

Intrinsic Absorption-Edge Spectrum of Gallium Phosphide

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The optical absorption edge has been measured at many temperatures between 1.6 and 300°K in exceptionally perfect single crystals of gallium phosphide. The corresponding transitions are of the allowed indirect type and involve the creation of free excitons and electron-hole pairs. Absorption components associated with four different phonon energies have been resolved, one of which is apparently due to a two-phonon process. The energies of the three single phonons are 12.8 ± 0.5 , 31.3 ± 0.5 , and 46.5 ± 1.0 meV. These are thought to be the respective energies of the transverse-acoustic, longitudinal-acoustic, and transverse-optic branches of the lattice dispersion curves at the $\langle 100 \rangle$ -type boundaries of the reduced zone, although the longitudinal-acoustic energy is ~ 10 meV larger than previous estimates for this phonon. Indirect absorption associated with the longitudinal optic phonon has not been resolved, apparently because these transitions are forbidden via the energetically favorable conduction-band minimum Γ_1 . The internal binding energy of the indirect exciton is 10.0 ± 1.0 meV. Fine structure, probably associated with an excited state of the indirect exciton and also with anomalies in the combined densities of states for the exciton and the acoustical phonons, has been resolved in the low-temperature spectra. The indirect energy gap is 2.339 ± 0.002 eV at 1.6°K and 2.259 ± 0.003 eV at 300°K. These values are considerably larger than previous estimates, especially at 300°K. The consequences of the larger energy gap in the quantitative analysis of donor-acceptor-pair fluorescence spectra and of the spectra of bound excitons in gallium phosphide are considered.

I. INTRODUCTION

EXTENSIVE studies of the photoluminescence properties of carefully prepared single crystals of gallium phosphide,¹⁻⁴ and also of the electroluminescence of *p-n* junctions prepared by alloying onto or diffusion into polycrystals or single crystals⁵⁻⁸ of gallium phosphide have been made during the last few years. Many of the luminescence systems have been identified either with the decay of bound-exciton complexes or with the recombination of electrons and holes respectively trapped at donor and acceptor centers (pair luminescence). The radiative transition energies can often be measured very accurately, since very sharp lines are involved. Correspondingly accurate information about the energies required to produce free excitons (the "exciton energy gap," E_{gx}) or free electron-hole pairs (the minimum forbidden energy gap, E_g) is required for the determination of the binding energies of excitons trapped at impurities, or for a comparison of the sum of the donor and acceptor ionization energies derived from the pair spectra⁹ with values derived from

transport properties.¹⁰ An accurate knowledge of the temperature dependence of E_g and E_{gx} is required to determine whether luminescence systems observed at high temperatures (say 300°K) are simply thermally broadened versions of systems which are prominent at low temperatures (below 77°K), or whether different transitions are involved at high temperatures. This question is particularly relevant to the green luminescence which has been observed at 300°K in spectra from gallium-phosphide diodes.^{7,8}

New measurements of the intrinsic electronic absorption edge of good single crystals of gallium phosphide grown by a modified wet-hydrogen transport process¹¹ are presented and analyzed in this paper. The structure is identified with phonon-assisted creation of free excitons and electron-hole pairs. Identification in the spectra recorded above $\sim 40^\circ\text{K}$ of electronic transitions associated with the *absorption* as well as the emission of phonons allows an unambiguous determination of E_{gx} , and therefore of E_g . The resulting values of E_g at 0°K and 300°K are, respectively, larger than previous estimates¹²⁻¹⁶ by 14 meV and 40 to 50 meV. The large discrepancy between the 300°K estimates is mainly due to neglect in the earlier work of the fact that the low-energy tail of the absorption is due to

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¹ D. G. Thomas, M. Gershenzon, and J. J. Hopfield, *Phys. Rev.* **131**, 2397 (1963).

² D. G. Thomas, M. Gershenzon, and F. A. Trumbore, *Phys. Rev.* **133**, A269 (1964).

³ D. G. Thomas, J. J. Hopfield, and C. J. Frosch, *Phys. Rev. Letters* **15**, 857 (1965).

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⁵ H. G. Grimmeiss, A. Rabenau, and H. Koelmans, *J. Appl. Phys.* **32**, 2123 (1961).

⁶ J. W. Allen, M. E. Moncaster, and J. Starkiewicz, *Solid-State Electron.* **6**, 95 (1962).

⁷ M. Gershenzon and R. M. Mikulyak, *Solid-State Electron.* **5**, 313 (1962).

⁸ M. Gershenzon, R. M. Mikulyak, R. A. Logan, and P. W. Foy, *Solid-State Electron.* **7**, 113 (1964).

⁹ F. A. Trumbore and D. G. Thomas, *Phys. Rev.* **137**, A1030 (1965).

¹⁰ H. C. Montgomery and W. L. Feldman, *J. Appl. Phys.* **36**, 3228 (1965).

¹¹ C. J. Frosch, *J. Electrochem. Soc.* **111**, 180 (1964).

¹² M. Gershenzon, D. G. Thomas, and R. E. Dietz, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 752.

¹³ W. G. Spitzer, M. Gershenzon, C. J. Frosch, and D. F. Gibbs, *J. Phys. Chem. Solids* **11**, 339 (1959).

¹⁴ H. C. Gorton, J. M. Swartz, and C. S. Peet, *Nature* **188**, 303 (1960).

¹⁵ R. Zallen and W. Paul, *Phys. Rev.* **134**, A1628 (1964).

¹⁶ S. A. Abagyan and V. K. Subashiev, *Dokl. Akad. Nauk SSSR* **156**, 763 (1964) [Engl. transl.: *Soviet Phys.—Doklady* **9**, 453 (1964)].

transitions associated with the *absorption* of phonons. The new estimates of the threshold energies of the phonon *emission* components of the absorption edge at 77°K are only ~ 2 meV lower than values published by Gross *et al.*¹⁷ However, Gross *et al.* did not observe the weaker absorption components associated with the absorption of phonons, and were therefore unable to make an absolute estimate of the phonon energies. The energy gap of 2.322 eV which they derived at 77°K, based upon a somewhat arbitrary choice of phonon energies, is in good agreement with the value found in the present work, although the phonon energies differ slightly.

II. EXPERIMENTAL

The crystals used for the optical measurements were grown by a modified wet-hydrogen transport technique¹¹ in quartz vessels. Care was taken to ensure the absence of nitrogen, which has recently been found to produce strong optical absorption near the absorption edge of gallium phosphide.³ Needles of length up to ~ 1 cm and cross section $\gtrsim 1$ mm can be grown rapidly by this technique, and have an amber-yellow color at room temperature. The optical-transmission measurements were made both along the axis of needles with polished end faces and also between natural and/or polished faces on the sides of the needles, which were triangular or hexagonal in cross section. Some measurements were also made on plates of gallium phosphide which had been seeded from gallium-arsenide substrates.

Most of the optical measurements were made using a Spex *f*/6.8 Czerny-Turner monochromator equipped with a Bausch and Lomb grating (1200 grooves/mm) and an EM1 9558 photomultiplier-detector. The crystals were placed in a variable-temperature cryostat in contact with the junction of a thermocouple.¹⁸ Temperatures between 23 and ~ 120 °K were obtained with liquid hydrogen in the Dewar-boiler. With liquid-nitrogen refrigerant, the temperature could be conveniently varied between ~ 105 and 300°K. Tests indicated that unfiltered light from the tungsten source raised the indicated temperature by nearly 1.5°K at 55°K, but the difference between the true temperature of the crystal and the temperature indicated by the thermocouple was < 0.5 °K. Spectra were also recorded with the crystals immersed in liquid nitrogen, in liquid oxygen, and in liquid helium. Transmission spectra were obtained at 1.6°K using a 2-m *f*/17 Bausch and Lomb grating spectrograph equipped with a scanning photomultiplier detector. A Rayleigh resolving power of ~ 15 000 was used in most of the measurements.

It was noticed that, in the low-temperature spectra, the light intensity I_T transmitted by the needles at

energies below the well-defined thresholds of the intrinsic absorption components accurately had the same energy dependence as the incident intensity I_0 . The geometry of the needles made it difficult to employ the conventional sample-in-sample-out technique to record the true transmittance $T = I_T/I_0$ with the desired accuracy. It was therefore assumed that the absorption coefficient was zero in the range where I_T and I_0 varied similarly with the photon energy $h\nu$. Some of the crystals, particularly those grown on gallium-arsenide substrates, exhibited a significant decrease in the magnitude of T with increase in $h\nu$ at energies well below the onset of appreciable intrinsic absorption. This extra absorption, which must be due to defects or impurities, was more noticeable at $\gtrsim 77$ °K than at 1.6°K, but never exceeded 0.3 cm^{-1} even close to the intrinsic thresholds. The crystals all have very high resistivities, which may be due to a close compensation between donor and acceptor concentrations and not always to low absolute magnitude of these quantities.

