

and the vacancy mechanism being equivalent to the two "chemical reactions" $A^\alpha + V^\beta \rightleftharpoons A^\beta + V^\alpha$ and $B^\alpha + V^\beta \rightleftharpoons B^\beta + V^\alpha$. The reaction rates in these models are derived in terms of the fundamental parameters of atom movements, and are themselves order-dependent.

(6) The vacancy-interchange model has been applied to the case of Cu_3Au , which has been studied experimentally by Burns and Quimby. $A-B$ symmetry was assumed, an activation energy and a pre-exponential factor were taken from the measurements of self-diffusion in pure copper and pure gold, and the remaining parameter of the theory was adjusted to produce agreement with the known critical temperature for ordering in this system. The theory then gives reasonably good agreement with relaxation times observed by

Burns and Quimby over the temperature range of the experiments, 338°C to 388°C .

(7) The developments outlined above have been concerned with homogeneous systems. The basic apparatus of multiparticle distribution functions and their equations of motion is equally applicable to inhomogeneous systems, including cases of domains of order in a disordered matrix, domains of antiphase order, and diffusion in alloys.

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Ionization Interaction between Impurities in Semiconductors and Insulators

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It is known that the free energy of an imperfect semiconductor or insulator crystal contains terms which arise from the ionizability of these imperfections and which represent chemical interactions between imperfections of the same and different kinds. We show that these ionization terms, which involve the Fermi level and the parameters of the energy band model, explain the systematic differences between n - and p -type semiconductors in lattice vacancy concentration, in substitutional atom diffusion coefficients, and in amphoteric impurity behavior. The ionization terms also explain the variation of solid-liquid impurity distribution coefficients with the crystal growth rate of certain semiconductors, and also the well-known "charge balance" effect in insulators.

1. INTRODUCTION

IT is well known¹⁻³ that the solubility of an ionizing impurity in a semiconductor is affected by the electron and hole concentrations. This happens because, roughly speaking, the free energy needed to insert, say, a donor atom in a semiconductor lattice is reduced by the energy liberated in the ionization of the donor, i.e. by an electron falling from the donor level to the Fermi level.

Reiss² has given a statistical treatment of this effect, showing that the chemical potentials of donor and acceptor impurities have the form

$$\mu_d = B_d(p, T) + kT \ln X_d + E_F - kT \ln \left(1 + 2 \exp \frac{E_F - E_d}{kT} \right), \quad (1.1a)$$

$$\mu_a = B_a(p, T) + kT \ln X_a - E_F - kT \ln \left(1 + 2 \exp \frac{E_a - E_F}{kT} \right), \quad (1.1b)$$

where X_d and X_a are the donor and acceptor concentrations, and E_F , E_d , and E_a are the Fermi level, donor level, and acceptor level, respectively. The main assumptions behind (1.1) are as follows:

(a) The energy band model is adequate. (For definiteness the donor and acceptor levels are assigned statistical weight 2.)

(b) The ionization interaction provides the only departure from regularity⁴ of the donor and acceptor solutions.

(c) The difference between Gibbs and Helmholtz free energy is negligible.

Using (1.1), Reiss calculated³ the distribution coefficient for an ionizing impurity atom between two phases, in terms of the concentration of other ionizing impurities. The results agree with experiment.³

In Sec. 2 of this paper, we present an alternative

¹ C. Wagner and K. Grunewald, *Z. Phys. Chem.* **B40**, 455 (1938); C. Wagner, *J. Chem. Phys.* **18**, 62 (1950), *J. Chem. Phys.* **19**, 626 (1951), K. Hauffe, *Halbleiterprobleme*, edited by W. Schottky (Friedrick Vieweg und Sohn, Braunschweig, 1954), Chap. 5; C. Goldberg, *Phys. Rev.* **88**, 920 (1952); F. A. Kroger and H. J. Vink, *Physica* **20**, 950 (1954); C. S. Fuller and H. Reiss, *Phys. Rev.* **99**, 624(A) (1955).

² H. Reiss, *J. Chem. Phys.* **21**, 1209 (1953).

³ H. Reiss and C. S. Fuller, *J. Metals* (to be published).

⁴ E. A. Guggenheim, *Mixtures* (Oxford University Press, Oxford, 1952).

method of derivation of Eqs. (1.1) which seems to us more simple and direct.

In the main part of this paper we shall analyze several other phenomena which are affected by the ionization interaction of imperfections in semiconductors and insulators. In Sec. 3 an expression is derived for the fraction of amphoteric atoms (of a certain kind) which act as donors and the fraction which act as acceptors, in terms of the concentration of other ionizing imperfections. Possible application to copper impurities in the germanium lattice and germanium atoms in the gallium arsenide lattice is considered.

In Sec. 4, the concentration of lattice vacancies is related to the concentration of other ionizing imperfections, assuming the vacancies act as acceptors. It is then shown that substitutional atom diffusion coefficients should be greater in n - than p -type semiconductors, under certain conditions.

In Sec. 5, we shall show that one may introduce as convenient intuitive concepts a chemical potential for lattice vacancies and also a separate chemical potential for donor amphoteric and acceptor amphoteric atoms.

In Sec. 6, we shall consider some questions concerning the distribution coefficients of ionizing impurities between two phases.

In Sec. 7, we shall show that the well-known phenomenon of "charge balance" in insulators is a consequence of the ionization interaction between impurities.

