

Metastability and lattice relaxation for D^0 and D^- donor centers

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Properties of strongly localized one-electron (D^0) and two-electron (D^-) donor centers in semiconducting compounds are studied with the help of the theoretical approach, which takes into account the influence of the conduction-band states and interactions with LA and LO phonons. The eigenvalue problem has been solved for the ground states of both the centers by the variational method in the wave-vector space. The description is given of the properties of the D^0 and D^- donor centers in GaAs under hydrostatic pressure. The calculated energy levels and pressure coefficients agree with the experimental results. Upper and lower bounds have been obtained for probabilities of radiative transitions from the extended electron states to the strongly localized D^- donor states. A large reduction received for these transition probabilities has been interpreted in terms of metastability of the donor centers. It is shown that the metastable behavior of donor centers results from a large difference in a lattice deformation around the center, which occurs between the states of different electron localization. It is found that the D^- center at the substitutional position in GaAs exhibits the properties that are characteristic for the DX center. The phonon representation of lattice vibrations has been applied to calculate the displacements from equilibrium positions of the ions surrounding the donor centers of different charge and localization. The results show that—even for the strongly localized donor state—the surrounding-lattice deformation encompasses a large number of ions. The number of ions that essentially contribute to the lattice relaxation energy is estimated to be several thousand. The present work takes into account the long-range component of the lattice deformation induced by the presence of the impurity in a crystal.

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I. INTRODUCTION

Experimental¹⁻⁶ and theoretical⁷⁻¹⁰ studies of donor centers in compound semiconductors have led to an identification of four types of donor states created on the same impurity atom at the substitutional site. These are the neutral (one-electron) donor centers of strong (D^0) and weak (d^0) electron localization and the negatively charged (two-electron) donor centers of strong (D^-) and weak (d^-) electron localization. For the strongly localized donor states (D^0 and D^-), the electron envelope wave function is confined within the unit cell, in which the impurity center is located, i.e., its Fourier transform is spread over the entire Brillouin zone. For the weakly localized states (d^0 and d^-), the envelope function is spread over many unit cells around the impurity atom, i.e., its Fourier transform is localized in the Brillouin zone near the \mathbf{k} point, which corresponds to a conduction-band minimum. The strongly localized donor states are created by the short-range component of the impurity-center potential, which mainly results from the difference in the atomic cores of the impurity and host crystal atoms. The weakly localized donor states result from an action of the long-range (Coulomb) component of the impurity-center potential, which arises due to the different nucleus charges of the impurity and host crystal atoms. The donor states of weak electron localization can be described by the effective-mass approximation. In III-V compounds, they can be treated as solid-state analogs of hydrogen atoms and ions with the properties slightly modified by the electron-phonon coupling. In II-VI and other more ionic compounds, the modification of the properties of the donor centers by the electron-LO phonon interaction becomes es-

sential and the weakly localized centers are described by the bound-polaron model.^{11,12} New physics is connected with the unusual properties of strongly localized donor centers. For the neutral donor centers, the anomalous anticrossing between energy levels [GaAs (Ref. 1), InSb (Ref. 13)] and metastability [CdF₂ (Ref. 2)] have been found. The negatively charged donor centers are responsible for the unusual DX -like properties observed in GaAs,^{4,5} Al_xGa_{1-x}As,¹⁴ CdTe,¹⁵ and Cd_xMn_{1-x}Te.¹⁶ The metastable occupation of the donor centers by the electrons has recently found new applications in a holographic recording, which was performed with CdF₂ (Ref. 17) crystals and Al_xGa_{1-x}As (Ref. 18) alloys.

The metastable behavior was observed for DX centers in GaAs (Refs. 4 and 5) under high hydrostatic pressure. The coexistence of the DX center with nonmetastable strongly localized donor centers D^0 has been found for Ge donors in GaAs (Ref. 19) and Si donors in Al_xGa_{1-x}As.²⁰ The most important characteristics of the DX centers are the large lattice relaxation and negative charge state.^{7,8,21} Among many models proposed in order to explain the behavior of the DX center, the following two models are of the subject of our interest. The first model proposed by Chadi and Chang^{7,21} is based on the bond-breaking mechanism, according to which the chemical bonding between the donor and host-lattice atoms is broken and the donor moves into the interstitial position leaving the vacancy. The stability of such a vacancy-interstitial configuration is achieved by the binding of two electrons on the donor center. The second model proposed by Chadi²² assumes the substitutional position of the donor center, which binds two electrons. The large lattice relaxation of breathing-mode type, which surrounds the center, is

responsible for their metastable behavior. In both the models, the formation of negatively charged two-electron centers is involved in either interstitial^{17,21} or substitutional position.²²

However, none of the existing models of the DX center describes—within the same formalism—the donor states of weak electron localization, i.e., d^0 and d^- centers, for which the effective-mass approximation has to be applied. Usually, the weakly and strongly localized donor states are treated by the different approaches. After the experimental observation^{3–5,19} of the coexisting d^0 , D^0 , and D^- donor centers in GaAs, the problem of unified theoretical description^{23–26} of the donor centers of different charge and localization appeared to be important.

For the one-electron (d^0 and D^0) donor centers, we elaborated^{23,24,26} the theoretical method of a description of the states with arbitrary electron localization. This approach allowed us to explain the metastability of donor states in CdF_2 (Ref. 23) and anomalous anticrossing between the donor energy levels in GaAs.^{24,26} We have shown that these properties result from the electron-phonon coupling, whereby in CdF_2 the polar Fröhlich coupling with LO phonons dominates and in GaAs the deformation-potential coupling with LA phonons is of crucial importance. The phonon states corresponding to the weakly and strongly localized one-electron donor centers are different, which leads to the reduction of the probability of radiative transitions between them. If the coupling with phonons is strong enough, as in CdF_2 , the transition probability is very small, which causes the electron states of higher energy to be occupied for a long time; i.e., the extended electron states are metastable with respect to the D^0 state of the lower energy. This result is in agreement with the observed metastable behavior of the In donor in CdF_2 .² We suggested^{26,27} that the mechanism of the metastability of the DX centers in GaAs is similar to that responsible for the metastable behavior of the D^0 donor centers.²³ The essence of this mechanism relies on the different lattice deformations between the donor states of different localization. The present paper provides the full proof of this hypothesis.

This paper mainly addresses the problem of the donor centers in GaAs. Moreover, the proposed method is also applicable to other materials. The paper is organized as follows. In Sec. II, we present the theory of D^- donor centers, which is a generalization of our approach²⁶ for D^0 donor centers. The results for the energy levels, pressure coefficients, and transition probabilities are presented in Sec. III. In Sec. IV, we describe our proposition for a description of a lattice deformation around the donor center in the frame of the phonon representation of lattice vibrations and present the results of calculations. Section VI includes the discussion of the results and Sec. VII is conclusions.

