Behavior of nitrogen impurities in III–V semiconductors

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Abstract

A detailed review on a few important issues related to the isoelectronic impurity nitrogen in III-V semiconductors GaP and GaAs are given in this article. These issues include (1) the binding mechanism for the nitrogen bound exciton, (2) the electron binding energy calculation, (3) the exciton binding energy calculation, (4) the exciton–phonon coupling, and (5) the behavior of the nitrogen in dilute nitride alloys. We conclude that a key problem that remains not well answered is the interplay of the short-range impurity potential originated from the atomic energy difference, the strain field caused by the lattice relaxation and the accompanying electronic polarization. The solution to this problem is essential to solve the long-standing mystery: what exactly are those pair's configurations? © 2000 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

In 1965, Thomas et al. [1,2] identified that a series of sharp emission lines in GaP : N were the results of the radiative decay of excitons bound to either isolated nitrogen centers or various nitrogen pair centers. The emission spectrum of a nitrogen center (either an isolated or a pair) consists of a zero-phonon line and a set of phonon sidebands. [1,2]. The zero phonon lines are usually labeled as A and NN_i ($i = 1$–10) for the isolated nitrogen and the nitrogen pairs, respectively. With increasing index i, the emission energy of NN_i converges to that of the A line. It was natural to assign NN_1 to the first nearest neighbor pair, NN_2 to the second nearest neighbor pair and so on [2]. Despite a more than 30 year long study of this system, the assign-

ments of these pair centers have still remained an unsolved mystery. There have been quite a few review articles on the subject of isoelectronic impurities [3–7]. In this contribution, we will review some of the later studies and only those related to nitrogen doping in the compound semiconductors GaP and GaAs. We will focus mostly on the two areas: (1) the binding mechanism and the binding energy; and (2) the exciton–phonon interaction. Also, we will try to correlate the early studies of nitrogen as an impurity and the very recent studies where nitrogens are incorporated in III–V materials to form a nitride alloy.

2. Binding mechanism of the isoelectronic impurity

The binding of an excitons to the nitrogen centers in GaP : N was explained qualitatively by Hopfield et al. [8] as a consequence of the difference in electronegativity χ between nitrogen and

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phosphor (the so called HTL model). More specifically, because of $\chi_N > \chi_P$, nitrogen tends to bind an electron; then, via the Coulomb interaction, an exciton is bound to nitrogen. Although the nitrogen bound state is very close to the band gap, in the sense of being able to capture an electron, it is considered a deep acceptor. The bound exciton is classified as an acceptor-like bound exciton. Similarly, Bi in GaP : Bi is a trap center for holes or a deep donor, and the Bi-bound exciton is classified as a donor-like bound exciton. The potential generated by the isoelectronic impurity is presumably short-range in nature according to the HTL model. Another approach [9] to understand the binding mechanism is to compare the depths of the atomic pseudopotentials for the s- and p-type states, which leads to the same qualitative trend as that from the electronegativity consideration.

The effect of the lattice deformation due to the atomic size difference was first considered by Allen [10]. Such a strain field is pure shear and is attractive to a particle associated with a degenerate band. Thus, in GaP the strain field can attract both electrons and holes, because both the conduction and valence band are degenerate. Furthermore, he explained the NN_i series as the results of an isolated nitrogen perturbed by the strain field induced by a second nitrogen at different distances. Indeed, the dependence of the binding energy on the pair distance can be fairly well described by a simple formula (especially for the deep pairs) [10]

$$E = E_N - \beta R_{NN}^{-3}, \tag{1}$$

where E_N is the energy of the isolated center, R_{NN} is the pair spacing and β is a constant. Here it was implicitly assumed that the Thomas and Hopfield's assignments [2] of the pair configurations were correct, despite the fact that a different binding mechanism was suggested. Later, he pointed out [11] that at least a considerable part of the exciton binding is due to the strain field around the nitrogen atom. Phillips [12] pointed out the importance of the electronic polarization. The strong localized nature of the trapping potential will result in the localization of the charge of the trapped electron in the central cell, and the atomic cores of the nearby atoms will then be positively charged. Because of the change in the charge distribution, the adjacent

lattice sites are expected to be distorted. Phillips [12] pointed out that the effect of the lattice distortion around the isoelectronic impurity was of equally important as the pseudopotential difference but that it had an opposite sign. To the first order, they should cancel each other. The residual screening (the anisotropy part of the screening correction) was responsible for the small binding energy of the isolated nitrogen center. Both Allen [11] and Phillips [12] suggested a long-range potential in the form of r^{-3} in additional to the short-range part. However, both of these models were qualitative or semi-quantitative. Another intuitive way of understanding the formation of the nitrogen bound state was given by Hjalmarson et al. [13]. They pointed out the "quasiatomic" nature of a deep impurity like nitrogen in GaP (a deep impurity is one whose short-range central-cell potential alone is sufficiently strong to have a bound state). The existence of the nitrogen bound state can be explained by a two-state model: the valence and conduction band are formed by the bonding and antibonding states of the P and Ga atomic energy levels, respectively. Because the N atomic energy level is much lower than that of P, the bonding and antibonding states of N and Ga form a deep resonant states in the valence band and a bound state below the GaP conduction band, respectively.

Another distinctly different model for the nitrogen bound state was proposed by Morgan, [14] and he called it the "weak bonding description" (WBD); this model was originally developed by him for the deep oxygen level in GaP. In this model, nitrogen weakly bonds to the surrounding Ga atoms, because the small nitrogen impurity has very deep 2s and 2p valence electrons. The nitrogen bound state is then a hybrid of a set of vacancy-like spin multiplets and nitrogen valence states. This model seems to be able to explain qualitatively a few properties of the so-called B line of the nitrogen bound exciton (the exchange interaction splitting of the exciton state) which cannot be explained in the conventional ways. However, there has not been any solid evidence for supporting this rather unusual model.