Only the results of measurements on crystals which did not exhibit this extra energy-dependent absorption will be discussed in this paper. The absorption coefficient α was calculated assuming that the transmitted intensity I_T in the energy region where I_T/I_0 was constant differed from I_0 solely because of reflection losses. α is related to T in a crystal of thickness t by the equation

$$T = I_T/I_0 = (1-R)^2 \exp(-\alpha t) / 1 - R^2 \exp(-2\alpha t), \quad (1)$$

which takes account of multiple internal reflections. R , the reflectivity of gallium phosphide, was taken as 30% in the energy region near the absorption edge.¹⁹ If $I_T = I_T'$ when $\alpha = 0$, then according to Eq. (1)

$$T' = I_T/I_T' = (1-R^2) \exp(-\alpha t) / 1 - R^2 \exp(-2\alpha t). \quad (2)$$

The value of α was determined from the experimental value of the apparent transmissivity T' using Eq. (2).

III. RESULTS

Figure 1 contains experimental data on the relationship between $\alpha^{1/2}$ and $h\nu$ obtained from transmission measurements on four crystals of thickness 0.0212, 0.058, 0.0724, and 0.362 cm, recorded at five temperatures between 0 and 300°K. The stepped structure characteristic of the intrinsic absorption edge of crystals with an indirect energy gap²⁰ is very well defined in the low-temperature spectra. The thresholds of the steps are labeled according to the type of phonon which assists the electronic transition which commences at that energy (see Sec. IVD). The subscripts denote whether the phonon is emitted (*E*) or absorbed (*A*) during the optical absorption process. The phonon absorption components are only observed above about

¹⁷ E. F. Gross, N. S. Kochneva, and D. S. Nedzvetskii, Dokl. Akad. Nauk SSSR 153, 574 (1963) [Engl. transl.: Soviet Phys.—Doklady 8, 1103 (1964)].

¹⁸ K. Maeda, J. Phys. Chem. Solids 26, 595 (1965).

¹⁹ D. F. Nelson (private communication).

²⁰ R. J. Elliott, Phys. Rev. 108, 1384 (1957).

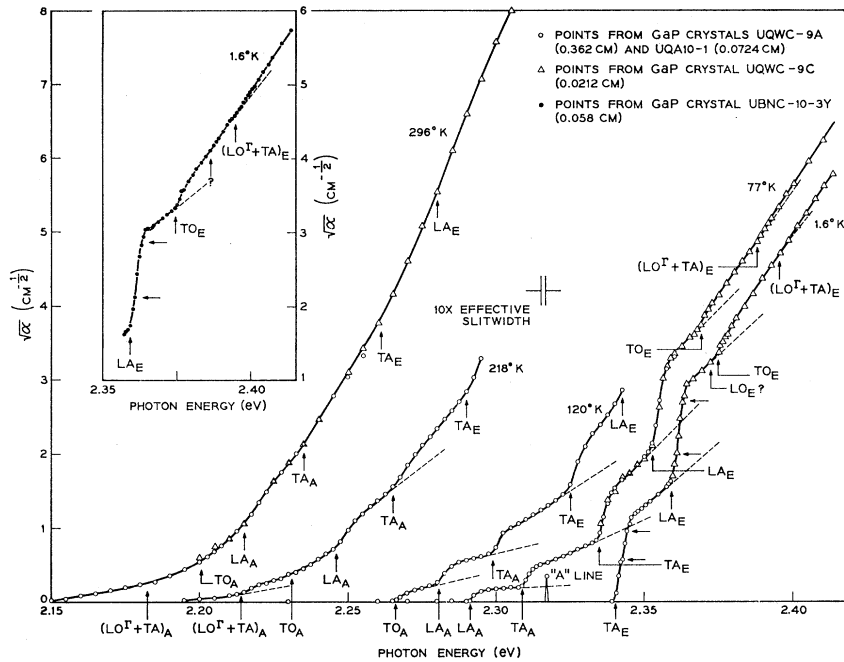


FIG. 1. The low-level edge-absorption spectrum of exceptionally perfect single crystals of gallium phosphide at various temperatures. The main curves were calculated from transmission spectra obtained from two crystals of different thickness, and the low-temperature spectrum of a third crystal is shown in the inset. Vertical arrows indicate the thresholds of different absorption components resulting from different phonon energies, horizontal arrows denote structure interpreted in terms of electronic degeneracy. The labeling of the phonons is discussed in the text.

40°K, and continuously increase in strength relative to the phonon-emission components as the temperature is increased towards 300°K. The whole absorption spectrum is translated to lower energies as the temperature increases, indicating the temperature dependence of E_g , and the structure becomes blurred due to a reduction in the lifetime of the free exciton due to lattice scattering, as observed for silicon²¹ and germanium.²²

The limited region of the 1.6°K spectrum shown in the inset of Fig. 1 was determined for a crystal for which the transmission spectrum was recorded as accurately as possible between 2.36 and 2.41 eV, with decreased but still adequate energy resolution. This spectrum shows the very sharp knee and nearly flat portion of the absorption spectrum near 2.365 eV, and also the very weak structure above 2.38 eV, more clearly than the complete 1.6°K spectrum.

Transmission spectra were recorded at intervals of $\lesssim 10^\circ\text{K}$ between 25 and 300°K, and the low-energy thresholds of the absorption components were located. Figure 2 shows the temperature dependence of these threshold energies between 0 and 300°K. The temperature dependence of the position of some strong optical-absorption lines due to the creation of bound exciton states, particularly the *A* line,¹ was also measured and found to be consistent with the shift of the intrinsic components shown in Fig. 2. The exciton energy gap

E_{gx} , denoted by the central dashed line in Fig. 2, is given as the arithmetic mean of the threshold energies of the pairs of absorption components identified with the same phonon energy. E_{gx} shows an essentially linear variation with temperature T above $\sim 140^\circ\text{K}$, when

$$E_{gx} = 2.355 \pm 0.001 - 3.57 \times 10^{-4} T. \quad (3)$$

E_{gx} (or E_g) cannot be conveniently represented in the range 0 to 300°K by a formula of the type $E_{gx} = A - BT^2$, were A and B are constant coefficients.¹² The value of dE_{gx}/dT given from Eq. (3) is significantly lower than previously reported values. The ratio of the (negative) coefficient dE_{gx}/dT for the indirect and direct ($\Gamma_{15} \rightarrow \Gamma_1$) transitions between 80 and 300°K is reduced from 1.15:1^{15,23} to 0.71:1.

IV. DISCUSSION

A. The Interrelationship of the Indirect-Transition Absorption-Threshold Energies

We will assume that the Coulomb interaction between the excited electrons and holes is strong enough for the creation of free excitons to play a significant role in the optical absorption spectrum in the considered temperature range, as is so for germanium and silicon.²⁴ Then, according to the theory of allowed indirect

²¹ G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, *J. Phys. Chem. Solids* **8**, 388 (1959).

²² T. P. McLean and E. G. S. Paige, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 450.

²³ V. K. Subashiev and G. A. Chalikyan, *Fiz. Tverd. Tela* **7**, 1237 (1965) [Engl. transl.: *Soviet Phys.—Solid State* **7**, 992 (1965)].

²⁴ T. P. McLean, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 5, p. 55.

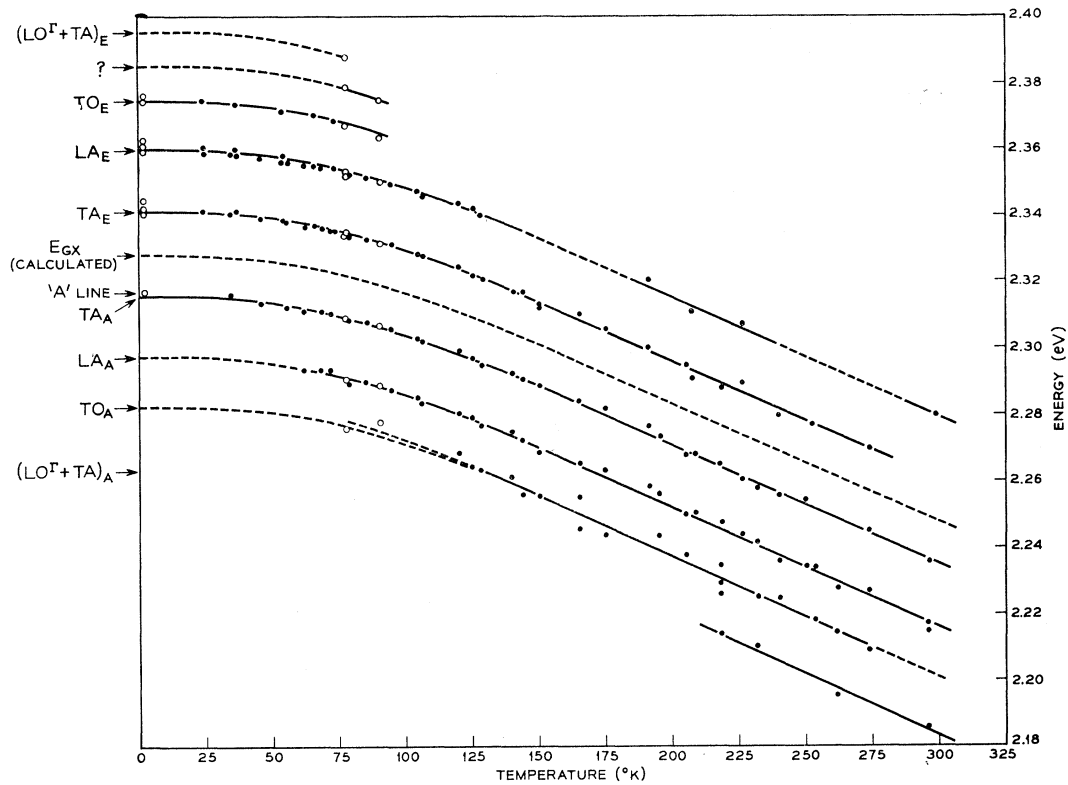


FIG. 2. The temperature dependence of the energies of the thresholds of the absorption components indicated in Fig. 1. The position of the "A" extrinsic absorption-emission line at 1.6°K is also shown. The \circ points were obtained with the crystals immersed in liquid refrigerant, and each represents the average value of measurements from several transmission spectra.

