

Electrical Resistivity of the Heavy Rare-Earth Metals*

R. V. COLVIN,† SAM LEGVOLD, AND F. H. SPEDDING

Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa

(Received June 8, 1960; revised manuscript received August 1, 1960)

The electrical resistivities of polycrystalline Gd, Tb, Dy, Ho, Er, Tm, and Lu have been measured between 1.3°K and room temperature. The slope of the resistivity curve for Gd changes near the Curie point. The curve for Tb is very much like that for Gd but there is some evidence that two ordering temperatures exist for this metal. Dy, Ho, and Tm all show peaks in resistivity near their Néel points, while Er shows only a change in slope at its Néel point. The change from ferromagnetism to antiferromagnetism in Dy is seen as a sharp rise in the resistivity.

I. INTRODUCTION

WE present here the temperature dependence of the electrical resistivities of Gd, Tb, Dy, Ho, Er, Tm, and Lu. All of these elements have the hexagonal close-packed crystal structure¹ and have very similar physical and chemical properties. For a given member of this group good correlations are found in the abnormal temperature dependence of such physical properties as specific heat, magnetic susceptibility, thermal expansion, thermoelectric effect, and electrical resistivity.

The measurements reported below were made on the best samples presently available in the Ames Laboratory. For Gd, Dy, and Er we believe these samples are superior to samples for which resistivities were reported previously.² This is manifested in more distinct breaks in the resistivity curves, lower values of the resistivity and smaller slopes in the curves. In other earlier work Bridgman³ reported the resistivities of a number of rare-earth metals from 0°C to room temperature. The resistivities of single crystals of Dy⁴ and Er⁵ have been measured and polycrystalline results have been predicted from these measurements. Agreement with the results reported here is good.

II. EXPERIMENTAL PROCEDURE

A. Apparatus

The variable temperature apparatus used for this investigation is shown in Fig. 1. A similar heat leak chamber was used and described by Anderson.⁶ Appropriate changes in the apparatus were made to permit

operation with liquid hydrogen and nitrogen as well as with liquid helium. Since operation of the apparatus at the higher temperatures was not economically feasible when helium was used as the cold reservoir, a nitrogen reservoir, which was refilled automatically, was used to maintain any temperature between 77.5°K and 400°K for indefinite periods of time.

Temperatures were changed by using pulses of electrical power in the 140 ohm heater coil to obtain the temperature desired. Automatic temperature control was used to maintain a temperature when it was desirable to do so. It was found that in the temperature regions where the resistivity was well behaved it was sufficient to have approximate equilibrium conditions to obtain good data. Temperatures and resistivities were measured simultaneously.

The sample resistance was determined by the usual

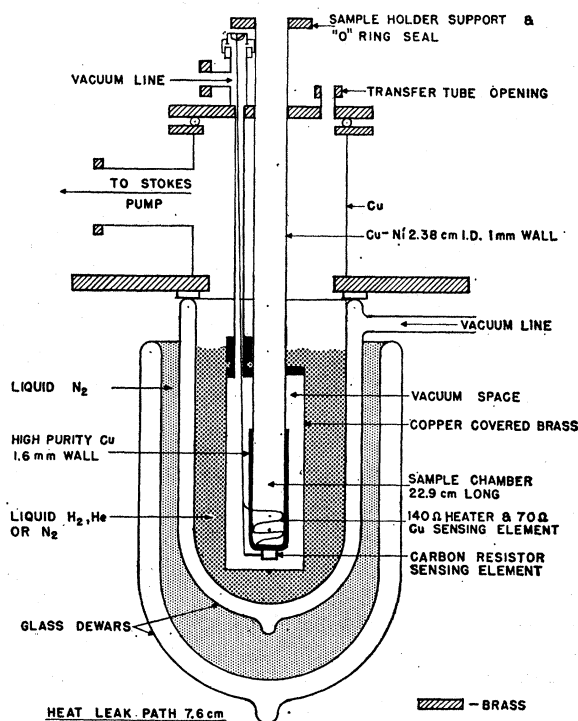


FIG. 1. Low-temperature heat leak chamber.

* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

† Now at the Edgar C. Bain Laboratory of the U. S. Steel Corporation, Monroeville, Pennsylvania.

¹ F. H. Spedding, S. Legvold, A. H. Daane, and L. D. Jennings, *Progress in Low-Temperature Physics* edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II.

² S. Legvold, F. H. Spedding, F. Barson, and J. F. Elliott, *Revs. Modern Phys.* **25**, 129 (1953).

³ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **83**, 1 (1954).

⁴ P. M. Hall, S. Legvold, and F. H. Spedding, *Phys. Rev.* **117**, 971 (1960).

⁵ R. W. Green, Ph.D. thesis, Iowa State University Library, Ames, Iowa, 1960 (unpublished).

⁶ G. S. Anderson, S. Legvold, and F. H. Spedding, *Phys. Rev.* **109**, 243 (1958).

TABLE I. Sample analysis.

Element	Analysis (in %)
Gadolinium (not distilled)	Dy ≥ 0.01 ; Y ≥ 0.05 ; Pb ≥ 0.01 ; Eu ≥ 0.01 ; Sm ≥ 0.05 ; Nd < 0.05 ; Mg < 0.01 ; Si, 0.025; Ca, 0.06; Fe, 0.02; Ta ≥ 0.1 ; C, 210 ppm; N, 130 ppm; Ag, Al, As, Au, B, Be, Bi, Co, Cr, Cu, Ga, Ge, Hg, Ir, Mn, Mo, Na, Pb, P, Pd, Rh, Ru, Sn, Sr, Ti, Tl, V, W, Zn, Zr not detected; Ni trace.
Terbium (not distilled)	Dy, 0.05; Gd, 0.05; Ca, 0.04; Eu, Fe, Ho, Si, Ta, Y, Yb, Tm, La, Lu, Nd, Pr, Er, not detected.
Dysprosium (distilled)	Y ≤ 0.01 ; Tb < 0.1 ; Yb < 0.005 ; Er < 0.02 ; Ho < 0.02 ; Ta, 0.2; Fe < 0.01 ; Si < 0.03 ; Ca < 0.05 ; C, 100 ppm; N, 15 ppm; Mg very faint trace.
Holmium (distilled)	Tm ≥ 0.01 ; Er < 0.02 ; Dy ≥ 0.04 ; Y < 0.01 ; Ta, 0.2; Fe, 0.01; Ca, 0.05; Si < 0.02 ; C, 75 ppm; N, 94 ppm; Ni, trace; Cu, trace; Mo, Cr, Al, Sc not detected.
Erbium (distilled)	Ca, < 0.01 ; Fe, 0.02; Mg < 0.01 ; Si < 0.01 ; Y < 0.01 ; Dy < 0.005 ; Yb < 0.0002 ; Tm < 0.002 ; Ho < 0.008 ; Ca, faint trace; Cu, trace; La, trace.
Thulium (distilled)	Lu ≥ 0.003 ; Yb ≥ 0.0005 ; Er ≥ 0.004 ; Ho ≥ 0.04 ; Y < 0.02 ; Ca < 0.05 ; Mg ~ 0.05 ; Fe, 0.02; Si < 0.01 ; C, 120 ppm; N, 9 ppm; Ta, 1.5; Ag, As, Au, Ba, Bi, Co, Ge, Hf, Hg, In, Mo, Na, Nb, Ni, Te, Ti, Tl, V, W, Zn, Zr, not detected. Cu, trace; Al trace; Mn, trace; Cr, trace.
Lutetium (not distilled)	Y ~ 0.05 ; Sc < 0.02 ; Yb < 0.005 ; Tm < 0.002 ; Ca < 0.05 ; Mg < 0.03 ; Cr < 0.02 ; Fe ~ 0.01 ; Si < 0.03 ; C, 66 ppm; N, 720 ppm; As, Au, Ba, Be, Cd, Co, Cr, Hf, Hg, In, Na, P, Pt, Ru, Te, Tl, V, Zr not detected, Cu, trace; Mn, trace; Nb, trace; Ni, trace; Sn, trace; Ta (strong line).

four-probe method using current reversal. An electronic constant-current power supply was used to supply 0.342 amp to all of the samples measured. Sharpened brass wedges approximately an inch apart mounted on a quartz block were used as potential contacts. Sample diameters were determined with a micrometer.

