A Note on the Pressure Dependence of the Ionization Energies of Some Donor States

M. POLLAK

Department of Physics, University of California, Riverside

AND

A. SAGAR

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

Abstract

A number of experiments on the strain dependence of transport properties in semiconductors indicate that the ionization energy of some donors is very pressure sensitive. In at least some of these situations the entity responsible for the donor states is known to be a vacancy. The effect of such vacancies on the band structure is investigated, and it is concluded that the cause for the strain dependence of the ionization energy is most likely to be the presence of an appreciable admixture of valence band wave functions to the donor wave function. The strain dependence of the ionization energy then arises from the strain dependence of the band gap. If the vacancies create appreciable local strains, the strain dependence of the ionization energy may be caused by an admixture of subsidiary conduction bands to the donor state.

Large pressure effects on the conductivity and Hall effect have been observed in a number of semiconductors [1–8], notably in some II–VI, and in some III–V compounds. In all cases the measurements could be successfully explained with the phenomenological assumption that there exists an appreciable strain dependence of the ionization energy of the donors. The materials where these observations were made have in common the following features: they are n-type, the lowest conduction band minimum lies at $k = (0, 0, 0)$, and they have higher conduction band minima at other k values. Except for GaSb they also have a separation between the lowest and next lowest conduction band comparable to the separation between the valence and conduction band. The case of GaSb is unique in that the two conduction bands are almost degenerate. For this reason the following discussion shall not apply to GaSb. While it is likely to apply to GaAs, the discussion will for the sake of specificity refer to II–VI compounds. In these, the donor state appears to be connected with a group VI vacancy. The typical donor ionization energies at low pressure are $\epsilon_i \simeq 0.01$ eV, and typical pressure dependences $\partial E_i/\partial P \sim 10^{-11}$ eV cm²/dyne.

To explain the pressure-dependent ionization energy of the donors Paul suggested that the donor wave function probably receives an appreciable contribution from the second lowest conduction band. The energy of the upper band is known to depend on pressure. Such a model yields results consistent with the experimentally observed pressure dependence of the donor ionization energy. It has also been suggested [4, 8, 9] that such an agreement may be obtained if an important admixture to the donor function comes from the valence band rather than from upper conduction bands. An argument in favor of the latter alternative was made in Bibliography [9].

In the following, the consequences of introducing a group VI vacancy into an otherwise perfect crystal are analyzed. The arguments are made in the framework of a one-electron approximation. It is shown that if strains around the vacancy are ignored, the strain dependence of the donor ionization energy is most likely to arise from the valence band; the upper conduction bands cannot contribute significantly to the donor wave function. However, when local distortions around the vacancy are taken into account this conclusion may well have to be altered. The following notation will be used for the electron eigenstates in the unperturbed crystal. The set of valence band states is annotated by φ, the set of states which form the lower conduction band by χ^1 and the set of states of the upper conduction band by χ^2, the wave functions in the crystal which include the vacancy then can be written

$$(1) \qquad\qquad \psi = a\varphi + b_1\chi^1 + b_2\chi^2$$

In accordance with experimental data the highest occupied of these states is a donor state, and thus must be a localized state. Equation (1) assumes that contributions from all bands other than φ, χ^1, and χ^2 are unimportant. The main effect of introducing a group VI vacancy is the removal of six positive charges from a perfect crystal, and the removal of six electrons from the valence band. Thus the vacancy modifies the Hamiltonian of the perfect crystal by introducing an additional term

$$\sum_j 6e^2/|r_v - r_j|$$

where r_v gives the position of the vacancy and r_j that of the j-th electron. The vacancy also converts the N-electron wave function of the valence electrons into an $(N - 6)$-electron wave function. The entire process can be imagined as accomplished by taking six electrons from the valence band and squeezing them into the core of the group VI atom. Obviously such a procedure will have a pronounced effect on the remaining valence electrons. Labelling the states ψ from the lowest to the highest state by 1 to $3N$, the state of interest, i.e. the donor state, is ψ_{N-6}. To apply the discussion to somewhat more general situations, the number of electrons which the defect deletes from the valence band will be sometimes annotated by n. Thus for the case of a group V vacancy in a III–V semiconductor $n = 5$, for a group III impurity in Si or Ge $n = 1$, for a group V impurity in Si or Ge $n = -1$.

