

and would probably be somewhat higher than that needed to cause the growth of a nucleus in a static experiment.

If this speculation were correct, the transition pressure at a given temperature would be lower in the static than in the dynamic experiments as is observed. Another conclusion is that the shock-induced transformation might be easier to analyze theoretically because the microscopic transition mechanism is subject to

severe constraint and should be relatively easily determined.

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Magnetoresistance of Single Crystals of Copper*

ROY OLSON† AND SERGIO RODRIGUEZ

Department of Physics, University of California, Berkeley, California

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Measurements of the magnetoresistance coefficients at 4.2° K and at 20.4° K in single crystals of copper, silver, and gold in the low magnetic field range, and in single crystals of silver for high magnetic field are reported. The low-field results were analyzed under the assumptions that a relaxation time exists and is a function of the energy alone, and that the Fermi surface is a single closed surface within the first Brillouin zone and not touching its boundary. It is found that for copper the magnetoresistance cannot be fitted very well on this model. We assume that at low temperature the hypothesis that a relaxation time exists is a good approximation, and suggest that in copper the Fermi surface touches the boundary of the first Brillouin zone. The magnetoresistance of silver in high magnetic fields shows marked anisotropy and no sign of saturation.

I. INTRODUCTION

THE change in the electrical resistance of a wire in the presence of a magnetic field (magnetoresistance) depends, among other factors, upon the nature and shape of the Fermi surface and its relationship to the first Brillouin zone. If we consider a spherical Fermi surface and a constant relaxation time, the electrical resistance will not be altered by the magnetic field. In order to account for the experimental phenomena, anisotropy of the energy surfaces and/or relaxation time have been postulated.¹

Recently²⁻⁴ considerable attention has been paid to the interpretation of magnetoresistance in high magnetic fields. By high magnetic fields we mean fields such that the radius R_c of the electron cyclotron orbits becomes smaller than the mean free path l of the electrons; this criterion can be expressed by

$$\frac{l}{R_c} = \omega\tau = \frac{H}{\rho N e c} > 1, \quad (1)$$

where ω is the cyclotron resonance frequency, τ the relaxation time, H the magnetic field, ρ the resistivity of the sample, N the number of conduction electrons per unit volume, and e the charge on a proton.

The usual Boltzmann transport theory seems to be unable to give a satisfactory explanation of high-field observations. The most peculiar of these effects is a linear increase in the electrical resistance with the magnetic field over a wide range. The discrepancies between theory and experiment seem to arise from the assumption that a relaxation time exists and is unaffected by the magnetic field.² For metals, even at high fields in the sense defined above, effects arising from the quantization of the orbits are negligible. In fact quantization is expected to become important only for fields of the order of 10^8 gauss such that $\frac{1}{2}\hbar\omega = \epsilon_F$ where ϵ_F is the Fermi energy.^{5,6} However, for low magnetic fields and low temperatures there are strong theoretical arguments that indicate that the Boltzmann transport theory is a good approximation.⁷ In particular this theory has been successful in interpreting magnetoresistance in bismuth.⁸ Our samples of copper, silver, and gold had $\omega\tau$ values ranging from 0 to about 0.2 for the low-field measurements and a maximum of $\omega\tau = 3$ for high-field measurements in silver. We shall assume

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† Now at Eitel-McCullough, Inc., San Bruno, California.

¹ R. Peierls, *Ann. Physik* **10**, 97 (1931); H. Jones and C. Zener, *Proc. Roy. Soc. (London)* **A145**, 268 (1934); L. Davis, *Phys. Rev.* **56**, 93 (1939).

² R. G. Chambers, *Proc. Roy. Soc. (London)* **A238**, 344 (1957).

³ Lifshitz, Azbel, and Kaganov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **31**, 63 (1956) [translation: *Soviet Phys. JETP* **4**, 41 (1957)].

⁴ D. K. C. MacDonald, *Phil. Mag.* **2**, 97 (1957).

⁵ S. Titeica, *Ann. Physik* **22**, 129 (1935).

⁶ I. M. Lifshitz, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **30**, 814 (1956).

⁷ R. Peierls, *Quantum Theory of Solids* (The Clarendon Press, Oxford, 1955), pp. 115-142.

⁸ B. Abeles and S. Meiboom, *Phys. Rev.* **101**, 544 (1956).

that the standard Boltzmann theory is adequate to interpret the low-field results.

