# Direct-band-gap structure of uniaxial-stressed $Si_xGe_{1-x}$/Ge [111] strained-layer superlattices

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The effects of both internal strain due to lattice mismatch and externally applied [111] uniaxial stress on $Si_xGe_{1-x}$/Ge [111] superlattices are predicted. In an $N_{Si}\times N_{Ge}$ $Si_xGe_{1-x}$/Ge [111] superlattice, the composition $x$ can always be chosen so that the superlattice conduction-band minimum is Ge derived. Then the Ge conduction-band minimum at $\mathbf{k}_L=(\pi/a_{Ge})$ (1,1,1) can be folded to the zone center with suitable choices of $N_{Si}$ and $N_{Ge}$, permitting the crystal-momentum selection rule for luminescence to be satisfied for the folded (1,1,1) minimum in the superlattice. However, internal strains raise the energy of the folded (1,1,1) conduction-band minimum relative to the unfolded $L$ minima at $(1,-1,-1)$, $(-1,1,-1)$, and $(-1,-1,1)$, causing the unfolded minima to be the lowest-energy conduction-band states into which injected electrons thermalize—and reinstating the selection rules against luminescence. Nevertheless, application of a [111] uniaxial stress of sufficient magnitude will overcome the internal strain, will make the folded (1,1,1) $L$ minimum (which has significant $s$ character) the lowest-energy conduction-band minimum, and will cause the Ge quantum wells in the superlattice to luminesce. These results obtained with use of the zone-folding approximation also hold when the electronic structure of the superlattice is evaluated properly.

## I. INTRODUCTION

Future generations of high-speed computers are likely to compute electronically, but communicate optically between chips, making it necessary to develop electro-optic materials that can convert electrical signals into light. Since silicon-processing technology is highly advanced over most other electronic-materials technologies, a silicon-based light emitter could play a central role in making Si compatible with electro-optics device applications. Bulk Si itself does not emit light, because its band structure is indirect: electrons injected into the conduction band thermalize to the indirect band minima at $(2\pi/a_{Si})$ (0.85, 0, 0), near the $X$ points of the Brillouin zone, while holes rise to the valence-band maximum at the zone center—leading to a situation such that an electron with finite crystal momentum and a hole of zero momentum cannot recombine to emit light (which has near-zero momentum) because of a selection rule. Superlattices of $Si_xGe_{1-x}$ and Ge, despite the fact that neither $Si_xGe_{1-x}$ nor Ge is a direct-gap-band-semiconductor, appear to offer some promise of circumventing this problem, because the simplest approximation to the band structure of the superlattice, the zone-folding approximation, produces a superlattice conduction-band minimum at or near the zone center, $\mathbf{k}_\Gamma=(0,0,0)$. In this paper we show that a direct band-gap electronic structure can occur for $Si_xGe_{1-x}$/Ge [111] superlattices.

## II. BAND OFFSET

Since the value of the valence-band offset (*extrapolated to unstrained conditions*) of Si/Ge superlattices is somewhat controversial,[1-6] we consider two models here: (i) one assuming a 0.2-eV offset and a band alignment such that the Ge conduction-band edge lies below that of $Si_xGe_{1-x}$ and (ii) a 0.455-eV offset, with the Ge conduction-band minima above those of Si (see Sec. V F). For $x=1$, namely, Si/Ge [111] superlattices, provided that the valence-band offset is less than 0.4 eV, the conduction-band minima of Ge will lie lower than those of Si (type-I alignment); but for an offset greater than 0.4 eV, the conduction-band alignment will be type II, with the superlattice conduction-band minimum being Si-like. The essential physics of this paper requires only that the stressed superlattice's conduction-band minimum be Ge derived: the band offset of [111] $Si_xGe_{1-x}$/Ge must be such that the conduction-band minima of stressed Ge lie below those of $Si_xGe_{1-x}$ (type-I alignment). Although this might not turn out to be the case for $x=1$ unstressed [111] Si/Ge, it certainly will be true for a sufficiently large applied stress, or for a range of compositions $x$ for unstressed $Si_xGe_{1-x}$/Ge [111] superlattices. Therefore, for simplicity of presentation, we illustrate our physical ideas first with calculations for Si/Ge superlattices, assuming a small offset of 0.2 eV (Ref. 2) and type-I alignment, while recognizing that a fully quantitative descrip-

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tion of these materials must await the final determination of [111] band offsets. All of the qualitative physics of the 0.2-eV-offset case will still hold for [111] $Si_xGe_{1-x}$/Ge superlattices, provided that the composition $x$ is chosen such that the conduction-band edge of stressed Ge lies below that of $Si_xGe_{1-x}$, as we also demonstrate in Sec. V F for an assumed Si/Ge offset of 0.455 eV, for $x=0.6$, and for a uniaxially stressed superlattice.

## III. QUALITATIVE PHYSICS

A perfect Si/Ge superlattice will luminesce if the fundamental band gap of the superlattice is direct: namely, if the conduction-band minimum lies at the same wave vector as the valence-band maximum (normally $\mathbf{k}=\mathbf{0}$). To determine if luminescence is possible, one must compute the band structure of the superlattice. An estimate of the superlattice band structure can be easily obtained in the zone-folding approximation, in which case the band structures of bulk Si and Ge are merely folded in $\mathbf{k}$ space to reflect the larger unit cell and smaller (mini-) Brillouin zone in the superlattice growth direction. The zone-folding approximation provides a qualitative estimate of the band structure which is very useful for thinking about the physics of superlattices, but is rarely quantitatively reliable. Therefore we shall employ the zone-folding approximation in discussing the physics of Si/Ge superlattices, but we shall confirm the conclusions obtained using the zone-folding approximation with a complete calculation of the superlattice electronic structure.

