Hall Effect, Resistivity, and Magnetoresistivity of Th, U, Zr, Ti, and Nb†

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The Hall effect, resistivity, and magnetoresistivity of Th, U, Zr, Ti, and Nb have been studied at temperatures between ~1°K and room temperature and in magnetic fields up to 30 kilogauss. Strong temperature and purity dependences were observed in the Hall coefficients of U, Ti, and Zr. In addition, the Hall coefficient of Zr was strongly dependent upon magnetic field strength at liquid helium temperatures. Comparisons with theory have been carried out, and it is concluded that existing theories are not sufficiently general to account quantitatively for the observed temperature and magnetic field dependences of the Hall effect and resistivity. Unusual behavior was observed in the magnetic-field-induced superconducting transition of Nb.

I. INTRODUCTION

THE results of measurements of the Hall effect and transverse magnetoresistivity on several samples of Th, U, Zr, Ti, and Nb are presented below for temperatures between ~1°K and 300°K and magnetic fields up to 30 kilogauss. It will be evident from the data that the relationship between electron transport properties and electronic structure is more complicated than is generally appreciated. The semiclassical isotropic two-band theory[1] has been widely invoked[2,3] in attempts to explain the magnetic field dependence of the Hall effect and magnetoresistivity, and parameters derived from such studies have been cited as indications of the numbers and mobilities of electrons and holes present. This model (with modifications in some instances for ellipsoidal constant energy surfaces) has been moderately successful in describing the behavior of some semiconductors.[4] However, a critical review of similar work on metals reveals that it is in general not possible to account for *both* the Hall effect and magnetoresistivity data with a single set of parameters. This is not surprising in view of the simplifying assumptions of the theory that the charge carriers exist in two isotropic bands, and collisions can be described by a field-independent relaxation time. Through the introduction of additional bands (or pockets of electrons and holes) in the theory, additional parameters can be made available, and better fits to experimental data can be achieved. However, such a process probably represents curve fitting in most instances, rather than a realistic interpretation of electronic structure.

A further criticism of the semiclassical theory is that the detailed quantum mechanical nature of the motion of the electron is ignored. A quantum mechanical treatment of the conductivity tensor has been carried out by Argyres[5] for the case of a single isotropic energy surface and scattering by phonons. Lifshitz,[6] on the other hand, considered the quantum mechanical case of equally spaced Landau levels, Fermi energy much greater than this spacing, elastic impurity scattering, and a closed Fermi surface. None of these theories is sufficiently general to account quantitatively for the temperature and magnetic field dependences of resistivity and Hall effect reported below. Nevertheless, a comparison between experiment and the semiclassical isotropic two-band theory is of interest as an illustration of the difficulties.

The two-band theory[1] yields the following expressions for the Hall coefficient R and the change of resistivity $\Delta\rho$ in a transverse magnetic field H divided by the resistivity ρ_0 in zero field.

$$R=\frac{-B}{Nec}\left[\frac{1+A(1/Nec)^2(H/\rho_0)^2/B}{1+(n_e-n_h)A(1/Nec)^2(H/\rho_0)^2}\right], \quad (1)$$

$$\frac{\Delta\rho}{\rho_0}=\frac{C(1/Nec)^2(H/\rho_0)^2}{1+(n_e-n_h)A(1/Nec)^2(H/\rho_0)^2}, \quad (2)$$

where

$$A=p^2(1-p)^2(n_e-n_h)/(n_en_h)^2, \quad (3)$$

$$B=p^2/n_e-(1-p)^2/n_h, \quad (4)$$

$$C=[p/n_e+(1-p)/n_h]^2p(1-p), \quad (5)$$

and n_e and n_h are the numbers *per atom* of electrons and holes, N is the number of atoms per unit volume, p is the fraction of the total current carried by the electrons in zero field, and e and c have their usual meanings. When $n_e=n_h$, $\Delta\rho/\rho_0$ is proportional to H^2 at all fields, R is field independent, and the ratio of the Hall electric field E_y to the longitudinal electric field E_x approaches

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[1] For a discussion of the isotropic two-band theory, see A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1953), second edition, pp. 212–218.

[2] For a review, see J.-P. Jan, in *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 1.

[3] E. S. Borovik, Izvest. Akad. Nauk S.S.S.R. **19**, 429 (1955) (translation: Columbia Technical Translations).

[4] G. Fischer and D. K. C. MacDonald, Can. J. Phys. **36**, 527 (1958). See also B. Abeles and S. Meiboom, Phys. Rev. **95**, 31 (1954).

[5] P. N. Argyres, Phys. Rev. **109**, 1115 (1958).

[6] I. M. Lifshitz, J. Exptl. Theoret. Phys. U.S.S.R. **32**, 1509 (1957) [translation: Soviet Phys. JETP **5**, 1227 (1957)].

TABLE I. Sample characteristics and purities.

