PHYSICAL REVIEW B VOLUME 12, NUMBER 8 15 OCTOBER 1975

Temperature dependence of the fundamental edge of germanium and zinc-blende-type semiconductors

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(Received 16 December 1974)

We calculate the theoretical temperature dependence of the minimum of the conduction band at $k = 0$ for Ge, GaAs, GaSb, InSb, GaP, CdTe, ZnTe, ZnSe, and ZnS. We find results strongly dependent on the parameters describing the symmetrical part of the pseudopotential, and we show that the use of slightly different sets of pseudopotential form factors give rise to very different values for the temperature coefficient of the fundamental edge. A comparison with experimental results (piezoreflectance measurements) permits discussion of the choice of these parameters.

INTRODUCTION

Since the pioneering work of Fan[1] and Yu and Brooks,[2] a large number of calculations[3-6] have been carried out to theoretically investigate the temperature dependence of the band structure of cubic semiconductors. Generally speaking most of these calculations achieve qualitative agreement with experiment, i.e., give a correct order of magnitude for the temperature coefficient of the main optical transitions, but they never fit closely the experimental data. No systematic attempt to improve the calculations was made because of the dispersion of the experimental results available for a given compound[6] and because of the lack of reliable experimental Debye-Waller factors.

However, a recent calculation of the temperature dependence of the band structure of germanium, silicon, and GaAs,[7] which uses the new pseudopotential parameters of Chelikoswky *et al.* including nonlocality of the V_0 pseudopotential,[8] concluded that the Yu-Brooks theory accounts well for the experimentally observed rigidity with temperature of the top valence band of these compounds. Indeed, increasing the temperature of a crystal, one increases first the lattice parameter and second the electron-phonon interaction. The effect of lattice expansion can be obtained from pressure experiments. For example, for the valence band of germanium in the X direction, it corresponds to a decrease in width with a rate -5.9×10^{-5} eV/°K. The Yu-Brooks theory permits one to calculate the second contribution and gives in this case a value $d(\Gamma_{25} - X_4)/dt = 7.9 \times 10^{-5}$ eV/°K which is positive. This gives, corresponding to the effect of electron-phonon interaction with increasing temperature, an increase in width which nearly cancels the decrease in width corresponding to the effect of lattice expansion. This corresponds well to the rigidity experimentally observed.[7]

In this paper we use the same method to calculate the theoretical temperature dependence of the minimum of the conduction band at $k=0$. It is well known that slightly different pseudopotential curves can give identical band structures even if the Fourier transform of the crystal potential has different $V_{(G^2)}$ components. We confirm that the use of these slightly different sets of band-structure parameters give rise to very different values for the temperature coefficient of the fundamental edge. In this case the calculated values of the temperature coefficients mostly depend on the symmetrical part of the pseudopotential[4] through the two form factors $V_{(G^2=8)}$ and $V_{(G^2=11)}$, and we show that this calculation in conjunction with both (i) a reliable set of experimental Debye-Waller factors, (ii) well-established experimental temperature coefficients, may constitute a separate check of these specific pseudopotential form factors.

In order to perform this comparison we give experimental results (piezoreflectivity measurements) on Ge, GaAs, GaSb, InSb, CdTe, ZnSe, ZnTe, and ZnS. As most of the dispersion observed in the previously published data comes from the room-temperature measurements, we focus our attention on the accuracy obtained at room temperature. In that way we achieve a set of accurate data which permits a systematic comparison with our calculated values.

I. THEORETICAL BACKGROUND

In this section, we perform a direct calculation of the temperature dependence of the fundamental edge of Ge, GaAs, GaSb, InSb, CdTe, ZnSe, ZnTe, and ZnS. For completeness, we also include GaP and Si which are indirect (the conduction-band minimum is in the X direction) and for which reliable data exist in the literature.[9,10] The electron-phonon interaction (Debye-Waller effect) is obtained in the pseudopotential formalism using the standard basis of 15 symmetrized combinations of plane waves.[11,12] We first obtain the unperturbed wave functions of the two states Γ_1^c and Γ_{15}^v ($T = 0$ °K) and then calculate in first order the effect of perturbation ($T \neq 0$ °K). In order to obtain a set of systematically reliable results, we take all the values of the mean-square displacement of atoms $\langle u^2 \rangle$ for zinc-blende materials from the work of Vetelino *et al.*[13] In the same way we always include[7] the effect of lattice expansion from the experimental work of Paul and co-workers.[14] Lastly our calculation completely neglects the electron self-energy effects (Fan term). A recent estimate for III-V compounds[15] has shown this correction to be of the order of $(4-9)\times 10^{-5}$ eV/°K for GaAs, GaP, and InP depending on the crystal considered and the parameters used in the calculation.

