Theory of Acceptor-Donor Pairing in Elemental Semiconductors

J. B. R. Franco* and M. Schoijet
Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional
Apartado Postal 14-740, *México* 14, *D. F.*, *México*
(Received 8 September 1970)

A theory of pairing for donor-acceptor atom pairs and for donor-atoms–vacancy-acceptor pairs with different states of charge in elemental semiconductors has been developed. A law of mass action for charged pairs $(N_{00}N_{-+}/N_{0+}N_{-0}) = e^{E_q/kT}$ has been obtained, where E_q is the Coulombic interaction energy between a positive donor and a negative acceptor at nearest-neighbor lattice sites.

I. INTRODUCTION

There are several reasons that make the study of the pairing of point defects in semiconductors necessary. First, pairing of impurities may affect diffusion either through pairing of impurity atoms or pairing of impurity atoms and vacancies. The effect of pairing on diffusion may occur in a direct way, for instance, through the change in mobility of a vacancy trapped by an impurity. But because vacancies in semiconductors are charged defects, [1–3] diffusion may be affected in an indirect way by pairing, through changes in the position of the Fermi level which will in turn influence the equilibrium concentrations of neutral and charged vacancies. Pairing will also affect other physical properties such as solubility of impurities and carrier mobility. [4] Pairing plays an important role in optical properties. The review article by Ferd Williams on acceptor-donor pairs[5] brings 14 references on luminescence properties in C (diamond), GaP, and ZnS attributed to impurity centers formed by the pairing of acceptor-donor impurities or pairing of vacancies and substitutional impurities in the case of ZnS. Pairing affects the transfer of energy between impurity centers in semiconductors, [5] which plays an important role in luminescence.

Another optical property affected by impurity pairing is infrared absorption. This has been observed in Si doped with Li and B. [6,7] Oxygen-defect interactions in Si have also been observed by infrared spectroscopy. [8–10] Photoconductive properties of Ge doped with Li and Hg have also been attributed to impurity pairing. [11]

The work of Watkins and co-workers has provided experimental evidence through the use of electron paramagnetic resonance EPR and electron-nuclear double resonance ENDOR on the existence of pairs of substitutional atoms with vacancies in Si. Sb-V (V is the vacancy), As-V, and P-V centers were observed which introduce acceptor levels at E_c-0.43, E_c-0.46, and E_c-0.47 eV (E_c is the conduction-band edge), i.e., new levels at a position different from the position of the unpaired impurity or vacancy. [12–14] Al-V pairs[15] and O-V[16–18] pairs in Si were observed by the same methods.

Pairing involves not only substitutional impurities. Substitutional Cu in Ge and Si is an acceptor while interstitial Cu is a donor. [19] Pairing between the substitutional and interstitial Cu atoms in Si seems to play an important role in the diffusion process. [20] Similar phenomena seem to operate in semiconductor compounds, where impurities may act like donors or acceptors according to which sublattice they occupy. This has been observed for Sn, Ge, and Si in GaAs. [21,22] Donor-vacancy association in ZnS has already been mentioned in connection with luminescence properties. Other cases of donor-vacancy association in III-V semiconductor compounds are given in the literature. [23]

The foundational theoretical work on chemical interactions among defects in Ge and Si was carried out by Reiss and his collaborators some 15 years ago. [4,24] Our approach is quite different from that of Reiss and collaborators and resembles that of Tredgold and Carter[25] and of Hu. [26]

In his first paper, Reiss proposed a scheme that led to laws of mass action for the ionization of donors and acceptors when they were simultaneously present in a semiconductor sample. This scheme is based on stating the electroneutrality condition and on postulating that the laws that give the ratio of charged to neutral defects are unchanged when both types of defect donors and acceptors are present. This kind of approach was later extensively exploited by Kröger. [27]

Reiss and his collaborators also carried out calculations on the pairing of donors and acceptors, on the assumption that the theory of ion pairing, derived by Bjerrum[28] and Fuoss, [29] should be applicable to donor-acceptor pairing in semiconductors. They postulate a law of mass action for paired and unpaired impurities [Eq. (9.4) of the paper[4]],

$$N_p/(N_A - N_p)(N_D - N_p) = \Omega\,, \tag{1}$$

where Ω is a complicated function of the temperature and the permittivity of the sample. In this way they are implying that the only pairs that exist are the positive-donor–negative-acceptor pairs and that all free donors and acceptors are ionized. This is a particular case, i.e., it should be valid when both donors and acceptors are shallow and the temperature is high enough.

