

## Interference between Intermediate States in the Optical Properties of Nitrogen-Doped Gallium Phosphide

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Nitrogen substituting for phosphorus in gallium phosphide forms an isoelectronic trap which strongly affects the optical properties of the crystal, particularly in the vicinity of the band-gap energy. Attention is directed to optical absorption and excitation spectra produced by the presence of nitrogen. The former shows a peak at the intrinsic exciton energy and unexpected dips at energies corresponding to phonon replicas of zero-phonon transitions. The fluorescence excitation spectra show quite different structure at the same energies, and this structure depends on the fluorescence that is being observed. Such anomalous structure in the absorption spectra can arise in several ways. It can occur when there are two paths to the same final state. In addition, it can occur when there are at the same energy two classes of states which are mixed by some perturbation. Absorption to each of these classes of states will have its own anomalous structure. Different final states often radiate with different efficiencies or in different spectral regions, and hence relative measurements can be made of the various absorption processes which occur at one energy. It is found that the excitation spectra confirm predictions made as a result of the interpretation of the total absorption spectra in terms of various interference effects.

### I. INTRODUCTION

THE isoelectronic substitution of nitrogen for phosphorus in GaP is a major perturbation because of the large difference between the cores of the nitrogen and phosphorus atoms. This strong short-range perturbation introduces new electronic bound states into the forbidden gap as well as causing the scattering of free-particle states. This paper is concerned with the optical effects due to the presence of nitrogen in GaP. These effects include line and continuum absorption and display the importance of electron-phonon coupling, particularly in the luminescence spectra.

The cross coupling between different scattering processes is a source of much "anomalous" structure for scattering cross sections in atomic and nuclear physics.<sup>1</sup> The strongly asymmetric absorption lines<sup>1</sup> of auto-ionization states of atoms<sup>2</sup> are a well-understood example of such a process. In this example, there are effectively two possible paths leading to the same final-continuum state. One of these paths is to go directly to the continuum state and the other is to go via the virtual bound (or resonant) auto-ionization state. The interference between the different paths to the same final state leads to the asymmetric absorption lines. This same interference between alternate routes to the same final state can also be thought of as the origin of the well-known structure in the elastic scattering cross section at the threshold for an inelastic process.<sup>3</sup>

Such anomalies become most pronounced when the couplings are strong. Effects of such interference also occur in a wide variety of solid-state problems.<sup>4</sup>

The present paper demonstrates that the many features of anomalous appearance in the absorption spectrum of nitrogen in GaP are due to these kinds of interference effects. Of particular importance in demonstrating these effects in GaP is the fact that *two* processes can be studied separately in this system. First, optical-absorption spectra, which sum over all final states, can be measured. Second, the quantum efficiency of fluorescence of an electron-hole pair depends strongly on the state of the pair. The measurement of fluorescence excitation spectra thus provides a method of separately investigating different processes whose absorptions overlap.

In Sec. II, detailed experimental results of optical-absorption studies are given. Section III describes several of the peculiar features of this spectrum which, from their form, appear related to the intermediate-state interference effects. The relation between these features and possible interacting intermediate states is discussed. The experimental results of fluorescence excitation spectra measurements and a description of the channels these are believed to measure, are described in Sec. IV, and compared to the qualitative predictions of Sec. III.

### II. ABSORPTION AND EMISSION SPECTRA

#### Experimental

GaP crystals deliberately doped with nitrogen were used in this work. Many were grown using a modified

<sup>3</sup> These effects were first experimentally observed by P. R. Malmberg, *Phys. Rev.* **101**, 114 (1956).