Most of the measurements below 20°K were made in the liquid hydrogen or liquid helium baths. Temperature measurements were made with a vapor pressure thermometer or with copper constantan thermocouples.

The probable error in the determination of the sample resistivities was about 1%. Temperatures were known to the nearest 0.1°K.

B. Samples

All of the samples were cast rods $\frac{3}{16}$ -in. in diameter and 2-in. long. The curves for Gd, Tb, Tm, and Lu were obtained after annealing. Annealing attempts on Ho and Er were unsuccessful. The curves reported for these two elements were obtained prior to annealing. No attempt was made to anneal Dy.

It has been observed that Ta impurities in a rare-earth metal will greatly reduce the resistivity and give erroneous results below the superconducting transition of Ta. Consequently, we have not plotted any points

below 4.4°K for Tm and Lu which apparently pick up Ta in the casting process. For the same reason we have taken the residual resistivity to be the 4.4°K value for all the samples.

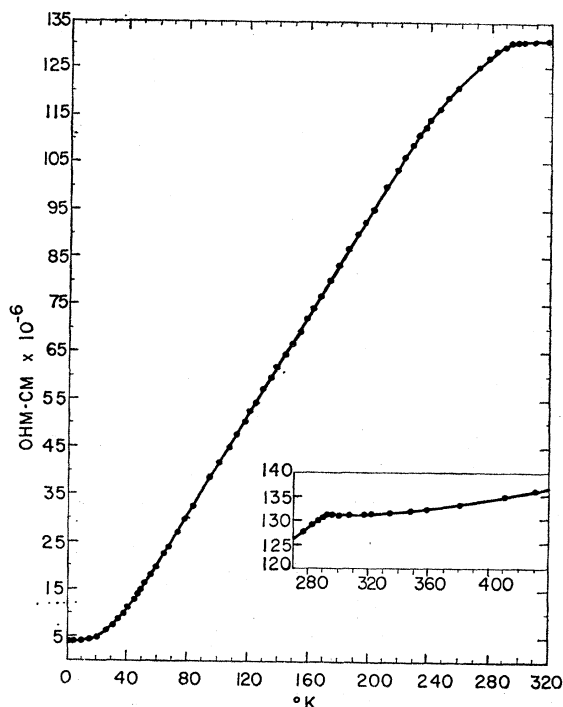


FIG. 2. Electrical resistivity of Gd vs temperature.

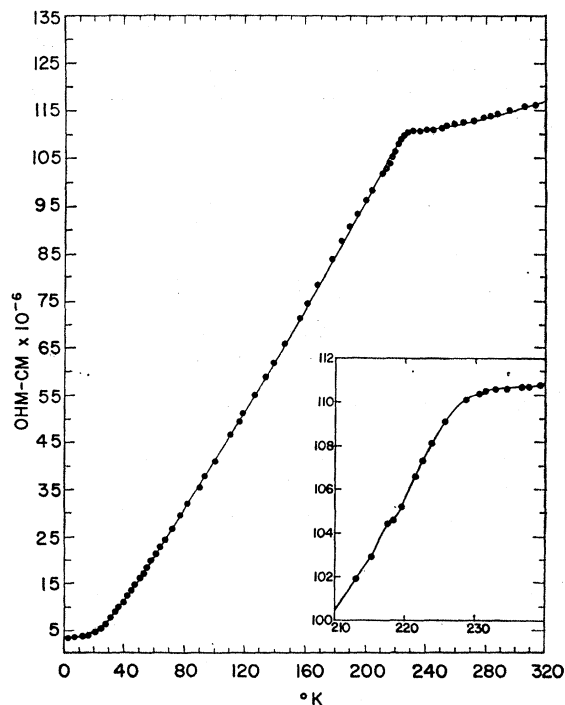


FIG. 3. Electrical resistivity of Tb vs temperature.

In Table I we show the results of spectrographic and other tests for impurities in the samples used in this work.

