

Temperature dependence of the band structure of germanium- and zinc-blende-type semiconductors

D. Auvergne, J. Camassel, and H. Mathieu

*Centre d'Etudes d'Electronique des Solides, Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cedex-France**

M. Cardona

Max-Planck-Institut für Festkörperforschung, Stuttgart, Federal Republic of Germany

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The top valence bands are known to vary little throughout the Ge-zinc-blende family of semiconductors (Ge, III-V, and II-VI compounds). We present in this paper, theoretical (Yu-Brooks calculations) and experimental evidence (piezoreflectance measurements) which suggests that these valence bands vary rigidly with temperature, in contrast to the behavior of the conduction bands. It is possible to combine this conclusion with the experimental temperature coefficients of the E_0 , E_1 , and E_2 energy gaps to predict the temperature coefficient of the separation between the Γ , L , and X - Δ conduction-band minima.

INTRODUCTION

The invariance of the width of the two top p -like valence bands for all germanium-type, III-V, and II-VI semiconductors was conjectured some time ago.¹⁻³ This invariance referred, in particular, to the relative energies of the X_4 , $\Gamma_{25'}$, and L_3 point (germanium notation). Local pseudopotential and other band calculations, however,⁴⁻⁶ indicated that these valence bands become flatter with increasing ionicity through the Ge, III-V, and II-VI sequence. Recent photoelectron spectroscopy measurements⁷ have made clear that the bands are indeed more rigid, independent of ionicity, than the semiempirical and non-self-consistent band calculations led us to believe. Such invariance of the width of the top valence bands is well reproduced, however, by self-consistent orthogonalized-plane-wave calculations⁸ and by pseudopotential calculations with allowance for nonlocality in the choice of an effective mass instead of a free-electron mass.⁹ Thus, the rigidity of the top p -like valence bands of Ge, III-V, and II-VI compounds must be regarded as an established fact. In contrast to it, the conduction bands deform considerably from one material of the family to another, a situation which results in the well-known switching of the various lowest conduction valleys and the transition from direct to various sorts (X , L) of indirect edges.

At this point, the question arises naturally as to whether the rigidity of the top valence bands is also preserved under the application of two standard symmetry-preserving perturbations: hydrostatic pressure and temperature. For instance, the pressure dependence of the E_1 gap (see Fig. 1) is 7.5×10^{-6} eV/bar,¹⁰ while that of the indirect gap $E_i(L)$ is only 5×10^{-6} eV/bar.¹¹ A look at Fig. 1 thus shows that the valence bands deform slightly with hydrostatic pressure, the $\Gamma_{25'} - L_3$ energy difference increases with increasing pressure at

the rate of 2.5×10^{-6} eV/bar. We show in this paper that this small pressure effect contributes to make the valence bands nearly independent of temperature. The explicit temperature dependence calculated with the Yu-Brooks theory¹²⁻¹⁵ produces also a slight change in the $\Gamma_{25'} - L_3$ energy separation which is mostly cancelled by the effect of the thermal expansion as obtained from the pressure coefficients discussed above.

Similar conclusions apply at the X point. The pressure coefficient of the indirect gap of Si ($\Gamma_{25'} - \Delta_1$, whereby Δ_1 is very close to X_1) is -1.5×10^{-6} eV/bar,¹¹ while that of the E_2 gap, which involves a large region of the Brillouin zone but which we assume, in view of considerable evidence, to be tied to the $X_4 - X_1$ gap, is $+3 \times 10^{-6}$ eV/bar.¹¹ The differences between these two pressure coefficients, which results in a slight deformation of the top valence bands along Δ , is compensated by the explicit temperature effects and yields nearly temperature independent bands along Δ .

The Yu-Brooks calculation, consisting simply in the multiplication of all pseudopotential form factors by the appropriate Debye-Waller parameters, are performed in a simple way by calculating the temperature dependence (diagonal matrix element) of the 15 Γ states which were used previously for the full zone $\vec{k} \cdot \vec{p}$ representation, and the off-diagonal elements between states of the same symmetry. Using the projections of the Bloch functions of any state in the Brillouin zone on those at Γ given in Ref. 16, it is possible to calculate from the temperature dependence of the basis states at $\vec{k} = 0$ that at any other point of the Brillouin zone. Calculations are presented for Ge and GaAs.

In order to find experimental evidence for the rigidity of the valence bands as a function of temperature, we have performed piezotransmission

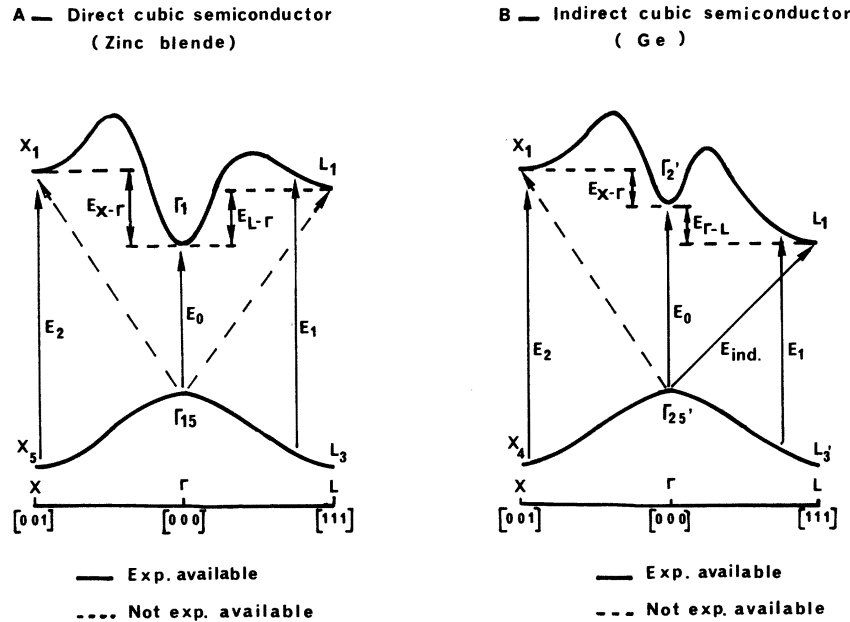


FIG. 1. Schematic band structures around the gap of a direct and an indirect gap semiconductor.

measurements of the indirect gaps of Ge and Si and piezoreflectance measurements of the E_1 and E_2 gaps as a function of temperature. This result enables us to conclude that to a high degree of accuracy the top valence bands of Ge along Λ and those of Si along Δ change rigidly with temperature. In view of the homology of both materials, we infer that these valence bands of Ge and Si change also rigidly along Δ and Λ , respectively.

