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Hydrostatic-pressure dependence of bound excitons in GaP

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We report for the first time an investigation of the low-temperature hydrostatic-pressure dependence of bound excitons in GaP. We have used a hydrostatic-pressure cell equipped with an optical window and filled with a transparent pressure-transmitting medium. Working with a sample temperature of about 5 K, we could reach a maximum pressure of 8 kbar and examined various recombination lines. This work reports the change in radiative recombination energy of (i) excitons bound to a single neutral donor (D^0X complex), (ii) excitons bound to a single isoelectronic impurity (NX complex), and (iii) excitons bound to a pair of isoelectronic defects (NNX complexes). We find nonlinear behaviors associated with the binding of an exciton around an isoelectronic trap. This is discussed in the light of existing model calculations.

I. INTRODUCTION

In the last twenty years, excitons bound to substitutional defects in semiconductors have attracted much theoretical and experimental interest.[1] As a result the electronic structure of some of these defects is now fairly well understood. Consider for instance the fine structure of the D^0X complex reported in Si, Ge, or GaP. It depends upon the various interparticle interactions which affect the electron-hole pair bound onto a neutral donor atom and has been extensively described in a series of recent theoretical papers by Chang and McGill.[2] On the experimental side, the situation is also very successful and, for instance, we notice in the literature concerning the sulfur-bound excitons in GaP: (i) a complete series of spectroscopic g values,[3] (ii) a piezospectroscopic determination of the amount of exchange energy (intervalley mixing) which lifts the degeneracy of excitons associated with adjacent valleys in $\vec{k}$ space,[4] or (iii) a complete description of the fine structure associated with the first excited state of the two-electron complex.[5]

Concerning excitons bound to isoelectronic centers, the situation is more confusing. Isoelectronic centers happen when one constituent of a "host" crystal is substituted by an atom of the same column of the Periodic Table. Since both have the same number of valence electrons, there is no simple Coulomb field to bind an extra particle (electron or hole). The trapping mechanism originates in this case mostly from the difference in core shells and atomic energy of valence electrons. Consider, for instance, an atom having its outer orbitals at lower (or higher) energy, by an amount Δ, when substituted into a host crystal. If Δ is large enough, such a center can bind an extra electron (or hole) added to the conduction (or valence) band. Such an idea, first developed by Hopfield-Thomas and Lynch constitutes the so-called HTL model.[6] It makes possible a classification of all isoelectronic centers into isoelectronic donors or acceptors, depending on whether the short-range potential of the impurity first attracts a hole or an electron.

The prototype of isoelectronic acceptors is nitrogen in GaP, but even in this case the binding mechanism is not yet understood. A first calculation of the electronic part of the binding energy was attempted by Faulkner.[7] Assuming that the bare potential of nitrogen in GaP is nothing but the difference of the two pseudopotentials of nitrogen and phosphorus, he ended up with a deep bound state localized at about 1 eV into the forbidden gap. By introducing an adjustable parameter to reduce the strength of the impurity potential, he demonstrated the great sensitivity of this level to the intensity of the perturbation and concluded that both lattice relaxation and electronic polarization of the host crystal should be accounted for in future calculations.

Some years later, Phillips[8] discussed the basic physics of lattice polarization. He concluded that binding an electron onto a nitrogen atom induces an electrostatic interaction between the charged impurity and the neighboring ions which expands the lattice in the vicinity of the impurity. This dynamic polarization, superimposed with the static deformation associated with the difference in bond length, should result in a total cancellation of the binding energy. With such a viewpoint, he expected the stable configuration to correspond with an unbound N^- state.

Even if the polarization of the lattice was overestimated by Phillips, all experimental results, starting with the pioneering work of Thomas and Hopfield,[9] show that in pure GaP crystals one is always dealing with a two-particle complex. The situation might be quite different in $GaAs_{1-x}P_x$ alloys[10] where a release of the bound hole, leaving behind a trapped electron, was recently reported in the range of composition of $0.4<x<0.6$.. The corresponding binding energy for the bound hole is about 30 meV and correlates satisfactorily with the 40-meV value reported for near-neighbor nitrogen pairs (NN) in GaP.[11]

Concerning the contribution to the binding energy which comes from the static relaxation of the lattice around the impurity, there is not much information available. Allen suggested first[12] that it constitutes the main contribution to the binding mechanism. Because it is an intermediate-range perturbation (varying as r^{-3}) he could fit satisfactorily the series of excitonic energies associated with the presence of NN pairs in GaP (indeed; $E_{\text{NN}} \sim r^{-3}$, after Ref. 13). In fact the experimental situation is certainly a more complicated one. Consider, for instance, that under hydrostatic pressure the nitrogen-nitrogen distance associated with a given pair *decreases.* Neglecting the change in lattice relaxation, one expects the binding energy to *increase.* In this case, the bound-exciton line should shift to lower energy faster than the free exciton. This is obviously not what is found[14,15]: By increasing the pressure, one *decreases* the binding energy of the bound exciton, which establishes, on a firm experimental basis, the complex nature of the isoelectronic interaction.[16]

We now understand why *ab initio* calculations have been difficult to carry out successfully over the years.

(i) Experimental binding energies are very small (of the order of a few meV) and *ab initio* calculations cannot reasonably achieve such an accuracy.

(ii) Additional perturbations (such as spin-orbit coupling, central-cell corrections, electronic polarizability, etc.,) cannot be ignored.

(iii) Lattice distortion, of which neither sign or magnitude can be *a priori* predicted without a massive minimization of the total energy of the crystal, must be included in the calculation.

(iv) Lastly, correlation effects must be accounted for. In fact, most calculations deal with one-particle (electron) states while experiments always deal with a two-particle (exciton) complex.

