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FERMI LEVELS IN SEMICONDUCTORS

by R. A. HUTNER, E. S. RITTNER and F. K. DU PRÉ^{*)}

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Summary

General formulae for determining the Fermi level and the density of free charge carriers in semiconductors are derived. Special semiconductor models are considered in detail and a few applications are discussed.

Résumé

Calcul de formules générales pour la détermination du niveau de Fermi et de la densité des porteurs de charge libres dans les semi-conducteurs. Les auteurs étudient en détail des modèles spéciaux de semi-conducteurs et discutent un certain nombre d'applications.

Zusammenfassung

Es werden allgemeine Formeln abgeleitet zur Bestimmung des Fermi-Niveaus und der Dichte der freien Ladungsträger in Halbleitern. Besondere Halbleitermodelle werden im einzelnen betrachtet und einige Anwendungen besprochen.

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1. Introduction

The Fermi-level concept is important in the theory of the electrical properties of solids, and particularly so in the case of semiconductors. For example, the general formula for thermionic emission current density is¹⁾

$$i = AT^2 e^{-(\chi-\zeta)/kT},$$

where χ is the electron affinity and ζ the position of the Fermi level with respect to the origin at the bottom of the conduction band. Furthermore,

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in the case of semiconductors, the conductivity, σ , and the Hall constant, R , are strongly dependent on the position of the Fermi level. This is readily illustrated for a conductor with only one type of charge carrier, assuming the mean free path, l , to be independent of velocity, by the formulae²⁾

$$\sigma = \frac{16\pi}{3} \frac{me^2}{h^3} l k T \ln (1 + e^{\zeta/kT}),$$

and

$$R = \pm \frac{3\pi}{8ec} \frac{G(\zeta/kT)}{n(\zeta, T)},$$

where $n(\zeta, T)$ is given below by either eq. (11a) or (11b), and $G(\zeta/kT)$ is a complicated expression, the value of which varies between unity and $8/3\pi$.

In section 2, general formulae are derived for determining the positions of the Fermi level in semiconductors^{*)}. In the remaining sections, these formulae are used to calculate the Fermi levels for special models, and some applications of the results are briefly discussed.

2. Derivation of the general formula for determining the Fermi level

Let us consider a general model of a semiconductor comprising a full band, a conduction band, and a series of localized impurity energy levels in the forbidden region (fig. 1).

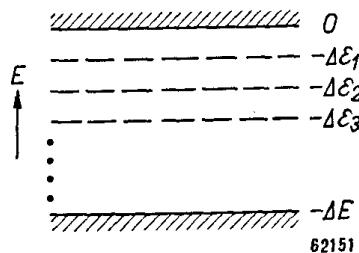


Fig. 1.

We assume that the charge carriers in the conduction band or in the full band behave like a free-electron gas or a free-hole gas, respectively. For simplicity, we neglect any change in the position of the localized levels which might occur as the concentration of the impurities is increased.

At $T = 0$ °K, let N be the number of electrons per cm^3 in the full band and N_d the number of electrons per cm^3 in the impurity levels; N_d is not necessarily equal to the total number of impurity states per cm^3 . Then, at any temperature,

$$\int_{-\infty}^{\infty} n(E) f(E) dE = N + N_d, \quad (1)$$

^{*)} The method used is essentially that given by Seitz³⁾ as a modification of Wilson's derivation.

where $n(E)dE$ is the number of energy states per cm^3 with energies between E and $E + dE$, and $f(E)$ is the probability that a given level is occupied.

For Fermi-Dirac statistics eq. (1) becomes

$$\int_{-\infty}^{\infty} \frac{n(E)}{e^{(E-\zeta)/kT} + 1} dE = N + N_d, \quad (2)$$

where ζ is the Fermi energy level or the thermodynamic potential per electron.

In order to evaluate the above integral, we divide the energy scale into three regions: $E > 0$, $-ΔE < E < 0$, and $E < -ΔE$.

For $E > 0$, the density of states for the lower part of the conduction band is³)

$$n(E) = \frac{4\pi}{h^3} (2m_e)^{3/2} E^{1/2}, \quad (3)$$

where m_e is the effective mass of the electrons.

For $-ΔE < E < 0$, let $n(E)$ at each impurity level be represented by a Dirac δ-function; then

$$n(E) = \sum_i n_i \delta(E + Δε_i), \quad (4)$$

where n_i is the total number of states per cm^3 corresponding to the i th impurity, and $Δε_i$ measures the position of the i th impurity level below the conduction band.

For $E < -ΔE$, the density of states for the upper part of the full band is

$$n(E) = \frac{4\pi}{h^3} (2m_h)^{3/2} (|E| - ΔE)^{1/2}. \quad (5)$$

In this region the number of electrons per cm^3 at any temperature equals N minus the number of holes per cm^3 .

When eqs (3), (4) and (5) are substituted in eq. (2), the latter becomes

$$\begin{aligned} & \frac{4\pi}{h^3} (2m_e)^{3/2} \int_0^{\infty} \frac{E^{1/2}}{e^{(E-\zeta)/kT} + 1} dE + \int_{-ΔE}^0 \frac{\sum_i n_i \delta(E + Δε_i)}{e^{(E-\zeta)/kT} + 1} dE + \\ & + N - \frac{4\pi}{h^3} (2m_h)^{3/2} \int_{ΔE}^{\infty} \frac{(E - ΔE)^{1/2}}{e^{(E-\zeta)/kT} + 1} dE = N + N_d. \end{aligned} \quad (6)$$

