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Statistics of multicharge centers in semiconductors: Applications

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A general formula is derived for the electron occupation numbers appropriate for multicharge centers in semiconductors, including excited states. The results are used to rederive and generalize several formulas of interest in the literature, in order to show exactly how the degeneracies of individual states enter in. Particular attention is paid to certain subjects which are sometimes confusing, such as how the statistics of band states differ from those of localized states. Another subject of much recent interest, negative- U centers, is dealt with in some detail. We show how the dependence of the average occupation number on Fermi energy and the temperature dependence of the free-carrier concentration differ between positive- and negative- U centers.

I. INTRODUCTION

It has long been known that the Fermi-Dirac distribution function,

$$f(\mathcal{E}) = 1/[1 + \exp(\mathcal{E} - \mathcal{E}_F/kT)],$$

which so well describes electrons in an energy band, is, in general, inapplicable to electrons in localized states, such as those that may arise from substitutional impurities in a semiconductor.^{1,2} For these latter cases, the distribution function is usually modified as follows:

$$f(\mathcal{E}) = 1/[1 + K \exp(\mathcal{E} - \mathcal{E}_F)/kT],$$

where K is a constant and the other symbols have their usual meanings. Thus, $K = 1$ for band electrons, and it has also been shown that $K = \frac{1}{2}$ for some shallow donors and $K = 4$ for some shallow acceptors.³ Usually, researchers use one of these three values but often in cases for which they have no apparent validity. In a more general sense, K is variously given as $1/g$ or as g_0/g_1 , where g_0 is the degeneracy of the unoccupied state of a single-charge-state impurity, and g or g_1 the degeneracy of the occupied state. Since band states are spin-degenerate, it might naively be expected that K should be one-half, not one, in this case. The reasons why this is not true are sometimes not made clear.

For discussions of double-charge-state centers (occupation by 0, 1, or 2 electrons), the starting point is usually either the law of mass action or a formula of Brooks.⁶ Evidently Brooks's formula has never been explicitly derived in the literature,

only quoted; in any case, it has not appeared, to our knowledge, with the various state degeneracies g_0 , g_1 , and g_2 , included in a general way. For centers with higher-order charge states, or with excited states, the situation is even less clear, at least for the general researcher. This problem becomes important when dealing with, say, negative- U centers, or with Cr in GaAs, for which four charge states (Cr^{1+} , Cr^{2+} , Cr^{3+} , and Cr^{4+}), along with important excited states, evidently exist.⁷

Many rather diverse treatments of this subject have appeared. Landsberg first introduced a thermodynamic approach based on minimizing the free energy.¹ Then Guggenheim suggested a method in which the equilibrium distribution function was written directly in terms of the absolute activity (Fermi level).⁸ Guggenheim's approach was essentially equivalent to formulating the problem in terms of the grand-partition function (GPF), and this formulation was then further developed and used by Landsberg,⁹ Teitler and Wallis,¹⁰ Clark,¹¹ and others. Different approaches have been utilized by Champness¹² and Shockley and Last.¹³

In spite of these excellent past efforts, we feel that a unified treatment, tying together the various results in the literature, as well as generalizing them, is lacking. In this paper we start from the familiar principle of maximum probability and derive general results, which are then used to obtain the following specific results: (1) free-electron and hole concentrations, (2) the charge balance equation, (3) the Fermi function for shallow donors with excited states, (4) the mass-action law, (5) the Brooks formula, (6) the Teitler-Wallis formula for acceptors in tetrahedral semiconductors, and (7)

the statistics of negative- U centers. In regard to item (1), we try to show in a very natural way why $K = 1$ for band electrons, and $K = \frac{1}{2}$ for donors in an orbital-singlet state. Also, we will discuss item (7), negative- U centers, in some detail since this is a topic of much current interest.

Our approach in this paper will be to start with the simplest problem, namely, the familiar single-charge-state center with no degeneracy and no excited states. Then we will consider some more complex problems of general interest and finally derive the general result. It is felt that this approach, rather than immediately deriving the general result, will lead to a better understanding of the concepts involved and make them more easily applicable by the interested researcher.

II. DERIVATION OF OCCUPATION PROBABILITIES

The maximum probability method of deriving energy-distribution functions is a familiar approach described in many textbooks on solid-state physics.¹⁴ The heart of the technique is in finding the number of distinguishable ways that a given number of particles can be distributed among a given number of boxes.¹⁵ The particles in this case are electrons and the boxes are the "elementary" eigenstates of the system. Here a "box" could be a band state, denoted by $k_x, k_y,$ and k_z quantum numbers, or an atomic impurity state, denoted by its own appropriate quantum numbers. Now an important assumption is that an electron in one box must interact only weakly with the electrons in other boxes. If this is the case, then the total Hamiltonian for the system will simply be the sum of the individual Hamiltonians, and the grand eigenstate can be written as a product of the individual eigenstates, properly symmetrized, of course. It should be noted here that, although the interaction between boxes must be weak, the interactions of electrons within a box may be strong indeed. We simply require that the eigenstate and eigenvalue for the box as a whole be known.

The available electrons in the system will come from the valence band and donor centers. These electrons can be distributed among states in the valence band, conduction band, donor centers, and acceptor centers. Each *distinguishable* arrangement of the electrons among all of these states results in a different grand eigenstate, and it is assumed that every grand eigenstate which leads to the same total energy is equally likely to occur.

The maximum probability principle then states that the electrons will distribute themselves among the possible energy cells of the system in such a way that the maximum number of grand eigenstates can be formed, consistent with a given total energy.

