High-precision determination of the temperature dependence of the fundamental energy gap in gallium arsenide

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The photoluminescence (PL) spectra of GaAs have been measured as a function of temperature between 2 and 280 K. Measurements have been performed on a high-quality nominally undoped sample grown by molecular-beam epitaxy. At the lower temperatures the recombination of free excitons in the $n=1$ and 2 states is observed. Increasing the temperature, the interband recombination appears and eventually dominates the PL spectra. The spectra have been successfully fitted by a spectral-line-shape theory that considers both excitonic and band-to-band transitions. The fits demonstrate that even at the highest temperatures a well-defined narrow peak due to the $n=1$ exciton is observable: its energy corresponds to the energy of the maximum of the PL spectra (E_M). Hence, by adding the exciton binding energy to E_M, the value of the energy gap (E_G) at each temperature has been deduced from the spectra. This way an accurate determination of the temperature dependence of E_G in GaAs is obtained; values for the parameters of the semiempirical relations describing $E_G(T)$ are found and compared with the literature.

I. INTRODUCTION

The temperature dependence of the energy of the fundamental gap of a semiconductor is usually described by a semiempirical relation also known as Varshni's equation:[1]

$$E_G(T)=E_G(0)-\alpha T^2/(\beta+T)\ , \tag{1}$$

where $E_G(T)$ is the energy gap at the temperature T and α and β are constants. If β is assumed to be of the order of the Debye temperature, Eq. (1) has low- and high-temperature trends consistent with the two mechanisms responsible for the temperature dependence of the energy gap:[1] (i) the thermal dilation of the lattice that results in a linear shift with T, which is important at high temperatures; (ii) the temperature-dependent electron-phonon interaction, which leads to a quadratic variation of the gap at low temperatures and to a linear one at high temperatures.

Another expression with more microscopic foundations, although still semiempirical, has been proposed:[2]

$$E_G(T)=E_B-a_B\left[1+\frac{2}{\exp(\Theta/T)-1}\right]\ , \tag{2}$$

where E_B and a_B are constants $[E_G(0)=E_B-a_B]$ and Θ is an average phonon frequency; in Eq. (2) the energy threshold decreases linearly in a term proportional to an average Bose-Einstein statistical factor for phonon emission and absorption. This equation has been used to describe the temperature dependence of the interband critical points of a number of group-IV and group-III-V semiconductors.[3]

The main difference between Eq. (1) and Eq. (2) is in the low-temperature region: the quadratic dependence given in (1) is replaced in (2) by an exponential dependence. The high-temperature trend, instead, is linear in both (1) and (2).

The effects of the thermal expansion and of the electron-phonon interaction are not explicitly considered or separately taken into account in the two relations (1) and (2); therefore, the physical meaning of the parameters appearing in them is not transparent. However, Manoogian and Woolley[4] have demonstrated that the phonon contribution to the energy shift coincides with Eq. (2) and that the Varshni equation (1) can be considered a second-order approximation of Eq. (2), valid at high temperatures ($\Theta/T\ll 1$).

As for GaAs, the most widely used[5] estimation of $E_G(T)$ is the Varshni relation (1) with the following values of the constants:

$$E_G(0)=(1519.2\pm0.2)\ \text{meV}\ ,$$
$$\alpha=(5.405\pm0.25)\times10^{-4}\ \text{eV/K}\ , \tag{3}$$
$$\beta=(204\pm45)\ \text{K}\ .$$

The $E_G(0)$ value has been obtained by Sell from low-temperature exciton absorption measurements.[6] The α and β parameters have been obtained fitting the difference $E_G(T)-E_G(T=0)$, where $E_G(T=0)=1519$ meV and the energy gap values refer to the 297–973-K temperature range;[7] the standard deviation of the experimental data from the fitting equation has been estimated to be some 3 meV. The agreement between this dependence and other low-temperature data previously published is good.[5,7]