A. Results

The 15 symmetrized combinations of [000], [111], and [200] plane waves used in the calculation are listed in Ref. 7 with the corresponding secular equation for a covalent crystal. Solving this equation one obtains a set of eight different wave functions:

$\Gamma_1^l, \Gamma_1^u, \Gamma_{2'}^l, \Gamma_{2'}^u, \Gamma_{25'}^l, \Gamma_{25'}^u, \Gamma_{15}$, and Γ_{12} which are (i) a pure $\{111\}_{\Gamma_{15}}$ combination, (ii) a pure $\{200\}_{\Gamma_{12'}}$ combination, (iii) two admixtures of the properly symmetrized $\{000\}_{\Gamma_1}$ and $\{111\}_{\Gamma_1}$ combinations, which we note

$$|\Gamma_1^l\rangle = \alpha_1^l \{000\}_{\Gamma_1} + \beta_1^l \{111\}_{\Gamma_1} ,$$
$$|\Gamma_1^u\rangle = \alpha_1^u \{000\}_{\Gamma_1} + \beta_1^u \{111\}_{\Gamma_1} , \tag{1}$$

and, (iv) four admixtures $|\Gamma_{2'}^l\rangle$, $|\Gamma_{2'}^u\rangle$, $|\Gamma_{25'}^l\rangle$, and $|\Gamma_{25'}^u\rangle$ of the properly symmetrized {111} and {200} combinations, which we note

$$|\Gamma_{2'}^l\rangle = \beta_{2'}^l \{111\}_{\Gamma_{2'}} + \gamma_{2'}^l \{200\}_{\Gamma_{2'}} , \tag{2}$$

with three other equivalent expressions.

We work under the standard assumption that the antisymmetric part of the pseudopotential in noncentrosymmetric crystals acts as a perturbation on the lone symmetric part of the pseudopotential which determines the pure $|\Gamma_{2'}^l\rangle$ and $|\Gamma_{25'}^l\rangle$ wave functions. This results in an admixture of $|\Gamma_1\rangle$ and $|\Gamma_{15}\rangle$ states with $|\Gamma_{2'}\rangle$ and $|\Gamma_{25'}\rangle$, respectively. One can write

$$|\Gamma_1^c\rangle = \alpha_1 |\Gamma_{2'}^l\rangle - j\beta_1 |\Gamma_1^l\rangle - j\gamma_1 |\Gamma_1^u\rangle ,$$
$$|\Gamma_{15}^v\rangle = \alpha_2 |\Gamma_{25'}^l\rangle - j\beta_2 |\Gamma_{15}\rangle , \tag{3}$$

where the factor j comes from the definition of the pseudopotential

$$V = V^S + jV^A .$$

In order to determine the numerical values of these coefficients α, β, γ we must calculate the three different antisymmetric matrix elements labeled, in the notation of Higginbotham *et al.*[16] V_1, V_2, and V_3. Each corresponds to a closed combination of the three classical antisymmetric form factors V_3^A, V_4^A, and V_{11}^A given by

$$V_1 = \langle \Gamma_{25'}^l | H^A | \Gamma_{15} \rangle = -\beta_{25'}^l V_4^A - \sqrt{2}\gamma_{25'}^l (V_3^A - V_{11}^A)$$
$$V_2 = \langle \Gamma_{2'}^l | H^A | \Gamma_1^u \rangle = V_3^A (2\alpha_1^u \beta_{2'}^l - \sqrt{6}\beta_1^u \gamma_{2'}^l)$$
$$+ V_4^A (\sqrt{6}\alpha_1^u \gamma_{2'}^l - 3\beta_1^u \beta_{2'}^l) - V_{11}^A (\sqrt{6}\beta_1^u \gamma_{2'}^l) , \tag{4}$$

with a similar expression for V_3. In that way we obtain the different wave functions of the conduction and valence bands at $k = 0$.

Now, since we know the different contributions (admixture coefficients) for a specific eigenstate, we can perform the temperature-dependent calculation once we have determined the variation versus temperature of each component. As an example, for the minimum of the conduction band we can write

$$\frac{d\Gamma_1^c}{dT} = \alpha_1^2 \frac{d\Gamma_{2'}^l}{dT} + \beta_1^2 \frac{d\Gamma_1^l}{dT} + \gamma_1^2 \frac{d\Gamma_1^u}{dT} + 2\alpha_1\beta_1 \frac{dV_3}{dT}$$
$$+ 2\alpha_1\gamma_1 \frac{dV_2}{dT} + 2\beta_1\gamma_1 \frac{d\langle \Gamma_1^l | H | \Gamma_1^u \rangle}{dT} , \tag{5}$$

with a similar expression for the valence band. The weighting coefficients α, β, γ depend on the semiconductor studied through the intensity of the antisymmetric coupling. For instance with the recent pseudopotential form factors of Chelikowsky *et al.*[8] we obtain for the conduction band in the horizontal sequence Ge-GaAs-ZnSe the contributions listed in Table I. As expected the $|\Gamma_{2'}\rangle$ contribution decreases with increasing ionicity from about 80% in GaAs to 50% in ZnSe as the $|\Gamma_1^l\rangle$ and $|\Gamma_1^u\rangle$ character increases. The same kind of result is found for the valence band.

Finally we need to calculate the temperature dependence of the different matrix elements in Eq. (5). In order to perform the calculation, we work under the standard assumption that because of the effect of the thermal vibrations of the lattice, each energy state experiences a shift which is (relative to its unperturbed value at 0 °K) simply obtained by

TABLE I. Change in admixture coefficients for the conduction and the valence band at $k = 0$ through the horizontal sequence Ge-GaAs-ZnSe.

