

## Dielectric Theory of Impurity Binding Energies. II. Donor and Isoelectronic Impurities in GaP

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The dielectric theory of chemical shifts based on valence-bond mismatch in the central cell applied in paper I to donor impurities in Si and Ge is here extended to donor and isoelectronic impurities in GaP. With one adjustable parameter, chemical shifts relative to Te of S and Se donor impurities in GaP are satisfactorily explained, as is the shift in binding energy of isoelectronic N impurities on replacing the GaP host lattice by GaAs. The good internal consistency found in the model provides strong support for the concept of valence-bond mismatch.

### 1. INTRODUCTION

IN a previous paper,<sup>1</sup> a dielectric theory of central-cell corrections to the binding energies of group-V donor impurities in Si and Ge was developed. Our theory stressed the role of dynamical rearrangement energies of valence electrons associated with accumulation of donor charge in the central cell. We now extend the preceding analysis to discuss central cell energies of group-VI donors substituting for P in GaP.<sup>2</sup> We also discuss by the same method the binding energies of isoelectronic N impurities in GaP and GaAs:GaP alloys.<sup>3</sup>

When the host crystal is homopolar (e.g., Si or Ge), one finds<sup>1</sup> that central-cell corrections are associated chiefly with the change in valence energy caused by mismatch between the bonds of the impurity and those of the host lattice. This mechanism is still present when the host is heteropolar GaP, but now a new mechanism becomes more important. This is the residual ionic charge on each atom in the unit cell, denoted by  $e^*$ .

We may estimate that  $e^*$  is of the same magnitude as the dynamical effective charge which is defined in terms of the dynamical dipole moment

$$\mathbf{p}_T = e_T^* \mathbf{u}, \quad (1.1)$$

where  $\mathbf{u}$  is the relative displacement of two atoms in the unit cell for a  $q \approx 0$  TO phonon. It has been suggested<sup>4</sup> that in terms of the effective charge  $e_c^*$  defined by Callen<sup>5</sup> one has

$$e_c^* = e_T^* / \epsilon_0 = \Delta Z / 2\epsilon_0, \quad (1.2)$$

where  $\Delta Z$  is the valence difference between two atoms in the unit cell. The experimental values<sup>6</sup> of  $e_T^*$  cluster around  $e_T^* = 2.0$  for  $\Delta Z = 2$  and 4, so that the valence dependence of (1.2) is not borne out. For either value

of  $\Delta Z$ , however, the constancy of  $e_T^*$  (rather than  $e_c^*$ ) is quite good.

According to the bond-charge model<sup>4</sup> the atom of larger valence carries a net positive charge. Thus when a group-VI impurity replaces P in GaP, the Coulombic impurity potential has the form

$$V_P(r) = -e/\epsilon_0 r \quad (1.3)$$

for  $r$  large compared to the radius  $R$  of the unit cell, and

$$V_P(r) = -e(e + e_T^*)/r \quad (1.4)$$

for  $r$  less than or of the order of an atomic radius  $R_a$ . (There is no appreciable dielectric screening<sup>7</sup> for  $r \lesssim R_a$ .)

Because  $e_T^* \neq 0$ , in heteropolar crystals there is a central-cell correction associated with  $e_T^*$  in (1.4). We estimate the magnitude of this correction in Sec. 2, and discuss in Sec. 3 N isoelectronic impurities in GaAs<sub>1-x</sub>P<sub>x</sub> alloys ( $x \lesssim 0.1$ ). In both cases the discussion is focused not on absolute binding energies, but rather on chemical shifts, because the strain field associated with the impurity and arising from its valence-bond mismatch is unknown. However, general arguments suffice to elucidate the relative importance of the different mechanisms contributing to the central-cell binding energy, and it is the competition between these mechanisms which has attracted our interest.