The approach of Reiss is not adequate for a complete description of the equilibrium involving pairs with all states of charge, i.e., neutral-donors–neutral-acceptors, neutral-donors–negative-acceptors, positive-donors–negative-acceptors.

Our approach is similar to the approach of Tredgold and Carter[25] and Hu.[26] This approach, which we consider more satisfactory, postulates an equation for the free energy of the system and then proceeds to obtain the amount of charged and neutral defects of each kind by minimizing the free energy. Tredgold and Carter applied this procedure to the pairing of donor and acceptor atoms and Hu to the pairing of donor atoms and acceptor vacancies.

Tredgold and Carter limit the usefulness of their results by assuming that only one type of pair (positive donors–negative acceptors) is present. The way in which the authors write the number of configurations implies double counting. Also, the authors state that they are considering the case of a compound semiconductor. However, this is not consistent with the way in which they write the number of configurations. This ambiguity leaves open the question of whether their results would be applicable to a compound semiconductor.

The results in Hu's paper come out in a rather cumbersome form. Also, the author failed to notice that a law of mass action for pairs could be derived from them. We prove this in the Appendix.

We believe that our approach is more general because we treat both the donor-atom–acceptor-atom pairs and the donor-atom–acceptor-vacancy pairs and we consider the pairs with all possible states of charge. We obtain a law of mass action for pairs and show that there is a law of mass action for each pair with a given state of charge and the free impurities with the corresponding states of charge, thus defining the range of validity of Reiss's results.

II. REDERIVATION OF LIDIARD'S RESULTS

We will rederive Lidiard's[30] results for the problem of pairing of neutral impurities with neutral vacancies. We will write down the number of configurations in a more careful way and we will obtain slightly different results.

We consider a crystal with N matrix atoms and N_1 impurities of which $N_i p$ are paired with vacancies. The number of lattice points will be given by

$$N_s = N + N_i(1+p) + N_v\,, \tag{2}$$

where N_v is the number of free vacancies.

For the first pair we can choose between N_s sites for the impurity atom and z nearest neighbors for the second. However, since each pair can be started from any of its two points, the number of ways of placing the first pair is given by $\frac{1}{2}zN_s$. The number of ways for the second is given by $\frac{1}{2}z[N_s - (z'+2)]$, where z' is the number of sites which are nearest neighbors of a pair of nearest neighbors. Then the number of ways of placing $N_i p$ pairs would be

$$W_p = [\tfrac{1}{2}z(z'+2)]^{N_i p} \prod_{s=0}^{N_i p-1} \left(\frac{N_s}{z'+z} - s\right) \Big/ (N_i p)! = [\tfrac{1}{2}z(z'+2)]^{N_i p} \frac{[N_s/(z'+2)]!}{[N_s/(z'+2) - N_i p]!\,(N_i p)!}\,. \tag{3}$$

Thus we write the free energy as

$$F = F_0 + N_v g_v + N_i p(g_v + \Delta g) - kT \ln \left([\tfrac{1}{2}z(z'+2)]^{N_i p} \frac{[N_s/(z'+2)]!}{[N_s/(z'+2) - N_i p]!\,(N_i p)!} \right.$$
$$\left. \times \frac{[N_s - N_i p(z'+2)]!}{N_s - N_i p(z'+2) - N_i(1-p)!\,N_i(1-p)!} \quad \frac{\{N_s - N_i[z+1+p(z'-z+1)]\}!}{\{N_s - N_i[z+1+p(z'-z+1)]\}!\,N_v!} \right)\,, \tag{4}$$

where F_0 is the free energy of the crystal without vacancies, g_v is the energy formation of a free vacancy, and Δg is the energy associated with impurity-vacancy pairing. We obtain the number of vacancies and paired impurities from the condition that the free energy be a minimum;

$$\frac{\partial F}{\partial N_v} = \frac{\partial F}{\partial p} = 0\,, \tag{5}$$

$$N_v/\{N_s - N_i[z+1+p(z'-z+1)]\} = e^{-g_v/kT}\,, \tag{6}$$

$$p/(1-p) = \tfrac{1}{2}z\, e^{-(g_v+\Delta g)/kT}\,. \tag{7}$$

III. PAIRING OF NEUTRAL IMPURITIES WITH CHARGED AND NEUTRAL VACANCIES

Let us consider now the case of neutral impurities interacting with neutral and negative vacancies. This might be the case of impurities of the same valence as the matrix in a semiconductor (let us say C or Si in Ge).

