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Binding to Isoelectronic Impurities in Semiconductors

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(Received 9 December 1971)

The potential produced by isoelectronic impurities is investigated and shown to be critically dependent upon screening. Two methods of calculation of the screened potential are used in this paper, one based on a first-principles wave-function approach and the other using the semiempirical theory of energy bands in semiconductors. The relaxation of the host crystal is also taken into account and shown to be important. The results are in satisfactory agreement with experiment.

Isoelectronic impurities in semiconductors may produce bound states in the forbidden gap,[1] binding a hole (or an electron). Experimental data are now available which suggest that an isoelectronic impurity may bind a hole (electron) only if its electronegativity is smaller (larger) than that of the host atom it replaces. This rule, however, does not indicate which systems will actually have a bound state. It is also found experimentally that only very large atoms (Te and Bi) or very small atoms (N and O) produce bound states (isoelectronic traps). On the theoretical side, the results achieved have been only qualitative[2,3] and even the binding mechanism is not yet clear. One would like to be able to calculate for a given semiconductor whether a particular isoelectronic substitution will bind a hole (or an electron).

In the present paper we make binding calculations on a model potential for isoelectronic impurities and apply it to the case of isoelectronic donors (i.e., hole traps). The bare impurity potential is assumed to be the difference of atomic pseudopotentials[4] and is then screened using a dielectric function which reflects the local electron density. The relaxation of the host lattice

TABLE I. Values of $\bar{E}$ and of the matrix element J as a function of lattice relaxation. J_{SO} is the spin-orbit contribution to the matrix element. The actual relaxation produced in the crystal is denoted $\bar{X}$. In the last two columns the predictions of the present model are compared with available experimental data. Numbers in parentheses are based on extrapolations. All energies are in eV.

	$\bar{E}$	J_{SO}	J(X=0) unscreened	J(X=0) average screening	J(X=0) local density screening	J(X=0) dielectric	J(X=1) pseudo-potential	J(X=1) dielectric	$\bar{X}$	Bound State? Theory.	Exp
Si:Ge	-1.8	0.04	0.32	0.09	0.08	0.10	(0.54)	0.63	0.41	No	No
Si:Sn	-1.8	0.14	1.96	0.45	0.40	0.37	(2.34)	2.44	0.36	No	
Si:Pb	-1.8	0.43	2.45	0.77	0.72	0.61	(3.63)	3.20	0.35	No	
GaP:As	-1.4	0.06	1.24	0.35	0.30	0.06	0.76	0.97	0.43	No	No
GaP:Sb	-1.4	0.20	4.49	1.26	1.07	1.06	2.80	3.70	0.37	Yes	No
GaP:Bi	-1.4	0.72	5.60	1.93	1.71	1.83	(4.12)	4.94	0.35	Yes	Yes
ZnS:Se	-0.9	0.11	4.81	1.67	1.20	0.24	1.01	1.63	0.51	No	No
ZnS:Te	-0.9	0.28	9.46	3.34	2.41	1.19	2.98	4.21	0.48	Yes	Yes

around the impurity is also studied and turns out to be important. The results obtained using the pseudopotential theory are compared with those we have calculated by using the semiempirical dielectric theory,[5] and reasonable agreement is found.

The potential produced by an isoelectronic substitution is short range and will bind a particle only if it is sufficiently strong. Using a one-band, one-site Koster-Slater approach, the binding condition is[2]

$$1+J/\bar{E} \leq 0, \qquad (1)$$

where J is the diagonal matrix element of the impurity potential on the appropriate Wannier function and $\bar{E}$ is an average energy related to the energy band $E(\vec{k})$ as follows

$$\bar{E}^{-1}=\Omega(2\pi)^{-3}\int E^{-1}(\vec{k})\,d^3k, \qquad (2)$$

where the integration is on the Brillouin zone and Ω is the unit cell volume. In the case of degenerate bands, an obvious generalization of Eq. (2) has to be used, but condition (1) is still valid.

The average energy $\bar{E}$, whose absolute value will be called threshold, depends only on the band structure of the host material and is very easily calculated. The first column of Table I shows a few values of $\bar{E}$ obtained neglecting spin-orbit effects, which are small for the crystals considered.

