

**Ultranarrow photoluminescence transitions of nitrogen cluster bound excitons in dilute GaAsN**

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High resolution photoluminescence spectroscopy on heavily doped GaAs:N reveals the existence of excitons bound to a nitrogen cluster. The observed transitions are exceedingly sharp, similar to those observed for excitons bound to nitrogen pairs in high quality GaAs with the narrowest transition being only  $94 \mu\text{eV}$ . Moreover, several other features can be observed originating most likely from phonon replicas of the nitrogen pair bound excitons and higher order clusters. However, the main transitions which dominate the photoluminescence spectra are thought to originate from excitons bound to a three nitrogen cluster. The sharp photoluminescence features are superimposed on a broad luminescence band indicating a strong perturbation induced by nitrogen atoms to the host GaAs lattice. The number of the allowed transitions and their polarization dependence provide important information about the arrangement of the nitrogen atoms in the cluster.

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**I. INTRODUCTION**

The physics of excitons bound to isoelectronic impurities has been the subject of numerous studies since their discovery three decades ago.<sup>1</sup> One of the reasons for this great interest has been the strong luminescence associated with the nitrogen (N) isoelectronic impurity in GaP, which has found applications in light-emitting devices in the green and yellow spectral region. In recent years, heavily nitrogen doped GaAs and GaInAs, have received considerable physical and technical attention due to their peculiar N-induced properties and potential for optoelectronic applications. The incorporation of a small amount of nitrogen leads to dramatic changes in the electronic band structure, such as a gigantic band gap reduction.<sup>2,3</sup> Strong efforts have been made to fabricate long wavelength lasers, high-efficiency multijunction solar cells, and heterojunction bipolar transistors using GaInNAs. These applications have provided a strong motivation for the effort of understanding the evolution of the electronic structure of these unconventional alloys with varying N content in a number of aspects, for instance, the impurity-impurity interaction, the impurity-host interaction, and the effect of external perturbation. With different emphasis on these interactions, several physical models have been proposed, such as the two-band anticrossing model (BAC),<sup>3</sup> the N-impurity band formation model<sup>4-6</sup> and the multiband hybridization model.<sup>7,8</sup>

In order to unveil the nature of the electronic properties of nitrogen doped GaAs a detailed study at different doping levels is necessary. It is known that a single N isoelectronic impurity introduces the resonant state  $N_x$  150–180 meV above the GaAs conduction band minimum, which can be observed in the dilute doping limit through the application of hydrostatic pressure.<sup>9</sup> When the nitrogen doping level reaches  $10^{16}$ – $10^{17} \text{ cm}^{-3}$ , below band gap N-related transitions can be observed which have been attributed to nitrogen pair bound excitons. This assignment has been supported by theoretical calculations and the photoluminescence (PL) transitions are referred to as  $NN_1$  and  $NN_4$  or  $X_1$  and  $X_2$ .<sup>10-13</sup>

They likely correspond to pair arrangements wherein if a nitrogen atom is located at the origin, the second atom is located either at  $[1/2, 1/2, 0]$  or  $[1, 1, 0]$  of the anion sublattice, respectively. If this configuration is exact, these pairs should have  $C_{2v}$  symmetry.<sup>13-17</sup> Both centers  $X_1$  and  $X_2$  should split under the biaxial crystal field into eight singlets ( $J=1$  triplet and  $J=2$  quintet). Two of the eight transitions are symmetry forbidden and only six transitions can be observed. As the N concentration is increased to  $10^{18}$ – $10^{19} \text{ cm}^{-3}$  broad N-related levels appear in the band gap which have been attributed to nitrogen cluster bound excitons.<sup>5,18-20</sup> Moreover, the emission associated with the GaAsN alloy band gap is observed to exhibit a rapid energy reduction and approach the N-related levels within the band gap with increasing nitrogen concentration.<sup>20,21</sup> The photoluminescence transitions assigned previously to nitrogen cluster bound excitons were very broad and little structure could be observed. Several broad peaks were observed superimposed with broad luminescence at nitrogen concentrations of  $10^{19} \text{ cm}^{-3}$  (0.1%), which motivated the impurity band model.<sup>5</sup> However, no assignment could be made on the number of nitrogen impurities in the cluster and their arrangement in the cluster. In this paper we provide the first detailed insight into the symmetry of such a cluster center, the preferred arrangement of the nitrogen atoms in the cluster, and based on these arguments, we provide strong evidence for the very existence of nitrogen cluster bound excitons in heavily doped GaAs, which has been so far only the most plausible explanation for the previously observed spectral features. We attribute the absence of such sharp features in the previous studies to either broadening induced by the heavier doping, or most likely due to the lower quality of the material. In order to incorporate large amounts of nitrogen, these samples were typically grown at a lower temperature leading most likely to lower quality material.

