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Dielectric Theory of Impurity Binding Energies. I. Group-V Donors in Si and Ge

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A dielectric theory of chemical shifts of ground-state donor energies of group-V impurities in Si and Ge is developed. With three disposable parameters, good agreement with experiment is obtained for P, As, and Sb impurities in Si and Ge and Bi in Ge. Predictions are made for N in Si and Ge.

1. INTRODUCTION

IMPURITY states in semiconductors have been the subject of intensive investigation for several decades. It was recognized at an early stage[1] that when the binding energy, labeled E_I, is small compared to the minimum energy gap ΔE_{cv} between the conduction and valence band edges, one may treat the particle in a bound state as a wave packet, moving with a kinetic energy described by an effective-mass tensor. Denote an appropriate average of the principal values of this tensor by m^* and let ϵ_0 represent the low-frequency limit of the electronic dielectric constant of the crystal. Then in the wave-packet or effective-mass approximation (EMA), the binding energy E_0 is given by dimensional analysis as

$$E_0 = (m^*/m\epsilon_0^2)\ \text{Ry}. \tag{1.1}$$

For group-V donor impurities in Si and Ge, Eq. (1.1) gives $E_0 \sim 0.03$ and 0.01 eV, respectively.

Experimentally, one finds that all p energy levels with principal quantum number $n \geq 2$ are independent of the particular impurity to which the electron is bound.[2] This means that the details of the interaction of the donor electron with a given impurity are unimportant, and one is justified in replacing the impurity potential with the potential of a point charge, screened by the dielectric polarization of the crystal. One is also justified in treating the kinematics of the electron motion by wave-packet techniques based on the energy bands $E_n(\mathbf{k})$ of the pure crystal.

The situation is quite different for the s states, and for the 1s state in particular. Because the impurity wave function $\Psi(\mathbf{R})$ is nonzero at $\mathbf{R}=0$ the 1s energy levels are found to vary with the potential of the given impurity. In the case of many-valley semiconductors the impurity potential lifts the degeneracy and the splittings can be treated by group theory.[2] It is clear, however, that specific calculations will be required to account for the variations in the central cell interaction from one impurity to another.

Although the impurity potentials are quite complicated, one might hope to be able to estimate the approximate magnitude of the corrections from macroscopic arguments. If we denote the locations of the symmetrically equivalent band edges in $\mathbf{k}$ space by $\mathbf{k}_\alpha$, then corrections to the hydrogenic model will arise from terms in $E_n(k-k_\alpha)$ which are fourth order in $(\mathbf{k}-\mathbf{k}_\alpha)$. Similarly, the EMA makes the approximation of neglecting variations in the impurity potential within one atomic cell of radius $\mathbf{a}$, compared to the Bohr radius a_0 of the orbit in question. These terms can be shown[2] to be of order q^{-1}, where the macroscopic quality factor q is given by

$$q = (\Delta E_{cv}/E_I)(a_0/a) \gg 1. \tag{1.2}$$

Kohn argued[2] that these terms would be small in semiconductors.

The fact that corrections to the EMA were not an important factor in determining central-cell interactions was brought out further by consideration of parallel terms in the exciton and substitutional rare-gas impurity levels of rare-gas solids. In that case it turned out that the central cell interaction could have either sign, although the corrections to the EMA always act to lower the 1s energy. Hermanson and Phillips[3] have noted that the macroscopic corrections associated with q give a poor account of the difference between the EMA ground-state energy E_0 and the observed energy E_I. It is convenient to define a relative hydrogenic defect d as

$$d = (E_I - E_0)/E_0. \tag{1.3}$$

One would expect that large values of the macroscopic quality factor q would correspond to small values of the hydrogenic defect d, and vice versa. If one compares[3] values of q and d in semiconductors with those in rare-gas solids, one finds that although q in the former exceeds q in the latter by factors of order 100, d in the former *exceeds* d in the latter by factors of order 3.

