

## Self-Compensation-Limited Conductivity in Binary Semiconductors. III. Expected Correlations With Fundamental Parameters\*

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The previously developed calculation of the degree of self-compensation in a binary semiconductor is used to obtain a useful correlation between the degree of self-compensation by singly ionized natural defects and the ratio of the electronic energy gap to certain generally known thermodynamic quantities. The latter quantities are related to the cohesive energy. It is shown, however, that the correlation factor given herein is more meaningful than the previously suggested ratio of the energy gap to the cohesive energy. The results are generalized to include compounds having a composition  $M_aN_b$ . One interesting conclusion is the prediction that  $M$ -atom vacancies will generally dominate interstitial  $N$  atoms when  $b < a$  and vice versa. It has previously been shown that the second ionization level of a compensating natural defect can be critical in determining the degree of self-compensation, particularly in the case of the II-VI compounds. A simple model of a singly ionized *vacancy* is presented which suggests that size considerations should play a major role in determining the second ionization level of such a defect. It is shown that the gross electrical properties of the II-VI compounds can be completely correlated with a single parameter, the ratio of the tetrahedral covalent radii of the elements. Finally, the over-all classification scheme described above is applied to a reasonably large group of compounds. The predicted gross electrical properties of these compounds are found to be in essential agreement with what is known experimentally, with the single exception of  $n$ -CdF<sub>2</sub>, for which an explanation is offered.

### I. INTRODUCTION

AN analysis of the expected degree of self-compensation in a simple binary semiconductor,  $MN$ , by isolated vacancies or interstitial atoms has been developed.<sup>1</sup> Several main conclusions were reached and are presented below:

(1) There exists a kind of 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.

(2) The degree of self-compensation by isolated *singly ionizable* vacancies or interstitial atoms (the position of the self-compensation boundary for that case) is expected to correlate with the ratio of the electronic energy gap  $E_g$  to the cohesive energy per gram atom, which is half the standard molar enthalpy change for the reaction

$$MN_{(s)} = M_{(g)} + N_{(g)}. \quad (1)$$

Essentially complete self-compensation by singly ionizable vacancies occurs for values of this ratio much above 1.0 while little self-compensation by such natural defects occurs for values below 0.5.

(3) There is a large class of compounds in which substantial but not complete self-compensation by singly ionized vacancies will occur ( $E_g/E_{\text{coh}} \approx 1$ ). The II-VI compounds fall into this group. Under these circumstances, the presence of a second ionization level within the bandgap associated with the compensating

vacancy results in complete self-compensation by a combination of singly and doubly ionized vacancies.

It has been shown that these results are largely in agreement with the available experimental information for a series of compounds ranging from the completely self-compensated relatively ionic KCl to the completely uncompensated relatively covalent GaAs.<sup>1</sup> Furthermore, in the intermediate case of ZnTe, for example, it is expected that complete self-compensation of  $n$ -type conductivity should occur in that the second ionization level of the compensating Zn vacancy is known to be shallow (close to the valence band).<sup>2</sup> It has, in fact, been recently experimentally demonstrated that complete self-compensation of  $n$ -ZnTe by a combination of singly and doubly ionized Zn vacancies does occur, regardless of the pressure of  $Zn_{(g)}$  in the system.<sup>3</sup>

We see that we seem able to describe the gross electrical behavior of simple binary semiconductors in terms of only three parameters: the ratio  $E_g/E_{\text{coh}}$  and, in the event this ratio has an intermediate value, the positions in energy of the second ionization levels of the compensating vacancies or interstitial atoms (one on the  $n$ -type side and one on the  $p$ -type side). There remain certain difficulties with this viewpoint, however.

Firstly, in regard to singly ionizable vacancies or interstitial atoms, the ratio  $E_g/E_{\text{coh}}$  does not take proper account of the relative volatility of the elements that comprise compound  $MN$ . As will be pointed out in Sec. II, this can lead to serious error if the heat of vaporization of at least one of the component elements of  $MN$  is very large.

Secondly, the second ionization levels associated with vacancies or interstitial atoms are unknown for most compounds. We cannot, therefore, predict the electrical

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<sup>1</sup> G. Mandel, Phys. Rev. 134, A1073 (1964).

<sup>2</sup> M. Aven and B. Segall, Phys. Rev. 130, 81 (1963).

<sup>3</sup> R. S. Title, G. Mandel, and F. F. Morehead (to be published).

properties of many compounds in the absence of extensive electrical measurements. This is a clearly unsatisfactory situation.

