# Isoelectronic Traps Due to Nitrogen in Gallium Phosphide

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Several sharp lines are seen in absorption and fluorescence in crystals of gallium phosphide containing nitrogen as an isolectronic substituent for phosphorus. These lines fall within about 0.15 eV of the band-gap energy. The most prominent line, the $A$ line, is due to a hole and an electron bound to an isolated nitrogen atom. A deeper series of lines, the $NN$ lines, are due to pairs of nitrogen atoms, each line corresponding to a particular internuclear pair separation. This follows from the observation that the $NN$-center concentrations vary as the square of the $A$-center concentration. The Zeeman patterns of the lines and several other pieces of evidence indicate that the deepest $NN$ line corresponds to closest-neighbor nitrogen pairs, the second deepest to second-neighbor pairs, and so on. Vibrational sidebands can be seen in fluorescence included among which are local-mode frequencies. The substitution of $N^{15}$ for $N^{14}$ caused these local modes to shift in exact accord with theoretical expectations. A brief qualitative discussion of the nature of isoelectronic traps in semiconductors is presented.

## I. INTRODUCTION

AT low temperatures the fluorescent spectra of certain crystals of gallium phosphide are remarkable for the large number of sharp lines which are present. Many of these arise from recombination of holes trapped on acceptors with electrons trapped on donors, there being separate lines for different donor-acceptor separations.[1] Other lines correspond to the decay of excitons bound to point defects; a reasonably well understood example of this is the so-called "C" line,[2] which gave a Zeeman pattern showing that an exciton was bound to a neutral donor which in this case is sulfur. It lies 0.018 eV below the intrinsic exciton,[3] a position which is at least consistent with the sulfur-donor binding energy of $0.085\pm0.02$ eV.[4] Two lines, $A$ and $B$, separated by $8\times10^{-4}$ eV, (which are often referred to simply as the "$A$ line"), and which are obviously connected, are seen in many crystals usually at the high-energy limit of the fluorescent spectrum.[2] The Zeeman effect of these lines shows that an exciton is bound to a "spinless" center. On the other hand the position of these lines, 0.011 eV below the intrinsic exciton or about 0.02 eV below the band gap, is inconsistent with this center being any known ionized donor or acceptor, the binding energies of which are all greater than 0.03 eV.[5] This fact together with unexpectedly strong phonon sidebands led to the suggestion that the bound exciton state might be derived from the direct-band-gap exciton rather than the lowest lying indirect-gap exciton. This suggestion was not subsequently supported by pressure investiga-

tions of the optical absorption of GaP.[6] Many other sharp no-phonon lines can be seen in certain crystals and among these are a series which were labeled[2] $D, E, F, G, H$ and which occur at energies lower than the $A$ line. The same lines were reported by Gross and Nedzvetskii[7] and were described by them as a converging hydrogen-like series arising from the decay of an exciton bound to a neutral acceptor. The transitions were supposed to leave the acceptor in an excited state and each excited state gave a different line in the series.

In this paper[8] it is shown that the $A$ line, and the series of lines below it, called here the $NN$ lines, are intimately connected, and that the $A$ line arises from an exciton bound to an isolated nitrogen atom substituted for a phosphorus atom, and that the $NN$ lines correspond to excitons bound to pairs of nitrogen atoms. The results are of interest because they demonstrate that isoelectronic substitutions for lattice atoms in a semiconductor can lead to bound states in the forbidden gap of the crystal.

## II. EXPERIMENTAL

### A. Crystals

Crystals of GaP grown from Ga solution[1] without special purification steps often show in fluorescence the $A$ line, and sometimes the $NN$ lines, but the spectra are usually dominated by donor-acceptor pair recombination. Fluorescence is therefore not a satisfactory method for following the $A$-center concentration (i.e., the nitrogen concentration). Absorption spectra, however, can be used for the measurement of the nitrogen concentration. It was found that if GaN was added to

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

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

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

[4] H. C. Montgomery and W. L. Feldmann, J. Appl. Phys. **36**, 3228 (1965).

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

[6] R. Zallen and W. Paul, Phys. Rev. **134**, A1628 (1964).

[7] E. F. Gross and D. S. Nedzvetskii, Dokl. Akad. Nauk. SSSR **154**, 64 (1964) [English transl.: Soviet Phys.—Doklady **9**, 38 (1964)].

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

the Ga solution before growth (from 1200°C), the resultant GaP crystals were doped with nitrogen. Several atomic percent of GaN could be added to the sealed quartz ampoules before undue pressures were developed. The controlled addition of GaN was a useful method for producing crystals containing variable quantities of nitrogen such as were used to compare the $A$-line and $NN$-line absorptions.

Crystals in which the donor-acceptor fluorescence is absent have been grown by Frosch using a modified wet hydrogen transport method.[9] Under favorable conditions, highly perfect needles were grown several millimeters long and with faces about 1 mm in width. When quartz vessels were used in the furnace the crystals had almost no fluorescence or absorption in the green region of the spectrum below the band edge. If, however, boron-nitride vessels were present, crystals were produced which had a reddish rather than an orange color, and which showed the $NN$ lines (and sometimes the $A$ line) in fluorescence, and which showed in absorption both the $NN$ lines and a very strong $A$ line. The strong $A$-line absorption accounts for the red color of the crystals. Boron or nitrogen were therefore suspected as impurities. While boron in quartz vessels did not produce the $A$ line or the $NN$ lines, when GaN was present in the oven-red crystals were produced just as if BN had been used, indicating that nitrogen was responsible for the absorption and fluorescence. Nitrogen added to the gas stream produced no strong effects because of the stability of the $N_2$ molecule. Small quantities of ammonia, however, resulted in red crystals. The ammonia was difficult to control as it tended to react first with the free gallium in the system. In fact a convenient way of introducing ammonia in suitable quantities was from BN or GaN which is hydrolyzed at the high temperatures by the water used in the transport process. To make crystals containing $N^{15}$, $N^{15}H_3$ was first reacted
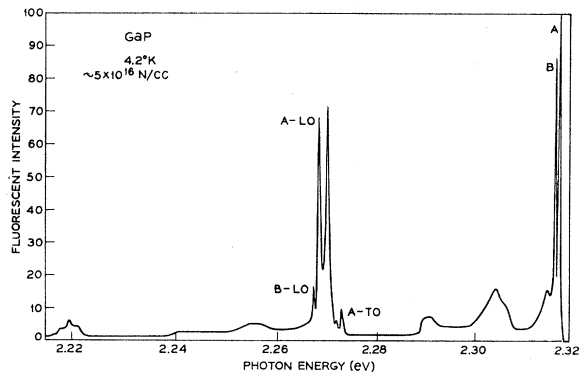


FIG. 1. The fluorescent spectrum of the $A$, $B$ lines, due to an exciton decaying at an isolated nitrogen atom, and associated vibrational (or phonon) sidebands. In other crystals the ratio of intensities of the no-phonon to the phonon lines can be quite different.

