

## NN<sub>2</sub> trap in GaP: A reexamination

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We present a simplified calculation of the nitrogen-related triplets in gallium phosphide in the Green's-function approach, using a phenomenological band structure. We get a binding energy for the electron bound to a nitrogen triplet where the second and third nitrogen atoms are located on two sites of the twelvefold second-nearest neighbors of the first nitrogen atom, which is in good agreement with the electron binding energy of the NN<sub>2</sub> center. Moreover, a comparison between the geometrical configuration of the triplet and its optical and piezospectroscopical properties suggests that the NN<sub>2</sub> trap may be associated with a triplet of nitrogen atoms where the relative locations of the impurities should be 000, 110, and 0 $\bar{1}$ 1, respectively, in order to make a planar defect.

### I. INTRODUCTION

Since the discovery of nitrogen in GaP,<sup>1</sup> much attention has been focused on studying this system both from the theoretical<sup>2-4</sup> and the experimental point of view.<sup>5</sup> A peculiar aspect of the 2-K luminescence spectrum of GaP:N consists of a series of sharp lines which correspond to the recombination of excitons bound to various NN<sub>*i*</sub> pairs of nitrogen atoms (Thomas and Hopfield<sup>1</sup> used NN<sub>*i*</sub> to label the defect corresponding to two phosphorus atom sites located in *i*th-neighbor positions, occupied by two substitutional nitrogen atoms). The corresponding binding energies vary from 143 meV for the deepest trap down to 17 meV for the asymptotic NN<sub>∞</sub> pair (isolated nitrogen pair). The shape of the luminescence spectra is not easy to understand, and the following strong features were noticed immediately by Thomas and Hopfield (TH).<sup>1</sup>

(i) The giant enhancement of the NN<sub>*i*</sub>-pair lines compared to the isolated nitrogen exciton line when the nitrogen concentration is increased. These observations of the NN<sub>*i*</sub>-pair relative intensities have been explained by taking into account the various transfer processes which could occur between the different nitrogen levels.<sup>6</sup> Direct tunneling at low temperature, multiple trapping, and variable range hopping at higher temperature have been selected from picosecond spectroscopy measurements versus temperature on both GaP:N where the NN<sub>*i*</sub> pairs dominate the 2-K luminescence spectra and derivative N-doped alloys (GaAs-P and Ga-InP) where the NN<sub>*i*</sub> pairs appear only at higher temperature.<sup>7</sup> For GaP:N, a stochastic model of exciton transfer has been developed<sup>6</sup> where nitrogen complex triplets such as NN<sub>*i*</sub>N<sub>*j*</sub> have been introduced in order to account for the very efficient transfer between the different exciton levels due to nitrogen pairs.

(ii) The very small cross section of NN<sub>2</sub> with respect to the other pairs and the absence of the NN<sub>2</sub> line in absorption experiments.

Although the nitrogen pairs have attracted a lot of attention which it is not the purpose of this paper to review, the NN<sub>2</sub> trap has not been intensively studied; most of the workers cite its small cross section which does not allow an unambiguous study. In our opinion this small cross section is due to the intrinsic character of NN<sub>2</sub>. We believe that the NN<sub>2</sub> trap is a triplet and not a pair as usually proposed. The purpose of the present paper is to describe the experimental and theoretical arguments, especially with regard to the local symmetry of the center and the electron binding energy, which support this belief.

The NN<sub>2</sub> trap demonstrates behavior which disagrees with the general trend of the other NN<sub>*i*</sub> traps. With the use of a tunable dye laser and luminescence excitation spectroscopy, Cohen and Sturge<sup>5</sup> measured the excited states of the nitrogen-pair-bound excitons. Their measurements, together with the Hopfield-Thomas-Lynch (HTL) model for an exciton bound to an isoelectronic trap<sup>8</sup> permitted determination of the hole contribution to the exciton binding energy. They found the following: Within the series of NN<sub>*i*</sub>-bound excitons the hole binding energy decreases monotonically when the exciton binding energy decreases, *except for* NN<sub>2</sub>. The accuracy of their measurement is clearly demonstrated in Fig. 3 of their paper.<sup>5</sup> This is, in our opinion, the first disagreement between the experimental findings and the common belief in universal behavior for the whole series of NN<sub>*i*</sub> traps.