II. THEORY OF D^- DONOR CENTERS

We start with the Hamiltonian of the two-electron donor center, which interacts with LA and LO phonons,

$$H = H_0 + H_{\text{el-el}} + H_{\text{el-ph}} + H_{\text{el-d}} + H_{\text{d-ph}}. \quad (1)$$

In Eq. (1), the first term is the Hamiltonian of noninteracting electrons and phonons and has the form²⁶

$$H_0 = \sum_{\mathbf{k}\sigma} E_{\mathbf{k}}^c b_{\mathbf{k}\sigma}^\dagger b_{\mathbf{k}\sigma} + \sum_{\mathbf{q}\nu} \hbar \omega_{\mathbf{q}\nu} a_{\mathbf{q}\nu}^\dagger a_{\mathbf{q}\nu}, \quad (2)$$

where $b_{\mathbf{k}\sigma}^\dagger$ ($b_{\mathbf{k}\sigma}$) is the creation (annihilation) operator of the conduction-band Bloch state of the electron with the energy $E_{\mathbf{k}}^c$, wave vector \mathbf{k} , and spin σ (we denote by \uparrow and \downarrow the states with spin-up and spin-down, respectively), $a_{\mathbf{q}\nu}^\dagger$ ($a_{\mathbf{q}\nu}$) is the creation (annihilation) operator of the phonon state with the energy $\hbar \omega_{\mathbf{q}\nu}$, wave vector \mathbf{q} , and branch index ν , where $\nu = \text{LA}$ and LO for longitudinal acoustic and longitudinal optical phonons, respectively. The second through the fifth terms in Eq. (1) are the Hamiltonians describing the interactions between the electrons,

$$H_{\text{el-el}} = \sum_{\mathbf{k}\mathbf{k}'\mathbf{q}\sigma\sigma'} U_{\mathbf{q}} b_{\mathbf{k}+\mathbf{q}\sigma}^\dagger b_{\mathbf{k}'-\mathbf{q}\sigma'}^\dagger b_{\mathbf{k}'\sigma'} b_{\mathbf{k}\sigma}, \quad (3)$$

electrons and phonons,

$$H_{\text{el-ph}} = \sum_{\mathbf{k}\mathbf{q}\sigma\nu} (F_{\mathbf{q}\nu} a_{\mathbf{q}\nu} b_{\mathbf{k}+\mathbf{q}\sigma}^\dagger b_{\mathbf{k}\sigma} + \text{H.c.}), \quad (4)$$

electrons and the donor center,

$$H_{\text{el-d}} = \sum_{\mathbf{k}\mathbf{k}'\sigma} V_{\mathbf{k}\mathbf{k}'} b_{\mathbf{k}\sigma}^\dagger b_{\mathbf{k}'\sigma}, \quad (5)$$

and phonons and the donor center,

$$H_{\text{d-ph}} = \sum_{\mathbf{q}\nu} (W_{\mathbf{q}\nu} a_{\mathbf{q}\nu} + \text{H.c.}). \quad (6)$$

The electron-electron interaction [Eq. (3)] is assumed to be the Coulomb interaction screened by the high-frequency dielectric constant ϵ_∞ , i.e.,

$$U_{\mathbf{q}} = U_{\mathbf{q}}^0 / \epsilon_\infty, \quad (7)$$

where

$$U_{\mathbf{q}}^0 = 4\pi e^2 / \Omega q^2 \quad (8)$$

is the potential energy of the bare Coulomb interaction in the wave-vector space and Ω is the crystal volume. In Eq. (5), $V_{\mathbf{k}\mathbf{k}'} = V_{\mathbf{k}-\mathbf{k}'}^C + V_{\mathbf{k}\mathbf{k}'}^S$ is the matrix element of the potential energy of the electron in the donor-center field, which consists of the long-range (Coulomb) component

$$V_{\mathbf{k}-\mathbf{k}'}^C = -U_{\mathbf{k}-\mathbf{k}'}^0 / \epsilon_\infty \quad (9)$$

and short-range (“central-cell”) component: $V_{\mathbf{k}\mathbf{k}'}^S$. In Eqs. (4) and (6), $F_{\mathbf{q}\nu}$ and $W_{\mathbf{q}\nu}$ are the electron-phonon and donor-phonon interaction amplitudes, respectively. We assume the deformation-potential interaction for LA phonons and polar Fröhlich interaction for LO phonons.²⁶

The separation of the donor-phonon interaction is the first step of calculations. This is done with the help of the Platzman transformation²⁸

$$U_p = \exp \left[\sum_{\mathbf{q}\nu} (-W_{\mathbf{q}\nu}^* / \hbar \omega_{\mathbf{q}\nu}) a_{\mathbf{q}\nu}^\dagger - \text{H.c.} \right], \quad (10)$$

which transforms Hamiltonian (1) into

$$\bar{H} = H_0 + H_{\text{el-el}} + H_{\text{el-ph}} + \bar{H}_{\text{el-d}} + \Sigma_d. \quad (11)$$

The Platzman transformation generates the constant self-energy term

$$\Sigma_d = - \sum_{\mathbf{q}\nu} |W_{\mathbf{q}\nu}|^2 / \hbar \omega_{\mathbf{q}\nu}, \quad (12)$$

which can be interpreted as the energy of the static lattice deformation around the ionized, i.e., positively charged, donor center. This constant term in Hamiltonian (11) shifts all the electronic energy levels by the same value, which is large in comparison with the donor binding energy, e.g., for GaAs, the contribution of LA phonons to Σ_d is estimated to be 600 meV, and that of LO phonons ≈ 80 meV, while the donor Rydberg is ≈ 5 meV. Throughout this paper, we discuss the relative energy separations; therefore, we neglect Σ_d , which is independent of the electron state. However, this term plays an important role in a treatment of the total energy of the system.

Transformation (10) also changes the electron-donor interaction. The new electron-donor potential can be split into two components,²⁶

$$\bar{V}_{\mathbf{k}\mathbf{k}'} = \bar{V}_{\mathbf{k}-\mathbf{k}'}^C + \bar{V}_{\mathbf{k}\mathbf{k}'}^S. \quad (13)$$

The short-range component $\bar{V}_{\mathbf{k}\mathbf{k}'}^S$ contains the previously introduced ‘‘central-cell’’ potential and short-range potential resulting from the coupling with LA phonons.²⁶ We approximate $\bar{V}_{\mathbf{k}\mathbf{k}'}^S$ by a constant in the wave-vector space.²⁶ The long-range component takes on the form of the Coulomb potential screened by the static dielectric constant, i.e.,

$$\bar{V}_{\mathbf{q}}^C = -U_{\mathbf{q}}^0 / \epsilon_0. \quad (14)$$

The result of the Platzman transformation [cf. Eqs. (1) and (11)] possesses the following physical interpretation. Before this transformation, the long-range component ($V_{\mathbf{k}-\mathbf{k}'}^C$) of the donor potential in Eq. (5) is the Coulomb potential screened by the high-frequency dielectric constant ϵ_∞ , [Eq. (9)] i.e., by the valence electrons. The additional screening of this interaction appears as the result of the polar coupling with LO phonons and is manifested as the change of the dielectric constant, i.e., $\epsilon_\infty \rightarrow \epsilon_0$. However, this additional screening does not occur in the electron-electron interaction, since transformation (10) is independent of the electronic coordinates. The phonon-mediated screening of the electron-electron interaction will result from further calculations. This remark is important because in some papers^{29–31} on the D^- center the screening of the electron-electron interaction by the static dielectric constant was introduced already in the starting Hamiltonian, in which the electron-phonon coupling was additionally taken into account. Such a treatment twice takes into account the corresponding correction to the interaction. This problem was correctly treated in Refs. 12 and 32.