[9] C. J. Frosch, *Proceedings of the International Conference on Crystal Growth, Boston, Massachusetts, 1966* (Pergamon Press, Inc., New York, 1966).
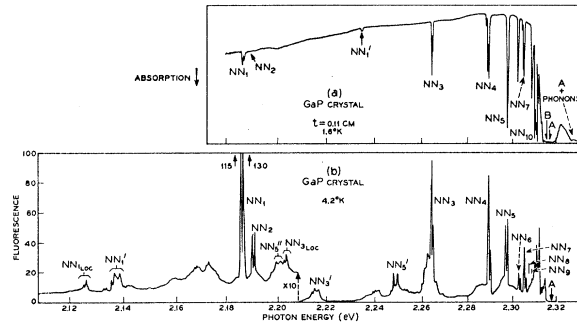


FIG. 2. (a) The absorption and (b) the fluorescent spectra of the $NN$ lines in a crystal containing about $10^{19}$ (atoms of nitrogen)/cc. The primed symbols such as $NN_1'$ represent phonon replicas of the no-phonon lines. Local modes are indicated as $NN_1$ loc, etc. Above 2.317 eV the absorption is dominated by the $A$ line and its phonon wings; there is, however, no $A$-line fluorescence.

with $Ga_2O_3$ to produce $GaN^{15}$, which was then used in the crystal-growing furnace.

Measurements by Montgomery showed that the vapor-grown crystals were of low conductivity and that nitrogen doping produced no obvious effects on the electrical properties of the crystals. Gershenzon showed that absorption at the $A$ line occurred equally well in both $p$- and $n$-type crystals.

### B. Optical Properties

Optical measurements were made at 20, 4.2, and 1.6°K with the crystals immersed in the refrigerant and mounted in a strain-free manner. Fluorescence was excited using the light from filtered high-pressure mercury lamps. In order to obtain sufficient path length for transmission measurements, it was sometimes necessary to polish the ends of the vapor-grown needles and pass the light down the length of the crystals. Similarly, for the solution-grown plates, light was passed in the plane of the plate. It was often convenient to use a magnified image of the crystal at the spectrograph entrance slit. A 2-m Bausch and Lomb spectograph was used employing photographic or photoelectric recording. The Zeeman pattern was observed using a magnet which could produce 31 kG. For certain orientations in the magnetic field the needles were mounted in the horizontal plane; a Dove prism was then used to produce a vertical image at the slit.

### III. RESULTS

#### A. The $A$ line and the $NN$ lines

Figure 1 shows the fluorescent spectrum of a vapor-grown crystal which grew with a low concentration of nitrogen as judged by its absorption spectrum; the analysis of Sec. III D indicates that it contains about $5 \times 10^{16}$ nitrogen atoms/cc. The no-phonon $A$ and $B$ lines are seen, as are various phonon replicas at lower energies.[2] The $B$ line corresponding to the $J = 2$ exciton state is a forbidden line and is only seen in fluorescence
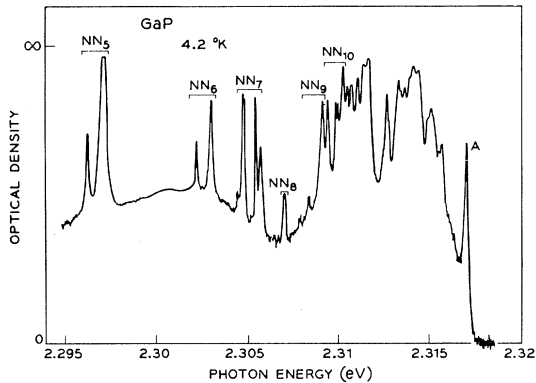
FIG. 3. The fluorescence of some $NN$ lines and, weakly, the $A$ line, in a crystal containing about $5 \times 10^{18}$ nitrogen atoms/cc. The results are taken from a photographic plate.

at low temperatures when the state is preferentially thermally populated.

As the concentration of nitrogen in the crystals is increased, the $NN$ lines appear and at high nitrogen concentrations they are present alone in fluorescence, the $A$ line having disappeared. Figure 2 shows the fluorescent and absorption spectra for such a crystal containing about $10^{19}$ nitrogen atoms/cc. In fluorescence the $NN$ lines consist of a series of multiplets the spacing between successive multiplets decreasing as the $A$ line is approached. In Fig. 2 they are labeled as $NN_1$, $NN_2$ etc.; the primed symbols in this figure refer to phonon replicas of the no-phonon lines and will be discussed in Sec. III E. Figure 3 shows similar results on an expanded scale at the high-energy end of the series where the lines converge. A somewhat less concentrated crystal has been used for the fluorescence, so that the $A$ line can be seen.

It is observed that the fluorescent lines in a multiplet all thermalize to lower energies; thus at 20°K the highest energy lines are usually strongest, at 4.2°K most of the lines have comparable strength, and at 1.6°K the lowest energy lines are strongest. This is illustrated for lines $NN_1$, $NN_6$, and $NN_7$ in Fig. 4. Thus there is thermalization within the multiplets, as there is for the $A$-$B$ lines, but there is no thermalization between the different multiplets. This makes it most unlikely that the same center is involved in all the lines, such as would be the case if excited states of the center were involved.[7] The $NN$ transitions have been numbered consecutively from the lowest energy observed multiplet $NN_1$. Beyond $NN_8$ the numbering is difficult because the separation between the multiplets is less than the multiplet structure itself. In general the multiplets appear to be derived from a pair of lines like $A$, $B$ but they have more fine structure. Thus the lines from the allowed $J = 1$ state can be recognized at higher energies as a singlet, doublet, or triplet. The lower energy set of lines are derived from the weaker $J = 2$ transition; their higher multiplicity is particularly clear

in a magnetic field (see Sec. III C). The fine structure indicates that the local symmetry at the centers responsible for the transitions is lower than the cubic symmetry of the crystal. The lowered symmetry causes mixing of the $J = 1$ and $J = 2$ states with a resultant relaxation of the selection rule that the $J = 2$ transition is forbidden, and it is observed that the larger the splittings of the multiplets, the stronger the "$J = 2$" lines. This evidence suggests that an isolated atom is responsible for the $A$ line, and that the $NN$ lines arise from pairs of atoms. Since the $NN$ lines appear when the nitrogen concentration is increased, the pairs might consist of two nitrogen atoms.