	$\rho(273)/\rho(4.2)$	Source and form	Impurities in % by weight Al	C	Ca	Cu	Fe	H	Mg	Mn	N	Ni	O	Si
Th 1	11.0	Ames (iodide Th wire)	← Unknown →											
Th 2[a]	18.2		← Unknown →											
U 1	6.5	Unknown	← Reactor grade →											
U 2	12.0	Argonne Nat. Lab. (rod)	0.0005	0.006	0.002	0.0001	0.001		0.0001			0.0005	0.0007	0.002
U 3	22.5 to 29.5	Argonne Nat. Lab. (single crystal)	← Unknown →											
Zr 1	170	Westinghouse			0.001	0.016	0.075	0.002			0.001		0.016	0.013
Zr 2	179	(crystal bar)			0.001	0.016	0.075	0.002			0.001		0.016	0.013
Zr 2′	176				0.001	0.016	0.075	0.002			0.001		0.016	0.013
Ti 1*u*	10.1	Heraeus (rolled	0.01			0.001	0.01	0.003	0.001			0.001	0.071	
Ti 1*a*[b]	11.0	sheet)	0.01			0.0001	0.01	0.0024	0.0001			0.001	0.074	
Ti 2*u*	7.7	Rem-Cru (rolled	0.01			0.001	0.01	0.0063	0.001	0.01		0.001	0.160	0.01
Ti 2*a*[b]	5.9	sheet)	0.01			0.0001	0.01	0.0012	0.001			0.001	0.148	
Ti 3	30.8	Mallory-Sharon (crystal bar)	0.001			0.0001	0.001		0.001					0.01
Nb 1*u*	10.4	United Kingdom		0.013			0.042	0.0002			0.012		0.024	0.014
Nb1*a*[c]	13.2	Atomic Energy	← Unknown →											
Nb 2[d]	17.3	Authority (1 mm sheet)	← Unknown →											

[a] Annealed 1 hour at 1200°C at 10^{-7} mm Hg prior to cold rolling.
[b] Annealed 1 hour at 1200°C at 7×10^{-7} mm Hg.
[c] Annealed ½ hour at 1600°C at 10^{-6} mm Hg.
[d] Annealed 5 hours with temperature increasing from 1500°C to 1800°C at 10^{-6} mm Hg.

0 at high fields. When $n_e \neq n_h$, $\Delta\rho/\rho_0$ saturates at high fields, R is field dependent, approaching a saturation value at high fields, and E_y/E_x becomes linear in H at high fields.

This model is in accord with Kohler's rule[7] in that R and $\Delta\rho/\rho_0$ are both functions only of H/ρ_0 for fixed n_e, n_h, and p. Additional temperature dependence (beyond that arising from the temperature dependence of ρ_0) may arise from a variation with temperature of any or all of the parameters n_e, n_h, and p. As noted earlier,[8] the Hall coefficients of Cu, Ti, and U are all characterized by weak temperature dependence in the residual-resistivity temperature region, strong temperature dependence in the small-angle electron-phonon scattering region, and weak temperature dependence in the linear-resistivity region. Indeed, the form of the R *versus* temperature curves for these metals is quite similar to the form of lattice specific heat curves. Such behavior in Cu suggests that changes in scattering mechanisms, rather than changes in the numbers of charge carriers, are responsible for the observed temperature dependence. In metals like Ti and U it is possible that changes in the numbers of charge carriers are important as well.

II. SAMPLES AND EXPERIMENTAL METHODS

Because much of the cryogenic, magnetic, and electrical equipment and most of the procedures used in this investigation have been described elsewhere,[9] this section will be devoted mainly to descriptions of the samples studied and the annealing treatments used.

Th 1 was a wire 4.90 cm long and 0.0508 cm in diameter; U 3 consisted of a single crystal 0.239 cm ×0.490 cm×0.180 cm; and Nb 2 consisted of a wire 1.25 cm long and 0.058 cm in diameter. The remaining samples were 2.3 cm long and 0.32 cm wide. Th 2 was cut from a 0.0183-cm thick strip fabricated from wire; U 1 was cut from 0.0244-cm thick rolled sheet; and Ti 1*u*, Ti 1*a*, Ti 2*u*, and Ti 2*a* were cut from 0.0127-cm thick rolled sheet. The remaining samples were machined from bulk material to the following thicknesses: U 2, 0.0259 cm; Zr 1 and Zr 2, 0.0378 cm; Ti 3, 0.0361 cm; and Nb 1, 0.0279 cm. It should be mentioned at this point that size effects of the type observed for Cu [9] should have been negligible for these thicknesses and sample resistivities. Current leads were attached to the ends of the sample with copper clamps, and the sample holder was so constructed that the sample could expand or contract thermally without constraint. Copper potential leads were forced against the sample edges with spring clips. The three-probe geometry[10] was employed for the Hall measurements, the voltage divider consisting of a specially constructed, all-copper potentiometer. In all Hall effect determinations, data were obtained on the magnetic field dependence of the Hall voltage, measurements being made up to 30 kilogauss at intervals of 5 kilogauss or less. All measurements carried out at 4.2°K were repeated at ~1°K, and, except for the case of the superconductivity data, no

[7] M. Kohler, Ann. Physik **32**, 211 (1938).
[8] T. G. Berlincourt, Bull. Am. Phys. Soc. Ser. II, **2**, 136 (1957).
[9] T. G. Berlincourt, Phys. Rev. **112**, 381 (1958).
[10] See J. K. Logan and J. A. Marcus, Phys. Rev. **88**, 1234 (1952).

changes beyond experimental error were observed in the liquid helium temperature region.

Sample characteristics and impurity contents, as determined by spectrographic and vacuum fusion techniques, are listed in Table I. The best over-all indication of sample quality is $\rho(273)/\rho(4.2)$, the ratio of the resistivity at the ice point, $\rho(273)$, to the residual resistivity, $\rho(4.2)$, measured at the normal boiling point of liquid helium. On this basis, the Zr samples were of rather high quality for such a reactive metal. The large observed resistivity ratios (~175) cast doubt on the spectrographic analysis, which indicated Fe impurity in the amount of ~0.075% by weight. Although the resistivity ratios of 30.8 and 29.5 observed, respectively, for Ti 3 and U 3 are the largest yet reported for these metals, they are nonetheless indicative of rather poor sample quality. The resistivity ratio of 17.3 observed for Nb 2 is likewise indicative of poor sample quality, although it is not greatly different from the value of 31 reported by White and Woods[11] for Nb. Comparative data on Th are conflicting in that other investigators[12,13] have reported room temperature resistivity values for Th which are about 25% less than the values observed in the present investigation. In view of the resistivity ratio of 18.2 reported herein for Th 2, a rather large violation of Mathiessen's rule[14] would be required to explain the discrepancy.