It is our purpose, in Sec. II, to modify the ratio  $E_g/E_{\text{coh}}$  to more closely correspond to the previously calculated degree of self-compensation by singly ionizable vacancies or interstitial atoms.<sup>1</sup> The resulting quantity takes proper account of relative volatility. In addition, we extend the analysis to include compounds of simple crystal structure having the composition  $M_aN_b$ , where  $a$  and  $b$  are no longer constrained to be unity.

In Sec. III, we consider a simple model for the second ionization level of a doubly ionizable vacancy. On the basis of this model, it is predicted that size considerations play a major role in the electrical behavior of those compounds in which substantial but not complete self-compensation by singly ionized vacancies takes place, e.g., the II-VI compounds. It is shown that the gross electrical behavior of the II-VI compounds can be completely correlated with a single parameter, the ratio of the tetrahedral covalent radii of the elements from which the compounds are made.

Finally, in Sec. IV, the classification scheme presented in Secs. II and III is applied to a reasonably large group of different compounds, including some to which the assumptions made in Secs. II and III do not apply. The gross electrical properties of these compounds are predicted and these predictions are found to be in reasonable agreement with what is known experimentally.

## II. CORRELATION OF SELF-COMPENSATION WITH ELECTRONIC ENERGY GAP AND COHESIVE ENERGY

As pointed out in Sec. I, it has been previously suggested,<sup>1</sup> based on theoretical arguments, that the degree of self-compensation by singly ionizable "natural" defects in a binary semiconductor should correlate with the ratio of the electronic energy gap  $E_g$  to the cohesive energy,  $E_{\text{coh}}$ ,  $E_{\text{coh}}$  being essentially determined by the reaction given in Eq. (1). It is obvious that  $E_{\text{coh}}$  has to be very large for compounds having at least one component element which has a very large heat of vaporization, e.g., CuI. For such compounds, the ratio  $E_g/E_{\text{coh}}$  is very low, apparently indicating a low degree of self-compensation. This is incorrect, however, in that a large heat of vaporization of  $M$ , for example, limits the maximum pressure of  $M_{(g)}$  that can be obtained at a given temperature. The pressure of  $M_{(g)}$  that is applied to the system serves to suppress the formation of  $M$  atom vacancies in the host  $MN$  lattice and to diminish the degree of self-compensation by such vacancies.

A better correlation may be obtained from a closer examination of the previously calculated degree of self-compensation by singly ionized natural defects.<sup>1</sup> For the case of  $n$ -type material doped with a donor  $D$  and compensated by acceptor  $M$  atom vacancies, we have

[Eq. (5) of Ref. 1].

$$n/D^+ = 1/(1+Q), \quad (2)$$

where  $n$  is the concentration of free electrons and  $D^+$  is the concentration of ionized donors. The minimum value of  $Q$  (maximum pressure of  $M_{(g)}$  in equilibrium with the system) is largely determined by a factor given by  $\exp[(E_g + \Delta H_M - \Delta H_M^{\text{vac}})/kT]$ , where  $\Delta H_M^{\text{vac}}$  is the enthalpy of neutral  $M$  vacancy formation,  $\Delta H_M$  is the enthalpy of vaporization of  $M$ , and  $T$  is the temperature of preparation of the sample.  $\Delta H_M^{\text{vac}}$  refers to the process whereby an atom of  $M$  is removed from the  $MN$  lattice and released to the vapor as  $M_{(g)}$ , leaving behind a neutral  $M$  vacancy.  $\Delta H_M$  is defined to refer to the reaction



Under some experimental conditions,  $M_{(s)}$  is more appropriate than  $M_{(l)}$ .<sup>1</sup>

Furthermore, it has been pointed out that  $\Delta H_M^{\text{vac}}$  may be written as<sup>1</sup>

$$\Delta H_M^{\text{vac}} = \Delta H_{MN} - E_r, \quad (4)$$

where  $\Delta H_{MN}$  refers to the reaction in Eq. (1) and is essentially  $2E_{\text{coh}}$ .  $E_r$  is referred to as the "relaxation energy" of the vacancy and is defined by Eq. (4).  $E_r$  is apparently small relative to  $\Delta H_{MN}$  in many simple cases,<sup>1</sup> although it has not been shown that it is generally small. Nevertheless, it is not difficult to envision simple bonding situations in which this is correct. The most obvious of these is a covalent crystal in which nearest-neighbor interactions provide most of the cohesive energy,<sup>4</sup> provided that the nearest neighbors to an  $M$  atom are all  $N$  atoms and vice versa. It can also be shown that  $E_r$  is small in the case of simple ionic crystals, although this arises from an apparently fortuitous approximate cancellation of several terms.

