# Experimental determination of the GaAs and  $Ga_{1-x}Al_xAs$  band-gap energy dependence on temperature and aluminum mole fraction in the direct band-gap region

M. El Allali, C. B. Sørensen, and E. Veje Oersted Laboratory, Universitetsparken 5, DK-2100 Copenhagen, Denmark

P. Tidemand-Petersson

TFL, Telecommunications Research Laboratory, Lyngsø Alle 2, DK-2970 Hørsholm, Denmark

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The band-gap energy of GaAs and  $Ga_{1-x}Al_xAs$  has been measured with the use of photoluminescence from 10 to 300 K, and at various values of the aluminum mole fraction  $x$ , in the direct band-gap region. The temperature dependence has been fitted with the Varshni relation, and a discussion of this fitting is given. The results for GaAs are discussed in relation to previous experimental and theoretical data and good agreement is found in some, but not all cases. The observed variation of the band-gap energy of  $Ga_{1-x}Al_xAs$  with x is presented and compared to previous results.

# I. INTRODUCTION

The band-gap energy of  $Ga_{1-x}Al_xAs$  has been studied extensively at low temperatures as a function of the mole fraction  $x$  (see Refs. 1–5 and references therein). Although all data in the literature do not agree, the bandgap energy dependence on the aluminum concentration seems to be fairly well established<sup>1</sup> at low temperatures; for a detailed discussion with references to earlier works, see Ref. 1. In contrast to this, the variation of the bandgap energy of  $Ga_{1-x}Al_xAs$  with temperature T, and for different values of  $x$ , has been studied only sparsely.<sup>6</sup> There is currently a great deal of interest in  $Ga_{1-x}Al_xAs$ , both in basic research and for applications to optical and electronic devices, which will have to operate over some temperature range. Therefore, we have carried out a series of measurements to obtain reliable data for the band-gap energy of  $Ga_{1-x}Al_xAs$  as a function of  $T$ , for different values of  $x$  in the range where the band gap at the  $\Gamma$  point is direct.

The experimental data presented here have been obtained with the use of photoluminescence (PL) spectroscopy, which is a very suitable technique to study the near-band-edge region. The band-gap energy can be determined with high precision with PL, provided that the sample quality is good, and also that the PL spectra are analyzed appropriately, so that the relative roles of excitonic radiation and band-to-band recombination radiation is sorted out at all temperatures. At low temperatures, the near-band-edge spectral region is dominated by excitonic recombinations rather than band-to-band transitions, and this has to be accounted for. By increasing the sample temperature, the band-to-band recombinations gradually take over, becoming the dominant feature at temperatures above approximately 100 K. At the same time, an appreciable thermal broadening appears, and this, together with the remaining excitonic radiation, may complicate the data analysis at higher temperatures. Grilli et  $al$ .<sup>7</sup> have recently carried out a very careful study of the temperature dependence of the fundamental energy gap in GaAs, based on PL. They evaluated the relative weights of the two above-mentioned recombination processes from 2 to 280 K. Therefore, as a test, we decided to study pure GaAs in our work, together with  $Ga_{1-x}Al_xAs$ . The satisfactory agreement with the results of Ref. 7 yields confidence in our measuring procedure as well as our data analysis, as we shall see.

The total change of band-gap energy as a function of the temperature, for fixed alloy composition, results from different contributions. (i) The effect of thermal expansion causes a well-established increase of the lattice constant with increasing  $T$ , leading to a change in the bandgap energy. Malloy and Van Vechten<sup>8</sup> have recently studied the role thermal expansion plays in determining the temperature dependence of band gaps and band offsets, by using a thermodynamic approach. (ii) The renormalization of the electronic energies due to electronphonon interaction gives rise to two terms, of which the Debye-Waller term leads to the dominant contribution,<sup>9</sup> and this can be calculated rather easily. The self-energy, though smaller, is, however, somewhat more dificult to treat theoretically,  $^{10}$  and an approach which neglects the self-energy may overestimate the band-gap shrinkage.<sup>9,10</sup> For discussions of these effects, see Refs. 8—10.

