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Modulation-spectroscopy study of the $Ga_{1-x}Al_xSb$ band structure

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We report a detailed study of the $Ga_{1-x}Al_xSb$ band structure over the entire composition range. We have determined the energies , as a function of temperature, at which the direct transitions $\Gamma_8^v \rightarrow \Gamma_6^c$ (E_0), $\Gamma_7^v \rightarrow \Gamma_6^c$ ($E_0+\Delta_0$), $L_{4,5}^v \rightarrow L_6^c$ (E_1), and $L_6^v \rightarrow L_6^c$ ($E_1+\Delta_1$) occur, and those at which the indirect transitions $\Gamma_8^v \rightarrow X_6^c$ (E_X) and $\Gamma_8^v \rightarrow L_6^c$ (E_L) occur. A simple physical model is proposed to explain the experimental values of the E_0, Δ_0, E_1, Δ_1 bowing parameters. A detailed comparison is made between our results and previously reported ones.

I. INTRODUCTION

Optical-fiber systems operating in the wavelength range 1.3–1.6 μm have been the subject of considerable research and development activity over the last few years.[1] This has given a great interest to the III-V ternary compounds, which are available in this window.[2–7] Some results have already been published concerning the potentiality of $Ga_{1-x}Al_xSb$ in the GaSb-rich composition range.[5–7] A precise knowledge of the band structure of this material is necessary to evaluate its expectable domain of application, and the direct-indirect transition crossover composition value is particularly of prime importance. A survey of the published literature[8–13] indicates dispersive results; therefore we have carried out a detailed study of this ternary system beginning with a precise determination of the transition-energy values of the limiting compounds GaSb and AlSb.[14,15] We have also compared our results with the existing ones. (For reference, a band-structure model of the $Ga_{1-x}Al_xSb$ ternary compound in the AlSb-rich domain of the composition x is displayed in Fig. 1.)

II. EXPERIMENT

A. $Ga_{1-x}Al_xSb$ elaboration techniques

$Ga_{1-x}Al_xSb$ alloys have been elaborated by a modified Bridgman method and by liquid-phase epitaxy. The Bridgman technique, described in another paper,[16] was adapted to solution growth. Bulk polycrystalline ingots of GaSb, AlSb, and $Ga_{1-x}Al_xSb$ alloys ($x < 0.87$) were obtained from antimony-rich liquid solutions using high temperature gradients (2 °C/mm) and slow growth rates (0.25 mm/h). The growth occurred under equilibrium conditions, and

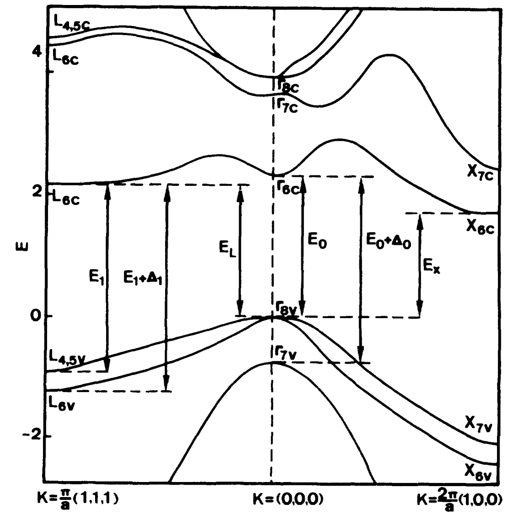

FIG. 1. $Ga_{1-x}Al_xSb$ band structure in the AlSb-rich composition domain.

the mean grain surface size often was about several mm^2.

Single-crystal GaSb and $Ga_{1-x}Al_xSb$ layers ($x < 0.70$) were grown by liquid-phase epitaxy[17] on $\langle 111 \rangle \bar{B}$-oriented GaSb substrates, taking advantage of the low temperature of liquid saturation (500–550 °C) and slightly supercooled solutions (3–5 °C). The epilayers were thick (50 μm) with a smooth shiny surface.

The solid compositions were determined by electron-microprobe analysis. The layer uniformity normal to the growth axis was controlled to be better than the accuracy of the microprobe analysis (±1 atomic fraction). The undoped samples had p-type conductivity. At room temperature, the residual carrier concentration was $(2-10) \times 10^{16}$ cm^{-3}, and the Hall mobility regularly decreases from 800 $cm^2 V^{-1} s^{-1}$ ($x = 0$) to 150 $cm^2 V^{-1} s^{-1}$ ($x = 1$).