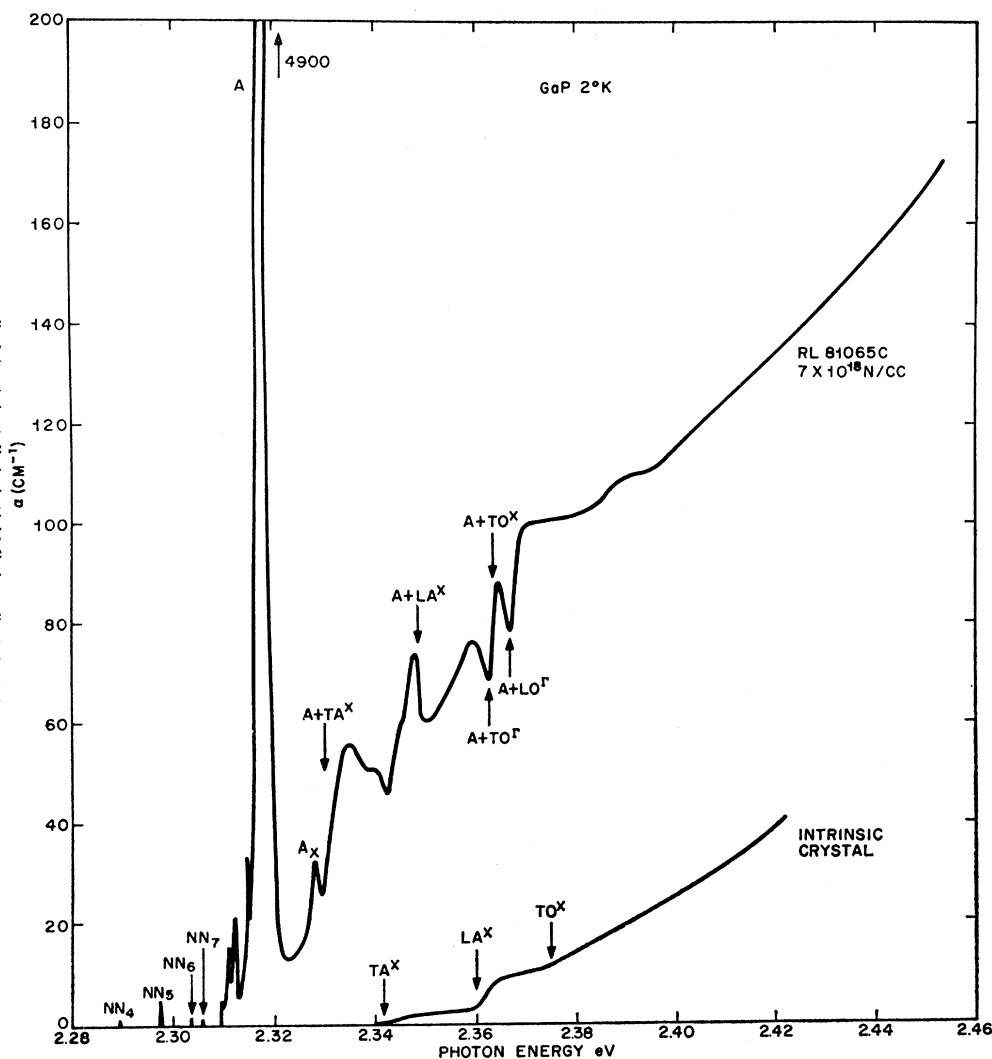
<sup>4</sup> J. J. Hopfield, Lecture from the Tokyo Summer Institute of Theoretical Physics (to be published).

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<sup>1</sup> The original asymmetric resonances were observed in nuclear physics, and the theory of Breit and Wigner for such experiments is found in any standard reference on nuclear physics; e.g., J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley & Sons, Inc., New York, 1952), p. 379 ff.

<sup>2</sup> See for example R. P. Madden and K. Codling, *Phys. Rev. Letters* **10**, 516 (1963).

FIG. 1. Low-temperature edge absorption spectra obtained from relatively heavily nitrogen-doped and from relatively perfect crystals of GaP. The arrows denote the thresholds of intrinsic interband electronic transitions involving different momentum-conserving phonons and also the positions of various phonon replicas of the  $A$  bound-exciton line (due to nitrogen) which might be anticipated. The absorption peak  $A_x$  marks the position of the free-exciton energy gap (see text).



wet hydrogen transport method,<sup>5</sup> but some were also grown from gallium solution using GaN as a controlled source of nitrogen.

Optical-absorption coefficients were computed using the technique discussed by Dean and Thomas.<sup>6</sup> Spectrally variable absorption neglected by this method was generally not greater than  $0.1 \text{ cm}^{-1}$ .

A Spex  $\frac{3}{4}$  m spectrometer or a Bausch and Lomb 2 m spectrometer was used for the absorption and luminescence excitation spectra measurements. In the latter the light emitted by the crystal was passed through a filter to remove the exciting radiation and then directly onto a photomultiplier.

### Results

Figure 1 shows the low-temperature absorption spectra of a pure GaP crystal<sup>6</sup> and one containing about

$7 \times 10^{18}$  (nitrogen atoms)/cc. Much phonon-induced structure is seen in the first  $0.050 \text{ eV}$  above the "A" absorption line, this line being due to a hole and electron trapped at an isolated nitrogen atom.<sup>7</sup> (The extent of the first-order phonon spectrum in GaP is  $0.050 \text{ eV}$ .) The energies at which the so-called "momentum conserving" (100) zone boundary (or X point) phonons occur are marked by arrows, their energies having been determined from the intrinsic absorption spectrum.<sup>6</sup> Such phonons clearly have no special importance in the nitrogen-induced absorption. It is true that the LA and TO (100) positions lie close to a peak in the absorption spectrum but the definite absence of exact agreement shows that this is of no particular significance. It is important to notice that there is strong coupling to phonons at almost all phonon wave vectors, not just at the (100) zone boundary values. Weak, sharp  $N-N$  absorption lines are also visible at this high nitrogen concentration, but

<sup>5</sup> C. J. Frosch, in *Proceedings of the International Conference on Crystal Growth, Boston, Massachusetts, 1966* (Pergamon Press, Inc., New York, 1966).

<sup>6</sup> P. J. Dean and D. G. Thomas, *Phys. Rev.* **150**, 690 (1966).

<sup>7</sup> D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **150**, 680 (1966).