transitions,²⁰ the optical absorption should be of the form

$$\alpha_i(h\nu) = \frac{a(T)}{\exp(\hbar\omega_i/kT) - 1} \{ (h\nu - E_{gx} + \hbar\omega_i)^{1/2} + [\rho_i \exp(\hbar\omega_i/kT)] (h\nu - E_{gx} - \hbar\omega_i)^{1/2} \} \quad (4)$$

for the pair of components associated with a given phonon of energy $\hbar\omega_i$, which has the momentum required to take the electron from the valence-band maxima to the conduction-band minima. $a(T)$ is a weakly temperature-dependent parameter containing the density-of-states effective masses of electrons and holes. k is Boltzmann's constant and ρ_i is given by

$$\rho_i = (\delta E + \hbar\omega_i)^2 / (\delta E - \hbar\omega_i)^2, \quad (5)$$

where δE is the difference in energy of the electron (or hole) between the principal intermediate state in the virtual transition and the final state.

Equation (4) shows that the threshold energies of the components are spaced symmetrically about E_{gx} with a separation of $2\hbar\omega_i$. This pairing is indicated in Figs. 1 and 2. Table I contains an analysis of these energies obtained from the 77°K absorption spectrum of Fig. 1 and also from the absorption spectra at 120°K (for TO_A) and at 218°K (for $(TA + LO^\Gamma)_A$), since the

latter components are not seen at 77°K. (TA = transverse acoustic; LO = longitudinal optic.) The assignment of the phonons to particular branches of the lattice dispersion curves is discussed in Sec. IV. The component with threshold near 2.378 eV is not clearly defined in the 77°K absorption spectrum, but it can be seen in the 1.6°K spectrum in the inset to Fig. 1. Inter-comparison of several transmission spectra suggested that a threshold definitely occurs near this energy. The corresponding phonon-absorption component is probably responsible for the exceptionally large broadening of the threshold of the TO_A component at high temperatures, for example in the 218°K spectrum shown in Fig. 1. (TO = transverse optic.) The four estimates of the exciton energy gaps obtained from the medians of the pairs of threshold energies are mutually consistent. This, together with the observation that the lower energy members of the pairs are successively frozen out as the temperature is reduced (Figs. 1 and 2), supports the pairing scheme adopted in Table 1. Equation 4 shows that, at a given temperature T , the magnitude ratio of the absorption coefficients for the phonon emission (second term in the curly bracket) and phonon absorption (first term in the curly bracket) components should be

$$(\alpha_i)_E / (\alpha_i)_A = \rho_i \exp(\hbar\omega_i/kT) \quad (6)$$

TABLE I. Analysis of the absorption-component threshold energies at 77°K.

Threshold Energy (eV)	Assignment	Phonon Energy (meV)	Exciton Energy Gap (eV)
2.3350±0.0005 2.3095±0.0005	$E_{gx} + \hbar\omega_{TA}$ $E_{gx} - \hbar\omega_{TA}$	$\hbar\omega_{TA} = 12.8 \pm 0.5$	2.3223±0.0005
2.3535±0.0005 2.2910±0.0005	$E_{gx} + \hbar\omega_{LA}$ $E_{gx} - \hbar\omega_{LA}$	$\hbar\omega_{LA} = 31.3 \pm 0.5$	2.3223±0.0005
2.3690±0.0005 2.2760±0.001	$E_{gx} + \hbar\omega_{TO}$ $E_{gx} - \hbar\omega_{TO}$	$\hbar\omega_{TO} = 46.5 \pm 1.0$	2.3225±0.001
2.3880±0.001 2.2595±0.001	$E_{gx} + \hbar\omega_{TA} + \hbar\omega_{LO}^\Gamma$ $E_{gx} - \hbar\omega_{TA} - \hbar\omega_{LO}^\Gamma$	$\hbar\omega_{TA} + \hbar\omega_{LO}^\Gamma = 64.3 \pm 1.0$	2.3228±0.001
2.379 ± 0.0015	$E_{gx} + \hbar\omega_{TA} + \hbar\omega_{TO}^\Gamma$ OR $E_g + \hbar\omega_{LO}$? $\left\{ \begin{array}{l} \hbar\omega_{TA} + \hbar\omega_{TO}^\Gamma = 57 \pm 2.0 \\ \text{OR } \hbar\omega_{LO} + E_x = 57 \pm 2.0^a \end{array} \right.$	

^a E_x is the internal binding energy of the indirect exciton.

for a given value of $(h\nu - E_{gx} - \hbar\omega_i)$ and $(h\nu - E_{gx} + \hbar\omega_i)$ and the same phonon. ρ_i is only slightly temperature-dependent through δE in Eq. (5). This equation was tested for the TA phonon, when α was measured at 12 meV above the two threshold energies in spectra between 35 and 200°K, and also for the LA phonon, when α was measured at 9 meV above the threshold energies between 60 and 200°K. A graph of $\log_{10}[(\alpha_i)_A/(\alpha_i)_E]$ versus T^{-1} (Fig. 3) gave a good straight line for the

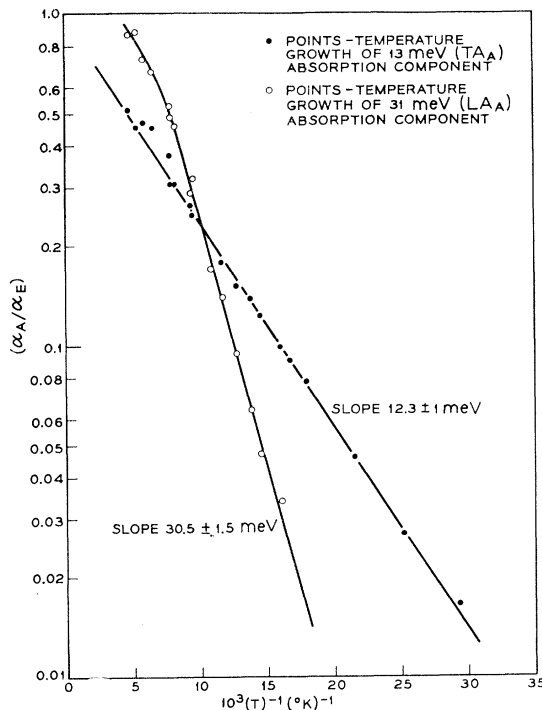


FIG. 3. The growth rate of the intensity of the optical-absorption components identified with the absorption of the TA (•-curve) and LA (○-curve) phonons. For the •-curve the optical absorption coefficient was measured 12 meV above the thresholds of the corresponding components, while for the ○-curve measurements were made at 9 meV above the threshold energies.

TA components with an exponent of 12.3 ± 1.0 meV, in excellent agreement with the value of $\hbar\omega_{TA}$ given in Table I. A similar plot for the LA components gave an exponent of 30.5 ± 1.5 meV between 60 and 130°K, but at higher temperatures the data indicated a lower exponent, probably because of an overestimate of the strength of the high-energy tails of the thermally broadened components associated with the higher energy phonons in the measurement of $(\alpha_i)_A$ for the longitudinal-acoustic (LA) phonon. Similar difficulties precluded a test of Eq. (6) for the TO and combination phonon components, but it is qualitatively evident from the temperature dependence data given implicitly in Fig. 1 that these components are associated with phonons of higher energy than $\hbar\omega_{LA}$, as suggested in Table I.

B. Fine Structure on the TA and LA Absorption Edges

At 1.6°K weak additional thresholds can be discerned on the TA_E and LA_E absorption edges. Although they are scarcely visible on the scale of Fig. 1, their positions have been marked by horizontal arrows on this figure. The structure is more clearly defined in Fig. 5 below. As well as can be determined, these additional thresholds fall at 1.6 ± 0.2 and 3.7 ± 0.3 meV above the lowest energy threshold for both the TA and LA edges. It seems likely that this structure arises in part from an excited electronic state of the exciton. This state may be similar to those discussed by McLean and Loudon,²⁵ having its origin in a splitting of the valence band produced by the anisotropy of the constant-energy surface for conduction-band electrons in minima which are not at $k=0$. j - j coupling between the hole and electron can also produce a splitting of the exciton energy levels.

²⁵ T. P. McLean and R. Loudon, J. Phys. Chem. Solids **13**, 1 (1960).

The splittings between these exciton states, expressed as a fraction of the exciton binding energy (10 meV according to Sec. IVC) are of the same order as the observed and calculated values for silicon and germanium, although only one excited state was seen.^{21,25} The calculation of these exciton levels depends upon a detailed knowledge of conduction- and valence-band parameters, which is not available at present for gallium phosphide.

The structure associated with the second excited state is discussed further in the next section.