We will illustrate these concepts by reviewing the common textbook problem of finding the density of electrons in the conduction band.¹⁴ Here the boxes are denoted by (k_x, k_y, k_z, σ) , where σ represents either spin up or spin down. Thus, each box can hold only one electron. [See Fig. 1(a).] We suppose that the states in the band can be split into small energy intervals of width $\Delta\mathcal{E}$, where $\Delta\mathcal{E}$ is large enough to envelop many states, but smaller than our maximum energy resolution, or at least smaller than the accuracy within which we wish to measure energy. Let N_k be the number of states in energy interval k and n_k be the number of electrons assigned to this energy interval. The first of these electrons can be assigned in N_k ways, the

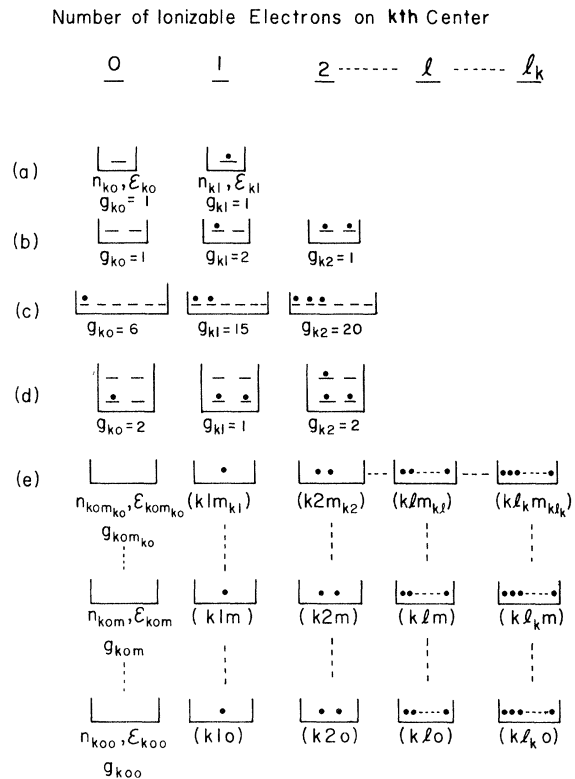


FIG. 1. Schematic representation of the number of ionizable electrons on the k th center. Here "ionizable" means that the electron can be excited to the conduction band by less than band-gap energy. See text for explanation of symbols.

second in $N_k - 1$, etc., for a total of

$$N_k(N_k - 1)(N_k - 2) \cdots (N_k - n_k + 1) \\ = N_k! / (N_k - n_k)!$$

ways. Since permutations of the n_k occupied states do not result in different grand eigenstates, the total number of distinguishable ways of arranging the electrons in the k th energy interval is

$$W_k = \frac{N_k!}{n_k!(N_k - n_k)!} \quad (1)$$

By taking into account states within the other energy intervals, we get the total number of distinguishable ways that electrons may be arranged in the whole conduction band:

$$W_c = \prod_k \frac{N_k!}{n_k!(N_k - n_k)!} \quad (2)$$

The constraints to this problem are

$$\sum_k n_k = n_t, \quad (3)$$

$$\sum_k n_k \mathcal{E}_k = \mathcal{E}_t, \quad (4)$$

where \mathcal{E}_k is the energy difference between the occupied and unoccupied states in the k th energy interval, n_t is the total number of electrons, and \mathcal{E}_t is the total energy. Note that in Eqs. (2)–(4) we have not included the contributions of electrons in the valence band and impurity levels. This is because the final result for conduction-band states will not explicitly depend on these other contributions, but only through a constant, α .

We now wish to find the set of n_k which will maximize W_c . (Actually it is more convenient to maximize $\ln W_c$ so that we can apply Stirling's formula: $\ln N! \simeq N \ln N - N$ for large N .) The method of Lagrange multipliers¹⁶ requires finding the maximum of the following function:

$$F = \ln W_c + \alpha \left[n_t - \sum_k n_k \right] + \beta \left[\mathcal{E}_t - \sum_k n_k \mathcal{E}_k \right], \quad (5)$$

where α and β are undetermined constants. By use of Stirling's approximation we get

$$\ln W_c = \sum_k [N_k \ln N_k - n_k \ln n_k \\ - (N_k - n_k) \ln (N_k - n_k)] \quad (6)$$

Although the n_k are not independent, they may be treated as such with respect to the Lagrange func-

tion, Eq. (5). The maximum of the Lagrange function is then found by setting $dF/dn_k = 0$, and the result is the well-known Fermi-Dirac distribution function:

$$n_k = \frac{N_k}{1 + \exp(\alpha + \beta \mathcal{E}_k)} \quad (7)$$

The constants α and β can be identified by comparison with a thermodynamic treatment of the problem.¹⁴ The results are $\alpha = -\mathcal{E}_F/kT$ and $\beta = 1/kT$, where \mathcal{E}_F is the chemical potential or Fermi energy.

The total density of electrons in the conduction band (CB) is then

$$n = \frac{1}{V} \sum_{k, \text{CB}} n_k = \frac{1}{V} \sum_k \frac{\phi_c(\mathcal{E}_k) \Delta \mathcal{E}}{1 + \exp[(\mathcal{E}_k - \mathcal{E}_F)/kT]} \\ = \frac{1}{V} \int_{\mathcal{E}_c^{\min}}^{\mathcal{E}_c^{\max}} \frac{\phi_c(\mathcal{E}) d\mathcal{E}}{1 + \exp[(\mathcal{E} - \mathcal{E}_F)/kT]} \\ = \frac{4\pi(2m_n^*)^{3/2}}{h^3} \int_0^\infty \frac{\mathcal{E}^{1/2} d\mathcal{E}}{1 + \exp[(\mathcal{E} - \mathcal{E}_F)/kT]}, \quad (8)$$

where we have set $\mathcal{E}_c^{\min} = 0$. The upper limit \mathcal{E}_c^{\max} can be extended to infinity since the integrand becomes very small for \mathcal{E} more than a few kT above \mathcal{E}_F . The density of states function used here is valid for simple parabolic energy bands, i.e., $\mathcal{E}(\vec{k}) = \hbar^2 k^2 / 2m_n^*$, where \vec{k} is the crystal momentum.