We solve the eigenvalue problem for the ground state of the system described by Hamiltonian (11) by the variational method. For the one-electron donor states, we apply the trial state vectors²⁶

$$|\Psi^0\rangle = \sum_{\mathbf{k}} \varphi_{\mathbf{k}}^0 b_{\mathbf{k}\uparrow}^\dagger |0\rangle_{\text{el}} |\chi^0\rangle, \quad (15)$$

and—for the two-electron singlet states—we propose the following trial state:

$$|\Psi^-\rangle = \sum_{\mathbf{k}\mathbf{k}'} \varphi_{\mathbf{k}\uparrow}^- \varphi_{\mathbf{k}'\downarrow}^- b_{\mathbf{k}\uparrow}^\dagger b_{\mathbf{k}'\downarrow}^\dagger |0\rangle_{\text{el}} |\chi^-\rangle. \quad (16)$$

In Eqs. (15) and (16), $|0\rangle_{\text{el}}$ denotes the electron vacuum state, which corresponds to an empty conduction band and fully occupied valence band. Eq. (16) corresponds to the Hartree-Fock approximation, according to which the electron-electron correlation is neglected.

The phonon states, which are associated with the donor charge states α , are taken on in the form

$$|\chi^\alpha\rangle = \exp\left(\sum_{\mathbf{q}\nu} g_{\mathbf{q}\nu}^\alpha a_{\mathbf{q}\nu}^\dagger - \text{H.c.}\right) |0\rangle_{\text{ph}}, \quad (17)$$

where we label the neutral and negatively charged donor by $\alpha = 0, -$, respectively, and $|0\rangle_{\text{ph}}$ is the phonon vacuum state. In Eqs. (15) and (16), the sums run over the first Brillouin zone. In order to perform the calculations, we replace these summations by the integrations over the Debye sphere.^{24,26} The functions $\varphi_{\mathbf{k}\sigma}^\alpha$ are the electron wave functions in the wave vector space. They are proposed in the form^{24,26}

$$\varphi_{\mathbf{k}}^\alpha = \frac{N_\alpha}{(k^2 + \lambda_\alpha^2)^2}, \quad (18)$$

where N_α are the normalization constants and λ_α are the variational parameters. If we performed the integration over the infinite wave vector space, we would become the Fourier transform of Eq. (18), which is proportional to the exponential function: $\exp(-\lambda_\alpha r)$. Therefore, the variational parameter λ_α can be interpreted as a measure of a localization of the electron at the donor center in the state α .

The phonon amplitudes $g_{\mathbf{q}\nu}^\alpha$ are obtained from the minimization of the expectation value of Hamiltonian (11) in the corresponding state, i.e.,

$$\frac{\delta E^\alpha}{\delta g_{\mathbf{q}\nu}^{\alpha*}} = 0, \quad (19)$$

which for the D^0 center yields

$$g_{\mathbf{q}\nu}^0 = -(F_{\mathbf{q}\nu}^* / \hbar \omega_{\mathbf{q}\nu}) \rho_{\mathbf{q}\sigma}^0 \quad (20)$$

and for the D^- center –

$$g_{\mathbf{q}\sigma}^- = -(F_{\mathbf{q}\nu}^* / \hbar \omega_{\mathbf{q}\nu}) (\rho_{\mathbf{q}\uparrow}^- + \rho_{\mathbf{q}\downarrow}^-), \quad (21)$$

where the one-electron probability densities are given by

$$\rho_{\mathbf{q}\sigma}^\alpha = \sum_{\mathbf{k}} \varphi_{\mathbf{k}\sigma}^{\alpha*} \varphi_{\mathbf{k}+\mathbf{q}\sigma}^\alpha. \quad (22)$$

For the ground state of the D^- center, we obtain the following variational estimate of the electronic energy:

$$E^- = 2T^0 + 2V^0 + V_{12} + W, \quad (23)$$

where the expectation values of the conduction-band energy T^0 and electron-donor center potential energy V^0 are calculated in the same manner as for the D^0 center.²⁶ The third term in Eq. (23) corresponds to the electron-electron interaction and has the form

$$V_{12} = \sum_{\mathbf{q}} U_{\mathbf{q}} \rho_{\mathbf{q}\uparrow}^- \rho_{\mathbf{q}\downarrow}^-, \quad (24)$$

and the last term is given by

$$\begin{aligned} W &= W_{\uparrow}^0 + W_{\downarrow}^0 + W_{12} \\ &= - \sum_{\mathbf{q}\nu} (|F_{\mathbf{q}\nu}|^2 / \hbar \omega_{\mathbf{q}\nu}) [(\rho_{\mathbf{q}\uparrow}^-)^2 + (\rho_{\mathbf{q}\downarrow}^-)^2 + 2\rho_{\mathbf{q}\uparrow}^- \rho_{\mathbf{q}\downarrow}^-]. \end{aligned} \quad (25)$$

In Eq. (25), we can separate out the corrections to the energy of the electron in the D^0 states (W_{\uparrow}^0 and W_{\downarrow}^0) and the phonon-mediated contribution to the electron-electron interaction (W_{12}). The contribution of LO phonons to W_{12} yields the correction to the interelectron interaction in the form of the Coulomb potential, which is screened by the effective dielectric constant ε^* , where $1/\varepsilon^* = 1/\varepsilon_{\infty} - 1/\varepsilon_0$. This results from the following calculation:

$$2 \frac{|F_{\mathbf{q}LO}|^2}{\hbar \omega_{\mathbf{q}LO}} = \frac{4\pi e^2}{\varepsilon^* \Omega q^2} = \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right) U_{\mathbf{q}}^0. \quad (26)$$

Substituting the expressions (25) and (26) into Eq. (23) and introducing the ground-state energy of D^0 center: $E^0 = T^0 + V^0 + W_{\uparrow}^0$, which is calculated according to Ref. 26, we obtain

$$E^- = 2E^0 + \bar{V}_{12} - 2 \sum_{\mathbf{q}} (|F_{\mathbf{q}LA}|^2 / \hbar \omega_{\mathbf{q}LA}) \rho_{\mathbf{q}\uparrow}^- \rho_{\mathbf{q}\downarrow}^-, \quad (27)$$

where the effective screened electron-electron interaction takes the form

$$\bar{V}_{12} = V_{12} + W_{12} = \frac{1}{\varepsilon_0} \sum_{\mathbf{q}} U_{\mathbf{q}}^0 \rho_{\mathbf{q}\uparrow}^- \rho_{\mathbf{q}\downarrow}^-. \quad (28)$$

Let us notice that the electron-electron interaction is screened by the static dielectric constant ε_0 and this screening appeared just at this stage of calculus. The last term in Eq. (27) describes the short-range attractive electron-electron potential, which results from the exchange of virtual LA phonons.

III. ENERGY LEVELS AND OPTICAL TRANSITIONS

The approach presented in Sec. II has been applied to the calculation of energy levels of the donor centers in GaAs as functions of the hydrostatic pressure (Fig. 1). The analytic form of the conduction band and the electron-phonon interaction amplitudes are taken on according to Ref. 26. The energy level associated with the ground state of the weakly localized d^0 center lies slightly below the Γ conduction-band minimum and follows its pressure change. At the ambient pressure, the separation between the Γ minimum and d^0 ground-state energy level is about one donor Rydberg, i.e., ≈ 5 meV. The ground-state energy level of the weakly local-

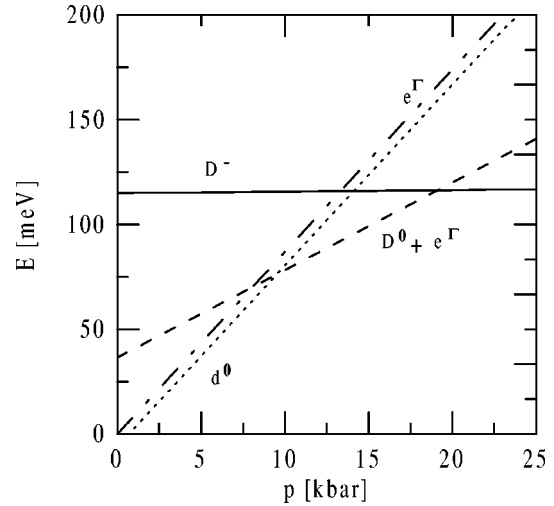


FIG. 1. Calculated ground-state energy per one electron for the D^- (solid curve) and d^0 (dotted curve) Ge-donor centers in GaAs as functions of hydrostatic pressure. Dash-dotted curve shows the energy of the e^Γ electron in the Γ conduction-band minimum and dashed curve shows the sum of the ground-state energy of D^0 center and e^Γ electron.

