$< \epsilon < 3.2$. Let us note that at practically all values of $l$ and $\epsilon$ there exist curves at which more than one solution of Eq. (4) appears. However, according to Eq. (5) the location of these curves on the phase diagram changes strongly. Thus, for example, the initial assumption of weak ionization may not be satisfied and the Debye-Hückel approximation may fail.

Let us note that vapor metallization under high pressure is one of the simplest examples of a chemical reaction near the critical point. Our model is capable of describing several different types of chemical transformations, for example, the variation of $N_A$ and $N_B$ with temperature, the reactions $A+B \rightleftarrows AB$, or $A \rightleftarrows B+C$, where the combined substance $C$ can precipitate, settle down in the interstitial positions, or move in the lattice. In the two last cases one may have to take into account the interaction between particles $AB$ and $C$ and the initial particles $A$ and $B$. The relevant results will be published elsewhere.

We think that one certainly expects anomalies of both the equilibrium and kinetic characteristics of the chemical reactions in substances whose thermodynamic parameters are close to their critical values. Unfortunately this problem has not been explored extensively either theoretically or experimentally.

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# Acceptorlike Excited $S$ States of Excitons Bound to Nitrogen Pairs in GaP

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The photoluminescence excitation spectra of excitons in GaP, bound to isoelectronic electron traps by more than 40 meV, show series of levels whose energies agree well with effective-mass calculations of the $nS$ levels of an acceptor, which are inaccessible by other techniques. This is the first detailed investigation of the internal structure of excitons bound to isoelectronic traps. It confirms the Hopfield-Thomas-Lynch model and establishes its range of validity.

Nitrogen pairs form isoelectronic traps in GaP,[1,2] binding an exciton by an amount ranging from 160 meV (nearest-neighbor pair) to 28 meV (infinite separation).[3-5] They are conventionally labeled $NN_1$, $NN_2$, ..., in order of decreasing binding energy. We report here the observation

of series of up to seven $S$-like levels of excitons bound to several different closely spaced nitrogen pairs. The energies of these levels, relative to the extrapolated series limit, are insensitive to the ground-state-exciton binding energy, in agreement with the Hopfield-Thomas-Lynch acceptor-like model of the isoelectronic electron trap.[6] The energies agree well with a variational calculation of $nS$ acceptor levels in GaP. This is the first observation of a series of acceptor levels of $S$ symmetry in any semiconductor,[7,8] and it makes a quantitative comparison between theory and experiment possible.

Excitons bound to a particular pair were selectively excited with a tunable dye laser, and their recombination fluorescence (usually in the no-phonon line) was monitored with a high-resolution double monochromator. This method permits the clear distinction of spectral features belonging to different pairs, and also improves the resolution of inhomogeneously broadened lines.[8] Measurements were made at 1.2 to 1.6 K on GaP crystals containing between $2\times 10^{17}$ and $2.5\times 10^{18}$ nitrogen atoms per cubic centimeter. The crystals were grown by Frosch,[9] and have an unwanted impurity level well below $10^{16}$ cm$^{-3}$. Excitation spectra of three representative pairs are shown in Fig. 1. Energy transfer causes the principal features of the isolated-nitrogen spectrum to appear in all the spectra. In the most concentrated crystals, some transfer from one pair to another manifests itself in the appearance of the "ground"-state absorption lines of one pair in the excitation spectrum of another with lower energy as noted in Fig. 1. Apart from this, the results reported here are independent of nitrogen concentration.

The most interesting features of the spectra shown in Fig. 1 are the series of lines labeled $nS$, $n\geq 2$. These lines are distinguished from phonon replicas of the $1S$ line by their sharpness, and by the absence of corresponding emission lines. Zeeman effect and stress splitting could be obtained in the stronger lines ($n\leq 3$). The splitting patterns are qualitatively similar, though not identical, to those of the $1S$ ground level. Only transitions to $S$-like exciton states are allowed,[10] and the differences in splitting may be connected with $D$ admixture in the higher states. One such stress splitting, for the $3S$ level of $NN_1$, is shown in the inset of Fig. 1.[11]

We interpret our data in terms of the Hopfield-Thomas-Lynch[6] model of an exciton bound to a deep isoelectronic electron trap. This model