From this discussion we see that to understand the nature of impurity binding energies it is necessary to go beyond macroscopic arguments and come to grips with the nature of the impurity potential, especially in the central cell occupied by the impurity itself. A dramatic example of the importance of the central-cell potential is afforded by isoelectronic impurities, where the macroscopic Coulombic potential is zero, yet electrons or holes can be bound by the short-range force associated with the central-cell impurity potential.[4]

There have been two apparently successful attempts

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[1] G. Wannier, Phys. Rev. 52, 191 (1937).

[2] W. Kohn and J. M. Luttinger, Phys. Rev. 98, 915 (1955); W. Kohn, Solid State Phys. 5, 257 (1957), see especially Eq. (5.44), pp. 281 and 290.

[3] See Table I in J. Hermanson and J. C. Phillips, Phys. Rev. 150, 652 (1966).

[4] D. G. Thomas and J. J. Hopfield, Phys. Rev. 150, 680 (1966).

to treat central-cell interactions quantitatively. For the rare-gas solids Hermanson and Phillips, using no adjustable parameters, succeeded in fitting energy levels and oscillator strengths quantitatively for Xe impurities in Ne, Ar and Kr, and excitons in Kr and Xe. The sign of the central-cell correction to the ground-state energy is reversed in Xe compared to Kr, and this too was explained with the aid of no adjustable parameters.

A different approach to the problem of ground-state donor binding energies in semiconductors was taken by Kohn and Luttinger.[2] They considered only one case in detail, P in Si. No attempt was made to calculate E_I. Instead this value was taken from experiment, and the hydrogenic wave equation was integrated inwards from $r=\infty$. Because E_I is not an eigenvalue of this Sturm-Liouville equation, the solution so obtained is a linear combination of the solutions which are regular and irregular at $r=0$. This means that for $r\lesssim a_0$, the solution grows rapidly (see Fig. 11, p. 293 of Ref. 2). In order to make $\psi(0)$ finite, it is assumed that $\psi(0)\approx\psi(a)$, where a is the atomic radius. It is then pointed out that the value of $\psi(0)$ so obtained is in good agreement with the value obtained by ENDOR studies of the hyperfine interaction. For other impurities in Si such as As and Sb, it is stated that the perturbation is much more violent, presumably because the cores are not isoelectronic to Si. How the hyperfine interactions are to be related to the cutoff parameter a is not stated.

While the agreement between theory and experiment for $|\psi(0)|^2$ obtained in this way is gratifying, one should note that one experimental number is explained through the introduction of one free parameter. Moreover, the central-cell correction for Sb is smaller than for P, yet $|\psi(0)|^2$ is larger. This is explained by assuming that the cutoff radius is larger for Sb. But Kohn and Luttinger also argue that $|\psi(0)|^2$ is insensitive to the choice of cutoff, because $a\ll a_0$. At the same time, one would expect a larger cutoff to give rise to a larger, and not a smaller, central-cell defect.

These questions become even more perplexing when we turn to the case of group-V donors in Ge. There the smallest central-cell correction occurs not for As impurities (whose cores are isoelectronic to those of the Ge host), but rather for Sb, where according to Kohn and Luttinger a "violent" perturbation is expected. It is evident that the approach based on using experimental values of E_I together with an adjustable cutoff radius to explain the hyperfine coupling has left us where we began. This is not surprising, because there is one free parameter (the cutoff radius) for each experimentally measured value of $|\psi(0)|^2$. Thus one is forced to conclude that little can be learned from $|\psi(0)|^2$ about the difference E_I-E_0.

Our view here is that central-cell interactions are best analyzed by employing, insofar as possible, scaling arguments which are free of specific assumptions concerning the behavior of $\psi(r)$ for $r\lesssim a_0$. For example, associated with each impurity there is undoubtedly a strain field which extends well beyond the central cell. Therefore we will not assume that $\psi(r)$ can be obtained from a hydrogenic wave equation valid in the region $a\lesssim r$. Instead we will examine the experimental values of E_I-E_0 and attempt without prejudice to construct a satisfactory model for the chemical shifts in E_I-E_0. By satisfactory we mean a model in which the ratio of free parameters to observables is, say, less than 0.5, compared to the Kohn-Luttinger value of 1.0.