C. Analysis of Individual Absorption Components

The component TA_A is most convenient for a detailed analysis of the form of α as a function of $h\nu$, since no other components obtrude within an energy interval of $2\hbar\omega_{TA}$, or ~ 25 meV, above its threshold, apart from the underlying components mainly consisting of the LA_A component, which is relatively weak if the temperature is correctly chosen. A suitable temperature is $\sim 75^\circ\text{K}$. Figure 4 shows the variation of α with $h\nu$ for components LA_A , TA_A , and TA_E at 77°K . Data obtained from two transmission runs show good mutual agreement. According to Eq. (4), the shape of TA_A absorption component should be given by

$$\alpha_{TA_A} = \frac{\alpha(T)}{\exp(\hbar\omega_{TA}/kT) - 1} [h\nu - E_{gx} + \hbar\omega_{TA}]^{1/2}. \quad (7)$$

Figure 4 shows that the initial portion of the TA_A component, obtained from the experimental spectrum after subtraction of the weak underlying LA_A component, follows this law fairly well, although the experimental curve has a slightly sharper knee than is allowed by Eq. (7). There is a systematically increasing deviation from Eq. (7) for $h\nu \gtrsim 2.320$ eV, however. The extra absorption shown in Fig. 4 is quite well represented by an expression like Eq. (7), but with an index of $\frac{3}{2}$, as is expected, theoretically close to the threshold of a component representing the phonon-assisted photogeneration of free electrons and holes with an optically allowed transition.²⁰ Similar effects are present for the TA_E (Fig. 4) and LA_E components, but are harder to analyze because of the relatively close spacing of adjacent components associated with different values of $\hbar\omega_i$. From Fig. 4, the 77°K TA_A component can be represented by

$$\alpha = 2.73(h\nu - 2.310)^{1/2} + 1150(h\nu - 2.320)^{3/2}, \quad (8)$$

where α is in cm^{-1} and $h\nu$ in eV. The exciton internal binding energy E_x is therefore 10.0 ± 1.0 meV, quite similar to the value derived for silicon.²¹

Using values of $0.9m_0$ and $0.5m_0$ as reasonable estimates of the density-of-states electron and hole masses in gallium phosphide,²⁶ where m_0 is the free-electron

mass, and a dielectric constant of 10.2,²⁷ the predicted value of E_x is ~ 40 meV on the simple hydrogenic theory. This type of estimate for E_x is known to give anomalously large results, however, because it neglects the reduction in the electron-hole correlation energy brought about by the complexities of the valence- and conduction-band energy surfaces.²⁸ E_x calculated from idealized values of the donor and acceptor binding energies in silicon is ~ 20 meV, whereas the directly measured value is only ~ 8 meV.²⁹

Figure 4 also shows a comparison of the shape of the experimental 77°K TA_E component with the theoretical expression of Eq. (4). The TA_E component is derived by subtraction of the linearly extrapolated LA_A component and the TA_A component extrapolated according to Eq. (8) from the experimental curve. The excess absorption near the knee of the experimental component is relatively stronger than observed for the TA_A component at the same temperature. Analysis of the 77°K LA_E component in the same way reveals even more pronounced deviations from Eq. (4) than for the TA_E component. The excess absorption is connected with the presence of the sharp discontinuity in these absorption components at 1.6°K , which is very pronounced for the LA_E component.

The fine structure discussed in Sec. IVB is seen most clearly at 1.6°K , as shown in the expanded spectrum in Fig. 5, since there is significant thermal broadening between 1.6 and 77°K .

Measurements made under optimum conditions of signal to noise, for example, in the inset of Fig. 1, show that the knee in the LA_E component near 2.365 eV is even sharper than shown in the main 1.6°K spectrum of Fig. 1 and in Fig. 5. The TO_E components from both of the 1.6°K spectra in Fig. 1 do not show this feature. Comparison of the shape of the experimental TO_E component with the theoretical expression in Eq. (4) does suggest the presence of unresolved substructure, but it is certain that this structure is not the same as for the LA_E component; otherwise, the sharp knee would be clearly visible in the TO_E component.

No such deviations from the predictions of Eq. (4) were detected in the edge absorption spectra of silicon or germanium²¹ and it is therefore unlikely that they are due to the known deviations of the band structure of these materials from the simple spherical form assumed in the theoretical analysis.²⁰ Similar deviations have been reported in absorption-edge spectra of certain modifications of silicon carbide, however, particularly the rhombohedral polytype 21R, in which exciton life-

²⁷ G. Giesecke and H. Pfister, *Acta Cryst.* **11**, 369 (1958).

²⁸ J. J. Hopfield, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris* (Dunod Cie., Paris, 1964), p. 725.

²⁹ J. R. Haynes, M. Lax, and W. F. Flood, in *Proceedings of the International Conference on the Physics of Semiconductors, Prague* (Academic Press Inc., New York, 1960), p. 423.

²⁶ D. F. Nelson (private communication).

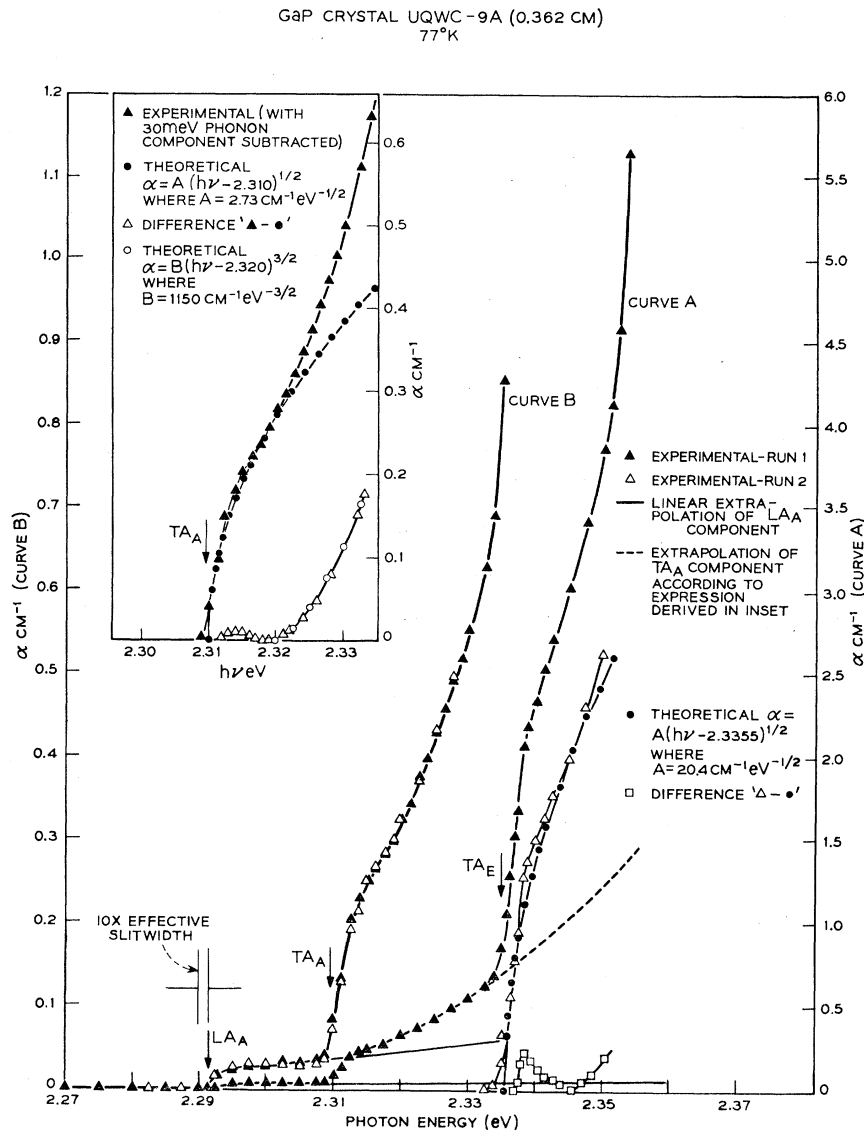


FIG. 4. A portion of the edge-absorption spectrum of gallium phosphide at 77°K. The inset shows the deviations between the experimental component associated with absorption of TA phonons and the theoretical expression for allowed indirect transitions to free-exciton states. The excess absorption above 2.32 eV in the experimental curve is attributed to the formation of unbound electron-hole pairs. Vertical arrows denote threshold energies of absorption components associated with different phonons. The component associated with the emission of TA phonons has also been extracted from the experimental spectrum and compared with the theoretical expression.

time broadening effects are relatively insignificant.³⁰ The effect is again particularly marked for the LA phonon emission component.

