

Lattice-distortion-induced electronic bistability of the donor defect in semiconductors

M. Grinberg

Institute of Physics, Nicolaus Copernicus University, ulica Grudzadzka 5/7, PL-87-100 Toruń, Poland

(Received 10 October 1989; revised manuscript received 8 January 1990)

The adiabatic approximation and a discrete lattice model are used for calculations of the electron-lattice interaction energy for an electron captured on a donor-type impurity. Thus the model describing the character of the electron-lattice interaction for a range of electron-impurity and electron-lattice coupling for any electron localization is obtained. The possibility of a large lattice-relaxation-induced bistability of the defect is investigated for the symmetrical and Jahn-Teller lattice distortion. The configurational-coordinate diagrams for the bistable substitutional donor (*DX* center) and As antisite (*EL2* center?) in GaAs are presented.

I. INTRODUCTION

During the last decade there appeared many papers concerning defects in semiconductors exhibiting bistable electronic properties. The bistability was reported for the complexes, such as the thermal donors in Si;¹ native defects, such as *EL2* centers in GaAs;² and impurities, such as In and Ga in CdF₂,³ Cl in CdTe,⁴ *DX* centers in Al_xGa_{1-x}As.⁵ The similar centers, such as *DX*, were observed in GaP_yAs_{1-y} (Ref. 6) and Al_xGa_{1-x}Sb.⁷ Due to the commercial applications of the devices based on GaAs the bistable defects in this semiconductor have been very intensively investigated. The *DX* centers in Al_xGa_{1-x}As were detected for Al concentrations greater than 0.2 when the donors of different species—group-IV elements (Si, Ge, and Sn) and group-VI elements (S, Se, and As) were incorporated.⁸ They were also found in GaAs under hydrostatic pressure.⁹ It is believed that the electron bound to the donor can occupy two states; first, the ordinary shallow state and second, the localized one, separated by the potential energy barrier. Several models based on the large lattice-relaxation (LLR) assumption have been proposed for explaining the physical nature of the centers.¹⁰⁻¹⁴ Also the small lattice relaxation (SLR) was proposed for describing the deep donor centers in Al_xGa_{1-x}As by Henning and Ansems.¹⁵ However, as was found later,^{16,17} two types of localized donor states, one accompanied with small lattice distortion and second with large lattice distortion, can exist in Al_xGa_{1-x}As. The theoretical basis of LLR models is the adiabatic energy approximation¹⁸ of an electron-lattice system used for describing the bistable donors by Toyozawa.¹⁹ According to Toyozawa's idea the electron can be localized due to the interaction with the acoustic phonons. In his model the system is described by the electron-phonon and electron-impurity coupling constants, which depend on the deformation potential of the conduction-band minimum and the electron and donor parameters given in the effective-mass approximation (EMA), respectively. The adiabatic energy of the system as a function of coupling constants for a given electron state can have two minima, one for the delocalized electron (the ordinary

EMA shallow donor state) and the second corresponding to the completely localized electron accompanied by LLR, or only one minimum corresponding to the localized or delocalized state. Unfortunately due to the continuum approximation of the crystal lattice the Toyozawa model cannot describe the localized electron. The only exact datum one can obtain in the framework of this model is the maximum of the electron-phonon coupling constant for which the EMA electron state can exist.²⁰ In addition the typical values of the deformation potentials for III-V and II-VI compound semiconductors are too small to be responsible for the bistability of donor centers in these materials.²¹

In this paper the alternative model based also on the adiabatic approximation is proposed but now the interaction of the electron with the discrete lattice is considered. Thus the electron-lattice interaction is given by the individual lattice ion potentials and displacements. In such a way one may obtain a description of the general behavior of the defect for arbitrary electron localization for a range of the electron-lattice interaction strength. In Sec. II the general properties of the model are presented. I investigate here the electron in the symmetric A_1 state interacting with the symmetric deformation of lattice (the breathing mode). Sections III and IV concern the negative- U system and the Jahn-Teller lattice distortion, respectively. The last section contains the calculations of the configurational-coordinate (CC) diagrams for the cases of *DX* and *EL2* centers in GaAs.

II. ADIABATIC ENERGY APPROXIMATION FOR THE LOCALIZED STATES

Let us consider the electron acting with the attractive impurity potential and the potentials created by the lattice ion displacements. The total energy of such a system in adiabatic approximation consists of three parts: electron, lattice, and electron-lattice interaction:

$$E(\varphi, \Delta) = \varepsilon_e(\varphi) + \varepsilon_{\text{latt}}(\Delta) + \varepsilon_{e-\text{latt}}(\varphi, \Delta). \quad (1)$$

Here φ and Δ are the electron wave function and lattice dilation, respectively. Since all the experiments suggest

that the electron captured at the lattice-distortion-induced state is localized in the volume of unit cell one may consider further only the interaction of an electron with the ions placed in the neighborhood of the defect. For the compound semiconductors and substitutional impurity we have four neighbors to be included. In dependence on the distortion symmetry, the ion displacements may be decomposed into the adequate collective coordinate complete set.²² In this section I considered only the electron occupying the symmetric A_1 state so only the interaction with the symmetric A_1 mode of the lattice distortion is taken into account. In such a way Δ is the real displacement of an individual lattice ion and the energy of the lattice and electron-lattice interaction may be given as follows:

$$\epsilon_{\text{latt}} = 2\Delta^2 C, \quad (2)$$

$$\epsilon_{e\text{-latt}} = \sum_s \int \varphi^*(\mathbf{r}) [V(\mathbf{r} - \mathbf{R}_s - \Delta_s) - V(\mathbf{r} - \mathbf{R}_s)] \varphi(\mathbf{r}) d\mathbf{r}. \quad (3)$$

Here C is the crystal elastic constant, $V(\mathbf{r})$ is the lattice ion potential, \mathbf{R}_s and Δ_s are the s th-ion position and displacement, respectively. After changing the integral variable in form (3) one obtains

$$\epsilon_{e\text{-latt}} = \sum_s \int V(\mathbf{r}) [\varphi^2(\mathbf{r} + \mathbf{R}_s + \Delta_s) - \varphi^2(\mathbf{r} + \mathbf{R}_s)] d\mathbf{r}. \quad (4)$$

The expansion φ^2 up to the linear term with respect to Δ_s results in

$$\epsilon_{e\text{-latt}} = 4\Delta \cdot \int V(\mathbf{r}) \text{grad} \varphi^2(\mathbf{r} + \mathbf{R}) d\mathbf{r}. \quad (5)$$

Here the direction of Δ and \mathbf{R} is (1,1,1) or arbitrary equivalent for T_d point-group symmetry. We may assume that only the short-range, core potentials of the ions significantly contribute to the electron-lattice interaction energy. The sum of the Coulomb potentials gives only the constant background independent of the individual ion positions. In such a way the Fröhlich interaction is not taken into account. For the III-V and II-VI semiconductors this approximation seems to be reasonable due to the small values of the electron-LO-phonon coupling constants. As far as the core potentials are nonzero only on a small distance from the ion centers one may approximate the gradient electron density by the constant and obtain

$$\epsilon_{e\text{-latt}} = 4\Delta \cdot \left. \frac{d}{dr} \varphi^2(r) \right|_{r=R} \int V(\mathbf{r}) d\mathbf{r}. \quad (6)$$