	$\lvert\Gamma_{2'}^l\rangle$	$\lvert\Gamma_1^l\rangle$	$\lvert\Gamma_1^u\rangle$	$\lvert\Gamma_{25'}^l\rangle$	$\lvert\Gamma_{15}\rangle$
Ge	1	0	0	1	0
GaAs	0.904	$-0.271j$	$-0.33j$	0.878	$-0.479j$
ZnSe	0.716	$-0.4j$	$-0.567j$	0.820	$-0.570j$

multiplying each pseudopotential form factor by the corresponding Debye-Waller-factor[2-7] amplitude:

$$V_m \to V_m \exp[-(m\Omega/6)\langle u^2\rangle] \qquad (6)$$

where $m = 3, 8, 11$ for the three symmetric form factors, $m = 3, 4, 11$ for the three antisymmetric form factors, $\Omega = (2\pi/a_0)^2$ where a_0 is the lattice constant in Bohr units, and $\langle u^2\rangle$ is the mean-square average displacement also in Bohr units.

This results in an attenuation of the potential seen by the electrons and for example in the simple picture of pure bonding and antibonding states of covalent crystals (see Fig. 1) one expects a positive variation of the valence band (bonding P state) and a negative variation of the conduction band (antibonding S state) with this decrease in potential. In order to calculate directly the numerical value $\langle \alpha\rangle$ of the corresponding temperature coefficients in the range of the linear variation between 100 and 300 °K we develop the perturbation and write

$$V_m \to V_m - \tfrac{1}{6} m\Omega V_m (\Delta\langle u^2\rangle)_{100^\circ\mathrm{K}}^{300^\circ\mathrm{K}}, \qquad (7)$$

where the first term corresponds to the unperturbed Hamiltonian and the second gives the temperature dependence of the matrix elements. With our explicit expressions of the wave functions [Eq. (3)], we limit the calculation to first order and obtain the numerical values given in the two first columns of Table II. In the last column, we give the references for the pseudopotential form factors used and list the corresponding parameters in Table III. In order to achieve a reliable set of results, we tried to refer all along the computation to the same work.[8] This has not been possible for GaSb,[17] ZnS, and ZnTe.[18] However a comparison between the calculations of Refs. 8 and 18 is possible through the use of the computations for CdTe and ZnSe with both series of parameters. In the same way all values of $(\Delta\langle u^2\rangle)_{100^\circ\mathrm{K}}^{300^\circ\mathrm{K}}$ are taken from the work of Ref. 13, except germanium (not given in Ref. 13) for which we use the recent experimental data of Jex.[19] The values of Ref. 13 are not experimental but computed from a rigid-ion model. However, we must outline that they compare well with the experimental results available for GaAs, GaP, InAs, ZnTe, and CdTe.

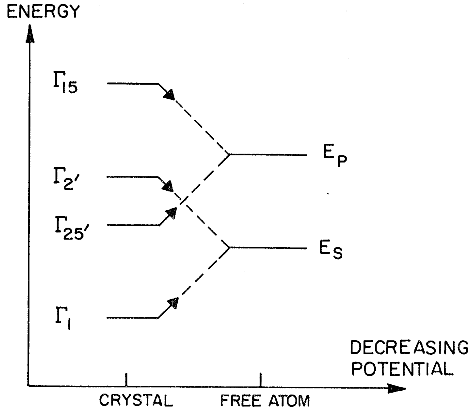

FIG. 1. Correspondence between atomic energies and crystal energies at $k = 0$ for a covalent semiconductor. A decrease in potential (effect of lattice expansion or thermal vibration) will give a positive temperature coefficient for the two bonding states Γ_1 and $\Gamma_{25'}$. An increase in potential (hydrostatic pressure) would give a negative pressure coefficient for these two states. In the same way, one expects for the two antibonding states $\Gamma_{2'}^{l}$ and Γ_{15} a negative temperature coefficient and a positive pressure dependence.

TABLE II. Details of the contributions which add to give the temperature coefficients of the fundamental gap in some cubic semiconductors.

