Photoluminescence in heavily doped GaAs. II. Hydrostatic pressure dependence

Diego Olego, Manuel Cardona, and Hans Müller
Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Federal Republic of Germany
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The photoluminescence at the direct E_0 gap of heavily doped p- and n-type GaAs has been measured as a function of hydrostatic pressure using a diamond anvil cell. In p-GaAs the emission at E_0 is still observed for pressures above that at which the material becomes indirect. The intensity of the emission at very high pressures normalized to that of zero pressure can be related to the radiative recombination and the intervalley scattering times. From the pressure dependence of the intensity, besides the pressure coefficient of the X_1^c minima, an average scattering time for transitions from Γ_1^c to X_1^c is obtained. Luminescence at the indirect gap X_1^c-Γ_8^v was observed in GaAs with 1.6×10^{18} holes cm^{-3} for pressures between 40 and 55 kbar. The E_0 gap, obtained from luminescence measurements, shows at room temperature the same sublinear behavior as a function of pressure as was reported by Welber *et al.* At low temperatures ($T = 120$ K), however, we measured a *linear* pressure dependence. The corresponding linear pressure coefficient is 30% lower than that at room temperature. In n-GaAs the linewidth of the emission changes drastically with increasing pressure; the emission disappears when the lowest gap becomes indirect. Both phenomena are due to the transfer of free electrons from Γ_1^c to X_1^c. The linear pressure coefficient of the luminescence lines is smaller than for the p samples because of the pressure dependence of the Burstein-Moss shift.

I. INTRODUCTION

The development of the diamond anvil cell and the ruby fluorescence manometer has given new impetus to the investigation of the electronic and vibronic states of semiconductors under very high hydrostatic pressure.[1,2] During the past four years, first and second-order Raman spectra,[3-5] absorption[6-8] and photoluminescence[5,8] have been investigated with the help of the diamond cell. In some cases materials were shown to undergo phase transitions at high pressures.[9] The general trends of the dependence of the energy gaps of germanium and zinc-blende-type semiconductors on hydrostatic pressure has been known for some time as a result of work at "low pressures" (~10 kbars).[10] With increasing pressure the Γ_1^c conduction-band states rise rapidly relative to the Γ_8^v valence-band states: the E_0 direct gap Γ_1^c-Γ_8^v increases. The X_1^c conduction-band minima along the $\{1,0,0\}$ directions move slowly towards the Γ_8^v valence-band states: the indirect gap X_1^c-Γ_8^v decreases slightly with increasing pressure. The L_1^c-Γ_8^v indirect energy gap also increases with pressure (L_1^c are the conduction-band minima at $L\{1,1,1\}$). The rate of increase, however, is roughly half that of the E_0 gap.

GaAs is a direct-gap semiconductor at normal pressure. Owing to the different signs of the pressure coefficients of the E_0 and X_1^c-Γ_8^v gaps a crossing between the Γ_1^c and X_1^c conduction-band minima takes place when the pressure is increased above 40 kbar. The lowest gap becomes indirect and the band structure resembles that of GaP. As a result of this crossing the luminescence efficiency decreases and, in the case of undoped GaAs, the E_0 emission completely disappears for pressures beyond 45 kbar.[5] A similar decrease of the E_0 luminescence was recently reported for InP at pressures around 100 kbar.[8] By fitting the pressure dependence of the emission intensity with a theoretical expression, Yu and Welber[5] and Müller *et al.*[8] were able to determine the pressure coefficient of the indirect energy gap X_1^c-Γ_8^v.

In this paper we report the hydrostatic pressure dependence of the photoluminescence from heavily doped p- and n-type GaAs. Owing to the enhancement of the luminescence by the free holes, the luminescence across the direct energy gap E_0 is still observed for the p-type samples when the material becomes indirect. The ratio of the intensities after and before the "Γ_1^c, X_1^c" crossing increases with increasing hole concentration and can be related to the hole concentration of the radiative recombination time. By fitting the measured dependence of the intensity on pressure, we obtain the pressure coefficient of the X_1^c-Γ_8^v indirect gap and the scattering time from the Γ_1^c to the X_1^c states.

The fact that the emission from E_0 is seen after the "Γ_1^c, X_1^c" crossing in heavily p-doped samples opens the possibility of performing temperature-dependence measurements of the pressure coefficients for pressures up to the phase transitions. Such measurements are difficult to perform with transmission techniques as it is difficult to focus the probing beam on the sample placed in a diamond cell inside a Dewar. Accurate focusing is not required for luminescence measurements.

At room temperature our measurements reproduce the sublinear pressure dependence of the direct energy gap E_0, as determined by Welber *et al.*[6] However, at low temperatures ($T \simeq 120$ K) we found the dependence of E_0 on pressure to be linear, with a slope around 30% lower than that found at room temperature (see Table II). The difference between the E_0 gap at 120 K and at room temperature shows a parabolic dependence on pressure.

We have reported in p-GaAs luminescence at the $E_0 + \Delta_0$ gap (Δ_0 the spin-orbit splitting), at the indirect gap X_1^c-Γ_8^v, and possibly from impurity levels associated with the X_3^c conduction-band minima.[12,13] We failed to observe these weak emissions when the sample was placed in the diamond cell: the small volume of sample and the poor collection efficiency of the pressure chamber allow only the stronger emission from E_0 to be observed. However, for samples with 1.6×10^{18} holes cm^{-3} a new emission line appears in the pressure range between 40 and 55 kbar. It can be identified as related to the X_1^c-Γ_8^v indirect gap.

The second part of the paper deals with the pressure dependence of the emission from heavily doped n-GaAs. As in the case of pure GaAs the intensity of the direct-gap luminescence vanishes for pressures above which the material is indirect. The transfer of the free electrons from the Γ_1^c minimum to the X_1^c minima with increasing pressure accounts for this behavior of the intensity. The shape of the emission line changes drastically for pressures near the "Γ_1^c, X_1^c" crossing as a result of a rapid decrease of the Fermi level with respect to the bottom of the Γ_1^c conduction band.