In Sec. 8, we discuss the solid-liquid interface, showing a connection between the rate of crystal growth and the resulting nonequilibrium distribution of impurities between the two phases.

2. CHEMICAL POTENTIALS OF IONIZING IMPURITIES IN SEMICONDUCTORS AND INSULATORS

We consider a semiconductor or insulating crystal which has an arbitrary uniform concentration of non-diffusing donors and acceptors in one region, a different uniform concentration in a second region, and a much smaller transition region⁵ between. Now we introduce N_d diffusing donor atoms and N_a diffusing acceptor atoms and calculate the equilibrium distribution of these diffusing atoms between the two regions. From this we shall finally be able to compute those parts of the chemical potentials of the diffusing impurities which arise from their ionizability.

The equilibrium values of N_d^1 , N_d^2 , N_a^1 , N_a^2 (the superscripts refer to the two regions) may be determined by minimizing the total Helmholtz⁶ free energy $F(V, T)$ which may be written as

⁵ Dr. H. Reiss (private communication) has suggested that it would be convenient to examine theoretically the chemical potential of ionizing impurities by means of a p - n junction.

⁶ Here we neglect the difference between Helmholtz and Gibbs free energy. The Gibbs free energy is the correct one to minimize at constant pressure and temperature, but the Helmholtz free energy is simpler to calculate.

$$F = F_1 + \sum_s n_s^1 E_s^1 - \sum_t p_t^1 E_t^1 + \sum_s n_s^2 E_s^2 - \sum_t p_t^2 E_t^2$$

$$-kT \left\{ (n_d^1 + n_d^2 + p_a^1 + p_a^2) \ln 2 \right. \\ + \ln \frac{N_{xd}^1!}{N_d^1! (N_{xd}^1 - N_d^1)!} \frac{N_{xd}^2!}{N_d^2! (N_{xd}^2 - N_d^2)!} \\ + \ln \frac{N_{xa}^1!}{N_a^1! (N_{xa}^1 - N_a^1)!} \frac{N_{xa}^2!}{N_a^2! (N_{xa}^2 - N_a^2)!} \\ + \sum_s \ln \frac{g_s^1!}{n_s^1! (g_s^1 - n_s^1)!} \frac{g_s^2!}{n_s^2! (g_s^2 - n_s^2)!} \\ \left. + \sum_t \ln \frac{g_t^1!}{p_t^1! (g_t^1 - p_t^1)!} \frac{g_t^2!}{p_t^2! (g_t^2 - p_t^2)!} \right\}. \quad (2.1)$$

In (2.1), E_s is a conduction band level or donor level (E_d); E_t is a valence band level or acceptor level (E_a); n_s is the electron occupation number of level E_s ; the maximum of n_s is g_s ; p_t is the hole occupation number of level E_t ; the maximum of p_t is g_t ; and N_{xd}^1 is the number of lattice sites available for donors in region 1. The $\ln 2$ term in (2.1) comes from the assumption that each donor may be, at most, singly occupied, but has statistical weight 2, and that each acceptor may be, at most, occupied by a single hole, but the statistical weight is 2. F_1 is the part of F unchanged by transfer of donors or acceptors across the junction or by changes in the valence electronic state.

We shall minimize F with respect to changes in N_d^1 , N_d^2 , N_a^1 , and N_a^2 and also with respect to changes in the set n_s^1 , n_s^2 , p_t^1 , p_t^2 : these two sets of occupation numbers are coupled by three sets of constraints on the system:

$$\sum_s n_s^1 - \sum_t p_t^1 - N_d^1 + N_a^1 = \text{const}, \quad (2.2a)$$

$$\sum_s n_s^2 - \sum_t p_t^2 - N_d^2 + N_a^2 = \text{const}, \quad (2.2b)$$

$$g_d^1 - N_d^1 = \text{const}, \quad (2.3a)$$

$$g_d^2 - N_d^2 = \text{const}, \quad (2.3b)$$

$$g_a^1 - N_a^1 = \text{const}, \quad (2.3c)$$

$$g_a^2 - N_a^2 = \text{const}, \quad (2.3d)$$

$$N_d^1 + N_d^2 = \text{const}, \quad (2.4a)$$

$$N_a^1 + N_a^2 = \text{const}. \quad (2.4b)$$

The constraints (2.2) are the condition for charge neutrality.⁷ The constraints (2.3) say that the addition of a donor (acceptor) increases the capacity of the donor (acceptor) levels by unity.⁸ The constraints (2.4) conserve the total number of donors and acceptors.

⁷ W. Shockley, *Holes and Electrons in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950).

⁸ The relative change in capacity of valence and conduction band levels is only of the order of the reciprocal of the total number of atoms, and we therefore neglect this relative change.

