

## Theory of Impurity Scattering in Semiconductors

E. CONWELL\* AND V. F. WEISSKOPF†  
*University of Rochester, Rochester, New York*  
 (Received October 5, 1949)

Experiments by Lark-Horovitz and collaborators on the Hall effect and resistivity of germanium semiconductors have shown that the simple theory of lattice scattering alone cannot explain the temperature dependence of the resistivity. Another probable source of resistance is scattering by ionized impurity centers. This resistance can be calculated by using the Rutherford scattering formula. Evaluation of the collision terms in the Lorentz-Boltzmann equation of state is made by assuming that scattering of an electron by one ion is approximately independent of all other ions. This results in a resistivity given by (in ohm cm):

$$\rho = 2.11 \times 10^2 \kappa^{-2} T^{-1} \ln \{1 + 36 \kappa^2 d^2 (kT)^2 e^{-4}\},$$

where  $d$  is half the average distance between impurity ions and  $\kappa$  the dielectric constant of the semiconductor.

**E**XPERIMENTS on the electrical properties of germanium semiconductors yield curves for resistivity as a function of temperature which cannot be explained by the theory of lattice scattering alone. The temperature behavior of the mobility indicates the existence of another scattering mechanism, especially at low temperatures.<sup>1</sup> It was pointed out by Lark-Horovitz† that another obvious source of resistance is scattering by the ionized impurity centers. This contribution to the resistivity is calculated here. Due to their relatively small density, the conduction electrons in a semiconductor obey Maxwell-Boltzmann statistics. Since the electrons have thermal energies and correspondingly large wave-lengths, their motion can be considered free and their scattering by the impurity ions is given by the Rutherford formula. The problem is then one of calculating the resistivity arising from Rutherford scattering of electrons (or holes) by a random distribution of impurity ions.

The system of free electrons in a semiconductor acted upon by a constant external field is in a state of dynamic equilibrium when a steady current is flowing. This implies that the number of particles per unit volume of phase space remains constant in time. From this condition it is possible to derive the form of the distribution function when there is an applied field by following the classical development of Lorentz.<sup>2</sup>

Consider a small volume of phase space  $d\tau$  around  $x, y, z, v_x, v_y, v_z$ . Then  $f(x, y, z, v_x, v_y, v_z)d\tau$  is the number of particles in  $d\tau$  at time  $t$ . There are two ways in which this number may change: by acceleration by the electric field and by collisions. In a homogeneous isotropic medium, with uniform field  $E_z$  applied in the  $z$

direction, the rate of change due to the field is given by:<sup>3</sup>

$$\left(\frac{\partial f}{\partial t}\right)_{\text{drift}} = \frac{E_z e}{m} \frac{\partial f}{\partial v_z}, \quad (1)$$

where  $\partial f/\partial v_z$  is to be evaluated in the particular volume of phase space under consideration. The rate of change due to collision is given by:

$$(\partial f/\partial t)_{\text{collision}} = b - a, \quad (2)$$

where  $b$  represents the number of particles entering a unit volume of  $d\tau$  in unit time as a result of collisions and  $a$  represents the corresponding number leaving in a similar manner. In the steady state:

$$\frac{df}{dt} = \left(\frac{\partial f}{\partial t}\right)_{\text{drift}} + \left(\frac{\partial f}{\partial t}\right)_{\text{collision}} = 0 \quad (3)$$

or, using (1) and (2):

$$-\frac{E_z e}{m} \frac{\partial f}{\partial v_z} = b - a. \quad (4)$$

The calculation of the collision term is simplified by assuming (1) infinite mass for the scattering center, (2) perfectly elastic collisions, and (3) that scattering of an electron by one ion can be treated to a first approximation as independent of all other ions. As a result of the second assumption, only the direction of the electron velocity changes in a collision. It is convenient to introduce the spherical coordinates  $v, \theta, \varphi$  instead of  $v_x, v_y, v_z$ . According to the third assumption, the electron is scattered by one ion at a time, i.e., by the one to which it is closest. If  $2d$  is the average distance between nearest neighbor impurity ions, then, to this approximation, an electron is scattered by a particular ion only when it comes within distance  $d$  of that ion. As a result, one can express the number of electrons scattered out of unit volume of  $d\tau$  in unit time into the solid

\* Now at Brooklyn College, Brooklyn, New York.