In a trial to rationalize all possible temperature-related effects, Varshni<sup>11</sup> suggested an empirical relation for the temperature dependence of the band-gap energy in semiconductors. In Sec. IV, we discuss our results in terms of the empirical relation proposed by Varshni.<sup>11</sup> Also, we the empirical relation proposed by Varshni.<sup>11</sup> Also, we compare our data for GaAs with a recent theoretical work by Gopalan, Lautenschlager, and Cardona.<sup>12</sup>

# II. EXPERIMENTAL DETAILS AND CONSIDERATIONS

# A. Sample production

The samples were produced by molecular-beam epitaxy (MBE) in a VARIAN Modular GEN II growth chamber.

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First, a 5- $\mu$ m-thick, unintentionally doped, GaAs buffer was grown on a semi-insulating GaAs wafer. This layer came out to be slightly  $p$  type, due to incorporation of carbon atoms during growth. On top of this buffer, a 15 nm unintentionally doped  $Ga_{1-x}Al_xAs$  layer was deposited, followed by a 500-nm-thick  $Ga_{1-x}Al_xAs$  layer, slightly n-type doped with silicon, and, to prevent oxidation of the Ga<sub>1-x</sub>Al<sub>x</sub>As layer, it was covered with a 5nm-thick GaAs cap, also lightly doped with silicon.

The thickness of 500 nm for the  $Ga_{1-x}Al_xAs$  layer of interest was chosen because this is sufficiently thin to make reabsorption-induced redshifts of PL negligible,  $13$ and at the same time sufficiently thick to make quantumconfinement effects and also surface-related distortions of the PL spectral shapes vanishingly small, as demonstrated by Wolford et al.<sup>14</sup> in their thorough study of interfacial effects of  $Ga_{1-x}Al_xAs$ . However, in passing it can be mentioned that they found decay kinetics to be strongly dependent on layer thickness, indicating that significant amounts of surface-related nonradiative decays may take place, but apparently this only reduces the overall intensity without disturbing the spectral shapes.<sup>14</sup>

The aluminum mole fraction  $x$  was determined from reflection high-energy electron-diffraction (RHEED) oscillations observed during growth on special, stationary test wafers, prior to growth on rotating wafers, from which the samples for PL studies were cut. Therefore, we felt it desirable to determine the values of  $x$  directly in the samples actually used for the PL measurements, and not only to rely on the RHEED data obtained from the stationary test wafers. For this purpose, high-resolution x-ray diffraction was applied. In addition, the homogeneity of the  $Ga_{1-x}Al_xAs$  layers was checked with PL carried out at room temperature across the wafers from which the samples were cut. Such measurements showed that  $x$  was constant across 40 mm of a 50-mm wafer to within  $\pm 0.001$ .

## B. X-ray diffractometry

The determination of the aluminum mole fraction  $x$  in  $Ga_{1-x}Al_xAs$  by x-ray-diffraction measurements has been  $Ga_{1-x}Al_xAs$  by x-ray-diffraction measurements has been<br>treated thoroughly in two recent papers. <sup>15,16</sup> The procedure followed in the present studies was essentially the same described in these papers, i.e, application of Vegard's law and comparison of measured diffraction spectra with similar ones obtained from calculations.

The calculations were performed using dynamical diffraction theory, which also takes account of the shift in position of the Bragg reflection of a thin epitaxial layer caused by interference effects.<sup>17</sup>

There has been some divergence in the lattice parameters and Poisson ratios reported in the literature, especially for A1As but also for GaAs. We used the parameters quoted by Goorsky et  $al$ .<sup>15</sup> in the calculations. However, before really applying these values, we made a control by measuring the lattice mismatch of an AlAs sample prepared according to the description given for our  $Ga_{1-x}Al_xAs$  samples above. The diffraction spectra measured with the AlAs sample were nicely reproduced by calculated spectra obtained with the parameters of

Goorsky et al.,<sup>15</sup> except that we improved the agreement by assuming a Poisson ratio for A1As of 0.270 instead of the 0.275 quoted by Goorsky *et al.* <sup>15</sup>

The measurements were performed with a Philips high-resolution diffractometer with a copper anode and a four-reflection ([440] of two channel cut germanium crystals) monocromator, selecting the Cu  $K_{\alpha 1}$  radiation for diffraction in the sample. For the actual determination the [004] diffraction in the samples was applied, but for the A1As sample the [224] diffraction was also measured to ensure that no relaxation had taken place.

