

Intracenter Coulomb correlations, charge states, and spectrum of group-III impurities in IV-VI narrow-gap semiconductors

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A model explaining the electroactivity, magnetic properties, and pinning of the chemical potential, which are observed in lead and tin tellurides and their alloys doped with Ga, In, or Tl, is proposed. © 1995 American Institute of Physics.

A model based on the idea of the closeness of the total (multielectronic) energies of different electronic configurations (s^2p^1 , s^1p^2 , and s^0p^3) of an impurity atom substituting for Pb or Sn at the site of a crystal lattice of a semiconductor is studied.¹ Metal atoms (Pb or Sn) in IV-VI semiconductors are in a divalent state (s^2p^2 configuration). Their s electrons form deep, completely filled bands, and the atomic p -orbitals form the valence and conduction bands.² It is therefore obvious that a group-III atom substituting for a divalent metal in the ground (univalent s^2p^1) atomic configuration is a singly charged acceptor; in the divalent configuration (s^1p^2) an impurity atom will be neutral and paramagnetic (unpaired spin in a s -shell); and, in a trivalent configuration (s^0p^3) it will become a singly charged donor. All electric and magnetic activities of these types were observed experimentally in Refs. 3 and 4. A change of the valence from 1 to 3 is, in itself, not surprising. It is well known, for example, that the compounds InCl, InCl₂, and InCl₃ exist (the second compound is metastable and decomposes into InCl and InCl₃). In these compounds the number of Cl atoms surrounding In in the molecule plays the role of the parameter that gives rise to the valence change. As a result, the energy gain due to the formation of an additional bond in the molecule compensates for the energy loss due to the change in the electronic configuration of the group-III atom. In a semiconductor, however, the environment around an impurity atom does not change when the valence changes. Nonetheless, a change in the chemical potential of the electrons (holes) changes the valence of group-III impurities. The point is that in contrast to a molecule, an atomic p -level in a crystal is smeared out into a band and the work function of the crystal, which is directly related to the change in the chemical potential, now plays the role of the parameter giving rise to a valence change.

MODEL HAMILTONIAN

The model Hamiltonian is

$$\hat{H} = \varepsilon_s \sum_{\sigma} n_{s\sigma} + \sum_{\sigma, \nu, \mathbf{k}} \varepsilon^{\nu}(\mathbf{k}) \hat{n}_{\mathbf{k}\sigma}^{\nu} + V_{ss} \hat{n}_{s\sigma} \hat{n}_{s-\sigma} + V_{sp} \sum_{\sigma} \hat{n}_{s\sigma} \sum_{\sigma, \nu} \hat{n}_{\sigma}^{\nu} + \frac{1}{2} V_{pp} \sum_{\substack{\nu, \nu' \\ \sigma, \sigma'}} \hat{n}_{\sigma}^{\nu} \hat{n}_{\sigma'}^{\nu'} \quad (1)$$

TABLE I.

V_{ss} , eV	V_{sp} , eV	V_{pp} , eV	$-\varepsilon_s$, eV	$-\varepsilon_p$, eV	$E_1 - E_0$, eV	$E_2 - E_0$, eV
In						
14,7	12,1	9,0	37,8	28,9	2,3	4,1
				31,0	0,3	~ 0
Ga						
15,5	12,0	8,55	38,9	29,1	2,8	5,6
				31,9	~ 0	0,1