Let

$$P = \frac{2(2\pi m_e k T)^{3/2}}{h^3}, \quad (7)$$

$$Q = \frac{2(2\pi m_h k T)^{3/2}}{h^3}, \quad (8)$$

$$F(\eta) = \int_0^{\infty} \frac{x^{1/2} dx}{e^{x-\eta} + 1}, \quad (9)$$

and

$$\eta = \zeta/kT. \quad (10)$$

Then eq. (6) becomes

$$\frac{2P}{\sqrt{\pi}} F(\eta) + \sum_i \frac{n_i}{e^{(-\Delta\epsilon_i - \zeta)/kT} + 1} - \frac{2Q}{\sqrt{\pi}} F(-\eta - \Delta E/kT) = N_d, \quad (11)$$

where the first term is the density of electrons in the conduction band, n_e ; the second term is the density of electrons in each $\Delta\epsilon_i$ impurity level; and the last term is the density of holes in the full band, n_h . Thus

$$n_e = \frac{2P}{\sqrt{\pi}} F(\eta), \quad (11a)$$

$$n_h = \frac{2Q}{\sqrt{\pi}} F(-\eta - \Delta E/kT). \quad (11b)$$

McDougall and Stoner⁴⁾ list values of $F(\eta)$ for η between -4 and $+20$. For values of $\eta > 20$, $F(\eta)$ can be approximated (with an error of -0.3% or less) by

$$F(\eta) = \frac{2}{3} \eta^{3/2}. \quad (12)$$

For values of $\eta < -4$, $F(\eta)$ can be approximated (with an error of $+0.7\%$ or less) by

$$F(\eta) = \frac{1}{2} \sqrt{\pi} e^\eta, \quad (13)$$

which is equivalent to the use of Maxwell-Boltzmann instead of Fermi-Dirac statistics.

Note that when eq. (13) applies, eq. (11a) simplifies to the form

$$n_e = P e^\eta, \quad (14)$$

corresponding to a Fermi level more than $4 kT$ below the conduction band. Similarly (11b) becomes

$$n_h = Q e^{-\eta - \Delta E/kT}, \quad (15)$$

corresponding to a Fermi level more than $4 kT$ above the full band. Finally, the product of eqs (14) and (15) yields

$$n_e n_h = P Q e^{-\Delta E/kT}, \quad (16)$$

which therefore holds when the Fermi level is more than $4 kT$ away from both the conduction and full bands. It must be stressed that eq. (16), which follows from classical statistical theory⁵⁾, is not of general validity.

The general expression is

$$n_e n_h = \frac{2P}{\sqrt{\pi}} F(\eta) \frac{2Q}{\sqrt{\pi}} F(-\eta - \Delta E/kT). \quad (17)$$

As it has been found that many important properties can be explained by assuming at most two impurity levels, one a donor and one an acceptor, we will simplify eq. (11) accordingly. We designate these levels *a* and *b*, and let

$$N_d = n_b, \quad (18)$$

thus making the *b* levels correspond to donors and the *a* levels to acceptors. (In the special case when the *b* levels are above the *a* levels, the words "donor" and "acceptor" apply before the electrons reach their equilibrium state.) Thus eq. (11) becomes,

$$\frac{2P}{\sqrt{\pi}} F(\eta) = \frac{n_b e^{-\Delta \varepsilon_b / kT}}{e^{-\Delta \varepsilon_b / kT} + e^\eta} - \frac{n_a e^\eta}{e^{-\Delta \varepsilon_a / kT} + e^\eta} + \frac{2Q}{\sqrt{\pi}} F\left(-\eta - \frac{\Delta E}{kT}\right), \quad (19)$$

that is to say,

$$\left\{ \begin{array}{l} \text{density of free} \\ \text{electrons in} \\ \text{conduct. band} \end{array} \right\} = \left\{ \begin{array}{l} \text{density of} \\ \text{bound holes} \\ \text{in "donors"} \end{array} \right\} - \left\{ \begin{array}{l} \text{density of} \\ \text{bound electr.} \\ \text{in "acceptors"} \end{array} \right\} + \left\{ \begin{array}{l} \text{density of free holes} \\ \text{in full band} \end{array} \right\},$$

where n_a and n_b are the densities of states of the *a* and *b* impurities; and $\Delta \varepsilon_a$, $\Delta \varepsilon_b$ and ΔE are indicated in figs 2*a* and *b*. Note that the $\Delta \varepsilon$ of an impurity level within the conduction band should have the opposite sign to that in eq. (19).

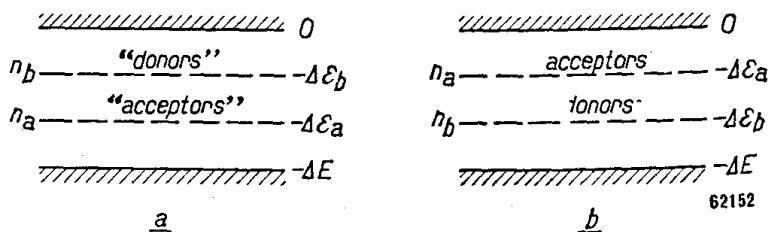


Fig. 2.

Eq. (19) applies for the most general case to be considered below; other models to be discussed are simplifications of this one, obtained by omitting one or two elements. Even the latter cases usually lead to equations that must be solved numerically. Only if still further assumptions are introduced, can simple analytical formulae then be obtained; however, their validity is usually restricted to narrow ranges of temperature and impurity parameters (see Appendix for an example).

In that which follows, we usually consider explicitly *n*-type semiconductors; analogous conclusions apply to *p*-type cases.

3. Semiconductors with one type of impurity level

A. Donor level, conduction band (or acceptor level, full band)

This is the original model proposed by Wilson, which has been employed extensively to interpret conductivity data (fig. 3).

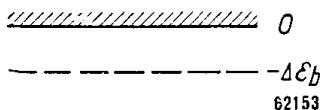


Fig. 3.