The difference between the HTL model [8] and the Allen model [10] has been understood as that for the former the formation of the exciton is

a two-step process: first the electron is bound, then the bound electron attracts a hole. For the latter, the exciton is bound as a whole (a single-step process). Thus, the study of the thermal quenching of the luminescence through the disassociation of the electron, hole or exciton was believed to be useful for determining the binding mechanism. If the thermal quenching of the luminescence has an activation energy close to the hole binding energy, it is considered as evidence supportive of the HTL model; if the activation energy is close to the difference between the free and bound exciton states, it is considered supportive of the Allen model. However, the observed thermal activation energy for the A line allowed the conclusion that the exciton formation was a two-stage process in some cases [15,16][1] and a single-step process in others [17]. We would like to point out that the thermal quenching process may not be directly related to the binding mechanism. In the Allen model, the major contribution to the exciton binding is the strain field around the nitrogen atom. The band edges of the conduction and valence bands are so deformed that a potential well is created for both electrons and holes. Thus, in such a picture, an electron and a hole can be independently trapped at the nitrogen site, depending on the availability of the two types of carriers. If a nitrogen atom indeed traps an electron and a hole, the Coulomb interaction between them forms an exciton, and the exciton binding energy is expected to be enhanced from the free exciton value due to the localization of the two particles. This picture is in fact very similar to that of strain-induced quantum wires and dots [18] where an electron and a hole are simultaneously trapped by a local strain field. Of course, the scale is drastically different in the two situations. In this sense, a nitrogen bound state may be considered as an atom-size GaN quantum dot. Allen's model may be considered as a type I, while the HTL model as a type II quantum dot, since for the latter the hole is not so close to the nitrogen or the electron and hole are spatially separated. If the electron binding energy is the same, the exciton binding energy is expected to be larger for the Allen

model than that for the HTL model. In principle, Allen's model can have three states: N^e, N^h and N^{ex}, while the HTL model can only have two: N^e and N^{ex}. However, there is no evidence for the existence of the N^h state. In general, experimental results tend to conclude that the HTL model is qualitatively correct for most of the pair centers, although to what extent the strain field and electronic polarization contribute to the binding potential is not at all clear. The most solid experimental evidence for the HTL model is perhaps the excitation spectra for the NN pairs measured by Cohen and Sturge [19], where they observed acceptor like hole excited states for NN_i centers with $i \leq 7$. Their conclusions were further supported by a subsequent luminescence thermal quenching study showing the thermal disassociation of the hole [20] and the observation of transitions between the NN^e and the acceptors [21].

The extension of the study to nitrogen doping of GaAs is very helpful for understanding the binding mechanism. In Allen's model, the degeneracy of the band edge is a necessary condition to generate a strain field from its shear components. In GaAs, the strain field is expected to be stronger for the hole, since the atomic size difference is larger between N and As than that between N and P while the deformation potentials are similar for most of the III–V compounds. According to the strain model, the electron bound state (N^e) would not exist in GaAs. However, it would still be possible to form a bound exciton through the Coulomb interaction if a hole was bound, just like in GaP : Bi. In reality, the nitrogen center produces a resonant state in the conduction band (~ 180 meV above the conduction band edge), as indicated by the Wolford et al.'s [22] study of the bound exciton state of the isolated nitrogen center under hydrostatic pressure. The difference between GaP : N and GaAs : N cannot be understood simply by considering the factors such as atomic size and electronegativity, since the atomic size or electronegativity difference is larger between N and As than between N and P. However, considering that the nitrogen state is an antibonding state of Ga and N with a quasiatomic nature, its absolute energy position remains more or less the same in the two hosts. Notice that the conduction band edge is

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[1] The 8 meV thermal activation energy was believed to be the electron binding energy [15].

lower in GaAs than in GaP, it is then not surprising that a bound state is easier to form in GaP. We will discuss more about the correlation between the formation of the bound state and the band edge alignment later. Recent theoretical calculations of the dilute GaAsN alloy or heavily doped GaAs : N have shown that the band gap decreases rapidly with increasing nitrogen doping, with most of the change occurring in the conduction band [23]. Such a result indicates that the strain effect can only be secondary to the atomic energy level difference.

3. Electron binding energies

The first elaborate calculation for the nitrogen bound exciton states was done by Faulkner [24]. In the framework of the short-range potential model, and using the impurity potential constructed by the pseudopotential difference of the impurity and the host atom, Faulkner's calculation gave a very large binding energy ~ 1 eV for the isolated nitrogen center. After introducing a correction factor to reduce the potential strength so that an 8 meV electron binding energy [15] was obtained for the isolated center, Faulkner was able to obtain the energies of the pair states in the same range as the experimental results, but with a sequence different from that suggested by Thomas and Hopfield [2]. Due to the multi-valley interference effect, the binding energy was not a monotonic function of the pair spacing. In light of Faulkner's results, if Eq. (1) is valid, one has to assume that the strain potential will be dominant over the short-range part so as to rearrange the sequence of the pair binding energy. Perhaps the most sophisticated calculation for the nitrogen states in GaP was carried out by Jaros and Brand [25,26], using a multiband model with a local self-consistent pseudopotential. Their impurity potential has a medium-range repulsive tail caused by the rearrangement of the valence electrons (screening) besides the usual short-range part due to the difference in ionic cores. Such a potential yields a nitrogen level almost exactly at the conduction band edge. Their calculated values for the pair binding energy range from ~ 0 to 100 meV. However, the sequence was again inconsistent with the

original assignments. They suggested that the strain or local distortion was responsible for these discrepancies.

Both Faulkner and Jaros and Brand's works indicate that the interference effect is very important in determining the correlation between the binding energy and the pair configuration. On the other hand, ignoring the interference effect, Benoit a la Guillaume [27] showed that the electron binding energy for pairs was a monotonic function of the pair spacing. If the strength of the nitrogen potential was adjusted to give the electron binding energies of pairs close to the experimental results obtained by Cohen and Sturge [19], then, the isolated center itself would not have an electron bound state. In this calculation, the binding energy exhibited a pair spacing dependence very close to r^{-3}, which indicates that the r^{-3} relation itself cannot be considered as solid evidence for the validity of the Allen model.