Applying Stirling's approximation to (2.1) and representing the constraints (2.2) and (2.4) by Lagrange multipliers E_F^1 , E_F^2 , α_d , α_a , the minimization of F is expressed by

$$0 = \delta F - E_F^1 \delta (\sum_s n_s^1 - \sum_t p_t^1 - N_d^1 + N_a^1) - E_F^2 \delta (\sum_s n_s^2 - \sum_t p_t^2 - N_d^2 + N_a^2) - \alpha_d \delta (N_d^1 + N_d^2) - \alpha_a \delta (N_a^1 + N_a^2). \quad (2.5)$$

In (2.5) the constraints (2.3) may be introduced explicitly. Carrying this process through, one finds the usual⁹ electron and hole distribution functions:

$$\frac{g_s}{n_s} = 1 + \exp\left(\frac{E_s - E_F}{kT}\right) \quad s \neq d, \quad (2.6a)$$

$$\frac{g_d}{n_d} = 1 + \frac{1}{2} \exp\left(\frac{E_d - E_F}{kT}\right) \quad (\text{donor levels}), \quad (2.6b)$$

$$\frac{g_t}{p_t} = 1 + \exp\left(\frac{E_F - E_t}{kT}\right) \quad t \neq a, \quad (2.6c)$$

$$\frac{g_a}{p_a} = 1 + \frac{1}{2} \exp\left(\frac{E_F - E_a}{kT}\right) \quad (\text{acceptor levels}), \quad (2.6d)$$

for both regions, and the following diffusing donor and acceptor distributions:

$$\ln \left[\frac{N_d^1}{N_{xd}^1 - N_d^1} \frac{1}{1 - n_d^1/g_d^1} \right] = \frac{\alpha_d - E_F^1}{kT}, \quad (2.7a)$$

$$\ln \left[\frac{N_a^1}{N_{xa}^1 - N_a^1} \frac{1}{1 - p_a^1/g_a^1} \right] = \frac{\alpha_a + E_F^1}{kT}, \quad (2.7b)$$

with corresponding expressions for region 2.

Now we shall express this same equilibrium in terms of the chemical potentials of the diffusing donors and acceptors, which we write as

$$\mu_d = \mu_{d1} + \mu_{de} \quad (\text{donors}), \quad (2.8a)$$

$$\mu_a = \mu_{a1} + \mu_{ae} \quad (\text{acceptors}), \quad (2.8b)$$

where

$$\mu_{d1} = M_d(p, T) + kT \ln [N_d / (N_{xd} - N_d)], \quad (2.9a)$$

$$\mu_{a1} = M_a(p, T) + kT \ln [N_a / (N_{xa} - N_a)]. \quad (2.9b)$$

Here μ_{d1} and μ_{a1} are the chemical potentials one would calculate if ionization were negligible and if the donors and acceptors there formed regular⁴ solutions. That is, in the absence of ionization effects the entropy corresponds to random mixing and the energy is linear in the numbers of solute atoms.

The thermodynamic condition for the equilibrium described by (2.7) is⁴

$$\mu_d^1 = \mu_d^2, \quad (2.10a)$$

$$\mu_a^1 = \mu_a^2. \quad (2.10b)$$

Substituting (2.7), (2.8), and (2.9) in (2.10), we find

$$\mu_{de}^1 - \mu_{de}^2 = E_F^1 - E_F^2 + kT \ln(1 - n_d^1/g_d^1) - kT \ln(1 - n_d^2/g_d^2), \quad (2.11a)$$

$$\mu_{ae}^1 - \mu_{ae}^2 = E_F^2 - E_F^1 + kT \ln(1 - p_a^1/g_a^1) - kT \ln(1 - p_a^2/g_a^2). \quad (2.11b)$$

Remembering that the total donor and acceptor concentrations are arbitrary, it follows from (2.11) that

$$\mu_{de} = E_F + kT \ln(1 - n_d/g_d) + \bar{\mu}_d, \quad (2.12a)$$

$$\mu_{ae} = -E_F + kT \ln(1 - p_a/g_a) + \bar{\mu}_a, \quad (2.12b)$$

where $\bar{\mu}_d$ and $\bar{\mu}_a$ are independent of the donor and acceptor concentration. μ_{de} and μ_{ae} have been defined so that

$$\mu_{de} \equiv 0, \quad \text{when ionization of donors is negligible,}$$

$$\mu_{ae} \equiv 0, \quad \text{when ionization of acceptors is negligible,}$$

i.e.,

$$\mu_{de} \equiv 0, \quad \text{when } E_F - E_d \gg kT, \quad (2.13a)$$

$$\mu_{ae} \equiv 0, \quad \text{when } E_a - E_F \gg kT. \quad (2.13b)$$

This means that $\bar{\mu}_d$ and $\bar{\mu}_a$ may be evaluated and (2.12) rewritten as

$$\mu_{de} = E_F - E_d + kT \ln 2 - kT \ln \left[1 + 2 \exp\left(\frac{E_F - E_d}{kT}\right) \right], \quad (2.14a)$$

$$\mu_{ae} = E_a - E_F + kT \ln 2 - kT \ln \left[1 + 2 \exp\left(\frac{E_a - E_F}{kT}\right) \right]. \quad (2.14b)$$

This puts (2.8) in agreement with (1.1). Thus (2.14) is the correction one must make to the chemical potential if one wishes to account for the effects of ionization. For the case, $E_F = \bar{E}_F \equiv (E_a + E_d)/2$,

$$\mu_{de} = \mu_{ae} = \frac{E_a - E_d}{2} + kT \ln 2 - kT \ln \left[1 + 2 \exp\left(\frac{E_a - E_d}{2kT}\right) \right]. \quad (2.15)$$

3. AMPHOTERIC IMPURITIES

If a certain impurity atom can occupy two kinds of site in a semiconductor or insulator lattice, acting as a donor in the one site and as an acceptor in the other, then the fraction of such amphoteric atoms in donor sites will depend upon the concentration of other ionizing imperfections. We shall calculate this dependence and, finally, discuss two possible applications.