We write down the free energy

$$F = F_0 + N_{vs}^0 g_v + N_{vs}^- (g_v + E_A) + N_i p (g_v + W_0) + N_i p' (g_v + W_0 + E_A)$$
$$- kT \ln \left([\tfrac{1}{2} z(z'+2)]^{N_i(p+p')} \frac{[N_s/(z'+2)]!}{[N_s/(z'+2) - N_i(p+p')]! [N_i(p+p')]!} \right.$$
$$\times \frac{[N_i(p+p')]!\, 2^{N_i p'}}{(N_i p)!\,(N_i p')!} \frac{[N_s - N_i(p+p')(z'+2)]!}{[N_s - N_i(p+p')(z'+2) - N_i(1-p-p')]! [N_i(1-p-p')]!}$$
$$\left. \times \frac{[N_s - N_i(p+p')(z'+2) - N_i(1-p-p')(z+1)]!}{[N_s - N_i(p+p')(z'+2) - N_i(1-p-p')(z+1) - N_{vs}]! N_{vs}!} \frac{N_{vs}!\, 2^{N_{vs}^-}}{N_{vs}^0! N_{vs}^-!} \right), \quad (8)$$

where N_{vs}^0 are the free neutral vacancies, N_{vs}^- are the free negative vacancies, $N_{vs} \equiv N_{vs}^0 + N_{vs}^-$, E_A is the acceptor level of the vacancies (the zero of energy is the edge of the valence band), W_0 is the pairing energy between the vacancy and impurity (it is taken as independent of the state of charge of the vacancy), $N_i p$ is the number of neutral vacancy-impurity pairs, $N_i p'$ is the number of negative vacancy-impurity pairs, and $N_i(1-p-p')$ is the number of free impurities. The factor $2^{N_{vs}^-}$ appears because of the degeneracy of the acceptor levels.

We obtain the values of N_{vs}^0, N_{vs}^-, p, and p' from the equations

$$\frac{\partial F}{\partial N_{vs}^0} = 0 , \quad (9a)$$

$$\frac{\partial F}{\partial N_{vs}^-} = \mu , \quad (9b)$$

$$\frac{\partial F}{\partial p} = 0 , \quad (10a)$$

$$\frac{\partial F}{\partial p'} = \mu , \quad (10b)$$

where μ is the chemical potential of the electrons in the acceptor levels.

The results are given by

$$\frac{N_{vs}^0}{N_s - N_i(p+p')(z'+2)} = e^{-g_v/kT} , \quad (11)$$

$$\frac{N_{vs}^-}{2[N_s - N_i(p+p')(z'+2)]} = e^{-(g_v + E_A - \mu)/kT} , \quad (12)$$

$$\frac{p}{(1-p-p')} = \tfrac{1}{2} z\, e^{-(g_v + W_0)/kT} , \quad (13)$$

$$\frac{p'}{(1-p-p')} = 2\, e^{-(g_v + W_0 + E_A - \mu)/kT} . \quad (14)$$

From Eqs. (11)–(14), we obtain

$$\frac{p'}{p+p'} = \frac{N_{vs}^-}{N_{vs}} = \frac{1}{1 + \frac{1}{2} e^{(E_A - \mu)/kT}} , \quad (15)$$

which agrees with the usual formula for the number of electrons in acceptor levels.[31]