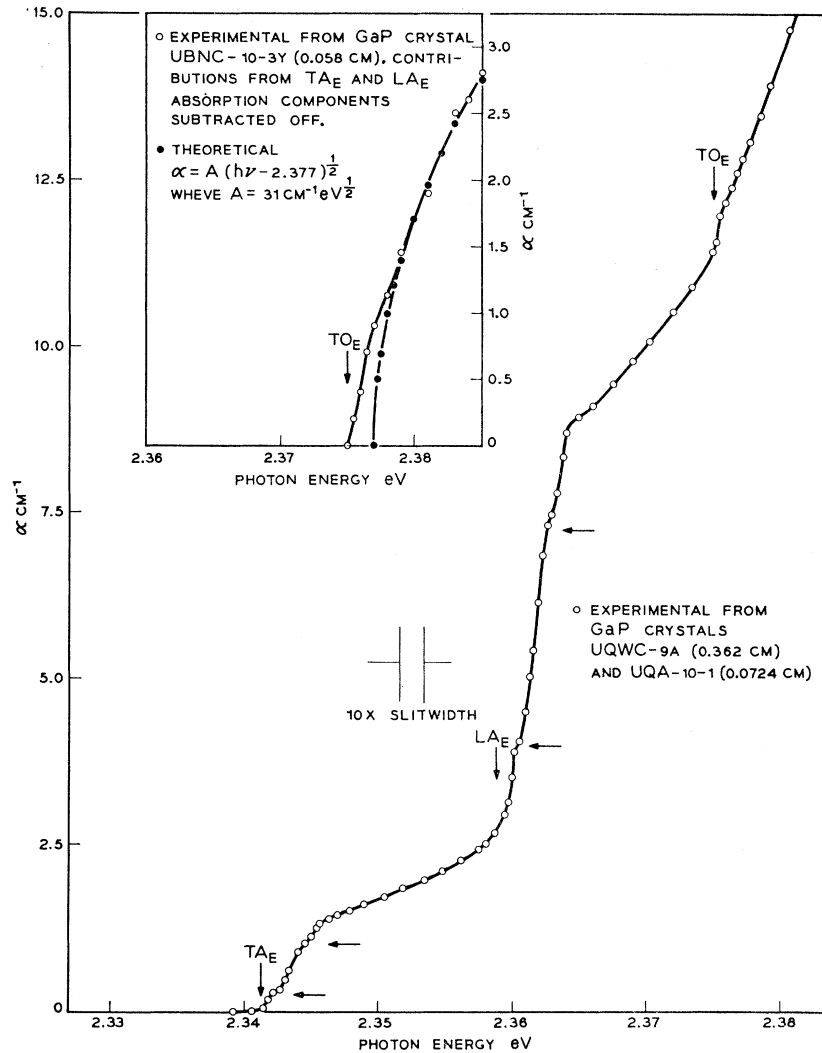
These effects may be attributable to an anomaly in the density-of-states parameter $a(T)$ of Eq. (4). A suitable type of anomaly could occur if the sum of the energies E_{gx} and $\hbar\omega_i$ reached a minimum value at equivalent points just inside the zone boundary on the $\langle 100 \rangle$ axes. The density of states function for the phonon-emission transition may then exhibit a P_0 -type³¹ critical point at the minimum value of $(E_{gx} + \hbar\omega_i)$ followed closely by a P_1 -type³¹ critical point corresponding to

the creation of excitons with zero kinetic energy associated with the minimum value of E_{gx} (or E_g). The shape of the LA_E absorption component suggests that the three resolved thresholds might arise from a splitting of each of the two states of the indirect exciton, discussed in Sec. IVB, into two further subcomponents. Two of the four subcomponents thus produced would be very closely spaced, and might make up the central resolved subcomponent, which is roughly twice as strong as each of the two outer subcomponents. If this additional fine structure arises from the density-of-states anomaly discussed above, then the lowest-energy subcomponent should have the characteristic shape of a P_0 critical point, having the energy dependence of Eq. (4), while the highest energy subcomponent should have a sharp knee like a P_1 critical point and the central subcomponent should be of mixed character. These

³⁰ D. R. Hamilton, L. Patrick, and W. J. Choyke, Phys. Rev. 138, A1472 (1965).

³¹ R. Loudon and F. A. Johnson, in *Proceedings of the International Conference on the Physics of Semiconductors, Paris* (Dunod Cie., Paris, 1964), p. 1037.

FIG. 5. The edge-absorption spectrum obtained from exceptionally perfect single crystals of gallium phosphide at 1.6°K showing the fine structure near the threshold of each main absorption component (horizontal arrows). The component associated with the emission of TO phonons, obtained by subtracting the extrapolated absorption components associated with the emission of TA and LA phonons from the experimental spectrum, is compared in the inset with the theoretical expression given by Eq. (4).



predictions appear to be in agreement with the experimental results, although the shapes of the two lower-energy subcomponents are difficult to establish because of the small energy separations involved. Analysis of the threshold energies on this model implies that the two exciton states are separated by ~ 1.5 meV, while each of these states is further split by ~ 2 meV into the P_0 and P_1 subcomponents. It is of particular interest that the upper subcomponent appears with such a well developed and characteristic shape, as shown in the inset in Fig. 1.

The origin of the anomalous structure proposed for the dispersion curve of $E_{gx} + \hbar\omega$ is not clear at present. The fine structure introduced into the conduction bands near the minima, which are at X ,³² and into the valence band by the lack of inversion symmetry in the zincblende structure of gallium phosphide³³ qualitatively

³² M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

³³ E. O. Kane, J. Phys. Chem. Solids **1**, 229 (1957).

produces the desired structure in the dispersion curve of E_{gx} , but the magnitude of the observed splitting is much too large to be explained by this effect alone. The clarity of the substructure in the LA_E absorption component, and the apparent absence of the sharp knee in the TO_E absorption component, suggests that the phonon dispersion curve makes a major contribution to the anomaly in $E_{gx} + \hbar\omega$. It is difficult to believe that the "effective mass" defined by the phonon dispersion curve near X is comparable with even the longitudinal exciton mass, however, as would be required by the latter hypothesis. No definitive interpretation of this anomalous structure can therefore be offered at present.

The ~ 1.5 meV splitting in the exciton states should appear in *all* the components of the indirect absorption spectrum, including those associated with the TO phonon. It was observed that the TO_E component at 1.6°K increased more *slowly* than allowed by Eq. (4), suggesting the presence of fine structure. This sub-structure could not be clearly resolved, however, presumably

TABLE II. Coefficients A [units $\text{cm}^{-1} (\text{eV})^{-1/2}$] in the expression $\alpha = A (h\nu - h\nu_0)^{1/2}$ for individual absorption components at various temperatures, compared with values calculated from the 1.6°K spectrum.

Temperature Phonon component	1.6°K		77°K		120°K		218°K	
	Coeffi- cient	Calculated from 1.6°K	Coeffi- cient	Calculated from 1.6°K	Coeffi- cient	Calculated from 1.6°K	Coeffi- cient	Calculated from 1.6°K
TA_E	17	17 ^a	20	20 ^a	25	24 ^a		
LA_E	64	64 ^a	67	65 ^a	68	67 ^a	74	79 ^a
TO_E	25	25 ^a	23	25 ^a				
$(\text{LO}^\Gamma + \text{TA})_E$			≤ 10	$\leq 10^a$				
TA_A	0	0	2.6	2.9 ^b	6.6	6.9 ^b	11	17 ^b
LA_A	0	0	0.36	0.63 ^b	1.6	3.5 ^b	5	16 ^b
TO_A	0	0			0.29	0.28 ^b		
$(\text{LO}^\Gamma + \text{TA})_A$	0	0					0.35	$\sim 0.3^b$

^a Calculated from the expression $(A_E)^T = (A_E)^0 / [1 - \exp(\hbar\omega_i/kT)]$.

^b Calculated from the expression $(A_A)^T = (A_A)^0 / [\exp(\hbar\omega_i/kT) - 1]$.

because of the small separation (~ 1.5 meV according to the above estimate) of the subcomponents and the unfavorable position of the TO_E component in the absorption spectrum. Thermal broadening probably prevented the observation of the expected fine structure in the phonon-absorption components (Fig. 4), since the structure was not resolved in the TA_E or LA_E components at the relevant temperatures.

The interpretation of the substructure in the LA_E and TA_E absorption components proposed above implies that the threshold value of $h\nu$ appropriate in the second (phonon-emission) term in Eq. (4) should correspond more closely with the threshold of the second subcomponent rather than the first. This prediction is supported by Fig. 2, where it is seen that the threshold energies of the TA_E and LA_E components extrapolate as the temperature is reduced to an energy distinctly higher than the thresholds of the corresponding components measured at 1.6°K.