It should be noted, however, that there are compounds for which  $E_r$  may not be small, even if only nearest-neighbor interactions are considered. In GaS, for example, the nearest neighbors around each Ga atom consist of three S atoms and one Ga atom, while those around each S atom consist of three Ga atoms and three S atoms.<sup>5</sup> If one Ga-Ga bond is not energetically equivalent to three S-S bonds, and if all of these are not small compared to three Ga-S bonds, then the cohesive energy, i.e.,  $\Delta H_{MN}$ , is not evenly shared and Eq. (4) with a small value of  $E_r$  does not make sense. In other words, the possible difficulty in this case is caused by the crystal structure in which Ga and S do not occupy energetically equivalent sites. Such complications do not, fortunately, arise in most cases of interest.

Using Eq. (4), with  $E_r$  neglected, and the discussion following Eq. (2), we come to the conclusion that a better correlation with the degree of self-compensation

<sup>4</sup> G. L. Hall, *Phys. Chem. Solids* **3**, 210 (1957).

<sup>5</sup> A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1962), 3rd ed.

by singly ionized  $M$  vacancies (or interstitial  $N$  atoms)<sup>1</sup> is obtained by considering the ratio  $E_g/(\Delta H_{MN} - \Delta H_M)$  rather than  $E_g/E_{\text{coh}} = 2E_g/\Delta H_{MN}$ . The denominator ( $\Delta H_{MN} - \Delta H_M$ ) is, of course, just the standard molar enthalpy change for the reaction

$$MN_{(s)} = M_{(l)} + N_{(g)}. \quad (5)$$

If we are considering self-compensation by singly ionized  $N$  vacancies (or interstitial  $M$  atoms), it is obvious that we need simply replace the products in Eq. (5) by  $M_{(g)} + N_{(l)}$ , i.e., we consider the ratio  $E_g/(\Delta H_{MN} - \Delta H_N)$ .

We would also like to extend these considerations to include compounds of composition  $M_aN_b$ , where  $a$  and  $b$  are not necessarily equal to unity. It is obvious that we may do this by rewriting Eq. (4),

$$\Delta H_M^{\text{vac}} = (1/a)\Delta H_{M_aN_b} - E_r, \quad (6)$$

where  $\Delta H_{M_aN_b}$  refers to the reaction,

$$M_aN_b_{(s)} = aM_{(g)} + bN_{(g)}. \quad (7)$$

Assuming  $E_r$  to be small in Eq. (6) is no worse than assuming it small in Eq. (4). For the simplest case to which Eq. (4) applies with neglect of  $E_r$ , i.e., nearest-neighbor  $M$ - $N$  interactions only, Eq. (6) also applies with  $a$  and  $b$  not necessarily equal to one. A compound for which these assumptions may very well be valid is  $\gamma$ -Ga<sub>2</sub>Se<sub>3</sub>, which crystallizes in a defect zinblende structure.<sup>5</sup>

Using Eq. (6), with  $E_r$  neglected, and the discussion following Eq. (2), we conclude that the degree of self-compensation in  $M_aN_b$  by singly ionized  $M$  vacancies should correlate with the ratio

$$\frac{E_g}{(1/a)(\Delta H_{M_aN_b} - a\Delta H_M)},$$

where we see that the denominator is simply  $1/a$  multiplied by the standard molar enthalpy change for the reaction

$$M_aN_b_{(s)} = aM_{(l)} + bN_{(g)}. \quad (8)$$

For self-compensation by singly ionized  $N$  vacancies, we simply replace the denominator by

$$(1/b)(\Delta H_{M_aN_b} - b\Delta H_N).$$

It should be noted that the essential equivalence of singly ionized  $M$  vacancies and singly ionized interstitial  $N$  atoms, which has been shown<sup>1</sup> to exist in a compound of composition  $MN$  (provided the binding energy of a neutral interstitial  $N$  atom in the lattice is small compared to  $\Delta H_{MN}$ ), is not valid in a compound of composition  $M_aN_b$  if  $a \neq b$ . We see this by noting that the concentration of neutral interstitial  $N$  atoms  $I_N$  depends on the pressure of  $M_{(g)}$ ,  $p_M$ , and  $N_{(g)}$ ,  $p_N$ , via