The general eq. (19) simplifies in this case to

$$\frac{2P}{\pi} F(\eta) = \frac{n_b e^{-\Delta\epsilon_b/kT}}{e^{-\Delta\epsilon_b/kT} + e^\eta}. \quad (20)$$

In fig. 4 we have plotted ζ against T obtained from the numerical solution of eq. (20) for $\Delta\epsilon_b = 0.2$ eV below the conduction band, and for $n_b = 10^{17}$, 3.10^{17} , and $10^{18}/\text{cm}^3$. It is evident that for this simple model the Fermi level falls indefinitely as the temperature is increased.

Fig. 5 shows ζ against T for a high value of n_b , $10^{20}/\text{cm}^3$, for varying values of $\Delta\epsilon_b$, both positive and negative (the donor level either in or below the conduction band, respectively). The humps which appear so prominently in fig. 5 are also a property of the curves in fig. 4, but for low concentrations they are too small and too close to $T = 0$ °K to appear in the drawing. For high values of n_b and small negative values of $\Delta\epsilon_b$, the Fermi level may enter the conduction band for a certain range of temperatures.

Fig. 6 gives a plot of $\log n_e$ against $10^4/T$ corresponding to the three Fermi-level curves of fig. 4. Note that at high temperatures, where the Fermi levels are below the donor level, strong ionization occurs. At sufficiently high temperatures, the number of electrons in the conduction band becomes constant, and the temperature dependence of the resistance will be like that of a metal. When the Fermi level is at the donor level, fifty per cent of the donors are ionized. In order to discuss the low-temperature region, where the curves are essentially straight lines, we first mention the formula commonly used for the density of free electrons, namely,

$$n_e = (n_b P)^{1/2} e^{-\Delta\epsilon_b/2kT} = \frac{(2n_b)^{1/2} (2\pi mk)^{3/4}}{h^{3/2}} T^{3/4} e^{-\Delta\epsilon_b/2kT}, \quad (21)$$

which is readily derived from eq. (20). However, eq. (21) is subject to the restrictions that the Fermi level be at least $2 kT$ below the conduction band and $2 kT$ above the donor level (for a maximum error of about 8%).

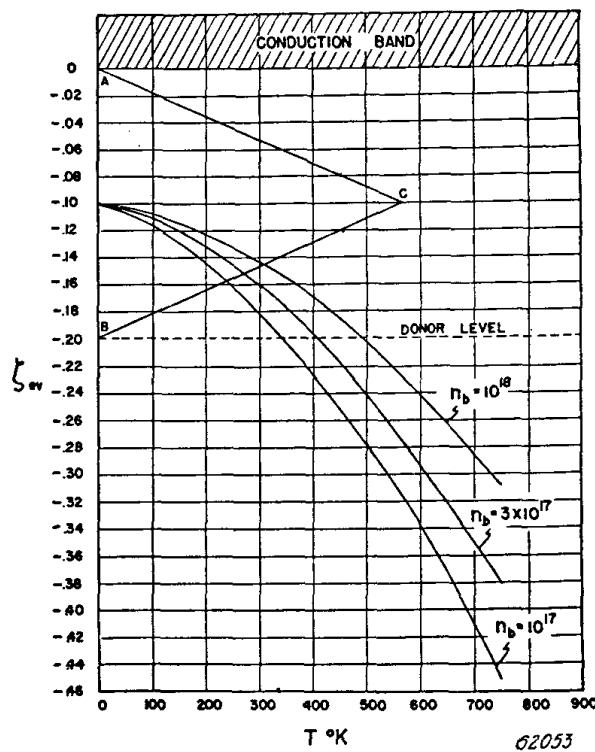


Fig. 4. Temperature dependence of Fermi level in simple *n*-type semiconductor

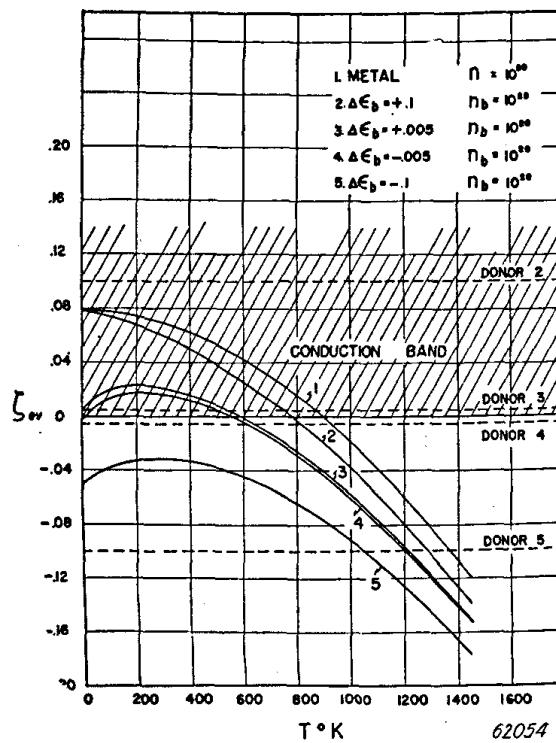


Fig. 5. Dependence of Fermi level on energy gap, $\Delta \epsilon_b$, in simple *n*-type semiconductor. Each curve represents the variation with temperature of the Fermi level when the correspondingly numbered donor level alone exists.

These conditions are fulfilled within the triangular region ABC of fig. 4, where AC represents a line $2 kT$ below the conduction band and BC a line $2 kT$ above the donor level. In fig. 6, the straight line portions below 250°K are all inside the range of validity of eq. (21), and the slopes of the curves $\log(n_e/T^{3/4})$ against $1/T$ (also straight lines in the regions considered) yield values close to $\frac{1}{2}\Delta\epsilon_b$.