## B. Absorption at the $A$ line and $NN$ lines

If the $A$ line arises from an exciton trapped at an isolated nitrogen atom, and the $NN$ lines from excitons trapped at pairs of nitrogen atoms, and if the nitrogens are distributed randomly, then the pair concentration should vary as the square of the $A$-center concentration. This comparison can be made by measuring the absorption of the $A$ line and the $NN$ lines in several crystals containing various concentrations of nitrogen.

In Figs. 5(a) and (b) are plotted the absorption curves taken at 1.6°K of two nitrogen-doped crystals, the second more heavily doped than the first. The absorption of a pure crystal at this temperature is essentially zero below a photon energy of 2.34 eV,[3] and this intrinsic absorption gives a negligible contribution to the absorption of these crystals above this energy. The $A$ line occurs in both crystals, and at higher energies
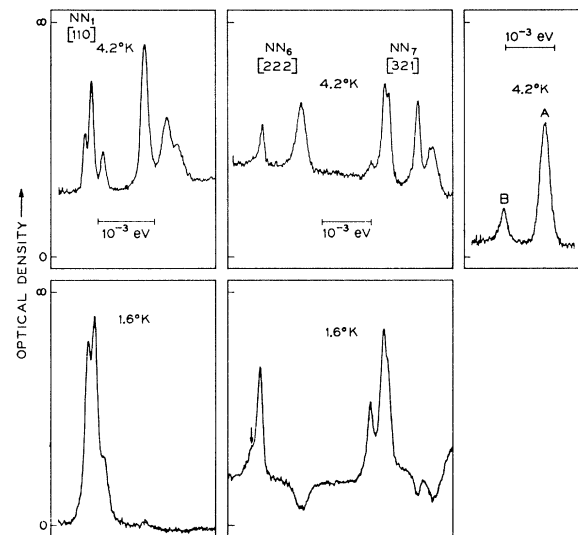


FIG. 4. Some of the $NN$ lines at 4.2 and 1.6°K, and the $A$, $B$ lines at 4.2°K. The $NN$ lines show more structure than the $A$, $B$ lines, but "$J = 1$" and "$J = 2$" components can still be classified. At 1.6°K the lower lines of each multiplet are emphasized; some of the allowed higher lines are now seen as "absorption" lines in the background fluorescent spectrum. The arrow on $NN_6$ at 1.6°K indicates an additional weak component of this multiplet. The results are taken from photographic plates.

there are absorption bands which correspond to the $A$-line transition with simultaneous emission of phonons. The shapes of these absorption bands are interesting and will be discussed elsewhere.[10] It is convenient to use the peak $A_X$ at 2.328 eV as a measure of the $A$-center concentration. Separate experiments have established that at 20°K the ratio of the absorption coefficient $\alpha$ at the peak of $A$ to that at $A_X$ is roughly 150.

In Fig. 5(b) the $NN$ lines are stronger compared to the $A$ line than they are in Fig. 5(a). This shows that at higher nitrogen concentrations the $NN$ lines are more prominent compared to the $A$ line, than at lower nitrogen concentrations. In Fig. 6 is shown a plot of the absorption at one of the $NN$ lines, $NN_{10}$, against the absorption at $A_X$ for several crystals containing different concentrations of nitrogen. The solid line has a slope of 2. A similar fit to a line of slope 2 has been found for line $NN_5$, and it is believed would be found for all the $NN$ lines. It is therefore reasonable to conclude



FIG. 6. The absorption at line $NN_{10}$ plotted against the absorption at $A_X$ for several crystals containing different quantities of nitrogen. The line is drawn with a slope of two and indicates that the $NN$ concentration varies as the square of the $A$-center concentration. The concentration scales are obtained as indicated in the text; it is estimated that they may be in error by a factor of 5.

that the $NN$ lines arise from pairs of atoms which alone are responsible for the $A$ line, namely, from two nitrogen atoms.

## C. Ordering of the $NN$ lines

Nitrogen introduced into GaP during growth will almost certainly substitute isoelectronically for a phosphorus atom. An isolated nitrogen atom evidently binds an exciton (the $A$ line). Two nitrogen atoms close together might be expected to bind an exciton more tightly. As the distance between the members of a pair increases the exciton will be bound with an energy that becomes increasingly close to that for the isolated atom. Thus a model may be tried in which the lowest energy line observed, $NN_1$, is ascribed to a nitrogen atom on a phosphorus site with another nitrogen atom on the nearest shell of phosphorus sites. $NN_2$ then has a nitrogen on the next nearest shell of phosphorus sites, and so on. From the geometry of the lattice, some of the properties of these successive pairs can be deduced. These include the number of equivalent pairs which can exist for each shell, the directions of the pairs in each shell and the number of sets of equivalent pairs in a particular shell when a magnetic field is applied in a particular direction. These properties are listed in Table I for the first 10 pairs. Some evidence can be adduced to support the suggested assignment of the lines, as follows:
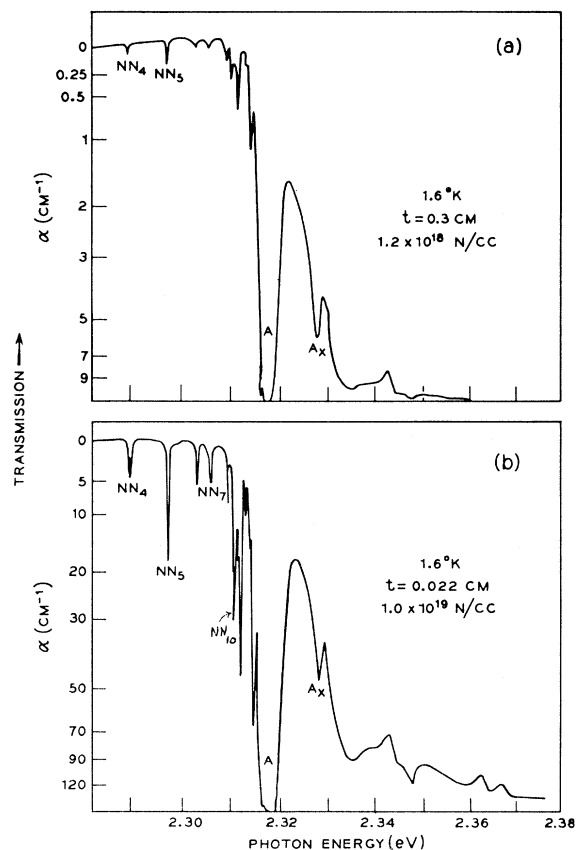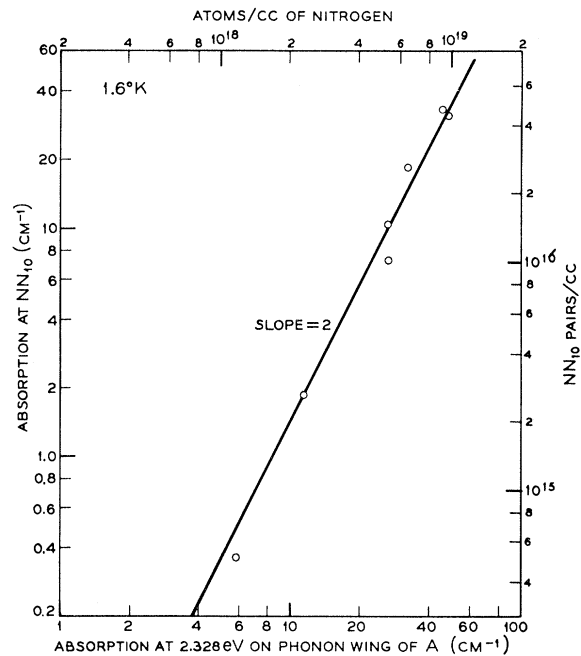