It is convenient to begin by considering the effect of the vacancy on the $\boldsymbol{\varphi}$ band alone, i.e. to consider solutions to the Schrödinger Equation in the presence of the vacancy, assuming that the set $\boldsymbol{\varphi}$ constitutes the complete set. Formally the only claim which can be made about the resulting solutions $\boldsymbol{\varphi}'$ is that they are related to the original set of functions $\boldsymbol{\varphi}$ by a unitary transformation. It will be shown *a posteriori*, however, that most of them are very good approximations to the actual solutions, that is that for a large number of functions $\psi_i \approx \varphi_i'$. Generally, however

(2)
$$\psi = a'\varphi' + b_1\chi^1 + b_2\chi^2$$

The interesting qualitative features of the functions can be established without the necessity to calculate them. In the one-electron approximation the new eigenfunctions are $(N - 6)$-fold products (Hartree approximation) or anti-symmetrized products (Hartree–Fock approximation) of one-electron functions. The primed functions and the unprimed functions must be related by a unitary transformation

(3)
$$\boldsymbol{\varphi}' = \mathbf{A}\boldsymbol{\varphi}$$

It is useful for the following discussion to consider the matrix $\boldsymbol{\varphi}'\boldsymbol{\varphi}'^+$. Since $\mathbf{A}$ is unitary, the trace of this matrix obeys

(4)
$$\mathrm{tr}\,(\boldsymbol{\varphi}'\boldsymbol{\varphi}'^+) = \mathrm{tr}\,(\boldsymbol{\varphi}\boldsymbol{\varphi}^+)$$

Because the defect Hamiltonian is repulsive, and is largest around the vacancy, the wave functions φ_i' with the lowest energies must be such that $\varphi_i'^*\varphi_i'$ (and hence $|\varphi_i'|$) is small near the vacancy. As a consequence, and because of (4), there must exist eigenfunctions φ_i' which have an appreciable amplitude only near the vacancy, and thus are of a localized nature. The degree of localization depends on the strength of the defect potential, that is on n. As is usual with localized states, the associated energies constitute a discrete set. These energies are higher than the energies of the valence band in the perfect crystal. This must be so because the difference in energy is primarily the value of

(5)
$$\Delta E_l = \int \varphi_l'^* V \varphi_l' \, d\tau$$

The integral is a positive quantity (for positive n), because of the repulsive nature of the defect. The value of the integral depends strongly on n for two reasons. First, V is proportional to n; secondly, the degree of localization of φ_l' increases with n. The nature of the functions $\boldsymbol{\varphi}'$ is schematically shown in Figure 1. The left half of the figure illustrates the one-electron wave functions of the perfect crystal. The vertical direction shows the energy, the horizontal shows the spatial extent of the functions. The heavy lines represent occupied states, the light lines unoccupied states. Thus the valence band $\boldsymbol{\varphi}$ is fully occupied, the conduction bands $\boldsymbol{\chi}^1$ and $\boldsymbol{\chi}^2$ are entirely empty. To conform with the actual situation in the materials of concern, the bands $\boldsymbol{\chi}^1$ and $\boldsymbol{\chi}^2$ are shown to overlap in energy.
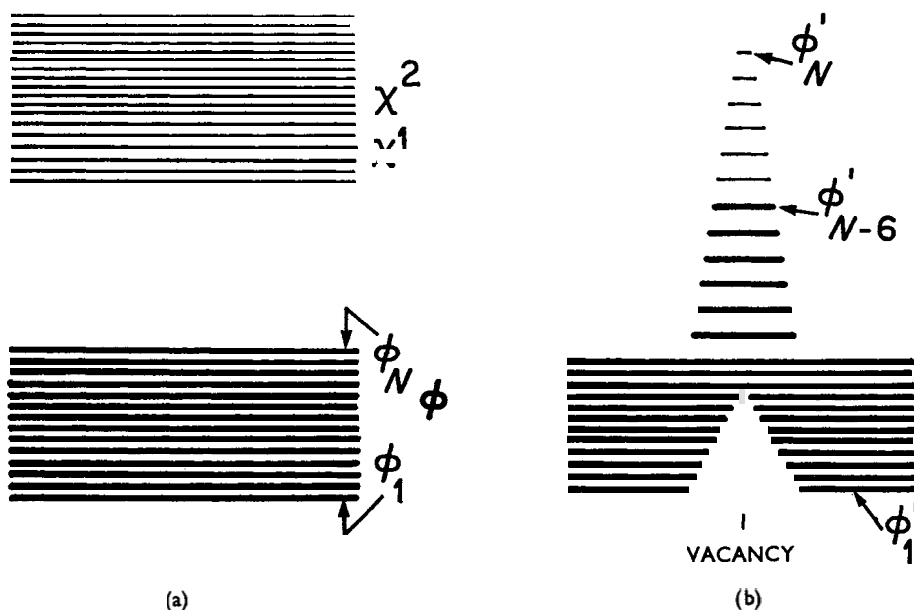
Figure 1. A schematic representation of the wave functions of the valence band φ and of two conduction bands χ^1 and χ^2. The heavy lines represent occupied states, the light lines vacant states. The vertical direction represents the energy, the horizontal the spatial extent of the functions. Figure 1a shows the wave functions in a perfect crystal, Figure 1b illustrates the wave functions of the valence band modified by the presence of a vacancy.