⁹ A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953).

The Helmholtz free energy of the system is

$$\begin{aligned}
 F = & F_1 + N_{1d}W_d + N_{1a}W_a + \sum_s n_s E_s - \sum_t p_t E_t \\
 & - kT \left\{ (n_d + p_a) \ln 2 + \ln \frac{N_{xd}!}{N_{1d}!(N_{xd} - N_{1d})!} \right. \\
 & \times \frac{N_{xa}!}{N_{1a}!(N_{xa} - N_{1a})!} + \sum_s \ln \frac{g_s!}{n_s!(g_s - n_s)!} \\
 & \left. + \sum_t \ln \frac{g_t!}{p_t!(g_t - p_t)!} \right\}, \quad (3.1)
 \end{aligned}$$

where $W_a - W_d$ is the energy to take an amphoteric atom from donor to acceptor site, N_{1d} and N_{1a} are the numbers of donor and acceptor amphoteric, N_{xd} and N_{xa} are the numbers of available sites for the donor and acceptor amphoteric, and F_1 is that part of F which is indifferent to transfer of amphoteric from donor to acceptor sites and to change in electron occupation numbers.

The equilibrium condition is that F be a minimum with respect to changes in the N_{d1} , N_{a1} and the n_s , p_t . These two sets of occupation numbers are coupled by the constraints

$$g_d - N_{1d} = \text{const}, \quad (3.2a)$$

$$g_a - N_{1a} = \text{const}, \quad (3.2b)$$

$$N_{1d} + N_{1a} = \text{const}, \quad (3.3)$$

$$\sum_s n_s - \sum_t p_t - N_{1d} + N_{1a} = \text{const}. \quad (3.4)$$

Equations (3.2) state that when an amphoteric changes from donor to acceptor site the number of donor levels decreases by unity and the number of acceptor levels increases by unity. Equation (3.3) conserves the total number of amphoteric atoms. Equation (3.4) is a form of the charge neutrality condition.⁷ Representing constraints (3.3) and (3.4) by Lagrange parameters μ and E_F , the minimization condition is

$$\begin{aligned}
 0 = & \delta F - \mu \delta (N_{1d} + N_{1a}) \\
 & - E_F \delta (\sum_s n_s - \sum_t p_t - N_{1d} + N_{1a}), \quad (3.5)
 \end{aligned}$$

in which (3.2) must be introduced explicitly. From this process there result the usual electron distribution functions (2.6) and the amphoteric atom distribution functions:

$$kT \ln \left(\frac{N_{1d}(1 - n_d/g_d)}{N_{xd} - N_{1d}} \right) = -(W_d + E_F - \mu), \quad (3.6a)$$

$$kT \ln \left(\frac{N_{1a}(1 - p_a/g_a)}{N_{xa} - N_{1a}} \right) = -(W_a - E_F - \mu). \quad (3.6b)$$

We shall consider the dilute case now:

$$N_{xd} \gg N_{1d}, \quad (3.7a)$$

$$N_{xa} \gg N_{1a}. \quad (3.7b)$$

In this case,

$$\frac{N_{1d}}{N_{1a}} = \frac{N_{xd}}{N_{xa}} \frac{1 - p_a/g_a}{1 - n_d/g_d} \exp \left(\frac{W_a - W_d - 2E_F}{kT} \right). \quad (3.8)$$

One can see from (3.8) that the ionization interaction makes amphoteric atoms prefer minority type sites.⁸ An alternate form of (3.8) is

$$\frac{N_{1d}^+}{N_{1a}^-} = \frac{N_{xd}}{N_{xa}} \exp \left(\frac{W_a - W_d - 2E_F}{kT} \right), \quad (3.9)$$

where N_{1d}^+ is the number of ionized amphoteric donors and N_{1a}^- is the number of ionized amphoteric acceptors.

We may compare N_{1d}/N_{1a} in an exhaustion semiconductor with its value N_{1d}^i/N_{1a}^i when the material is intrinsic:

$$\frac{N_{1d}/N_{1a}}{N_{1d}^i/N_{1a}^i} = \exp \left(2 \frac{E_F^i - E_F}{kT} \right); \quad (3.9b)$$

using Eq. (A5b),

$$\frac{N_{1d}/N_{1a}}{N_{1d}^i/N_{1a}^i} = \left\{ \frac{N}{2n_i} + \left[\left(\frac{N}{2n_i} \right)^2 + 1 \right]^{1/2} \right\}^{-2} \quad (3.10a)$$

$$= n_i^2/N^2, \quad \text{when } N \gg 2n_i, \quad (3.10b)$$

where N is the total $N_d - N_a$.

As an example of an amphoteric impurity of the type considered above, one may mention germanium in the gallium arsenide lattice, with germanium acting as a donor in a gallium site and as an acceptor in an arsenic site.

As a second example, one may consider an atom which acts as an acceptor when occupying a substitutional site in a germanium lattice and as a donor when occupying an interstitial site. Copper may be an impurity of this type.

In the latter example it may be anticipated that the diffusion coefficient is a linear combination of an interstitial atom coefficient and a substitutional atom coefficient, with the proportion of each depending upon the fraction of amphoteric in the two kinds of site.