### 2. DONOR IMPURITIES IN GaP

The conduction-band structure in GaP is quite similar to that of Si. The conduction-band edge in Si lies near  $\mathbf{k} = X_1$ ; in GaP, it is at  $X$ . Reasonable values of the transverse and longitudinal effective masses which are consistent with band calculations<sup>8</sup> and the Faraday rotation<sup>9</sup> mass  $m_F^* = 0.35m$  are

$$m_{\perp}/m = 0.22, \quad m_{\parallel}/m = 1.2. \quad (2.1)$$

<sup>1</sup> J. C. Phillips, preceding paper, Phys. Rev. B 1, 1540 (1970).

<sup>2</sup> P. J. Dean *et al.*, Phys. Rev. Letters 18, 122 (1967).

<sup>3</sup> P. J. Dean and R. A. Faulkner, Appl. Phys. Letters 14, 210 (1969).

<sup>4</sup> J. C. Phillips, Phys. Rev. 168, 905 (1968).

<sup>5</sup> H. B. Callen, Phys. Rev. 76, 1394 (1949).

<sup>6</sup> E. Burstein, M. H. Brodsky, and G. Lucovsky, J. Quantum Chem. 15, 759 (1967).

<sup>7</sup> Srinivasan, Phys. Rev. 178, 1244 (1969).

<sup>8</sup> F. H. Pollak, C. W. Higginbotham, and M. Cardona, J. Phys. Soc. Japan 21S, 20 (1966).

<sup>9</sup> T. S. Moss, A. K. Walton, and B. Ellis, in *Proceedings of the International Conference on Semiconductors*, Exeter, 1962 (The Institute of Physics and The Physical Society, London, 1962), p. 295.

The low-frequency electronic dielectric constant<sup>10</sup> is  $\epsilon_0 = 9.1$ , the static dielectric constant<sup>10</sup> (including lattice polarizability) is  $\epsilon_s = 11.1$ . Because the donor binding energies are comparable to the Debye energy of the crystal, we use  $\bar{\epsilon} = \frac{1}{2}(\epsilon_0 + \epsilon_s)$  in estimating effective-mass binding energies and Bohr radii. This gives<sup>11</sup>

$$E_H = 45 \text{ meV}, \quad (2.2)$$

while the probability  $P_H$  that a hydrogenic donor electron will be found in the central cell  $\mathbf{R} = 0$  is given in terms of the envelope function  $\Psi(\mathbf{R})$  by

$$P_H = \frac{3}{4}a^3 |\Psi(0)|^2 = 0.012. \quad (2.3)$$

In (2.3),  $\frac{3}{4}a^3$  is the volume of the unit cell, the factor 3 represents the number of band edges ( $X$  points) in GaP, and  $|\Psi(0)|^2$  is calculated from variational effective-mass wave functions<sup>11</sup> using  $m_{11}$ ,  $m_{\perp}$ , and  $\bar{\epsilon}$ .

The binding energy associated with the effective impurity potential (1.4) in the impurity atomic cell is approximately

$$E_c = \gamma \frac{(e + e_c^*)^2}{R_a} P_H, \quad (2.4)$$

where  $\gamma$  is a number of order unity. Strictly speaking, we should calculate the central-cell probability  $P_c$  not in the hydrogenic approximation, but using a more accurate form for  $\Psi(\mathbf{R})$  which allows for the presence of (1.4), i.e., allows for dielectric breakdown and electronegativity differences. We shall see, however, that in this case the effects of the latter are small. Moreover, it appears from *I* that  $P_H$  actually gives a reasonably good estimate of  $P_c$ , possibly because most of the effects of dielectric breakdown are cancelled by the effects of lattice strain. Because the latter are difficult to calculate, we absorb all uncertainties in  $\gamma$ .