We shall now give arguments supporting the assumption that, in the residual resistance temperature range, a relaxation time exists. In the residual resistance range the main contributions to the resistivity come from elastic scattering by impurity atoms and lattice defects. The relaxation time $\tau(\mathbf{k})$ is the characteristic time in which the electron distribution function $f(\mathbf{k})$ returns to its thermal equilibrium value after it has been momentarily perturbed. In Appendix 1 it is proved that, provided the collisions giving rise to the relaxation mechanism are elastic, the isotropy of the scattering is a necessary and sufficient condition for a relaxation time to exist for an arbitrary energy surface. The elastic scattering is said to be isotropic if the transition probability $w(\mathbf{k},\mathbf{k}')$ from the state characterized by the wave vector \mathbf{k}' to that characterized by \mathbf{k} is a function of the energy alone. It is also shown that, under these conditions (elastic isotropic scattering), the relaxation time $\tau(\mathbf{k})$ is furthermore a function of the energy alone. Thus, if we assume that a relaxation time exists, there is no loss of generality if it is taken to be constant over the Fermi surface whatever its shape. However, strictly speaking a relaxation time does not exist. We have not been able to calculate the effect of this on the magnitude of the magnetoresistance, but we believe the effect to be small. For the samples used in our experiments, we presume that the resistivity arising from point defects is more important than that due to dislocations. Point defects give rise to deviations from the periodic potential that can be represented by a potential well in the case of impurities from the same column in the periodic table of elements or by a screened Coulomb potential for atoms from another column or for other point defects like vacancies, etc. We could not treat the scattering of electrons by such a perturbing potential in a realistic fashion, but we believe that the transition probability $w(\mathbf{k},\mathbf{k}')$ is fairly isotropic. The total scattering, as measured for example by the time between collisions $[\int w(\mathbf{k},\mathbf{k}')d\mathbf{k}']^{-1}$, is much more isotropic than $w(\mathbf{k},\mathbf{k}')$ due to the averaging over the energy surfaces. In particular the time between collisions is not proportional to the density of states at \mathbf{k} but rather to the integrated density of states at \mathbf{k}' . Thus, although this is not in general the relaxation time $\tau(\mathbf{k})$, we believe that it indicates that the scattering mechanism (whatever its form) is considerably more isotropic than the density of states and contributes proportionally less to the magnetoresistance. Furthermore, in the limit of low fields the curvature of the electron paths will be negligible and, consequently, the relaxation time will not be appreciably altered by the magnetic field. Therefore we shall base our arguments on the transport theory with the assumption that an isotropic relaxation time exists.

In this paper we shall describe measurements of low-

field magnetoresistance in single crystals of copper, silver, and gold for different crystal orientations and at liquid helium and liquid hydrogen temperatures. A few high-magnetic-field measurements were also done on silver. In this case the change in resistance shows no sign of saturation and is markedly anisotropic.

The low-field experimental results are analyzed according to the Boltzmann transport theory with the assumption that a relaxation time exists and that the Fermi surface is a single closed surface, within the first Brillouin zone and not touching the zone surface. It was found that for copper this model could not be made to account for the experimental results, particularly as regards the ratio of transverse to longitudinal magnetoresistance. This leads us to conclude that the Fermi surface probably touches the boundary of the Brillouin zone.

II. EXPERIMENTS

The crystals of copper and silver used in these experiments were made from 99.999%-pure rods obtained from Johnson, Mathey, and Company. Cleaned bars, 0.008 in. \times 0.008 in. \times 1 in., were prepared, melted in a spectrographically pure graphite mold and allowed to crystallize from one end in a temperature gradient. The gold used was 99.9% pure wire prepared in the same way.

Two three-mil copper or silver wire potential leads were spot welded approximately fifty mils from each end on the same side of the crystal. The crystals thus prepared were then cemented in a slot along one edge of a micarta block and current leads soldered to the ends. The orientation of the crystallographic axes with respect to the edges of the micarta block was determined by x-ray techniques.

The resistivity of the crystals was not determined directly from their resistance as their dimensions could not be measured accurately. Instead it was determined by measuring the resistance of the wire at 4.2°K and at room temperature (293°K), and using the known values of the ideal lattice resistivity at the latter temperature. For copper and silver the resistivity at 4°K of most samples ranged from 2.4×10^{-8} to 8.4×10^{-8} ohm-cm. For the gold samples it ranged from 8.0×10^{-8} to 18×10^{-8} ohm cm. The errors in the resistivity measurements were less than 3%. The resistivity of copper at liquid hydrogen temperature was about 5% larger than that at liquid helium temperature. For silver and gold this difference was about 15%. From these results we conclude that, at 4°K, the lattice resistivity contributes less than one part in ten thousand to the total resistivity.

The results of our magnetoresistance measurements are most conveniently expressed in terms of certain coefficients that we shall now define. For a cubic crystal in a sufficiently weak magnetic field and for electric fields within the range of validity of Ohm's law, the

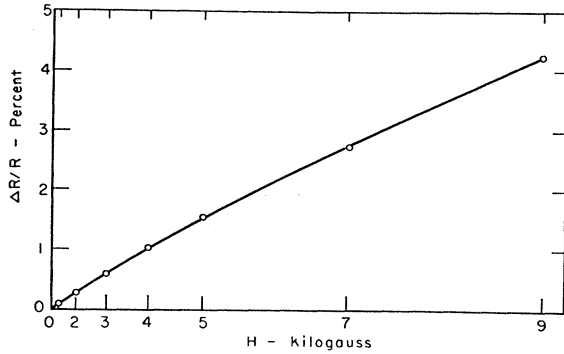


FIG. 1. Fractional change in resistance as a function of H^2 for a copper sample whose resistivity at 4°K is 4.00×10^{-8} ohm-cm. The current direction makes angles of 78°, 62°, and 34° with the [100], [010], and [001], axes. The magnetic field forms angles of 80°, 28°, and 61° with the same axes.