Compound	$\frac{d\Gamma_1^c}{dT}$ (eV/°K)	$\frac{d\Gamma_{15}^v}{dT}$ (eV/°K)	$\left(\frac{dE_0}{dT}\right)_{\mathrm{DW}}$ (10^4 eV/°K)	$\left(\frac{dE_0}{dT}\right)_{\mathrm{vol}}$ (10^4 eV/°K)	$\left(\frac{dE_0}{dT}\right)_{\mathrm{calc}}$ (10^4 eV/°K)	Reference (V_m)
Ge	-5×10^{-6}	2.7×10^{-4}	−2.75	−1.65	−4.4	8
GaAs	-7×10^{-5}	2.45×10^{-4}	−3.15	−1.3	−4.45	8
GaSb	-4×10^{-5}	2×10^{-4}	−2.4	−1.35	−3.75	17
InSb	1×10^{-5}	2.5×10^{-4}	−2.4	−0.9	−3.3	8
GaP	-1×10^{-4}	2×10^{-4}	−3	−1.5	−4.5	8
CdTe	-1.6×10^{-4}	5.5×10^{-4}	−7.1	−0.4	−7.5	8
	-4×10^{-5}	3.5×10^{-4}	−3.9	−0.4	−4.3	18
	5×10^{-5}	3.4×10^{-4}	−2.9	−0.4	−3.3	20
ZnSe	-2.5×10^{-4}	5.2×10^{-4}	−7.7	−0.7	−8.4	8
	-9×10^{-5}	3.54×10^{-4}	−4.44	−0.7	−5.1	18
ZnTe	-1.1×10^{-4}	3.8×10^{-4}	−4.9	−0.6	−5.5	18
ZnS	-2.6×10^{-4}	3.9×10^{-4}	−6.5	−0.6	−7.1	18

TABLE III. Pseudopotential form factors and lattice constant a_0(Å) used in the calculation.

Compound	a_0(Å)	V_3^S	V_8^S	V_{11}^S	V_3^A	V_4^A	V_{11}^A	Reference
Si	5.43	−0.257	−0.040	0.033				
Ge	5.65	−0.269	0.038	0.035				8
GaAs	5.64	−0.252	0.000	0.080	0.068	0.066	0.012	8
GaSb	6.12	−0.21	0.015	0.04	0.09	0.03	0.01	17
InSb	6.47	−0.25	0.010	0.044	0.049	0.038	0.01	8
GaP	5.45	−0.249	0.017	0.083	0.081	0.055	0.003	8
CdTe	6.48	−0.245	−0.015	0.073	0.089	0.084	0.006	8
		−0.207	0.006	0.032	0.145	0.0715	0.026	18
		−0.20	0.012	0.027	0.168	0.075	0.028	20
ZnSe	5.65	−0.261	0.011	0.113	0.151	0.130	0.016	8
		−0.239	0.014	0.0529	0.2807	0.0978	0.0525	18
ZnTe	6.07	−0.2256	0.0022	0.035	0.087	0.1257	0.035	18
ZnS	5.41	−0.2472	0.0412	0.0526	0.301	0.1215	0.0475	18

B. Discussion of results

As expected, the Debye-Waller temperature coefficient of the valence band is positive and this is true for the entire family: The valence band goes up with increasing temperature and gives the most important contribution to the experimental value of the temperature coefficient of the band gap. Roughly this contribution is of the order of 3×10^{-4} eV/°K. The exact value depends essentially on the symmetrical part of the pseudopotential through the V_{11} form factor. In the isoelectronic sequence Ge-GaAs-ZnSe, computed with the parameters of Ref. 8, the temperature coefficient given for germanium is greater than the corresponding value for GaAs. This result arises from the different origin of the mean-square displacement $\langle u^2\rangle$ for germanium and explains our choice of a reliable unique source of data for all the rest of the calculation.

The temperature coefficient of the conduction band is less important. As expected, for germanium it is negative but very small: -5×10^{-6} eV/°K. Generally speaking, the calculated value increases through the isoelectronic sequence (Ge-GaAs-ZnSe with increasing strength for the antisymmetric coupling) but remains negative. The numerical values obtained strongly depends on the semiconductor (Ge: -5×10^{-6} eV/°K, GaAs: -7×10^{-5} eV/°K) and on the set of parameters used. Consider for example the strongly varying values obtained for ZnSe (-2.5×10^{-4} eV/°K with the parameters of Ref. 8 and -9×10^{-5} eV/°K with those of Ref. 18). An even more interesting result is obtained in the isoelectronic sequence InSb-CdTe. For InSb the calculated value is very low and positive. This results in a small Debye-Waller contribution to the temperature coefficient α_0 of the band gap which correlates well with the small experimental value of α_0 obtained on this compound. For CdTe we performed the calculation with three different sets of parameters. The values obtained range between -1.6×10^{-4}, and $+5\times10^{-5}$ eV/°K which also gives a positive shift for the conduction band versus temperature and a small Debye-Waller contribution. As previously observed for InSb this also correlates well with our experimental results on CdTe: The two compounds exhibit nearly identical temperature coefficients which are the lowest for the whole germanium-zinc-blende family. As the most important difference between the parameters of Refs. 8, 18, and 20 is in the successive decrease of the V_{11} symmetric form factor this confirms that the calculated values mainly depend on the symmetrical part of the pseudopotential (through V_8^S and V_{11}^S which should vary little through the horizontal sequence).

The third column of Table II gives the total Debye-Waller contribution obtained from the difference of columns 1 and 2. In order to perform the calculation, we must add to this contribution the effect of lattice expansion given in column 4. We can calculate this contribution from the experimental pressure and compressibility coefficients listed by Paul and co-workers[14] through the standard expression

$$\frac{dE_0}{dT}=-\frac{3\alpha}{\chi}\frac{dE_0}{dP}\ .$$

The linear-dilatation coefficients are taken in the work of Novikova[21] and one obtains the values given in column 4. This volume or dilatation contribution is always smaller than the Debye-Waller contribution but is also negative, and hence, contributes to increase the temperature coefficients to the final values listed in column 5.