From (2.4) we obtain the heteropolar contribution  $\delta E_T$  to the central-cell binding energy. It is

$$\begin{aligned} \delta E_T &= (2ee_T^*/\epsilon_0 R_a) \gamma P_H \\ &= 13 \gamma \text{ meV}. \end{aligned} \quad (2.5)$$

Faulkner has suggested<sup>10</sup> a somewhat different interpretation of the observed luminescence spectra of excitons bound to group-VI donors in GaP from the one that was originally proposed.<sup>2</sup> With his interpretation, the donor binding energies are shifted from the original values<sup>2</sup> of 107, 105 and 93 meV for S, Se and Te, respectively, to 101, 99, and 87 meV. The difference between the two interpretations is small for our purposes, but we shall use the latter values for specific purposes of discussion.

If we compare these values with those observed for group-V impurities in Si (see *I*), we are struck by two

qualitative points:

(a) The average central-cell correction is about 20 meV in Si. Using (2.2), we see that the average correction in GaP is about 55 meV. The values of  $P_H$  in Si and GaP differ by only 20% (0.010 and 0.012, respectively) so that  $\Delta E_c$  is more than twice as large in GaP as in Si, even allowing for differences in effective masses and  $\bar{\epsilon}$ .

(b) While large chemical shifts were found for P, As, and Sb in Si ( $\Delta E_c \sim 14, 22$ , and 11 meV, respectively), the chemical shifts for S, Se, and Te are smaller, especially on the scale of the average central-cell correction. Moreover, for group-VI donors in GaP, the shifts are monotonic.

We shall deal first with the chemical trends. Consider the term associated with covalent-bond rearrangement energies and denoted by  $\Delta E_b$  in Eq. (2.3) of *I*:

$$\Delta E_b = 2a_{\text{GaP}} |E_g(\text{GaP}) - E_g(\text{ZnY})| P_H(\text{GaP}), \quad (2.6)$$

where  $Y = \text{S, Se, or Te}$ . The values<sup>12</sup> of  $E_g$  needed in (2.6) are: GaP: 5.72; ZnS: 7.78; ZnSe: 7.07, ZnTe: 5.77 (all in eV).

From these numbers we see that (2.6) accounts semiquantitatively for the dependence of  $\Delta E_c$  on  $Y = \text{S, Se, or Te}$ . However, with  $a_{\text{GaP}} \sim a_{\text{Si}} \sim 0.8$ , the predicted variation is 36 meV, while the observed variation is only 14 meV. This suggests that  $a_{\text{GaP}} = 0.3$  is a good choice.

We saw in *I* that the ratio  $a_{\text{Ge}}/a_{\text{Si}} \approx 5$  is expected from the relative sensitivities of  $L_1 - \Gamma_{25'}$  and  $X_1 - \Gamma_{25'}$  to chemical changes in Ge-Si alloys and to hydrostatic pressure. These ratios (as well as that of  $\Gamma_{2'} - \Gamma_{25'}$ ) are reproduced rather well in homopolar grey Sn by derivatives of the corresponding gaps with respect to the pseudopotential parameter  $V_{220}^S = V_8^S$  according to Cohen and Bergstresser.<sup>13</sup> On the other hand, in heteropolar InSb,  $\partial(X_1 - \Gamma_{25'})/\partial V_8^S$  is only half as large as in homopolar Sn, and of opposite sign. Thus the small value of  $a_{\text{GaP}}$  is not unreasonable.

We are now left with the bulk of the central-cell correction (denoted by  $\Delta E_1$ ) to explain. Because  $\Delta E_b(\text{Te}) = 0$ , this is just the central-cell correction for Te impurities, of order 50 meV, and it is constant, independent of  $Y$ . This contribution was absent for Si or Ge hosts. We suggest that  $\Delta E_1 = \Delta E_T$ , and that  $\gamma$  in (2.5) should be about 4.

### 3. ISOELECTRONIC N IMPURITIES IN $\text{GaAs}_y\text{P}_{1-y}$

The localization energy of excitons at N impurities in GaP is 0.011 eV, but studies of  $\text{GaAs}_y\text{P}_{1-y}$  ( $y \lesssim 0.2$ ) indicate that the same energy in GaAs would be relatively large,  $\sim 0.080$  eV, were the minimum in the conduction band to be at  $X$  in GaAs as it is in GaP.