The most common superlattices are grown in the [001] direction,[7,8] in which case Brillouin-zone folding cannot easily map two of the six relative conduction-band minima of bulk Si near the $X$ point of the Brillouin zone to wave vectors near the zone center, because the minima are not exactly at the $X$ point. In bulk Ge the conduction-band minima are exactly at the $L$ points, equivalent to $(\pi/a_{\mathrm{Ge}})$ (1,1,1), not near the $X$ point, and so the lowest folded conduction-band minimum of the [001] superlattice is not at the zone center either. However, in a [111] 1×1 superlattice (alternating two-atom-thick layers of Si and Ge (Ref. 9) grown in the [111] direction), the Ge band structure in the [111] direction is folded in half, mapping the conduction-band minimum of bulk Ge at the $L$ point into the zone center for this superlattice (see Fig. 1). (Such folding can also be achieved with larger-period superlattices by suitably choosing the thicknesses of the Ge and Si layers. If the total number of the two-atom-thick layers is even, for example, 1×3 and 2×2 but not 1×2, Si/Ge superlattices will achieve the desired zone folding.) Thus one of the four conduction-band minima has the same crystal momentum as the valence-band maximum and light emission is possible—in principle. However, bulk Ge has a larger lattice constant than Si by about 4%, and so the Ge layers in a 1×1 Si/Ge strained-layer superlattice will be compressed and sheared (a positive shear strain as well as a compressive dilational strain), and the shear will raise the energy of the folded (1,1,1) $L$ valley of this band structure relative to the unfolded $L$ valleys in the (1,−1,−1), (−1,1,−1), and (−1,−1,1) directions—making the superlattice an indirect-gap semiconductor once more.

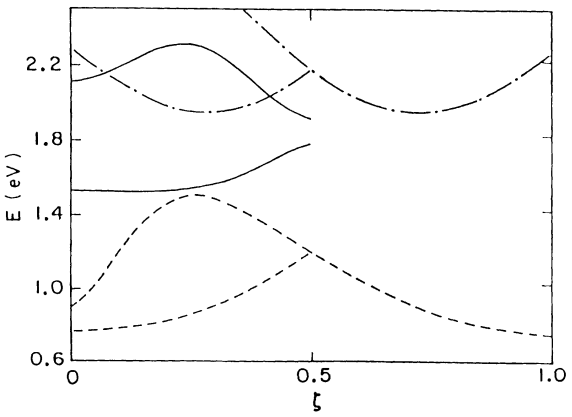


FIG. 1. Illustration of the zone-folding approximation for the lowest conduction-band state of an unstrained 1×1 Si/Ge superlattice: the computed conduction band (in eV) vs reduced wave vector $\zeta$ in the [111] direction, where we have $\mathbf{k}=(\pi/a_L)(\zeta,\zeta,\zeta)$ and $a_L$ is the relevant lattice constant. The bulk Ge band and its folding are denoted by dashed lines; comparable results for Si are chained. The computed superlattice band structure is denoted by solid lines—and differs significantly from the band structure obtained by the zone-folding approximation. The band offset is assumed to be 0.2 eV.

This internal shear strain of the superlattice can be overcome, however, by the application of a [111] uniaxial stress, as we show here, establishing the folded (1,1,1) $L$ minimum as the conduction-band minimum, lower in energy than the other three $L$ minima. Furthermore, we shall show that this minimum has significant Ge $s$ character, in contrast to the $p$ character of the valence-band maximum, suggesting that luminescence involving electrons confined in a Ge quantum well of a Si/Ge superlattice should be reasonably strong.

In Sec. IV we develop a theory of the electronic structure of such [111] superlattices, based on an empirical tight-binding scheme.[10] Although theoretical studies of [001] Si/Ge superlattices have been reported,[6,11] we believe that this is the first calculation of its sort for [111] Si/Ge superlattices. In Sec. V we present our main results and show that the qualitative physics of the zone-folding approximation holds when the superlattice band structure is evaluated properly. Section VI summarizes our findings.

## IV. FORMALISM

### A. Tight-binding Hamiltonian for the unstrained [111] superlattice

We treat a periodic Ge/Si superlattice whose layers are perpendicular to the [111] direction, with respect to the usual cubic axes. We employ a nearest-neighbor tight-binding Hamiltonian with an $s^*sp^3$ basis[10] of five orbitals centered on each atomic site. The superlattice we consider has $N_{\mathrm{Ge}}$ two-atom-thick Ge layers and $N_{\mathrm{Si}}$ two-atom-thick Si layers repeated periodically. The tight-binding Hamiltonian has a block-tridiagonal form as shown on p. 4. Here we have $k=2N_{\mathrm{Ge}}$, $L=2(N_{\mathrm{Ge}}+N_{\mathrm{Si}})$, and all the

$\underline{H}(m,n)$ for $m=1,2,\ldots,L$, and $n=1,2,\ldots,L$ are $5\times5$ matrices. $\underline{0}$ is the $5\times5$ null matrix.

The matrices $\underline{H}(n,n)$ are diagonal:

$$\underline{H}(n,n)=\begin{bmatrix} E_s* & 0 & 0 & 0 & 0 \\ 0 & E_s & 0 & 0 & 0 \\ 0 & 0 & E_p & 0 & 0 \\ 0 & 0 & 0 & E_p & 0 \\ 0 & 0 & 0 & 0 & E_p \end{bmatrix},$$

where $E_s*$, $E_s$, and $E_p$ are tight-binding parameters for Ge or Si, depending on whether $n$ refers to Ge or Si, of Vogl *et al.*[10] To account for the valence-band-edge discontinuity of $|\Delta E_{\rm VB}|$,[2] a constant $-|\Delta E_{\rm VB}|$ is added to the energies $E_s*$, $E_s$, and $E_p$ for Si. This constant causes the valence-band maximum of Si to be $|\Delta E_{VB}|$ below the valence-band maximum of Ge.

Here we are, in effect, assuming that this band-offset $\Delta E_{\rm VB}$ is independent of strain, an effect that has been discussed by Priester *et al.*[12] We do, however, include the effects of strain in the Hamiltonian using elasticity theory (see below), and so we do compute a superlattice band edge that does depend on the strain. The philosophy guiding this work is that the band offset and its dependence on strain are parameters whose precise values can be determined experimentally, and do not affect the qualitative conclusions of this work.