4. LATTICE VACANCIES AND DIFFUSION

In those semiconductors and insulators in which lattice vacancies act as acceptors, it may be expected that the equilibrium vacancy concentration will depend upon the concentration of other ionizing imperfections. We shall calculate this dependence and then discuss how it affects the diffusion of substitutional impurity atoms. (The corresponding results for vacancies which act as donors may be obtained by similar arguments.)

The equilibrium number of vacancies, N_v , is calculated by minimizing the free energy, which we write as

$$F = F_1 + N_v W_v + \sum_s n_s E_s - \sum_t p_t E_t - kT \left\{ (n_d + p_a) \ln 2 + \ln \frac{N_x!}{N_v!(N_x - N_v)!} + \sum_s \ln \frac{g_s!}{n_s!(g_s - n_s)!} + \sum_t \ln \frac{g_t!}{p_t!(g_t - p_t)!} \right\}. \quad (4.1)$$

Here W_v is the energy of formation of a vacancy, N_x is the number of lattice points which may be vacant, and F_1 is the part of F which is independent of N_v, n_s, p_t . We are ignoring, for simplicity, the change in vibrational free energy¹⁰ caused by changes in N_v . The minimization of F is with respect to changes in N_v and p_t, n_s . These occupation numbers are coupled by the constraints

$$g_a - N_v = \text{const}, \quad (4.2)$$

$$\sum_s n_s - \sum_t p_t + N_v = \text{const}. \quad (4.3)$$

Equation (4.2) is the assumption that each new vacancy adds one new acceptor level (of weight 2). Equation (4.3) is the condition of charge neutrality.⁷

If (4.3) is represented by a Lagrange parameter E_F , and (4.2) introduced explicitly, the minimization is expressed by

$$0 = \delta F - E_F \delta (\sum_s n_s - \sum_t p_t + N_v). \quad (4.4)$$

From (4.4), there result the usual electron distribution functions (2.6) and

$$N_v/N_x = \{1 + (1 - p_a/g_a) \exp[(W_v - E_F)/kT]\}^{-1}. \quad (4.5)$$

Plainly the equilibrium number of vacancies is greater in n -type than p -type semiconductors.

When

$$N_v \ll N_x, \quad (4.6)$$

then

$$\frac{N_v}{N_x} = \frac{\exp[(E_F - W_v)/kT]}{1 - p_a/g_a} \quad (4.7)$$

or

$$N_v^-/N_x = \exp[(E_F - W_v)/kT], \quad (4.8)$$

where N_v^- is the number of ionized vacancies.

It is interesting to compare N_v for an exhaustion semiconductor with its value N_v^i when the semiconductor is intrinsic. In an exhaustion semiconductor, $p_a/g_a \ll 1$, so that

$$N_v/N_v^i = \exp[(E_F - E_F^i)/kT]. \quad (4.9)$$

Using (A5a), one finds

$$N_v/N_v^i = N/2n_i + [(N/2n_i)^2 + 1]^{\frac{1}{2}}. \quad (4.10)$$

When

$$N \equiv N_d - N_{a1} - N_v \gg n_i, \quad (4.11a)$$

one finds

$$N_v/N_v^i \approx N_d/n_i. \quad (4.11b)$$

When

$$N \equiv N_d - N_{a1} - N_v \ll -n_i, \quad (4.12a)$$

one finds

$$N_v/N_v^i \approx n_i/(N_{a1} + N_v). \quad (4.12b)$$

Consider the relevance of the foregoing to diffusion theory. If one assumes that the diffusion of substitutional impurities proceeds by the vacancy mechanism,¹¹ then the diffusion coefficient will be proportional to the vacancy concentration. If the vacancy concentration has its equilibrium value¹² it will be greater in n -type than in p -type semiconductors. Under these assumptions, one may then expect systematically greater substitutional atom diffusion coefficients in n -type than p -type material.^{13,14} Such a systematic difference can be seen in data taken by Dunlap.¹⁵

Finally, we consider the analog of (4.10) for insulators, i.e., we calculate the ratio of N_v to its value $\bar{N}_v = N_d - N_{a1}$ when $N = 0$ ($N_{a1} \equiv N_a - N_v$ and $E_F \equiv \bar{E}_F$ when $N = 0$).

$$N_v/\bar{N}_v = \exp[(E_F - \bar{E}_F)/kT]. \quad (4.13)$$

Using (A8a)

$$\frac{N_v}{\bar{N}_v} = \frac{1}{4N_a} [Ne^{\Delta/2} + (N^2 e^{\Delta} + 16N_a N_d)^{\frac{1}{2}}]. \quad (4.14)$$

Now consider the case where $N^2 > 16N_d N_a e^{-\Delta}$: we find

$$N_v/\bar{N}_v = Ne^{\Delta/2}/2N_a. \quad (4.15)$$

Because $e^{\Delta/2}$ is so large, we must have

$$N/N_a \sim 0,$$

i.e.,

$$N_d - N_{a1} - N_v \sim 0, \quad (4.16)$$

so that the vacancy density must very nearly cancel out the net unbalance of donors and other acceptors. We discuss the significance of this result for "charge balance" in Sec. 7.

5. AMPHOTERIC IMPURITY ATOM AND LATTICE VACANCY CHEMICAL POTENTIALS

We shall show, in this section, that one may introduce, as convenient concepts, a chemical potential for lattice

¹¹ F. Seitz, *Phase Transformations in Solids*, edited by Smoluchowski, Mayer, and Weyl (John Wiley and Sons, Inc., New York, 1951).