C. Minimum X of indirect materials

For the sake of completeness it is interesting to calculate the temperature dependence of the X indirect gap of GaP and silicon. The corresponding $|X_1^c\rangle$ wave function is an admixture of the two symmetrized combinations of plane waves $\{100\}_{X_1}$ and $\{011\}_{X_1}$ given in Ref. 11 through the effect of both symmetric and antisymmetric coupling:

$$\begin{array}{ccc} & \{100\}_{X_1} & \{011\}_{X_1} \\ \{100\}_{X_1} & \Omega - v_4^- & \sqrt{2}(v_3 - v_3^-) \\ \{011\}_{X_1} & \sqrt{2}(v_3 - v_3^-) & 2\Omega + v_8 - 2_{v4}^- \end{array}$$

with the parameters of Ref. 8, a straightforward calculation gives for the temperature coefficient of the $|X_1^c\rangle$ minimum of GaP $dX_1^c/dT = -1.25\times 10^{-4}$ eV/°K. Taking account of the two values calculated in Table II for $d\Gamma_1^c/dT$ and $d\Gamma_{15}^v/dT$, we have the three coefficients needed to account for the experimental temperature dependence of both the direct and the indirect gap in this material. Adding the effect of the two strongly different corrections for lattice expansion, one obtains the results given in Table IV in excellent agreement with the experimental values.

TABLE IV. Comparison of both calculated and experimental values for the temperature dependence of the direct and indirect gaps of GaP.

	$\frac{dE_{(\Gamma-X)}}{dT}$	$\frac{dE_0}{dT}$
Debye-Waller contribution	-3.25×10^{-4}	-3×10^{-4}
Volume contribution	0.15×10^{-4}	-1.5×10^{-4}
Calculated value	-3.1×10^{-4}	-4.5×10^{-4}
Experimental value (100–300 °K)	-3.1×10^{-4} [a]	-4.1×10^{-4} [b]

[a] Experimental result obtained from the relation $E_g = 2.388 - 6.2\times 10^{-4}T^2/(T+460)$. [M. B. Panish and H. C. Casey (Ref. 9)].

[b] Value obtained from the experimental results of Dean *et al.* (Ref. 9).

For silicon, we used the recent nonlocal pseudopotential of Chelikowsky and Cohen[8] and obtained for the temperature coefficient of the indirect gap the values given in Table V. In Ref. 8 the authors calculated the optical, photoemissive, and x-ray properties, as well as the cyclotron masses of silicon, with both a local and a nonlocal pseudopotential. For comparison, we give also the results of our computation with the set of parameters corresponding to the purely nonlocal pseudopotential. One obtains only a good agreement with the parameters corresponding to the nonlocal pseudopotential: $(dE_{\text{ind}}/dT)_{\text{calc}} = -2.7\times 10^{-4}$ eV/°K compared with the experimental value[10] $dE_{\text{ind}}/dT = -2.4\times 10^{-4}$ eV/°K in the range 200–300 °K. With the parameters corresponding to the local pseudopotential the agreement is poor: we find $(dE_{\text{ind}}/dT)_{\text{calc}} = -4.7\times 10^{-4}$ eV/°K. These two examples show that, with accurate pseudopotential form factors, (i) the Debye-Waller coefficients which we independently associate with each extrema of the band structure are correct and (ii) our calculation of the lattice-expansion effect from experimental hydrostatic-pressure coefficients is also sufficiently accurate to permit a fine comparison with experiment. This is the goal of Sec. II.

II. EXPERIMENTS

The experimental apparatus has been previously described[22,23] and enables us to work in a large range of experimental conditions independent of the spectral range investigated and of the doping

TABLE V. Comparison of calculated and experimental values for the temperature dependence of the indirect gap of silicon (eV/°K).

Pseudopotential parameters	local [a]	nonlocal [a]
Debye-Waller contribution $\frac{dX_1}{dT}$	-1.66×10^{-4}	-1.07×10^{-4}
Debye-Waller contribution $\frac{d_{25'}}{dT}$	3.14×10^{-4}	1.77×10^{-4}
Volume contribution	1.1×10^{-5}	1.1×10^{-5}
Calculated values	-4.7×10^{-4}	-2.73×10^{-4}
Experimental value [b] (200–300 °K)	-2.4×10^{-4}	-2.4×10^{-4}

[a] J. R. Chelikowsky and M. L. Cohen (Ref. 8b).

