PHYSICAL REVIEW B VOLUME 27, NUMBER 8 15 APRIL 1983

Temperature dependence of the direct gap of Si and Ge

P. B. Allen
Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794

M. Cardona
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80,
Federal Republic of Germany

(Received 18 October 1982)

The temperature dependences of the lowest direct gaps of germanium and silicon are calculated. They result from the effect of electron-phonon interaction on the corresponding electronic states. Both Debye-Waller (second-order interaction Hamiltonian) and "self-energy" (first-order interaction Hamiltonian) are included. It is shown that the latter are by no means negligible. They *reduce* the calculated temperature coefficients at constant volume by a factor of 1.7 in the case of Si and 1.3 in the case of Ge. Agreement with experimental data is satisfactory.

I. INTRODUCTION

The measured temperature dependence of energy bands at constant pressure derives partly from thermal expansion and partly from the renormalization of band energies by electron-phonon interactions.[1] The former effect can be calculated by finding the volume dependence of band energies and combining this with measured values of the thermal expansion coefficient $\alpha = L^{-1}(dL/dT)_P$. This paper describes theoretical calculations of the latter effect, which is usually the larger contribution but is much harder to evaluate. We compare our calculations with experimental values,[2] measured at constant pressure but reduced to constant volume by means of the measured coefficient $(\partial E_g/\partial P)_T$. We have

$$\left[\frac{\partial E_g}{\partial T}\right]_P = \left[\frac{\partial E_g}{\partial T}\right]_V + \left[\frac{\partial E_g}{\partial T}\right]_{\text{thermal exp}},$$

$$\left[\frac{\partial E_g}{\partial T}\right]_{\text{thermal exp}} = -3B\alpha\left[\frac{\partial E_g}{\partial P}\right]_V . \quad (1)$$

Here B is the bulk modulus. Our results are summarized in Table I for the direct gaps at $\vec{k}=0$ in Si and Ge. Experimental values of $(\partial E_g/\partial T)_V$ are -1.9×10^{-4} eV/K for Si and -2.8×10^{-4} eV/K for Ge.

There are two types of electron-phonon contributions, Debye-Waller terms[3] and "self-energy" terms.[4] This terminology is widely used and is explained in our previous paper,[5] hereafter denoted as I. A perturbative calculation[6] of the electron self-energy to second order in atomic displacement u yields both terms, but only the second is commonly named a self-energy, the first being independent of frequency. Both are necessary to preserve translational invariance.[7,8] As can be seen from the last two lines of Table I the Debye-Waller term overestimates the experimental value of $(dE_g/dT)_V$ by about a factor of 2, but when the self-energy term is added, agreement between theory and experiment improves. For Si the agreement seems excellent, but this is marred by the difficulty of observing the $\vec{k}=\vec{0}$ which is degenerate with the E_1 gap arising from states in the $\{111\}$ directions. Thus it is impossible to be certain that the experimental value -1.9×10^{-4} eV/K should be assigned to the $\vec{k}=\vec{0}$ state. In Ge the discrepancy is larger but not nearly so large as our incorrect original calculations in I indicated. The present paper corrects the errors of paper I for Ge and extends the calculations to Si.

II. FORMALISM AND METHOD OF CALCULATION

We use the same method as in I and only the most important equations will be repeated. We subdivide the electron energy shift $\Delta E_{\vec{k}n}$ into contributions from the various phonons $\vec{Q},j$,

TABLE I. Room-temperature data and calculations for the direct gap at $\vec{k}=\vec{0}$ in Si and Ge. Data are from Ref. 2 unless otherwise specified.

Experimental	Si	Ge
B (10^{11} N/m^2)	0.98	0.75
α (10^{-6} K^{-1})[a]	2.0	5.5
$\left[\dfrac{\partial E_g}{\partial P}\right]_T$ (meV/kbar)	5.2	13.
$\left[\dfrac{\partial E_g}{\partial T}\right]_{\text{thermal exp}}$ (10^{-4} eV/K)	-0.3	-1.6
$\left[\dfrac{\partial E_g}{\partial T}\right]_P$ (10^{-4} eV/K)	-2.2[b]	-4.4[c]
$\left[\dfrac{\partial E_g}{\partial T}\right]_V$ (10^{-4} eV/K)	-1.9	-2.8
Theoretical calculations at constant volume		
$\left[\dfrac{\partial E_g}{\partial T}\right]_{\text{DW}}$ (10^{-4} eV/K)	-3.2	-4.9
$\left[\dfrac{\partial E_g}{\partial T}\right]_{\text{tot}}$ (10^{-4} eV/K)	-1.9	-3.9

[a] Average value between 200—300 K.

[b] From Ref. 2 for E_1 edge which contains the $\Gamma'_{25}\rightarrow\Gamma_{15}$ gap plus transitions along {111}.