Since we are interested in the minimum value of the adiabatic energy we minimize functional (1) with respect to Δ and φ . Putting (6) into (1) and minimizing with respect to Δ one obtains

$$\Delta = -\frac{1}{C} \left. \frac{d}{dr} \varphi^2(r) \right|_{r=R} \int V(\mathbf{r}) d\mathbf{r} \quad (7)$$

and

$$E = \epsilon_e(\varphi) - \frac{2}{C} \left[\int d\mathbf{r} V(\mathbf{r}) \left. \frac{d}{dr} \varphi^2(r) \right|_{r=R} \right]^2. \quad (8)$$

To proceed further one needs some details about the electronic energy of the system. In general we may use the electronic Hamiltonian with the kinetic energy operator defined by the real dispersion of the electron in the conduction band and the real potential of the impurity. Thus, since a number of conduction-band minima must be included, the reference energy level is connected rather with Brillouin-zone average energy¹⁴ defined by the symmetry points Γ , X , and L (Ref. 23) than with the position of the lowest conduction-band minimum. In fact, since we are interested in the character of electron-lattice interaction not in the absolute value of the energy, we do not need the exact electronic Hamiltonian. According to the variational principle we may introduce the parametrized electron wave function satisfying the adequate symmetry conditions and vary the total energy with respect to their parameters. It is useful to have a function with one parameter describing the electron localization. For the electron in A_1 state we may use the s -type Gaussian function

$$\varphi(r, a) = 2^{3/4} a^{-3/2} \exp(-\pi r^2 a^{-2}), \quad (9)$$

where the effective radius of the state a is the variational parameter. Using the parameter $\eta = a/R$ one can transform Eq. (8) as follows:

$$E = \epsilon_e(\eta) - P_1 \exp(-4\pi\eta^{-2}) \eta^{-10} \quad (10)$$

where the constant P_1 is given by

$$P_1 = \frac{256\pi^2}{R^8 C} \left[\int V(\mathbf{r}) d\mathbf{r} \right]^2. \quad (11)$$

The minimization of functional (8) with respect to φ may be replaced by the minimization of functional (10) with respect to η . The equation $dE/d\eta = 0$ gives the relation between P_1 and η ,

$$P_1 = -\frac{d\epsilon_e}{d\eta} \eta^{11} \exp(4\pi\eta^{-2}) (10 - 8\pi\eta^{-2})^{-1}. \quad (12)$$

One may investigate the dependence of the right side of Eq. (12) on η . Due to the fact that $P_1 > 0$ [see Eq. (11)] we are interested in a certain range of η only. It is evident that if the value of the right side of (12) changes monotonically with η the equation has only one solution and the energy of the system has only one minimum for the electron localization given by $\eta(P_1)$. There is a different situation when it changes nonmonotonically. In this case for a certain range of P_1 Eq. (12) has several solutions which correspond to the minima and the maxima of the energy. For further analysis I assumed that the pure electronic energy $\epsilon_e(\eta)$ has only one minimum for $\eta = \eta_e$ and that $d\epsilon_e/d\eta$ is slowly varying in comparison to $\eta^{11} \exp(4\pi\eta^{-2})$. Under these conditions for both $\eta_e > (0.8\pi)^{1/2}$ and $\eta_e < (0.8\pi)^{1/2}$ Eq. (12), in dependence on the value of P_1 , may have only one or three solutions. For the case of three, for $\eta_1 < \eta_2 < \eta_3$, η_1 and η_3 corre-

spond to the minima of the energy, and η_2 corresponds to the maximum. One may see that the system is then bistable and can exist in the state with localization parameter equal either to η_1 or η_3 . To picture the model one may assume that the electronic energy of the system may be approximated by the following function:

$$\varepsilon_e = B(\eta^{-2} - g_l \eta^{-1}) \quad (13)$$

where B and g_l are the parameters describing the kinetic energy and the ratio of the potential to the kinetic energy of an electron for $\eta=1$. Formally the approximation (13) is similar to EMA where g_l and B are constants for the whole range of η and can be given by electron effective mass m , dielectric constant ε_∞ , and the charge of defect Z :

$$g_l = \frac{2^{5/2} Z R m}{3 \pi \varepsilon} \quad (14)$$

$$B = \frac{3 \pi}{2 m R^2} \quad (15)$$

In fact we need only B and g_l to be constants for the range of η close to the resolutions of Eq. (12)— η_1 and η_3 . If the system can exist either in strongly localized or delocalized states this approximation seems to be reason-

able. A similar concept was proposed by Bourgoïn and Mauger²⁴ for describing the intervalley mixing shallow-deep instability of L -point donor level in GaAs. Using this approximation one may obtain the dependence of the right side of Eq. (12) on η for different electronic energy parameters [see Figs. 1(a) and 1(b)]. I know that in fact the dependence of the electronic energy on η is much more complicated. However, I maintain that the conclusions concerning the character of the electron-lattice interaction deriving from this picture are qualitatively valid in general. To consider further the physical conditions of bistability one may treat Eq. (12) formally as the dependence P_1 on η and find the extreme values of $P_1(\eta)$ given by (12). Taking $dP_1/d\eta=0$ one obtains

$$\frac{\eta(d^2\varepsilon_e/d\eta^2)}{d\varepsilon_e/d\eta} = \frac{16\pi^2\eta^{-4} - 23\pi\eta^{-2} + 110}{10 - 8\pi\eta^{-2}} \quad (16)$$

The graphical solutions of this equation are presented in Fig. 2. The solid curves represent the right side of the equation, others correspond to the left side for different values of g_l . For $g_l=0.39$ (dotted curve) there are two solutions labeled as I and II corresponding to the maximum and minimum P_1 , respectively. Adequate dependence of P_1/B on η is presented in Fig. 1(a). For $2000 < P_1/B < 8000$ the energy of the system has two minima: first for η slightly smaller than η_{II} (the localized electron) and second for η slightly greater than η_I (the delocalized electron). For other values P_1/B the energy has only one minimum; for $P_1/B > 8000$ and $P_1/B < 2000$ the electron is localized and delocalized, respectively. For $g_l=1.1$ (dashed-dotted curves) there are no solutions for positive P_1 (the inflection point labeled as i appears for $P_1 < 0$). The dependence of P_1/B on η for this type of electron-lattice interaction is presented in Figs. 1(a) and 1(b) for $g_l=0.7$ and $g_l=1.7$, respectively. For sufficiently large g_l the system is again bistable: for $g_l=2.3$ (dashed curve) Eq. (16) has two solutions labeled as III and IV. From Fig. 1(b) it is seen that for