B. Experimental measurement techniques

In the past decade, optical modulation techniques have been extensively applied to the determination of semiconductors band structure.[18] All techniques modulate the reflectance or transmittance of a sample through a periodic change of an external parameter, such as an electric field, pressure, or temperature. Modulation of the reflected or transmitted beam is detected synchronously and phase-sensitively, separated from the unmodulated background, and amplified. In contrast to the usual rather featureless reflectance or transmittance curves, a modulated spectrum is rich in structures, which are compressed into narrow regions of photon energy and easily relatable to the transitions energies, thus yielding their precise values.

In the present study, we have successfully used electromodulation, piezomodulation, and wavelength modulation, of which experimental details are described elsewhere.[18–21] We note that whenever possible, we have applied the electroreflectance technique, even though it is the most difficult technique because of the requirment for the construction of a heterojunction barrier on the sample, which was often made possible by evaporating a thin layer of Cu_2S on the reflective face of the sample. To avoid transmission-backreflection structures, the unpolished rear face was deliberately made nonparallel to the reflective face. An Ohmic contact is taken on this face by diffusion of In in a H_2HCl atmosphere.

C. Results

Typical experimental spectra are reported in Figs. 2–5. This illustrates the reason for the preference that we have shown for the electroreflectance technique: It gives very well-resolved spectra rich in information content. Our study has been based on twenty samples evenly distributed over the entire composition range.

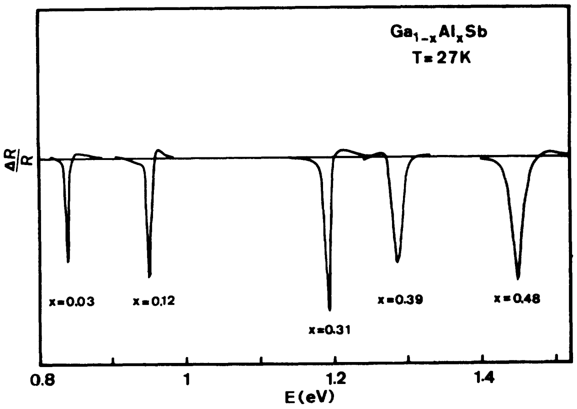

FIG. 2. Piezoreflectance spectra near the $\Gamma_8^v \rightarrow \Gamma_6^c$ (E_0) transition obtained at 27 K for different values of the composition x between 0.03 and 0.48.

III. GaSb AND AlSb

Most of our original results obtained on these materials have been previously reported.[14,15] We have summarized in Table I the transition-energy values we have determined with great precision in the very pure material that we have prepared.

We will now report on the original determination of the $\Gamma_8^v \rightarrow X_6^c$ (E_x) AlSb transition energy by wavelength modulation (Fig. 6). This spectrum is obtained by detecting the signal at a frequency twice

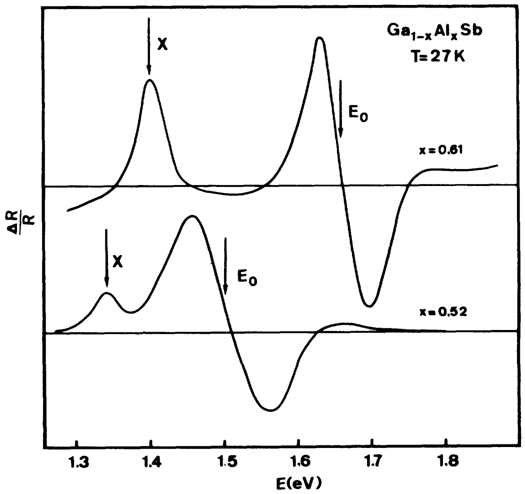

FIG. 3. Electroreflectance spectra of $Ga_{1-x}Al_xSb$ near the $\Gamma_8^v \rightarrow \Gamma_6^c$ (E_0) and the $\Gamma_8^v \rightarrow X_6^c$ (E_X) transitions at 27 K for two samples of different compositions.

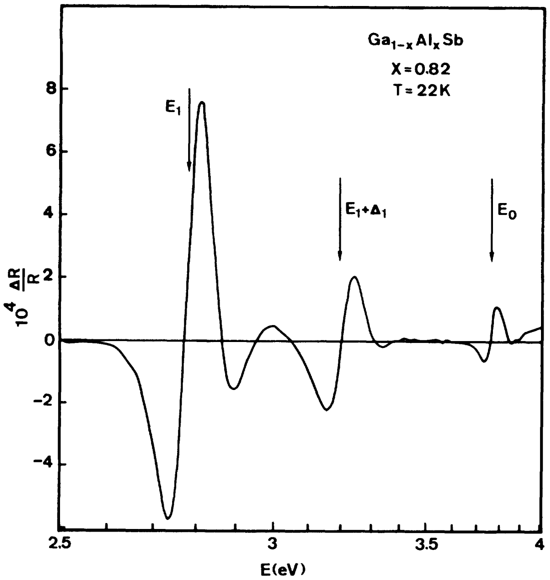

FIG. 4. Low-temperature spectra near the transitions $L^v_{4,5}\rightarrow L^c_6$ (E_1) and $L^v_8\rightarrow L^c_6$ ($E_1+\Delta_1$). An upper structure associated with the $\Gamma^v_8\rightarrow\Gamma^c_7$ (E'_0) appears on this example.