Jaros and Brand's multiband model seems to conclude that no quantitative analysis of the problem is possible unless the whole band structure is taken into account. However, after they adjusted the strength of the self-consistent pseudopotential in order to place the NN pair bound states in an appropriate range, their results did not have an over all better agreement with the experiment than that of the simple one-band one-site Koster-Slater model. This puzzle can probably be explained by the Swarts et al.'s [28] calculation where an extended Hückel theory was used. They found that the energy of the impurity bound state is insensitive to its atomic energy, and attributed this to the strong level repulsion of the impurity state by the valence band. The valence-band repulsion compensated the actual impurity potential, and yielded a weak effective potential for the one-band model.

There have been a few other calculations attributing to understand the pair bound states [29–32]. Li et al.'s [29] approach was based on the Koster–Slater Green's function and the center-cell defect-potential approximation. They used two potential parameters to fit the experimental results [19], and obtained the same energy sequence as suggested by Thomas and Hopfield [2], except for the NN₃ center. Their potential gave a 10 meV electron binding energy for the isolated N center.

Shen et al. [30] proposed a multi-band model including the lattice relaxation effect. This is the only model, which is able to give the same energy sequence for the pairs as suggested by Thomas and Hopfield. An approximate r^{-3} pair-spacing dependence was produced and explained as being due to the strain relaxation around the nitrogen. The strain potential was adjusted by varying the bond length to make the electron binding energy of the isolated center equal to the "experimental value" of 11 meV for GaP. However, in reality, an absolute experimental value has never been established. The 11 meV binding energy is the difference between that of the nitrogen-bound exciton and the free exciton [2], which may be considered as the upper bound of the electron binding energy. This work also predicted that NN_1 was a bound state in GaAs, and that all the other pair states are resonant in the conduction band. It had been shown by Wolford et al. [22] that the isolated nitrogen center produced a resonant state 150 – 180 meV above the conduction band edge. According to the Shen et al.'s calculation, though the short-range impurity potential was still responsible for the electron binding to the nitrogen centers, the strain potential could significantly change the actual values of the binding energies so that the sequence of the energy levels would be altered from that of a theory which did not take into account the strain field. However, the strain field itself could not give rise to those bound states. Thus, it appears that the r^{-3} rule does not have any significance and is nothing more than a coincidence. It appears that the Shen et al.'s calculation could give the sequence of the pair energy levels in better agreement with the intuitive assignments of the pair configurations [2] than those given by Faulkner's and the Jaros and Brand calculations. However, how the strain effect could change forbidden into allowed states was not addressed.

Gil et al. [31] and Zhang et al. [32] have further explored the pair bound states using the one-band one-site Koster–Slater model. Gil et al. [33] investigated the stress induced splittings of the pair emission lines, and found that the local symmetries of the NN pairs did not fully match the symmetries of the conventional assignments. In fact, they found that only the symmetries of NN_1, NN_3 and NN_4

agreed, having symmetries of C_v, C_s and C_{2v}, respectively. The symmetries of NN_2 and NN_7 were identified as C_s and C_{2v}, respectively. However, symmetry considerations are still not able to determine whether, for instance, NN_1 is associated with the [110] or [220] pair. Also, the lattice-relaxation might change the pair symmetry based purely on geometrical considerations. In Gil et al.'s model calculation [31], results qualitatively similar to Faulkner's and Jaros and Brand's were obtained, although the sequencing was slightly different for certain pairs. They adjusted the potential strength so that the isolated center had a binding energy of 1 meV. Taking into account the local symmetry established by the stress experiment, they suggested a set of tentative assignments between the NN pair states and the pair configurations.

Let us briefly summarize the mathematical description of the one-band one-site Koster–Slater model for the nitrogen problem [24].

For the isolated nitrogen center, the electron bound state ψ is represented as

$$\psi = \sum_{BZ} a_k \phi_c(\boldsymbol{k}), \tag{2}$$

with

$$a_k = \frac{A}{E - E_c(k)}, \tag{3}$$

where E is the electron bound state, $E_c(\boldsymbol{k})$ is the dispersion of the conduction band, and A is a normalization constant. The electron bound state is the solution of the following Green's function equation:

$$JG(E) = 1, \tag{4}$$

where $G(E)$ is the Greens function defined as

$$G(E) = \frac{\Omega}{(2\pi)^3} \int_{BZ} \frac{\mathrm{d}\boldsymbol{k}}{E - E_c(\boldsymbol{k})}, \tag{5}$$

and $J < 0$ is the potential parameter. For a nitrogen pair with one atom at the origin and the other at $\boldsymbol{R}_m$, the corresponding equations are

$$J[G(E) \pm G(E, \boldsymbol{R}_m)] = 1, \tag{6}$$

where $G(E, \boldsymbol{R}_m)$ is defined as

$$G(E, \boldsymbol{R}_m) = \frac{\Omega}{(2\pi)^3} \int_{BZ} \frac{\exp(i\boldsymbol{k} \cdot \boldsymbol{R}_m)\mathrm{d}k}{E - E_c(\boldsymbol{k})}. \tag{7}$$

The wavefunction of a NN_i pair state takes a similar form as Eq. (2) and now a_k is given as

$$a_k = A \frac{1 \pm \exp(-i\boldsymbol{k} \cdot \boldsymbol{R}_m)}{E - E_c(\boldsymbol{k})}. \tag{8}$$