III. RESULTS

The electrical resistivities observed on the heavy rare-earth metals are shown in Figs. 2-8 and are discussed below:

Gadolinium. A sharp change in slope occurs in the resistivity of Gd between 291 and 292°K (Fig. 2). Measurements of magnetic moments,² thermal expan-

sion,⁷ thermoelectric effect⁸ and specific heat⁹ indicate abnormal behavior near this temperature and suggest that the sharp change in slope should be associated with ferromagnetic ordering.

Terbium. There is a sharp change in the slope of the resistivity curve for terbium at 229°K as seen in Fig. 3. A careful study of the resistivity just below this tem-

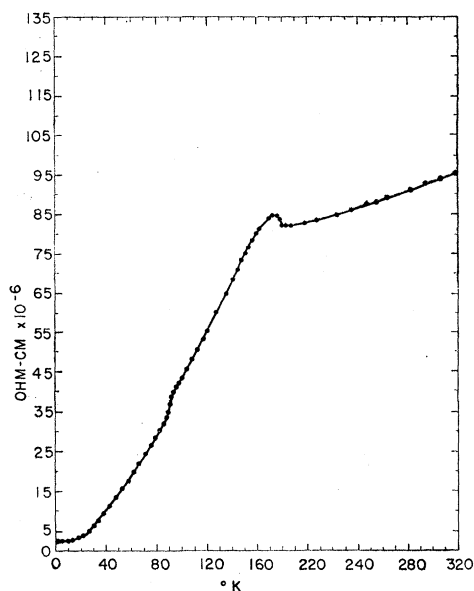


FIG. 4. Electrical resistivity of Dy vs temperature.

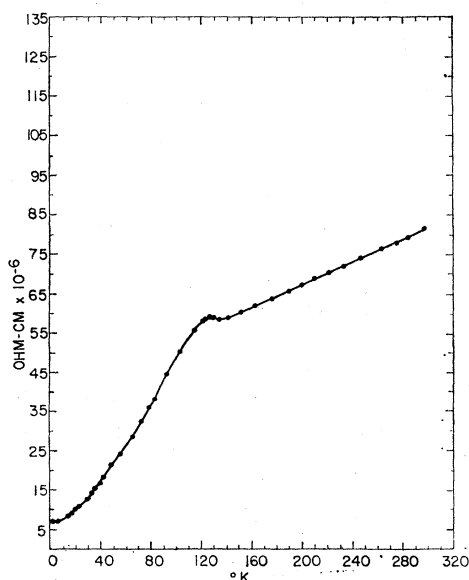


FIG. 5. Electrical resistivity of Ho vs temperature.

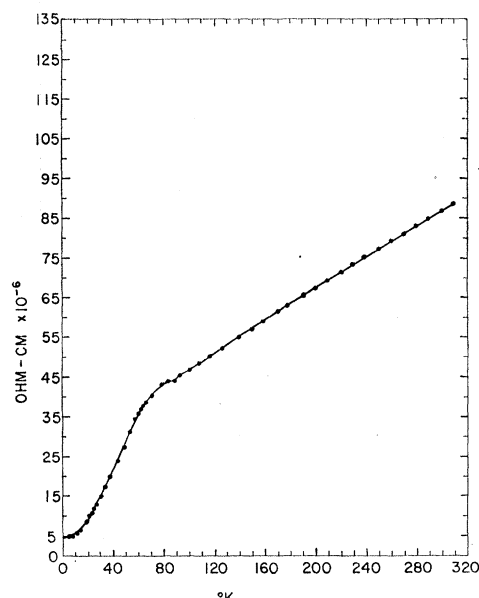


FIG. 6. Electrical resistivity of Er vs temperature.

