau\rangle\rangle$ is small, is of the form,

$$\lim_{\gamma\to 0}\frac{\sigma}{\sigma_0}=\begin{Vmatrix} a_{xx}{}^2\gamma^2 & (\alpha D+\beta N)a_{xy}{}^1\gamma+a_{xy}{}^2\gamma^2 & a_{xz}{}^1\gamma \\ -(\alpha D+\beta N)a_{xy}{}^1\gamma+a_{xy}{}^2\gamma^2 & Da_{yy}{}^0+a_{yy}{}^2\gamma^2 & Da_{yz}{}^0+a_{yz}{}^1\gamma \\ -a_{xz}{}^1\gamma & Da_{yz}{}^0-a_{yz}{}^1\gamma & a_{zz}{}^0 \end{Vmatrix}. \tag{2}$$

In an exactly compensated metal, the term in σ_{xy} linear in γ is zero,[11,12] and the linear term proportional to N in Eq. (2) results from a small deviation from compensation. A band of open orbits is equivalent in some sense to a deviation from compensation, which gives a similar term linear in γ and proportional to D in σ_{xy}. But the open orbits also give terms of order zero in γ and proportional to D in σ_{yy}, σ_{yz}, and σ_{zy} because of their tendency in the high-field limit to behave like a two-dimensional conductor in the y-z plane.[11] The coefficients $a_{ij}{}^p$ may be evaluated in principle by integrating the appropriate functions of the Fermi velocity and the scattering probability along each cyclotron orbit and summing over all orbits on all sheets of the Fermi surface.[11,12] For the present purposes, it is sufficient to note that all $a_{ij}{}^p\sim 1$.

When the tensor (2) is inverted to obtain the resistivity tensor, the term in σ_{xy} linear in γ for $D\neq 0$ or $N\neq 0$ gives rise to a leading term in ρ_{xy} linear in H, which corresponds to the Hall effect. In general, the coefficients of $D\gamma$ and $N\gamma$ in this term will not be equal and it is simply a notational convenience to write it in the form given, with α, β of order unity. The field-independent terms in σ_{yy}, σ_{yz}, and σ_{zy} are a consequence of the lack of harmonicity of the electron motion in an open cyclotron orbit. The importance of these terms in determining the form of the resistivity tensor was first pointed out by Lifshitz *et al.*[11]

A simplified form of the resistivity tensor, which shows the field dependence of each component in the high-field limit, is obtained by inverting the conductivity tensor.[13] We write

$$\alpha=\beta=1,$$

and

$$a_{ef}{}^r a_{gh}{}^s a_{ij}{}^t+a_{kl}{}^u a_{mn}{}^v a_{pq}{}^w+\cdots=1 \tag{3}$$

for all sums of coefficients of the same order ($r+s+t=u+v+w=\cdots$). In the expansion of each element of the tensor in ascending powers of γ we retain terms up to order $(m+2)$, where m is the order of the lowest order term, and obtain[14]

$$\lim_{\gamma\to 0}\frac{\rho}{\rho_0}=\begin{Vmatrix} D+D^2+\gamma^2 & (D+N)\gamma+\gamma^2 & [D+D(D+N)]\gamma+(D+N)\gamma^2+\gamma^3 \\ -(D+N)\gamma+\gamma^2 & \gamma^2 & (D+N)\gamma^2+\gamma^3 \\ -[D+D(D+N)]\gamma+(D+N)\gamma^2-\gamma^3 & (D+N)\gamma^2-\gamma^3 & [D+(D+N)^2]\gamma^2+\gamma^4 \end{Vmatrix} \times\{[D+(D+N)^2]\gamma^2+\gamma^4\}^{-1}. \tag{4}$$

[11] I. M. Lifshitz, M. Ya. Azbel, and M. I. Kaganov, Zh. Eksperim. i Teor. Fiz. **31**, 63 (1956) [English transl.: Soviet Phys.–JETP **31**, 41 (1957)].

[12] R. G. Chambers, Proc. Roy. Soc. (London) **A237**, 344 (1956).

[13] A. Baratoff has given the resistivity tensor in a similar form in unpublished work.

[14] The effect on the transverse magnetoresistance of a small deviation from compensation and a band of open orbits has also been given by N. E. Alekseevskii, Yu. P. Gaidukov, I. M. Lifshitz, and V. G. Peschanskii, Zh. Eksperim. i Teor. Fiz. **39**, 1201 (1960) [English transl.: Soviet Phys.–JETP **39**, 837, Eq. (8) (1961)].

