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Temperature Dependence of Energy Gaps of Some III-V Semiconductors *

Y. F. Tsay, B. Gong, † and S. S. Mitra
Department of Electrical Engineering, University of Rhode Island, Kingston, Rhode Island 02881

and

J. F. Vetelino
Department of Electrical Engineering, University of Maine, Orono, Maine 04473

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The Brooks-Yu theory is applied to the calculation of the band structure of some III-V semiconductors at finite temperatures. The theory is applied in the context of the empirical pseudopotential method, and utilizes a recent lattice-dynamical calculation of the Debye-Waller factors. The temperature dependence of several band gaps are determined and compared with available experimental data and, in general, good agreement is obtained.

I. INTRODUCTION

It is well known that the band gaps of semiconductors change noticeably with temperature in most experiments and applications. There are two reasons for this change: (i) The thermal-expansion effect, or what is often called the dilation contribution, accounts for the effect of the change of lattice constant on the energy gaps. This is expected since the electronic energy bands are formed because of the "overlappings" of electronic wave functions, the extent of which is dependent upon the distances between neighboring atoms (ions). (ii) The major contribution, however, comes from electron-phonon interactions. The one-electron theory of electronic energy bands of a crystalline solid is based on the assumption that the crystal is perfect, which is true only at absolute-zero-degree temperature. At finite temperatures, the energy of the electron is subject to change because of the interactions between electrons and phonons. This is reflected in the change of the energy gap with temperature.

Fan[1] was among the first to calculate the shift of electronic energies with temperatures. Treating the electron-phonon interactions as a perturbation to simple parabolic bands, he calculated $\partial E_g / \partial T$ for Ge and Si. Although the model used was crude, it did predict the correct order of magnitude for this coefficient. During the past two decades there have been numerous experimental measurements of band gaps of semiconductors as functions of temperature.[2] The reliability of some of their measurements is, however, questionable. Considerable scatter in the experimental data exists due to the difficulty in the interpretation and analysis of the data, as well as the limited resolution of various experimental techniques. Hence, systematic and reliable results over extended temperature ranges are relatively sparse.[2]

Recently, a simple theory by which the energy bands of crystalline solids at finite temperatures can be calculated within the framework of the empirical pseudopotential method[3] was proposed by Brooks and Yu.[4] The temperature-dependent band structure can be calculated by this method provided the corresponding Debye-Waller factors of the solids are available.

Calculations based on this approach have been performed for GaAs,[5] GaP,[6] PbTe[7,8] SnTe,[8] and HgTe.[9] The Debye-Waller factors used in the aforementioned work were experimentally obtained. Also the previous calculations were primarily limited to the fundamental gaps.

For the III-V compounds of the zinc-blende structure the reliability of the small amount of experimental data on Debye-Waller factors that exists is questionable. In some of the experimental work no explicit correction due to thermal diffuse-scattering intensity has been made. This contribution has been shown to have a significant effect in some alkali halides[10] and in HgTe[11] of the zinc-blende structure.

It is the purpose of the present paper to theoretically calculate the temperature dependence of several energy gaps in a large number of III-V zinc-blende-type semiconductors. The appropriate empirical pseudopotential form factors will be combined with theoretical Debye-Waller factors. The eigenfrequencies and the eigenvectors of the phonon states as obtained from the modified rigid-ion model[12] of lattice dynamics has been used to calculate the Debye-Waller factors for these crystals.[13] We regard these Debye-Waller factors to be more systematic and reliable than existing experimental data. Where experimental data on Debye-Waller factors did exist for the III-V compounds, agreement with our calculated value was found[13] to be (a) excellent in the case of GaP and GaAs, (b) tolerably good for InAs, and (c) decidedly poor for GaSb, InP, and InSb. The range of agreement is not surprising due to the questionable experimental Debye-Waller-factor measurements. Explicit calculations of the temperature dependence of the energy gaps at Γ, X, and L critical points have been performed for six III-V semiconductors, viz., GaP, GaAs, GaSb, InAs, InSb, and InP. Spin-orbit interaction has not been included in this work.