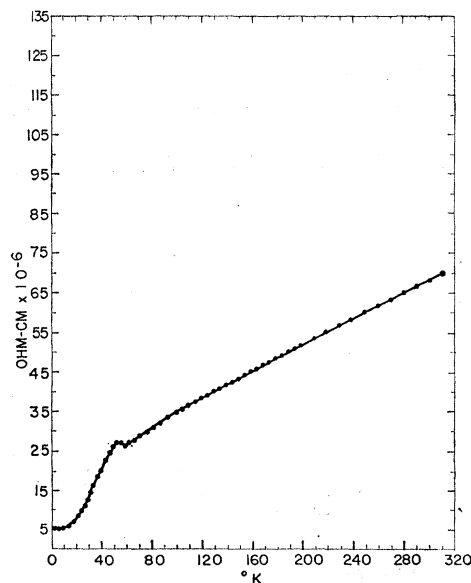


FIG. 7. Electrical resistivity of Tm vs temperature.

⁷ F. Barson, S. Legvold, and F. H. Spedding, *Phys. Rev.* **105**, 418 (1957).

⁸ H. Born, Ames, Iowa, 1959 (private communication).

⁹ M. Griffel, R. E. Skochdopole, and F. H. Spedding, *Phys. Rev.* **93**, 657 (1954).

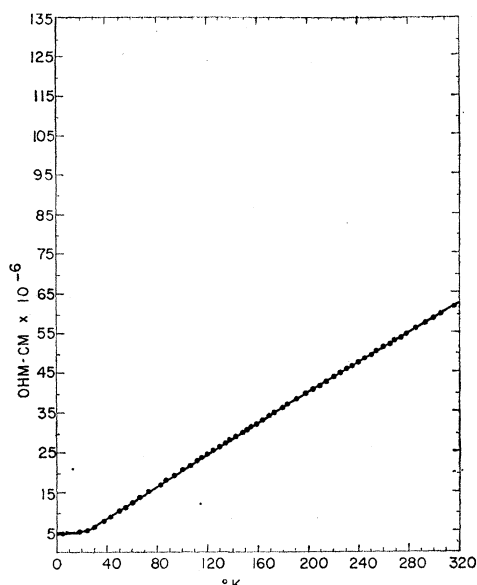


FIG. 8. Electrical resistivity of Lu vs temperature.

perature (see insert in figure) showed a slight increase in slope with increasing temperature at 219°K. Measurements of magnetic moments,¹⁰ specific heat,¹¹ thermal expansion⁷ and thermoelectric effect⁸ suggest that from 219°K to 229°K terbium is in a weak antiferromagnetic state and that below 219°K it is ferromagnetic.

Dysprosium. As seen in Fig. 4, a sharp increase in resistivity with increasing temperature occurs at 90°K. A peak was found at 174°K. This is in good agreement with the single crystal observations of Hall *et al.*⁴ An applied magnetic field of 22.4 kilo-oersteds will remove most of the peak and will suppress the resistivity jump at 90°K. Measurements of specific heat,¹² magnetic

moments,^{13,14} thermoelectric effect⁸ and thermal expansion⁷ suggest antiferromagnetism from 90°K to 174°K and ferromagnetism below 90°K.

Holmium. A change in slope (see Fig. 5) occurs near 19°K. A peak was found at 127°K. Measurements of specific heat,¹⁵ magnetic moments¹⁶ and thermoelectric effect⁸ suggest ferromagnetism below 19°K and antiferromagnetism from 19°K to 127°K.

Erbium. A pronounced minimum occurs in the curve for erbium at 80°K as seen in Fig. 6. All the points were taken with the temperature increasing from 4.2°K. Measurements of magnetic moments^{2,5,17} and specific heat¹⁸ suggest that the metal is ferromagnetic below 20°K and antiferromagnetic between 20° and 80°K. The ferro-antiferromagnetic transition is not detectable in the polycrystalline resistivity curve reported here.

Thulium. A peak occurs at 54.5°K. Measurements of specific heat¹⁹ and magnetic moments¹⁶ suggest Tm is antiferromagnetic below 54.5°K. The resistivity data below this temperature do not indicate a change to a ferromagnetic state.

Lutetium. The resistivity of Lu was found to be well behaved over the temperature region investigated.

TABLE II. Magnetic and residual resistivities (ohm cm $\times 10^{-6}$).