For all samples two measurements were performed with the sample rotated by 180° in between in order to account for possible tilt of the epitaxial layers with respect to the crystal planes of the GaAs substrate. The resulting mole fractions are in reasonable agreement with the values from the RHEED measurements, considering that these measurements were performed on different stationary samples. The values applied in the following are those resulting from the x-ray-diffraction measurements.

#### C. Photoluminescence measurements

For determination of the band-gap energy, the samples were mounted strain free in a closed-cycle helium refrigeration system and studied with PL from 10 to 300 K. The light sources were an Ar-ion laser ( $\lambda$ =488 nm), a He-Ne laser (633 nm), and also a diode laser (670 nm). The different light sources revealed the same spectral features on relative scales. Also, with the Ar-ion laser, the light spot on the sample was changed from being well focused, to obtain a high excitation density, to being defocused, for weak excitation densities, and such measurements yielded identical results. In all cases, the irradiance at the sample was sufficiently low to assure no local heating of the sample due to the illumination.<sup>18</sup>

The PL radiation was analyzed with a 1-m scanning spectrometer (McPherson model 2051) and detected with a photomultiplier (Hamamatsu model R943-02), using single-photon counting. The PL facility is described in detail in Ref. 19.

At the lowest temperatures applied in this work, narrow excitonic transitions were observed with high intensities, whereas at higher temperatures broader band-toband transitions showed up with lower intensities. The slits of the spectrometer were always adjusted so that a sufficient amount of light was admitted to depress statistical fluctuations to be negligibly small, at the same time as the resultant spectral widths were set by the sample and its temperature, and not by the instrumental resolution of the spectrometer.

Some electronic nonlinear effects may in principle distort the PL spectra.<sup>20</sup> Most important is the Burstein-Moss effect, which is the increase of band-gap energy due to filling of the band states, and the band-gap shrinkage due to screening of the crystal field by photoexcited carriers.<sup>20</sup> To circumvent errors caused by these two effects, we used only lightly doped samples and low excitation intensities.

The conversion from wavelength  $\lambda$ , in nm, to photon energy  $E$ , in eV, was performed by using the product value  $E\lambda = 1239.513$  eV nm, which is based on a constant value of 1.0002749 for the refractive index of air (see, e.g., Ref. 21 and references therein). The wavelength scale of the spectrometer was carefully calibrated by using suitable spectral lamps.

# III. DATA TREATMENT AND RESULTS

Our GaAs PL spectra were very similar to those reported by Grilli et  $al.$ <sup>7</sup>, i.e., dominated by excitonic transitions at low temperatures, and at higher temperatures by band-to-band recombination showing high-energy Maxwell-Boltzmann tails. The identifications of the various spectral features as well as their relative intensities at different temperatures are so detailed and precisely described in Ref. 7 that we refer the reader to Ref. 7 for a detailed discussion. Also, we agree with Grilli et  $al.$ <sup>7</sup> that even at room temperature not only is the  $n = 1$  exciton observable, but the intensity maximum in the PL spectrum appears at the excitonic transition rather than at the band-to-band recombination radiation. For a detailed spectral deconvolution with discussion, based on the theory given by Elliot;<sup>22</sup> see Ref. 7. This finding allows a straightforward determination of the band-gap energy from each PL spectrum, simply by adding the exciton binding energy to the photon energy at which the PL intensity maximum is located. For that purpose, the exciton binding energy can be calculated in the hydrogenic effective-mass approximation, which is known to hold for GaAs,<sup>23</sup> by using the values of the effective masses and the dielectric constant given in Ref. 24, combined with the temperature dependencies of the electron effective mass and the dielectric constant given in Ref. 25. The temperature dependencies of the effective hole masses are not well established, but it seems fair to use a linear interpolation between the low- and high-temperature values. Anyway, the overall uncertainty related to the various approximations and simplifications concerning the determination of the exciton binding energy versus temperature is not crucial here, because the binding energy is well established to be 4.2 meV at  $T = 0$  K (see Ref. 26), and it is approximately 3 meV at  $T = 300$  K, so its temperature variation amounts to roughly 1 meV.