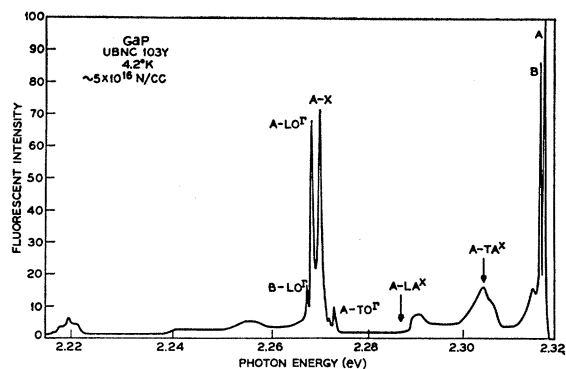


FIG. 2. The low-temperature fluorescence spectrum of excitons bound to nitrogen impurities in GaP. The phonon replicas are to be contrasted with the structure above  $A$  in absorption (Fig. 1).

contribute negligibly to the total absorption. These lines are due to holes and electrons bound to pairs of nitrogen atoms, the internuclear separation varying from one line to the next.<sup>7</sup>

The fluorescence spectrum due to isolated nitrogen atoms in lightly doped GaP is shown in Fig. 2 for a temperature of 4.2°K. At this low temperature, the "B" line fluorescence is visible as well as the "A" line, due to the large population of the lower-energy  $J=2$  excited state. Strong phonon cooperation with phonons from many parts of the Brillouin zone is evident, and many Van Hove singularities can be discerned. The  $LO^T$  and  $TO^T$  zone center phonon frequencies are observed as strong peaks. The strong critical point singularities do not correspond in general to the (100) zone boundary phonons, again indicating no special role for these phonons in processes induced by nitrogen. The fluorescence shows that nitrogen is a sufficiently strong perturbation that the optical-matrix element it directly induces is greater than that which comes about by use of momentum conserving phonons. Additional support for this view comes from the absorption spectrum. Thus only  $\sim 10^{18}$  (nitrogen impurities)/cc introduce much more continuous absorption, even well above the band gap (Fig. 1), than is present via the usual momentum conserving phonons for the unperturbed lattice, containing about  $2 \times 10^{22}$  (phosphorus atoms)/cc.

In simple situations, the phonon cooperation for a bound-state transition shows a "mirroring" about a zero-phonon line. The present experiments show a radical departure from this simple situation. For example, the LO and TO phonon replicas of  $A$  which show up as emission peaks occur as absorption *dips*; the peak  $A_x$  in absorption has no emission counterpart, and the general structure of the spectra are qualitatively different. The emission spectrum has the general shape of phonon wings normally observed—a shape approximately characterized by the phonon density of states, although it is unusual for such a weakly bound exciton state to the extent that it is little influenced by momentum conservation requirements for the indirect

transition. The peculiar form of the absorption spectrum is the main problem to be understood.

### III. INTERPRETATION OF THE ABSORPTION SPECTRUM

The electronic state whose excitation is responsible for the "zero-phonon" emission and absorption line lying at 2.3171 eV, (the  $A$  line) is an exciton bound to a nitrogen impurity.<sup>7</sup> This excited state will be called  $N^*$ . There are, in fact, two excited states  $A$  and  $B$ , split slightly by electron-hole spin-spin interactions. One of them, however, has a negligible oscillator strength, and can be ignored in absorption considerations. The study of the intrinsic absorption<sup>6</sup> of pure GaP shows that the bandgap is indirect, and that the lowest-energy exciton lies at 2.328<sub>5</sub> eV at low temperatures. This exciton energy gap  $E_{gx}$  will for convenience be taken as the zero of energy. The exciton binding energy is  $0.010 \pm 0.001$  eV.<sup>6</sup>

These basic experimental numbers define the stable electronic states of the system. These states are schematically shown in Fig. 3(a). They include  $N^*$ , a free-exciton continuum starting at zero energy, various excited-exciton continua beginning at energies above zero, and an electron-hole pair continuum beginning at an energy of +0.010 eV. Each free-exciton continuum has an  $(E-E_0)^{1/2}$  form for its density of states. The free-electron-hole pair continuum has an  $(E-E_0)^2$  form for its density of states. (The superposition of many different excited-exciton continua and the presence of Coulomb effects on matrix elements for free-electron-hole pair states will lead to smooth results for all physical measurements in the vicinity of the free-pair threshold; cf. the absorption edge of intrinsic indirect semiconductors). No other excited states of  $N^*$  have been seen, though the existence of such states [ $N^{*'} in Fig. 3(a)] is plausible. These electronic states, which$

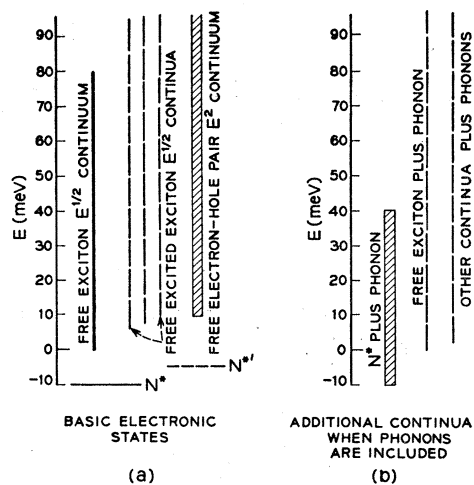


FIG. 3. Schematic representations of the energy states near the indirect band gap of GaP doped with nitrogen (a) without and (b) with the inclusion of interactions with phonons.

in fact may be reached because of the presence of nitrogen in the crystal, account for the grossest details of the spectra, and for the absorption line and the existence of an absorption continuum at high energies.

On the other hand, other states are clearly needed to understand all the detailed structure in the observed absorption spectrum, due to the presence of nitrogen, which is shown in Fig. 1. The electronic states described themselves produce (a) no continuous absorption below  $E=0$ , (b) a  $\sqrt{E}$  threshold at  $E=0$ , and (c) no reason for structure above  $E=0.010$  eV. All the details in the region  $-0.010$  to  $+0.040$  eV clearly require the inclusion of phonons to explain them, a result not surprising in view of the obvious importance of phonons in the emission spectrum due to nitrogen (Fig. 2).