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By the analysis of the dielectric function measured over a wide temperature range, Lautenschlager *et al.*[3] determined the temperature dependence of the interband critical points energy. In particular, between 20 and 500 K, $E_G(T)$ can be described by the Varshni equation (1) with parameters[8]

$$E_G(0)=(1517\pm4)\ \text{meV}\ ,$$
$$\alpha=(5.5\pm0.7)\times10^{-4}\ \text{eV/K}\ , \quad (4)$$
$$\beta=(225\pm89)\ \text{K}$$

or by expression (2) with the parameters[8]

$$E_B=(1571\pm12)\ \text{meV}\ ,$$
$$a_B=(57\pm15)\ \text{meV}\ , \quad (5)$$
$$\Theta=(240\pm52)\ \text{K}\ .$$

The values of the parameters (3) and (4) are in reasonable agreement. However, the uncertainties are large. This fact can be justified if we consider that these values are deduced from the fit of a limited number of experimental data over a wide temperature region.

In this paper we present an accurate determination of the direct energy gap in GaAs for temperatures from 2 to 280 K obtained by means of photoluminescence (PL) measurements. Photoluminescence is very suitable to study near-band-edge transition and thus, if the quality of the sample is high enough, it allows the determination of the fundamental energy gap in a very accurate way. The measured E_G values are characterized by a scattering which is significantly lower than that of the literature data (see, for instance, Table III of Ref. 3). Hence we propose relations for the temperature dependence of E_G with new values of the parameters and we discuss the capability of Eqs. (1) and (2) to describe the experimental data.

II. EXPERIMENT

The photoluminescence measurements were performed on an undoped GaAs layer 3 μm thick grown by molecular-beam epitaxy (MBE).

The sample was mounted strain free in an exchange gas cryostat, whose temperature can be varied between 2 and 300 K. The sample temperature was measured by an Au:Fe vs Chromel thermocouple in good thermal contact with the sample; the precision of the temperature determination is estimated to be ±2 K; the temperature stability during each spectrum was better than ±0.5 K.

The PL was excited by a He-Ne laser; the laser power incident at right angle on the sample surface was 0.05 mW with a laser spot diameter of $\sim250\ \mu$m, corresponding to an intensity of ~0.1 W/cm^2. For $T>100$ K, the laser power has been increased to 1 mW in order to compensate for the decrease of the radiative recombination efficiency; the laser spot diameter was correspondingly enlarged to keep the incident power density constant. Due to the low power density used we rule out any significant sample heating by the laser excitation.

The PL was focused on the entrance slit of a 0.5-m Jarrel Ash grating monochromater with a 1200 grooves/mm grating blazed for 0.5 μm and detected by a cooled GaAs photomultiplier. The spectral band pass during the low-temperature ($T<30$ K) measurements was 0.16 nm (0.3 meV); at high temperatures it was progressively increased up to 1.1 nm (2 meV) in order to keep a reasonable signal-to-noise ratio despite the reduction of the PL intensity. The absolute precision of the wavelength determination was ±0.1 nm, corresponding to ±0.2 meV.

III. RESULTS

A PL spectrum measured at 2 K is reported in Fig. 1.[9] Several lines are visible. With reference to the detailed study of Heim and Hiesinger[10] we identify them as the $n=1$ free-exciton recombination (line at 1515.3 meV), excitons bound to neutral donor recombination (D^0,X) (line at 1514.3 meV), and recombination of excitons bound to neutral acceptors (A^0,X) (strong line at 1512.6 meV). Finally, the two weak and broad peaks at 1493.0 and 1491.0 meV are attributed to free-electron–neutral-carbon-acceptor (e,C^0_{As}) and neutral-donor–neutral-carbon-acceptor (D^0,C^0_{As}) transitions, respectively. Between the excitonic structures and the carbon-related recombination peaks, in the 1504–1512-meV spectral region, the well-known "defect-induced bound excitons" (d,X) (Ref. 11) appear.