A number of III-V semiconductors (GaAs, GaSb, GaP, AlSb) have conduction band minima within a small energy range. The temperature dependence of their energy separations is of importance in a number of technological applications (Gunn effect, semiconductor laser). It is not always possible to obtain directly these temperature coefficients since indirect gaps cannot be observed once they occur above a direct one. We therefore suggest to use the rigidity of the valence bands and to determine the relative temperature shifts of the L_1 , X_1 , and Γ_2 (Γ_1) minima from the temperature coefficients of the corresponding direct gaps E_1 , E_2 , and E_0 . Some examples are presented.

THEORY

Germanium

The full zone $\vec{k} \cdot \vec{p}$ representation of the band structure of germanium and zinc-blende-type materials¹⁸ uses as a basis the following Bloch states at Γ [listed by order of increasing energy for Ge]: Γ_1^I , $\Gamma_{25'}^I$ (threefold), Γ_2^I , Γ_{15} (threefold), Γ_{12}^I (twofold), Γ_1^II , $\Gamma_{25'}^II$ (threefold). The eigenvalues and eigenfunctions of these states can be determined in the pseudopotential formalism as mixtures

of plane waves of wave vectors $(2\pi/a)(1, 1, 1)$ and $(2\pi/a)(2, 0, 0)$.¹⁷ The states Γ_{12}^I and Γ_{15} do not have any mate in the basis above. They are therefore pure, properly symmetrized $[200]$ and $[111]$ plane waves, respectively [we represent by $[ijk]$ the normalized plane wave of wave vector $(2\pi/a)(i, j, k)$]. We list in Table I the $[111]$ and $[200]$ waves properly symmetrized to have the symmetries of our basis states.

We use for Ge, the symmetric pseudopotential¹⁷: $V = V_3 + V_8 + V_{11}$, where the subindex represents the sum of the squares of the indices j, k, l which determine the corresponding Fourier-component plane wave $\exp[(2\pi/a)(jx + ky + lz)] = [jkl]$. The symmetrized partial pseudopotentials are

$$V_{m=j^2+k^2+l^2} = v_i \cos \frac{1}{4}\pi (l+j+k), \quad (1)$$

where v_i is the atomic form factor and the cosine gives the corresponding structure factor. Within the bases of Table I, the eigenvalues and pseudo-eigenvectors are trivial for the "lone" Γ_{15} and Γ_{12}^I states:

$$\Gamma_{15}: \text{eigenvalue } 3\Omega - v_8, \\ \text{eigenvector, see } \langle 111 \rangle \text{ combination,} \\ \text{Table I;}$$

$$\Gamma_{12}^I: \text{eigenvalue } 4\Omega - 2v_8, \\ \text{eigenvector, see } \langle 200 \rangle \text{ combination, (2)} \\ \text{Table I;}$$

$$\Omega = (2\pi/a)^2.$$

In Eq. (2), all energies are in rydbergs and the lattice constant a in Bohr radii.

TABLE I. Symmetrized combinations of [000], (111) and (200) plane waves to be used in the pseudopotential analysis of the $k=0$ states. For the doubly ($\Gamma_{12'}$) and triply degenerate states ($\Gamma_{25'}$, Γ_{15}) we have given only one of the degenerate combinations.

	(000)	(111)	(200)
Γ_1	[000]	$\frac{1}{\sqrt{8}} \{ 111\rangle - 1\bar{1}\bar{1}\rangle - \bar{1}1\bar{1}\rangle - \bar{1}\bar{1}1\rangle - \bar{1}\bar{1}\bar{1}\rangle - \bar{1}11\rangle - 1\bar{1}1\rangle - 11\bar{1}\rangle \}$	
$\Gamma_{25'}$		$\frac{1}{\sqrt{8}} \{ 111\rangle - 1\bar{1}\bar{1}\rangle + \bar{1}1\bar{1}\rangle + \bar{1}\bar{1}1\rangle - \bar{1}\bar{1}\bar{1}\rangle - \bar{1}11\rangle + 1\bar{1}1\rangle + 11\bar{1}\rangle \}$	$\frac{1}{\sqrt{2}} \{ 200\rangle + \bar{2}00\rangle \}$
$\Gamma_{2'}$		$\frac{1}{\sqrt{8}} \{ 111\rangle - 1\bar{1}\bar{1}\rangle - \bar{1}1\bar{1}\rangle - \bar{1}\bar{1}1\rangle - \bar{1}\bar{1}\bar{1}\rangle + \bar{1}11\rangle + 1\bar{1}1\rangle + 11\bar{1}\rangle \}$	$\frac{1}{\sqrt{6}} \{ 200\rangle + 020\rangle + 002\rangle - \bar{2}00\rangle - 0\bar{2}0\rangle - 0\bar{0}2\rangle \}$
Γ_{15}		$\frac{1}{\sqrt{8}} \{ 111\rangle - 1\bar{1}\bar{1}\rangle - \bar{1}1\bar{1}\rangle - \bar{1}\bar{1}1\rangle - \bar{1}\bar{1}\bar{1}\rangle - \bar{1}11\rangle - 1\bar{1}1\rangle - 11\bar{1}\rangle \}$	
$\Gamma_{12'}$			$\frac{1}{2} \{ 200\rangle - 020\rangle - \bar{2}00\rangle + 0\bar{2}0\rangle \}$

The eigenvalues and vectors of the pairs of states (Γ_1^u, Γ_1^l), ($\Gamma_{25'}^u, \Gamma_{25'}^l$), ($\Gamma_{2'}^u, \Gamma_{2'}^l$) are obtained by diagonalization of 2×2 matrices. The matrix for the Γ_1 states is

$$\begin{pmatrix} 0 & -2v_3 \\ -2v_3 & 3\Omega + 3v_8 \end{pmatrix}, \quad (3)$$

which yields for the form factors and lattice constant used in Ref. 9 ($v_3 = -0.269$, $v_8 = 0.038$, $v_{11} = 0.035$ Ry, $a = 5.65$ Å) the eigenvalues and eigenvectors