The off-diagonal matrices $\underline{H}(m,n)$, with $m\neq n$, have three different forms. The first is $\underline{H}(m+1,m)$, where $m$ is an odd number; here both $m$ and $n$ refer to sites in the same materials:

$$\underline{H}(m+1,m)=\begin{bmatrix} 0 & 0 & -C_0V_6 & -C_0V_6 & -C_0V_6 \\ 0 & C_0V_1 & -C_0V_4 & -C_0V_4 & -C_0V_4 \\ C_0V_7 & C_0V_5 & C_0V_2 & C_0V_3 & C_0V_3 \\ C_0V_7 & C_0V_5 & C_0V_3 & C_0V_2 & C_0V_3 \\ C_0V_7 & C_0V_5 & C_0V_3 & C_0V_3 & C_0V_2 \end{bmatrix}.$$

Here we have $C_0=g_0^*$, where we have $4g_0=\exp(i\mathbf{k}\cdot\mathbf{x}_0)$, where we have $\mathbf{x}_0=(a_L/4)(1,1,1)$, with $a_L$ being the lattice constant of either Si or Ge, whichever is relevant, and $\mathbf{k}$ being the wave vector, respectively. In addition, we have

$$V_1=V(s,s)\,,$$
$$V_2=V(x,x)\,,$$
$$V_3=V(x,y)\,,$$
$$V_4=V(sa,pc)\,,$$
$$V_5=V(sc,pa)\,,$$
$$V_6=V(s^*a,pc)\,,$$

and

$$V_7=V(s^*c,pa)\,,$$

in the notation of Vogl *et al.*[10] The parameters of Ge are used for $m<2N_{\rm Ge}$, and Si parameters are employed for the case $2N_{\rm Ge}<m<2(N_{\rm Ge}+N_{\rm Si})$.

The second form of off-diagonal matrix is $\underline{H}(m+1,m)$, where $m$ is an even number:

$$\begin{bmatrix} 0 & 0 & V_6(g_1-g_2-g_3) & V_6(-g_1+g_2-g_3) & V_6(-g_1-g_2+g_3) \\ 0 & V_1(g_1+g_2+g_3) & V_4(g_1-g_2-g_3) & V_4(-g_1+g_2-g_3) & V_4(-g_1-g_2+g_3) \\ -V_7(g_1-g_2-g_3) & -V_5(g_1-g_2-g_3) & V_2(g_1+g_2+g_3) & V_3(-g_1-g_2+g_3) & V_3(-g_1+g_2-g_3) \\ -V_7(-g_1+g_2-g_3) & -V_5(-g_1+g_2-g_3) & V_3(-g_1-g_2+g_3) & V_2(g_1+g_2+g_3) & V_3(g_1-g_2-g_3) \\ -V_7(-g_1-g_2+g_3) & -V_5(-g_1-g_2+g_3) & V_3(-g_1+g_2-g_3) & V_3(g_1-g_2-g_3) & V_2(g_1+g_2+g_3) \end{bmatrix}.$$

In the case $m=2N_{\rm Ge}$, one is treating an interface between a Ge layer and a Si layer, the parameters are taken to be an average of the corresponding parameters for Ge and Si. Here we have

$$4g_1=\exp(i\mathbf{k}\cdot\mathbf{x}_1)\,,$$
$$4g_2=\exp(i\mathbf{k}\cdot\mathbf{x}_2)\,,$$

and

$$4g_3=\exp(i\mathbf{k}\cdot\mathbf{x}_3)\,.$$

Here we have $\mathbf{x}_1=(a_L/4)(1,-1,-1)$, $\mathbf{x}_2=(a_L/4)(-1,1,-1)$, and $\mathbf{x}_3=(a_L/4)(-1,-1,1)$.

The third form corresponds to another interface: $\underline{H}(L,1)$, where $L=2(N_{\rm Ge}+N_{\rm Si})$.

$$\begin{bmatrix} 0 & 0 & V_6(C_1-C_2-C_3) & V_6(-C_1+C_2-C_3) & V_6(-C_1-C_2+C_3) \\ 0 & V_1(C_1+C_2+C_3) & V_4(C_1-C_2-C_3) & V_4(-C_1+C_2-C_3) & V_4(-C_1-C_2+C_3) \\ -V_7(C_1-C_2-C_3) & -V_5(C_1-C_2-C_3) & V_2(C_1+C_2+C_3) & V_3(-C_1-C_2+C_3) & V_3(-C_1+C_2-C_3) \\ -V_7(-C_1+C_2-C_3) & -V_5(-C_1+C_2-C_3) & V_3(-C_1-C_2+C_3) & V_2(C_1+C_2+C_3) & V_3(C_1-C_2-C_3) \\ -V_7(-C_1-C_2+C_3) & -V_5(-C_1-C_2+C_3) & V_3(-C_1+C_2-C_3) & V_3(C_1-C_2-C_3) & V_2(C_1+C_2+C_3) \end{bmatrix}.$$

$$
\begin{array}{|cccccccccccccccccc|}
\underline{H}(1,1) & \underline{H}(1,2) & \underline{0} & \underline{0} & \cdots & & & & & & & & & & & & \underline{0} & \underline{H}(1,L) \\
\underline{H}(2,1) & \underline{H}(2,2) & \underline{H}(2,3) & \underline{0} & \cdots & & & & & & & & & & & & \underline{0} & \underline{0} \\
\underline{0} & \underline{H}(3,2) & \underline{H}(3,3) & \underline{H}(3,4) & & & & & & & & & & & & & \underline{0} & \underline{0} \\
\underline{0} & \underline{0} & \underline{H}(4,3) & \underline{H}(4,4) & & & & & & & & & & & & & \underline{0} & \underline{0} \\
\underline{0} & \underline{0} & \underline{0} & \underline{H}(5,4) & & & & & & & & & & & & & \underline{0} & \underline{0} \\
 & & & & \ddots & & & & & & & & & & & & \vdots & \vdots \\
 & & & & & \underline{H}(k,k-1) & \underline{H}(k,k) & \underline{H}(k,k+1) & & & & & & & & & \underline{0} & \underline{0} \\
 & & & & & \underline{0} & \underline{H}(k+1,k) & \underline{H}(k+1,k+1) & \underline{H}(k+1,k+2) & & & & & & & & \underline{0} & \underline{0} \\
 & & & & & \underline{0} & \underline{0} & \underline{H}(k+2,k+1) & \underline{H}(k+2,k+2) & \underline{H}(k+2,k+3) & & & & & & & \underline{0} & \underline{0} \\
 & & & & & & & & & & \ddots & & & & & & \vdots & \vdots \\
 & & & & & & & & & & & \underline{H}(L-1,L-2) & \underline{H}(L-1,L-1) & \underline{H}(L-1,L) & & & \underline{0} & \underline{0} \\
 & & & & & & & & & & & \underline{0} & \underline{H}(L,L-1) & \underline{H}(L,L) & & & \underline{0} & \underline{0} \\
\underline{0} & \underline{0} & \underline{0} & \underline{0} & \cdots & & & & & & & & & & & & \underline{0} & \underline{0} \\
\underline{H}(L,1) & \underline{0} & \underline{0} & \underline{0} & \cdots & & & & & & & & & & & & \underline{0} & \underline{H}(L,L)
\end{array}
$$

The parameters are also taken from the average of the corresponding parameters of Ge and Si, and here we have $C_i = g_i^*$.