The spectrum in Fig. 1 is typical of a nominally undoped MBE GaAs, the carbon acceptor being the dominant residual impurity; the very good quality of the sample is proved by the appearance at 1518.2 meV of the recombination of free excitons in the $n=2$ excited state and by the linewidth of the $n=1$ exciton recombination (~0.7 meV); the splitting of the (A^0,X) recombination, which is of the order of our spectral band pass (~0.3 meV), is not resolved.

When the temperature increases, the features of the photoluminescence spectra change smoothly but significantly [see Figs. 2(a) and 2(b)]. Between 2 and 25 K

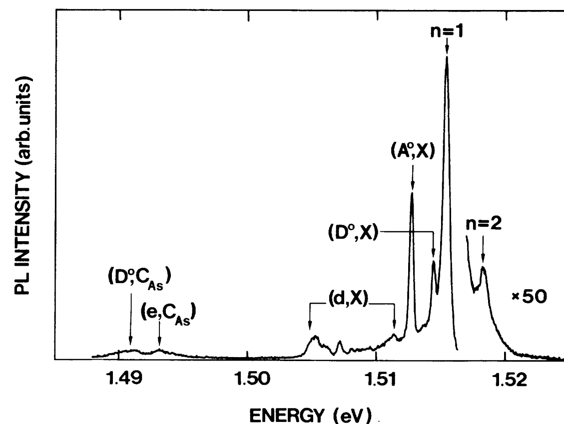

FIG. 1. Photoluminescence spectrum measured at 2 K with an exciting power density of ~100 mW/cm^2. The attribution of the spectral lines to transitions involving excitons and shallow donors and acceptors is indicated.

the weakening and the disappearance of the bound excitons recombination is observed due to thermal dissociation of the complex. In the same temperature range, the $n=2$ exciton recombination increases and the band-to-band transitions appear. The relative strength of the interband recombination increases at high temperatures and finally ($T>100$ K) the interband transition become the dominant recombination process.

In order to evaluate the relative weight of the different recombination processes, the PL spectra have been fitted using Elliot theory.[12] The luminescence intensity $I_{\mathrm{PL}}(E)$ is related to the absorption coefficient $\alpha(E)$ through the energy balance relation[13]

$$I_{\mathrm{PL}}(E) \propto \alpha(E) f(E) , \quad (6)$$

where $f(E)$ is a suitable thermal function. Using Elliot theory, which includes excitonic effects, the absorption coefficient[14] is

$$\alpha(\hbar\omega)=\frac{4\pi e^2}{cn\omega m_0^2}|M_{c-v}|^2\left\{\frac{1}{a_B^3}\left[CA_x(E_g-R-\hbar\omega)+\sum_{n\geq 2}\frac{1}{n^3}A_b\left[E_g-\frac{R}{n^2}-\hbar\omega\right]\right] + \left[\frac{2\mu}{\hbar^2}\right]^{3/2}\frac{\sqrt{R}}{2}\int_{E_g}^{\infty}\frac{A_b(E-\hbar\omega)}{1-\exp[-2\pi\sqrt{R/(E-E_g)}]}dE\right\} . \quad (7)$$

$E_g-R/n^2=E_n$ is the energy of the nth excited state of the free exciton. The empirical factor C is due to the assumption of a different relaxation mechanism between the $n=1$ exciton and the other high index excitons or free carriers.[15] The functions $A_x(E)$ and $A_b(E)$ account for a broadening of the states through a suitable function (e.g., a Gaussian function or a Lorentzian one). In the limit of nondegenerate carrier density, the thermal function $f(E)$ is approximated by a Boltzmann function.