**II. SAMPLE AND EXPERIMENT**

The present sample was grown at a higher temperature while still incorporating a large amount of nitrogen. It should

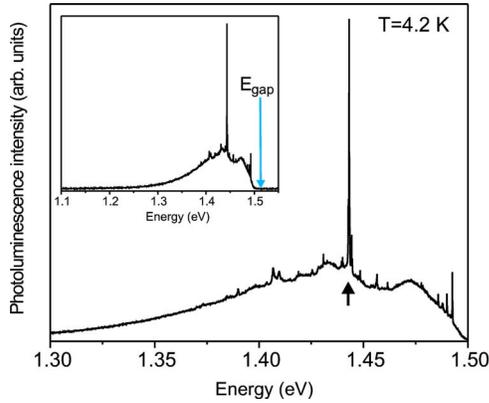


FIG. 1. (Color online) Photoluminescence spectra of the GaAsN sample at 4.2 K showing the cluster bound exciton luminescence lines marked by the vertical black arrow. Multiple weaker transitions can be observed originating from phonon replicas of the nitrogen pair bound excitons and possible higher order clusters. The inset shows a larger energy region in order to better display the entire photoluminescence region of interest. The vertical (blue) dark gray arrow marks the estimated location of the band gap at this nitrogen concentration based on the electroreflectance studies (Ref. 2).

be mentioned that although we show spectra from one sample only, identical spectra were observed in several samples grown in the same or slightly different conditions. The photoluminescence spectra were collected with samples mounted in strain a free manner and immersed in liquid helium. The detections system included a SPEX1403 double-grating spectrometer equipped with liquid nitrogen cooled charged coupled detector (CCD) and a cooled RCA C31034 GaAs photomultiplier tube. The excitation at 650 nm was provided by a coherent dye laser using the RG6 dye. The polarization dependence of the emitted light was measured by manually rotating a waveplate placed in front of the spectrometer slit. The 300 nm thick GaAs:N layer was grown by molecular beam epitaxy at 630 °C. The nitrogen concentration was measured by secondary ion mass spectroscopy to be  $1 \times 10^{18} \text{ cm}^{-3}$ .

### III. RESULTS AND DISCUSSION

In Fig. 1 PL spectra of the GaAsN sample at 4.2 K are shown. The main stronger transition is marked by the vertical arrow. The inset shows a larger energy region in order to better display the entire photoluminescence region of interest. The only observed transitions originating from excitons bound to nitrogen pairs below the band gap have been attributed to the  $X_1$  and  $X_2$  pair configurations and lie much higher in energy (1.5095 eV and 1.4986 eV, respectively).<sup>13</sup> Therefore, and due to the higher concentration of nitrogen in the present sample, the strong transition marked by the vertical arrow most likely originates from excitons bound to a three nitrogen cluster. Moreover, the relatively high binding energy of the center, 74.3 meV, compared to 8.2 meV for the  $X_1$  and 19.1 meV for the  $X_2$  centers suggests a larger nitrogen complex. The three nitrogen assignment is further sup-