IV. PAIRING OF NEUTRAL AND NEGATIVE VACANCIES WITH SUBSTITUTIONAL DONORS

We consider a system formed by a semiconductor crystal with N matrix atoms and N_D impurities which act like singly ionizable donors. There are N_v vacancies and the vacancies act like singly ionizable acceptors. Pairing of donors and vacancy acceptors as nearest neighbors is considered, any other pairing effect is neglected. We consider $N_D \ll N$. We consider that the energy of formation of a vacancy at a nearest-neighbor position of an impurity is different than the energy of formation away from an impurity. We consider that neither the vacancy- nor the donor-impurity levels are affected by pairing. Four possible kinds of pairs are considered: neutral-vacancy–neutral-donor (N_{00}); neutral-vacancy–ionized-donor (N_{0+}); ionized-vacancy–ionized-donor (N_{-+}); ionized-vacancy–neutral-donor (N_{-0}). The total number of pairs is given by

$$N_p = N_{00} + N_{0+} + N_{-+} + N_{-0} \quad (16)$$

and the number of unpaired impurities is given by

$$N_{Ds} = N_D - N_p . \quad (17)$$

The total number of sites will be given by

$$N_s = N + 2N_p + (N_D - N_p) + N_{vs}^0 + N_{vs}^- ,$$
$$N_s = N + N_p + N_D + N_{vs}^0 + N_{vs}^- . \quad (18)$$

Let us now define N_{Ds}^+ as the number of unpaired ionized donors and N_{Ds}^0 as the number of unpaired neutral donors. Donor impurities have a ground-state impurity level at E_D eV below the conduction

band E_c, and the vacancies have an acceptor level E_A above the valence band. We take the top of the valence band as the zero of energy. Then we write down the free energy

$$F = F_0 + N^0_{vs} g_v + N^-_{vs}(g_v + E_A) + N^+_{Ds}(E_c - E_D) + N_{0+}(g_v + W_0 + E_c - E_D) + N_{00}(g_v + W_0)$$
$$+ N_{-+}(g_v + E_A + W_0 + E_c - E_D + E_q) + N_{-0}(g_v + E_A + W_0) - kT \ln\Big([\tfrac{1}{2} z(z'+2)]^{N_p} \frac{[N_s/(z'+2)]!}{[N_s/(z'+2) - N_p]! N_p!}$$
$$\times \frac{N_p!\, 2^{(N_{00}+N_{-0})} 2^{(N_{-0}+N_{-+})}}{N_{0+}! N_{00}! N_{-+}! N_{-0}!} \frac{[N_s - N_p(z'+2)]!}{[N_s - N_p(z'+2) - N_D + N_p]!\,(N_D - N_p)!} \frac{(N_D - N_p)!\, 2^{(N_D - N_p - N^+_{Ds})}}{(N_D - N_p - N^+_{Ds})! N^+_{Ds}!}$$
$$\times \frac{[N_s - N_p(z'+2) - (N_D - N_p)(z+1)]!}{[N_s - N_p(z'+2) - (N_D - N_p)(z+1) - N^0_{vs} - N^-_{vs}]!\,(N^0_{vs} + N^-_{vs})!} \frac{(N^0_{vs} + N^-_{vs})!\, 2^{N^-_{vs}}}{N^0_{vs}! N^-_{vs}!} \Big) , \quad (19)$$

where W_0 is the energy of interaction of the vacancy and impurity as nearest neighbors excepting the Coulomb interaction. E_q is the Coulomb-interaction energy between negative vacancy and positive donor at nearest-neighbor positions. In the case we are considering, E_q is negative. We divide the number of configurations into two factors, one for the vacancy donor pairs and the other for single impurities and vacancies. For the unpaired donors and vacancies we write the number of configurations in a way similar to that of Lidiard,[30] generalized to include the states of different charge. The factors $2^{(N_{00}+N_{-0})}$ and $2^{(N_{-0}+N_{-+})}$ arise from the degeneracy of the donor and acceptor levels. In the way the free energy is written down we have the implicit condition that the number of donors is constant.

In order to get the number of pairs, neutral free vacancies, negative free vacancies, and positive donors for the state of equilibrium we apply the following equations plus (9a) and (9b):

$$\frac{\partial F}{\partial N_{0+}} = -\mu , \quad (20a)$$

$$\frac{\partial F}{\partial N_{00}} = 0 , \quad (20b)$$

$$\frac{\partial F}{\partial N_{-+}} = 0 , \quad (20c)$$

$$\frac{\partial F}{\partial N_{-0}} = \mu , \quad (20d)$$

where μ is the chemical potential for electrons in impurity levels.