II. METHOD OF CALCULATION

The pseudopotential method of energy-band calculations involves the solving of the wave equation

$$[-\nabla^2 + V(\vec{r})]\,\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\,\psi_{\vec{k}}(\vec{r}), \tag{1}$$

where $V(\vec{r})$ is the crystal pseudopotential, which is considered to be weak. The Fourier transform of $V(\vec{r})$ completely determines the band structure of the crystal. Assuming the crystal pseudopotential to be the superposition of that of the constituent atoms (ions), one obtains

$$V(\vec{G}) = \textstyle\sum_j S_j(\vec{G})\, V_j(\vec{G}), \tag{2}$$

where

$$S_j(\vec{G}) = e^{i\vec{G}\cdot\vec{\tau}_j}.$$

$S_j(\vec{G})$ is the structure factor, $\vec{G}$ the reciprocal-lattice vector, and $\vec{\tau}_j$ the position vector of the jth atom in the reference primitive unit cell. $V_j(\vec{G})$ is the Fourier transform of the jth atomic pseudopotential. According to the Brooks-Yu theory, at finite temperatures $S_j(\vec{G})$ is replaced by a temperature-dependent one given as

$$S_j(\vec{G}, T) = e^{i\vec{G}\cdot\vec{\tau}_j}\, e^{-W_j(\vec{G},T)}. \tag{3}$$

$W_j(\vec{G}, T)$ is the Debye-Waller factor for the jth atom, and is defined as

$$W_j(\vec{G}, T) = (\tfrac{1}{6}\,|\vec{G}|^2\,\langle U_j^2\rangle), \tag{4}$$

where $\langle U_j^2\rangle$ is the total mean-square displacement of the jth atom. This amounts to replacing $V_j(\vec{G})$ by a temperature-dependent pseudopotential $V_j(\vec{G}, T)$ defined as[7,8]

$$V_j(\vec{G}, T) = V_j(\vec{G})\,\exp(-\tfrac{1}{6}\,|\vec{G}|^2\,\langle U_j^2\rangle). \tag{5}$$

This accounts for the effect of the electron-phonon contribution. The dilation contribution is taken into account by using the lattice constant at finite temperatures and scaling the zero-temperature atomic pseudopotential form factors. This scaling is done according to the dependence of the form factor on the lattice constant,[8] and also assuming the atomic pseudopotential in real space to be independent of temperature. Lattice constants and the mean-square displacements for constituent atoms are listed in Tables I and II, respectively.

Throughout the calculation, use was made of the form factors deduced from zero-temperature empirical pseudopotential energy-band calculations.[3,14,15] No further adjustments were made for exact agreement of the theoretical gaps with the experimental ones which are concerned in the present work. This was done for two reasons. First, the form factors mentioned above were adjusted, in general, to yield band structures in good agreement with experiment at several critical points of the first Brillouin zone. Some of them also predict optical constants consistent with experiment.[14,15] A set of form factors which gives the exact band gap at only one point of the first Brillouin zone does not necessarily assure good agreement at other critical points. In fact, a set of form factors which gives reasonable but approximate agreement at many critical points might be superior to another set which gives exact agreement at only one critical point. Second, it is not uncommon in the literature that a particular band gap reported by different authors, using different experimental techniques, may differ by as much as 0.2 eV.[2,16] The present interest is in the changes of band gaps with temperature. Therefore, no further adjustments on the form factors were made to correct the small discrepancy that might exist between theoretical and experimental values of the particular band gap at 0° temperature.

TABLE I. Lattice constants[a] (Å).

T (°K)	0	50	100	150	200	250	300
GaAs	5.64	5.6399	5.6402	5.6410	5.6423	5.6438	5.6453
GaSb	6.12	6.1198	6.1202	6.1214	6.1230	6.1249	6.1268
InP	5.86	5.8596	5.8601	5.8610	5.8624	5.8638	5.8653
InSb	6.48	6.4797	6.4801	6.4812	6.4826	6.4842	6.4858
InAs	6.04	6.0398	6.0397	6.0401	6.0409	6.0420	6.0432

T (°K)	0	100	200	300	400	500	600	700	800	900
GaP[b]	5.44	5.4401	5.4422	5.4460	5.4487	5.4514	5.4547	5.4580	5.4612	5.4650

[a] All data except GaP are obtained from A. Novikova [in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), Chap. 2].

[b] Data of GaAs taken as an approximation.

TABLE II. Mean square atomic displacements (in 10^{-16} cm^2).

