Fundamental Energy Gaps of AlAs and AlP from Photoluminescence Excitation Spectra

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The measurement of photoluminescence excitation spectra is shown to be a powerful method to obtain information on the lower fundamental energy gaps in materials where suitable samples for transmission measurements cannot readily be prepared. In this work this method is used to derive accurate values for the lowest indirect *and* direct excitonic band gaps of the "exotic" compounds AlAs and AlP. The indirect $\Gamma_{15v} - X_{1c}$ excitonic edge was found as 2.229 ± 0.001 eV at 4 K, 2.223 ± 0.001 eV at 77 K and 2.153 ± 0.002 eV at 300 K. The X-point phonon energies observed for AlAs are $E_{LO(X)}$, 50.0 ± 1.0 meV; $E_{TO(X)}$, 41.5 ± 1.0 meV; $E_{LA(X)}$, 27.5 ± 1.5 meV; and $E_{TA(X)}$, 13.5 ± 1.0 meV, giving an X-point deviation from the Brout sum rule $\Delta_K(X) = 0.09$ for AlAs. The lowest direct $\Gamma_{15c} - \Gamma_{1c}$ excitonic edge in AlAs was found to vary from 3.13 ± 0.01 eV at 4 K to 3.03 ± 0.01 eV at 300 K. For AlP, the corresponding values found experimentally for excitonic band gaps are 2.505 ± 0.01 eV at 4 K for the indirect $\Gamma_{15v} - X_{1c}$ transition and 3.63 ± 0.02 eV at 4 K for the lowest direct gap (probably $\Gamma_{15v} - \Gamma_{1c}$).

I. INTRODUCTION

Investigations of the lowest fundamental energy gaps of semiconductors are usually performed by straightforward transmission measurements. This method is the most reliable way of determining the correct energy dependence of the absorption coefficient. However, in many cases, serious experimental limitations of its applicability occur. For instance, the study of details in a weak indirect absorption structure requires access to large optically perfect single crystals (of thickness preferably several mm) to get satisfactory resolution in transmission data. The other extreme occurs in the investigation of structures at high absorption coefficients ($\alpha \approx 10^4$ cm^{-1}) characteristic of, e.g., direct band gaps. Here, a transmission measurement with reasonable resolution ($\alpha d \approx 1$) requires an optically perfect crystal with a thickness of not more than a few microns. If thin as-grown crystal platelets of the proper thickness and purity cannot be obtained, the preparation of strain-free thin specimens without appreciable damage from mechanical polishing is a very delicate problem. For conventional materials, such as Ge, Si, GaAs, and GaP, careful investigations of the lowest indirect and direct absorption edges have been performed by transmission measurements owing to access to reasonably good samples.[1-5] For other more "exotic" III-V compounds, such as AlAs and AlP, the situation can be quite different due to inadequate techniques of crystal growth.

Apparently other methods have to be used to obtain reliable information on the detailed structure at the onset of interband transitions in materials where suitable samples for optical transmission measurements cannot yet be prepared. A method to estimate the lowest-direct-gap energy for an indirect-gap material has recently been proposed by Dumke *et al.*[6] Their method makes use of accurate experimental data about the absorption coefficient from transmission measurements in an energy region *well below* the direct edge to be explored. A more attractive method of resolving direct-gap structures should involve experiments which reveal details of the edge for energies both *above* and *below* the direct gap, without the need for optical-quality thin crystals. Results for GaP by Dean at low temperature indicated[7] that measurements for photoluminescence excitation spectra (PLE) in the region of fundamental absorption can provide such a simple method. In this work, we apply the PLE method to the "exotic" indirect-gap compounds AlAs and AlP and we demonstrate its usefulness in revealing details in lowest indirect and direct absorption edges (for crystals not suitable for optical transmission experiments in the edge regions). Since good radiative efficiency was maintained up to room temperature, we could for AlAs determine (for the first time) the indirect "exciton" band gap to within 0.002 eV between 0 and 300 K and the direct exciton gap to within 0.01 eV in the same temperature region. These results represent roughly an order-of-magnitude improvement on the corresponding data at present available in the literature.