† Now at Massachusetts Institute of Technology, Cambridge, Massachusetts. This paper was completed in 1943 and its publication was delayed by a number of circumstances.

<sup>1</sup> Lark-Horovitz, Middleton, Miller, and Walerstein, *Phys. Rev.* **69**, 258 (1946). K. Lark-Horovitz, Contractor's Final Report NDRC 14-585 (November, 1945), pp. 27-33.

‡ Personal communications.

<sup>2</sup> A. A. Lorentz, *Theory of Electrons* (G. E. Stechert and Company, New York, 1923), pp. 266.

<sup>3</sup> Reference 2, p. 268.

angle  $d\Omega'$  at  $\theta', \varphi'$  as:

$$f(v, \theta, \varphi)N\sigma(\theta, \theta')vd\Omega',$$

where  $N$  is the number of impurity ions per  $\text{cm}^3$ ,  $\sigma(\theta, \theta')$  the Rutherford scattering cross section,  $v$  the relative velocity of the electron and the scattering center (which, by the first assumption, is just the electron velocity). The term  $a$  is the integral of the above expression over  $\theta', \varphi'$ . From the previous considerations, however, it is apparent that the integration is not to be carried out over all  $\theta'$ . The limitation on impact parameter is equivalent to a limitation on  $\theta'$  which can be expressed by the relationship:

$$\tan[(\theta' - \theta)/2] = Ze^2/(\kappa mv^2\beta), \quad (5)$$

where  $\kappa$  is the dielectric constant of the medium and  $\beta$  the impact parameter. For the largest possible impact parameter,  $d$ :

$$\theta' - \theta = (\theta' - \theta)_{\min} = 2 \arctan Ze^2/(\kappa mv^2d). \quad (6)$$

This gives the lower limit for integration over  $\theta'$ . Since this formula and the Rutherford scattering cross section depend only on the change of direction or  $\theta' - \theta$ , it is possible to choose axes to set  $\theta$  equal to  $0^\circ$ . The expression for  $a$  is then:

$$a = Nv \int_{\theta'=\theta'_{\min}}^{\pi} \int_{\varphi'=0}^{2\pi} f(v, \theta, \varphi)\sigma(\theta')d\Omega'. \quad (7)$$

The term  $b$  is evaluated in much the same manner as  $a$ . The final result for  $b - a$  is:

$$b - a = Nv \int_{\theta'=\theta'_{\min}}^{\pi} \int_{\varphi'=0}^{2\pi} [f(v, \theta', \varphi') - f(v, 0, \varphi)]\sigma d\Omega'. \quad (8)$$

When substituted in (4) this gives the integral equation:

$$\begin{aligned} & -\frac{E_z e}{m} \left( \frac{\partial f}{\partial v_z} \right) \\ & = Nv \int_{\theta'=\theta'_{\min}}^{\pi} \int_{\varphi'=0}^{2\pi} [f(v, \theta', \varphi') - f(v, 0, \varphi)]\sigma d\Omega'. \quad (9) \end{aligned}$$

The form for the solution of this equation used by Lorentz and others in conductivity problems is suggested by physical considerations. The effect of applying the field is to superimpose on the random thermal motion a small net drift of electrons in the direction opposite to the field (in the field direction for conduction by holes). This suggests for the new distribution function the expression:

$$f = f_0 - v_z \chi(v) = f_0 - v \cos\theta \chi(v), \quad (10)$$

where

$$f_0 = A \exp(-mv^2/2kT); \quad A = n(m/2\pi kT)^{3/2}, \quad (11)$$

$n$  being the number of conduction electrons per  $\text{cm}^3$  and  $\chi(v)$  a function to be determined.