Now an important point about the familiar formula given in Eq. (8) is that both the spin-up and spin-down states, which are degenerate, were included among our elementary eigenstates. However, spin degeneracy cannot be treated so easily when the wave functions are localized, as on impurity atoms. To illustrate the differences, we will consider the slightly more complicated arrangement shown in Fig. 1(b), in which each box may hold two electrons. From the energy-band point of view a box here may represent a given (k_x, k_y, k_z) eigenfunction, which can hold both spin-up and spin-down electrons, while for localized levels a box may represent a donor impurity atom, which can have either one or two electrons in an s state. The representation in Fig. 1(b) differs from that in Fig. 1(a) in two ways. First of all, there are additional permutations possible. These arise because the electrons in the singly occupied boxes can be in either of two states (e.g., spin up or spin down). Since there are n_{k1} double permutations possible, W_k becomes

$$W_k = \frac{2^{n_{k1}} N_k!}{n_{k0}! n_{k1}! n_{k2}!} . \quad (9)$$

Second, a new energy, \mathcal{E}_{k2} , must be assigned to the two-electron state. Here \mathcal{E}_{k2} is the energy difference between the two-electron state and the zero-electron state. Normally, $\mathcal{E}_{k2} > 2\mathcal{E}_{k1}$ because of electron-electron repulsion, although the reverse will be true for "negative- U " centers, to be discussed later. The constraints are now

$$n_{k0} + n_{k1} + n_{k2} = N_k , \quad (10)$$

$$n_{k1} + 2n_{k2} + \sum_{\substack{k' \neq k \\ l'}} l' n_{k'l'} = n_l , \quad (11)$$

$$n_{k1} \mathcal{E}_{k1} + n_{k2} \mathcal{E}_{k2} + \sum_{\substack{k' \neq k \\ l'}} n_{k'l'} \mathcal{E}_{k'l'} = \mathcal{E}_l , \quad (12)$$

where Eq. (10) is included as a new constraint rather than being explicitly substituted into Eq. (9) for n_{k2} . The summations over index k' simply represent other electrons in the system, which will not affect the final result. We introduce a new Lagrange multiplier γ for Eq. (10), set up a function similar to that of Eq. (5), and take derivatives with respect to n_{k0} , n_{k1} , and n_{k2} , respectively. The results are

$$-1 - \ln n_{k0} - \gamma = 0 , \quad (13)$$

$$\ln 2 - 1 - \ln n_{k1} - \gamma - \alpha - \beta \mathcal{E}_{k1} = 0 , \quad (14)$$

$$-1 - \ln n_{k2} - \gamma - 2\alpha - \beta \mathcal{E}_{k2} = 0 . \quad (15)$$

(Note that by taking second derivatives it is easily seen that this extremum corresponds to a maximum.) These equations may be solved, by use of Eq. (10), to give

$$n_{k0} = \frac{N_k}{1 + 2e^{(-\mathcal{E}_{k1} + \mathcal{E}_F)/kT} + e^{(-\mathcal{E}_{k2} + 2\mathcal{E}_F)/kT}} , \quad (16)$$

$$n_{k1} = \frac{N_k}{1 + \frac{1}{2}e^{(\mathcal{E}_{k1} - \mathcal{E}_F)/kT} + \frac{1}{2}e^{(\mathcal{E}_{k1} - \mathcal{E}_{k2} + \mathcal{E}_F)/kT}} , \quad (17)$$

$$n_{k2} = \frac{N_k}{1 + e^{(\mathcal{E}_{k2} - 2\mathcal{E}_F)/kT} + 2e^{(\mathcal{E}_{k2} - \mathcal{E}_{k1} - \mathcal{E}_F)/kT}} . \quad (18)$$

Here, all energies are referenced to the valence band, and this will be true in the rest of the paper unless otherwise noted. Thus, for example, \mathcal{E}_{k2} is

the energy necessary to place two electrons from the top of the valence band onto a center of group k . We have chosen $\mathcal{E}_{k0} = 0$, since this level is presumed degenerate with the valence band. Later, if we wish to refer energies to the conduction-band edge, they will be designated by a superscript C .

We first apply these results to the previous problem, i.e., electrons in a conduction band. In this case, the wave functions are spread throughout the whole crystal so that the electron-electron repulsion energy, due to having two electrons (spin up and spin down) in the same (k_x, k_y, k_z) box, is small. Thus, $\mathcal{E}_{k2} = 2\mathcal{E}_{k1}$ and, with a little algebra, we can show that

$$n_k = n_{k1} + 2n_{k2} = \frac{2N_k}{1 + e^{(\mathcal{E}_{k1} - \mathcal{E}_F)/kT}} . \quad (19)$$

This is exactly the same result as before [Eq. (7)] because we started with twice as many boxes in that case; i.e., each spin state led to a separate box in the previous example. We might note here, for later reference, that the number of *holes* in the k th cell (or center) is given by

$$p_k = 2n_{k0} + n_{k1} = \frac{2N_k}{1 + e^{(\mathcal{E}_F - \mathcal{E}_{k1})/kT}} . \quad (20)$$

(Note the transposition of the energy argument.) Equation (20) will be of use later, when dealing with the valence band.

We next apply Eqs. (16)–(18) to a *localized* wave-function situation, e.g., a donor impurity in an s state. Here there will be a strong repulsive term from having two electrons on the same atom. Thus, we might expect $\mathcal{E}_{k2} \gg \mathcal{E}_{k1}$, giving

$$n_{k1} = \frac{N_k}{1 + \frac{1}{2}e^{(\mathcal{E}_{k1} - \mathcal{E}_F)/kT}} . \quad (21)$$

These considerations explain the origin of the well-known degeneracy factor of one-half. It arises simply from the much higher energy normally required to place two electrons in *localized* orbits near each other. This point has sometimes been confused in the literature. It should also be noted here that in some cases lattice relaxation effects can overcome the repulsion effects to actually give $\mathcal{E}_{k2} < 2\mathcal{E}_{k1}$. This situation will be discussed later.

The above results can be easily generalized to include arbitrary degeneracy. We first note that g_0 is not always equal to unity. Consider, for example, the neutral anion vacancy in a III-V compound. In an unrelaxed state, this defect presumably has two paired electrons in a filled a_1 state, and, at a

higher energy, one electron in a t_2 state. The t_2 state is threefold orbitally degenerate and twofold spin degenerate. If the single t_2 electron were resonant with the valence band, and if this center could accept up to two more t_2 electrons with energies in the band gap, then the situation would be described by the example in Fig. 1(c), in which $g_0 = 6!/5!1! = 6$, $g_1 = 6!/4!2! = 15$, and $g_2 = 6!/3!3! = 20$. Therefore, $g_0 \neq 1$ in this case. The number of *extra* distinguishable permutations for a double-charge-state system in general is simply $g_{k0}^{n_{k0}} g_{k1}^{n_{k1}} g_{k2}^{n_{k2}}$, giving

$$W_k = \frac{g_{k0}^{n_{k0}} g_{k1}^{n_{k1}} g_{k2}^{n_{k2}} N_k!}{n_{k0}! n_{k1}! n_{k2}!} . \quad (22)$$

