If a critical drift velocity  $v_{dc}$  is defined as that velocity at which the Ohm's law and the  $E^{\frac{1}{2}}$  regions intersect when extrapolated, we obtain from Eqs. (3) and (4) a critical drift velocity given by

$$v_{dc} = (1.23)^2 c = 1.51c, \tag{5}$$

and a corresponding critical field given by

$$E_c = 1.51c/\mu_0.$$
 (6)

Table I shows a comparison of the experimental and calculated values of critical drift velocity and critical field for silicon and germanium at 298°K. The observed values are from two to four times those calculated from Eqs. (5) and (6). Evidently then, electrons and holes are able to deliver their energy to the lattice up to higher fields than simple theory would predict. Shockley has proposed that the constant energy surfaces in the Brillouin zone are nonspherical and deeply re-entrant.<sup>2</sup> This concept serves also to explain the magnetoresistance increase of some sevenfold found by Suhl.<sup>11</sup>

<sup>11</sup> H. Suhl, Phys. Rev. 78, 646 (1950).

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In the saturation range at the higher fields the electrons are "heated" sufficiently so that they can transfer energy to optical modes of lattice vibration. These modes are much more effective than the acoustical modes in absorbing energy from the electrons. Theory predicts that the drift velocity is independent of the field in this range and is of the order of  $6(10)^6$  cm per sec.<sup>2</sup> This value is in very good agreement with that shown in Figs. 2 and 5 for *p*-type and *n*-type germanium at room temperature and is in fair agreement with the observed value of  $8(10)^6$  shown in Fig. 3 for *n*-type silicon.

The author is indebted to many of his associates for their assistance in this work and, in particular, to W. Shockley for his encouragement and advice.

Note added in proof:-In Fig. 2 the low field mobility of holes varies as  $T^{-1.5}$  for the particular sample of germanium which was used. F. Morin and M. Prince (private communication) find a similar dependence for somewhat impure material and a  $T^{-2.3}$ dependence for purer material.

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### High Field Mobility in Germanium with Impurity Scattering Dominant\*

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Experimental measurements show a variation of mobility with electric field intensity of electrons in n type germanium which differs at 20°K from that observed in the same specimen at 77°K and higher temperatures. This difference can be accounted for by scattering by ionized impurities. A crude quantitative treatment is carried out along the lines of Shockley's treatment for the case of lattice scattering. As in that case, the resulting theory fits the data well if the rate of energy loss is taken several times higher than that given by the theory assuming that the surfaces of constant energy are spherical.

#### INTRODUCTION

**T**SING a pulse technique to apply high voltages to a sample of n type germanium, Ryder<sup>1</sup> has obtained the data shown in Fig. 1 for current density vs electric field intensity at 77°K and 20°K. Since the number of carriers and the temperature of the sample are kept constant, Ryder's experiment measures essentially the variation of drift velocity or mobility with electric field intensity at constant lattice temperature.<sup>1a</sup>

Now with Sylvania Electric Products, Inc., Bayside, New York. <sup>1</sup> E. J. Ryder (preceding paper), Phys. Rev. **90**, 766 (1953).

The significance of Ryder's data can perhaps be made clearer if they are replotted as mobility vs electric field intensity. This plot is shown in Fig. 2. The number of conduction electrons per unit volume was taken from Hall effect data.

The 77° behavior is of the same type as has been observed previously in samples at 77°K and higher temperatures. It has been explained by Shockley in the following way.<sup>2,3</sup> In the samples which show this behavior mobility is determined by interaction with acoustical modes of lattice vibration. This mechanism. at these temperatures, gives rise to a constant mean free path and isotropic scattering. In low fields, the

<sup>\*</sup> Presented at the Washington meeting of the American Physical Society, May 1, 1952. Also presented in preliminary form at the Twelfth Annual Conference on Physical Electronics, Massachusetts Institute of Technology. Figure 1 in the written report of this conference is incorrect, however. The corrected version constitutes Fig. 2 of this paper. † On leave from Brooklyn College, Brooklyn, New York.

