

Tractable Approach for Calculating Lattice Distortions around Simple Defects in Semiconductors: Application to the Single Donor Ge in GaP

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A self-consistent, parameter-free approach is described which allows one to calculate the lattice distortion around neutral and charged simple defects. The method is applied to the Ga-site single donor Ge in GaP. It is predicted that the nearest-neighbor atoms of the impurity move towards the impurity. The influence of an ionization of the defect on this lattice relaxation is found to be very small. The results are interpreted in terms of simple mechanisms.

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The knowledge of the lattice distortion around a defect in a crystal is crucial for a theoretical description of its electronic structure. In the absence of direct experimental information about the atomic positions and in the face of the complexity of a reliable theoretical calculation of the lattice geometry, the approach in most theoretical investigations has usually been to neglect the influence of the lattice distortion completely. In fact, accurate self-consistent calculations of the electronic structure of simple undistorted defects are already quite complicated and those calculations became possible only during the last few years (see, e.g., Scheffler,¹ Jaros,² and references therein). Only for a few cases has the influence of lattice distortions on the electronic structure been studied, and such investigations have shown that a change of theoretical ionization energies of about half an electronvolt is in fact possible as a consequence of a lattice distortion (see for example Ref. 1, or Fig. 1 below). These results thus indicate the range of uncertainty that may affect the predictions based on calculated charge densities and ionization energies, when the actual lattice reconstruction is unknown.

Parameter-free, self-consistent calculations of the lattice distortion around a defect have only been performed so far with the repeated supercell method.^{3,4} However, this method is limited to neutral unit cells and usually to quite small distortions: The interaction between the different

unit cells implies that the impurity induces a band within the gap rather than a discrete level. As a consequence, the method usually breaks down for distortions where the impurity band enters the valence band.

In this paper we describe a parameter-free, self-consistent scheme which allows us to calculate the lattice distortion for neutral and charged states of simple defects. The approach is based on the self-consistent pseudopotential Green's-function method^{5,6} for the calculation of the electronic charge density at the defect. In the additional step we then calculate directly the force acting on the atoms. The zero of the force gives the equilibrium distortion.⁷ The theory is applied to the Ge single donor in GaP. These calculations show that the nearest-neighbor atoms around the impurity move towards the Ge_{Ga} center, which is found to induce a deep A_1 level in the gap. The corresponding wave function is antibonding between the impurity and its nearest neighbors. For a neutral center this antibonding level is filled with one electron, and for a singly positively charged state the deep level is empty. It is plausible and in fact also confirmed by our calculations for the two different charge states that the inward relaxation is stronger when this deep level is empty. However, the amount of the change in the lattice relaxation upon ionization of the deep defect is very small.

We briefly outline our method.⁸ If \vec{q} is a vector,

giving a point in configuration space, which describes the geometry of the nuclei, the force on these nuclei is given by⁹

$$F_i(\vec{q}) = \int \frac{\partial V(\vec{r}, \vec{q})}{\partial q_i} n(\vec{r}, \vec{q}) d^3r + \frac{\partial}{\partial q_i} E^{\text{ion}}. \quad (1)$$

The first term is the Hellmann-Feynman force due to the electronic charge density $n(\vec{r}, \vec{q})$. As we use the frozen-core approximation, $V(\vec{r}, \vec{q})$ describes the ionic potential of all nuclei together with their core electrons. This potential is replaced in our actual calculations by ionic pseudopotentials. The second term in Eq. (1) describes the electrostatic interaction between the ions. Because q_i is a generalized coordinate in configuration space, $F_i(\vec{q})$ is a component of a generalized force. Usually, a great difficulty arises in using Eq. (1), because this expression depends sensitively on the charge density $n(\vec{r}, \vec{q})$. In an actual calculation it is therefore important to ensure that $n(\vec{r}, \vec{q})$ is converged with respect to the basis set.¹⁰ We note that this difficulty is significantly reduced if a Green's-function method is used for the calculation of the electronic structure. Then the different contributions to $n(\vec{r}, \vec{q})$, namely the perfect-crystal charge density $n^0(\vec{r})$ and the defect-induced charge density $\Delta n(\vec{r}, \vec{q})$, can be calculated with two different basis sets (see Scheffler *et al.*¹¹). This allows us to study the convergence of each contribution separately. Furthermore, the flexibility of the basis set for the calculation of $\Delta n(\vec{r}, \vec{q})$ is no longer determined by the long-range wave functions, but by the very localized defect-induced potential. It is convenient to split the force into two contributions, $F_i(\vec{q}) = F_i^0(\vec{q}) + F_i^1(\vec{q})$, with