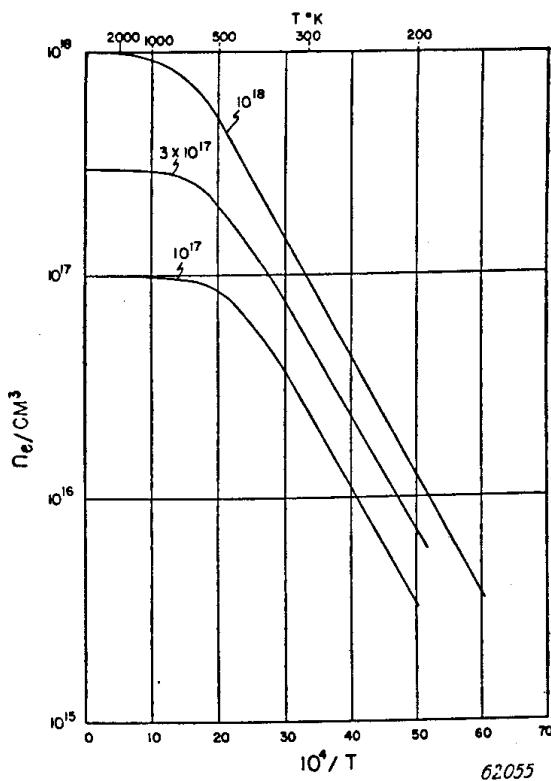


Fig. 6. Density of free electrons in simple *n*-type semiconductor; $\Delta\epsilon_b = -0.2 \text{ eV}$. Values of n_b as indicated.

However, when straight lines are obtained in experimental $\{\log(n_e/T^{3/4}), 1/T\}$ plots for a limited temperature interval, it cannot be considered a proof that eq. (21) applies. For example, in the strong ionization region, where eq. (21) does not apply, such plots may appear linear, with a small slope, over a fairly large temperature range. Similar difficulties may be encountered in determining $\Delta\epsilon_b$ from the slope of straight line portions of experimental plots of $\log \sigma$ against $1/T$. Moreover, the interpretation of conductivity data is subject to another difficulty, namely, that the negative temperature coefficient of the resistance often arises from the presence of barriers. Thus it is dangerous to draw conclusions regarding the energy-level diagram based only upon d.c. conductivity data over a narrow temperature range.

B. Full band, donor (or acceptor) level, conduction band. Application to germanium

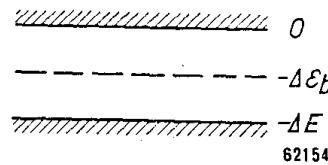


Fig. 7.

In this case (fig. 7) the equation is

$$\frac{2P}{\sqrt{\pi}} F(\eta) = \frac{n_b e^{-\Delta\epsilon_b/kT}}{e^{-\Delta\epsilon_b/kT} + e^\eta} + \frac{2Q}{\sqrt{\pi}} F\left(-\eta - \frac{\Delta E}{kT}\right). \quad (22)$$

The solid curves *) in the upper half of fig. 8 were calculated from eq. (22) for $\Delta\epsilon_b = 0.005$ eV below the conduction band, $\Delta E = 0.75$ eV, $m_h/m_e = 1.2$, and for various values of n_b . These values are appropriate to *n*-type germanium. The only important difference from the simple *n*-type case of section A is that the Fermi-level curves undergo an inflection and join the intrinsic line at high temperatures instead of falling indefinitely. By the intrinsic line is meant the Fermi-level curve for a model consisting of a full band and a conduction band only **).

The corresponding curves of $\log n_e$ against $1/T$ are shown in fig. 9. All the curves characterizing the impurity conduction at low temperatures merge at higher temperatures into the same line with a steep slope which characterizes the intrinsic conduction.

The solid curves in the lower half of fig. 8 were calculated for $\Delta\epsilon_a = 0.01$ eV above the full band and for two values of n_a . These curves for the *p*-type semiconductor are entirely analogous to those in the upper half of the figure for the *n*-type semiconductor.

Putley ⁶⁾ has made similar Fermi-level calculations which he has employed to explain his conductivity data on *n*-type germanium from 100 to 500 °K. He assumed that only lattice scattering was present; the conductivity formula applicable to this case is

$$\sigma = \sigma_0 \ln(1 + e^{\xi/kT}), \quad (23)$$

where σ_0 is a constant, which Putley determined empirically. Since he

*) Incidental to a discussion of the effect of surface states on the temperature variation of the work function of semiconductors, Markham and Miller ¹³⁾ have published similar curves based only on the use of classical statistics.

**) When m_h/m_e is equal to unity, the intrinsic line is at $\frac{1}{2}\Delta E$, independent of temperature; when the mass ratio is greater than unity, it rises with increasing temperature. At sufficiently high mass ratios and for sufficiently small values of ΔE it is possible for the intrinsic line to reach into the conduction band at reasonable temperatures. However, even in such cases, the temperature coefficient of resistance remains negative.

claims eq. (23) is in good agreement with his experiments, he concludes that it is not necessary to invoke Rutherford scattering by ionized centres as has been done by Lark-Horovitz et al.⁷).

