PHYSICAL REVIEW VOLUME 168, NUMBER 3 15 APRIL 1968

Energy-Dependent Capture Cross Sections and the Photoluminescence Excitation Spectra of Gallium Phosphide above the Threshold for Intrinsic Interband Absorption

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(Received 11 December 1967)

Oscillatory structure connected with intrinsic absorption processes involving the $\Gamma_{15} \rightarrow X_1$ indirect energy gap and an enhanced response near the $\Gamma_{15} \rightarrow \Gamma_1$ direct energy gap have been observed in the luminescence excitation spectra of excitons bound to nitrogen and bismuth isoelectronic substituents in gallium phosphide. The oscillation period indicates that hot photogenerated indirect excitons rapidly lose energy by the cascade emission of low-wave-number longitudinal optical phonons without undergoing dissociation. The oscillatory structure appears in the luminescence excitation spectra of these centers, although it cannot be seen in absorption, because *excitons* of *low* kinetic energy are preferentially captured by the isoelectronic impurities. Thus the impurity center induces an energy-dependent capture cross section because of the presence of a shallow bound state. A lifetime effect is the only one of several mechanisms suggested for the oscillatory structure observed in interband photoconductivity excitation spectra of several direct-gap semiconductors which can be relevant in luminescence excitation spectra. Just below the $\Gamma_{15} \rightarrow \Gamma_1$ direct energy gap, near the onset of the second region of anomalous luminescence response, indirect absorption is predominantly due to transitions which produce *low* kinetic-energy *holes*. It is believed that these absorption transitions preferentially contribute to the luminescence excitation spectra because the probability of forming the excited states of these impurity complexes, particularly for nitrogen, is much greater for cold holes. Excitation spectra of shallow donor-acceptor pair luminescence in gallium phosphide do not show either of these selective excitation effects. The shape of the spectra can be accounted for solely from a consideration of the intrinsic absorption spectrum, including processes involving the creation of free-electron hole pairs as well as free excitons, and surface recombination processes. The latter processes depend in detail upon the particular crystal and, as previously reported by Gershenzon and Mikulyak, upon which of the principal ⟨111⟩ faces of solution-grown platelets is illuminated. The $\Gamma_{15} \rightarrow \Gamma_1$ direct exciton transition appears as a well-defined dip in the low-temperature excitation spectra of pair luminescence.

I. INTRODUCTION

It is well known that impurity luminescence can be efficiently excited in semiconductors by intrinsic absorption processes which involve the creation of free excitons and/or free electron-hole pairs. The form of the luminescence excitation spectrum is generally very similar to the intrinsic absorption spectrum, subject to a monotonic decrease in the excitation efficiency due to the increasing influence of the generally strong and radiationless surface recombination at the higher absorption coefficients.[1] This will be true if impurity-induced absorption, particularly that of the activating impurity, is negligible compared with the intrinsic absorption. In addition, either the relevant capture cross sections of the luminescent and competing nonradiative centers must be independent of the kinetic energies of the free photoexcited quasiparticles, or, alternatively, these particles must come to thermal equilibrium with the lattice before capture occurs. The present paper shows that this simple behavior is exhibited in the excitation spectra of shallow (green) donor-acceptor pair luminescence in gallium phosphide, as was previously found for deep (red) pair luminescence.[2] The $\Gamma_{15} \rightarrow \Gamma_1$ direct exciton transition and the transition from the component of the Γ_{15} valence band split off by spin-orbit interaction are clearly observed as minima in these excitation spectra, since they occur well above the peak in the luminescence response.

The present paper draws attention to complications which may occur in the low-temperature excitation spectra of dilutely doped crystals if the above conditions are not realized and if the luminescence efficiency is significantly less than unity, as is usually so. Two possible sources of complication arise. First, the impurity-induced partial absorption coefficient representing processes in which the luminescence center is left in its discrete excited state may be enhanced, relative to other possible absorption processes, in the luminescence excitation spectrum. The enhancement occurs since these excitations produce efficient luminescence at low temperatures.[3] The partial absorption coefficient due to the stokes phonon-assisted creation of excitons bound to isoelectronic nitrogen substituents in gallium phosphide has already been examined in this way, and a variety of interference effects between different partial absorption coefficients were noted.[4] Second, the luminescence center may act as a selective indicator of particular final states reached in *intrinsic* absorption processes ("selective excitation" effect). Oscillatory structure just above the

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[1] "Dead-layer" effects due to surface recombination are a well-known feature of cathodoluminescence. See, for example, G. Gergely, Acta. Phys. Hungary **12**, 253 (1960); D. B. Wittry and D. F. Kaiser, J. Appl. Phys. **38**, 375 (1967). For a quantitative discussion of surface recombination in photoluminescence, see J. Vilms and W. E. Spicer, J. Appl. Phys. **36**, 2815 (1965).

[2] M. Gershenzon and R. M. Mikulyak, Appl. Phys. Letters **8**, 245 (1966).

[3] There is no possibility of Auger recombination within the isoelectronic impurity-bound exciton complexes considered in this paper because only two electronic particles are present. See D. F. Nelson, J. D. Cuthbert, P. J. Dean, and D. G. Thomas, Phys. Rev. Letters **17**, 1262 (1966).

[4] J. J. Hopfield, P. J. Dean, and D. G. Thomas, Phys. Rev. **158**, 748 (1967).

$\Gamma_{15} \rightarrow X_1$ indirect energy gap and a broad anomalous response near the $\Gamma_{15} \rightarrow \Gamma_1$ direct energy gap in excitation spectra of the luminescence of excitons bound to bismuth[5] and nitrogen[6] isoelectronic substituents in gallium phosphide, but not for shallow donor-acceptor pair luminescence, are reported in the present paper. These anomalous luminescence excitation features, which do not appear in the optical-absorption spectra, are attributed to selective excitation effects involving preferential capture cross sections at these centers for free quasiparticles of low kinetic energy.

II. EXPERIMENTAL

A. Crystals

Gallium phosphide single crystals deliberately doped with the isoelectronic impurities nitrogen or bismuth or with group II and VI acceptor and donor impurities were studied. Some of these crystals were grown from the vapor using a modified wet hydrogen transport method.[7] Most were grown from gallium solution to which the impurities were added as described by Trumbore *et al.*[8] and by Thomas and Lynch.[9]

B. Optical Measurements

Optical-absorption and luminescence-excitation spectra were obtained with the crystal cooled to near 20°K by means of the gas-cooling technique described by Maeda,[10] but using liquid helium instead of liquid hydrogen. Some luminescence-excitation spectra were recorded with the crystals immersed in liquid helium. For the excitation measurements, light from a 650-W tungsten-iodine lamp was passed through a Spex $\frac{3}{4}$-m monochromator and focused onto the crystals. The luminescence was measured with an EMI 9558 QA photomultiplier placed as near to the crystal as was practicable. A Corning filter between the crystal and photomultiplier cathode blocked the exciting radiation

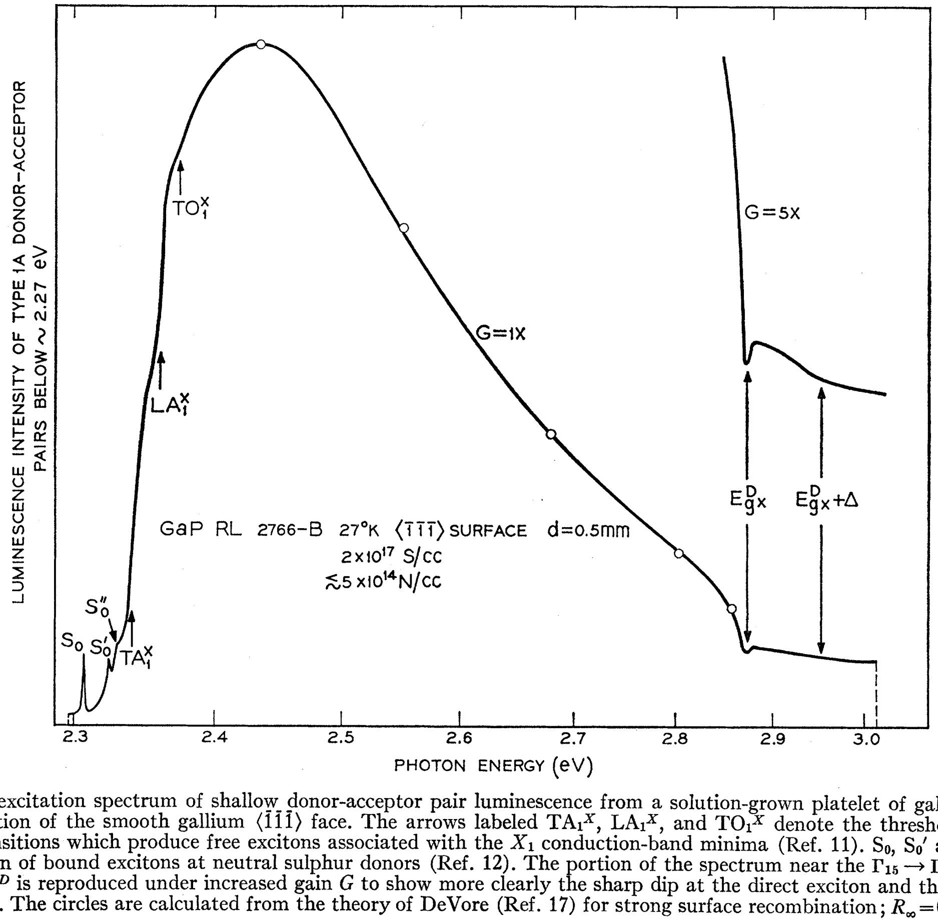

FIG. 1. The excitation spectrum of shallow donor-acceptor pair luminescence from a solution-grown platelet of gallium phosphide under illumination of the smooth gallium $\langle\bar{1}\bar{1}\bar{1}\rangle$ face. The arrows labeled TA_1^X, LA_1^X, and TO_1^X denote the thresholds of intrinsic absorption transitions which produce free excitons associated with the X_1 conduction-band minima (Ref. 11). S_0, S_0' and S_0'' are due to the formation of bound excitons at neutral sulphur donors (Ref. 12). The portion of the spectrum near the $\Gamma_{15} \rightarrow \Gamma_1$ direct exciton energy gap E_{gx}^D is reproduced under increased gain G to show more clearly the sharp dip at the direct exciton and the much broader dip at $E_{gx}^D + \Delta$. The circles are calculated from the theory of DeVore (Ref. 17) for strong surface recombination; $R_\infty = 0.1$ and $d/\ell = 10$ (see text).