Each electronic state can now be convoluted with a phonon density of states to obtain the densities of states for various one-phonon processes. These have been schematically indicated in Fig. 3(b).

The presence of such a large variety of states makes the detailed calculation of the absorption spectrum produced by nitrogen extremely difficult. Nor is the form of the optical matrix elements due to the nitrogen perturbation known in detail. What we shall attempt to do is to understand the structure in the optical absorption through the application of appropriate general theories of line shape. Only a few of the many states are in fact capable of contributing to the experimentally observed structure.

Structure in the data will be interpreted in terms of two general theories of interference applicable to different state distributions. First, in the theory of Fano<sup>8</sup> (following Breit and Wigner) of a resonant

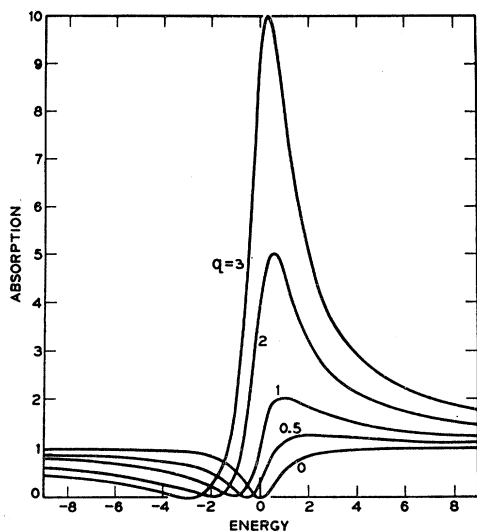


FIG. 4. Possible forms of the partial absorption coefficient to continuum states (after Fano, Ref. 8). The mirror images of these curves about zero energy result if  $q$  is negative. When, as in the present problem, several continua are superposed, a superposition of several such curves results.

<sup>8</sup> U. Fano, Phys. Rev. **124**, 1866 (1961).

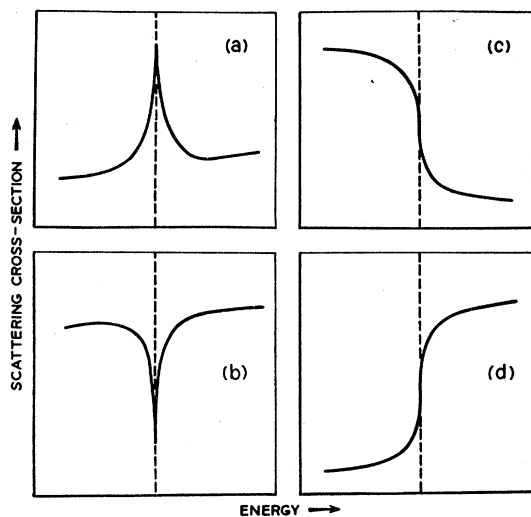


FIG. 5. The possible spectral forms for elastic processes at inelastic thresholds. The coefficients of the square-root term on the two sides of the threshold are not necessarily identical, so the most general curves possible are less symmetric than shown (after Baz', Ref. 9).

“state” imbedded in a continuum, the interference between this state and the continuum leads to a variety of possible forms for the cross section for transitions to the continuum, as shown in Fig. 4. As a result of having several different final states for the absorption process in a single physical situation, different physically observable effects may have different resonant shapes. Second, in the theory of Wigner and Baz'<sup>9</sup> when several reactions are possible, and one of them has a threshold  $E_T$  above which (or below which, *mutatis mutandis*) its reaction rate is proportional to  $(E-E_T)^{1/2}$ , the cross sections for each of the other processes will in general have one of the four forms of Fig. 5 at  $E_T$ . These forms are characterized by a vertical tangent at  $E_T$ .

One striking anomaly in the shape of the nitrogen-induced absorption of Fig. 1 is the form observed at the location of  $A+TO^\Gamma$  and  $A+LO^\Gamma$  phonon replicas. In the emission spectrum, the analogous processes produce strong peaks. The dips in the absorption process must be due to the interference between the peaks expected for the state

$$N^* + LO \text{ (or TO) (virtual),}$$

and the continuum on which it lies. This continuum, which of course is proportional in strength to the nitrogen concentration, is chiefly due to the processes

$$\text{photon} \rightarrow \text{electron-hole pair}$$

and

$$\text{photon} \rightarrow \text{free exciton.}$$

<sup>9</sup> E. P. Wigner, Phys. Rev. **73**, 1002 (1948); A. I. Baz', Zh. Eksperim. i Teor. Fiz. **33**, 923 (1957) [English transl.: Soviet Phys.—JETP **6**, 33 (1958)]; L. G. Landau and E. M. Lifschitz, *Quantum Mechanics; Non-Relativistic Theory* (Pergamon Press, Inc., London, 1958), 2nd ed., pp. 565-571.

The final electron-hole pair state can be reached in many ways; for example, via

$$\text{photon} \rightarrow N^* + \text{LO (virtual)} \rightarrow e-h \text{ pair}$$

(where the last step is due to electron-phonon interactions) or directly

$$\text{photon} \rightarrow e-h \text{ pair.}$$

Because the LO and TO phonon bands are quite flat, the state  $N^* + \text{LO}$  can be approximately characterized as having a single energy, and the relevant theory is that of Fano.