To refine the analysis of the lowest direct-gap structures observed for AlAs and AlP, a comparative study was made with results from PLE measurements on GaP crystals of a similar purity. This gives valuable information on the broadening effects in the direct-gap excitonic region at different temperatures in an impure crystal, since the direct exciton peak in pure GaP is accurately known at different temperatures from transmission data.[5]

II. EXPERIMENTAL

A. Crystals

The AlAs crystals used in this work were grown by a synthesis technique by the reaction of AsH$_3$ (diluted with H$_2$) with liquid Al in an open system at 1100 °C, as described by Kischio.[8] Electrical-probe measurements indicated n-type conductivity with varying degrees of compensation. From these measurements, from the growth conditions, and the appearance of the optical spectra, the total impurity concentration in these crystals was estimated to be in the high-10^{18}-cm^{-3} range for the crystals referred to in this work. The AlP crystals were grown by a similar synthesis method by the reaction of PH$_3$ with liquid Al in an open system at 1500 °C, as described by Grimmeiss $et\,al.$[9] The crystals used were about $3\times3\times0.1$-mm large-grained polycrystals or smaller single crystals. They were not intentionally doped, but the presence of a thin surface-oxide layer made electrical measurements unreliable. From the high-temperature growth conditions, the total defect concentration is believed to have been about 10^{19} cm^{-3}. The GaP crystals used in some comparative measurements with AlAs were rather strongly doped solution-grown single crystals, exhibiting the red Zn-O complex emission, and with a total impurity concentration in the low-10^{18}-cm^{-3} range. For comparison with AlP data, we used polycrystalline GaP crystals cut from large ingots, with impurity concentration near 10^{19} cm^{-3}. To avoid surface degradation of the AlAs and AlP crystals, these were stored and handled in vacuum, dry He gas, or liquid nitrogen.

B. Optical Measurements

Photoluminescence excitation spectra were obtained at low temperatures with crystals cooled in a liquid-He cryostat, either immersed in the liquid (at 1.5–4.2 K) or in cooled He gas. At 77 K or higher temperatures, liquid-N$_2$ or N$_2$ gas was used as coolant. The temperature was measured with thermocouples and was maintained with an accuracy of 1 K during a single measurement. The excitation was performed by a 250-W tungsten halogen lamp together with a Zeiss MM12 double-prism monochromator with quartz or glass optics, allowing a spectral resolution of 0.0008 eV between 2 and 4 eV. The luminescence was detected with a cooled EMI9659 photomultiplier placed close to the cryostat. The exciting radiation was blocked by placing suitable filters between the cryostat and the detector, the spectral range of luminescence covered being thus determined by the choice of filters and the cutoff of the photomultiplier (extended S20) cathode response. Since the crystals had a high efficiency of luminescence, a simple

dc measuring technique could be used, and excitation spectra were continuously recorded on a recorder. All spectra shown in Figs. 1–7 are normalized for constant photon flux of exciting radiation at each energy.

III. EXPERIMENTAL RESULTS

A. General Shape of Excitation Spectra

In Fig. 1 is shown the over-all shape of the photoluminescence excitation spectrum of an AlAs crystal at 4 K. The measured quantity is the integrated photomultiplier response for the emission intensity between 2.2 and 1.45 eV, but the dominating contribution to the luminescence at these temperatures comes from shallow donor-acceptor pair spectra peaking at 2.15 and 2.11 eV.[10] The general appearance of this spectrum is that expected for luminescent transitions in which selective excitation effects are not important. In the region of fundamental absorption, the spectrum is very similar to the absorption spectrum at low absorption coefficients, but at higher absorption levels strong and nonradiative surface recombination causes a gradual decrease in excitation efficiency.[7,11–13] An abrupt rise in absorption coefficient caused, for example, by the onset of a direct-gap transition in an indirect-gap material will therefore show up as a corresponding abrupt decrease in the excitation spectrum as can be seen at about 3.1 eV in Fig. 1 (see also Ref. 7). Exceptions from this typical behavior of PLE spectra in III-V compounds have been observed only when shallow isoelectronic centers (such as N or Bi in GaP) dominate the radiative transitions de-
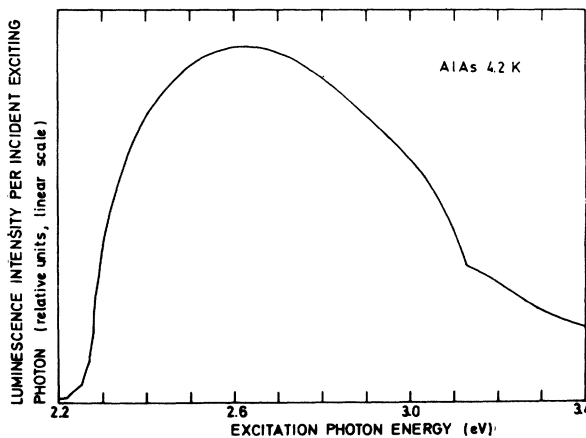