the modulation frequency; so it represents a second-derivative transmission spectrum. A systematic study as a function of temperature (Fig. 7) allowed us to separate the absorbed and emitted phonons whose energies have been compared with the values previously reported in the literature (Table II). Our results are in good agreement with those given by Turner and Rees.[22]

We have deduced, from these structures,

$$E_x(300\text{ K})=1.615\pm0.003$$

$$E_x(27\text{ K})=1.686\pm0.001$$

measured in eV, with a temperature coefficient -3.05×10^{-4} eV/K fitted in the linear part of the curve (Fig. 7).

IV. $Ga_{1-x}Al_xSb$ DIRECT GAPS

A. The $\Gamma^v_8\rightarrow\Gamma^c_6$ (E_0) and $\Gamma^v_7\rightarrow\Gamma^c_6$ ($E_0+\Delta_0$) transitions

Within a good approximation, the energies associated with these transitions follow a parabolic variation as a function of the (fractional) composition x. This law is generally expressed as

$$E=a+bx+cx(x-1)\ .$$

Such an equation shows clearly the $cx(x-1)$ quadratic deviation from a linear $a+bx$ variation between the limiting-compound energy gaps a ($x=0$) and $a+b$ ($x=1$). c is known as the bowing parameter.

The low-temperature experimental data reported in Fig. 8 have been fitted by the least-squares method to obtain, at 27 K,

$$E_0=0.81+1.57x+0.48x(x-1)\ ,$$

$$E_0+\Delta_0=1.57+1.48x+0.78x(x-1)\ .$$

Hence,

$$\Delta_0=0.76-0.09x+0.30x(x-1)\ .$$

$E_0+\Delta_0$ was not observable for the alloys with composition $x>0.55$ in which the associated structure was mixed with the $L^v_{4,5}\rightarrow L^c_6$ (E_1) transition. We could observe it in AlSb above the E_1 structure.[15]

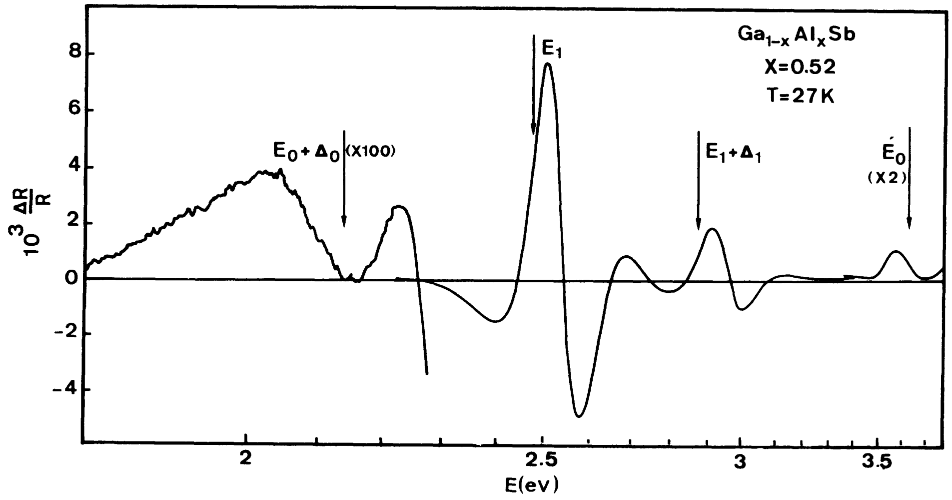

FIG. 5. Low-temperature result showing a structure associated with the $\Gamma^v_7\rightarrow\Gamma^c_6$ ($E_0+\Delta_0$) transition.

TABLE I. Experimental values of the limiting-compound transitions energies (in eV). The asterisk indicates an extrapolated value.