FIG. 5. The absorption spectra of two crystals of GaP containing different concentrations of nitrogen. (a) is a less concentrated crystal than (b), and in it the $NN$ lines are weaker compared to the $A$-line absorption than in (b). The absorption at energies higher than that of $A$ is entirely due to the phonon wings or excited states of $A$. The absorption at $A_X$ is often used as a measure of the $A$-line absorption.

[10] P. J. Dean, J. J. Hopfield, and D. G. Thomas (to be published).

TABLE I. Properties of $NN$ lines and $A$ line at 4.2°K.

| | Wavelength in air of lowest "$J=1$" line (Å) | Energy of lowest "$J=1$" line (eV) | Energy from exciton (eV) | Separation (Å) | Coordinate of one member of pair with other at origin | No. of equivalent sites $n_m$ | Shift of line to higher energy when $N^{14}$ is replaced by $N^{15}$ ($10^{-4}$ eV) |
|---|---|---|---|---|---|---|---|
| $NN_1$ | 5671.3 | 2.1854 | 0.143 | 3.85 | (110) | 12 | 1.6 |
| $NN_2$ | 5659.3 | 2.1901 | 0.138 | 5.45 | (200) | 6 | 2.8 |
| $NN_3$ | 5473.5 | 2.2644 | 0.064 | 6.67 | $\left\{\begin{matrix}(211)\\(2\bar{1}1)\end{matrix}\right\}$ | $\left\{\begin{matrix}12\\12\end{matrix}\right\}$ | |
| $NN_4$ | 5413.8 | 2.2894 | 0.039 | 7.71 | (220) | 12 | |
| $NN_5$ | 5395.7 | 2.2971 | 0.031 | 8.62 | (310) | 24 | 1.0 |
| $NN_6$ | 5381.2 | 2.3033 | 0.025 | 9.45 | $\left\{\begin{matrix}(222)\\(\bar{2}\bar{2}2)\end{matrix}\right\}$ | $\left\{\begin{matrix}4\\4\end{matrix}\right\}$ | 1.1 |
| $NN_7$ | 5375.1 | 2.3059 | 0.022 | 10.2 | $\left\{\begin{matrix}(321)\\(3\bar{2}1)\end{matrix}\right\}$ | $\left\{\begin{matrix}24\\24\end{matrix}\right\}$ | 1.1 |
| $NN_8$ | 5371.1 | 2.3076 | 0.020 | 10.9 | (400) | 6 | |
| $NN_9$ | 5365.3 | 2.3101 | 0.018 | 11.56 | $\left\{\begin{matrix}(411)\\(4\bar{1}1)\\(330)\end{matrix}\right\}$ | $\left\{\begin{matrix}12\\12\\12\end{matrix}\right\}$ | |
| $NN_{10}$ | 5363.2 | 2.3110 | 0.017 | 12.19 | (420) | 24 | |
| $A$ line | 5349.0 | 2.3171 | 0.011 | $\infty$ | $\cdots$ | $\cdots$ | 0.7 |

## 1. Zero-Field Patterns

As already described, the zero-magnetic-field structure of each $NN$ multiplet is more complex than that of the simple $A$, $B$ lines. This can arise from the local deviation from cubic symmetry produced by the pair of atoms. The deviation will of course reflect the arrangement of



(a) FLUORESCENCE $NN_1$, (110), 4.2°K 31KG

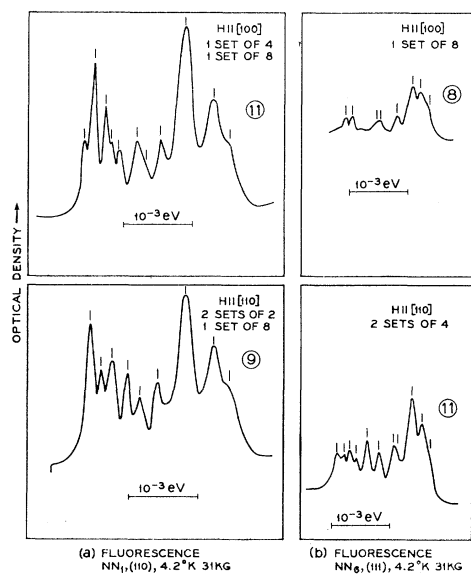(b) FLUORESCENCE $NN_6$, (111), 4.2°K 31KG

FIG. 7. The spectra of $NN_1$ and $NN_6$ in the different orientations of a magnetic field of 31 kG. Also indicated are the number of inequivalent sets of pairs for each field orientation, and the number of pairs in each set, assuming the $NN$ properties given in Table I. It is significant that for $NN_6$ with a field in the (100) direction a maximum of eight lines are predicted and only eight lines are seen. The data are taken from photographic plates.

the pairs. It is a result of symmetry considerations that pairs arranged in $\langle 100 \rangle$ or $\langle 111 \rangle$ directions can split the "$J=1$" state of the bound exciton into a doublet only, while pairs in other directions can split the $J=1$ state into a triplet. In accord with this, Fig. 4 shows that the $J=1$ state of $NN_1$ ($\langle 110 \rangle$ direction) is split into a triplet, whereas that of $NN_6$ ($\langle 111 \rangle$ direction) is not perceptibly split. $NN_2$ and $NN_8$ which are both in $\langle 100 \rangle$ directions have $J=1$ states which are, respectively, observed as a doublet and a singlet. Unfortunately, $NN_8$ is difficult to examine, since it is very weak. While this evidence is not conclusive, since the splittings might be too small to be observed, it is consistent with the proposed model.