	T (°K)	10	50	100	150	200	250	300
GaAs	Ga	0.0044	0.0050	0.0066	0.0088	0.0111	0.0135	0.0159
	As	0.0043	0.0049	0.0065	0.0087	0.0110	0.0134	0.0159
GaSb	Ga	0.0048	0.0057	0.0080	0.0108	0.0137	0.0168	0.0199
	Sb	0.0038	0.0048	0.0073	0.0103	0.0133	0.0164	0.0196
InP	In	0.0040	0.0048	0.0072	0.0101	0.0130	0.0160	0.0191
	P	0.0067	0.0074	0.0093	0.0117	0.0143	0.0171	0.0200
InAs	In	0.0041	0.0053	0.0081	0.0114	0.0148	0.0182	0.0218
	As	0.0048	0.0059	0.0086	0.0117	0.0151	0.0185	0.0219
InSb	In	0.0043	0.0060	0.0096	0.0136	0.0177	0.0219	0.0261
	Sb	0.0042	0.0059	0.0095	0.0136	0.0177	0.0219	0.0261

T (°K)		10	100	200	300	400	500	600	700	800	900
GaP	Ga	0.0043	0.0060	0.0097	0.0139	0.0182	0.0226	0.0270	0.0314	0.0358	0.0602
	P	0.0060	0.0074	0.0107	0.0146	0.0188	0.0230	0.0273	0.0316	0.0359	0.0402

III. RESULTS AND DISCUSSION

A. Fundamental Band Gap

1. GaAs

In some early work on absorption measurements, Oswald[17] reported the fundamental gap for this crystal as 1.53 eV at 5 °K and 1.38 eV at 300 °K, i.e., a change of 0.15 eV. Sturge[18] later, also by absorption measurements, reported the fundamental gap to be 1.52 eV at 5 °K and 1.43 eV at 300 °K. Recently, Shay and co-workers,[19] based on photoreflectance data obtained from an ultrapure epitaxial layer of GaAs, deduced the gap to be 1.52 eV at 0 °K, 1.43 eV at 300 °K, in good agreement with Sturge's results. The first theoretical calculation with spin-orbit interaction was done by Walter *et al.*[5] in which they used, as an approximation, the phonon spectrum of Ge to calculate the Debye-Waller factors of Ga and As, hence assuming the Debye-Waller factors of the constituent atoms to be identical. The results of their calculation are $E_g = 1.52$ eV at 5 °K and 1.36 eV at 300 °K, a change of 0.16 eV, which is in good agreement with Oswald's results, but they are 0.07 and 0.06 eV larger, respectively, than those reported by Sturge and Shay. Shay,[20] repeating the calculation using the same Debye-Waller factors, argued, however, that the discrepancy may result from the arbitrary truncation of the pseudopotential form factors. The result of the present calculation is given along with the available experimental data in Fig. 1. In the present work, the Debye-Waller factors given in Table I have been used. The mean-square displacements of Ga and As are essentially identical, justifying Walter's assumption. Our values, however, differ substantially from theirs. Using the form factors given by Walter and Cohen,[14] a change of 0.136 eV from $T = 0$ to 300 °K was predicted. Although this is still appreciably higher than the experimental result of Sturge and Shay, it is, however, an improvement. The disagreement between

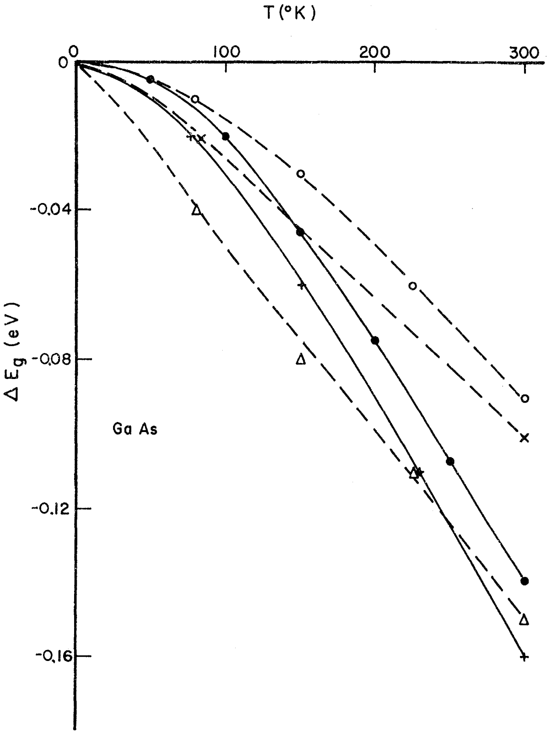

FIG. 1. Change of the direct gap ($\Gamma_{15,v} \rightarrow \Gamma_{1,c}$) of GaAs as a function of temperature. Solid lines: theoretical calculations; dots: present calculation; pluses: calculations from Ref. 5; dashed lines: approximate curves to experimental data; triangles: Ref. 17; open circles: Ref. 18; crosses: Ref. 19.