The direct consequence of these difficulties is that most of our common understanding of the physics of isoelectronic centers comes from a direct comparison of model calculations with experimental results.[17,18] Moreover, model calculations can be made self-consistent, and, in this case, they account for the electron-hole exchange interaction and the hole excitation energy.[19] In this way, through a comparison of a refined treatment of the $(\text{NN})^-$ ground state with experimental data,[11] it was concluded that N^- is indeed unstable in GaP.[19]

To give more insight into the problem of excitons bound to electronic centers, we report the change under hydrostatic pressure, and at low temperature, of the radiative recombination line of (i) excitons bound to a single neutral donor: *C* line; (ii) excitons bound to a single nitrogen center: *A-B* doublet; and (iii) excitons bound to pairs of nitrogen atoms: NN_i-pair spectra (where i runs from $i=1$ to $i=9$). We find a linear behavior for shallow excitons associated with simple neutral donors and nonlinear behaviors for most excitons associated with nitrogen. However, in the range of investigated pressure, this is not true for the deep traps NN_1, NN_2, and NN_3. Resolving most components of the *J-J* manifolds associated with both isolated nitrogen and NN-pair spectra,[20] we find a change in the electron-hole exchange interaction. Comparing this with the predictions of a recent self-consistent model,[19] we find satisfactory agreement. From the same model we estimate also the change in ionization energy of the bound hole to about 10% of the total change in binding energy of the complex. Lastly, in order to check whether or not the change in electron binding energy associated with most NN-pair spectra can be satisfactorily accounted for by just changing the strength of a model potential, we model the pair by two spherical wells. In this case we find necessary to decrease the short-range potential by ~0.5% per kbar in order to account for the experimental data.

II. EXPERIMENTAL DETAILS

We have used a heavily nitrogen-doped GaP crystal kindly provided to us by Dr. Poiblaud from La Radiotechnique Compelec (R.T.C.) Laboratories (Caën, France). The nitrogen concentration was in the range 10^{20} cm^{-3} with a residual donor concentration of about 4×10^{16} cm^{-3}. This allowed the simultaneous observation, on the same sample, of the different radiative recombination lines discussed in this work.

The hydrostatic-pressure cell was a conventional one made of beryllium copper and fitted with an optical window. At room temperature the device was charged with a transparent pressure-transmitting medium and compressed to a maximum value of about 12 kbar. After cooling down to liquid-helium temperature, an indium an-

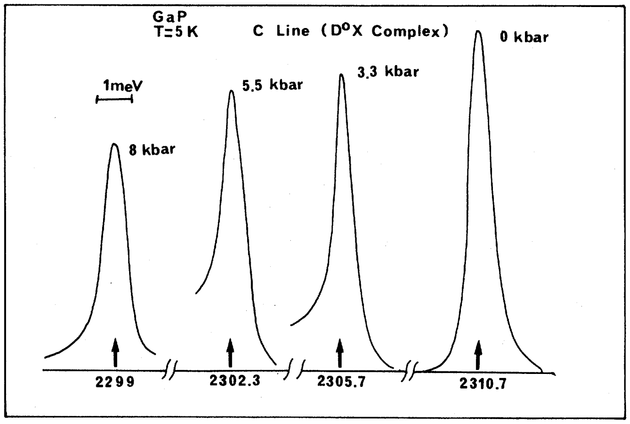

FIG. 1. Examples of resolution obtained in this work under hydrostatic pressure at 5 K. Note the width of the *C* line which is always smaller than 1 meV and independent of the hydrostatic pressure. Any shear component larger than 250 bar would result in a splitting of the $J=\frac{3}{2}$ bound-exciton complex in two components, $M_J=\pm\frac{3}{2}$ and $\pm\frac{1}{2}$, with an energy separation larger than 1 meV. This is obviously not found.

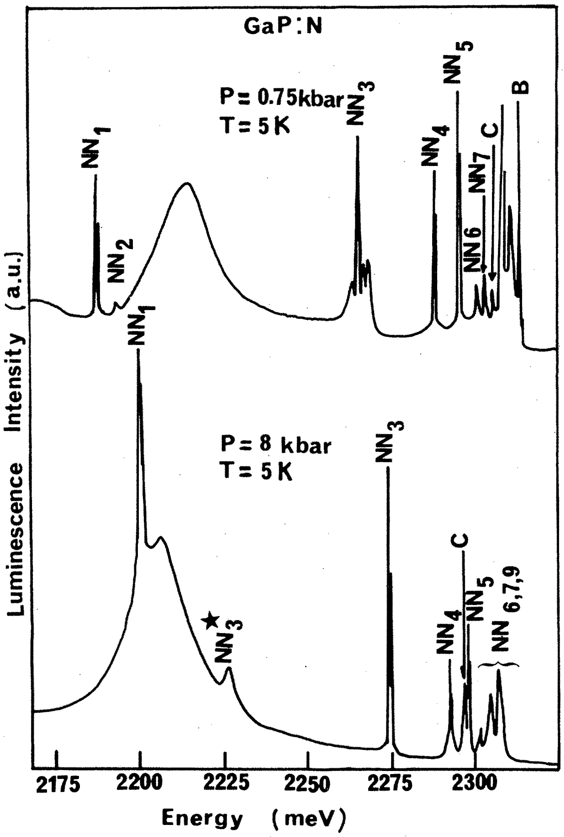

FIG. 2. Typical luminescence spectra associated with the decay of an exciton bound to (i) an isolated sulfur atom (*C* line), (ii) an isolated nitrogen atom (*B* line), and (iii) pairs of nitrogen atoms (NN_i lines). Two different spectra correspond with two different pressures. Close comparison shows that the *C* line exhibits a negative shift (it moves toward lower energy) while, opposingly, all N bound excitons become less tightly bound. Also seen in the figure are the recombination line associated with a donor-acceptor pair (*D*-*A*) and the phonon replica of the NN_3 no-phonon line (NN_3^*).

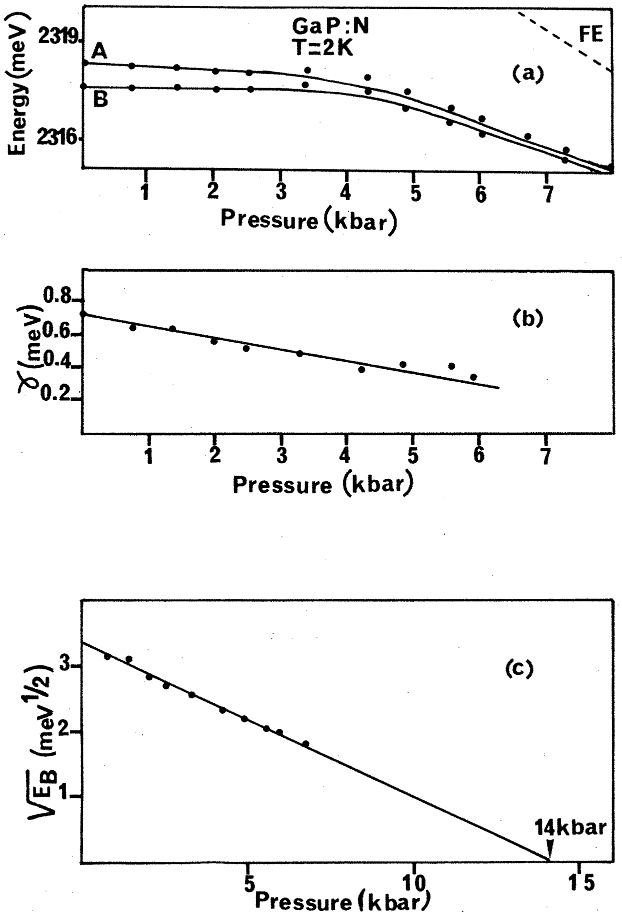

FIG. 3. (a) Pressure dependence of the $J=1$ (*A*) and (*B*) zero-phonon lines associated with one single-nitrogen atom $J=2$. (b) Corresponding change in the splitting exchange parameter γ. (c) Linear relationship between the square root of the binding energy and the hydrostatic pressure. From the straight line we deduce an exciton ionization pressure of about 14 kbar.