For each pair, there are two possible solutions corresponding to the " + " and " − " signs respectively. The one with $a_0 \neq 0$ is interpreted as a diople allowed transition and the other one with $a_0 = 0$ a dipole forbidden transition. For simplicity, the Green's functions are approximated by the sum of contributions from valleys associated with three special $\boldsymbol{k}$ points (Γ, L and X) [34]:

$$G(E) = G_\Gamma(E) + 4G_L(E) + 3G_X(E), \tag{9}$$

and

$$\begin{aligned} G(E, \boldsymbol{R}_m) = f_\Gamma(\boldsymbol{R}_m)G_\Gamma(E, \boldsymbol{R}_m) + f_L(\boldsymbol{R}_m)G_L(E, \boldsymbol{R}_m) \\ + f_X(\boldsymbol{R}_m)G_X(E, \boldsymbol{R}_m), \end{aligned} \tag{10}$$

where $f_{k_0}(\boldsymbol{R}_m)$ for $k_0 = \Gamma$, L and X are defined as

$$f_{k_0}(\boldsymbol{R}_m) = \sum_{K_j \in k_0} \exp(i\boldsymbol{K}_j \cdot \boldsymbol{R}_m). \tag{11}$$

The interference effect is reflected in the value of $f_{k_0}(\boldsymbol{R}_m)$. For all the possible pairs, $f_X(\boldsymbol{R}_m)$ equals either $+3$ or -1. In general, if the isolated center has a finite binding energy, a pair with $f_X(\boldsymbol{R}_m) = +3$ will have a deeper allowed state (bonding state) and possibly a shallow forbidden state (anti-bonding state); while for a pair with $f_X(\boldsymbol{R}_m) = -1$, there will be a deeper forbidden state and possibly a shallow allowed sate. The contribution of the L valleys does not change this classification established by the X-valleys. Faulkner [24] found that the binding energy is not a monotonic function of the pair spacing, even within a group of a fixed $f_X(\boldsymbol{R}_m)$ value. Gil et al. [31] pointed out that the nitrogen pair states could be classified into 2×3 classes ($f_X(\boldsymbol{R}_m) = 3$ or -1 and $f_L(\boldsymbol{R}_m) = 4$, -4 and 0), and within each class the binding energy is a monotonic function of $|\boldsymbol{R}_m|$. This conclusion is in fact invalid based on their own numerical results. For instance, in the class of $f_X(\boldsymbol{R}_m) = 3$ and

$f_L(\boldsymbol{R}_m) = -4$, the binding energy of the [420] pair is larger than that of [222] although $|\boldsymbol{R}_{[222]}| < |\boldsymbol{R}_{[420]}|$. More interesting observations were made by Zhang et al. [32]. The possible nitrogen pair configurations are in fact the same as the so-called type I donor-acceptor pairs [35]. If $\boldsymbol{R}_m = [u, v, w]a/2, u + v + w$ is even and $u^2 + v^2 + w^2 = 2m$, where $m = 1, 2, \dots$ is the shell number. There are so-called empty shells where no lattice points can occur (for instance, $m = 14, 30, 46, \dots$). The pair spacing is $|\boldsymbol{R}_m| = (m/2)^{1/2} a$, where a is the lattice constant. Table 1 lists all the pair configurations for $m \leq 48$ [35]. Zhang et al. found that (1) all pairs with odd m have $f_X(\boldsymbol{R}_m) = -1$, thus, the deeper bound state for each pair in this group is a forbidden state; (2) all pairs with even m have $f_X(\boldsymbol{R}_m) = 3$, thus, the deeper bound state is an allowed state; (3) the even m pairs can be further divided into two subgroups, I and II, in which the binding energy in each group is a monotonic function of the pair spacing. All pairs belonging to subgroup II have $f_X(\boldsymbol{R}_m) = -4$, and tend to have smaller binding energies than those belonging to subgroup I, because for the former pairs the contribution of the X and L valleys cancel each other. In this calculation, the electron binding energy of the isolated center was assumed to be 9 meV. Note that in both the Gil et al. and the Zhang et al. model calculations, the effective mass anisotropy was ignored, which led to a degeneracy for pairs with a same $|\boldsymbol{R}_m|$. Such a degeneracy is removed if the mass anisotropy is considered [24]. Fig. 1 shows experimental and theoretical results of Refs. [19,24,26,29–32], Fig. 1(a) for the allowed pairs and Fig. 1(b) for the forbidden pairs. Another interesting trend was found in Zhang et al. calculation [32], that is, the pressure coefficients for the pairs in subgroup II were much smaller than those for the pairs in the subgroup I as well as those measured by Gil et al. [31]. Thus, they tentatively associated the experimentally observed pair states to those pair configurations in subgroup I. In this way, both the energies and the pressure coefficients were consistent with the experimental results, although such an agreement could be just a coincidence.

　　In summary, although all the model calculations seem to be able to place the pair states in the energy

Table 1
Isoelectronic impurity pairs in Zincblende semiconductors[a]