$$\hat{n}_\sigma^\nu = \sum_{\mathbf{k}} \hat{n}_{\mathbf{k}\sigma}^\nu,$$

with the electric neutrality condition

$$\sum_{\sigma} n_{s\sigma} + \sum_{\sigma,\nu} n_{\sigma}^\nu = 3. \quad (2)$$

In accordance with the genesis of the valence bands and the conduction bands from the atomic p -orbitals,² the index ν runs through the values $\{x,y,z\}$, σ is the spin index, $n_{s\sigma}$ is the density, ε_s is the bare one-electron energy of s electrons with a definite spin, $\varepsilon^\nu(\mathbf{k})$ is the dispersion relation, $\hat{n}_{\mathbf{k}\sigma}^\nu$ is the density operator for p electrons with definite spin and momentum, the constants V_{ss} , V_{sp} , and V_{pp} approximate the Coulomb interaction between the corresponding orbitals, and the prime in the last sum in Eq. (1) means that the self-action is excluded from the summation (terms with like values of ν and σ are excluded). The constants in the Hamiltonian (1) are chosen in such a way that, on the one hand, the energies of the configurations s^2p^1 and s^0p^3 (the case of In) or s^2p^1 and s^1p^2 (the case of Ga) would be, in accordance with the experimental data of Refs. 3 and 4, approximately the same and, on the other, the Hartree-Fock energies would not differ markedly from the atomic calculations [the Hartree-Fock values of the energies are: $\tilde{\varepsilon}_s = -10.12$ eV, $\tilde{\varepsilon}_p = -4.69$ eV for In and $\tilde{\varepsilon}_s = -11.37$ eV, $\tilde{\varepsilon}_p = -4.9$ eV for Ga (Ref. 5)]. As the zeroth approximation for the constants, the Hamiltonian (1) can be replaced by the Hamiltonian of an isolated impurity and the numerical values can be chosen for it by a similar procedure. Such a Hamiltonian is similar to (1), but the term $\sum \varepsilon^\nu(\mathbf{k}) \hat{n}_{\mathbf{k}\sigma}^\nu$ is replaced by $\varepsilon_p \hat{n}_\sigma^\nu$. For an isolated atom the values presented in Table I are obtained for the constants (for ε_p we give the initial and modified values, for which the many-electron energies become equal to one another).

STABILIZATION OF THE CHEMICAL POTENTIAL

The valence changes at the moment the thermodynamic potentials of the two configurations are equal to one another. According to the experimental data (see, for example, Ref. 4), pinning occurs near the band gap. When the valence changes, the electrons therefore flow into the region near the L -point. It can be assumed, to a good degree of accuracy, that the thermodynamic potential of the valence and conduction bands changes only as a result of a change in the occupancy near the L -points, which play the role of reservoirs, therefore, for electrons from the s -level. The conditions for pinning can

then be determined by studying the thermodynamic potential of the system “ s -level + L -point.” The thermodynamic potential of the s -level is determined, by virtue of Eq. (1), by the formula

$$\Omega_s(n_s, \mu) = (\varepsilon_s - \mu)n_s + V_{ss}n_{s\sigma}n_{s-\sigma} + V_{sp}n_s \sum n_{\sigma}^{\nu} + \frac{1}{2}V_{pp} \sum n_{\sigma}^{\nu}n_{\sigma'}^{\nu'}$$

and the thermodynamic potential of the L -point is

$$\Omega_L = \int_0^{\mu} (\varepsilon - \mu)n_L(\varepsilon)d\varepsilon. \quad (3)$$

The thermodynamic potential of an s -level in different electronic configurations has the form

$$\begin{aligned} \Omega_{s0} &= 2(\varepsilon_s - \mu) + V_{ss} + 2V_{sp} \sum n_0 + \frac{1}{2}V_{pp} \sum n_0 n_0', \\ \Omega_{s1} &= (\varepsilon_s - \mu) + V_{sp} \sum n_1 + \frac{1}{2}V_{pp} \sum n_1 n_1', \\ \Omega_{s2} &= \frac{1}{2}V_{pp} \sum n_2 n_2'. \end{aligned} \quad (4)$$

Here μ is the chemical potential, $n_0(n_1, n_2)$ is the number of particles at an impurity site with a filled (singly and doubly ionized, respectively) s -level (the indices σ and ν are dropped for brevity), $n_L(\varepsilon) \sim \sqrt{\varepsilon}$ is the density of states near the L -point (the reading is made from the bottom of the conduction band), and μ is determined from the condition

$$(2 - n_s)c = \int_0^{\mu} n_L(\varepsilon)d\varepsilon, \quad (5)$$

where c is the number of impurity atoms transferred into the excited state. Stabilization occurs for values of μ , for which $\Delta\Omega_{\text{tot}} = 0$, where

$$\Delta\Omega_{\text{tot}} = \begin{cases} \Omega_L + c(\Omega_{s2} - \Omega_{s0}) & (\text{In}) \\ \Omega_L + c(\Omega_{s1} - \Omega_{s0}) & (\text{Ga}) \end{cases} \quad (6)$$

$$\Omega_L = -\frac{2}{5}\mu c(2 - n_s) = \begin{cases} -\frac{4}{5}\mu c & (\text{In}) \\ -\frac{2}{5}\mu c & (\text{Ga}) \end{cases} \quad (7)$$