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[5] F. A. Trumbore, M. Gershenzon, and D. G. Thomas, Appl. Phys. Letters **9**, 4 (1966).

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

[7] C. J. Frosch, *Crystal Growth* (Pergamon Press, Inc., New York, 1967), p. 305.

[8] F. A. Trumbore, H. G. White, M. Kowalchik, and R. A. Logan, J. Electrochem. Soc. **112**, 1208 (1965).

[9] D. G. Thomas and R. T. Lynch, J. Phys. Chem. Solids **28**, 433 (1967).

[10] K. Maeda, J. Phys. Chem. Solids **26**, 595 (1965).

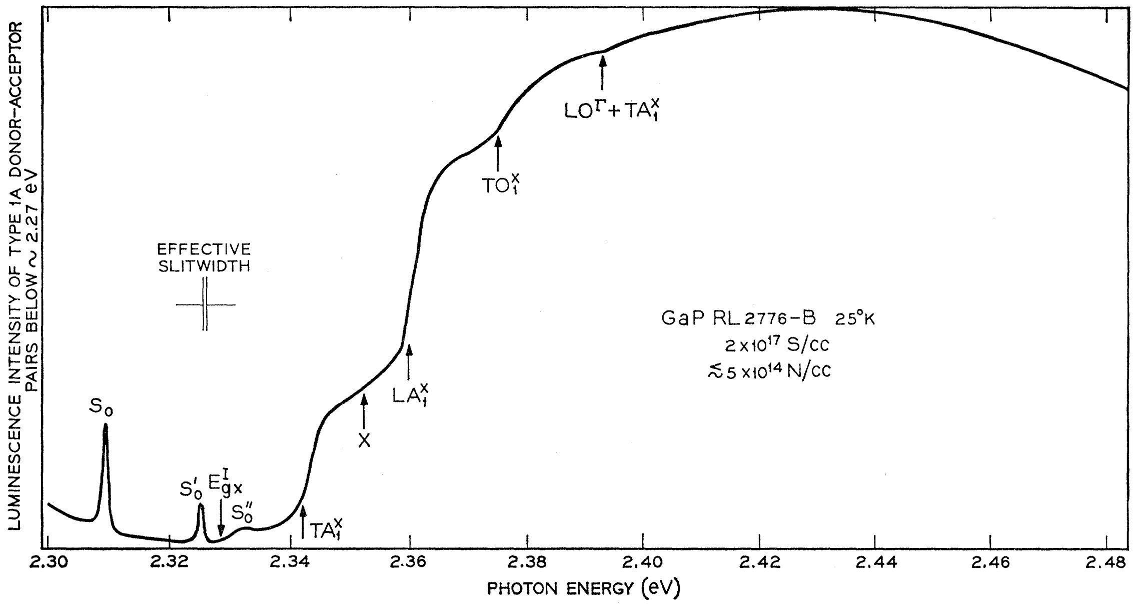

FIG. 2. Detail in the excitation spectrum of shallow donor-acceptor pair luminescence near the indirect energy gap. The indirect exciton energy gap is denoted by E_{gx}^I. The threshold of a two-phonon assisted absorption component $LO^\Gamma + TA_1^X$ can be clearly seen in addition to the indirect gap thresholds marked in Fig. 1. The onset of free-carrier absorption assisted by the transverse acoustical MC phonon TA_1^X occurs near X (Ref. 11).

and, usually in conjunction with the low-energy response of the S-20 type photomultiplier (~1.5 eV), served to define the energy interval within which luminescence could be detected.

III. RESULTS: GENERAL SHAPE OF LUMINESCENCE EXCITATION SPECTRA

A. Donor-Acceptor Pair Luminescence

1. Detailed Structure near the Indirect and Direct Energy Gaps

The luminescence excitation spectrum in Fig. 1 contains well-defined low-energy thresholds due to the photoexcitation of indirect free excitons with the emission of the indicated momentum-conserving (MC) phonons.[11] The threshold associated with the $LO^\Gamma + TA_1^X$ two-phonon-assisted transition is more clearly defined in the expanded luminescence-excitation spectrum of Fig. 2 than in the intrinsic-absorption spectrum. Above ~2.34 eV, the spectra in Figs. 1 and 2 are otherwise quite similar to the intrinsic absorption spectra, apart from the general decrease in excitation efficiency with increase in photon energy discussed in Sec. III A 2. The inflection near X in Fig. 2, ~10 meV above the TA^X intrinsic exciton threshold, is due to the onset of absorption into free-electron pole-pair states.[11]

The sharp lines S_0 and S_0' are due to bound exciton states at neutral sulphur donors.[12] The intensities of these lines increase significantly relative to the broad intrinsic peak near 2.42 eV with increasing temperature between 4 and ~60°K. Thermal dissociation of this bound exciton complex is significant in this temperature range.[12] The luminescence-excitation spectra show that many of the free-electron hole pairs thereby produced recombine at shallow donor-acceptor pairs. The intensity ratio S_0'/S_0 is ~2.5 times larger in Fig. 2 than in the absorption spectra of the sulphur-exciton complex[13] because the probability of thermal ionization is significantly higher at a given temperature for the less tightly bound excited exciton state. Tunneling energy-transfer processes are probably responsible for the weak contribution of these bound-exciton absorption lines in the luminescence-excitation spectra recorded at 4.2°K. Tunneling processes are believed to be responsible for the quenching of low-temperature luminescence due to excitons weakly bound at isoelectronic nitrogen impurities observed in relatively heavily doped crystals of gallium phosphide.[14]

The structure near E_{gx}^I and E_{gx}^D is more clearly defined in the low-temperature luminescence-excitation spectrum of Fig. 1 than in the 90°K spectrum recently reported by Gorban' and Kosarev for luminescence of deep donor-acceptor pairs.[15] In particular, direct transitions to the broadened exciton state involving holes from the lower component of the valence band, split off by spin-orbit coupling, can be clearly seen as a broad dip in the high-gain detail in Fig. 1. The spin-orbit splitting Δ obtained from the luminescence-excita-

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[11] P. J. Dean and D. G. Thomas, Phys. Rev. **150**, 690 (1966).

[12] P. J. Dean, Phys. Rev. **157**, 655 (1967).

[13] See Fig. 4 of Ref. 12.

[14] D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966).

[15] I. S. Gorban' and V. M. Kosarev, Fiz. Tverd. Tela **8**, 3697 (1966) [English transl.: Soviet Phys.—Solid State **8**, 2967 (1967)].

tion spectra ($\sim$80 meV) agrees well with the value recently obtained from absorption spectra of thin vapor-grown single-crystal ribbons.[16] As a result of surface recombination (Sec. III A 2), the $\Gamma_{15} \rightarrow \Gamma_1$ direct exciton transitions, which produce high values of the absorption coefficient $\alpha \gtrsim 10^4$ cm^{-1}, always appear as *minima* in excitation spectra of shallow donor-acceptor pair luminescence. Crystal RL 2766-B exhibits the minimal half-height bandwidth for the lowest energy $\Gamma_{15} \rightarrow \Gamma_1$ direct exciton transition, $\sim$7.5 meV, observed in the luminescence-excitation spectra.