The second point we want to make concerns the fine structure of the NN<sub>2</sub>-bound exciton seen in luminescence measurements. If we model the anisotropic character of the NN<sub>*i*</sub> traps using a phenomenological parameter which splits the Γ<sub>8</sub>-like valence-band states, we can estimate, after a close comparison between theory and experiment, the magnitude of the strain field surrounding the defect and experienced by the bound hole. The greatest value has been found for NN<sub>2</sub>; simultaneously the electron-hole exchange splitting takes its maximum value.<sup>9</sup> This is a consequence of a strain field larger for NN<sub>2</sub> than for the

remaining pairs and of a significant quadrupolar contribution to the electron-hole exchange splitting.<sup>10</sup>

The third strange behavior has been observed in hydrostatic pressure measurements.<sup>11</sup> All pairs exhibit a pressure dependence which diminishes from  $NN_1$  up to  $NN_\infty$  except  $NN_2$  which does not follow the general trend.

A fourth discrepancy between experiment and the common belief has been observed under uniaxial stress.<sup>12</sup> The symmetry of the  $NN_2$  trap does not agree with TH's assignment; the experimental results are consistent with the trap having a planar behavior as a function of uniaxial stress; as detailed in Ref. 12, the relative location of the two nitrogen impurities in some of the  $NN_i$  traps does not correspond to the  $i$ th-neighbor position in the anionic sublattice.

A fifth peculiar experimental characteristic of the  $NN_2$  level is the energy shift obtained for the luminescence line when using isotope  $^{15}\text{N}$  instead of  $^{14}\text{N}$ . It was observed<sup>1</sup> to be 0.7 meV for isolated nitrogen centers, between 1 and 1.6 meV for all the  $NN_i$  pairs except the  $NN_2$ , and 2.8 meV for the so-called  $NN_2$  level.

Finally, outside the frame of these experimental results we must mention the tentative model calculations of the pairs. This is a well-documented subject,<sup>2,3,13-15</sup> but no pair model calculation, even the most elaborate one, can account for the small difference in the electron binding energies between  $NN_1$  and  $NN_2$ . The experimental difference is 7 meV (the electron binding energies are, respectively, 113 meV and 120 meV for the  $NN_2$  and  $NN_1$  traps), whereas it has been found to be around 50 meV in the theoretical models. In the framework of our earlier calculation of nitrogen in III-V compounds we could deduce general features concerning the strength of the isoelectronic potential in the binary and the ternary alloys;<sup>14</sup> this calculation has been also recently applied with success to the several luminescence bands related to change in the local environments of nitrogen in  $\text{Ga}_{1-x}\text{In}_x\text{P}$ ,<sup>16,17</sup> and gives us a way to estimate the energy of nitrogen triplets.<sup>18</sup> We will find that a triplet configuration of three nitrogen atoms can explain the experimental findings and gives the correct exciton binding energy for the so-called  $NN_2$  level. In this paper, our calculation applied to the  $NN_1N_1$  triplet centers is first presented by pointing out the approximations, the algebraic treatment and the geometrical considerations that we made. In Sec. III the numerical results are given, and in Sec. IV the new assignment of the  $NN_2$  level is discussed in detail with respect to all the experimental data.

## II. BINDING TO $NN_1N_1$ TRIPLETS

According to our previous work, we write down the excitonic Hamiltonian as follows:

$$H = H_0(e) + V_i(e) + H_0(h) + V_i(h) + V_c(e-h),$$

where  $H_0(e)$  [ $H_0(h)$ ] represents the Hamiltonian of the electron [hole] in the host perfect crystal,  $V_i(e)$  [ $V_i(h)$ ] is the short-range attractive [repulsive] triplet potential experienced by the electron [hole] and  $V_c(e-h)$  denotes the mutual Coulomb and exchange interactions between the electron and the hole.

