Nitrogen pairs, triplets, and clusters in GaAs and GaP

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The electronic and atomic structure of substitutional nitrogen pairs, triplets, and clusters in GaP and GaAs is studied using the multiband empirical pseudopotential method with atomistically relaxed supercells. A single nitrogen impurity creates a localized $a_1(N)$ gap state in GaP, but in GaAs, the state is resonant above the conduction-band minimum. We show how the interaction of multiple a_1 impurity levels, for more than one nitrogen, results in a nonmonotonic relationship between energy level and impurity separation. We assign the lowest (NN1) line in GaP to a [2,2,0]

nonmonotonic behavior. In our calculations we find that multiband-coupling *alone* produces a nonmonotonic ordering, even for similarly oriented pairs, e.g., pairs oriented on the [1,1,0] axis: In GaP, for unrelaxed supercells we find NN4 [2,2,0] to be *deeper* than NN1 [1,1,0], while for relaxed pairs along the [1,1,0] axis we find, from deepest to shallowest level, NN4 [2,2,0], NN1 [1,1,0], then NN9 [3,3,0], and more distantly spaced pairs.

(ii) *Are all of the assigned PL lines due to nitrogen pairs?* When first discovered,[4,5] it was proposed that the sharp ''NN'' lines observed in PL were due to pairs of nitrogen atoms at increasing separation. This assignment has remained contentious to the present day. Uniaxial pressure measurements of GaP:N (Ref. 8) find that, except for NN1, NN3, and NN4, the stress-induced splittings cannot be assigned to mth nearest-neighbor pairs as originally proposed, suggesting the other lines are due to other small aggregates of nitrogen atoms (triplets, clusters, etc.), despite the low nitrogen concentration. In particular, the NN2 PL line of GaP:N displays several anomalies: (1) the amplitude in PL is significantly smaller than for NN1 or NN3,[4–6] (2) the hydrostatic pressure coefficient for the level is larger than for NN1 or NN3,[7] and (3) the local symmetry is C_s,[8] while a second nearest-neighbor pair would display D_{2d} symmetry. In our calculations, we find the second nearest-neighbor pair levels to be both forbidden and high in energy (Figs. 1 and 2), i.e., in agreement with Ref. 7, a second nearest-neighbor pair cannot explain the experimental observation of the NN2 line. We considered several symmetry-compatible triplet and cluster geometries.[26] Our calculations find a planar triplet with symmetry compatible with the NN2 line (inset to Fig. 1) has

measured ~36 meV.[6,7] Our model thus predicts the overall trends for isolated impurities and clusters.

(iv) *Does a model considering nitrogen pairs at the unrelaxed sites of the host lattice preserve the essential physical picture of the relaxed description*? Many previous models (e.g., those of Refs. 24, 12, and 21), have assumed that the