FIG. 1. Excitation spectrum of mainly shallow donor-acceptor pair luminescence from a nominally undoped AlAs single crystalline platelet at 4.2 K. The structure just above 2.2 eV is related to the indirect Γ_{15v}-X_{1c} edge, while the "inverted" lowest direct-gap threshold is clearly visible just above 3.1 eV.
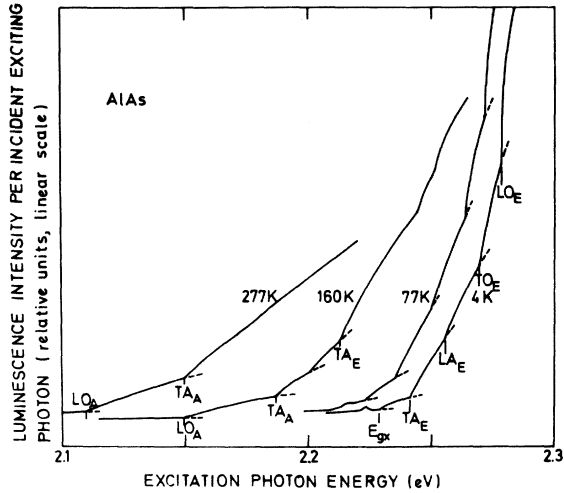
FIG. 2. Excitation spectrum of the same crystal as in Fig. 1 for four different temperatures in the vicinity of the indirect Γ_{15v}-X_{1c} edge. The high-temperature curves would tend to flatten off if extended beyond the high-energy limits drawn in the figure, due to the increased importance of surface recombination. The low-temperature curves should represent only slightly distorted absorption curves.

tected, which can cause selective excitation effects in certain energy regions.[7] From the appearance of the photoluminescence spectra, it was clear that such impurity luminescence did not play a dominant role at any temperature covered in this work.

B. Indirect Γ_{15v}-X_{1c} Edge of AlAs

Figure 2 shows in more detail that part of the AlAs excitation spectrum from Fig. 1 which falls in the immediate vicinity of the indirect Γ_{15v}-X_{1c} edge. A well-defined structure is observed in the whole temperature region studied (4–290 K) due to the photoexcitation of indirect free excitons with the emission (subscript E in Figs. 2 and 3) or absorption (subscript A) of momentum-conserving phonons typical for indirect transitions.[4,14] In spite of a rather high impurity concentration, the "smearing" of the structure expected from lifetime broadening of the excitons was not appreciable, and the sharpness of the onset of a new transition seemed, at least at low temperatures, to be limited by instrumental resolution. With increase of temperature, the high-energy phonon emission components faded out, due to a more rapid surface recombination process, and instead phonon absorption components arise below the free exciton energy. At temperatures below 200 K, it was also possible in some crystals to observe a weak no-phonon structure probably due to the presence of small concentrations of a shallow isoelectronic center at 2.223 eV (4 K) similar to N in GaP (Fig. 2).

Thus it was possible to locate at least two phonon-assisted edges in this excitation spectrum at any temperature below 290 K with an accuracy not worse than 0.002 eV for each measured point. In Fig. 3 is shown the temperature dependence of the different phonon-assisted edges obtained from measurements at a large number of temperatures up to room temperature. (Above 290 K the luminescence was too weak to allow detection of the structure in the excitation spectra with adequate resolution with the simple detection method employed). From the results presented in Fig. 3, the value of the indirect excitonic band gap is 2.229 ± 0.001 eV at 4 K, 2.223 ± 0.001 eV at 77 K, and 2.153 ± 0.002 eV at 300 K. The accuracy of the results are apparently as good as could possibly be obtained from accurate transmission measurements on purer and larger single crystals, as judged from similar results on GaP reported in Ref. 4. The phonon energies observed are $E_{TA(X)}$ = 13.5 ± 1.0 meV; $E_{LA(X)}$ = 27.5 ± 1.5 meV; $E_{TO(X)}$ = 41.5 ± 1.0 meV; and $E_{LO(X)}$ = 50.0 ± 1.0 meV. The assignment of these phonons is discussed in Sec. IV.