The photon energy of the emission from degenerate n-type semiconductors is very sensitive to the Burstein-Moss effect.[11] At 120 K the emission from n-GaAs moves to higher energies with increasing pressure with a linear pressure coefficient smaller than that measured for the p-type samples. The difference between both linear pressure coefficients can be explained by considering the pressure dependence of the Burstein-Moss shift.

II. EXPERIMENT

The GaAs samples were cut from single crystals and the carrier concentrations determined from Hall-effect measurements. After a wafer was polished to a thickness from 20 to 40 μm, it was broken into small pieces. A fragment was selected under the microscope and inserted into the 200-μm hole of the pressure cell gasket together with a ruby chip for the determination of the pressure.[2] A 4:1 mixture of methanol and ethanol was used as a pressure transmitting fluid.

The experiments were performed in the backscattering configuration using the high-pressure diamond cell described in Ref. 14. For the low-temperature measurements the cell was placed in an evacuated cryostat and held by a copper cold finger in contact with a liquid-nitrogen bath. The pressure could be varied from outside even when the system was cold. It was monitored by the ruby fluorescence technique.[1,2,15] The ruby lines did not show any asymmetry or abnormal behavior at higher pressures even at low temperature; we thus exclude possible pressure gradients or uniaxial stress components (maximum estimated strength of such components $\simeq \frac{1}{10}$ of the pressure shift which corresponds to the ruby fluorescence width, $\simeq\pm1$ kbar). The temperature in the pressure chamber was determined in two independent ways, the energy of the E_0 gap at very low pressures[12] and the temperature dependence of the ruby lines.[15] Both determinations agree to within ±10 K.

The photoluminescence was excited with either the 4880- or 4579-Å lines of an Ar^+-ion laser and analyzed with a Spex 0.8-m double monochromator. The detection was performed with an RCA 31034 photomultiplier with photon-counting electronics. The recorded spectra were corrected for spectral response of the monochromator-multiplier setup.

III. RESULTS AND DISCUSSION

A. Pressure dependence of the intensity (p-GaAs)

Figure 1 displays the emission around the E_0 gap for various pressures at 120 K in p-GaAs with 9×10^{19} holes cm^{-3}. In the range of pressures between 30 and 45 kbar the intensity of the luminescence decreases exponentially as a result of the crossing between Γ_1^c and X_1^c conduction-band states. However, the emission lines do not disap-

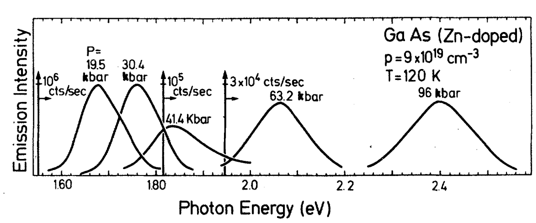

FIG. 1. Typical emission spectra around the E_0 direct gap as a function of pressure at 120 K for a heavily Zn-doped p-GaAs with 9×10^{19} holes cm^{-3}. With increasing pressure the emission lines shift to higher energies. Their intensity decreases for pressures between 30 and 45 kbar because of the "Γ_1^c, X_1^c" crossing. Although the material becomes indirect after this crossing, the emission from E_0 can still be observed.

pear completely when the material becomes indirect, as is the case for undoped GaAs.[5] This behavior of the luminescence across the direct gap E_0 as a function of pressure is observed for hole concentrations above 10^{17} holes cm^{-3}; it is shown in Fig. 2 for a series of samples of various hole concentrations. The intensity of the emission has a "steplike" dependence on pressure. The ratio of the intensity above 60 kbar to that at low pressures increases with increasing hole concentration as shown by the experimental points of Fig. 3.

The pressure dependence of the emission can be described with the expression

$$I \simeq I_0\left\{\left[1 + A\exp\left(\frac{(\alpha_\Gamma - \alpha_X)(P - P_0)}{kT}\right)\right]^{-1} + \frac{\tau_{\Gamma\to X}}{\tau_{\text{rad}}}\right\}, \tag{1}$$

where I_0 is a constant, P_0 the pressure at which Γ_1^c and X_1^c are degenerate, α_Γ and α_X the linear pressure coefficients for the E_0 and X_1^c-Γ_8^v energy gaps, $\tau_{\Gamma\to X}$ represents an average intervalley scattering time of the electrons from the conduction band at Γ to the conduction-band minima at or near X; τ_{rad} is the radiative recombination time for optical transitions across the direct gap. The parameter A is given by

$$A = 6\left(\frac{m_{\parallel X} m_{\perp X}^2}{m_\Gamma^3}\right)^{1/2}\frac{\tau_\Gamma}{\tau_X}, \tag{2}$$

where $m_{\parallel X}$, $m_{\perp X}$ are the longitudinal and transverse

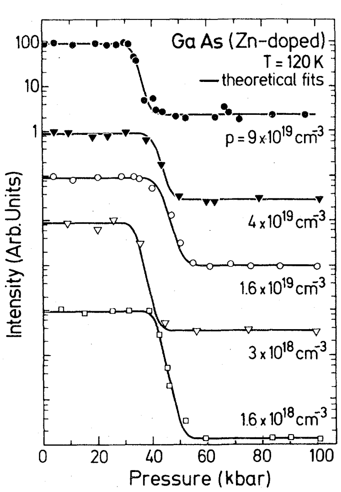

FIG. 2. Pressure dependence of the emission across the E_0 gap for a series of hole concentrations. For each hole concentration the vertical scale has been displaced. The solid lines correspond to fits performed with Eq. (1). The obtained parameters are listed in Table I.