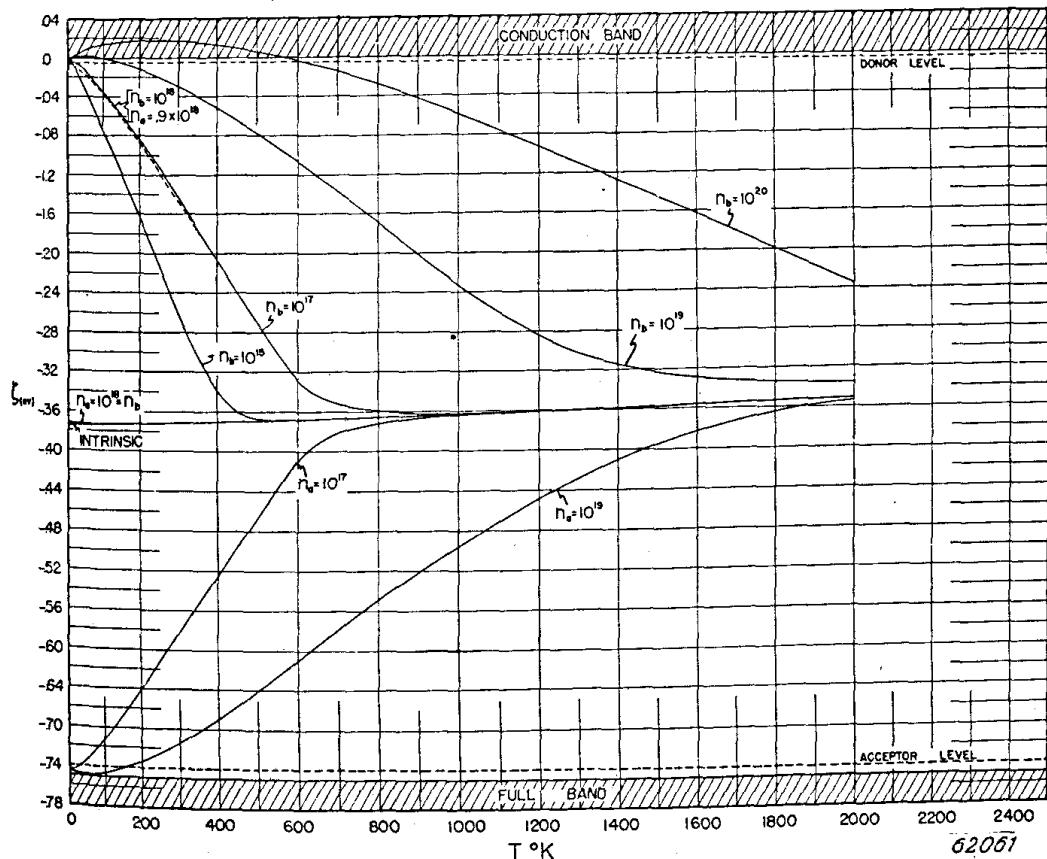


Fig. 8. Variation of Fermi level with temperature in germanium.

Because of this dilemma we have analyzed Putley's data carefully and have found that eq. (23) fits the data from 500 to 150 °K; however, it gives values that are clearly too small for lower temperatures. This discrepancy is particularly marked for the sample with the highest impurity content. Since Lark-Horovitz et al. have obtained both Hall and conductivity data on a number of germanium specimens, thus permitting an experimental determination of the mobility, we have analyzed such data for a sample, 11 Q, the conductivity of which behaved in a manner similar *) to that of Putley's specimens. The mobility, b , for this sample at low temperatures was found to be considerably below that expected for lattice scattering alone ($b \sim T^{-1/2}$). For example, at 100 °K the experimental value of b is about 800, while the value for lattice scattering is 6700 cm/sec per volt/cm. As, furthermore, the mobility values can be explained, as to

*) We have applied Putley's analysis to this sample, and have obtained values of n_b and $\Delta\epsilon_b$ in good agreement with those mentioned in his paper.

order of magnitude, by the inclusion of Rutherford scattering, and assuming additivity of the resistance contributions, we believe that Putley's assumption of lattice scattering only seems unwarranted.

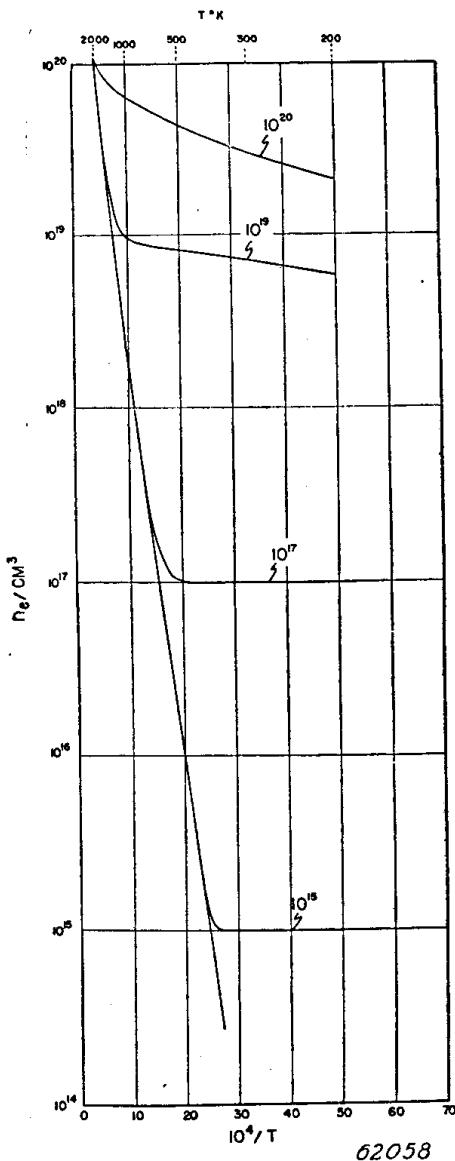


Fig. 9 Density of free electrons in germanium.

4. Semiconductors with two types of impurity level *)

A. Acceptor level, donor level, conduction (or full) band

The formula applicable in each case (figs 10 a and b) is

$$\frac{2P}{\sqrt{\pi}} F(\eta) = \frac{n_b e^{-\Delta_{eb}/kT}}{e^{-\Delta_{eb}/kT} + e^\eta} - \frac{n_a e^\eta}{e^{-\Delta_{ea}/kT} + e^\eta}. \quad (24)$$

*) As pointed out by Dr J. W. Mitchell (Bristol) in a private discussion with one of us, a semiconductor model containing donors and acceptors simultaneously is not always chemically stable. If either or both impurity centres are sufficiently mobile, they may destroy each other by recombination. A tentative suggestion for a physical picture, which is perhaps not subject to this objection, is interstitial donors and lattice-defect acceptors.