timonide pressure gauge was used to control the stress.[21] A maximum value of about 8 kbar could be reached. Changing the pressure required warming up the system to 300 K and then cooling it down again.

The complete hydrostatic character of the pressure achieved in this work is demonstrated in Fig. 1. Comparing the width of the *C* line (D^0X complex) for different pressures ranging from 0 to 8 kbar, we find values always smaller than 1 meV. Since any uniaxial stress component would split the valence band with a rate of roughly 4 meV/kbar, we estimate the stress homogeneity to be better than 200 bar.

Typical spectra obtained under excitation with about 200 mW of the 5145-Å line of an Ar^+-ion laser are shown in Fig. 2. Starting from the low-energy side, we successively resolve all NN_i pairs with $1 \leq i \leq 7$. NN_8 is not found. This point has been already noticed[20] and will not be discussed further. The broad peak around 2.21 eV in Figs. 2(a) and 2(b) corresponds to a donor-acceptor pair. Since the position of its maximum varies slightly with excitation intensity, we did not seriously attempt to deduce responding pressure coefficient. Also resolved are two sharp lines labeled *B* and *C*, respectively. The first one corresponds to the low-energy $J=2$ component of the single exciton bound to a single-nitrogen atom.[9] The companion peak ($J=1$) appears under higher excitation or increased sensitivity. Lastly, the *C* line corresponds with a single exciton bound to a single neutral donor.

Since hydrogenic energy levels depend only on effective masses and dielectric constants, which are practically not affected by the application of a low hydrostatic pressure, we deduce the pressure dependence of the band gap from the pressure coefficient of the *C* line. Next we discuss the N*X* complex and lastly we examine all NN_i pair spectra.

III. EXPERIMENTAL RESULTS

A. D^0X complex

Typical experimental data have been already presented in Fig. 1. The sharp recombination line associated with the radiative decay of an exciton bound to a single neutral donor shifts with a rate of -1.46 meV/kbar. This negative slope parameter corresponds satisfactorily with the negative change in band gap widely reported for GaP.[22–25] It also corresponds with the pressure coefficient of the indirect Γ—X transition recently reported for GaAs,[26] -1.4 meV/kbar.

B. N*X* complex

Both components, *A* and *B*, of the *J*-*J* doublet could be resolved up to about 6 kbar. This is shown in Fig. 3(a), where the free-exciton energy is indicated for clarity. At very low pressure the two lines exhibit weak pressure coefficients,

$$\frac{dA}{dP}=-0.09,\quad \frac{dB}{dP}=-0.02\ ,$$

in units of meV/kbar, for the *A* line and *B* line, respectively. Within experimental uncertainty, both agree with the experimental values reported from uniaxial stress experiments.[15]

The slightly different slopes associated with the two recombination lines correspond with a change in exchange parameter,

$$\frac{d\gamma}{dP}=-0.07\ ,$$

in meV/kbar, which is illustrated in Fig. 3(b). It corresponds with a decrease in the *J*-*J* coupling coefficient associated with a decrease in binding energy, and qualitatively speaking, correlates satisfactorily with the prediction of Ref. 19. We shall come back on this point later.

Around 4 kbar we find a continuous change in slope parameters. From the experimental data, it is not clear whether the bound excitons tend to be parallel to the band gap with some constant binding energy or whether they cross the free-exciton line and ionize. This point will be discussed in the next section.

C. NN*X* pairs

For illustrative purpose two series of experimental spectra have been displayed in Fig. 4. The fine structure associated with a given pair was identified in a previous work[20] and comes from a simple admixture of *J*-*J* coupling and local-field effects. In this case, *J* being no longer a good quantum number, two manifolds can be identified which have predominant *A*-like and *B*-like character.

Consider, for instance, NN_1. We resolve four components associated with two "forbidden" (*B*-like) and two

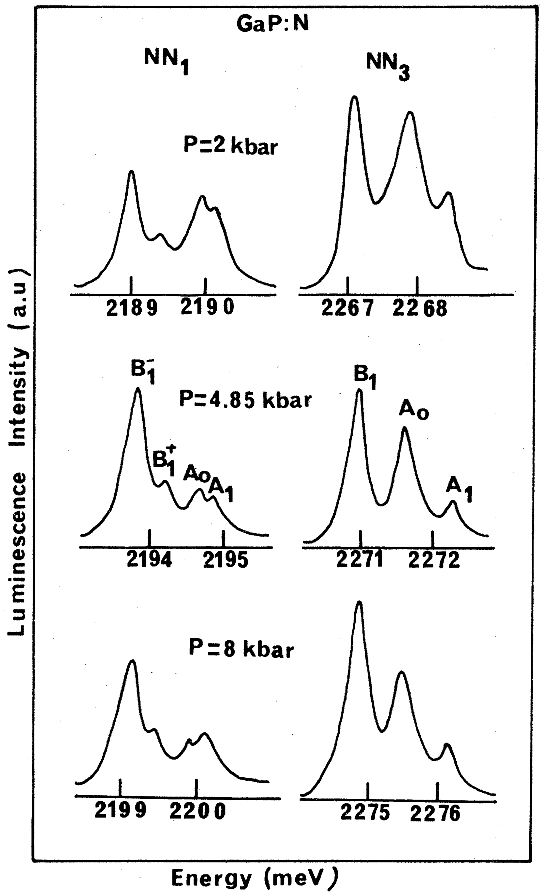

FIG. 4. Fine structure of (a) NN_1 and (b) NN_3 recombination lines. From the line shape of the spectra, we estimate the sample temperature to be about 5 K. Next, analyzing the stress dependence of the *A*-like and *B*-like manifolds, we obtain information concerning the change in *J*-*J* coupling and local-field effects.