[b] Value obtained from the experimental results of W. Bludau, A. Onton, and W. Heinke (Ref. 10).

level of the sample. All samples studied are mechanically polished and chemically etched by standard techniques to a final thickness of 100 μm and then glued on piezoelectric transducers in order to perform a derivative spectroscopy. With standard values of the electric field, $E \sim (3-5)\times 10^3$ V/cm, this corresponds to the application of an alternative stress $\Delta T \sim 50$ kg/cm^2 on the sample and gives a modulation amplitude of the fundamental edge:

$$\Delta E_0 \simeq \frac{dE_0}{dP}\,\Delta T \sim 5\times 10^{-4}\ \text{eV}\,.$$

In order to obtain an accurate determination of a temperature coefficient it is most important to determine precisely the experimental value of the transition in the highest-temperature range of data. Consider for example GaAs, which is a well-known semiconductor. In the recent literature one can find values of the band gap at room temperature ranging from[24] 1.380 to[25] 1.435 eV which constitutes simply a dispersion in crystals quality, broadening effects, interpretation of data, etc. On the other hand, most of the results converge at helium temperature, resulting in a dispersion of 2×10^{-4} or 3×10^{-4} eV/°K which constitutes 50% of the true coefficient. The situation is worse for II-VI compounds in which the range of uncertainty at room temperature is of the order of 100 meV.[23]

A typical example of the resolution obtained at room temperature is given in Fig. 2(a). The line shape is characteristic of the first derivative of a two-dimensional M_0 critical point and permits an accurate determination of the absorption edge.[26] In this case, for intrinsic germanium the broadening parameter Γ which corresponds to half the energy separation between the two extrema is less than 3 meV and the accuracy of the data competes with the best results obtained in low-field electroreflectance[27] [(see Fig. 2(b)]. The same kind of spectrum is obtained on high-purity GaAs and GaSb. In contrast, InSb always contains an im-

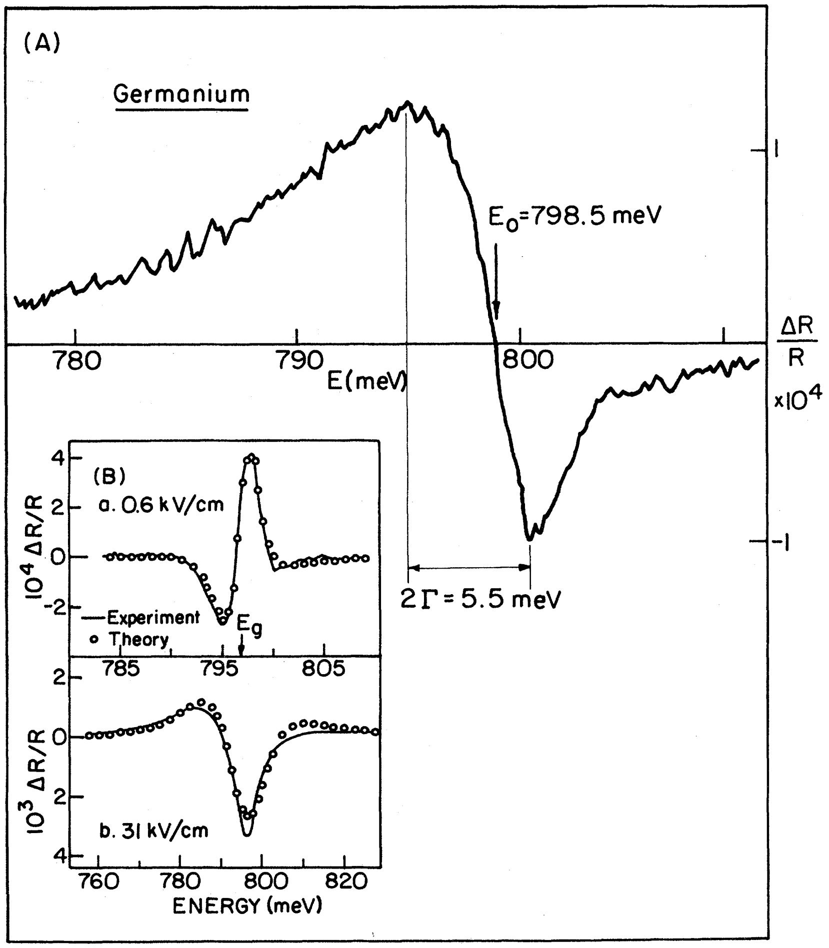

FIG. 2. Differential reflectivity spectrum of the fundamental edge of germanium (300 °K): (a) piezoreflectivity (this work) $E_0 = 798.5 \pm 1$ meV; (b) electroreflectivity (a: low field $E = 600$ V/cm, b: high field $E = 3.1$ kV/cm, after Ref. 27). In both cases $E_0 = 797 \pm 2$ meV.

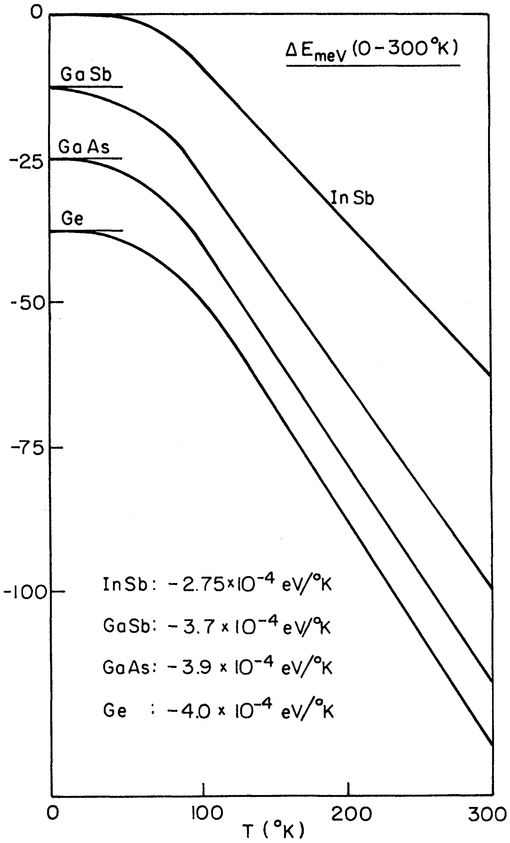

FIG. 3. Relative shift of the band gap in Ge, GaAs, GaSb, and InSb.