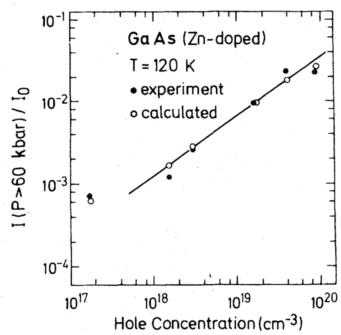

FIG. 3. Hole-concentration dependence of the intensity of the E_0 luminescence for pressures above 60 kbar normalized to that at very low pressures. The calculated points were obtained with Eq. (4). The solid line has been drawn as a visual aid.

effective masses of the X_1^c minima and m_Γ that of Γ_1^c; τ_Γ and τ_X are the lifetimes of the minority carriers at Γ_1^c (mostly radiative) and X_1^c (nonradiative), respectively. The factor 6 accounts for the degeneracy of the X_1^c minima.[16]

The first term on the right-hand side (rhs) of Eq. (1) represents the transfer of the photoexcited electrons to the X_1^c minima when the material becomes indirect, and has been used by Yu and Welber[5] and Müller *et al.*[8] to describe the exponential decrease of the luminescence in undoped GaAs and InP, respectively. In a heavily doped p-type material, however, an enhancement of the emission [i.e., decrease of τ_{rad} (Ref. 17)] occurs because of the large number of free holes on the top of the valence bands. It implicitly assumes that the recombination times τ_Γ and τ_X are longer than the intervalley scattering time $\tau_{\Gamma\to X}$ so that thermal equilibrium between Γ and X can be reached. As the ratio $\tau_{\Gamma\to X}/\tau_{\text{rad}}$ increases a small fraction of electrons will recombine radiatively without reaching thermal equilibrium. This fraction is represented by the second term in the rhs of Eq. (1). It gives rise to the luminescence observed above 45 kbar in heavily doped samples.

Casey and Stern[18] have performed a calculation of τ_{rad} for several hole concentrations. From the data in Table IV and Fig. 9 of Ref. 18 we infer the expression for τ_{rad}.

$$\frac{1}{\tau_{\text{rad}}} = (26.7 - 0.56\ln p)p \times 10^{-10}\ \text{sec}^{-1} \tag{3}$$

with p the hole concentration in cm^{-3}. Recently Nelson and Sobers[19] have determined τ_{rad} from photoluminescence decay time measurements and found a very good agreement with Casey and Stern's estimates in the range of hole concentrations we are dealing with.

In summary, the meaning of Eq. (1) is the following: The luminescence intensity depends on the electron population of the Γ_1^c states. When the material becomes indirect after the "Γ_1^c, X_1^c" crossing, part of the electrons at Γ_1^c relax to the lower X_1^c minima, while the others recombine radiatively because of the presence of the free holes. We fitted the pressure dependence of the luminescence intensity with Eq. (1) and used for τ_{rad} the values given by Eq. (3). The resulting fits are represented by the solid lines in Fig. 2. From the fitting procedure the parameters A, α_X, P_0, and $\tau_{\Gamma\to X}$ at $T=120$ K are determined. They are listed in Table I, together with those corresponding to undoped GaAs. For comparison the values reported by Yu and Welber[5] at $T=380$ K are also tabulated. The results for α_X at $T=120$ K were obtained using our own measurements for α_Γ at the same temperature (see Table II and subsection III B).

From the data in Table I we find the average value of α_X at 120 K; $\alpha_X = -(1.8\pm 0.6)\times 10^{-3}$ eV/kbar, which agrees within the experimental error with the value of $-(2.7\pm 0.5)\times 10^{-3}$ eV/kbar determined by Yu and Welber at $T=380$ K.[5]

Our results at $T=120$ K for P_0 (the pressure at which Γ_1^c and X_1^c become degenerate) are higher than those of Ref. 5. This is consistent with the fact that we measure at low temperatures a smaller α_Γ than that obtained at room temperature (see subsection III B). From the data of Table I a mean value of 3.9×10^{-12} sec for $\tau_{\Gamma\to X}$ is obtained. $\tau_{\Gamma\to X}$ represents the time needed for the photoexcited electrons to scatter from the conduction band near the Γ point to the conduction band near the X points. This time can be compared with the lifetime of the carriers at the X_1^c minima estimated from Eq. (2) with the value of $A=7$ resulting from the fits. With $m_\Gamma = 0.067$,[20] $m_{\perp X} = 0.27$,[16] $m_{\parallel X} = 1.3$,[21] and $\tau_\Gamma \simeq \tau_{rad}$ we estimate $\tau_X \simeq 15\tau_{rad}$. Using the expression given by Eq. (3) for τ_{rad}, one can see that $\tau_{\Gamma\to X}$ is shorter than τ_X for all the hole concentrations, in agreement with the assumption implicit in Eq. (1).

As already mentioned, Fig. 3 displays the ratio of the luminescence intensity for pressures above 60 kbar to that at very low pressures as a function of hole concentration. From Eq. (1) one sees that for $P<P_0$ the intensity of the luminescence $I\simeq I_0$ and for $P>P_0$ $I\simeq I_0\,\tau_{\Gamma\to X}/\tau_{rad}$. Hence

$$I(P>60\ \text{kbar})/I_0 \simeq \tau_{\Gamma\to X}/\tau_{rad}\,. \qquad (4)$$

The calculated points of Fig. 3 are obtained using 3.9×10^{-12} sec for $\tau_{\Gamma\to X}$ and τ_{rad} from Eq. (3). The hole-concentration dependence of the ratio of intensities is well described by the hole-concentration dependence of the radiative recombination time τ_{rad}. This description confirms the model of the enhancement of the emission due to the pressure of the free holes.

