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Excited states of excitons bound to nitrogen pairs in GaP

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We report the luminescence excitation spectra of bound excitations in GaP:N below 2 K. A dye laser was used as a tunable excitation source. The spectra of excitons bound to NN_i pairs and to single N traps reveal a series of sharp transitions to excited states for those pairs having total exciton binding energy of more than 40 meV. For the shallower NN_i traps ($i \geq 7$) and the single N, the excited states overlap the free-exciton continuum and are broad. The sharp excited states are identified as nS states of an acceptorlike series resulting from the motion of a hole in the Coulomb field of the tightly bound electron. The dependence of the excited-state energies on the principal quantum number n agrees very well with the effective-mass calculations of Baldereschi and Lipari. The observed core correction is negative, contrary to the case of normal acceptors. These observations provide direct proof of the validity of the Hopfield-Thomas-Lynch model for isoelectronic traps. Besides these acceptorlike excited hole states, we find evidence for a possible excited state of the electron bound to NN_1, 85 meV above the ground state.

I. INTRODUCTION

Excitons bound to isoelectronic traps in semiconductors have been studied extensively for several reasons.[1,2] First there is the basic problem of how an electron-hole pair can bind to an uncharged impurity center.[3-5] Secondly, in contrast to the decay of excitons bound to neutral donors and acceptors, the Auger effect cannot take place for those bound to isolated isoelectronic traps. Their radiative efficiency is therefore high, making semiconductors doped with isoelectronic traps useful as light-emitting devices.[6] Out of the few known cases of isoelectronic traps which can actually produce bound states within the band gap, the traps produced by nitrogen in GaP are perhaps the most interesting.[7,8] One reason for this is the technical importance of the green-light-emitting diode using GaP : N. A more fundamental reason is illustrated in Fig. 1. It summarizes Thomas and Hopfield's[7] results of the binding energies of excitons to various pairs of nitrogen atoms on phosphorus sites. Excitons can bind not only to a single N atom but also to pairs, labeled NN_i, $i = 1, 2, \ldots$, in order of increasing separation. The greater the pair separation, the smaller the exciton binding energy. Therefore, GaP : N exhibits a series of isoelectronic traps with different binding energies (a series which converges on the value for isolated N). This is a unique situation for the study of various properties of bound excitons. With one exception,[9] previous work has dealt with properties of the lowest state of the exciton bound to each NN pair. This is because the usual methods of excitation (carrier injection or band-gap irradiation) excite all NN_i simultaneously and in the low-temperature range emission takes place from the lowest state of each NN_i. Most of the properties of the lowest states are therefore known (radiative lifetimes,[10] crystal-field and exchange splittings,[7] effects of external perturbations[7-9,11]).

Several theoretical attempts have been made at explaining the binding of excitons to NN_i. Allen's theory[12] invokes strain fields arising from the difference in size between N and P to explain the binding of the exciton as a single entity. Another approach[4,13] is based on the fact that N is electronegative relative to P and therefore provides an attractive short-range potential for electrons. If this potential is strong enough, it can bind an electron. Once an electron is bound it provides a Coulomb potential which binds the hole. Similarly an electropositive impurity such as bismuth binds a hole first. This separation into primary and secondary particles is the basic assumption of the Hopfield-Thomas-Lynch (HTL) model,[14] which will be discussed in more detail below. It should be noted that only in a few cases, all in GaP [Bi,[9,15] and the nearest-neighbor pairs (Zn, O) and (Cd, O) which act essentially as isoelectronic electron traps[16]], has the existence of a bound state for a single particle been demonstrated.[9] Also, the currently available theoretical calculations do not agree well with the experimentally determined binding energies of excitons to NN_i,[13] or to any other isoelectronic trap.

A better insight into the binding mechanism might be attained through a more detailed knowledge of the excited states of bound excitons. This paper is addressed to the problem of finding the excited states of the NN_i centers. This is done by measuring the excitation spectrum of the fluorescence of each center. This method enables us to detect transitions to S-like bound states. The analysis of

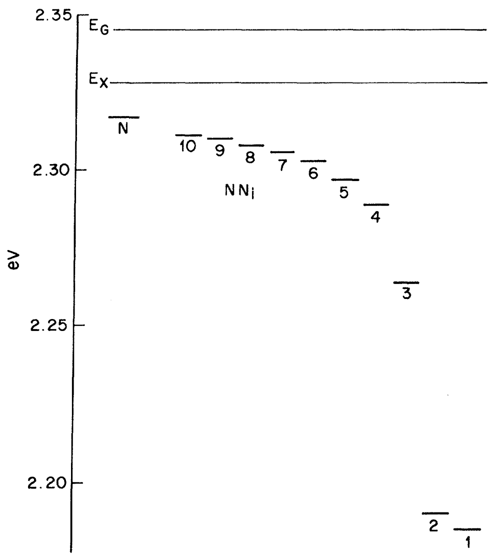

FIG. 1. "Ground" state energies of excitons bound to nitrogen pairs in GaP. E_G is the indirect band gap; E_x is the free-exciton ground state; "N" is that of an exciton bound to isolated nitrogen; "NN_i" is that of an exciton bound to a nitrogen pair in the ith nearest-neighbor position. Data from Ref. 7.

these excited states directly verifies that the HTL model applies quantitatively to NN_i, $i \leq 5$, and indicates that it may also apply to NN_6 and NN_7. Our data are also relevant to the analysis of nonradiative decay processes of excitons bound to NN_i.[17]

The paper is laid out as follows: Sec. II details the experimental method and results. Section III describes the model and calculations of nS acceptorlike excited states using Baldereschi and Lipari's[18] method, and compares them with the experimental data. Other possible excited states are also discussed. Our conclusions are summarized in Sec. IV.

A Letter on part of this work has previously been published.[19]

II. EXCITATION SPECTRA

A. Experimental procedure

In principle, excited states of excitons bound to impurities can be detected in the absorption spectrum of the crystal. Some excited states of excitons bound to neutral sulphur in GaP have been observed[20] in this way. Absorption spectra of nitrogen-doped GaP did not yield any definite information on excited states.[7,21] Even in heavily doped crystals, the excited states of excitons bound to NN_i escape detection because of the relatively low concentration of nitrogen pairs.[22] Even if transitions to these states could be detected in this way, it would be difficult to assign the observed lines to the correct center. The method of luminescence excitation spectroscopy is much more sensitive and, being selective, overcomes the latter difficulty. The crystal is irradiated by monochromatic light from a tunable source. The resulting luminescence is monitored at an energy corresponding to radiative recombination of excitons bound to the particular center of interest. Relaxation from excited states to the "ground" (i.e., the lowest) state of any particular exciton is normally very rapid, so that emission only occurs from this state.