This Hamiltonian for $N_{\mathrm{Si}}=0$ will give exactly the same band structure as obtained from the Ge tight-binding Hamiltonian of Vogl *et al.*; for $N_{\mathrm{Ge}}=0$ it will give the band structure of Si. Spin-orbit splitting ($\simeq 0.3$ eV) is not included here because it is small and affects primarily the valence band, whereas the essential physics of this paper concerns the conduction-band minimum of the superlattice, its $L$ parentage, and its dependence on strain.

### B. Internal strain

Si/Ge superlattices are not perfectly lattice matched, however, and so internal strains cause the atoms to move from the perfect-lattice sites and to change the bond lengths and angles between nearest-neighbor atoms. These altered bond lengths and angles lead to modifications of the strain-free Hamiltonian. To determine these modifications, we first obtain expressions for the dilation $\Delta$ and the shear $\epsilon$ in both Si and Ge layers, and then we express the bond lengths of atoms in the strained superlattice as functions of the dilation and shear.

The dilation and shear result from internal strains due to the difference of Ge and Si lattice constants: the lattice constant of Ge, $a_{\mathrm{Ge}}$, is 5.66 Å, about 4% larger than the lattice constant of Si, $a_{\mathrm{Si}}=5.43$ Å.[13] In [111] Ge/Si superlattices, the in-plane lattice constant of Ge, $a_{\parallel\mathrm{Ge}}$, and the in-plane lattice constant Si, $a_{\parallel\mathrm{Si}}$, should be equal to each other:

$$a_{\parallel\mathrm{Ge}} = a_{\parallel\mathrm{Si}}$$

But we have

$$a_{\parallel\mathrm{Ge}} = a_{\mathrm{Ge}}(1+\Delta_{\mathrm{Ge}}-\epsilon_{\mathrm{Ge}})$$

and

$$a_{\parallel\mathrm{Si}} = a_{\mathrm{Si}}(1+\Delta_{\mathrm{Si}}-\epsilon_{\mathrm{Si}}) ,$$

where we have $\Delta = u_{xx} = u_{yy} = u_{zz}$, which is the dilational strain, and $\epsilon = u_{xy} = u_{yz} = u_{zx}$, which is the shear strain.

Because there is dilation and shear in both the Ge and the Si layers, the elastic energies $W$ of both types of layers increase:[14]

$$\begin{aligned} W_{\mathrm{Ge}} &= (\tfrac{1}{2})c_{1111,\mathrm{Ge}}(u_{xx}^2+u_{yy}^2+u_{zz}^2) \\ &\quad + c_{1122,\mathrm{Ge}}(u_{xx}u_{yy}+u_{yy}u_{zz}+u_{zz}u_{xx}) \\ &\quad + 2c_{1212,\mathrm{Ge}}(u_{xy}u_{xy}+u_{yz}u_{yz}+u_{zx}u_{zx}) \\ &= (\tfrac{3}{2})(c_{11,\mathrm{Ge}}+2c_{12,\mathrm{Ge}})\Delta_{\mathrm{Ge}}^2 + 6c_{44,\mathrm{Ge}}\epsilon_{\mathrm{Ge}}^2 . \end{aligned}$$

A similar expressions holds for Si. The elastic stiffness constants[15] $c_{11}$, $c_{12}$, and $c_{44}$ have been tabulated for Ge and Si.[16]

The total elastic energy of the superlattice is

$$W = N_{\mathrm{Ge}}W_{\mathrm{Ge}} + N_{\mathrm{Si}}W_{\mathrm{Si}} .$$

By minimizing the total elastic energy of the superlattice subject to the constraint

$$a_{\mathrm{Ge}}(1+\Delta_{\mathrm{Ge}}-\epsilon_{\mathrm{Ge}})=a_{\mathrm{Si}}(1+\Delta_{\mathrm{Si}}-\epsilon_{\mathrm{Si}}) ,$$

for fixed layer thicknesses $N_{\mathrm{Ge}}$ and $N_{\mathrm{Si}}$, we determine $\Delta_{\mathrm{Ge}}$, $\Delta_{\mathrm{Si}}$, $\epsilon_{\mathrm{Ge}}$, and $\epsilon_{\mathrm{Si}}$:

$$\epsilon_{\mathrm{Si}}=D_{11}(a_{\mathrm{Ge}}-a_{\mathrm{Si}})/D ,$$

$$\epsilon_{\mathrm{Ge}}=-D_{12}(a_{\mathrm{Ge}}-a_{\mathrm{SI}})/D ,$$

$$\Delta_{\mathrm{Ge}}=-4c_{44,\mathrm{Ge}}\epsilon_{\mathrm{Ge}}/(c_{11,\mathrm{Ge}}+2c_{12,\mathrm{Ge}}) ,$$

and

$$\Delta_{\mathrm{Si}}=-4c_{44,\mathrm{Si}}\epsilon_{\mathrm{Si}}/(c_{11,\mathrm{Si}}+2c_{12,\mathrm{Si}}) .$$

Here we have

$$D_{11}=12N_{\mathrm{Ge}}c_{44,\mathrm{Ge}}/a_{\mathrm{Ge}} ,$$

$$D_{12}=12N_{\mathrm{Si}}c_{44,\mathrm{Si}}/a_{\mathrm{Si}} ,$$

$$D_{21}=\frac{(c_{11,\mathrm{Ge}}+2c_{12,\mathrm{Ge}}+4c_{44,\mathrm{Ge}})a_{\mathrm{Si}}}{c_{11,\mathrm{Ge}}+2c_{12,\mathrm{Ge}}} ,$$

$$D_{22}=-\frac{(c_{11,\mathrm{Si}}+2c_{12,\mathrm{Si}}+4c_{44,\mathrm{Si}})a_{\mathrm{Ge}}}{(c_{11,\mathrm{Si}}+2c_{12,\mathrm{Si}})} ,$$

and

$$D=D_{11}D_{22}-D_{12}D_{21} .$$

These equations give the correct dependence on elastic constants and on layer thicknesses. Consider, for example, the dependence on layer thickness for growth on a Si substrate; then for $N_{\mathrm{Si}}\gg N_{\mathrm{Ge}}$, we have $D_{12}\gg D_{11}$ and $D\simeq -D_{12}D_{21}$; thus we find $\epsilon_{\mathrm{Si}}\simeq(a_{\mathrm{Ge}}-a_{\mathrm{Si}})D_{11}/D_{12}D_{21}\simeq 0$, $\Delta_{\mathrm{Si}}\simeq 0$, $a_{\parallel}\simeq a_{\mathrm{Si}}$, as it should be. We also find that the magnitudes of the strains $\epsilon_{\mathrm{Ge}}$ and $\Delta_{\mathrm{Ge}}$ decrease as the Ge layer thickness increases—as expected.