Γ_1^u : $E = 1.405$ Ry,

$$|\Gamma_1^u\rangle = 0.935 \{ |111\rangle_{\Gamma_1} + 0.356 \{ |000\rangle_{\Gamma_1} \}, \quad (4)$$

Γ_1^l : $E = -0.205$ Ry,

$$|\Gamma_1^l\rangle = +0.356 \{ |111\rangle_{\Gamma_1} - 0.935 \{ |000\rangle_{\Gamma_1} \},$$

where $\{ |111\rangle_{\Gamma_1}$ and $\{ |000\rangle_{\Gamma_1}$ are the symmetrized plane waves of Table I. The matrices for the ($\Gamma_{25'}^u, \Gamma_{25'}^l$) and the ($\Gamma_{2'}^u, \Gamma_{2'}^l$) pairs can be found in Ref. 17. The eigenvectors are

$$\begin{aligned} |\Gamma_{2'}^u\rangle &= 0.582 \{ |111\rangle_{\Gamma_{2'}} - 0.812 \{ |200\rangle_{\Gamma_{2'}} \}, \\ |\Gamma_{2'}^l\rangle &= 0.812 \{ |111\rangle_{\Gamma_{2'}} + 0.582 \{ |200\rangle_{\Gamma_{2'}} \}, \\ |\Gamma_{25'}^u\rangle &= 0.540 \{ |111\rangle_{\Gamma_{25'}} - 0.845 \{ |200\rangle_{\Gamma_{25'}} \}, \\ |\Gamma_{25'}^l\rangle &= 0.845 \{ |111\rangle_{\Gamma_{25'}} + 0.540 \{ |200\rangle_{\Gamma_{25'}} \}. \end{aligned} \quad (5)$$

Once these wave functions are available for all the states at Γ , it is possible to obtain their explicit temperature dependence by using the Yu-Brooks method of Debye-Waller factors.¹²⁻¹⁴ To this explicit temperature dependence one must add the effect of thermal expansion, obtained either from the experimental pressure coefficients or from a pseudopotential calculation.¹⁷

The idea of the Yu-Brooks method is to describe the temperature dependence of the band structure by multiplying the pseudopotential form factors by the amplitude Debye-Waller factors

$$\begin{aligned} \exp\left[-\frac{1}{6} \Omega \langle u^2 \rangle (j^2 + k^2 + l^2)\right] \\ \simeq 1 - \frac{1}{6} \Omega \langle u^2 \rangle (j^2 + k^2 + l^2), \end{aligned} \quad (6)$$

where $\langle u^2 \rangle$ is the mean-square average of the atomic displacements due to the lattice vibrations. In the region of interest between 100 and 300 K, it is justified to use only the two terms in the power series expansion of Eq. (6). Since the eigenvalues of the unperturbed (\equiv no lattice vibrations) system are known, it is reasonable to calculate the effect of the Debye-Waller factor in first-order perturbation theory. The matrix elements of the perturbation Hamiltonian between plane waves are obtained by replacing into Eq. (3) and the analogous equa-

TABLE II. Expectation values and off-diagonal matrix elements of the Debye-Waller temperature perturbation Hamiltonian for the 15 states of the full-zone $k \cdot p$ basis.

	$dE/d\langle u^2 \rangle$ (eV/bohr ²)	$(\partial E/\partial T)_v$ (eV/°C)	
$\Gamma_{25'}^u$	-1.13	-2.24×10^{-4}	
$\Gamma_{25'}^l$	-1.63	-3.24×10^{-4}	$\langle \Gamma_{25'}^u H' \Gamma_{25'}^l \rangle = -0.144 \langle u^2 \rangle$ eV
$\Gamma_{12'}$	0.497	9.85×10^{-5}	$\langle \Gamma_{12'}^u H' \Gamma_{12'}^l \rangle = -0.732 \langle u^2 \rangle$ eV
$\Gamma_{2'}^u$	-1.52	-3×10^{-4}	$\langle \Gamma_{25'}^u H' \Gamma_{25'}^l \rangle = -0.465 \langle u^2 \rangle$ eV
Γ_{15}	0.25	4.9×10^{-5}	
$\Gamma_{2'}^l$	-0.028	-5.5×10^{-6}	
$\Gamma_{25'}^l$	1.37	2.71×10^{-4}	
Γ_1^l	0.778	1.54×10^{-4}	

TABLE III. Temperature coefficients of the E_0 and E_0' gaps (in units of 10^{-4} eV/°C).

	Calculated	Experiment
$\frac{dE_0}{dT}$	-4.4	-4.0 ± 0.2^a
$\frac{dE_0'}{dT}$	-2.4	-1.5 ± 0.2^b

^aUnpublished data.

^bD. E. Aspnes, Phys. Rev. Lett. **28**, 913 (1972).

tions for other states the form factors v by

$$H'_m = -\frac{1}{6} \Omega m \langle u^2 \rangle v_m \quad (7)$$

A trivial calculation yields for the 15 basis states the temperature shifts (in eV and per unit $\langle u^2 \rangle$) listed in Table II. We reiterate that this calculation was done for Ge by using the new pseudopotential parameters of Chelikowsky *et al.*,⁹ given above, which include nonlocality of the v_0 pseudopotential as required by recent photoemission measurements. Using the temperature dependence of $\langle u^2 \rangle$ obtained from x-ray data and from lattice-dynamical calculations by Jex¹⁸

$$\frac{d\langle u^2 \rangle}{dT} = 1.98 \times 10^{-4} \text{ bohr}^2/\text{K}$$

one finds the temperature coefficients of the basis states given also in Table II.

From Table II we can find the explicit temperature dependence of the $E_0(\Gamma_2^I - \Gamma_{25'}^I)$ and the $E_0'(\Gamma_{15} - \Gamma_{25'}^I)$ gaps. In order to obtain the total temperature coefficients of these and other gaps one must add the effect of the thermal expansion obtained from the volume dependence of the gap and the linear expansion coefficient α ($\alpha = 5.7 \times 10^{-6}$ K⁻¹ for Ge). The volume coefficient $dE_0/d \ln v$ equals -9.8 eV,¹⁹ and $dE_0'/d \ln v$ equals -0.9 eV,¹⁰ for Ge. Using these values we find the total temperature coefficients of Table III which compare well with the experimental results also listed in this table. A slight decrease in the value used for $d\langle u^2 \rangle/dT$ would suffice for bringing the calculated values into even better agreement with experiment.