By changing the energy of the bare s -level and the constants V_{ss} , V_{sp} , and V_{pp} by very small amounts, it is possible to place the values

$$\mu_{\text{pin}} = \begin{cases} \frac{(\Omega_{s2} - \Omega_{s0})_{\mu=0}}{1.2} & (\text{In}) \\ \frac{(\Omega_{s1} - \Omega_{s0})_{\mu=0}}{0.6} & (\text{Ga}) \end{cases} \quad (8)$$

in the band gap (for Ga) or at the bottom of the conduction band (for In).

INTERACTION OF ELECTRONS AT THE L -POINT WITH HOLES IN THE s -LEVEL

If an impurity atom in the semiconductor is in a nondominant configuration (s^1p^2 or s^0p^3), then there arises for the electrons in the bands an attractive potential due to the interaction of the electrons with deep holes in the s -level of the impurity. When this interaction force is sufficiently strong, it can be expected that a state in the band gap will be split off from the bottom of the conduction band at the L -point.

In the presence of an attractive potential at an impurity site the Green's function of the electrons near the L -point is determined by the standard equation

$$\tilde{G}_{kk'} = G_k \delta_{kk'} - G_k \sum_{k'' \in L} U_0 \tilde{G}_{k''k'} \quad (9)$$

Here all momenta lie near the L -point in k space, and the symbol $\sum_{k \in L}$ indicates summation over k near the L -point ($|k| < \Lambda$). To determine the level that is split off, it is necessary to solve the equation, taking into account the fact that the neighborhood of the L -point is described by the Dirac equation (see, for example, Ref. 6). Taking into account, to second order in perturbation theory, transitions of the type " L -point \rightarrow other points in the Brillouin zone," whose spectrum is quasi-one-dimensional,⁷ we easily find

$$U_0 = g + g^2/\xi \quad (10)$$

(the sign of U_0 is taken into account). Here $\xi \sim 6 - 10$ eV is the band gap, and g is the strength of the attractive potential in the model of quasi-one-dimensional bands. This potential is defined below.

If U_0 and the Green's function describing the neighborhood of the L -point are known, we can calculate the level that is split off:

$$\begin{pmatrix} \Delta_g - U_0 \delta(\mathbf{r}) & v \sigma \mathbf{p} \\ v \sigma \mathbf{p} & -\Delta_g \end{pmatrix} \Psi = E \Psi \quad (11)$$

Here v is a matrix element with the dimensions of velocity ($v \sim 10^8$ cm/s). For brevity, we have written the half width of the band gap in IV-VI semiconductors ($\varepsilon_g \approx 0.1 - 0.2$ eV) as $\Delta_g = 1/2\varepsilon_g$, and the short-range attractive potential is approximated by a δ function (the momenta are limited by the condition $|p| < \Lambda$, and this approximation will not lead to a divergence).

After the potential U_0 is introduced, there arise matrix elements which transfer an electron from the neighborhood of a given L -point into a neighborhood of any other L -point (thus far we have assumed that the four different L -points remain stationary). Since the perturbation that displaces the L -points is approximately the same as $U_0 \delta(\mathbf{r})$, equations of the type (11) for all L -points can be transformed into Eq. (11) with the constant U renormalized by a factor of 4.

SELF-CONSISTENT DETERMINATION OF THE CONSTANT g

To determine the constant g , the model of quasi-one-dimensional bands is adequate.⁷ The point is that, as will be shown below, g is determined by the total electron density at

an impurity site. The volume of a neighborhood of the L -point in phase space (and, correspondingly, the contribution to the density), however, is approximately $10^{-2} - 10^{-3}$ of the total volume of the Brillouin zone.