The right half of Figure 1 is a schematic illustration of the functions φ'. Again, the heavy lines correspond to occupied, the light lines to unoccupied functions. The fact that the vacancy removes six electrons from the valence band is clearly indicated, as is the high energy and localized nature of the function φ'_{N-6}.

At first sight it may seem peculiar to have localized states associated with a repulsive potential. The reason for this to happen lies in the fact that the φ set is of finite dimensionality, as distinct from the usually considered infinite set of free-electron wave functions.

The interesting state for a group VI vacancy in a II–VI semiconductor is the highest occupied state φ'_{N-6} (i.e., the seventh highest state) rather than the unoccupied state. This is so because the large value of n is likely to make the value of ΔE_l of (5) so large that the energy of the highest occupied state may be comparable to the energy of the edge of the conduction band, or even larger. The result of such a situation is a donor state. This is, in fact, the only way in which a group

VI vacancy in a II–VI semiconductor can give rise to a donor state and thus be consistent with the experimental observations. Thus we are led to conclude that φ'_{N-6} cannot have an energy much below the conduction band edge.

We now examine the magnitude of the components of the matrices $\mathbf{b}_1$ and $\mathbf{b}_2$. This will decrease with the size of energy differences $E(\chi_i) - E(\varphi'_j)$, and increase with the magnitude of the matrix elements $\langle \chi_i \mid V\varphi'_j \rangle$. For the low-lying states the energy difference is large and the matrix elements small. The reason for the latter lies in the fact that for small indexes $i \mid \varphi'_i \mid$ is small where V is large and vice versa. The contributions from the χ bands to ψ is therefore very small. On the other hand, for the localized functions φ'_j both the energy differences and the matrix elements make the contribution particularly from χ' considerably more important. However, the important fact is that unless the energy of φ'_{N-6} is considerably higher than the energy of the bottom of the χ^1 band, the contribution of φ'_{N-6} to the highest occupied (i.e. donor) state must also be important. This is what is needed to account for the experimental observations.

The alternative possibility, that the energy of the function φ'_{N-6} is so much higher than the energy of the lowest χ' function that its contribution to the donor state wave function can be neglected, must now be considered. Since we wish to examine the hypothesis that at least some of the coefficients $(b_2)_{k,N-6}$ are sufficiently large to account for the observed pressure effects we will now assume that all the φ' functions are so much removed from the donor state that all coefficients $a'_{i,N-6}$ in (2) are negligible. In this situation the only importance of the φ' electrons for the formation of the donor state is to provide a part of the potential for the total Hamiltonian (in a way similar to the role of the σ electrons in the $\sigma - \pi$ separation procedure). The potential experienced by the electron which has been postulated here to fall from the high φ'_{N-6} state into a χ state differs from the potential that an electron in a χ state experiences in a perfect lattice by the potential V due to the charge of $-6e$ which represents the vacancy, and by the potential V' arising from an altered charge distributions $\rho_1(\mathbf{R})$ of the φ' electrons compared to $\rho_0(\mathbf{R})$ in a perfect crystal. In the one-electron approximation used here