In order to analyze the rigidity of the top valence band with varying temperature we now calculate the temperature coefficient of the $L_{3'}$ and X_4 valence states. The corresponding periodic Bloch functions are linear combinations of the 15 $\vec{k}=0$ basis states.¹⁶ From Ref. 16, we find

$$\begin{aligned} |L_{3'}\rangle &= 0.827 |\Gamma_{25'}^I\rangle + 0.402 |\Gamma_{15}\rangle \\ &+ 0.098 |\Gamma_{25'}^u\rangle - 0.381 |\Gamma_{12'}\rangle \quad (8) \end{aligned}$$

The expectation value of the perturbation Hamiltonian H' in the state $|L_{3'}\rangle$ of Eq. (8) can be calculated by using the matrix elements of Table II.

We find

$$\left(\frac{\partial L_{3'}}{\partial T}\right)_v = 2 \times 10^{-4} \text{ eV/K} \quad (9)$$

a value slightly smaller than that of the $\Gamma_{25'}$ states. The volume coefficients of these states, however, are known to be different: this difference can be obtained from the difference between the volume coefficient of the indirect gap (-3.7 eV¹¹) and that of the E_1 gap (-5.6 eV^{11,19}) (see Fig. 1). This difference contributes a term

$$\frac{d(\Gamma_{25'} - L_{3'})}{dT} = -3 \times 10^{-5} \text{ eV/K} \quad (10)$$

to the temperature dependence of the valence-band width $\Gamma_{25'} - L_{3'}$. Adding this term to the difference

$$\left(\frac{\partial \Gamma_{25'}}{\partial T}\right)_v - \left(\frac{\partial L_{3'}}{\partial T}\right)_v = 7.1 \times 10^{-5} \text{ eV/K} \quad (11)$$

we find a nearly negligible temperature dependence of the width of the top valence band along Λ (4.1×10^{-5} eV/K). One can perform a similar calculation for the X_4 valence state

$$\begin{aligned} |X_4\rangle &= 0.716 |\Gamma_{25'}^I\rangle - 0.672 |\Gamma_{15}\rangle \\ &- 0.193 |\Gamma_{25'}^u\rangle \quad (12) \end{aligned}$$

Using the matrix elements of Table II, one obtains

$$\left(\frac{\partial X_4}{\partial T}\right)_v = +1.92 \times 10^{-4} \text{ eV/K} \quad (13)$$

a value considerably smaller than the explicit temperature coefficient of the $\Gamma_{25'}$ state. We can estimate the thermal expansion contribution to the temperature coefficient of the $\Gamma_{25'} - X_4$ width by looking at the difference between the pressure coefficients of the E_2 gap of silicon ($+3 \times 10^{-6}$ eV/bar) and the corresponding $\Gamma_{25'} - X_1$ indirect gap (-1.5×10^{-6} eV/bar): Pressure coefficients of the same gap are known to be nearly the same for a given family of materials.¹¹ These coefficients could also be calculated from the corresponding wave functions and the derivatives of the pseudopotential with respect to the wavevector.¹⁷ We prefer, however, to use experimental values because of the inaccuracies involved in estimating the derivatives of the pseudopotentials. We thus find, for the volume contribution,

$$\frac{d(\Gamma_{25'} - X_4)}{dT} = -5.9 \times 10^{-5} \text{ eV/K} \quad (14)$$

Adding this term to explicit temperature effects [Eq. (13) and Table II], we find

$$\frac{d(\Gamma_{25'} - X_4)}{dT} = +2 \times 10^{-5} \text{ eV/K} \quad (15)$$

a very small temperature dependence, indeed. For the sake of completeness, we have also cal-

TABLE IV. Calculated values of the explicit temperature coefficients of the L_1 and X_1 states of Ge, together with the experimental and calculated values of the total temperature coefficients of the E_1 and E_2 gaps (in units of 10^{-4} eV/K).

	$\left(\frac{\partial L_1}{\partial T}\right)_v$	$\frac{dE_1}{dT}$	$\left(\frac{\partial X_1}{\partial T}\right)_v$	$\frac{dE_2}{dT}$
Calculated	-0,72	-3,7	-0,54	-2,85
Experimental		$-4,1 \pm 0,2^a$		$-3,9 \pm 0,9^a$
		$-4,2 \pm 0,4^b$		$-2,4 \pm 0,4^b$
		$-4,2 \pm 0,4^c$		$-1,8 \pm 0,5^c$

^aThis work.

^bReference 28.

^cReference 1.

culated the explicit temperature coefficients of the L_1 and X_1 conduction states. They are listed in Table IV together with the total temperature coefficients of the E_1 and E_2 gaps obtained from them and also with the experimental values.

GaAs

The calculations are made under the standard assumptions that the potential of GaAs is the sum of that of Ge plus an antisymmetric potential

$$V^- = iv_m^- \sum_{l,j,k} \sin \frac{1}{4} \pi (l+j+k) e^{(2\pi i/a)(xl+yj+zk)}, \quad (16)$$

$$m = l^2 + j^2 + k^2.$$

We take, as usual, only the three antisymmetric form factors $v_3^- = 0.068$, $v_4^- = 0.066$, $v_{11}^- = 0.012$ Ry.⁹ Through the antisymmetric potential the $\Gamma_{25'}^i$ state of germanium becomes mixed with Γ_{15} and $\Gamma_{25'}^u$. We take the admixture coefficients from $\vec{k} \cdot \vec{p}$ calculations²⁰

$$\begin{aligned} |\Gamma_{15}^u\rangle_{\text{GaAs}} = & 0.81 |\Gamma_{25'}^i\rangle + 0.083 |\Gamma_{25'}^u\rangle \\ & - 0.464 i |\Gamma_{15}\rangle. \end{aligned} \quad (17)$$

For evaluating the expectation value of the Debye-Waller perturbation Hamiltonian, we need the expectation values and matrix elements of Table II plus the antisymmetric coupling between $\Gamma_{25'}^i$ and Γ_{15} . Using the wave functions of Eq. (5) and Table I, we find

$$\begin{aligned} \langle \Gamma_{25'}^i | H' | \Gamma_{15} \rangle &= i \times 0.228 \langle u^2 \rangle \text{ eV}, \quad (18) \\ \langle \Gamma_{25'}^u | H' | \Gamma_{15} \rangle &= i \times 0.047 \langle u^2 \rangle \text{ eV}. \end{aligned}$$