Since the additive term is much smaller than  $f_0$ , it can be neglected in evaluating  $(\partial f/\partial v_z)$  at  $v, 0, \varphi$ . Integration of  $b - a$  is completely straightforward. From Eq. (9) one obtains the following expression for  $\chi$ :

$$\chi(v) = \frac{\kappa^2 m^2 v^3 A E_z \exp(-mv^2/2kT)}{\pi N e^3 k T \ln G}, \quad (12)$$

where

$$G = 1 + \kappa^2 m^2 v^4 d^2 e^{-4}. \quad (13)$$

From  $\chi(v)$  either the mean free path for this type of scattering or the resistivity can be obtained simply. To obtain the former, one uses:<sup>2</sup>

$$\chi(v) = (l/v) e E_z [(\partial f_0)/(\partial \epsilon)] \quad (14)$$

which gives

$$l(v) = \kappa^2 m^2 v^4 / \pi N e^4 \ln G. \quad (15)$$

To obtain the resistivity, we use:<sup>4</sup>

$$j = \sigma E_z = -e \int_{v=0}^{\infty} \int_{\theta'=0}^{\pi} \int_{\varphi'=0}^{2\pi} v^4 \chi \cos^2 \theta' \sin \theta' dv d\theta' d\varphi'. \quad (16)$$

From (16), after integration over  $\theta', \varphi'$ , one gets

$$\sigma = \frac{2\kappa^2 m^2 A}{3N e^3 k T} \int_{v=0}^{\infty} \frac{v^7 \exp(-mv^2/2kT) dv}{\ln(1 + \kappa^2 m^2 v^4 d^2 e^{-4})}. \quad (17)$$

This integral converges. Since the logarithm is a slowly varying function, a good approximation to the value of the integral can be obtained by substituting for the logarithm its value at the maximum of the function in the numerator. This maximum occurs at

$$v^2 = 6kT/m. \quad (18)$$

The simplified integral is readily evaluated. This yields a resistivity (in ohm cm) (all constants in c.g.s. units):

$$\rho = 9 \times 10^{11} \pi^{3/2} e^2 m^{3/2} 2^{-7/2} \kappa^{-2} (kT)^{-3/2} \times \ln\{1 + 36\kappa^2 d^2 (kT)^2 e^{-4}\}. \quad (19)$$

When there is no intrinsic\* conductivity,  $n$  is equal to  $N$ , the number of ionized impurity centers and hence  $N$  and  $n$  do not explicitly appear in Eq. (19). So the dependence on the density of impurity centers occurs only in the logarithmic term, through the factor  $d^2$ .

Generally the temperature behavior of the resistivity due to impurity scattering is more strongly influenced by the  $T^{-3/2}$  in Eq. (19) than by the  $T^2$  term in the logarithm, and hence this resistivity rises as the temperature decreases. This increase is due to the decrease of mean electron velocity with drop in  $T$  and the consequent increase in the scattering effect of the impurity

<sup>4</sup> Reference 2, p. 272.

\* Observed at higher temperature, due to electrons in the conduction band equal in number to the holes in the full band.

ions. On the other hand, for an impurity semiconductor, the resistivity due to lattice scattering generally decreases with decreasing temperature because of the  $T^{-1}$  dependence of the mean free path.<sup>5</sup> Hence, the im-

portance of the impurity ion scattering resistivity in determining total resistivity increases as temperature decreases.<sup>6</sup>

<sup>5</sup> A. Sommerfeld and H. Bethe, *Handbuch der Physik XXIV* (1933), Vol. 12, p. 560.

<sup>6</sup> K. Lark-Horovitz and V. A. Johnson, *Phys. Rev.* **69**, 258 (1946). K. Lark-Horovitz, Contractor's Final Report, NDRC 14-585 (November, 1945), pp. 36-41.