TABLE I. Central-cell corrections in meV to group-V donor impurity binding energies. The EMA values are from Ref. 6, and the remaining three columns are from this paper. One may compare $\Delta E_d=\Delta E_b+\Delta E_{pd}$ with $(\Delta E_c)_{\text{expt}}$ the experimental values. The latter are based for Ge on J. H. Reuszer and P. Fisher [Phys. Rev. **135**, A1125 (1964)] and for Si on R. L. Aggarwal [Solid State Commun. **2**, 163 (1964)]. The values actually quoted are corrected values obtained from Ref. 8. The values marked by an asterisk have been adjusted to fit experiment.

Si	Impurity	$(\Delta E_c)_{\text{expt}}$	$(\Delta E_c)_{\text{EMA}}$	ΔE_b	ΔE_{pd}	ΔE_d
$(E_0=31.27)$	N	···	···	98	16	114
	P	14.26	7	14*	0*	14*
	As	22.46	17	7	9	16
	Sb	11.46	19	0	11*	11*
	Bi	39.68	···	2	13	15
Ge	Impurity	$(\Delta E_c)_{\text{expt}}$		ΔE_b	ΔE_{pd}	ΔE_d
$(E_0=9.81)$	N	···		36	2.5	39
	P	3.09		7.0	−2.5	4.5
	As	4.38		4.4*	0.0	4.4*
	Sb	0.52		1.0	0.5	1.5
	Bi	2.98		3.0	0.7	3.7

An obvious approach to the nature of the central-cell potential is a chemical one based on electronegativity differences.[5,6] The values of E_I-E_0 are shown in Table I for group-V donors in Si and Ge. At first the chemical shifts appear random, with the possible exception of the fact that E_I-E_0 is smallest for Sb in either Si or Ge.

The purpose of this note is to suggest that the eight values of E_I-E_0 can be explained in terms of three basic mechanisms, the difference in bond strengths between impurity and host, the difference in core-core repulsive forces,[6] and the difference in p-d hybridization.[6] We believe that the electronegativity difference is important not primarily through its contribution to the central-cell potential, but through the way it affects the valence-bond energy, and the dynamical changes in this bond energy produced by the presence of the impurity electron. The latter alters bond energies and produces additional local strains near the impurity of an electrostrictive character. These dynamical strains in turn affect the energy associated with core-core repulsion. All these energies contribute to E_I-E_0.

An interesting discussion of E_I-E_0 for shallow donor levels in Si from the EMA point of view has been given by Morita and Nara.[7] Local strain effects on the static

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[5] J. A. Van Vechten, Phys. Rev. **182**, 891 (1969).

[6] J. C. Phillips, Phys. Rev. Letters **22**, 285 (1969); **22**, 645 (1969).

[7] A. Morita and H. Nara, J. Phys. Soc. Japan **21**, S234 (1966); G. Weinreich, J. Phys. Chem. Solids **8**, 216 (1959).

EMA impurity potential are estimated from deformation potentials. Agreement with experiment is only fair, as shown in Table I. The EMA calculation omits dynamical rearrangement energies of central-cell valence electrons.

The dynamical corrections to the long-range (Coulombic) part of the impurity potential arising from electron-electron interactions have been discussed by Sham,[8] who has shown that as $r\to\infty$ an additional term of order br^{-2} may be present in the Coulombic potential. The importance of this term can be estimated by studying np impurity levels with $n=2$ and 3, for which central-cell corrections are negligible. Faulkner has shown[9] that the ratio of these binding energies is given correctly (within the limits of experimental error) by the Coulomb potential, with $b=0$. The error is at most 0.05 meV, compared to central-cell corrections of order 10 meV. Sham's long-range dynamical corrections are therefore 200 times smaller than the short-range dynamical ones discussed here.