### C. Tight-binding Hamiltonian for the strained superlattice

After the strains have been determined, we need to find the relative positions of the nearest atoms in order to determine the new tight-binding Hamiltonian under the internal strain. If, without strain, a central atom and its four nearest-neighbor atoms are located at (0,0,0), $(a_L/4)(1,1,1)$, $(a_L/4)(1,-1,-1)$, $(a_L/4)(-1,1,-1)$, and $(a_L/4)(-1,-1,1)$, then, with strain, the new atomic positions are $(2\xi\epsilon,2\xi\epsilon,2\xi\epsilon)$, $(a_L/4)(1+\Delta+2\epsilon,1+\Delta+2\epsilon,1+\Delta+2\epsilon)$, $(a_L/4)(1+\Delta-2\epsilon,-1-\Delta,-1-\Delta)$, $(a_L/4)(-1-\Delta,1+\Delta-2\epsilon,-1-\Delta)$, and $(a_L/4)(-1-\Delta,-1-\Delta,1+\Delta-2\epsilon)$, respectively. Here $\xi$ is the internal displacement parameter[17] and $\epsilon$ and $\Delta$ are the corresponding shear strain and dilation. The internal displacement parameters for both Si and Ge are taken to have the measured value of 0.7 for Ge.[18,19] After the relative positions of the nearest-neighbor atoms have been determined, the new tight-binding Hamiltonian of the superlattice under strain can be easily deduced. The diagonal Hamiltonian matrix elements, which are independent of bond length,[10] will remain the same as those without strain. The off-diagonal matrix elements $V_{\alpha\beta}$ between atomic orbitals $\alpha$ and $\beta$ centered on adjacent sites depend both on the distance between the two atoms and on the direction cosines of the corresponding orbitals. The distance dependence of the matrix elements $V_{\alpha,\beta}$ can be treated as in previous work:[20–22]

$$V_{\alpha,\beta}=V^0_{\alpha,\beta}(d_0/d)^{\eta_{\alpha,\beta}} .$$

Here $d_0$ and $d$ are the distances between the nearest-neighbor atoms, namely, the ones that are the centers for the orbitals $\alpha$ and $\beta$, for the unstrained and strained cases, respectively. $V^0_{\alpha,\beta}$ is the matrix element for the unstrained crystal, and $\alpha$ and $\beta$ range over $s$, $p_x$, $p_y$, $p_z$, and $s^*$, in addition to specifying the site. By fitting to the experimental pressure variations of the band gaps of Si and Ge, we found the following exponents for Ge (Si): $\eta_{s,s}=4.4$ (3.0), $\eta_{s,x}=\eta_{x,s}=2.4$ (1.6), $\eta_{x,x}=2.3$ (3.42), $\eta_{x,y}=2.5$(2.6), and $\eta_{s^*,x}=\eta_{x,s^*}=3.982$ (3.327).[23]

The direction cosine variations of the off-diagonal matrix elements $V_{\alpha,\beta}$ for the strained superlattice are due to stress-induced bond-angle distortions, and can be easily obtained using the Slater-Koster definitions[24] of these matrix elements. For example, for the matrix element between $s$ and $p_x$ states on neighboring sites we have

$$V_{s,p_x}=V^0_{s,p_x}(\cos\theta/\cos\theta_0)(d_0/d)^{\eta_{s,p}} ,$$

with similar expressions for the variations of the other off-diagonal matrix elements on $d$ and $\theta$. Here $\theta_0$ and $\theta$ are the zero- and finite-stress bond angles relative to the crystal axes.

With these new values for the matrix elements of the Hamiltonian $H_0$, the calculation of the electronic properties proceeds as for the unstrained superlattice. It is noteworthy that, for the case of bulk Ge, the deformation potentials calculated[25] using this method are in reasonable agreement with data.[26,27]

### D. Applied [111] compressive uniaxial stress

Under an applied compressive [111] uniaxial stress of magnitude $P$ (force per unit area), the Hamiltonian for the superlattice is determined from the combination of induced and internal strains, as in the case of internal strains alone.

The induced strains $u_{xx}$, $u_{yy}$, $u_{zz}$, $u_{xy}$, $u_{yz}$, and $u_{zx}$ in Ge and Si can be obtained from the stress tensor[28]

$$\sigma_{xx}=\sigma_{yy}=\sigma_{zz}=P/3 ,$$

$$\sigma_{xy}=\sigma_{yz}=\sigma_{zx}=P/3 ,$$

using elasticity theory,[15] with the net strains being a linear superposition of the external and internal strains. The expressions given above for the dilations $\Delta$ and shears $\epsilon$ undergo the following changes:

$$\delta\Delta=P(S_{11}+S_{12})/3$$

and

$$\delta\epsilon=PS_{44}/6 ,$$

where $S_{11}$, $S_{12}$, and $S_{44}$ are the elastic compliance constants.[15]

## V. RESULTS

### A. Unstrained Si/Ge [111] superlattices

The electronic structure of a $1\times1$ (Ref. 9) Si/Ge [111] superlattice is displayed in Fig. 1, in comparison with the folded band structures of bulk Si and Ge. Here we assume $\Delta E_{VB}=0.2$ eV. The conduction-band minimum is near $\mathbf{k}=\mathbf{0}$ for the $1\times1$ superlattice (see Fig. 1). and at $\mathbf{k}=\mathbf{0}$ for the $2\times2$ superlattice, directly above the valence-band maximum, indicating that luminescence is allowed.