<sup>10</sup> R. A. Faulkner (private communication); A. S. Barker, Jr., Phys. Rev. **165**, 917 (1968).

<sup>11</sup> R. A. Faulkner, Phys. Rev. **184**, 713 (1969).

<sup>12</sup> J. A. Van Vechten, Phys. Rev. **182**, 891 (1969).

<sup>13</sup> M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, A789 (1966).

(Actually, it is at  $\Gamma$ , where  $m_e^*$  is so much smaller that one would not expect to find isoelectronic bound states.) Here we wish to discuss the implications of this chemical shift for the mechanisms responsible for forming isoelectronic bound states.

At first one might attempt to explain this shift in terms of changes in the position of  $X_1$  in the host band structure. (The band structure of the alloy  $\text{GaAs}_y\text{P}_{1-y}$  can be treated in the "virtual-crystal" approximation because energy levels shift almost linearly<sup>14</sup> as a function of  $y$ .) However, one must be careful to measure  $X_1$  not relative to  $\Gamma_{15}^v$  (the top of the valence band) which also changes with  $y$ , but relative to vacuum. The dielectric theory of ionization potentials (I.P.) (I.P. = vacuum -  $\Gamma_{15}^v$ ) estimates<sup>15</sup> that I.P. changes by  $0.41 \pm 0.06$  eV on going from  $y=0$  to 1, and the measured<sup>14</sup> shift in  $X_1$  is 0.40 eV. Thus within the limits of experimental accuracy the position of  $X_1$  does not change relative to vacuum as a function of  $y$ . As we shall see below, a change of order 0.4 eV would be required to explain the change in  $\Delta E_c$  if no other mechanism were operative.

It is our thesis, however, that corrections to valence-bond energies make a dynamical contribution to the energy of conduction electrons localized near the isoelectronic N impurities. This contribution scales with  $|E_g(\text{host}) - E_g(\text{GaN})|$ , where in this case the host is either GaP or GaAs.

In the case of charged impurities the long-range hydrogenic potential automatically provides a calibration for this self-energy through the factor  $P_H$  in Eq. (2.6). For isoelectronic impurities different calibration procedures must be developed. In order to make the situation as simple as possible, we neglect the effects of lattice strain and represent the impurity potential  $V_I$  by a single attractive spherical well of volume equal to an atomic volume centered at the impurity site. (A more sophisticated model<sup>16</sup> would utilize a stronger attractive well of the same volume together with a weaker repulsive well of about five times greater volume to include the effects of lattice strain. The parameters of the more realistic model might be related to the strengths of phonon side bands seen in recombination of excitons bound to the isoelectronic impurity. Development of the latter model is a task which lies outside the scope of this paper.)

Solution of the crystalline wave equation with realistic host energy bands (unperturbed Hamiltonian  $H_0$ ) is a formidable task.<sup>17,18</sup> Even in the effective-mass approximation (which is not valid for short-range potentials) the results are quite sensitive to the form assumed for the impurity potential. In a three-valley model (appropriate to GaP) one must consider both

intravalley and intervalley matrix elements of  $V_I$ , denoted by  $V_I^{\alpha\alpha}$  and  $V_I^{\alpha\alpha'}$ . If the impurity potential is very short range,  $V_I^{\alpha\alpha} = V_I^{\alpha\alpha'}$ . If the impurity potential is always attractive and of longer range,  $V_I^{\alpha\alpha'} < V_I^{\alpha\alpha}$ . However, in our case the potential is probably oscillatory<sup>16</sup> with a wavelength of order the radius of the unit cell. In that case  $V_I^{\alpha\alpha'}$  may easily be larger than  $V_I^{\alpha\alpha}$  and one can easily show that this would imply only one bound state from the three band edges.