ized d^- state (not shown in Fig. 1) is located at about 5% of the donor Rydberg below the d^0 level and also follows the pressure evolution of the Γ minimum. The energy levels of the strongly localized donor centers (D^0 and D^-) are almost pressure independent, since the applied hydrostatic pressure possesses a very weak influence on the states with the electron localization within the elementary cell. This property is correctly reproduced by the results of the present calculation. In Fig. 1, the solid curve shows the ground-state energy (E^-) of the D^- state and the dashed curve shows the energy ($E^0 + E^\Gamma$) of the ionized two-electron state, i.e., the system composed of one electron in the strongly localized D^0 state and the second in the Γ conduction-band minimum. One should note that Fig. 1 shows the energy of two-electron states calculated per one electron, i.e., half of the total energy.

The results shown in Fig. 1 have been obtained with the use of one-element trial states [Eqs. (15) and (16)], which provide the variational estimates only for the ground states of the considered donor centers. Therefore, the correct upper bounds are shown by the parts of the curves that correspond to the lowest energy. For the D^0 state, the corresponding range of pressure is $p \geq 9$ kbar, while for the D^- center, the range is $p \geq 19$ kbar. This last interval of pressure results from the condition

$$E^- \leq E^0 + E^\Gamma. \quad (29)$$

For the lower values of pressure, the corresponding curves in Fig. 1 can be treated as the extrapolations. The results of Fig. 1 show that the negatively charged D^- center is the ground state of the system for $p \geq 19$ kbar, which is consistent with the experimental data.¹⁹ We also see that for $p \geq 15$ kbar the following reaction is exothermic:



which means the negative- U behavior of the donor centers.²²

At the ambient pressure, both the strongly localized states D^0 and D^- are resonant with the conduction band (Fig. 1). The corresponding energy levels are located at 75 and 115 meV above the conduction-band minimum. We note that Fig. 1 displays half of the energy for the $(D^0 + e^\Gamma)$ system, for which $E^\Gamma = 0$ at $p = 0$. These calculated values agree with the experimental data (i.e., 66 and 105 meV) for the Ge donor impurity in GaAs.^{4,5} The calculated pressure coefficients (with respect to the conduction-band minimum) are nearly equal to each other for both the centers. The value (-9 meV/kbar) obtained in the present paper also agrees with the experimental results, which are estimated to be -8.6 meV/kbar for the D^0 center^{1,5} and -10 meV/kbar for D^- center.⁵ According to Fig. 1, the D^- energy level enters the gap for $p \approx 13$ kbar, which is consistent with the experiment for Ge donor.¹⁹ The present results have been obtained in the frame of the one-band approximation, which takes into account the nonparabolicity and finite width of the conduction band.²⁶ We neglect the effect of the subsidiary minima at X and L points of the Brillouin zone of GaAs. This is justified by the fact that, in the interval of pressure $p < 25$ kbar, the properties of the considered shallow-level donor centers are insensitive to the X and L conduction-band states because these minima lie high above the Γ minimum ($E^\Gamma = E^X$ only for $p \approx 40$ kbar). The pressure dependence of the parameters of the present model has been discussed in Ref. 26.

In our previous paper,²⁶ we discussed the reduction of the probability of radiative transitions for the D^0 states, which results from the large difference in the lattice deformation between the donor states of different localization. In this paper, we consider the D^- states, for which this difference of the lattice deformation is considerably increased, which results from the fact that the phonon amplitude [Eq. (21)] for the two-electron state is about two times larger than that for the one-electron D^0 state [Eq. (20)]. Therefore, the probability of the dipole-allowed transitions from the weakly localized $2p$ state of the d^0 center to the strongly localized ground state of the D^- center is further reduced. Using the method proposed,²⁶ we have estimated the phonon factor P_{ph} of the transition probability. Figure 2 shows the upper and lower bounds on P_{ph} for GaAs as functions of the energy separation ΔE between the initial state ($2p$ state of the weakly localized d^0 center) and one of the ground states of the strongly localized D^0 and D^- centers. The upper bound allows us to draw conclusions about the appearance of the metastability, while the lower bound allows us to draw conclusions about the disappearance of this effect. Considering the radiative transitions to the ground state of the D^- center, we see that for the small energy separation ΔE the transition probability is reduced by the phonon factor 10^{-17} . The transition probability increases with increasing ΔE and reaches the value 10^{-10} for $\Delta E \approx 120$ meV. A comparison of the results of Figs. 1 and 2 leads to the conclusion that in GaAs the metastability related with the D^- center can occur at the hydrostatic pressure larger than about 15 kbar. The results of Fig. 2 have been obtained under the assumption that the energy of the D^- state is smaller than that of the weakly localized states. Very similar results can be obtained if the extended conduction-band states are the initial states for the considered transitions, since these states have energies and

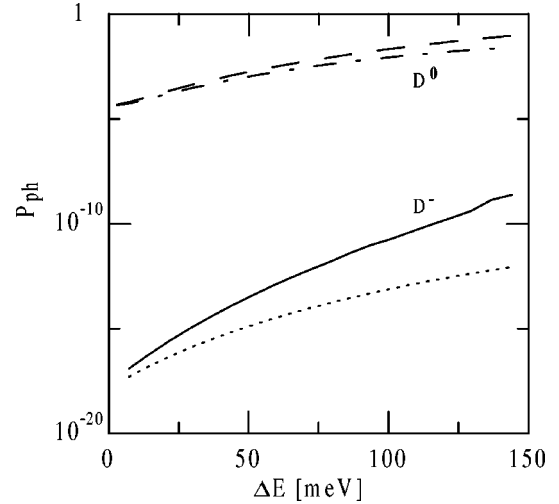


FIG. 2. Phonon factor P_{ph} of the probability of radiative transitions from the initial state ($2p$ state of d^0 center) into the final states (ground states of D^0 and D^- centers) in GaAs as functions of the energy difference ΔE between the initial and final states. Solid (dotted) curve shows the upper (lower) bound on the P_{ph} for the D^- final state, dashed (dash-dotted) curve shows the corresponding bounds for the D^0 final state.

localizations that only slightly differ from those of the weakly localized donor states. This means that the extended electron states of either the conduction band or weakly localized donors are metastable with respect to the strongly localized D^- state of the lower energy. Therefore, the electrons can occupy the extended states for a long time before they are trapped by the donor centers. This provides an explanation of the persistent photoconductivity observed in GaAs under high hydrostatic pressure.³³ Similarly, after occupying the D^- centers by the electrons and reducing the pressure, which results in a shift of the D^- energy level above the conduction-band minimum, the electrons will occupy the D^- state for a long time too. In this case, the D^- states are metastable with respect to the extended electron states.