The state ( $N^* + \text{LO phonon}$ ) when the LO phonon wave packet is well removed from the vicinity of the  $N^*$  is a stable final state. The excitation of the "resonance" at energy  $A + \text{LO}$  can be thought of as the excitation of an LO phonon in the vicinity of  $N^*$ . The phonon may escape to a distant part of the crystal, resulting in the stable final state  $N^* + \text{LO}$ . This transition has very sharp peaks in its density of states (as long as the optical-phonon branches are nearly flat) and will cause absorption "lines" near TO and LO. Alternatively, the virtual excitation of  $N^* + \text{LO}$  near the impurity results in a second interaction of the LO phonon with  $N^*$  in which the phonon is reabsorbed and a free exciton or electron-hole pair generated. For this process, the state  $N^* + \text{LO}$  is simply a resonant intermediate state, and the final state is a continuum exciton or pair state. For this process, an absorption like that of the one of the forms of Fig. 4 will result, the essential reason being that the presence of nitrogen results in there being two routes to the same final state. In fact, because several continua are present, a superposition of several forms like those of Fig. 4 is possible.

In summary of the general considerations for excitations in the vicinity of  $N^*$  plus the LO and TO phonons (whose dispersions are small), two final states corresponding to each phonon are possible. The absorption to the final state  $N^* + \text{LO}$  (or TO) will have the general shape of an ordinary absorption line. The absorption to the final continuum state with no phonon present can show the more complicated forms of Fig. 4. The experimental absorption (Fig. 1) is clearly dominated by the final continuum state in the vicinity of the  $\text{LO}^\Gamma$  and  $\text{TO}^\Gamma$  energies. The spectrum closely resembles Fig. 4 with  $q=0$  in the vicinity of a resonant energy.

A second anomaly of definable origin in the absorption spectrum occurs at the exciton energy gap. It is seen as a peak and is labeled  $A_x$  in Fig. 1. It occurs at the threshold for the process

$$\text{photon} \rightarrow \text{free exciton.}$$

The optical-matrix element for this process is due to the nitrogen impurities, and an absorption is expected, due to this free-exciton creation, of the form  $(E - E_{\text{ex}})^{1/2}$  proportional to the nitrogen concentra-

tion.<sup>10</sup> In this same energy region, the only other process which can take place (see Fig. 3) is

$$\text{photon} \rightarrow N^* + \text{phonon.}$$

This excitation with phonon cooperation provides a continuum of states above the "A" line transition. Using the general theory of interference effects at square-root thresholds,<sup>3,4</sup> one can conclude that at the threshold of free-exciton production there will be produced one of the characteristic forms of Fig. 5. The total absorption, the sum of the two processes, will also show a form like one of those in Fig. 5.

At higher energies, there are so many interaction processes occurring between different states that it is difficult to sort out the relevant processes. In general, however, the fact that the one-phonon sideband of the electronic transition producing  $N^*$  overlaps an electronic continuum means that each critical-point square-root singularity in the phonon cooperation density-of-states curve (Fig. 2) will be mirrored in absorption *not* as a square-root singularity, but as one of the forms<sup>11</sup> of Fig. 5. The drastic failure to "mirror" the spectral envelopes is thus demonstrated as an interference effect.

#### IV. INVESTIGATION OF SEPARATE CHANNELS; PHOTOEXCITATION

In the absence of detailed calculations on this complicated system, verification of the qualitative description of the interference phenomena described in Sec. III is lacking. An experimental verification of many of the details would be possible, however, if one could (as in nuclear physics) measure separately the reaction rates (partial absorption coefficients) due to different final states. From the explanation of the spike in the total absorption at the exciton energy gap (defined above as zero energy), using the model described in Sec. III, two predictions can be made about the *partial* absorption coefficients. First, the partial absorption coefficient due to the process

$$\text{photon} \rightarrow N^* + \text{phonon}$$

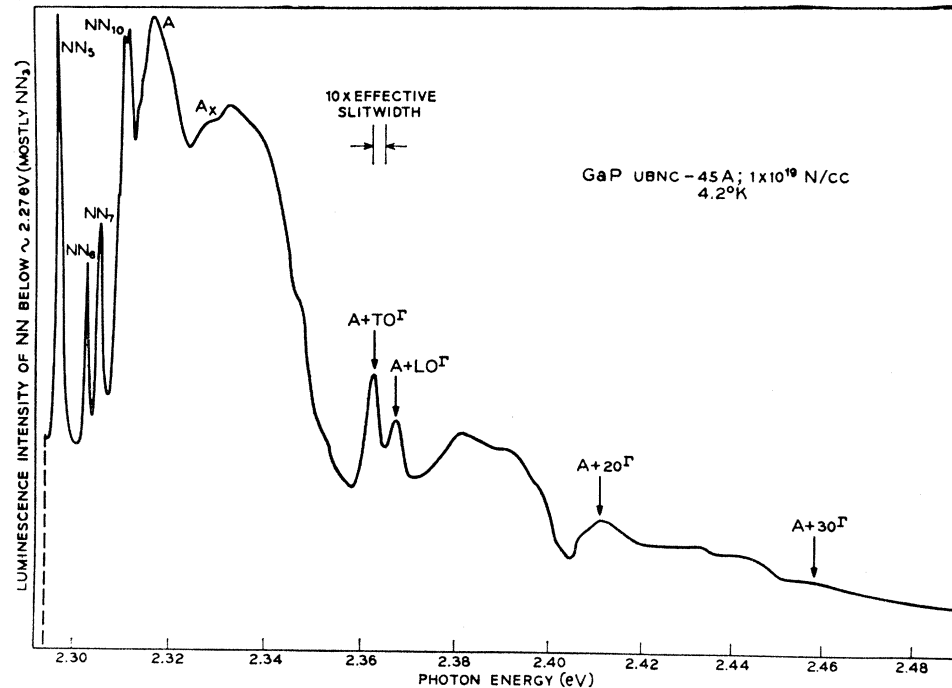
has a spike at zero energy. Second, the partial absorption coefficient due to free-exciton creation (via a nitrogen atom) will have a normal  $\sqrt{E}$  threshold at zero energy. Similarly in order to obtain the "inverted" absorption "lines" at the  $\text{LO}^\Gamma$  and  $\text{TO}^\Gamma$  phonon energies above the A line, the partial absorption coefficient due to the process