2. *General Shape of the Luminescence-Excitation Spectra: Surface Recombination*

The broad maximum generally observed in the excita-spectra, near 2.435 eV for the n-type crystal in Fig. 1, is produced by surface recombination. The donor-acceptor pair luminescence is nonselectively excited by free excitons and free-electron hole pairs (Sec. III A 1) and is linearly related to the low-level excitation intensity. The spectral shape should therefore be adequately described by a theory due to DeVore which uses the minority carrier diffusion length ℓ and the ratio of surface-to-volume recombination rates as adjustable parameters.[17] From the value of αd at the peak response in Fig. 1 ($\sim$2.5), where d is the crystal thickness, ℓ can be calculated from the simple expression appropriate to strong surface recombination:

$$\ell = d/[(\exp\alpha d) - \alpha d - 1]. \tag{1}$$

The resulting value, $\sim 50\,\mu$, is slightly larger than 20°K values previously obtained by Gershenzon and Mikulyak[2] for the smooth gallium $\langle\bar{1}\,\bar{1}\,\bar{1}\rangle$ faces of solution-grown p-type crystals, but is comparable with 90°K values reported for an n-type crystal by Gorban' and Kosarev.[15] For n-type crystals, ℓ is reported to increase exponentially with increasing temperature between 90 and $\sim$200°K,[15] whereas ℓ decreases with temperature between 20 and 300°K for smooth $\langle\bar{1}\,\bar{1}\,\bar{1}\rangle$ faces of p-type crystals.[2]

The surface recombination velocity S can be calculated from the asymptotic luminescence response at large αd, R_∞ (measured relative to the peak response) and the minority carrier diffusion constant D using the relationship

$$R_\infty = D/S\ell. \tag{2}$$

With $\ell = 50\,\mu$, $D \sim 4.5 \times 10^{-3}$ cm^2 sec^{-1} at 27°K,[2] and $R_\infty \sim 0.085$ (Fig. 1), S is $\sim$10 cm sec^{-1}. This result is similar to values reported by Gershenzon and Mikulyak for fresh $\langle\bar{1}\,\bar{1}\,\bar{1}\rangle$ surfaces, although R_∞ is lower than reported by them, since the effect of the decreased high-energy response is cancelled in the calculation of S by the larger value of ℓ observed in the present work. Typical values of R_∞ observed in the present work were $\lesssim 0.1$, indicating low shallow donor-acceptor pair photoluminescence excitation efficiency for gallium phosphide under 3650 Å ($\sim$3.4 eV) Hg arc excitation at temperatures $\lesssim$25°K (see Ref. 2).

Low-temperature excitation spectra for the yellow shallow donor-acceptor pair luminescence were compared for the rough $\langle 111\rangle$ phosphorus faces and smooth $\langle\bar{1}\,\bar{1}\,\bar{1}\rangle$ gallium faces of solution-grown platelets freshly etched in hydrochloric acid. Like the excitation spectra of deep donor-acceptor pairs,[2] the $\langle 111\rangle$ faces showed significantly increased surface recombination and decreased minority carrier diffusion lengths, but the values of ℓ and S were consistently larger near 20°K than those reported by Gershenzon and Mikulyak. For the n-type crystal illustrated in Fig. 3, ℓ and S are $\sim 80\,\mu$ and $\sim$20 cm sec^{-1} for the $\langle 111\rangle$ surface and are $\sim 10\,\mu$ and $\sim$120 cm sec^{-1} for the $\langle\bar{1}\bar{1}\bar{1}\rangle$ surface according to Eq. (2), with $D = 2.7 \times 10^{-3}$ cm^2 sec^{-1} at 16°K. The values of ℓ reported here and in Ref. 2 correspond to surprisingly large values of the minority carrier lifetime, $\sim$1 msec. The lifetime estimated by this method is probably not simply the lifetime of free carriers, but may be extended by minority carrier tunneling between impurity centers before recombination occurs.

The minimum due to the $\Gamma_{15} \rightarrow \Gamma_1$ direct exciton is ill defined in Fig. 3 compared with Fig. 1. This may be due in part to the higher concentration of sulphur donors in crystal C-11 compared with RL 2766-B ($\sim 2.5 \times 10^{17}$ cm^{-3} neutral sulphur donors), but internal strain may also contribute significantly to the broadening of this transition.[16]

Excitation spectra recorded from mechanically polished $\langle\bar{1}\bar{1}\bar{1}\rangle$ or $\langle 111\rangle$ faces of solution-grown crystals generally show values of ℓ comparable with etched $\langle 111\rangle$ faces, but significantly larger values of S. The luminescence response decreases very rapidly with increasing energy at the low-energy tail of the direct exciton transition, becoming immeasurably low near 2.86 eV in extreme cases.

B. Exciton Luminescence at Isoelectronic Nitrogen Impurities

1. *General Shape below 2.8 eV*

The general shape of the excitation spectrum for the luminescence of excitons weakly bound to isoelectronic nitrogen impurities is quite different from the spectra in Figs. 1–3. Figure 4 shows that the peak intensities occur at appreciably higher energies, corresponding to lower values of the minority carrier diffusion length ℓ. In particular, the 20°K peak luminescence intensities of crystals showing pronounced oscillatory response just above $E_{gx}{}^I$ at 4.2°K occurred at values of αd between $\sim$20 and $\sim$40 (peak response near 2.68 or 2.76 eV for a 0.4-mm crystal) corresponding to 30 Å$\gtrsim \ell \gtrsim$3 Å according to Eq. (1). If $D \sim 3.5 \times 10^{-3}$ cm^2 sec^{-1} at 20°K, such small values of ℓ are anticipated for these crystals

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[16] P. J. Dean, G. Kaminsky, and R. B. Zetterstrom, J. Appl. Phys. **38**, 3551 (1967).

[17] H. B. DeVore, Phys. Rev. **102**, 86 (1956).

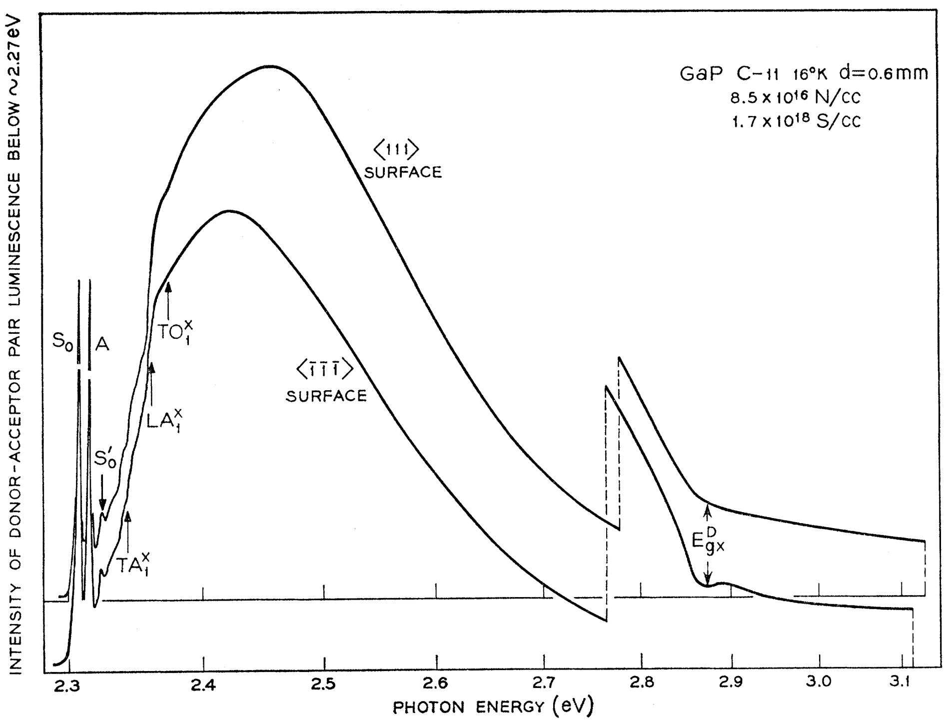

FIG. 3. Typical excitation spectra of shallow donor-acceptor pair luminescence from a solution-grown platelet of gallium phosphide for illumination of the smooth gallium $\langle\bar{1}\bar{1}\bar{1}\rangle$ face and the rough opposite phosphorous $\langle 111\rangle$ face etched by HCl. Note the energy shift in the maximum near 2.45 eV due to the relatively larger minority carrier diffusion length near the $\langle\bar{1}\bar{1}\bar{1}\rangle$ surface. The spectra and notation are similar to Fig. 1 except that the sharp band A due to excitons bound at nitrogen isoelectronic substituents (Ref. 6) is also present.

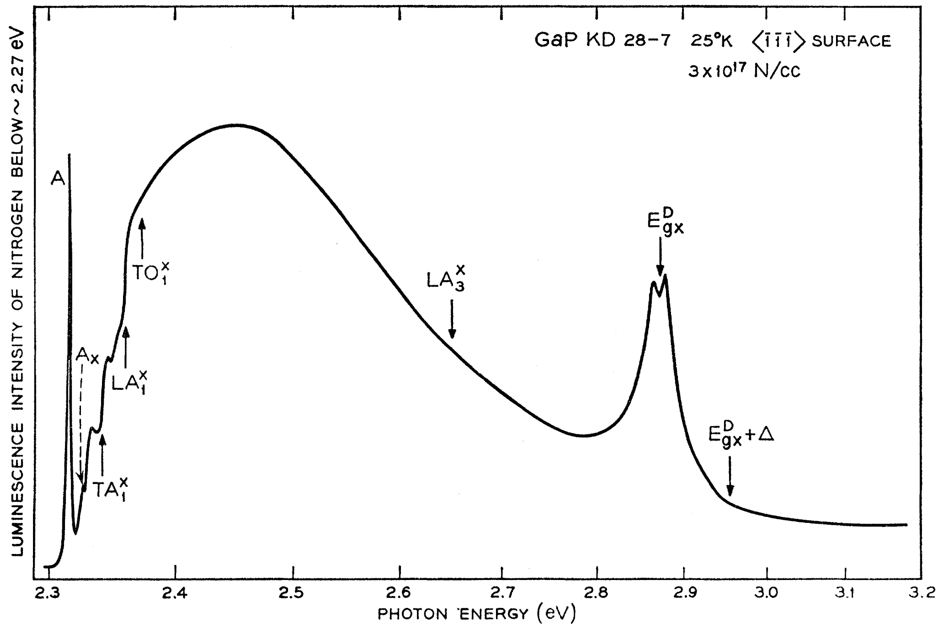

FIG. 4. The excitation spectrum of nitrogen luminescence from the smooth gallium $\langle\bar{1}\bar{1}\bar{1}\rangle$ surface of a solution-grown crystal of gallium phosphide which contains slightly more nitrogen than is typical for an "undoped" crystal. The notation is similar to Figs. 1 and 3, but in addition the nitrogen-induced line A_X, which marks the indirect exciton energy gap (Ref. 4), is noted. The very broad luminescence response centered near E_{gx}^{D} distinguishes this spectrum from those for donor-acceptor pair luminescence (Figs. 1–3). In addition, a weak inflection appears near LA_3^X, associated with the onset of transitions to the X_3 conduction-band minima (Ref. 16).

according to the very short lifetimes, ~10^{-12} sec, discussed in Sec. VI B2 for the capture of electrons or excitons at isoelectronic nitrogen impurities. The rough $\langle 111 \rangle$ faces of these crystals also generally exhibited significantly lower values of ℓ than the $\langle \bar{1}\bar{1}\bar{1} \rangle$ faces. Crystal KD 28-7 contains appreciably more nitrogen than crystals C-11 and RL 2766-B. No simple general relationship was observed between the value of ℓ and the nitrogen concentration, however, probably because of uncontrolled concentrations of other impurities in the crystals which were used.