<sup>&</sup>lt;sup>1a</sup> Note added in proof.—A similar, although steeper, increase of current density with voltage has been observed at 4°K by Sclar, Burstein, Turner, and Davisson, Bull. Am. Phys. Soc. 28, No. 2, 17 (1953) and attributed by them to increase in carrier density through impact ionization of neutral impurities. The current pulses

in their experiment had a visible rise time for fields beyond the breakdown field, as would be expected for the mechanism of impact ionization, while the pulses in Ryder's case were flat. <sup>2</sup> W. Shockley, Bell System Tech. J. **30**, 990 (1951).

<sup>&</sup>lt;sup>a</sup> W. Snockley, Bell System 1ecf. J. **50**, 990 (1951). <sup>a</sup> The problem of electron drift in high fields was treated earlier in essentially this manner by H. Frohlich and F. Seitz, Phys. Rev. **79**, 526 (1950), and F. Seitz, Phys. Rev. **76**, 1376 (1950). The Seitz paper also contains a review of the literature.



FIG. 1. Current density and drift velocity vs electric field intensity for a sample of n-type germanium at 20°K and 77°K.

electrons are able to dissipate in collisions with the lattice the power they get from the electric field without an appreciable rise in their "temperature." As long as this is the case, they have a constant collision rate and constant mobility of  $\mu_0$ . When the field becomes high enough, the electron "temperature" is raised, the rate of collision increases, and the mobility decreases. After a short transition region, the mobility is observed to be proportional to  $E^{-\frac{1}{2}}$  or the drift velocity to  $E^{\frac{1}{2}}$ , which has also been derived theoretically.<sup>2</sup>

In the case of the data at 20°K, scattering by ionized impurities is more important than lattice scattering for electron temperatures of the order of the lattice temperature. Scattering by ionized impurities is Rutherford scattering, with a differential x-section proportional to  $1/v^4$ . When the average electron speed is increased by a high field, the deflection of an electron passing an ionized impurity is decreased, and the average drift velocity the electrons can develop per unit field is increased. This increase in mobility means in turn an increased rate of power input from the field. As a result, the mobility has an initial steep increase. After a small range of fields, this increase results in the impurity scattering becoming less effective than the lattice scattering, and the  $E^{-\frac{1}{2}}$  variation characteristic of that mechanism sets in. The deviation from this which is observed at the highest fields obtained will be discussed later.

#### QUANTITATIVE THEORY OF THE VARIATION OF MOBILITY WITH FIELD

A quantitative treatment for the case with impurity scattering dominant at low fields will now be carried out under the assumption that the surfaces of constant energy in the Brillouin Zone are spherical. Although there is reason to suspect that this assumption is not true,<sup>4</sup> such a treatment, it will be seen, leads to semiquantitative agreement with experiment. Under this assumption it can be shown that the mobility  $\mu$  is related to the relaxation time  $\tau$  by

$$\mu = \frac{q}{3m} \left\langle \frac{1}{v^2} \frac{d}{dv} (\tau v^3) \right\rangle,\tag{1}$$

where q and m are the electron charge and effective mass, respectively, and the average indicated is to be taken over all electrons.<sup>5</sup> This is valid at high as well as low electric fields provided the energy loss of an electron in a collision is small, which is the case for the scattering mechanisms involved here.

Under the assumption that equipartition is valid for the lattice oscillators which the electron interacts with, the relaxation time for lattice scattering,  $\tau_L$ , is given by

$$\tau_L = l/v, \tag{2}$$

where l, the mean free path, is independent of electron velocity.6 Since the range of velocities over which the impurity scattering term contributes is small, the log term in the relaxation time for impurity scattering can be considered constant, and  $\tau_I$  is given by<sup>7</sup>

$$\tau_I = B v^3. \tag{3}$$

The relaxation processes are additive, giving

$$\tau = \tau_I \tau_L / (\tau_I + \tau_L). \tag{4}$$

When Eqs. (2) through (4) are substituted in Eq. (1), one obtains

$$\mu = (2q/3m) \langle \tau_L (1 + 3\tau_L/\tau_I) / (1 + \tau_L/\tau_I)^2 \rangle.$$
 (5)

To carry out this averaging and complete the solution of the problem rigorously, it is necessary to solve the Boltzmann equation to find the velocity distribution at all fields. A crude but mathematically much simpler treatment was used instead. This is described in the next section.