[c] Linear coefficient at high T from Ref. 21.

$$\Delta E_{\vec{k}n}(T)=\sum_{\vec{Q},j}\left[\frac{\partial E_{\vec{k}n}}{\partial n_{\vec{Q}j}}\right][n_{\vec{Q}j}(T)+\tfrac{1}{2}]$$
$$=\int_0^{\omega_{\max}} d\Omega\, g^2F(\vec{k},n;\Omega)$$
$$\times[(e^{\Omega/T}-1)^{-1}+\tfrac{1}{2}]\ , \qquad (2)$$

where $n_{\vec{Q}j}$ is the occupation number of the phonon mode. The second line of Eq. (2) uses the electron-phonon spectral function g^2F,

$$g^2F(\vec{k},n;\Omega)=\sum_{\vec{Q},j}\left[\frac{\partial E_{\vec{k}n}}{\partial n_{\vec{Q}j}}\right]\delta(\Omega-\omega_{\vec{Q}j})\ , \qquad (3)$$

where $\omega_{\vec{Q},j}$ is the phonon energy. The contribution from phonon $\vec{Q},j$ to the electron energy shift $\partial E_{\vec{k}n}/\partial n_{\vec{Q}j}$ is the sum of the Debye-Waller (DW) and self-energy (SE) contributions, given by

$$\left[\frac{\partial E_{\vec{k}n}}{\partial n_{\vec{Q}j}}\right]_{\text{SE}}=\frac{1}{2}\sum_{n'}\frac{[\vec{\Gamma}(\vec{k},n,n';\vec{Q})\cdot\vec{u}(\vec{Q},j;+)+\vec{\Theta}(\vec{k},n,n';\vec{Q})\cdot\vec{u}(\vec{Q},j;-)]^2}{\epsilon_{\vec{k}n}-\epsilon_{\vec{k}+\vec{Q},n'}}\ , \qquad (4)$$

$$\left[\frac{\partial E_{\vec{k}n}}{\partial n_{\vec{Q}j}}\right]_{\text{DW}}=-\frac{1}{2}{\sum_{n'}}'\frac{[\vec{\Gamma}(\vec{k},n,n';\vec{0})\cdot\vec{u}(\vec{Q},j;+)]^2+[\vec{\Theta}(\vec{k},n,n';\vec{0})\cdot\vec{u}(\vec{Q},j;-)]^2}{\epsilon_{\vec{k}n}-\epsilon_{\vec{k}n'}}\ . \qquad (5)$$

Explicit formulas for the vectors $\vec{\Gamma}$ and $\vec{\Theta}$ are given in Eq. (16) of paper I in terms of pseudo-wave-functions and pseudopotentials. The prime in the summation in (5) indicates that only interband terms $n'\neq n$ are summed. The displacements $u\,(\pm)$ are the even and odd combinations of displacements of the two atoms (labeled 1 and 2) in the unit cell, namely

$$\begin{aligned}\vec{u}(\vec{Q},j;+)&=(\hbar/2MN\omega_{\vec{Q}j})^{1/2}\\&\quad\times[\vec{\epsilon}(\vec{Q},j;1)+\vec{\epsilon}(\vec{Q},j;2)]\ ,\\ i\vec{u}(\vec{Q},j;-)&=(\hbar/2MN\omega_{\vec{Q}j})^{1/2}\\&\quad\times[\vec{\epsilon}(\vec{Q},j;1)-\vec{\epsilon}(\vec{Q},j;2)]\ ,\end{aligned}\tag{6}$$

where $\vec{\epsilon}$ is a (complex) polarization vector, which in diamond structure obeys $\epsilon_2=\epsilon_1^*$.[9] Thus the amplitudes $u(\pm)$ are real as is everything else in Eqs. (4) and (5).

The DW term (5) can be written in a more familiar form,

$$\left[\frac{\partial E_{\vec{k}n}}{\partial n_{\vec{Q}j}}\right]_{\rm DW}=-\frac{1}{2}\left\langle \vec{k},n\left|\sum_{\vec{G}}|\vec{G}\cdot\vec{u}_{\vec{Q}j}|^2V(\vec{G})e^{i\vec{G}\cdot\vec{r}}\right|\vec{k},n\right\rangle\ ,\tag{7}$$

where V is the pseudopotential, $\vec{G}$ is a reciprocal-lattice vector, and $|\vec{u}_{\vec{Q}j}|^2$ is the square modulus of the displacement of either atom 1 or 2 and equals $[\vec{u}(\vec{Q},j;+)^2+\vec{u}(\vec{Q},j;-)^2]/2$. Equation (5) is much more difficult to evaluate than (7) because it involves summing squared off-diagonal matrix elements of $\vec{\nabla}V$ over many intermediate states. However, the form (5) has the advantage that it is easily compared to the SE term (4) (which cannot be simplified). In particular, consider the limit of (4) as $\vec{Q}$ gets small. For an acoustic phonon $\vec{u}(\vec{Q},j;-)$ goes to zero so the term involving $\vec{\Theta}$ is irrelevant. The diagonal part of $\vec{\Gamma}$, $\vec{\Gamma}(\vec{k},n,n;\vec{Q})$, vanishes as $\vec{Q}$ goes to zero by the deformation-potential theorem.[10] Then Eqs. (4) and (5) exactly cancel as required by translational invariance.[8] A long-wavelength acoustic phonon becomes a rigid translation of the lattice which cannot alter the electron energy. Our calculations use the form (5) rather than (7), but we have verified that (7) gives exactly the same result.

The error in I arose from the labeling of atoms 1 and 2 located at positions $\vec{\tau}_1$ and $\vec{\tau}_2$. Our energy-band program used $\vec{\tau}_1=(a/8)(1,1,1)$ and $\vec{\tau}_2=-\vec{\tau}_1$. For the phonon frequencies and eigenvectors we used bond-charge—model[11] programs[12] of Weber which had chosen the opposite convention. Unfortunately we did not notice this inconsistency until after I was published. Thus, although the formulas in I are correct, the amplitude $\vec{u}(\vec{Q},j;-)$ had the wrong sign in the calculations. It can be seen from Eqs. (4) and (5) that the sign of $\vec{u}(\vec{Q},j;-)$ does not affect the DW term. Further, the SE term is unaffected at values of $\vec{Q}$ near $\vec{Q}=\vec{0}$ where the modes are purely acoustic $[\vec{u}(\vec{Q},j;-)=\vec{0}]$ or purely optic $[\vec{u}(\vec{Q},j;+)=\vec{0}]$. Thus extensive tests at $\vec{Q}=\vec{0}$ reported in I failed to detect the error. The present calculations have been checked at all symmetry lines and we find that $\vec{Q}\neq\vec{0}$ electron-phonon selection rules are strictly obeyed, whereas the previous calculations contained violations.