		(E_0) $\Gamma_8^v \to \Gamma_6^c$	($E_0+\Delta_0$) $\Gamma_7^v \to \Gamma_6^c$	(E_1) $L_{4,5}^v \to L^c$	($E_1+\Delta_1$) $L_8^v \to L_6^c$	(E_x) $\Gamma_8^v \to X_6^c$	(E_L) $\Gamma_8^v \to L_6^c$
AlSb	27 K	2.384	3.060	3.001	3.417	1.686	2.327
	300 K	2.300	2.975*	2.890	3.310	1.615	2.211
GaSb	27 K	0.808	1.569	2.185	2.622		0.871
	300 K	0.725	1.485	2.055	2.490		0.761

The main source of uncertainties—we have evaluated 10 meV on the coefficients a, b, and c—originates from the concentration measurements by electron microphone analysis. Because they represent a fit to the whole data set, it is not surprising to obtain $a=0.81$ eV and $a+b=2.38$ eV with less precision then the directly measured values $E_0(\mathrm{GaSb})=0.808$ eV and $E_0(\mathrm{AlSb})=2.384$ eV.

An identical study made at room temperature (300 K) gave

$$E_0=0.73+1.57x+0.47x(x-1) .$$

We observe that the bowing coefficient is practically independent of temperature, whose effect on the $E_0(x)$ curve is limited to a translation.

This analysis is confirmed by a systematic study of the E_0 variation versus temperature for five samples, whose conclusion is a linear dependence between 100 and 300 K with the same linear temperature coefficient, $-(3.5\pm0.1)\times10^{-4}$ eV/K, within the experimental uncertainties.

The $E_0+\Delta_0$ transition is generally not observable at room temperature, but we have verified on GaSb that Δ_0 does not vary with temperature, confirming the valence-band rigidity of the III-V compounds.[25]

B. The $L_{4,5}^v \to L_6^c$ (E_1) and $L_6^v \to L_6^c$ ($E_1+\Delta_1$) transitions

These transitions are observable throughout the entire composition range. We have obtained, at 27 K (Fig. 9),

$$E_1=2.19+0.81x+0.63x(x-1)$$

$$E_1+\Delta_1=2.62+0.81x+0.67x(x-1)$$

Hence,

$$\Delta_1=0.43+0.04x(x-1) .$$

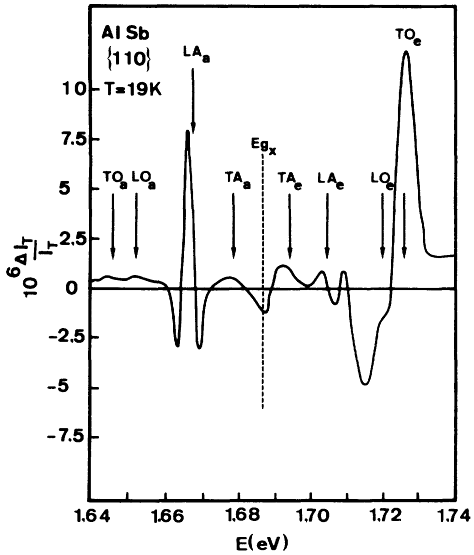

FIG. 6. AlSb second-derivative transmission spectrum obtained by wavelength modulation near the $\Gamma_8^v \to X_6^c$ (E_X) transition.

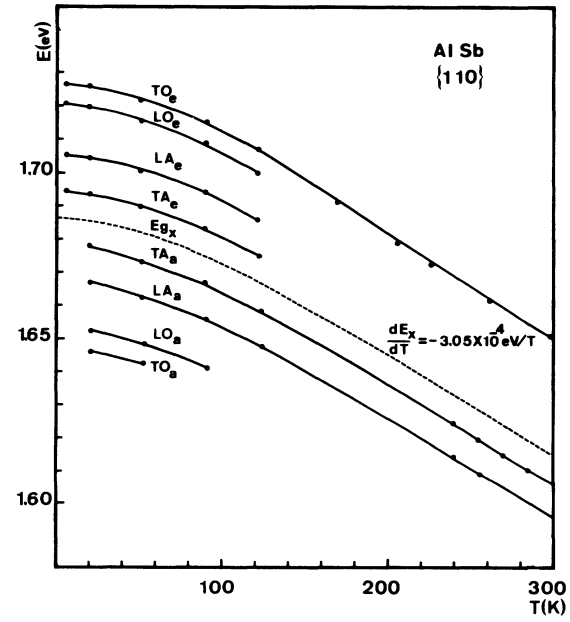

FIG. 7. Variations of the AlSb phonon energies vs temperature.

TABLE II. AlSb phonon energies (in meV). Turner and Rees (Ref. 22) used the infrared-absorption technique; Rowe, Cardona, and Shaklee (Ref. 23) and Sirota and Lukomskii (Ref. 24) used the wavelength modulation technique.