Caution must be exercised in the analysis of nitrogen luminescence-excitation spectra according to the DeVore theory, however. Some solution-grown crystals showed a monotonically *increasing* response from 2.34 eV to the onset of the broad response peak near 2.8 eV shown in Fig. 4. This behavior is characterized by an unrealistically small value of ℓ ($\ll$1 Å) according to the surface-recombination theory. Under certain conditions, the nitrogen luminescence can be superlinearly dependent upon the excitation intensity. In addition, the nitrogen centers introduce a strong absorption cross section at energies well above the indirect energy gap of gallium phosphide,[4] unlike donor-acceptor pairs or bismuth isoelectronic centers. The absorption induced directly by only ~3×10^{18} cm^{-3} nitrogen atoms is comparable with the intrinsic absorption near the peak response of the excitation spectra for donor-acceptor pair luminescence (Figs. 1 and 3). These complications, which are particularly important at relatively high nitrogen concentrations ($\gtrsim 10^{18}$ cm^{-3}), invalidate the straightforward application of DeVore's theory of surface-recombination effects to excitation spectra of nitrogen luminescence in gallium phosphide.

2. *Luminescence Response near the Direct Energy Gap*

The broad peak in the luminescence response, centered near E_{gx}^D, is the most remarkable feature in the nitrogen luminescence excitation spectrum in Fig. 4. This peak cannot be explained on the surface-recombination theory of DeVore (Sec. III A *2*), since an *increase* of luminescence response with increasing energy can only occur above the over-all intensity peak in the luminescence-excitation spectrum as a result of a *decrease* in the absorption coefficient. This effect is responsible, for example, for the increased response just above E_{gx}^D in Fig. 1. There is no energy-dependent *decrease* in the intrinsic absorption coefficient α to account for the rise in the response between ~2.82 and ~2.87 eV in Fig. 4. In fact α *increases* very rapidly with energy in this region.[16]

It should be noted particularly that the anomalous response can be detected in Fig. 4 at least 0.1 eV below E_{gx}^D, i.e., well below the significant absorption in the tail of the broadened direct exciton transition in a good crystal (Fig. 1 and Ref. 16). Two effects appear to influence the shape of the broad response. A selective excitation effect, discussed in Sec. IV B1, produces exceptionally large nitrogen photoluminescence efficiencies at energies near the $\Gamma_{15}\rightarrow\Gamma_1$ direct energy gap. Surface recombination competes with this selective-excitation effect, as expected at the high values of αd in this region.[16] The relatively narrow dip near the maximum of the broad response peak is the most clearly distinguishable effect of surface recombination in this region in Fig. 4. This dip coincides with E_{gx}^D. The two effects are not clearly separable at other energies, but are presumably jointly responsible for the rapid decrease in the luminescence response just above E_{gx}^D.

The dip at E_{gx}^D has a half-height bandwidth of ~7 meV, as expected for the exciton absorption peak in a good solution-grown crystal (Sec. III A1). This confirms the fact that the anomalous luminescence response near E_g^D cannot be attributed to nitrogen-induced abnormal behavior of the intrinsic absorption coefficient in these crystals. Indeed, crystals containing *less* nitrogen than crystal C-11 (Fig. 3) also exhibit the anomalous luminescence response near E_g^D provided that their donor-acceptor pair concentration is sufficiently low that the detected luminescence originates predominantly at the nitrogen centers.

These observations can be understood if the anomalous luminescence response is attributed to a selective-excitation effect arising from the sensitivity of the nitrogen centers to the details of the excitation channel. The nature of this effect is discussed further in Sec. IV B1.

3. *Oscillatory Structure near Indirect Energy Gap*

Periodic fluctuations appear in the low-temperature excitation spectra of nitrogen luminescence above ~2.38 eV and can be followed to ~2.5 eV (Fig. 5). These oscillations are more difficult to see near 25°K, unlike bismuth luminescence-excitation spectra (Sec. III C). Crystal RL 52465-G used for Fig. 5 is very lightly nitrogen-doped, and its absorption spectrum above ~2.34 eV shows only the stepped structure associated with the phonon-assisted creation of free excitons (Fig. 6). The nitrogen-induced absorption features are much more prominent below 2.38 eV in the luminescence excitation spectrum (Fig. 5). This effect has been discussed in Ref. 4.

Despite the absence of the oscillations in the absorption spectrum, there are two pieces of evidence for their association with intrinsic indirect $\Gamma_{15}\rightarrow X_1$ transitions, rather than with absorption induced by the presence of the nitrogen impurities. First, the oscillations are not present in the excitation spectra at nitrogen concentrations ~10^{19} cm^{-3}, where the absorption induced directly by the nitrogen is considerably greater than the intrinsic absorption to well above 2.5 eV. This is consistent with the form of the nitrogen-induced absorption, which is substantially smooth above ~2.37 eV.[4] The oscillations can still be discerned (Fig. 7) at an intermediate nitrogen concentration, ~10^{18} cm^{-3}, where the nitrogen-induced absorption predominates below ~2.38 eV and

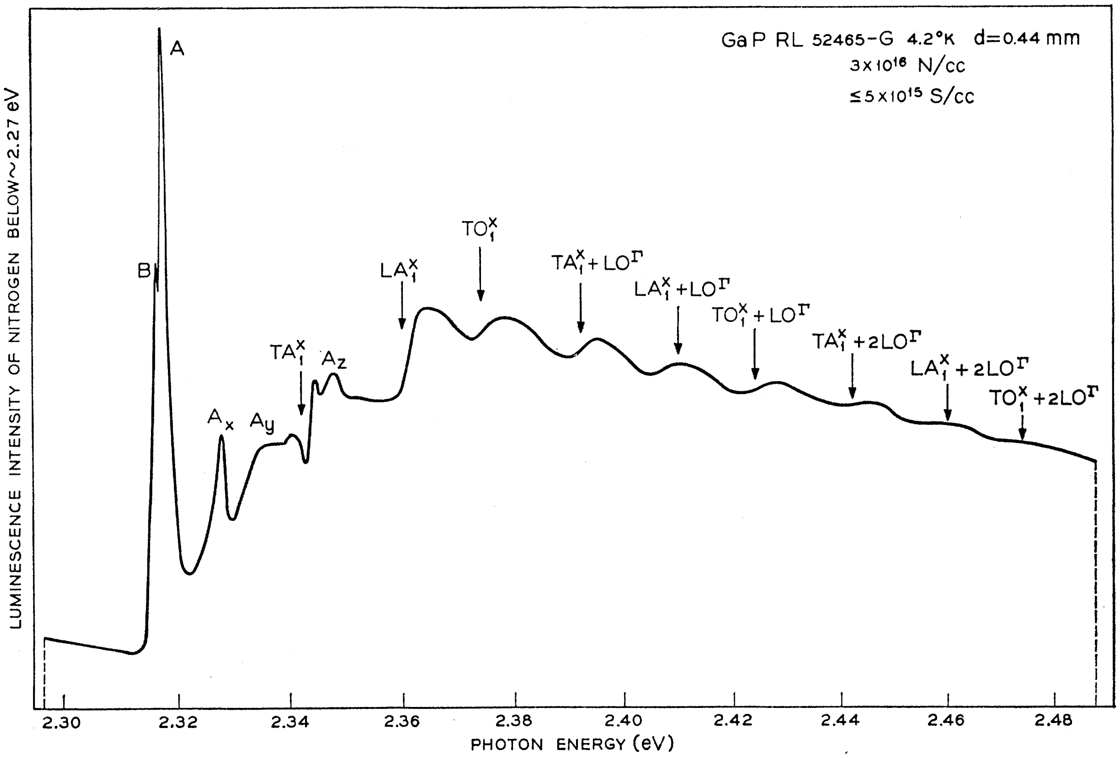

FIG. 5. The low-temperature excitation spectrum of nitrogen luminescence from a lightly nitrogen-doped solution-grown crystal of gallium phosphide uncorrected for the spectral variation in the excitation intensity. The A, B bound exciton lines are prominent, as are the line A_x and the nitrogen-induced structure at A_y and A_z. The oscillatory structure above ~2.38 eV, not present for the donor-acceptor pair luminescence, is labeled according to an interpretation given in the text.