IV. LATTICE DEFORMATION AROUND DONOR CENTERS

The characteristic properties of D^0 and D^- donor centers mainly result from the different lattice deformation associated with these centers. In Secs. II and III, these deformations were described with the help of phonon states (17), which are dependent on the charge state of the impurity. Having at disposal the phonon states [Eq. (17)], we can transform the lattice vibrations from the phonon representation into the configuration-space representation, which will allow us to obtain displacements of ions from equilibrium positions. We consider the zinc-blende crystal with N elementary cells and lattice vectors \mathbf{R}_n . Each elementary cell consists of the two ions located at $\boldsymbol{\tau}_1 = 0$ and $\boldsymbol{\tau}_2 = (a/4)(1,1,1)$, where a is the lattice constant. We assume that the impurity atom substitutes the ion at the origin of the coordinate system. The operator of the displacement of the host-crystal ion from the equilibrium position $\mathbf{R}_{ns} = \mathbf{R}_n + \boldsymbol{\tau}_s$ is given by

$$\mathbf{u}_{ns} = \sum_{\mathbf{q}\nu} \left(\frac{\hbar}{2NM_s\omega_{\mathbf{q}\nu}} \right)^{1/2} [\mathbf{e}_{\mathbf{q}\nu}^s a_{\mathbf{q}\nu} \exp(i\mathbf{q} \cdot \mathbf{R}_{ns}) + \text{H.c.}], \quad (31)$$

where M_s are the masses of the ions and $\mathbf{e}_{\mathbf{q}\nu}^s$ are the polarization vectors, which are taken on in the long-wavelength forms, i.e.,

$$\mathbf{e}_{\mathbf{q}\text{LA}}^s = i \left(\frac{M_s}{M_1 + M_2} \right)^{1/2} \frac{\mathbf{q}}{|\mathbf{q}|} \exp(i\mathbf{q} \cdot \boldsymbol{\tau}_s) \quad (32)$$

and

$$\mathbf{e}_{\mathbf{q}\text{LO}}^s = (-1)^s \left[\frac{M_1 M_2}{(M_1 + M_2) M_s} \right]^{1/2} \frac{\mathbf{q}}{|\mathbf{q}|} \exp(i\mathbf{q} \cdot \boldsymbol{\tau}_s). \quad (33)$$

In this section, we apply the interaction picture, which is commonly used in the phonon representation of lattice vibrations. This means that the phonon operators explicitly depend on the time, i.e.,

$$da_{\mathbf{q}\nu}/dt = -i\omega_{\mathbf{q}\nu} a_{\mathbf{q}\nu}. \quad (34)$$

Therefore, we can introduce the operator of the velocity of the ion, i.e., $d\mathbf{u}_{ns}/dt$, and calculate the kinetic energy of the ions, which consists of the sum of the following expectation values:

$$\frac{M_s}{2} \left\langle \chi^\alpha \left| \left(\frac{d}{dt} \mathbf{u}_{ns} \right)^2 \right| \chi^\alpha \right\rangle = \frac{1}{4N} \sum_{\mathbf{q}\nu} \hbar \omega_{\mathbf{q}\nu} |\mathbf{e}_{\mathbf{q}\nu}^s|^2. \quad (35)$$

According to Eq. (35), the kinetic energy of the ions is independent of the donor state α , which means that at $T=0$ this energy contributes to the zero-point vibrations only. Therefore, the different energetic contributions for the different donor charge states α originate from the static lattice deformation, i.e., the displacements of the ions from their initial equilibrium positions. We can calculate these displacements as the expectation values of operators (31) in phonon states (17). Since we have taken into account the dominant interactions with the longitudinal phonons, the calculated lattice deformation results from these interactions only. Therefore, the longitudinal displacements of the ions, i.e.,

$$L_{ns}^\alpha = \langle \chi^\alpha | \mathbf{u}_{ns} \cdot \mathbf{R}_{ns} | \chi^\alpha \rangle / |\mathbf{R}_{ns}| \quad (36)$$

correspond to the main contribution to the deformation.

We attach the ionized-donor center d^+ to the present treatment. The lattice deformation around the d^+ center is described by the Platzman transformation [Eq. (10)]. Therefore, the phonon-state vector for the d^+ center has the form

$$|\chi^+\rangle = \mathcal{U}_P |0\rangle_{\text{ph}} \quad (37)$$

and determines the host-crystal ion positions with respect to the ideal-crystal lattice (phonon vacuum state). According to Eq. (10), the phonon amplitudes for the d^+ center are given by

$$g_{\mathbf{q}\nu}^+ = -W_{\mathbf{q}\nu}^* / \hbar \omega_{\mathbf{q}\nu}, \quad (38)$$

i.e., they depend on the amplitudes $W_{\mathbf{q}\nu}$ of the interaction of the donor center with phonons. We assume the following long-wavelength approximation for these amplitudes: $W_{\mathbf{q}\nu} = -F_{\mathbf{q}\nu}$, which allows us to describe correctly the long-

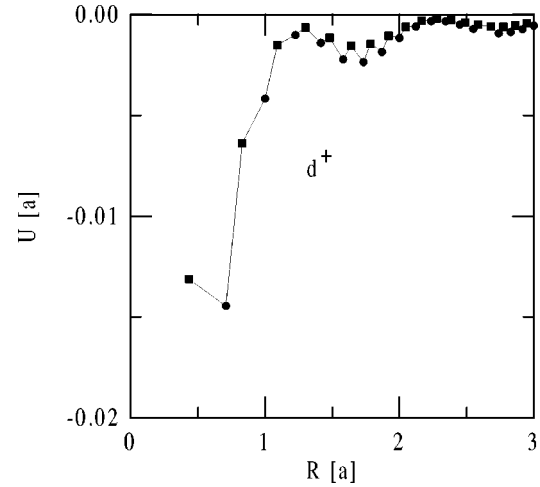


FIG. 3. Longitudinal displacements of ions $L=L_{ns}^+$ from equilibrium positions around the d^+ center vs the ion-donor center distance for Ge impurity in GaAs. Squares correspond to anions, circles to cations. Solid lines are guides for the eye. The lattice constant a is the unit of length.

range part of the lattice deformation. This approximation is well justified for the polar coupling with LO phonons, which changes the sign when changing the negative electron charge to the positive charge of the donor center. The calculated ion displacements around the d^+ center in GaAs are given in Fig. 3. The shifts are the largest for the nearest-neighbor ions; however, they do not exceed 1.5% of the lattice constant. For the weakly localized d^0 and d^- states, the lattice deformations are similar to those shown in Fig. 3 because of the delocalized character of the electronic charge in these states, which is neutralized at large distances (in GaAs, the donor Bohr radius is about 100 Å). Due to the approximation used for the donor-phonon interaction amplitude, the results of Fig. 3 possess mainly a qualitative character and are used as a reference for the shifts of ions obtained in further calculations (Figs. 4 and 5).

The static lattice deformation around the d^+ center (Fig. 3) can be decomposed into the long- and short-range components. The long-range component is mainly induced by the long-range coupling with LO phonons, i.e., it corresponds to the dipole polarization field of the surrounding lattice, and is responsible for the additional screening of the Coulomb potential of the donor center, which leads to the change of the high-frequency dielectric constant ϵ_∞ to the static dielectric constant ϵ_0 [cf. the remark below Eq. (14)]. The results of Fig. 3 show the origin of this screening. The second component of the range of about one lattice constant (Fig. 3) results from the short-range coupling with LA phonons and yields the short-range correction to the donor potential, which has been included into the term $\bar{V}_{\mathbf{k}\mathbf{k}}^S$, [Eq. (13)].