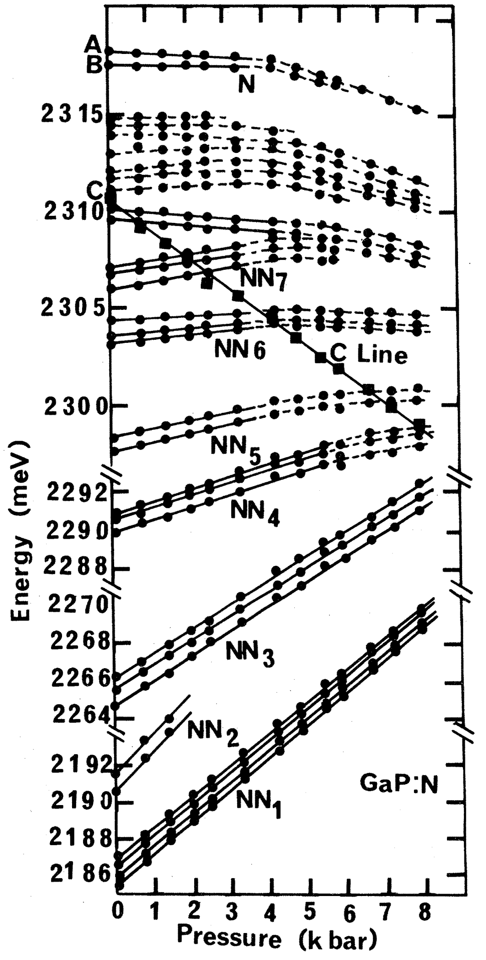

FIG. 5. Stress dependence of the radiative recombination lines observed in GaP at 5 K. Labeled in the figure are all isolated and pair defects discussed in the text.

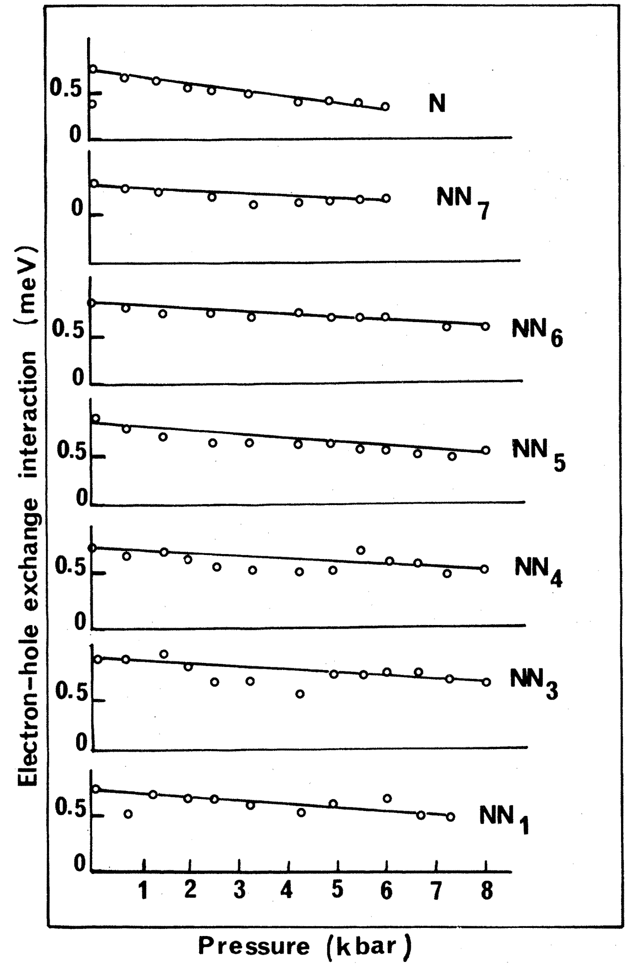

FIG. 6. Detailed evolution of the *J*-*J* coupling parameter γ vs hydrostatic pressure.

"allowed" (*A*-like) recombination lines, respectively. This is shown in Fig. 4(a). By simple inspection of the shape of the spectrum, we could deduce a sample temperature of about 5 K which is confirmed by consideration of the shape of NN_3 [see Fig. 4(b)]. By changing the pressure, we did not sacrifice the experimental resolution and could follow all recombination lines separately. The corresponding data have been summarized in Fig. 5 which also includes, for the sake of completeness, the simple case of a single exciton bound to a single neutral donor (*C* line) and a single exciton bound to a single-nitrogen atom (*A*-*B* doublet).

We find the following.

(i) Except for NN_9, all recombination lines shift to higher energy with increasing pressure. The deeper the line the larger the pressure coefficient. There are only two exceptions to this monotonic series: NN_2 and NN_7 shifting faster than NN_1 and NN_5 or NN_6, respectively.

(ii) Concerning NN_9, we find a negative slope. This is in contrast with the preceding series and is not clearly understood. As a consequence we shall discuss only data for NN_i with $i \leq 7$.

(iii) Deeply bound excitons (NN_1, NN_2, and NN_3) exhibit linear dependences but shallow excitons, starting with NN_4, all exhibit nonlinear stress behaviors. This resembles the nonlinear behavior already noticed for the single-nitrogen complex and, roughly speaking, one can define at low stress an asymptotic regime associated with a constant slope, and at high stress, a departure from linearity. The deeper the pair, the longer the linear regime. Indeed, concerning NN_1, NN_2, and NN_3, no departure from linearity is observed in our range of experimental pressure, while, concerning NN_4, it appears around 7 kbar next, 6 kbar for NN_5, and then saturates around 4.5 kbar up to NN_8 to NN_∞.

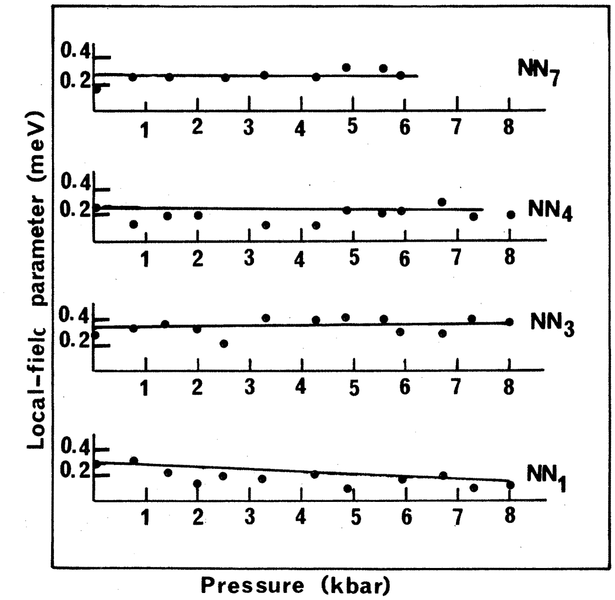

FIG. 7. Change in local-field parameter ϵ_1 vs external stress.