The annealing technique used in attempts to improve sample quality was originally developed by Meechan[12] and is particularly applicable in the case of reactive metals. The sample is placed in a vacuum of 10^{-7} to 10^{-6} mm Hg, and heating is accomplished by the passage of an electrical current through the sample. The walls of the vacuum chamber are maintained at liquid nitrogen temperature so that contamination from outgassing of the vacuum chamber walls is minimized, and volatile sample contaminants can condense on the walls. A further advantage of the method is that the hot portion of the sample does not contact bodies with which it could react. All samples annealed by this technique exhibited more lustrous surfaces after treatment, and all samples except Ti 2*a* exhibited improved electrical characteristics. Because the surface of Ti 2*a* was quite dull before the annealing treatment, it is possible that a large amount of surface contaminant diffused into the interior of the sample causing deleterious effects. The annealing temperatures listed in Table I are only approximate because sublimation took place in some instances, and the glass walls of the vacuum chamber were darkened to such an extent that accurate optical pyrometer temperature determinations could not be made.

TABLE II. Hall effect and resistivity data for Th samples.

Sample	T (°K)	$R\times10^5$ (cm³/coulomb)	$\rho\times10^6$ (ohm cm)
Th 1	4.2		1.59
	77		5.53
	297		18.9
Th 2	4.2	−9.70	0.859
	77	−10.35	4.29
	297	−11.16	17.2
Ames measurements[a]	300	−8.8	...
Measurements of Bodine[b] (two samples)	300	−11	...
	300	−13	...

[a] Ames Laboratory Staff, ISC-283, Quarterly Summary Research Report in Physics, April–June 1952, (unpublished), p. 13.
[b] J. H. Bodine, Jr., Phys. Rev. **102**, 1459 (1956).

[11] G. K. White and S. B. Woods, Can. J. Phys. **35**, 892 (1957).
[12] C. J. Meechan, Advances in Nuclear Engr. **2**, 209 (1957).
[13] W. Meissner and B. Voigt, Ann. Physik **399**, 892 (1930).
[14] See H. Jones, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19, p. 255.

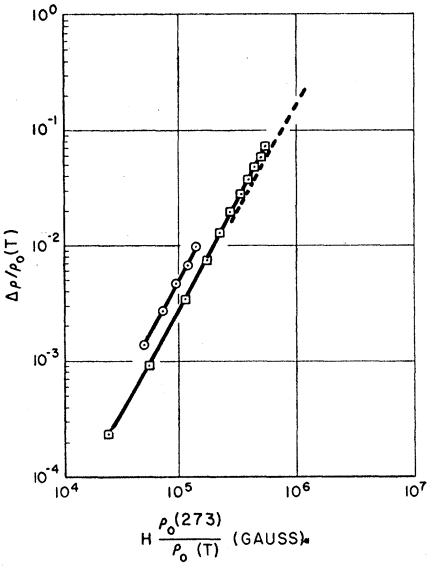

FIG. 1. Kohler plot for the transverse magnetoresivity of Th 1 (circles) and Th 2 (squares) at 4.2°K. The dashed line corresponds to data obtained by Kapitza[15] at 88°K and 193°K.

III. EXPERIMENTAL RESULTS

A. Thorium

The Hall voltage for Th 2 was a linear function of magnetic field strength from ~1°K to room temperature. The corresponding Hall coefficient values are presented in Table II and indicate only weak temperature dependence. Values reported by other investigators are included in Table II for comparison.

The transverse magnetoresistivity was determined for Th 1 and Th 2 at liquid helium temperatures, and the results are in fair accord with the earlier higher temperature measurements of Kapitza[15] as shown by the Kohler plot of Fig. 1. The magnetoresistance for both samples was proportional to H^2 to within 2%. Thus the data are consistent with the two-band theory for the case $n_e=n_h$, and values for n_e, n_h, and p could

[15] P. Kapitza, Proc. Roy. Soc. (London) **A123**, 292 (1929).

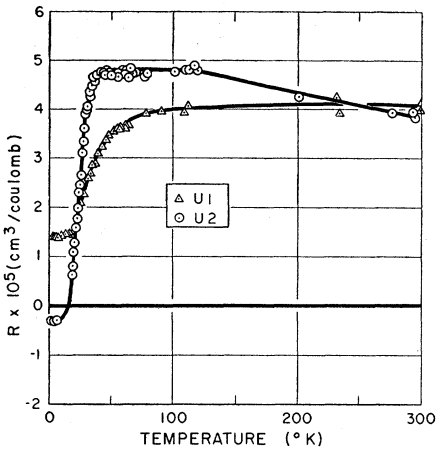

FIG. 2. Hall coefficient *versus* temperature for U 1 and U 2.

be derived. However, because of the low effective fields (H/ρ_0) attained, there is little justification for attaching any physical significance to such values.

B. Uranium

The Hall voltage was a linear function of magnetic field strength for U 1 and U 2 for the temperature and field ranges investigated. The Hall coefficient proved to be impurity sensitive, and a strong dependence upon temperature was detected as illustrated in Fig. 2 and Table III. The rapid variation in the range 20°K to 40°K is suggestive of a phase transformation. However, electrical resistivity measurements carried out on U 2 revealed no evidence in support of this possibility (see Fig. 3).