current density \mathbf{J} is given by⁹

$$\mathbf{J} = \sigma_0 \mathbf{E} + \alpha \mathbf{E} \times \mathbf{H} + \beta \mathbf{H} \cdot \mathbf{H} \mathbf{E} + \gamma (\mathbf{H} \cdot \mathbf{E}) \mathbf{H} + \delta \mathbf{T} \cdot \mathbf{E}, \quad (2)$$

where σ_0 is the zero magnetic field conductivity, α , β , γ , and δ are constants, \mathbf{E} the total electric field, \mathbf{H} the magnetic field and \mathbf{T} a second rank tensor which, when referred to the crystal axes is diagonal and has components H_1^2 , H_2^2 , H_3^2 . Here and in what follows the crystal axes are denoted by suffixes 1, 2, 3; the components of a vector \mathbf{A} on the crystal axes being A_1 , A_2 , A_3 . We notice that the only anisotropic term in (2) is $\delta \mathbf{T} \cdot \mathbf{E}$. Equation (2) is just a consequence of the symmetry and is, therefore, perfectly general. Since experimentally we measure the resistivity tensor rather than the conductivity tensor, it is convenient to invert (2) and express the electric field \mathbf{E} in terms of the current density \mathbf{J} . For a sufficiently small magnetic field the result is¹⁰⁻¹²

$$\mathbf{E} = -\frac{1}{\rho_0} [\rho_0^2 \mathbf{J} + a' (\mathbf{J} \times \mathbf{H}) + b' \mathbf{H} \cdot \mathbf{H} \mathbf{J} + c' (\mathbf{J} \cdot \mathbf{H}) \mathbf{H} + d' \mathbf{T} \cdot \mathbf{J}], \quad (3)$$

TABLE I. Values of coefficients (4) in units of 10^{-25} (ohm-cm/gauss)².

	Cu	Ag	Au
b'	7.0 ± 0.3	22 ± 3	40 ± 15
c'	-8.0 ± 0.6	-22 ± 5	-33 ± 20
d'	10.6 ± 1.2	44 ± 6	60 ± 40

⁹ F. Seitz, Phys. Rev. **79**, 372 (1950).

¹⁰ G. L. Pearson and H. Suhl, Phys. Rev. **83**, 768 (1951); C. Goldberg and R. E. Davis, Phys. Rev. **94**, 1121 (1954).

¹¹ H. Y. Fan, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 338.

¹² We have used dashes on a' , b' , c' , d' to distinguish them from the coefficients $a = a'/\rho_0^2$, $b = b'/\rho_0^2$, $c = c'/\rho_0^2$, $d = d'/\rho_0^2$ that are frequently found in the literature (see reference 11).

where $\rho_0 = 1/\sigma_0$ is the zero-field resistivity and

$$\begin{aligned} a' &= -\alpha \rho_0^3, & b' &= -(\beta + \rho_0 \alpha^2) \rho_0^3, \\ d' &= -\delta \rho_0^3, & c' &= -(\gamma - \rho_0 \alpha^2) \rho_0^3. \end{aligned} \quad (4)$$

The increase in resistance $\Delta\rho$ due to the magnetic field is given by

$$\frac{\rho_0 \Delta\rho}{H^2} = b' + c' \cos^2(\mathbf{J}, \mathbf{H}) + d' \sum_{i=1}^3 \cos^2(\mathbf{i}, \mathbf{J}) \cos^2(\mathbf{i}, \mathbf{H}), \quad (5)$$

where $\cos(\mathbf{A}, \mathbf{B})$ is the cosine of the angle between the vectors \mathbf{A} and \mathbf{B} . Within experimental error b' , c' , d' were independent of the sample and of the temperature in the range 4°K and 20°K. This constitutes a verification of Kohler's rule,¹³ i.e., it shows that the scattering probabilities $w(\mathbf{k}, \mathbf{k}')$ in the different samples differ only by constant factors. This is to be expected since they were all in the residual resistance range. The values of b' , c' , and d' are given in Table I.

$\Delta\rho/\rho_0$ was found to be proportional to H^2 within 3% up to $\omega\tau = 0.024$ for copper and $\omega\tau = 0.08$ for silver. Gold crystals presented a special problem since even for very low fields no H^2 law was observed. The values for gold given in Table I are extrapolations to zero magnetic field.

In Figs. 1 and 2 we give the fractional change in resistance of typical samples of copper and gold plotted against H^2 .

A silver sample with resistivities 0.33×10^{-8} ohm cm and 0.83×10^{-8} ohm cm at 4°K and 20°K, respectively, was prepared. For this sample $\omega\tau = 1$ at 3 kilogauss. The resistivity of this sample is shown as a function of the magnetic field at 4°K in Fig. 3. The current was directed in approximately the [111] direction.