(iv) Additional information can be obtained concerning the change in the electron-hole exchange parameter and the local-field effects experienced by the hole which participates in the bound exciton. Consider, for instance, NN_1, for which the following four different slopes have been resolved:

$$\frac{dA(1)}{dP}=+1.64\ ,\quad \frac{dA(0)}{dP}=+1.68\ ,$$

$$\frac{dB(+1)}{dP}=1.67,\quad \frac{dB(-1)}{dP}=+1.67\ ,$$

in units of meV/kbar.

Analyzing the data with a simple model of axial perturbations including both *J*-*J* coupling and local fields,[20] we note the following.

(i) We resolve a slight but finite difference between the pressure shifts experienced by the *A* components with respect to the *B* ones. It corresponds to a pressure dependence of the electron-hole exchange interaction. This is found for all pairs up to NN_7 and is illustrated in Fig. 6.

(ii) Depending on the pair separation, the bound hole might experience a change in uniaxial perturbation, ϵ_1. Within experimental uncertainty this is only found for the deep states associated with NN_1. The corresponding data have been displayed in Fig. 7.

(iii) Since the two components of the *B*-like manifold

TABLE I. Pressure coefficients and deformation potential successively reported for the interband transition Γ_8-X_6 in GaP.

	Uniaxial			Hydrostatic	
Stress configuration	Ref. 24 $\langle 1,1,1,\rangle$ $\langle 1,1,0\rangle$ $\langle 1,1,2\rangle$	Ref.25 $\langle 1,1,1,\rangle$ $\langle 0,0,1\rangle$	Ref. 22 $\langle 1,1,1\rangle$ $\langle 0,0,1\rangle$ $\langle 1,1,0\rangle$	Ref. 23	This work
$\frac{dE_g}{dP}$ (meV/kbar)	-4.5 ± 1.5	-1.8 ± 0.2	-2.6 ± 0.5	-1.1 ± 0.1	-1.46 ± 0.07
$E_1+a_1+a_2$ (eV)	3.7 ± 0.6	1.6 ± 0.2	2.3 ± 0.5	$1\ \pm0.1$	$1.3\ \pm0.06$
E_2 (eV)	$7\ \pm0.5$	6.5 ± 0.5	6.3 ± 0.9		
T (K)	77	2	2	300	5

shift with identical rate, there is no change in the biaxial field parameter (ϵ_2) experienced by the hole.

IV. ANALYSIS OF DATA

A. Excitons bound to a neutral sulfur donor

The negative stress dependence displayed for the C line in Fig. 5 satisfactorily correlates with the negative change in band gap widely reported for GaP.[22–25] This was already noticed. By using experimental elastic compliance constants,[27] we deduce a deformation potential for the radiative recombination line,

$$E_0+E_1+a_1+a_2=1.3\ ,$$

in units of eV, where E_0 accounts for the change in binding energy and E_1, a_1, and a_2 refer to the change in electronic energy of the lowest conduction band and topmost valence band, respectively. Neglecting the change in binding energy for Wannier excitons bound to a large Coulombic orbital (which is not a bad approximation for the D^0X complex) we are left with the free-exciton–interband deformation potential.

A quantitative comparison with previously published values, however, is difficult to perform since a large variation in the experimental data on this parameter exists in the literature. From the results listed in Table I, together with an indication of the experimental technique used, we find that most of the discrepancy comes from the uniaxial stress experiments. It originates from the difficulty in finding a reliable deformation potential E_2 associated with the shear-induced splitting of the conduction band. Since in this work we perform truly hydrostatic measurements, we get an experimental value which we believe to be very accurate. In the following section, it will be taken as a representative of the band gap.

B. Excitons bound to one single-nitrogen atom

As already noticed, the change in binding energy reported in Fig. 3(a) for the two components of the bound exciton is nonlinear: The initial slope is about -1.4 meV/kbar and decreases to roughly -0.8 meV/kbar around 8 kbar. To understand whether the bound states cross the band gap and ionize after some critical value of the pressure, or whether they tend to follow the free-exciton line with a constant binding energy, in Fig. 3(c) we plot the square root of the binding energy versus pressure. We know from elementary quantum mechanics that the binding energy of a short-range potential (simple square well, for instance) is a nonlinear function of the potential. In first order $(E_B)^{1/2}$ varies as the potential strength and vanishes below some critical value. In other words, we expect $(E_B)^{1/2}$ to be a linear function of the pressure if the exciton tends to ionize. This is indeed what is found. In Fig. 3(c) we define a nice straight line which extrapolates to a predicted pressure of ionization of about 14 kbar. This shows that, for such a pressure, the fast renormalization of the lattice around the impurity reduces the attractive part of the potential to a point where an exciton cannot be bound.

Such a situation also appears for isoelectronic donors. It has been qualitatively discussed for GaP:Bi by Baldereschi and Hopfield.[28] This was done in an effort to account for the series of isoelectronic hole traps in Si, GaP, and ZnSe. The potential produced by an isoelectronic impurity is short range and only binds a particle if it is sufficiently strong. The binding condition for a hole trap is determined by the relative values of the impurity potential (J) and the average kinetic energy ($\bar{E}$) which depends only on the structure of the valence band of the host material. The binding condition is well known,

$$J/\bar{E}>1\ .$$

To predict the dependence of the bound state versus pressure, one must discuss $\bar{E}$ and J separately.

For a hole trap, $\bar{E}$ is directly related to the width of the valence band. A plot of Phillip's ionicity (f_i) suggest the following empirical relationship[29]:

$$\bar{E}=1.7(1-f_i)\ .$$

A decrease in ionicity is related to a delocalization of the valence-band wave functions and a higher average kinetic energy per electron. A simple numerical estimate can be made from the change in LO-TO splitting associated with Raman-active modes in ZnS-type crystals.[30] It comes from the standard relationship,

$$\omega_{\mathrm{LO}}^2-\omega_{\mathrm{TO}}^2=\frac{4e_T^{*2}}{VM\epsilon_\infty}\ ,$$

where e_T^* means the transverse dynamic charge, V is the volume of the unit cell, M is the reduced mass of atoms, and $1/\epsilon_\infty$ accounts for the screening of the macroscopic field by the interband electronic transitions.