Shell number (m)	Lattice vector $[u, v, w]$ (unit $a/2$)	Degeneracy	Shell number (m)	Lattice vector $[u, v, w]$ (unit $a/2$)	Degeneracy
1	[1, 1, 0]	12	26	[6, 4, 0]	24
			27a	[7, 2, 1]	48
			27b	[6, 3, 3]	24
2	[2, 0, 0]	6	27c	[5, 5, 2]	24
3	[2, 1, 1]	24	28	[6, 4, 2]	48
4	[2, 2, 0]	12	29	[7, 3, 0]	24
5	[3, 1, 0]	24	30	Empty	0
6	[2, 2, 2]	8	31	[7, 3, 2]	48
7	[3, 2, 1]	48	32	[8, 0, 0]	6
			33a	[8, 1, 1]	24
			33b	[7, 4, 1]	48
8	[4, 0, 0]	6	33c	[5, 5, 4]	24
9a	[4, 1, 1]	24	34a	[8, 2, 0]	24
9b	[3, 3, 0]	12	34b	[6, 4, 4]	24
10	[4, 2, 0]	24	35	[6, 5, 3]	48
11	[3, 3, 2]	24	36a	[8, 2, 2]	24
			36b	[6, 6, 0]	12
12	[4, 2, 2]	24	37a	[8, 3, 1]	48
			37b	[7, 5, 0]	24
			37c	[7, 4, 3]	48
13a	[5, 1, 0]	24	38	[6, 6, 2]	24
13b	[4, 3, 1]	48	39	[7, 5, 2]	
14	Empty	0			
15	[5, 2, 1]	48			48
16	[4, 4, 0]	12	40	[8, 4, 0]	24
			41a	[9, 1, 0]	24
17a	[5, 3, 0]	24	41b	[8, 3, 3]	24
17b	[4, 3, 3]	24	42	[8, 4, 2]	48
18a	[6, 0, 0]	6			
18b	[4, 4, 2]	24	43a	[9, 2, 1]	48
19a	[6, 1, 1]	24	43b	[7, 6, 1]	48
19b	[5, 3, 2]	48	43c	[6, 5, 5]	24
20	[6, 2, 0]	24	44	[6, 6, 4]	24
			45a	[9, 3, 0]	24
			45b	[8, 5, 1]	48
			45c	[7, 5, 4]	48
21	[5, 4, 1]	48	46	Empty	0
22	[6, 2, 2]	24	47a	[9, 3, 2]	48
			47b	[7, 6, 3]	48
23	[6, 3, 1]	48	48	[8, 4, 4]	24
24	[4, 4, 4]	8			
25a	[7, 1, 0]	24			
25b	[5, 5, 0]	12			
25c	[5, 4, 3]	48			

[a]Inverse sets $[u, v, w]$ and $[\bar{u}, \bar{v}, \bar{w}]$ are equivalent for the isoelectronic pairs but not for donar–acceptor pairs.
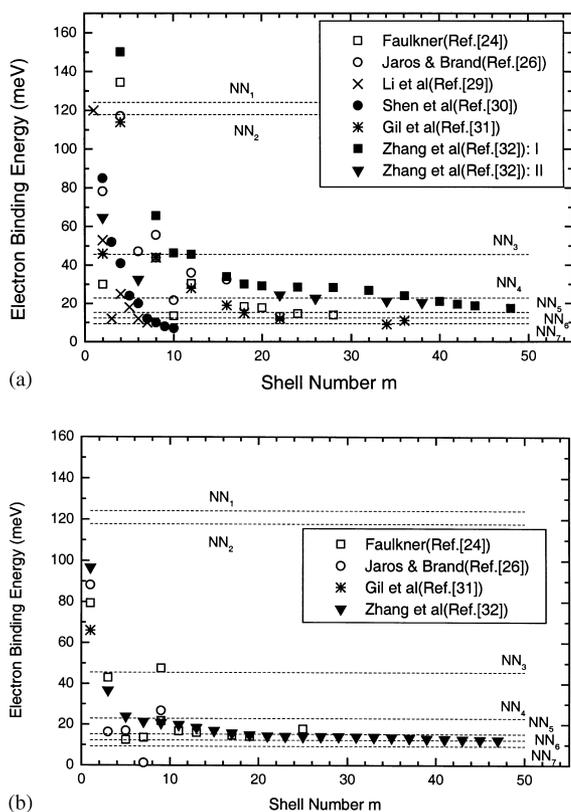
Fig. 1. Summary of the theoretical results for the electron binding energy as a function of shell number. Dashed lines are the experimental results of Cohen and Sturge [19]. (a) For pairs whose transitions are dipole-allowed, and (b) for pairs whose transitions are dipole-forbidden.

range observed in experiments, none except for Ref. [30] could yield a sequence in agreement with the assignments of Thomas and Hopfield [2]. Since the order of the pair states are sensitive to the calculation methods, the potential strength and other band structure parameters, all the theoretical results currently obtained are only meaningful in a qualitative way. A more rigorous theory for the isoelectronic problem is called for. Although more sophisticated first-principles calculations have been conducted for relatively high nitrogen concentration well beyond the impurity regime [36], a true impurity limit (an isolated center or a pair) has still remained difficult to compute due to the limitation of the computer power or lack of better computation techniques.

4. Exciton bound states

Still an open question is whether the isolated nitrogen center can bind an electron. Since an accurate impurity potential is hard to obtain, an alternative approach to answer this question was first adopted by Faulkner [24], and was then modified by others [37–39]. In principle, if one knows the functional form of the impurity or the bound electron wavefunction, the exciton binding energy can be calculated as a function of, for instance, the strength of the potential. Then, by comparing with known experimental results for the total exciton energy, the electron bound state can be determined. Using the Koster–Slater one-band one-site approximation for the electron and a hydrogen-like model for the hole and considering only the X-valleys, Faulkner [24] found the electron and hole binding energies to be 10.4 and 9.6 meV, respectively, based on the 20 meV total binding energy assumed at that time. Taking the same approach but using much more sophisticated trial wavefunctions for both the electron and hole, Masselink and Chang [37][2] concluded that the electron binding energy was only 0.6 meV, assuming the total binding energy to be 28 meV. However, if a more accurate total binding energy of 33 meV [21] was used, the electron binding energy became ~ 2.8 meV. The Gilinskii and Loginova [38] calculation for the pair centers led to an extrapolated value of 3.7 eV for the electron binding energy of the isolated center. Using an approach practically equivalent to that of Faulkner's but considering X, L and Γ valleys in the electron wavefunction, Zhang [39][3] obtained an electron binding energy of 5.8 meV with a total binding energy of 33 meV [21]. It is also worth while to mention that the oscillator strength calculated by Masselink and Chang [37] was only $\sim 1/20$ of the experimental value, which is presumably due to the underestimation of the Γ component of the electron wavefunction or the electron

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[2] The oscillator strength calculated by the authors should be compared with the total oscillator strength $f = 0.1$ rather than that of the zero phonon line, as pointed out by T.N. Morgan [14].