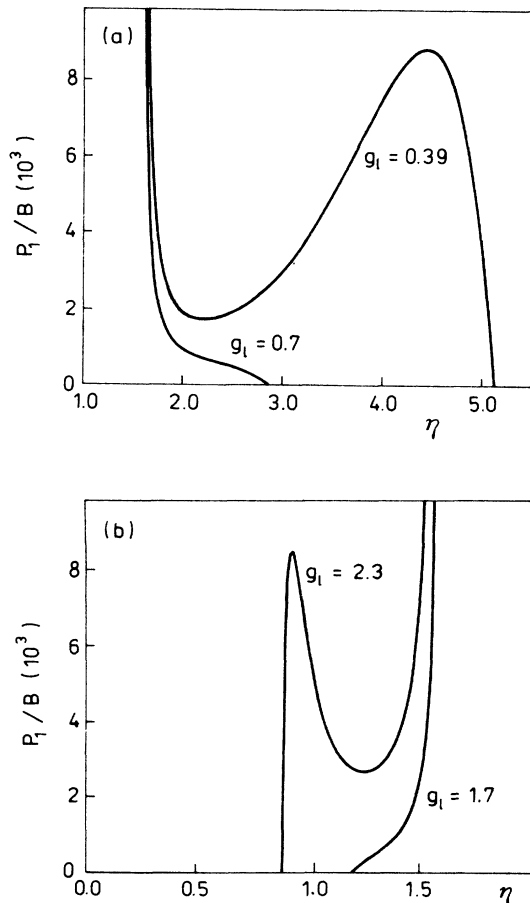


FIG. 1. Graphical representation of Eq. (12) for different values g_l .

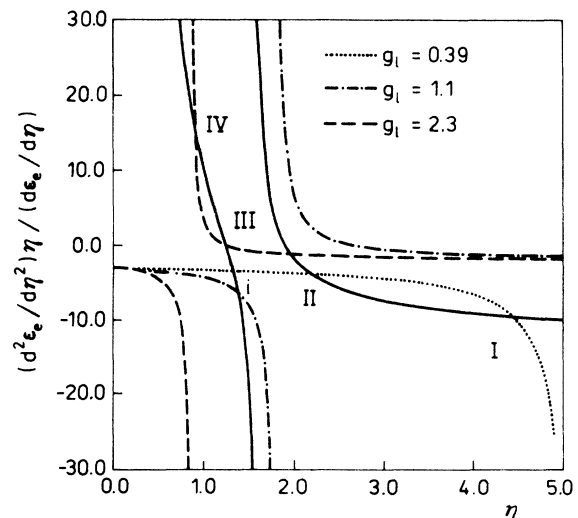


FIG. 2. Graphical solutions of Eq. (16) for different values g_l .

$2500 < P_1/B < 8200$ the two minima of energy exist: first for $\eta < \eta_{IV}$ and second for $\eta > \eta_{III}$. However, here the electron in both states is strongly localized. As was mentioned before the parametrization of the electronic energy given by (13) is not strictly valid for intermediate values of η . Nevertheless one may see from Fig. 2 that the crossing points IV and I, which appear for strongly localized and delocalized states, respectively, and the asymptotic behavior ($d^2\varepsilon_e/d\eta^2 \eta / (d\varepsilon/d\eta)$) for large and small η forced the existence of the crossing points III and II for intermediate electron localization, for any reasonable particular dependence $\varepsilon_e(\eta)$. Therefore the conclusions concerning the possibility of the existence of the two types of donors, the normal and the bistable donors, are quite general. It is interesting also to consider the distortion of the lattice. Using forms (7) and (9) we may see that ion displacement Δ is significant only for the states for which the localization parameters are close to $\eta = (0.8\pi)^{1/2}$. In Fig. 3 the normalized ion displacement is presented versus the localization of the electron. All the results are summarized in Fig. 4 which is the phase diagram describing the character of the electron-lattice interaction in dependence on P_1/B and g_l . One may see that for the values of the parameters corresponding to the area labeled as I the system is bistable and can exist either in the delocalized, ordinary shallow donor state or in the localized state accompanied by LLR. The area labeled as II corresponds to the normal states (the energy of the system has only one minimum). Here the electron-lattice interaction for given P_1 depends on g_l and reaches the maximum for $g_l = 2(0.8\pi)^{-1/2}$. For the area labeled as III the system is again bistable and can exist alternatively in two different localized states; first, with the electron localized inside the core of the impurity ion without lattice distortion and second with the electron localized on one of the nearest-neighbor ions accompanied by LLR. One may see that the defects which are defined by the parameters from region I (bistability with localized and delocalized states) have all properties of *DX* centers. The bistable defect with the localized stable and

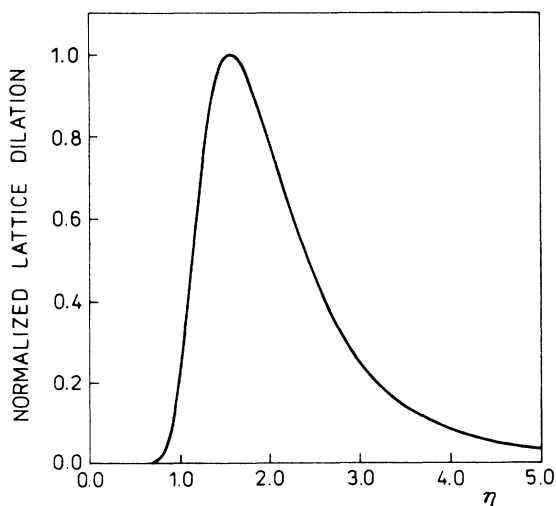


FIG. 3. The normalized lattice dilation vs localization of electron wave function.

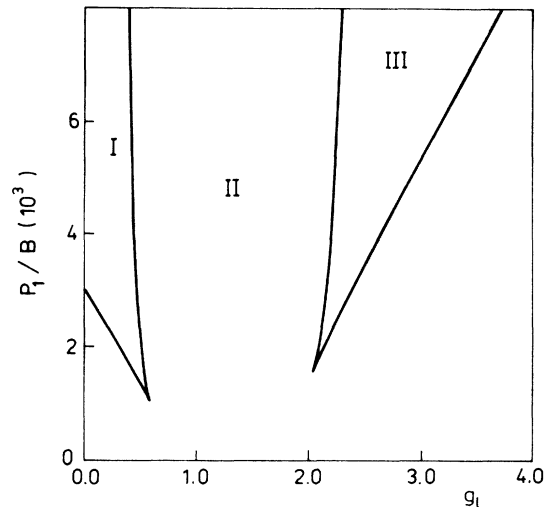


FIG. 4. The phase diagram for existence of normal and bistable states in semiconductors.