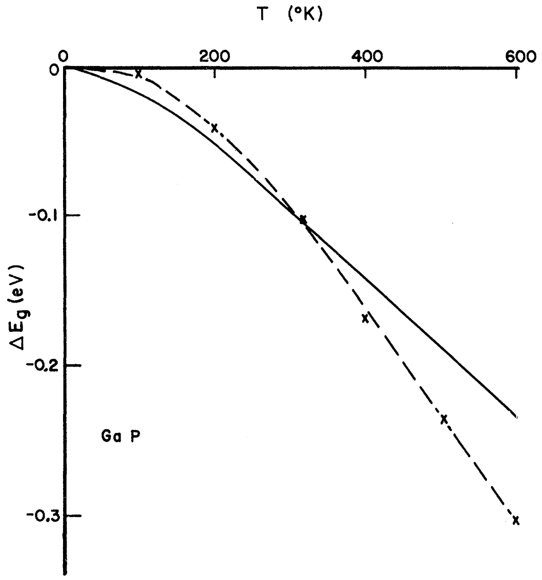

FIG. 2. Change of the direct gap ($\Gamma_{15,v} \rightarrow \Gamma_{1,c}$) of GaP as a function of temperature. Solid line: present calculation; dashed line: approximate curve to experimental data from Ref. 22.

theory and experiment might be due to the arbitrary truncation of the form factors or the values of the Debye-Waller factors used.

2. GaP

The minimum gap in GaP corresponds to the indirect transition from $\Gamma_{15,v} \rightarrow X_{1,c}$. Early experiments[21] reported a gap of 2.4 eV at 0 °K and 2.25 eV at 300 °K. Recently, experimental data on the energy gap over an extended temperature range have become available. Absorption measurements by Subashiev and Chalikyan[22] showed that the gap is 2.31 eV at 0 °K and 2.2 eV at 700 °K. Lorenz *et al.*,[23] determining the indirect gap for $T < 400$ °K, from an absorption line due to the creation of excitons at isolated nitrogen atoms substituted on P sites, and $T > 400$ °K from intrinsic absorption data, reported a gap of 2.338 eV at 0 °K and 1.975 eV at 900 °K. The first attempt at the theoretical calculation of the temperature dependence of the energy gaps of this crystal was performed by Liang *et al.*[6] They used experimentally determined mean-square displacements and found the temperature coefficients of the direct and the indirect gaps to be -3.8×10^{-4} and -2.8×10^{-4} eV/°K, respectively, in the temperature range 80–300 °K. The results of the present calculation are presented in Figs. 2 and 3.

Assuming a linear variation for the energy gaps above 200 °K, our calculated temperature coefficient of the direct gap is -4.5×10^{-4} eV/°K, which compares fairly well with the experimental value of -6.5×10^{-4} eV/°K found by Subashiev *et al.* As for the indirect gap, the calculated temperature coefficient of the present work is -4.25×10^{-4} eV/°K, which is in good agreement with the value of -4.67×10^{-4} eV/°K determined from the experimental data of Lorenz *et al.* There are apparent discrepancies between our calculated values of the coefficients and those given by Liang *et al.* However, it is to be noted that they do not refer to the same temperature range. In the present work, the predicted variations of the energy gaps are not linear until $T > 200$ °K due to the fact that the Debye-Waller factors are not linear at lower temperatures. However, if a straight line is drawn from energy-gap shifts at 80 °K to their values at 300 °K, the calculated coefficients are -4.3×10^{-4} and -2.75×10^{-4} eV/°K, respectively, for the direct and indirect gaps, which are in good agreement with those reported by Liang *et al.* In Liang's work the mean-square displacement of the Ga atom is greater than that of the P atom. The converse is true in the present work, but this apparently has little effect on the resulting temperature coefficients.