Now, we consider the relative displacements of the ions around the D^0 and D^- centers with respect to those for the d^+ center (or the centers d^0 and d^- of weak electron localization). These relative displacements are determined by the electron-phonon interaction amplitudes, which are known better than the donor-phonon interaction amplitudes. Therefore, these results should be correct as well quantitatively. Using the phonon amplitudes given by Eq. (20) for the D^0 center and by Eq. (21) for the D^- , we have calculated the ion

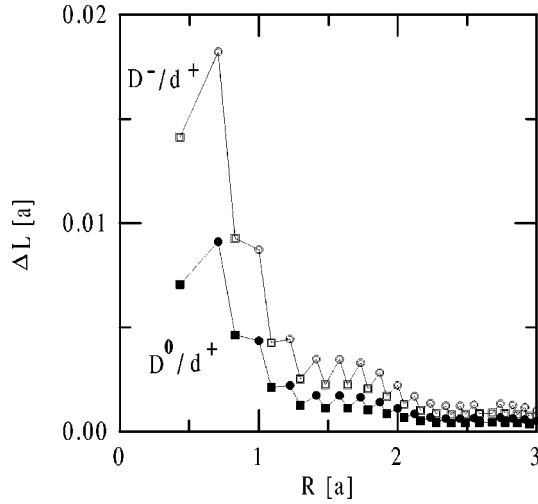


FIG. 4. Relative longitudinal displacements of ions $\Delta L = L_{ns}^\alpha - L_{ns}^+$ around the D^0 ($\alpha=0$, full symbols) and D^- ($\alpha=-$, open symbols) centers determined with respect to those for the d^+ center vs the ion-donor center distance R for Ge impurity in GaAs. Squares correspond to anions, circles to cations. Solid lines are guides for the eye. The lattice constant a is the unit of length.

displacements around both the centers. The results are displayed in Fig. 4, which shows that the lattice deformation around the neutral D^0 center is smaller than that for the negatively charged D^- center. The results in Figs. 3 and 4 indicate that the crystal lattice exhibits an inward relaxation for the d^+ center and an outward relative relaxation for the D^0 and D^- centers. Figure 4 shows that the dependences of the ion displacements on the distance from the donor center possess the forms of vanishing oscillations. A distinct deviation from a breathing-mode character of the lattice deformation results from an influence of LO phonons.

The range of the local lattice deformation is an important quantity, which allows us to determine the main contribution of the displaced ions to the total energy of the system. Since the energetic contributions of both the LA and LO phonon

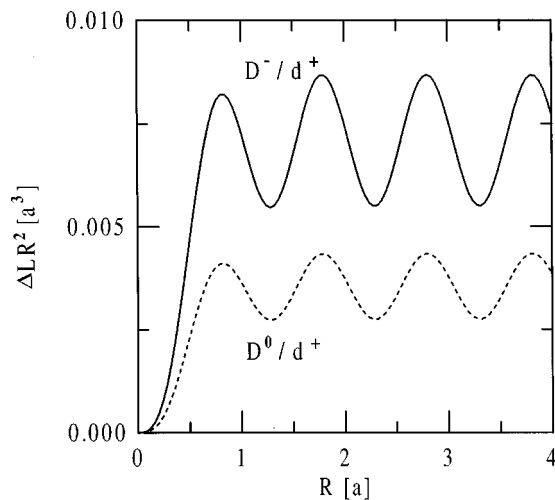


FIG. 5. Product of the longitudinal-acoustic component ΔL of the relative displacements of ions by the square of the ion-donor center distance R vs R . Solid (dashed) curve corresponds to the D^- (D^0) center in GaAs. a is the lattice constant.

branches are additive, we can treat them separately. In the following—for an illustration only—we will discuss the breathing-mode relaxation, which is determined by the LA phonons. Figure 5 shows the product of the LA component of the ion displacements by the square of the distance of the ion from the donor center, which allows us to determine the rate of decay of the amplitudes of these displacements. The nonvanishing oscillations obtained for both the centers (Fig. 5) mean that the corresponding shifts of ions are inversely proportional to the square of the ion-donor center distance. We have found²⁷ that the envelope of the relative ion displacements can be parametrized by a function $0.0084R^{-2}$ (in the lattice-constant units), which proves the long-range character of the lattice deformation around the donor center. We mention that due to the long-wavelength approximations applied to the electron-phonon interaction amplitudes and polarization vectors, the calculated ion displacements are correct at large distances from the donor center. The results of Figs. 4 and 5 for the nearest-neighbor ions should be regarded as qualitative.

The present results permit us to determine the range of the lattice deformation, which yields the major contribution to the lattice-relaxation energy. For this purpose, we estimate the elastic energy of the deformed lattice inside the sphere with the center at the impurity atom and the radius R . Assuming the elastic energy to be proportional to the square of the ion displacement and using the R^{-2} dependence for these displacements, we receive the R^{-4} dependence of the relaxation energy of the ions on the ion-donor center distance. The number of ions at the distance R from the donor center is proportional to R^2 . Thus, after summing up the contributions from all the ions, we obtain the total lattice-relaxation energy varying like R^{-1} . This result once again proves that the lattice deformation around the strongly localized donor centers possesses the long-range character. Therefore, the large contribution to the lattice-relaxation energy originates from the ions, which are quite remote from the donor center. The corresponding ion-donor separations several times exceed the nearest-neighbor interatomic distance. We have estimated²⁷ the range of the lattice deformation, which gives the essential energetic contribution to the lattice relaxation, to be 3–4 lattice constants. Therefore, the corresponding region of crystal contains several thousands of ions.

V. DISCUSSION

Before we discuss the results, we comment on the approximations used in the present work. The majority of these approximations was thoroughly discussed in our previous paper.²⁶ Therefore, we confine ourselves to the approximations, which are characteristic for the two-electron systems. They are related with the electron-electron correlation and the screening of Coulomb potentials by valence electrons.

As mentioned below Eq. (16), the Hartree-Fock-type electronic trial wave function proposed in the present paper for the D^- center does not include the electron-electron correlation. It is well known that—for the H^- ion and for the hydrogenlike weakly localized d^- center—the incorporation of the correlation into the variational wave function leads to the substantial improvement of the variational upper bounds on the ground-state energy. For the two-electron atoms and

ions,³⁴ the absolute value of the correlation energy slowly increases with the increasing electron localization. However, the relative contribution of the correlation energy to the ground-state energy rapidly decreases with the localization.³⁴ As a result, already for the He atom, the Hartree-Fock approximation yields a fairly good estimate of the ground-state energy. For the strongly localized D^- center, the dominating contributions to the ground-state energy originate from the kinetic energy (band energy), the short-range potential, and the direct Coulomb (Hartree) energy. Taking into account the correlation would slightly improve the present upper bounds for the energy, but will not change our results substantially and will not affect our conclusions.

In Sec. II, we have assumed [cf. Eqs. (7) and (9)] that—for the Bloch electrons—the electron-electron and electron-donor Coulomb interactions are screened by the high-frequency dielectric constant ϵ_∞ , which is the simplest approximation for the dielectric function. When discussing the problem of screening in the real space, we can consider the average electron-donor and electron-electron separations, i.e., $\langle r_1 \rangle$ and $\langle r_{12} \rangle$, respectively, as relevant auxiliary quantities. We have estimated these separations for the D^- ground state. The results are the following: $\langle r_1 \rangle = 3.5a_B = 0.33a$ and $\langle r_{12} \rangle = 8.6a_B = 0.81a$, where a_B is the hydrogen Bohr radius and a is the lattice constant of GaAs. This means that the two-electron wave function is spread over the unit cell, which consists of several atoms and several tens of valence electrons. Therefore, the screening of the Coulomb interactions by the valence electrons should be significant even for the strongly localized D^- center.