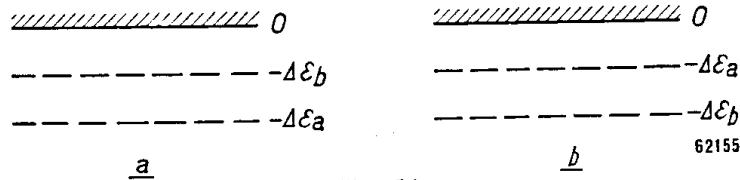
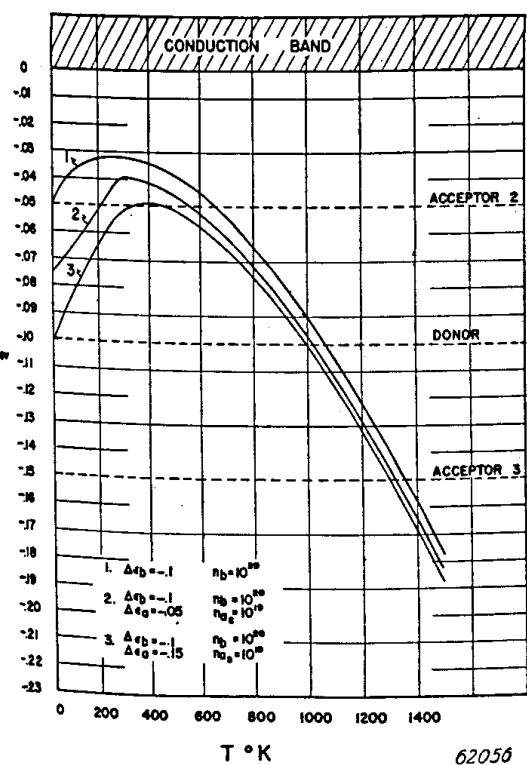
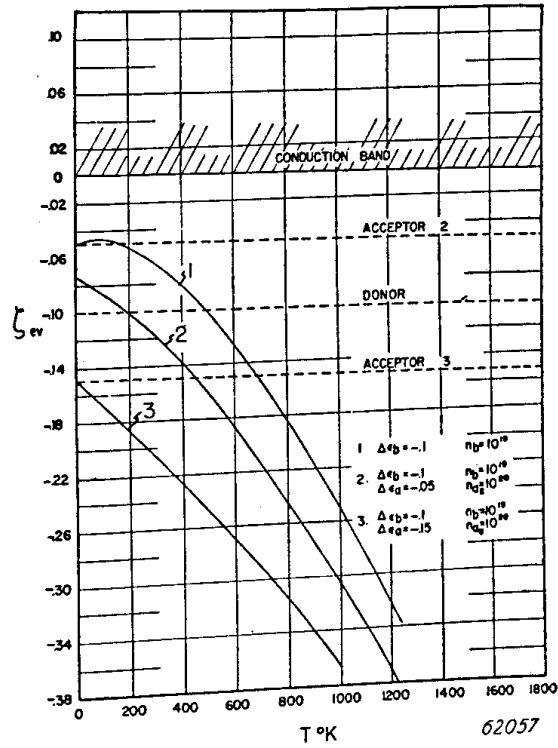


Fig. 10.

Fig. 11 shows the effects of traps on the Fermi level when $n_b > n_a$ for the trap first above and then below the donor level. Fig. 12 corresponds to fig. 11 except that here $n_a > n_b$. In all cases the traps depress the Fermi level.

Fig. 11. Effect of traps, $n_b > n_a$.Fig. 12. Effect of traps, $n_a > n_b$.

The corresponding $\{\log n_e, 1/T\}$ curves are shown in fig. 13. It is observed that the presence of traps, in all cases, lowers n_e and increases the effective activation energy. This is particularly marked for the series in which the trap concentration exceeds the donor concentration. Since the conductivity can be represented by

$$\sigma = n_e e b, \quad (25)$$

the increase in activation energy for n_e in the presence of traps is reflected in an increase in activation energy for conductivity.

Von Hippel and Rittner⁸), however, have interpreted the influence of traps in another manner. They give the following reason for including the effect of traps in a mobility term rather than in n_e : "The motion of charge carriers in semiconductors is normally an intermittent process. The electron or hole travels a mean distance \bar{w} in the field direction for an average time, t_f , and is then trapped for a time t_t . The mobility of the carrier is thus given by

$$b = \bar{w}_0 / (t_f + t_t) ,$$

where $\bar{w}_0 = \bar{w}/E$ ". Since they have thereby defined a mobility *) depending on the trapping time, it is evident that their mobility is not the conventional one obtained from Hall and conductivity data. The latter mobility