the following equations<sup>1,6</sup>:

$$\begin{aligned} \frac{I_N}{N_I} &= p_N \exp\left(-\frac{\Delta S_{I_N}}{k}\right) \exp\left(\frac{\Delta H_{I_N}}{kT}\right) \\ &= \frac{1}{p_M^{a/b}} \exp\left(\frac{(1/b)\Delta S_{M_aN_b} - \Delta S_{I_N}}{k}\right) \\ &\quad \times \exp\left(-\frac{(1/b)\Delta H_{M_aN_b} - \Delta H_{I_N}}{kT}\right), \quad (9) \end{aligned}$$

where  $N_I$  is the concentration of interstitial sites in the lattice,  $\Delta S_{M_aN_b}$  is the standard molar entropy change of Eq. (7), and  $\Delta H_{I_N}$  and  $\Delta S_{I_N}$ , the "binding" enthalpy and entropy, are defined by Eq. (9). The concentration of neutral  $M$  vacancies,  $V_M$ , on the other hand, is related to  $p_M$  by the following equation<sup>1,6</sup>:

$$\frac{V_M}{N_M} = \frac{1}{p_M} \exp\left(\frac{\Delta S_M^{\text{vac}}}{k}\right) \exp\left(-\frac{\Delta H_M^{\text{vac}}}{kT}\right), \quad (10)$$

where  $N_M$  is the concentration of  $M$  sites in the lattice. We use Eq. (6) for  $\Delta H_M^{\text{vac}}$ . For  $\Delta S_M^{\text{vac}}$ , we assume

$$\Delta S_M^{\text{vac}} = \Delta S_M + \Delta S_R, \quad (11)$$

where  $\Delta S_M$  refers to the simple vaporization reaction in Eq. (3), while  $\Delta S_R$  is termed the "relaxation" entropy of the vacancy and is believed to be relatively small.<sup>1</sup> Similarly, we expect that

$$\Delta S_{I_N} = \Delta S_N - \Delta S_{I_N}', \quad (12)$$

where  $\Delta S_N$  refers to a similar vaporization process and  $\Delta S_{I_N}'$  is a similar small "relaxation" entropy referring to relaxation of the lattice around an interstitial  $N$  atom.

Combination of Eqs. (6) and (10)–(12) and comparison with Eq. (9) indicate that the difference in behavior between neutral interstitial  $N$  atoms and neutral  $M$  vacancies resides in a factor given by  $\exp(\Delta S^*/k) \times \exp(-\Delta H^*/kT)$ , where

$$\begin{aligned} \Delta S^* &= \left(\frac{1}{b}\Delta S_{M_aN_b} - \Delta S_N - \frac{a}{b}\Delta S_M\right) + (\Delta S_{I_N}' - \Delta S_R), \\ \Delta H^* &= (1/b - 1/a)\Delta H_{M_aN_b} \\ &\quad + (E_R - \Delta H_{I_N}) + (1 - a/b)\Delta H_M. \end{aligned} \quad (13)$$

We expect that  $\Delta S_{I_N}'$  and  $\Delta S_R$ , the "relaxation" entropies, are small and comparable in magnitude. Furthermore, we expect  $(1/b)\Delta S_{M_aN_b}$  to be comparable in magnitude to  $(1/b)(b\Delta S_N + a\Delta S_M)$  so that  $\Delta S^*$  is essentially zero in the general case.

We expect  $E_R$  and  $\Delta H_{I_N}$ , the "relaxation" energy of a neutral vacancy and the binding energy of a neutral

<sup>6</sup> F. A. Kroger and H. J. Vink, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. III, p. 310.

interstitial atom, to be small compared to  $\Delta H_{M_a N_b}$  and comparable in magnitude with each other. It is clear, however, that  $\Delta H^*$  will not, in general, be close to zero except when  $a=b$ .

Returning to the discussion following Eq. (7), we conclude, simply by adding  $\Delta H^*$  to

$$(1/a)(\Delta H_{M_a N_b} - a\Delta H_M),$$

that the degree of self-compensation in  $M_a N_b$  by singly ionized interstitial  $N$  atoms should correlate with the ratio

$$\frac{E_g}{(1/b)(\Delta H_{M_a N_b} - a\Delta H_M)},$$

where the denominator is now  $1/b$  multiplied by the standard molar enthalpy change for Eq. (8).