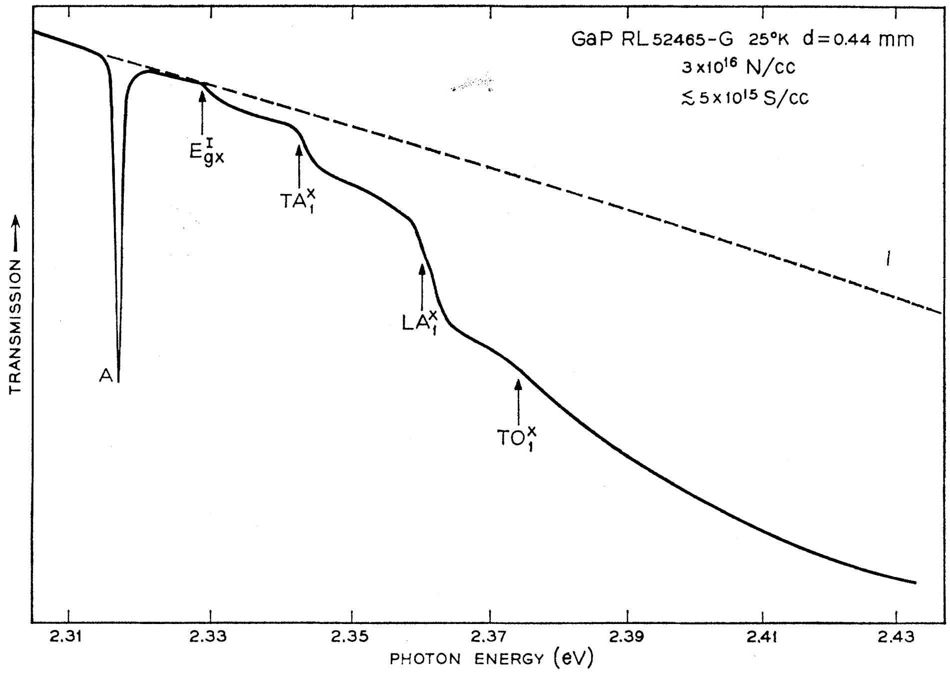

FIG. 6. The transmission spectrum of the lightly nitrogen-doped gallium phosphide crystal used for Fig. 5. The dashed line indicates 100% transmission. The $(\Delta E)^{1/2}$ form of the component starting at $E_{gx}{}^{I}$ is evident; likewise for the intrinsic phonon-assisted components with thresholds $TA_1{}^X$, $LA_1{}^X$ and $TO_1{}^X$. The no-phonon components at A and at $E^I{}_{gx}$ are induced by the nitrogen impurities (Ref. 4). Note that component A_X cannot be seen in absorption although it is prominent in Fig. 5.

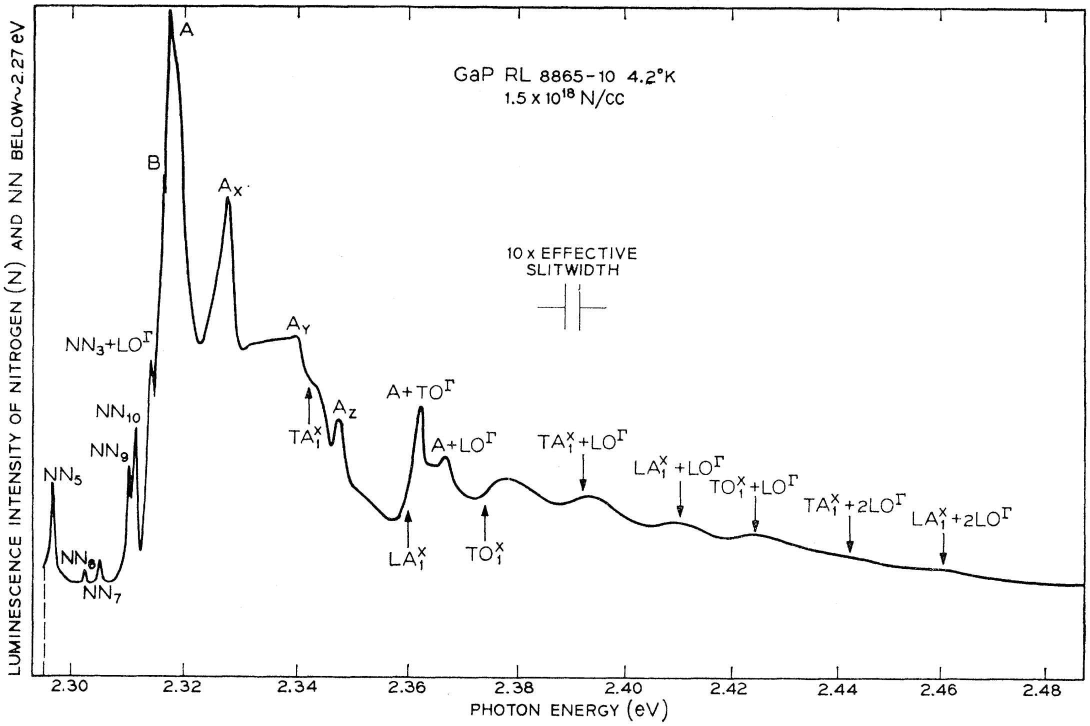

FIG. 7. The excitation spectrum of nitrogen luminescence from a moderately heavily nitrogen-doped solution-grown crystal of gallium phosphide uncorrected for the spectral variation in the excitation intensity. Some of the *NN* lines, due to transitions at pairs of nitrogen atoms (Ref. 14), can be seen below *A*, *B*. The nitrogen-induced component A_x and the optical-phonon replicas of the *A* line are clearly evident, as is component A_z, which is probably an acoustical-phonon replica of the *A* line. Nitrogen-induced component A_y is discussed in the text. The periodic oscillations above ~2.38 eV are quenched in spectra from more heavily nitrogen-doped crystals when the nitrogen-induced absorption predominates over intrinsic absorption to $\gtrsim$2.5 eV.

the intrinsic absorption predominates above this energy. Second, the analysis in Table I shows that the threshold energies $h\nu$ of the oscillations, allowing for broadening effects, extrapolate to the threshold energies of the intrinsic absorption bands at which free excitons are created together with the *X*-point MC phonons, energy $\hbar\omega^X$, according to the equation

$$h\nu=E_{gx}+\hbar\omega^X+n\hbar\omega_{\mathrm{LO}}{}^\Gamma, \tag{3}$$

where $\hbar\omega_{\mathrm{LO}}{}^\Gamma$ is the zone center longitudinal optical (LO) phonon.

TABLE I. Analysis of peak energies of oscillatory structure present in excitation spectra of luminescence from nitrogen and bismuth isoelectronic substituents in gallium phosphide.

Peak energy[a] (eV)	Assignment	Calc energy (eV) Eq. (3)
2.394	$TA_1{}^X+LO^\Gamma$	2.392
2.410	$LA_1{}^X+LO^\Gamma$	2.410
2.427	$TO_1{}^X+LO^\Gamma$	2.424
2.445	$TA_1{}^X+2LO^\Gamma$	2.442
2.462	$LA_1{}^X+2LO^\Gamma$	2.460
2.477	$TO_1{}^X+2LO^\Gamma$	2.474
2.493	$TA_1{}^X+3LO^\Gamma$	2.492
2.510	$LA_1{}^X+3LO^\Gamma$	2.510
2.526	$TO_1{}^X+3LO^\Gamma$	2.524

[a] Figures 5, 7, and 8 show that the most clearly defined oscillations are asymmetric, with relatively steeply rising low-energy sides. The energies calculated according to Eq. (3) agree better with the low-energy thresholds of the well-defined oscillations (see particularly the $TO_1{}^X$ series in Fig. 8), as would be expected from the interpretation presented in the text. The threshold energies of the broadened high-energy members of the $TA_1{}^X$ and $LA_1{}^X$ series are ill defined, however, so the peak energies are listed in column 1. Comparison with column 3 shows that the broadening tends to bring the peak energies closer to the calculated energies.

Oscillatory structure has never been observed in the excitation spectra of donor-acceptor pair luminescence, even at 4.2°K. There, the luminescence response conforms to the intrinsic absorption spectrum, modified smoothly by the effects of surface recombination (Fig. 2). It is inherently impossible to account for this oscillatory structure on the surface-recombination theory, since the absorption coefficient is a monotonically increasing function of energy in this region. It is shown in Sec. IV B2 that these oscillations, like the anomalous response near $E_g{}^D$, can be explained by a selective-excitation effect associated with a differential response of the nitrogen centers to particular final states reached in intrinsic optical absorption.