[3] A factor of two was missing in the summation over spin states for the oscillator strength calculation.

binding energy. Zhang's calculation [39] yielded an oscillator strength $\sim 1/5$ of the experimental value. Although we still don't know the accurate value of the electron binding energy, all these different calculations seem to suggest that the binding energy is likely to be finite. The only reported experimental evidence for the electron bound state was a differential absorption measurement made by Lupal and Pikhtin [40] where they believed that the 2S and 3S exciton excited states were observed for the isolated nitrogen center.

In the exciton binding energy calculation, all approaches have ignored the correlation between the electron and hole, i.e., the exciton wavefunction is approximated simply as the product of the electron and hole wavefunctions. Such an approximation omits the interaction of the hole with the impurity potential, which is repulsive [24]. Benoit a la Guillaume [27] justified this approximation by noticing the large difference between the electron and hole wavefunctions. Zhang [39] pointed out that this approximation is equivalent to saying that the valence band or the exciton ground state is unperturbed by nitrogen doping. This can be understood intuitively in terms of the atomic level model of Hjalmarson et al. [13]: the Ga–N bonding state is far below the top of the valence band and the antibonding state is very close to the conduction band, which leaves an energy range between the two levels in which the influence of nitrogen is expected to be small. A recent first-principles calculation [23] has indeed shown that the valence band is perturbed very little in the dilute GaAsN alloy.

Zhang [39] calculated the exciton binding energy as a function of the electron binding energy in the energy region of the pair states. Strictly speaking, such a functional dependence is not applicable to the pairs. However, in view of the fact that the pair spacing is usually much smaller than the exciton radius, they can be approximately treated as a single center. As shown in Fig. 2, the hole binding energies for most of the pairs obtained experimentally by Cohen and Sturge [19] lie fairly close to the theoretical curve. The deviation for those wider spaced pairs NN_3 through NN_7 is probably because the single center approximation is not good enough. Note that there is no adjustable parameter in this calculation. The result indicates that
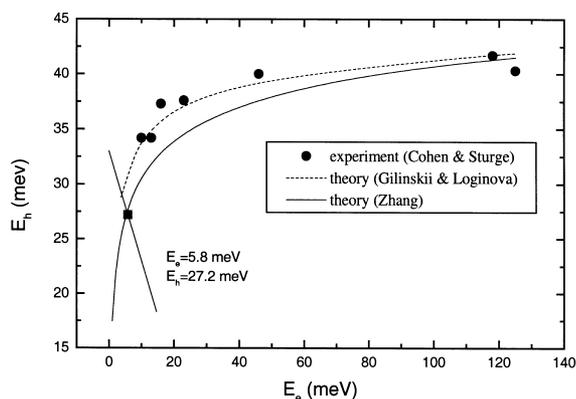

Fig. 2. The hole binding energy E_h as a function of the electron binding energy E_e [19,38,39].

the deviation of the hole binding energy from that of the acceptor based on the effective mass theory can be largely explained as the result of partial delocalization of the electron bound state. The deviation was usually explained as a result of a "chemical shift" or a "central-cell correction". Glinskii and Loginova [38] did a similar calculation for the pairs where they allowed the central-cell correction and the valence-band effective mass to be adjustable parameters to fit all the excited states of the pairs. Their results indeed agreed better with the experimental results, as shown in Fig. 2.

5. Exciton–phonon coupling

It was known from the very beginning [2] that the decay of a nitrogen bound exciton results in a series phonon sidebands in addition to the zero-phonon line. For the isolated center, the phonon sidebands appear in the energy regions of TA, LA, TO and LO phonons, although their energies do not always match the phonon energies at special k-points (the most significant one is the X-point). The phonon sideband structure of the pair states is very similar to that of the isolated center, except for an extra phonon sideband associated with the nitrogen local mode. The intensity of the local mode tends to increase with increasing exciton binding energy, which can be understood as a result of increasing confinement [2]. Fig. 3 shows a typical
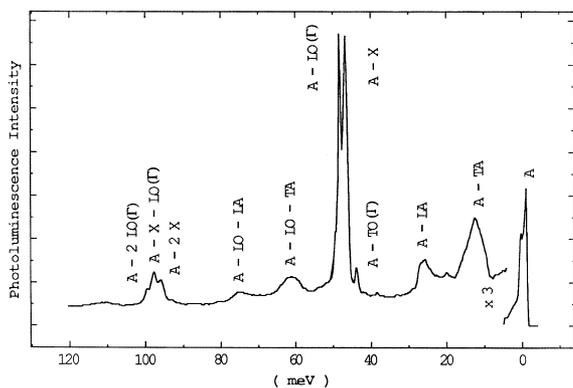
Fig. 3. Photoluminescence spectrum of the isolated nitrogen bound exciton in GaP : N (4.2 K, [N] = 10^{16} cm^{-3}, A line at 2.317 eV) [20].

photoluminescence spectrum for the isolated center. Even though the origins of those phonon sidebands were not clear, it was almost always taken for granted that the decay of a phonon sideband was the same as that of the zero-phonon line, ignoring the temperature dependence of the phonon population.

The LO phonon sideband was used to measure the exciton decay time by Cuthbert and Thomas [15] and to investigate the thermal quenching process by Sturge et al. [20]. In Ref. [20], each pair state was selectively excited at its zero-phonon line to avoid the complication caused by inter-center exciton transfer under above band-gap excitation. However, it was claimed by Chang et al. [41–43] that the LO phonon sideband of the nitrogen center was inappropriately treated as a conventional phonon sideband, based on their experimental results of abnormal temperature dependence of the relative intensity between the phonon sideband and zero-phonon line for NN_4–NN_6. They interpreted the abnormality in terms of a new type of impurity-exciton-phonon complex, the so called "dressed exciton". It was later shown by Zheng and Zhang [44], Zhang et al. [45] and Ge et al. [46] that the anomalous temperature dependence of the LO phonon sidebands was due to the erroneous assignments of the spectral lines. The error arose because the overlap between the optical phonon sidebands of NN_4–NN_6 and the acoustic

phonon sidebands of NN_3, the difference in the thermal quench rates and the effect of thermally activated exciton transfer among these centers were overlooked. These complications were avoided by selective excitation [20,47]. The existence of the so called "dressed exciton" was not been proven in GaP : N.