III. PSEUDOPOTENTIAL AND DEFORMATION POTENTIAL

The DW terms (5) or (7) require the pseudopotential $V(\vec{q})$ only at reciprocal-lattice vectors $\vec{G}$, and the value $V(\vec{0})$ at $\vec{G}=\vec{0}$ occurs with vanishing weight. The values $V(\vec{G})$ are taken from band theory.[13] Unfortunately there is ambiguity in the pseudopotential $V(\vec{Q}+\vec{G})$ for $\vec{Q}\neq\vec{0}$ which enters the SE terms. Strictly speaking, this should not be exactly the same pseudopotential as occurs in band theory. In place of $(\vec{Q}+\vec{G})V(\vec{Q}+\vec{G})$ there should be

$$\sum_{G'}\epsilon^{-1}(\vec{Q}+\vec{G},\vec{Q}+\vec{G}')(\vec{Q}+\vec{G}')V_b(\vec{Q}+\vec{G}')\ ,\tag{8}$$

i.e., the screened gradient of the bare potential. Note that the screening and the gradient operators only commute in a homogeneous system. Also the band-structure pseudopotential V only equals the screened bare potential $\epsilon^{-1}V_b$ if the potential V_b is very weak although the discrepancy is probably not large for Si and Ge.[14]

The rigid-atom model ignores these difficulties and assumes that when an atom moves the pseudopotential moves rigidly. This model becomes very reliable at large $|\vec{Q}+\vec{G}|$ corresponding to $V(\vec{r})$ for small $\vec{r}$ where the inner electrons reside. However, for small $|\vec{Q}+\vec{G}|$ or large r the outer valence electrons deform in a way which remains largely unknown.

There is an infinite variety of rigid-atom models, one for each possible way of splitting the total potential of the periodic crystal into a sum of identical potentials centered on each atom. In reciprocal space we can draw any curve $V(\vec{G})$ which passes through the known values $V(\vec{G})$ when $\vec{q}=\vec{G}$. Each curve corresponds to a possible splitting of the total potential. In I we drew a curve which passed through $V(\vec{0})=-2\epsilon_F/3$ where ϵ_F is the free-electron Fermi energy, following guidelines reviewed in Ref. 13. However, this choice for $V(\vec{0})$ is not compulsory except in a nearly-free-electron metal.

Recently,[15] Glembocki and Pollak (GP) calculated $\vec{Q}\neq\vec{0}$ matrix elements for phonon-assisted indirect transitions in Si and Ge. Their model, nearly identical to ours, yielded good agreement with experiment. However,[16] Bednarek and Rössler (BR) improved the agreement by making a very different extrapolation of $V(\vec{q})$ for small q. The idea is that the BR potential might represent a more realistic rigid-pseudoatom model, or more likely, contains empirical adjustments which make up for a possible inadequacy of the rigid-pseudoatom model at small q. The ideal test of the model for $V(\vec{q})$ at small q would be a study of the electron interaction with small-q acoustic phonons, i.e., the acoustic deformation potentials. Unfortunately this is a subject full of confusion.

Suppose the crystal is given a homogeneous external strain $\epsilon_{\alpha\beta}$. Then the shift $\delta E_{\vec{k}n}$ of the energy of the state $\vec{k},n$, to linear order in strain, is given by the deformation potential $\Xi_{\alpha\beta}$,

$$\delta E_{\vec{k}n} = \Xi_{\alpha\beta}(\vec{k},n)\epsilon_{\alpha\beta} . \tag{9}$$

If the strain is hydrostatic, $\epsilon_{\alpha\beta} = (\delta V/V)\delta_{\alpha\beta}$, the volume dependence of the energy is

$$V\frac{dE_{\vec{k}n}}{dV} = \frac{1}{3}\,\mathrm{tr}\,\Xi(\vec{k},n) . \tag{10}$$

Relative shifts of different levels with strain (for example, dE_g/dV) are easily calculated and directly measurable by optical techniques. Absolute shifts are hard to calculate because of ambiguity in the appropriate fixed-energy reference. For example, the muffin-tin zero is not a meaningful reference. There is no ambiguity in Eq. (8), which would correctly give acoustic-phonon scattering. Another unambiguous procedure would be a long-wavelength "frozen-phonon" calculation of the change in electron potential. Recently Vergés *et al.*[17] have described a simpler method for calculating absolute energy shifts by specifying that the self-consistent potentials have long-range Coulombic tails which vanish at infinity. Their procedure yields numbers which agree well with experimental values of Ξ from dc transport in III-V—compound semiconductors. For Si and Ge the data scatter widely; the comparison with theory is satisfactory but less meaningful. The rigid-ion model makes a prediction about volume deformation potentials which has absolute meaning only if the rigidly moved potential is correctly chosen. This can be checked by comparison with the calculation of Ref. 17. The simplest procedure for doing the calculation is to alter the lattice constant from a to $a(1+\alpha)$ where α is $\frac{1}{3}\delta V/V$, V being the volume. When the potentials are moved rigidly, the Schrödinger equation becomes

$$0 = \det\left[\left[\frac{(\vec{k}+\vec{G})^2}{(1+\alpha)^2} - \epsilon\right]\delta_{\vec{G}\,\vec{G}'} + \frac{1}{(1+\alpha)^3}V\left[\frac{\vec{G}-\vec{G}'}{1+\alpha}\right]\right] , \tag{11}$$