A least-squares fit of $I_{\mathrm{PL}}(E)$ to the experimental data has been made for different spectra between 22 and 280 K. A Gaussian broadening has been assumed; the use of a Lorentzian broadening results in identical values of the fitting parameters but in larger χ^2 values. Five fitting parameters have been used: (i) Γ_x in $A_x(E)$, which represents the broadening of the $n=1$ excitonic state; (ii) Γ_b in $A_b(E)$, which represents the broadening of the high-index excitons and of the continuum states; (iii) the empirical factor C; (iv) the total luminescence intensity; and (v) the band-gap energy E_G.

The exciton binding energy (R) is not a fitting parameter, but has been calculated in the hydrogenic effective-mass approximation, which is known to hold for GaAs.[16] The low-temperature values of the effective masses and of the dielectric constants have been taken from Ref. 17; an estimation of their high-temperature values is proposed in Ref. 5, together with the temperature dependence of the electron effective mass m_e^* and of the electric constant. Detailed information on the temperature dependence of the hole masses is lacking in the literature and we assumed a linear interpolation between the low- and high-temperature values. This approximation cannot significantly influence the value of the reduced exciton mass, due to the smallness of the electron effective mass with respect to the hole masses.

Some fits are reported in Fig. 3. For $T=22$ K the $n=1$ exciton transition dominates the spectrum. Transitions associated with higher-index excitons are visible as a separated peak at about 1518 meV. The contribution of the band-to-band recombination appears as a high-energy tail. The low-energy tail of the $n=1$ exciton peak is not very well reproduced by our fit, which tends to overestimate the broadening of the $n=1$ exciton state. This is due to the use of a Gaussian function for the low-temperature broadening; a Lorentzian function gives better results in this temperature range. This problem is no more present at higher temperatures, as indicated by the $T=111$ and 280 K results. For $T=111$ K, thermal population of high-energy states occurs and the relative intensity of the band-to-band and exciton transition is now comparable. The excitonic transitions ($n=1$ and higher-index excitons) have merged in a single wide band due to the thermal broadening of the excitonic states. For $T=280$ K the free-carrier contribution to the photoluminescence dominates the spectrum. However, the peak position is still determined by the excitonic transitions due to their smaller linewidth with respect to that of the broad band-to-band line. In general, our calculations justify *a posteriori* our assertion of no laser-induced thermal heating. In fact, the fit of the high-energy tail of the free-carrier band, which is due to the interband thermalization, is pretty good.

The fits, as mentioned before, show that, for our sample, even at the highest temperatures a well-defined peak due to the $n=1$ exciton is observable: its energy correspond to the energy of the maximum of the PL spectrum (see Fig. 3). This fact allows a straightforward evaluation of the band-gap energy at each temperature: we simply add to the peak energy of each spectrum the value of R calculated at the corresponding temperature. The values of the energy gap obtained this way are reported as a function of the temperature in Fig. 4, together with the errors on T and on E_G. These errors are three times the standard deviations deduced from the accuracy of the experiment. The error in the band-gap energy includes, together with the sources of error discussed in Sec. II, the uncertainty regarding the determination of the peak energy. Also the exciton Rydberg bears some uncertainty,