The mechanism for the phonon sidebands in GaP : N posed a very interesting issue. In GaP, the phonon sideband structure of the isolated nitrogen center appears different from that of a donor. Even though the binding energy of the A line is much smaller than that of a donor, the phonon sidebands are much stronger and richer for the A line. Intuitively, the cause for the difference is that the nitrogen is spatially very localized, thus, its coupling to the phonons is strong. Another long-standing mystery is the origin of the phonon sideband "X". The LO phonon sideband is a doublet, one peak located at 50.1 meV of the LO(Γ) phonon energy and the other peak usually labeled as X at 48.4 meV; this value does not match the energy of the LO(X) phonon at the X point of the conduction band minimum. The peak energies of LA and TA phonon sidebands also deviate from the corresponding phonon energies at the X-point, especially for the LA phonon sideband. Snyder et al. [48,49] have explained the phonon sideband structure of the A line in terms of wavefunction delocalization in the k-space: the phonon sideband consists of a combination of phonons from all the k-points weighted by the components of the wavefunction at these k-points and the phonon density of states. Dai et al. [50] applied the indirect transition model or the _momentum conservation_ (MC) model in calculating the phonon sideband spectrum of the isolated nitrogen center. They concluded that the indirect transition was the mechanism for all the phonons sidebands, except for the LO(Γ) sideband which could be explained by the _configuration coordinate_ (CC) model. Even though their calculated spectrum shape appeared very close to the experimental result, the absolute strength of the phonon sideband was not considered. In fact, the lineshape was largely determined by the phonon density of states, because of wavefunction delocalization in the k-space. Zhang (Chang) et al. [51] and Hong et al. [52] tried to

explain the previously reported anomalous temperature dependence of the LO phonon sidebands [41–43] with such an indirect transition model. They concluded that the abnormality was due to a different temperature dependence in the LO(Γ) and X components of the LO phonon sideband. As later pointed out by Ge et al. [46], such an explanation contained serious inconsistency, beside having made erroneous assignments of the spectral lines [44,45].

The electron–phonon coupling for an impurity state was treated in a comprehensive way by Zhang et al. [53]. In principle, the electron-phonon coupling affects both electron and phonon wavefunctions. If the electron and phonon wavefunctions are Φ_j^0 and χ_n^0 for the independent electron and phonon subsystems, respectively, the electron–phonon interaction H_{EL} will change the wavefunctions to Φ_{jn} and χ_{jn}. An optical transition should be understood as occurring between two states of the coupled system which may be denoted as $\{\Phi_{jn}\chi_{jn}\}$ within the Born–Oppenheimer approximation. Two frequently adopted approaches to treat the coupling lead to the two above-mentioned models: the MC model and CC model. For the MC model, only the electronic part of the total wavefunction is perturbed by the coupling, that is, the optical transition is between two set of states described by $\{\Phi_{in}\chi_n^0\}$ and $\{\Phi_{fn'}\chi_{n'}^0\}$, where i and f stand for the initial and final electronic state, respectively, and n and n′ for different phonon states [54]. Such a description is equivalent to the second order perturbation theory developed for indirect transitions [55]. For the CC model [56,57], within the commonly adopted Condon approximation, the optical transition occurs between $\{\Phi_i^0\chi_n\}$ and $\{\Phi_f^0\chi_n\}$, which in general leads to multi-phonon spectral lines. The relative strength of the one-phonon sidebands to the zero-phonon line is described by the Huang-Rhys factor S [56]. Both the CC and MC models were applied to interpret the phonon replicas of the impurity spectra in semiconductors [58]. Zhang et al. [53] demonstrated that for a localized state the contribution of the MC mechanism is usually much smaller that of the CC mechanism. Even for the case like the isolated nitrogen center in GaP with a fairly small binding energy, the contribution of the CC mechanism is
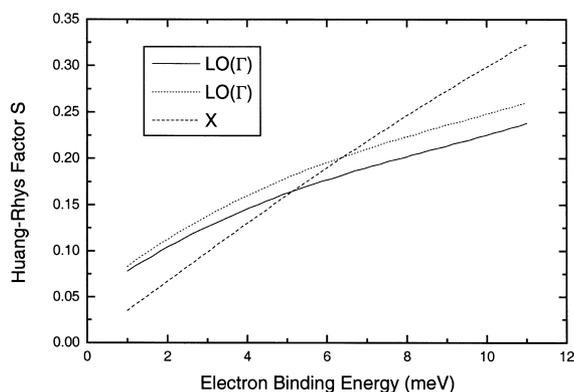

Fig. 4. Calculated Huang–Rhys factors of the LO phonon sidebands versus the electron binding energy for the isolated nitrogen bound exciton in GaP [53]. Full line: Fröhlich interaction, calculated with using k-space wave function. Dotted line: Fröhlich interaction, using real space wave function. Dashed line: deformation potential interaction, using real space wave function.

still dominant over that of the MC mechanism. It was concluded [53] that indeed the LO(Γ) sideband is due to the Fröhlich interaction, while the X sideband as well as the TA and LA sidebands are due to the deformation potential interaction, and the CC model is appropriate to describe the phonon sideband spectrum. It is very interesting to find that the dependence of $S_{LO(\Gamma)}$ and S_X on the electron binding energy is different, but they are nearly equal when electron binding energy is about 6 meV, as shown in Fig. 4. Both the relative and the absolute coupling strengths with the 6 meV binding energy agree very well with the experimental results shown in Fig. 3. Also, such a binding energy is consistent with that derived from the exciton binding energy calculation [39].