metastable states such as *EL2* in GaAs can be placed into region III. For region II the extremely weak electron-lattice interaction characteristic for ordinary shallow donors corresponds to the small g_l and P_1/B values. The intermediate or strong electron-lattice coupling without bistability characteristic for $0.6 < g_l < 2.1$ corresponds to the properties of transition metal ions. The strong localization of electron with very weak or without electron-lattice interaction characteristic for region II for $g_l > 2.1$ corresponds to the properties of rare earth ions. Using form (14) we may calculate g_l for several types of impurities. Using the typical EMA parameters one obtains for shallow donors $g_l < 0.2$; using the true electron mass, $\epsilon_\infty = 1$, and $Z = 1$ one obtains for transition metals $g_l = 2.2$; using $Z = 8$ for rare earth ions one obtains $g_l = 18$. The model also may be used for describing the electron traps in InSb. Here the residual oxygen impurity introduces three types of states: tied to the Γ , L , and X minimum of the conduction band, respectively.^{25,26} The first one is the typical shallow donor state without the electron-lattice interaction. The second and third are localized accompanied by intermediate and strong electron-lattice coupling, respectively. It is easy to find that for InSb $g_l^\Gamma \ll g_l^L \cong g_l^X$ and $B^\Gamma \gg B^L \cong B^X$. Thus for the same P_1 the interaction with the lattice should be stronger for the state connected with the L and X minima.

III. NEGATIVE-*U* SYSTEM

Anderson²⁷ suggested that the strong electron-phonon coupling may result in phonon-mediated attraction which overcomes the Coulomb repulsion between two electrons at the same defect. One may calculate the binding energy of the defect occupied by two electrons E_{2e} and the energy of defect with only one electron E . The sign of

$$U = E_{2e} - 2E \quad (17)$$

decided which electronic configuration is energetically preferable. The negative-*U* systems were found in semi-

conducting glasses²⁷ and crystalline semiconductors.²⁸ Toyozawa¹⁹ has investigated theoretically the possibility of the existence of the negative charged donors in the framework of his model. He found that for the bistable defects being in the state accompanied by LLR $U < 0$. The lack of electron paramagnetic resonance (EPR) signal for semiconductors with DX centers leads to the conclusions that they may be in fact the negative- U systems. In the model presented we also considered the case of two electrons captured on the one defect. Assuming that two electrons with opposite spin occupied the same orbital φ and using the approximation (13) one obtains the following expression on the electronic energy of the two-electron system:

$$\varepsilon_{2e}(\eta) = B[(2\eta^{-2} - 2g_I\eta^{-1}) + g_{\text{int}}\eta^{-1}]. \quad (18)$$

Here g_{int} is the measure of interelectron interaction. Taking into account that each electron interacts with the lattice in the same way one obtains the following expression on the adiabatic energy:

$$E_{2e} = \varepsilon_{2e}(\eta) - 4P_1 \exp(4\pi\eta^{-2})\eta^{-10} \quad (19)$$

where P_1 is given by Eq. (11). Minimization of Eq. (19) with respect to η yields

$$P_1 = 0.25 \frac{d\varepsilon_{2e}}{d\eta} \eta^{11} (10 - 8\pi\eta^{-2})^{-1} \exp(4\pi\eta^{-2}). \quad (20)$$

Comparing Eqs. (12) and (20) and taking into account that for $g_{\text{int}} \ll g_I$, $d\varepsilon_{2e}/d\eta \cong 2d\varepsilon_e/d\eta$, one may see that the system of two electrons becomes bistable for a P_1/B parameter about two times smaller than the one-electron system does. For given g_I and g_{int} one may obtain the terminal values of P_1 : $P_1^m(2e)$ and $P_1^m(1e)$ for which the defect with two and one electrons becomes bistable. The calculation performed for $g_{\text{int}} < g_I$ results in $P_1^m(2e) < P_1^m(1e)$. In addition it was found that for the range of parameters P_1/B and g_I for which both the one- and two-electron systems are bistable the U energy is negative for the states with LLR and positive for the states where the interaction with the lattice is small. It yields that stable and metastable states of the defect should be the different charge states. This conclusion concerns especially the case of simple donors which, without lattice distortion, usually bound only one electron ($Z=1$). For other defects which may bound more than one electron due to the Coulomb potential ($Z \geq 2$) the situation is qualitatively different and the center in both states may have the same charges.

IV. JAHN-TELLER DEFORMATION

In the preceding sections I have considered the symmetrical distortion of the lattice. It is clear that it is not the only possibility. For instance, Morgan,¹² describing the properties of DX centers, suggested that the localized relaxed state is in fact the T_2 excited state of the donor, tied to the L minimum of the conduction band which becomes metastable due to the interaction with the T_2 symmetry lattice deformation. A similar model was proposed

by Kobayashi *et al.*,¹⁰ Oshiyama and Ohnishi,²⁹ and Chadi and Chang.¹⁴ Actually, according to the Jahn-Teller theorem the system being in the degenerated T_2 state is unstable without the lattice relaxation. It is very probable that the adiabatic energy reaches the second minimum due to displacement of the donor or one of the nearest-neighbor ions to the interstitial position. This type of distortion was found to play an important role in the creation of metastable state of the $EL2$ center.^{30,31} For analysis of this case one may represent the distortion by a sum of totally symmetric ion displacements given by the configuration coordinate Q_1 (A_1) describing the symmetrical mode and the sum of Q_4 (T_2), Q_5 (T_2), Q_6 (T_2) the normal coordinates defining the displacement of T_2 symmetry:²²

$$\begin{aligned} Q_1 &= 0.25(\Delta_1 + \Delta_2 + \Delta_3 + \Delta_4), \\ Q_4 &= 0.25(\Delta_1 + \Delta_2 - \Delta_3 - \Delta_4), \\ Q_5 &= 0.25(\Delta_1 - \Delta_2 + \Delta_3 - \Delta_4), \\ Q_6 &= 0.25(\Delta_1 - \Delta_2 - \Delta_3 + \Delta_4). \end{aligned} \quad (21)$$

Here Δ_i are the nearest-neighbor ions' relative shifts. Due to the fact that this distortion contains the symmetrical part it is "felt" also by the electron being in A_1 state. To obtain electron-lattice interaction energy one may use the electron wave function which is a linear combination of Bloch waves with the momentum for the entire Brillouin zone. In one band approximation we have

$$\phi(\mathbf{r}) = \sum_{\mathbf{k}} f(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) u_{\mathbf{k}}(\mathbf{r}). \quad (22)$$

One may see that for almost all semiconductors the energy increases very quickly with the momentum in the vicinity of the Γ minimum (small effective mass). Taking into account the results of preceding sections: the "heavier" electron may be localized for smaller electron-lattice interaction, one may predict that the summation on \mathbf{k} in (22) in the close vicinity of Γ should not take the significant contribution to the lattice-distortion-trapped electron wave function, the more so as the volume corresponding to the Γ minimum in k space is small in comparison to the total volume of the Brillouin zone. Therefore considering the strong electron-lattice interaction we may treat the localized electron states as tied to the X and/or L minima only. In such a way summation on \mathbf{k} in (22) is extended around the four equivalent points for the L minimum and around the six points for the X minimum of the conduction band. Thus for both cases one obtains

$$\begin{aligned} \phi(\mathbf{r}) &= \sum_j \exp(i\mathbf{K}_j \cdot \mathbf{r}) \sum_{\mathbf{k}}' f(\mathbf{k}) u_{\mathbf{K}_j + \mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) \\ &= \sum_j \alpha_j \varphi(\mathbf{r}) \exp(i\mathbf{K}_j \cdot \mathbf{r}), \end{aligned} \quad (23)$$

where φ is independent of \mathbf{K}_j and is given by

$$\varphi(\mathbf{r}) = \sum_{\mathbf{k}}' f(\mathbf{k}) u_{\mathbf{K}_j + \mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}). \quad (24)$$