According to the HTL model<sup>8</sup> we concentrate on the one-electron Hamiltonian; the localized electron acts as an acceptor which binds a hole with an energy  $E_I$  (in the case of  $NN_2$ ,  $E_I = 41$  meV according to Ref. 5). The electron binding energy is consequently close to 113 meV. The energies of the bound states are given by the zeros of the equation  $\det |(1 - GV)| = 0$ , where  $G(E) = (E - H_0)^{-1}$  is the Green's function of the host crystal. Using a Wannier's representation one gets

$$\det \left| \left| \delta_{nn'} \delta_{ij} - \sum_l G_{n,il}(E) \langle nl | V | n'l' \rangle \right| \right| = 0,$$

where

$$G_{n,il}(E) = \langle ni | (E - H_0)^{-1} | nl \rangle,$$

and  $|ni\rangle$  denotes the Wannier function of band  $n$  at site  $i$ . The  $\langle nl | V | n'l' \rangle$  matrix element concerns the short-range triplet potential.

### A. Approximations

We first make the so-called one-band approximation. After a complicated calculated calculation Banks and Jaros<sup>19</sup> obtained the expansion of the real-space nitrogen wave function along the ten lowest energy bands. The nitrogen wave function is mainly built from Bloch states originating from band 5; this justifies the one-band approximation used here. One interesting point to mention concerns the impurity charge distribution; it is isotropic out to a radius of 1 a.u. from the impurity, and beyond this becomes strongly anisotropic with charge accumulated along the antibonding  $\langle 110 \rangle$  directions. To calculate the Green's function one can use the model density of states introduced by Kleiman<sup>20</sup> and applied with success by Mariette *et al.*<sup>21</sup> and Gil *et al.*<sup>14</sup> for GaP and its ternary alloys and for  $\text{GaAs}_{1-x}\text{P}_x$  under hydrostatic pressure ( $x = 1, 0.957$ , and 0) up to 9 kbars.<sup>14</sup> With the use of this partition of the first Brillouin zone (BZ), the Green's function,

$$G(\epsilon, R) = (\Omega/2\pi^3) \sum_{\text{BZ}} e^{ikR} / [\epsilon - E(k)] d^3R,$$

can then easily be shown to be given as

$$G(\epsilon, R) = \sum_i F_i(R) g_i(\epsilon, R),$$

where

$$F_i(R) = \sum_{l \in i} \exp(iK_{il}R),$$

and  $g_i(\epsilon, R)$  is the Green's function calculated around the minimum  $K_i$  of the band structure. More details are given in the appendix of Ref. 14.

We next focus on the model potential for the triplet. The simplest way to describe the triplet potential consists of a short-range single-site potential,

$$V_T = V(|0\rangle\langle 0| + |1\rangle\langle 1| + |2\rangle\langle 2|),$$

where  $|i\rangle$  denotes the site function centered on each of the three impurities of the cluster. An "extended" Slater-Koster- (SK) type potential can be used, which affects

both the site of the impurity and the first shell of its nearest (anionic) neighbors. Previous investigations along this line were concerned with isolated N traps in GaAs<sub>1-x</sub>P<sub>x</sub>,<sup>22</sup> and found that such a model potential might simulate the strain field surrounding the impurity. Within the energy range of interest here (0–150 meV) this extended SK model is formally equivalent to an energy-dependent single-site potential.<sup>22</sup> Such results were also obtained by Mariette *et al.*<sup>21</sup> who used a single-site potential in a coherent-potential-approximation (CPA) medium and took into account the different local configurations As-P surrounding the nitrogen centers. Figure 1 displays the variations of this effective potential versus electron binding energy in the typical case where 15.6% of the electronic charge lies on the first neighbor shell; the situation is deduced from the works of Banks and Jaros.<sup>19</sup>

### B. Algebraic treatment

We focus on the simple case where one nitrogen atom of the triplet is located at the coordinate origin and the remaining two are located on two sites of the twelffold first-neighbor shell. Let  $|0\rangle$ ,  $|1\rangle$ , and  $|2\rangle$  be the corresponding Wannier functions.