Element	ρ_{ext}	ρ_{res}	$\rho_{\text{mag}} = \rho_{\text{ext}} - \rho_{\text{res}}$
Gd	110.8	4.4	106.4
Tb	89.2	3.5	85.7
Dy	60.0	2.4	57.6
Ho	39.3	7.0	32.3
Er	28.3	4.7	23.6
Tm	20.5	5.6	14.9
Lu	4.4	4.5	-0.1

Measurements of specific heat¹⁹ and thermoelectric effect⁸ also indicate normal behavior for a metal.

IV. MAGNETIC DISORDER RESISTIVITY

Following proposals by Elliott,²⁰ Kasuya,²¹ Schmitt,²² deGennes and Friedel,²³ Coles,²⁴ and Weiss and Marotta²⁵ we may expect a contribution to the resistivity from

¹³ J. F. Elliott, S. Legvold, and F. H. Spedding, Phys. Rev. **94**, 1143 (1954).

¹⁴ D. R. Behrendt, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 1544 (1958).

¹⁵ B. C. Gerstein, M. Griffel, L. D. Jennings, R. E. Miller, R. E. Skochdopole, and F. H. Spedding, J. Chem. Phys. **27**, 394 (1957).

¹⁶ B. L. Rhodes, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 1547 (1958).

¹⁷ J. F. Elliott, S. Legvold, and F. H. Spedding, Phys. Rev. **100**, 1595 (1955).

¹⁸ R. E. Skochdopole, M. Griffel, and F. H. Spedding, J. Chem. Phys. **23**, 2258 (1955).

¹⁹ L. D. Jennings (private communication). (To be published.)

²⁰ R. J. Elliott, Phys. Rev. **94**, 564 (1954).

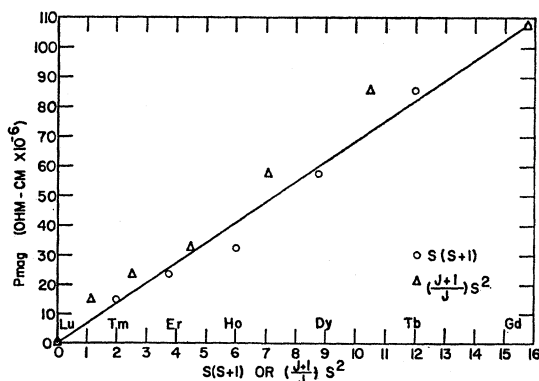
²¹ T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 58 (1956).

²² R. W. Schmitt, Phys. Rev. **103**, 83 (1956).

²³ P. G. deGennes and J. Friedel, J. Phys. Chem. Solids **4**, 71 (1958).

²⁴ B. R. Coles, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1958), Vol. 7, p. 40.

²⁵ R. J. Weiss and A. S. Marotta, J. Phys. Chem. Solids **9**, 302 (1959).

FIG. 9. The magnetic disorder contribution to the electrical resistivity vs $S(S+1)$ and $(J+1)S^2/J$ for the heavy rare earths, Gd to Lu.

¹⁰ W. C. Thoburn, S. Legvold, and F. H. Spedding, Phys. Rev. **112**, 56 (1958).

¹¹ L. D. Jennings, R. M. Stanton, and F. H. Spedding, J. Chem. Phys. **27**, 909 (1957).

¹² M. Griffel, R. E. Skochdopole, and F. H. Spedding, J. Chem. Phys. **25**, 75 (1956).

magnetic scattering. We consider the resistivity as a sum of the residual resistivity (ρ_{res}), the magnetic contribution (ρ_{mag}), and the phonon contribution (ρ_{ph}).

We assume that by extrapolating the linear high-temperature part of the resistivity curve back to zero degrees K we eliminate ρ_{ph} . The resistivity intercepts thus obtained are shown as ρ_{ext} in Table II. Also shown in Table II are the ρ_{res} and the ρ_{mag} . The latter are obtained by subtracting the ρ_{res} from the ρ_{ext} . This method is somewhat simpler than the method used by Anderson and Legvold²⁶ and follows the free electron model.²⁷ The two methods yield about the same results.

²⁶ G. S. Anderson and S. Legvold, Phys. Rev. Letters **1**, 322 (1958).

²⁷ A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, part 2, p. 499.