III. CALCULATIONS

The phenomenological constants σ_0 , α , β , γ , δ in (2) can be expressed as averages over the Fermi surface. The functions that are to be averaged are complicated expressions containing the relaxation time τ , the gradient in \mathbf{k} space of the energy $\epsilon(\mathbf{k})$ of the electron characterized by wave vector \mathbf{k} , and the operator

$$\Omega = (\text{grad}_{\mathbf{k}} \epsilon) \times \text{grad}_{\mathbf{k}}. \quad (6)$$

These formulas are given by Seitz.⁹

It is convenient to express these integrals in terms of a different set of variables. It turns out that these integrals become simpler if we choose the energy ϵ and the polar angles θ , ϕ of the reduced wave vector \mathbf{k} with the 3 axis as the polar axis as independent variables. By an elementary transformation the operator (6) becomes

$$\Omega = \left(\frac{\partial \mathbf{k}}{\partial \epsilon} \sin \theta \right)^{-1} \left(\frac{\partial \mathbf{k}}{\partial \phi} \frac{\partial}{\partial \theta} - \frac{\partial \mathbf{k}}{\partial \theta} \frac{\partial}{\partial \phi} \right), \quad (7)$$

where $k = |\mathbf{k}|$. This expression can be rewritten using

¹³ M. Kohler, Ann. Physik **32**, 211 (1938).

the usual quantum mechanical angular momentum operators L_1, L_2, L_3 . We obtain

$$\Omega_{3,\pm} = i \left(\frac{\partial k}{k^2} \right)^{-1} \Lambda_{3,\pm}, \quad (8)$$

where

$$\Omega_{\pm} = \Omega_1 \pm i\Omega_2, \quad (9)$$

and

$$\Lambda_3 = kL_3 + \frac{1}{2}[(L_+k)L_- - (L_-k)L_+], \quad (10)$$

$$\Lambda_{\pm} = kL_{\pm} \pm \frac{1}{2} \frac{y_1^{\pm 1}}{y_1^0} [(L_+k)L_- - (L_-k)L_+]. \quad (11)$$

Here $L_{\pm} = L_1 \pm iL_2$ and $y_l^m(\theta, \phi)$ are the spherical harmonics as defined by Jeffreys and Jeffreys.¹⁴ The operators Λ_j ($j=1,2,3$) are Hermitian and Λ_{\pm} are Hermitian conjugates of one another. We now use the cubic symmetry, the identity $\Omega_1(\tau \partial \epsilon / \partial k_1) + \Omega_2(\tau \partial \epsilon / \partial k_2) + \Omega_3(\tau \partial \epsilon / \partial k_3) = 0$, and the fact that for temperatures much lower than the Fermi degeneracy temperature, the function $-\partial f_0 / \partial \epsilon$ behaves as $\delta(\epsilon - \epsilon_F)$ where δ is the Dirac δ function. We obtain for the quantities in (2)

$$\sigma_0 = \frac{e^2}{4\pi^3} \int d\Sigma_{\theta, \phi} \frac{k^2}{\tau} \lambda_s^2, \quad (12)$$

$$\alpha = -\frac{e^3}{8\pi^3 \hbar^2 c} \int d\Sigma_{\theta, \phi} \lambda_- \Lambda_3 \lambda_+, \quad (13)$$

$$\beta = -\frac{e^4}{8\pi^3 \hbar^4 c^2} \int d\Sigma_{\theta, \phi} \frac{\tau}{k^2} \frac{\partial k}{\partial \epsilon} |\Lambda_3 \lambda_+|^2, \quad (14)$$

$$\beta + \gamma + \delta = \frac{e^4}{4\pi^3 \hbar^4 c^2} \int d\Sigma_{\theta, \phi} \frac{\tau}{k^2} \frac{\partial k}{\partial \epsilon} \{\Lambda_3 \lambda_3\}^2, \quad (15)$$

$$3\beta + 3\gamma + \delta = \frac{e^4}{16\pi^3 \hbar^4 c^2} \int d\Sigma_{\theta, \phi} \frac{\tau}{k^2} \frac{\partial k}{\partial \epsilon} (\Lambda_+ \lambda_+ - \Lambda_- \lambda_-)^2. \quad (16)$$

In these formulas $\lambda_j = (\tau/\hbar) \partial \epsilon / \partial k_j$ ($j=1,2,3$), $\lambda_{\pm} = \lambda_1 \pm i\lambda_2$, and $d\Sigma_{\theta, \phi} = \sin \theta d\theta d\phi$; also the integration is performed over the whole solid angle. In all expressions where the energy ϵ appears, it is understood that all differential coefficients should be evaluated at the Fermi level.

It will now be assumed that the energy surfaces can

¹⁴ H. Jeffreys and B. S. Jeffreys, *Methods of Mathematical Physics* (The University Press, Cambridge, 1956), third edition, pp. 626-666.