The large band-gap Si layers cause quantum confinement in the small-gap Ge quantum wells. To illustrate this effect, we fix the Si layer thickness at 5.43 Å (four Si atoms thick) and vary the Ge-layer thickness. The fundamental band gap of the superlattice, corresponding to the gap between the Ge valence-band maximum and the Ge folded (1,1,1) conduction-band minimum, increases dramatically as the Ge-layer thickness decreases (Fig. 2). This effect is most dramatic, as expected, for small $N_{Ge}$ and for the [111] valley (1,1,1), which is folded into the $\mathbf{k}=\mathbf{0}$, $\Gamma$ point of the superlattice Brillouin zone. Note in particular that the (1,1,1) valley folded into $\Gamma$ is at a lower energy than the other $L$ minima for large $N_{Ge}$ and at a higher energy for small $N_{Ge}$—an effect not contained in the folded-band approximation.

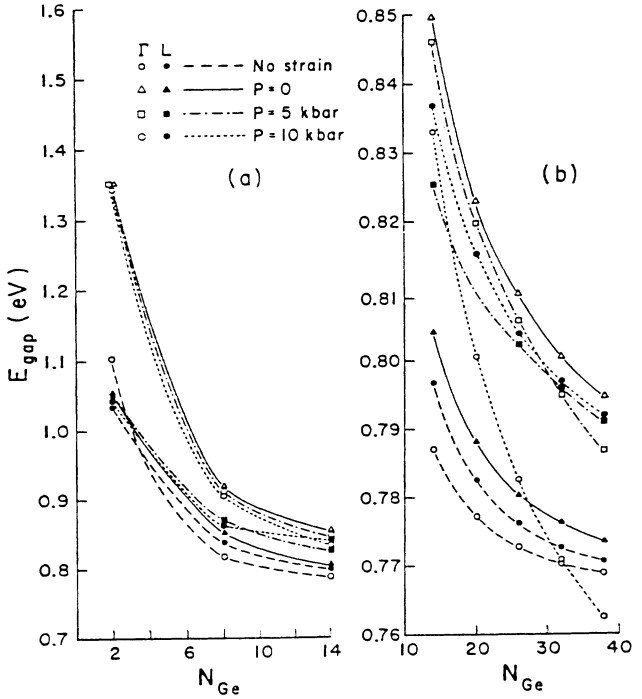


FIG. 2. Band gaps of $2\times N_{Ge}$ free-standing superlattices as a function of the number of Ge layers $N_{Ge}$ (i) computed without internal or applied stress (long dashed lines, open circles for $\Gamma$, closed circles for the unfolded $L$ minima), (ii) computed with internal strain, but with $P=0$ (solid lines, open triangles for $\Gamma$, closed triangles for the unfolded $L$ minima), and (iii) computed with internal strain and $P=5$ kbar (dash-dotted lines, open squares for $\Gamma$, closed squares for the unfolded $L$ minima) and $P=10$ kbar (short dashed lines, open hexagons for $\Gamma$, closed hexagons for the unfolded $L$ minima). The gap derived from the zone-folded (1,1,1) minimum of Ge is labeled $\Gamma$ because it is at $\mathbf{k}=\mathbf{0}$ of the superlattice Brillouin zone. The gap labeled $L$ is derived from the $(1,-1,-1)$, $(-1,1-1)$, or $(-1,-1,1)$ minima of the bulk band structure of Ge. The zero of energy is the valence band maximum of the superlattice and the assumed valence-band offset is 0.2 eV. Parts (a) and (b) of the figure correspond to different ranges of $N_{Ge}$.

### B. Effects of internal strain

Because the lattice constant of bulk Si is about 4% smaller than that of bulk Ge, and because the in-plane lattice constants of Si and Ge layers in the [111] superlattice must match, there is a positive shear strain and negative dilation in the Ge layers (together with negative shear and positive dilation in Si). The positive shear strain in Ge raises the energy of the (1,1,1) valley and lowers the other three valleys such as $(1,-1,1)$ (Refs. 29 and 30) (Fig. 2). This effect is not negligible: the (1,1,1)-$(1,-1,1)$ strain splitting is typically $\simeq0.3$ eV for a $2\times2$ superlattice, whereas in the absence of strain it is about a factor of 4 smaller. This strain splitting is bad for luminescence because electrons tend to thermalize into the lowest-energy conduction-band states, namely, the indirect minima such as $(1,-1,1)$ (where they are forbidden from emitting light by recombination with holes at the valence-band maximum), rather than the optically-active, folded (1,1,1) minimum at the $\Gamma$ point of the mini-Brillouin-zone. The effect is minimized if there is very little strain in the Ge layers, that is, if the Ge layers are thick and the Si layers are thin. Unfortunately making the ratio of the Ge to Si large will also minimize the effect of zone folding on the optical matrix element, because the superlattice will be very Ge-like, having a very small optical matrix element despite the zone folding. Thus it is best to keep the thickness of the Ge layers small, too. Hence to make [111] Si/Ge superlattices luminesce, we must construct small-period superlattices and find a way to overcome the internal strain (e.g., with strain-absorbing buffer layers between the Si and the Ge) and make the (1,1,1) $\Gamma$ minimum the lowest-energy conduction-band state.

### C. Effects of applied compressive [111] uniaxial stress

One way to drive the (1,1,1) $L$ valley of the conduction band of bulk Ge to lower energy is to apply a compressive [111] uniaxial stress; this will induce a negative shear strain and will lower the (1,1,1) conduction band minimum and raise the othe three $L$ minima, as shown in the theory of Herring and Vogt[29] and as Chandrasekhar and Pollak demonstrated experimentally.[19,31] Thus a sufficiently large compressive [111] stress applied to a [111] Si/Ge superlattice should overcome the internal strain splitting and drive the folded (1,1,1) minimum of the Ge conduction band to lower energy than the other three $L$ minima—making the fundamental band gap of the superlattice direct and permitting luminescence.

This reasoning indicates that favorable conditions for light emission from a Si/Ge [111] superlattice include (i) small Si-layer thicknesses or periods, (ii) periods such that the Ge (1,1,1) $L$ minimum is folded into the

Brillouin-zone center of the superlattice, and (iii) applied uniaxial stress strong enough to overcome the internal strain splitting and make the superlattice band gap direct.

These ideas are supported by our calculations. Figure 2 shows the calculated fundamental band gaps of $2\times N_{Ge}$ [111] Si/Ge superlattices subjected to uniaxial stresses $P=5$ and 10 kbar. The $2\times N_{Ge}$ superlattice is a direct-band-gap semiconductor for $P=5$ kbar and $N_{Ge}\geq 30$, whereas the $2\times N_{Ge}$ superlattice is direct for $P=10$ kbar and $N_{Ge}\geq 12$.

