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Self-Compensation Limited Conductivity in Binary Semiconductors. I. Theory*

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The techniques of Kroger and Vink and Brebrick are extended to allow a calculation of the minimum extent of self-compensation by simple vacancies or interstitial atoms in heavily doped binary semiconductors. The resulting equations are applied to a series of compounds, and it is found that the degree of self-compensation by singly ionizable vacancies varies from essentially complete in KCl (all but $\sim 10^{-9}$ of the impurities compensated) to practically none in GaAs (only $\lesssim 10^{-3}$ of the impurities compensated). The II-VI compounds occupy an intermediate position with about ~ 99 and 99.9% self-compensation in CdTe and ZnTe, respectively. These theoretical conductivity limitations are not sufficient to account for the experimental limitations found in, for example, *n*-ZnTe or *p*-CdS. The above results are extended to include multiply ionizable vacancies, the ionization levels of which fall within the bandgap. It is found that essentially complete self-compensation by a combination of singly and doubly ionized vacancies will occur in the higher bandgap II-VI compounds. As a consequence, for example, the Fermi level in ZnTe cannot be pushed closer to the bottom of the conduction band than half the energy separation between the second ionization level of the acceptor vacancy and the bottom of the conduction band. Some specific implications of the above calculations with respect to CdTe and GaAs are discussed. Finally, certain solubility effects (of impurities) related to stoichiometry and the above calculations are discussed.

I. INTRODUCTION

IT is well known that the introduction of electrically active impurities into a semiconductor host crystal induces the formation of electrically active "natural" defects (vacancies, interstitial atoms, etc.), which tend to at least partially compensate the electrical activity of the impurity. This phenomenon has been considered by a number of workers, particularly in a review article by Kroger and Vink[1] and, somewhat more rigorously and recently, by Brebrick.[2,3] This self-compensation may be analyzed simply in terms of an energy balance equation, i.e., energy must be supplied by the crystal to produce the "excess" concentration of defect centers while energy is gained by the crystal by the interaction of the defects with the free carriers produced by the added impurity centers. Clearly, if the energy of defect formation is large compared to the energy gained by compensation, very little self-compensation will take place. On the other hand, if the energy of defect formation is small compared to the energy gained by compensation, all free carriers will be compensated by the formation of defects and only insulating crystals will be accessible by equilibrium processes.

The purpose of this paper is the calculation, in terms of the energy parameters of the host crystals, of the minimum extent of self-compensation by simple vacancies in a series of binary compounds, i.e., KCl, ZnTe, CdTe, and GaAs. Qualitatively, we expect to observe a trend in this series due to the fact that the more ionic compounds, e.g., KCl, have electronic bandgaps which are large compared to their cohesive energies while the reverse is true for the more covalent compounds, e.g., GaAs. Roughly speaking, the energy gained by the system upon "recombination" of a free carrier at a vacancy is expected to correlate with the bandgap, while the energy required to generate a vacancy, i.e., the energy required to remove an atom from the lattice, is expected to correlate with the cohesive energy.

The possibility of obtaining appreciable *n*- and *p*-type conductivity in the II-VI compounds, e.g., CdTe and ZnTe, is a question of increasing technological importance because of possible application toward an injection luminescence device operating in the visible region of the spectrum. These compounds appear to be an intermediate case requiring somewhat more careful analysis.

In Sec. II, we calculate the degree of self-compensation by simple singly ionizable acceptor vacancies in a binary semiconductor *MN*, into which we have introduced a large concentration of shallow donors, *D*. (A precisely analogous situation will exist for acceptors.) This calculation is based essentially upon the equation for charge neutrality and Fermi statistics as applied to a nondegenerate semiconductor.[1-3]

In Sec. III, we apply the resulting equations to the series of compounds under consideration and find the expected trend in the results. Of particular interest are the results for CdTe and ZnTe, which indicate that the degree of self-compensation by singly ionizable vacancies calculated theoretically is *not* sufficient to account for the observed conductivity limitations in the II-VI compounds, ZnTe being a particularly appropriate example.