The zero-field patterns provide support for the belief that both members of the pairs are identical atoms. Since GaP lacks a center of symmetry pairs in directions such as $\langle 111 \rangle$ (e.g., $NN_6$) or $\langle 321 \rangle$ (e.g., $NN_7$), would have extra structure if the atoms were not identical, for $X$-$Y$ would not be equivalent to $Y$-$X$. Pairs in $\langle 110 \rangle$ directions, for instance (such as $NN_1$), would not have this inequivalence. However, no peculiar fine structure has been observed for those multiplets in which it could occur.

## 2. Zeeman Patterns

The magnetic splittings of the $NN$ lines are in general anisotropic and complex. The behavior of $A$, $B$ in a magnetic field was on the other hand very simple.[11] In spherical symmetry, the electron and hole angular moments ($\frac{1}{2}$ and $\frac{3}{2}$, respectively), combine to yield the basic $J=1$ and $J=2$ states, $A$ and $B$, respectively. The low-

[11] Y. Yafet and D. G. Thomas, Phys. Rev. **131**, 2405 (1963).

FIG. 8. A comparison of the observed absorption and fluorescent intensities of the $NN$ lines, with the number of equivalent pairs in each multiplet as given in Table I. The absorption at $NN_2$ and $NN_8$ is too weak to measure reliably.
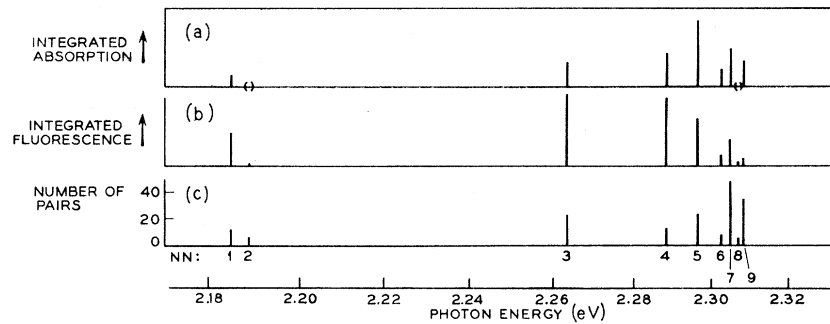
field Zeeman pattern will then consist of a triplet and a quintet. The cubic field terms are quite small; experimentally, the line patterns are very close to the simple spherical model. The cubic zero-field splitting of the $J=2$ state is unobservably small.

An exciton bound to a pair of nitrogen atoms has in its Hamiltonian additional terms representing potentials of lower symmetry. The simplest such term might be represented as one of axial symmetry around the line joining the pair. Such a term splits the degeneracy of the $A$ and $B$ lines, mixes $A$ and $B$ states, and gives rise to the multiplet structure in zero field discussed in the previous section. The magnetic effects must now be calculated in the presence of such splittings. For any particular pair of atoms, there will still be eight magnetic levels, but the Zeeman pattern will now depend on the orientation of the pair axis with respect to the magnetic field.

A given $NN$ pair line in zero field contains contributions from equivalent pairs in different physical orientations. The magnetic field now produces different Zeeman splittings for the pairs in different orientations, resulting in a line pattern which is a superposition of several octets, many of whose lines are not experimentally resolved. Figure 7 shows the Zeeman splitting of the $NN_1$ and $NN_6$ multiplets in a magnetic field of 31 kG for fields oriented in the $\langle 100 \rangle$, and $\langle 110 \rangle$ directions. $NN_6$ consists of pairs lying along the four $\langle 111 \rangle$ lines. A magnetic field in the $\langle 100 \rangle$ direction makes the same angle with each of these $\langle 111 \rangle$ lines, so in this case all pairs should have the same Zeeman splitting. Eight lines are thus expected, and are observed. For a magnetic field in the $\langle 110 \rangle$ direction, on the other hand, 11 Zeeman components can be resolved for $NN_6$, out of a total of two octets (16 lines) which could have been expected. For $\langle 110 \rangle$ pairs such as, for example, $NN_1$ there is no geometry in which only one octet is expected. Eleven and nine lines can be seen in the two magnetic geometries shown. These results are in accord with the model. No cases were found which violated the model, although it often happens that fewer lines can be resolved than are theoretically predicted.

An attempt was made to parametrize the fine structure of $NN$ pair lines in the presence of a magnetic field in terms of a "spin Hamiltonian" for the eight levels

involved. The parameters of importance are: (1) the electron hole $\mathbf{J} \cdot \mathbf{J}$ coupling (isotropic component); (2) the electron hole $\mathbf{J} \cdot \mathbf{J}$ coupling (cubic component); (3) the uniaxial or biaxial "strain" splitting of the valence band; (4) two lower symmetry $\mathbf{J} \cdot \mathbf{J}$ coupling terms; (5) the anisotropy of the hole $g$ value. Extensive calculations were made of the positions and intensities of the pair lines in a magnetic field using this parametrization of the problem. While these calculations produced plausible line patterns very similar to patterns observed, the ambiguities of interpretation (due in part to the failure to resolve a sufficient number of lines and in part to the lack of identification of those lines which were well resolved) prevented the quantitative understanding of the details of the fine structure.

### 3. The Intensity of the Lines

It is assumed that the nitrogen atoms are arranged randomly in the lattice. The strength of the absorption lines should then be in the ratio of the number of possible pairs for each shell multiplied by the corresponding optical transition probabilities. To say that the transition probabilities remain constant as the $N$-$N$ separation changes is an approximation. It is expected that the transition probabilities will vary with the separation and also with the orientation of the pairs, for the hole and electron wave functions are not spherically symmetrical. However, there is a qualitative difference between the $NN$ pairs and the donor-acceptor pairs. In the latter case the transition probabilities become steadily less as the separation increases because the overlap between the hole and the electron becomes steadily less. Infinite separation of the nitrogen atoms, however, corresponds to the $A$ line, in which an exciton is entirely bound to one atom. As the second nitrogen atom is brought closer to the first, one can imagine the $A$ line being modified by the presence of a foreign atom. It is convenient therefore as a first approximation to suppose the transition probabilities to be the same for all the $NN$ lines and the $A$ line.

Figure 8 plots the number of pairs for the first nine shells. Also shown is the integrated experimentally observed absorption for the $NN$ lines. (The absorption at $NN_2$ and $NN_8$ is too weak to measure accurately.) There is generally qualitative correspondence between the

number of pairs possible and the absorption intensity. Notice that $NN_2$, $NN_6$, and $NN_8$ are all expected to be weak and are observed to be so.