As a check, we also deduced the band-gap energy from those parts of the PL spectra which were due to band-toband recombination radiation, by using the relation<sup>18,27</sup>

$$
E_{I,\max} = E_g + \frac{1}{2}kT \tag{1}
$$

where  $E_{I, \text{max}}$  is the photon energy at which the intensity maximum of the band-to-band radiation is located,  $E<sub>g</sub>$  is the band-gap energy, k is Boltzmann's constant, and  $\tilde{T}$  is the electron temperature, which in our case was identical to the lattice temperature (see Sec. II C). The two methods agreed within experimental uncertainty limits, but the accuracy of the latter is reduced by the neighboring intense maximum in the PL spectra from the excitonic transition, making the precise localization of the broader maximum of the band-to-band radiation somewhat difficult.

The spectra recorded for  $Ga_{1-x}Al_xAs$  were mainly similar to those reported by Mihara et  $al$ . <sup>28, 29</sup> Therefore, we have used their identifications. For all mole fractions used, the emission line due to radiative recombination of the bound  $Ga_{1-x}Al_xAs$  bulk exciton was identified. Next, the photon energy  $h v_{BE}$  of the bound-exciton radiative recombination was determined, and, from this, the band-gap energy  $E_g$  was deduced by using an exciton binding energy  $E_b$  given at 10 K by

$$
E_b = (0.0042 + 0.007x) \text{ eV} \tag{2}
$$

This is a linear interpolation based on an exciton binding energy of 4.2 meV for GaAs (Ref. 26) and 11 meV for A1As (Ref. 30), in accordance with Refs. 31 and 32. At higher temperatures, the Ga<sub>1-x</sub>Al<sub>x</sub>As exciton binding energy was estimated as described above for GaAs.

The derived band-gap energies are shown in Fig. <sup>1</sup> as functions of the sample temperature  $T$ , for the five different mole fractions investigated. For GaAs, several samples grown under different conditions were studied, yielding identical data within  $\pm 1$  meV, and this scatter equals essentially our overall uncertainty, related to each point in Fig. 1, as estimated from reproducibility and uncertainty in reading the spectral charts.

As seen from Fig. 1, in all cases the band-gap energy decreases smoothly with increasing sample temperature, and in quite similar ways. However, the reduction in band-gap energy when going from 0 to 300 K increases slightly with increasing  $x$ , being 0.096 eV for pure GaAs, and 0.103 eV for  $x = 0.38$ .



FIG. 1. The temperature dependence of the band-gap energy  $E_g(T)$  in eV of  $Ga_{1-x}Al_xAs.$   $\bullet, \triangle, \circ, \square, \times$  are experimental data for  $x = 0$ , 0.10, 0.18, 0.27, and 0.38, respectively. The solid curves are the best fits obtained from Eq. (3).

TABLE I. The table presents the values of  $E_g(0)$ ,  $\alpha$ , and  $\beta$  used in the Varshni relation, Eq. (3) for obtaining the curves shown in Fig. 1, and also the ratio  $\alpha/\beta$ . The data for  $x = 0.37$  have been taken from Ref. 6.

Mole fraction						
$\boldsymbol{x}$		0.10	0.18	0.27	0.38	0.37
$E_g(0)$ , eV $\alpha$ , 10 <sup>-4</sup> eV K <sup>-1</sup>	1.519	1.658	1.773	1.895	2.053	
	8.95	6.44	8.06	9.00	7.82	11.78
$\beta$ , K	538	304	451	507	383	548
$\alpha/\beta$ , 10 <sup>-6</sup> eV K <sup>-2</sup>	1.66	2.12	1.79	1.77	2.04	2.15

#### IV. DISCUSSION AND CONCLUSIONS

#### A. Band-gap energies versus temperature

Traditionally, the variation of the band-gap energy with temperature  $T$  is discussed in terms of an empirical relation of the form

$$
E_g(T) = E_g(0) - \alpha T^2 / (T + \beta) , \qquad (3)
$$

where  $E_g(0)$  is the band-gap energy at  $T=0$ , and  $\alpha$  and  $\beta$ are constants which are determined by fitting the righthand side of Eq. (3) to an experimental data set. The relation given in Eq.  $(3)$  was first introduced by Varshni<sup>11</sup> in a trial to rationalize the different effects mentioned in Sec. I.