ported by the symmetry of the bound exciton center, obtained by polarization studies. The spectral structure of the new feature differs significantly from those observed for nitrogen pairs, in the number of transition lines, the separation between the lines, and their polarization behavior. While at this resolution for the pair bound exciton transition in lower doped samples only four lines can be resolved, for the newly observed cluster bound exciton six transitions can be observed. Multiple weaker transitions at higher and lower energy can also be observed, surrounding the cluster bound exciton transition. Some of these transitions show striking similarities to the nitrogen pair bound excitons in their spectral structure and may originate from phonon replicas of the nitrogen pair bound excitons. Some of the weaker transitions at lower energies are rather unique in their spectral structure and may arise from excitons bound to higher order nitrogen clusters, or to three-nitrogen clusters with a different arrangement of the nitrogen atoms in the lattice. The preceding studies reported spectral features originating most likely from cluster bound excitons at this energy, as well as at higher and lower energies. The transitions reported in the previous studies are listed in Ref. 5 without assignment on the number of nitrogen atoms involved or their configuration in the lattice.

The ground state of the exciton corresponds to the electron localized in the  $\Gamma_6$  minimum of the conduction band and the hole is associated with the top of the  $\Gamma_8$  valence band. The exchange interaction or  $\mathbf{J}\text{-}\mathbf{J}$  coupling, splits the  $\Gamma_6 \times \Gamma_8$  excitonic state into a  $\mathbf{J}=1$  triplet and a  $\mathbf{J}=2$  quintet. In the case of a single nitrogen impurity bound exciton, the crystal field of  $T_d$  symmetry ( $\Gamma_6 \times \Gamma_8 = \Gamma_3 + \Gamma_4 + \Gamma_5$ ) leads to a  $\mathbf{J}=1$  like state  $\Gamma_5$  and further splits the  $\mathbf{J}=2$  like state into a  $\Gamma_3$  doublet and a  $\Gamma_4$  triplet. The local symmetry is further reduced for excitons bound to nitrogen pairs. Depending on the location of the nitrogen atoms in the lattice, the center can have  $C_{3v}$ ,  $D_{2d}$ ,  $C_{2v}$ ,  $C_s$ , or  $C_2$  local symmetry, which can lift the degeneracy partially or completely. The center symmetry of nitrogen pairs has been discussed in detail for the nitrogen bound exciton transitions in GaP.<sup>15,16</sup> The situation gets further complicated for three nitrogen cluster centers, due to the large number of possible arrangements of the nitrogen atoms. The local symmetry of such centers has also been discussed in connection with the nitrogen bound exciton transitions in GaP. By using photoluminescence spectroscopy under uniaxial stress along the symmetry directions, the symmetry of the center, and as a result, the arrangement of the nitrogen atoms in the lattice was determined.<sup>17</sup>

In Fig. 2 the PL spectra of the nitrogen cluster bound exciton at 4.2 K and 1.8 K are shown. In total, six transitions can be observed marked by the vertical ticks, with the narrowest transition being only 94  $\mu\text{eV}$ . Decreasing the temperature from 4.2 K to 1.8 K the higher energy transitions thermalize to the lower energy ones indicating that all six transitions originate from the same center. In order to unveil the configuration of the nitrogen atoms in the cluster the polarization dependence of the PL transitions was recorded and the polarization map is shown in Fig. 3. There are many possible configurations the three nitrogen atoms can have in the cluster leading to different local symmetries. However, the only nitrogen impurity arrangement that would allow for

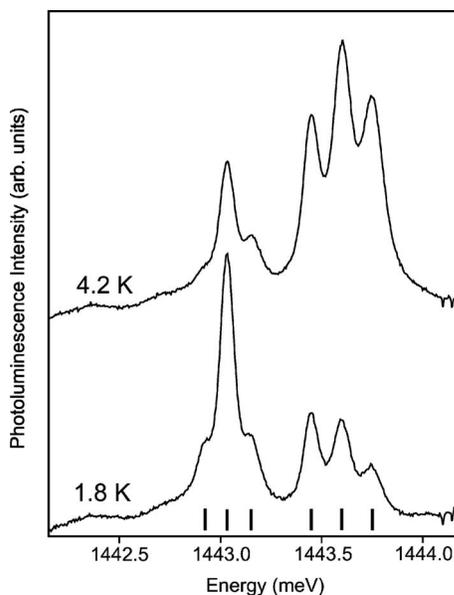


FIG. 2. Photoluminescence spectra of the nitrogen cluster bound exciton at 4.2 K and 1.8 K. Six sharp transitions can be observed marked by the vertical ticks, with the narrowest transition being only 94  $\mu\text{eV}$ . Decreasing the temperature from 4.2 K to 1.8 K the higher energy transitions thermalize to the lower energy ones indicating that all six transitions originate from the same center.