In fluorescence, since the transitions are not saturated, the intensities of the lines may be expected to be related to the number of pairs multiplied by their respective capture cross section. This will only be true for the more tightly bound centers. For small binding energies the exciton may be thermally released before recombination. Also, as the binding energy becomes less and the bound hole and electron covers a greater volume of the system, there will be an opportunity for the exciton to tunnel to a lower energy state and decay there. This latter process will be particularly important for the more concentrated samples, and explains the absence of the higher $NN$ lines and the $A$ line in Fig. 2. The result is particularly striking for the $A$ line, since its concentration far exceeds those of the $NN$ lines. Comparing therefore the intensity of the lower $NN$ lines in fluorescence with the theoretical number of pairs, assuming a constant capture cross section, one sees from Fig. 8 that there is generally qualitative agreement with the expected pattern, although $NN_4$ appears anomalously strong.

### 4. The Positions of the Lines

Table I lists the energies of the strongest component of the $NN$ lines (the lowest energy line of those derived from the "$J=1$" state), and also their energies below the exciton together with the separation of the $NN$ atoms in angstroms.

The binding of a particle to a short-range potential well is a function of both the well depth and range of the potential. For a short-range potential, it is easily possible for near-neighbor pairs to bind an exciton strongly when an isolated impurity binds the exciton weakly, or even if the isolated impurity did not bind an exciton at all. Unlike the donor-acceptor-pair problem, in which the asymptotic $e^2/\epsilon r$ form of the energy as a function of separation was independent of wave function details, in the isoelectronic-pair case it is impossible to calculate any energies for pairs without an explicit wave function. It is to be expected that the binding energy should decrease rapidly with separation, an effect quite clear in Table I. Equally apparent is the irregularity of the energy levels, a symptom of the dependence of the binding energy on details—note, for example, the closeness of $NN_2$ and $NN_1$.

Nitrogen lacks $P$ orbitals in its core states, so its pseudopotential is much more attractive for electrons than is that of phosphorus. While this fact provides a qualitative understanding of why nitrogen is so different from phosphorus, the complicating effects of the polarization of the valence band by the impurity must be taken into account before the mechanism of the binding of the exciton can be understood.

In this section strong circumstantial evidence has been presented supporting the proposed ordering of the $NN$ lines. No experimental evidence has been uncovered which is in conflict with the model.

### D. The Concentration of Nitrogen in GaP Crystals

Assuming that the model is correct, that the nitrogen is distributed randomly and that the optical transition probability is the same for the $NN$ lines and for the $A$ line, it is possible, from measurements of optical absorption alone, to estimate the concentration of nitrogen present in the crystals.

The $A$-line absorption is always much stronger than that of the $NN$ lines, so the isolated nitrogen concentration exceeds that of the nitrogen pairs. Let the nitrogen concentration be $N$ atoms/cc. The probability of any phosphorus site being occupied is

$$N/N_0,$$

where $N_0$ is the number of phosphorus sites/cc. The probability of any site being occupied by a nitrogen atom which in turn has a nitrogen neighbor on the surrounding $m$th shell is

$$\frac{N}{N_0} \times n_m \frac{N}{N_0},$$

where $n_m$ is the number of sites on the $m$th shell (see Table I). The concentration of $m$th-neighbor pairs is therefore

$$n_m \frac{N^2}{N_0^2} \times N_0 \times \tfrac{1}{2} = \frac{n_m}{2} \frac{N^2}{N_0}.$$

Since the pair concentration is small, the concentration of isolated nitrogen is approximately $N$. Assuming now the same proportionality constant between absorption strength and concentration for all the lines, we have

$$\frac{\text{Strength of } NN_m \text{ in Absorption}}{\text{Strength of } A \text{ in Absorption}} = \frac{n_m N}{2N_0}. \tag{1}$$

$N_0$ is known ($2.5 \times 10^{22}$/cc), $n_m$ is known (Table I) and so $N$, and the pair concentration can also be determined. One of the higher energy $NN$ lines, namely $NN_{10}$, was chosen to compare with the peak of the $A$-line absorption, since its transition probability might be supposed to be close to that of the $A$ line, and any preferential pairing would be small for so large a separation. The peak absorption coefficient of the zero-phonon lines for $NN_{10}$ and $A$ are compared (the value for $A$ being obtained using the absorption at 2.328 eV and the factor of 150 mentioned in Sec. III A); it is assumed that the strength in the phonon wings will be comparable for $A$ and $NN_{10}$. The results of the analysis lead to the concentration scales given on Fig. 6. The various assumptions, and the difficulty of measurement of extremely sharp lines are estimated to lead to an uncertainty in the absolute value of this concentration scale of a factor of 5.

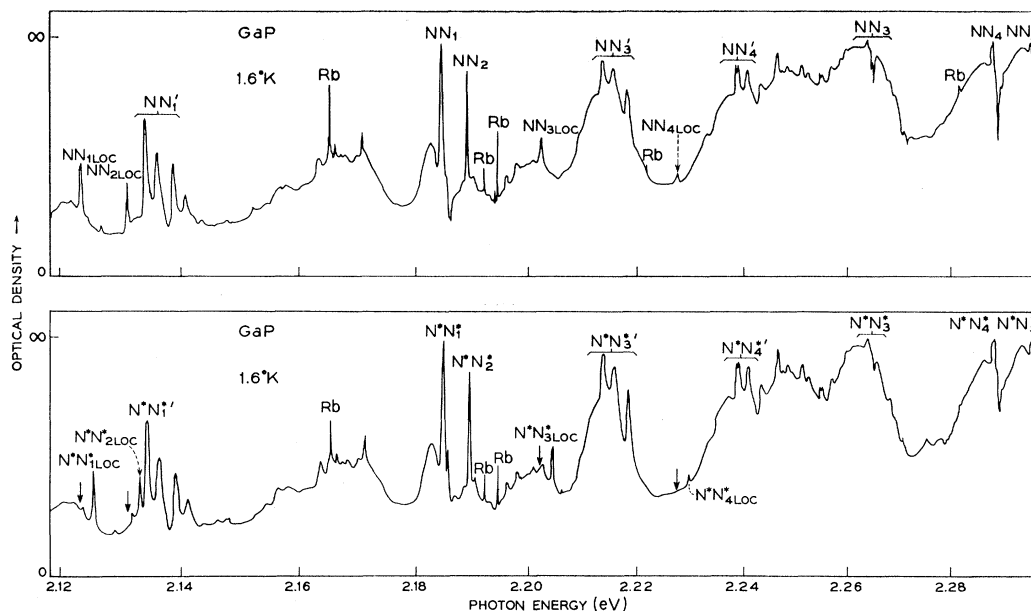Using these concentration scales it is interesting to

