Stress dependence of the metal-insulator transition in doped semiconductors

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The single-particle energy bands are calculated for a lattice of donors in many-valley semiconductors with a *moderately strong central-cell potential* using a pseudopotential constructed by the method of polarized orbitals. The variation of the metal-insulator transition with uniaxial stress is found to be in a direction *opposite* to that expected for effective-mass donors, as seen experimentally in phosphorus-doped silicon and arsenic-doped germanium.

Doped semiconductors are unique among random systems in that the metal-insulator (MI) transition in shallow impurity bands can be "tuned" by application of uniaxial stress readily available in the laboratory. This versatility arises from a strong coupling of the impurity band to a uniaxial strain field, and allows the study of the localization transition in a single sample of impurity density, n, as the density at the MI transition, n_{MI}, is swept through it.[1] Thus the physical properties (e.g., dc conductivity) of the system near n_{MI} can be explored in detail with greater control than using different samples[2] to vary n through n_{MI}.

Many calculations have recently been done[3–6] of a correlation-driven MI transition in a lattice of hydrogenic atoms, based on the ideas of Mott,[7] without radical simplifying assumptions as, e.g., in the Hubbard model.[8] Effects of disorder emphasized by Anderson,[9] which would modify n_{MI} somewhat, are not included. However, in a stress experiment, only the donor wave functions (and their overlap) are altered while the disorder is effectively held fixed; hence these calculations may yield relatively accurate results for the *variation* in n_{MI} with stress.[10] In fact, for effective-mass (em) donors in many-valley semiconductors (e.g., *Ge*:Sb) *the same result* is obtained[11] for the ratio of n_{MI} at high stress and the stress-free case, within both the Mott-Hubbard, and Anderson pictures of the MI transition.

Despite this simplification, these calculations cannot be readily applied to systems such as *Si*:P or *Ge*:As—the predicted increase in n_{MI} with uniaxial stress[11] is the reverse of the experimental situation.[1,12] This can be traced to the presence of a moderately strong central-cell potential which removes the degeneracy of the em ground state.[13] Here we investigate the case of a large central-cell splitting of the donor ground state, which persists even at $n \approx n_{MI}$. (Besides the stress variation of n_{MI}, evidence for this comes from Raman measurements on *Si*:P and *Ge*:As which exhibit the valley-orbit splitting for densities near, and even somewhat beyond n_{MI}.[14]) We show that in this case, using the method of polarized orbitals,[15] a calculation of the same degree of sophistication as for hydrogenic donors[6] is possible. The variation of n_{MI} with uniaxial stress comes out to be not only of the right sign, but of approximately the correct magnitude, for systems with moderate central-cell effects. In light of recent experiments,[1] calculations are presented for phosphorus-doped silicon; results for other donors in Si (or Ge) with a nondegenerate ground state can be computed similarly.

The idea, in brief, is as follows. Application of uniaxial stress mixes the ground state of the isolated donor with the somewhat more extended valley-orbit split excited states.[13] This, in turn, causes both a broadening of the occupied (D^+, or hole) band, and a lowering of the empty (D^-, or electron) band because of change in the effective potential due to the occupied band. Both these effects (the latter being the dominant) reduce n_{MI}, which is signaled by crossing of the D^+ and D^- bands.[16]

The envelope functions for the ground and excited states are assumed to have a spherically symmetric hydrogenic form with radii a_g and a_e, respectively.[17] Thus

$$\Psi_g(\vec{r}) = f_g(r) \sum_j \phi_j(\vec{r})/\sqrt{6} \;; \qquad \psi_e^\alpha = f_e(r) \sum_j A_j^\alpha \phi_j \;, \tag{1}$$

where $\phi_j(\vec{r}) \sim \exp(i\vec{k}_j \cdot \vec{r})$, $\vec{k}_j = \pm k_0\hat{x}, \pm k_0\hat{y}, \pm k_0\hat{z}$ are the Bloch waves at the conduction-band minima and $f_g(r) = (\pi a_g^3)^{-1/2}\exp(-r/a_g)$ and $f_e(r) = (\pi a_e^3)^{-1/2}\exp(-r/a_e)$ are the ground- and excited-state envelope functions, respectively. For the two excited states of interest the vectors A^α are $A^1 = (1, 1, -1, -1, 0, 0)/2$ and $A^2 = (1, 1, 1, 1 -2, -2)/\sqrt{12}$.