Now we consider the effect of a band of open orbits in the x direction on the transverse magnetoresistance of a compensated metal, i.e., we write $N=0$, $D\neq 0$ in Eq. (4). The open orbits have no effect on the quadratic field dependence of the component ρ_{xx}. But the component ρ_{yy} has the form

$$\frac{\rho_{yy}}{\rho_0}=\frac{1}{D+\gamma^2}=\frac{t^2}{1+Dt^2}, \tag{5}$$

where we have written $t=1/\gamma=\langle\omega_c\tau\rangle$, and neglected D^2 compared with D for the case $D\ll 1$. We see that this component of the resistivity tensor saturates, and in the limit $t\gg 1$ approaches $1/D$. This is the value shown for the magnetoresistance at the bottom of the minimum in Fig. 4. The ratio of the magnetoresistance with the field in a direction producing open orbits to its value t^2 at neighboring field directions producing no open orbits is Dt^2. Thus, from the facts that the magnetoresistance of the tungsten sample is $\gtrsim 10^5$ and its anisotropy shows no narrow minimum attributable to open orbits greater than one percent of the total magnetoresistance, we can conclude that $D\lesssim 10^{-7}$. For the molybdenum sample the magnetoresistance is $\gtrsim 10^2$, so that $D\lesssim 10^{-4}$. These estimates are accurate only to the extent that the approximations in Eqs. (3) are valid. The absence of narrow minima in the transverse magnetoresistance[1] shows that accidental cancellations of the coefficients in Eqs. (3) are unlikely. The variation with field direction of the transverse magnetoresistance by about a factor two suggests that the upper limits for D are accurate to within a factor two. We conclude that there are no open orbits along the $\langle 100\rangle$ axis in molybdenum and tungsten to the accuracy indicated. This does not imply a rejection of the Lomer model for the reasons given in Sec. 2 but does show that magnetic breakdown does not occur at point X in Fig. 1 in fields up to 83 kOe.

We now consider the effect of a small deviation from exact compensation in a compensated metal, i.e., we write $D=0$, $N\neq 0$ in Eq. (4) and obtain,[15]

$$\frac{\rho_{xx}}{\rho_0}=\frac{\rho_{yy}}{\rho_0}=\frac{\gamma^2}{N^2\gamma^2+\gamma^4}=\frac{t^2}{1+N^2t^2}. \tag{6}$$

In the tungsten sample there is no deviation from a quadratic field dependence greater than one percent up to a value of $t^2\sim 300\,000$ for $\theta=90°$ (see Fig. 5). This means that $N^2t^2/\ln t<0.02$; i.e., $N<0.07\%$.[16]

This result has some relevance to the observation[17,18] in the uncompensated metals that the algebraic sum n_e-n_h of the numbers of electrons and holes differs by about 5% from the expected integral values.[19] Chambers and Jones[18] have suggested that this deviation may be attributable to many-body effects. However, it seems most unlikely that many-body effects would be so similar on the different sheets of the Fermi surface of a compensated metal that compensation would be maintained to an accuracy of 0.07%. We believe the latter result strongly suggests that to this accuracy the total number of carriers per atom in a metal is an exact integer, i.e., the number of quasiparticles in a many-body scheme is equal to the number of particles in a one-electron scheme, as indicated by the treatment of the electron-electron interaction to all orders of perturbation theory.[20]

ACKNOWLEDGMENTS

The authors are indebted to P. H. Schmidt and G. F. Brennert for technical assistance in preparing and mounting the samples.

[15] M. I. Kaganov and V. G. Peschanskii, Zh. Eksperim. i Teor. Fiz. **35**, 1052 (1958) [English transl.: Soviet Phys.–JETP **35**, 734 (1959)].

[16] Similarly high values of magnetoresistance and therefore low values of N have been observed in high-purity samples of other compensated metals, e.g., Zn, Ga, Sn, and Pb (see Ref. 19).

[17] F. E. Rose, M. T. Taylor, and R. Bowers, Phys. Rev. **127**, 1122 (1962).

[18] R. G. Chambers and B. K. Jones, Proc. Roy. Soc. (London) **A270**, 417 (1962).

[19] E. Fawcett and W. A. Reed, Phys. Rev. **131**, 2463 (1963).

[20] J. M. Luttinger and J. C. Ward, Phys. Rev. **118**, 1417 (1960); J. M. Luttinger, *Proceedings of the International Conference on the Fermi Surface* (John Wiley & Sons, Inc., New York, 1960), p. 2.