FIG. 9. Part of the fluorescent spectra at 1.6°K of two crystals of GaP. The top spectrum comes from a crystal containing $N^{14}$, the lower from a crystal containing $N^{15}$. The differences between the spectra are extremely small with the exception of the local-mode lines. For the heavier isotope these have all shifted to higher energies. In the lower section the solid arrows mark the positions of the local mode lines for $N^{14}$. The data are taken from photographic plates. The lines marked Rb are rubidium calibration lines.

notice how the fluorescence of the crystals depends on the nitrogen concentration. At a nitrogen concentration near $10^{19}/cc$ the $A$ line is not seen in fluorescence, only the $NN$ lines. Near a concentration of $10^{18}$ both the $A$ line and the $NN$ lines can be seen, and at $10^{17}$ nitrogen atoms/cc crystals show the $A$ line and no $NN$ lines in fluorescence. If crystals containing nitrogen are grown from gallium solution, donor-acceptor pair lines are often seen in addition to the lines due to nitrogen.

### E. Vibrational Sidebands and Local Modes

The $A$ line and the $NN$ lines all have vibrational sidebands. These are most easily studied in fluorescence. For the $A$ line and the higher $NN$ lines the vibrational replicas which can be seen can be reasonably accounted for in terms of lattice phonons.[2] Apart from multiple-phonon effects the largest phonon interval is observed to be $0.050_4$ eV which corresponds to a longitudinal optic (LO) phonon at the zone center. The upper section of Fig. 9 shows a section of the fluorescent spectrum of a crystal of GaP taken from a photographic plate. The crystal was at 1.6°K in order to produce some simplification of the spectrum; at this temperature most of the fluorescence is concentrated in the lowest energy line of the no-phonon multiplets, so that there is only one no-phonon line from which replicas occur. A consequence of this is that the strong allowed no-phonon lines falling above the lowest energy lines can appear as absorption lines in the spectrum, for they absorb the background light generated by phonon processes. Examples of this can be seen at $NN_1$ and $NN_4$.

The spectra show much structure most of which can be recognized as being derived from various lattice phonons if acoustic branches and phonon combinations are included. The sets of lines labeled $NN_1'$, $NN_3'$, etc. represent phonon replicas involving a group of optical phonons which can also be seen off the $A$ line. The lowest-energy lines of these groups corresponds to the LO phonon. The intensities of the phonon replicas of the $NN$ lines are considerably weaker than the corresponding no-phonon $NN$ lines. The intensities of the phonon replicas of the $A$ line are usually relatively much stronger. It has been observed, however, that for the $A$-line system there can be a wide variation of the relative strength of the no-phonon line and its phonon replicas. It appears that in crystals in which the no-phonon line is abnormally broad, the phonon replicas are relatively weaker than for crystals in which the no-phonon line is sharp. At present this phenomenon is not well understood. The effect is not believed to be due to self-absorption and re-emission of the fluorescent light, since it is not found to be drastically affected by the size of the crystals.

At energies below those corresponding to the LO phonons, other phonon replica lines can sometimes be seen. These become relatively stronger the greater the binding energy of the hole and electron to the $NN$ pair. These lines have been marked in the figure as $NN_{1\ loc}$, $NN_{2\ loc}$, etc. $NN_{1\ loc}$ is comparable in strength to the $NN_1'$ lines, but $NN_{4\ loc}$ is much weaker than the $NN_4'$ lines. Certain additional weak lines can also be discerned near these lines.

TABLE II. Isotope shifts of local-mode energies at 1.6°K, in eV. Experimental accuracy ±0.0002 eV.

| | $NN_1$ | | | $NN_2$ | | | $NN_3$ | | | $NN_4$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | "J=2" line | Local-mode line | Local-mode energy | "J=2" line | Local-mode line | Local-mode energy | "J=2" line | Local-mode line | Local-mode energy | "J=2" line | Local-mode line | Local-mode energy |
| $N^{14}$ | 2.1844 | 2.1234 | 0.061 | 2.1891 | 2.1311 | 0.058 | 2.2635 | 2.2022 | 0.0613 | 2.2887 | 2.2273 | 0.0614 |
| $N^{15}$ | 2.1845 | 2.1255 | 0.059 | 2.1894 | 2.1332 | 0.0562 | 2.2637 | 2.2042 | 0.0595 | 2.2888 | 2.2292 | 0.0596 |
| Observed isotope shift | | | −0.002 | | | −0.0018 | | | −0.0018 | | | −0.0018 |
| Predicted isotope shift [Eq. (6)] | | | −0.00207 | | | −0.00197 | | | −0.00207 | | | −0.00207 |

Since these new lines occur outside the allowed lattice vibrational modes, and since nitrogen is lighter than phosphorus, it is reasonable to suppose that the lines correspond to the excitation of local modes. Presumably one of the nitrogen atoms is set vibrating against its surrounding gallium atoms. There may be more than one type of vibrational mode, particularly since two nitrogen atoms are present, and this may account for some of the weaker lines. The most tightly bound centers are expected to have the strongest local-mode effects since for these the bound-exciton wave function will be more concentrated at the foreign atom. Local modes derived from the $A$ line itself are not seen. This is probably because in the electronic decay of the state "breathing" modes of the system are predominantly excited. For the isolated nitrogen atom, these do not involve motion of the nitrogen atom but for the $NN$ pairs the nitrogen atoms will be set into vibrational motion.