$$F_i^0(\vec{q}) = \int \frac{\partial V(\vec{r}, \vec{q})}{\partial q_i} n^0(\vec{r}) d^3r + \frac{\partial}{\partial q_i} E^{\text{ion}}. \quad (2)$$

Here $n^0(\vec{r})$ is the electronic charge density of the perfect crystal. Thus Eq. (2) is independent of the defect electronic structure and can be calculated very easily: As $n^0(\vec{r})$ is a periodic function the integral is evaluated in Fourier space. The second term in Eq. (2) involves a summation over all ions in the system, which is easily evaluated with the Ewald technique. We note that for the perfect crystal each term in Eq. (2) vanishes as a result of symmetry at the undistorted geometry. The other contribution, $F_i^1(\vec{q})$, to the force requires the knowledge of $\Delta n(\vec{r}, \vec{q})$, the defect-in-

duced change in the electronic charge density:

$$F_i^1(\vec{q}) = \int \frac{\partial V(\vec{r}, \vec{q})}{\partial q_i} \Delta n(\vec{r}, \vec{q}) d^3r. \quad (3)$$

Because $\Delta n(\vec{r}, \vec{q})$ is very localized, this integral can be evaluated numerically very fast and accurately.

The above theory has been applied to the Ga-site single donor Ge in GaP. The group-IV single donors Si, Ge, and Sn have been systematically investigated from an experimental point of view in the last few years,¹²⁻¹⁵ and it is well established that Ge_{Ga} exhibits some special properties,¹⁶ which clearly contrast with the electronic properties of the shallow centers Si_{Ga} and Sn_{Ga} . There is experimental evidence that Ge_{Ga} is deep with a deep-level wave function belonging to the A_1 representation and with an ionization energy $\epsilon(+0) = E_{\text{CB}} - 0.2 \text{ eV}$.^{14, 15} The Ge_{Ga} center is thus one of the best-known deep-level defects. Therefore we have used this system as the first example to be studied with the above-described method in order to test the theory and to get a better understanding of the effects which determine lattice distortions. For the impurity ion we use a norm-conserving Hamann-Schlüter-Chiang pseudopotential¹⁷ and for the host ions we use local pseudopotentials which have been successfully used in previous defect calculations and give a good description of the band structure and the electronic charge density.^{11, 18}

Our results for the undistorted geometry show that both Ge_{Ga}^0 and Ge_{Ga}^+ have an A_1 level in the gap. There is no Jahn-Teller effect and therefore we studied the influence of a symmetry-conserving breathing-mode relaxation. Our coordinate q is then a scalar, and also the generalized force has only one component. The coordinate q is defined by the positions of the four neighboring atoms with respect to the impurity, $\vec{R}_k^{\text{relaxed}} = q \vec{R}_k$. Here \vec{R}_k ($k = 1, \dots, 4$) are the positions of the four P atoms in the perfect crystal.