Before we discuss the details of our dielectric model, we estimate the order of magnitude of central-cell dynamical corrections for a frozen lattice. If the valence-bond energy associated with the impurity were the same as that of a host atom, there would be no local strain (apart from core effects) and no valence contribution to $\Delta E_c=E_I-E_0$. The valence bond energy is of order the average energy gap E_g, where

$$E_g^2=E_h^2+C^2 \tag{1.4}$$

and where E_h and C are the dielectrically defined[10] covalent and ionic energy gaps. Introduction of the group-V impurity alters *both* E_h and C, although only the latter measures electronegativity differences. We expect that four bond energies will contribute a term to ΔE_c of order

$$\Delta E_b\sim4|E_g(\text{host})-E_g(\text{impurity})|P_c, \tag{1.5}$$

where P_c is the EMA probability (based on the macroscopic parameters of the host crystal) that the impurity electron will find itself in the central cell of volume $\frac{1}{4}a^3$, where a is the lattice constant. In terms of the EMA envelope wave function $\Psi(r)$ one has[11]

$$P_c=\tfrac{1}{4}|\Psi(0)|^2a^3. \tag{1.6}$$

From the EMA expressions[2] for $|\Psi(0)|^2$, one finds $P_c=0.010$ and 0.0006 in Si and Ge, respectively, allowing for the multivalley nature of the conduction-band edges. As we shall see, energy-gap differences are of order 1 eV, so that (1.5) predicts values of ΔE_b of order 40 meV in Si and 2.4 meV in Ge, in rough agreement with the experimental values shown in Table I.

2. DIELECTRIC ESTIMATES OF CHEMICAL SHIFTS

In the presence of the donor impurity, but in the absence of the donor electron, there is local strain around the impurity. Qualitatively speaking this strain arises from mismatch of the valence bonds of the impurity with valence bonds of the host lattice. The addition of donor charge to the central cell displaces some valence charge from that cell. We may expect that the bond mismatch reduces the itinerant part[6] of the total valence energy, regardless of the sign of $[E_g(\text{host})-E_g(\text{impurity})]$. This loss in energy is itself reduced by the displacement of valence charge by the donor charge. Thus the presence of an energy-gap difference between host and impurity may *increase* the binding of the donor electron regardless of the sign of this difference, which accounts for the absolute value used in (1.5). We believe this valence resonance argument is also important for isoelectronic impurities.[4,6]

The magnitude of the local lattice deformation induced by bond mismatch is determined primarily by valence-electron deformation potentials, which are similar for Si and for Ge. However, because the conduction-band edges in the two crystals fall, respectively, at points along [100] and [111] symmetry directions, where the deformation potentials are very different, the amount of lattice deformation required to reduce P_c to a value consistent with the local strain is different for the two crystals. We therefore multiply (1.5) by two adjustable constants, one for Si and one for Ge, chosen so that for P in Si,

$$\Delta E_b(\text{calc, P})=\Delta E_c(\text{expt, P}) \tag{2.1}$$

and similarly for As in Ge. These cases are chosen because the cores of P and Si, as well as As and Ge, are isoelectronic, so that the core-core energies discussed in the following section make little contribution to ΔE_c.

We may define $E_g(\text{impurity})$ as follows. Let B denote the impurity, and let $E_g(AB)$ denote the average energy gap of the AB crystal, where $A=\text{Al}$ when Si is the host crystal, and $A=\text{Ga}$ when Ge is the host crystal. Then the definition is

$$E_g(B)=\tfrac{1}{2}[E_g(\text{host})+E_g(AB)]. \tag{2.2}$$

Values of $E_g(AB)$ so defined are taken from tabulated values[5] of E_h and C and are listed for group-V donors in Si and Ge in Table II. The definition (2.2) is analogous to the one used to extract atomic form factors from symmetric and antisymmetric pseudopotential form factors.[12] It also corresponds to noticing that the situation in the host-B bond is halfway between that of the host-host bond and an A-B bond.