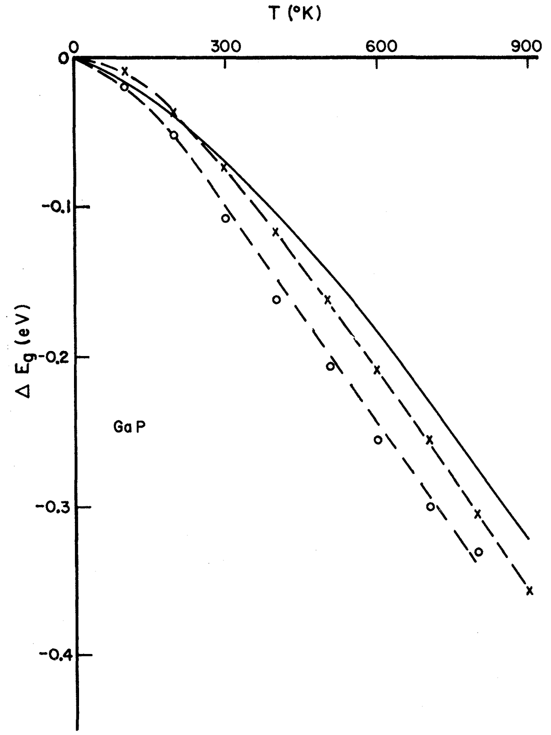

FIG. 3. Change of the indirect gap ($\Gamma_{15,v} \rightarrow X_{1,c}$) of GaP as a function of temperature. Solid line: present calculation; dashed lines: approximate curves to experimental data; crosses: Ref. 23; open circles: Ref. 22.

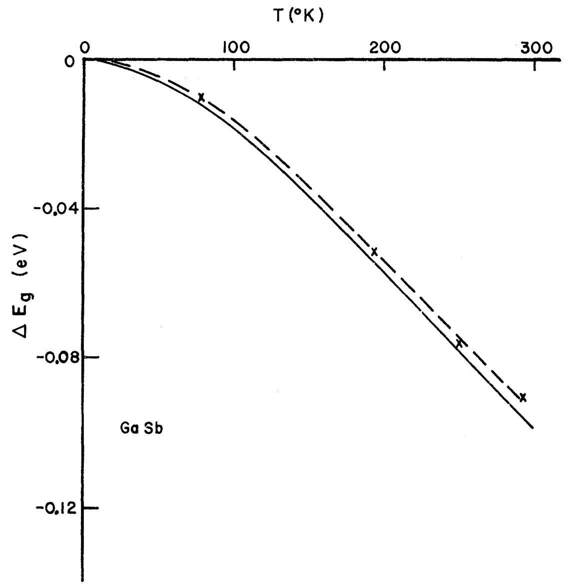

FIG. 4. Change of the direct gap ($\Gamma_{15,v} \rightarrow \Gamma_{1,c}$) of GaSb as a function of temperature. Solid line: present calculation; dashed line: approximate curve to experimental data from Ref. 24.

3. GaSb

By extrapolating to zero the steepest parts of $(Kh\nu)^{1/2}$ curves at various temperatures, where K is the absorption constant and $h\nu$ is the photon energy, Roberts and Quarrington[24] determined very accurately the fundamental gap at five temperatures ranging from 20 to 289 °K. The present calculations are compared with this experimental data in Fig. 4. The agreement with the experimental data of Roberts and Quarrington is excellent throughout the whole temperature range. The temperature coefficient as calculated from their experimental data, assuming a linear variation from 100 to 300 °K, is -3.6×10^{-4} eV/°K in good agreement with the present calculated value of -4.0×10^{-4} eV/°K, also assuming a linear variation in the same temperature range.

4. InAs, InSb, InP

The empirical pseudopotential energy-band calculation for these crystals was performed by Cohen *et al.*[3] A similar calculation has also been done[25] for InSb. However, owing to the lack of significantly new experimental data, no refined calculations by the same method are available. The pseudopotential form factors used in the present work are those given by Cohen *et al.*[3,15]

For InAs, Oswald[17] reported a temperature coefficient of the fundamental gap of -3.5×10^{-4} eV/°K, which was deduced from absorption measurements. Pidgeon *et al.*[26] recently, based on magnetoabsorption data, determined the temperature coefficient to be -2.55×10^{-4} eV/°K. The result of the present calculation is presented and compared with experimental data in Fig. 5. The present calculated value of -3.47×10^{-4} eV/°K is in excellent agreement with the result given by Oswald.