and $V(dE_{\vec{k}n}/dV)$ (V being the volume) is $\frac{1}{3}d\epsilon_{\vec{k}n}/d\alpha$. Because of the volume factor $(1+\alpha)^{-3}$ which normalizes $V(\vec{G}-\vec{G}')$, the results depend on $V(\vec{0})$ sensitively. Specifically, the answer is that $V(dE_{\vec{k}n}/dV)$ equals $-V(\vec{0})$ plus the results obtained with $V(\vec{0})$ set to zero. The BR potential for Si has $V(\vec{0})=0$ and gives $V(dE/dV) = -8.0$ and -9.0 eV, respectively, for the conduction-band (Γ_{15}) and valence-band (Γ_{25}') states at $\vec{k}=\vec{0}$. This agrees fairly well with the values -8.2 and -7.9 eV found by Vergés *et al.*[17] However, the GP potential has $V(\vec{0}) = -\frac{2}{3}\epsilon_F \cong -8.4$ eV which gives $V(dE/dV)$ close to zero for the states at $\vec{k}=\vec{0}$. Note that the directly observable shifts of the gap E_g (or any other interband gaps) with volume remain independent of $V(\vec{0})$.

This result convinced us that the BR potential is a serious alternative to the potentials used by GP and by us in I. Therefore we constructed two pseudopotentials for Si, shown in Fig. 1. Both are chosen to pass through the Cohen-Bergstresser[18] empirical values of $V(\vec{G}\neq\vec{0})$ and to vanish beyond $\vec{G}=(2\pi/a)(4,0,0)$. The potential labeled V_A is extrapolated to $V(\vec{0})=0$, while potential V_B uses $V(\vec{0}) = -2\epsilon_F/3$. The potentials V_A and V_B closely resemble the BR and GP potentials but no attempt was made to reproduce these potentials exactly.

The significance of deformation potentials in the electron-phonon problem is that they give the long-wavelength intraband matrix elements for scattering by acoustic phonons:

$$\langle \vec{k}+\vec{Q},n \mid V_{e\text{-ph}}^{\text{acoustic}} \mid \vec{k},n \rangle = iQ_\alpha u_\beta(\vec{Q},j)\Xi_{\alpha\beta}(\vec{k},n) . \tag{12}$$

This is simply the deformation potential theorem,[10] and $iQ_\alpha u_\beta$ is the strain $\epsilon_{\alpha\beta}$. From Eq. (15) of paper I we find

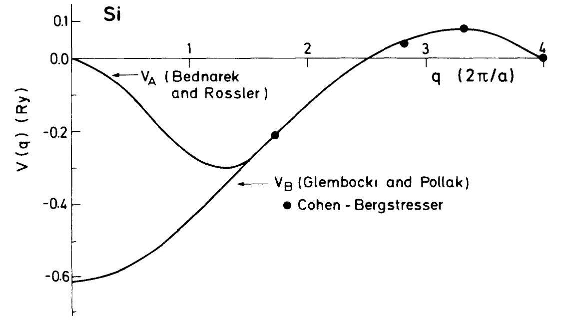

FIG. 1. Two pseudopotentials used for Si. Both agree with V_G of Cohen and Bergstresser (Ref. 18). V_A is patterned after Ref. 16 and is used in all the final calculations. V_B, patterned after Ref. 15 and I (Ref. 5), gives very similar results. For Ge, see Fig. 2 of I.

$$\Xi_{\alpha\beta}(\vec{k},n)=\left.\frac{\partial\Gamma_\beta(\vec{k},n;n,\vec{Q})}{\partial Q_\alpha}\right|_{\vec{Q}=\vec{0}} . \tag{13}$$

We verified that the same volume deformation potentials emerged from Eqs. (13) and (11).

IV. RESULTS

As in I we used 59-plane-wave band structures and performed the $\vec{Q}$ sums on a discrete mesh of 89 $\vec{k}$ points in the irreducible $\frac{1}{48}$th of the Brillouin zone. The spectral functions $g^2F(\vec{k},n;\Omega)$ were computed for valence- and conduction-band states at $\vec{k}=\vec{0}$ in Si and Ge with the use of the tetrahedron method.[19] These calculations took ~ 8 h of central-processing unit (CPU) time for each element on a Honeywell-Bull 66-80P computer. Because of the large time required all calculations were debugged with the use of 15-plane-wave energy bands, which needed only ~ 10 min of CPU time. We found to our surprise that the potentials V_A and V_B gave virtually indistinguishable results for g^2F in Si using 15 plane waves. The reason is partly because the DW terms which yield the main contribution to the energy shift are the same for potentials V_A and V_B. In the SE terms only acoustic phonons are sensitive to the difference between potential V_A and potential V_B and acoustic phonons tend to contribute less than optic phonons. For example, in the table of Ref. 16, potentials 1 and 2 are essentially V_A and V_B. For $Q=(2\pi/a)(0.85,0,0)$ the optic-phonon effects are large and not sensitive, whereas acoustic-phonon effects are small and sensitive. However, the insensitivity to the small-q pseudopotential is greater than can be explained this way. A phonon $\vec{Q},j$ contributes to the SE part of $\partial E_{\vec{k}n}/\partial n_{\vec{Q}j}$ via virtual transitions to all available intermediate states. It must be that this sum over states is less sensitive than the individual matrix elements to $V(\vec{q})$ at small q.