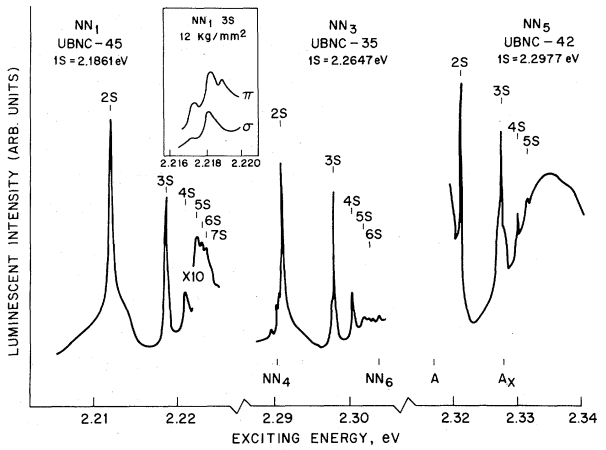


FIG. 1. Excitation spectra of emission from the $1S$ "ground" level of the $NN_1$, $NN_3$, and $NN_5$ nitrogen-pair traps in GaP. Sample UBNC-45 contains $2.5\times 10^{18}$ N atoms/cm$^3$; UBNC-42, $2\times 10^{18}$ N atoms/cm$^3$; UBNC-35, $2\times 10^{17}$ N atoms/cm$^3$. (The concentrations are chosen to give the cleanest spectra.) Unlabeled structure can be assigned to phonon replicas of the transition to the $1S$ state. Labels below the spectra refer to no-phonon lines of other centers, labeled as in Ref. 1. Inset: Splitting of the $3S$ level of $NN_1$ under 12 kg/mm$^2$ stress parallel to [111]. Two polarizations of the exciting light are shown: $\pi$, $\vec{E}\parallel[111]$; $\sigma$, $\vec{E}\perp[111]$.

was proposed for a point defect, but is applicable here since the separation of the nitrogen atoms in the pairs of interest is always much less than the Bohr radius of the exciton (about 25 Å). The electron is bound by a short-range interaction to the trap, while the hole is held in a relatively extended orbit by the Coulomb attraction of the trapped electron. The higher excited states of the hole should therefore resemble those of an acceptor. The lower ones will be somewhat perturbed by the core potential (repulsive for holes) and by the finite extent of the electron wave function, both of which act to reduce the binding energy, and by electron-hole correlation, which tends to increase it.

Accurate variational calculations of acceptor levels of cubic semiconductors have been reported previously.[12] Recently[13] this method has been extended to include the cubic contributions to the $S$-like states. The accuracy is reduced for $n\geq 5$ because of the limited set ($L\leq 3$) of basis functions used. The results for the five lower $S$-like acceptor states in GaP are given in Table I. The valence-band parameters of Lawaetz[14] are used. The calculated energies of the acceptor levels fit the following semiempirical formula within a few

TABLE I. Binding energy of the five lowest $S$-like levels of acceptors and indirect excitons in GaP. $X_6$ and $X_7$ refer to the exciton symmetry with electron spin neglected. We have used the valence-band parameters of Lawaetz (Ref. 14), $\epsilon_0 = 10.75$, $m_{e\parallel} = 1.7 m_0$, and $m_{e\perp} = 0.191 m_0$ (Ref. 4). The energy unit is meV.

| $n$ | Acceptor | Free indirect exciton $X_7$ | $X_6$ |
|---|---|---|---|
| 1 | 49.49 | 16.80 | 18.64 |
| 2 | 14.36 | 4.45 | 5.16 |
| 3 | 7.25 | 2.09 | 2.61 |
| 4 | 4.36 | 1.19 | 1.52 |
| 5 | 2.85 | 0.78 | 0.93 |

percent:

$$E_i - E(n) = E_0 n^{-\alpha}, \quad (1)$$

where for GaP, $E_0 = 49$ meV, $\alpha = 1.76$; $E_i$ is the ionization energy of the 1$S$ level.

In Fig. 2 we plot the observed levels of the six deepest traps against $n^{-1.76}$. $E_i$ is taken to be the extrapolated series limit. We see that for $n \geq 3$ the first five traps show the predicted acceptor-like behavior, within experimental error. The 2$S$ and 1$S$ levels have less binding energy than predicted by Eq. (1). The deviation of the 1$S$ level only varies with pair separation from 9 to 11 meV, while the electron binding energy (i.e., the total 1$S$ exciton binding energy less $E_i$) varies from 120 to 10 meV. Even for the much deeper Zn-O and Cd-O isoelectronic electron traps, the 1$S$ deviation is much the same ($12 \pm 4$ meV).[15] The order of magnitude of the deviation for 1$S$ agrees with the theoretical estimate of the effect of electron spread, which is 5 meV in the case of the Zn-O trap.[16] For $n > 1$ it varies roughly as $n^{-3}$, as expected.