In (23) and (24) the prime denotes that the summation on

\mathbf{k} does not extend over the entire Brillouin zone for each \mathbf{K}_j but over the smaller areas which together give the entire zone. It should be noted that since φ depends on the Bloch function it is not the EMA envelope function. The sets of α coefficients are³²

$$\begin{aligned} \alpha_{A_1(L)} &= 0.5(1, 1, 1, 1), \\ \alpha_{A_1(X)} &= 1/\sqrt{6}(1, 1, 1, 1, 1, 1) \\ \alpha_{T_2(L)} &= \frac{1}{2} \begin{pmatrix} 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix}, \\ \alpha_{T_2(X)} &= 1/\sqrt{2} \begin{pmatrix} 1 & 0 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & 0 & -1 \end{pmatrix}. \end{aligned} \quad (25)$$

The function (23) is not normalized. Using the φ given by (9) in (23) one obtains the following normalization factors:

$$\begin{aligned} N(A_1(L)) &= 1 + 3 \exp(-3\pi\eta^2/16), \\ N(A_1(X)) &= 1 + 4 \exp(-3\pi\eta^2/16) + \exp(-3\pi\eta^2/8), \\ N(T_2(L)) &= 1 - \exp(-3\pi\eta^2/16), \\ N(T_2(X)) &= 1 - \exp(-3\pi\eta^2/8). \end{aligned} \quad (26)$$

It should be mentioned here that for the T_2 symmetry state the trial electron wave function defined by (23) should also contain the p -type Gaussians. However, the variational calculations give the electron-lattice interaction energy, defined for the individual ion by (6), very small and almost not dependent on lattice distortion, for reasonable ion displacements, when the trial function is given by the sum of p -type Gaussians.

Using forms (21)–(26) I have calculated the electron-lattice interaction energy for the electron states of A_1 and T_2 symmetry tied to L and X minima. The results obtained are presented in Table I (the details are given in the Appendix). Here

$$\begin{aligned} I_1 &= \int V(\mathbf{r}) d\mathbf{r}, \\ I_2 &= \frac{\pi^2}{3R^2} \int V(\mathbf{r}) r^2 d\mathbf{r}, \\ \Theta &= (d\varphi^2/dr)_{r=R} \Delta. \end{aligned} \quad (27)$$

One may see that the T_2 state in both cases, for states tied to L and X minimum, splits into A_1 and E states. Knowing which state is the ground one (A_1 or A_1 originated from T_2) we may minimize the total energy with respect to Δ and obtain the following expression on the total energy of the system:

$$E = \varepsilon_e(\eta) - P_1 \eta^{-10} \exp(-4\pi\eta^{-2}) N^{-2}. \quad (28)$$

One may see that the values of the P_1 parameters depend here on the symmetry of the state (see Table I).

Comparing Eqs. (28) and (10) one may see that the difference between them is in the normalization factor which, in fact, does not strongly depend on η . Therefore the conclusions concerning the type of electron-lattice interaction drawing from Eq. (28) are generally the same as in the preceding sections. We may consider now which distortion, the totally symmetric A_1 or the Jahn-Teller distortion, produce in fact the bistability of the defect. It depends of course on the value of the P_1 parameter. For the A_1 distortion P_1 is given by the form (11). It is easy to find that, including the intervalley interaction P_1 , for A_1 state the breathing modes have the values $256\pi^2(I_1 + 1.5I_2)^2/R^8/C$ and $2304\pi^2I_2^2/R^8/C$ for the states tied to the L and X minima, respectively. One may then see that if $I_1 > 4.5I_2$ and $I_1 > 1.5I_2$ for the states from L and X , respectively, P_1 for the interaction with the Jahn-Teller mode is greater than P_1 for the breathing mode. In this case for positive I_1 and I_2 (the local pseudopotentials of the lattice ions are repulsive for electrons) the A_1 state originated from T_2 is bistable and becomes the ground one when the electron is trapped by the lattice distortion. The A_1 state which was the ground state without the interaction with the lattice due to the smaller

TABLE I. The electron-lattice interaction energy and coupling constants P_1 for A_1 and T_2 donor states pinned to L and X of conduction band. The integrals I_1 and I_2 and Θ are defined by Eq. (27).

Minimum	State	Electron lattice interaction		Energy	P_1
		Energy	Splitting		
L	A_1	$(I_1 + 1.5I_2)\Theta/N$		$\frac{(I_1 + 1.5I_2)\Theta}{N(A_1(L))}$	$\frac{64\pi^2(I_1 + 1.5I_2)^2}{R^8C}$
	T_2	$(I_1 - 0.5I_2)\Theta/N$	$\begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}$	E	O
X	A_1	$3I_2\Theta/N$		$\frac{3I_2\Theta}{N(A_1(X))}$	$\frac{64\pi^2(3I_1 - 1.5I_2)^2}{R^8C}$ $\frac{576\pi^2I_2^2}{R^8C}$
	T_2	$(2I_1 - I_2)\Theta/N$	$\begin{pmatrix} 1 & 1 & -1 \\ 1 & 1 & -1 \\ -1 & -1 & 1 \end{pmatrix}$	E	O
				A_1	$\frac{256\pi^2(3I_1 - 1.5I_2)^2}{R^8C}$

values of P_1 is the "normal" state and becomes excited for the distorted system. In general the bistability of the state depends also on the values of B and g_l . This problem will be discussed in the next section for the case of donors in GaAs.