It is interesting to note that these results suggest that isolated neutral interstitial  $N$  atoms will dominate isolated neutral  $M$  vacancies whenever  $b > a$  and vice versa. This will also be true for ionized interstitial  $N$  atoms or  $M$  vacancies, provided that the electronic energy levels associated with these defects are not too different. No conclusion can be drawn when  $b=a$  inasmuch as only the relatively small differences  $E_R - \Delta H_{I_N}$  and  $\Delta S_{I_N}' - \Delta S_R$  are involved, and insufficient information exists regarding them. The assumptions that have been necessary to obtain these results should also be borne in mind, particularly the overly simplified bonding picture leading to Eq. (6).

### III. SECOND IONIZATION LEVEL OF A VACANCY

The significance of the second ionization level of a compensating natural defect has been pointed out for the intermediate case of a binary compound which is substantially, but not completely, self-compensated by singly ionized natural defects.<sup>1</sup> In this section, we shall consider a simple model for the second ionization level of an isolated vacancy (interstitials will not be discussed). We have in mind particularly the II-VI compounds, in which the second ionization level of a vacancy may be analyzed in terms of a single carrier (electron or hole) bound to a charged cavity in a dielectric medium.

The model we take as appropriate to this situation is a semicontinuum model of the "*F* center" (see Gourary and Adrian<sup>7</sup>). Such a model consists of cavity in a dielectric medium such that the effective field at large distances from the cavity is  $2e/kr^2$ , where  $e$  is the electronic charge,  $k$  is an "effective" dielectric constant, and  $r$  is the distance from the cavity. The potential inside the cavity is some constant value determined by the host lattice. Superimposed upon these potentials is that due to the trapped carrier.

An approximate solution to the energy eigenvalue

<sup>7</sup> 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. X, p. 188ff.

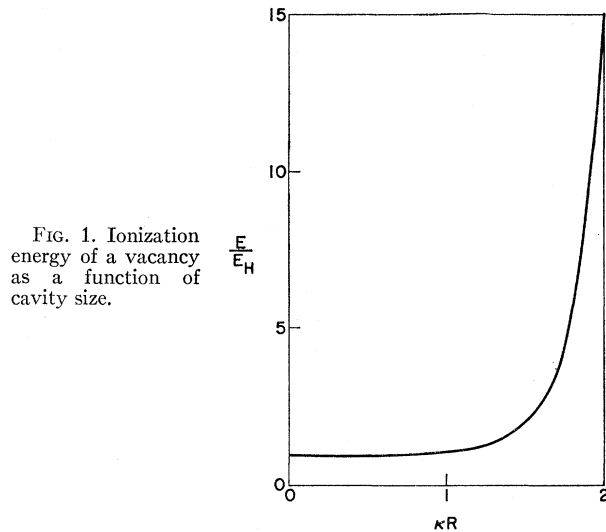


FIG. 1. Ionization energy of a vacancy as a function of cavity size.

problem associated with the above physical model has been obtained by Krumhansl and Schwartz<sup>7,8</sup> in the form of an equation which must be solved numerically and which we shall not reproduce here. The solutions to this equation possess certain interesting properties when the effective dielectric constant is sufficiently high and the cavity radius is sufficiently small. This is illustrated in Fig. 1, in which we have plotted  $E/E_H$  against  $\kappa R$ , where  $E$  is the ionization energy (ground state relative to bottom of conduction band for a donor vacancy),  $E_H$  is the "hydrogenic" value of  $E$  (including dielectric constant and effective mass),  $\kappa$  is a parameter determined by  $(V_0)^{1/2}$ ,  $V_0$  being the potential inside the cavity, and  $R$  is the cavity radius. For purposes of illustration, we have taken static dielectric constant = "optical" dielectric constant = 20 and  $V_0 = 12$  V.  $R$  varies from 0-3 atomic units (0-1.6 Å).

The most significant feature of the result illustrated in Fig. 1 is the fact that the ionization energy has its "hydrogenic" value for  $R$  below some critical value and then rises very rapidly as  $R$  increases beyond this critical value. Physically, the trapped carrier spends most of its time inside the cavity when the cavity is sufficiently large.

Unfortunately, a quantitative theory based on the work of Krumhansl and Schwartz cannot be developed since the value of  $V_0$  cannot be calculated for the systems of interest. We have too simple a model which we cannot, in any event, solve quantitatively. Nevertheless, we may draw certain qualitative conclusions from Fig. 1 from which a potentially very useful semi-empirical relationship results.