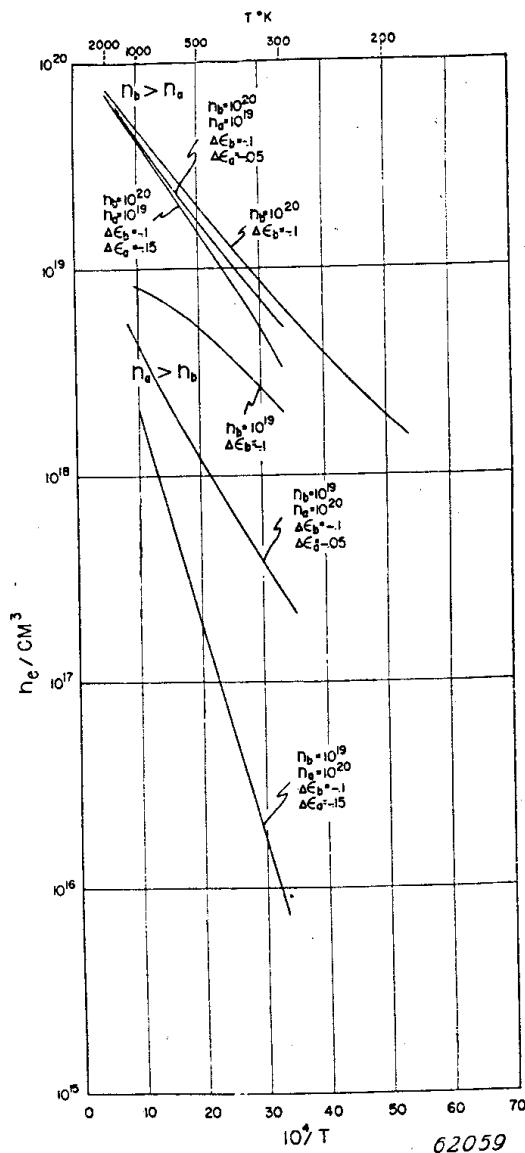


Fig. 13. Effect of traps on density of free electrons.

*) The mobility so defined is, however, appropriate to their discussion of the origin of secondary photocurrents.

refers only to the time spent in the conduction band and not to the time spent in the traps. With the use of the terms in their conventional sense, it is clear that, although the traps influence the mobility by way of additional scattering, their main effect on the conductivity is to decrease the number of free electrons.

B. Full band, acceptor level, donor level, conduction band

This is the general model introduced in section 2, and eq. (19) applies.

1. Change of activation energy with impurity concentration

Calculations⁹⁾ have already been made to determine the behaviour of Fermi levels for a special model of this type with the acceptors below the donors. This model was chosen to explain, among other things, the process of activation of (Ba-Sr)O cathodes, which process was presumed to consist of an increase in the donor concentration while the acceptor concentration remained constant. In fig. 14, taken from reference⁹⁾, is shown

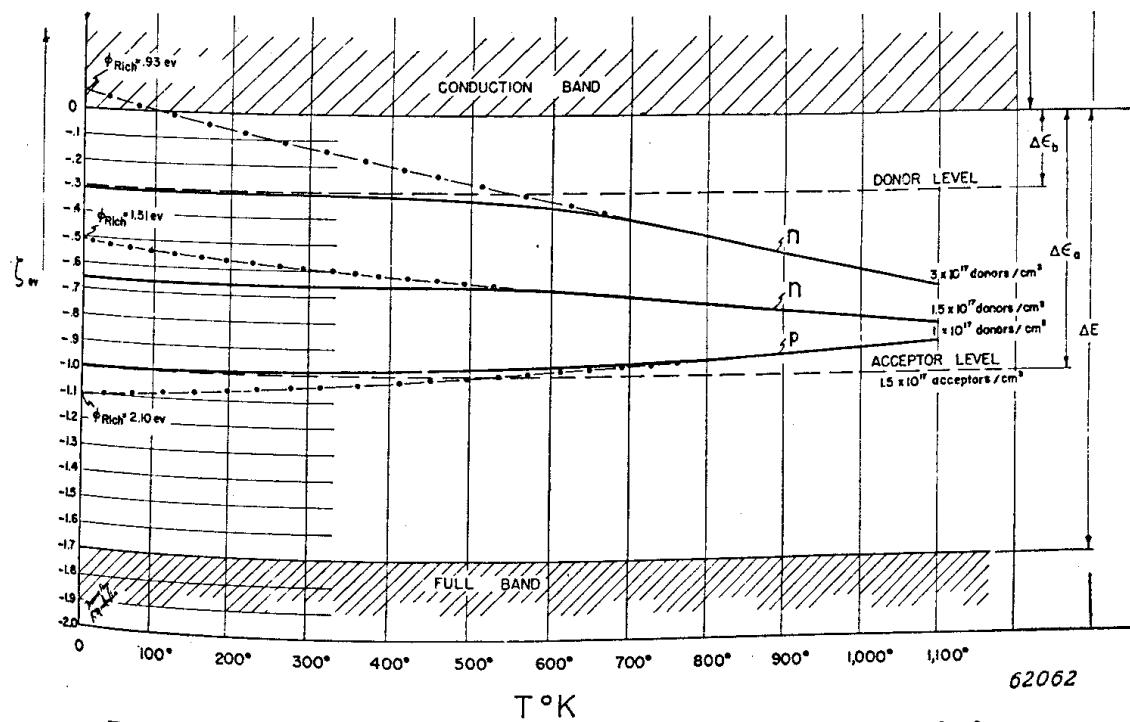


Fig. 14. Variation of Fermi level with temperature for (Ba-Sr)O cathodes.

the variation of the Fermi level with temperature for three donor concentrations; fig. 15 presents the corresponding curves of $1/(n_e + n_h)$. One of the prominent features of fig. 15 is the decrease in activation energy with increasing donor concentration. This interesting property is not at all dependent on the presence of the full band, but is caused simply by the presence of donor levels above acceptor levels. Thus the occurrence

of this configuration of energy levels may represent a possible explanation of the frequently observed large decreases in activation energy with impurity content, unless the semiconductor behaviour is caused by barriers.