Before the advent of the tunable dye laser, Faulkner and Dean[9] observed some excited states of NN_1 by this technique, using a spectrometer as the monochromatic exciting source. They were limited to the deepest center because the emission was selected by the use of optical filters (due to weak signals). In the present study we used a cw dye laser as an excitation source and selected the emission band by monitoring through a Spex double monochromator. The energy resolution was determined by the dye laser linewidth (0.3 Å corresponding to ~0.12 meV in this part of the spectrum). By using a double monochromator of fairly high resolution (typically 0.4 Å) we obtained good rejection of scattered laser light, so that the emission could be measured accurately to within 1.5 Å of the laser line. We could also achieve a slight reduction in the linewidth of transitions to excited states by judicious selection of a narrow fluorescing band within the inhomogeneous linewidth of the emission line.

The dye laser output varied with wavelength and also fluctuated somewhat with time. To eliminate error from this, we automatically recorded the ratio between the luminescent intensity and the dye laser output. All the excitation spectra shown below are normalized in this way. Although the combination of a dye laser for excitation and a spectrometer for analyzing the luminescence improves the resolution and selectivity, there are still two sources of interfering signals which cannot be straightforwardly eliminated. First, there could be overlapping emission from another NN_i trap which is excited into one of its bound states. This problem is resolved by monitoring different parts of the emission spectrum of the NN_i under study: usually the no-phonon line and the (sharp) optical phonon sidebands. Secondly, there could be excitation transfer from other traps (usually other NN_i pairs of N) to the NN_i under study.[7,23] This transfer is usually manifested by the appearance of the "ground states" of the various other NN_i's as peaks in each excitation spectrum (cf. Fig. 2). These lines are easily identified by their energies and by their decreasing intensity in lower-

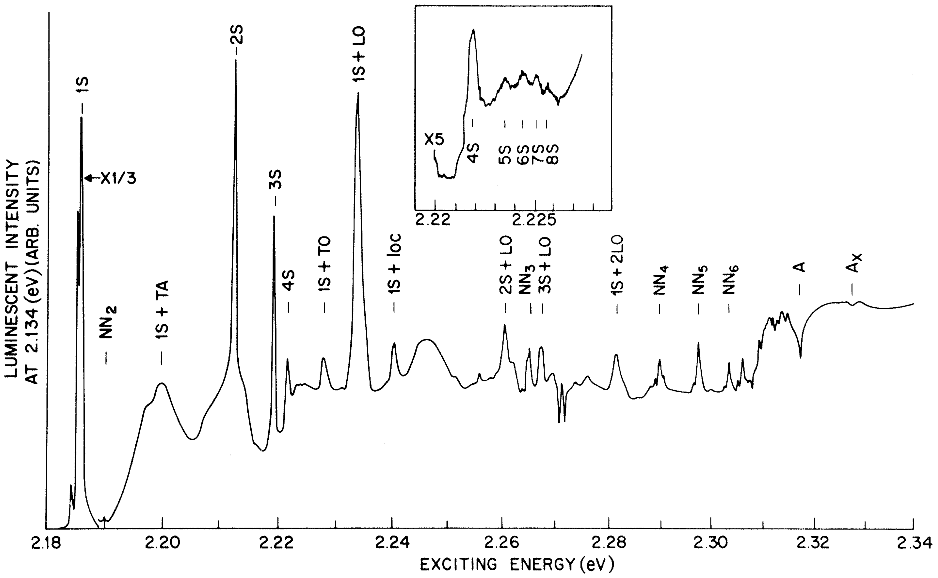

FIG. 2. Excitation spectrum at 1.75 K of the 2.134-eV LO-phonon-assisted emission from the NN$_1$ bound exciton in GaP. Nitrogen concentration [N] $=2.5\times10^{18}$ cm^{-3}. Phonon-assisted absorption gives rise to features with labels like "1S + TO," which refers to excitation to the 1S level of NN$_1$, accompanied by the emission of a TO phonon. Other labels are explained in the text. Gain is reduced $\times\frac{1}{3}$ in the region of the 1S line. Insert: expansion of the region near 2.225 eV. (Note displaced origin of intensity).

concentration crystals.

The crystals used in the bulk of this study were grown by either one of the two methods: (a) vapor transport in which case they were long, unstrained needles of about 0.1 mm^2 cross section, and (b) from Ga solution which yielded small platelets.[24] Nitrogen doping was in the bulk and ranged from 10^{16} to 2.5×10^{18} cm^{-3}, as determined by absorption measurements.[25] The "pure N" crystals were mostly weakly n-type but a few were p-type. The excess carrier concentration, as determined at room temperature, corresponded to $|N_D - N_A| \sim 10^{15}$ cm^{-3}. Another indication of the relative purity of these crystals was the fact that no donor-acceptor pair spectra were found under band-gap excitation at $T > 60$ K. Since absorption into the excited states of excitons bound to NN$_i$ is extremely weak, epilayers are not suitable for the present study in spite of the fact that they can be produced with high degree of purity. The contribution of the substrate cannot be eliminated and it cannot be produced with the same purity level as the epilayer.

B. Results

The "ground" 1S state of the bound exciton is split by the exchange interaction into a $J=1$ and $J=2$ level,[7] about 1 meV apart, with the $J=2$ level lowest. The uniaxial "crystal field" of an NN$_1$ pair produces further splittings, which, however, are usually small relative to the exchange splitting. Radiative transitions from the $J=2$ level to the ground state of the crystal are forbidden in spherical symmetry; however, below 2 K only this level is occupied and emission is made possible by various symmetry-breaking processes. Only transitions to $J=1$ levels can be seen in absorption or excitation from the ground state of the crystal; this applies to excited states as well as to the "ground" state of the exciton. Because of the good rejection of scattered laser light by the double monochromator, it was possible in most cases to monitor emission from the lowest $J=2$ level while pumping into the 1S $J=1$ level.

A well-known selection rule for the creation of excitons in a parity-allowed transition requires that they be created in nS states.[26] The transition probability falls off rapidly with n, and for high n the transitions became very difficult to distinguish from the strong background of phonon-assisted transitions to the 1S state. Furthermore, for the shallower (higher i) NN$_i$ traps, the excited states overlap the strong transitions to the free-exciton continuum. While such transitions are forbidden in a pure crystal, because of the indirect energy gap, they are made allowed in our crystals by scattering at the nitrogen impurity.[13,21]

These problems are least significant for the deeper traps, and we will begin with them. Figure 2 shows the excitation spectrum of the NN$_1$ exciton in a crystal containing 2.5×10^{18} N cm^{-3} (new calibration[25]) which is near the solubility limit. Almost identical spectra are obtained at lower concentration. There are a number of features of secondary interest which will be disposed of first. The broad features and some of the sharper ones, are phonon-assisted transitions to the 1S "ground" state. Superimposed on the multiphonon continuum are lines (marked NN$_3$, NN$_4$, etc.) which are the 1S transitions of excitons bound to these centers, which appear in the NN$_1$ spectrum because of energy transfer. The dip marked A is at the position of the "A line," which is the very strong absorption line of excitons bound to isolated nitrogen. It appears as a dip in a concentrated sample because the light cannot penetrate. Consequently, excitons are created very close to the surface, and rapid surface recombination reduces the quantum efficiency.[27] Above the A line the excitation curve is flat in the most concentrated sample, since the absorption length is less than the sample thickness. A_x is the position of the free exciton, where continuum absorption (induced by the nitrogen) begins.