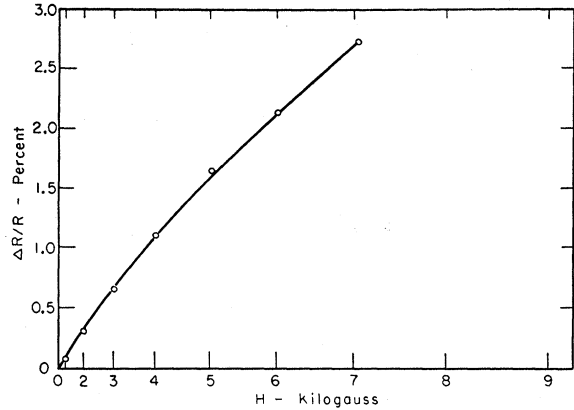


FIG. 2. Fractional change in resistance as a function of H^2 for a gold sample whose resistivity at 4°K is 7.16×10^{-8} ohm-cm. The current direction makes angles of 73°, 61°, and 35° with the [100], [010], and [001], axes. The magnetic field forms angles of 19°30', 72°, and 81° with the same axes.

be described by¹⁵

$$\epsilon = \frac{\hbar^2 k_0^2}{m^*} \left[\frac{1}{2} \left(\frac{k}{k_0} \right)^2 + r \left(\frac{k}{k_0} \right)^4 \right] \times \left\{ K_4(\theta, \phi) + t \left(\frac{k}{k_0} \right)^2 K_6(\theta, \phi) \right\}, \quad (17)$$

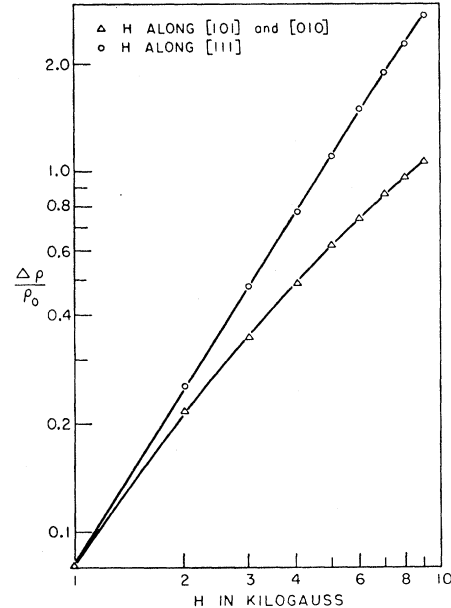


FIG. 3. Logarithmic plot of magnetoresistance of a single crystal of silver at 4°K. The current makes angles of 60°, 50°, 54° with the directions [010], [001], [100]. Errors in H and $\Delta\rho/\rho_0 + 1$ are 0.5% and 2.5%, respectively. At $H=3$ kilogauss, $\omega\tau=1$.

¹⁵ In this approximation it is easy to find an expression for the Fermi energy by means of the requirement,

$$N = \frac{2}{(2\pi)^3} \int f_0(\mathbf{k}) d\mathbf{k} = \frac{2}{(2\pi)^3} \int_0^{\epsilon_F} d\epsilon \int d\Sigma_{\theta, \phi} k^2 \frac{\partial \epsilon}{\partial \mathbf{k}}$$

$k^2(\partial k/\partial \epsilon)$ has cubic symmetry and therefore can be expanded in

where $k_0 = (12\pi^2)^{1/3}/a$ is the radius of the Fermi surface if it were a sphere containing one electron per atom. Here a is the lattice constant for the face-centered cubic crystal, m^* an electron effective mass, and r and t two dimensionless parameters. The functions $K_4(\theta, \phi)$ and $K_6(\theta, \phi)$ are the cubic harmonics of degree 4 and 6, respectively. They are given by¹⁶

$$K_4(\theta, \phi) = \frac{5}{2}(\xi^4 + \eta^4 + \zeta^4 - \frac{3}{2}), \quad (18)$$

and

$$K_6(\theta, \phi) = \frac{231}{2} \left\{ \xi^2 \eta^2 \zeta^2 + \frac{1}{55} K_4(\theta, \phi) - \frac{1}{105} \right\}, \quad (19)$$

where $\xi = \sin\theta \cos\phi$, $\eta = \sin\theta \sin\phi$, $\zeta = \cos\theta$ (see Appendix 2). We have omitted terms in k^4 and k^6 in (17) because they give rise to no anisotropy of the energy surfaces and, consequently, do not contribute significantly to the magnetoresistance.