The smooth curves shown in Fig. <sup>1</sup> were obtained by fitting Eq. (3) to the data sets, and evidently, in all five cases, satisfactory agreement was obtained. The parameter values offering the best fits are listed in Table I. In the following we discuss our data, first for GaAs, with a comparison to previous results, and subsequently for  $Ga_{1-x}Al_xAs.$ 

Our data for GaAs at low temperatures agree with previous recent measurements. The band-gap energy we find at 300 K agrees within uncertainty limits with the value obtained by using the Varshni relation [Eq. (3)j with the parameter values given by Grilli et  $al.$ <sup>7</sup> Thus, our data for GaAs confirm Ref. 7, and this in turn yields confidence to our  $Ga_{1-x}Al_xAs$  data.

Table II gives the presently obtained values for the Varshni parameters  $\alpha$  and  $\beta$  for GaAs, together with values from previous works. Obviously, the various values from previous works. Obviously, the various<br>values of  $\alpha$  and  $\beta$  scatter rather much. Therefore, the<br>table also presents (third column)  $\Delta E_g \equiv E_g (T = 0$  TAI table also presents (third column)  $\Delta E_g \equiv E_g(T=0 \text{ K}) - E_g(T=300 \text{ K})$ , calculated from the various sets of the Varshni parameters. Concerning  $\Delta E_g$ , and disregarding the fairly low value obtained from the 25-year-old data given in Ref. 11, it is seen that the other four values are very close together with an average of 96 meV, which equals our result. Thus the rather different values of  $\alpha, \beta$ listed in Table II lead to almost identical results at room temperature. Hence, fitting an experimental data set to Eq. (3) does not necessarily lead to a very precise determination of the two fitting parameters  $\alpha$  and  $\beta$ , but, on the other hand, despite this, a reliable determination of the band-gap energy versus temperature can be obtained from Eq. (3) with a suitable combination of  $\alpha$  and  $\beta$ . This can be understood by the following arguments.

By differentiating Eq. (3), one obtains to first order

$$
\Delta(E_g(T))_V = \frac{-T^2}{T+\beta}\Delta\alpha + \frac{\alpha T^2}{(T+\beta)^2}\Delta\beta\;, \tag{4}
$$

where the subscript  $V$  indicates a band-gap energy obtained from Eq. (3). Evidently, for all temperatures  $T \ll \beta$ , variations of  $\alpha$  and  $\beta$  fulfilling  $\Delta \alpha / \alpha = \Delta \beta / \beta$ , will to first order imply no change in  $\Delta(E_g(T))_V$ . Hence, fitting band-gap energies measured only in a limited temperature interval  $0 < T \ll \beta$  with Eq. (3) does not permit a precise determination of  $\alpha$  and  $\beta$ , but only of the ratio  $\alpha/\beta$ .

If the condition  $T \ll \beta$  is not fulfilled for the whole temperature interval under study, Eq. (4) shows that the change of  $\Delta (E_g(T))_V$  induced by a given, fixed value of  $\Delta \alpha$  or  $\Delta \beta$  increases with T. Also, for a fixed value of T  $(T=T_0)$ , if  $\alpha$  and  $\beta$  are changed such that  $\Delta \alpha/\alpha = \Delta \beta/(T_0+\beta)$  still,  $\Delta (E_{\alpha}(T_0))_V$  will be zero. Consequently, a precise determination of  $\alpha$  and  $\beta$  and a detailed test of the validity of Eq. (3) can only be done by fitting Eq. (3) to precise measurements covering a large temperature interval, at least up to  $T \simeq \beta$ , and preferably also above. However, such a test may well be much more than the simple relation Eq.  $(3)$  warrants.<sup>35,36</sup>

Returning now to the  $Ga_{1-x}Al_xAs$  data presented in Table I, it is noted that the values of  $\alpha$  and  $\beta$  for the five different mole fractions are fairly close to each other, as expected. However, there are some deviations, and especially, whereas  $\alpha$  and  $\beta$  change irregularly with increasing x, the variation of the ratio  $\alpha/\beta$  is not so pronounced,

TABLE II. The first two columns present previous and present values of  $\alpha$  and  $\beta$  obtained by applying the Varshni relation  $[Eq. (3)]$  to experimental results for GaAs. The third column gives  $\Delta E_g(300 \text{ K}) \equiv E_g(0) - E_g(300 \text{ K})$  calculated from Eq. (3) and using the values of  $\alpha$  and  $\beta$  listed in the first two columns. The fourth column gives the ratio  $\alpha/\beta$ . References to previous works are given in the last column.