	Our values	Turner *et al.* (Ref. 22)	Rowe *et al.* (Ref. 23)	Sirota *et al.* (Ref. 24)
TA	8	8	8	8
LA	19	16	29	16
LO	34	37	36	33.7
TO	40	39	41	

Δ_1 does not vary with the temperature, and the value of the E_1 temperature coefficient remains the same over the entire composition range within the experimental uncertainties. The numerical value of the temperature coefficient is -5×10^{-4} eV/K. The effect of temperature on the $E_1(x)$ curve is just a translation.

C. Comments on the bowing parameter *c*

1. E_0 *and* E_1

In the virtual-crystal approximation several approaches have been proposed to explain the quadratic variation of the III-V ternary-compound transition energies with the composition. The Van Vechten dielectric theory,[26] the empirical pseudopotential method,[27] and the Hill method[28,29] give a theoretical bowing parameter in good agreement with the experimental values, except in the case of $Ga_{1-x}Al_xSb$ and $Ga_{1-x}Al_xAs$, whose limiting-compound crystalline parameters are too similar. In the case of $Ga_{1-x}Al_xSb$, only the dielectric theory predicts a nonzero c value ($c=0.16$), but it is still too small compared with the previous experimental values of 0.28,[11] 0.38,[12] and 0.40,[21] and with our result of 0.47 for the E_0 transition. This theory assumes, in the composition range between the limiting compounds, a linear variation of the ionic heteropolar gap C introduced by Phillips[30]:

$$E_g^2=E_h^2+C^2 ,$$

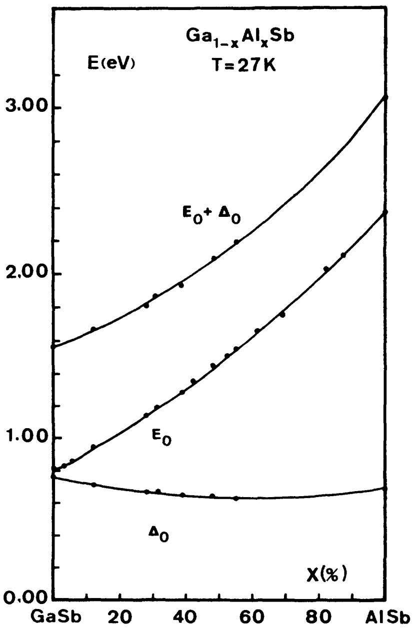

FIG. 8. Variation of the $\Gamma_8^v\rightarrow\Gamma_6^c$ (E_0), $\Gamma_7^v\rightarrow\Gamma_6^c$ ($E_0+\Delta_0$), and $\Gamma_8^v\rightarrow\Gamma_7^v$ (Δ_0) energies vs composition x for the $Ga_{1-x}Al_xSb$ ternary system.

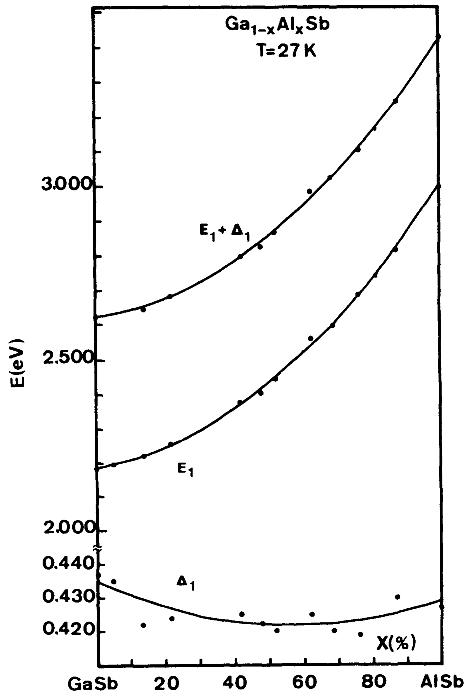

FIG. 9. Variation of the $L_{4,5}^v\rightarrow L_6^c$ (E_1), $L_8^v\rightarrow L_6^c$ ($E_1+\Delta_1$), and $L_{4,5}^v\rightarrow L_6^v$ energies vs composition x for the $Ga_{1-x}Al_xSb$ ternary compound.

where E_h is the homopolar gap. We have proposed a parabolic law of variation of C and, to take into account the spin-orbit splitting in this simple group theory, we have proposed in our model $E_0+\Delta_0/3$ and $E_1+\Delta_1/2$ as the corresponding energy gaps associated with the $\Gamma^V \rightarrow \Gamma^C$ and $L^v \rightarrow L^c$ transitions. These hypotheses modify the intrinsic contribution c_i of the bowing parameter $c=c_i+c_e$, the extrinsic contribution c_e being very small (0.004). In Table III we have reported c_i(linear) (the value of c_i deduced from a linear variation of C with the composition), c_i(parabolic) (the value of c_i deduced from the parabolic variation we have proposed), and c_{expt} (our experimental value). There is a very good agreement between c_i(parabolic) and c_{expt} for the E_0 transition. The E_1 bowing parameter is also closely fitted.