#### APPROXIMATE TREATMENT OF STEADY STATE DISTRIBUTION

This treatment makes use of the fact that in the steady state average power gain from the field must balance average power loss in collisions, or symbolically,

$$q\mu E^2 + \left[ d\mathcal{E}/dt \right]_c = 0, \tag{6}$$

where  $\left\lceil d\mathcal{E}/dt \right\rceil_c$  represents power loss in collisions. Both  $\mu$  and  $\left[ d\mathcal{E}/dt \right]_c$  can be expressed as averages over the electron distribution of some function of velocity, this being Eq. (5) for the former. If the electrons are assumed to have some simple velocity distribution, such as a  $\delta$ -function, the averaging can be carried out and the resulting functions of v substituted in Eq. (6). The solution of this equation in the case of the  $\delta$ -function distribution, gives the electron speed as a function of electric field intensity. This combined with Eq. (5) gives the

<sup>&</sup>lt;sup>4</sup> Pearson, Haynes, and Shockley, Phys. Rev. 78, 295 (1950).

<sup>&</sup>lt;sup>5</sup> E. Conwell, Phys. Rev. 88, 1379 (1952).

<sup>&</sup>lt;sup>6</sup> W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), Chap. 17. <sup>7</sup> E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950).

variation of  $\mu$  with electric field intensity. Such a procedure will give the correct dependence of  $\mu$  on E. except for a multiplying factor of the order of 1, when  $\mu$  and  $\left[ \frac{d\mathcal{E}}{dt} \right]_c$  are both in the form of a constant times  $\langle v^n \rangle$ , *n* of course being different for the two. This is the case in the regions of constant slope in the log-log plot.

The calculation indicated was carried out for a  $\delta$ -function distribution. From Eqs. (1) through (3) the impurity mobility  $\mu_I$  and the lattice mobility  $\mu_L$  for such a distribution are

$$\mu_I = (2q/m)Bv^3, \tag{7a}$$

$$\mu_L = (2/3)(q/m)(l/v), \tag{7b}$$

and in terms of these

$$\mu = \mu_L (1 + 9\mu_L/\mu_I) / (1 + 3\mu_L/\mu_I)^2. \tag{8}$$

It will be useful for what follows to use the dimensionless quantities x and a defined by

$$x = v/v_0,$$
 (9a)  
 $a = 3\mu_{L0}/\mu_{I0},$  (9b)

$$a = 3\mu_{L0}/\mu_{I0},$$
 (9)

where the subscript 0 indicates the value of the quantity in a small electric field. In terms of these, Eq. (8) can be written,

$$\mu = (\mu_{L0}/x) [(1+3a/x^4)/(1+a/x^4)^2].$$
(10)

It is easily seen that this gives the type of behavior shown in Fig. 2. At low fields, from the definition,  $x \simeq 1$  and this gives the low field mobility. As the field increases, x starts to increase from 1. For large a, or dominant impurity scattering at low fields, this gives the 20° behavior as x increases. For small a, this gives the 77° behavior.

We consider now the power loss terms. Losses to ionized impurities are certainly small, and will be neglected. The rate of energy loss to acoustical lattice modes has been evaluated by Shockley for the case in which equipartition is valid for the lattice oscillators the electron interacts with.<sup>2</sup> For the  $\delta$ -function distribution his result is

$$\left[d\mathcal{E}/dt\right]_{c} = -\left(v/l\right)\left[\left(mc^{2}/kT\right)mv^{2} - 4mc^{2}\right], \quad (11)$$

where c is the average velocity of sound in the lattice. The condition that there be thermal equilibrium between electrons and lattice in the absence of the field requires that this expression vanish when  $v = v_0$ , or

$$v_0 = (4kT/m)^{\frac{1}{2}}.$$
 (12)