The integrals (12) to (16) have been performed under the following assumptions:

- (i) the energy surfaces are given by (17);
- (ii) the relaxation time is constant over the Fermi surface as discussed in the introduction and Appendix 1;
- (iii) the Fermi surface is a single closed surface inside the first Brillouin zone and not touching its boundary;
- (iv) we have $r \ll 1$, so that r^4 and higher powers can be neglected. Then we find:

$$\alpha_0 = (N e^2 \tau / m^*) [1 - r^2(0.190 + 1.85t^2)], \quad (20)$$

$$\alpha = -N e c (e \tau / m^* c)^2 [1 - r^2(5.14 + 81.2t^2)], \quad (21)$$

$$\beta = -N e c (e \tau / m^* c)^3 [1 + r^2(26.3 + 224t^2)], \quad (22)$$

$$\gamma = N e c (e \tau / m^* c)^3 [1 + r^2(67.3 - 43.6t + 716t^2)], \quad (23)$$

$$\delta = -N e c (e \tau / m^* c)^3 3r^2 [13.7 - 7.83t + 368t^2]. \quad (24)$$

From these the coefficients (4) can be obtained:

$$b' = \frac{81 \times 10^{22}}{(N e c)^2} r^2 [36.4 + 414t^2], \quad (25)$$

$$c' = -\frac{81 \times 10^{22}}{(N e c)^2} r^2 [77.4 - 43.6t + 877t^2], \quad (26)$$

$$d' = \frac{81 \times 10^{22}}{(N e c)^2} r^2 [41.0 - 23.5t + 1103t^2], \quad (27)$$

where the units are (ohm cm/gauss)².

IV. INTERPRETATION

From the magnetoresistance coefficients given in Table I, information concerning the shape of the Fermi surface in terms of cubic harmonics. The average of a cubic harmonic of order greater than zero over the unit sphere vanishes. This leads to the relation

$$\epsilon_{F^2} = (\hbar^2 / 2m^*) (3\pi^2 N)^{1/3}.$$

¹⁶ F. C. von der Lage and H. A. Bethe, Phys. Rev. 71, 612 (1947).

surface can be found. The experimental results will now be interpreted in the light of some possible models.

For a state with wave vector near the boundary of the first Brillouin zone it is reasonable to expect the energy to be depressed with respect to its value corresponding to a spherical Fermi surface, as found for instance in aluminum.¹⁷ If we suppose that the Fermi surface is nearly spherical, it may, in this model, bulge outwards in the direction in which the first Brillouin zone has the smallest dimension. For the simple cubic structure the first Brillouin zone has its smallest dimension in the [100] direction. Then the radius vectors k_F of the Fermi surface in k space is expected on this argument to be such that

$$k_F[100] > k_F[110] \gtrsim k_F[111].$$

This condition is satisfied by the cubic harmonic K_4 but not by K_6 since

$$K_4[100] = 1, \quad K_4[110] = -\frac{1}{4}, \quad K_4[111] = -\frac{2}{3},$$

and

$$K_6[100] = 1, \quad K_6[110] = -13/8, \quad K_6[111] = 16/9.$$

The coefficients r and t represent the amount of anisotropy and the qualitative shape of the Fermi surface respectively. Thus, for a simple cubic crystal it may be sufficient to take $K_4(\theta, \phi)$ alone in the expression for ϵ , i.e., to assume $t=0$ in (17), (25), (26), and (27). For the face centered cubic structure we expect by similar reasoning that

$$k_F[111] > k_F[100] \gtrsim k_F[110];$$

to satisfy this relation we need to take $t \lesssim -0.48$. It turns out from (25), (26), (27), and Table I that the experimental values b' , c' , d' cannot be fitted within the experimental error by any choice of r and t . For copper the best fit is found with $t = -0.5$ and $r = 0.08$ (within 5%). For these values the radius k vector at the Fermi surface in the [111] direction is $1.124k_0(1 \pm 0.004)$. However, the dimension $k_{BZ}[111]$ of the first Brillouin zone in this direction is only $1.108k_0$, and thus in the [111] direction the radial k vector on the Fermi surface would be larger than the dimension of the Brillouin zone. As r measures the deviation of the Fermi surface from a sphere, this means that the observed magnetoresistance is larger than it could be if the Fermi surface did not touch the zone surface. We conclude, therefore, that for copper the Fermi surface probably touches the first Brillouin zone in the [111] direction.

Band structure calculations for copper, performed by Howarth^{18,19} indicate a completely different model. If we use Howarth's results¹⁸ to fit (17), the corresponding calculated magnetoresistance coefficients are 3 times larger than the experimental values. Howarth's calculation by the augmented-plane-wave method¹⁹ indicates

¹⁷ V. Heine, Proc. Roy. Soc. (London) A240, 340 (1957).

¹⁸ D. J. Howarth, Proc. Roy. Soc. (London) A220, 513 (1953).

¹⁹ D. J. Howarth, Phys. Rev. 99, 469 (1955).

that the Fermi surface touches the Brillouin zone in the [110] direction. This would indicate that the calculated magnetoresistance is still larger than in the previous case. Hence these band structure calculations are in disagreement with magnetoresistance measurements. However, if we assume that Howarth's calculations give the right qualitative shape of the Fermi surface bulging in the [110] direction but not touching the boundary of the Brillouin zone, we would have

$$k_F[100] \lesssim k_F[111] < k_F[110],$$

i.e., $0.122 < t \lesssim 2.14$. Here again the experimental values cannot be fitted by appropriate choice of r and t , the ratio of b' to c' being off by a factor of 2. The best fit is obtained with $t=2.0$, $r=2.4 \times 10^{-2}(1 \pm 0.05)$. For these values, $k_F[110]=1.087k_0(1 \pm 0.001)$ while $k_{BZ}[110]=1.357k_0$.