The most significant qualitative feature of Fig. 1 is, of course, the strong cavity size dependence mentioned above, i.e., the *smaller* the size of the vacancy, the *smaller* the ionization energy of the vacancy and,

<sup>8</sup> J. A. Krumhansl and N. Schwartz, *Phys. Rev.* **89**, 1154 (1953).

TABLE I. Accessible conductivity in II-VI compounds as a function of the sizes of the atoms involved.

Compound $MN$	$R_M/R_N$	Accessible conductivity type
ZnO	1.98	$n$
ZnS	1.26	$\dots$
ZnSe	1.15	$n$
ZnTe	0.99	$p$
CdS	1.42	$n$
CdSe	1.30	$n$
CdTe	1.12	$n$ and $p$

therefore, the stronger the tendency of the vacancy to compensate.

Furthermore, we expect a dependence on "effective" dielectric constant which is at least partially and perhaps largely determined by the polarizability of the nearest-neighbor atoms surrounding the vacancy. This polarizability is related to the size of these nearest-neighbor atoms. Thus, the larger the nearest-neighbor atoms, the larger the "effective" dielectric constant and, therefore, the smaller the ionization energy of the vacancy and the stronger the tendency of the vacancy to compensate.

These two size effects are in opposite directions with respect to conductivity limitations; a result which has interesting implications. For example, in a compound  $MN$ , a large size of the  $M$  atoms implies a large cavity size for an  $M$  vacancy and a large second ionization energy for such a vacancy. If  $M$  vacancies are acceptors (while  $N$  vacancies are donors), and if self-compensation by singly ionized vacancies is substantial but not complete, as in a II-VI compound, appreciable  $n$ -type conductivity will still be obtainable. This results from the fact the position of the Fermi level is determined by the position of the second ionization level of the compensating defect<sup>1</sup> and can be close to the conduction band for such a deep acceptor level. On the other hand, the postulated large size for  $M$  atoms implies a large polarizability for the nearest-neighbor  $M$  atoms surrounding an  $N$  vacancy and, therefore, a low second ionization energy for an  $N$  vacancy, which has been postulated to be a donor. This results in complete self-compensation of  $p$ -type conductivity.<sup>1</sup> A similar situation in which  $p$ -type conductivity is allowed while  $n$ -type conductivity cannot be obtained results if  $N$  atoms are large relative to  $M$  atoms. We expect, therefore, that, except for a range of comparable  $M$  and  $N$  sizes, most binary compounds which are substantially, but not completely, self-compensated by singly ionized vacancies will display only one type of conductivity, a result in obvious qualitative agreement with the known properties of the II-VI compounds.

Even more specifically, we expect a strong correlation between the ratio of the radii  $R_M/R_N$  in a II-VI compound (or other intermediate case) and its gross electrical behavior. It is not clear as to how these radii are

to be defined, although any consistent set of radii would probably suffice. In Table I, we display the ratios of the tetrahedral covalent radii<sup>9</sup> for most of the II-VI compounds as contrasted with their known electrical behavior. It is expected that only  $n$ -type conductivity will be accessible when  $R_M/R_N \gg 1$  while only  $p$ -type conductivity will be accessible when  $R_M/R_N \ll 1$  (as explained above).

We indeed see that the gross electrical behavior of the II-VI compounds is qualitatively described very well by the radius ratio  $R_M/R_N$ . (Appreciable conductivity of either type is apparently not accessible in ZnS because of the high degree of self-compensation by singly ionized vacancies.) If we combine the information in Table I with some preliminary experimental data<sup>10</sup> on  $Cd_xZn_{1-x}Te$ , which indicates that  $n$ -type conductivity is accessible when  $x \leq 0.5$ , we conclude that both  $n$ - and  $p$ -type conductivity are accessible only when  $1.12 \geq R_M/R_N \geq 1.06$ . The upper limit of the range is slightly uncertain (perhaps as high as 1.15). The fact that the center of the range occurs at  $R_M/R_N = 1.90$  rather than at  $R_M/R_N = 1.00$  should not be a matter of concern in that the tetrahedral covalent radius is merely a self-consistent measure of relative size and probably has little absolute significance in the present context.

It is presently an unanswered question as to whether the semiempirical relationship between electrical properties and  $R_M/R_N$  can be applied to systems of intermediate nature other than the II-VI compounds.