If Eq. (7b) is used to eliminate l from Eq. (11), it can be written in the form

$$[d\mathcal{E}/dt]_{c} = -(8/3)(qc^{2}/\mu_{L0})x^{3}(1-1/x^{2}).$$
(13)

The substitution of Eqs. (10) and (13) in the conservation of energy equation leads to the desired relationship between v, which is proportional to x, and E. Since this equation is of eighth degree in x and second degree in E, it was solved for E in terms of x, giving

$$E = (8/3)^{\frac{1}{2}} \frac{c}{\mu_{L0}} \left[ x^4 (1 - 1/x^2) \frac{(1 + a/x^4)^2}{1 + 3a/x^4} \right]^{\frac{1}{2}}.$$
 (14)

The drift velocity can then also be expressed in terms of x by using  $v_d = \mu E$ , leading to

$$v_d = (8/3)^{\frac{1}{2}} c \left[ x^2 (1 - 1/x^2) \frac{1 + 3a/x^4}{(1 + a/x^4)^2} \right]^{\frac{1}{2}}.$$
 (15)

## COMPARISON WITH EXPERIMENT

The density of conduction electrons at 20°, taken from Hall measurements, was  $8.7 \times 10^{13}$ /cm<sup>3</sup>. The average velocity of sound in germanium is taken, somewhat arbitrarily, as the velocity measured in the [110] direction,  $5.4 \times 10^5$  cm/sec. The value of *a*, which determines the shape of the curve, cannot be computed theoretically because the acceptor concentration in the sample is unknown. The closest approximation to the shape was obtained for a=9. To fit the low field data with this value of a,  $\mu_{L0}$  must be taken as  $2.56 \times 10^5$ cm<sup>2</sup>/volt sec. The value obtained for 20°K by taking the lattice mobility at room temperature as 3600 and assuming the theoretically predicted  $T^{-\frac{3}{2}}$  dependence<sup>6</sup> is  $2.12 \times 10^5$  cm<sup>2</sup>/volt sec. There is evidence, however, from other germanium data that the lattice mobility decreases somewhat more steeply than  $T^{-\frac{3}{2}}$  and is perhaps even higher than  $2.56 \times 10^5$  at  $20^{\circ}$ K.<sup>8</sup> These values of a and  $\mu_{L0}$  fix  $\mu_{I0}$  as  $8.5 \times 10^4$  cm/volt sec. If the effective mass of the electron is taken as one-quarter the free electron mass,<sup>9</sup> this leads to a total ionized impurity concentration of about  $4 \times 10^{14}$ /cm<sup>3</sup>, which is a reasonable value for this particular sample.

With these numerical values, it is found that the departure from constant mobility and the transition to the  $1/\sqrt{E}$  dependence of  $\mu$  all take place at fields about one-third as high as those found experimentally. If a factor of 2.8 is inserted on the right side of Eq. (14), the theoretical curve agrees quite well with the experimental one, as is shown in Fig. 1. It can be shown that this discrepancy is not a result of the use of a  $\delta$ -function distribution. An exact theory, based on spherical energy surfaces, has been obtaind by Shockley for the case in



FIG. 2. Mobility vs electric field intensity for a sample of n-type germanium at 20°K and 77°K.

<sup>8</sup> P. P. Debye, Bell Laboratories (private communication). <sup>9</sup> Experimental evidence for such a value of m is presented by P. P. Debye and E. Conwell, Phys. Rev. 87, 1131 (1952).

which the scattering is entirely due to lattice vibrations.<sup>2</sup> In the analysis of a number of samples with lattice scattering only, he found it necessary to multiply by a factor of 3.2 to obtain agreement of this exact theory with experiment. Comparison of the lattice scattering part of the 20° data with this theory shows about the same discrepancy.

Since the value of the mobility could not be incorrect by such a factor, this disagreement would seem to indicate that the rate of energy loss in collisions is higher than the previous considerations indicate by a factor of about nine. This could be the case, as Shockley points out, if the edge of the conduction band were degenerate. This would give rise to complex energy surfaces, which might give more effective energy dissipation for the electrons without affecting their mobility.