There seems to be no other reasonable shape of the Fermi surface. Then, probably, the only possible way to account for the experimental values of the magnetoresistance coefficients is to assume that the Fermi surface touches the boundary of the Brillouin zone in the [111] direction.

V. FURTHER REMARKS

If it is considered that magnetoresistance is due to the anisotropy of the relaxation time and that the Fermi surface is spherical, then it is concluded, according to Seitz,⁹ that c' is positive. This result holds if we consider τ expanded in cubic harmonics and retain those terms up to and including the fourth-order harmonic. Under the assumptions made in the present work c' turns out to be negative which is in agreement with our experiments (see Table I).

It is now convenient to give an expression for the magnetoresistance coefficients in terms of r and t for a polycrystalline sample. In this case there is no anisotropic term and the change in resistance of the sample in a magnetic field is given by the equation,

$$\Delta\rho/\rho_0 H^2 = B_t \sin^2(\mathbf{J}, \mathbf{H}) + B_l \cos^2(\mathbf{J}, \mathbf{H}), \quad (28)$$

where B_t and B_l are the transverse and longitudinal magnetoresistance coefficients respectively. By means of an averaging process over all possible directions of the crystal and keeping the angle (\mathbf{J}, \mathbf{H}) between \mathbf{J} and \mathbf{H} constant, it is found that

$$\rho_0^2 B_t = b' + (5/18)d' \quad (29)$$

and

$$\rho_0^2 B_l = b' + c' + (7/9)d'. \quad (30)$$

VI. ACKNOWLEDGMENTS

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APPENDIX 1

We shall prove here that if the relaxation mechanism is due to elastic collisions, a necessary and sufficient condition for a relaxation time to exist for an arbitrary Fermi surface is that the scattering be isotropic. Furthermore it will be shown that in this case the relaxation time is a function of the energy alone.

A relaxation time of a system we understand to be a characteristic time which describes the return of the system to the condition of thermal equilibrium after a deviation from this condition has been established, for example, by an electric field. In order for the relaxation time to be meaningful, it should be independent of the particular form of the deviation from the equilibrium state. In other words, the rate of change of the distribution function at a point in k space must be independent of the distribution function at other points. The distribution function $f(\mathbf{k})$ is defined as the probability that the state characterized by \mathbf{k} be occupied. We assume furthermore that the temperature of the substance at hand is uniform so that f is independent of the position.

The rate of change of the distribution due to scattering is given by

$$\left[\frac{\partial f(\mathbf{k})}{\partial t} \right]_{\text{collisions}} = \frac{1}{8\pi^3} \int d\mathbf{k}' \{ w(\mathbf{k}, \mathbf{k}') f(\mathbf{k}') [1 - f(\mathbf{k})] - w(\mathbf{k}', \mathbf{k}) f(\mathbf{k}) [1 - f(\mathbf{k}')] \}, \quad (\text{A1.1})$$

where

$$w(\mathbf{k}, \mathbf{k}') = w(\mathbf{k}', \mathbf{k}) = \frac{2\pi}{\hbar} |\langle \mathbf{k} | \mathcal{H}' | \mathbf{k}' \rangle|^2 \delta[\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}')] \quad (\text{A1.2})$$

is the transition probability for elastic scattering from state \mathbf{k}' to state \mathbf{k} and \mathcal{H}' is the deviation from the periodic potential of the lattice. Let

$$f(\mathbf{k}) = f_0(\epsilon(\mathbf{k})) + \phi(\mathbf{k}), \quad (\text{A1.3})$$

where $\phi(\mathbf{k})$ is the deviation of the distribution function from the equilibrium distribution $f_0(\epsilon)$ with the same total energy. Conservation of energy and of the number of particles implies that on each constant energy surface the number of electrons will remain constant, i.e.,

$$\int d\mathbf{k}' \phi(\mathbf{k}') \delta[\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}')] = 0. \quad (\text{A1.4})$$

Since no mechanism for the release of the energy has been provided, the equilibrium distribution carries no current but is not necessarily equal to the Fermi function. In an actual metal there will, of course, be

inelastic processes by means of which the thermal equilibrium Fermi function will be attained. But these collisions will have, in our case, a small transition probability and therefore, will give rise to a large relaxation time whose contribution to the resistivity is negligible.