#### IV. APPLICATION OF OVER-ALL CLASSIFICATION SCHEME TO A VARIETY OF BINARY COMPOUNDS

We now apply the results of Secs. II and III to a number of different binary compounds. The necessary thermodynamic data is taken from Kubaschewski and Evans<sup>11</sup> and Stull and Sinke.<sup>12</sup> Electronic energy gaps are taken from Aigrain and Balkanski<sup>13</sup> except for KCl,<sup>14</sup> CuI,<sup>15</sup> CuBr,<sup>16</sup> AgI,<sup>16</sup> Cu<sub>2</sub>O,<sup>17</sup> GaSe,<sup>18</sup> GaS,<sup>18</sup> CdF<sub>2</sub>,<sup>19</sup> and CaF<sub>2</sub>.<sup>20</sup> All data refers to room temperature unless otherwise specified.

It should be realized that it is unreasonable to con-

<sup>9</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948), 2nd ed., p. 179.

<sup>10</sup> F. F. Morehead and G. Mandel (to be published).

<sup>11</sup> O. Kubaschewski and E. Evans, *Metallurgical Thermodynamics* (Pergamon Press, Inc., New York, 1958).

<sup>12</sup> D. R. Stull and G. C. Sinke, *Adv. Chem. Ser.* **18**, (1956).

<sup>13</sup> P. Aigrain and M. Balkanski, *Selected Constants Relative to Semiconductors* (Pergamon Press, Inc., New York, 1961).

<sup>14</sup> J. E. Eby, K. J. Teegarden, and D. B. Dutton, *Phys. Rev.* **116**, 1099 (1959).

<sup>15</sup> S. Nikitine and R. Reiss, *Phys. Chem. Solids* **16**, 237 (1960).

<sup>16</sup> R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960), p. 233.

<sup>17</sup> J. Bloem, *Philips Res. Rept.* **13**, 167 (1958).

<sup>18</sup> G. Fischer, *Helv. Phys. Acta* **36**, 317 (1963).

<sup>19</sup> J. S. Prener and J. D. Kingsley, *J. Chem. Phys.* **38**, 667 (1963).

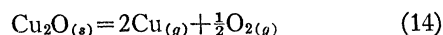
<sup>20</sup> D. C. Stockbarger, *J. Opt. Soc. Am.* **39**, 731 (1949).

TABLE II. Expected electrical behavior of various binary compounds.

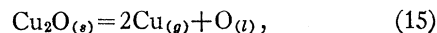
Compound $M_aN_b$	$E_g$		$R_M/R_N$	Comments
	$(1/a)(\Delta H_{M_aN_b} - a\Delta H_M)$	$(1/b)(\Delta H_{M_aN_b} - b\Delta H_N)$		
KCl	1.50	1.63		$(p/A^-)^{\max}$ calculated to be $4.7 \times 10^{-9}$ (Ref. 1).
ZnTe	0.66	0.88	0.99	$(n/D^+)^{\max}$ calculated to be $3 \times 10^{-3}$ if only singly ionized vacancies present (Ref. 1). Due to low value of $R_M/R_N$ , $n$ -type conductivity completely compensated by singly and doubly ionized vacancies (Ref. 3). Only partial compensation of $p$ -type conductivity occurs.
CdTe	0.48	0.69	1.12	$(n/D^+)^{\max}$ calculated to be $3 \times 10^{-2}$ (Ref. 1). $(p/A^-)^{\max}$ calculated to be $1 \times 10^{-3}$ (Ref. 1). Doubly ionized vacancies are not important due to favorable value of $R_M/R_N$ (Sec. III).
GaAs	0.32	0.33		$(n/D^+)^{\max}$ calculated to be 0.998 (Ref. 1).
CuBr	1.26	0.65		It is predicted that $n$ -type conductivity is almost completely compensated while $p$ -type conductivity is only partially compensated.
CuI	1.59	0.73		
AgI( $\alpha$ )	1.41	0.71		
Cu <sub>2</sub> O	1.00	(0.53) <sup>a</sup>		
ZnO	0.51	0.64	1.98	Complete compensation of $p$ -type conductivity by a combination of singly and doubly ionized $N$ vacancies is predicted, based on the high values of $R_M/R_N$ . Substantial but not complete compensation of $n$ -type conductivity by singly ionized $M$ vacancies is predicted.
ZnS(cub.)	0.77	1.01	1.26	
ZnSe(cub.)	0.70	0.90	1.15	
CdS	0.60	0.89	1.42	
CdSe	0.55	0.76	1.30	
GaN	0.55	0.85	1.80	Same as for five II-VI compounds immediately above although identical $R_M/R_N$ correlation may not apply.
AlN	0.66	0.82	1.80	
GaS	0.57	0.54	1.21	Same as immediately above.
GaSe	0.54	0.46	1.10	
				Predicted to be similar to CdTe. Favorable value of $R_M/R_N$ suggests that doubly ionized vacancies are unimportant. All predictions relating to GaS and GaSe are thrown into doubt, however, by the crystal structure of these compounds (see Sec. II).
Ga <sub>2</sub> Se <sub>3</sub> ( $\gamma$ )	(0.51) <sup>a</sup>	0.55	1.10	
				Compensation is predicted to be by Se interstitials on $n$ -type side and Se vacancies on $p$ -type side. Should be similar to CdTe (and GaSe, above). Prediction is thrown into some doubt by defect nature of crystal structure.
CdF <sub>2</sub>	(1.36)*	1.43		
CaF <sub>2</sub>	(1.40)*	1.39		Compensation is predicted to be by F interstitials on $n$ -type side and F vacancies on $p$ -type side and should be essentially complete in both cases. It is known, however, that considerable $n$ -type conductivity can be obtained in CdF <sub>2</sub> , Ref. 19.