C. Exciton Luminescence at Isoelectronic Bismuth Impurities

Excitation spectra of the luminescence of relatively tightly bound excitons at bismuth isolectronic impurities in gallium phosphide are much more comparable with those for nitrogen luminescence (Fig. 4) than for

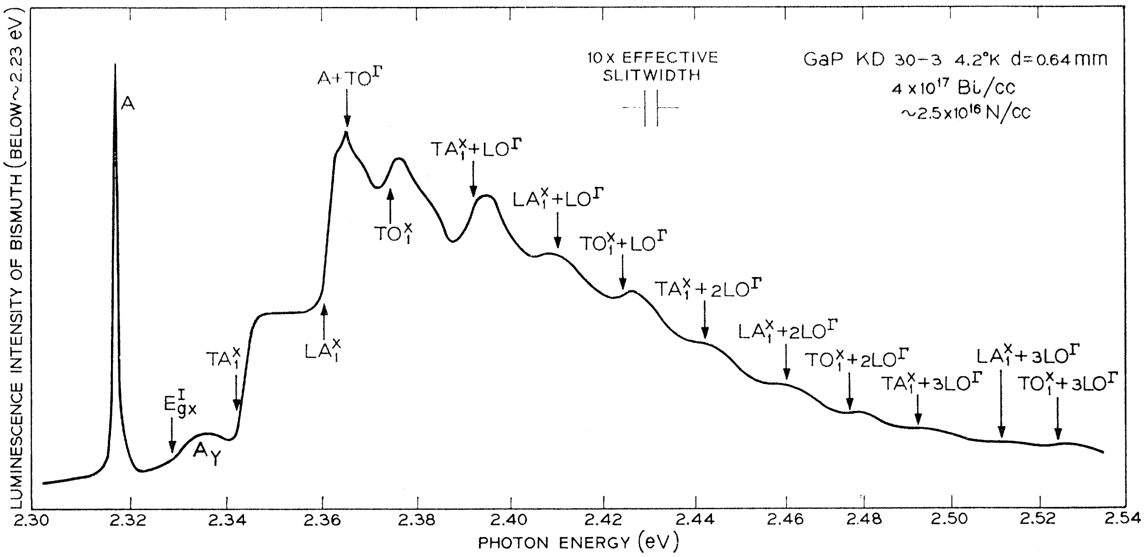

FIG. 8. The excitation spectrum of bismuth luminescence in a relatively lightly nitrogen-doped solution-grown crystal of gallium phosphide uncorrected for the spectral variation in the excitation intensity. The oscillatory structure above 2.38 eV is clearly present, as in Fig. 5. The A, B line and the nitrogen-induced structure between 2.32 and 2.35 eV, prominent in Fig. 5, is suppressed relative to the intrinsic structure in this region when bismuth rather than nitrogen luminescence is recorded.

donor-acceptor pair luminescence (Figs. 1 and 3). Unlike the case of nitrogen (Sec. III B1), however, the over-all shape of the excitation spectra for bismuth luminescence is not very specimen-dependent. The values of ℓ derived from the peak response are comparable with those reported for shallow donor-acceptor pair luminescence (Sec. III A2). The bismuth luminescence is invariably a linear function of the excitation intensity, and the absorption introduced directly by the bismuth at the maximum attainable concentration (a few $\times 10^{17}$ cm^{-3})[18] is negligible compared with the intrinsic absorption.[19] The surface-recombination theory of DeVore should therefore be applicable to the general shape of the excitation spectra for bismuth luminescence, unlike nitrogen luminescence-excitation spectra.

Noteworthy differences between the excitation spectra for bismuth and nitrogen luminescence also occur in the "anomalous-response" regions discussed in Secs. III B2 and III B3. Typically, a smooth slowly varying response is observed near $E_g{}^D$ for bismuth luminescence, with a relatively weak broad positive peak and often a weak narrow superimposed dip at $E_{gx}{}^D$. Comparison with Fig. 1 shows that there must be a significant selective-excitation effect operative in this energy region in the bismuth luminescence excitation spectra, although it is generally weaker than in the nitrogen luminescence-excitation spectra.

The oscillatory response just above $E_{gx}{}^I$, by contrast, is more clearly defined in the bismuth than in the nitrogen spectra, especially at higher temperatures (Fig. 8). The oscillations can be discerned to over 50°K. This difference is due to the greater thermal stability of the bismuth exciton complex[5,18] and possibly also to differences in the relative values of the lifetimes discussed in Sec. IV B2 between nitrogen and bismuth-doped gallium phosphide. Because of thermal dissociation of the nitrogen-exciton complexes, an appreciable fraction of the luminescence detected from most crystals at $\gtrsim$25°K under the low pumping levels used in the luminescence-excitation spectra is due to donor-acceptor pair recombinations. As closely as can be determined, threshold energies of the oscillations in Fig. 8 are identical with those in Fig. 5, and are therefore also associated with intrinsic absorption processes (Table I).

Although it has not been possible to examine the excitation spectrum for bismuth luminescence in a crystal entirely free from nitrogen, it is believed that the oscillatory structure in these crystals is not connected with the residual nitrogen. This conclusion is supported by a comparison of Figs. 5 and 8, where it is seen that the absorption features A, A_x, A_y, and A_z, which are introduced directly by the nitrogen impurities,[4] are much weaker in the bismuth excitation spectrum, although the nitrogen concentrations are similar in these crystals. The nitrogen concentration is very low in Fig. 8, and transfer of energy to the bismuth centers after tunneling exchange of excitation between the nitrogen centers should be inefficient. The excitation of the bismuth luminescence is therefore predominantly due to intrinsic absorption processes.[19] The oscillations indicate that the excitation efficiency is sensitive to the nature of the excited states, i.e., that the bismuth centers also exhibit the second type of selective-excitation effect introduced in Sec. III B3.

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[18] J. D. Cuthbert and D. G. Thomas, Phys. Rev. **154**, 763 (1967).

[19] This is shown implicitly in Fig. 1 of Ref. 5.

IV. DISCUSSION

A. Excitation Spectra of Donor-Acceptor Pair Luminescence

It has been shown in Sec. III A that there is no evidence for selective-excitation effects, as defined in Sec. I, in excitation spectra for shallow donor-acceptor pair luminescence in gallium phosphide. These excitation spectra may be derived from the absorption spectra of the corresponding crystals subject only to the smoothly varying influence, as a function of transition energy, of surface recombination which becomes more important at high absorption coefficients. The absorption due to shallow donor-acceptor pairs is weak compared with the intrinsic absorption,[20] and was not observed in this work. Excitation structure due to the creation of excitons bound to neutral donor or isoelectronic nitrogen impurities was observed. This structure was weak compared with intrinsic processes in crystals suitably doped to exhibit low-temperature luminescence predominantly from shallow donor-acceptor pairs.

Free excitons and free electron-hole pairs generated by intrinsic interband absorption appear to be comparably efficient in exciting the donor-acceptor pair luminescence. Presumably the free excitons dissociate through interaction with acoustical phonons and crystal defects. Ionized donors and acceptors have large Coulomb-attractive capture cross sections for free-electron hole pairs. In dilutely doped gallium phosphide crystals at low temperatures, pairs of neutral donors and acceptors thereby produced relax predominantly through the detected interimpurity (pair) radiative transition. No significant dependence of the luminescence efficiency on the energy of the photoexcited electrons or holes is apparent. Since the experimentally observed capture cross sections of ionized centers increase rapidly with decreasing temperature, as explained by the "cascade-capture" theory proposed by Lax,[21] this result implies that the electrons and holes reach substantial equilibrium with the lattice before capture takes place.[22]

B. Excitation Spectra for Luminescence of Excitons at Isoelectronic Nitrogen and Bismuth Impurities

The anomalous-response regions of the nitrogen luminescence excitation spectra indicated in Secs. III B2 and III B3 suggest that, unlike the donor-acceptor pairs, the isoelectronic nitrogen center acts as a selective indicator of particular final states reached in the intrinsic absorption process; a selective-excitation effect. The nature of the two selective-excitation effects observed for nitrogen luminescence will now be discussed in turn.

1. *Enhanced Luminescence Efficiency near the* $\Gamma_{15} \rightarrow \Gamma_1$ *Direct Energy Gap*

An important clue to the nature of the process responsible for this anomalous luminescence response is afforded by the observation that there is no well-defined threshold energy for the enhanced efficiency. The tail of the broad response peak extends at least 0.1 eV below E_g^D. In this energy region the absorption is still indirect. Transitions to the X_1 and X_3 conduction-band minima have been resolved.[16,23] The matrix element for the indirect transition is proportional to $(\delta E)^{-1}$, where δE is the energy between the real conduction- or valence-band state and the virtual state used in the indirect transition.[24] Indirect transitions such as A in Fig. 9 will predominate in gallium phosphide at energies approaching E_g^D, since δE becomes very small for transitions via the intermediate state associated with the Γ_1 minimum compared with the values for all other possible indirect transitions. The hole states involved in these transitions have *low* kinetic energies. Other

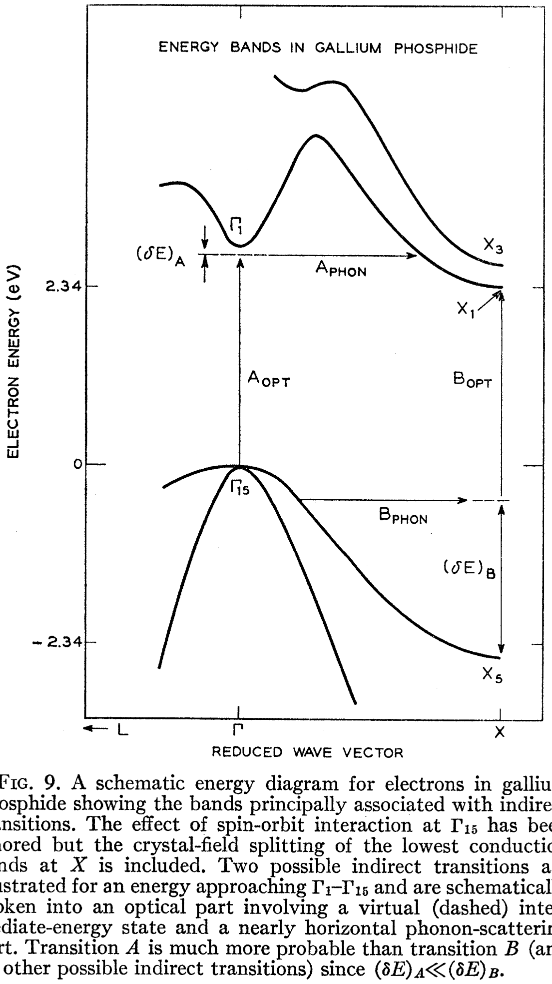

FIG. 9. A schematic energy diagram for electrons in gallium phosphide showing the bands principally associated with indirect transitions. The effect of spin-orbit interaction at Γ_{15} has been ignored but the crystal-field splitting of the lowest conduction bands at X is included. Two possible indirect transitions are illustrated for an energy approaching Γ_1–Γ_{15} and are schematically broken into an optical part involving a virtual (dashed) intermediate-energy state and a nearly horizontal phonon-scattering part. Transition A is much more probable than transition B (and all other possible indirect transitions) since $(\delta E)_A \ll (\delta E)_B$.