C. Direct Γ_{15v}-Γ_{1c} Edge of AlAs

The absorption coefficient near the onset of the lowest-direct gap absorption in an indirect-gap
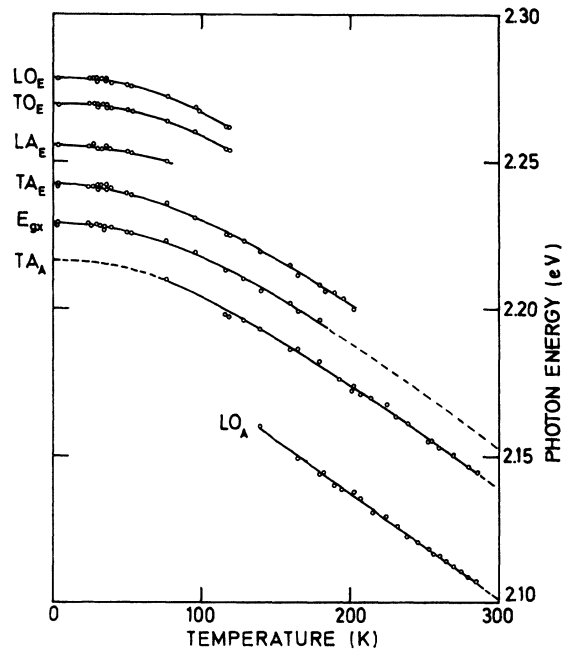

FIG. 3. Temperature dependence of the various threshold energies observed in the indirect Γ_{15v}-X_{1c} edge excitation spectrum. From the measured value of the low-temperature TA(X)- and LO(X)-phonon energies, the exciton band gap could be extrapolated up to room temperature with good accuracy.

material rises with an increasing slope towards this edge, due to the combined effects of a decrease in energy denominators for transition probabilities in the indirect phonon-assisted transitions[6] and an exponential rise due to the direct-exciton-gap absorption tail. At energies above $E^x_{g\,d} - 0.05$ eV, the exponential tail generally dominates and gives rise to a steeper *descent* in the excitation spectrum due to the surface-recombination effect mentioned above. Just above the direct gap, the fractional increase in the absorption coefficient is lower than immediately below the edge, which causes a much slower decrease of the excitation spectrum in this region. In purer materials, the direct-gap exciton peak manifests itself as a pronounced well-defined dip in the excitation spectrum,[7] but in our AlAs crystals the rather high impurity concentrations would cause a broadening of the exciton absorption edge as well as a certain decrease of the whole exciton part of the direct-gap absorption spectrum, so that only a weak broad dip was observed in PLE spectra at low temperatures (Fig. 4). To extract an accurate value for the direct exciton band gap in the pure material from a broadened structure such as the one shown for AlAs in Fig. 4, the simplest way experimentally is to correlate the position of one well-defined point at the edge with the position of the exciton energy gap for a pure crystal. This has been done, in our case, by selecting the point as the crossing point be-
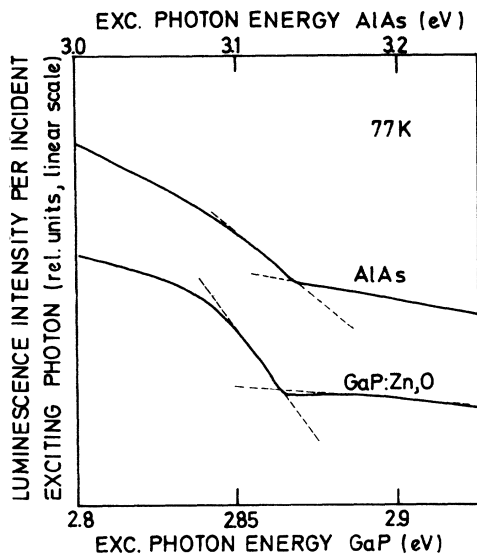