In the case of the samples with 1.6×10^{18} holes cm^{-3} a new emission line is observed in the range of pressures between 40 and 55 kbars as shown in Fig. 4. This line (labeled $X_1^c\to\Gamma_8^v$) shifts to lower energies with increasing pressure. This behavior suggests that the observed emission arises from indirect transitions between the X_1^c conduction-band minima and the valence-band states Γ_8^v. The pressure dependence of this line is displayed in Fig. 5, where the solid line represents a linear-least-squares fit to the experimental points with the expression

$$(X_1^c-\Gamma_8^v)_P = (X_1^c-\Gamma_8^v)_0 + \alpha_X P\,. \qquad (5)$$

The parameters resulting from the fit are:

$$(X_1^c-\Gamma_8^v)_0 = (1.946\pm 0.020)\ \text{eV}\,,$$
$$\alpha_X = -(2.8\pm 0.8)\times 10^{-3}\ \text{eV/kbar}\,.$$

The value of (1.946 ± 0.020) eV at 120 K for the energy difference $X_1^c-\Gamma_8^v$ agrees with that of 1.961 eV proposed by Aspnes[22] at the same temperature

TABLE I. Parameters obtained with Eq. (1) by fitting the pressure dependence of the E_0 photoemission intensity at 120 K for various hole concentrations. Also listed are our own determinations for undoped GaAs at the same temperature and those reported by Yu and Welber at 380 K.

p (cm^{-3})	A	P_0 (kbar)	$\alpha_X/(10^{-3}$ eV/kbar)	$\tau_{\Gamma\to X}/(10^{-12}$ sec)
9×10^{19}	7	36	−2.3	3.5
4×10^{19}	7	44	−1	6
1.6×10^{19}	7	46	−2.4	3.7
3×10^{18}	7	37	−1.4	4
1.6×10^{18}	7	43.5	−1.2	2.6
undoped	7 [a]	38 [a]	−2.7 [a]	
($n\simeq 10^{16}$)	7 [b]	33 [b]	−2.7 [b]	

[a] Our results for undoped GaAs at 120 K.
[b] Reference 5, 380 K.

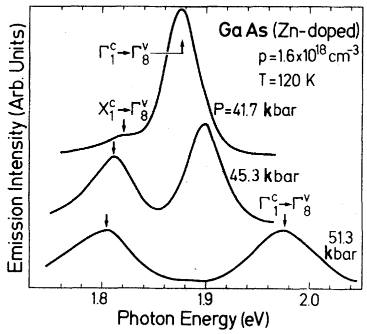

FIG. 4. Typical luminescence spectra at 120 K from the samples with 1.6×10^{18} holes cm^{-3} for pressures between 40 and 55 kbar. They show two lines. One corresponds to emission from the direct gap E_0 (Γ_1^c-Γ_8^v); it shifts to higher energies with pressure. The other line shifts to lower energies with increasing pressure and is related to indirect transitions across the X_1^c-Γ_8^v indirect gap.

and the value (1.935 ± 0.010) eV reported at 100 K.[13] The coefficient $\alpha_X=-(2.83\pm0.8)\times10^{-3}$ eV/kbar agrees within the experimental error with the values obtained by fitting the pressure dependence of the intensity of E_0: $-(1.8\pm0.6)\times10^{-3}$ eV/kbar (this work) and $-(2.7\pm0.5)\times10^{-3}$ eV/kbar (Yu and Welber, Ref. 5). Thus our interpretation of the nature of the new line is confirmed by the fit parameters of Eq. (5).

To our knowledge this is the first direct measurement of the pressure coefficient of the indirect gap X_1^c-Γ_8^v in GaAs and also the first observation of indirect-gap luminescence when the material becomes indirect. Noack and Holzapfel[23] have reported luminescence in GaSb associated with the L_1^c conduction-band minima for pressures near that at which L_1^c and Γ_1^c become degenerate.

Before closing this section we want to make a remark concerning the pressure dependence of the L_1^c conduction-band minima in GaAs. At normal pressure it is now generally accepted that the L_1^c minima lie lower in energy than the X_1^c minima.[22] Aspnes has proposed a pressure coefficient of 5.5×10^{-3} eV/kbar for the L_1^c-Γ_8^v gap. Assuming this value and taking a value of 9×10^{-3} eV/kbar for the pressure coefficient α_Γ of the direct gap E_0 (see subsection III B), we expect a "Γ_1^c, L_1^c" crossing at around 90 kbar. If this crossing takes place another decrease of the luminescence intensity should occur. However, this is not observed in our experiments. With one sample ($p=1.6\times10^{19}$ holes cm^{-3}) we performed measurements up to 140 kbar in order to elucidate the temperature dependence of the pressure coefficient: no evidence of the "Γ_1^c, L_1^c" crossing was observed. Hence the value proposed by Aspnes[22] for the pressure coefficient of the L_1^c-Γ_8^v gap may have to be revised (upwards) unless the $\Gamma\rightarrow L$ scattering time turns out to be very low.

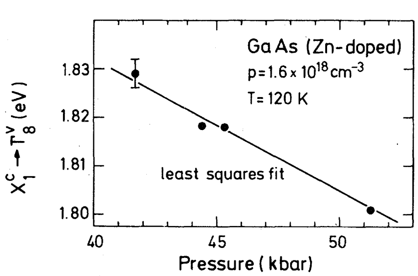

FIG. 5. Pressure dependence of the $X_1^c\rightarrow\Gamma_8^v$ emission line described in Fig. 4. The solid line represents a least squares fit with Eq. (5).

B. Temperature dependence of the pressure coefficients (p-GaAs)

Welber *et al.*[6] have determined the pressure dependence of the direct gap E_0 of undoped GaAs by measuring the absorption edge at room temperature up to pressures near the phase transitions (~180 kbar). They found that the energy gap E_0 shows a sublinear dependence on pressure due, in part, to nonlinearities in the bulk modulus. Resonant Raman scattering measurements at $T\simeq380$ K have confirmed the nonlinear dependence of E_0.[5] The same behavior was reported for Ge (Ref. 7) and recently for InP.[8] If a quadratic fit of the sublinear data is performed, a linear coefficient is obtained which is somewhat higher than that obtained with conventional large-volume, low-pressure cells (typical pressures up to ~10 kbar, see Table I in Ref. 6).