Carrying out the partial differentiations, we obtain

$$N_{0+} = \tfrac{1}{2} z N^0_{Ds} \exp[-(g_v + W_0 + E_c - E_D + \mu)/kT] , \quad (21)$$

$$N_{00} = z N^0_{Ds} \exp[-(g_v + W_0)/kT] , \quad (22)$$

$$N_{-+} = z N^0_{Ds} \exp[-(g_v + E_A + W_0 + E_c - E_D + E_q)/kT] , \quad (23)$$

$$N_{-0} = 2 z N^0_{Ds} \exp[-(g_v + E_A + W_0 - \mu)/kT] . \quad (24)$$

From these four equations, we obtain

$$N_{00} N_{-+} / N_{0+} N_{-0} = e^{E_q/kT} . \quad (25)$$

Let us now obtain N^0_{vs}. Using (9a) and $(\partial N_s/\partial N^0_{vs}) = 1$ after neglecting higher-order terms, we obtain

$$N^0_{vs} / [N_s - N_p(z'+2)] = e^{-g_v/kT} ; \quad (26)$$

for the negative vacancies, we obtain

$$N^-_{vs} / 2[N_s - N_p(z'+2)] = e^{-(g_v + E_A - \mu)/kT} . \quad (27)$$

Combining Eqs. (26) and (27), we get

$$N^-_{vs} / N_{vs} = 1/(1 + \tfrac{1}{2} e^{(E_A - \mu)/kT}) \quad (28)$$

as should be expected for any acceptor-impurity level. For donors using $\partial F/\partial N^0_{Ds} = \mu$ and $\partial N_s/\partial N^+_{Ds} = 1$, we obtain

$$N^0_{Ds} / N_{Ds} = 1/(1 + \tfrac{1}{2} e^{-(E_c - E_D + \mu)/kT}) . \quad (29)$$

V. CONSIDERATIONS OF DIFFERENT PAIRING ENERGIES FOR PAIRS WITH DIFFERENT CHARGE STATES

Let us now consider the case in which the impurity levels of the pairs do not change but the energy of pairing changes because of the state of charge of the pair. The energy of pairing of the neutral-neutral pair is called W_0, the energy of the neutral-positive pair W_1, and the energy of the negative-neutral pair W_2. Then by rewriting the free energy (19) and following the same procedure as above, we get

$$N_{-+} N_{00} / N_{0+} N_{-0} = \exp\{-[2W_0 - (W_1 + W_2) - E_q]/kT\} . \quad (30)$$

VI. LAWS OF MASS ACTION INVOLVING PAIRS AND SINGLE DEFECTS

Assuming the number of donors to be a constant we have obtained explicit equations for N_p, N_{0+}, N_{00}, N_{-+}, N_{-0}, and N^0_{vs}. From there we obtained the following laws of mass action involving pairs and single defects: For the "reaction"

$$N_{0+} \rightleftharpoons N^0_{vs} + N^+_{Ds} , \quad (31)$$

$$\frac{N^0_{vs}N^+_{Ds}}{N_{0+}} = \frac{N_s}{\frac{1}{2}z}\,\frac{1+\frac{1}{2}e^{-(E_c-E_D+\mu)/kT}}{1+2e^{(E_c-E_D+\mu)/kT}} \times e^{(W_0+E_c-E_D+\mu)/kT}, \quad (32)$$

For the reaction

$$N_{00} \rightleftarrows N^0_{vs}+N^0_{Ds}, \quad (33)$$

we obtain

$$\frac{N^0_{vs}N^0_{Ds}}{N_{00}} = (N_s/z)\,e^{W_0/kT}. \quad (34)$$

For the reaction

$$N_{-+} \rightleftarrows N^-_{vs}+N^+_{Ds}, \quad (35)$$

we obtain

$$\frac{N^-_{vs}N^+_{Ds}}{N_{-+}} = \frac{N_s}{\frac{1}{2}z}\,\frac{1+\frac{1}{2}e^{-(E_c-E_D+\mu)/kT}}{1+2e^{(E_c-E_D+\mu)/kT}} \times e^{(W_0+E_c-E_D+\mu+E_q)/kT}. \quad (36)$$