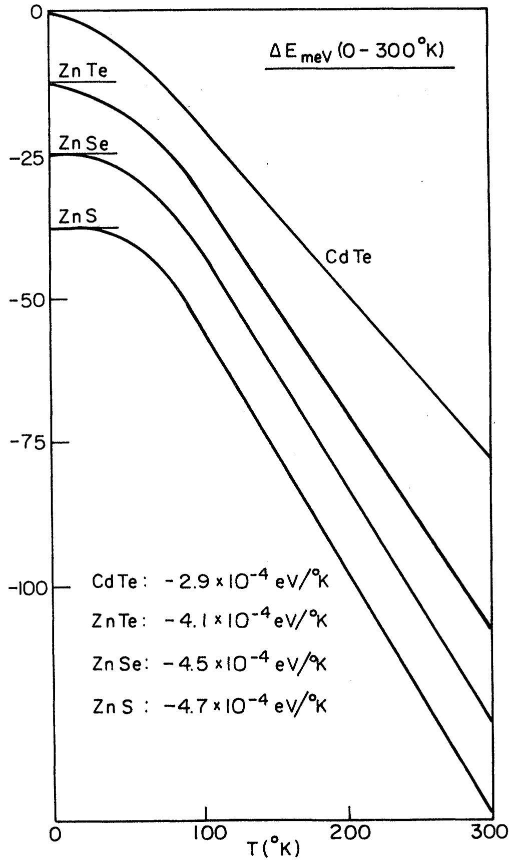

FIG. 4. Shift of the band gap in the II-VI compounds CdTe, ZnTe, ZnSe, and ZnS.

portant concentration of free carriers and is characterized by a three-dimension (nonexcitonic) M_0 critical point.[22]

The temperature dependence of the band gap in these compounds is given in Fig. 3. In Fig. 4 we give the temperature dependence observed in the II-VI compounds.[23] As expected from the results of our calculation, we see that the semiconductors of the same isoelectronic sequence are characterized by nearly the same experimental value (see Fig. 5). This experimental result confirms the predominent role played by the symmetrical part of the pseudopotential in the calculation of the temperature coefficients. The numerical values of the absorption edge at 0 and 300 °K are given in Table VI together with the experimental and calculated values of the temperature coefficients in the range 100–300 °K. A comparison of these two series of results show that for Ge, GaAs, GaSb, and InSb the agreement obtained between the experimental values and the result of our calculation is fairly good.

It is interesting to verify how a small change of V_{11}^S is able to greatly modify this result. In Table

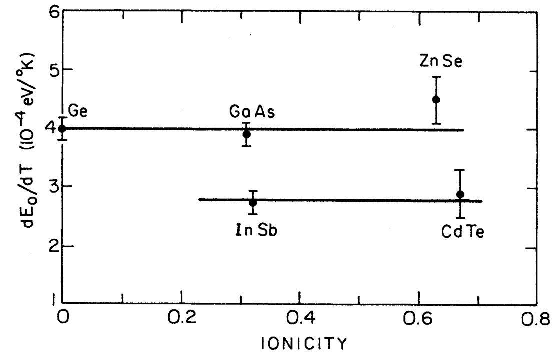

FIG. 5. Temperature dependence of the fundamental edge versus ionicity for the two isoelectronic sequences Ge-GaAs-ZnSe and InSb-CdTe. The estimated error is $+0.2\times10^{-4}$ eV/°K for Ge and the III-V compounds and $\pm 0.4\times10^{-4}$ eV/°K for the II-VI compounds. We did not find in the recent literature any value for the temperature coefficient of the inverted bandgap of α-Sn. According to the present scheme it should be positive $dE_g/dT \sim 3 \times10^{-4}$ eV/°K.

TABLE VI. Variation of the band gap versus temperature in cubic compounds. Experimental values for Ge, GaAs, GaSb, and InSb do not include the binding energy of excitons. Values for CdTe, ZnTe, ZnSe, and ZnS include excitonic effect according to the work of Ref. 23.