six transitions to be observed based on group theoretical selection rules has  $C_{2v}$  local symmetry.<sup>17</sup> Assuming that one nitrogen atom is located at the origin, such a symmetry can only be achieved if the other two nitrogen atoms occupy the  $[1/2,1/2,0]$  and  $[1,1,0]$  lattice positions, leading to a linear defect. Moreover, the  $C_{2v}$  symmetry allows only one polar-

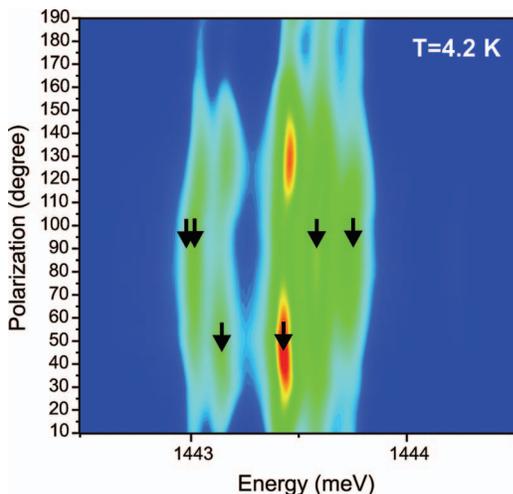


FIG. 3. (Color) Two-dimensional map of the polarization dependence of the nitrogen cluster bound exciton photoluminescence transitions. The color PL intensity in arbitrary units increases from blue to red. The six vertical black arrows at 90°, 90°, 45°, 45°, 90°, and 90°, respectively, indicate the polarizations at which the transitions maximize. The number of the allowed transitions and their polarization behavior of the emitted light provide information about the symmetry of the cluster, i.e., the arrangement of the nitrogen atoms in the host lattice.

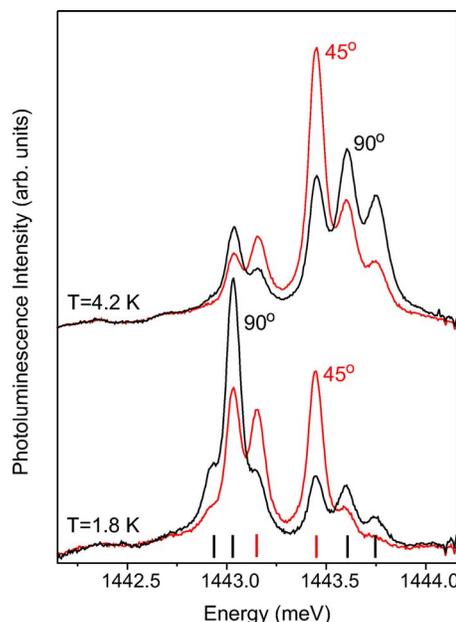


FIG. 4. (Color online) Selected photoluminescence spectra at 4.2 K and 1.8 K at the polarizations of interest, 45° (red), dark gray and 90°, black. At 1.8 K the lower energy transitions are more strongly populated, and weaker transition are enhanced. The vertical ticks indicate the positions of the six transitions.