The constraints in this problem are the same as before [Eqs. (10)–(12)], and the final result is

$$n_{k0} = \frac{N_k}{1 + \frac{g_{k1}}{g_{k0}} e^{\eta_F - \eta_{k1}} + \frac{g_{k2}}{g_{k0}} e^{2\eta_F - \eta_{k2}}} , \quad (23)$$

$$n_{k1} = \frac{N_k}{1 + \frac{g_{k0}}{g_{k1}} e^{\eta_{k1} - \eta_F} + \frac{g_{k2}}{g_{k1}} e^{\eta_{k1} - \eta_{k2} + \eta_F}} , \quad (24)$$

$$n_{k2} = \frac{N_k}{1 + \frac{g_{k0}}{g_{k2}} e^{\eta_{k2} - 2\eta_F} + \frac{g_{k1}}{g_{k2}} e^{\eta_{k2} - \eta_{k1} - \eta_F}} , \quad (25)$$

where $\eta_{kl} = \mathcal{E}_{kl}/kT$. Here, as before, all energies are referenced to the valence band. Equations (23)–(25), of course, revert to Eqs. (16)–(18), respectively, when $g_{k0} = 1$, $g_{k1} = 2$, and $g_{k2} = 1$.

We now consider the most general case, including excited states [Fig. 1(e)]. Let n_{klm} denote the m th excited state of the l th charge state of the k th impurity, or defect, or energy cell in a band. Here we are assuming that the zeroth charge state is resonant with the valence band so that an energy greater than the band gap would be required to excite an electron from a center in this charge state into the conduction band. Let l_k be the number of charge states within the band gap for the k th center; then $l = 0, 1, 2, \dots, l_k$. The $(l_k + 1)$ th charge state is presumed to be resonant with the conduction band, and thus unstable. For a given l , assume that there are m_{kl} excited states, i.e., $m_l = 0, 1, 2, \dots, m_{kl}$. Finally, let the degeneracy of klm th state be g_{klm} . Each excited state is now a

separate box in this problem, and from the above considerations it should be clear that

$$W = \prod_k \prod_{l=0}^{l_k} \prod_{m=0}^{m_{kl}} \frac{g_{klm}^{n_{klm}} N_k!}{n_{klm}!} . \quad (26)$$

The constraints are

$$\sum_{l,m} n_{klm} = N_k \quad \text{for each } k , \quad (27)$$

$$\sum_{k,l,m} l n_{klm} = N_e , \quad (28)$$

$$\sum_{k,l,m} n_{klm} \mathcal{E}_{klm} = \mathcal{E}_t . \quad (29)$$

Let the Lagrange multipliers be γ_k , $k = 1, 2, \dots$ for Eq. (27), α for Eq. (28), and β for Eq. (29). Then the derivative with respect to n_{klm} of the total Lagrange function will give

$$\ln g_{klm} - 1 - \ln n_{klm} - \gamma_k - l\alpha - \beta \mathcal{E}_{klm} = 0 . \quad (30)$$

When $l = 0$ and $m = 0$ we get

$$\ln g_{k00} - 1 - \ln n_{k00} - \gamma_k - \beta \mathcal{E}_{k00} = 0 . \quad (31)$$

Thus, by combining Eqs. (30) and (31) we get

$$\begin{aligned} n_{klm} &= \frac{g_{klm}}{g_{k00}} n_{k00} e^{-l\alpha - \beta(\mathcal{E}_{klm} - \mathcal{E}_{k00})} \\ &= \frac{g_{klm}}{g_{k00}} n_{k00} e^{l\eta_F - (\eta_{klm} - \eta_{k00})} \end{aligned} \quad (32)$$

where, again, $\eta \equiv \mathcal{E}/kT$. Equation (27) can be written

$$\begin{aligned} N_k &= \sum_{l,m} n_{klm} \\ &= \frac{n_{k00}}{g_{k00}} \sum_{l,m} g_{klm} e^{l\eta_F - (\eta_{klm} - \eta_{k00})} \end{aligned} \quad (33)$$

so that the final result is

$$n_{klm} = \frac{N_k}{1 + \sum_{l',m' \neq l,m} \frac{g_{kl'm'}}{g_{klm}} e^{\eta_{klm} - \eta_{kl'm'} - (l-l')\eta_F}} . \quad (34)$$

The restriction on the summation is that $l' \neq l$ and $m' \neq m$ at the same time. Here \mathcal{E}_{klm} is the energy required to place l electrons from the valence band into the m th excited state on one of the centers in group k .

III. APPLICATIONS

In this section we will use the above results to derive, and in certain cases generalize, a number of formulas which exist in the literature. One purpose is to enhance the applicability of some of these well-known results for the general researcher. Also, we will consider negative- U centers in some detail.

A. Conduction and valence bands

The total density of electrons in the conduction band was already derived [Eq. (8)]. Similarly, the total density of holes in the valence band (VB) may be obtained from Eq. (20):

$$\begin{aligned}
 p &= \frac{1}{V} \sum_{k, \text{VB}} p_k = \frac{1}{V} \sum_k \frac{2N_k}{1 + \exp[(\mathcal{E}_F - \mathcal{E}_k)/kT]} \\
 &\rightarrow \frac{1}{V} \int_{\mathcal{E}_v^{\min}}^{\mathcal{E}_v^{\max}} \frac{2\phi_v(\mathcal{E})d\mathcal{E}}{1 + \exp[(\mathcal{E}_F - \mathcal{E})/kT]} = \frac{4\pi(2m_p^*)^{3/2}}{h^3} \int_{-\infty}^{\mathcal{E}_v^{\max}} \frac{(-\mathcal{E} + \mathcal{E}_v^{\max})^{1/2}d\mathcal{E}}{1 + \exp[(\mathcal{E}_F - \mathcal{E})/kT]} \\
 &= \frac{4\pi(2m_p^*)^{3/2}}{h^3} \int_0^{\infty} \frac{X^{1/2}dX}{1 + \exp[(X + \mathcal{E}_F - \mathcal{E}_v^{\max})/kT]}, \quad (35)
 \end{aligned}$$

where, again, non-parabolic-band effects are ignored. When \mathcal{E}_F is more than a few kT from either band edge, we obtain the well-known results¹⁷

$$n = \frac{2(2\pi m_n^* kT)^{3/2}}{h^3} e^{\mathcal{E}_F/kT} \equiv N_c e^{\mathcal{E}_F^C/kT}, \quad (36)$$

$$p = \frac{2(2\pi m_p^* kT)^{3/2}}{h^3} e^{(\mathcal{E}_v^{\max} - \mathcal{E}_F)/kT} \equiv N_v e^{(-\mathcal{E}_F^V)/kT}. \quad (37)$$