E_0 (eV)	Ge	InSb	GaSb	GaAs	CdTe	ZnTe	ZnSe	ZnS
300 °K	0.7985	0.172	0.722	1.424	1.529	2.300	2.724	3.731
0 °K	0.888	0.235	0.810	1.515	1.606	2.395	2.823	3.833
$\left(\frac{dE_0}{dT}\right)_{\text{expt}}$ (10^{-4} eV/°K)	-4 ± 0.2	-2.75 ± 0.20	-3.7 ± 0.2	-3.9 ± 0.2	-2.9 ± 0.5	-4.1 ± 0.5	-4.5 ± 0.5	-4.7 ± 0.5
$\left(\frac{dE_0}{dT}\right)_{\text{calc}}$ (10^{-4} eV/°K)	-4.4	-3.3	-3.75	-4.45	-7.5 -4.3 -3.3	-5.5	-8.4 -5.1	-7.1

VII we compare the results obtained for InSb with only a slight adjustment of V_{11}^S, changing from the value[8] 0.044 Ry to the value 0.040 Ry.[28] This results in an improvement of the calculation which gives now -2.9×10^{-4} eV/°K, in much better agreement with the experimental value of -2.75×10^{-4} eV/°K.

For the II-VI compounds the comparison of both series of results (experiment and theory) shows a systematic improvement when a set of pseudopotential form factors are used which give Fourier components of the symmetrical part of the pseudopotential lower in a II-VI compound as compared with the corresponding III-V. This result is absolutely general and is expected to provide a probe to check one or two specific form factors.[29] For example, we give in Table VIII a systematic comparison between our experimental values, the results of this calculation, and the results obtained by Tsay *et al.*,[6] with the same values of the Debye-Waller factors but the pseudopotential form factors of Cohen and Bergstresser.[28] The improvement is general and reflects well the progress achieved in band-structure calculation during the last ten years.

III. CONCLUSION

We have performed a direct calculation of the temperature dependence of the fundamental edge in germanium and zinc-blende-type semiconductors. This calculation shows that the most sensitive level to temperature is the maximum of the valence band Γ_{15}^v. As the temperature increases, the valence band goes up toward the conduction band with a rate of $\sim3\times10^{-4}$ eV/°K and gives the most important contribution to the temperature coefficient of the band gap. In contrast, the temperature coefficient of the conduction band at $k=0$ is very small. Lastly, in both cases, the calculated values are mostly sensitive to the symmetrical part of the pseudopotential. This effect is supported by experimental observations on semiconductors of the two most important isoelectronic sequences which exhibit experimental temperature coefficients nearly independent of ionicity, i.e., roughly independent of the effect of antisymmetric couplings.

In this way, a careful comparison of the experimental values with the results of the calculation for different sets of parameters shows a systemat-

TABLE VII. Example of adjustment of $V^S(G^2=11)$ performed on InSb.

Pseudopotential form factors	$\frac{d\Gamma_1^c}{dT}$	$\frac{d\Gamma_{15}^v}{dT}$	$\left(\frac{dE_0}{dT}\right)_{\text{theor}}$	$\left(\frac{dE_0}{dT}\right)_{\text{expt}}$
a	1×10^{-5}	2.5×10^{-4}	-3.3×10^{-4}	-2.75×10^{-4}
b	4×10^{-5}	2.4×10^{-4}	-2.9×10^{-4}	-2.75×10^{-4}

[a] See Ref. 8, $V^S(G^2=11)=0.044$ Ry.

[b] All pseudopotential form factors have the values of Ref. 8, except $V^S(G^2=11)=0.04$ Ry (see Ref. 28).

TABLE VIII. Comparison of experimental results and calculated values, first in this work, second in the works of Tsay *et al.* (Ref. 6) with a systematic use of the pseudopotential form factors of Ref. 28.

	Experimental value (10^{-4} eV/°K)	Calculated value (this work) (10^{-4} eV/°K)	Reference of the pseudopotential form factors (this work)	Other works (Refs. 6 and 28)
Ge	−4.0	−4.4	8	
Si ($X_1-\Gamma_{25'}$)	−2.4	−2.7	8	
GaAs	−3.9	−4.45	8	−6.3
GaSb	−3.7	−3.75	17	−4.0
InSb	−2.75	−2.9	8 with $V_{11}=0.04$	−3.5
GaP ($\Gamma_1^c-\Gamma_{15}^v$)	−4.1	−4.5	8	−4.3
GaP ($X_1^c-\Gamma_{15}^v$)	−3.1	−3.1	8	−2.75
CdTe	−2.9	−3.3	20	−6.2
ZnSe	−4.5	−5.1	18	−6.5
ZnTe	−4.1	−5.5	18	−6.7
ZnS	−4.7	−7.1	18	−6.7

ic dependence on the value of the V_{11}^S. This result could give a new probe to check the results of different band-structure calculations and a more detailed comparison could be made if a complete set of experimental Debye-Waller factors for the germanium–zinc-blende family becomes available. A critical check is to perform on HgTe and HgTe-CdTe alloys. Indeed, two recent attempts[30,31] to calculate the temperature dependence of the band gap of these compounds have been unsuccessful, even in the sign of the variation, and the question is to know (i) if the Yu-Brooks theory in this case is inadequate[30] or (ii) if simply the potential used in the calculation must be modified.[31]

ACKNOWLEDGMENTS

We would like to thank Professor M. Cardona for helpful comments during the course of this work and Professor M. L. Cohen for a critical reading of the manuscript.

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