In Sec. IV, we generalize the results of Sec. II to in-

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clude multiply ionizable vacancies, in particular, doubly ionizable vacancies, such as might be expected to be important in the II-VI compounds. It is demonstrated that multiply ionizable vacancies can be of critical importance in determining the degree of self-compensation under certain circumstances, these circumstances being most probably appropriate to the II-VI compounds. In particular, under these circumstances, we find that the Fermi level cannot be pushed appreciably closer to the bottom of the conduction band than half the energy separation between the second ionization level of a simple doubly ionizable acceptor vacancy and the bottom of the conduction band.

Some specific implications of Secs. II and IV are discussed with respect to GaAs and CdTe in Sec. V. In particular, it is predicted that the concentration of simple vacancies in GaAs must be small, and certain experimental evidence supporting this view is cited. With respect to CdTe, it is pointed out that the assignment of a level much below the conduction band to the second ionization of a Cd vacancy cannot be correct.

Finally, in Sec. VI, we discuss certain effects of vacancies on the solubility of impurities, in view of the above calculations.

II. SINGLY IONIZABLE VACANCIES

Let us consider a binary compound semiconductor, *MN*, into which we have introduced a large concentration of donors, D, at the temperature T. The pressures of the various species in the vapor phase are fixed, particularly the pressures of $M_{(g)}$ and $N_{(g)}$, p_M and p_N. The only defects in the host crystal which we consider are simple singly ionizable vacancies, an M atom vacancy being assumed to be an acceptor while an N atom vacancy is assumed to be a donor. For simplicity, we will analyze only the case of *heavy* doping in which the concentration of ionized donors, D^+, is large compared to the concentration of ionized N vacancies, V_N^+, or holes in the valence band, p. [The calculations can easily be extended to include V_N^+ by simply writing $(D^+ + V_N^+)$ in place of D^+ throughout.]

It will be shown in Sec. III that self-compensation by interstitial atoms rather than vacancies is essentially equivalent and leads to similar results.

The charge conservation equation, which is sufficient to describe the system[1–3] is given by

$$D^+ = n + V_M^-, \tag{1}$$

where n is the concentration of electrons in the conduction band and V_M^- is the concentration of ionized M vacancies. The competition between n and V_M^- in maintaining charge neutrality is clearly the question at hand.

The interactions between defects in equilibrium in a nondegenerate semiconductor are given by the equations of Fermi statistics

$$n = N_c \exp(E_F - E_c/kT), \tag{2}$$

$$V_M^-/V_M = g_M \exp(E_F - E_A/kT), \tag{3}$$

where N_c is the density of states near the bottom of the conduction band (given in terms of the electronic effective mass and T), E_F is the Fermi level, E_c is the energy at the bottom of the conduction band, V_M is the concentration of neutral M vacancies, E_A is the acceptor energy level associated with an M vacancy, and g_M is a degeneracy factor (generally we assume $g_M = 2$ for a singly ionizable level). An equivalent description is given by the mass action formalism.[1–3]

$$nV_M/N_cV_M^- = 1/g_M \exp(E_A - E_c/kT), \tag{4}$$

where the right-hand side of Eq. (4) is an equilibrium constant describing the ionization of an ionized M vacancy to yield a neutral M vacancy and an electron in the conduction band.

Combining Eqs. (1) and (4), we obtain immediately

$$n/D^+ = 1/1 + Q, \tag{5}$$

$$Q = g_M V_M/N_c \exp(E_c - E_A)/kT = g_M V_M/N_c \times \exp(E_g - E_A')/kT, \tag{6}$$

where E_g is the electronic bandgap and E_A' is the acceptor level of the M vacancy relative to the valence band.

Equations (5) and (6) are our central result. All the quantities in Eq. (6) except V_M, the concentration of neutral M vacancies, are generally known with sufficient accuracy (with the possible exception of E_A' in some cases). We note that, except for the temperature, T, only V_M is under experimental control. V_M will be determined by the pressure of $M_{(g)}$ in the system, p_M, which can take on a range of values. The connection between V_M and p_M is written[1–3]

$$p_M V_M/N_M = \exp\Delta S_M/k \exp(-\Delta H_M/kT), \tag{7}$$

where N_M is the concentration of M sites in the lattice, and where the right-hand side of Eq. (7) is an equilibrium constant referring to the process in which an atom of M is removed from the *MN* lattice and placed into the vapor, the pressure of $M_{(g)}$ being maintained at 1 atm (standard state), leaving behind an M vacancy in the lattice. The quantities ΔS_M and ΔH_M are defined as the entropy and enthalpy of M vacancy formation, respectively. Note that we have not assumed that $M_{(g)}$ is the only species in the vapor phase but are simply using p_M as a convenient measure of the chemical potential of M in the system.