Let us now discuss the impurity potential and its matrix element J. An isoelectronic substitution implies more than the replacement of an atomic core. The *unperturbed* covalent bond between the impurity and its neighbors has a length R_i generally different from the bond length R_h of the host crystal and consequently a strain field is produced. If we suppose that all atoms, beyond the nearest neighbors, move according to the elastic continuum theory, the displacement R of nearest neighbors will completely define the strain field present in the crystal. As a measure of this field we will use the dimensionless quantity $X=R/(R_i-R_h)$ which ranges between $X=0$ (no relaxation) to $X=1$ (maximum relaxation).

Let us consider first the case $X=0$. To make a specific example, let us consider GaP:Bi. The lattice is perfectly rigid and the impurity potential can be assumed to be the difference between the bare atomic pseudopotentials[4] of Bi and P. The potential thus obtained must be screened, and to begin we use the dielectric constant of the host crystal as given by Penn's model.[6] Furthermore, effects due to spin-orbit must be included, and can be described as the difference of the model spin-orbit pseudopotentials of Bi and P as given by Animalu.[7] The estimated spin-orbit corrections to J are given in the second column of Table I. The total matrix element J of the impurity potentials defined in this way are given in the third and fourth columns of Table I for unscreened and screened potentials, respectively. A comparison between the results immediately reveals the importance of screening. Substituting the numbers so far obtained into the binding condition (1), we see that screened potentials give better agreement with experiment. Still some discrepancies exist and they seem to

increase with increasing ionicity of the host material (Se would produce a deeply bound state in ZnS!). The explanation we propose is that Penn's screening, based on the average electron density, cannot be used for a potential whose range is less than the atomic radius. Walter and Cohen[8] show that the valence charge density of semiconductors has strong deviations from the average value of eight electrons per unit cell. In particular, the average charge density around Si, around P in GaP, and around S in ZnS can be estimated to be 12.5, 21.0, and 35.0 electrons per unit cell, respectively. Under these circumstances, a screening based on the *local* electron density is needed. We have estimated such screening by using Penn's interpolation formula[6] in which quantities such as the Fermi momentum and energy, and the plasma frequency, are evaluated according to the average *local* electron density. The Penn's gap, which does not effect the results in the range of interest here, is left unchanged. Using this crude model of local screening, we obtain the results shown in the fifth column of Table I. The agreement with experiment improves but J is still systematically too large for traps in ZnS. It should be noted that it is the more ionic crystals which are changed by using local density screening but that the change is not large enough. We will return later to this point.

If we now allow the lattice to relax, the additional potential produced by the displacement of atoms has to be considered. For maximum relaxation ($X=1$), the total impurity potential can be obtained by subtracting the pseudopotential of a GaBi crystal from that of GaP and then retaining only that portion of the potential which is inside the unit cell containing the impurity atom. We have used, whenever possible, the pseudopotentials given by Cohen and Bergstresser,[4] with the undetermined constant potential V_0 evaluated from the experimental values of the ionization potentials. The matrix elements J obtained in this way are shown in the seventh column of Table I. These numbers include the spin-orbit correction which we assume to be the same as that for $X=0$, since spin-orbit effects have been shown[9] to depend only slightly on pressure. For those crystals for which pseudopotential form factors are not available, the matrix element J has been estimated on the basis of electronegativity differences. The effect of relaxation is to make the potentials more attractive to holes, as was expected since in all cases here considered, relaxation makes the bonds longer and therefore weaker (i.e., more attractive to holes). Note that in this $X=1$ limit, we have circumvented the problem of screening by being able to use the empirical screened pseudopotentials.

The potential matrix element J can also be evaluated by using a different approach to semiconductor band structures: the dielectric theory.[5] The isoelectronic substitution GaP:Bi can also be described as follows: A unit cell of GaP is substituted with a unit cell of GaBi in the limit $X=1$, and with a compressed unit cell of GaBi (so as to match lattice constants) for $X=0$. The matrix element $J(X=0)$ can be obtained by subtracting the average ionization potentials[10] of GaP and compressed GaBi, where for average we define the mean at Γ, X, and L with weights 1, 3, and 4, respectively. The ionization potential of a compressed crystal is calculated from the deformation potentials of the valence band recently obtained by Lawaetz.[11] The same method can also be used for $J(X=1)$. In this case the difference in average ionization potentials includes also kinetic differences which must not appear in J. Kinetic contributions are subtracted off using an average value of the kinetic energy in the top valence bands equal to $1.76(2\pi\hbar)^2/2ma^2$ which is the free-electron value for a crystal with lattice constant a. The results obtained in the two limits $X=0$ and $X=1$, corrected for spin-orbit contributions, are given in the sixth and eighth columns of Table I.