The remaining features, which cannot be accounted for either by phonon effects (since there are no corresponding features in emission), nor by energy transfer, are two sharp dips near 2.271 eV, and the series of sharp lines marked nS, $n = 2, \ldots$. In the insert it is seen that this series extends to $n = 7$ or 8 (the $n = 8$ member being doubtful). The dips have some highly anomalous properties which will be described in Sec. II C. The nS series, which qualitatively resembles a hydrogenic series, will be shown in Sec. III to arise from transitions to acceptorlike excited states of a hole bound to the negative center (NN_1 +electron), as predicted by the HTL model.

Parts of the excitation spectra of excitons bound to NN_2, NN_3, and NN_4 are shown in Fig. 3. The nS series is clearly visible. The $1S$ line (not shown) is at the energy given on the figure.

The excitation spectra for higher NN_i are shown in Fig. 4. Here the excited states overlap the continuum beginning at A_x. In spite of the strong absorption in this concentrated crystal, they show up as weak peaks. There is also some weak phonon structure, exhibiting "interference" with the free-exciton continuum similar to that observed for the exciton bound to isolated nitrogen.[21] The positions and intensities (relative to the $1S$ lines) of the nS peaks are independent of concentration, but at low concentration structure in the background makes them more difficult to identify. The highest-energy peaks (optimistically marked $5S$ and $6S$ in NN_5, $4S$ and $5S$ in NN_6 and NN_7, and $2S$ in NN_8) are not clearly visible in more dilute samples and their assignments are to be regarded as doubtful. The excitation spectrum of NN_9 ($1S = 2.3102$ eV) resembles that of NN_8 except that the peak marked "$2S$" is missing. That of NN_{10} ($1S = 2.3115$ eV) resembles the last spectrum in Fig. 4, marked B. Here the highest-energy emission peak in the 2.5×10^{18} cm^{-3} sample, at 2.3132 eV, is monitored. At this energy there is overlapping emission of distant nitrogen pairs, not clearly distinguishable from the acoustic sideband of the B-line emission from isolated nitrogen. Unlike the NN_i excitation spectra, it shows no well-defined $1S$ ($J = 1$) line.

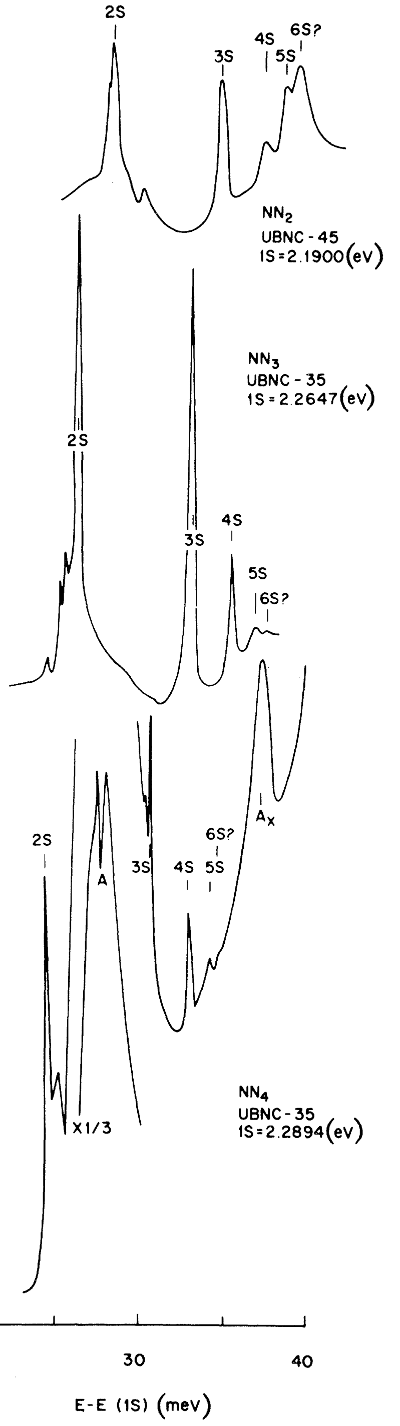

FIG. 3. Part of the excitation spectra at 1.75 K of the no-phonon emission from excitons bound to NN_2, NN_3, and NN_4 nitrogen pairs. The nitrogen concentrations [N] are, for NN_2, 2.5×10^{18} cm^{-3}, for NN_3 and NN_4, 2×10^{17} cm^{-3}. Intensity scale is arbitrary.

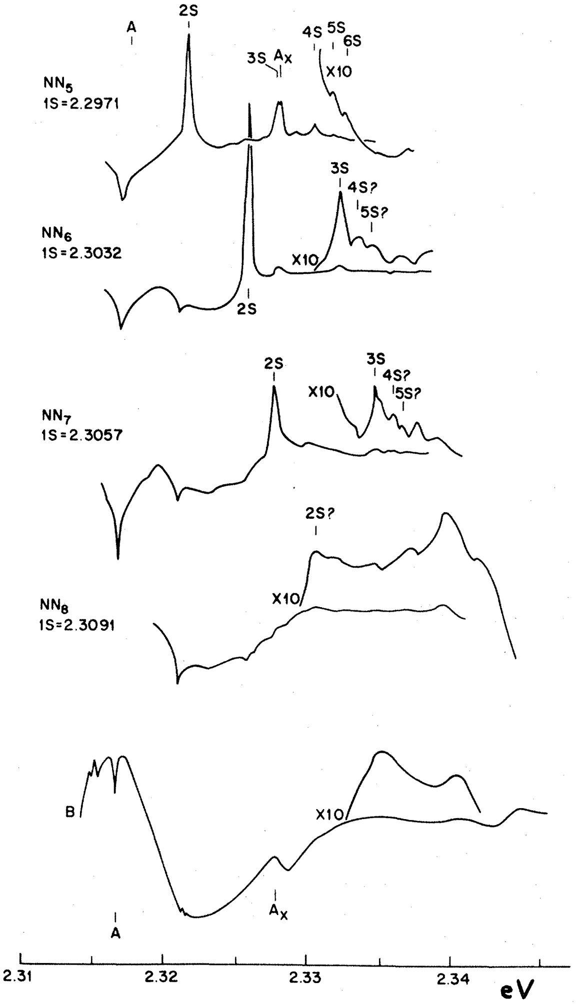

FIG. 4. Excitation spectra at 1.75 K of the no-phonon emission from excitons bound to NN$_5$, NN$_6$, NN$_7$, and NN$_8$, and to distant pairs (B). Nitrogen concentration [N] = 2.5×10^{18} cm^{-3}. Intensities are normalized to agree in the flat region around 2.335 eV. In the B spectrum, emission at 2.3132 eV was monitored.