The eigenenergies can be found as solutions of the equation system

$$1/V = G_0 - G_{12} (E_1),$$

$$1/V = G_0 + \frac{1}{2} G_{12} [1 + (1 + 8G_{10}^2/G_{12}^2)^{1/2}] (E_2),$$

$$1/V = G_0 + \frac{1}{2} G_{12} [1 - (1 + 8G_{10}^2/G_{12}^2)^{1/2}] (E_3),$$

where  $1/V$  is the proper value of the site potential; it may be energy dependent in the case of an extended impurity potential. It is a straightforward exercise to find the expansion of the three corresponding states along the Bloch functions of the conduction band. We, respectively, find:

$$\phi(k) = AV(e^{ikR_1} - e^{ikR_2})/[E_1 - E(k)],$$

$$\phi(k) = A'V[2B/(\mu + C/2) + e^{ikR_1} + e^{ikR_2}]/[E_2 - E(k)],$$

$$\phi(k) = A''V[2B/(-\mu + C/2) + e^{ikR_1} + e^{ikR_2}]/[E_3 - E(k)],$$

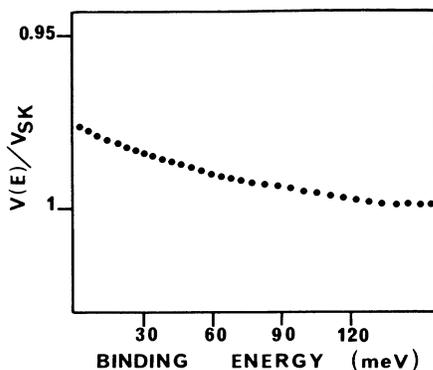


FIG. 1. Variation of the extended impurity potential as a function of the Slater-Koster one-site potential  $V_{SK}$ .  $V_{SK}$  is an adjustable parameter which has been fitted in order to give a vanishing binding energy in the case of a single impurity.

where  $A$ ,  $A'$ , and  $A''$  are the normalization constants  $B = -VG_{10}$ ,  $C = -VG_{12}$ , and  $\mu = (2B^2 + C^2/4)^{1/2}$ .

As already noticed by Faulkner,<sup>3</sup> it is clear from the preceding equation that different situations occur. States with  $\phi(k=0)=0$  cannot be associated with the direct creation and/or recombination of a bound exciton at  $k=0$ ; they are said to be dipole forbidden. The states corresponding to the  $E_1$  solution are dipole forbidden; the two remaining ones generally are not.

### C. Geometrical considerations

Various topological configurations have to be distinguished for such triplet clusters; Fig. 2 summarizes the four geometrical configurations which can be classified into two types. For type-I clusters, all three impurities are nearest neighbors to each other and the local symmetry of the defect is  $C_{3v}$ . For type-II clusters, the impurities are further apart; we can select three subtypes corresponding to the impurities 1 and 2 in second-neighbor position ( $E\langle 001 \rangle$  local symmetry), third-neighbor position ( $E\langle 111 \rangle$  local symmetry), and fourth-neighbor position ( $C_{2v}$  local symmetry). Table I summarizes the relative positions of the atoms for these two types of clusters together with the corresponding structure factors related to  $\Gamma$ ,  $X$ , and  $L$  extrema of the lowest conduction band.

### III. NUMERICAL RESULTS

The numerical calculations have been performed for the two types of clusters and of course for the three subtypes of type-II clusters. One interesting point to outline concerns the sign of the Green's function. Of course  $V$  and  $G_0$  are both negative since the single-impurity problem must satisfy the simple equation  $1 - VG_0 = 0$  (obeyed

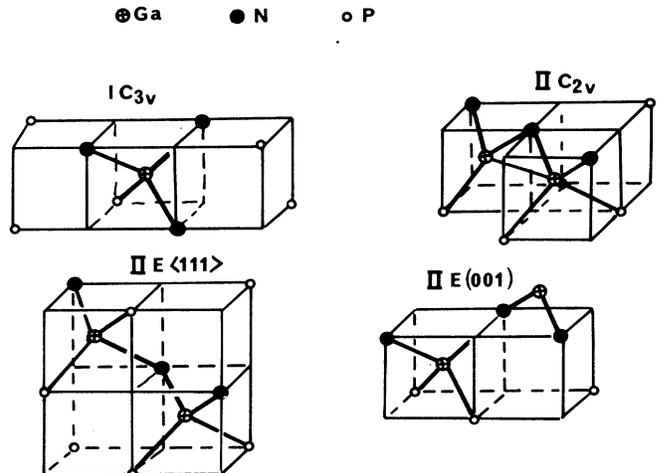


FIG. 2. Geometrical configurations of the clusters. The four topological defects are gathered into two classes. Type-I clusters correspond to three atoms in near-neighbor position, and to a  $C_{3v}$  point symmetry. Type-II clusters correspond to three atoms in the other remaining configurations with two atoms further than the near-neighbor location. Type-II clusters are linear or planar defects.