The results presented in Secs. III and IV have been obtained for the donor center located at the substitutional site in the crystal lattice. The calculated positions of energy levels and pressure coefficients agree with those measured^{4,5} for the Ge-doped GaAs under the hydrostatic pressure. We have obtained the large reduction of the probability of radiative transitions from the extended electron states to the strongly localized D^- states of the lower energy. This result can be interpreted as a proof of the metastability of the delocalized (conduction-band) and weakly localized electron states with respect to the strongly localized electron states, which correspond to the electrons bound in the ground state of the D^- center. Therefore, the electrons can occupy the conduction band for a long time, before they are trapped at the localized impurity centers, which explains the persistent photoconductivity observed in GaAs.³³ All these results are compatible with those attributed to the DX center in GaAs under the hydrostatic pressure. This allows us to conclude that the observed^{4,5} DX -type behavior can be explained as resulting from the formation of the strongly localized D^- donor centers at the substitutional position with the surrounding lattice deformation.

Several groups of authors^{8,10,21,35} performed the total-energy *ab initio* calculations for the DX center and found two minima of the total energy, which correspond to the D^- center located at the substitutional position and interstitial position. According to the results of Dąbrowski and Scheffler⁸ and Chadi *et al.*²¹ the first position corresponds to the local minimum and the second to the global one. These results give support to the bond-breaking mechanism^{7,9} of the formation of DX centers. This mechanism leads to a

creation of a vacancy-interstitial defect pair, which is stabilized by the binding of two electrons on the impurity center at the interstitial position. Recently, Schmidt *et al.*¹⁰ obtained the different arrangement of total-energy minima for the negatively charged Ge and Si centers in GaAs, namely, the global minimum at the substitutional position and the local one at the interstitial position. The authors¹⁰ pointed out that the opposite result received in Ref. 8 resulted from a too small number of \mathbf{k} points used in the Brillouin-zone summation. We mention that Chadi, the main inventor of the bond-breaking mechanism, also analyzed²² the two atomic configurations of the negatively charged DX centers and found that the D^- center at the substitutional site with the symmetric breathing-mode relaxation can be responsible for the DX -like properties of the Sn, Se, and Te impurities in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. This interpretation is consistent with the observed coexistence of two different DX -like centers in Te-doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$.³⁶

The similar effects are observed for other donor impurities in GaAs under hydrostatic pressure. For example, Maude *et al.*³³ and Suski *et al.*³⁷ observed the DX -like properties for Si, Sn, S, and Te donors. The experimental results^{33,37} differ from those for the Ge donor merely by the values of energy levels and pressure, at which the energy levels of the strongly localized states enter the energy gap. The present calculations have been performed for a Ge donor in GaAs, for which the observed¹ anticrossing between the energy levels of D^0 and d^0 states enables us to determine the short-range potential.²⁶ The present approach applied to the other donors in GaAs should lead to the same qualitative results.

The microscopic structure of the DX center in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ has been experimentally studied by positron-annihilation spectroscopy.³⁸ The authors³⁸ argue that their observations can be interpreted as resulting from the vacancy associated with the DX center, which would support the vacancy-interstitial model⁷ of the DX center in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. However, the change of the core-annihilation parameter was observed³⁸ for Si donors only. Similar experiments performed on the isocoric Ge impurity in GaAs or $\text{Al}_x\text{Ga}_{1-x}\text{As}$ would provide more decisive arguments for or against the substitutional position of the DX center.

In Sec. IV, we have presented the results for the lattice deformation induced by a donor center in a crystal. We have shown that this deformation possesses the range of several lattice constants and encompasses the large number of ions. The number of displaced ions that essentially contribute to the lattice-relaxation energy is estimated to be several thousand. The total-energy *ab initio* calculations^{8–10,21} include only up to about 100 ions in a supercell. Based on the results of Sec. IV, we argue that such supercells are too small to correctly account for the total elastic energy of the lattice deformed by the presence of the donor impurity. So far, only empirical methods allow us to study the clusters with large enough number of ions. For example, Cai and Song³⁹ applied the semiempirical approach to a description of metastability of the neutral donor states d^0 and D^0 associated with the In donor in CdF_2 . The results³⁹ agree with both the experimental data² and the results of our previous papers^{23,40} for the metastable donor states in CdF_2 .

The present paper describes the lattice deformation in the phonon representation, which can be applied if the displace-

ments of the ions from the equilibrium positions are small. Under this assumption, the present approach provides the correct description of the local lattice deformation around the impurity center. The shifts of the distant ions are always small and can be described by the long-range component of the lattice deformation obtained in Sec. IV. This means that the present approach can be useful for a description of the long-range lattice deformation induced by any defect. In particular, the displacements of the remote ions associated with the formation of the broken-bond DX configuration⁷ can also be reproduced in the frame of the present method.

The phonon representation of the lattice deformation, applied in the present paper, does not allow for a calculation of the energy of the defect with the broken-bond configuration, since the shift of the impurity atom into the interstitial position is not small as compared with the lattice constant. We cannot therefore answer the question of which position (substitutional or interstitial) the donor center possesses the lower energy. However, due to the large difference in the local lattice deformation between both the configurations, we expect the coexistence of the two types of D^- donor centers (one at the substitutional position and the second at the interstitial position). This coexistence should occur independently of the sign of energy difference between both the states. Recently, Jia and Grimmeiss⁴¹ observed in $Al_xGa_{1-x}As$ three donor states with metastable properties. According to the authors' interpretation⁴¹ and the results of the present paper, the two of them can be attributed to the D^- centers: one at the substitutional site and the second at the interstitial site.

VI. CONCLUSIONS

The present paper (together with our previous paper²⁶) provides a unified theoretical method for a description of one-electron and two-electron shallow-level donor centers of electron arbitrary localization. Our approach is based on the one-band approximation for the electrons and includes the interaction with LA and LO phonons, which allows us to describe the reaction of the crystal lattice on the presence of impurity. The present theory can be helpful in a description of the four types of shallow-level donor states, i.e., d^0 , D^0 , d^- , and D^- , which are formed in semiconducting compounds on the impurity atoms of the same species. We have applied our method to the description of the properties of donors in GaAs and CdF₂.²⁶ In both these materials, the metastable behavior of donors is observed. Our results allow us to give an explanation of this metastability. In the strongly polar CdF₂, the interaction with the LO phonons is of crucial importance and—already at the ambient pressure—leads to

the occurrence of metastability for the neutral donor states associated with Ga and In impurities. In the weakly polar GaAs, the deformation-potential interaction with LA phonons is responsible for the metastability. In this material, the metastability appears at the high hydrostatic pressure for the negatively charged D^- donor centers. According to the present treatment, the metastability of both the donor centers in both the materials results from the large difference of the lattice deformation around the donor center, which occurs between the states of different electron localization. The corresponding phonon states are also different; therefore, the overlap between them is very small, i.e., the dipole-matrix elements determining the transition probability are as well very small. This means that the probability is considerably reduced for the radiative transitions from the delocalized state of the higher energy to the localized ground state of the system. This result is compatible with the metastable behavior of DX centers observed^{4,5} in Ge-doped GaAs under high hydrostatic pressure.