The required stresses are quite large and perhaps can be achieved in practical devices more easily internally, for example, by using Sn as well as Si between the Ge layers to absorb some of the strain created by the Si.

### D. Optical selection rules

A complete calculation of the frequency-dependent dielectric function of these superlattices is in progress and will be reported in subsequent work. Nevertheless we have cause for some optimism concerning the luminescence intensity: the bottom of the Ge conduction band that is folded has 56% $s$ character in the present model.[10] Thus optical transitions are allowed and should have significant strength.

### E. $Si_xGe_{1-x}/Si_yGe_{1-y}$ [111] superlattices

Virtually everything we have predicted for Si/Ge [111] superlattices with $|\Delta E_{VB}|=0.2$ eV should hold qualitatively for $Si_xGe_{1-x}/Si_yGe_{1-y}$ superlattices as well, provided they have type-I zero-strain ideal band offsets. Quantitative differences should arise from the smaller lattice mismatches, which should lead to direct-gap behavior at lower applied stresses $P$. However, the optical matrix elements are likely to be weaker as well.

### F. Larger band offsets

If the magnitude of the Si/Ge valence-band offset is not smaller than 0.4 eV, and some recent measurements indicate that it is larger,[1] then the desired luminescence can be achieved by "engineering" the alloy composition $x$ and the externally applied uniaxial stress $P$ of a $Si_xGe_{1-x}/Ge$ superlattice. Figures 3 and 4 illustrate this point, assuming a Si/Ge band offset of $\Delta E_{VB}=0.455$ eV. Figure 3 shows the predicted conduction band-edge energies of $2\times N_{Ge}$ Si/Ge type-II superlattices, as functions of applied uniaxial stress $P$. When the applied stress is sufficiently large, the direct $\mathbf{k}=\mathbf{0}$ conduction-band edge lies below the corresponding indirect $L$ edge. Similarly, Fig. 4 gives the results for a $Si_xGe_{1-x}/Ge$ type-I superlattice with a band offset of $0.455x$ eV, assuming $x=0.6$. In this case also, the appropriate choice of alloy composition $x$ and applied uniaxial stress $P$ makes the superlattice a direct-gap material.

### G. Si/Ge [111] superlattices grown on Ge substrates

The calculations of this paper have been for a free-standing Si/Ge superlattice. However, it is clear from the physics that a Si/Ge superlattice grown on a Ge substrate would exhibit similar behavior and that the desirable strain effects would be enhanced, because the strain in the Ge superlattice layers would be near zero while the Si layers would be highly strained. In such a case, a relatively small [111] uniaxial compressive stress would be needed to drive the [111] $L$ valley below the others and to

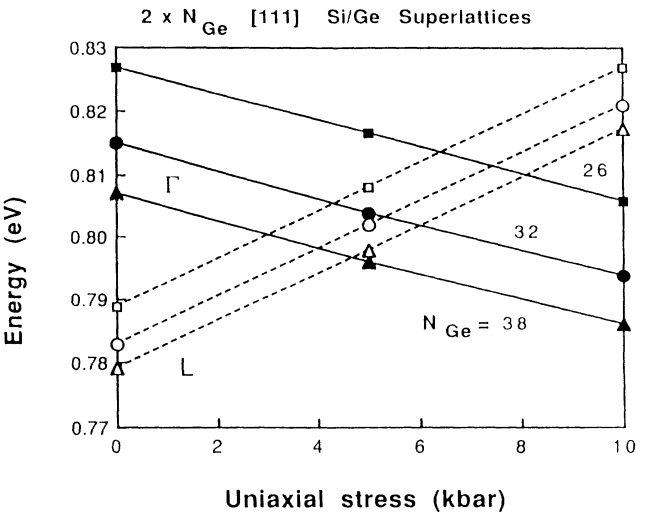


FIG. 3. Predicted conduction-band edge energies (in eV) for $2\times N_{Ge}$ [111] Si/Ge type-II superlattices, assuming a valence-band offset of 0.455 eV, as functions of applied uniaxial stress $P$ (in kbar). Solid (dashed) lines denote the $\Gamma$ ($L$) edges. Triangles, circles, and squares denote $N_{Ge}=38$, 32, and 26, respectively.

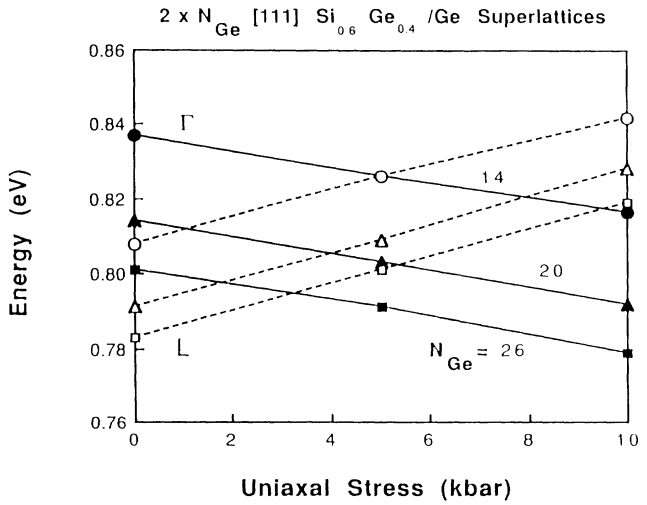


FIG. 4. Predicted conduction-band edge energies (in eV) for $2\times N_{Ge}$ [111] $Si_xGe_{1-x}/Ge$ type-I superlattices for $x=0.6$, and assuming a valence band offset of 0.455 eV, as functions of applied uniaxial stress $P$ (in kbar). Solid (dashed) lines denote the $\Gamma$ ($L$) edges. Circles, triangles, and squares denote $N_{Ge}=14$, 20, and 26, respectively.

satisfy the condition for luminescence, even for rather large Si/Ge thickness ratios.