V. BISTABLE DONORS IN GaAs

In this section I would like to present some quantitative results obtained in the framework of the model. Let us focus on the donor centers in GaAs. As was shown, the type of the electron-lattice interaction depends on the constant P_1 and electron energy parameters B and g_l (see Fig. 4). To obtain P_1 I have calculated the integrals I_1 and I_2 using the symmetric local part of pseudopotentials given by Bachelet *et al.*³³ The elastic constant was calculated from the longitudinal-optical phonon energy [285 cm^{-1} (Ref. 34)]. I have obtained the following values of I_1 and I_2 : $I_1=17.8$ and $I_2=2.1$ a.u. and $I_1=33.8$ and $I_2=4.1$ a.u. for donors in Ga and As position, respectively. According to the conclusions of the preceding section these values suggest that the bistability of the centers is connected rather with the Jahn-Teller distortion than with the breathing distortion. It is known that the substitutional donors of the IV and VI groups give the additional localized shallow states tied to Γ , L , and X minima of the conduction band. Due to very small effective mass for the Γ point we may consider further only the L and X minima. According to group theory the fourfold degenerated state under the L minimum splits into the symmetric A_1 state and threefold degenerated T_2 state. The situation for the X minimum is more complicated. For compound semiconductors the conduction band in X point of the Brillouin zone is split into X_1 and X_3 bands. It was found³⁵ that the symmetry of donor states tied to the specified bands depends on whether an impurity substitutes anion or cation. Thus for a donor substituting As ion the electron wave function in the lower band belongs to an X_1 representation and in the upper to an X_3 representation, and for a donor in the Ga sublattice the symmetry of the proper wave function is X_1 in the upper and X_3 in the lower band. For T_d symmetry group X_1 representation reduces to the A_1 and E irreducible representations and X_3 transforms as T_2 irreducible representation. Thus considering the defect bistability for the donors substituting Ga one should take into account the T_2 state tied to X and L minima. Using the data from Table I it is easy to find that P_1 for the state tied to lower X minimum is greater than P_1 for L . This suggests that the greatest contribution to the electron wave function defined by (22)–(24) comes from the summation on the X minima of the conduction band. Omitting the other ones, one may use the band parameter from X minimum to obtain the electronic energy ε_e of the system. Taking it into account one may obtain the CC diagram describing the bistability of Ga substitutional donor center [see Fig. 5(a)]. To calculate this diagram I have used B and g_l obtained from (14) and (15) with effective mass $m=0.8$, high-frequency dielectric constant $\varepsilon_\infty=10$, and the impurity nearest-neighbor distance $R=4.61$ a.u. I have used $m=0.8$, which is the reasonable value for X minimum, to fit the

model to the energy of the metastable state of DX center with respect to Γ minimum for Si-doped GaAs–0.17 eV, the value obtained by Thesis *et al.*¹³ The energy of electron-electron interaction for the doubly occupied state ($2e$) was calculated including only the Coulomb repulsion between the electrons. It was found that due to the Jahn-Teller distortion the T_2 electron state splits into A_1 and E states and when the center captured an additional electron on the A_1 state the system lowered its en-

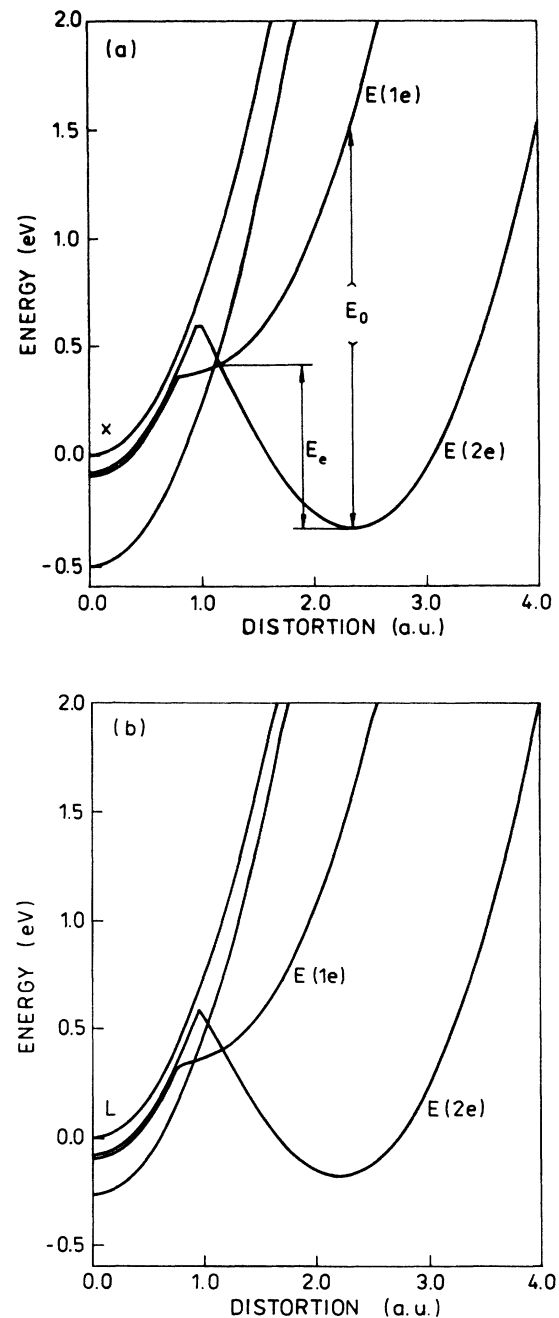


FIG. 5. Configurational-coordinate diagram for donor substituted Ga (a) and As (b) lattice ions in GaAs. Curves denoted as $E(1e)$ and $E(2e)$ correspond to $A_1(T_2)$ state occupied by one and two electrons, respectively.

ergy due to the lattice relaxation. Thus the doubly occupied A_1 state is bistable [curve $E(2e)$]. When the center bound only one electron [curve $E(1e)$] both states originated from T_2 are the normal states but the strong unharmonicity for the interaction with the lattice was obtained for the A_1 one. When the center is in metastable negative charge state one electron can be excited to the conduction band. For such a process the obtained activation energy for thermal emission is $E_e = 0.76$ eV and the energy of the optical transition is $E_o = 1.88$ eV. These data are about two times greater than the observed values: 0.33 eV (Refs. 13 and 11) and >0.8 eV.¹¹ It should be mentioned, however, that the fitting may be much better if we introduce an additional parameter ϵ_∞ describing the effective screening of the impurity potential. The similar CC diagram one may obtain for donor substituting As in the lattice [Fig. 5(b)]. In this case the P_1 parameters are much larger due to the large values of the I_1 and I_2 integrals. However, here the states tied to the lower X conduction band have A_1 and E symmetry and therefore do not interact strongly with the lattice. On the other hand, the upper X conduction band is characterized by small effective mass. Thus the trapped electron wave function [(22)–(24)] contains only the contributions from the summation on L equivalent points of the Brillouin zone. To obtain a CC diagram for this case the effective mass $m = 0.84$ was used. It should be mentioned that the values of the effective masses for X and L minima used in the calculations are in qualitative agreement with those obtained from the EMA donor T_2^X and T_2^L state energies: 122 and 70 meV, respectively.³⁶ The CC diagrams presented in Figs. 5(a) and 5(b) are almost identical. Especially in both cases the center is in the metastable state when the ion is displaced about 2.2 a.u. from its lattice position. Also the stable and metastable states are characterized by different charges. One may see that the crossing over the energy surfaces $E(1e)$ and $E(2e)$ yields to diminishing and smoothing of the energy barrier between the stable and metastable states. This explains why the thermal emission energy E_e for the DX center does not depend on Al concentration in $Al_xGa_{1-x}As$ (Ref. 37) and also the independence or very weak dependence of E_e on pressure for DX in GaAs-doped Si and S.³⁸ Unfortunately, this model does not allow one to judge which ion, the impurity or that of the nearest neighbor, is really displaced. However, due to the higher mobility of cations we may predict that in the case of IV and VI group donors the donor and the lattice ion is shifted, respectively. Recently Chadi and Chang³⁹ using the *ab initio* pseudopotential calculations have obtained the energy of DX center formation in GaAs and $Al_xGa_{1-x}As$. They found that (1) DX is a highly localized negative U defect center which appears when the impurity ion and Al or Ga ion for Si and S dopants, respectively, is shifted in (1,1,1) direction from the substitutional to the interstitial position. The displacements were found to be 1.17 and 1.13 Å for Si and the host ion, respectively. (2) Because of the strong instability of the neutral DX the excitation of one of the electrons to the conduction band results in the return of the interstitial