¹² J. Bardeen and C. Herring, *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley and Sons, Inc., New York, 1952).

¹³ R. L. Longini, *Phys. Rev.* **99**, 636(A) (1955).

¹⁴ At a colloquium given at the University of Pittsburgh (October 1955), C. Ramasastry reported that a group at University of Illinois (J. Bardeen *et al.*) have measured the coefficient of self diffusion of germanium at 800°C and found it greater in n -type than p -type material. Assuming the vacancy mechanism of diffusion operating, they concluded that the vacancy concentration was higher in the n -type material because of the interaction, through the Fermi level, between donor impurities and vacancies acting as acceptors.

¹⁵ W. C. Dunlap, Jr., *Phys. Rev.* **94**, 1531 (1954).

¹⁰ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940).

vacancies, a chemical potential for donor amphoteric atoms, and also a chemical potential for amphoteric atoms in acceptor states.

Denoting the chemical potential for an amphoteric atom by μ , we define

$$\mu_{d1} \equiv \mu - \mu_{de}, \quad (5.1a)$$

$$\mu_{a1} \equiv \mu - \mu_{ae}, \quad (5.1b)$$

with μ_{de} and μ_{ae} defined by (2.14). The equilibrium condition (3.6) may be written now as

$$\mu_{d1} - \mu_{a1} = E_a + E_d - 2E_F$$

$$\begin{aligned} & -kT \ln \left[1 + 2 \exp \left(\frac{E_a - E_F}{kT} \right) \right] \\ & + kT \ln \left[1 + 2 \exp \left(\frac{E_F - E_d}{kT} \right) \right]. \end{aligned} \quad (5.2)$$

Now using (2.6), the condition that the electron distribution function also be that of equilibrium, (3.6) becomes

$$\begin{aligned} & kT \ln \left[\frac{N_{1d}}{N_{xd} - N_{1a}} \frac{N_{xa} - N_{1a}}{N_{1a}} \right] \\ & = -2E_F + W_a - W_d + kT \ln \left[1 + 2 \exp \left(\frac{E_F - E_d}{kT} \right) \right] \\ & - kT \ln \left[1 + 2 \exp \left(\frac{E_a - E_F}{kT} \right) \right]. \end{aligned} \quad (5.3)$$

Comparing (5.3) with (5.2), we see that

$$\begin{aligned} & kT \ln \left[\frac{N_{1d}}{N_{xd} - N_{1d}} \frac{N_{xa} - N_{1a}}{N_{1a}} \right] \\ & = W_a - W_d + \mu_{d1} - \mu_{a1} - E_a - E_d. \end{aligned} \quad (5.4)$$

Now for the case

$$E_F = \bar{E}_F \equiv (E_a + E_d)/2,$$

(5.4) becomes [using (2.15)]

$$kT \ln \left[\frac{\bar{N}_{1d}}{N_{xd} - \bar{N}_{1d}} \frac{N_{xa} - \bar{N}_{1a}}{\bar{N}_{1a}} \right] = W_a - W_d - 2\bar{E}_F. \quad (5.5)$$

Thus

$$\begin{aligned} & kT \ln \left[\frac{N_{1d}}{\bar{N}_{1d}} \frac{N_{xd} - \bar{N}_{1d}}{N_{xd} - N_{1d}} \frac{\bar{N}_{1a}}{N_{1a}} \frac{N_{xa} - N_{1a}}{N_{xa} - \bar{N}_{1a}} \right] \\ & = \mu_{d1} - \mu_{a1} = \mu_{ae} - \mu_{de}. \end{aligned} \quad (5.6)$$

This is just what one would expect on the basis of a naïve use of separate chemical potentials, $\mu_{d1} + \mu_{ae}$ and $\mu_{a1} + \mu_{de}$, for donor and acceptor amphoteric atoms.

For lattice vacancies, we define a "chemical potential"

$$\mu_{av} \equiv \mu_{av1} + \mu_{ave}, \quad (5.7)$$

where μ_{ave} is defined by (2.14b) and μ_{av1} has the form (2.9b). (Again we assume the vacancy acts as an acceptor. If it acts as a donor quite similar arguments can be made.)

$$\mu_{av} = \mu_{av1} + E_{av} - E_F + kT \ln 2$$

$$-kT \ln \left[1 + 2 \exp \left(\frac{E_a - E_F}{kT} \right) \right]. \quad (5.8)$$

From (4.7), the dilute case, and (2.6d)

$$\ln \left(\frac{N_v}{N_x} \right) = \frac{E_F - W_v}{kT} + \ln \left[1 + 2 \exp \left(\frac{E_a - E_F}{kT} \right) \right], \quad (5.9)$$

and, from (5.8)

$$\ln \left(\frac{N_v}{N_x} \right) = \frac{-W_v - \mu_{ave} + E_{av}}{kT} - \ln 2. \quad (5.10)$$

Comparing this with the intrinsic case

$$\ln \left(\frac{N_v}{N_v^i} \right) = \frac{\mu_{ave}^i - \mu_{ave}}{kT}, \quad (5.11)$$

which corresponds to Eq. (4.9).

Thus also in the case of lattice vacancies, when their density is small compared to the density of lattice sites, we can again use the simple electronic chemical potential approach.