$$\text{photon} \rightarrow \text{free exciton (or free-electron-hole pair)}$$

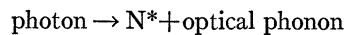
<sup>10</sup> Such an absorption shape has been seen at the exciton threshold in AgBr containing small quantities of AgCl. B. L. Joesten and F. C. Brown, Phys. Rev. 148, 919 (1966).

<sup>11</sup> A similar conversion of simple square-root Van Hove singularities to the forms of Fig. 5 was shown by Toyozawa, in the theory of the optical absorption of insulators when electron-hole interactions (short-range only) are taken into account. [Y. Toyozawa, lectures from the Tokyo Summer Institute of Theoretical Physics (to be published); Proceedings of the 1966 International Semiconductor Conference, Kyoto (to be published)].

FIG. 6. Low-temperature luminescence excitation spectrum for indirect electronic interband transitions in a heavily nitrogen-doped crystal of GaP. The optical phonon replicas of the  $A$  line appear as *peaks* in contrast to the absorption spectrum (Fig. 1). The structure near  $A$  and  $A_x$  is heavily distorted because essentially all the incident radiation is absorbed within the crystal by processes which efficiently excite the detected luminescence.



occurring in the presence of nitrogen must be the dominant process in the total optical absorption at this energy. The process



also occurs in this energy region, but would have a partial absorption cross section with peaks at the  $\text{LO}^\Gamma$  and  $\text{TO}^\Gamma$  frequencies. A measurement of these partial absorption coefficients to compare with the above predictions was the object of the excitation studies.

Typical nitrogen-doped GaP crystals have a rather low fluorescent efficiency  $\eta$ , even at 4.2°K, due to unidentified nonradiative traps. While  $\text{N}^*$ , once formed, apparently radiates with nearly unit efficiency, a typical free exciton or electron-hole pair is only rarely captured by nitrogen. Thus in the *excitation* spectrum of nitrogen fluorescence the absorption processes in which  $\text{N}^*$  is left in the final state has a weight 1.0, the absorption process in which a free electron or electron-hole pair is formed has only weight  $\eta$ . The study of the excitation spectrum for nitrogen fluorescence thus provides a measure of the partial absorption coefficient for processes which directly make  $\text{N}^*$  when  $\eta$  is small.

Figure 6 shows the excitation spectrum of a crystal containing  $10^{19}$  (N atoms)/cc. [At nitrogen concentrations as large as this, there is a strong tendency for the excitation to hop to nearby lower-energy NN pairs before recombining, and the fluorescence observed is chiefly nitrogen pair emission. This complication has no major consequences on the general line of reasoning.] At this nitrogen concentration, intrinsic absorption is negligible over the energy range of Fig. 6 (see Fig. 1).

Both the  $A$  line and the NN pair lines can be seen in the excitation spectrum. Two strong maxima marked  $A+\text{TO}^\Gamma$  and  $A+\text{LO}^\Gamma$  occur, lying 45.4 and 50.1 meV, respectively, above the  $A$  line. They therefore correspond to the zone-center TO and LO phonons, and fall at precisely the *minima* seen in the absorption curves of Fig. 1.

At this high nitrogen concentration, the  $\sim 1$ -mm thickness of this irregular crystal was sufficient to absorb all the light at photon energies above 2.33 eV. If the efficiency for fluorescence due to the generation of free-electron-hole pairs were negligible and that for excitons bound to nitrogen were unity, the measured luminescence excitation spectrum when all the light is absorbed is proportional to

$$\alpha_{\text{bound}}/\alpha_{\text{total}},$$

where  $\alpha_{\text{total}}$  is the (total) absorption coefficient and  $\alpha_{\text{bound}}$  that partial absorption coefficient due to processes which leave an exciton bound to nitrogen. The variation of the total absorption coefficient in the vicinity of  $A+\text{TO}^\Gamma$ ,  $A+\text{LO}^\Gamma$ , and at 2.348 eV is less than 10%. Since there is a 50% rise in the excitation spectrum at the  $\text{TO}^\Gamma$  and  $\text{LO}^\Gamma$  positions in the excitation spectrum, it is clear that the partial absorption coefficient due to bound states  $\alpha_{\text{bound}}$  in fact possesses strong maxima at the  $A+\text{LO}^\Gamma$  and  $A+\text{TO}^\Gamma$  energies, as predicted in Sec. III.