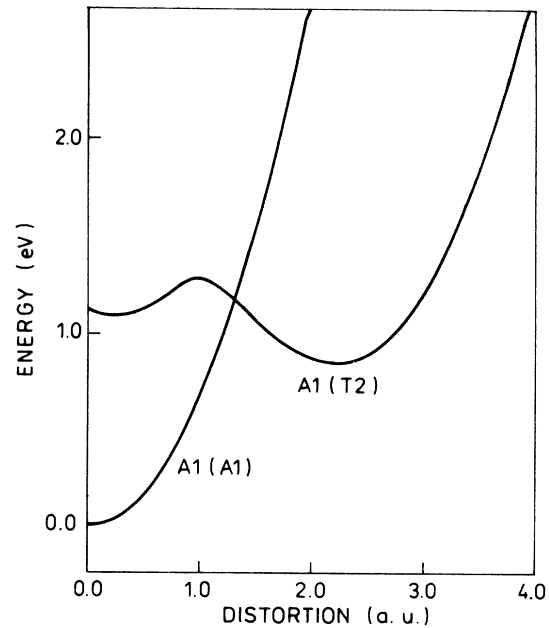


FIG. 6. Configurational-coordinate diagram for As antisite in GaAs. The energy of fundamental A_1 state is taken as zero.

ions to their lattice position and the disappearance of the DX center. One may see that these conclusions are in good agreement with what can be drawn from our CC diagrams.

Finally, let us consider the special case of double donor in Ga position (As antisite). For this case in the same way as for the single donor the strong Jahn-Teller distortion may create the bistability of the electron state. However, here both the stable and metastable states are localized. Using $B = 0.38$ a.u. and $g_l = 2.34$ one may obtain the CC diagram presented in Fig. 6. Here the fitting parameters are the energy barrier between the fundamental $A_1(A_1)$ and metastable $A_1(T_2)$ state (0.34 eV) and the energy of internal optical transition (1.15 eV).⁴⁰ The electron being in the $A_1(A_1)$ ground state almost does not interact with the lattice due to the small electron-lattice interaction energy for the A_1 state. For the excited state of T_2 symmetry the interaction is much stronger. As in the former case this state splits into A_1 and E states due to the interaction with the T_2 lattice distortion and the A_1 is bistable. Both the stable and metastable configurations are accompanied by the Jahn-Teller distortion. The obtained value of small Jahn-Teller relaxation is about 0.05 eV. Because of the fact that the absolute value of the total energy is calculated here independently of the band structure the presented diagram rather pictures the possibility of the bistability of double donors than the physical model. However, it describes well the electronic properties of the $EL2$ center in GaAs. Comparing the presented estimation with the more sophisticated calculations done by Chadi and Chang³⁰ and Dabrowski and Sheffler³¹ one may see that the general conclusions are the same in both cases. Especially the symmetry of the fundamental and metastable state is A_1 , the charges of the center being in fundamental and metasta-

ble state are the same, the small Jahn-Teller effect in the internal optical transition should be observed, and in metastable configuration the As ion is displaced about 2 a.u. in the (1,1,1) direction from the substitutional position.

ACKNOWLEDGMENTS

This work was supported in part by Polish Research Program No. CPBP-01-06.

APPENDIX

To obtain the energy of electron-lattice interaction including the intervalley interaction for the electron being

$$M_{m,n}(\Delta) = \langle \phi_m | dV(\Delta) | \phi_n \rangle \\ = 0.25 \sum_{j,j',s} \alpha_{m,j} \alpha_{n,j'} \int \varphi^2(\mathbf{r}) \exp[i(\mathbf{K}_j - \mathbf{K}_{j'}) \cdot \mathbf{r}] [V(\mathbf{r} - \mathbf{R}_s - \Delta_s) - V(\mathbf{r} - \mathbf{R}_s)] d\mathbf{r} \quad (\text{A2})$$

where \mathbf{R}_s and Δ_s are the impurity-sth-nearest-neighbor-ion distance and displacement, respectively. Using the linear approximation and applying transformations similar to those in Sec. II one obtains

$$M_{m,n} = 0.25 \sum_{j,j',s} \alpha_{m,j} \alpha_{n,j'} \int V(\mathbf{r}) \exp[i(\mathbf{K}_j - \mathbf{K}_{j'}) \cdot \mathbf{R}_s] \exp[i(\mathbf{K}_j - \mathbf{K}_{j'}) \cdot \mathbf{r}] [\text{grad}\varphi^2 \cdot \Delta_s + i(\mathbf{K}_j - \mathbf{K}_{j'}) \cdot \Delta_s \varphi^2] d\mathbf{r} \quad (\text{A3})$$

When one takes into account only the short-range ion pseudopotentials the exponent $\exp[i(\mathbf{K}_j - \mathbf{K}_{j'}) \cdot \mathbf{r}]$ can be linearized and the real part of (A3) is

$$M_{m,n} = 0.25 \sum_{j,j',s} \alpha_{m,j} \alpha_{n,j'} \exp[i(\mathbf{K}_j - \mathbf{K}_{j'}) \cdot \mathbf{R}_s] \\ \times \left[\int V(\mathbf{r}) d\mathbf{r} [\text{grad}\varphi^2(\mathbf{r})]_{\mathbf{r}=\mathbf{R}_s} \cdot \Delta_s - (\mathbf{K}_j - \mathbf{K}_{j'}) \cdot \Delta_s \int (\mathbf{K}_j - \mathbf{K}_{j'}) \cdot \mathbf{r} V(\mathbf{r}) \varphi^2(\mathbf{r} + \mathbf{R}_s) d\mathbf{r} \right] \quad (\text{A4})$$

Using only the symmetric potentials of the ions after some algebra one obtains

$$M_{m,n} = 0.25 \sum_{j,j',s} \alpha_{m,j} \alpha_{n,j'} \exp[i(\mathbf{K}_j - \mathbf{K}_{j'}) \cdot \mathbf{R}_s] \left[\int V(\mathbf{r}) d\mathbf{r} - \frac{[(\mathbf{K}_j - \mathbf{K}_{j'}) \cdot \mathbf{R}_s]^2}{3R_s^2} \int V(\mathbf{r}) r^2 d\mathbf{r} \right] [\text{grad}\varphi^2(\mathbf{r})]_{\mathbf{r}=\mathbf{R}_s} \cdot \Delta_s \quad (\text{A5})$$

After the summation over j , j' , and s one obtains the electron-phonon interaction energy matrix elements given in Table I.

in the A_1 or T_2 state one may use the electron wave function whose components can be given in r space as a linear combination of Gaussian functions centered in k space on the L or X points of the Brillouin zone. Thus the m th component of the function is given by

$$\phi_m = \sum_j \alpha_{m,j} \exp(i\mathbf{K}_j \cdot \mathbf{r}) \varphi(\mathbf{r}) \quad (\text{A1})$$

where φ is defined by (9) and the coefficients $\alpha_{m,j}$ are given by (25). The vectors \mathbf{K}_j correspond to the four equivalent L points and six X points of the Brillouin zone. The matrix element describing the electron-lattice interaction may be given as follows:

¹See, for review, A. Chantre, *Appl. Phys. A* **48**, 3 (1989).