Owing to the enhancement of the luminescence in the p-type samples, the pressure dependence of E_0 can be studied with the luminescence techniques up to the phase transition. These measurements can be performed at room and at low temperatures. Transmission measurements at low temperatures are difficult to perform with the diamond cell because of focusing difficulties inside of a Dewar. We actually have performed most of our luminescence work at low temperatures ($T\simeq120$ K) because the emission lines are narrower and easier to observe, especially after the "Γ_1^c, X_1^c" crossing.

We found at $T\simeq120$ K a *linear* dependence of the E_0 gap on pressure in all the samples measured. No evidence of a sublinear pressure dependence was present. In Table II we summarize the linear pressure coefficients α_Γ we obtained at $T\simeq120$ K from least squares fits of the observed

TABLE II. Linear pressure coefficients α_Γ of the direct-energy gap E_0 observed for heavily doped and pure GaAs at $T=120$ K.

p (cm^{-3})	$\alpha_\Gamma/(10^{-3}$ eV/kbar)
9×10^{19}	10.1
4×10^{19}	8.2
1.6×10^{19}	8.5
3×10^{18}	9.1
1.6×10^{18}	9.0
pure	9.5

linear pressure dependences of E_0. These coefficients are also systematically lower than those found from transmission measurements at room temperature.[6] In order to confirm these differences on one and the same sample we performed measurements as a function of pressure at room and low temperatures with samples which had 1.6×10^{19} holes cm^{-3}. We chose these samples as they represent a compromise between the intensity of the luminescence after the "Γ_1^c, X_1^c" crossing and the width of the line.

In Fig. 6 we display the pressure dependence at room temperature and at 120 K of the luminescence across the direct gap E_0 for one of these samples. We have plotted the energy position of E_M (see Paper I): its pressure dependence is the same, within our experimental error, as that of E_0. In this figure one can clearly observe the linear behavior at low temperature and the sublinear dependence at room temperature. The experimental data have been fitted with

$$E_M(P) = E_M + \alpha_\Gamma P + \beta_\Gamma P^2 , \tag{6}$$

where α_Γ and β_Γ are the linear and quadratic pressure coefficients of the direct gap, respectively, and P the pressure in kbar. The resulting coefficients are tabulated in Table III and compared with those reported by Welber *et al.*[6] The agreement at room temperature is good and confirms a temperature effect in the pressure coefficients of GaAs. Work performed with uniaxial stress[24] also suggests that the *hydrostatic* coefficient of the E_0 gap indeed increases with increasing temperature.

The difference of the luminescence peaks E_M at $T=120$ K and 300 K as a function of pressure is shown in Fig. 7. A parabolic dependence on pressure is obtained for this difference. It is tempting to attribute the anomalously and unexpectedly large temperature dependence of the variation of E_0 with pressure just reported to a dependence on pressure of the effect of temperature on the band structure. This effect is known to consist of two terms: a Debye-Waller effect and a self-energy of the electrons due to emission and reabsorption of phonons.[25] The latter contribution contains cancellations of terms due to energy denominators of opposite sign. These energy denominators can be changed drastically by the application of pressure and thus the cancellation mentioned can be offset. Therefore changes in the temperature coefficients of gaps are possible, in principle, as pressure is applied. It would be of interest to test this conjecture by means of a calculation of the temperature dependence of the band structure of GaAs under several applied pressures. It should also be mentioned that theoretical calculations (performed for $T=0$) (Ref. 6) do not easily reproduce the sublinearity of the gap on the lattice constant obtained at room temperature. They agree better with the supralinearity which follows from our low-temperature measurements.

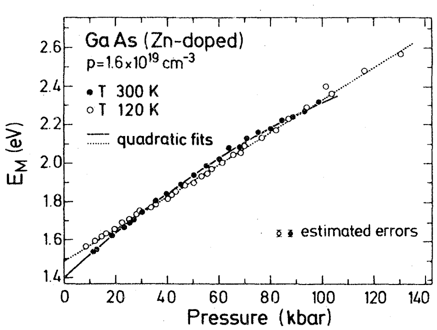

FIG. 6. Pressure dependence of the emission-peak maximum E_M at low and room temperature for p-GaAs with 1.6×10^{19} holes cm^{-3}. At 120 K the direct gap depends linearly on pressure, while at 300 K a sublinear behavior is observed. The quadratic fits were performed with Eq. (6) and the obtained pressure coefficients are summarized in Table III.

C. Pressure dependence of the intensity (n-GaAs)

Figure 8 shows typical emission lines at $T=120$ K in n-GaAs with 7×10^{18} electrons cm^{-3} for various pressures. With increasing pressure not only the intensity but also the width of the luminescence

TABLE III. Pressure coefficients at room and low temperatures of the direct-energy gap of GaAs obtained by fitting the data of Fig. 6 with Eq. (6). Also, values reported by Welber *et al.*

Temperature (K)	$\alpha_\Gamma/(10^{-3}$ eV/kbar)	$\beta_\Gamma/(10^{-5}$ eV/kbar^2)
120	8.5 ± 0.03 [a]	0 [a]
300	12.3 ± 0.02 [a]	-3.1 ± 0.1 [a]
	12.6 ± 0.1 [b]	-3.77 ± 0.1 [b]

[a] This work.
[b] Welber *et al.*, Ref. 6.