Since, on the other hand, a general relationship holds for diamond and related compounds,[31]

$$e_T^{*2}/\epsilon_\infty \sim f_i \ ,$$

one can deduce the change in threshold energy $\Delta\bar{E}$ with only experimental values of the phonon frequencies and Gruneisen-mode parameters as input data,

$$\Delta E = 1.7 f_i \left[1 + 2\frac{\gamma_{\mathrm{TO}}\omega_{\mathrm{TO}}^2 - \gamma_{\mathrm{LO}}\omega_{\mathrm{LO}}^2}{\omega_{\mathrm{LO}}^2 - \omega_{\mathrm{TO}}^2} \right] (S_{11} + 2S_{12}) X \ .$$

We find for GaP,

$$\Delta\bar{E} = +84 \ ,$$

in units of meV/kbar. This shows that, even if one assumes a constant matrix element for the impurity potential, the binding energy should decrease versus pressure since the average kinetic energy of valence electrons increases.

However, the impurity potential J also scales with pressure.[28,29] For instance, for isoelectronic hole traps such as Bi, Sb, or As in GaP, it varies linearly from a minimum value associated with ideal lack of relaxation of the host crystal to a maximum value corresponding to hypothetical total relaxation of the lattice. To predict the change of J upon hydrostatic pressure, we should know the relaxation which exists in the crystal, independently of the stress just by introduction of the foreign atom. Consider for instance GaP:Bi. Ga—Bi bonds around the impurity are longer but more compressible than normal GaP bonds. Therefore under external stress they tend to match. This corresponds with a decrease in lattice relaxation which in turn should correspond with a decrease in the potential of the impurity.

The same *qualitative* arguments hold for electron trap, and in both cases the change in kinetic energy added to the change in lattice relaxation must result in a decrease of the binding energy. However, we could not perform a quantitative comparison on such a basis and we had to go through a model calculation in order to account *quantitatively* for the experimental results.

Working in the framework of the model calculation first presented by Benoit à la Guilluame,[19] we assume the change in local potential extending around the defect to be a linear function of the perturbation. We take the isoelectronic potential acting on the electron only as a square well of radius a and depth

$$V = V_0(1+\epsilon) \ ,$$

where V_0 is the minimum depth to have one bound state. As a function of ϵ, the main parameter of the model, a Hartree calculation[19] predicts that the square root of the

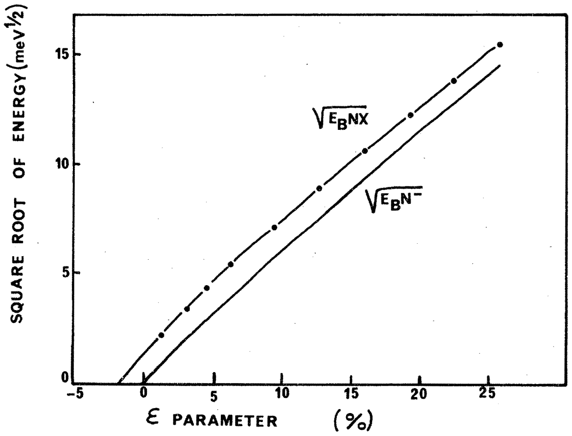

FIG. 8. Results of the Hartree calculation. This gives the square root of the binding energy of the exciton vs the depth $V_0(1+\epsilon)$ of the model isoelectronic potential. For comparison, the square root of the binding energy of the electron $(\mathrm{N})^-$ is also given.

TABLE II. Average slope parameter associated with a given bound-exciton complex (meV/kbar) and corresponding change in exciton binding energy (also in meV/kbar).

Bound-exciton complex	$\left\langle \frac{d\,\mathrm{NN}_i}{dP} \right\rangle$	$\frac{dE_{BX}}{dP}$
NN_1	1.67	−3.13
NN_2	2.06	−3.52
NN_3	1.26	−2.72
NN_4	0.64	−2.10
NN_5	0.45	−1.91
NN_6	0.19	−1.65
NN_7	0.35	−1.81
NN_9	−0.15	−1.31

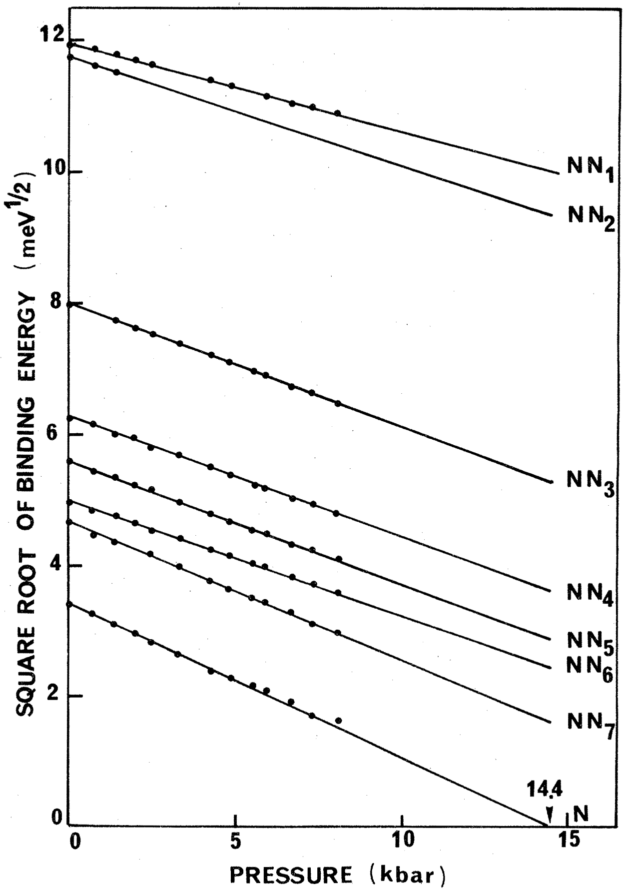

FIG. 9. Same as Fig. 3(c) but for all NN_i pairs discussed in the text. Corresponding ionization energies are listed in Table III.

TABLE III. Predicted ionization pressure for excitons bound to a single (N) and a pair (NN_1 to NN_7) of isoelectronic defects.