$\alpha$ , 10 <sup>-4</sup> $eVK^{-1}$	B. Kelvin	$\Delta E_{o}$ $(300 \text{ K})$ , eV	$\alpha/\beta$ , 10 <sup>-6</sup> $e$ VK $^{-2}$	Reference
8.871	572	0.092	1.55	11
5.405	204	0.097	2.65	33
10.6	671	0.098	1.58	
5.5	225	0.094	2.44	34
8.95	538	0.096	1.66	present work

in accordance with the above-given discussion. As a further illustration, we have compared  $E_g(0) - E_g(T)$  for the data sets with  $\alpha T^2/(T+\beta)$ , using the average values for  $\alpha$  and  $\beta$ . All five data sets showed only small individual deviations from such an average function. This makes us conclude that the irregular changes in  $\alpha$  and  $\beta$  may be real, but, being irregular, they may be sample dependent, in the sense that they may be related to imperfections in the samples such as, e.g., built-in strain or stress or defects, so that other samples grown at other conditions may show similar, but different, individual irregularities. The values for  $\alpha$  and  $\beta$  reported by Waters<sup>6</sup> for  $x = 0.37$ are included in Table I, and, as seen, his data are in fair agreement with the present ones.

The way  $\alpha$  was introduced by Varshni<sup>11</sup> did not relate this parameter directly to some measurable quantity. Later, Manoogian and Woolley<sup>35</sup> showed that the Varshni relation can be regarded as a second-order approximation to the part of the band-gap temperature dependence related to electron-phonon interactions. Still,  $\alpha$  is essentially a fitting parameter, so we cannot advance the discussion of the values obtained for  $\alpha$  any further here. cussion of the values obtained for  $\alpha$  any further here.<br>Contrary to this, according to Varshni,<sup>11</sup>  $\beta$  is expected to be related to the Debye temperature  $\theta_D$ , and from the work of Manoogian and Woolley,<sup>35</sup> it follows that  $\beta=3\theta_D/8$ . For GaAs, the recommended value (Refs. 37) and 38) for  $\theta_D$  is 370 K, and similar for  $Ga_{1-x}Al_xAs$ (Ref. 37) increasing slightly with increasing  $x$ . From this, one would expect  $\beta \approx 140$  K, but obviously, all values for GaAs, listed in Table II, and also for  $Ga_{1-x}Al_xAs$  in Table I, are substantially larger, so that such a comparison is clearly disappointing, despite the fact that the Varshni fits to the present and also to previous data sets are satisfyingly good, cf. Fig. 1. Thus the agreement with the Varshni fits obtained with the use of Eq. (3) may be fortuitous, and it may be that Eq. (3) gives merely a good numerical representation but not necessarily a basic physical one.

For the sake of completeness, we mention that



FIG. 2. The band-gap energy reduction for GaAs vs temperature. The full curve shows the theoretica1 results by Gopalan, Lautenschlager, and Cardona (Ref. 12), and the filled circles are experimental data taken from Ref. 12. Our experimental results are given by crosses.

O'Donnell and Chen<sup>36</sup> have successfully applied a simple three-parameter fit to the temperature dependence of semiconductor band gaps, and naturally, our data can also be reproduced by such three-parameter fits. However, to proceed along such trends, a larger temperature range than used here is required.

In Fig. 2, we compare our experimental data for GaAs (crosses) with the result of a recent theoretical work carried out by Gopalan, Lautenschlager, and Cardona<sup>12</sup> (full curve). In the figure are also included some experimental points which were presented in Ref. 12. We note that our data fall close to the other experimental results (but show much less scattering). However, from medium temperatures and up, both experimental data sets fall above the theoretical curve, the deviation between theory and experiment increases with increasing temperature.