We have implicitly assumed that $\langle u_{\text{Ga}}^2 \rangle = \langle u_{\text{As}}^2 \rangle = \langle u^2 \rangle$. The work of Vetelino *et al.*²¹ shows that this assumption holds to within 1% for GaAs. It holds rather well ($\sim 10\%$) even in materials with

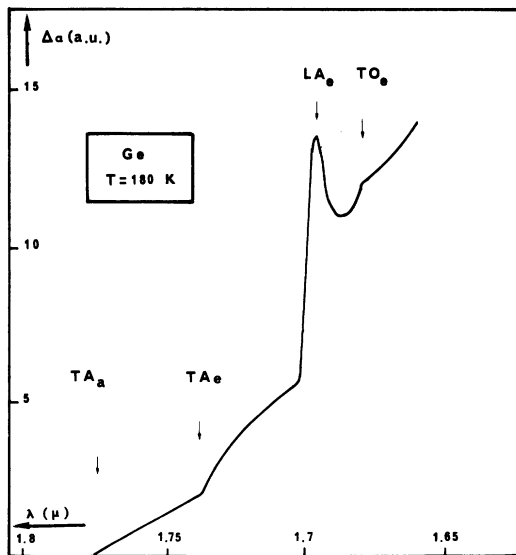


FIG. 2. Piezotransmission spectrum of Ge at 180 K.

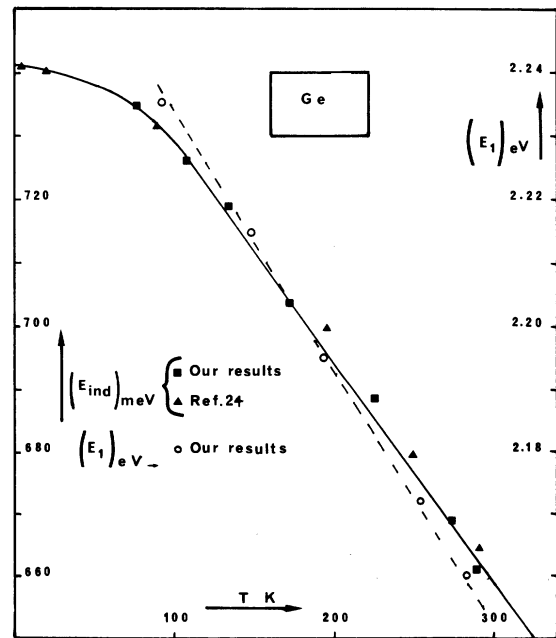


FIG. 3. Temperature dependence of the indirect and the E_1 gap of Ge.

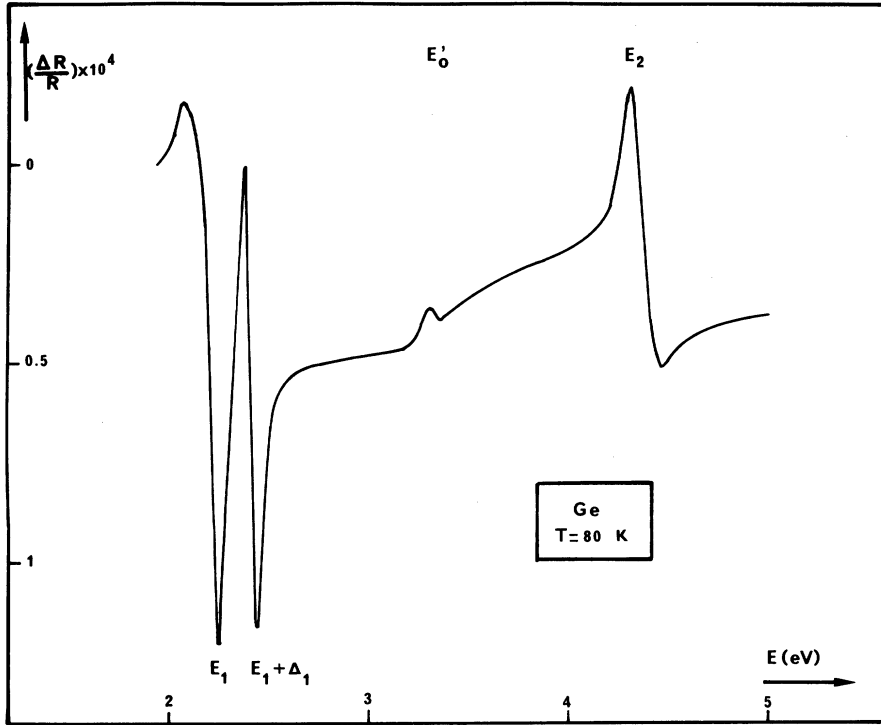


FIG. 4. Piezoreflectance spectrum of the E_1 , $E_1 + \Delta_1$, E'_0 , and E_2 transitions of Ge at 80 K.

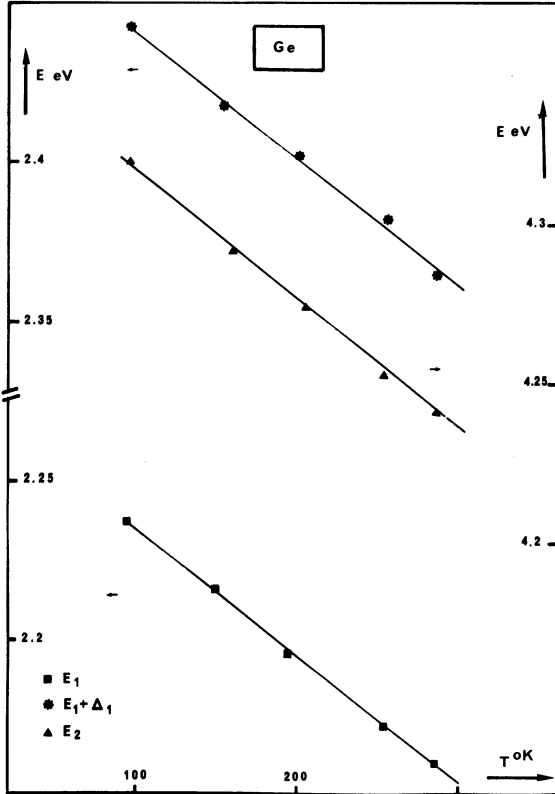


FIG. 5. Temperature dependence of the E_1 , $E_1 + \Delta_1$, and E_2 transitions of Ge.