B. Charge balance equation

The left-hand side of Eq. (28) is

$$\begin{aligned}
 \sum_{k, l, m} \ln_{klm} &= n + (N_{vt} - p) \\
 &+ \sum_{\mathcal{D}} \sum_{k, l, m} \ln_{klm} + \sum_{\mathcal{A}} \sum_{k, l, m} \ln_{klm}, \quad (38)
 \end{aligned}$$

where N_{vt} is the total density of states in the valence band, \mathcal{D} denotes donors, and \mathcal{A} denotes acceptors. (All numbers now are normalized to unit volume to give densities.) The right-hand side of Eq. (28), N_e , is just the total number (density) of electrons available for distribution among the various electronic states. Thus,

$$N_e = N_{vt} + \sum_{\mathcal{D}} l_k N_k. \quad (39)$$

Equation (28) can, therefore, be rearranged as

follows:

$$n + \sum_{\mathcal{A}} \sum_{k, l, m} \ln_{klm} = p + \sum_{\mathcal{D}} \left[l_k N_k - \sum_{l, m} \ln_{klm} \right]. \quad (40)$$

Equation (40) is simply a statement of charge balance since the left-hand side is the total density of negative charges and the right-hand side, positive charges. For single donors and acceptors ($l=0, 1$), with no excited states, Eq. (40) attains the familiar form

$$n + \sum_{\mathcal{A}} n_k = p + \sum_{\mathcal{D}} (N_k - n_k). \quad (41)$$

where, according to Eq. (34),

$$n_k = \frac{N_k}{1 + \frac{g_{k0}}{g_{k1}} e^{(\mathcal{E}_{k1} - \mathcal{E}_F)/kT}}. \quad (42)$$

C. Excited states of shallow donors

In dealing with the detailed electrical properties of shallow donors in GaAs, it is sometimes necessary to take account of excited states.¹⁸ For the Fermi level near the conduction band, we can ignore p and assume that all acceptors are ionized, with total negative charge N_A . Then, if there is only one dominant donor species, which can bind one electron, Eq. (40) becomes

$$n + N_A = N_D - \sum_m n_{D1m} = \sum_m n_{D0m} = n_{D0}, \quad (43)$$

where we have assumed that the *unoccupied* state n_{D0} has no excited states within the band gap.

From Eq. (34) we now get

$$\begin{aligned}
 n_{D0} &= \frac{N_D}{1 + \sum_{m'} \frac{g_{1m'}}{g_{00}} e^{(-\mathcal{E}_{1m'} + \mathcal{E}_F)/kT}} \\
 &= \frac{N_D}{1 + \frac{g_{10}}{g_{00}} e^{\mathcal{E}_F/kT} e^{-\mathcal{E}_{10}^C/kT}} \\
 &\quad \times \left[1 + \sum_{m' \neq 0} \frac{g_{1m'}}{g_{10}} e^{(\mathcal{E}_{10}^C - \mathcal{E}_{1m'}^C)/kT} \right] \\
 &= \frac{N_D}{1 + \frac{g_{10}}{g_{00}} e^{E_D/kT} \frac{n}{N_c} (1+F)}, \quad (44)
 \end{aligned}$$

where energies have been referenced to the conduction band, as is common when dealing with shallow donors. Here we have set $\mathcal{E}_{10}^C = -E_D$, and have assumed the nondegenerate (Boltzmann) form of n [Eq. (36)]. By combining Eqs. (43) and (44), it can be shown that

$$\frac{n(n+N_A)}{N_D - N_A - n} = \frac{g_{00}}{g_{10}} \frac{N_c e^{-E_D/kT}}{1+F}, \quad (45)$$

where

$$F = \sum_{m' \neq 0} \frac{g_{1m'}}{g_{10}} e^{(\mathcal{E}_{10}^C - \mathcal{E}_{1m'}^C)/kT}. \quad (46)$$

If there are no excited states, then, of course, $F=0$. Equation (45) is a form which has often been used in the analysis of temperature-dependent Hall-effect measurements,¹⁸ except that in these applications it

was assumed that $g_{00}=1$. This assumption is correct for a simple donor in an s state, such as that illustrated in Fig. 1(b). It must also be assumed that the *two-electron* state lies at a much higher energy.

D. Mass-action law

The mass-action law has often been used as a starting point in the discussion of multivalence impurities or defects.¹⁹ This law can be derived immediately from Eqs. (32) and (36). If the k and m indices are suppressed, we get

$$\frac{n_{l+1}}{n_l} = \frac{g_{l+1}}{g_l} e^{\eta_F - (\eta_{l+1} - \eta_l)} = \frac{g_{l+1}}{g_l} \frac{n}{N_c} e^{\eta_c + \eta_l - \eta_{l+1}} \quad (47)$$

or

$$\frac{nn_l}{n_{l+1}} = N_c \frac{g_l}{g_{l+1}} e^{\eta_{l+1} - \eta_l - \eta_c} \equiv K_{l,l+1}^{(n)},$$

where η_c denotes the conduction-band edge. The right-hand side of Eq. (47) is simply the equilibrium constant for the reaction $n + n_l \rightarrow n_{l+1}$. For holes we can use Eq. (37) to get

$$\frac{pp_j}{p_{j+1}} = \frac{g_j}{g_{j+1}} N_v e^{\eta_{j+1} - \eta_j} \equiv K_{j,j+1}^{(p)}, \quad (48)$$

which describes the reaction $p + p_j \rightarrow p_{j+1}$. (Here the subscripts j and $j+1$ refer to *hole* occupation numbers.) Equation (48) was the starting point for a recent discussion of negative- U centers by Hoffmann,¹⁸ except that his degeneracy factors were given as unknown constants. It should be remembered that these mass-action formulas are valid only in the nondegenerate limit since we have used Eqs. (36) and (37).