2. Δ_0 *and* Δ_1

We have experimentally shown a quadratic variation of Δ_0 and Δ_1 with the concentration, with corresponding bowing parameters

$$c_{\Delta_0}=0.30$$

and

$$c_{\Delta_1}=0.04 ,$$

measured in eV. The two-thirds rule[31] $(\Delta_1/\Delta_0=2/3)$ is better verified in the AlSb-rich compounds than in the GaSb-rich compounds, but the disagreement is less than 12/100.

The Δ_0 and Δ_1 quadratic variation cannot be explained by the Braunstein[32] theory, which predicts a linear variation of the $Ga_{1-x}Al_xSb$ spin-orbit splittings. We have used the Hill model, which attributes to the nonlinearity of E_0 and Δ_0 the same physical origin: a charge density decreasing near the core in the ternary compounds. In this hypothesis it seems reasonable to assume an identical maximum relative effect of this nonlinearity on Δ_0 and E_0, corresponding to an $x=0.50$ compound:

$$\frac{\Delta_{0,\text{lin}}-\Delta_0}{\Delta_{0,\text{lin}}}=\frac{E_{0,\text{lin}}-E_0}{E_{0,\text{lin}}} .$$

TABLE III. Comparison of theoretical and experimental values of the bowing parameter (in eV) for the E_0 and E_1 transitions of the $Ga_{1-x}Al_xSb$ system.

	c_e	c_i(linear)	c_i(parabolic)	c_{expt}
E_0	0.004	0.31	0.47	0.47
E_1	0.004	0.20	0.51	0.63

Hence

$$c_{\Delta_0}/\Delta_{0,\text{lin}}=c_{E_0}/E_{0,\text{lin}}$$

$\Delta_{0,\text{lin}}$ and $E_{0,\text{lin}}$ are the values of Δ_0 and E_0 linearly extrapolated from the limiting compounds. In these conditions we deduced from $c_{E_0}=0.48$ eV,

$$c_{\Delta_0}=0.22 ,$$

in eV. This value agrees better with our experimental determination (0.30 eV) than that of Van Vechten (0.16 eV).

An identical treatment applied to the Δ_1 gap using $c_{E_1}=0.63$ eV gives

$$c_{\Delta_1}=0.10 ,$$

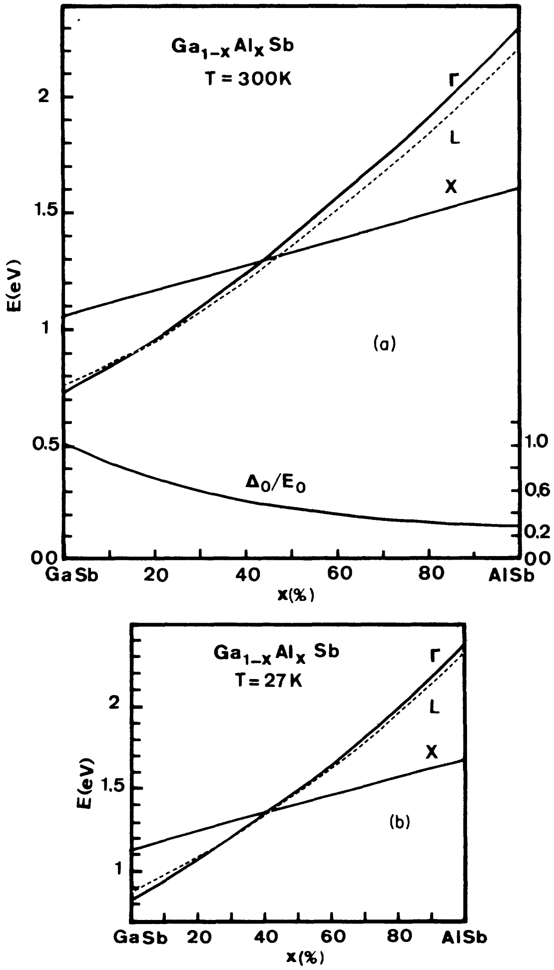

FIG. 10. $Ga_{1-x}Al_xSb$ $\Gamma_8^v \rightarrow \Gamma_6^c$ (E_0), $\Gamma_8^v \rightarrow L_6^c$ (E_L), and $\Gamma_8^v \rightarrow X_6^c$ (E_X) energy variations vs composition x (a) at room temperature and (b) at 27 K. We have drawn in the room-temperature ($T=300$ K) figure the Δ_0/E_0 variation vs composition. This ratio is important in the device conception.