In view of these complications, and the paucity of information concerning the local strain associated with the oscillatory part of the potential, we have adopted a simple model to fit the energy level of the N impurity in the GaP host. The model enables us to see whether the binding energy of isoelectronic N in GaAs (relative to the  $X_1$  edge) may reasonably be eight times larger than it is in GaP.

In our model we treat the conduction electron as a free electron of mass  $m$ , with an "effective" impurity potential (including valence-bond deformation energies) described by a well of depth  $V_0$  and radius  $R_a$  determining<sup>19</sup> the bound energy levels through the combination  $V_0 R_a^2$ . Let

$$T_0 = \hbar^2 / 2mR_a^2, \quad (3.1)$$

which is 1.3 eV in GaP. When  $V_0$  reaches the critical value  $V_{00}$  defined by

$$V_{00} = -(\frac{1}{2}\pi)^2 T_0 = -3.2 \text{ eV} \quad (3.2)$$

the first  $s$ -wave bound state appears. Let  $V_0 = V_{00} - \delta V_0$ . Then the bound-state energy is

$$E = -(1/4T_0)(\delta V_0)^2. \quad (3.3)$$

In GaP, electrons are bound to N impurities by about 0.008 eV. According to (3.2) this implies that  $\delta V_0 = 0.2$  eV. Similarly, in hypothetical GaAs ( $X_1$  lowest conduction-band edge) the electron binding energy may be of order 0.06 eV, giving  $\delta V_0 = 0.6$  eV.

The values of  $E_g$  in GaN, GaP, and GaAs are estimated<sup>12</sup> to be 11.5, 5.7, and 5.2 eV, respectively. In analogy with (2.6) we suggest that the effective well depth  $V_0$  is related to gap differences. Thus for N in GaP we estimate

$$\begin{aligned} V_0(\text{N: GaP}) &= -2a_{\text{GaP}} |E_g(\text{GaP}) - E_g(\text{GaN})| \\ &= -(0.6)(5.8) \text{ eV} = -3.5 \text{ eV}, \end{aligned} \quad (3.4)$$

where we have used  $a_{\text{GaP}} = 0.3$  as deduced in Sec. II from analysis of the chemical shifts of group-VI donor impurities in GaP. According to (3.2) and (3.3), the value of  $V_0$  in the single-well model is

$$V_0(\text{N: GaP}) = V_{00} - \delta V_0 = -3.4 \text{ eV}. \quad (3.5)$$

The very good agreement between the two differently derived estimates (3.4) and (3.5) must be con-

<sup>14</sup> A. G. Thompson and J. C. Wooley, Can. J. Phys. **45**, 255 (1967).

<sup>15</sup> J. A. Van Vechten, Phys. Rev. **187**, 1007 (1969).

<sup>16</sup> J. C. Phillips, Phys. Rev., Letters **22**, 285 (1969).

<sup>17</sup> J. Callaway and A. J. Hughes, Phys. Rev. **156**, 860 (1967).

<sup>18</sup> R. A. Faulkner, Phys. Rev. **175**, 991 (1968).

<sup>19</sup> L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1949).

sidered quite fortuitous. That this good agreement is not entirely fortuitous can be seen by using (2.6) to estimate  $V_0$  for N in GaAs:

$$V_0(\text{N:GaAs}) = V_0(\text{N:GaP}) - (0.6)(0.5) \text{ eV} \\ = -(3.5 \pm 0.3) \text{ eV}, \quad (3.6)$$

i.e.,  $V_0$  shifts by 0.3 eV on going from the GaP host to GaAs host, whereas to fit the observed binding energies a shift of 0.4 eV is needed. Considering that the only disposable parameter in (3.4) and (3.6) was obtained from analysis of chemical shifts of hydrogenic-donor binding energies, we regard this success as strong evidence for the internal consistency of (2.6), (3.4), and (3.6). If one wishes, one may call this approach the dielectric valence-bond method of treating chemical shifts of impurity states in semiconductors.

