CANCELATION THEOREM FOR ISOELECTRONIC IMPURITY BINDING ENERGIES

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Substitutional impurities in undeformed covalent crystals theoretically generate localized states with binding energies of order 1 eV even when the valence of the impurity is equal to that of the atom it has replaced. The weakness of observed binding energies is ascribed to lattice deformations. The observed binding energies are therefore identified as remnants of the original large binding energy.

Central-cell corrections to impurity binding energies are surprisingly small in covalent crystals. These corrections are observed as departures of 1s impurity binding energies E_{1s} from the continuum wave-packet value for ordinary donors or acceptors,

$$R_1 = m^*/m\epsilon_s^2 \text{ Ry}, \tag{1}$$

where m^* is an average band-edge effective mass and ϵ_s is the static dielectric constant. The normalized central-cell correction is defined by

$$d = (E_{1s} - R_1)/R_1. \tag{2}$$

Within the framework of continuum wave-packet theory Kohn and Luttinger identified[1] two mechanisms which contribute to d. One is breakdown of dielectric screening (in the central cell the effective value of $\epsilon_s \to 1$) and the other is mass enhancement at short wavelengths ($m^*/m \to 1$). Both mechanisms make positive contributions to d. A third mechanism, core polarization, was proposed by Hermanson and Phillips[2] to explain the very small and sometimes even negative values of d found for excitons and substitutional rare-gas impurities in solid rare gases. In contrast to the Kohn-Luttinger theory the Hermanson-Phillips approach yielded for the first time results for d in good agreement with experiment for a number of rare gases with no adjustable parameters.[3]

The solid rare gases are particularly simple because of the closed-shell character of the valence states. Faulkner[4] has recently carried out similar Slater-Koster calculations for isoelectronic impurities N in GaP. He finds that the energy of the particle bound to the isoelectronic impurity will typically be of order the smaller of two energies, the energy gap between valence and conduction band, or the conduction-band width, i.e., the binding energy should be of order 1 eV. (This would also hold for ordinary donors and acceptors.) The actual binding energy of GaP:N electrons[4,5] is only 8×10^{-3} eV, and of GaP:Bi holes[6] only 40×10^{-3} eV.

Two mechanisms have been suggested as important in determining the binding energies of isoelectronic impurities. One is the electronegativity difference[5] between the impurity and the host atom it replaces. All electronegativity tables[7] agree, however, that the difference in electronegativity between N and P is at least three times greater than that between P and Bi, whereas the binding energy of a hole to Bi is some five times greater than that of an electron to N. This suggests that the lattice deformation around the impurity is critical,[8] but no theory of this general deformation has been proposed.

In this note it is argued that under rather general conditions the lattice around an isoelectronic impurity deforms in such a way that the binding energy is not 1 eV but zero; to first order this explains the experimental results. We then examine the terms omitted from the model and compare with the observed trend in binding energies to identify the mechanism responsible for binding.

Assume that the potential $V(\vec{R})$ in the Wannier representation is short range and is characterized by a strength parameter $g > 0$:

$$V(\vec{R}) = g\varphi(\vec{R}), \tag{3}$$

where $\varphi(R) \gtrless 0$ for electrons or holes, respectively. Let the value of g at which the first bound state appears be g_c. Assume that $g = g_c$ and that the lattice is in its equilibrium (deformed) state around the impurity. Now increase g to $g_c + \delta g$, thereby increasing the binding energy from 0 to δE. The envelope wave function of the bound state for a spherical well has the form[9]

$$\psi = (\gamma/2\pi)^{\frac{1}{2}} e^{-\gamma r}/r, \tag{4}$$

$$\gamma = (2m^*\delta E/\hbar^2)^{1/2}. \tag{5}$$

The charge e_c^* in the central cell is

$$e_c^*/e = 2\gamma R, \tag{6}$$

where R is the radius of the central cell, defined so that $\frac{1}{3}4\pi R^3$ is the central cell volume.