It should be noted that whereas the positions of the 1S lines agree with Thomas and Hopfield's[7] values for all other NN$_i$ ($i \leqslant 10$) to within ±0.2 meV, that for NN$_8$ does not. We find no level corresponding to their 2.3076-eV "NN$_8$" line.

In Tables I and II we list the positions and intensities (relative to 1S) of the nS lines. Doubtful assignments are indicated. Faulkner and Dean[9] observed the transitions of NN$_1$ that we assign to 2S and 3S. Their assignments were different, because they found no splitting of the 3S state under stress. We have discussed this point in a previous publication.[19] We find that the Zeeman patterns and stress splittings of the 2S and 3S lines of NN$_1$, NN$_3$, and NN$_5$ are qualitatively similar to those of the 1S lines, confirming our assignment.

Figure 5 shows the excitation spectrum of the emission from the $J=2$ level of excitons bound to isolated N in a dilute sample (10^{16} N cm^{-3}). There is no feature in this spectrum which can reliably be assigned to a transition to an excited state of the bound exciton. The weak but extremely sharp feature at 2.3304 eV corresponds exactly to the excitation of a bound exciton plus a TA(X) phonon of 13.2 meV.[28] The sharpness indicates that some of the exciton wave function is confined to an extremely limited volume of k space. The broad feature next to it, already noted by Dean[27] and called by him "A_y," comes to an abrupt end 18.5 meV above the A line. This energy corresponds exactly to the highest point in the TA dispersion surface, approximately (0, 0.6, 0.6).[29] This band can therefore be assigned to transitions involving phonons of general $\vec{k}$, coupling to the spatially localized part of the exciton wave function. The dispersionlike feature at 2.3441 eV has been previously reported,[21,27] and attributed to interference between the continuum of phonon-assisted bound-exciton transitions and the sharp edge due to the creation of a free exciton plus TA phonon. The fine structure, which corresponds qualitatively to the fine structure in the wavelength-derivative absorption spectrum,[30] may be associated with the structure that is known to exist in the ground state of the indirect exciton.[28]

C. Further structure in the NN$_1$ spectrum

It was mentioned in connection with Fig. 2 that two sharp dips appear in the NN$_1$ excitation spectrum at 2.2704 and 2.2715 eV. These are shown on an expanded scale in Fig. 6(a). Very weak peaks appear in the excitation spectra of NN$_2$ and NN$_3$ at the same energy. There are no corresponding absorption lines in the crystal, showing that the dips are not due to competition from another center. In samples containing only N (other impurities being well below the 10^{16} cm^{-3} level) the strength of the dips relative to their background is independent of N concentration.

In p-type samples ($N_A - N_D \sim 10^{18}$ cm^{-3}) the dips are also present, although they appear relatively weak because of the donor-acceptor pair background to the NN$_1$ emission. However, in strongly n-type samples ($N_D - N_A \gtrsim 3\times10^{17}$ cm^{-3}) two peaks appear in the NN$_1$ excitation spectrum. These are at the identical positions of the dips in the purely N-doped samples, as shown in Fig. 6(b). The multiphonon continuum is relatively weak, and the 2.271-eV doublet is the strongest feature of the NN$_1$ excitation spectrum below the energy of the

TABLE I. Excited-state energies of NN_i in GaP,[a] in meV above the $1S$ $J=1$ level.

i	1	2	3	4	5	6	7	8	9	10
E_B [b]	160	155	81	56	48	42	39	36	35	33
$2S$	26.4	28.1	26.2	24.5	24.1	22.5	21.9	(21.6)		
$3S$	33.1	35.1	33.2	30.9	30.4	28.8	28.9			
$4S$	35.6	37.4	35.8	33.4	32.9	(30.1)	(30.2)			
$5S$	37.3	38.6	37.2	34.6	(34.1)	(31.1)	(30.9)			
$6S$	38.2	(39.3)	(38.0)	(35.4)	(34.9)					
$7S$	38.9									
$8S$	(39.4)									
E_I	40.3	41.7	40.0	37.6	37.3	(34.2)	(34.2)			
E_e [c]	120	113	41	18	11	8	5			

[a] Doubtful assignments in parentheses.

[b] Binding energy of the $1S$ level relative to free particles assuming that the free exciton binding energy is 17 meV.

[c] Defined by $E_e = E_B - E_I$.

A line. The nature of the majority donor (S, Te, or Si) does not appreciably affect the relative strength of the peaks. However, Si is present to some extent in all our *n*-type samples. Corresponding dips appear in the NN_2 and NN_3 spectra. There is also an extra peak in the NN_2 spectrum at 2.2778 eV, but its significance is unknown. There is no structure in the NN_2 spectrum of any of the samples at 2.275 eV, which is as far above the NN_2 $1S$ level as the dips are above the NN_1 $1S$. A possible intrepretation of this structure is given in Sec. III E.

Some of our samples show a weak dip in the NN_1 excitation spectrum at 2.2942 eV (64 meV above the $1S$ "ground" state). Its presence is not correlated with the presence of dips or peaks at 2.271 eV, and its significance is obscure.

Under ⟨111⟩ stress, the splitting of the 2.271 doublet increases, initially quadratically. The splitting fits the approximate formula

$$\Delta E^2(p) = \Delta E^2(0) + (Ae)^2 ,$$

where e is the uniaxial strain ($e = e_4 + e_5 + e_6$). We find $A \sim 1$ eV, less by an order of magnitude than a typical deformation potential.

III. MODEL AND INTERPRETATION

A. Basic Hamiltonian–HTL model

The transitions described in Sec. II are from the crystalline ground state to various states of a system consisting of an electron-hole pair bound to NN_i. The electron and hole are perturbed by the presence of the impurity and mutually attracted by their Coulomb potential. In the effective-mass approximation, the Hamiltonian can be written[5,26]

$$\mathcal{H} = E_c(-i\vec{\nabla}_e) + V_e(\vec{r}_e) - E_v(-i\vec{\nabla}_h) - V_h(\vec{r}_h) - e^2/|\vec{r}_e - \vec{r}_h| . \qquad (1)$$

If the impurity potential terms were small, then the problem would reduce to that of a perturbed exciton. We would expect a series of excited states with its limit corresponding to the dissociation

TABLE II. Relative intensities[a] of transitions to nS acceptorlike levels of excitons bound to NN_i in GaP, for $[N] = 2.5 \times 10^{18}$ cm^{-3}.