TABLE I. Relative location of the three impurities, the first impurity is located at the coordinate origin  $R_0=0$ , the second one at  $R_1=110$ . We denote by  $R_2$  the position of the third atom. Given  $R_0$  and  $R_1$ , eleven configurations are allowed for the third nitrogen atom on the twelvefold nearest-neighbor shell in the anion sublattice; this gives two types of clusters: type I and type II. We also give the local lowering of crystal symmetry and the structure factor useful to calculate the Green's functions. The local symmetry is noted according to Schoenflies convention. In the case of type-II clusters, we also give the crystallographic direction perpendicular to the plane containing the three impurities. Type-II  $C_{2v}$  defects are linear defects.

$R_2$	$F_x$	$F_L$	Local symmetry	Type
011	-1	0	$C_{3v}$	I
01 $\bar{1}$	-1	0	$C_{3v}$	I
101	-1	0	$C_{3v}$	I
10 $\bar{1}$	-1	0	$C_{3v}$	I
$\bar{1}\bar{1}0$	3	+4	$C_{2v}$	II
$\bar{1}\bar{1}0$	3	-4	$E\langle 001 \rangle$	II
$1\bar{1}0$	3	-4	$E\langle 001 \rangle$	II
0 $\bar{1}\bar{1}$	-1	0	$E\langle 1\bar{1}\bar{1} \rangle$	II
0 $\bar{1}\bar{1}$	-1	0	$E\langle \bar{1}\bar{1}\bar{1} \rangle$	II
$\bar{1}01$	-1	0	$E\langle 1\bar{1}\bar{1} \rangle$	II
$\bar{1}0\bar{1}$	-1	0	$E\langle \bar{1}\bar{1}\bar{1} \rangle$	II

when the electron binding energy vanishes<sup>2</sup>)  $G_{01}$  and  $G_{12}$  (type-II  $E\langle 111 \rangle$  defects) are negative while  $G_{12}$  ( $E\langle 001 \rangle$  and  $C_{2v}$  triplets) are positive quantities. It is clear from the form of the Dyson equation that the lowest-energy state will be  $E_3$  for both type-I  $C_{3v}$  and type-II  $E\langle 111 \rangle$  clusters because a negative quantity has to be added to  $G_0$  in order to satisfy the eigenequation ( $E_3$ ). In the remaining two cases of type-II  $E\langle 001 \rangle$  and  $C_{2v}$  clusters, it is clear that both  $E_1$  and  $E_2$  will give an electronic level in the band gap, but it is not possible to say *a priori* which one will correspond to the lowest electronic state. Table II summarizes the numerical results obtained for the triplet clusters and for the two pairs of interest:  $\langle 110 \rangle_p$  and  $\langle 220 \rangle_p$  (labeled  $NN_1$  and  $NN_4$  in Ref. 1). The pair energies have been obtained after pairing the two identical potentials at the proper lattice position according to our previous work.<sup>14</sup> Without any consideration except an examination of the energy range scaled by the electronic levels (150–36 meV), we find a result in striking disagreement with the work of Goede and Hennig.<sup>23</sup> This is not surprising because they had made large approximations

TABLE II. Numerical values of the electron binding energies calculated for the triplets in GaP. The pair energies are 65 meV for  $\langle 110 \rangle_p$  and 114 meV for  $\langle 220 \rangle_p$ . The  $E_1, E_2, E_3$  states correspond to the notations of the text and the dipole-forbidden states are starred. The resonant states are marked with the dashes.

$NN_1N_1$	$E_1$	$E_2$	$E_3$
I $C_{3v}$	—	—	150
II $C_{2v}$	99*	36	—
II $E\langle 001 \rangle$	37*	58	—
II $E\langle 111 \rangle$	—	—	107

and dropped the multivalley character of the GaP conduction band. On the other hand, our finding agrees with the one obtained by Tchakpelé *et al.*<sup>24</sup> for isovalent clusters in II-VI compounds when using a realistic description of the band structure.