Inasmuch as we wish to calculate the minimum extent of self-compensation, we must estimate the minimum value of V_M and, therefore, the maximum value of p_M. Clearly p_M must always be less than the value associated with the presence of a pure condensed phase of M (generally $M_{(l)}$ in cases of interest).[3] For temperatures several hundred degrees centigrade below the maximum melting point of MN, or lower, the maximum achievable value of p_M is fairly well approximated by that associated with $M_{(l)}$, p_M^{vap}, for most cases of interest. We will confine our calculations to such temperatures that $p_M \cong p_M^{\text{vap}}$ and simply point out that the results will represent a lower bound to the degree of self-compensation at other temperatures where $p_M < p_M^{\text{vap}}$, e.g., the maximum melting point. We write,

$$p_M^{\text{vap}} = \exp \Delta S_M^{\text{vap}}/k \exp(-\Delta H_M^{\text{vap}}/kT)\,, \tag{8}$$

and obtain, finally, from Eqs. (6)–(8),

$$\begin{aligned} kTlnQ^{\min} = E_g - E_A' - \Delta H_M + \Delta H_M^{\text{vap}} \\ + T(\Delta S_M - \Delta S_M^{\text{vap}}) + kT\ln(g_M N_M/N_c)\,. \end{aligned} \tag{9}$$

Thus, with Eqs. (5) and (9) we can calculate the maximum relative concentration of free carriers that we can introduce into $MN_{(s)}$ at the temperature T. If T is sufficiently large, these carriers will be equal in concentration to the "uncompensated" donor impurities present. If the temperature at which we measure the conductivity is much less than T, some of these carriers may "freeze out." The extent of this "freeze-out" is determined largely by the energy level associated with the donor impurity (for the case of singly ionizable vacancies only). We will not be concerned with this "impurity limitation" on the accessable carrier concentration and conductivity but merely state that Eqs. (5) and (9) allow us to calculate the maximum relative concentration of uncompensated shallow impurities (virtually all ionized at temperature T) that can be introduced into $MN_{(s)}$.

III. CALCULATION OF RESULTS; KCl, ZnTe, CdTe, AND GaAs

We now apply Eqs. (5) and (9) to p-KCl, n-ZnTe, n- and p-CdTe, and n-GaAs. The energy bandgaps, E_g, are available in the literature.[4–9] The energy levels of the compensating vacancies, E_A' are available for p-KCl (F center),[10] n-ZnTe,[11] n-CdTe,[8] and p-CdTe.[8,12] No data are available on E_A' in GaAs and we will simply assume $E_A' = 0$ in this case to put an upper bound on the extent of self-compensation.

The enthalpy of compensating vacancy formation, ΔH_M, is available as such only for n-CdTe.[8] The enthalpy of formation of interstitial Cd atoms in p-CdTe is reported,[8] however, according to the equation

$$I_{\text{Cd}}/N_{\text{Cd}}p_{\text{Cd}} = \exp - \Delta S_{\text{Cd}}^{I}/k \exp \Delta H_{\text{Cd}}^{I}/kT\,, \tag{10}$$

where I_{Cd} is the concentration of interstitial Cd atoms. It is, in practice, impossible to distinguish between interstitial Cd atoms and Te vacancies by electrical measurements.[1] If we reinterpret the data in terms of Te vacancies and use Eq. (7) (with $M = \text{Te}$) in place of Eq. (10), it is easy to demonstrate that the "equivalent" enthalpy of Te vacancy formation is given as

$$\Delta H_{\text{Te}} = \Delta H_{\text{CdTe}} - \Delta H_{\text{Cd}}^{I}\,, \tag{11}$$

where ΔH_{CdTe} is the standard molar enthalpy change for the reaction

$$\text{CdTe}_{(s)} = \text{Cd}_{(g)} + \text{Te}_{(g)}\,. \tag{12}$$

ΔH_{CdTe} is essentially twice the cohesive energy per gram-atom of $\text{CdTe}_{(s)}$ and is available in the literature.[13,14] On the basis of such reinterpretation, we have obtained ΔH_{Te} for the calculation appropriate to p-CdTe. It is apparent that, for our purposes, no significant difference exists between interstitial atoms and vacancies and that the available data can always be interpreted without error in terms of vacancies, as above.