For the reaction

$$N_{-0} \rightleftarrows N^-_{vs}+N^0_{Ds}, \quad (37)$$

we obtain

$$\frac{N^-_{vs}N^0_{Ds}}{N_{-0}} = (N_s/z)\,e^{W_0/kT}. \quad (38)$$

From Eqs. (34) and (36), we obtain a new law of mass action involving pairs and single defects

$$N_{-+}N^0_{vs}N^0_{Ds}/N_{00}N^-_{vs}N^+_{Ds} = e^{E_q/kT} \quad (39)$$

which corresponds to the "reaction"

$$N_{00}+N^-_{vs}+N^+_{Ds} \rightleftarrows N_{-+}+N^0_{vs}+N^0_{Ds}. \quad (40)$$

The law of mass action (39) coupled with (25) implies

$$N_{0+}N_{-0}N^0_{vs}N^0_{Ds} = N^2_{00}N^-_{vs}N^+_{Ds}. \quad (41)$$

VII. PAIRING OF DONOR AND ACCEPTOR ATOMS IN SUBSTITUTIONAL POSITIONS

We consider single-level donor and acceptor atoms and only nearest-neighbor pairs. Then we write down the free energy

$$F = F_0 + N^+_{Ds}(E_c - E_D) + N^-_{As}E_A + N_{0+}(W_0+E_c-E_D) + N_{00}W_0 + N_{-+}(E_A+E_c-E_D+W_0+E_q) + N_{-0}(E_A+W_0)$$
$$-kT\ln\Bigg(\left[\tfrac{1}{2}z(z'+2)\right]^{N_p}\frac{[N_s/(z'+2)]!}{\{[N_s/(z'+2)]-N_p\}!\,N_p!}\,\frac{N_p!\,2^{(N_{00}+N_{-0})}\,2^{(N_{-+}+N_{-0})}}{N_{0+}!N_{00}!N_{-+}!N_{-0}!}\,\frac{[N_s-N_p(z'+2)]!}{[N_s-N_p(z'+2)-N_{Ds}]!N_{Ds}}$$
$$\times\frac{1}{!}\,\frac{N_{Ds}!\,2^{N^0_{Ds}}}{N^0_{Ds}!N^+_{Ds}!}\,\frac{[N_s-N_p(z'+2)-N_{Ds}(z+1)]!}{[N_s-N_p(z'+2)-N_{Ds}(z+1)-N_{As}]!N_{As}!}\,\frac{N_{As}!\,2^{N_{As}}}{N^0_{As}!N^-_{As}!}\Bigg), \quad (42)$$

where N^-_{As} is the number of free negative acceptors; F_0 is the free energy of the pure matrix. We neglect the effect of vacancies. Now we consider the number of donor and acceptor atoms to be constant. Equations (20) apply to this case, and instead of Eq. (9b) we use

$$\frac{\partial F}{\partial N^-_{As}} = \mu. \quad (43)$$

The number of sites is now a constant and is given by $N_s = N+N_A+N_D$. We obtain

$$N_{0+} = \tfrac{1}{2}\gamma e^{-(W_0+E_c-E_D+\mu)/kT}, \quad (44)$$

$$N_{00} = \gamma e^{-W_0/kT}, \quad (45)$$

$$N_{-+} = \gamma e^{-(W_0+E_A+E_c-E_D+E_q)/kT}, \quad (46)$$

$$N_{-0} = 2\gamma e^{-(W_0+E_A-\mu)/kT}, \quad (47)$$

$$N^0_{Ds}/N_{Ds} = 1/(1+\tfrac{1}{2}e^{-(E_c-E_D+\mu)/kT}), \quad (48)$$

$$N^0_{As}/N_{As} = 1/(1+2e^{-(\mu-E_A)/kT}), \quad (49)$$

where we have defined

$$\gamma \equiv zN^0_{Ds}N^-_{As}/[N_s-N_D-N_p(z'-z+1)]. \quad (50)$$

Combining Eqs. (44)–(49) we obtain again (25). This means that the law of mass action for pairs applies both for pairing of vacancy acceptors with donor atoms and for donor-acceptor atoms. In a similar way an equation involving pairs and single defects is obtained which is like (39) except that we replace N^0_{vs} and N^-_{vs} by N^0_{As} and N^-_{As} which corresponds to a "reaction" analogous to (40). From (46), (48), and (49), we obtain, assuming $N_p \sim N_{-+}$,