Because of the fact that $e_c^* \neq 0$, the lattice will now deform further. We make three assumptions in order to characterize this deformation.

(I) The valence Wannier wave functions in the deformed lattice are such that each atomic cell outside the central cell remains effectively neutral. The only effect of lattice and valence polarization is to replace the potential $-e_c^*/r$ by $U(r) = -e_c^*/r\epsilon(r)$, where $\epsilon(r)$ is a dispersive dielectric function[10] which is bounded for all r and tends to ϵ_s as $r \to \infty$. (The least upper bound is actually only slightly larger than ϵ_s.)

(II) Neglect core-core or Born-Mayer closed-shell repulsive forces. These are small in semiconductors and metals such as Al or Na.[11]

(III) Neglect anisotropic screening corrections to $U(r)$ associated with umklapp terms described in the unstrained lattice by the response function $\epsilon(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$, where $\vec{G}$ and $\vec{G}'$ are reciprocal lattice vectors and $\vec{G} \neq \vec{G}'$. Although these terms represent bonding forces, they are small compared with the isotropic screening terms.[10,11]

Granted (I)-(III), we can conclude that $e_c^* < 0$ exerts an attractive force on each nucleus. For the specific case of N impurities in GaP, at $g = g_c$ the GaP lattice was already extended in the neighborhood of the impurity because Ga-N bonds are shorter than Ga-P bonds. A chemical survey of hydrostatic deformation potentials[12] at Γ_{15}^v (valence band edge), Δ_1^c, Γ_1^c, or L_1^c shows that the hydrostatic deformation potentials for electrons (holes) may be all positive (negative), corresponding to a diminution of g with lattice contraction for holes or lattice expansion for electrons. (Such deformation potentials describe, strictly speaking, only long-wavelength strains. Examination of pseudopotential form factors[13] shows, however, that so long as the wave numbers $\vec{q}$ associated with the strain are small compared with $2k_F$, the sign of the band-edge shift is determined by the sign of the $q = 0$ deformation potential.)

We conclude that because e_c^* induces further extension of GaP bonds, δg and thus δE are reduced, thereby reducing e_c^*. This process continues until $0 = U(r) = e_c^* = \delta E$. The lattice automatically deforms to reduce the binding energy to zero. The observed binding energies, of order 10^{-2} eV, represent the effect of small lattice forces described by (II) and (III).

One can estimate Born-Mayer forces from Hartree-Fock calculations[14] for He-Ne, He-Ar, and Ne-Ar. These show that α-core-β-core repulsive potentials can be closely approximated by

$$\varphi_{\alpha\beta}(r) = A_{\alpha\beta} e^{-\lambda(\alpha,\beta)r}. \tag{7}$$

The functional form (7) can also be used to fit the outermost core wave functions of each atom with $\lambda^* = \lambda^*(\alpha)$. A good representation of $A_{\alpha\beta}$ and $\lambda(\alpha,\beta)$ is obtained with

$$\lambda(\alpha,\beta) = \lambda^*(\alpha) + \lambda^*(\beta), \tag{8}$$

$$A_{\alpha\beta} = 2[E_c(\alpha)E_c(\beta)]^{1/2} n_\alpha n_\beta, \tag{9}$$

where λ^* is obtained by fitting Hartree-Fock-Slater atomic wave functions[15] and $E_c(\alpha)$ and n_α represent, respectively, the Hartree-Fock-Slater energy and number of least strongly bound core electrons.