$$(6) \quad V'(\mathbf{r}') = \int [(\rho_1 - \rho_0)/r] \, d^3R = \int \left(e \sum_{i=1}^{N-7} \varphi_i'^* \varphi_i'/r \right) d^3R - \int (\rho_0/r) \, d^3R$$

$$= \int \left(e \sum_{i=1}^{N} \varphi_i'^* \varphi_i'/r \right) d^3R - \int \left(e \sum_{i=N-6}^{N} \varphi_i'^* \varphi_i'/r \right) d^3R - \int (\rho_0/r) \, d^3R;$$

$$r = |\mathbf{R} - \mathbf{r}'|$$

The first term of the right hand side of (6) is identical to the last term because of (4). Therefore

$$(7) \qquad\qquad V' = - \int \left(e \sum_{i=N-6}^{N} \varphi_i'^* \varphi_i'/r \right) d^3R$$

which means that V' corresponds to a potential arising from seven positive electron charges localized around the vacancy. The potential $V + V'$ then corresponds to one positive electron charge (as is indeed required by the charge neutrality of the crystal) which is localized around the vacancy to a degree determined by the functions φ'_{N-6} to φ'_N,

$$(8) \qquad V_t = V + V' = \int \left\{ e \left[6\delta(r_v) - \sum_{i=N-6}^{N} \varphi_i'^* \varphi_i \right] / r \right\} d^3 R$$

That this localization must be very strong is apparent from the energies which separate the states φ_{N-6} to φ_N from the valence band. The general situation is therefore quite similar (except perhaps for a slightly more delocalized positive charge) to that of the more familiar donor states, such as for example a group V impurity in germanium or in silicon. It thus seems surprising that the properties of the donor states should be quite different. From the considerations thus far it is reasonable to assume that the energy of the function φ'_{N-6} is not much greater than that of the lowest χ^1 function and that the pressure dependence arises from the importance of the coefficient $a'_{N-6,N-6}$ in (2) rather than of the coefficients $(b_2)_{k,N-6}$. It is, in fact, possible to argue on theoretical basis that this must be expected.

If all coefficients $a'_{k,N-6}$ are negligible, the ground state donor function ψ_{N-6} can be expressed as

$$(9) \qquad \psi_{N-6} = \beta_1 \bar{\chi}^1 + \beta_2 \bar{\chi}^2$$

where

$$(10) \qquad \bar{\chi}^1 = \sum_i (b_1)_{i,N-6} \chi_i^1 \qquad \bar{\chi}^2 = \sum_i (b_2)_{i,N-6} \chi_i^2$$

The knowledge of the coefficients $(b_1)_{i,N-6}$ and $(b_2)_{i,N-6}$ is unimportant at present. Since the basis set χ^1, χ^2 is taken as the eigenfunction set of the Hamiltonian for a perfect crystal,

$$(11) \qquad \langle \chi_i^1 | \chi_j^1 \rangle = \delta_{ij} \qquad \langle \chi_l^2 | \chi_m^2 \rangle = \delta_{lm} \qquad \langle \chi_n^1 | \chi_k^2 \rangle = 0$$

The ratio β_2^2/β_1^2 is a measure of the contribution of the subsidiary minimum to the ground state donor wave function, and is determined by the variational principle

$$(12) \qquad \delta \langle \psi_{N-6} | H \psi_{N-6} \rangle = 0 \qquad H = H_0 + V_t$$

with the result

$$(13) \qquad \beta_2^2/\beta_1^2 = \frac{(1 + d^2)^{1/2} - 1}{(1 + d^2)^{1/2} + 1} \qquad d = 4 \frac{(V_t)_{12}}{H_{22} - H_{11}}$$

$$A_{ij} = \langle \bar{\chi}^i | A \bar{\chi}^j \rangle \qquad i = 1, 2 \qquad A = H, V_t$$