6. Implication of the early work to the current understanding of the GaAs$_{1-x}$N$_x$ and GaP$_{1-x}$N$_x$ alloys

During the time period when the nitrogen in GaP was intensively studied, the concept of band offset was not an issue of interest to most scientists. In fact, the large enhancement of the electron binding energy from an isolated center to a pair implies a type II band alignment between the GaP and
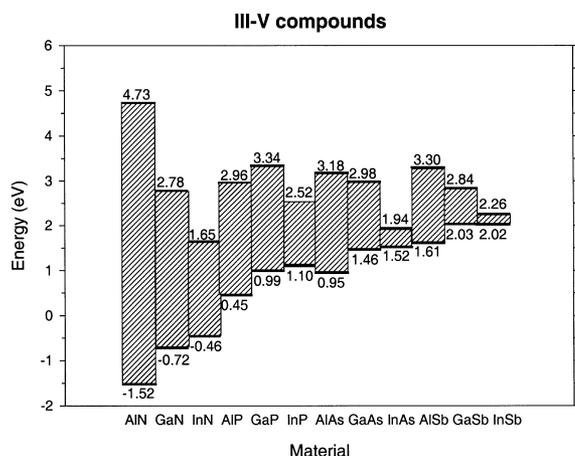
Fig. 5. Band alignments of III–V semiconductors.

GaN, as was recently calculated by Bellaiche et al. [23]. The similar situation happens between GaAs and GaN. The valence band alignments for almost all III–V semiconductors were calculated by Wei and Zunger [59]. In Fig. 5, we plot band alignments for both conduction and valence bands [59,60]. For a III–V alloy, an isoelectronic bound state tends to form in the dilute limit of an alloy $A^{III}B^{V}_{1-x}C^{V}_{x}$ of which the hosts materials $A^{III}B^{V}$ and $A^{III}C^{V}$ have type II band alignments with large band offsets: for instance, GaP : N [1], GaAs : N [22], GaN : As and GaN : P [61]. Such an observation is easy to understand in terms of the Hjalmar-son et al. model [13]. In these cases, either the antibonding state (for GaP : N and GaAs : N) or the bonding state (for GaN : P and GaN : As) are more likely to be a bound state, compared to the cases like GaP : As and GaAs : P where the band offsets between GaP and GaAs are relatively small and the band alignment between them is type I. However, the ultimate factor for having a bound state is the large difference in the atomic energy levels and not the band alignment. It appears that the crucial difference between alloys like $GaAs_{1-x}N_x$ and $GaAs_{1-x}P_x$ is the existence of the bound state in the former case. Thus, the formation of an impurity band is anticipated for the former case with a high N concentration.

The earlier work on GaP : N had been limited to doping level below $1-2 \times 10^{19}$ cm^{-3} or $x < 0.1\%$.

New epitaxial growth techniques have been able to achieve a doping level of a few percents of nitrogen in GaP [62–64]. It has been shown by emission and excitation spectroscopy studies that the sharp ni-trogen pair related transition lines exist up to a level of [N] $\sim 1 \times 10^{20}$ cm^{-3} [62–64]. Beyond that, these pair transition lines are severely broadened. We notice that the broadened NN_1 state becomes effectively a new band edge state in the high doping region. The situation is somewhat different in $GaAs_{1-x}N_x$. NN_1 and NN_2 as well as NN_3 was were observed in moderately doped GaA : N ([N] $\sim 5 \times 10^{17}$ cm^{-3}) samples [65–67]. However, for x as small as 0.01% or [N] $\sim 2 \times 10^{18}$ cm^{-3}, the sharp NN_1 line became unobservable, and the emission spectrum is not well understood [68]. On the other hand, a resonant state was observed in $GaAs_{1-x}N_x$ with $x > 1\%$ by Perkins et al. [69] as well as in GaInAsN by Shan et al. [70]. This reson-ant level was found to move toward higher energy while the band-gap decreased with increasing nitro-gen composition. The relationship between this res-onant state [69] and the resonant state of the isolated nitrogen center observed in the dilute limit [22] is not clear so far. The extrapolation of the Perkins et al. results yielded a level at ~ 250 meV above the GaAs band edge for $x = 0$, while in the dilute limit the extrapolation to the zero pressure led to a level at 150 – 180 meV above the band edge [22]. Shan et al. [70] explained the newly observed resonant level being the same as that in the dilute limit [22], and they interpreted the movement of the band-gap in an opposite direction to the reson-ant level as due to the two level repulsion. Perkins et al. [69] pointed out there is yet another possible origin for the resonant level, as a GaAs L-point related transition. A recent theoretical calculation [71] indicated that the L-point was "folded" into the Γ-point due to alloy scattering and the four-fold degeneracy at the L-point was lifted because of the interaction with the nitrogen. A similar result might have been observed in GaP : N long time ago [2], that is, the band-gap free exciton transition became allowed without any phonon assistance. The transition was labeled as A_x, and its intensity in-creased linearly with the nitrogen concentration. This transition can perhaps be associated with one of the three-fold degenerate states at the X-point

split due to the perturbation of the nitrogen impurity (more specifically, the A_1 state). In fact, the A_x level was found to be slightly lower than the bulk free exciton level [72]. A new wave of interest in the nitride related materials will definitely leads to a better understanding of the behavior of the nitrogen as an isoelectronic impurity in III–V materials.

7. Summary

We have given a rather detailed review on a few important issues related to the isoelectronic impurity nitrogen in GaP and GaAs. These issues include (1) the binding mechanism, (2) the electron binding energy calculation, (3) the exciton binding energy calculation, (4) the exciton–phonon coupling, and (5) the behavior of the nitrogen in dilute nitride alloys. A key problem that remains not well answered is the interplay of the short-range impurity potential, the strain field and the electronic polarization. The solution to this problem is essential to solve the long-standing mystery: what exactly are those pair's configurations?

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