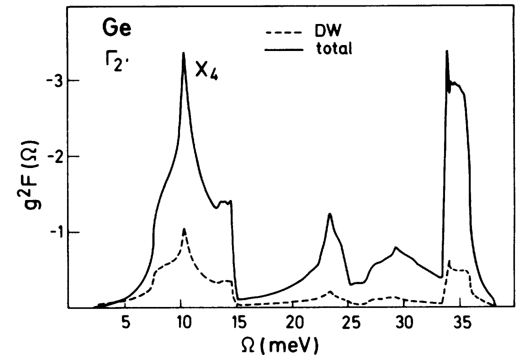

FIG. 3. Spectral function g^2F for the Γ_2' (conduction-band) state of Ge. This corrects Fig. 5 of I.

The insensitivity of g^2F and $E_{\vec{k}n}(T)$ to $V(\vec{0})$ is a happy result because as mentioned in Sec. III there is no unique prescription for this part of the pseudopotential in pseudoatom theory. Our final calculations for Si used potential V_A. For Ge we continued to use the potential of I which has the form of potential V_B.

At low temperatures, $\ll \Theta_D$, the T dependence of $E_{\vec{k}n}$ derives mainly from long-wavelength acoustic phonons and thus is sensitive to $V(\vec{q})$ at small q. However, the shift $\Delta E_{\vec{k}n}$ is very small and probably not measurable in semiconductors. However, in noble metals, de Haas–van Alphen measurements of the T dependence of neck areas[20] has shown a T^4 behavior which can be attributed to $\Delta E_{\vec{k}n}(T)$ scaling as T^4.

The calculated spectral functions $g^2F(\Omega)$ are shown in Figs. 2–5 for the states at the $\vec{k}=\vec{0}$ gap, i.e., Γ_{25}' and Γ_{15} in Si and Γ_{25}' and Γ_2' in Ge. The Γ_{25}' valence-band states (Figs. 2 and 4) show very similar behavior in the two elements. The SE terms suppress strongly the acoustic phonons and enhance

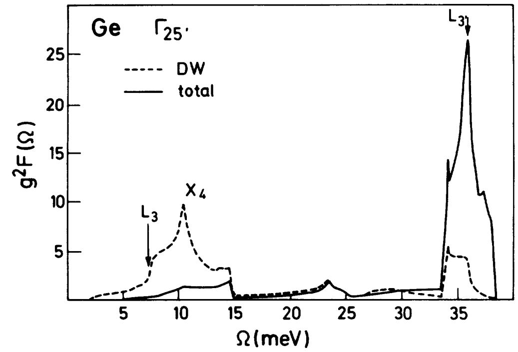

FIG. 2. Spectral function $g^2F(\Omega)$ for the Γ_{25}' (valence-band) state of Ge. This corrects Fig. 6 of I. Dashed curve is the DW contribution proportional to $F(\Omega)/\Omega$.

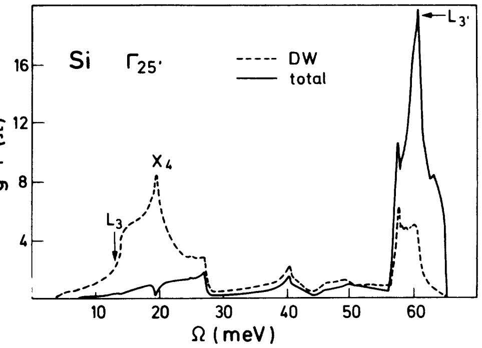

FIG. 4. Spectral function g^2F for the Γ_{25}' (valence-band) state of Si.

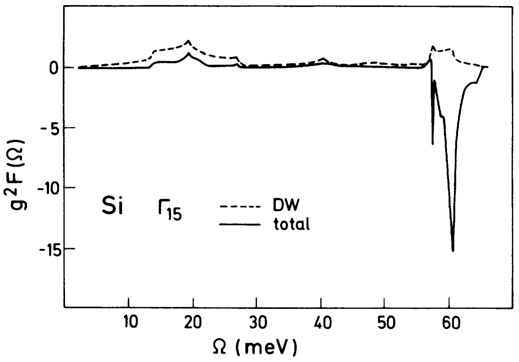

FIG. 5. Spectral function g^2F for the Γ_{15} (conduction-band) state of Si.

strongly the optic phonons. The behavior of the Γ_2' state (Fig. 3) is surprisingly different: All phonons except small-Q acoustic ones are enhanced. The error made in I had very little effect on the Γ_2' state, but a major effect on the Γ_{25}' acoustic-phonon contribution. The Γ_{15} state (Fig. 5) has a third kind of behavior. The DW term acts to increase the energy of the Γ_{15} state, unlike the case for the Γ_2' state in Ge which decreased in energy. The SE term suppresses the acoustic contribution (while leaving it positive) and gives a large negative contribution for optic phonons which overwhelms the small DW effect. A partial explanation will be given shortly.

The temperature shifts $\Delta E_{\vec{k}n}(T)$ of the four states is shown in Fig. 6. Note that zero-point motion gives significant shifts, ~ 50 meV upwards for valence-band states and ~ 15 meV downwards for conduction-band states, or a total reduction of ~ 0.065 eV of the band gap. Band theorists currently strive for accuracy at this level and zero-point shifts need to be recognized as a significant factor limiting the accuracy of energy-band theory. To our knowledge this is the first calculation of the zero-point renormalization which correctly treats SE as well as DW effects. For all states studied except Γ_2', the DW terms by themselves overestimate the thermal shifts. However, the zero-point shifts are often underestimated by DW. The reason is that at $T=0$ the shift $\Delta E(0)$ is proportional to the area under $g^2F(\Omega)$, whereas the high-T shift $\Delta E(T)$ contains an extra factor $2k_BT/\hbar\Omega$ in the integrand which weights acoustic phonons more heavily than optic ones. Thus for the Γ_{25}' state in Ge, the area under g^2F is enhanced by the SE terms but the thermal shift (minus first moment) is reduced because of the suppression of acoustic phonons. In Si the Γ_{25}' state has the area under g^2F unchanged by SE terms but the thermal shift is again reduced. The Γ_{15} state has the sign of the area (and the zero-point effect) reversed by SE terms. The thermal shift is only very weakly T dependent because of a strong tendency for the positive effect of acoustic phonons to cancel the negative effect of optic phonons.