E. A formula derived by Brooks

Centers with two charge states are often discussed in terms of a formula derived by Brooks.^{6,20} The derivation, however, was not published. The two-charge-state system is described by Eqs. (23)–(25). Let $a \equiv (g_0/g_1)\exp(\eta_1 - \eta_F)$, and $b \equiv (g_2/g_1)\exp(\eta_1 - \eta_2 + \eta_F)$. The average number of electrons per center is then given by

$$\begin{aligned}
 n_{av} &= \frac{n_1 + 2n_2}{N} = \frac{1}{1+a+b} + \frac{2}{1+ab^{-1}+b^{-1}} = \frac{1}{1+a+b} + \frac{2b}{1+a+b} = \frac{1}{\frac{1}{2} + \frac{1+a}{1+2b}} \\
 &= \frac{2}{1 + \frac{1+2a}{1+2b}} = \frac{2}{1 + \frac{1+2(g_0/g_1)\exp(\eta_1 - \eta_F)}{1+2(g_2/g_1)\exp(\eta_1 - \eta_2 + \eta_F)}}. \quad (49)
 \end{aligned}$$

For an impurity in an s state (or a state with a_1 orbital symmetry), $g_0 = g_2 = 1$, $g_1 = 2$, so that

$$n_{av} = \frac{2}{1 + \frac{1 + \exp(\eta_1 - \eta_F)}{1 + \exp(\eta_1 - \eta_2 + \eta_F)}}. \quad (50)$$

Brooks did not write his formula in terms of the g_l 's, but only for two specific situations, one of which gave Eq. (50), and the other of which gave factors of four in front of the exponential terms.²⁰ In this latter case we would need $g_0 = g_2$, and $g_1 = g_0/2$; a possible state which would lead to this result is shown in Fig. 1(d).

F. Acceptors in tetrahedral semiconductors

Teitler and Wallis¹⁰ have used the grand-partition-function scheme to analyze acceptors in semiconductors with tetrahedral coordination. In such semiconductors the valence bands at $k = 0$

may often be described in terms of two degenerate p -like bands at an energy $|\mathcal{E}_g|$ below the conduction-band edge: one spin-orbit-split p -like band lying below the two degenerate bands, and an s -like band lying much lower. Each of these four bands is spin degenerate. We assume that an acceptor can be described in a similar manner, i.e., of the eight possible electrons in its outer (valence) shell, the four highest lying electrons are degenerate, and the other four electrons are paired off and lie at much lower energies. Thus, in this model our box has four compartments, containing from zero to four electrons. As an example, neutral gold in silicon would have one electron in this box (and four in the lower levels), and gold in its triple-acceptor state would have four electrons in the box. The degeneracies in this problem are easily calculated: $g_0 = 4!/4! = 1$, $g_1 = 4!/3!1! = 4$, $g_2 = 4!/2!2! = 6$, $g_3 = 4$, and $g_4 = 1$. Consider the doubly occupied state ($l = 2$). Then from Eq. (34),

$$n_2 = \frac{N}{1 + \sum_{l' \neq 2} \frac{g_{l'}}{g_2} e^{\eta_2 - \eta_{l'} + (l' - 2)\eta_F}} = \frac{N}{1 + \frac{1}{6} e^{\eta_2 - \eta_0 - 2\eta_F} + \frac{2}{3} e^{\eta_2 - \eta_1 - \eta_F} + \frac{2}{3} e^{\eta_2 - \eta_3 + \eta_F} + \frac{1}{6} e^{\eta_2 - \eta_4 + 2\eta_F}}, \quad (51)$$

where we have suppressed the k and m indices. It is sometimes more convenient to work with "ionization" energies, i.e., $E_l = \mathcal{E}_l - \mathcal{E}_{l-1}$, since these are the experimentally measured quantities. Then it is easily seen that $\mathcal{E}_4 - \mathcal{E}_0 = E_4 + E_3 + E_2 + E_1$, $\mathcal{E}_3 - \mathcal{E}_0 = E_3 + E_2 + E_1$, etc., and Eq. (51) becomes

$$\frac{n_2}{N} = \left\{ 1 + \frac{1}{6} \exp[(E_1 + E_2 - 2E_F)/kT] + \frac{2}{3} \exp[(E_2 - E_F)/kT] + \frac{2}{3} \exp[(-E_3 + E_F)/kT] + \frac{1}{6} \exp[(-E_3 - E_4 + 2E_F)/kT] \right\}^{-1}. \quad (52)$$

This result agrees with the corresponding formula in the Teitler-Wallis paper.¹⁰ Formulas for n_0 , n_1 , n_3 , and n_4 may be derived similarly. In dealing with ionization energies, we must be careful not to assign more meaning to them than is due. For example, in the four-electron state we *do not* have four different orbitals, corresponding to energies E_1 , E_2 , E_3 , and E_4 , respectively. That is, we cannot assign these electrons individual positions in energy space, say with respect to the band edges. As a group, however, we can assign an energy, and that is what our script notation \mathcal{E} stands for. For example, the energy required to place four electrons from the valence band onto a previously unoccupied center is just $\mathcal{E}_4 - \mathcal{E}_0$.

G. Negative- U centers

In general, we would expect that a two-electron state would have more than twice the energy of a

one-electron state, because of electron-electron repulsion. However, in order to explain certain electronic and magnetic properties of chalcogenide glasses, Anderson²¹ introduced the concept of "negative- U " centers in which this condition does not hold. Recently, Baraff, Kane, and Schluter²² predicted that the Jahn-Teller relaxation energy for the Si vacancy in the two-electron state might be large enough to overcome the repulsive energy between the electrons, and thus lead to a negative- U center. Indeed, Watkins and Troxell²³ confirmed this prediction experimentally. Hoffmann¹⁹ has discussed some of the expected electrical properties of negative- U centers. Our treatment is an improvement in that degeneracy factors are explicitly taken into account and their effects are noted in particular cases.

Consider a center which can bind either one or two electrons with energy states in the bandgap.