In the case of InSb, early experimental data from absorption measurenents by Roberts *et al.*[24] gave a temperature coefficient of the fundamental energy gap of -2.9×10^{-4} eV/°K. The result of the present work, which is presented in Fig. 6, yields a temperature coefficient of -3.5×10^{-4} eV/°K in reasonable agreement with the experimental value.

For InP, early experiments[21] gave

$$E_g = (1.41 - 4.7\times 10^{-4} T) \text{ eV} .$$

Recently, experiments on optical absorption and electroreflectance on this crystal[27] suggest that the approximate fundamental energy gap is, respectively, 1.43, 1.41, and 1.35 eV at 0, 77, and 300 °K. The temperature coefficient of the energy gap calculated from these data is -2.8×10^{-4} eV/°K. The result of the present calculation is given in Fig. 7 from which a temperature coefficient of -4.0×10^{-4} eV/°K is obtained.

B. E_1 and E_2 Reflectivity Peaks

The temperature coefficients of the E_1 and E_2 reflectivity peaks of the six III-V compounds were also calculated. In the single group notation, the E_1 peak corresponds to the combined effect of the

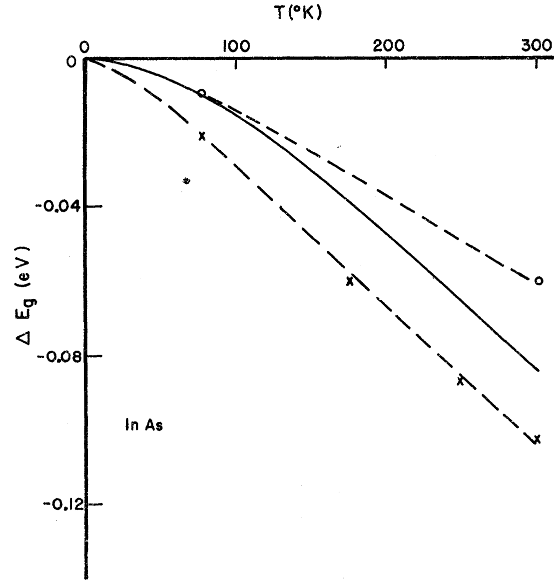

FIG. 5. Change of the direct gap ($\Gamma_{15,v} \rightarrow \Gamma_{1,c}$) of InAs as a function of temperature. Solid line: present calculation; dashed lines: approximate curves to experimental data; crosses: Ref. 17; open circles: Ref. 26.

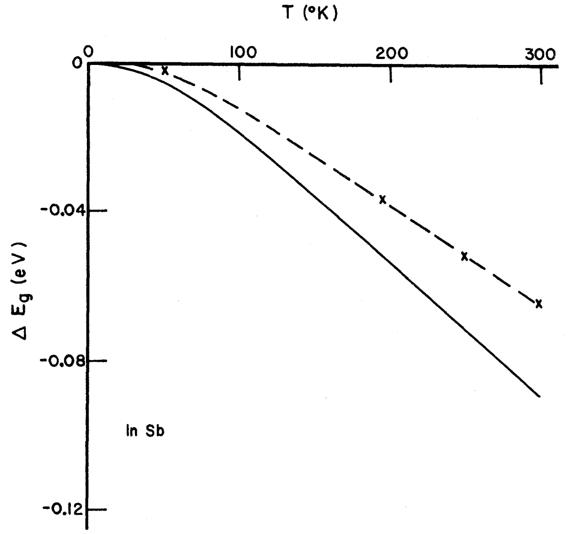

FIG. 6. Change of the direct gap ($\Gamma_{15,v} \rightarrow \Gamma_{1,c}$) of InSb as a function of temperature. Solid line: present calculation; dashed line: approximate curve to experimental data from Ref. 24.

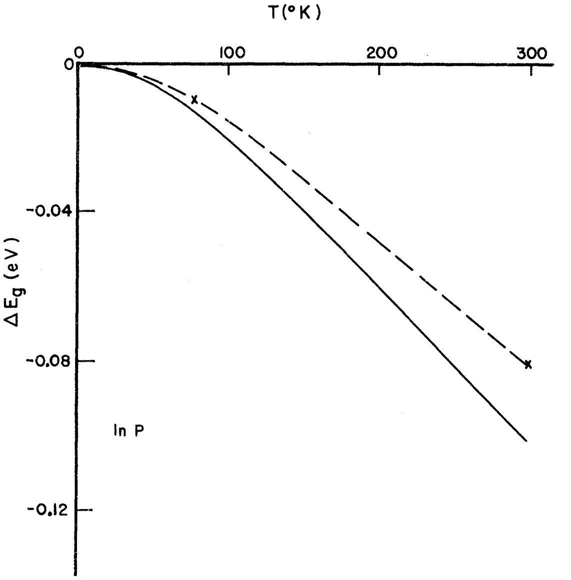

FIG. 7. Change of the direct gap ($\Gamma_{15,v} \rightarrow \Gamma_{1,c}$) of InP as a function of temperature. Solid line: present calculation; dashed line: approximate curve to experimental data from Ref. 27.