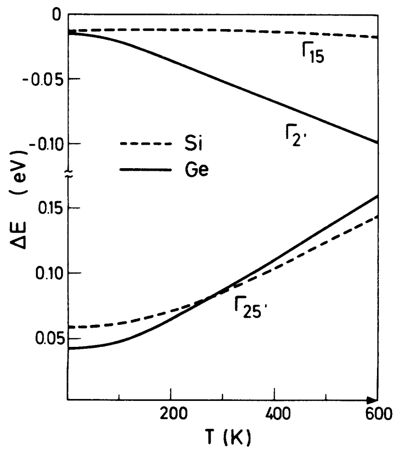

FIG. 6. Temperature-dependent shifts $\Delta E_{\vec{k}n}(T)$ of $\vec{k}=\vec{0}$ states in Si and Ge. Zeros correspond to rigid-crystal bands. Shifts are not zero at $T=0$ because of zero-point renormalizations.

The directly measurable quantity is the shift of the lowest direct gap $\Delta E_0(T)$ shown in Fig. 7. The experimental points for germanium were obtained by subtracting from the data of Ref. 21 the effect of thermal expansion [Eq. (1)] obtained from the temperature-dependent expansion coefficients of

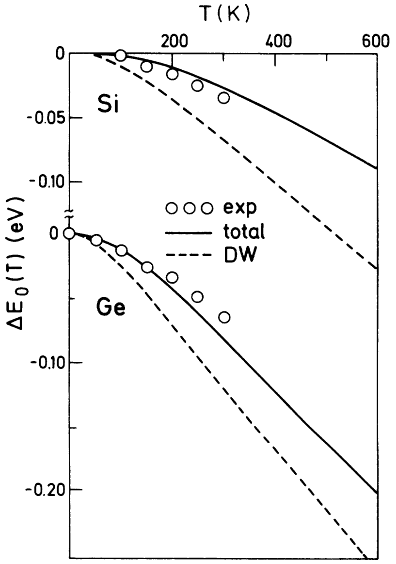

FIG. 7. Calculated shifts of the $\vec{k}=\vec{0}$ gaps $\Delta E_0(T)$ vs temperature (solid lines). Dashed curves are the DW contributions. Dots are experimental (see text).

TABLE II. Electron two-phonon deformation potentials D_1 in eV as defined by Eq. (14) for states at $\vec{k}=\vec{0}$ in Si and Ge and phonons at points X and L. In addition to the total, the DW part is given, and the contributions to the SE part from the lowest eight intermediate states are listed separately. When the intermediate state is doubly degenerate, the contribution shown is half the total contribution of the doublet. Similarly, when the phonon is doubly degenerate, the contribution shown is one-half the contribution of the pair. Occasional small contributions ($\lesssim 0.3$ eV) represent forbidden transitions which appear as weakly allowed because of small truncation errors. The contribution to $dE_{\vec{k}n}/dT$ at $T>\Theta_D$ is given by $2D_1k_BT/3NM\omega_{\vec{Q}j}^2a^2$. This table corrects Tables I—IV of I.

			Deformation potential (eV)	
Initial	Intermediate		Phonon branch	
state	state	X_3(TA)	X_1(LA,LO)	X_4(TO)
Ge Γ_{25}'	$X_1(v)$	1.	21.	100.
	$X_4(v)$	0.	130.	83.
	$X_1(c)$	$-82.$	$-60.$	$-2.$
	$X_4(c)$	0.	$-16.$	$-36.$
	DW	160.	160.	160.
	Total	$-18.$	250.	360.
Si Γ_{25}'	$X_1(v)$	0.2	9.	73.
	$X_4(v)$	0.	100.	51.
	$X_1(c)$	$-140.$	$-58.$	$-2.$
	$X_4(c)$	0.	$-10.$	$-29.$
	DW	190.	190.	190.
	Total	$-110.$	210.	300.
Ge Γ_2'	$X_1(v)$	0.	0.	0.
	$X_4(v)$	0.	0.	0.
	$X_1(c)$	0.	$+230.$	0.
	$X_4(c)$	$-12.$	0.	$-1.$
	DW	$-18.$	$-18.$	$-18.$
	Total	$-50.$	$+420.$	$-74.$
Si Γ_{15}	$X_1(v)$	0.2	1.	15.
	$X_4(v)$	10.	32.	0.
	$X_1(c)$	2.	47.	71.
	$X_4(c)$	$-1.$	$-8.$	-0.1
	DW	48.	48.	48.
	Total	36.	130.	18.