## Evaluation of the Stiffness Coefficients for Beryllium from Ultrasonic Measurements in Polycrystalline and Single Crystal Specimens\*

LOUIS GOLD

*Air Force Cambridge Research Laboratories, Cambridge, Massachusetts*

(Received August 15, 1949)

The pulsed ultrasonic method has been applied to the determination of the stiffness coefficients for beryllium. The constants  $c_{11}=30.8 \times 10^{11}$  dynes/cm<sup>2</sup>,  $c_{33}=35.7$  were evaluated from compressional wave velocities in single crystals by extrapolating a plot of the effective stiffness coefficient *versus*  $\sin^2\theta$  ( $\theta$  being the angle between the hexagonal axis and the direction of wave propagation) to the points  $\theta=\pi/2$  and 0. The values  $c_{12}=-5.8$ ,  $c_{44}=11.0$  were derived from an analysis relating the average effective stiffness coefficients for compressional and shear waves with the shear modulus and Lamé's constant. The latter data were calculated from measurements of longitudinal and transverse body wave velocities in polycrystalline metal. To find

the coefficient  $c_{13}=0.87$ , the established values for the other constants were employed in the general relation for the effective stiffness coefficient of the form  $C_{ij}=f(c_{ijk's}, \theta)$ .

Several criteria have been used to assess the validity of the  $c_{ijk}$  data: (1) The ratio of  $c_{11}/c_{33}$  is in accord with the  $c/a$  ratio for the hexagonal close-packed structure of beryllium; (2) the compressional and shear wave anisotropy factors of  $c_{33}/c_{11}=1.16$  and  $c_{44}/\frac{1}{2}(c_{11}-c_{12})=1.68$ , respectively are in harmony with the observed transmission properties of polycrystalline beryllium; and (3) the experimental and theoretical curves for the directional variation of the effective compressional stiffness coefficient agree quite well.

### 1. INTRODUCTION

THE literature contains the stiffness coefficients of only three hexagonal metals, these being magnesium, zinc, and cadmium.<sup>1</sup> Some recent work on the preparation of large beryllium crystals has made available several adequate-sized single crystals of beryllium for ultrasonic velocity measurements from which the  $c_{jk}$  constants were determined.<sup>2</sup>

It was found that essentially all of the crystal specimens were so oriented that measurements along ideal directions were virtually precluded. This condition eliminated any hope of obtaining the best possible accuracy, and, therefore, redetermination would be warranted when better crystals could be had. Nevertheless, the values for the  $c_{jk's}$  of beryllium are determinable to the order of accuracy common to the other hexagonal metals.

The method employed for evaluating the stiffness coefficients of beryllium is unique and has not been reported previously. It is based upon the following experimental data:

- (1) Compressional and shear wave velocities in polycrystalline metal.
- (2) Compressional wave velocities in single crystal

specimens having their crystallographic axes differently oriented with respect to the direction of propagation. Deriving the coefficients from this information requires the conditions, (1) the crystal belongs to classes 21-27 of Voigt's designation, thus having five independent constants, (2) the crystal is not too anisotropic.

The first of these conditions permits one to considerably simplify the expressions for the various wave velocities;<sup>3</sup> the functions  $v=f(\alpha, \beta, \gamma, c_{jk's}, \rho)$  can be reduced to  $v=F(\theta, c_{jk's}, \rho)$  where  $\theta$ , the angle between the hexagonal axis and the direction of wave propagation, takes the place of the three direction cosines  $\alpha, \beta$ , and  $\gamma$ . The second condition makes possible certain extrapolation and approximations which will be described in detail. If the crystal is too anisotropic it becomes very difficult to obtain velocity data for polycrystalline specimens because of the poor multiple echo patterns.<sup>4</sup> Beryllium exhibited excellent patterns, so it appeared reasonable at the outset to infer that it was not a highly anisotropic crystal. The significance of this feature will be accounted for later.

### 2. EXPERIMENTAL ASPECTS

Apparatus for the pulsed-ultrasonic measurements was of the nature already described in a number of

\* This paper is based on work performed at the Metallurgical Project, Massachusetts Institute of Technology, under Contract No. W-7405-eng-175 for the AEC.

<sup>1</sup> R. F. S. Hearmon, *Rev. Mod. Phys.* **18**, 409 (1946).

<sup>2</sup> L. Gold, *Rev. Sci. Inst.* **20**, 115 (1949).

<sup>3</sup> H. E. Mueller (private communication).

<sup>4</sup> W. P. Mason and H. J. McSkimin, *J. Acous. Soc. Am.* **19**, 464 (1947). W. Roth, *J. App. Phys.* **19**, 901 (1947).