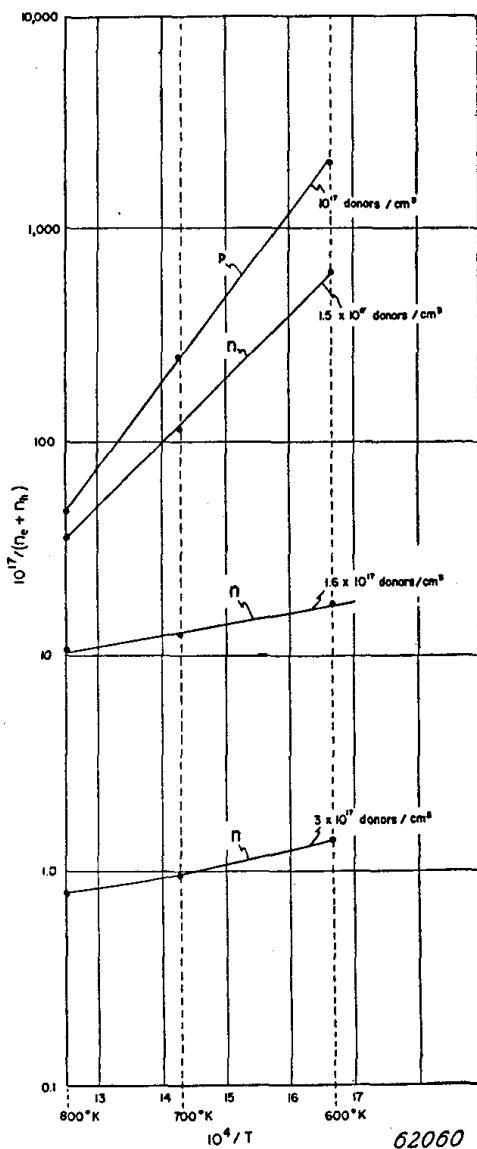


Fig. 15. Calculated values of log "resistance" against $1/T$ for $(\text{Ba-Sr})\text{O}$ cathodes.

2. The occurrence of $n-p$ barriers

In fig. 8, two curves (dashed) have been included which refer to the type of model considered in this section. The concentrations employed were $n_a = n_b = 10^{18}/\text{cm}^3$ and $n_a = 0.9 \cdot 10^{18}$, $n_b = 10^{18}/\text{cm}^3$. In the former case, the Fermi-level curve starts, at $T = 0$ °K, half-way between the two impurity levels and gradually merges with the intrinsic curve at higher temperatures. Thus, in such an idealized situation, the substance behaves approximately like an intrinsic semiconductor. In the case of $n_a = 0.9 \cdot 10^{18}$

$n_b = 10^{18}/\text{cm}^3$, the Fermi-level curve starts, at $T = 0^\circ\text{K}$, at the donor level and merges with the curve corresponding to $(10^{18} - 0.9 \cdot 10^{18}) = 10^{17}$ donors/ cm^3 . In the analogous case of surplus acceptors (not shown), namely, $n_a = 10^{18}$, $n_b = 0.9 \cdot 10^{18}/\text{cm}^3$, the Fermi curve starts at the acceptor level and merges with the curve 10^{17} acceptors/ cm^3 . Thus, when the concentration of donors and acceptors are almost equal, the Fermi level is very sensitive to slight variations in their relative concentrations, especially at low temperatures, since a slight shift in the concentration from excess donors to excess acceptors displaces the Fermi level from the neighbourhood of the donor level to that of the acceptor level *).

If a semiconductor has both donors and acceptors in nearly equal concentrations, local variations in composition may cause the substance to be divided into *n*-type regions and *p*-type regions. Owing to the equilibrium condition that the Fermi level be everywhere the same, at the contacts between adjacent *n*- and *p*-type regions *n-p* barriers are formed the height of which may be considerable, namely, of the order of the energy difference between donor and acceptor levels. Such *n-p* barriers have already been invoked by Sosnowski, Starkiewicz and Simpson¹²⁾ and by James¹¹⁾ to explain photoconductivity in oxidized PbS, and by Wannier¹⁰⁾ to explain secondary photocurrents in insulators.

APPENDIX

To illustrate the manner in which simple analytical formulae are obtained from eq. (19) by making certain approximations, consider the case of a full band, a conduction band, and a donor level. Then, since n_a is zero, eq. (19) reduces to eq. (22).

If we assume that the Fermi level is at least $2kT$ away from both the full and conduction bands, then

$$Pe^\eta = \frac{n_b e^{-\Delta_{eb}/kT}}{e^{-\Delta_{eb}/kT} + e^\eta} + Q e^{-\eta - \Delta E/kT},$$

which leads to a cubic in e^η . Further simplification requires an additional assumption. An interesting case is that in which the Fermi level is at least $2kT$ above the donor level, i.e. when

$$e^{-\Delta_{eb}/kT} \ll e^{-|\zeta|/kT}.$$

Then we obtain

$$Pe^\eta = n_b e^{-\eta - \Delta_{eb}/kT} + Q e^{-\eta - \Delta E/kT},$$

$$e^\eta = \left(\frac{n_b}{P} e^{-\Delta_{eb}/kT} + \frac{Q}{P} e^{-\Delta E/kT} \right)^{\frac{1}{1_3}},$$

*) This fact has already been mentioned by Wannier¹⁰⁾ and by James¹¹⁾.

$$n_e = (n_b P e^{-\Delta \epsilon_b / kT} + P Q e^{-\Delta E / kT})^{1/2}.$$

Thus the density of free electrons, in this approximation, is not given simply by a sum of the contributions from the donor level and from the full band, as is often assumed.

It is worth repeating that analytical formulae derived in a similar manner to that shown above have a very limited range of validity and should be used with caution.

New York, February, 1950

Note added in proof:

Bardeen has recently reported (American Physical Society meeting, February 1950, New York) a wide variety of data indicating a temperature dependence of the band separation in solids; the variation is of the order of 10^{-4} eV/degree in Si, Ge and Te. This effect has not been taken into account in the numerical calculations presented above. It is obvious how this should be done as eq. (19) must be solved for η at each value of T . Although the temperature variation of ΔE will not materially alter the shape of the Fermi-level curves, it may change the free charge carrier density appreciably. However, the difficulty remains that the variation with temperature of the impurity-level positions is not yet well known.

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