FIG. 5. The upper curve shows the experimentally determined temperature dependence of the GaP direct Γ_{15v}-Γ_{1c} gap free-exciton ground-state energy for a pure GaP crystal (Ref. 5). The experimental points shown are values for the crossing points in the lower curve of Fig. 4 in the same temperature range, showing that this procedure for the actual impurity concentration of the Zn, O-doped GaP crystal (low 10^{18} cm^{-3} range) is a accurate within a few meV. The lower curve shows the experimentally determined direct edge of AlAs from curves such as the upper curve in Fig. 4. Different notations for experimental points refer to different samples. Due to a somewhat higher impurity concentration in the AlAs samples compared with the GaP sample, this curve is believed to represent an energy a few meV above the exciton edge in pure AlAs.

FIG. 4. Details of the excitation spectra for AlAs and GaP in the vicinity of the direct Γ_{15v}-Γ_{1c} edge at 77 K, showing the crossing-point procedure adopted to evaluate the exciton energy. The broad exciton dip is not very much more pronounced at 4 K and could not therefore be used as an accurate measure of the excitonic gap position for pure material.
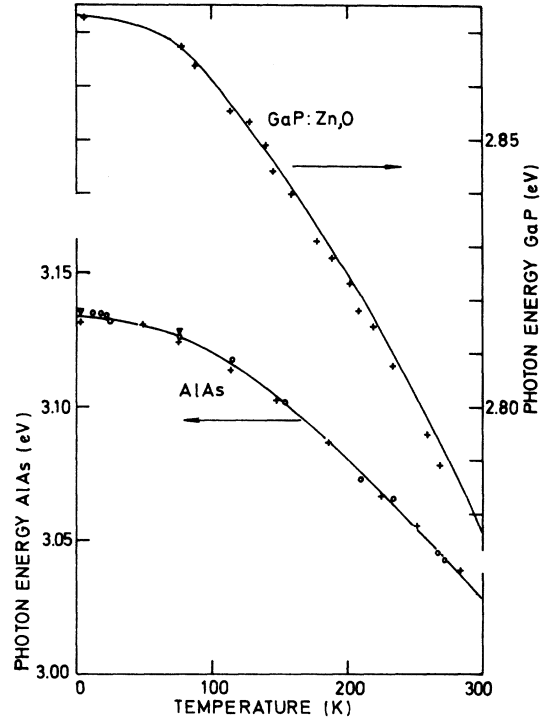
tween the approximately linear portions of the excitation spectrum just below and just above the edge, respectively (Fig. 4).

As a check, we applied the above procedure to a ZnO-doped GaP crystal with impurity concentration in the low-10^{18}-cm^{-3} range. The excitation spectrum for the well-known red emission from this type of crystal showed a broadened exciton dip below 150 K as expected for this impurity concentration, and the accuracy of the "line-crossing" procedure (Fig. 4) could be tested in the whole temperature range 4–290 K. The experimental edge energies found in this way are compared in Fig. 5 with accurate values for the direct-gap ground-state exciton peak of GaP obtained from absorption measurements on thin platelets of high

purity by Dean et al.[5] It is obvious that the pro-
cedure in this case gives the correct energy de-
pendence of the exciton edge to within a few meV,
and also gives an accurate absolute value for the
exciton energy of the pure material. Since the
AlAs results show a somewhat more depressed ex-
citon structure, the crossing point might move
somewhat towards higher energies as compared
with the exciton peak for a pure crystal. How-
ever, this analysis gives us strong confidence that
the AlAs curve in Fig. 5 represents the direct
Γ_{15v}-Γ_{1c} gap exciton energy E_{gd}^{x} to within 0.01 eV
at all temperatures below 300 K.