	Theoretical [b]								
n	Acceptor	Exciton	NN_1	NN_2	NN_3	NN_4	NN_5	NN_6	NN_7
1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
2	0.14	0.12	0.13	0.11	0.08	(0.05)	0.045	0.025	0.01
3	0.45	0.02	0.10	0.09	0.08	0.02	0.017	0.001	
4	0.022 [c]	0.01	0.02	0.03	0.03	(0.01)	0.005	(0.0005)	
5	0.014	0.0006	0.004		0.004		(0.0007)		

[a] Normalized to $1S = 1.0$. Values in parentheses are subject to uncertainties of a factor of 2.

[b] N. O. Lipari (private communication).

[c] Interpolated.

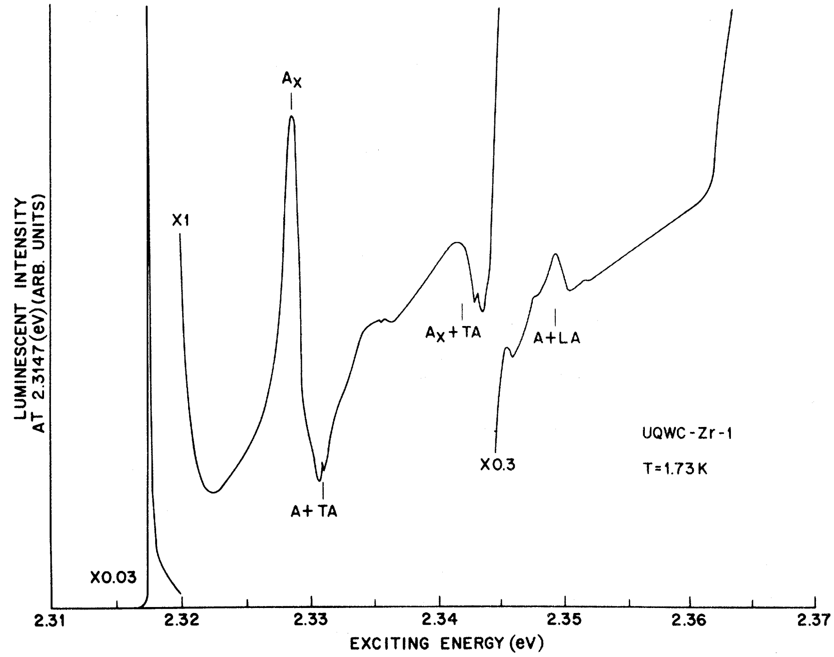

FIG. 5. Excitation spectrum at 1.75 K of the sharp acoustic sideband of the *B*-line emission (2.3147 eV) in a sample with $[\mathrm{N}] = 1.0 \times 10^{16}\ \mathrm{cm}^{-3}$.

of the exciton, i.e., the excited states would converge at the bottom of the conduction band. This is definitely not observed experimentally. As can be seen in Figs. 3 and 4 and in Table I, they converge at a limit about 40 meV above the lowest level, for all NN_i, $i \leq 5$, virtually independent of the total binding energy (E_B in Table I), indicating that the excited states are those of one of the particles, with the other one remaining in basically its "ground" state. This is the essence of the HTL model for isoelectronic traps.[14] It postulates binding of one particle (the so-called primary particle) by the short-range potential of the isoelectronic trap. Once it is bound, it provides a Coulomb field which attracts the other (secondary particle), thereby producing a bound exciton. This approximation leads to separation of variables in Eq. (1). The primary particle in the case of NN_i is the electron,[14] and its Hamiltonian will simply be

$$\mathcal{H}_e = E_c(-i\vec{\nabla}_e) + V_e(\vec{r}_e)\,. \qquad (2)$$

Various sources have been proposed for V_e (Ref. 4); however, its precise form is irrelevant to the present model. All that the Thomas-Hopfield model requires is that V_e produce at least one bound state. The electron wave function for this state will describe a charge distribution $\rho(\vec{r}_e)$ which is concentrated around NN_i but is certainly spreading out and can only be approximated by a point charge. In Fig. 7 we sketch the electron wave function around a simple one-dimensional square well (this

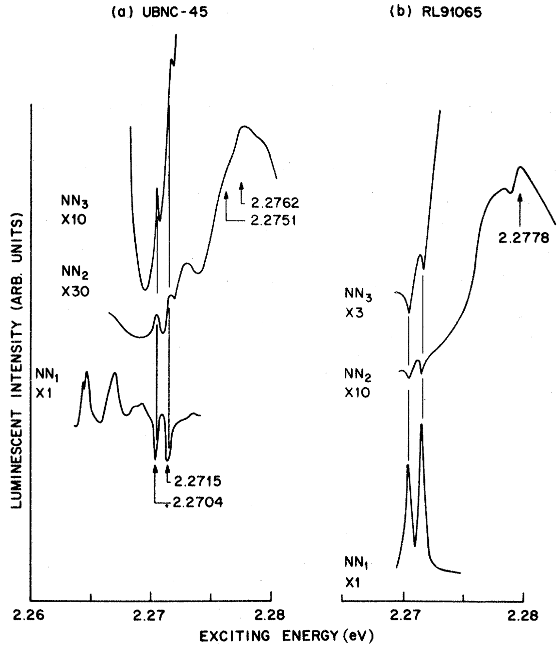

FIG. 6. Excitation spectra at 1.75 K of NN_1 no-phonon emission at 2.1845 eV, NN_2 emission at 2.1890 eV, and NN_3 emission at 2.2640 eV, in the region of 2.271 eV. (a) A typical "pure" nitrogen-doped sample, with $[\mathrm{N}] = 2.5 \times 10^{18}\ \mathrm{cm}^{-3}$ and $|N_D - N_A| \lesssim 10^{15}\ \mathrm{cm}^{-3}$. (b) A typical *n*-type sample, with $[\mathrm{N}] == 1.8 \times 10^{18}\ \mathrm{cm}^{-3}$ and $N_D - N_A = 1.0 \times 10^{18}\ \mathrm{cm}^{-3}$. Intensities in NN_2 and NN_3 spectra are plotted relative to displaced origins.