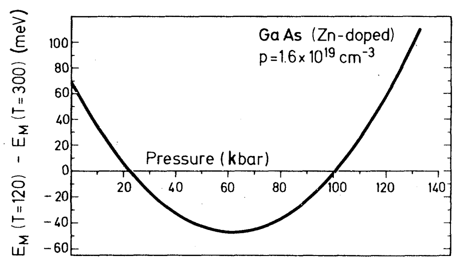

FIG. 7. Energy difference at $T=120$ and 300 K of the emission lines across the direct gap as a function of pressure.

lines decreases. The pressure dependence of the intensity for this sample is plotted in Fig. 9. As in the case of pure GaAs, the emission at the E_0 gap disappears for pressures above the critical one, P_0.

The free electrons occupy the conduction-band states Γ_1^c up to the Fermi level in heavily doped n-type GaAs. At very low pressures for samples with 7×10^{18} electrons cm^{-3} the Fermi level lies at around 200 meV above the bottom of the conduction band at the Γ point.[26] With increasing pressure the free-electron concentration at the Γ point decreases due to the carrier transfer to the X_1^c minima. Neglecting lifetime effects one can assume that the intensity of the emission across the E_0 gap is proportionl to the concentration of the free carriers (n_Γ) present at Γ:

$$I=I_0 n_\Gamma\,, \qquad (7)$$

where I_0 is a constant. We do not include in n_Γ the photoexcited *electrons*. Their concentration, at the laser powers used, is two or three orders of magnitude smaller than the free-electron concentration present from the donors.

The solid line of Fig. 9 is a theoretical fit to the pressure dependence of the intensity with Eq. (7). The free-electron concentration at the Γ_1^c

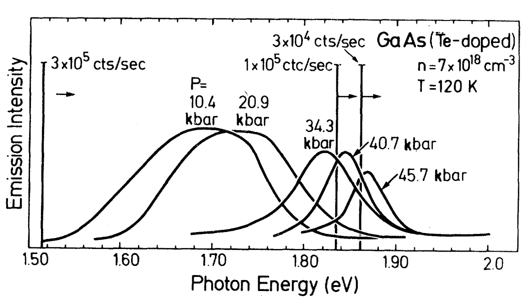

FIG. 8. Typical emission lines at $T=120$ K across the direct gap E_0 in n-type GaAs for various pressures. With increasing pressure the intensity of the lines decreases and they become narrower. Both effects can be related to the transfer of the free electrons from the Γ_1^c states to the X_1^c minima.

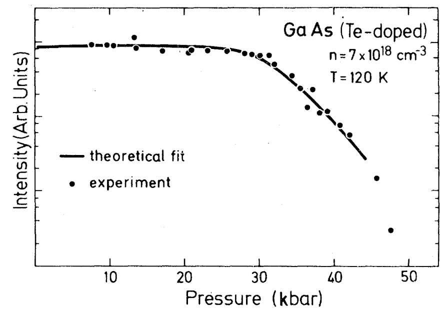

FIG. 9. Pressure dependence of the emission intensity across the direct gap E_0 in n-type GaAs. The emission cannot be observed after the gap becomes indirect. The solid line is a theoretical fit with Eq. (7).

conduction-band states as a function of pressure has been calculated taking into account the pressure and carrier-concentration dependence of the effective conduction mass m_Γ. The pressure dependence of the longitudinal and transversal effective masses of the X_1^c minima has been neglected. The details of the calculation are given in the Appendix, where the parameters used are also given.

The best fit to the experimental data of Fig. 9 was obtained with a pressure coefficient for the X_1^c-Γ_8^v energy gap of $\alpha_X=-(1.9\pm0.2)\times10^{-3}$ eV/kbar. It agrees with the values reported in subsection IIIA for the p-type samples.

When pressure is applied, the position of the Fermi level with respect to the bottom of the conduction band at the Γ point decreases due to carrier transfer to the X_1^c minima. The change of the emission line shape with pressure can be explained by this decrease of the Fermi level. In the case of degenerate n-type semiconductors the luminescence is shifted to higher energies in comparison with a pure material due to the Burstein-Moss effect.[11] The photon energy of the emission is determined by the optical gap:

$$E_{\rm op}=E_0+E_F\,, \qquad (8)$$

where E_0 is the actual band gap of the material and E_F represents the Fermi level degenerate with the Γ_1^c conduction-band states. Recently Vilkostkii *et al.*[11] while analyzing the emission in heavily doped n-InAs have realized that $E_{\rm op}$ corresponds to the point on the high-energy side of the emission line where the intensity is 0.8 times the intensity of the maximum.

Using this procedure we have determined $E_{\rm op}$ and E_0 in the way described in Paper I. Their difference represents E_F. Figure 10 displays the so obtained E_F as a function of pressure and the results of theoretical calculation performed as discussed in the Appendix. Theory and experiment are in close agreement thus confirming the assign-

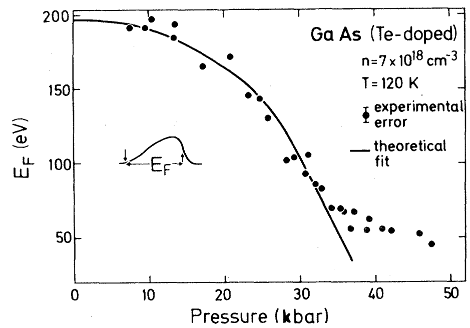

FIG. 10. Pressure dependence of the Fermi level (E_F) measured from the bottom of the conduction band Γ_1^c in n-GaAs with 7×10^{18} electron cm^{-3}. E_F was determined from the difference between the optical gap and the direct gap with Eq. (8). The theoretical fit was performed in a way described in the Appendix.

ment made for E_{op}' and E_F. For pressures above 40 kbar the experimental points are to be interpreted as the natural line width of the emission in nondegenerate n-type GaAs.[27]

D. Pressure coefficients (n-GaAs)

Figure 11 displays the pressure dependence of the E_0 luminescence at $T=120$ K in n-GaAs with 7×10^{18} electrons cm^{-3}. The emission lines shift to higher energies with a pressure coefficient (7.2×10^{-3} eV/kbar) much smaller than that for the p samples at the same temperature (see Table II). For pressures above 30 kbar the shift occurs at even a lower rate.