D. Results for AlP

The excitation spectra observed for the AlP
crystals give appreciably less information than
those for AlAs, due to the larger defect concentra-
tion in the former. Thus, even the lowest tem-
perature excitation spectra (Fig. 6) show a con-
siderable broadening of the indirect Γ_{15v}-X_{1c} edge,
with a dominating tail down to about 2.1 eV. This
tail has also been obsf rved in transmission mea-
surements, where its obscured the structure con-
nected with indirect exciton formation near 2.5
eV.[15,16] In our crystals, the tail absorption usual-
ly started with a line structure with a zero-phonon
line at 2.078 eV and phonon replica at higher ener-
gies from a 25-meV phonon. This structure indi-
cates that the observed luminescence is excited
partly via some localized complex, and strengthens
our assumption of a defect-induced origin for this
tail. Some structure connected with the indirect
Γ_{15v}-X_{1c} edge was indeed observed at low tempera-
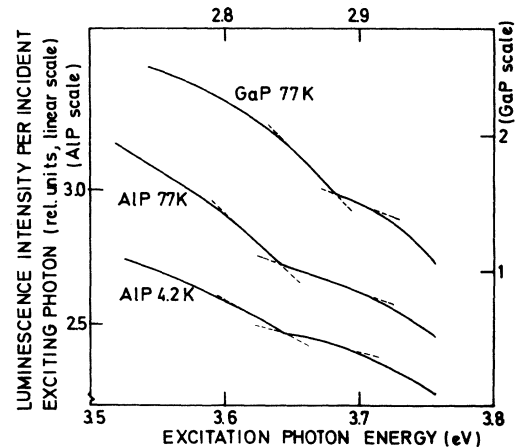
FIG. 7. Details of the lowest direct gap structure
from the corresponding portion of the excitation spectra
for AlP at 4 and 77 K and for a polycrystalline dirty GaP
bulk sample used for comparison (see text). The cross-
ing point for this GaP sample lies roughly 15-meV above
the exciton peak for a pure crystal, and a similar cor-
rection is therefore applied to the AlP data to evaluate
the direct exciton gap for pure AlP.

tures (Fig. 6) and the dominant threshold at 2.565
± 0.01 eV is believed to be due to the creation of
an indirect exciton with emission of an LO(X) pho-
non, from selection rule arguments (see below).
It was also possible to resolve a weak structure prob-
ably due to the onset of the lowest direct-gap transi-
tion, as is shown in more detail in Fig. 7. This
broadened direct-gap structure is similar to that
observed in polycrystalline samples of GaP with
impurity concentration about 10^{19} cm^{-3} (Fig. 7).
The line-crossing procedure for this GaP crystal
(Fig. 7) gives an energy 2.883 eV for the crossing
point at 77 K, which is 15-meV above the exciton
peak for pure GaP (Fig. 5). Applying a similar
correction to the AlP results in Fig. 7, we obtain
the lowest direct-gap exciton energies for AlP as
3.63 ± 0.02 eV at 4 K and 3.62 ± 0.02 eV at 77 K.
This larger uncertainty in the energy values com-
pared with the AlAs values would make a plot of
the temperature dependence of the direct AlP
edge too arbitrary, although it could be obtained
up to 200 K.

IV. DISCUSSION

The results presented in this paper finally re-
solve the scatter in the values previously reported
for the lowest band gaps of AlAs. An analysis of
the structured indirect absorption edge of AlAs
at three low temperatures (4, 77, and 143 K) re-
ported by Lorenz et al.[16] was based on the assump-
tion of the existence of a prominent anomalous
step without momentum-conserving phonon inter-
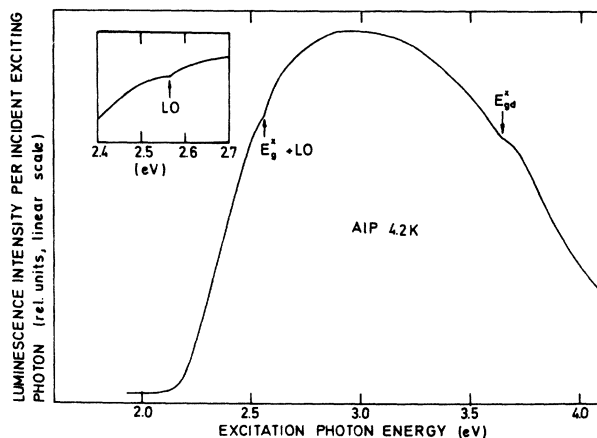action at the free exciton energy, which was be-