$L_{3,v} \rightarrow L_{1,c}$ transition and the saddle point $\Lambda_{3,v} \rightarrow \Lambda_{1,c}$ transition somewhere along the [111] direction. The E_2 peak, which is the strongest of the reflectivity peaks, is thought to arise mainly from the $X_{5,v} \rightarrow X_{1,c}$ transition and the $\Sigma_{2,v} \rightarrow \Sigma_{1,c}$ transition along the [110] direction. In the presence of spin-orbit interaction, the E_1 peak splits into two components E_1 and $E_1 + \Delta_1$, which are the well-known doublet peaks in the reflectivity spectra of zinc-blend-type crystals. Since the spin-orbit interaction is not included in the present work, it is not possible to predict the temperature dependence of the doublet peaks separately. In Table III, the temperature coefficients of the E_1 and E_2 peaks from the present calculation are listed along with some experimental data. All the calculated values, except those of GaP, are obtained assum-

TABLE III. Temperature coefficients of the E_1 and E_2 peaks (in 10^{-4} eV/°K).

Materials	$-\frac{dE_1}{dT}$ Calc.	$\left(-\frac{dE_1}{dT}\right)$[a,b] Expt.	$\left[-\frac{d(E_1+\Delta_1)}{dT}\right]$[b] Expt.	$-\frac{dE_2}{dT}$ Calc.	$-\frac{dE_2}{dT}$ Expt.
GaAs	4.7	4.2 ± 0.5[c]; 4.6 ± 0.3[d]	...	3.7	3.6[e] 3.3[f]
GaSb	3.3	4.0 ± 0.4[c]; 4.2 ± 0.6[d]	3.6 ± 0.5[c]	3.1	4.1[e] 6.2[g]
InP	3.6	4.2 ± 0.6[d]	...	3.2	...
InAs	3.6	...	...	3.1	5.6[e]
InSb	3.4	4.0 ± 0.2[c]	3.6 ± 0.2[c]	3.0	3.6[e] 5.4[f]
GaP	2.8	2.5 ± 0.6[d]	...	2.5	4.5[f]

[a] M. Cardona, J. Appl. Phys. 325, 2151 (1962).

[b] M. Cardona and G. Harbeke, J. Appl. Phys. 34, 813 (1963).

[c] Absorption data.

[d] Reflectivity data.

[e] R. R. L. Zucca and Y. R. Shen (unpublished); values were measured at 5 °K.

[f] A. G. Thompson, J. C. Woolley, and M. Rubenstein, Can. J. Phys. 44, 2927 (1966).

[g] F. Lukes and E. Schmidt, *Proceedings of the International Conference of the Physics of Semiconductors*, 1962 (The Institute of Physics and the Physical Society, London, 1962), p. 389.

ing a linear variation of the energy gaps for $T > 100$ °K. For GaP, a linear variation for $T > 200$ °K is assumed. We also take the transitions $L_{3,v} \rightarrow L_{1,c}$ and $X_{5,v} \rightarrow X_{1,c}$ as corresponding to the E_1 and E_2, peaks respectively. Values calculated for contending critical points give essentially the same results. As can be seen in Table III, the agreement is quite good for the E_1 peaks and reasonable for the E_2 peak. The calculated temperature coefficients are approximately equal to the average value of those corresponding to the two spin-orbit-split components. It is to be noted also that for the III-V compounds the difference of the temperature coefficients between the two components is small.

IV. CONCLUSIONS

Given a set of pseudopotential form factors for the zero-temperature band structure and reliable Debye-Waller factors, the Brooks-Yu theory seems adequate to predict the temperature dependence of the energy gaps of most III-V semiconductors. Agreement of calculated values are within 30% of the experimentally determined values. It is also concluded that the agreement between theory and experiment is about as good in many cases as the agreements between different experimental results.