The enthalpy of vacancy (F center) formation in KCl has not been reported. Data are available, however, as to the concentration of F centers as a function of potassium pressure, p_{K}, at one temperature (697°C).[15] In particular, the concentration of F centers is reported to be proportional to $p_{\text{K}}^{0.85}$, rather than the expected linear dependence. We may handle these data in several ways, with slight variation in the calculated results. Firstly, we arrive at the minimum value of V_{Cl} by extrapolating the reported data to a value of p_{K} consistent with the highest possible value of p_{Cl} ($p_{\text{Cl}}^{\text{vap}}$), an extrapolation of perhaps a factor of 10^{20}, and use Eq. (6). Secondly, we may assume a linear dependence and carry out the same extrapolation with a resultant difference of a factor of 10^3 (fewer vacancies). Finally, in a fashion equivalent to the linear extrapolation, we may estimate the standard molar entropy change appropriate to the removal of a Cl atom to the vapor as half the standard molar entropy change of the reaction.

$$\text{KCl}_{(s)} = \text{K}_{(g)} + \text{Cl}_{(g)}\,, \tag{13}$$

plus a small contribution due to the presence of the vacancies,[2,3,16] which we somewhat arbitrarily estimate as ~4 e.u.[16] On the basis of our estimate of the total entropy change, we use Eq. (7) and the data mentioned above to calculate ΔH_{Cl}. Use of this calculated value in Eq. (9) leads, as expected, to essentially the same result

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as the linear extrapolation, and is probably the most reliable method.

No thermodynamic data on vacancy formation is available for either ZnTe or GaAs. We may, however, follow Swalin[16] and write

$$\Delta H_M = \Delta H_{MN} - E_r \simeq 2E_{\mathrm{coh}} - E_r\,, \qquad (14)$$

where ΔH_{MN} is the standard molar enthalpy change for the reaction

$$MN_{(s)} = M_{(g)} + N_{(g)}\,. \qquad (15)$$

E_{coh} is the cohesive energy per gram-atom and E_r is a "relaxation" energy associated with the vacancy. Eq. (14) is based on the assumption of constancy of bond energy and may be expected to apply to covalent crystals. An equation of the same form can actually also be derived for ionic crystals.[17] If we put the data for n-CdTe[8] into the form of Eq. (14), we find $E_r/\Delta H_{MN} = 0.24$. Similarly, for Ge,[15] $E_r/\Delta H_{MN} = E_r/2E_{\mathrm{coh}} = 0.19$. We will assume that Eq. (14) applies to both ZnTe and GaAs. Further, we will assume that $E_r/\Delta H_{MN}$ has the same value for ZnTe as for CdTe. For GaAs, we will assume a value of $E_r/\Delta H_{MN}$ midway between that of CdTe and Ge, i.e., $E_r/\Delta H_{MN} = 0.21$, and use the data of ΔH_{GaAs}.[18]

The enthalpies and entropies of vaporization [Eq. (8)], are available for all the elements involved.[14]

For each case, we take the temperature, T, to be several hundred degrees centigrade below the maximum melting point of the host crystal in order that the maximum value of p_M be reasonably accurately described by p_M^{vap}.

The entropies of vacancy formation, ΔS_M, are generally unknown. The over-all entropy term in Eq. (9), $(\Delta S_M - \Delta S_M^{\mathrm{vap}})$, is clearly the standard molar entropy change that occurs upon transfer of one mole of M atoms from $MN_{(s)}$ to $M_{(l)}$, leaving M vacancies in the crystal. This must be given by approximately minus half the standard molar entropy of formation of $MN_{(s)}$ from the solid elements ($\sim$2 e.u.) plus the standard molar entropy of fusion of $M_{(s)}$ ($\sim$3 e.u. for most elements) plus a contribution due to the "excess" entropy of the vacancies[2,3,16] (which is $\sim$4 e.u.).[15] We therefore take $(\Delta S_M - \Delta S_M^{\mathrm{vap}})$ as $\sim$9 e.u. in each case.

The degeneracy factor, g_M, is taken as 2 for all cases and the concentration of available M sites, N_M, is calculated from the densities of the host crystals, which are easily available.