Table II lists the energies of the no-phonon lines and of the strongest local mode lines derived from them. The differences give the local-mode energies. These range from 58 to 61.4 meV. A crude estimate of the expected energy may be made as follows. An "average" optical lattice-vibration frequency may be written

$$\bar{\omega} = k^{1/2} \left\{ \frac{1}{M_{Ga}} + \frac{1}{M_P} \right\}^{1/2}, \qquad (2)$$

where $M_{Ga}$, etc. represents the mass of a gallium atom and $k$ represents a force constant. Here the whole gallium lattice is vibrating against the phosphorous lattice. If the phosphorus is replaced by nitrogen and if the force constant remains the same,

$$\omega_{loc} \approx k^{1/2} \left\{ \frac{1}{\alpha M_{Ga}} + \frac{1}{M_N} \right\}^{1/2}, \qquad (3)$$

where $\alpha$ is a parameter which will be larger the more localized is the mode. As a guess $\alpha$ may be taken as 4, suggesting that one nitrogen atom is vibrating against its four nearest neighbors. So long as $\alpha > 1$, the value of $\omega_{loc}$ is not very sensitive to $\alpha$. Combining the two

relations,

$$\omega_{loc} = \bar{\omega} \left\{ \frac{1/4M_{Ga} + 1/M_N}{1/M_{Ga} + 1/M_P} \right\}^{1/2} = 1.27\bar{\omega}. \qquad (4)$$

As an approximation for $\bar{\omega}$ we may use

$$\bar{\omega} = \frac{2\omega_{TO} + \omega_{LO}}{3} = 47.1 \text{ meV}, \qquad (5)$$

where $\omega_{TO}$, the doubly degenerate transverse vibrational energy, is 45.4 meV,[2] and $\omega_{LO} = 50.4$ meV (TO = transverse optic, LO = longitudinal optic). Hence we expect

$$\omega_{loc} \approx 1.27 \times 47.1 \approx 60 \text{ meV}.$$

This value is certainly within the range of the observed values and therefore provides some confirmation of the model.

Isotopic substitution for the nitrogen should provide much more convincing proof. The lower section of Fig. 9 shows the fluorescent spectrum of a crystal containing $N^{15}$ rather than $N^{14}$. Although it is not visible on the diagram, when $N^{15}$ is used the $NN$ lines and the $A$ line and their phonon replicas, all show very small shifts to higher energies. The shifts of some of the lines are given in Table I. The local-mode lines alone, show a large shift to higher energy. The solid arrows in the lower section of Fig. 9 show the positions of the local modes for $N^{14}$; these are absent and have been replaced by similar peaks at about 2-meV higher energies. The results are summarized in Table II.

The isotope shift of the local-mode frequency can be approximated as follows: First-order perturbation theory applied to any harmonic system of masses and springs shows that the change in frequency of a normal mode of frequency $\omega_{loc}$ when a particular mass $M$ is changed to $M + \Delta m$ is given by

$$\Delta\omega_{loc} = -\frac{1}{2}\omega_{loc}\frac{\Delta m}{M} \left( \frac{T_m}{T} \right), \qquad (6)$$

where $T_m$ is the fraction of the kinetic energy $T$ of the normal mode which is due to the motion of the mass $M$. For a model of the local mode in which the nitrogen

vibrates against four gallium atoms, the parenthesis has the value $4M_{Ga}/(4M_{Ga}+M_N)=0.952$. For a completely localized mode, $(T_m/T)$ is unity. Clearly putting $(T_m/T)=1.0$ will yield in this present case a good approximation to the isotope shift for any realistic model of the local mode. The shifts predicted by this relation are given in Table II; they are seen to be in good agreement with the observed shifts, and provide strong confirmation of the correctness of the model.

## IV. CONCLUSIONS

The substitution of nitrogen for phosphorus in gallium phosphide has been shown to lead to several discrete energy levels for bound holes and electrons in the forbidden gap. The most prominent of these is a state 0.011 eV below the intrinsic exciton or about 0.02 eV below the band-gap energy which is due to an isolated nitrogen atom. It consists of two lines, $A$ and $B$. In crystals with small concentrations of nitrogen (e.g., about $10^{17}$ atoms/cc), these lines can be the only ones seen in absorption and fluorescence. As the nitrogen concentration increases many lines are seen at lower photon energies, the deepest, $NN_1$, being 0.143 eV below the intrinsic exciton. These lines are called $NN_1$, $NN_2$, etc. The concentration of the $A$ center and the $NN$ centers is proportional to their absorption strengths. It is found that the concentration of the $NN$ centers varies as the square of the $A$-center concentration, indicating that the $NN$ centers consist of two nitrogen atoms. Strong circumstantial evidence has been cited showing that the $NN_1$ center arises from two nitrogen atoms on the closest possible sites, the $NN_2$ center from two nitrogen on the second nearest sites and so on. Unlike the bound states arising from donor-acceptor pairs, the binding energy here becomes less the greater the internuclear-pair separation. It has been possible to estimate the absolute concentration of nitrogen present in a crystal by purely optical methods.

Nitrogen can be introduced into the crystals during growth by several methods. If the crystals are grown from gallium solution, gallium nitride is a convenient source of nitrogen. If the crystals are grown from the vapor by the method of Frosch, ammonia is a useful source of nitrogen. The most striking proof that nitrogen is involved in the $NN$ lines and hence in the $A$ line, is the effect that the substitution of $N^{15}$ for $N^{14}$ has on the fluorescent spectrum. All the lines and their vibrational sidebands remain essentially unchanged except for certain "local-mode" lines, which shift by about 0.002 eV,

in excellent agreement with the isotope shift expected of a nitrogen atom substituted at a phosphorus site.

The substitution of nitrogen for phosphorus may be termed an isoelectronic substitution of a host lattice atom, since no unpaired holes or electrons are created and all valence bonds are satisfied. Such substitutions have not usually been expected to give rise to discrete band-gap states although the substitution of Te for S in CdS appears to be another example.[12] Here one discrete state is inferred from fluorescence, absorption, and photoconductivity results. In many cases isoelectronic substitutions evidently do not give discrete states, at least not for an isolated foreign atom. Thus small quantities of arsenic in GaP do not lead to an absorption line analogous to the $A$ line, and large quantities result in a continuous shift of the band gap from that of GaP to that of GaAs. Whether or not pairs of arsenic atoms might bind excitons is not known. It is interesting to remark that the band gap of GaN is 3.25 eV,[13] considerably larger than that of GaP (2.3 eV), yet nitrogen in GaP causes absorption below the band gap of GaP. There is as yet no quantitative theory to account for isoelectronic binding. In general terms a hole and electron are bound to a potential well formed by the foreign atom. From this point of view two foreign atoms close together could provide a deeper well and so tighter binding as is observed. It is possible that isoelectronic traps can bind holes or electrons separately. Such trapping should be apparent for the deeper traps in Hall-effect measurements. From a naive point of view, nitrogen and other elements in the second row of the Periodic Table with a large electron affinity due to a relatively exposed nuclear charge, may tend to bind an electron, whereas elements in the last row may tend to bind holes. In between isolated isoelectronic atoms may not bind at all, although it is possible that two such atoms close together may give rise to bound states.

[12] A. C. Aten, J. H. Haanstra, and H. de Vries, Philips Res. Rep. 20, 295 (1965); A. C. Aten and J. H. Haanstra, Phys. Letters 11, 97 (1964).
[13] E. Kaner and A. Rabenau, Z. Naturforsch. 12a, 942 (1957).