In the above equations H_0 is the Hamiltonian of the perfect crystal, and V_t is the potential of the defect given by (8). Equation (13) implies that the contribution from the subsidiary minima can be, at most, comparable to the contribution from the band edge. In order that the value of β_2^2/β_1^2 is of any significance at all, the value of $(V_t)_{12}$ must be at least comparable to the value of $H_{22} - H_{11}$. The value of $(H_0)_{22} - (H_0)_{11}$, i.e., the energy separation of the minima, is known to be about 2 eV. This would imply that either $(V_t)_{12}$ must be of this magnitude, or that $(V_t)_{11}$ and $(V_t)_{22}$ should be able to change significantly the value of $(H_{11} - H_{22})$ from the value of $(H_0)_{11} - (H_0)_{22}$.

The following demonstrates that neither is very likely. It is easy to show that the functions $\bar{\chi}^1$ and $\bar{\chi}^2$ are solutions of the variational principles

$$\delta \int |\psi_{N-6} - \bar{\chi}^1|\, d\tau = 0 \quad \text{and} \quad \delta \int |\psi_{N-6} - \bar{\chi}^2|\, d\tau = 0,$$

respectively. Such functions are close [10] to functions obtained from the variational principles

$$\delta \langle \bar{\chi}^1 \,|\, H\bar{\chi}^1 \rangle = 0 \quad \text{and} \quad \delta \langle \bar{\chi}^2 \,|\, H\bar{\chi}^2 \rangle = 0$$

However, the latter are the conventional ground state donor functions formed in the first case from the band χ^1 when no band χ^2 exists, and, in the second case, from the band χ^2 when no band χ^1 exists. $(V_t)_{11}$ and $(V_t)_{22}$ are then ionization energies of such states from their respective bands and are known to be considerably smaller than 2 eV. The value of $(V_t)_{12}$ is less than $(V_t)_{22}$ and therefore is also considerably less than 2 eV. Thus, under the conditions of the above arguments, it is most unlikely that the ground-state donor function can have a significant admixture from the subsidiary minimum.

However this conclusion is based on two implicit assumptions which have been made in the foregoing. The one is the assertion that the creation of a vacancy corresponds to the deletion from the lattice of six positive charges, together with six electrons from the valence band. In actual fact, many more positive charges are deleted, together with many additional electrons which are in very tight orbits. The consequence of the deletion of these additional positive charges together with the tightly bound electrons can be represented by a very localized pseudopotential, and can certainly be neglected in comparison to the effects which were considered. The other assumption which has been implicitly made is that the position of the atoms has not been affected by the creation of the vacancy. This is certainly an improper assumption particularly for atoms in the neighborhood of the vacancy. It is known that a defect such as a vacancy has a rather long range effect on the position of the atoms around it. It is known that there is a very significant dependence of the band structure on strain. It is thus quite conceivable that the strains associated with the vacancy can locally create an inversion

of the χ^1 and χ^2 bands. If this is the case, and if the region in which this inversion happens is comparable to the size of the donor state, the contribution of the subsidiary conduction band to the donor function must of course be appreciable.

Bibliography

[1] R. J. Sladek, Proc. Int. Conf. Phys. Semicond. 7th, Paris, 1964, p. 545.
[2] R. J. Sladek, Phys. Rev. **140,** A1345 (1965).
[3] A. R. Hutson, A. Jayaraman and A. S. Coriell, Phys. Rev. **155,** 786 (1967).
[4] A. G. Foyt, R. E. Halsted and W. Paul, Phys. Rev. Letters **16,** 55 (1966).
[5] A. Sagar and M. Rubenstein, Phys. Rev. **143,** 552 (1966).
[6] B. B. Kosicki and W. Paul, Phys. Rev. Letters **17,** 246 (1966).
[7] B. B. Kosicki, W. Paul, A. J. Strauss and G. W. Iseler, Phys. Rev. Letters **17,** 1175 (1966).
[8] A. Sagar, M. Pollak and W. Lehman, Phys. Rev. **174,** 859 (1968).
[9] M. Pollak, A. Sagar and W. Lehman, Westinghouse Report 66-1F5-TPROP-P3 (unpublished).
[10] W. Kutzelnigg and V. H. Smith, J. Chem. Phys. **41,** 896 (1964).