In Fig. 9 we have plotted the ρ_{mag} contributions as functions of two different parameters. The $S(S+1)$ parameter is the one used by Anderson and Legvold²⁶ and the parameter $[(J+1)/J]S^2$ has been suggested by Brout and Suhl.²⁸

ACKNOWLEDGMENTS

The authors are indebted to Dr. J. Powell for preparing the pure rare-earth salts needed, and to G. Wakefield and C. Habermann for producing the metal samples used. J. Alstad gave much valuable assistance in the treatment of data.

²⁸ R. Brout and H. Suhl, Phys. Rev. Letters **2**, 387 (1959).

Impurity Conduction at Low Concentrations*†

ALLEN MILLER‡ AND ELIHU ABRAHAMS

Physics Department, Rutgers University, New Brunswick, New Jersey

(Received June 23, 1960)

The conductivity of an n -type semiconductor has been calculated in the region of low-temperature T and low impurity concentration n_D . The model is that of phonon-induced electron hopping from donor site to donor site where a fraction K of the sites is vacant due to compensation. To first order in the electric field, the solution to the steady-state and current equations is shown to be equivalent to the solution of a linear resistance network. The network resistance is evaluated and the result shows that the T dependence of the resistivity is $\rho \propto \exp(\epsilon_3/kT)$. For small K , $\epsilon_3 = (e^2/\kappa_0)(4\pi n_D/3)^{1/3}(1-1.35K^{1/3})$, where κ_0 is the dielectric constant. At higher K , ϵ_3 and ρ attain a minimum near $K=0.5$. The dependence on n_D is extracted; the agreement of the latter and of ϵ_3 with experiment is satisfactory. The magnitude of ρ is in fair agreement with experiment. The influence of excited donor states on ρ is discussed.

I. INTRODUCTION

At sufficiently low temperatures, transport effects in doped semiconductors are not due to free carriers but occur as a result of charge transport between impurity states. The term *impurity conduction* denotes this type of transport. When the impurity concentration is high, the impurity states overlap strongly and lose their localized character. It is often said that an *impurity band* is formed and that conduction takes place in this "band." At low concentrations banding does not occur and conduction takes place by *hopping* of electrons from occupied to unoccupied localized donor states.

In recent years, many interesting experimental data on impurity transport have been published. Data are

available for the resistivity and Hall effect,¹⁻⁷ effects of strain,⁸ and magnetoresistance^{2,9} in the temperature range of impurity transport.

We restrict our discussion throughout to those cases in which impurity "banding" does not occur and the hopping process is important. The hopping process was suggested by Conwell¹⁰ and by Mott.¹¹ The same mechanism was independently proposed by Pines, Abrahams, and Anderson¹² in connection with the study of electron relaxation processes in Si.

¹ C. S. Hung and J. R. Gleissman, Phys. Rev. **79**, 726 (1950).

² H. Fritzsche, Phys. Rev. **99**, 406 (1955).

³ S. Koenig and G. Gunther-Mohr (Appendix by P. J. Price), J. Phys. Chem. Solids **2**, 268 (1957).

⁴ H. Fritzsche, J. Phys. Chem. Solids **6**, 69 (1958).

⁵ H. Fritzsche and K. Lark-Horovitz, Phys. Rev. **113**, 999 (1959).

⁶ T. A. Longo, R. K. Ray, and K. Lark-Horovitz, J. Phys. Chem. Solids **8**, 259 (1959).

⁷ J. S. Blakemore, Phil. Mag. **4**, 560 (1959).

⁸ H. Fritzsche, J. Phys. Chem. Solids **8**, 257 (1959).

⁹ R. Keyes and R. J. Sladek, J. Phys. Chem. Solids **1**, 143 (1956).

¹⁰ E. M. Conwell, Phys. Rev. **103**, 51 (1956).

¹¹ N. F. Mott, Can. J. Phys. **34**, 1356 (1956).

¹² D. Pines, Can. J. Phys. **34**, 1367 (1956).

* This work is based on a dissertation submitted by one of us in partial fulfillment of the requirements for the Ph.D. degree at Rutgers University.

† This work was supported in part by the Office of Naval Research.

‡ Present address: Physics Department, University of Illinois, Urbana, Illinois.