The occupational probabilities for this system have already been given in Eqs. (23)–(25), and the average number of electrons is found from the generalized Brooks formula, Eq. (49). Suppose we rewrite Eq. (49) as

$$n_{av} = \frac{2}{1 + \frac{1+2\phi_{n1}/n}{1+2n/\phi_{n2}}} = \frac{2}{1 + \frac{1+2p/\phi_{p1}}{1+2\phi_{p2}/p}}, \quad (53)$$

where

$$\phi_{n1} = \frac{g_0}{g_1} N_c e^{\eta_1^c}, \quad (54a)$$

$$\phi_{n2} = \frac{g_1}{g_2} N_c e^{\eta_2^c + \eta_V^c - \eta_1^c}, \quad (54b)$$

$$\phi_{p1} = \frac{g_1}{g_0} N_V e^{-\eta_1^v}, \quad (54c)$$

$$\phi_{p2} = \frac{g_2}{g_1} N_V e^{\eta_1^v - \eta_2^v}. \quad (54d)$$

Here, all of the subscripts refer to *electron* occupation numbers. Then it is easy to see that the relative values of ϕ_{n1}/n and n/ϕ_{n2} (or p/ϕ_{p1} and ϕ_{p2}/p) will determine n_{av} . The conditions necessary to get $n_{av}=0, 1$, and 2 , respectively, are given in Table I. Now the definition of a *positive-U* center becomes immediately obvious by glancing at

TABLE I. Requirements to obtain $n=0, 1$, and 2 respectively. The zero of energy is at the valence-band maximum. It is assumed that $\exp \mathcal{E}/kT \gg 1$ if $\mathcal{E} > 2kT$.

n_{av}	General requirements	\mathcal{E}_F requirement if $\mathcal{E}_2 > 2\mathcal{E}_1 + kT \ln(4g_0g_2/g_1^2)$ (positive U)	\mathcal{E}_F requirement if $\mathcal{E}_2 < 2\mathcal{E}_1 + kT \ln(4g_0g_2/g_1^2)$ (negative U)
0	(A) $2p/\phi_{p1} \gg 1$ and $p/\phi_{p1} \gg \phi_{p2}/p$ or (B) $2p/\phi_{p1} \gg 2\phi_{p2}/p \gg 1$	$\mathcal{E}_F < \mathcal{E}_1 - kT(2 + \ln g_1/2g_0)$	$\mathcal{E}_F < \mathcal{E}_2/2 - kT(2 + \ln g_2/g_0)/2$
1	(A) $p/\phi_{p1} = \phi_{p2}/p$ or (B) $2p/\phi_{p1} \ll 1$ and $2\phi_{p2}/p \ll 1$	$\mathcal{E}_F = (\mathcal{E}_2 + \ln g_0/g_2)/2$ $\mathcal{E}_2 - \mathcal{E}_1 - kT(2 + \ln 2g_2/g_1) > \mathcal{E}_F$ $\mathcal{E}_F > \mathcal{E}_1 + kT(2 + \ln 2g_0/g_1)$	$\mathcal{E}_F = (\mathcal{E}_2 + \ln g_1/g_2)/2$ not applicable
2	$2\phi_{p2}/p \gg 1$ and $\phi_{p2}/p \gg p/\phi_{p1}$	$\mathcal{E}_F > \mathcal{E}_2 - \mathcal{E}_1 + kT(2 + \ln g_1/2g_2)$	$\mathcal{E}_F > \mathcal{E}_2/2 + kT(2 + \ln g_0/g_2)/2$

the requirements to have an $n_{av}=1$ state, i.e., either $\mathcal{E}_F = (\mathcal{E}_2 + kT \ln g_0/g_2)/2$, or $\mathcal{E}_2 - \mathcal{E}_1 > \mathcal{E}_F > \mathcal{E}_1$ (at $T=0$). The first condition here is irrelevant since it occurs at only one value of \mathcal{E}_F . The second condition gives $\mathcal{E}_2 > 2\mathcal{E}_1$. Thus, the condition for a *negative-U* center is just the opposite, i.e., $\mathcal{E}_2 < 2\mathcal{E}_1$, again at $T=0$. The condition at finite T is $\mathcal{E}_2 < 2\mathcal{E}_1 + kT \ln(4g_0g_2/g_1^2)$. For the cases shown in Figs. 1(b), 1(c), and 1(d), the last term adds $0, 0.76kT$, and $2.8kT$, respectively. The physics here is quite clear: At $T=0$, if it takes less energy to place two electrons on one center than one electron each on two centers, the one-electron state will not exist. At finite T , an entropy factor, shown as a function of the various charge-state degeneracies, must also be taken into account. This phenomenon is illustrated in Fig. 2. The various parameters for the curves in Fig. 2 are given in Table II. Note that for curve (a), n_{av} goes directly from zero to two as \mathcal{E}_F is raised; this is the prime characteristic of a *negative-U* center. The effects of different degeneracy factors are also shown. The temperature dependences of the free hole concentrations in GaAs for the same sets of parameters are shown in Fig. 3. To obtain p the following charge-balance equation was solved [cf. Eq. (40)]:

$$\frac{n_1^2}{p} + N_{AS} = p + N_{DS} + 2N_D - \frac{2N_D}{1 + \frac{1+2p/\phi_{p1}}{1+2\phi_{p2}/p}}. \quad (55)$$

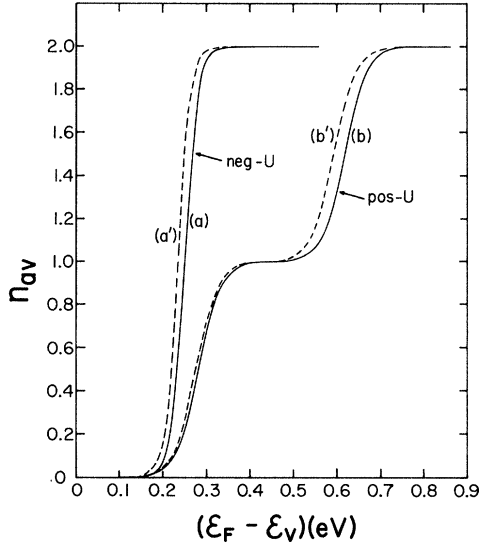


FIG. 2. Average number of electrons on a double-charge-state center at 296 K as a function of Fermi energy. The values of \mathcal{E}_1 , \mathcal{E}_2 , g_0 , g_1 , and g_2 are given in Table II.

where n_i is the intrinsic carrier concentration, N_{AS} is the “shallow” acceptor concentration, N_{DS} is the “shallow” donor concentration, and ϕ_{p1} and ϕ_{p2} are defined in Eq. (54). Here “shallow” means with respect to \mathcal{E}_F ; it is assumed that no significant concentrations of donors or acceptors, other than the double-charge-state donor of interest, lie within the range of \mathcal{E}_F considered here. It is also assumed that \mathcal{E}_1 and \mathcal{E}_2 are temperature independent, i.e., tied to the valence band, but the temperature dependence of n_i is included in the calculation.