The type-I  $C_{3v}$  cluster gives a 150-meV-deep electronic level; it is deeper than the  $\langle 220 \rangle_p$  level. Concerning the type-II clusters, we find an electronic level 7 meV above  $\langle 220 \rangle_p$  (107 meV for type-II  $E\langle 111 \rangle$ ) which can lead to the direct recombination of the electron with a valence-band hole since  $\phi(k=0) \neq 0$ . Both type-II  $E\langle 001 \rangle$  and type-II  $C_{2v}$  give a dipole-active state corresponding to weaker binding energies (58 meV for type-II  $E\langle 001 \rangle$  and 36 meV for type-II  $C_{2v}$ ).

#### IV. DISCUSSION

We can reject some configurations of the triplet clusters, since they disagree with the experimental results. The most selective experimental result was obtained from uniaxial-stress experiments.<sup>12</sup> The  $NN_2$  defects split into two separate families of defects under uniaxial stress oriented along  $\langle 001 \rangle$ ; <sup>12</sup> a  $C_{3v}$  planar cluster would not, as has been pointed out by Kaplyanskii.<sup>25</sup> Next, the experimental splitting under  $\langle 111 \rangle$  stress permits us to select three types of defects; a  $C_{2v}$  noncubic center would split into two only. Finally a  $\langle 110 \rangle$  stress gives four families of defects. These three orientations of the stress allow us to keep only  $E\langle 111 \rangle$  type-II clusters as potential candidates.

Therefore, we propose to associate the  $NN_2$  isoelectronic trap with the type-II  $E\langle 111 \rangle$  triplet (whose electronic binding energy is calculated to be 107 meV) and not to a pair of nitrogen atoms. The probability of occurrence of such a triplet is lower than the probability of pair formation. A lot of isoelectronic centers arise from association of several (more than two) impurities: four lithium atoms in silicon,<sup>26</sup> two beryllium atoms in silicon,<sup>27</sup> the copper- and copper-lithium-related centers in the III-V compounds,<sup>28</sup> the Li-Li-O triplets in GaP.<sup>29</sup> Concerning the associates of isoelectronic species, in addition to  $N_p-N_p$  pairs some heteropolar triplets  $B_{Ga}-N_p-N_p$  had been previously recognized<sup>30</sup> with a reasonable probability of occurrence. As a consequence, the probability of occurrence for a nitrogen triplet could not be negligible except for low nitrogen concentrations.

We have reinvestigated the  $NN_2$  luminescence spectrum collected at liquid-helium temperature using a high-quality sample specially grown for that work.<sup>31,32</sup> The nitrogen concentration has been calibrated using the method proposed by Lightowers *et al.*<sup>33</sup> and found to be  $2.9 \times 10^{18} \text{ cm}^{-3}$ .

The deconvolution of the luminescence spectrum given in Fig. 3 permits us to select unambiguously four optical transitions corresponding to  $B_1, B_2, A_0, A_1$  according to the notations of Gil *et al.*<sup>9</sup> This splitting pattern reflects the anisotropy of the crystal field surrounding the defect. The three atoms lie in a plane perpendicular to a  $\langle 111 \rangle$  direction. The defect creates a local strain field whose magnitude varies as a function of the distance from the triplet; simultaneously the crystal field tends to recover

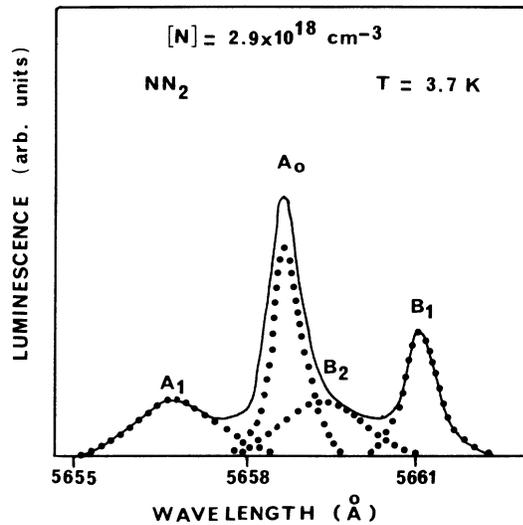


FIG. 3. A typical luminescence spectrum obtained for NN<sub>2</sub> in a sample with  $[N]=2.9 \times 10^{18} \text{ cm}^{-3}$ . Clearly, we resolve four transitions. The dotted lines correspond to the fitting of the luminescence with four sublevels. The relative ordering, magnitude, and width of each sublevel is given in the bottom of the figure.