## VI. SUMMARY

$Si_xGe_{1-x}$/Ge [111] superlattices with periods chosen to fold the (1,1,1) Ge conduction-band maximum into the center of the Brillouin zone appear to offer the possibility of direct-gap recombination, provided the internal strains are compensated. Although we performed the calculations first for $x=1$ and an assumed valence band offset of 0.2 eV, we have also shown that the basic physics will still hold for $x<1$ and for other values of the band offset, provided the Ge conduction band edge lies below that of the $Si_xGe_{1-x}$ (type-I alignment). For example, if the currently unknown (unstrained) Si/Ge valence band offset should turn out to be greater than 0.4 eV so that the superlattice has type-II alignment, then type-I alignment can be restored either by reducing $x$ or by applying larger uniaxial stress,[1] and the qualitative predictions of the present theory will still be valid, as shown in Figs. 3 and 4. Only three physical features are required to produce the desired direct-gap structure in [111] $Si_xGe_{1-x}$/Ge superlattices: (i) band alignments that result in the unstrained or strained superlattice's conduction-band minimum being derived from the Ge minima, (ii) band folding, and (iii) the fact that applied uniaxial stress drives the (1,1,1) $L$ minimum down in energy with respect to the $(1,-1,1)$ minimum.

## ACKNOWLEDGMENTS

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*Present address.

[1]The valence-band offset we consider has not been measured, and is the difference in positions of the valence-band maxima of *unstrained bulk Ge and unstrained bulk Si, both grown in the [1,1,1] direction.* The corresponding value for [001] superlattices, which should be different from the [111] value is a subject of controversy (Refs. 2–6), with the most recent measurements (Ref. 3) implying (Ref. 4) a value of 0.455±0.13 eV, compatible with either type-I or type-II band alignment. Measured offsets for [001] superlattices (which include strain) range from 0.17 to 0.74 eV (Refs. 2, 3, and 5). Van der Walle and Martin (Ref. 6) have predicted a large offset, 0.54±0.04 eV, and type-II alignment. Resolution of this controversy concerning the precise value of the valence-band offset is beyond the scope of this paper. Nevertheless we do point out that, even if the ideal unstrained band offset of Si/Ge [111] is greater than 0.4 eV, it can be overcome simply by the application of sufficient compressive uniaxial stress, and luminescence should occur. Furthermore, there will always exist a range of values of $x$ for which the $Si_xGe_{1-x}$/Ge [111] system exhibits the required type-I alignment.

[2]G. Margaritondo, A. D. Katnani, N. G. Stoffel, R. R. Daniels, and T. X. Zhao, Solid State Commun. **43**, 163 (1982). See also H. Kroemer, in *Molecular Beam Epitaxy and Heterostructures,* Vol. 87 of *NATO Advanced Study Institute, Series E,* edited by L. L. Chang and K. Ploog (Nijhoff, The Netherlands, 1983), p. 331.

[3]G. P. Schwartz, M. S. Hybertsen, J. Bevk, R. G. Nuzzo, J. P. Mannaerts, and G. J. Gualtieri, Phys. Rev. B **39**, 1235 (1989).

[4]S. Y. Ren (unpublished).

[5]R. People and J. C. Bean, Appl. Phys. Lett. **48**, 538 (1986).

[6]C. G. Van de Walle and R. M. Martin, Phys. Rev. B **34**, 5621 (1986), and references therein.

[7]J. C. Bean, L. C. Feldman, A. T. Fiory, S. Nakahara, and I. K. Robinson, J. Vac. Sci. Technol. A **2**, 436 (1984).

[8]T. P. Pearsall, J. Berk, L. C. Feldman, J. M. Bonar, J. P. Mannaerts, and A. Ourmazd, Phys. Rev. Lett. **58**, 729 (1987).

[9]Because Si and Ge have two atoms per unit cell, the layers of a $1\times1$ superlattice are each two atoms thick.

[10]P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).

[11]M. S. Hybertsen and M. Schlüter, Phys. Rev. B **36**, 9683 (1987), and references cited therein.

[12]C. Priester, G. Allan, and M. Lannoo, Phys. Rev. B **38**, 13 451 (1988).

[13]*Numerical Data and Functional Relationships in Science and Technology,* edited by O. Madelung, M. Schulz, and H. Weiss, Landolt-Börnstein, New Series, Vol. 17a (Springer-Verlag, Berlin, 1982), pp. 61 and 103.

[14]L. D. Landau and E. M. Lifshitz, *Theory of Elasticity,* 3rd ed. (Pergamon, London, 1986), p. 35.

[15]C. Kittel, *Introduction to Solid State Physics,* 4th ed. (Wiley, New York, 1971), p. 139.

[16]H. B. Huntington, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7, p. 213.

[17]See, for example, W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980), p. 198.

[18]A. Segmuller, Phys. Lett. **4**, 227 (1963).

[19]See also I. Goroff and L. Kleinman, Phys. Rev. **132**, 1080 (1963). Theoretically the internal displacement parameters of Si and Ge are predicted to be nearly equal (see Ref. 17, pp. 196 and 208).

[20]S. Y. Ren, J. D. Dow, and D. J. Wolford, Phys. Rev. B **25**, 7661 (1982).

[21]R.-D. Hong, D. W. Jenkins, S. Y. Ren, and J. D. Dow, Phys. Rev. B **38**, 12 549 (1988); D. W. Jenkins, R.-D. Hong, and J. D. Dow (unpublished).

[22]See also W. A. Harrison and S. Ciraci, Phys. Rev. B **10**, 1516 (1974); W. A. Harrison, *Electronic Structure and the Properties of Solids* (Ref. 17).

[23]These exponents are the same as those determined in Ref. 21.

[24]J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[25]For pure Ge, the calculated deformation potentials are $d=-3.22$ in comparison with the experimental value $-4.85\pm0.15$ (Ref. 26) and $\Xi_u^L=7.68$ in comparison with the experimental value 16.2±0.4 (Ref. 27). The difference between theory and data is attributable partly to the nearest-neighbor tight-binding Hamiltonian approximation and partly to the internal displacement we used. Because, in this paper, what matters is the relative movement of the different

valleys of Ge under strain, an experimentally larger deformation potential than $\Xi_u^L = 7.68$ will make the effect described in this paper even easier to be seen.

[26]L. D. Laude, F. H. Pollak, and M. Cardona, Phys. Rev. B **3**, 2623 (1971).

[27]I. Baslev, Phys. Rev. **143**, 636 (1966).

[28]See, for example, M. Lannoo and J. Bourgoin, *Point Defects in Semiconductors I, Theoretical Aspects* (Springer-Verlag, Berlin, 1981), p. 24.

[29]C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

[30]H. Fritzshe, Phys. Rev. **115**, 336 (1959).

[31]M. Chandrasekhar and F. H. Pollak, Phys. Rev. B **15**, 2127 (1977).