Our expression for ΔE_b is therefore

$$(E_1-E_0)_b=\Delta E_b=2a_{\text{Si,Ge}}|E_g(\text{host})-E_g(AB)|P_c(\text{Si,Ge}) \tag{2.3}$$

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[8] L. J. Sham, Phys. Rev. **150**, 720 (1966).

[9] R. A. Faulkner, Phys. Rev. **184**, 713 (1969).

[10] J. C. Phillips, Phys. Rev. Letters **20**, 550 (1968).

[11] W. Kohn and J. M. Luttinger, Phys. Rev. **97**, 883 (1955).

[12] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

TABLE II. Average energy gaps for group-V donors in Si and Ge in eV. All of the values are obtained from the tables of Ref. 10 using the methods discussed in the text, except for Bi. There a covalent radius (Ref. 14) of Pb which is 6% greater than Sn has been used together with the methods of Ref. 10.

Si	Impurity	E_g(impurity)
($E_g=4.7$)	N	7.8
	P	5.15
	As	4.92
	Sb	4.70
	Bi	4.63
Ge	Impurity	E_g(impurity)
($E_g=4.3$)	N	7.9
	P	5.0
	As	4.75
	Sb	4.20
	Bi	4.0

with

$$a_{\mathrm{Si}}=0.78\,, \quad a_{\mathrm{Ge}}=4.0 \tag{2.4}$$

fixed by (2.1). The resulting values for ΔE_b are shown in Table I. The large difference between a_{Si} and a_{Ge} in (2.4) is attributed to the fact that L_1 is about five times more sensitive[13] to pressure and to chemical shifts than is X_1.

From the table we see that the bond theory correctly predicts that the central-cell correction is smallest in either Si or Ge for Sb impurities. Good quantitative agreement is also obtained for Sb and Bi in Ge. Poor quantitative agreement is obtained for P in Ge, and for As, Sb, and Bi in Si.

3. VALENCE HYBRIDIZATION

A striking feature of the cases where ΔE_b fails to account for ΔE_c is that it fails for P (no *d* core) in Ge (*d* core) and for As, Sb, and Bi (*d* core) in Si (no *d* core). Moreover, in the former case, $\Delta E_b > \Delta E_c$, whereas in the latter cases $\Delta E_b < \Delta E_c$. This suggests that *d* states play an especially important role in the valence rearrangement energies.

From cohesive energies of diatomic molecules it has long been known[14] that strong *p-d* hybridization enhances bond energies. The enhancement is greatest for atoms from the Si row, because of the smallness of 3*p*-3*d* promotion energies. We have recently suggested[6] that the magnitude of the enhancement for saturated molecules in crystals can be estimated from scaling arguments. These arguments assume that in the absence of *p-d* hybridization the cohesive energy of diamond-type lattices should scale like d^{-n} with $n=2$ (where d is the nearest-neighbor distance). Deviations from this behavior are attributed to *p-d* hybridization, which is assumed to be negligible in diamond itself (because the 2*p*-3*d* promotion energy is so large). The significance of $n=2$ can be understood by scaling the cohesive energies of $M\mathrm{H}_4$, where M is a group-IV element. Then one finds[15] $n=\frac{3}{2}$, which suggests that four of the eight electrons (those on M) are itinerant, corresponding to $n=2$, while the other four (those centered on the protons) are localized, corresponding to $n=1$. Other examples, such as $M\mathrm{H}_3$, where M is a group-V element, confirm the analysis. (In the case of $M\mathrm{H}_3$, one finds $n=1.0$, corresponding to the fact that the three bonds are almost at right angles, and therefore fully localized.)

The *p-d* enhancements δE_{pd} of valence-bond energies estimated in this way are (in eV/atom): diamond, 0.0 eV; Si, 0.90 eV; Ge, 0.45 eV; Sn, 0.36 eV. To estimate the effect of group-V impurities, assume that *p-d* valence enhancement is similar for SiP as for Si_2, for SiAs as for SiGe, etc.