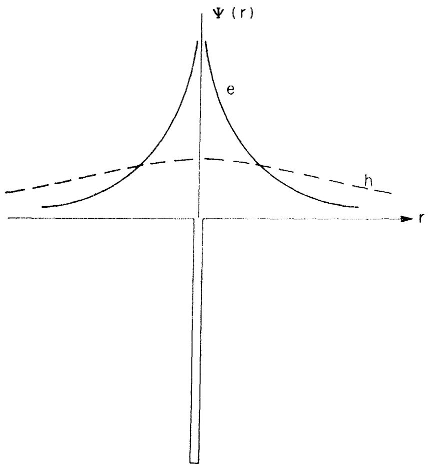

FIG. 7. HTL model for an acceptorlike isoelectronic trap. Electron wave function is concentrated near the core (the behavior within the core is unknown) while that of the hole is spread out over many lattice spacings.

would presumably be double in the case of distant NN pairs). Within the well (corresponding to the isoelectronic core) the wave function is highly oscillatory but outside it decays exponentially with distance. If V_e is sufficiently localized, the radial exponent of the wave function outside V_e is determined by the binding energy; as is the normalization (and hence the amount of charge which is delocalized).[31] The value of V_e necessary to give binding is uncertain since the effective mass in the small region within the range of V_e is not necessarily the same as the bulk value. However, it can easily be shown that if $|V_e|$ is large relative to the binding energy, its precise value is irrelevant; most of the charge is outside the core.

In the case of NN_i traps the potential well arises from two neighboring point defects. The electron is presumably equally shared between the two centers, so that its wave function spreads at least over the pair separation. This varies from 3.85 Å for NN_1 to 8.62 Å for NN_5. For excitons bound to NN_i, $i \leq 5$, the excited-state energies are virtually identical, as seen in Table I. Thus the change in pair separation, while it affects the total binding energy E_B enormously, hardly affects the hole at all. It is therefore reasonable, as far as the hole is concerned, to approximate the electron distribution by a point negative charge, and to write the Hamiltonian for the hole (secondary particle) as

$$\mathcal{H}_h = -E_v(-i\vec{\nabla}_h) - V_h(\vec{r}_h) - e^2/r_h \, . \qquad (3)$$

The hole coordinates are taken with respect to the electron which is assumed to be localized midway between the members of NN_i. This expression is identical in form to the Hamiltonian for an acceptor. We can expect the observed excited states of NN_i to resemble those of an acceptor, and will try to fit them to the predicted acceptor levels in GaP.

B. Identification of the excited states

Now that we have formulated the model Hamiltonian for the NN_i system we can calculate its eigenvalues and eigenfunctions. Elliott[26] has shown that in the case of dipole-allowed direct interband transitions, the oscillator strength is the atomic interband transition strength multiplied by the probability $|\Phi(\vec{r}=0)|^2$ for the electron and hole to be found at the same location ($\vec{r}=0$). This probability is nonzero only for S states and therefore only these are observed. In GaP the transition is indirect, but in the case of excitons bound to NN_i, the transitions from the crystalline ground state into bound states are made possible by the admixture of $\vec{k}_e = 0$ states of the electron by the short-range isoelectronic potential so that the transitions are effectively direct. In the HTL model, the electron has S symmetry in its ground state, since it is bound by the short-range potential and cannot have a node at the origin. Therefore, the observed acceptorlike states are nS type. The observed transitions of isoelectronic traps provide a means of studying the nS states of an "acceptor," which are unaccessible by the conventional method of far-infrared absorption.

C. Calculation of energy levels

In order to obtain the excited-state energies we have to diagonalize the Hamiltonian given in Eq. (1) corresponding to a perturbed exciton. For the case of an acceptorlike isoelectronic center, the Hamiltonian of Eq. (3) has to be diagonalized. Such calculations taking into account the perturbing terms are unavailable. However, extensive effective mass calculations have been made by Baldereschi and Lipari for acceptors[18] and indirect excitons.[19] Because the band structure [introduced through $E_v(-i\vec{\nabla}_h)$ and $E_c(-i\vec{\nabla}_e)$ of Eq. (1)] is anisotropic, states of different angular momentum are admixed. In particular, S states are admixed with D, G states, etc. Baldereschi and Lipari's calculations take into account D admixture only and are less accurate for high principal quantum number n. The calculations for GaP assumed the following mass parameters (in units of m_0): $\gamma_1 = 4.20$, $\gamma_2 = 0.98$, and $\gamma_3 = 1.66$ for the hole[32] and $m_\parallel = 1.7$ and $m_\perp = 0.191$ for the electron.[33] The dielectric constant used was[34] $\epsilon_0 = 10.75$. Although the recently determined[35,36] hole parameters are somewhat different than the above-mentioned calculated values, the resulting acceptor and exciton levels are found not to be very sensitive to small variations in these parameters. We can therefore use the results of these calculations. The best value of the dielectric constant has recently been revised to 11.02 (Ref. 37): this simply introduces a scaling factor 0.95 by which all the calculated energies have been multiplied. The calculated energies of the nS ($n=1,\ldots,5$) states for acceptors and excitons in GaP are shown in Fig. 8, on a log-log plot. The acceptor energy levels can be fitted to the semiempirical relation

$$E(nS) = -E_0 n^{-1.76}, \qquad (4)$$

with $E_0 = 47.1$ meV.

For the exciton the situation is slightly more complicated. There are two sets of free exciton levels, arising from the electron mass anisotropy. The calculated binding energy is[38] 17.7 meV and the 1S state splitting is 1.75 meV. However, the impurity potential eliminates this splitting for S-like states in the case of bound excitons, and the energies shown in Fig. 8 were calculated with an averaged electron mass. Then the levels can be fitted with the relation

$$E(nS) - E_0 n^{-1.86}, \qquad (5)$$

with $E_0 = 16.9$ meV.

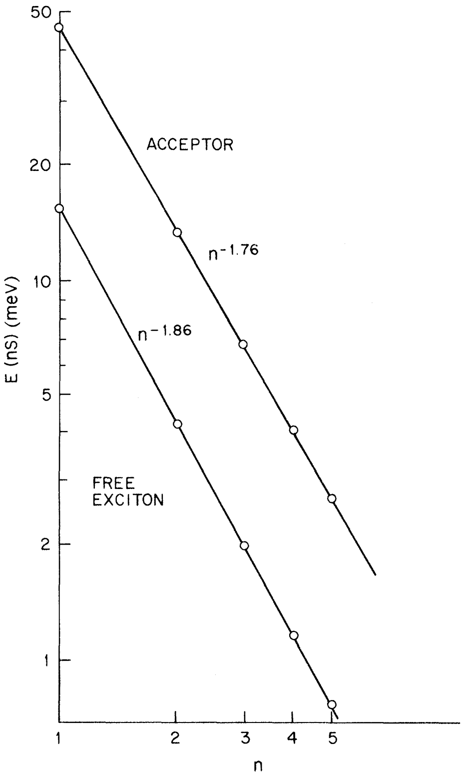

FIG. 8. Calculated $E(nS)$ in the effective mass approximation of acceptors and free excitons in GaP. In the case of the exciton the points were calculated assuming an isotropic conduction band [setting $\mu_{\text{el}} \equiv 3m_{\parallel}m_{\perp}/(2m_{\parallel}+m_{\perp})$].