We can explain the observed behavior by considering that in heavily doped n-GaAs

$$\frac{dE_M}{dP}\simeq\frac{d}{dP}(E_0+E_F), \tag{9}$$

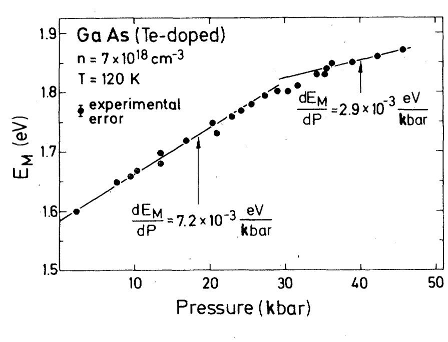

FIG. 11. Pressure dependence of the emission at $T=120$ K around the direct gap E_0 in heavily doped n-GaAs. With increasing pressure the emission shifts to higher energies with a smaller pressure coefficient than that of the p samples at the same temperature. This behavior is explained considering the pressure dependence of the Fermi level.

where E_M represents the maximum of the luminescence line (plotted in Fig. 11) and E_F corresponds to the Fermi energy measured from the bottom of the conduction band Γ_1^c. Taking for E_F,

$$E_F=\frac{\hbar^2}{2m_\Gamma}(3\pi^2 n_\Gamma)^{2/3}, \tag{10}$$

with m_Γ and n_Γ the conduction effective mass and the free-electron concentration at the Γ point, respectively, it is easy to see that for pressures below 25 kbar

$$\frac{dE_F}{dP}\simeq-\frac{E_F}{E_0}\frac{dE_0}{dP} \tag{11}$$

because $dn_\Gamma/dP\simeq0$. We have used the approximation[28,29]:

$$\frac{dm_\Gamma}{m_\Gamma}\simeq\frac{dE_0}{E_0}.$$

With $dE_0/dP=9\times10^{-3}$ eV/kbar, $E_F/E_0\simeq0.2/1.5$, we get with Eq. (9) for $P<25$ kbar: $dE_M/dP\simeq7.8\times10^{-3}$ eV/kbar, close to the observed value.

For pressures higher than 25 kbar the derivative of the Fermi energy with respect to pressure is dominated by the term dn_Γ/dP due to the relaxation of the free electrons to the X_1^c conduction minima where the density of states is very high. From our calculations (Appendix) we estimate for $P\gtrsim25$ kbar that $dE_F/dP\simeq-7\times10^{-3}$ eV/kbar; hence $dE_M/dP\simeq2\times10^{-3}$ eV/kbar, which is again close to the experiment.

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APPENDIX: CALCULATION OF n_Γ AND E_F AS A FUNCTION OF PRESSURE IN n-GaAs

The conduction band in GaAs near the Γ point can be described by[30]:

$$E_\Gamma(k)=\tfrac12E_0+\tfrac12E_0(1+4k^2\gamma^2/E_0^2)^{1/2}$$
$$\simeq E_0+k^2\gamma^2/E_0-k^4\gamma^4/E_0^3, \tag{A1}$$

where k is the magnitude of the wave vector, γ represents the matrix element of the linear momentum operator, and E_0 is the direct-energy gap. The origin of energies has been taken at the top of the valence band (Γ_8^v). We use the parabolic approximation for the conduction band near the X points:

$$E_X(k)=X_0+\frac{\hbar^2}{2}\left(\frac{k_x^2+k_y^2}{m_\perp}+\frac{k_z^2}{m_\parallel}\right), \tag{A2}$$

where we have written for simplicity X_0 for the indirect-energy gap X_1^c-Γ_8^v. The other symbols have their usual meaning. The parabolic approximation for E_X is justified because of the large gaps at X.

The free-electron concentration obeys the charge balance equation

$$7\times 10^{18}\ \text{cm}^{-3} = n_\Gamma + n_X\,, \tag{A3}$$

where n_Γ and n_X are the electron concentrations at the Γ_1^c and X_1^c conduction-band states. With the origin of energies we have chosen, we can express[30]:

$$n_\Gamma = \frac{\sqrt{2}}{\pi^2}\,\frac{m_{\Gamma,0}^{3/2}}{\hbar^3}\,(kT)^{3/2}\left(F_{1/2}(\mu) + \frac{10}{4}\frac{kT}{E_0}F_{3/2}(\mu)\right)$$

$$\simeq \frac{\sqrt{2}}{\pi^2}\,\frac{m_\Gamma^{3/2}}{\hbar^3}\,(kT)^{3/2}F_{1/2}(\mu) \tag{A4}$$

and

$$n_X = \frac{6\sqrt{2}}{\pi^2}\,\frac{(m_\perp^2 m_\parallel)^{1/2}}{\hbar^3}\,(kT)^{3/2}F_{1/2}(\mu')\,, \tag{A5}$$

where $m_{\Gamma,0}$ is the mass of the bottom of the band and $F_{1/2}$ and $F_{3/2}$ are Fermi integrals.[31] The approximation on the rhs of Eq. (A4), while not necessary, simplifies the calculations. It can be shown to be satisfactory in our case. The arguments of the Fermi integrals are:

$$\mu = \frac{E_F - E_0}{kT} = \frac{E_F - [E_0(0) + \alpha_\Gamma P]}{kT}\,, \tag{A6}$$

$$\mu' = \frac{E_F - X_0}{kT} = \frac{E_F - [X_0(0) + \alpha_X P]}{kT}\,. \tag{A7}$$

The meaning of the different terms are discussed in the previous sections.