When the impurity charge e_c appears in the central cell, it displaces valence charge of roughly the same amount to other cells.[16] For P in Si, this leads to little change in valence energy. For As in Si, however, there is an energy gain of

$$\Delta E_{pd}(\mathrm{As:Si}) = b a_{\mathrm{Si}} P_c(\mathrm{Si})[\delta E_{pd}(\mathrm{Si}) - \delta E_{pd}(\mathrm{Ge})]\,, \tag{3.1}$$

where b is a number of order unity. Fixing b by the value of $\Delta E_c = \Delta E_d$, i.e.,

$$\Delta E_d - \Delta E_b = \Delta E_{pd} \tag{3.2}$$

for Sb in Si, we obtain 2.5. One can then calculate $\Delta E_{pd}(\mathrm{Sb:Si})$ by replacing Ge in (3.1) by Sn. Then (3.2) gives ΔE_c for Sb in Si shown as ΔE_d in the last column of Table I. A reasonable guess for δE_{pd} in Pb is 0.30 eV; this gives the value of ΔE_d for Bi also shown in the last column of Table I.

We see that our model gives good results for As, but poor results for Bi. This is explained by *d*-core repulsive energies, which are[11] especially large for Bi.

For Si we have fitted three values of ΔE_c with two parameters, not an impressive result. For Ge, however, we now have only one free parameter (a_{Ge}) which is fixed by $\Delta E_c(\mathrm{As:Ge})$. Our remaining three values of ΔE_d for P, Sb, and Bi in Ge are given by, e.g.,

$$\Delta E_d(\mathrm{P:Ge}) = \Delta E_b + b a_{\mathrm{Ge}} P_c(\mathrm{Ge}) \times [\delta E_{pd}(\mathrm{Ge}) - \delta E_{pd}(\mathrm{Si})] \tag{3.3}$$

in analogy with (3.1) and (3.2). As seen from Table I, the reversal of sign of $\Delta E_{pd}(\mathrm{P:Ge})$ compared to $\Delta E_{pd}(\mathrm{As:Si})$ materially improves agreement with experiment.

4. CONCLUSIONS AND DISCUSSION

We have used three parameters to construct a model which produces values of ΔE_d which agree with experimental values of ΔE_c to within 2 meV for seven of the eight cases of group-V impurities in Si and Ge for which

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[13] J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18.

[14] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, N. Y., 1960), p. 142 ff.

[15] J. C. Phillips, *Covalent Bonding in Crystals and Molecules* (University of Chicago Press, Chicago, 1970).

[16] G. Srinivasan, Phys. Rev. **178**, 1244 (1969).

data are available. The case which fails (Bi in Si) is not surprising, as Bi also behaves oddly[11] as an isoelectronic impurity in GaP.

A theory which contains three parameters and roughly fits only seven observables is scarcely unique. However, Eqs. (3.1)–(3.3) predict rather large central-cell corrections for N impurities in Si or Ge. As can be seen from Table I, these corrections arise primarily from ΔE_b, although ΔE_{pd} is also significant for N in Si.

We believe that although the present theory is not unique, it does give a useful qualitative picture of the hitherto mysterious variations of ΔE_c shown in Table I. Our theory explains why ΔE_c is smallest in Si or Ge for Sb impurities, and it shows that the role of d states is important in accounting for differences between second-row host or impurity compared to third–fifth-row host or impurities. Differences between first-row host or impurity and other-row host or impurities are found to be dependent chiefly on the large difference in size between first-row atoms and atoms from other rows.

Because the dielectric-bond method of representing dynamical central-cell energies is so different from a conventional one-electron wave-packet (EMA) treatment, it may be useful to indicate here some of the salient differences.