The imperfect fit in the region of sharp ascent can be ascribed to two factors: (1) the crude theoretical treatment, and (2) nonuniformity of the field in the sample because of variations in impurity concentration and cross section. It is also observed that at the very highest fields obtained, the experimental points fall below the line of slope  $\frac{1}{2}$ . This is expected if equipartition ceases to be valid for the lattice oscillators which scatter the electron, as can be seen from the following considerations. The probability of scattering of an electron by a particular mode of lattice vibration is proportional to the dilatation or deformation produced by the mode, which is in turn proportional to its energy. As the electron gets faster, it interacts with

shorter lattice waves. Under equipartition, fast electrons see no bigger deformation than slow ones, and the mean free path is independent of electron velocity. When the energy of the lattice oscillators is essentially the zero point energy, however, faster electrons see a more deformed lattice, and this leads to a mean free path which decreases with v or x, and a mobility which decreases more rapidly than 1/v or 1/x. At the field intensity for which the departure from the line of slope  $\frac{1}{2}$  becomes evident, the electron speed has been multiplied by a factor of about 6. If the effective mass of the electron were the free electron mass, the departure from equipartition should occur at much lower fields. An electron of smaller effective mass, however, would have smaller momentum for the same energy, and therefore interact with phonons of smaller energy. To account for the validity of equipartition out to the high fields observed, the effective mass would have to be of the order of one-sixth the mass of a free electron, which is in fair agreement with the previously stated value.

It can be concluded that a combination of scattering by ionized impurities and lattice vibrations accounts semiquantitatively for the variation of mobility with field that has been observed by Ryder. It is quite satisfactory, in the present state of the theory, that application of a theory assuming spherical energy surfaces to this case shows the same discrepancy as it does in the case where only lattice scattering is present.

I am indebted to Dr. W. Shockley for a number of valuable discussions on this subject.

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# Surface Barrier Analysis for the Highly Refractory Metals by Means of Schottky Deviations\*

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The theory for the deviation from the Schottky effect is redeveloped for the thermionic case, using the Herring and Nichols coefficients  $\mu$  and  $\lambda$ , which are typical of the two reflection regions of the metallic surface barrier. The assumptions of Guth and Mullin are used, but correction of their calculations leads to new results; a method of data analysis based on these results is described. In this method the Guth-Mullin assumptions regarding the form of the barrier are taken as a first approximation to the real case. The method is applied to available experimental data on tungsten, tantalum, and molybdenum. One may draw the following conclusions: The outer  $(\lambda)$  reflection region behaves in accordance with the mirror-image law, while the innermost ( $\mu$ ) is field-independent. The phase change suffered by an electron wave crossing the  $\mu$ -region is less than that computed for the theoretical box model. All three metals studied are mutually similar as regards the potential form in the  $\mu$ -region. Apparently, it is not yet possible to evaluate the zero-field reflection coefficient from deviation amplitudes; this is probably due to the parabolic approximation used for the  $\lambda$ -region in the theory.

## I. INTRODUCTION

HE phenomenon of periodic deviations from the Schottky effect<sup>1-3</sup> has been accounted for by

<sup>\*</sup> This research was sponsored by the U. S. Navy Bureau of Ships.

Now at the U.S. Naval Ordnance Test Station, Inyokern, California.

Guth and Mullin<sup>4</sup> in terms of the interference between electron waves reflected from the emitter surface and the region of the barrier maximum. Herring and

 <sup>&</sup>lt;sup>1</sup> R. L. E. Seifert and T. E. Phipps, Phys. Rev. 56, 652 (1939).
<sup>2</sup> D. Turnbull and T. E. Phipps, Phys. Rev. 56, 663 (1939).
<sup>3</sup> Munick, LaBerge, and Coomes, Phys. Rev. 80, 887 (1950).
<sup>4</sup> E. Guth and C. J. Mullin, Phys. Rev. 59, 575 (1941).