$$\frac{N_{-+}}{(N_D-N_p)(N_A-N_p)} = \frac{2\gamma'\exp[-(W_0+E_c-E_D+E_A+E_q)/kT]}{(N_D-2\gamma'\exp[-(W_0+E_c-E_D+E_A+E_q)/kT]} \times\frac{1}{N_A-2\gamma'\exp[-(W_0+E_c-E_D+E_A+E_q)/kT]} \equiv \Delta \quad (51)$$

and from there we get

$$N_{-+} = \frac{1+(N_A+N_D)\Delta-\{[1+(N_A+N_D)\Delta]^2-8\Delta^2N_AN_D\}^{1/2}}{2\Delta}. \quad (52)$$

Reiss, Fuller, and Morin get instead of this [Eq. (9.5) of their paper]

$$N_{-+}=\tfrac{1}{2}(N_D+N_A+1/\Omega)-[\tfrac{1}{4}(N_D+N_A+1/\Omega)^2-N_A N_D]^{1/2}\ ,$$

where

$$\Omega\equiv 4\pi\int_a^b r^2 e^{q^2/\epsilon r k_B T}\,dr\ ,$$

q being the charge of an ion, ϵ the permittivity, r the radial distance, a the distance of nearest approach, and b a distance for which the distribution function of ions of opposite sign to the ion located at the origin has a minimum.

Equation (46) does not agree with the result of Tredgold and Carter.[25] Using our notation for their equation (16) they obtain

$$\frac{N_{-+}}{(N_A^-N_{-+})(N_D^+-N_{-+})}=\frac{z}{N}e^{-E_q/kT}\ .$$

VIII. SUMMARY OF RESULTS AND DISCUSSION

We have obtained a law of mass action for charged pairs of vacancy acceptor—donor atoms and for acceptor and donor atoms in an elemental semiconductor. The law of mass action is independent of the position of the Fermi level. We also obtained laws of mass action describing the interaction of pairs and single impurities.

The law of mass action for pairs could also be obtained from Hu's results. Since Hu's uses general degeneracy factors for the impurity levels, it seems that the law of mass action does not depend on the degeneracies of the levels.

The ratio of ionized to neutral unpaired vacancies agrees qualitatively with previous results.[32]

A more refined treatment would include the change in the position of the impurity levels because of pairing. To know this and to know the pairing energies of pairs of different states of charge would require an effort to develop the quantum chemistry of the quasimolecule formed by impurity pairing in a semiconductor.

ACKNOWLEDGMENT

One of the authors (M. S.) became interested in the subject through a lecture given by Dr. L. A. Girifalco, of the Department of Metallurgy and Materials Science of the University of Pennsylvania, in 1967.

APPENDIX: DERIVATION OF THE LAW OF MASS ACTION FOR DONORS AND ACCEPTOR VACANCIES FROM HU'S RESULTS

In Hu's paper the quantities derived from the free energy are the total number of pairs, the number of positive-donor–negative-vacancy pairs, the number of pairs having a positive donor, and the number of pairs having a negative acceptor. These are given in Eqs. (2.19)–(2.22) of his paper. They are connected to the number of pairs with given states of charge, which we use, by Eqs. (2.13)–(2.15) of the same paper. Using these equations, we obtain

$$N_{-+}=\frac{N_v}{N_s}\frac{N_A}{K}\frac{\alpha\beta\xi}{1+\xi}\frac{\xi}{1+\zeta}\ , \tag{A1}$$

$$N_{-0}=\frac{N_v}{N_s}\frac{N_A}{K}\frac{\alpha\xi}{(1+\xi)(1+\zeta)}\ , \tag{A2}$$

$$N_{0+}=\frac{N_v}{N_s}\frac{N_A}{K}\frac{\alpha\zeta}{(1+\zeta)(1+\xi)}\ , \tag{A3}$$

$$N_{00}=\frac{N_v}{N_s}\frac{N_A}{K}\frac{\alpha}{(1+\xi)(1+\zeta)}\ , \tag{A4}$$