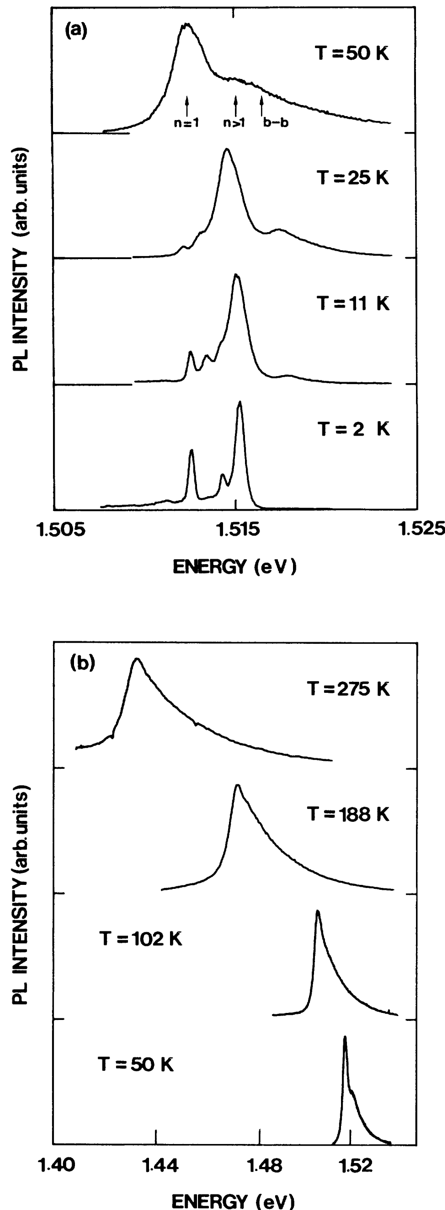

FIG. 2. (a) Photoluminescence spectra measured at different temperatures with an exciting power density of ~100 mW/cm^2. The recombinations of the $n=1$ exciton ($n=1$), of the high index excitons ($n>1$), and of free carrier ($b-b$) are indicated on the spectrum measured at $T=50$ K. (b) Photoluminescence spectra measured at different temperatures with an exciting power density of ~100 mW/cm^2.

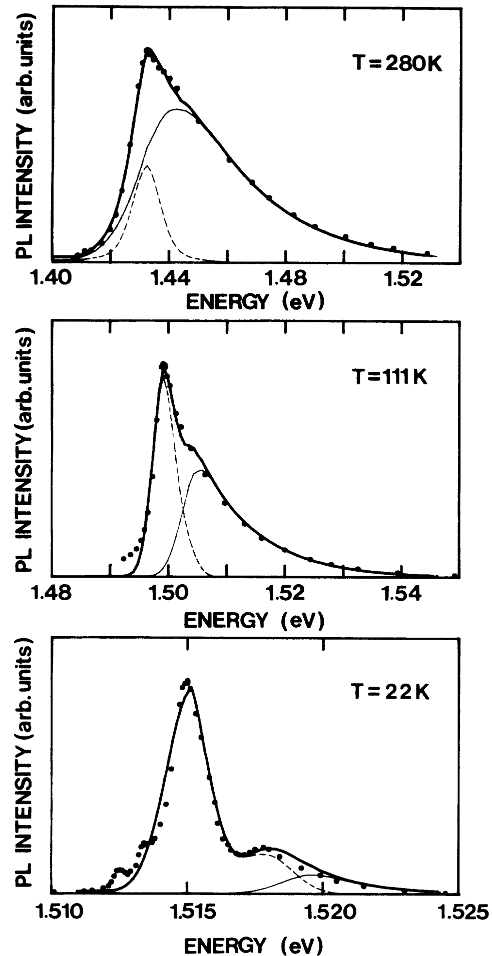

FIG. 3. Line-shape fits (thick lines) to the photoluminescence spectra of GaAs (dots) at various temperatures. The thin dashed lines and the thin solid lines indicate the excitonic and the free-carriers contribution to the total photoluminescence intensity, respectively. The parameters used in the fits are the following. For $T=22$ K: $\Gamma_x=2.2$ meV, $\Gamma_b=2.1$ meV, $C=0.21$, and $E_G=1519.1$ meV; for $T=111$ K: $\Gamma_x=4.5$ meV, $\Gamma_b=5.2$ meV, $C=0.54$, and $E_G=1502.9$ meV; for $T=280$ K: $\Gamma_x=11.4$ meV, $\Gamma_b=28.5$ meV, $C=1.11$, and $E_G=1435.9$ meV.

which is impossible to evaluate; indeed any information on the errors and on the temperature dependence of the hole masses is lacking. However, the impossibility to estimate the uncertainty on R is not important, due to the smallness of the Rydberg (3–4 meV).