That the structure observed in the excitation spectrum is explicitly not due to a surface effect coupled with the variation of the total absorption coefficient is demonstrated from the fact that the dip at 2.352 eV

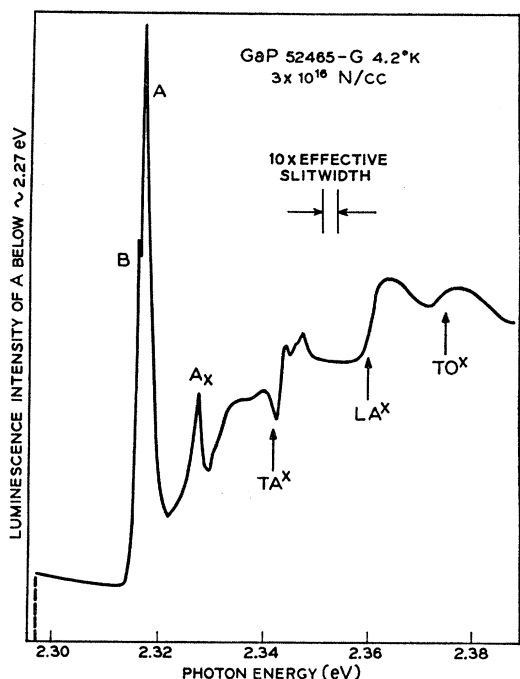


FIG. 7. Low-temperature luminescence excitation spectrum in the vicinity of the indirect absorption edge of a lightly nitrogen-doped crystal of GaP. This crystal was  $\geq 30\%$  transparent over the whole of the energy range shown. The notation is as in Fig. 1.

in Fig. 1 is as strong as the  $A+LO^{\Gamma}$  or  $A+TO^{\Gamma}$  dips, and would cause an "absorption length" effect very similar to that at the  $A+LO^{\Gamma}$  or  $A+TO^{\Gamma}$  energies. The fact that there is no prominent peak at 2.352 eV in the excitation spectrum of Fig. 6 is an experimental demonstration that the excitation spectrum shape is *not* simply a reflection of the absorption coefficient, but in fact has its shape determined in part by the nature of the electronic final states.

The spectrum of  $\alpha_{\text{bound}}$  provided from the excitation measurements is not simply the mirror image of the fluorescence spectrum about the no-phonon line, however. In particular the coupling of  $N^*$  to  $TO^{\Gamma}$  phonons is much larger in absorption (Fig. 6) than in emission (Fig. 2). However, several conditions must be met before exact mirroring can be expected. One of these which does not hold in the present circumstances, is that the electronic states must be well separated compared with the energies of the relevant phonons, since only then can the electronic and vibrational parts of the wave function be separated.

In some but not all of the region below 2.33 eV the absorption in this crystal was quite strong but not complete, and the analysis in the region of  $A$  and  $A_x$  is therefore difficult. The analysis of the data of Fig. 7 in this energy region is much easier. In crystals having a nitrogen concentration of  $\sim 3 \times 10^{16}$  N/cc, the absorption below the intrinsic threshold at 2.341 eV is weak (and nitrogen-induced). If again the efficiency of the

" $A$ " fluorescence due to free excitons is negligible and that due to bound excitons is unity at 4.2°K, then the excitation spectrum will be simply proportional to  $\alpha_{\text{bound}}$  below the intrinsic threshold. This spectrum (Fig. 7) shows the usual sharp peak at  $A$ , and shows  $A_x$ , the "cusp" at the free-exciton threshold, clearly—more clearly, in fact, than does  $\alpha_{\text{total}}$ . That the cusp should occur in  $\alpha_{\text{bound}}$  is expected from Sec. III. That it shows up more clearly in this spectrum is due to the fact that the free-exciton square-root threshold, which also contributes to  $\alpha_{\text{total}}$ , and which if large enough would eliminate the cusp in  $\alpha_{\text{total}}$ , is not present in  $\alpha_{\text{bound}}$ .

In the final class of excitation experiments, small amounts of bismuth were added to crystals also containing low concentrations of nitrogen. Bismuth also binds an exciton, but its emission below  $\sim 2.22$  eV is easily resolved from nitrogen.<sup>12</sup> The addition of bismuth introduces a weak absorption line at 2.2315 eV, but the absorption due to bismuth in the vicinity of  $A$  and  $A_x$  is negligible. At energies just below the intrinsic threshold, the absorption in these crystals is due to nitrogen. If the nitrogen fluorescence efficiency when an exciton is bound at nitrogen is high, an excitation process which results in an exciton bound to nitrogen is