A uniaxial stress leads to a strain Hamiltonian H_ϵ with nonzero matrix elements[18]:

$$\langle \phi_x | H_\epsilon | \phi_x \rangle = \langle \phi_{-x} | H_\epsilon | \phi_{-x} \rangle = \Delta(2\epsilon_{xx} - \epsilon_{yy} - \epsilon_{zz}) \tag{2}$$

and permutations for $\phi_{\pm y}$ and $\phi_{\pm z}$, where 3Δ is the deformation potential and $\epsilon_{\mu\nu}$ the strain tensor. This mixes the wave functions Ψ_g and Ψ_e^α; restricting one-

self to this subspace, the total Hamiltonian matrix relative to the ground state energy in the unstrained crystal becomes

$$H - E_g I = \begin{pmatrix} 0 & \sqrt{3}\Delta\epsilon_1 & \sqrt{3}\Delta\epsilon_2 \\ \sqrt{3}\Delta\epsilon_1 & E_0 + \sqrt{3/2}\Delta\epsilon_2 & \sqrt{3/2}\Delta\epsilon_1 \\ \sqrt{3}\Delta\epsilon_2 & \sqrt{3/2}\Delta\epsilon_1 & E_0 - \sqrt{3/2}\Delta\epsilon_2 \end{pmatrix} . \quad (3)$$

$\epsilon_1 = (\epsilon_{xx} - \epsilon_{yy})/\sqrt{2}$ and $\epsilon_2 = (\epsilon_{xx} + \epsilon_{yy} - 2\epsilon_{zz})/\sqrt{6}$ are the orthorhombic and tetragonal strain components and E_0 is the energy of the excited states in the unstrained crystal relative to the ground state.

For small strains the ground-state wave function is given by

$$\Psi_g(\epsilon) \approx \langle \Psi_g(\epsilon) | \Psi_g \rangle \left[\Psi_g + \sqrt{3} \left(\frac{\Delta}{E_0} \right) \sum_{\alpha=1}^{2} \epsilon_\alpha \Psi_e^\alpha \right] . \quad (4)$$

We now come to the computation of the D^- band. The D^- state, in the one-electron picture, is the "outer" electron in a donor with two electrons. The outer electron sees very little of the central cell; thus the D^- state has the full valley degeneracy of 6. Because of this, as it hops from site to site it is unlikely to encounter a donor with an inner electron possessing the same spin and valley quantum number. Consequently, the exchange repulsion may be ignored, and the appropriate D^- bandwidth is that for a "ferromagnetic" configuration of the occupied donor levels.[6]

The effective one-electron pseudopotential for the D^- band $V(r)$ is determined by adding to the Hartree term

$$U_0(r) = \int d^3r' |\Psi_g(\vec{r}')|^2 v(\vec{r}, \vec{r}') , \quad (5)$$

the second-order shift in the energy of the inner electron ($\vec{r}'$);

$$U_2(r) = -\langle \Psi_g | v (H - E_g)^{-1} v | \Psi_g \rangle , \quad (6)$$

where $v(\vec{r}, \vec{r}') = (2/|\vec{r}' - \vec{r}| - 2/r)$ is the perturbation due to the outer electron ($\vec{r}$).

By allowing for the virtual excitation of the inner electron to a p state, this "polarized orbitals" method[15] yields the asymptotically exact $U(r)$ both for $r \to \infty$ and 0, and gives a binding energy for the D^- ion within 0.01 Ry.[6] Further, we find that it is readily generalized to the many-valley finite central-cell case, and for the wave function (4), the potential U can be evaluated analytically. This is because (i) the interaction $v(\vec{r}, \vec{r}')$, being a long-range one, does not mix different valleys; and (ii) the intermediate p state in Eq. (6) has no amplitude at the impurity site. Consequently $(H - E_g)^{-1}$ is effectively diagonal in valley space, despite the central-cell potential. We thus obtain

$$U(r) = |\langle \Psi_g(\epsilon) | \Psi_g \rangle|^2 \left[u_g(r) + 3(\Delta^2/E_0^2) \left(\sum_{\alpha=1}^{2} \epsilon_\alpha^2 \right) u_e(r) \right] \quad (7)$$

with

$$u(r) = -2e^{-2x}(1+x)a_0/r - x^{-4}[9/2 - e^{-2x}(9/2 + 9x + 9x^2 + 6x^3 + 3x^4 + 2x^5/3)] . \quad (8)$$

Here $x = r/a_g$ for u_g and r/a_e for u_e; a_0 is the em Bohr radius and u is in em Rydbergs.