Using the phonon state vectors obtained from variational calculations for the donor states, we have calculated a distribution of displacements from equilibrium positions for the ions surrounding the donor center. The corresponding lattice relaxation involves both the LA and LO phonons, i.e., is more complicated than the symmetric breathing-mode relaxation. The present paper shows that—even for the strongly localized D^0 and D^- donor states—the corresponding lattice deformations encompass a large number of ions around the impurity center. The number of ions that essentially contribute to the local lattice relaxation energy can reach several thousand. Such a large number of ions is out of the scope of the recent total-energy *ab initio* calculations. To the best of our knowledge, the present method is the only one that fully takes into account the long-range lattice deformation around the donor center.

In summary, we can state that a certain consensus has been reached among different groups of authors studying the problem of the microscopic structure of the DX center in GaAs; namely, the authors agree that this is the two-electron center (D^-), which is surrounded by the deformed crystal lattice, which plays an essential role in any explanation of the DX -like properties. Based on the results of the present paper, we expect the coexistence of the two types of D^- donor centers in GaAs: one at the substitutional site and the second at the interstitial site.

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¹Z. Wasilewski and R. A. Stradling, *Semicond. Sci. Technol.* **1**, 264 (1986).

²J. E. Dmochowski, J. M. Langer, Z. Kaliński, and W. Jantsch, *Phys. Rev. Lett.* **56**, 1735 (1986).

³J. E. Dmochowski and R. A. Stradling, *Jpn. J. Appl. Phys., Suppl.* **32**, 227 (1993).

⁴M. Baj, L. H. Dmowski, and T. Słupiński, *Phys. Rev. Lett.* **71**, 3529 (1993).

⁵P. J. van der Wel, P. Wisniewski, T. Suski, J. Singleton, C. Skierbiszewski, L. J. Giling, R. Warburton, P. J. Walker, N. J. Mason, R. J. Nicholas, and M. Eremets, *J. Phys.: Condens. Matter* **5**, 5001 (1993).

- ⁶L. Dobaczewski and P. Kaczor, *Phys. Rev. B* **44**, 8621 (1991).
- ⁷D. J. Chadi and K. J. Chang, *Phys. Rev. Lett.* **61**, 873 (1988).
- ⁸J. Dąbrowski and M. Scheffler, *Mater. Sci. Forum* **83–87**, 735 (1992).
- ⁹C. H. Park and D. J. Chadi, *Phys. Rev. B* **52**, 11 884 (1995).
- ¹⁰T. M. Schmidt, A. Fazzio, and M. J. Caldas, *Phys. Rev. B* **53**, 1315 (1996); T. M. Schmidt and M. J. Caldas, in *Proceedings of the 23rd International Conference on the Physics of Semiconductors*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), p. 2745.
- ¹¹J. Adamowski, *Phys. Rev. B* **32**, 2588 (1985).
- ¹²J. Adamowski, *Phys. Rev. B* **39**, 13 061 (1989).
- ¹³S. Porowski, M. Kończykowski, and J. Chroboczek, *Phys. Status Solidi A* **63**, 291 (1974); Z. Wasilewski, A. M. Davidson, R. A. Stradling, and S. Porowski, *Physica* **117B–118B**, 89 (1983).
- ¹⁴P. M. Mooney, *J. Appl. Phys.* **67**, R1 (1990).
- ¹⁵D. Wasik, J. Przybytek, M. Baj, G. Karczewski, T. Wojtowicz, A. Zakrzewski, and J. Kossut, *Mater. Sci. Forum* **182–184**, 247 (1995); A. K. Zakrzewski, L. Dobaczewski, T. Wojtowicz, J. Kossut, and G. Karczewski, in *Proceedings of the 23rd International Conference on the Physics in Semiconductors* (Ref. 10), p. 3005.
- ¹⁶D. Wasik, J. Przybytek, M. Baj, G. Karczewski, T. Wojtowicz, and J. Kossut, *J. Cryst. Growth* **159**, 392 (1995).
- ¹⁷B. Koziarska, J. M. Langer, A. I. Ryskin, A. S. Shcheulin, and A. Suchocki, *Mater. Sci. Forum* **196–201**, 1103 (1995).
- ¹⁸R. A. Linke, T. Thio, D. J. Chadi, and G. Devlin, *Appl. Phys. Lett.* **65**, 16 (1994).
- ¹⁹C. Skierbiszewski, T. Suski, P. Wisniewski, W. Jantsch, G. Ostermayer, Z. Wilamowski, P. G. Walker, N. J. Mason, and J. Singleton, *Appl. Phys. Lett.* **63**, 3209 (1993).
- ²⁰A. Baraldi, P. Frigeri, C. Ghezzi, A. Passini, A. Bosacchi, S. Franchi, E. Gombia, and R. Mosca, *Phys. Rev. B* **53**, 10 715 (1996).
- ²¹D. J. Chadi and K. J. Chang, *Phys. Rev. B* **39**, 10 063 (1989); S. B. Zhang and D. J. Chadi, *Phys. Rev. B* **42**, 7174 (1990).
- ²²D. J. Chadi, *Phys. Rev. B* **46**, 6777 (1992).
- ²³S. Bednarek and J. Adamowski, *Mater. Sci. Forum* **65–66**, 427 (1990); **83–87**, 493 (1992).
- ²⁴S. Bednarek and J. Adamowski, *Phys. Rev. B* **51**, 4687 (1995).
- ²⁵Y. Toyozawa, *Mater. Sci. Forum* **196–201**, 1 (1995).
- ²⁶S. Bednarek and J. Adamowski, *Phys. Rev. B* **55**, 2195 (1997).
- ²⁷S. Bednarek and J. Adamowski, in *Proceedings of the 23rd International Conference on the Physics of Semiconductors* (Ref. 10), p. 2781.
- ²⁸P. M. Platzman, *Phys. Rev.* **125**, 1961 (1962).
- ²⁹A. B. Dzyubenko and A. Yu. Sivachenko, *Phys. Rev. B* **48**, 14 690 (1993).
- ³⁰J. M. Shi, F. M. Peeters, and J. T. Devreese, *Phys. Rev. B* **51**, 7714 (1995).
- ³¹Y. Wan, G. Ortiz, and P. Phillips, *Phys. Rev. Lett.* **75**, 2879 (1995).
- ³²D. M. Larsen, *Phys. Rev. B* **23**, 628 (1981).
- ³³D. K. Maude, J. C. Portal, L. Dmowski, T. Foster, L. Eaves, M. Nathan, M. Heiblum, J. J. Harris, and R. B. Beall, *Phys. Rev. Lett.* **59**, 815 (1987).
- ³⁴H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957).
- ³⁵E. Yamaguchi, K. Shiraishi, and T. Ohno, *J. Phys. Soc. Jpn.* **60**, 3093 (1991).
- ³⁶R. E. Peale, Y. Mochizuki, H. Sun, and G. D. Watkins, *Phys. Rev. B* **45**, 5933 (1992); R. E. Pearle, H. Sun, and G. D. Watkins, *Phys. Rev. B* **45**, 3353 (1992).
- ³⁷T. Suski, R. Pietrzowski, P. Wiśniewski, E. Litwin-Staszewska, and L. Dmowski, *Phys. Rev. B* **40**, 4012 (1989).
- ³⁸J. Mäkinen, T. Laine, K. Saarinen, P. Hautojärvi, C. Corbel, V. M. Airaksinen, and J. Nagle, *Phys. Rev. B* **52**, 4870 (1995).
- ³⁹Y. Cai and K. S. Song, *J. Phys.: Condens. Matter* **7**, 2275 (1995).
- ⁴⁰S. Bednarek and J. Adamowski, *Solid State Commun.* **91**, 429 (1994).
- ⁴¹Y. B. Jia and H. G. Grimmeiss, *J. Appl. Phys.* **80**, 4395 (1996).