very different masses such as InP. From Ref. 21 we find, between 100 and 300 K for GaAs, $d\langle u^2 \rangle / dT = 1.67 \times 10^{-4}$ bohr²/K. The explicit temperature dependence of the Γ_{15}^v state of GaAs thus becomes

$$\left(\frac{\partial \Gamma_{15}^v}{\partial T}\right)_v = 1.82 \times 10^{-4} \text{ eV/K} \quad (19)$$

It is also possible using the same method to calculate the explicit temperature dependence of the L_3 and X_5 top valence states. We have²⁰

$$\begin{aligned} |L_3\rangle = & (0.688 - 0.355i)|\Gamma_{25'}^i\rangle + (0.198 - 0.480i)|\Gamma_{15}\rangle, \\ & + (0.200 - 0.042i)|\Gamma_{25'}^u\rangle \\ & + (-0.377 + 0.106i)|\Gamma_{12'}\rangle, \end{aligned} \quad (20)$$

$$\begin{aligned} |X_5\rangle = & (0.710 - 0.0789i)|\Gamma_{25'}^i\rangle + (-0.666 - 0.077i)|\Gamma_{15}\rangle \\ & + (-0.175 - 0.103i)|\Gamma_{25'}^u\rangle. \end{aligned}$$

A straightforward calculation yields, for the explicit temperature dependence of L_3 and X_5 ,

$$\left(\frac{\partial L_3}{\partial T}\right)_v = 1.62 \times 10^{-4} \text{ eV/K} \quad (21)$$

$$\left(\frac{\partial X_5}{\partial T}\right)_v = 1.22 \times 10^{-4} \text{ eV/K} \quad .$$

The coefficients of Eq. (21) become nearly the same as those of Eq. (19) (Γ_{15}^v) after the contribution of the thermal expansion, assumed to be the same as that obtained from experimental data for germanium, is added.

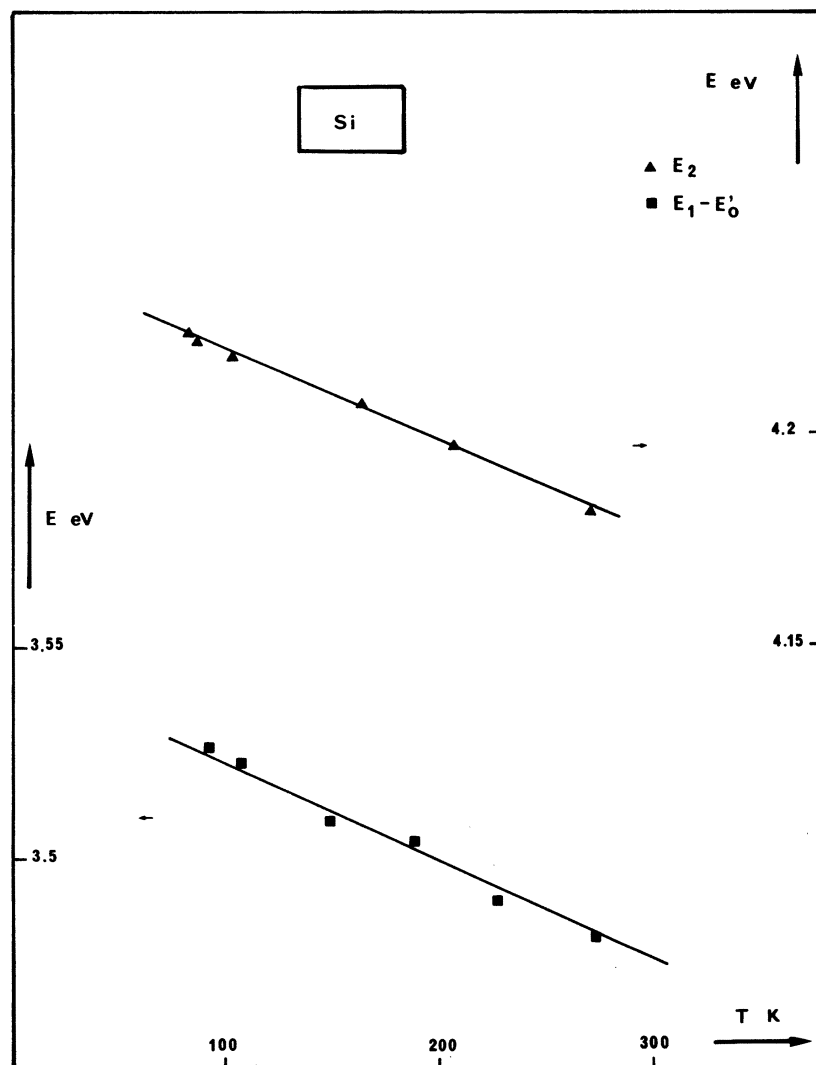


FIG. 6. Temperature dependence of the $E_1 - E_0'$ and the E_2 transitions of Si.

The calculations just presented show that the top valence band changes rigidly with temperature for Ge and GaAs. We have also found similar results for silicon. The homology of the germanium-zinc-blende family enables us to expect similar results for all group-IV and III-V compounds, and possibly also for the II-VI compounds, except maybe those of very large band gap.

EXPERIMENTS

In order to confirm the rigidity of the top valence bands of germanium and silicon, we have performed piezotransmission measurements of the temperature dependence of the indirect gaps of these materials and piezoreflectance measurements of the temperature dependence of the E_1 and E_2 gaps. From the indirect and the E_1 gaps of germanium we obtain information about the top valence band along Λ . From the indirect and E_2 gaps of

silicon, the rigidity along Δ is confirmed (see Fig. 1). We should point out that recent measurements of the indirect gap of GaP (Ref. 22) yield a temperature coefficient of -3.6×10^{-4} eV/ $^\circ\text{C}$, very close to that obtained by Varea *et al.*²³ for the E_2 gap [$(-3.5 \pm 0.4) \times 10^{-4}$ eV/K]. This confirms experimentally the rigidity of the top valence bands along Δ for at least one III-V compound.