From (A1.1), using (A1.2) and (A1.3), we find

$$\left[\frac{\partial f(\mathbf{k})}{\partial t} \right]_{\text{collisions}} = -\frac{1}{8\pi^3} \phi(\mathbf{k}) \int d\mathbf{k}' w(\mathbf{k}, \mathbf{k}') + \frac{1}{8\pi^3} \int d\mathbf{k}' w(\mathbf{k}, \mathbf{k}') \phi(\mathbf{k}'). \quad (\text{A1.5})$$

A relaxation time exists if, and only if,

$$\left[\frac{\partial f(\mathbf{k})}{\partial t} \right]_{\text{collisions}} = -\frac{f(\mathbf{k}) - f_0\{\epsilon(\mathbf{k})\}}{\tau(\mathbf{k})}. \quad (\text{A1.6})$$

From (A1.5) this condition reduces to the one, that there exists a function $F(\mathbf{k})$ which is independent of the choice of $\phi(\mathbf{k})$ consistent with the subsidiary condition (A1.4), and satisfies

$$\int d\mathbf{k}' w(\mathbf{k}, \mathbf{k}') \phi(\mathbf{k}') = F(\mathbf{k}) \phi(\mathbf{k}). \quad (\text{A1.7})$$

We see that this is not possible for arbitrary $w(\mathbf{k}, \mathbf{k}')$. In fact, if we make an arbitrary variation $\delta\phi$ of ϕ consistent with (A1.4), we find, by use of Lagrange's method of undetermined multipliers and the fundamental theorem of the calculus of variations, that F will remain unchanged if, and only if,

$$w(\mathbf{k}, \mathbf{k}') = F(\mathbf{k}) \delta(\mathbf{k} - \mathbf{k}') + C(\epsilon) \delta(\epsilon - \epsilon'), \quad (\text{A1.8})$$

where $C(\epsilon)$ depends only on the energy. The first term in (A1.8) represents no scattering at all and therefore gives no contribution to the rate of change of the distribution function. The second term represents an isotropic scattering and gives rise to a constant relaxation time

$$\tau(\epsilon) = 1/[n(\epsilon)C(\epsilon)], \quad (\text{A1.9})$$

where $n(\epsilon)$ is the total density of states at energy ϵ . This completes the proof of the assumptions made in Sec. 1.

APPENDIX 2

Cubic harmonics are linear combinations of spherical harmonics which transform, under the operations of the cubic group O_h , according to an irreducible represen-

tation of this group. They are characterized by three symbols; one corresponds to the degree of the function and the other two to the irreducible representation and to the row in the representation to which the function belongs. Methods to obtain cubic harmonics have been given by von der Lage and Bethe¹⁶ and by Bell.²⁰ Here we give a more convenient procedure.

Let $F_l(x, y, z)$ be a homogeneous polynomial of degree l in x, y, z and which belongs to a certain irreducible representation Γ of O_h . This polynomial would be a spherical harmonic if it satisfied Laplace's equation. But even if this is not the case, we can construct from it the cubic harmonic

$$K_l(\Gamma; \theta, \phi) = r^{l+1} F_l \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \left(\frac{1}{r} \right). \quad (\text{A2.1})$$

This transforms under rotations in the same way as $F_l(x, y, z)$ and furthermore it satisfies the associated Legendre equation. The polynomials $F_l(x, y, z)$ can be found by inspection. The expression (A2.1) can then be written as a linear combination of spherical harmonics by using the equation

$$\left(\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right)^m \left(\frac{\partial}{\partial z} \right)^{l-m} \left(\frac{1}{r} \right) = (-1)^m l! r^{-l-1} y_l^m(\theta, \phi) \quad (\text{A2.2})$$

(see reference 14, p. 633).

As examples we give a few of the cubic harmonics which have been used in the present calculation. We designate the irreducible representations of O_h by the symbols used by Bouckaert, Smoluchowski, and Wigner²¹ where in addition we have explicitly indicated whether the particular representation is even or odd with respect to inversion by superscripts \pm .

$$K_0(\Gamma_1^+; \theta, \phi) = 1,$$

$$K_4(\Gamma_1^+; \theta, \phi) = y_4^0(\theta, \phi) + (1/14)y_4^4(\theta, \phi) + (1/14)y_4^{-4}(\theta, \phi),$$

$$K_6(\Gamma_1^+; \theta, \phi) = y_6^0(\theta, \phi) - \frac{1}{2}y_6^4(\theta, \phi) - \frac{1}{2}y_6^{-4}(\theta, \phi),$$

$$K_8(\Gamma_1^+; \theta, \phi) = y_8^0(\theta, \phi) + (14/99)y_8^4(\theta, \phi) + (14/99)y_8^{-4}(\theta, \phi) + (1/198)y_8^8(\theta, \phi) + (1/198)y_8^{-8}(\theta, \phi),$$

$$K_3^{(0)}(\Gamma_{15}^-; \theta, \phi) = 4y_3^0(\theta, \phi),$$

$$K_3^{(+)}(\Gamma_{15}^-; \theta, \phi) = -3y_3^1(\theta, \phi) - y_3^{-3}(\theta, \phi),$$

$$K_3^{(-)}(\Gamma_{15}^-; \theta, \phi) = 3y_3^{-1}(\theta, \phi) + y_3^3(\theta, \phi).$$

²⁰ D. G. Bell, Revs. Modern Phys. 26, 311 (1954).

²¹ Bouckaert, Smoluchowski, and Wigner, Phys. Rev. 50, 58 (1936).