FIG. 6. Excitation spectrum for a nominally undoped
AlP large-grained polycrystal at 4.2 K. The rise in the
curve just above 2 eV is believed to be of an extrinsic
nature. The step observed above 2.5 eV (enlarged in the
inset) is correlated to the indirect Γ_{15v}-X_{1c} edge, the
structure above 3.6 eV to the lowest direct edge.

lieved to be caused by an unidentified shallow iso-
electronic impurity. The results presented here
reflect essentially the "normal" behavior of an in-
trinsic indirect absorption edge, practically un-
perturbed by isoelectronic states.[4] Thus, the
close agreement of our results for the structure
of the low-temperature absorption edge with those
from transmission measurements on polycrystal-
line samples[16] indicates that the analysis made in
Ref. 16 was indeed correct, and our value for the
exciton band gap agrees to within the stated uncer-
tainties (0.001 eV) with the values reported in Ref.
16. One advantage of our measuring technique is
that it provides an extension of these accurate
measurements of the exciton band gap up to room
temperature, where phonon structure could not
be resolved by Lorenz et al.[16] In view of these re-
sults, the indirect absorption structure claimed
to be observed by Hörig et al.[17] up to room tem-
perature seems to be questionable since an exci-
ton band gap about 0.1 eV too low was reported.
It is astonishing that reliable transmission mea-
surements could be performed at these low ab-
sorption levels (~ 5 cm^{-1}) on a crystal only 92-μm
thick.[17] We believe their observed structure must
have been of an extrinsic nature, since such a
large shift of the indirect exciton band gap with
moderate impurity content would indeed be anom-
alous.

The assignment of phonon energies observed in
our excitation spectra are also quite consistent
with those from transmission data of Lorenz et
al.[16] Recent band-structure calculations[18-20] all
seem to agree that the lowest conduction-band
minimum has X_1 symmetry in AlAs (as in GaP)
and the lowest conduction band at Γ point has Γ_1
symmetry. Selection rules for the optical transi-
tion between the X_1-conduction-band minimum and
the Γ_{15}-valence-band maximum via the lowest in-
termediate conduction-band minimum Γ_1 (which
should be favored due to a smaller energy denomi-
nator in the transition matrix element) are in
favor of the LO-phonon mode for AlAs (since
$M_{Al} < M_{As}$), while for GaP the same transition
mainly proceeds via the LA-phonon (since here
$M_{III} > M_V$).[21,22] The most prominent phonon-as-
sisted step in the low-temperature excitonic Γ_{15v}-
X_{1c} edge should therefore be the $[E_g^x + LO(X)]_E$
mode, and that was made the starting point for the
analysis of the spectra in the present work. Since
three additional steps occur at lower energies in
the low-temperature spectra, they could hardly
be assigned to anything else than TA(X), LA(X),
and TO(X) phonons in that energetic order, since
shallow isoelectronic centers were not prominent.

The statement made in Ref. 17 that the TO-phonon
energy would be expected to be the largest one
at the X point in AlAs is thus in conflict with our

interpretation of excitation spectra. This state-
ment goes back to the theory of Mitra,[23] which
states that a crossing over of LO- and TO-phonon
branches should occur between Γ and X in the
Brillouin zone, if the value of the Szigeti effective
charge parameter $q*$ is less than 0.7, which is the
case for AlAs as well as for GaP.[24] However, this
simple theory is inadequate for GaP, where the
LO(X)-phonon energy still exceeds the TO(X)-
mode energy,[25] and might therefore also be inade-
quate for AlAs which has a very similar value of
$q*$ parameter.[24] We thus believe that selection
rules should be a more adequate starting point for
the analysis of phonon structure in intrinsic ab-
sorption spectra (and corresponding PLE spectra).
It is also interesting to consider the deviation
from the Brout sum rule[26]

$$\Delta_K(X) = \left(\sum_{i=1}^{6} E_i(X) - \sum_{i=1}^{6} E_i(\Gamma) \right) \Big/ \sum_{i=1}^{6} E_i(\Gamma) ,$$

which can be calculated from the above X-point
phonon energies and the corresponding Γ-point
phonon energies obtained from Raman work and
ir-reflection work.[27,28] A value for $\Delta_K(X)$ as 0.09
is found, which is somewhat less than the value
0.15 found for GaP. The value of this deviation
can be considered as a measure of the nonelectro-
static forces between the atoms (in this case main-
ly next-nearest neighbors) in the solid.[29]