Table II contains the parameters

$$a(T) / [\exp(\hbar\omega_i/kT) - 1]$$

and

$$\frac{a(T) \exp(\hbar\omega_i/kT)}{\exp(\hbar\omega_i/kT) - 1},$$

denoted A^T , derived directly from the experimental data for several components at various temperatures. It is noticeable that, at a given temperature T , the magnitudes of $(A_A)^T$ calculated from the strength of the corresponding component, $(A_E)^0$, measured at 1.6°K using the expression

$$(A_A)^T / (A_E)^0 = 1 / [\exp(\hbar\omega_i/kT) - 1], \quad (9)$$

are in reasonable agreement with the experimental values for the TA , TO , and $(\text{LO}^\Gamma + \text{TA})$ components, but are considerably larger for the LA component. Equation (4) shows that the right-hand side of (9) should be multiplied by $(\rho_i)^{-1}$, and Eq. (5) shows that ρ_i is appreciably greater than unity only if $\hbar\omega_i$ is significant compared with δE . It is shown in Sec. IVD that δE is ~ 0.52 eV for the LA phonon-assisted transition

at 77°K, and decreases slowly with increase in temperature (Sec. III), whereas the minimum value of δE is ~ 2.5 eV for allowed indirect transitions involving phonons from the other branches of the lattice dispersion curves. Thus, ρ_{LA} is ~ 1.26 , whereas ρ_{TA} , ρ_{LO} , and ρ_{TO} are all ~ 1.05 . The temperature growth rate of the LA_A component presented in Table II implies that ρ_{LA} is ~ 1.75 at 77°K and is larger at higher temperatures, whereas ρ_{TA} , ρ_{TO} , and probably $\rho_{(\text{LO} + \text{TA})}$ also, are in the range $1.0 \lesssim \rho \lesssim 1.1$. This observed value of ρ_{LA} suggests that δE of Eq. (5) is only ~ 0.22 eV, much lower than values observed in reflectivity¹⁵ and absorption²³ spectra. Good agreement has been obtained between observed and calculated values of ρ for indirect transitions in germanium, however.²¹ The temperature dependence of ρ_{LA} implies that δE decreases with increasing T , consistent with the results given in Sec. III if δE is identified with the energy difference between conduction-band minima at Γ_1 and X_1 (see also Sec. IVD). The relatively large discrepancy between the calculated and observed values of $(A_E)^T$, as well as $(A_A)^T$, at 218°K is largely due to the difficulties of quantitative analysis of the absorption data at high temperatures caused by thermal broadening of the structure (Sec. IVA).

D. Phonon Assignments and Selection Rules for the Indirect Transitions

The four phonons which assist the indirect transitions have been labeled in Sec. IVA as transverse acoustical (TA , 12.8 meV), longitudinal acoustical (LA , 31.3 meV), transverse optical (TO , 46.5 meV), and a combination of longitudinal optical and transverse acoustical ($\text{LO}^\Gamma + \text{TA}$, 64.3 meV). This identification is based upon the following considerations:

(1) The energies of the LO and TO phonons at the center of the reduced zone (symmetry point Γ) have been shown to be respectively 50.0 and 45.4 meV from measurements of first-order Raman scattering,³⁴ and

³⁴ M. V. Hobden and J. P. Russell, Phys. Letters 13, 39 (1964).

an earlier analysis of the reststrahlen band in the infrared indicated a similar value for $\hbar\omega_{\text{TO}}$.³⁵ Bound-exciton and donor-acceptor-pair luminescence spectra also support the view that $\hbar\omega_{\text{LO}}$ is ~ 50 meV.^{1,2} The dispersion curves of zinc-blende lattices are such that the energies of all single-phonon lattice modes should be less than this quantity.³⁶

(2) The ordering of the single-phonon energies at the boundary of the reduced zone depends upon the value of the effective ionic charge in the Ga-P bonds.³⁶ Measurements of these energies for gallium arsenide, by inelastic neutron scattering, indicate that $\hbar\omega_{\text{TO}} > \hbar\omega_{\text{LO}}$ over the outer region of the reduced zone, while $\hbar\omega_{\text{LA}}$ is much greater than $\hbar\omega_{\text{TA}}$ throughout the zone, except at Γ .³⁷ These results suggest a relatively small effective ionic charge for gallium arsenide. Although the fact that the ratio $(\hbar\omega_{\text{LO}} - \hbar\omega_{\text{TO}}/\hbar\omega_{\text{LO}})^{\Gamma}$ is $\sim 1.5\times$ greater for gallium phosphide than for gallium arsenide suggests that the effective ionic charge is larger for gallium phosphide, it is still expected that $\hbar\omega_{\text{TO}}$ is significantly larger than $\hbar\omega_{\text{LO}}$ at the zone boundary.^{34,36} This, together with the value of $\hbar\omega_{\text{TO}}^{\Gamma}$, implies that the 46.5-meV phonon should be assigned to the TO rather than to the LO branch.

(3) The wave vector of the phonons observed in the indirect absorption-edge transitions is equal to $\mathbf{K}_c - \mathbf{K}_v$, where \mathbf{K}_c and \mathbf{K}_v represent the momenta of electrons at the conduction-band minima and valence-band maxima. Theoretical comparative studies of the band structure of III-V compounds,^{32,38} and the magnitude of the anisotropy of the g factor of holes in bound-exciton complexes in gallium phosphide,³⁹ suggest that $\mathbf{K}_v = 0$. The symmetry classification of the upper valence bands is Γ_{15} . Correlation of the measured shifts of the indirect absorption edge of GaP under hydrostatic pressure with similar properties of other group IV and III-V crystals,¹⁵ and also theoretical considerations,³² suggest that $K_c = K_{\text{max}}\langle 100 \rangle$, i.e., that the conduction-band minima are at X (symmetry classification X_1). The phonons from the absorption-edge spectrum should therefore be fitted to the lattice dispersion curves at X .

Analysis of the infrared combination absorption bands and of the second-order Raman scattering spectrum is thought to provide energies of phonons at principal symmetry points at the reduced zone boundaries.^{31,40} The most explicit assignment yet produced for gallium phosphide was derived from the Raman spectrum.³⁴ The single-phonon energies listed in Table I are compared in Table III with those inferred from the Raman data. The single entry in column 4 represents

TABLE III. Comparison of phonon energies derived from the Raman spectrum and from the infrared absorption spectrum of gallium phosphide with values derived from the indirect absorption edge.

Phonon	Energy from indirect absorption (meV)	Energy from ^a Raman spectrum (meV)	Energy from ^b infrared absorption (meV)
TA	12.8	12.8	14.3
LA	31.3	21.4	
LO	absent	44.4	
TO	46.5	47.0	

^a Reference 34.

^b Reference 35.

the phonon TA_1 derived by Kleinman and Spitzer from the infrared combination absorption bands.³⁵ No attempt was made by the latter workers to assign single-phonon energies to particular regions of the reduced zone, other than at Γ , however.

The energies in columns (2) and (3) agree very well for the TA and TO phonons, but there is a large difference, well outside the limits of experimental error, between the two estimates of $\hbar\omega_{\text{LA}}$. Since there is no unambiguous method for separating individual phonon energies from the second-order Raman spectrum and from the multiphonon infrared absorption spectrum, or for making the zone-boundary assignments, we believe that the estimates made in column (2) are the most reliable. Although only one of the phonon energies at X is altered by this comparison, this quantity appears in three assignments made from the Raman data.³⁴ It therefore does not appear that the Raman spectrum can be completely interpreted in the way suggested by Hobden and Russell. For instance, there is no component present in the published Raman spectrum with the Raman shift predicted for $\hbar\omega_{\text{TO}} + \hbar\omega_{\text{LA}}$ at X on the new assignment (~ 77 meV).

It is interesting to note that the new value of $\hbar\omega_{\text{LA}}$ given in Table III would bring the phonon energies of gallium phosphide into good agreement with the correlation graph between $\hbar\omega_{\text{LA}}$ and $\hbar\omega_{\text{TO}}$ exhibited by the zinc-blende-structure semiconductors,³⁶ and in particular into agreement with the scaled zone-boundary phonon energies of gallium arsenide, where it has been observed that $\hbar\omega_{\text{LA}}$ is roughly isotropic at the zone boundary.³⁷ The phonon energies listed in Table III also suggest that the present assignments of the two and three phonon combination infrared absorption bands^{34,41} require revision.

Support for the phonon assignments made in Tables I and III can be derived from a consideration of the selection rules for the indirect transitions. Transitions in which the lowest direct conduction-band minimum (at Γ_1) acts as a virtual intermediate state should possess a favorably large transition moment if the transition is optically allowed.²⁴ Group theory shows that a transition via this state is allowed only for scat-

⁴¹ R. J. Cherry, Phys. Letters 4, 234 (1963).

³⁵ D. A. Kleinman and W. G. Spitzer, Phys. Rev. 118, 110 (1960).

³⁶ S. S. Mitra, Phys. Rev. 132, 986 (1963).

³⁷ J. L. T. Waugh and G. Dolling, Phys. Rev. 132, 2410 (1963).

³⁸ H. Ehrenreich, J. Appl. Phys. Suppl. 32, 2155 (1961).

³⁹ Y. Yafet and D. G. Thomas, Phys. Rev. 131, 2405 (1963).

⁴⁰ W. Cochran, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 467.

tering by the LA phonon, however. Indirect transitions via the higher Γ_{15} conduction-band minimum are only allowed for scattering by LO, TA, and TO phonons, whereas indirect transitions via the X_5 valence-band intermediate state are allowed for all phonons.⁴² The energy differences Γ_1-X_1 , $\Gamma_{15}-X_1$ (conduction band) and $\Gamma_{15}-X_5$ (valence band), are ~ 0.5 , ~ 3.1 , and ~ 2.4 eV in gallium phosphide,³² and represent the quantity δE introduced in Sec. IVC. The matrix element for the indirect transition is proportional to $(\delta E)^{-1}$, so that the strength of LA-assisted transitions via the Γ_1 minimum are $\sim 25\times$ larger than via the X_5 intermediate state.