IV. DISCUSSION

The data in Fig. 4 have been fitted with both relations (1) and (2). The fitting parameters are reported in Table I, together with the literature results we discussed in Sec. I.[3,7] The uncertainties of the fitting parameters and the estimated standard deviations of the fits are included in the table together with the $\tilde{\chi}^2$ values. The estimated standard deviation is defined as[18]

$$s=(\tilde{\chi}^2/\bar{\sigma}^2)^{1/2}\,, \qquad (8)$$

where

$$\bar{\sigma}^2=\left[\frac{1}{N}\sum_{i=1}^{N}1/\sigma_i^2\right]^{-1}.$$

σ_i are the standard deviations of the data points. The goodness of the fit is given by the value of $\tilde{\chi}^2$. With the number of our data points a good fit is defined by $\tilde{\chi}^2\leq 1.5$; in this case the uncertainty of the fitting param-

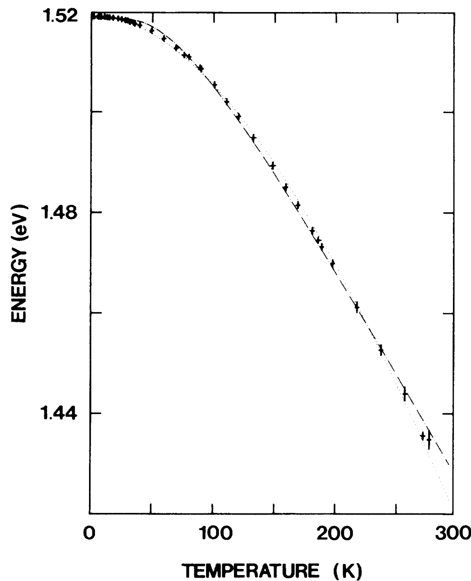

FIG. 4. Experimental values of the fundamental energy gap of GaAs for $T < 300$ K. The errors on T and on E_G are reported; these errors are three times the standard deviations deduced from the accuracy of the experiment. The fits of the data with Eq. (1) (dotted line) and Eq. (2) (dash-dotted line) are also shown; the fitting parameters are reported in Table I.

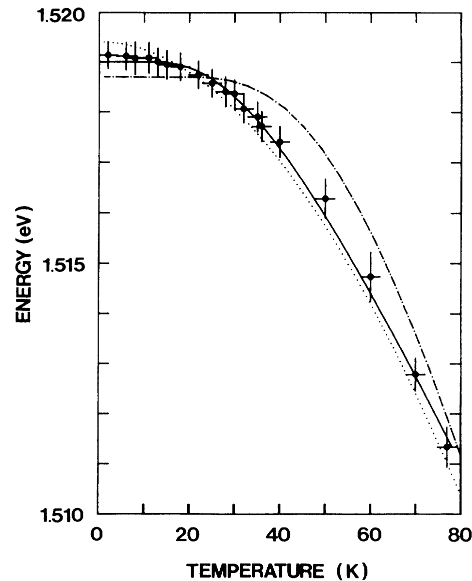

FIG. 5. Experimental values of the fundamental energy gap of GaAs for $T < 80$ K. The errors on T and on E_G are also reported; these errors are three times the standard deviations deduced from the accuracy of the experiment. The lines represent the fitting curves: curve obtained from the fit of the data at $T \leq 77$ K with Eq. (2) (solid line); curve obtained from the fit of the data at $T \leq 280$ K with Eqs. (1) and (2) (dotted line and dash-dotted line, respectively). The fitting parameters are reported in Table I.

eters can be effectively estimated. When $\tilde{\chi}^2$ is greater, the function is not appropriate;[18] in any case, the function with the parameters obtained from the fit provides a curve that describes the data points with an approximation of the order of the estimated standard deviation s.