Transverse magnetoresistivity measurements were carried out at liquid helium temperature on U 2 and for several orientations of a single crystal U 3. A miniature sample holder was used for the latter studies, and the single crystal was trimmed with a dental-type sandblaster so that in all cases the current direction coincided with the largest dimension of the crystal. The results are presented in Fig. 4. In all cases the magnetoresistivity was approximately parabolic in H at low fields and approached linearity in H at high fields. For fixed magnetic field strength and current along a principal crystallographic direction, plots of magnetoresistivity *versus* orientation of the magnetic field in a plane perpendicular to the current direction proved to be approximately sinusoidal. In all cases the maxima and minima corresponded to principal crystallographic directions. Zero-field resistivities for the three principal axes are listed in Table IV. The large probable errors arose because of inaccuracies in dimensional determinations on the small crystal.

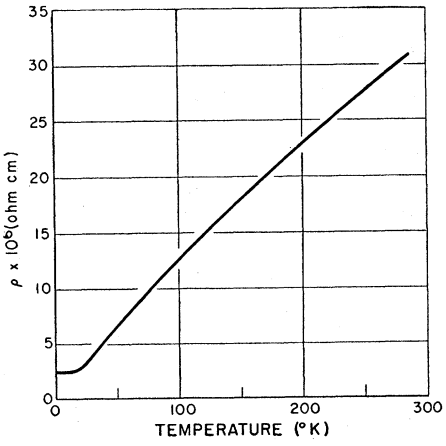

FIG. 3. Electrical resistivity *versus* temperature for U 2. Data points were too numerous to show on the graph. The scatter did not exceed the width of the line.

C. Zirconium

At room temperature and 77°K the Hall voltages for the Zr samples were linear functions of magnetic field strength. The corresponding Hall coefficients are summarized in Table V along with resistivity data and the results of earlier measurements on high-purity Zr by Foner[16] and on 97% pure Zr by Frank.[17] Marked differences are apparent in the Hall coefficients of Zr 1 and Zr 2, which were machined, respectively, from transverse and longitudinal sections of the same crystal bar. The third and still different results listed after Zr 2′ correspond to a remounting of Zr 2 in such a position that all potential leads were shifted about 3 mm along the length of the sample. Such behavior might be expected for a sample composed of a few large anisotropic grains. However, such an explanation does not appear to be applicable in this instance in view of (1) an almost negligible anisotropy in $\Delta\rho/\rho_0$ ($\sim$1%) at liquid helium temperatures for rotation of the magnetic field in a plane perpendicular to the sample length, and (2) close agreement of the liquid helium temperature magnetoresistivity data for the three samples. The difficulty could stem from an inhomogeneous impurity content and an extreme sensitivity of the Hall coefficient

TABLE III. Hall effect and resistivity data for U 1 and U 2.

Sample	T (°K)	$R\times10^5$ (cm³/coulomb)	$\rho\times10^6$ (ohm cm)
U 1	4.2	+1.45	4.8
	77	+3.9	11.9
	300	+4.1	34.0
U 2	4.2	−0.31	2.43
	77	+4.75	10.0
	273	+3.93	29.7
Measurements of Boeschoten and Huiszoon[a]	293 to 573	+3.4±10%	...

[a] F. Boeschoten and C. Huiszoon, Physica **23**, 704 (1957).

[16] S. Foner, Atomic Energy Commission Report NYO-7257 (unpublished), Suppl. 2.
[17] V. Frank, Appl. Sci. Research **B7**, 41 (1957).

to impurity content, a sensitivity not shared by the resistivity and magnetoresistivity. As will be evident from the Ti studies to be described below, such sensitivity to impurity exists for Ti.

Measurements carried out on the Zr samples at 4.19°K revealed an interesting magnetic field dependence of the Hall coefficient as shown in Fig. 5. The transverse magnetoresistivity data for the same samples are presented on a Kohler plot in Fig. 6, and E_y/E_x is plotted against field in Fig. 7. Hall coefficient, resistivity, and magnetoresistivity data obtained on Zr 2 at 1.55°K were in agreement with the 4.19°K data to better than 0.3%. The transverse magnetoresistivity data are in fair general accord with Kohler's rule in that

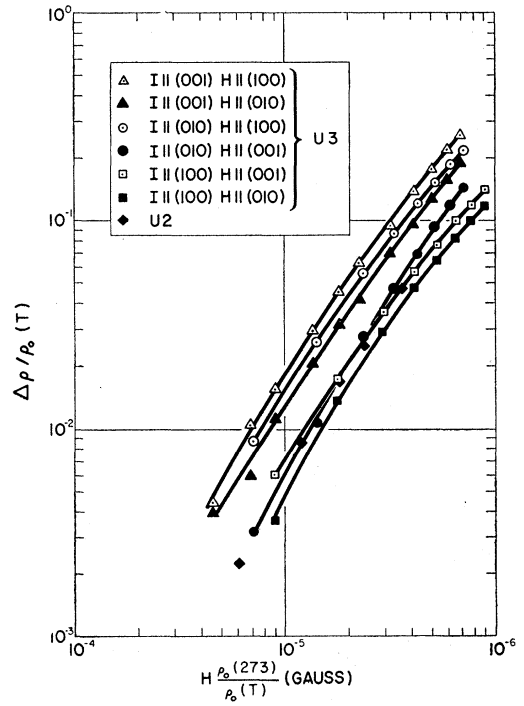

FIG. 4. Kohler plots for the transverse magnetoresistivity of polycrystalline sample U 2 and single crystal sample U 3 at 4.2°K.

the curves in Fig. 6 are nearly superposed for all three samples. On the other hand, the Hall coefficient data do not obey Kohler's rule, the variation from sample to sample far exceeding what could be accounted for if R were plotted against $H\rho(273)/\rho(4.2)$.