Ref. 2. We used $(\partial E_g/dP)_T = 13$ meV/kbar (Ref. 2), a value obtained for $P<10$ kbar. Values as high as 15.3 meV/kbar are obtained through quadratic fits to data for $P \lesssim 100$ kbar. We feel that the linear data for the lower pressure are more suitable to our purpose. The agreement between theory and experiment shown both for Ge and Si in Fig. 7 can be considered as satisfactory. In both cases inclusion of SE terms improves considerably this agreement and corrects most of the discrepancy found with the use of only the DW terms.[22] One should point out, however, that the experimental data for silicon correspond to the E_1 edge ($\sim$3.4 eV) which is nearly degenerate with the $\Gamma_{25}' \rightarrow \Gamma_{15}$ edge but also contains transitions between valence and conduction bands along the {111} directions. A detailed calculation of temperature coefficients of the {111} gaps as a function of $\vec{k}$ would be of interest. We have not performed it here as each $\vec{k}$ point would require 6 times more computer time than at point Γ.

We have listed in Table I all relevant calculated and experimental linear temperature coefficients of the lowest direct gap of Ge and Si in the (200—300)-K range. It is apparent that when SE and DW effect are combined, the result depends strongly on which state is considered. Further insight can be obtained by examining contribution of individual phonons. Table II gives an analysis for X- and L-point phonons. The results are expressed in terms of the two-phonon deformation potentials

TABLE II. (*Continued.*)

Initial state	Intermediate state	Deformation potential (eV) Phonon branch L_3(TA)	L_2(LA)	L_1(LO)	L'_3(TO)
Ge Γ'_{25}	$L'_2(v)$	0.	12.	0.	120.
	$L_1(v)$	0.5	0.	180.	0.
	$L'_3(v)$	0.	190.	0.	640.
	$L_1(c)$	−54.	0.	−140.	0.
	$L_3(c)$	−51.	0.	−11.	0.
	$L'_2(c)$	0.	−0.3	0.	0.
	DW	160.	160.	160.	160.
	Total	−25.	530.	3.	1460.
Si Γ'_{25}	$L'_2(v)$	0.	2.	0.	84.
	$L_1(v)$	0.3	0.	110.	0.
	$L'_3(v)$	0.	170.	0.	460.
	$L_1(c)$	−79.	0.	−83.	0.
	$L_3(c)$	−47.	0.	−12.	0.
	$L'_2(c)$	0.	−0.1	0.	0.
	DW	190.	190.	190.	190.
	Total	−25.	490.	62.	1120.
Ge Γ'_2	$L'_2(v)$	0.	0.	0.	0.
	$L_1(v)$	0.	3.	0.	0.
	$L'_3(v)$	4.	0.	0.	0.
	$L_1(c)$	0.	560.	0.	0.
	$L_3(c)$	0.	0.	0.	−17.
	$L'_2(c)$	0.	0.	−4.	0.
	DW	−18.	−18.	−18.	−18.
	Total	−42.	540.	−56.	−90.
Si Γ_{15}	$L'_2(v)$	7.	0.	18.	0.
	$L_1(v)$	0.	9.	0.	16.
	$L'_3(v)$	23.	0.	52.	0.
	$L_1(c)$	0.	80.	0.	19.
	$L_3(c)$	0.	−80.	0.	−660.
	$L'_2(c)$	−29.	0.	−14.	0.
	DW	48.	48.	48.	48.
	Total	30.	−45.	−52.	−1350.

D_1. Suppose the phonon $\vec{Q},j$ has amplitude $u_{\vec{Q}j}$. Then D_1 can be defined in terms of the shift in energy of the state $\vec{k},n$ due to virtual emission and reabsorption of this phonon, i.e.,

$$\frac{\partial \epsilon_{\vec{k}n}}{\partial n_{\vec{Q}j}} = \tfrac{2}{3} D_1(\vec{k},n;\vec{Q},j)\left(\frac{u_{\vec{Q}j}}{a}\right)^2 , \qquad (14)$$

where a is the lattice constant. The typical value shown for D_1 is ~340 eV for Γ'_{25} states, about 70 eV for the Γ'_2 state and ~−200 eV for the Γ_{15} state. The DW terms do not vary but the total D_1's show large fluctuations around these averages, i.e., between a minimum of 3 eV (for Ge, Γ'_{25} electron and L_1 phonon) and a maximum of 1500 eV (same electron with L'_3 phonons). The small value came from an accidental cancellation. The largest values always occur in SE terms when a strongly allowed phonon couples *via* an intermediate electron state with a small energy denominator. For Γ'_{25} valence bands the small denominators occur for Λ_3 and L'_3 states in the [111] direction. The denominator $E(\Gamma'_{25})-E(L'_3)$ is 0.75 and 0.9 eV in Ge and Si, respectively. The L_2(LA) and L'_3(TO) phonons are allowed (where LA is longitudinal acoustic and TO is transverse optical) but the latter couple more strongly than the former. This is the origin of the enhancement of optic phonons seen in Figs. 2 and 4. The corresponding acoustic suppression is related to the fact that the L_3(TA) (where TA is transverse acoustic) phonon is forbidden to couple Γ'_{25} to L'_3. An unfortunate large and erroneous violation of this selection rule (Table IV of I) was responsible for our incorrect finding in I that acoustic phonons were enhanced.

Ge and Si differ strongly in details of conduction bands. The Ge Γ'_2 state is nearly degenerate with both X_1 $[E(\Gamma'_2)-E(X_1)\simeq .08$ eV] and L_1 $\{E(\Gamma'_2)-E(L_1)\simeq 0.3$ eV] states. Only the X_1(LA,LO) (where LO is longitudinal optic) phonons at $\Omega=28.7$ meV couple Γ'_2 to X_1. The anomalously large D_1 at this point has little effect on g^2F because of two factors: (1) Little phase space carries phonons of this energy, and (2) nearby electronic states have energy denominators of opposite sign so that the contributions from states in this region tend to cancel. The $\vec{Q}$-space summation suffers from computational ambiguities in this region because of the vanishing energy denominators which occur on a surface in $\vec{Q}$ space. To handle this a phenomenological Lorentzian damping factor $\Gamma=0.1$ eV was used in the denominator. Reasons were given in I for believing that our results are not sensitive to the exact choice of Γ.