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[20] In fact, this type of absorption has never been observed.

[21] M. Lax, Phys. Rev. **119**, 1502 (1960).

[22] The considerable reductions reported in the intensity of the relatively inefficient deep donor-acceptor pair luminescence intensity in diamond under external electric fields which produce hot carriers [P. J. Dean and J. C. Male, J. Phys. Chem. Solids **25**, 1369 (1964)] probably arise from this strong dependence of the capture cross sections on the carrier "temperature."

[23] V. K. Subashiev and G. A. Chalikyan, Phys. Status Solidi **13**, K91 (1966).

[24] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

possible indirect transitions at this energy which can produce one cold carrier, such as B in Fig. 1 involving an intermediate state from the X_s valence band, involve relatively large values of δE and are therefore much less strongly weighted.

At high excitation energies near A in Fig. 9, the nitrogen excited states are mainly formed by the successive capture of free carriers rather than free indirect excitons. It has been suggested that an electron is captured first[25] with a small ionization energy, possibly ~8 meV.[18] Two effects may then contribute to the anomalously strong luminescence response if indirect transition A is involved. First, the capture cross section of a hole at the Coulomb attractive center will decrease very rapidly with increasing hole kinetic energy, as discussed by Lax.[21] Second, hot holes may release the weakly bound electron to the conduction band through impact ionization. The nitrogen luminescence efficiency is significantly less than unity in general, even at the response peak for interband excitation,[4] so that there will be an appreciable probability that the ejected electrons will be captured by the competing recombination centers, and the fraction of radiative electron-hole recombinations at the nitrogen impurities will be reduced. The isoelectronic nitrogen recombination centers can therefore act as selective indicators for slow holes.

The nitrogen luminescence response may also be enhanced near the threshold for the $\Gamma_{15}\rightarrow X_3$ indirect transition, again because of the low-kinetic-energy holes produced there. This should make the very weak absorption threshold $\mathrm{LA}_3{}^X$ more clearly defined in the luminescence-excitation spectrum. An inflection can indeed be observed in Fig. 4 close to the energy anticipated from the absorption spectrum,[16] but the structure is still too ill defined to enable indirect $\Gamma_{15}\rightarrow X_3$ transitions involving the individual MC phonons to be reliably identified.

Bismuth isoelectronic centers in gallium phosphide are believed to trap holes first,[25] and the ionization energies are ~5 times larger than for the nitrogen-exciton complex. Although slow holes may still be preferentially trapped by the uncharged bismuth center, the energy dependence of this effect should be much less than for the nitrogen center.[21] This may account for the reduced relative magnitude of the anomalous response for bismuth luminescence (Sec. III C). The probability of impact ionization by the hot electrons will also be relatively small for the relatively tightly bound holes at the bismuth center.

2. *Oscillatory Structure Associated with the $\Gamma_{15}\rightarrow X_1$ Indirect Transition*

The oscillations in the energy region ~2.38 to >~2.5 eV of the excitation spectra of nitrogen and bismuth luminescence correspond with intrinsic absorption structure involving the phonon-assisted creation of free indirect excitons [Eq. (3) and Table I]. The results presented in Secs. III B3 and III C can be understood, again provided that the luminescence efficiency is less than unity, if the excited electronic states of these isoelectronic centers are preferentially formed from free excitons and, to a lesser extent, from free-electron hole pairs. The absence of the threshold for the creation of free-electron hole pairs from Fig. 8, although it is clearly marked at **X** in Fig. 2, can therefore be understood.

Component A_y in Fig. 8 is due to the no-phonon creation of free excitons induced by the nitrogen impurities. The deviations of this component and the intrinsic $\mathrm{TA}^X\mathrm{MC}$ component from the expected square-root forms seen in absorption[11] indicate that the excitation efficiency for bismuth luminescence decreases with increasing free exciton kinetic energy (see below). These deviations cause the oscillatory response at higher energy to be more clearly marked. Similar deviations may occur in the nitrogen luminescence response, but the observed excitation spectra (Figs. 5 and 7) are complicated between ~2.33 and ~2.37 eV by the strong features due to absorption processes in which the final state is an exciton bound to the nitrogen atoms[26] and by various interference effects.[4]

Free excitons whose initial energy is $>\hbar\omega_{\mathrm{LO}}\Gamma$ rapidly lose energy by the cascade emission of LO phonons[27] until their residual energy is $<\hbar\omega_{\mathrm{LO}}\Gamma$. The lifetime τ_0 for optical phonon emission may be as low as 10^{-14} sec in gallium phosphide.[28] Free excitons whose initial kinetic energy is close to $n\hbar\omega_{\mathrm{LO}}\Gamma$ therefore become cold in a time short compared with other lifetimes for energy loss or recombination. The rapid increase in the luminescence efficiency for these cold excitons (Table I) might arise in two ways. Either the exciton dissociation lifetime τ_d or the lifetime τ_i against free exciton capture could be a decreasing function of the residual exciton kinetic energy after the cascade emission of optical phonons. In either case, we presuppose that recombinations at other centers are favored at high residual exciton kinetic energies. These centers may include neutral donors[29] and, after exciton dissociation, ionized donor-acceptor pairs. An energy-dependent luminescence response can be obtained from the first mechanism only if scattering processes in which the exciton kinetic energy is reduced *without* exciton dissociation are in-

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[25] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Letters **17**, 312 (1966).

[26] These features include phonon-assisted transitions.

[27] Momentum must be conserved at each step of the cascade process, presumably by the selection of an LO phonon of appropriate wave vector. If the combined electron-hole mass for the $\Gamma_{15}\rightarrow X_1$ indirect exciton is of the order of the free-electron mass, the wave vector change for the emission of a 50-meV phonon is only ~10% of the crystal wave vector at X. Plausible LO dispersion curves for gallium phosphide indicate that the energy of this phonon will be indistinguishable from $\hbar\omega_{\mathrm{LO}}\Gamma$ to the accuracy of the data in Table I.

[28] This estimate was made from Eq. (25) of H. J. Stocker and H. Kaplan, Phys. Rev. **150**, 619 (1966) using the parameters appropriate to gallium phosphide and the estimate that $\tau_0=10^{-12}$ sec for indium antimonide.

[29] Neutral donors are important nonradiative recombination centers for excitons in gallium phosphide at low temperatures; see D. F. Nelson, J. D. Cuthbert, P. J. Dean, and D. G. Thomas, Phys. Rev. Letters **17**, 1262 (1966).

significant and from the second mechanism only if the time τ_i is shorter than the time τ_a for energy loss to acoustical phonons.

The first mechanism proposed above seems improbable since the radiative recombination of free excitons at equilibrium with the lattice observed from a number of materials whose band structure is similar to gallium phosphide (for example, diamond and silicon) shows negligible dependence upon the kinetic energy of the recombining excitons.[30] Intrinsic recombinations in these indirect-gap materials involve scattering by acoustical or optical phonons to conserve momentum. A significant dependence of τ_d on the exciton kinetic energy would be expected to reduce the luminescence intensity in the high-energy tails of the intrinsic bands.

The second mechanism also seems unattractive initially since τ_a is very short, probably $\lesssim 10^{-11}$ sec for gallium phosphide at 20°K.[31] Faulkner and Hopfield[32] have recently calculated the scattering cross section of isoelectronic nitrogen substituents in gallium phosphide, however, and find it to be very large, $\sim 10^{-12}$ cm^{-2}, because of a resonance condition due to the presence of a very shallow bound state. This large scattering cross section implies a large capture cross section for free electrons, and therefore free excitons.[33] The resonance condition implies that both of these cross sections should decrease rapidly with increase in the electron or exciton kinetic energy, in agreement with the suggested interpretation of the form of the luminescence-excitation spectra. At 20°K an exciton capture cross section $\sim 10^{-12}$ cm^{-2} corresponds to $\tau_i \sim 3\times 10^{-12}$ sec in a typical crystal containing $\sim 10^{17}$ nitrogen impurities. Thus the exciton trapping time τ_i at the nitrogen atoms may be less than τ_a even at 20°K. This inequality becomes more marked at lower temperatures and at low exciton kinetic energies, since both of these conditions increase τ_a. We therefore conclude that the enhanced luminescence response observed at energies corresponding to the photocreation of cold excitons can be explained by a velocity-dependent capture cross section for these excitons at the isoelectronic nitrogen impurities. The very short values of τ_i which are required for this mechanism are also of the order required to account for the very small values of the minority carrier diffusion length estimated from the position of the peak luminescence response of these crystals using the theory of DeVore (Sec. III B1).