The compensation ratio, $R = (N_{AS} - N_{DS})/N_D$, was allowed to assume values of 0.5 and 1.5. For a positive- U center, case (b) in Fig. 3 and Table II, this difference is seen to have a large effect. When $R = 1.5$, the one-electron state is approximately

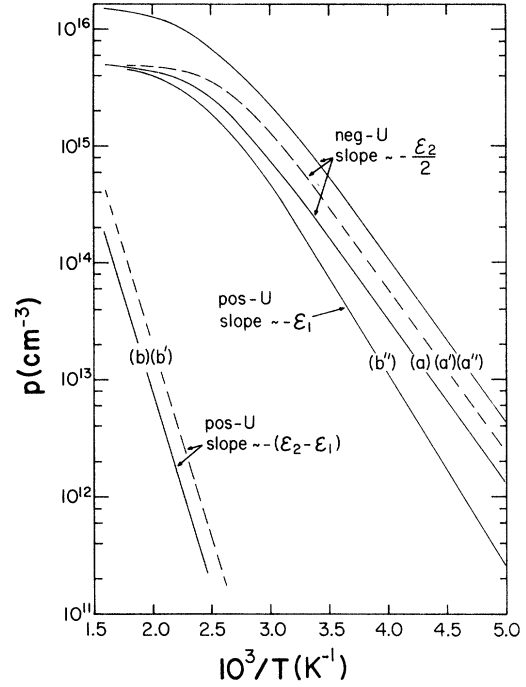


FIG. 3. Temperature dependence of the free hole concentration for both negative- U and positive- U double donors of concentration $1 \times 10^{16} \text{ cm}^{-3}$ in GaAs. The energies are referenced to the valence band and are assumed independently of temperature. The various parameters are given in Table II.

half-occupied and the Arrhenius plot of p has a low-temperature slope of $-\mathcal{E}_1/k$. When $R = 0.5$, on the other hand, the two-electron state is approximately half-occupied, and the slope is $-(\mathcal{E}_2 - \mathcal{E}_1)/k$. Now for a negative- U center, case (a) of Fig. 3 and Table II, the one-electron state is never significantly occupied, and the Arrhenius plot gives a slope of $-\mathcal{E}_2/2k$ for both compensation ratios. It is clear from these considerations

TABLE II. Temperature dependence of the free hole concentration in GaAs under various conditions for both positive- U and negative- U centers. Energies are measured from the valence-band edge. Also, $N_D = 1 \times 10^{16} \text{ cm}^{-3}$.

Designation	Type	\mathcal{E}_1 (eV)	\mathcal{E}_2 (eV)	g_0	g_1	g_2	$(N_{AS} - N_{DS})/N_D$	n_{av} (296 K)	Low-temperature Arrhenius slope
(a)	Negative U	0.3	0.5	1	2	1	0.5	1.54	$-\mathcal{E}_2/2k$
(a')		0.3	0.5	6	15	20	0.5	1.56	$-\mathcal{E}_2/2k$
(a'')		0.3	0.5	1	2	1	1.5	0.59	$-\mathcal{E}_2/2k$
(b)	Positive U	0.3	0.9	1	2	1	0.5	1.51	$-(\mathcal{E}_2 - \mathcal{E}_1)/k$
(b')		0.3	0.9	6	15	20	0.5	1.50	$-(\mathcal{E}_2 - \mathcal{E}_1)/k$
(b'')		0.3	0.9	1	2	1	1.5	0.52	$-\mathcal{E}_1/k$

that one must be quite careful in interpreting Arrhenius plots of Hall-effect data for cases in which a multicharge center may exist, and especially, if this center might be of the negative- U type. If, however, the negative- U nature can be independently established by some other means, say by deep level transient spectroscopy²³ or magnetic susceptibility, then the Hall-effect data, fitted to Eq. (55), can be quite useful in determining the two-electron energy level and the concentration of the center involved. Although in Eq. (55) the dominant center was considered to be a donor, acceptors may be treated similarly.

It is useful to relate the present discussion of negative- U centers to that of Baraff, Kane, and Schluter (BKS).²² Their center of interest is the vacancy in p -type Si. The *undistorted* vacancy has two electrons in a sixfold degenerate state of t_2 -orbital symmetry, such as that shown in Fig. 1(c). However, a Jahn-Teller distortion splits off an orbital singlet (spin doublet) of b_2 symmetry, so that the final picture is like that of Fig. 1(b). Thus,

$g_0(V^{++})=1$, $g_1(V^+)=2$, and $g_2(V^0)=1$. At their respective minima in configuration-coordinate space, the following potential energies are obtained: $\mathcal{E}_0=0$, $\mathcal{E}_1=\mathcal{E}_L-\mathcal{E}_{JT}-\mathcal{E}_F$, and $\mathcal{E}_2=2\mathcal{E}_L+U-4\mathcal{E}_{JT}-2\mathcal{E}_F$, where \mathcal{E}_L is the energy of the *undistorted* one-electron state above the valence band, \mathcal{E}_{JT} is the *one-electron* Jahn-Teller relaxation energy, \mathcal{E}_F is the Fermi energy, and U is the electron-electron repulsion energy. The various assumptions employed may be found in the BKS paper, but our condition for a negative- U center at $T=0$, $\mathcal{E}_2 < 2\mathcal{E}_1$, gives $U^{\text{eff}} \equiv U - 2E_{JT} < 0$, in agreement with the BKS result. Thus, the terminology "negative- U " really refers to "negative- U^{eff} " in which U^{eff} includes the Jahn-Teller stabilization energy as well as the electron-electron repulsion energy.

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