Similarly, only one phonon branch, L_2(LA), couples Γ'_2 to L_1. Little effect can be seen at $\omega(L_2)=25.7$ meV in g^2F. The uniform enhancement by SE terms of nearly all phonons for Ge Γ'_2 is a result which depends on all of $\vec{Q}$ space and the absence of any sharp enhancement at particularly resonant energy denominators.

The Si Γ_{15} conduction-band state is quite far in energy from X_1. At the L point, two nearby states occur, $E(\Gamma_{15})-E(L_1)=1.4$ eV and $E(\Gamma_{15})-E(L_3)=-0.5$ eV. From Table II it can be seen that neither allowed phonon has a large coupling to L_1 and only the L'_3(TO) phonon couples Γ_{15} strongly to L_3. The large negative D_1 arising from this transition accounts for the sharp negative resonance of g^2F at $\omega(L'_3)=60.9$ meV for the Si Γ_{15}. Thus we are able to account *a posteriori* for much of the odd behavior of g^2F. Clearly it would be difficult to guess *a priori* the relative quantitative importance of the various special points in the Brillouin zone.

V. CONCLUSIONS

The main conclusion of this work is that SE effects are very important. Earlier work reviewed in Ref. 1 had suggested that DW terms alone could explain most of the results. This now seems incorrect. Figures 2–5 show clearly that the complete theory (DW + SE) is distorted away from the simple DW theory. The integrated effect on dE_0/dT is to reduce the DW predictions by factors of 1.7 (Si, 300 K) and 1.3 (Ge, 300 K). The details of the physics are more strongly affected. The early successes of DW theory must be somewhat spurious, deriving from the flexibility of empirial nonlocal pseudopotential models, as suggested in Ref. 1, and from the fact that sometimes the *total* measured temperature coefficient is compared with the calculated $(\partial E_g/\partial T)_V$ without subtracting the thermal-expansion effect. The discrepancy is then smaller than if the comparison is carried out for $(\partial E_g/\partial T)_V$ correctly.

Contrary to our earlier paper (I), we are now encouraged to believe in the suitability of a rigid-pseudopotential model for these calculations. The insensitivity of our results to $V(\vec{q})$ at small q removes the largest source of uncertainty on this question.

Finally we find that the SE effects are sensitive to small details of near degeneracy in the band structure. However, selection rules at symmetry points are helpful in reducing the number of near resonances and allow rough interpretations to be made.

ACKNOWLEDGMENTS

One of us (P.B.A.) thanks H. Bilz for hospitality at the Max-Planck-Institut für Festkörperforschung, Stuttgart, where most of this work was done. We thank P. Vogl and M. L. Cohen for helpful conversations and U. Rössler for pointing out to us the inconsistencies which led us to find the error in I. The work of (P.B.A) was supported in part by the National Science Foundation under Grant No. DMR-81-21954.

---

[1] M. L. Cohen and D. J. Chadi, in *Semiconductor Handbook*, edited by M. Balkanski (North-Holland, Amsterdam, 1980), Vol. 2, Chap. 4b.

[2] See Landolt-Börnstein Tables, Group III, Vol. 17a, in *Physics of Group IV Elements and III-V Compounds*, edited by O. Madelung (Springer, Berlin, 1982).

[3] E. Antončik, Czech, J. Phys. 5, 449 (1955); J. Camassel and D. Auvergne, Phys. Rev. B 12, 3258 (1976).

[4] H. Y. Fan, Phys. Rev. 82, 900 (1951).

[5] P. B. Allen and M. Cardona, Phys. Rev. B 23, 1495

(1981). [hereafter denoted I]; Phys. Rev. B 24, 7479(E) (1981).

[6] P. B. Allen, Phys. Rev. B 18, 5217 (1978).

[7] S. K. Sinha, Phys. Rev. 169, 477 (1968).

[8] P. B. Allen and V. Heine, J. Phys. C 9, 2305 (1976).

[9] M. Lax, *Symmetry Principles in Solid State and Molecular Physics* (Wiley, New York, 1974), p. 342.

[10] L. J. Sham and J. M. Ziman, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 15, p. 221.

[11] W. Weber, Phys. Rev. B 15, 4789 (1977).

[12] O. H. Nielsen and W. Weber, Comput. Phys. Commun. 18, 101 (1979).

[13] M. L. Cohen and V. Heine, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24, p. 37.

[14] J. A. Appelbaum and D. R. Hamann, Phys. Rev. B 8, 1777 (1973).

[15] O. J. Glembocki and F. H. Pollak, Phys. Rev. Lett. 48, 413 (1982); Phys. Rev. B 25, 7863 (1982).

[16] S. Bednarek and U. Rössler, Phys. Rev. Lett. 48, 1296 (1982).

[17] J. A. Vergés, D. Glötzel, M. Cardona, and O. K. Andersen, Phys. Status Solidi B 113, 519 (1982).

[18] M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).

[19] G. Lehmann and M. Taut, Phys. Status Solidi B 54, 469 (1972); (b) 57, 815 (1973).

[20] N. S. Cooper and G. G. Lonzarich (unpublished).

[21] Y. P. Varshni, Physica (Utrecht) 34, 149 (1967).

[22] M. Cardona, in *Atomic Structure and Properties of Solids,* edited by E. Burstein (Academic, New York, 1972), p. 514.