The density of states, N_c, is calculated from the temperature, T, and the appropriate effective mass, m^*, which is available for n-CdTe,[19,20,8] p-CdTe[8] (with some uncertainty) and n-GaAs.[21] We will take m^* for n-ZnTe as identical to that of n-CdTe and that for p-KCl as equal to the free-electron mass.

Finally, the only implicit temperature dependence in Eq. (9) that we consider is that of the bandgap, E_g. Estimates of this dependence are available for CdTe[8,22] and CdAs.[22] The value for ZnTe is interpolated from data for CdTe, CdSe, and ZnSe.[22] The value of $(\partial E_g/\partial T)$ for KCl is arbitrarily estimated as -10^{-3} eV/°C.

The inputs for Eq. (9) are given in Table I, excluding $(\Delta S_M - \Delta S_M^{\mathrm{vap}}) = 9$ e.u. $= 3.9\times10^{-4}$ eV/°C and $g_M = 2$.

The results of the calculation based on Eq. (9) and the data in Table I are presented in Table II, along with data on E_g and E_{coh}. It is clear from the above discussion relating to the data in Table I that the results in the second and third columns in Table II are reliable only as to order of magnitude. Nevertheless, we may draw certain firm conclusions from these results:

1. There does exist a self-compensation "boundary" such that certain compounds, falling beyond the "boundary," cannot be doped by any equilibrium process to have appreciable electronic conductivity, e.g., the alkali halides. A rough rule of thumb for determining the position of the self-compensation "boundary" is given by the ratio of the bandgap, E_g, to the cohesive energy per gram-atom, E_{coh}; essentially complete self-compensation occurring for values of this ratio much above unity while little self-compensation occurs for values below 0.5. The expected trend from ionic to covalent compounds is observed.

2. The II-VI compounds constitute a class in which considerable self-compensation may be expected to occur ($E_g/E_{\mathrm{coh}} \approx 1$). Nevertheless, the calculated degree of self-compensation by singly ionizable vacancies for these compounds is *not* sufficient to explain the well-known difficulty of obtaining, for example, appreciable conductivity in n-ZnTe or p-CdS. Similar results are expected for compensation by simple singly ionizable interstitial atoms [see discussion of data in Table I for p-CdTe and Eq. (14)]. We conclude, therefore, that some other limitation on the accessible carrier concentration and conductivity in II-VI compounds must be involved. There may, of course, be *impurity* limitations related to solubility or position of energy levels within the electronic bandgap. There may also be other "natural defects" involved, e.g., impurity-vacancy pairs, etc. A particular possibility that we will consider in more detail is the presence of doubly ionizable vacancies, of which both ionization levels fall within the electronic bandgap.

IV. MULTIPLY IONIZABLE VACANCIES

In the general case, we designate the concentration of M vacancies, which have been ionized to a charge of

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TABLE I. Inputs for Eq. (9).

Compound	T (°K)	$E_g(T)$ (eV)	E_A' (eV)	ΔH_M (eV)	ΔH_M^{vap} (298°K) (eV)	N_M (cm^{-3})	N_c (cm^{-3})
p-KCl	970	8.03^{a,c}	2.40^{h}	6.20^{a}	1.36^{b,m}	1.38×10^{22}	1.50×10^{20} ^{a}
n-ZnTe	1500	1.36^{d,e,a}	0.05^{i}	3.43^{a}	1.21^{m}	1.83×10^{22}	1.03×10^{19} ^{a}
n-CdTe	1250	1.02^{f}	0.15^{f}	3.20^{f}	1.07^{m}	1.55×10^{22}	7.76×10^{18} ^{f}
p-CdTe	1250	1.02^{f}	0.02^{f}	3.37^{a}	1.86^{m}	1.55×10^{22}	3.49×10^{19} ^{f,k,l}
n-GaAs	1250	0.95^{g,e}	0.00^{a}	5.81^{a,j}	2.76^{m}	1.01×10^{22}	4.12×10^{18}

[a] See text in Sec. III.
[b] T is above the critical temperature of Cl_2 so that $Cl_{2(S)}$ is the condensed phase of interest rather than $Cl_{2(1)}$. We will neglect the small effect of this however.
[c] See Ref. 4.
[d] See Refs. 5–7.
[e] See Ref. 20.
[f] See Ref. 8.
[g] See Ref. 9.
[h] See Ref. 10.
[i] See Ref. 11.
[j] See Ref. 16.
[k] See Ref. 17.
[l] See Ref. 18.
[m] See Ref. 13.