	NN_1	NN_2	NN_3	NN_4	NN_5	NN_6	NN_7	N
Ionization pressure (kbar)	86	73	38	36	30	28	23	14

binding energy of the exciton to the isoelectronic center is linear in ϵ (for ϵ small) similarly to the square root of the binding energy of the electron. We believe that an exact calculation would preserve this feature, but just push the limit of binding towards a more negative value of ϵ without much change in the slope (Fig. 8). A comparison of the slopes in Figs. 3(c) and 8 gives a change $d\epsilon/dP=-0.5\%$ per kbar.

Other evidence of the strong renormalization of the potential surrounding the defect can be obtained to first order by considering the exchange energy within a given electron-hole pair. Indeed, any fast renormalization must modify, in real space, the localization of the wave functions and induce a change in electron-hole overlap (i.e., in the *J-J* coupling coefficients).

Around normal pressure conditions the calculation predicts

$$\frac{1}{E_B}\frac{dE_B}{dP}=3\frac{1}{\gamma}\frac{d\gamma}{dP},$$

while the experimental value is

$$\frac{1}{E_B}\frac{dE_B}{dP}\sim 1.4\frac{1}{\gamma}\frac{d\gamma}{dP},$$

(-0.14 kbar^{-1} for the binding energy to be compared with -0.1 kbar^{-1} for the exchange splitting parameter). Taking into account the approximations in the model, this is not a bad result.

C. Excitons bound to a pair of nitrogen atoms

Listed in Table II are pressure-induced changes in binding energy for excitons associated with NN_i pairs ($1\leq i<7$). We assume $dE_g/dP=-1.46$ meV/kbar and derive the change in binding energy from the constant slope observed around atmospheric pressure in the asymptotic regime. We are now in a position to check whether the simple renormalization of the potential assumed for one single-nitrogen atom also accounts for the trends of experimental results observed for NN_i pairs. Let us first check if the square root of the exciton binding energies are linearly dependent on the external pressure. A plot of $E_B\times(NN)$ versus pressure is shown in Fig. 9. We find linear behaviors for all NN_i pairs from NN_1 to NN_7, and the corresponding slopes are close to that of the single-nitrogen bound exciton. The series of predicted ionization pressures are listed in Table III.

We now attempt a more quantitative comparison. We take $\Delta\epsilon$ to be -5% and obtain, from Ref. 19, the changes in electron and hole binding energy listed in Table IV. The corresponding pressure coefficients, assuming $d\epsilon/dP=-0.5\%$ per kbar, agree satisfactorily with the experimental values and we did not try to get any better fit.

Until now we have found that the model calculation of Ref. 19 accounts satisfactorily for the overall trend of experimental data. It describes both the nonlinear behavior of exciton bound to one single-nitrogen atom and the change in pressure coefficients of excitons bound to pairs of nitrogen atoms. It shows also that most of the contribution comes from the change in potential experienced by the electron, the contribution which comes from the hole being roughly 1 order of magnitude lower. Finally it accounts for the change in electron-hole exchange interaction which appears under hydrostatic pressure. However, it does not provide much physical insight about the microscopic mechanism which originates in the change in potential surrounding the impurity and it is clear that, in the framework of such a phenomenological model, one cannot choose between a linear change in the potential depth ΔV and a linear change in the potential radius Δa (or an appropriate combination of both) provided that $\Delta V/V=2\Delta a/a$.

In order to check whether a simple change in lattice relaxation would be sufficient to explain the reduction in potential strength, we have performed a second model calculation. We use a simple square-well potential whose width a_0 is characteristic of the lattice relaxation surrounding the impurity.[13] Solving variationally for NN_i pairs we get the electron binding energies listed in Table

TABLE IV. Summary of contributions which result in the change of exciton binding energy computed for NN pairs. We take $d\epsilon/dP=-0.5\%$ per kbar and find values in satisfactory agreement with the experimental data.

i	$\Delta E_e(NN_i)$ ($\Delta\epsilon=-5\%$)	ΔE_h ($\Delta\epsilon=-5\%$)	ΔE_{BX} ($\Delta\epsilon=-5\%$)	dE_B/dP ($\Delta\epsilon=0.5\%$ per kbar)	dE_B/dP (Expt.)
2	32	0.5	32.5	-3.25	-3.5
3	21	1.5	22.5	-2.25	-2.9
4	15	2	17	-1.7	-2.1
5	12	1.5	13.5	-1.4	-1.9
6	10	1.5	11.5	-1.2	-1.65

TABLE V. Comparison of experimental and theoretical electron binding energy E_e (meV). Experimental values are deduced from the work of Cohen and Sturge (Ref. 11) with an exciton binding energy of 17 meV. Calculation assumes two spherical nitrogen potentials of depth 1.15 eV and radius 2.7 Å separated by a nitrogen distance d. Effective mass was $m^* = 0.59 m_0$. Pressure coefficients dE_e/dP are obtained assuming a shrinkage of the potential radius by 0.25% per kbar.

	NN_1	NN_2	NN_3	NN_4	NN_5	NN_6	NN_7	NN_8	NN_9	NN_{10}
d (Å)	3.85	5.45	6.67	7.71	8.62	9.45	10.2	10.9	11.56	12.19
Experimental electron binding energies (after Ref. 11)	120	113	41	18	11	8	5			
Electron binding energies	150	6	28	17	11	8	6	5	4	3
Bohr radius	3.4	4.4	5.3	5.9	6.6	7.1	7.6	8.0	8.4	8.8
Pressure coefficients	−3.1	−1.6	−1.1	−0.8	−0.6	−0.5	−0.4			

V. To compare them with experimental values we follow the path of Cohen and Sturge[11] and assume an exciton binding energy of 17 meV with the hole binding energies deduced from luminescence excitation. Both series of data are in satisfactory agreement (see Table V).

We can now deduce what is the change in binding energy driven by the compressibility of the perfect crystal. We assume the following.

(i) A change in potential radius with a rate

$$a = a_0[1 + (S_{11} + 2S_{12})P] .$$

(ii) A change in distance between the two nitrogen atoms associated with a given pair,

$$d = d_0[(1 + (S_{11} + 2S_{12})P] .$$

We then obtain all values listed in Table VI. Both contributions have opposite signs and partially cancel. The change in nitrogen-nitrogen separation induces a small and *positive* contribution which cannot account for the experimental data. The change associated with the radius of the potential well is more interesting to discuss. Under atmospheric pressure we assume $a_0 = 2.7$ Å. This was chosen intentionally close to the first nearest-neighbor distance in GaP and roughly corresponds to the extent of the short-range interaction associated with the difference in core potentials. In this case, assuming that the variation must correspond with the simple effect of the compressibility, we get results 1 order of magnitude below the experimental values.