The direct Γ_{15v}-Γ_{1c} edge of AlAs at room tem-
perature has previously been estimated by differ-
ent experimental methods. Photoresponse measure-
ments indicated values of 2.9[30] and 2.86 eV,[31] and
transmission measurements carried out on inade-
quately thick crystals have indicated direct absorp-
tion edges at 3.1[10] and 3.14 eV[32] at 300 K from a
rather crude analysis. The most reliable previous
result should be the electroreflectance value re-
ported by Onton to be 2.95 eV at 300 K.[27] The
present work is thus the first thorough investiga-
tion of the position of the direct Γ_{15c}-Γ_{1c} edges
below 300 K, and the accuracy in the determination
allows a quantitative conclusion for the tempera-
ture dependence of this edge. Just as was found
for GaP,[5] the direct Γ_{15v}-Γ_{1c} edge moves considera-
bly faster to lower energies with rising tempera-
ture than does the indirect Γ_{15v}-X_{1c} edge, which
reflects the corresponding difference in the influ-
ence of the electron-phonon interaction for the
different conduction-band extremes at X and Γ.[33]
(Quantitative estimates of the expected tempera-
ture variations may be carried out using different
theoretical methods,[34,35] but the accuracy involved
does not seem to be sufficient to resolve separately
the dilatation and electron-phonon contribution to
this temperature dependence, judged from com-
parison with experimental data for other com-
pounds.[35]) It is interesting to note that our low-

temperature value of the direct Γ_{15v}-Γ_{1c} gap of AlAs (E^x_{gd} = 3.13 ± 0.01 eV) is in good agreement with the value obtained by Dumke et al. (3.13 ± 0.02 eV) by the aforementioned extrapolation procedure.[6] Theoretically calculated values for this lowest direct AlAs gap vary between 2.50[18] and 3.14 eV.[19]

The AlP results reflect the difficulties involved in reducing the defect concentration in the high-temperature growth procedure of this compound, and the final analysis of the details in the AlP indirect Γ_{15v}-X_{1c} edge will probably require a further step in crystal growth. Previously reported transmission measurements on these crystals have established the indirect nature of the band gap around 2.5 eV at low temperature from a crude analysis for rather thin single crystals.[15] The phonon step observed in the excitation spectrum at 2.565 ± 0.01 eV at 4 K in this work is identified with the LO_g-phonon mode, since the same principal lower conduction-band structure in AlP[36,37] as in AlAs will give the same phonon selection rules in the optical transitions ($M_p > M_{Al}$). The LO(Γ) energy of AlP is accurately known from Raman work[27,38] to be 62.6 meV and the LO(X)-mode energy could thus be estimated to be roughly 60 meV. This places the 4-K indirect exciton band gap of AlP at 3.505 ± 0.01 eV, in good agreement with previous estimates by Lorenz et al.[16] The lowest direct (probably Γ_{15v}-Γ_{1c}) gap energy found in this work represents the first reported experimental measurement of this quantity, and the results appear to be in good agreement with a linear extrapolation

from the direct-gap variation with composition for $Al_xIn_{1-x}P$ alloys.[39] This indicates a low value for the corresponding bowing parameter for the Γ_{15v}-Γ_{1c} gap in this alloy, compared with, e.g., $Ga_xAl_{1-x}As$, where the same gap exhibits a substantial bowing in its composition dependence, as can be seen from the AlAs end-point data provided in the present work.[40]

The evaluation of the true band gaps from the excitonic gap values reported here requires a knowledge of excitonic binding energies in the different cases. These binding energies are not readily obtained experimentally even in a highly pure material, and could therefore not be deduced from the present results. Theoretically, the estimation of this quantity is also a nontrivial matter, due to the light-hole-heavy-hole degeneracy of the Γ_{15} valence-band maximum.[41,42] Since reliable values for the appropriate effective masses are not known for AlAs or AlP, an order-or-magnitude estimate for indirect free-exciton ground-state binding energies should be the corresponding values for GaP, which are 10 meV for the Γ_{15v}-X_{1c} exciton[4] and 11 meV for the Γ_{15v}-Γ_{1c} exciton.[42]

ACKNOWLEDGMENTS

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