We compute the position of the D^- band by approximating the Wigner-Seitz cell of volume n^{-1} around each donor by a sphere [radius $r_{WS} = (3/4\pi n)^{1/3}$]. The total potential is the sum of $U(r)$ due to the central and the neighboring donors. For the latter, we take a uniform distribution of donors outside r_{WS}, with density n, leading to a potential $V(r) = n \int_{r_{WS}}^{\infty} d^3r' \, U(\vec{r} - \vec{r}')$. The bottom of the D^- band is then given by the energy of the nodeless solution to the radial Schrödinger equation in the potential $[U(r) + V(r)]$ with the boundary condition of zero derivative at r_{WS}.

Turning next to the D^+ band, we note that a moderately strong central cell leads to a marked reduction in the bandwidth. This effect is similar to the reduction of the exchange interaction between donor pairs,[19] and is due to the phase mismatch of different Bloch waves at neighboring donor sites. Specifically, for the wave function (1), the transfer integral between sites a distance $\vec{R} = (X, Y, Z)$ apart is given by

$$T_0(\vec{R}) = \tfrac{1}{3}(\cos k_0 X + \cos k_0 Y + \cos k_0 Z) T_g(R) , \quad (9)$$

where $T_g(R) = 2(1 + R/a_g)\exp(-R/a_g)$ is the transfer integral for the envelope function f_g in em Rydbergs.[20] The rapid oscillations of the cosine factors (on the scale of the lattice spacing) imply an averaging of $T_0(\vec{R})$ for even *very small randomness.* Consequently the bandwidth [$\propto |T_0(\vec{R})|$ in a tight-binding description] is reduced relative to the corresponding hydrogenic case by a factor[19]

$$\langle |T(\vec{R})| \rangle / T_g(R) = \langle |\cos k_0 X + \cos k_0 Y + \cos k_0 Z| \rangle / 3 \approx 0.33 . \quad (10)$$

There is a further reduction, by a factor ≈ 0.75 due to the antiferromagnetic arrangement of the donors in the ground state.[6] These reductions in bandwidth, which carry through for strain-induced

changes, imply that the variation in n_{MI} with strain is dominated by the D^- band for which there is neither a phase mismatch dictated by the central cell, nor the spin-flip scattering effect.

Since we are interested in only the energy gap between the D^+ and D^- bands, we incorporate diagonal shifts of the D^+ band in the D^- band energy. These include (a) a lowering of the energy to form a hole by $V(0)$ because the ionized donor left behind polarizes the lattice, and (b) the lowering of the isolated donor energy due to strain [$\delta E = -3\Delta^2(\epsilon_1^2+\epsilon_2^2)/E_0$ to lowest order]. Then with the reduced bandwith of the D^+ band, we may use the change in transfer integral to compute the *relative* broadening due to strain (as in a tight-binding description), without affecting results much.[21] For the wave function (4), after averaging over the phase factors, this relative broadening is given to quadratic order in ϵ_i by

$$\langle |T_\epsilon(\vec{R})|\rangle / \langle T_0(\vec{R})|\rangle - 1 = 3(\Delta/E_0)^2[T_e(R)/T_g(R)-1](\epsilon_1^2+\epsilon_2^2) \ , \quad (11)$$

where T_g and T_e are the transfer integrals for the ground- and excited-state envelope functions.