It is to be noted that in both cases the dependence on n deviates from the hydrogenic series n^{-2}. The power-law form of Eqs. (4) and (5) has no theoretical justification and the exponents depend on the mass parameters.

The calculations also yield the Φ_{nS} wave functions. The intensities of transitions from the ground state to the various nS states are proportional to $|\Phi_{nS}(0)|^2$, whose values are given in Table II.

D. Comparison of experiment and calculation

The true acceptor energy levels will deviate from the calculated ones due to the influence of the core (central cell correction). This effect is most pronounced for S states since they have a nonzero probability at the origin and thus sense the short-range part of the core potential. Among the S states, those with higher n are less affected. Therefore, any comparison between theory and experiment should rely mainly on the higher nS states rather than on 1S and 2S. The observed energy levels for NN$_i$, $i=1,\ldots,6$ have been fitted to the formula

$$E(nS) = E_I - E_0 n^{-1.76}, \qquad (6)$$

with $E_0 = 47$ meV. The value of E_I represents the ionization energy of the hole in the 1S state and is determined experimentally from the series limit. Figure 9 shows the function $E_I - E(nS)$ vs $n^{-1.76}$ for NN$_i$, $i=1,\ldots,7$. Only states with $n \geq 2$ are shown. The solid curve is the function given by Eq. (4). The experimental values found for E_I are indicated in the figure. Up to NN$_5$ there is no ambiguity about the fit: E_I can be determined to within ±0.5 meV by simple extrapolation of Eq. (6) to $n=\infty$. For NN$_6$ and NN$_7$ there is ambiguity: only the 2S and 3S levels are well established, and they are not sufficient for a reliable extrapolation. If we extrapolate from the more doubtful 4S and 5S levels, we find the quoted values for E_I. The 2S and 3S levels then fall below the positions predicted by Eq. (6).

The good agreement observed indicates that the acceptor model is indeed an excellent approximation to the excitons bound to NN$_i$, $i \leq 5$. It thus proves the applicability of the HTL model for these NN$_i$ and shows that these isoelectronic traps can bind an electron independently of the hole. This is the most complete series of acceptorlike states to be observed in any semiconductor and it agrees closely with the calculated energies of Baldereschi and Lipari.[18]

Knowing E_I we could find E_e, the electron bind-

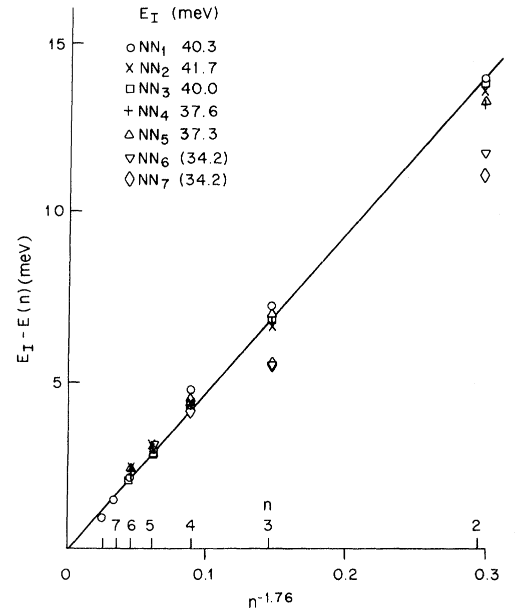

FIG. 9. Equation (7) (solid line) fitted to the energy-level data for NN_1–NN_7. Values of E_I given were obtained by fitting Eq. (7) to the highest levels observed and are doubtful for NN_6 and NN_7.

ing energy, if we knew the total binding energy E_B of the 1*S* exciton, which is simply $E_I + E_E$ in the HTL model. While the 1*S* energy relative to the free exciton is accurately known, the precise binding energy of the free exciton itself is not. The generally accepted value is 10 meV. Dean and Thomas[28] obtained this value from a detailed analysis of the absorption edge. However, their analysis depends critically on unsupported assumptions concerning the effect of the higher states of the exciton, and probably gives too low a value. Recently, Auvergne *et al.*[39] have proposed a new value of 13 meV, but again the evidence is weak: a small bump on the piezoabsorbance curve, assigned to the interband absorption edge. For definiteness we have taken the theoretical value[38] (corrected for ϵ) of 17 meV. The values of E_B and E_e thus obtained are given in Table I.

The observed ionization energy E_I is *smaller* than the calculated (effective mass theory) value of 47 meV. In normal acceptors the core acts to increase the binding of the *nS* states over their effective mass values (positive core correction). In the present case of an acceptorlike isoelectronic center the core repels the hole and thus we find a negative core correction. While the core correction for 1*S* is about 7 meV (for NN_i, $i \leq 3$) it is less than 1 meV for 2*S*. This relative magnitude is consistent with the calculated ratio $|\Phi_{1S}(0)/\Phi_{2S}(0)|^2 = 7$ given in the acceptor column of Table II. The negative core correction for the hole arises from two contributions: (a) the short-range potential is repulsive for holes (since it is attractive for electrons), and (b) the Coulomb potential due to the electron is reduced from that of a point charge due to its spreadout wave function. It is difficult to estimate how the first contribution will depend on NN_i, though one would expect it to decrease as E_e decreases. On the other hand, we would expect the second contribution to increase as the E_e decreases and the electron wave function spreads out. There will also be a contribution of uncertain sign from electron-hole correlation.

In Fig. 10 we plot the hole binding energy E_I vs E_e. The hole binding energy seems to be almost independent of E_e, at least up to NN_5, and possibly up to NN_7. At this point the apparent value of E_e has fallen almost to zero and it would be quite unreasonable to expect the HTL model to work. However, it does seem that the lowest states are still acceptorlike. It is of interest to note that E_I is the same (37 ± 4 meV) for the very deep traps (Zn-O) and (Cd-O) in GaP.[16] This supports the view[40,41] that such centers are more profitably to be viewed as isoelectronic traps than as close donor-acceptor pairs.