Despite this difficulty, a comparison with the two-band theory is of interest. Upon being casually inspected, the curves of Figs. 5 through 7 appear to approximate the curves to be expected for $n_e \neq n_h$. The case of $n_e = n_h$ can be ruled out immediately because of the observed magnetic field dependence of R. The dashed line of Fig. 5 represents a reasonable fit of Eq. (1) to the Zr 2′ Hall data obtained for $A = 102.0$, $B = 1.034$, and $n_e - n_h = 3.494$. These values yield a set

TABLE IV. Electrical resistivity of a uranium single crystal U 3.

Current direction	$\rho(273)\times10^6$ (ohm cm)	$\rho(273)/\rho(4.2)$
(100)	39.4±10%	29.5
(010)	25.5± 5%	23.5
(001)	26.2±10%	22.5

TABLE V. Hall effect and resistivity data for Zr samples.

Sample	T (°K)	$R\times10^5$ (cm³/coulomb)	$\rho\times10^6$ (ohm cm)
Zr 1	4.2	a	0.224
	77	−5.28	6.11
	298.6	...	42.6
Zr 2	4.2	a	0.213
	77	−1.47	6.08
	300.1	+1.30	42.6
Zr 2′	4.2	a	0.216
	77	−0.58	6.08
	300.0	+2.27	42.6
Measurements of Foner[b]	300	+12.6	...
Measurements of Frank[c]	77	+10.8	...
on impure Zr	273	+14.0	40.5
	500	+9.0	...
	800	+2.8	...

[a] In these cases R was dependent on magnetic field.
[b] See reference 16.
[c] See reference 17.

of parameters $n_e = 1.964\times10^{-3}$, $n_h = -3.492$, and $p = 3.887\times10^{-2}$. The negative value for n_h is not acceptable physically. However, if one considers the case of two bands of electrons instead of one band each of electrons and holes, Eqs. (1) through (5) are modified only in that n_h is replaced by $-n_e'$ where n_e' is the number of electrons per atom in the second band. For this case the Hall data for Zr 2′ can be characterized by the parameters $A = 102.0$, $B = 1.034$, $n_e = 1.964$

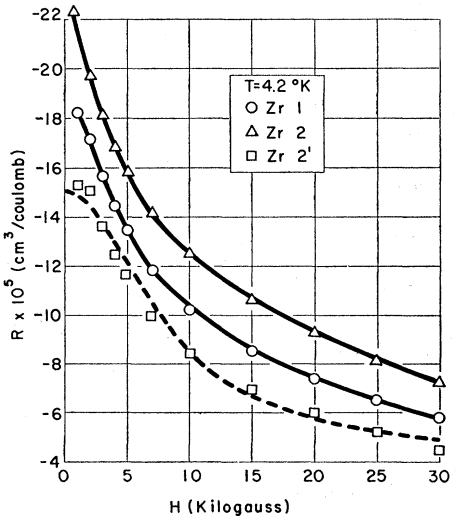

FIG. 5. Hall coefficient *versus* magnetic field strength for Zr samples at 4.2°K. The dashed line represents a fit of the isotropic two-band theory to the Zr 2′ data.

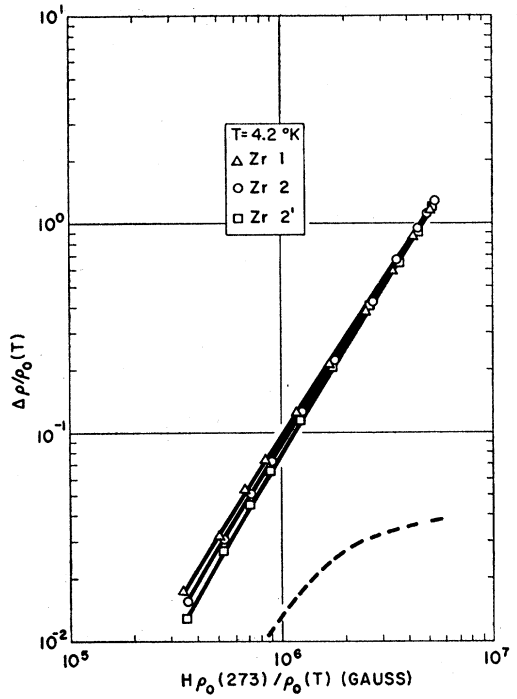

FIG. 6. Transverse magnetoresistivity *versus* magnetic field strength for Zr samples at 4.2°K. The dashed line was calculated using the isotropic two-band theory and the parameters used to fit the Hall effect data.

10^{-3}, $n_e'=3.492$, and $p=3.887\times10^{-2}$. Although these parameters appear to be acceptable physically, a calculation of the transverse magnetoresistivity using these parameters in Eq. (2) yielded the dashed curve appearing in Fig. 6. A large discrepancy is apparent in both functional form and magnitude, the observed and calculated magnetoresistivities differing by a factor of 33 at the highest fields. The same difficulties arose in a comparison of the Zr 1 data with Eqs. (1) and (2). It is thus clear that the isotropic two-band theory is incapable of accounting for the observed behavior.