δE is of similar magnitude (2.5 \rightarrow 3 eV) for transitions involving all four phonons in silicon. Intrinsic indirect absorption or emission transitions assisted by the LO and LA phonons are not detectable, however,^{24,29} even though they are allowed by group theory. If we speculate that the strength of the LO- and LA-assisted absorption components in gallium phosphide might be similar, were it not for the relative enhancement of the LA transition arising from the magnitude of the relevant δE term, then we may calculate that the strength of the missing LO-assisted absorption component is only $\sim 1/25$ th of that of the observed LA-assisted component. The calculated value of A (Table II) is therefore only ~ 2.6 cm⁻¹ (eV)^{-1/2}. The position of the threshold of the LO_E component derived using the value of $\hbar\omega_{LO}$ given in Table III, column 3, is noted in Fig. 1. Since the strength of the LO_E component thus estimated is only $\sim 10\%$ of that of the TO_E component which commences at an energy only ~ 2 meV higher, it is clear from the transmission spectra that the LO-phonon-assisted component cannot readily be detected in the intrinsic absorption spectrum.

The value of $\hbar\omega_{LO}^x$ obtained from half the Raman shift of a prominent peak in the second-order Raman spectrum³⁴ is probably correct. We may then evaluate the quantity

$$\Delta_{K_x} = \left[\sum_{i=1}^6 \omega_i^2(K_x) - \sum_{i=1}^6 \omega_i^2(0) \right] / \sum_{i=1}^6 \omega_i^2(0) \quad (10)$$

for phonons at the $\langle 100 \rangle$ zone boundaries in gallium phosphide, using the phonon energies given in Table III, column 2, together with this value of $\hbar\omega_{LO}^x$. According to the Brout sum rule,⁴³ Δ should be zero independent of the phonon wave vector. In fact $\Delta_{K_x} = 0.15$ for gallium phosphide. Rosenstock has pointed out⁴⁴ that Brout's rule is satisfied for germanium (and silicon), but not for diamond. Using more recently determined lattice dispersion data for diamond,⁴⁵ $\Delta_{K_x} = 0.22$ and $\Delta_{K_L} = 0.15$ (at the $\langle 111 \rangle$ zone boundaries). Δ_{K_x} and Δ_{K_L}

are, respectively, 0.11 and 0.09 for gallium arsenide, according to the energies given in reference.³⁷ Patrick *et al.*⁴⁶ have applied the sum rule to phonon energies in silicon carbide, and conclude that Δ_{K_x} is 0.16 for the wurtzite polytype 2H and is 0.14 for cubic (zinc-blende) silicon carbide. The importance of the "nonelectrostatic" interatomic forces defined by Rosenstock⁴⁴ therefore appears to increase with the energy gap of these zinc-blende-structure crystals, rather than with the scale of the phonon energy spectra.

E. Application of the New Experimental Value of E_g to the Determination of $E_A + E_D$ from Donor-Acceptor-Pair Spectra

Good self-consistency has been obtained in derivations of the quantity $E_g - (E_A + E_D)$ from pair spectra recorded from crystals of gallium phosphide counter-doped with many different types of donor and acceptor centers.⁹ This quantity is determined from the limiting zero-phonon transition energy for radiative electron-hole recombination at donor-acceptor pairs given from the equation

$$E(r) = E_g - (E_A + E_D) + e^2/\epsilon r - (e^2/\epsilon)(\alpha^5/r^6), \quad (11)$$

when r , the separation between donor and acceptor ions, tends to infinity, e is the electronic charge, α is an adjustable van der Waals parameter and ϵ is the low-frequency dielectric constant. Because the value of E_g was taken as 2.325 + 0.005 eV (at 1.6°K) in the previous analysis,⁹ rather than 2.339 \pm 0.001 eV, as deduced from the present work, the estimates of $E_A + E_D$ obtained previously are 14 meV too low. A revised list of these quantities is presented in Table IV.

If the Hall measurements are taken at their face value ($E_D = 89$ meV for sulphur, 78 meV for silicon, 76 meV for tellurium, all ± 20 meV),¹⁰ Table IV implies that the ionization energies of Zn, Si, and Cd acceptors are, respectively, 79, 63, and 111 meV, with a large uncertainty of ± 20 meV associated with the Hall data.

TABLE IV. Sum of donor and acceptor ionization energies obtained from a quantitative analysis of donor-acceptor pair spectra.

Spectral type ² and impurities	$E_g - (E_A + E_D)$ ± 0.002 eV	$E_A + E_D$ ± 0.003 eV
I _A (Si _P Se _P)	2.1856	0.1534
I _C (Si _P Se _P)	2.1867	0.1523
I _B (Si _P Te _P)	2.2007	0.1383
II _A (Zn _{Ga} Se _P)	2.1701	0.1689
II _D (Zn _{Ga} Se _P)	2.1718	0.1672
II _C (Zn _{Ga} Te _P)	2.1848	0.1542
II _B (Cd _{Ga} Se _P)	2.1369	0.2021
II _E (Cd _{Ga} Se _P)	2.1383	0.2007
II _F (Cd _{Ga} Te _P)	2.1517	0.1873

⁴⁶ L. Patrick, D. R. Hamilton, and W. J. Choyke, Phys. Rev. **143**, 526 (1966).

⁴² R. Loudon (private communication).

⁴³ R. Brout, Phys. Rev. **113**, 43 (1959).

⁴⁴ H. B. Rosenstock, Phys. Rev. **129**, 1959 (1963).

⁴⁵ J. L. Warren, R. G. Wenzel, and J. L. Yarnell, Symposium on the Inelastic Scattering of Neutrons in Solids, Bombay, 1964 (unpublished); see also P. J. Dean, E. C. Lightowers, and D. R. Wight, Phys. Rev. **140**, A352, 1965.

These results suggest that the variation of E_A between different acceptor centers is appreciably larger than the variation of E_D between these donors, but that E_A and E_D are generally of the same order for these substitutional impurities.

The values of E_A for Zn and Cd acceptors derived from the pair spectra are rather higher than previous estimates obtained from Hall measurements,⁷ although there is agreement in the conclusion that $(E_A)_{Cd}$ is significantly greater than $(E_A)_{Zn}$.

F. Ionization Energies of Bound-Exciton Complexes

The increased value of E_{gx} at 1.6°K, proposed in this paper (increased from 2.315 ± 0.003 eV¹² to 2.3285 ± 0.001 eV) implies a considerable increase in the binding energies E_{Bx} of the bound-exciton complexes which have been identified in gallium phosphide.^{1,3} E_{Bx} is determined from the energy difference between E_{gx} and the observed zero-phonon transition energies. The new estimates are given in column 3 of Table V and are

TABLE V. Optically determined binding energies E_{Bx} of excitons in various bound-exciton complexes which have been identified in gallium phosphide (measured at 1.6°K).

Nature of center binding exciton (all substitutional)	Observed zero-phonon transition energy (eV)	Revised E_{Bx} (meV)
Single N (isoelectronic) (<i>A</i> line)	2.3171	11
Single N (isoelectronic) (<i>B</i> line)	2.3162	12
Neutral S donor (<i>C</i> line)	2.3095	19
Pairs of nitrogen atoms on phosphorus sites. The subscripts refer to first-nearest neighbor, second-nearest neighbor, etc.	NN ₁₀ 2.3110 NN ₇ 2.3059 NN ₆ 2.3033 NN ₅ 2.2970 NN ₄ 2.2894 NN ₃ 2.2644 NN ₂ 2.1901 NN ₁ 2.1854	18 22 25 31 39 64 138 143

13 meV larger than the previous values. E_{Bx} was previously thought to be only 1 or 2 meV for the *A* center. The transition energies given in column 2 are 0.6 meV lower than previously reported values¹ because of the neglect of an air-to-vacuum wavelength correction factor. Fine structure has been neglected in the energies listed for the "NN" lines, the energies refer to the most intense absorption component.

G. Comments on the Nature of the Green Electroluminescence Observed at 300°K from Gallium-Phosphide Diodes

The most prominent spectral component in the electroluminescence or photoluminescence of gallium phosphide at 300°K is the broad band centered at ~ 1.8 eV ("red" band), which has been identified with pair recombination of holes trapped on shallow zinc acceptors

with electrons trapped on relatively deep oxygen donors.^{4,47} Much weaker "green" emission bands have also been observed at photon energies closer to the energy gap. The "green" luminescence from heavily doped *p-n* junctions at 77°K has been clearly identified with pair radiation involving the shallow donors and acceptors discussed in Sec. IVE.^{8,48}

The transitions involved in the green luminescence at 300°K are less certain. Two green bands have been recently reported at 300°K which are separated by an energy equal to the difference of the ionization energies of the sulphur and tellurium donors with which the crystals were doped. Consequently these bands were ascribed to Zn-S and Zn-Te pair recombination.⁴⁸ The reported energies of the peak intensities of these bands lie ~ 90 and 65 meV below E_g for Zn-S and Zn-Te pairs, respectively, using the value of $2.248 + E_x = 2.26$ eV obtained from Fig. 2 at 300°K. The comparable photoluminescence energies at 1.6°K are 139 and 124 meV, respectively. It seems unlikely that more than ~ 10 to 20% of the discrepancy of 50 to 60 meV could be attributed to a shift due to the higher pumping levels possible in electroluminescence compared with photoluminescence.^{2,8}

Considerations of the thermal stability of these neutral donor-acceptor pairs at 300°K suggest that pair transitions should not play an important part in the recombination process, since it has been observed that at 20°K the pair luminescence takes between 10^{-5} and 10^{-4} sec to decay to 50% of its initial value,⁴⁹ and also since the ionization energies of individual donor and acceptor centers will be significantly reduced from their "isolated" values of 0.06 to 0.11 eV (Sec. IVE) because of the donor-acceptor interaction.²⁸ These reduced ionization energies will be only $\lesssim 2kT$ at 300°K for the relatively close pairs which would satisfy the observed peak energies.⁴⁸

It is more likely that this type of green luminescence arises from the radiative recombination of free holes at neutral donor centers, which is a more favorable recombination mechanism at high temperatures.⁵⁰ The peak intensity would then be expected to lie below E_g by an energy E_1 equal to the donor ionization energy, subject to slight corrections for the kinetic energy of the free holes (reduces E_1) and for possible phonon cooperation (increases E_1). The observed values of E_1 are consistent with this expectation when compared with the Hall values of E_D .¹⁰

A careful analysis of the variation in this green emission spectrum between 77 and 300°K is required in order to observe the expected transformation from the "pair" spectrum to the "free-to-bound" spectrum.