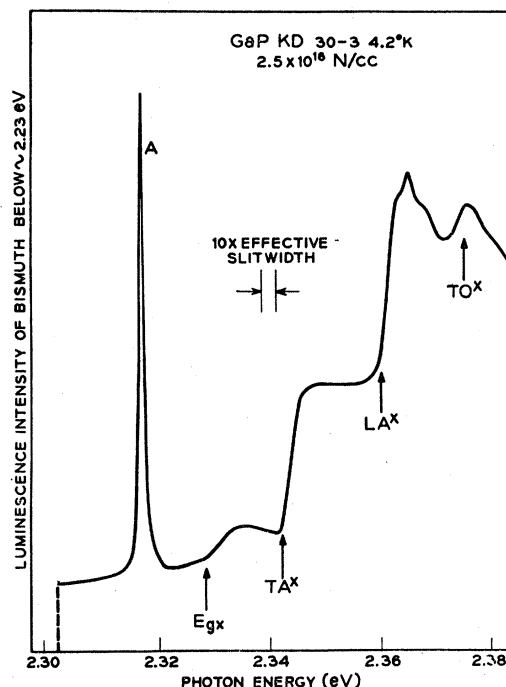


FIG. 8. Low-temperature luminescence excitation spectrum in the vicinity of the indirect absorption edge of a lightly nitrogen-doped crystal of GaP. This crystal was also  $\geq 30\%$  transparent over the whole of the energy range shown, but unlike Fig. 7 the detected luminescence does not originate at the nitrogen ( $A$ ) centers.

<sup>12</sup> F. A. Trumbore, M. Gershenzon, and D. G. Tomas, Appl. Phys. Letters 9, 4 (1966).

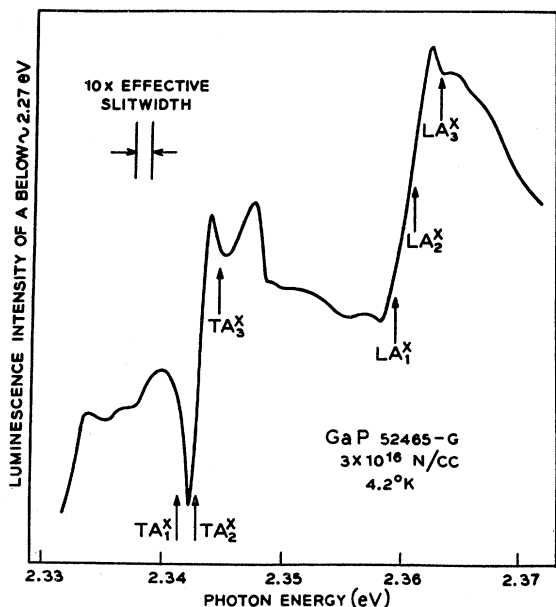


FIG. 9. Detail in the low-temperature luminescence excitation spectrum from the lightly nitrogen-doped crystal of Fig. 7, showing characteristic interference shapes (cf. Fig. 5) near the thresholds for phonon-assisted creation of free indirect excitons. There is no detailed correspondence between the positions of the arrows, which mark the thresholds of fine structure observed in the intrinsic absorption edge (Ref. 6), and the structure in the excitation spectrum.

inefficient in producing bismuth emission compared to an excitation which creates a free exciton or a free electron-hole pair. This excitation spectrum should be dominated (below the intrinsic threshold) by the partial absorption coefficient for generating free particles due mainly to the presence of nitrogen. The observed spectrum is shown in Fig. 8. An absorption threshold is evident at the exciton energy gap  $E_{gz}$ .  $A_x$  is not visible, just as predicted in Sec. III.  $A$ , which ideally should also be missing, does have a much smaller band area than in Fig. 7 relative to the intensity in the intrinsic absorption region near 2.37 eV.

Many other kinds of interference effects are visible in the excitation spectrum. For example, the excitation spectra of a relatively weakly nitrogen-doped crystal in the vicinity of the intrinsic absorption thresholds, shown in Fig. 9, have shapes which strongly suggest interference. In this sample, the interference would be between intrinsic absorption and nitrogen-induced absorption. The exact form of the excitation structure above the threshold for intrinsic absorption is therefore expected to be very sensitive to the magnitude of the

nitrogen concentration near  $5 \times 10^{16}$  atoms/cc, in agreement with observation.

## V. DISCUSSION AND CONCLUSION

The couplings between different processes which, by themselves, would have simple spectral shapes lead to a variety of well-known interference-induced spectral forms. The shape of the absorption spectrum due to substitutional nitrogen in GaP strongly indicates the presence of such effects. The effects are consistent with the current understanding of the energy levels of GaP containing nitrogen.

Two different classes of electronic final states are involved in the transitions studied: final states with an exciton bound to nitrogen and final states having a free exciton or electron-hole pair. The explanation of the structures observed in the total absorption coefficient in terms of interference contained several predictions about the partial absorption coefficients associated with these two classes of final states.

When absorption leads to several different electronic final states and these radiate with different probabilities, the measurement of fluorescence excitation spectra provide a means of measuring partial absorption coefficients. The quantitative determination of partial absorption coefficients for the present system has not been attempted. The simple suppositions of the present analysis are certainly not rigorously correct, though qualitatively acceptable. For example, the fluorescent efficiency for intrinsic absorption is low but not zero and probably depends on the excitation intensity. The fluorescent efficiency of nitrogen at 4.2°K is probably not 100% in crystals of high concentration, where the excitation can "hop" over large distances. (This may lead to nonradiative recombination at other centers, or to nonradiative Auger recombination.) The separation of "total-absorption-coefficient effects" from final-state effects is also nontrivial. Yet such problems do not prevent the interpretation of the observed excitation spectra as a qualitative description of appropriate partial absorption coefficients. These qualitative partial absorption coefficients agree well with the predictions based on the interference description of the total absorption coefficient.

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