The calculated energy bands near the *MI* transition for *Si*:P are shown in Fig. 1 for various values of the strain parameter $\epsilon = (\Delta/E_0)(\epsilon_1^2+\epsilon_2^2)^{1/2}$. The following input parameters[2,22] have been used: 1 Ry = 31.3 meV, $E_0 = 13.1$ meV, $a_e = a_0 = 20$ Å, $a_g = 0.82a_e$, and

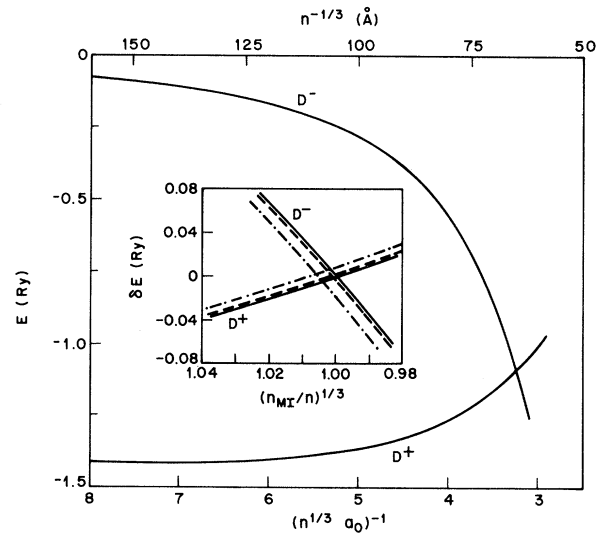

FIG. 1. The bottom of the electron (D^-) and top of the hole (D^+) band for Si:P as a function of donor separation ($n^{-1/3}$). Inset: Region near n_{MI} enlarged for different values of strain (solid lines, $\epsilon = 0$; dashed line, $\epsilon = 0.07$; dot-dashed line, $\epsilon = 0.14$).

$n_{MI}(\epsilon = 0) = 3.7 \times 10^{18}$ cm^{-3}. (The tight-binding band is for a simple cubic lattice; results for bcc and diamond structures are virtually identical.[21]) The change in n_{MI} is quadratic for small ϵ,[23] and is easily shown to be

$$\delta n/n_{MI} = -3\epsilon^2(R_-/r_-)[1+(E_D+/E_{D-})(R_+/R_-)][1+(E_{D+}/E_{D-})(r_+/r_-)]^{-1} \ , \quad (12)$$

where $2E_{D+}$ is the D^+ bandwidth and E_{D-} is the isolated D^- state energy relative to the bottom of the D^- band discussed above. $R_\pm = (1/E_{D\pm}) \times (\partial E_{D\pm}/\partial\epsilon^2)$ and $r_\pm = (n_{MI}/E_{D\pm})(\partial E_{D\pm}/\partial n)$. Using *only relative* values for the D^+ bandwidth, we find $R_-/r_- \approx 0.4$, while $R_+/R_- \approx r_+/r_-$ within 20%, so $\delta n/n_{MI}$ is not sensitive to the ratio E_{D+}/E_{D-}. We therefore use the nominal value (Fig. 1). Using the elastic constant $(c_{11}-c_{12}) = 1.026 \times 10^{12}$ dyn cm^{-2} and $\Delta = 2.7$ eV for Si,[22] Eq. (12) implies that for a 3% change in n_{MI}, a stress $S \approx 2$ kbar in a plane normal to the (111) axis [e.g., $(1\bar{1}0)$] is necessary. This is in reasonable agreement with the experimentally required stresses of 2–6 kbar to convert insulating samples believed to be within 5% of n_{MI} into metals. More detailed comparison is precluded on the one hand by the experimental uncertainty in δn and on the other by the limit applicability of the lowest-order expression, Eq. (12). The agreement between theory and experiment on this scale is nevertheless encouraging, especially in light of the opposite sign expected for em donors, and validates the basic idea behind the calculation. Inclusion of higher-order terms in the strain and mixing of excited states by the potentials of neighboring donors would both increase the calculated stress needed for a given change in n_{MI}, and thus shift the theoretical result in the direction of experiment.

Thus a calculation of the variation of n_{MI} with uniaxial stress in multivalley semiconductors with a moderately strong central-cell potential is in fairly good agreement with experimental results on *Si*:P. This indicates that central-cell effects are nonnegligible even at densities $\approx n_{MI}$, as seen in Raman scattering. Experimental study of other donors in silicon and germanium, as well as a theoretical treatment to include higher-order terms in the (nonlinear) stress variation of n_{MI}, are called for to further check the above ideas.

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[21]The absolute magnitude of the bandwidth for Fig. 1 is determined by requiring that the energy gap vanish at the *experimental* n_{MI} in the stress-free case; this requires ≈15% adjustment of the tight-binding bandwidth for sc, bcc, and diamond structures.

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