Replacing Eqs. (A4) and (A5) in Eq. (A3) and using the tabulated values for $F_{1/2}$ (Ref. 31), for each μ there exists only one μ' that allows Eq. (A3) to be satisfied. With each pair (μ, μ') so obtained, the pressure can be determined from Eqs. (A6) and (A7):

$$P = \frac{[X_0(0) - E_0(0)] - kT(\mu - \mu')}{\alpha_\Gamma - \alpha_X}\,. \tag{A8}$$

With the relationship between P and μ the pressure dependence of both n_Γ and the position of E_F relative to the Γ_1^c conduction-band minimum is easily estimated from Eqs. (A4) and (A6), respectively. The calculation should be performed iteratively because of the pressure dependence of m_Γ. The effective conduction mass at the Γ point depends on pressure, through its dependence on E_0 and n_Γ.[28] This dependence can be represented by

$$\frac{1}{m_\Gamma} = \frac{2(E_F - E_0)}{\hbar^2 k_F^2} = \frac{1}{\hbar^2}\left(\frac{2\gamma^2}{E_0} - \frac{2k_F^2\gamma^4}{E_0^3}\right), \tag{A9}$$

where Eq. (A1) was used to relate E_F with k_F. This expression for m_Γ is a good approximation provided $E_F \gg kT$. Equation (A9) must also be calculated iteratively.

We neglected the pressure dependence of $m_\parallel$ or $m_\perp$ since the density of states at the X_1^c minima is two orders of magnitude larger than at the Γ_1^c minimum and thus the corresponding Fermi energy is very small. Also, because of the large gaps at X, the pressure dependence of $m_\parallel$ and $m_\perp$ should be negligible.

The following parameters were used: $m_\parallel = 1.37$,[21] $m_\perp = 0.27$,[16] $m_\Gamma = 0.075$ (Ref. 32) (at $P = 0$), $T = 120$ K, $\alpha_\Gamma = 9\times 10^{-3}$ eV/kbar (Table II), $\gamma = 0.6188$ (Ref. 29) (in atomic units), $E_0(0) = 1.46$ eV (taking into account the gap shrinkage, Paper I), $X_0(0) = 1.961$ eV.[22]

[1] J. D. Barnett, S. Block, and G. J. Piermarini, Rev. Sci. Instrum. 44, 1 (1973).
[2] G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, J. Appl. Phys. 46, 2774 (1975).
[3] R. Trommer, E. Anastassakis, and M. Cardona, in *Light Scattering in Solids*, edited by M. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flammarion, Paris, 1976), p. 396.
[4] R. Trommer, H. Müller, M. Cardona, and P. Vogl, Phys. Rev. B 21, 4869 (1980), and references therein.
[5] P. Yu and B. Welber, Solid State Commun. 25, 209 (1978).
[6] B. Welber, M. Cardona, C. Kim, and S. Rodriguez, Phys. Rev. B 12, 5729 (1975).
[7] B. Welber, M. Cardona, Y. Tsay, and B. Bendow, Phys. Rev. B 15, 875 (1977).
[8] H. Müller, R. Trommer, M. Cardona, and P. Vogl, Phys. Rev. B 21, 4879 (1980).
[9] S. C. Yu, I. L. Spain, and E. F. Skelton, Solid State Commun. 25, 49 (1978).
[10] See, for instance, W. Paul, in *Optical Properties of Solids*, edited by J. Tauc (Academic, New York, 1966), p. 257.
[11] V. A. Vilkotskii, D. S. Domanevskii, R. D. Kakanakov, V. V. Krasovskii, and V. D. Tkachev, Phys. Status Solidi B 91, 71 (1979).
[12] D. Olego and M. Cardona, Paper I, Phys. Rev. B 22, 886 (1980).
[13] D. Olego and M. Cardona, Solid State Commun. 32, 1027 (1979).
[14] R. S. Hawke, K. Syassen, and W. Holzapfel, Rev. Sci. Instrum. 45, 1598 (1974).
[15] R. Noak and W. Holzapfel, in *High-Pressure Science and Technology*, edited by K. D. Timmerhaus and M. S. Barber (Plenum, New York, 1979), Vol. 1, p. 748.
[16] A. Pinczuk, S. Louie, B. Welber, J. Tsang, and

J. Bradley, in *Physics of Semiconductors 1978*, edited by B. Wilson (Institute of Physics, London, 1978), p. 1191.

[17]H. B. Bebb and E. W. Williams, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1972), Vol. 8, p. 181.

[18]H. C. Casey and F. Stern, J. Appl. Phys. 47, 631 (1976).

[19]R. Nelson and R. Sobers, J. Appl. Phys. 49, 6103 (1978).

[20]R. Lawaetz, Phys. Rev. B 4, 3460 (1971).

[21]H. Neumann, I. Topol, K. Schulze, and E. Hess, Phys. Status Solidi B 56, K55 (1973); and E. S. Meieran, J. Appl. Phys. 36, 2544 (1965).

[22]D. Aspnes, Phys. Rev. B 14, 5331 (1976).

[23]R. Noack and W. Holzapfel, Solid State Commun. 28, 177 (1978).

[24]M. Chandrasekhar and F. H. Pollak, Phys. Rev. B 15, 2127 (1977).

[25]P. B. Allen, Phys. Rev. B 18, 5217 (1978).

[26]C. Hwang, J. Appl. Phys. 41, 2668 (1970). Our estimate (Appendix) reproduces this value for this concentration.

[27]H. Casey and R. Kaiser, J. Electrochem. Soc. 114, 149 (1967).

[28]W. DeMeis, Harvard University Technical Report No. HP-15, 1965 (unpublished).

[29]See, for example, M. Cardona, in *Atomic Structure and Properties of Solids*, edited by E. Burstein (Academic, New York, 1972), p. 514.

[30]M. Cardona, Phys. Rev. 121, 752 (1961).

[31]See, for example, V. I. Fistul, in *Heavily Doped Semiconductors* (Plenum, New York, 1969).

[32]A. Raymond, J. Robert, and C. Bernard, J. Phys. C 12, 2289 (1979).