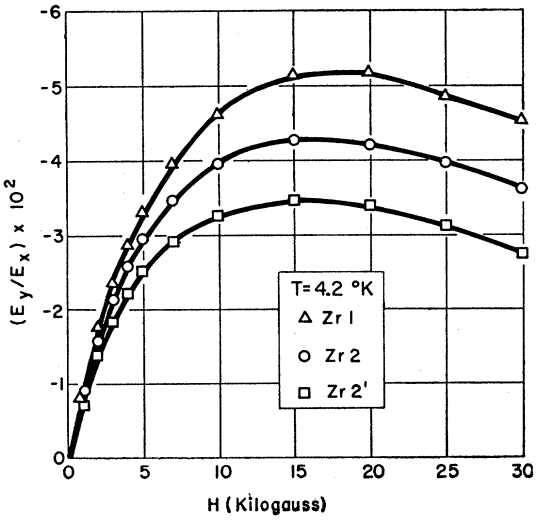

FIG. 7. E_y/E_x *versus* magnetic field strength for Zr samples at 4.2°K.

D. Titanium

The Hall voltage was a linear function of magnetic field strength from ~1°K to room temperature for all Ti samples studied. The corresponding Hall coefficients are presented, along with resistivity data, in Table VI and Fig. 8. Hall coefficient values obtained by other investigators[16,18] are also included in Table VI. As in the case of Zr, the data reveal a very great sensitivity of the Hall coefficient to impurity content. It is probable that preferred orientation also contributed to the broad spectrum of observed values, inasmuch as all Ti samples except Ti 3 were cut from rolled sheet. This view is supported by the fact that the resistivity curves in Fig. 8 for the rolled samples are in fair accord with Mathiessen's rule,[14] but are crossed by the curve for Ti 3.

TABLE VI. Hall coefficient and resistivity data for Ti.

Sample	T (°K)	$R\times10^5$ (cm³/coulomb)	$\rho\times10^6$ (ohm cm)
Ti 1*u*	4.2	−4.10	4.43
	77	−0.95	8.81
	296.5	−0.05	48.7
Ti 1*a*	4.2	−4.68	3.91
	77	−3.46	8.07
	297.5	−4.29	47.3
Ti 2*u*	4.2	−10.9	5.83
	77	−6.48	10.5
	296	−4.09	48.8
Ti 2*a*	4.2	−7.52	8.18
	77	−5.22	12.5
	295.0	−4.50	50.0
Ti 3	4.2	−10.52	1.46
	77	−4.58	6.00
	297.0	−3.55	49.2
Measurements of Foner[a]			
Ti I	300	−1.06	...
Ti II	291	−2.59	...
Ti III	294	+1.02	...
Measurements of Scovil[b]	300 to 1100	−2.0 to +3.3	40 to 175

[a] See reference 18.
[b] G. Scovil, J. Appl. Phys. **27**, 1196 (1956).

The temperature dependence of R was determined in some detail for Ti 1*u*. The behavior for the other samples is probably of the same general form with weak temperature dependence in the residual- and linear-resistivity temperature regions and strong temperature dependence in the small-angle electron-phonon scattering region.

The transverse magnetoresistivity was determined at 4.2°K for Ti 3 and can be represented to an accuracy of ±5% by the expression $\Delta\rho/\rho_0=1.50\times10^{-11}H^2$. It is worthy of mention that magnetoresistivity measurements carried out on a Ti single crystal containing

[18] S. Foner, Phys. Rev. **107**, 1513 (1957).

between 0.01% and 0.1% Mn impurity revealed a decrease of resistivity of ~10% in a field of 30 kilogauss at 4.2°K. The effect is similar to that occurring in Cu doped with small amounts of Mn,[19] and is attributed to a cooperative magnetic phenomenon.

E. Niobium

Because Nb becomes superconducting[20] below about 9°K, the data in this section refer to measurements carried out either at temperatures above the transition temperature or in fields great enough to restore the normal state. The Hall voltage was a linear function of magnetic field strength from ~1°K to room temperature for Nb 1 both before and after annealing. Furthermore, as is evident from the tabulation of data in Table

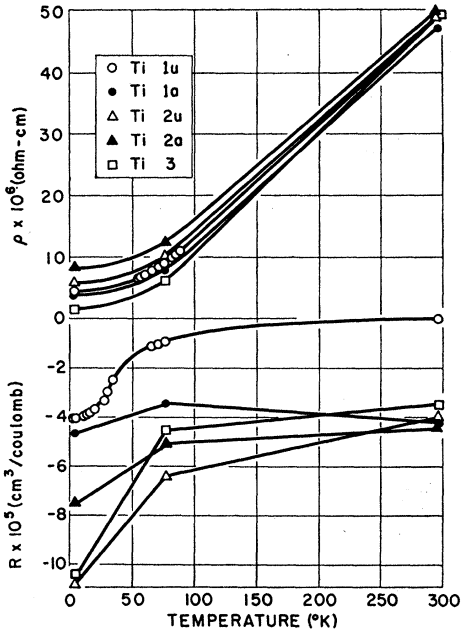

FIG. 8. Resistivity and Hall coefficient *versus* temperature for Ti samples.

VII, the Hall coefficient of Nb is only weakly temperature dependent and is nearly insensitive to the annealing treatment. Excellent agreement with Frank's earlier measurements[17] on Nb is also indicated.

The observed magnetoresistivity at liquid helium temperatures was small, $\Delta\rho/\rho_0 \sim 10^{-2}$ at 30 kilogauss, but the relatively large critical fields for the superconducting transition made an accurate determination of the normal magnetoresistivity unfeasible.

F. Superconductivity of Niobium

Data were obtained on the superconducting transition of Nb in a magnetic field as determined by resistivity

TABLE VII. Hall coefficient and resistivity data for Nb.