where

$$\alpha=ze^{W_0/kT}\ ,\qquad \beta=e^{-E_q/kT}\ ,$$

$$\zeta=g_A^{-1}e^{(E_A-\mu)/kT}\ ,\qquad \xi=g_v e^{(\mu-E_v)/kT}\ ,$$

$$K=1+\left[\frac{N_A}{N_s}\frac{\alpha}{1+\xi}\left(1+\frac{1+\beta\zeta}{1+\zeta}\xi\right)+(z+1)\right],$$

g_A and g_v are spin-degeneracy factors of the A (impurity) and vacancy centers, and E_A is either a donor or an acceptor level. E_v is the vacancy energy level, that we call E_A.

Combining Eqs. (A1)–(A4) we obtain Eq. (25).

---

*Supported by a scholarship from the Instituto Nacional de la Investigación Cientifica, México.

[1]R. L. Longini and R. F. Greene, Phys. Rev. 102, 1992 (1956).

[2]M. W. Valenta and C. Ramasastry, Phys. Rev. 106, 73 (1957).

[3]A. Seeger and K. P. Chik, Phys. Status Solidi 29, 445 (1968).

[4]H. Reiss, C. S. Fuller, and F. J. Morin, Bell System Tech. J. 35, 535 (1956).

[5]F. Williams, Phys. Status Solidi 25, 493 (1968).

[6]M. Balkanski and W. Nazarewicz, J. Phys. Chem. Solids 25, 437 (1964).

[7]W. G. Spitzer and M. Waldner, Phys. Rev. Letters 14, 223 (1965).

[8]H. Y. Fan, in *Proceedings of the International Conference on Semiconductors, Prague*, 1960 (Academic, New York, 1961).

[9]A. K. Ramdas and M. G. Rao, Phys. Rev. 142, 451 (1966).

[10]R. E. Whan, J. Appl. Phys. 37, 3378 (1966).

[11]R. L. Williams and B. H. Breazeale, Phys. Rev. Letters 18, 1129 (1967).

[12]E. L. Elkins and G. D. Watkins, Phys. Rev. 174, 881 (1968).

[13]M. Hirata, Ma. Hirata, and H. Saito, J. Appl. Phys. (Japan) 5, 252 (1966).

[14]E. Sonder and L. C. Templeton, J. Appl. Phys. 34, 3295 (1963).

[15]G. D. Watkins, Phys. Rev. 155, 802 (1967).

[16]G. D. Watkins and J. W. Corbett, Discussions Faraday Soc. 31, 86 (1961).

[17]G. D. Watkins and J. W. Corbett, Phys. Rev. 121, 1001 (1961).

[18]G. D. Watkins, J. W. Corbett, R. M. Chrenko, and R. S. McDonald, Phys. Rev. 121, 1015 (1961).

[19]R. N. Hall and J. H. Racette, J. Appl. Phys. 35, 379 (1964).

[20]V. V. Voronkov, G. I. Voronkova, and M. I. Iglitsyn, Fiz. Tverd. Tela 11, 1660 (1969) [Sov. Phys. Solid State 11, 1344 (1969)].

[21]Review article by D. L. Kendall, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1968), Vol. 4, p. 163, and four references there.

[22]F. A. Kröger, *The Chemistry of Imperfect Crystals* (North-Holland, Amsterdam, 1964), references cited on p. 702.

[23]Reference 21, references cited on p. 178.

[24]H. Reiss, J. Chem. Phys. 21, 1209 (1953).

[25]R. H. Tredgold and J. Carter, J. Phys. Chem. Solid 29, 2121 (1968).

[26]S. M. Hu, Phys. Rev. 180, 773 (1969).

[27]F. Kröger, Ref. 22, p. 618ff.

[28]N. Bjerrum, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. 7, 9 (1926).

[29]R. M. Fuoss, Trans. Faraday Soc. 30, 967 (1934).

[30]A. B. Lidiard, Phil. Mag. 5, 1171 (1960).

[31]For example, R. Kubo, *Statistical Mechanics* (North-Holland, Amsterdam, 1965), p. 272.

[32]M. F. Millea, J. Phys. Chem. Solids 27, 315 (1966).