The above estimate that the lifetimes τ_i and τ_a become comparable near 20°K is consistent with the observation that broadening of the oscillatory structure occurs at $T \gtrsim 20$°K. The lifetime calculations are not sufficiently precise to justify a close comparison between experiment and theory, however.

Similar considerations are believed responsible for the oscillatory structure in the excitation spectra of bismuth luminescence. Here τ_i may be larger since the bismuth hole traps are significantly farther from the resonant threshold condition for binding, but this effect tends to be reduced by the uniformly high bismuth concentration ($\sim 4\times 10^{17}$ cm^{-3}) in the crystals studied.

The oscillations should be observable at very high energies if the lifetime against LO phonon emission is sufficiently small compared with other possible energy loss mechanisms. In practice, Figs. 5 and 8 show that this criterion is inadequately fulfilled. The oscillation amplitude decreases considerably with n in Eq. (3) well before the onset of absorption due to $\Gamma_{15} \rightarrow X_3$ transitions, which would complicate the spectrum.

An effect not discussed in Ref. 4 is the sharp decrease in response near 2.34 eV in crystals where nitrogen-induced absorption predominates at this energy (A_y in Fig. 7). This energy marks the threshold for the no-phonon creation of free electron-hole pairs if the ionization energy of the indirect exciton is $\sim$10 meV.[11] The exact spectral form in this region is determined by interference effects between different nitrogen-induced absorption channels, but the decrease in response is also consistent with a low efficiency for excitation of nitrogen luminescence by free-electron hole pairs compared with free excitons.

3. *Comparison with Oscillatory Structure in Excitation Spectra Reported for Various Materials*

Similar oscillatory structure, also involving a bound exciton transition, has been observed in luminescence[34] and photoconductivity[35] excitation spectra of natural diamond, which also has an indirect band gap. Minima in the photoconductivity spectra coincide with the luminescence excitation maxima, as expected if the optical-phonon cascade reduces the free-carrier lifetime. Periodic minima have been observed in the photoconductivity of several II–VI direct band gap semiconductors.[36–38] The interpretation offered for the structure in CdS [36] and CdSe [38] differs from the above, and is difficult to understand since the most prominent cascade process is assumed to involve free electrons

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[30] See P. J. Dean, in *Luminescence in Inorganic Solids*, edited by P. Goldberg (Academic Press Inc., New York, 1966), Chap. 3.

[31] This estimate was made from an equation given by M. A. Habegger and H. Y. Fan, Phys. Rev. Letters **12**, 99 (1964), assuming that $\tau_a = 3\times 10^{-7}$ sec for an exciton kinetic energy ϵ of 10 meV in indium antimonide. This lifetime is proportional to $\epsilon^{-1/2}$ and is therefore appreciably larger at low ϵ.

[32] R. A. Faulkner and J. J. Hopfield, in Proceedings of the Irvine Conference on Localized Excitations, 1967 (to be published).

[33] For neutron-proton scattering, the zero-energy elastic scattering cross section is $\sim$10 times the cross section for radiative neutron-proton capture. J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley & Sons, Inc., New York, 1952), Chaps. II and XII. We assume in the text that these two cross sections are of the same order for interactions between electrons and nitrogen impurities.

[34] P. J. Dean and J. C. Male, Proc. Roy. Soc. (London) **277A**, 330 (1964).

[35] P. Denham, E. C. Lightowlers, and P. J. Dean, Phys. Rev. **161**, 762 (1967).

[36] Y. S. Park and D. W. Langer, Phys. Rev. Letters **13**, 392 (1964).

[37] R. E. Nahory and H. Y. Fan, Phys. Rev. Letters **17**, 251 (1966).

[38] D. W. Langer, Y. S. Park, and R. N. Euwema, Phys. Rev. **152**, 788 (1966).

although the oscillation energies clearly extrapolate to the *A* and *B* intrinsic excitons rather than to the associated free-carrier energy gaps. The energy origin of the oscillatory minima in ZnTe, by contrast, is associated with the direct free-carrier energy gap.[37] Unlike CdS and CdSe, the effect of the finite curvature of the valence band on the oscillation period was detected for ZnTe.

Oscillatory structure has also been reported in the region of intrinsic absorption for two direct gap III–V semiconductors InSb[39–41] and GaSb.[40] In addition to, or instead of, the assumption of an energy-dependent free-carrier lifetime against LO phonon scattering,[39] the presence of the oscillatory structure has been attributed to an energy-dependent free-carrier mobility[41] or to preferential momentum loss due to LO phonon emission from a nonequilibrium distribution of the injected electrons.[42] These latter considerations are of no consequence to the presence of oscillations in the *luminescence* excitation spectra. The extrinsic luminescence itself reveals the presence of the recombination center which is essential to the energy-dependent lifetime interpretation.

Oscillatory structure associated with the $\Gamma_{15} \rightarrow \Gamma_1$ direct transition, but not in the region of indirect absorption, has been reported in photoconductivity excitation spectra of gallium phosphide.[43] No oscillations in the luminescence spectral response were observed above E_g^D in the present work.

V. CONCLUSIONS

Luminescence excitation spectra in the region of interband absorption in semiconductors can yield information about the details of the energy transfer between the intrinsic absorption process and recombination at an impurity. In the present work, a comparison is made of excitation spectra of luminescence at two quite different types of recombination center in gallium phosphide, namely, donor-acceptor pairs and isoelectronic substituents.

For shallow donor-acceptor pair luminescence, intrinsic absorption processes involving the creation of free excitons and free-electron hole pairs are both important. As previously reported from measurements on deep donor-acceptor pair luminescence,[2] fresh solution-grown crystals of gallium phosphide exhibit strong surface recombination, which severely attenuates the luminescence response near 3 eV and controls the over-all spectral response function at lower energies. The minority carrier diffusion length and the surface recombination velocity may be derived from the form of the excitation spectra above the band gap. Absorption into shallow bound exciton states also contributes to the excitation spectrum. Thermal ionization and inter-impurity tunneling both contribute to the energy-transfer process from these exciton states to the deeper pair radiative recombination centers. There is no appreciable effect of the initial energy of the photoexcited excitons or free carriers on the shape of the excitation spectrum for pair luminescence.

The excitation spectra for luminescence at nitrogen and bismuth isoelectronic centers also show evidence of surface recombination. The position of the peak response in the excitation spectra for nitrogen luminescence for many crystals suggests very low values of the minority carrier diffusion length and carrier lifetime (down to $\sim 10^{-12}$ sec) according to the theory of DeVore.[17] This simple theory of the excitation spectrum may be inapplicable to luminescence in relatively heavily nitrogen-doped ($>10^{18}$ cm^{-3}) gallium phosphide. Two regions of anomalous response, where the spectral dependence of the isoelectronic center luminescence excitation intensity is not simply related to that of the absorption coefficient, were noted. Both are connected with intrinsic absorption processes. Oscillatory structure above the $\Gamma_{15} \rightarrow X_1$ indirect energy gap indicates that photogenerated free excitons lose energy rapidly by the cascade emission of LO phonons. This process is apparent in the luminescence excitation spectra, though it cannot be seen in the absorption spectrum, because the isoelectronic impurity-exciton complexes responsible for the detected luminescence are preferentially formed from low-energy excitons. A similar conclusion is obtained from a comparison of the shapes of individual free-exciton components in the excitation spectra and in the absorption spectra. Near the $\Gamma_{15} \rightarrow \Gamma_1$ direct energy gap, consideration of the indirect transition matrix elements shows that the predominant transitions involve intermediate states derived from the Γ_1 minimum. These transitions produce low-energy holes near Γ_{15}. A broad anomalous luminescence response in the excitation spectra for bismuth and, particularly, nitrogen luminescence is attributed to the preferential formation of the excited luminescent states from these low-energy free holes. Neither of these anomalous response effects would be visible if the efficiency of the detected luminescence was unity under intrinsic photoexcitation. This ideal situation is never achieved in practice, but variations in the quantum efficiency can account for the appreciable variations in the modulation depth of the oscillatory structure observed from different crystals.

ACKNOWLEDGMENTS

It is a pleasure to thank C. H. Henry, J. J. Hopfield, D. G. Thomas, and P. A. Wolff for several enlightening discussions concerning this work. Thanks are also due to J. C. Tsang and G. Kaminsky for experimental assistance. The crystals were grown by R. T. Lynch, M. Kowalchik, and R. B. Zetterstrom.

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[39] H. J. Stocker, C. R. Stannard Jr., H. Kaplan, and H. Levinstein, Phys. Rev. Letters **12**, 163 (1964).

[40] M. A. Habegger and H. Y. Fan, Phys. Rev. Letters **12**, 99 (1964).

[41] V. J. Mazurczyk, G. V. Ilmenkov, and H. Y. Fan, Phys. Letters **21**, 250 (1966).

[42] H. J. Stocker and H. Kaplan, Phys. Rev. **150**, 619 (1966).

[43] D. N. Nasledov, V. V. Negreskul, S. I. Radautsan, and S. V. Slobodchikov, Fiz. Tverd. Tela **7**, 3671 (1965) [English transl.: Soviet Phys.—Solid State **7**, 2965 (1966).]