the  $T_d$  host symmetry. For a medium-range distance from the triplet [remember that the hole Bohr radius is about 25 Å (Ref. 5)], the luminescence pattern suggests a trigonal point symmetry. Keeping in mind the trigonal symmetry of the  $\langle 111 \rangle$  direction which is perpendicular to the plane of the defect, this is not surprising. Elementary group theory permits support of this belief: the  $\Gamma_6(T_d) \times \Gamma_8(T_d)$  exciton splits into a series of irreducible representations ( $\gamma_i$ ) in a trigonal  $C_{3v}$  crystal field. According to Koster's tables<sup>34</sup> we find

$$\Gamma_6 \times \Gamma_8 = \gamma_1 + \gamma_2 + \gamma_3 + \gamma_3 + \gamma_3.$$

Four of these five levels are dipole active,  $\gamma_1$  and the three  $\gamma_3$  levels.  $\gamma_1$  being a singlet corresponds to the  $A_0$  transition; the three  $\gamma_3$  doublets correspond to  $B_1$ ,  $B_2$ , and  $A_1$  respectively. The local-field parameter  $2\epsilon_1$  introduced in Ref. 9 reflects the anisotropy of the diluted wave function of the bound hole.

This characteristic uniaxial behavior induces a vanishing difference of the local lowering of symmetry along

$\langle 110 \rangle$  and  $\langle 112 \rangle$  directions at a distance of a hole Bohr radius from the cluster. This is no longer true when considering the localized bound electron. Under uniaxial stress, we selectively split the zone-boundary extrema of the Brillouin zone. A  $\langle 001 \rangle$  stress, for instance, splits the  $K_z$  Bloch state with respect to  $K_x$  and  $K_y$ . The electronic states are a sensitive function of the uniaxial stress; according to Kaplyanskii<sup>25</sup> we expect 3-4-6 families of defect under  $\langle 001 \rangle$ ,  $\langle 111 \rangle$ , and  $\langle 110 \rangle$  stress, respectively. The experimental results do not give as many transitions as expected (see Fig. 4 of Ref. 12) and is compatible with a monoclinic type-I symmetry. This reflects a peculiar sensitivity of the electronic state to the deformation in the  $\langle 211 \rangle$  direction where the density of charge of the electronic state is important.

Finally, we have calculated the variations of the electron binding energy versus pressure, according to our common method of renormalization.<sup>11,14</sup> We find  $\partial E_e / \partial p = -4.3 \text{ meV kbar}^{-1}$  with  $[(1/V)(\partial V / \partial p)] = -0.5\% \text{ kbar}^{-1}$  while we have measured<sup>11</sup>  $\partial E_e / \partial p = -3.52 \text{ meV kbar}^{-1}$ .

## V. CONCLUSION

We have presented a detailed review of the physical properties of excitons bound to the trap labeled NN<sub>2</sub> in gallium phosphide. These properties have been experimentally found to be at variance with the general trend for the rest of the series of nitrogen-pair-bound excitons. A careful examination of the experimental results given in the literature together with a numerical calculation suggests that the NN<sub>2</sub> trap is associated not with a pair but with a triplet NN<sub>1</sub>N<sub>1</sub> of three nitrogen atoms which make a planar defect. This work is the first one to be in agreement with the experimental results for (i) the symmetry of this defect, (ii) its binding energy (we found a NN<sub>1</sub>N<sub>1</sub> level 7 meV above the deepest nitrogen level), and (iii) its small cross section with respect to the remaining NN<sub>i</sub> traps (the probability of occurrence of a triplet is always smaller than that of a pair).

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