6. REMARKS ON DISTRIBUTION COEFFICIENTS

Reiss and Fuller³ have calculated distribution coefficients for donor (acceptor) atoms between two phases when the acceptor (donor) concentrations are *fixed*. We wish to remark that lattice vacancies may form an appreciable fraction of the net imbalance of ionizing imperfections and that this fraction is not fixed but depends (in equilibrium) upon the position of the Fermi level. Therefore it would be preferable to express the equilibrium distribution coefficients in terms of the Fermi level directly. This is easily done.

We wish to compare the number, N^s , of impurity atoms in the solid with the number, N^{is} , which would be in equilibrium with the same liquid if the solid were intrinsic. Denoting the chemical potentials of this impurity atom by μ^s and μ^{is} in those two cases, we must have

$$\mu^{is} = \mu^s. \quad (6.1)$$

Using (2.8) and (2.9) again

$$\mu_1^{is} + \mu_e^{is} = \mu_1^s + \mu_e^s \quad (6.2)$$

and

$$kT \ln \left[\frac{N^s}{N_x^s - N^s} \frac{N_x^s - N^{is}}{N^{is}} \right] = -\mu_e + \mu_e^i. \quad (6.3)$$

Now using (2.14) we have, for donors

$$kT \ln \left[\frac{N_d^s}{N_{xa}^s - N_d^s} \frac{N_{xa}^s - N_d^{is}}{N_d^{is}} \right] = E_F - E_F^i - kT \ln \left[1 + 2 \exp \left(\frac{E_F - E_d}{kT} \right) \right], \quad (6.4a)$$

and, for acceptors

$$kT \ln \left[\frac{N_a^s}{N_{xa}^s - N_a^s} \frac{N_{xa}^s - N_a^{is}}{N_a^{is}} \right] = E_F^i - E_F - kT \ln \left[1 + 2 \exp \left(\frac{E_a - E_F}{kT} \right) \right]. \quad (6.4b)$$

These formulas may be reduced to Reiss' and Fuller's formula³ (2.10), for the special case of exhaustion semiconductors using (A5).

The distribution coefficients, $K \equiv C_s/C_L$, in semiconductors are ordinarily measured for intrinsic materials. In the dilute case $N^s \ll N_x^s$ and Eq. (6.3) reduces to

$$\ln(K/K^i) = (\mu_e^i - \mu_e)/kT. \quad (6.5)$$

7. CHARGE BALANCE IN INSULATORS

Charge balance in insulators (i.e., the number of donor impurities equals the number of acceptor impurities) is a condition that has long been in current usage.¹⁰ We shall here show that charge balance is a thermodynamic equilibrium condition which arises from the ionization interaction between impurities and from the presence of a large energy gap.

In an insulator, $|E_F - \bar{E}_F| \gg kT$ even for only slight imbalance of donor and acceptor concentrations, according to (A8). But when $(E_F - \bar{E}_F) \gg kT$, say, the crystal will strongly tend to "suck in" acceptor imperfections in order to lower its free energy. Acceptor imperfections may be available in the form of impurity atoms, in which case (6.4) is relevant, or as lattice vacancies, in which case (4.16) and accompanying remarks are relevant. Thus, an insulator decreases its free energy strongly by moving its Fermi level toward the gap center, thereby suppressing the free carrier density. Thus an insulator will remain insulating even with high-impurity concentrations.

8. SOLID-LIQUID INTERFACE AND CRYSTAL GROWTH

The Fermi level is displaced relative to the center of the energy gap by unbalance in impurity type. Then, since in equilibrium the Fermi level is the same in solid and liquid phase, it is clear that there is a variable step in electric potential of magnitude $|E_F^i - E_F|$ at the interface between solid and liquid (metallic) impure germanium. (This is in addition to the potential step arising from difference in work function in the intrinsic case.)

This potential step is smoothed over a layer of about 10^{-6} cm in the semiconductor (rather than in the metal) phase. The spatial variation in potential produces a difference in equilibrium impurity concentration in the surface layer from the bulk. The surface layer concentration is, in fact, nearly independent of the bulk concentration.

It is clear that too rapid crystal growth will result in a nonequilibrium bulk concentration, *viz.*, some compromise between the surface layer and equilibrium bulk concentration determined by the relative speed of crystal growth and diffusion. This effect is intensified when the impurity-produced potential step has the same sign as the intrinsic step and weakened when the two steps have opposite sign. Indeed such a dependence of distribution coefficient upon growth rate is observed¹⁶ in *n*-type but not *p*-type germanium. This suggests that the intrinsic potential step makes the surface layer *p*-type by about 0.15 ev. (See Fig. 1.) It may also be

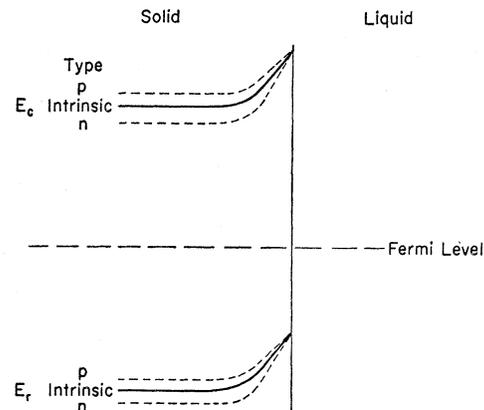


FIG. 1. Band model for solid-liquid interface in germanium.

noted that diffusion of acceptor type impurities from the surface layer to the bulk is aided by the potential step while the diffusion of donor-type impurities is impeded.