The piezotransmission spectrum of the indirect edge of Ge at 180 K is shown in Fig. 2. Three phonon-emission-induced transitions (TA_e , LA_e , TO_e) and one phonon-absorption-induced (TA_a) are observed. We take for the determination of the temperature dependence of the indirect edge the shift of the most prominent LA_e peak with $\hbar\Omega_{LA} = 27.6$ meV. The results are shown in Fig. 3 together with the indirect gap data of Ref. 24. Both sets of data agree and give through a least-squares fit a temperature coefficient

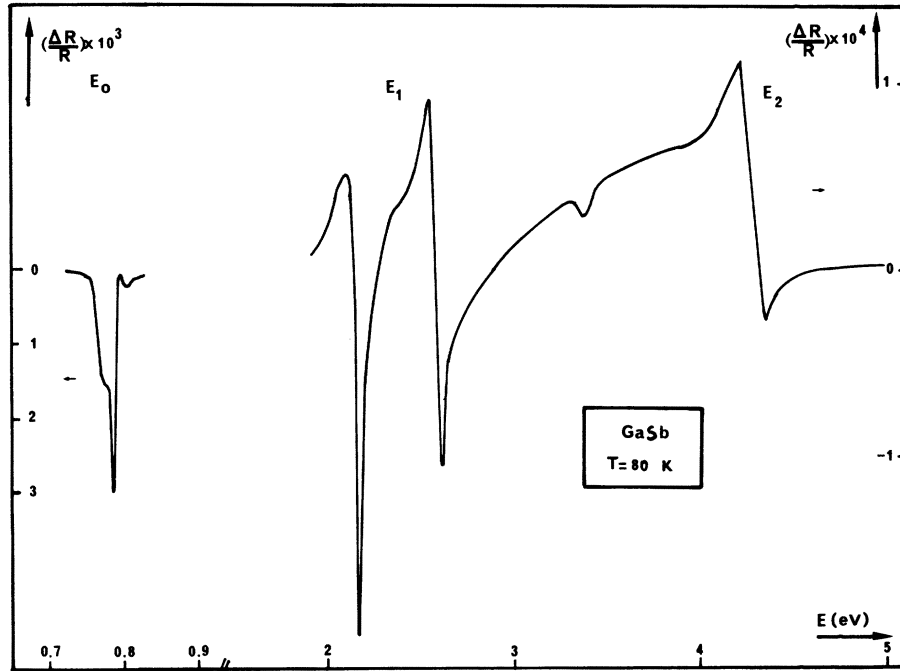


FIG. 7. Piezoreflectance spectrum of the E_0 , E_1 , and E_2 transitions of GaSb at 80 K.

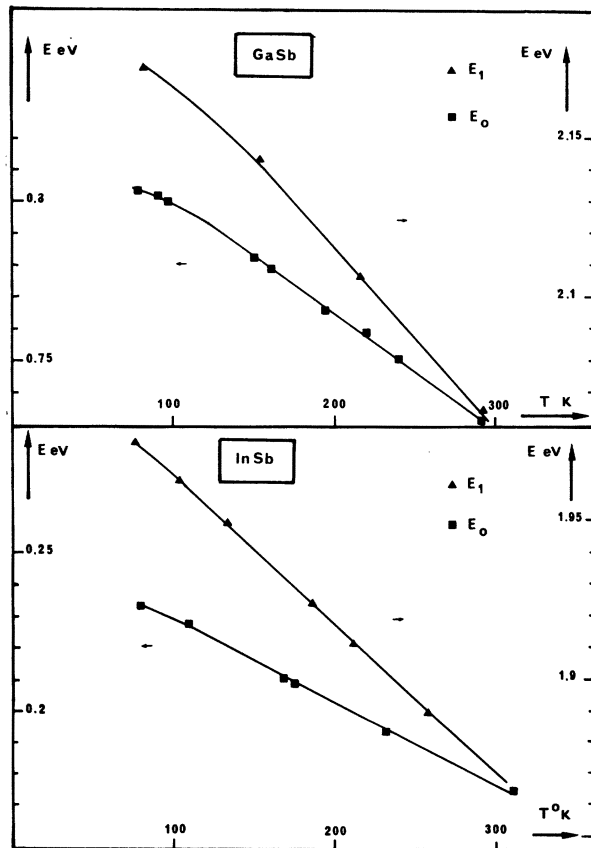


FIG. 8. Temperature dependence of the E_0 and E_1 gaps of GaSb and InSb.

$$\frac{dE_{1\text{nd}}}{dT} = -(3.7 \pm 0.2) \times 10^{-4} \text{ eV/K} \quad (22)$$

We have also plotted in Fig. 3 the shift of the E_1 gap (see Fig. 5) in order to exhibit its similarity to that of the indirect edge and thus illustrate the rigidity of the valence band (see Fig. 1). A least-squares fit to the E_1 data gives a coefficient

$$\frac{dE_1}{dT} = -(4.1 \pm 0.2) \times 10^{-4} \text{ eV/K} \quad (23)$$

which agrees reasonable with the calculated one (see Table IV).

The shift of the E_1 , $E_1 + \Delta_1$ [$-(4.1 \pm 0.2) \times 10^{-4}$ eV/K] and that of the E_2 [$-(3.9 \pm 0.2) \times 10^{-4}$ eV/K] gaps of germanium were obtained from piezoreflectance spectra like that of Fig. 4. The corresponding temperature shifts are illustrated for the E_1 , $E_1 + \Delta_1$, and E_2 gaps of Ge in Fig. 5. The shifts of the $E_1 - E'_0$ [$-(2.2 \pm 0.3) \times 10^{-4}$ eV/K], and the E_2 [$-(2.3 \pm 0.1) \times 10^{-4}$ eV/K] gaps of Si are illustrated in Fig. 6.

Once the rigidity of the valence bands has been

TABLE V. Measured temperature coefficients of the E_0 and E_1 gaps of GaSb and InSb, together with the estimated coefficient of the $L_{1c} - \Gamma_{1c}$ separation (in eV/K).