Introducing an attractive potential of the form $V_{ij} = -g \delta_{i0} \delta_{j0} \delta_{\sigma\sigma'} \delta_{\nu\nu'}$, where σ and σ' are spin indices, ν and ν' are band indices, i and j enumerate the sites, and $g > 0$ (the problem is similar to the work of Koster and Slater,⁸ but the semiconductor is described by a different model), it is not difficult to find the electron density at an impurity site as a function of g (see, for example, Ref. 9) and, knowing this density, to determine self-consistently [using the Hamiltonian (1)] the effective interaction potential between a hole in a deep s -level and the electrons in a band.

The terms

$$V_{sp} \sum_{\sigma} n_{s\sigma} \sum_{\nu, \sigma} n_{\sigma}^{\nu} + \frac{1}{2} V_{pp} \sum_{\sigma} n_{\sigma}^{\nu} n_{\sigma}^{\nu'} \quad (12)$$

correspond to the interaction of s and p electrons in Eq. (1). In the Hartree-Fock approximation the self-consistency equation in g is obtained from Eq. (12):

$$g = (2 - n_s) V_{sp} - 5 V_{pp} (n_{\sigma}^{\nu} - n_{0\sigma}^{\nu}) \quad (n_s = 0, 1), \quad (13)$$

where $n_{0\sigma}^{\nu}$ is the unperturbed density. Both the site electron density and the effective interaction constant g are determined from Eq. (13).

DETERMINATION OF THE SPLIT-OFF LEVEL

Using solution (13), we obtain from (11) an equation for E :

$$U \int \frac{d^3 p}{(2\pi)^3} \frac{E + \Delta_g}{E^2 - \Delta_g^2 - v^2 p^2} = -1. \quad (14)$$

The integration in Eq. (14) extends over the region $|p| < \Lambda$, $U = [(2\pi)^3 / V_B] 4U_0$, and U_0 is determined from Eq. (10). The minimum value of U , for which a solution of Eq. (14) exists, is

$$U_{\min} = \frac{(2\pi)^3 v^2}{4\pi \Lambda \epsilon_g} V_B. \quad (15)$$

For arbitrary energy

$$\frac{4\pi U}{(2\pi)^3} \frac{(\Delta_g + E)}{v^2} \left(\Lambda - \frac{\pi}{2} \frac{\sqrt{\Delta_g^2 - E^2}}{v} \right) = 1. \quad (16)$$

For $U \sim U_{\min}$ the level lies near the bottom of the conduction band. Then

$$E - \Delta_g = \Delta_g \frac{(U - U_{\min})^2}{2\lambda^2 U^2}. \quad (17)$$

Setting $\varepsilon_g \approx 0.2$, $v \sim 10^8$ cm/s, and $\Lambda^3 \sim 10^{-2} - 10^{-3} V_B$, the energy of the split off level is $\varepsilon = E - \Delta_g \approx 5 - 10$ meV. The radius of this state is $r \approx v/2\sqrt{\varepsilon_g \varepsilon} \approx 10^3$ Å. These values confirm the assumption made in Ref. 3 that a shallow bound state with an energy of the order of 60 K is present in the band gap of PbTe.

In conclusion, the large role of the intracenter Coulomb correlations (described by the constants V_{ss}, V_{sp}, V_{pp}) in the present model should be noted. The energy as a function of the occupation numbers has a local minimum at points corresponding to integers (configurations s^2p^1, s^1p^2 , and s^0p^3) only in the presence of these correlations. These configurations are separated by potential barriers. It is assumed that the slow relaxation phenomena are due to the presence of these barriers,⁴ if the deformation effects appearing near an impurity as a result of charge transfer on the impurity are assumed to be small. Moreover, the fact that the charge states depend mainly on the work function suggests that the pinning phenomenon should be used to determine experimentally the work function of materials with different chemical compositions (for example, by investigating the position of the pinning relative to the bands at the L -point it is possible to determine the contact potential difference in the series PbTe–SnTe).

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