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APPENDIX: THE POSITION OF THE FERMI LEVEL IN THE BAND STRUCTURE

The position of the Fermi level relative to the band structure is determined by the donor and acceptor populations, N_d and N_a , through the charge neutrality equation,⁷

$$-\sum_s n_s + \sum_t p_t = N_d - N_a \equiv N, \quad (A1)$$

together with the formulas (2.6a), (2.6b), (2.6c), (2.6d).

¹⁶ R. N. Hall, Phys. Rev. 88, 139 (1952).

(Slightly different formulas would result from different assumptions concerning the donor and acceptor degeneracies.) Solving the resulting transcendental equation for E_F is complicated, (the case of nondegenerate donor and acceptor levels has been reviewed by Blakemore¹⁷) but simple expressions for E_F can be got in two important cases: the exhaustion semiconductor having nondegenerate carriers, and the insulator.

In the exhaustion semiconductor (A1) reduces to

$$N = n_c - p_v, \quad (\text{A2})$$

where n_c is the conduction band electron population and p_v is the valence band hole population. If these obey nondegenerate statistics

$$n_c = n_i \exp(E_F - E_{F^i})/kT, \quad (\text{A3a})$$

$$p_v = n_i \exp(E_{F^i} - E_F)/kT, \quad (\text{A3b})$$

where n_i is the value of n_c when $N_d = N_a = 0$ and where

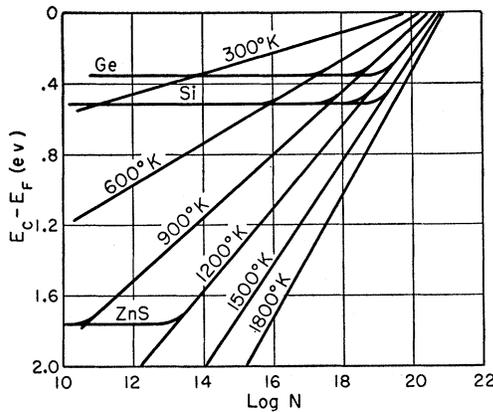


FIG. 2. Fermi levels in semiconductors. The conduction band energy, E_c , is taken as reference level for all semiconductors.

E_{F^i} is the corresponding⁷ value of E_F .

$$E_{F^i} = (E_c + E_v)/2 + kT \ln(N_c/N_v), \quad (\text{A4})$$

where N_c and N_v are the effective⁷ number of states in the conduction and valence bands. Putting (A3) into (A2) gives

$$\exp\left(\frac{E_F - E_{F^i}}{kT}\right) = \frac{N}{2n_i} + \left[\left(\frac{N}{2n_i}\right)^2 + 1\right]^{\frac{1}{2}} \quad (\text{A5a})$$

or

$$\exp\left(\frac{E_F - E_{F^i}}{kT}\right) = \left\{ -\frac{N}{2n_i} + \left[\left(\frac{N}{2n_i}\right)^2 + 1\right]^{\frac{1}{2}} \right\}^{-1}. \quad (\text{A5b})$$

(See Fig. 2.)

¹⁷ J. S. Blakemore, Elec. Commun. 29, 131-153 (1952).

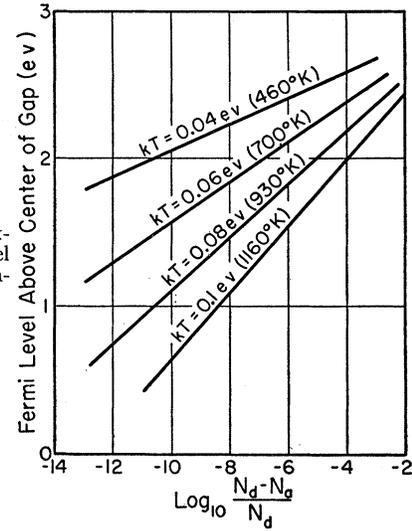


FIG. 3. Approximate Fermi level versus impurity concentration in NaCl.

In an insulator, in addition to a large energy gap, one has

$$\frac{n_c}{n_d} = \frac{N_c}{N_d} \exp\left(\frac{E_d - E_c}{kT}\right) \ll 1, \quad (\text{A6a})$$

$$\frac{p_v}{p_a} = \frac{N_v}{N_a} \exp\left(\frac{E_v - E_a}{kT}\right) \ll 1, \quad (\text{A6b})$$

so that (A2) becomes

$$N = n_d - p_a. \quad (\text{A7})$$

Using (2.6b) and (2.6d) in (A7), one finds

$$\exp\left(\frac{E_F - \bar{E}}{kT}\right) = \frac{1}{4N_d} [N e^{\Delta/2} + (N^2 e^{\Delta} + 16N_a) N_d] \quad (\text{A8a})$$

or

$$\exp\left(\frac{E_F - \bar{E}}{kT}\right) = 4N_d [-N e^{\Delta/2} + (N^2 e^{\Delta} + 16N_a N_d)^{\frac{1}{2}}]^{-1}, \quad (\text{A8b})$$

where

$$\bar{E} \equiv (E_a + E_d)/2 \quad (\text{A9a})$$

and

$$\Delta \equiv (E_d - E_a)/kT. \quad (\text{A9b})$$

(See Fig. 3.)