The central qualitative conclusion that emerges from evaluation of (8) and (9) for Ga-α bonds (where α is a group-V element) is that the magnitude of the core-core forces increases rapidly with $l_c(\alpha)$, the angular momentum of the outermost core state of α. Thus $\lambda_{1s}^*(\mathrm{N}) = 5.10$, $\lambda_{2p}^*(\mathrm{P}) = 3.06$, $\lambda_{3d}^*(\mathrm{Ga}) = 1.38$, and $\lambda_{5d}^*(\mathrm{Bi}) = 1.52$. One now balances $U'(r)$ against the difference between Ga-P repulsive forces and Ga-α forces described by (7),

$$\frac{\partial}{\partial r}\left[\frac{3ee_c^*}{\epsilon(r)r}\right] = \frac{\partial}{\partial r}\left[\varphi_{\mathrm{Ga}\alpha}(r) - \varphi_{\mathrm{GaP}}(r)\right]. \tag{10}$$

From (10) one finds $e_c^*/e = 3\times10^{-4}$ for $\alpha = \mathrm{N}$ and 0.2 for $\alpha = \mathrm{Bi}$. On the other hand from (6) one estimates that $e_c^*/e = 0.1$ for $\alpha = \mathrm{N}$, and 0.2 for $\alpha = \mathrm{Bi}$.

We conclude that Born-Mayer forces may indeed be responsible for the remnant binding energy of 40×10^{-3} eV of holes in GaP:Bi, but that their contribution to binding electrons in GaP:N is negligible. In the latter case we believe anisotropic screening corrections could account for the observed binding. Umklapp terms in $\epsilon(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$ have yet to be calculated in detail. However, Martin has noted[11] that it is just the umklapp terms that give rise to "bond-charge" forces in his microscopic calculation of lattice vibration frequencies. From the difference in dielectric constants[7] between GaP and GaN it appears that e_c^*/e in GaP:N is about equal to the difference in bond charge Z_b between GaN and GaP, or about a quarter of the difference in charge $Z^* = 4Z_b$ between tetrahedrally bonded N and P atoms. If we allow for the effects of lattice distor-

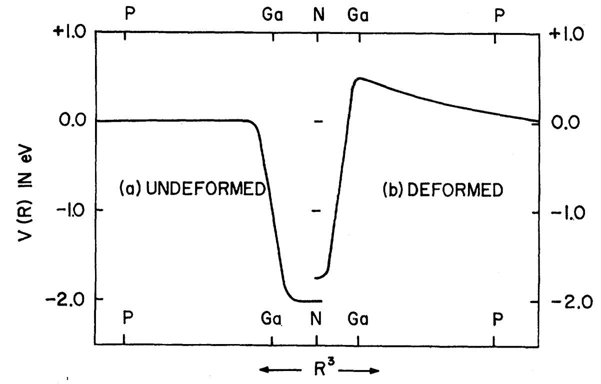

FIG. 1. A sketch of the additional crystal potential generated by a substitutional isoelectronic impurity in (a) an undeformed lattice and (b) a deformed lattice. The energies indicated (–2 eV in the central cell, +0.2 eV in neighboring cells) are meant to be representative but not accurate.

tion, which reduce e_c^*, then it appears that local-field or bond-charge effects may account for the binding of electrons in GaP:N.

To place the foregoing discussion on a quantitative basis requires a rather detailed knowledge of the lattice deformation around an impurity. We believe, however, that the mechanisms proposed here represent a preliminary explanation of the observed binding energies of substitutional isoelectronic impurities. Our model suggests that the form of $\varphi(\vec{R})$ is as shown in Fig. 1. In (a) we have the effective potential of the undistorted lattice, consisting of an attractive square well in the central cell generated by electronegativity differences. In (b) the lattice deformation has superimposed on this a repulsive potential varying approximately as $B|\vec{R}|^{-3}$. The magnitude of B is fixed by a self-consistency condition [such as (10) when (II) dominates]. The form of potential proposed in (b) can be checked by calculation[4] of recombination spectra of GaP:N_2. Also it appears that (b) provides a plausible explanation[16] for why (at least so far) all isoelectronic bound states have been observed for V impurities (in III-V crystals) or VI impurities (in II-VI crystals). For these cases the Bloch functions which multiply the X_1 band-edge envelope function ψ give greater weight to the attractive part of φ (centered on the V atom) than to the repulsive part. The converse holds for III or II impurities. The pure IV case (e.g., C or Sn in Si) is too delicate to be decided from general considerations.

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