Sample	T (°K)	$R\times10^5$ (cm³/coulomb)	$\rho\times10^6$ (ohm cm)
Nb 1*u*	4.2	+9.37	1.43
	77	+9.67	4.08
	299.5	+8.78	16.3
Nb 1*a*	4.2	+9.54	1.10
	77	+8.50	3.74
	295.0	+8.72	15.7
Nb 2	4.2	...	0.817
	297.7	...	15.4
Measurements of Frank[a]	77	+9.2	...
	273	+8.7	14.2
	800	+9.1	...

[a] See reference 17.

measurements. The results for Nb 1 before annealing are displayed in Fig. 9 for the case of the magnetic field perpendicular to the plane of the flat strip sample. The fields required to restore the normal resistivity were considerably greater than critical fields determined from earlier magnetic moment measurements.[20] Such an apparent discrepancy is common among "hard" superconductors in which, because of physical and chemical inhomogeneities, fine threads of superconducting material can be present when the main bulk of the material is normal.[21] Such superconducting threads provide a zero resistance path but make only a very small contribution to the magnetic moment.

The effect of annealing on the superconducting properties of Nb 1 was quite marked, as is evident from Fig. 10. The fields required to restore the normal resistivity were about half as great as before annealing but were still more than twice as large as critical fields determined from magnetic moment measurements. Anomalous peaks can be seen at the knees of the transitions. Most of the data were taken in decreasing fields, but cycling over the 2.003°K curve revealed negligible hysteresis. A possible qualitative explanation for the observed behavior follows the argument[22] used to account for anomalous behavior in the thermal

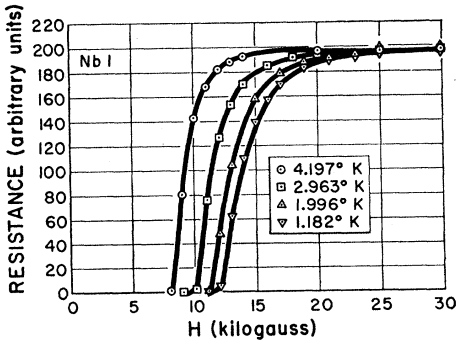

FIG. 9. Superconducting transitions (resistive) in a magnetic field for Nb 1.

[19] R. W. Schmitt and I. S. Jacobs, Can. J. Phys. **34**, 1285 (1956).
[20] For a review, see J. Eisenstein, Revs. Modern Phys. **26**, 277 (1954). Also see reference 11.
[21] J. K. Hulm and B. B. Goodman, Phys. Rev. **106**, 659 (1957).
[22] See D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), p. 86.

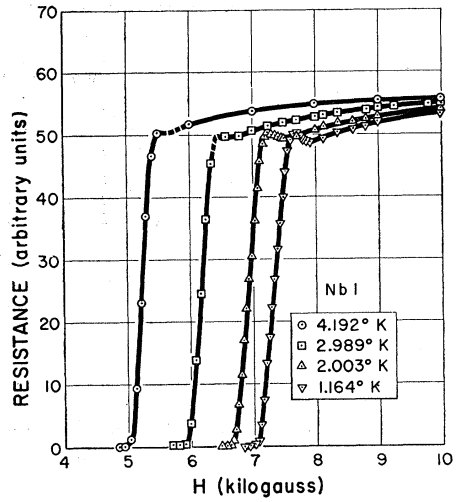

FIG. 10. Superconducting transitions (resistive) in a magnetic field for Nb 1 after anneal. Note anomalous peaks at knees of curves.

conductivity of superconductors in the intermediate state. As the magnetic field is decreased, portions of the sample become superconducting, decreasing the resistance. As the field is further decreased and more superconducting regions are created, scattering from the normal-superconducting boundaries dominates, and the resistance increases. As the field is still further decreased, the superconducting regions grow and merge to form continuous superconducting paths, and the resistance decreases to zero. Of course, it is also possible that the observed behavior was merely the consequence of a fortuitous combination of the geometry of the experiment, the magnitude of the measuring current, and the sample inhomogeneities. Subsequent measurements on the wire sample, Nb 2, in a transverse magnetic field did not reveal such behavior.

IV. DISCUSSION

Many of the earlier investigations of the Hall coefficients of metals were confined to room temperature measurements on a single sample of a given metal. The present investigation, as well as other recent investigations,[3,16,17,23,24] has revealed strong temperature, magnetic field, and purity dependences of the Hall coefficient. A satisfactory quantitative interpretation of the observed phenomena in terms of realistic electronic parameters is beyond the scope of existing theories.

The magnetic field dependences of R, $\Delta\rho/\rho_0$, and E_y/E_x reported above for Zr are similar to the results of Coles and Taylor[25] on Rh and the results of Borovik[26] on Zn and Be. Furthermore, they share the difficulty that it is not possible to fit *both* the Hall effect and magnetoresistivity data with a single set of two-band theory parameters. Conclusions regarding electronic structure based upon parameters which fit only part of the conductivity tensor are without justification.