Table II gives the observed and theoretical intensities of the transitions, relative to the 1*S* transition. The absolute strength of this transition can be found from absorption measurements, if one assumes a random distribution of N atoms. After correction for differences in phonon coupling, the 1*S* strength varies by less than a factor of 2 from NN_1 to the *A* line, except for NN_2, which, anomalously, is too weak to measure. The agreement of the relative intensities for NN_1, NN_2, and NN_3 with theory is reasonable (allowing for experimental error) except that the 3*S* transition is always anomalously strong. For higher NN_i, however,

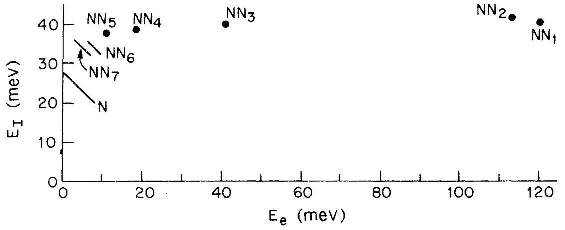

FIG. 10. Hole binding energy E_I plotted against electron binding energy E_e (defined by $E_e = E_B - E_I$) for NN_1–NN_7. E_B and hence E_e is uncertain because the free-exciton binding energy is not accurately known; we have assumed 17 meV (see text). For given E_B, the uncertainty in E_I for the shallower traps leads to the uncertainty indicated in the figure by the diagonal bars.

the intensities drop off much more rapidly with increasing n than predicted for the acceptor. The rapid drop-off *is* predicted for the exciton, and its observation may indicate that the higher-excited states are excitonlike. However, it is possible that these transitions only appear to be weak, because energy is being transferred to excitons which are free, or bound to other centers. Indeed it is clear from Fig. 4 that broad transitions do exist in the energy region just below the band gap and resonant transfer is possible. Far-infrared-absorption experiments, which make possible the observation of P-like states, may clarify this problem. P states should be much less broadened than S states by interaction with the free-exciton continuum.

While the data in the critical region of NN_6 through NN_8 are not conclusive, it appears that the binding energy E_I of the hole is almost independent of the electron binding energy E_e, and that the latter drops to zero for $i \sim 8$ ($E_B \sim 40$ meV). This supports Allen's[12] view that the isolated nitrogen impurity (and by implication, the shallower pairs, $i \gtrsim 8$) cannot bind an electron by itself; V_e in Eq. (2) is just not strong enough. The addition of the Coulomb interaction permits a bound state to form.

We now turn to several additional observations which can be made. Examination of Figs. 2 and 3 reveals that the transitions to the excited states are unsplit and their width is ≤ 1 meV. The transition to the $1S$ state for all NN_i is split by the electron-hole exchange interaction and noncubic crystal-field terms in $\tilde{V}_e$ and V_h. The transition to the $1S$ state of N is split by 0.7 meV (into the A and B lines) by exchange interaction. The absence of observable splitting in the excited states is to be expected for the following reasons: (a) The transition to the $J=2$ state is very weak. (b) The exchange and crystal-field splitting of the excited states is likely to be much smaller than of the $1S$ state, since the amplitude $\Phi_{nS}(\vec{r}=0)$ is smaller so that the hole senses the core potential less, and also its contact interaction with the electron is reduced.[42]

E. An excited state of the bound electron?

Finally, we turn to the problem of identifying the doublet structure in the NN_1 spectrum which was described in Sec. II C. We cannot at present give definite assignments. Its position, 85 meV above the $1S$ level, suggests at first that it might be due to acceptorlike states associated with the split-off (Γ_7) valence band. According to Sell and Lawaetz[43] this band is 78 ± 2 meV below Γ_8. Excitation into states associated with this low mass band might possibly make hole ionization easier. This would account for the dips in the NN_1 spectrum, but not the peaks in the NN_2 and NN_3 spectra; nor would it explain the peaks in the n-type samples.

A more plausible explanation is that this is an excited bound state of the exciton involving excitation of the electron rather than the hole. The electron wave function in the excited state will be more spread out, so that exciton tunneling to other centers will be enhanced, accounting nicely for the dips in the NN_1 and the corresponding peaks in the NN_2 and NN_3 spectra. A possible explanation of the effect of donors is as follows. Of the donors studied, S and Te have excited states near 85 meV,[44,45] while Si has an ionization energy of 82 meV.[33,37] A resonant energy transfer process is possible in which the NN_1 exciton, initially in its excited state, falls to its "ground" $1S$ state, simultaneously exciting or ionizing a neutral donor. If this happens so rapidly that the exciton has no time to migrate, fluorescence from the NN_1 "ground" state will be enhanced rather than diminished by occupation of the excited state.[46] Another possibility is that the transition to the excited state, normally forbidden, is made allowed by the random electric fields of neighboring ionized impurities.

The most plausible origin of this putative excited state of the electron lies in the valley-orbit splitting produced by the strong short-range potential. If we assume for the moment that the conduction-band minima (valleys) are at the zone boundary, they are mixed to produce the A_1 ground state and an excited E state. Since the latter state has $|\Phi(0)|^2=0$, its binding is small, and optical transitions to it weak. The anisotropic "crystal field" of the nitrogen pair combines with the electron-hole exchange to remove most of the 16-fold degeneracy of this state.

This interpretation is still speculative, although it fits all the known facts, and more work is necessary. If it is true that there is a second bound state of the electron in the NN_1 trap, with a binding energy of about 35 meV, important theoretical consequences ensue. The potential V_e could not possibly be a square well of atomic dimensions, since for so small a binding energy of the A_1 state (120 meV) the binding energy of the E state would be extremely small. A more extended potential, such as the strain field visualized by Allen,[3] would be indicated. Recent results on nitrogen traps in $GaAs_{1-x}P_x$ alloys may support this view.[47]

IV. CONCLUSIONS

Three firm and two tentative conclusions can be drawn from this work.

(i) The deeper nitrogen-pair traps in GaP obey the HTL model quantitatively, even when the electron (primary particle) is bound more weakly than the hole.

(ii) This fact makes it possible to determine the positions of a whole series of acceptorlike states of *S* symmetry, which are difficult to study in a normal acceptor since they are inaccessible from the ground state by dipole transitions.[48] The positions of these excited states, relative to the ionization limit, agree well with the predictions of effective-mass theory.

(iii) The core correction to the 1*S* level is negative, and is remarkably constant, near −10 meV, as the electron binding energy varies over two orders of magnitude, from 0.011 eV (NN_5) to 1.4 eV (Cd, O).

(iv) There appears to be an excited doublet state of the NN_1 exciton 85 meV above the ground state, involving excitation of the electron, probably into the *E* symmetry valley-orbit state. If confirmed, the large binding energy of this state (35 meV) seems to rule out models of the isoelectronic trap which assume that the primary particle moves in a short-range potential of atomic dimensions.

(v) The electron is bound only weakly, if at all, to the shallower traps. It therefore seems unlikely that the electron can bind by itself to isolated nitrogen.

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