ization for each transition, which would explain the polarization dependence observed in Figs. 3 and 4. Other possible arrangements of the nitrogen atoms and resulting symmetries, such as  $C_{3v}$  or others, would lead to a different number of transitions and allow more than one polarization. In the  $C_{2v}$  point group following the notation introduced in Ref. 14, the exciton states reduce to  $\Gamma_6 \times \Gamma_8 = 2\Gamma_1 + 2\Gamma_2 + 2\Gamma_3 + 2\Gamma_4$ . The transitions from the  $\Gamma_1$  ground state to the  $\Gamma_3$  state are forbidden by the selection rules, leading to six allowed transitions, each of them being polarized in  $x$ ,  $y$ , or  $z$  direction. Three of these states ( $\Gamma_1, \Gamma_2, \Gamma_4$ ) are  $J=1$  like and the remaining three are  $J=2$  like. In Fig. 2 two triplets can be observed which can be tentatively assigned to the exchange split  $J=1$  and  $J=2$  states. Based on the temperature behavior the lower energy triplet appears to correspond to the  $J=2$  like states and the higher energy triplet to  $J=1$  like states.<sup>15</sup> However, it should be pointed out that  $J$  is no longer a good quantum number.

Figure 3 shows the two-dimensional map of the polarization dependence of the cluster bound exciton photoluminescence transitions. The six vertical black arrows at 90°, 90°, 45°, 45°, 90°, and 90°, respectively, indicate the polarizations at which the transitions maximize. The polarization dependence observed further supports the arrangement of the nitrogen atoms along the  $[110]$  direction. There are in total 12 indistinguishable arrangements of the nitrogen atoms in the cluster. Four of them are located in the planes parallel to the surface and eight in the two planes perpendicular to the surface. The  $[001]$  direction is perpendicular to the sample surface and the sample is cleaved along  $[110]$  and  $[1\bar{1}0]$  directions. The two cleaved sides correspond to the 0 (vertical) and 90 (horizontal) degree polarizations in the detection.

Assuming this orientation, the later eight configurations are expected to show transitions polarized along (0 or 180) and 90 degree, while the other four nitrogen configurations are expected to have transitions polarized along 45 and 135 degrees, which are observed for two transitions in Fig. 3. While four transitions polarized along 90 degree can also be observed, and are marked by vertical black arrows in Fig. 3, the transitions polarized along 0 or 180 degree could not be unambiguously labeled. The convolution of transitions originating from the 12 indistinguishable orientations leads to some extent to mixed polarizations, and makes the assignment of the polarization to specific transitions difficult. In fact the intensity of the transitions does not always completely vanish when the polarization of the waveplate is aligned perpendicular to the polarization of the emitted light, indicating that weaker transitions with a different polarization are underlying. Only the dominating polarization for each transition can be observed. In Fig. 4 selected photoluminescence spectra at 4.2 K and 1.8 K at the polarizations of interest are shown (45° red and 90° black). At 1.8 K the lower energy transitions are more strongly populated, and weaker transitions are enhanced.

At this concentration, very strong nitrogen cluster levels seem to have already formed below the band gap and the broad luminescence on which the cluster levels are superimposed indicates a strong perturbation induced by the nitrogen atoms to the host GaAs lattice, which has a strong impact on the electronic properties of this material. Theoretical and experimental studies suggest that this strong perturbation to the

GaAs host lattice, caused by the nitrogen impurity atoms, can lead to a splitting of the quadruply degenerate conduction band at the  $L$  point of the Brillouin zone, into a singlet and a triplet. Moreover, nitrogen substitution into GaAs destroys the formal translational symmetry underlying momentum conservation based optical selection rules and thereby may make normally forbidden indirect transitions optically active.<sup>2,7,22-24</sup> At higher nitrogen concentrations, such strongly trapping cluster levels become resonant in the conduction band leading to electron scattering that may be the cause for the relatively low electron mobility in this material.

In conclusion, ultranarrow excitonic transitions were observed, originating most likely from excitons bound to a three nitrogen cluster. The relatively large binding energy of the center and the spectral structure of the transitions, which differs from those of pairs, suggest the three nitrogen assignment. Polarizations studies support the arrangement of the nitrogen atoms along the [110] direction forming a line defect. The broad luminescence, on which the cluster bound exciton transitions are superimposed, indicates strong perturbation induced by the nitrogen atoms to the host lattice.

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