Interesting trends have been noted by Foner,[16] by Gelhoff, Justi, and Kohler[27] and by Frank[17] in the dependence of the room temperature Hall coefficient upon atomic number for the first, second, and third transition series. Nevertheless, strong temperature and purity dependences of the type reported above for U, Zr, and Ti should temper conclusions drawn from such correlations. It would be tempting to ascribe all such temperature and purity dependences to very sensitive band-overlap conditions which could exist in metals like U, Zr, and Ti. A small change in overlap, such as might be induced by a change of temperature or purity, could then greatly modify the Hall coefficient. However the form of the temperature dependence of R (i.e., the similarity of R *versus* temperature curves to lattice specific heat curves) and effects of alloying, as discussed by Coles,[28] suggest that scattering is comparable in importance with charge carrier concentration in determining R. In this connection, it is also of interest that Hall coefficient measurements by Kevane, Legvold, and Spedding[24] on several of the rare earth metals between 20°K and room temperature revealed strong temperature dependences in the small angle electron-phonon scattering region. A magnetic effect such as accompanies the approach to a Curie point was proposed as a possible explanation for some of the strong temperature dependences. Although such a mechanism might very well apply in instances where strong magnetism is known to occur, it is not unlikely that in cases such as that of Pr continuation of the data to liquid helium temperature might reveal behavior similar to that reported herein for U and Ti rather than a continuing strong temperature dependence as required for the approach to a Curie point.

An ideal theory for the conductivity tensor would probably have to take into account the anisotropy of the Fermi surface, the anisotropy of the scattering, a magnetic field dependence of the relaxation time, and quantum mechanical effects. It appears doubtful, even if such a theory were available, that the shape of the energy surface could be determined from comparisons with data of the type described herein. The use of single crystals would be necessary so that the anisotropy could be taken into account. However, because reliable means for determining the shapes of energy surfaces

[23] T. Fukuroi and T. Ikeda, Sci. Repts. Sendai Univ. **A8**, 205 (1956).
[24] Kevane, Legvold, and Spedding, Phys. Rev. **91**, 1372 (1953).
[25] B. R. Coles and J. C. Taylor, J. Phys. Chem. Solids **1**, 270 (1957).
[26] E. S. Borovik, J. Exptl. Theoret. Phys. U. S. S. R. **23**, 83 (1952). [Translation: Naval Research Laboratory Report NRL-462 (unpublished)].
[27] Gelhoff, Justi, and Kohler, Z. Naturforsch. **5a**, 16 (1950).
[28] B. R. Coles, Phys. Rev. **101**, 1254 (1956).

already exist in the use of de Haas-van Alphen[29] and cyclotron resonance[30] techniques, transport property measurements might better be used for tests of transport theories for cases in which the shapes of the energy surfaces are already known.

[29] For a review, see D. Shoenberg, in *Progress in Low-Temperature Physics*, edited by J. C. Gorter (North Holland Publishing Company, Amsterdam, 1957), Vol. 2, p. 226.
[30] For a review, see B. Lax, Revs. Modern Phys. **30**, 122 (1958).

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Impurity Scattering in Superconductors

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With the Bardeen-Cooper-Schrieffer theory as a starting point, perturbation theory is used to determine the reduction in superconducting transition temperature due to scattering by impurities dissolved in the superconductor. Two cases are discussed: scattering due to a localized exchange interaction between the spins of the conduction electrons and impurity spins, and purely orbital scattering by nonmagnetic impurities. In the former case good quantitative agreement with observations is obtained. In the latter case numerical agreement is less good, but the qualitative feature, that the initial reduction in T_c is a universal function of residual resistivity is made evident. It is further shown that indiscriminate application of perturbation theory of B.C.S. states leads to the wrong result in predicting the transition temperature, if the transition is of second order.

1. INTRODUCTION

IT has been known for some time that the addition of impurities to a superconductor can have a major effect on its transition temperature.[1,2] The difficulty in the interpretation of most such results is that the impurities will change several characteristics of the material at the same time, and it is not always clear which change is the most important. Thus, if host and solute atoms have different numbers of valence electrons, there may be a modification in the electron concentration upon which, according to the current theory,[3] the criterion for superconductivity sensitively depends. Alternatively, there might be a change in the effective electron-electron interaction due to the solute, and this interaction enters current theory in a similarly critical way. Finally at the larger concentrations, there might be some upset in the phonon spectrum.

To overcome such objections, and at the same time to investigate relationships between superconductivity and ferromagnetism, Matthias and co-workers[4] studied solutions of the various rare earths in lanthanum. The rare earths differ from lanthanum only in the number of inner-shell, f, electrons. Hence changes in the conduction-electron density should be minimal in this case. Also the field near an impurity should not be too different from that near a lanthanum atom. No very large, purely orbital, scattering effects are therefore to be expected.

Yet it turned out that the reduction in transition temperature was surprisingly large: just over one atomic percent of gadolinium reduced it almost to zero. Furthermore the reduction depended more nearly on the spin, rather than on the magnetic moment, of the solute, being largest by far for gadolinium, which has the largest spin ($S=\frac{7}{2}$) and much smaller for holmium and dysprosium whose ions have the largest magnetic moments. (We assume here that the rare earths are present in their trivalent form, the outer electrons having joined the sea of conduction electrons.) This led Herring[5] to suggest that an exchange interaction between the conduction electrons and the f-shell spins is responsible for the reduction in transition temperature, and his rough estimate showed that with an exchange constant of about 0.2 volt one would indeed obtain the observed reduction in T_c. Part of this paper is concerned with a calculation of this effect. That the magnetic dipole fields of the solute ions are too weak to account for the observations is demonstrated in Appendix I.

[1] Lynton, Serin, and Zucker, J. Phys. Chem. Solids **3**, 165 (1957).
[2] B. Serin, International Conference on Electronic Properties of Metals at Low Temperatures, Geneva, 1958 (unpublished).
[3] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957). Hereafter referred to as B.C.S.
[4] Matthias, Suhl, and Corenzwit, Phys. Rev. Letters **1**, 93 (1958).
[5] C. Herring, Kamerlingh Onnes Memorial Conference on Low-Temperature Physics, Leiden, Holland, 1958 [Suppl. Physica **24**, (September, 1958)].