TABLE II. Results from Eq. (9).

Compound	$Q_{\text{calc}}^{\text{min}}$	$\left(\frac{n}{D^+}\right)^{\text{max}}$ or $\left(\frac{p}{A^-}\right)^{\text{max}}_{\text{calc}}$	E_g (298°K) (eV)	$\Delta H_{MN}=2E_{\text{coh}}$ (eV)	E_g/E_{coh}
p-KCl	2.12×10^{8}	4.71×10^{-9}	8.70^{a}	6.70^{e}	2.61
n-ZnTe	3.09×10^{2}	3.22×10^{-3}	2.20^{b}	4.51^{e}	0.97
n-CdTe	3.23×10	3.00×10^{-2}	1.50^{c}	4.20^{e}	0.72
p-CdTe	8.70×10^{2}	1.15×10^{-3}	1.50^{c}	4.20^{e}	0.71
n-GaAs	1.70×10^{-3}	0.998	1.43^{d}	7.35^{f}	0.39
CdS					0.94
ZnS					1.22

[a] See Ref. 4.
[b] See Refs. 5–7.
[c] See Ref. 8.
[d] See Ref. 9.
[e] See Refs. 12 and 13.
[f] See Refs. 16 and 13.

$-i$ as V_M^{-i} and follow Sec. II in writing a charge neutrality equation,

$$n+\sum_{i=1}^{N} iV_M^{-i}=D^+, \tag{16}$$

where N is the highest charge state to fall within the bandgap. We also write an equilibrium constant for ionization of a vacancy in the ith charge state,

$$nV_M^{-i+1}/N_cV_M^{-i}=g_{i-1}/g_i\exp(E_{A_i}-E_c/kT), \tag{17}$$

where g_i is a degeneracy factor and E_{A_i} is an energy level describing the ith charge state of the vacancy. As before, E_c is the energy at the bottom of the conduction band. It follows from use of Eq. (17) in Eq. (16) that Eq. (5) still applies, with Q given by

$$Q=Q_1\left\{1+\sum_{i=2}^{N}(ig_i/g_1)\left(\frac{n}{N_c}\right)^{i-1}\times\exp\left[(1/kT)\sum_{j=2}^{i}(E_c-E_{A_j})\right]\right\}, \tag{18}$$

where

$$Q_1=g_1V_M/N_c\exp(E_c-E_{A_1})/kT, \tag{19}$$

as in Eq. (6).

For the II-VI compounds, it is believed that $N=2$ and we write, for these compounds,

$$Q=Q_1\{1+(2g_2/g_1)(n/N_c)\exp(E_c-E_{A_2}/kT)\}. \tag{20}$$

Certain general features of Eqs. (18) and (20) should be noted. We see that the effect of the second ionization level of the vacancy only becomes significant in Eq. (20) if the doping level is such that the Fermi level rises above the second ionization energy level [see Eq. (2)]. If we attempt to dope the host crystal so heavily that the Fermi level does rise above the second ionization level of the acceptor vacancy, we see from Eqs. (1) and (20) that the situation is soon reached in which

$$n/N_c=\exp(E_F-E_c)/kT=(g_1D^+/2g_2Q_1N_c)^{1/2}\times\exp(E_{A_2}-E_c/2kT). \tag{21}$$

It is clear that $Q_1\gg1$ for the higher bandgap II-VI compounds (see Table II). Further $(g_1D^+/2g_2Q_1N_c)^{1/2}\lesssim1$. It follows that the Fermi level in the II-VI compounds cannot be pushed closer to the bottom of the conduction band than half the energy separation between the second ionization level of the acceptor vacancy and the bottom of the conduction band. In other words, shallow impurities will be completely compensated by a combination of singly and doubly ionized vacancies in a II-VI compound if the second ionization level of the compensating vacancy falls within the bandgap.

Even if the Fermi level does not rise above the second ionization level of the acceptor vacancies, these levels will still contribute to the temperature dependence of the carrier concentration. If the donor impurities are sufficiently shallow, the position of these second ionization levels will entirely determine this temperature dependence. However, as long as $Q_1\gg1$, "freeze-out" of carriers onto these levels cannot push the Fermi level higher than the maximum value discussed above. Complete compensation of impurities by a combination of singly and doubly ionized vacancies will then always occur as long as the energy level of the added donor impurities is shallower (closer to the conduction band) than the second ionization level of the vacancies. If the energy level of the donor impurity is sufficiently deep, the donors will not be completely compensated, but cannot then contribute appreciable conductivity.