## B. Band-gap energy dependence on aluminum mole fraction

Figure 3 shows our data for the band-gap energy at  $T=0$  and 300 K versus the mole fraction x. At both temperatures the relationship is almost linear, with a very slight tendency toward curvature downward. Both data sets can be fitted with a relation of type



FIG. 3. The band-gap energy of  $Ga_{1-x}Al_xAs$  vs mole fraction x, at  $T = 0$  and 300 K. Our data points at  $T = 0$  K are given with filled circles and at  $T = 300$  K with crosses, and the second-order polynomial fits are given by solid curves; see the text. Previous results are shown as follows:  $---:$  Ref. 1;  $\cdots$ , Ref. 4; -----, Ref. 20; - $\cdots$ , Ref. 40; and  $-\cdots-\cdots$ , Ref. 3.

TABLE III. Representations of the direct-energy-gap dependence on the aluminum mole fraction  $x$ , as reported in the literature, and for low temperatures ( $T \approx 0$  K). *a* and *b* are coefficients of a second-order polynomial  $E_g(x) = E_{g,\text{GaAs}}$  $+ax+bx^{2}$ , as described in the text.

$a$ (eV)	$b$ (eV)	Reference	
1.60	0	40	
1.247	0	20	
1.45	0	3	
1.34	0	4	
1.36	0.22		
1.447	$-0.15$	this work	
1.415	0	this work	

 $E_g(x) = E_{g,GaAs} + ax + bx^2$ . The best fits were obtained with  $a = 1.447$  eV and  $b = -0.15$  eV for  $T = 0$  K, and  $a = 1.429$  eV and  $b = -0.14$  eV for  $T = 300$  K. These fits are shown as full curves in Fig. 3. However, although second-order polynomials can be used, there is clearly no evidence for the quadratic terms, and, if linear fittings are employed, the values obtained for a are 1.415 eV at  $T=0$ K, and 1.395 eV at  $T=300$  K. For the sake of completeness, we mention that according to the theoretical work of Hill, $39$  one should expect a positive contribution from a quadratic term, and not negative, as our data might indicate. This fact casts further doubt on the significance of the values for b found here.

Whereas both the linear and quadratic fits to our data obviously can be used with confidence for interpolations for  $0 < x < 0.4$ , neither of them are suited for extrapolations of the band-gap energy at the  $\Gamma$  point to 0.4 < x < 1, because both fits underestimate the AlAs limit<sup>30</sup> (3.13 eV at  $T = 0$  K), with 0.2 and 0.3 eV, respectively. To reach this limit correctly, at least one positive, higher-order term has to be added, which actually is evident already from inspection of Fig. 5 in Ref. 30. However, the physical background behind such a higher-order fitting is by no means clear, and furthermore, to proceed like that, new experimental data are needed in the region  $x > 0.4$ .

The value we find for  $a$  at  $0$  K is slightly larger than at 300 K, but only by  $1\%$ . This is consistent with the increase in  $E_g(T=0 \text{ K})-E_g(T=300 \text{ K})$  we observe with increasing x. In contrast to this, Oelgart et  $al.$ <sup>3</sup> found a to be reduced by 6%.

Results from previous experimental works at low temperatures are also included in Fig. 3. Such data sets are represented either with linear curves or with a secondorder polynomial (see Table III for details), but individual data points of previous investigations have been omitted in Fig. 3, to avoid obscuring the figure.

The work of Bosio et  $al$ <sup>1</sup> is the most recent one, and from Fig. 3 it can be seen that, for  $x < 0.3$ , our results agree essentially with theirs, though for increasing  $x$  the two data sets seem to start diverging slightly (as all of the sets seem to do). However, our low-temperature data come very close to the average values of all previous works, which can be taken as support of our results.

Our data at  $T=300$  K are also in close agreement with an average of previously published data sets. The latter are not included in Fig. 3, but can be found in Ref. 1.

In conclusion, we can state that we have made an experimental determination of the  $Ga_{1-x}Al_xAs$  band-gap energy variation in the temperature range 10—300 K for selected values of  $x$ . The results can partly be taken as a confirmation of earlier data, mainly for GaAs corresponding to  $x = 0$ , but they also represent an extension of the investigated area. The  $x$  values applied in our studies belong to the interval corresponding to a direct band gap. For all values, the observed temperature dependence could be reproduced by the Varshni relation, although scattered parameter values resulted from this procedure, thus indicating the necessity of investigating a wider temperature range for extraction of consistent values of the Varshni coefficients.

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