In most cases, where discrepancy between theory and experiment exists, it is of the order of a few hundredths of an electron volt. It is reasonable to expect that it can be corrected by better zero-temperature pseudopotential form factors as well as more accurate Debye-Waller factors. For finite-temperature energy-band calculations, in addition to the zero-temperature form factors, $V_S(|G|^2=4)$ and $V_A(|G|^2=8)$ are also needed because the thermal motions of the two constituent atoms are, in general, different. It is a common practice to obtain these two "missing" components by numerical interpolations.[15] However, at least in the case where thermal vibrations of the two constituent atoms are sufficiently different, e.g., GaP and InP,[13] it might be possible to use the two idle form factors as adjusting parameters to fix the discrepancy between the theoretical and experimental temperature dependence of the energy gap and leave the zero-temperature pseudopotential form factors intact if they already give an accurate zero-temperature band structure. Finally the omission of spin-orbit interaction in the present calculations does not seem to be a serious shortcoming so far as the temperature effect is concerned.

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

[2] See, for example, O. Madelung, *Physics of III-V Compounds* (Wiley, New York, 1964).

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

[4] S. C. Yu, Ph.D. thesis (Harvard University, 1964) (unpublished); S. C. Yu and H. Brooks (unpublished).

[5] J. P. Walter, R. Zucca, M. L. Cohen, and Y. R. Shen, Phys. Rev. Letters 24, 102 (1970).

[6] K. S. Liang, C. S. Guenzer, and A. Bienenstock, Bull. Am. Phys. Soc. 15, 1637 (1970).

[7] C. Keffer, T. M. Hayes, and A. Bienenstock, Phys. Rev. Letters 21, 1676 (1968); Phys. Rev. B 2, 1966 (1970).

[8] Y. W. Tsang and M. L. Cohen, Phys. Rev. B 3, 1254 (1971).

[9] C. S. Guenzer and A. Bienenstock, Phys. Letters 34A, 172 (1971).

[10] W. J. L. Buyers and T. Smith, J. Phys. Chem. Solids 25, 483 (1964); 29, 1051 (1968); J. C. Abraham and J. L. Bernstein, Acta Cryst. 18, 926 (1965).

[11] E. F. Skelton, P. L. Radoff, P. Bolsaitis, and A. Verbalis, Phys. Rev. B 5, 3008 (1972).

[12] J. F. Vetelino and S. S. Mitra, Phys. Rev. 178, 1349 (1969).

[13] J. F. Vetelino, S. P. Gaur, and S. S. Mitra, Phys. Rev. B 5, 2360 (1972).

[14] J. P. Walter and M. L. Cohen, Phys. Rev. 183, 763 (1969); R. N. Cahn and M. L. Cohen, Phys. Rev. B 1, 2569 (1970).

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

[16] A. M. Gray, Phys. Status Solidi 37, 11 (1970).

[17] F. Oswald, Z. Naturforsch. 10a, 927 (1955).

[18] M. D. Sturge, Phys. Rev. 127, 768 (1962).

[19] J. L. Shay, Phys. Rev. B 2, 803 (1970); J. L. Shay and R. E. Nahory, Solid State Commun. 7, 945 (1969); R. E. Nahory and J. L. Shay, Phys. Rev. Letters 21, 1569 (1968).

[20] J. L. Shay, Phys. Rev. B 4, 1389 (1971).

[21] See, for example, L. Pincherle and J. M. Radcliffe, Advan. Phys. 5, 272 (1956).

[22] V. K. Subashiev and G. A. Chalikyan, Phys. Status Solidi 13, K91 (1966).

[23] M. R. Lorenz, G. D. Pettit, and R. C. Taylor, Phys. Rev. 171, 876 (1968).

[24] V. Roberts and J. E. Quarrington, J. Electron. 1, 152 (1955).

[25] The band sturcture of InSb using the empirical pseudopotential method with spin-orbit interaction has been done by S. Bloom and T. K. Bergstresser [Solid State Commun. 6, 465 (1968)]. Their pseudopotential form factors are, however, the same as those given in Ref. 3.

[26] C. R. Pidgeon, D. L. Mitchell, and R. N. Brown, Phys. Rev. 154, 737 (1967); C. R. Pidgeon, S. H. Groves, and J. Feinleib, Solid State Commun. 5, 677 (1967).

[27] See, for example, D. Long, *Energy Bands in Semiconductors* (Interscience, New York, 1968), p. 100.