V. SPECIFIC IMPLICATIONS: GaAs, CdTe

The magnitude of the concentrations of vacancies in GaAs is of interest because it has been suggested that the concentration of some natural defects can be quite high ($\sim 10^{19}/\text{cm}^3$).[23] The estimated value of the energy of vacancy formation used in Sec. III, however, leads to the conclusion that the total concentration of simple vacancies, neutral or ionized, must be low. In particular, the maximum concentration of neutral Ga vacancies (under the maximum pressure of As) is calculated to be $\sim 10^{14}/\text{cm}^3$. If the Ga vacancies were *shallow* acceptors, the total concentration of Ga vacancies could hardly exceed $10^{18}/\text{cm}^3$ in a crystal of GaAs grown from an As-rich melt and doped to be degenerately *n*-type (at the growth or equilibration temperature). This view is supported by the well-known fact that GaAs can be prepared either *n*- or *p*-type at the $10^{17}/\text{cm}^3$ level without appreciable compensation. Thus under "normal" preparation conditions, the concentrations of electrically active natural defects must be low, i.e., $\lesssim 10^{15}/\text{cm}^3$.

As regards CdTe, it has been suggested that the second ionization level of the acceptor Cd vacancy is 0.6 eV below the conduction band.[8,12] It is, however, well known that CdTe can be doped degenerately *n*-type.[8,20] From the results of Sec. IV, it is clear that this contradicts the assignment of the 0.6-eV level to the second ionization level of the isolated Cd vacancy. This conclusion does not depend on the results of Sec. III but simply requires that Q_1 not be much smaller than unity. The experimental observation that substantial self-compensation is observed in *n*-CdTe[8] demonstrates that this requirement is met. There is, in fact, some support for the estimated energy of vacancy formation in CdTe used in Sec. III in that large concentrations of singly ionized Cd vacancies can be introduced into *p*-CdTe.[12]

It would thus appear that the 0.6-eV level must be assigned to some other center, possibly some complex involving a doubly ionized Cd vacancy.[12] The second ionization level of the isolated Cd vacancy in CdTe must, in fact, be much closer to the conduction band and may be the level recently observed by Lorenz *et al.*[24,25] in CdTe and some other II-VI compounds (all of which can be doped heavily *n* type). The exclusion of ZnTe (which apparently cannot be doped *n* type) from this group is significant.

VI. SOLUBILITY EFFECTS

Inasmuch as an impurity must reside on either an M site or an N site in $MN_{(s)}$,we expect that the solubility of impurities in binary compounds must, in general, be a function of the stoichiometry of the system, i.e., the concentration of vacancies. In Sec. II, we have a situation in which the concentration of added donor impurities in $MN_{(s)}$ is held fixed. Under these circumstances, it was pointed out, the maximum *relative* amount of uncompensated donor impurities will occur in a system in which the concentration of compensating acceptor vacancies is a minimum. What is generally held constant in the laboratory, however, is, to a first approximation, the thermodynamic activity of the added donor impurities. As a consequence of the dependence of the solubility of the impurities on the vacancy concentration, it is not necessarily true, then, that the maximum *total* concentration of uncompensated impurities will occur in a system in which the concentration of acceptor vacancies is a minimum.

For, example, let us consider a compound semiconductor $MN_{(s)}$, which is brought into equilibrium at the temperature T with a total constant activity of added donor impurities, i.e., the partial pressure of atomic $D_{(g)}$ is held constant at a value p_D. These impurities are presumed to reside on M sites in the host crystal for this system. The pressure of $M_{(g)}$ is again designated p_M and we assume, as in Sec. II, that only singly ionizable acceptor M vacancies need be taken into account.

The concentration of neutral donors, D, in the host crystal is determined by the equilibrium constant.[1–3]

$$D/p_D V_M = K(T)\,, \tag{22}$$

which refers to the process in which an atom of $D_{(g)}$ "fills" an M vacancy to yield a neutral donor impurity in the lattice.