This confirms that in order to come back to a more reasonable agreement we have to introduce an extra change in the strength of the potential. As pointed out earlier this can be a change in the depth or a change in the radius. For instance, we list in Table V all pressure dependences obtained for the electron assuming a change in the radius by 0.25% per kbar. This rate corresponds to the results of our preceding discussion and we have not attempted to get any better fit.

However, the important conclusion in this case is that the nitrogen potential would decrease 1 order of magnitude faster than the GaP band gap. More likely, both the radius *and* the depth of the potential change versus pressure. This is a situation commonly admitted in the alloys,[17] and the analogy between alloying and hydrostatic pressure has been noticed for a long time.

V. CONCLUSIONS

We have investigated the hydrostatic pressure dependence of three different series of bound excitons in GaP. Our major findings are the following.

TABLE VI. Details of the two contributions driven by the perfect-crystal compressibility which contribute to (i) a change in nitrogen-nitrogen distance and (ii) a change in the potential radius. All values are in (meV/kbar) and give results roughly 1 order of magnitude below the experimental data.

	NN_1	NN_2	NN_3	NN_4	NN_5	NN_6	NN_7
$\left[\frac{\partial E_e}{\partial P}\right]_{V,a}$	0.14	0.06	0.04	0.02	0.02	0.01	0.01
$\left[\frac{\partial E_e}{\partial P}\right]_{V,d}$	−0.49	−0.26	−0.18	−0.14	−0.11	−0.10	−0.02
$\left[\frac{\partial E_e}{\partial P}\right]_{V}$	−0.35	−0.20	−0.14	−0.12	−0.10	−0.08	−0.01

(i) Concerning the neutral donor complex, the recombination line shifts linearly toward lower energy with a slope of -1.46 meV/kbar. This reflects satisfactorily the change in the indirect band gap versus pressure.

(ii) Concerning the single exciton bound to a single-nitrogen atom, we find a nonlinear behavior. Considering the change in binding energy versus potential strength, this is satisfactorily accounted for. An ionization pressure of 14 kbar is predicted.

(iii) Lastly, concerning the series of excitons bound to pairs of nitrogen atoms, the experimental behavior depends on the pair index "*i*." The deepest pairs, NN_1-NN_3, exhibit constant and positive slope parameters, while starting from NN_4 we find nonlinear dependences. This agrees again with the simple models of linearly pressure-dependent potential strength. The effect of the host crystal compressibility is computed to give results about 1 order of magnitude lower than the experimental values, and we find it necessary to relax the potential strength with a rate equal to -0.5% per kbar.

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[1] For a recent review, see P. J. Dean and D. G. Herbert, in *Excitons,* edited by K. Cho (Springer, New York, 1979).

[2] Y. C. Chang and T. C. McGill, Phys. Rev. B 25, 3945 (1982); B 25, 3963 (1982).

[3] P. J. Dean, D. Bimberg, and F. Mansfield, Phys. Rev. B 15, 3906 (1977); see also D. Bimberg and P. J. Dean, *ibid.* 15, 3917 (1977).

[4] H. Mathieu, B. Archilla, P. Merle, and J. Camassel, Phys. Rev. B 20, 4268 (1979).

[5] H. Mathieu, J. Camassel, and P. Merle, Phys. Rev. B 21, 2466 (1980).

[6] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. 17, 312 (1966).

[7] R. A. Faulkner, Phys. Rev. 175, 991 (1968).

[8] J. C. Phillips, Phys. Rev. Lett. 22, 285 (19690.

[9] D. G. Thomas and J. J. Hopfield, Phys. Rev. 150, 680 (1966).

[10] J. A. Kash, J. H. Collet, D. J. Wolford, and J. Thompson, Phys. Rev. B 27, 2294 (1983).

[11] E. Cohen and M. D. Sturge, Phys. Rev. B 15, 1039 (1977).

[12] J. W. Allen, J. Phys. C 1, 1136 (1968); also see 4, 1936 (1971).

[13] F. Thuselt, K. Kremer, and H. J. Wunsche, Solid State Commun. 36, 563 (1980).

[14] J. L. Mertz, A. Balderschi, and A. M. Sergent, Phys. Rev. B 6, 3082 (1972).

[15] H. Mathieu, L. Bayo, J. Camassel, and P. Merle, Phys. Rev. B 22, 4834 (1980).

[16] For a recent review, see M. Jaros, *Deep Levels in Semiconductors* (Adam Hilger, Bristol, 1982).

[17] W. Y. Hsu, J. D. Dow, D. J. Wolford, and B. G. Steetman, Phys. Rev. B 16, 1597 (1977).

[18] C. A. Swarts, D. L. Miller, D. R. Franceschetti, H. P. Hjalmarson, P. Vogl, and J. D. Dow, Phys. Rev. B 21, 1708 (1980).

[19] C. Benoit à la Guillaume, in *Proceedings of the 16th International Conference on the Physics of Semiconductors* (North-Holland, Montpellier, 1982), p. 105.

[20] B. Gil, J. Camassel, P. Merle, and H. Mathieu, Phys. Rev. B 25, 3987 (1982).

[21] N. Konczykowsi, M. Baj, E. Szafarkiewicz, L. Konczewicz, and S. Porowski, *High pressure and Low Temperature Physics* (Plenum, New York, 1978), p. 537.

[22] H. Mathieu, P. Merle, E. L. Ameziane, B. Archilla, J. Camassel, and G. Poiblaud, Phys. Rev. B 19, 2209 (1979).

[23] R. Zallen and W. Paul, Phys. Rev. 134, Al628 (1964).

[24] I. Balslev, J. Phys. Soc. Jpn. 21, Suppl. 101 (1966).

[25] R. G. Humphreys, U. Rossler, and M. Cardona, Phys. Rev. B 18, 5590 (1978).

[26] J. A. Bradley, D. J. Wolford, H. E. King, K. Fry, K. E. Newman, and J. D. Dow, Bull. Am. Phys. Soc. 28, 330 (1983).

[27] W. Boyle and R. J. Sladek, Phys. Rev. B 11, 2933 (1975).

[28] A. Baldereschi and J. J. Hopfield, Phys. Rev. Lett. 28, 171 (1972).

[29] A. Baldereschi, J. Lumin. 7, 79 (1973).

[30] R. Trommer, H. Muller, M. Cardona, and P. Vogl, Phys. Rev. B 21, 4869 (1980).

[31] R. M. Martin, Phys. Rev. B 1, 4005 (1970).