²See, for review, G. M. Martin and S. Markman-Ebid, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 399.

³J. M. Langer, *Radiat. Eff.* **72**, 55 (1983); J. E. Dmowski, W. Jantsch, D. Dobosz, and J. M. Langer, *Acta Phys. Pol. A* **73**, 247 (1988).

⁴M. Baj, L. Dmowski, M. Kończykowski, and S. Porowski, *Phys. Status Solidi A* **33**, 421 (1976); M. Baj, Ph.D. thesis, Warsaw University, 1979.

⁵See, for review, P. Bhattacharya, *Semicond. Sci. Technol.* **3**, 1145 (1988); D. W. Lang, in *Deep Centers in Semiconductors*, Ref. 2, p. 486.

⁶R. A. Caren and D. J. Finn, *J. Appl. Phys.* **50**, 6334 (1979).

⁷L. Koncewicz, E. Litwin-Staszewska, S. Porowski, A. Iller, R. L. Aulombard, J. L. Robert, and A. Joulie, *Physica B+C* (Amsterdam) **117B&118B**, 92 (1983).

⁸O. Kumagai, H. Kawai, Y. Mori, and K. Kaneko, *Appl. Phys. Lett.* **45**, 1322 (1984).

⁹M. Tachikawa, T. Fujisawa, H. Kukimoto, A. Shibata, G. Oomi, and S. Minomura, *Jpn. J. Appl. Phys. Pt. 2* **24**, L893 (1985); N. T. Theis, B. D. Parker, P. M. Solomon, and S. L. Wright, *Appl. Phys. Lett.* **49**, 1542 (1986); D. K. Maude, J. C. Portal, L. Dmowski, T. Foster, L. Eaves, M. Nathan, M. Heiblum, J. J. Harris, and R. P. Beall, *Phys. Rev. Lett.* **59**, 815 (1987).

¹⁰K. L. I. Kobayashi, Y. Uschida, and H. Nakaschima, *Jpn. J. Appl. Phys. Pt. 2* **24**, L928 (1985).

¹¹P. M. Mooney, G. A. Northrop, T. N. Morgan, and H. G. Grimmeiss, *Phys. Rev. B* **37**, 8298 (1988).

¹²T. N. Morgan, *Phys. Rev. B* **34**, 2664 (1986).

¹³T. N. Theis, P. M. Mooney, and S. L. Wright, *Phys. Rev. Lett.* **60**, 361 (1988).

¹⁴D. J. Chadi and K. J. Chang, *Phys. Rev. Lett.* **61**, 873 (1988).

¹⁵J. C. M. Henning and J. P. M. Ansems, *Appl. Phys. A* **44**, 245 (1987); *Semicond. Sci. Technol.* **2**, 1 (1987).

¹⁶J. C. M. Henning, J. P. M. Ansems, and P. J. Roksnor, *Semicond. Sci. Technol.* **3**, 631 (1988).

- ¹⁷E. A. Montie and J. C. M. Henning, *J. Phys. C* **21**, L311 (1988).
- ¹⁸D. Emin and T. Holstein, *Phys. Rev. Lett.* **36**, 323 (1976).
- ¹⁹Y. Toyozawa, *Physica B+C (Amsterdam)* **116B**, 7 (1983).
- ²⁰M. Grinberg, *Phys. Rev. B* **39**, 8443 (1989).
- ²¹Y. Toyozawa, *Physica B+C (Amsterdam)* **117B&118B**, 23 (1983).
- ²²See, for example, D. M. Struge, in Vol. 20 of *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1967), p. 92.
- ²³D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **7**, 692 (1973).
- ²⁴J. C. Bourgoin and A. Mauger, *Appl. Phys. Lett.* **53**, 749 (1988).
- ²⁵S. Porowski and W. Trzeciakowski, *Phys. Status Solidi B* **128**, 11 (1985).
- ²⁶S. Porowski, in *Proceedings of the International Conference on High Pressure Science and Technology*, Ref. 38.
- ²⁷P. W. Anderson, *Phys. Rev. Lett.* **34**, 953 (1975).
- ²⁸N. O. Lipari, J. Bernholc, and S. T. Pantelides, *Phys. Rev. Lett.* **43**, 1354 (1979); G. A. Baraff, E. O. Kane, and M. Schlüter, *ibid.* **43**, 956 (1979); R. D. Harris, J. L. Newton, and G. Watkins, *ibid.* **48**, 1271 (1982).
- ²⁹A. Oshiyama and S. Ohnishi, *Phys. Rev. B* **33**, 4320 (1986).
- ³⁰D. J. Chadi and K. J. Chang, *Phys. Rev. Lett.* **60**, 873 (1988).
- ³¹J. Dabrowski and M. Sheffler, *Phys. Rev. Lett.* **60**, 2183 (1988).
- ³²W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 257.
- ³³G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982).
- ³⁴G. Dolling and J. L. T. Waugh, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, Oxford, 1965), p. 19.
- ³⁵T. N. Morgan, *Phys. Rev. Lett.* **21**, 819 (1968).
- ³⁶J. C. M. Henning, in *DX Center in III-VI Ternary Compound*, edited by J. C. Bourgoin (Trans Tech, Aedermannsdorf, Switzerland, in press).
- ³⁷P. M. Mooney, E. Calleja, S. L. Wright, and M. Heiblum, in *Defect Semiconductors*, edited by H. J. von Bardeleben (Trans Tech, Aedermannsdorf, Switzerland, 1986), p. 417.
- ³⁸P. Wisniewski, R. Piotrkowski, and T. Suski, in *Proceedings of the International Conference on High Pressure Science and Technology, Paderborn, 17-21 July 1989* (in press).
- ³⁹D. J. Chadi and K. J. Chang, *Phys. Rev. B* **39**, 10063 (1989).
- ⁴⁰W. Kuszko, P. J. Walczak, P. Trautman, M. Kaminska, and J. M. Baranowski, in *Defect Semiconductors*, Ref. 37, p. 317.