The high $\tilde{\chi}^2$ values (see Table I for the 2–280-K temperature range) show that the two equations are in significant disagreement with the experimental trend of $E_G(T)$. However, the estimated standard deviations (0.4 and 0.5 meV in the two cases) are of the same order of the experimental uncertainties. Then the approximation of the data points with the calculated curve could be reasonable for many practical uses. The difference between our experimental determination and the Varshni equation with the parameters (3), which is the most widely used $E_G(T)$ dependence,[5] reaches 4–5 meV in the 100–200-K temperature range. The accepted low-temperature value of the energy gap of GaAs [1519.2±0.2 meV (Ref. 6)] is in reasonable agreement with the $E_G(0)$ value deduced from the fit of our data with Eqs. (1) and (2): 1519.4 meV and $E_G(0)=E_B-a_B=1518.7$ meV, respectively.

A closer insight into the fitting curves shows that in the low-temperature region ($T < 100$ K) there are small

TABLE I. Values of the parameters obtained from the fit of the GaAs energy gap with Eqs. (1) and (2). The uncertainty of the fitting parameters obtained in the present work is reported only if the fit is good ($\tilde{\chi}^2 \leq 1.5$). $\tilde{\chi}^2$ and s are the reduced χ^2 and the estimated standard deviation, respectively.

Fit with Varshni's equation (1)						
$E_G(0)$ (meV)	α (10^{-4} eV/K)	β (K)	Temperature (K)	s (meV)	$\tilde{\chi}^2$	Ref.
1519.4	10.6	671	2–280	0.36	4.13	a
1519.2±0.2	5.405±0.25	204±45	297–973			b
1517±4	5.5±0.7	225±89	20–500			c
Fit with Eq. (2)						
E_B (meV)	a_B (meV)	Θ (K)	Temperature (K)	s (meV)	$\tilde{\chi}^2$	Ref.
1529.4±1.1	10.4±1.1	102.4±5.7	2–77	0.10	0.62	a
1562.0	43.3	202	2–280	0.49	7.47	a
1571±12	57±15	240±52	20–500			c

[a]Present work.
[b]References 6 and 7.
[c]Reference 3.

but systematic differences between the trend of the experimental data and of the calculated curve both in the case of expression (1) and expression (2) (Fig. 5). In any case, the fitting curves proposed in the literature do not fit our experimental data in this temperature range at all (Fig. 6).

However when we fit with Eq. (2) the low-temperature data only ($T \leq 77$ K), we get a good fit, as shown in Fig. 5.[19] The $\tilde{\chi}^2$ value is now 0.6 and the estimated standard deviation is 0.1 meV. Also the low-temperature $E_G(T)$ value (1519.0 meV) is in full agreement with the accepted one.[6] The large value of the uncertainty on both E_B and a_B indicates the presence of some correlation between these parameters.

The better quality of this fit with respect to the two performed on all the data points is consistent with the fact that Eq. (2) gives essentially the dynamic part of the energy shift.[4] This contribution dominates at low temperatures. Indeed the curve calculated this way does not fit the experimental points for $T \geq 100$ K. In fact, the thermal-expansion contribution to the energy shift becomes important. An estimation of this contribution can be deduced from the difference between the fitted curve and the experimental data at high temperatures (including the values at $T > 300$ K from Ref. 20); these differences are of the same order of the effects of the thermal expansion on the energy gap shift in GaAs reported in Table I of Ref. 21.

In order to get $E_G(T)$ relations valid in a wider temperature region, we have tried to fit our data together with the four high-temperature ($T > 300$ K) values of E_G reported in Ref. 20. The fit has failed ($\tilde{\chi}^2 \geq 10$). The disagreement is higher for $T > 300$ K than for $T < 300$ K. We think that a more-detailed determination of E_G for $T > 300$ K is needed.