\* Calculated on the basis of interstitials rather than vacancies, as indicated in text.

sider a condensed phase in equilibrium with certain compounds at the temperature of preparation because of the very high vapor pressures involved, e.g.,  $O_{(l)}$  in equilibrium with  $Cu_2O_{(s)}$ . In such a case, it is probably more correct to write



instead of



as in Eq. (8). However, inasmuch as the boiling point of  $O_{(l)}$  is low, the difference in enthalpy between Eqs. (14) and (15) is negligibly small, i.e., the heat of vaporization of a very volatile species such as  $O_2$  is small. We neglect such effects and use Eq. (15), i.e., the system outlined in Sec. II, as written.

The results of the calculations are presented in Table II. The compound  $M_aN_b$  under consideration is listed in the first column. The correlation factor relating to

the degree of compensation of  $n$ -type conductivity by  $M$  vacancies is listed in the second column while that relating to compensation of  $p$ -type conductivity by  $N$  vacancies is listed in the third column. The factor relating to compensation of  $n$ -type conductivity by  $N$  interstitials is also listed in the second column *in parentheses*. This is appropriate when  $b > a$  (see Sec. II). The factor relating to compensation of  $p$ -type conductivity by  $M$  interstitials is listed in the third column *in parentheses* and is appropriate when  $b < a$ . The ratio of the tetrahedral covalent radii,  $R_M/R_N$ , is listed in the fourth column and is significant for intermediate cases when compensation is by vacancies (see Sec. III). Comments and predictions are listed in the fifth column, including calculated values of the maximum number of carriers ( $n$  or  $p$ ) relative to the number of ionized donors or acceptors ( $D^+$  or  $A^-$ ) when available.<sup>1</sup>

We see that the predicted behavior of most of the compounds listed in Table II is in substantial agreement with their known properties, with the single exception of  $\text{CdF}_2$  (and  $\text{GaS}$ ,  $\text{GaSe}$ , and  $\text{Ga}_2\text{Se}_3$ , which

have not been extensively investigated). The known  $n$ -type conductivity of  $\text{CdF}_2$  is in marked disagreement with the prediction (although compensation by F interstitials is correct).<sup>19</sup> The only explanation we can offer is that the acceptor level associated with an interstitial F atom must be very deep (far from the valence band). This is plausible, since the interstitial site is surrounded by negatively charged  $\text{F}^-$  ions in the fluorite structure and is small relative to the size of a  $\text{F}^-$  ion. If this explanation is correct, it may have interesting implications with respect to  $\text{CaF}_2$ .

It is clear from the results in Table II and the above discussion that further experimental study is required to determine the limits of validity of the classification scheme we have used. In particular,  $\text{GaS}$  and  $\text{GaSe}$  possess an almost pathological crystal structure from our point of view and the effects of this require investigation. The discrepancy in  $\text{CdF}_2$  suggests that  $\text{CaF}_2$  and  $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2$  should be investigated as semiconductors (using the techniques of Prener<sup>19</sup>). The defect nature of  $\text{Ga}_2\text{Se}_3$  may result in peculiar effects in that compound.