The differences in band structure between GaP and Si are rather small for the purposes of treating short-

range potentials. Therefore it is of some interest to see what the present model has to say about C substitutional impurities in Si. One has  $E_g(\text{SiC}) - E_g(\text{Si}) = 4.5$  eV, compared to  $E_g(\text{GaN}) - E_g(\text{GaP}) = 5.8$  eV. Thus the gap shift is smaller. However, as we saw in Sec. 2,  $a_{\text{Si}} \sim 0.8$ ,  $a_{\text{GaP}} \sim 0.3$ , so that according to (3.3),

$$V_0(\text{C:Si}) = -(1.6)(4.5) \text{ eV} = -7.2 \text{ eV}, \quad (3.7)$$

which is approximately twice the effective depth of N impurities in GaP. In this case the threshold formulas (3.2) and (3.3) no longer apply, but one can say that bound states for C impurities in Si should be deep, with binding energies of order 0.55 eV (half the indirect gap energy).

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### Experimental Determination of the Low-Temperature Grüneisen Parameter of Silicon from Pressure Derivatives of Elastic Constants\*

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Pressure derivatives of the elastic constants of Si are obtained in fluid and gaseous He at 4 and 77°K on samples in the resistivity range 150–500 Ω cm. The doping level was found to have no effect on these derivatives, and the 4°K values were essentially indistinguishable from those at 77°K. Thus the disparity between the low-temperature limit of the Grüneisen parameter determined from thermal-expansion measurements from 2 to 15°K by Sparks and Swenson and from the 77°K elastic-constant work of McSkimin and Andreatch is not resolved.

#### I. INTRODUCTION

THE low-temperature limit of the Grüneisen parameter  $\gamma_0$  can be obtained experimentally in two ways. The first method uses directly measured thermodynamic data and the relation  $\gamma = \beta B_T V / C_V$ , where  $\beta$  is the thermal-expansion coefficient,  $B_T$  is the isothermal bulk modulus, and  $C_V / V$  is the heat capacity at constant volume per unit volume. The second method, discussed by Daniels,<sup>1</sup> involves a combination of the volume (or pressure) derivatives of the elastic constants. Recent determinations<sup>2,3</sup> of  $\gamma_0$  by the two techniques have resulted in values differing by more than a factor of 2 in the case of Si in spite of the fact that the estimated uncertainties in each of the methods is of the order of 10%.

This discrepancy might be attributed to the use of 77°K rather than 0°K pressure derivatives in the calculation. However, McSkimin and Andreatch<sup>2</sup> saw essentially no difference between the room-temperature and 77°K values for these derivatives. An examination of the form of the relation between  $\gamma_0$  and the pressure derivatives of the elastic constants shows that the major contribution stems from  $dC_{44}/dP$ . Mason and Bateman<sup>4</sup> have shown that the temperature dependence of  $C_{44}$  below 80°K is strongly dependent on doping. While the samples used in the two sets of experiments in question were of relatively high purity, the resistivities of the specimens used by Sparks and Swenson<sup>3</sup> in their thermal-expansion measurements differed from those used by McSkimin and Andreatch<sup>2</sup> in their elastic-constants studies by a factor of 3.

The purpose of this study, then, was to determine whether the pressure dependence of the elastic constants

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<sup>1</sup> W. B. Daniels, Phys. Rev. Letters **8**, 3 (1962).

<sup>2</sup> H. J. McSkimin and P. Andreatch, Jr., J. Appl. Phys. **35**, 2161 (1964).

<sup>3</sup> P. W. Sparks and C. A. Swenson, Phys. Rev. **163**, 779 (1967).

<sup>4</sup> W. P. Mason and T. B. Bateman, Phys. Rev. Letters **10**, 151 (1963).