Excellent agreement between the two methods is obtained for $X=0$ in Si and GaP. For ZnS the dielectric theory predicts a much weaker potential and since this theory has been shown to be valid for all values of ionicity, we believe that the discrepancy is due to our crude model of local screening and/or the need for nonlinear screening since the bare potentials for ZnS are very deep. In this limit therefore we will trust more the method based on the dielectric theory. Satisfactory agreement is obtained for $X=1$, since the discrepancies between the two methods do not seriously affect the final result. In fact actual relaxations are always far from this limit. No argument has been found in favor of one method or the other and we arbitrarily use the pseudopotential method in this limit.

The behavior of J for intermediate relaxation has been obtained by linear interpolation between the two limits $X=0$ and $X=1$. Figure 1 shows the dependence of J on relaxation for traps in GaP and indicates the importance of relaxation for this problem.

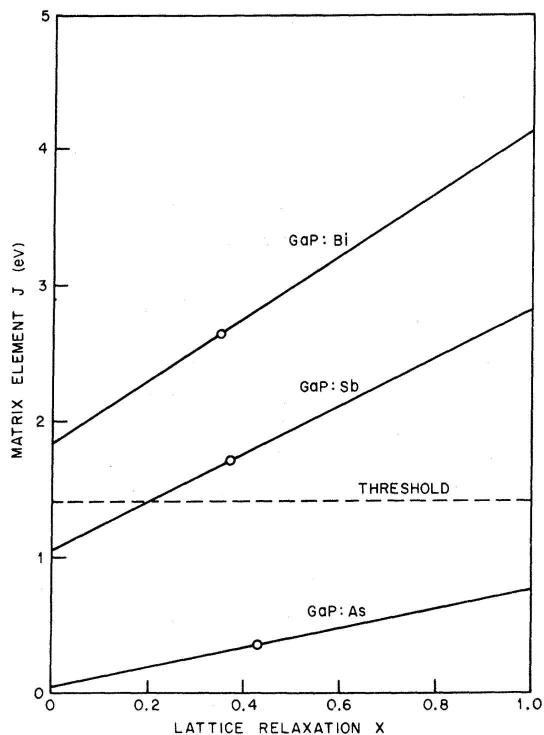

FIG. 1. Dependence of the matrix element J on lattice relaxation for GaP:As, GaP:Sb, and GaP:Bi. The broken line represents the threshold $|\overline{E}|$. The dots indicate the actual relaxation and show that according to the present model Bi and Sb are traps in GaP whereas As is not. Note that Sb will produce a barely bound state while experimental data seem to indicate a barely unbound state.

At this point, to find out if a bound state exists or not, we need only to know the actual relaxation $\overline{X}$, the one which minimizes the strain energy. Using the previously defined model for strain field, usual values of the elastic constants and the force constants given by Martin,[12] we obtain for $\overline{X}$ the values shown in Table I and the dots of Fig. 1.

The binding mechanism here proposed agrees with the experimental observation that a hole can be bound in GaP by Bi and in ZnS by Te. The only discrepancy is for GaP:Sb where we predict a barely bound state whereas experiment shows a barely unbound state. No isoelectronic traps are predicted in Si due to its high threshold.

As shown by Faulkner[2] and by Phillips,[3] the binding energy of these traps is a delicate quantity and we do not attempt an evaluation here, but the strong effect of relaxation we have found seems to indicate that the binding energy must be very sensitive to an externally applied pressure. In this respect, isoelectronic traps would differ from traditional donors and acceptors which are bound by pressure-independent Coulomb forces and therefore rigidly follow the associated energy-band extremum. A strong pressure dependence of the binding energy of isoelectronic traps has indeed been observed in GaP.[13]

It is a pleasure to thank C. H. Henry for his generous contributions throughout this work, J. C. Phillips and E. O. Kane for many helpful discussions, and R. A. Faulkner who provided a copy of his computer code for pseudopotential band-structure calculations.

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