In discussing chemical trends involving either a series of impurities in one host or an impurity in a series of host crystals, one must carefully distinguish the microscopic characteristics of the impurities from the macroscopic ones of the host. The latter include principally the EMA binding energy E_0 of the 1s ground state, and the EMA probability P_c that the additional particle will be found in the central cell. If one wishes to develop a modified wave-packet or EMA theory of central-cell corrections containing as input E_0 and P_c, then it is clearly necessary, in order to account for variations from one impurity to another, to add[2] some microscopic information, e.g., the observed binding energy $E_I(\alpha)$ for each impurity α. But if one wishes to *understand* the trends in $E_I(\alpha)$, this procedure suffers from the obvious defect that it begs the question.

To circumvent this situation we have inserted here the macroscopic parameters E_0 and P_c and scaled $E_I(\alpha)-E_0$ to first order in P_c, which plays the role of a macroscopic scaling factor. It is clear that as soon as $|E_I(\alpha)-E_0|>0$, the value of P_c must change, and that microscopic change should be calculated self-consistently if one wishes to determine $E_I(\alpha)-E_0$ to better than first order in P_c. We have settled here for a first-order model $\{$although $d=|[E_I(\alpha)-E_0]/E_0|$ is not always small compared to one$\}$ because the higher-order corrections would require evaluation of valence strain energies, a calculation not appropriate to our present knowledge of deformation potentials of the valence bands.

Our dynamical model fits the observed central-cell corrections in seven cases with only three parameters, which suggests that the model is at least semiquantitative. No mention is made of two one-electron effects, dielectric breakdown and mass enhancement, which had previously been invoked[2] to explain the origin of the central-cell corrections. What became of these terms?

In order to estimate the magnitude of these terms, we consider a case in which many-electron effects associated with gap mismatch and differences in p-d hybridization are almost absent. Such a case is Sb in Ge, as shown in Table I. It is estimated that the one-electron effects are of order 1 meV in Ge and 3 meV in Si, i.e., they are about three to seven times smaller than the observed values of ΔE_c.

It is thought that the one-electron terms are small because in addition to dielectric breakdown and mass enhancement (which make negative contributions to E_I) there is a third one-electron term,[3] the change in repulsive potential (orthogonality terms) of valence states seen by conduction states. This term was not considered in early work,[2,7] but it has been shown[17] that in the rare-gas solids this positive term approximately cancels the two negative terms, thereby accounting for the small values of ΔE_c and even its reversal of sign in some cases. To first order the electronegativities of the rare gases are all the same, so that they represent the best test case of one's theory of one-electron effects.

Our theory contains two microscopic scaling factors a_{Si} and a_{Ge} for describing dynamical effects. It was found that their ratio is characteristic of the strain and chemical properties of the valence contributions to the self-energies of the band edges of the host crystals. The ratio is consistent with experimental values of band-edge sensitivities obtained both from studies of Si-Ge alloys and from the effects of hydrostatic pressure. Thus the dielectric theory has produced a deep result which would never appear in a superficial one-electron theory based on macroscopic mechanisms only. If the cancellation of one-electron effects found both for closed-shell systems (rare-gas solids) and covalent systems (Si and Ge) holds for other cases, then the general theory of impurity states may emphasize electronegativity as the most important parameter determining central-cell interactions.

The argument has sometimes been made that all central-cell corrections can be accounted for in terms of differences in impurity and host atomic radii. No one has actually done so, however. Some reasons why such an approach is inadequate are the following: (a) In A^NB^{8-N} crystals the atomic radii for all atoms belonging to column N can be increased by an arbitrary amount providing that the radii for all atoms belonging to column $8-N$ are decreased by the same amount. Thus the "difference in radius" between an $N=5$ impurity and an $N=4$ host atom is a meaningless phrase. (b) Even if the "difference in radius" could be defined, converting this difference, with dimensions of length, into a central-cell correction, with dimensions of energy, is a formidable task indeed.

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[17] J. Hermanson, Phys. Rev. **150**, 660 (1966).