⁴⁷ M. Gershenson, F. A. Trumbore, R. M. Mikulyak, and M. Kowalchik, J. Appl. Phys. **37**, 483 (1966).

⁴⁸ L. M. Foster and M. Pilkuhn, Appl. Phys. Letters **7**, 65 (1965).

⁴⁹ D. G. Thomas, J. J. Hopfield, and W. M. Augustiniak, Phys. Rev. **140**, A202 (1965).

⁵⁰ K. Colbow, Phys. Rev. **141**, 742 (1966).

However, the reported values for the peak energies of the green band in Zn-Te doped diodes at 77 and 300°K are very similar,⁴⁸ whereas a decrease of ~ 75 meV should have been observed between these temperatures according to Fig. 2, if the emission is due to pair transitions at both temperatures. This energy probably represents the ionization energy of Zn acceptors (Sec. IVE) which must be subtracted from E_g to give the position of the luminescence band at 77°K, but not at 300°K, according to the models proposed above.

Gershenson *et al.*, have shown that a green emission system spectrally quite different from the one discussed above appears in the electroluminescence spectrum of relatively lightly doped gallium-phosphide diodes as the temperature is increased from 77 to 300°K and above.⁸ It was suggested⁸ that this system is due to recombinations of holes with the donor center then thought to be responsible for the *A*, *B* exciton luminescence at low temperatures.¹ It is now known that the *A*, *B* lines are due to excitons bound to an isoelectronic substitutional impurity, however.³

SUMMARY

The analysis of new accurate measurements of the dependence of the indirect-edge-absorption coefficient of gallium phosphide on the photon energy at many temperatures between 1.6 and 300°K has shown that the magnitude of this energy gap is larger than previous estimates, especially at the higher temperatures. The energies of phonons which assist in these optical transitions have been measured from the energy intervals between optical thresholds and (for two low-energy phonons) from the temperature dependence of the intensity of optical components which involve phonon absorption (anti-Stokes components). The classification of these phonons has been considered, and it is found that the new set of phonon energies can only be partially reconciled with the phonon energies previously derived from the intrinsic infrared absorption spectrum of gallium-phosphide, and from Raman-scattering measurements. Since the derivation of the energies of single phonons from the edge-absorption spectrum is more direct than from the other measurements, it is probable that the infrared and Raman spectra should be reinterpreted using the phonon energies found in the present work. Information about the virtual electronic states associated with the phonon-scattering processes in the indirect transitions can be derived from the absorption spectra, and an estimate of the internal binding energy of the indirect exciton has also been obtained. Fine structure has been observed in the main absorption components at 1.6°K, and is attributed to the creation of indirect excitons in two slightly different energy states. Significant deviations between the observed shape of some of the individual absorption sub-components and the theoretical predictions for indirect transitions have been observed. No definitive explana-

tion for the origin of these deviations can be offered at present but they apparently arise from anomalies in the combined exciton-phonon dispersion curves for the indirect transitions in gallium phosphide and were not seen in indirect absorption spectra of silicon or germanium. The new values of E_g and E_{gx} necessitate revisions in the quantitative analysis of the spectra of donor-acceptor pairs and bound excitons in gallium phosphide, and also enable new interpretations of some green room-temperature luminescence systems to be made. No evidence has been obtained for absorption components associated with the split-off valence band. Since the spin-orbit splitting of the valence band is ~ 0.13 eV⁵¹ it is likely that the broadening of these absorption components at 1.6°K will be nearly two orders of magnitude greater than for the indirect components associated with the upper pair of valence bands because of intervalence band scattering processes.²²

Two papers relevant to the work discussed above have recently come to the authors attention. Russell has reported new Raman scattering measurements on gallium phosphide at 20°K⁵² containing more structure than the earlier room temperature measurements.³⁴ The energies of individual phonons at the *X* point consistent with Russell's assignments of the new spectra differ considerably from his previous values listed in column 3 of Table III, except for $\hbar\omega_{TA}$. The new Raman value for $\hbar\omega_{LA}$ is increased by 14 to 35.3 meV, and is now 4 meV larger than the estimate from the absorption edge. According to the new data, $\hbar\omega_{TO}$ is also increased to 48.6 meV, now also significantly higher than the absorption edge value given in Table III. The present authors feel that the assignments made from the new Raman data should also be viewed with caution because of these discrepancies.

The results of a recent study of the edge-absorption spectrum of gallium phosphide made by Gorban and Kosarev⁵³ are inconsistent with those reported in this paper. The spectra were recorded between 103 and 290°K from crystals which exhibited a relatively strong absorption line close to the exciton energy gap. It was suggested that this line arises from the creation of free excitons without phonon participation in the presence of high concentrations ($\sim 5 \times 10^{18}$ cm⁻³) of unknown impurities. Although the transition energy reported for this line (2.315 eV) is ~ 10 meV greater than for the *A* line at 103°K, the threshold energy of the principal intrinsic absorption-edge component, identified as LA_E in Fig. 1 of this paper, is ~ 8 meV higher than the 103°K value obtained from Fig. 2 of this paper. The present authors therefore believe that the 2.315-eV line

⁵¹ J. W. Hodby, Proc. Phys. Soc. (London) **82**, 324 (1963).

⁵² J. P. Russell, J. Phys. (Paris) **26**, 629 (1965).

⁵³ I. S. Gorban and V. M. Kosarev, Fiz. Tverd. Tela **7**, 3641 (1965) [English transl.: Soviet Phys.—Solid State **7**, 2934 (1966)].

is the incorrectly located A line since no strong impurity absorption lines have been observed at higher energies than the A line, other than satellites of the A line, during an extensive investigation of the edge absorption spectra of gallium phosphide including doped as well as undoped crystals. The origin of the A absorption line is fully discussed in Ref. (3). Some of the absorption structure attributed by Gorban and Kosarev to intrinsic processes, such as that involving an 8-meV phonon, is not intrinsic but is associated with the presence of the strong A no-phonon line. For these reasons the inter-

pretation of the absorption-edge structure of gallium phosphide proposed by Gorban and Kosarev is incorrect.

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Measurements of X-Ray Lattice Constant, Thermal Expansivity, and Isothermal Compressibility of Argon Crystals*

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Crystals of 99.998% purity argon were prepared by directional solidification of the liquid. The x-ray lattice constant was measured by means of a rotating-camera method, and the volume coefficient of thermal expansion was determined over the range 2.3 to 83.2°K with a precision of about 5 ppm deg⁻¹. The lattice constant extrapolated to 0°K is 5.30017 ± 0.00008 kxu. X-ray diffraction was also used to obtain a value for the isothermal compressibility at 4.25°K of $(3.75 \pm 0.05) \times 10^{-11}$ cm² dyn⁻¹. A critical synthesis of existing measurements of elastic-wave velocity and of isothermal compressibility is attempted because comparison of the present results with various theoretical models for crystalline argon is limited by the inaccuracies of elastic data. A set of compressibility values is adopted and new values for several thermodynamic functions of argon are compiled. The observed temperature variations of the Grüneisen parameter and of the Debye temperature are compared with several lattice-dynamical models.

INTRODUCTION

MANY theoretical models for noble gas crystals have been studied. Precise and extensive experimental data on the actual crystals are, of course, also necessary. Existing work, primarily on argon, has been summarized in several review articles.¹⁻⁴ According to these, much of the experimental information presently available is qualitative and practically none has been obtained from single-crystal specimens. The present paper reports a study, by means of x-ray diffraction, of several properties of pure massive crystals of argon:

lattice constant, thermal expansivity, and isothermal compressibility.

X-ray measurements of the lattice structure and lattice constant of solid argon at a single temperature were reported as early as 1924 by Simon and von Simon⁵ and in 1925 by De Smedt and Keesom.⁶ More extensive determinations of lattice constants of microcrystalline specimens in a range above 20°K were made by Dobbs and co-workers⁷ in 1956 by means of a powder camera. They achieved an accuracy of 0.06%, but were forced to stop taking measurements at 60°K because of grain growth. Powder diffractometers have been used more recently over a wider temperature range by Bolz and Mauer⁸ and by Barrett and Meyer.⁹ Barrett and Meyer were able to extend their measurements to 64°K by cold working their specimens and then annealing them to produce suitable polycrystalline x-ray samples. They also obtained one single-crystal measurement at 81°K with the same diffractometer

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