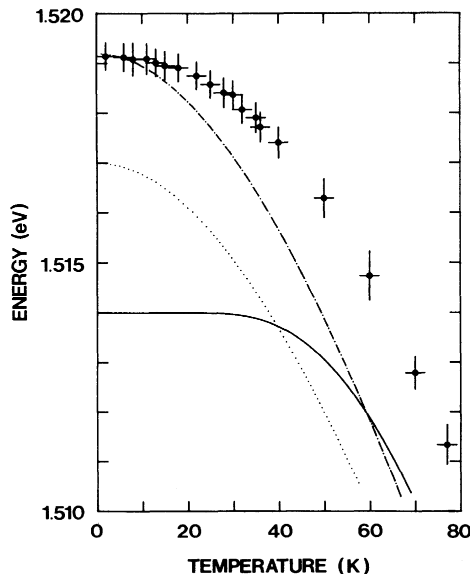

FIG. 6. Comparison of the experimental values of the fundamental energy gap of GaAs for $T < 80$ K with the fitting curves reported in the literature; the solid line represents Eq. (2) with the parameters (5); the dash-dotted and the dotted lines represent Eq. (1) with the parameters (3) and (4), respectively.

The preceding discussion warrants some final comments on the capability of Eq. (1) and (2) to describe the temperature dependence of the energy gap in GaAs.

(i) At low temperatures ($T < 80$ K) the effects of the lattice dilation are negligible (see Table I in Ref. 21): Equation (2), which is an expression for the dynamic contribution to $E_G(T)$, gives a good description of the data in this temperature range.

(ii) In GaAs the contribution of the electron-phonon interaction to $E_G(T)$ is always greater than the contribution of the lattice dilation.[21] Therefore, Eq. (2) and its approximate form (1) give a useful fit of the data, also if data at high temperatures ($T \leq 280$ K) are considered. The effective dependence on the temperature, however, is only approximately described by the empirical relations.

(iii) Consequently, the values of the parameters with which a given empirical law describes the experimental data depend on the temperature interval in which the data have been fitted and are valid only in that interval.

V. CONCLUSIONS

We determined the width of the energy gap versus temperature in GaAs by means of PL measurements for temperatures below 280 K. The uncertainty of our determination progressively increases with temperature from 0.3 meV for $T \leq 30$ K to 1.9 meV for $T = 280$ K. This way we get experimental data that are more accurate than those available in the literature (see, for instance, the scattering of the data collected in Table III of Ref. 3).

The temperature dependence of these data has been fitted using two semiempirical relations: Eqs. (1) and (2). At low temperatures ($T < 80$ K), where the effect of the thermal dilation on $E_G(T)$ is negligible, the fit of the data with Eq. (2) is good.

For temperatures below 280 K, Eqs. (1) and (2) fit the data with comparable $\tilde{\chi}^2$ and s values but none of them provides a good fit. It is important to point out that the previously published fitting parameters were obtained with a limited number of data points[3] or with no points at all[7] between 2 and 300 K. Therefore, our determination of the fitting parameters can be considered the most reliable one in this temperature region. When high-temperature literature data are included, the fits get worse: a more-detailed determination of E_G for $T > 300$ K would be useful.

In any case, we have shown that neither of the two relations proposed for the temperature dependence of the energy gap describes in an appropriate way the experimental data in the case of GaAs. We feel that this is a more general problem connected with the inadequacy of the proposed semiempirical relations to account for a complex physical problem.

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[15]A tentative fit to the PL spectra with $C=1$, i.e., assuming a thermodynamic equilibrium between the $n=1$ exciton and the rest, has failed. We note that also the absorption coefficient of GaAs is not fitted by the Elliot theory [D. E. Hill, Solid State Commun. **11**, 1187 (1972)]. The oscillator strengths for high-index excitons or for continuum states are well described by Elliot theory, whereas the ratio between the $n=1$ and the $n=2$ exciton oscillator strength is missed. Some speculations on this point are possible, but an explication goes beyond the objective of the present paper.

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