The concentration of ionized impurity atoms in the crystal, D^+, is determined by the equilibrium constant for the ionization of a neutral impurity to yield a free electron.

$$nD^+/N_cD = (1/g_D)\exp(E_D - E_c/kT)\,, \tag{23}$$

where g_D is a degeneracy factor and E_D is the energy level associated with the donor impurity.

It follows, from Eqs. (5) and (23), that

$$n^2 = [1/(1+Q)](N_cD/g_D)\exp(E_D - E_c)/kT)\,. \tag{24}$$

At constant p_D and T, D is proportional to V_M according to Eq. (22). On the other hand, according to

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[23] J. Blanc, R. H. Bube, and L. R. Weisberg, Phys. Rev. Letters **9**, 252 (1962).

[24] M. R. Lorenz and H. H. Woodbury, Phys. Rev. Letters **10**, 215 (1963).

[25] M. R. Lorenz, M. Aven, and H. H. Woodbury, Phys. Rev. **132**, 143 (1963).

Eq. (6), Q is also proportional to V_M at constant T. We see, therefore, that the total concentration of free carriers, n, is a maximum when V_M is a *maximum*, despite the fact that the relative amount of uncompensated donors, n/D^+, is a minimum under the same conditions. When $Q \gg 1$, as in the II-VI compounds (see Sec. III), the *total* concentration of free carriers is essentially independent of V_M. Thus, as p_M is varied in these systems, only the concentration of compensated donors varies.

It should be noted that the situation is entirely different if the donor impurities reside on N sites rather than M sites. Under such circumstances, the solubility of the impurities is maximized and the degree of self-compensation minimized when V_M is minimized, i.e., when p_M is maximized.

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Theory of the Optical and Magnetic Properties of the Self-Trapped Hole in Lithium Fluoride*

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Using a semiphenomenological method, the energy and wave functions of a self-trapped hole (V_k center) in LiF are obtained as a function of the separation between the two F^- ions at which the hole is assumed trapped. The lattice distortion energy due to the changes in Madelung, repulsive, and polarization energies is calculated as a function of the totally symmetric displacement of the two participating F^- ions and six positive ions adjacent to the F^- ions. This lattice energy is combined with the calculated energy for the F_2^- molecule to obtain the total energy as a function of the distance between the participating F^- ions for both the symmetric (Σ_g) and antisymmetric (Σ_u) states of the hole on the V_k center. Only the energy curve for the ground (Σ_u) state exhibits a minimum in the expected region of F^--ion separation. From the resulting configurational coordinate curves, the optical absorption energy and width are computed and found to be in order-of-magnitude agreement with experiment. Computed values of the experimentally known isotropic and anisotropic hyperfine constants are used to assess the validity of our molecular wave functions, which were obtained in a one-electron approximation.

I. INTRODUCTION

In recent years, a fairly detailed understanding of the F center in alkali halides has been achieved by concerted theoretical and experimental studies of its electronic structure.[1] The F center consists of an electron bound to a negative-ion vacancy, and is the simplest of several "electron" color centers such as the M, R, and F' centers.[2] A series of "hole" color centers also exists (V_1,H,V_k); these are characterized by optical absorption bands lying at somewhat higher energies than those of electron centers, are generally stable only at low temperatures, and must be formed by high-energy irradiation. The best understood of these, a center which consists of a self-trapped hole, has been studied elaborately by Castner and Känzig.[3] Electron resonance data have conclusively shown that this center is not associated with a vacancy but instead resembles a negative halogen molecule-ion with a hole shared between two adjacent negative ions. Two previous theoretical attempts[4,5] have been made to explain the stability of this self-trapped holes. Yamashita[4] tried to calculate the energy of the hole in KCl as a function of the displacement of the Cl^- ions which trap it. He could not obtain a minimum in the energy as a function of this displacement but suggested that the repulsion between the core electrons of the Cl^- ions, which he had neglected, might provide a minimum in the energy curve at half the usual distance between the ions in the crystal. A subsequent attempt by Nettel[5] gave the result that the energy of a hole trapped as a Cl_2^- ion in the crystal had higher energy than a chlorine atom

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[1] See, for example, the review article by B. S. Gourary and F. J. Adrian in *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

[2] See, for example, J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, Inc., New York, 1963).

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[5] S. J. Nettel, Phys. Rev. **121**, 425 (1961).