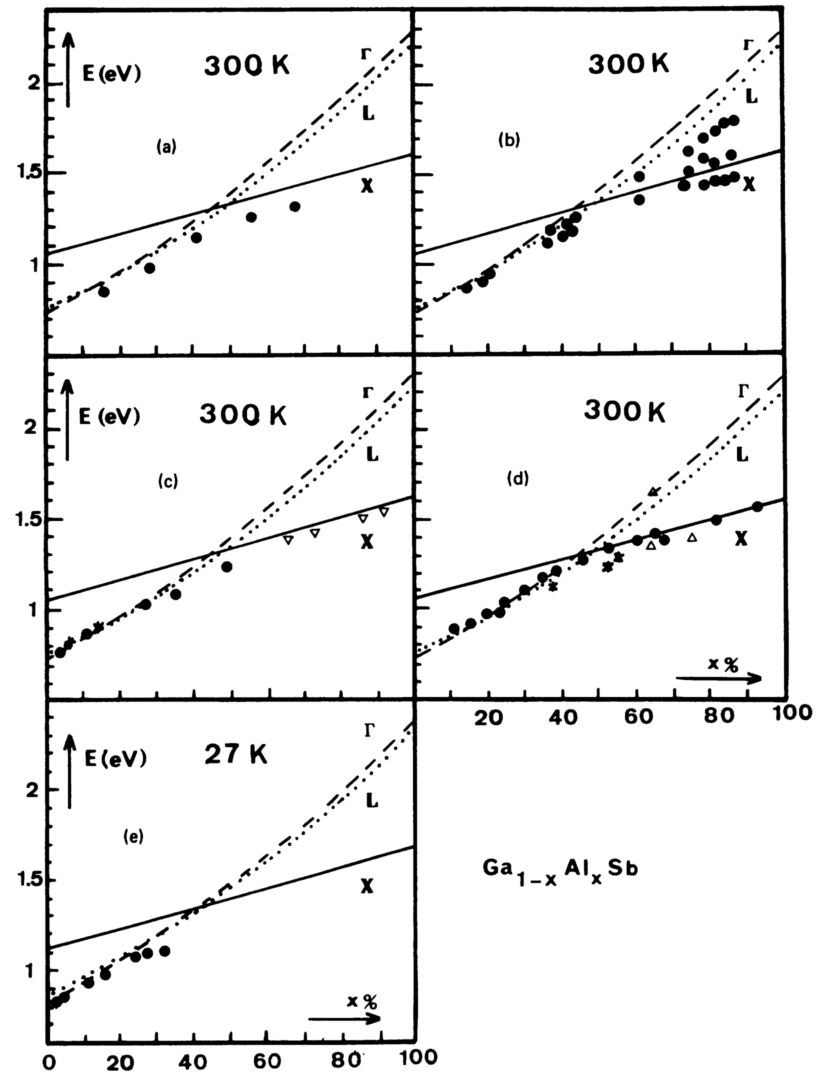

FIG. 11. Comparison between the previous results and — our E_X variation, — — our E_Γ variation, and ··· our proposed E_L variation. (a) ●, piezoreflectance by Auvergne *et al.* (Ref. 8). (b) ●, photovoltage by Bedair (Ref. 10). (c) ●, optical absorption; ✱, photoluminescence; ∇, wavelength modulation by Cheng (Ref. 7). (d) ●, photovoltage; △, absorption; ✱, photoluminescence by Anderson *et al.* (Ref. 11). (e) ●, photoluminescence by Allegre *et al.* (Ref. 12).

in eV, greater than the experimental result 0.04 eV. This must confirm the Hill hypothesis: a negative bowing of Δ_1 induced by a potential decreasing at the anion-cation contact in the alloys. This negative bowing is prominent in numerous III-V compounds[21] but in the $Ga_{1-x}Al_xSb$ case a decrease of the density near the core is insufficient for a reversal of the sign of the positive bowing.

V. $Ga_{1-x}Al_xSb$ INDIRECT GAPS

A. The $\Gamma_8^v \to X_6^c$ (X) transition

This transition has been observed on seven samples with composition $x > 0.52$ by electroreflectance technique. Within experimental uncertainties, it appears linearly dependent on x:

$$E_X = a + bx ,$$

with, at room temperature, $a = 1.05$ eV and $b = 0.56$ eV, and, at 27 K, $a = 1.12$ eV and $b = 0.56$ eV.