The Hopfield-Thomas-Lynch model presumably breaks down for traps whose total exciton binding energy is less than that expected for the hole alone. Near the excitonic limit, the electron-trap interaction must be regarded as a perturbation on the exciton as a whole, and it is possible that neither particle can bind wtihout the other. We expect the excited states to approach those of the free exciton.

Calculations of indirect-free-exciton states, using perturbation theory, have been reported.[4] Recently,[5] a more accurate description has been obtained through the tensor-operator technique previously used for acceptor states.[12] The five lowest $S$-like levels of the free indirect exciton in GaP are shown in Table I. Each level is split

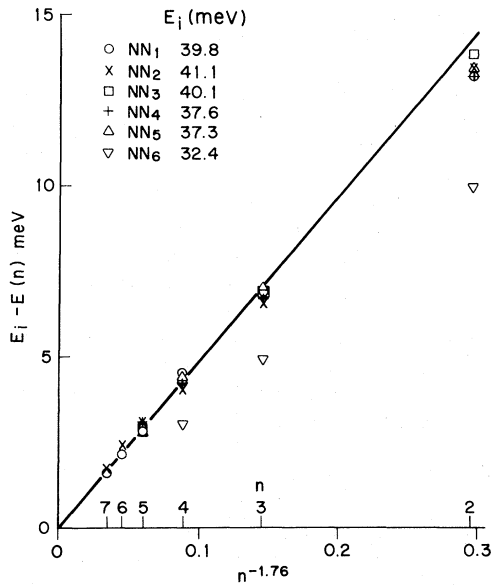


FIG. 2. Observed excited levels of excitons bound to nitrogen pairs plotted according to Eq. (1). The origin of energy $E_i$, relative to the 1$S$ level, is given for each center. The theoretical points all lie within 0.2 meV of the line shown.

by the electron-mass anisotropy and the mean positions obey Eq. (1) with $E_0 = 17$ meV, $\alpha = 1.85$. Unfortunately, excited states of shallow traps ($NN_i$, $i \geq 7$) are found to be very broad, probably because they overlap the continuum due to free-exciton dispersion. $NN_6$, with a total binding energy of 42 meV, appears to be an intermediate case, with $E_0 = 33$ meV. This suggests a rapid, but continuous, transition to excitonlike behavior. However, it remains to be seen whether the excitonic limit is reached in the case of isolated nitrogen.

In summary, we have demonstrated the acceptorlike nature of the excited states of excitons bound to close nitrogen pairs in GaP. The results support the Hopfield-Thomas-Lynch model of the isoelectronic trap and agree with the effective-mass calculations of excited acceptor levels.

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# Photoemission for Xe Physisorbed on W(100): Evidence for Surface Crystal-Field Effects

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Photoemission spectra at $h\nu = 21.2$ eV reveal two 5*p* levels for xenon physisorbed on a tungsten (100) surface. The spin-orbit splitting of the two levels and their intensity ratio correspond closely to gas-phase measurements, while the $5p_{3/2}$ peak is significantly broadened with respect to the $5p_{1/2}$. We interpret the broadened structure as an unresolved doublet resulting from splitting the Xe $5p_{3/2}$ states in the tungsten-surface crystal field.

One of the most challenging problems confronting surface science is understanding the adsorption of gases on the surfaces of transition metals, whose properties are intimately connected with catalytic and other chemical processes. A prototype system for studying the interaction of atoms with a metal surface is provided by rare-gas physisorption. This system is particularly interesting since the interaction energies involved are at least an order of magnitude smaller than those for chemisorbed species, and the Van der Waals forces responsible for the interaction are reasonably well understood.[1] Physisorption thus offers the possibility of delineating some of the mechanisms governing the interaction of an adsorbate with a metal surface whereas chemisorption, with its much stronger forces, involves competing effects which generally preclude unambiguous identification of structure observed in photoemission spectra. In this communication we report ultraviolet photoelectron spectroscopy (UPS) measurements for xenon physisorbed on a tungsten (100) surface. Specifically, we observe two well-defined peaks arising from the Xe 5*p* levels; the $5p_{3/2}$ peak is appreciably broadened with respect to its spin-orbit companion, and we suggest that the broadening results from splitting of the Xe $5p_{3/2}$ states in the tungsten-surface crystal field. To our knowledge this is the first UPS evidence for surface-crystal-field effects.

A description of the photoemission apparatus employed in these investigations has been given