	$\frac{dE_0}{dT}$	$\frac{dE_1}{dT}$	$\frac{d(L_{1c} - \Gamma_{1c})}{dT}$
GaSb	-3.7 ± 0.1	-5.4 ± 0.3	-1.7 ± 0.4
InSb	-2.75 ± 0.1	-4.7 ± 0.2	-2.1 ± 0.3

TABLE VI. Summary of experimental values of $\Delta E_c = E(L_1) - E(\Gamma_1)$ and its temperature coefficient obtained for GaSb by various techniques. The fourth column lists the density-of-states mass m_{2d} (including degeneracy factor) used for processing the data or obtained from experiment.

Experiment	ΔE_c (meV)	$\frac{d\Delta E_c}{dT}$ (eV/K)	$\frac{m_{2d}}{m_0}$
Hall effect, resistivity with hydrostatic and uniaxial pressure ^a	74 (300 K)	-3×10^{-4}	0.55
Infrared reflectivity ^b	80 (300 K)	1×10^{-4}	0.55
Hall effect, magnetoresistance ^c	80 (4 K)		0.9
Faraday rotation ^d		1.1×10^{-4}	0.7
Magnetoresistance ^e	84 (4 K)	0.8×10^{-4}	0.43
Hall effect, Faraday rotation ^f		0.59×10^{-4}	0.74
Magnetoresistance, Faraday rotation ^g		0 to 2×10^{-5} doping dependent	0.57
Hall effect ^h	70	0	
Faraday rotation, reflectivity ⁱ	72 (90 K)	5.5×10^{-5}	0.72
Resistivity with hydrostatic and uniaxial pressure ^j	120 (300 K)	2×10^{-4}	0.815
Magnetoresistance ^k	77 (4 K)	-2×10^{-4}	0.24
Tunnel effect ^l	80 (4 K)	-2.1×10^{-4}	0.25

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established it is possible to use the measured temperature coefficients of the E_0 , E_1 , and E_2 gaps to obtain experimental information about the relative shifts of the three main conduction minima (Γ , L , $X-\Delta$) with temperature. Figure 7 shows a typical piezoreflectance spectrum from which the temperature shifts of the E_0 , E_1 , and E_2 gaps can be obtained. The E_0 and E_1 shifts are shown in Fig. 8 for InSb and GaSb and the corresponding temperature coefficients listed in Table V. Assuming the rigidity of the top valence band along Λ , we find for the temperature coefficient of the separation between the L_1 and the Γ_1 conduction minima the values listed in Table V.

DISCUSSION

We show in Table VI the temperature dependence of the $\Delta E_c = E(L_1) - E(\Gamma_1)$ gap obtained for GaSb by a number of different authors and experimental techniques. Enormous discrepancies appear in the sign and magnitude of these coefficients. Our assumption of a rigid valence band yields, using the temperature coefficients of Table V, a coefficient $d\Delta E_c/dT = (-1.7 \pm 0.4) \times 10^{-4}$, which tends to support the values of footnotes a, k, and l of Table VI.

The density of states mass m_{2d} of the L_1 minima (including valley degeneracy factor) used for or obtained in the experiments is also listed in Table VI. This mass is expected to have a value very similar to that of Ge,²⁵ namely, $0.55m_0$. This mass agrees with that of footnote a but those of footnotes k and l are significantly smaller. We do not find an explanation for this discrepancy but we believe that the present work supports indeed a negative temperature coefficient, of the order of -2×10^{-4} eV/K for ΔE_c . A similar coefficient is expected for InSb according to Table V. These coefficients are of particular interest since they describe the variation with temperature of the valley separation which determines the Gunn effect.

The postulated rigidity of the valence bands can also be used to predict the temperature coefficient of the separation between the Γ_1 minimum and the X_1 minima in GaAs, which are at low temperature (2 K), 483 ± 15 meV above Γ_1 ,²⁶ and play a dominant role in the Gunn effect. The temperature coefficient of the E_0 gap of GaAs is -3.6 eV/K,²⁷ that of the E_2 gap is also $-(3.6 \pm 0.4)$ eV/K,²⁸ and therefore the $E(\Gamma_1) - E(X_1)$ gap should have a nearly zero-temperature coefficient, a result which deviates from the coefficient -2.4×10^{-4} eV/K pro-

posed by Pitt²⁹ by interpolating between data obtained in different experiments.

In InP, the L_1 minima lie between the X_1 and Γ_1 minima and they all are involved in the Gunn effect.³⁰ The $X_1 - \Gamma_1$ separation is 960 meV at low temperatures²⁶ while the $L_1 - \Gamma_1$ separation is 610 meV at 300 K.³¹ Using for the E_0 gap the coefficient $-(2.9 \pm 0.2) \times 10^{-4}$ eV/K,³² for that of E_1 $-(4.2 \pm 0.4) \times 10^{-4}$ eV/K,²³ and for that of E_2 $-(3.1 \pm 0.4) \times 10^{-4}$ eV/K,²³ we find for the temperature coefficient of the $L_1 - \Gamma_1$ gap -1.3×10^{-4} eV/K and for that of the $X_1 - \Gamma_1$ gap -0.2×10^{-4} eV/K.

Our procedure to obtain temperature coefficients of separations between conduction minima is based on two assumptions. The first one, the rigidity of the valence bands, has been discussed in detail and can be assumed to hold on the basis of the theoretical and experimental data to better than $\pm 5 \times 10^{-5}$ eV/K. The other assumption is that the E_1 and E_2 gaps are indeed representative of transitions ending at the L_1 and X_1 conduction minima.

The E_1 gap is known to be due to transitions along most of the $\langle 111 \rangle$ lines, including the L point. The exact parallelism of valence and conduction bands along the region of these transitions for all zinc-blende- and germanium-type materials suggests that the temperature coefficient of the gap is the same regardless of the position of the Λ point. A Debye-Waller calculation along Λ should be performed to confirm this conjecture.

The situation is somewhat more complex with regards to the E_2 gap, to which the transitions at X contribute rather little in spite of occurring at about the same energy. It has been suggested in a recent paper³³ that the E_2 transitions occur in a region rather localized around $(2\pi/a) (\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ certainly not too far from the X point $(2\pi/a) (1, 0, 0)$. One may therefore argue, by continuity, that the E_2 gap has indeed the same temperature coefficient as the $X_5 - X_1$ gap. This conjecture seems confirmed by the analysis of the pressure dependence of refractive indices.¹⁴

*Centre Associé au Centre Nationale de la Recherche Scientifique.

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