A systematic temperature-dependence study on three samples gave a linear temperature coefficient, in eV/K:

$$\frac{dE_X}{dT} = -(3.1 \pm 0.2) \times 10^{-4} .$$

B. The $\Gamma_8^v \rightarrow L_6^c$ (E_L) transition

The precise determination of this transition energy is quite important for device applications. Unfortunately, because of its location we have not observed in the $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{Sb}$ alloy spectra any structure that we could unambiguously attribute to the E_L transition. In only one sample ($x=0.03$) was found a low-temperature electroreflectance structure at 900 meV that could be identified as E_L, but it was not observable above 45 K because it overlapped with the structure associated with E_0. In the limiting compounds we have obtained the E_L transition-energy value with good precision (Table I).

To evaluate the position of E_L we have applied the previously evoked Hill model. The Γ_8^v, Γ_6^c, and L_6^c levels taking part in the indirect transition E_L, we have proposed for c_L the mean value of c_{E_0} and c_{E_1},

$$c_L = 0.55 \ .$$

in units of eV. From this value and the limiting-compound transition energies E_L we have deduced a reasonable evaluation of the position of E_L throughout the entire composition range.

VI. CONCLUSION

Figure 10 illustrates the $\Gamma_8^v \rightarrow \Gamma_6^c$ (E_0), $\Gamma_8^v \rightarrow L_6^c$ (E_L), and $\Gamma_8^v \rightarrow X_6^c$ (E_X) transition-energy variations versus the composition x. At room temperature the conduction-band minimum is Γ_6^v between $x=0$ and $x=0.16$, L_6^c between $x=0.16$ and $x=0.48$, and X_6^c between $x=0.48$ and $x=1$. At 27 K this minimum is Γ_6^c between $x=0$ and $x=0.35$, L_6^c between $x=0.35$ and $x=0.46$, and X_6^c between $x=0.46$ and $x=1$.

We propose now a comparison of our results with previously reported ones. In 1975 three different teams published results on the band structure of $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{Sb}$. A piezoreflectance study on three samples with composition 0.16, 0.28, and 0.40 gave a first approximation of the E_0 variation by Auvergne and Mathieu[8,9]:

$$E_0 = 0.721 + 1.479x + 0.69x(x-1) \ .$$

The E_0(GaSb) value they determined is comparable to ours (0.725 eV), but they used the AlSb $E_0=2.2$ eV reported by Cardona,[33,34] which is very different from our precise determination, 2.300 ± 0.008 eV. The few samples studied, always in the GaSb-rich domain, and the error on the E_0(AlSb) can explain the disagreement of the parameters b and c. They also evaluated the E_X variation on two samples with compositions 0.56 and 0.68. Figure 11(a) gives a comparison of our respective results.

Photovoltage technique allowed Bedair[10] to obtain a rather imprecise transition-energy measurement, but it showed clearly that the conduction-band minimum is L_6^c between $x=0.36$ and $x=0.45$ and X_6^c between $x=0.60$ and $x=1$. Our corresponding results are compared Fig. 11(b).

Cheng[7] examined eleven samples by optical absorption, photoluminescence, and wavelength modulation. The E_0 transition is measured on four samples with compositions less than 0.16, E_L on three samples between $x=0.27$ and $x=0.49$, and E_X on four samples between $x=0.66$ and $x=1$. The comparison in Fig. 11(c) shows good agreement for the direct-gap determination, the E_X values are systematically less than ours, and the E_L evaluation is very different from ours.

In 1977 Anderson[11] determined, by photovoltage, optical absorption, and photoluminescence,

$$E_0 = 0.72 + 1.50x + 0.28x(x-1) \ ,$$

$$E_X = 1.03 + 0.59x + 0.06x(x-1) \ ,$$

$$E_L = 0.80 + 0.80x \ .$$

The photovoltage determination of E_L is imprecise and can be 0.11 eV less than the true values, according to Bedair.[10] Comparison between our corresponding results is given in Fig. 11(d).

Allegre[12] (1978) obtained by photoluminescence at 4.2 K the experimental points, shown in Fig. 11(e). There is good agreement for compositions less then 0.16. The more important deviation for the other samples can be due to a lack of structures in the photoluminescence spectra. Aulombard[13] (1981) interpreted conductivity measurements under hydrostatic pressure and high magnetic field by a E_0-E_L crossing at $x=0.2$.

In summary, with twenty samples evenly distributed throughout the entire composition range and of excellent crystalline quality, we have achieved higher precision and given new information on the $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{Sb}$ band structure.

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