The results of the study of Ge_{Ga}^+ are summarized in Fig. 1. We find that the four nearest-neighbor P atoms move towards the Ge impurity, reducing their bond length to the center by 3.5% compared to the geometry of the perfect crystal. This result can be understood as follows. The impurity core is of similar size as that of the Ga atom which is being replaced. However, the Ge ion has a higher ionic charge than the Ga ion. As a consequence, this higher positive charge repels the nearest-neighbor P ions. The force F^0 is therefore repulsive at the lattice geometry of the

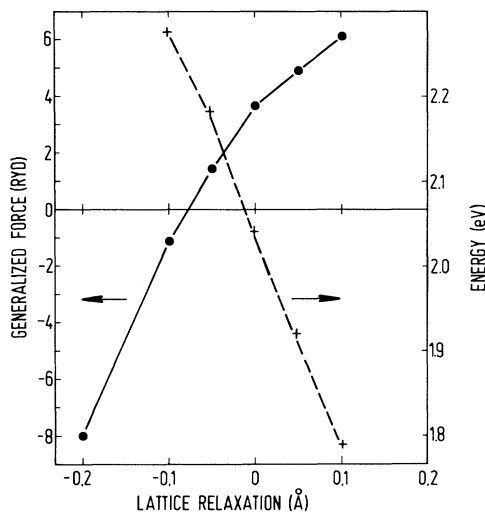


FIG. 1. The generalized force (solid line) acting on the nearest-neighbor P atoms around $\text{GaP:Ge}_{\text{Ga}}^+$ as a function of a breathing relaxation of the four P neighbors. A positive force drives the neighbor atoms towards the impurity; a negative relaxation refers to a relaxation towards the impurity. The zero of the generalized force gives the equilibrium lattice distortion. The dashed line shows the corresponding eigenvalue of the deep level with respect to the top of the valence band. The calculated points are connected for visual clarity.

perfect crystal. [The first term in Eq. (2), which depends on the unperturbed electronic charge density, $n^0(\vec{r})$, vanishes at this geometry as a result of symmetry.] A further consequence of the higher nuclear charge of the Ge atom compared to that of Ga, however, is an increase of electronic charge at the Ge (see Fig. 2), which because of the higher electronegativity of Ge not only screens the additional nuclear charge, but even attracts further electronic charge towards the impurity. As a consequence the force F^1 is attractive at zero distortion and it even overcompensates the force F^0 . This gives a net force on the nearest neighbors which pulls them towards the center (see Fig. 1).

The ionization energy of this center as obtained with the transition-state approach¹⁹ is $\epsilon(+/0) = E_{\text{CB}} - 0.1$ eV, which compares well with the experimental value ($E_{\text{CB}} - 0.2$ eV).^{14, 15} It is clear from Fig. 1 that a small error in the determination of the equilibrium distance would have led to a significant error in eigenvalues and ionization energies. Thus the comparison between the theoretical and experimental ionization energies provides a test of the calculated lattice distortion.

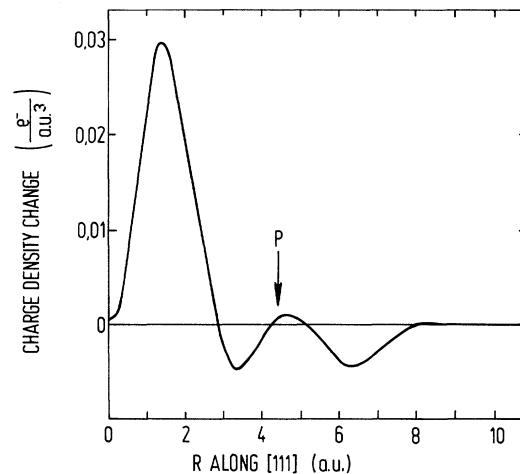


FIG. 2. The change in the electronic charge density induced by $\text{GaP:Ge}_{\text{Ga}}^+$ along the $[111]$ direction. The atomic geometry is that of the perfect crystal. The impurity sits at $R = 0$ and the position of the nearest-neighbor P atom is indicated by the arrow.

For the neutral Ge_{Ga} center the calculated equilibrium lattice relaxation is found to be reduced compared to that of the Ge_{Ga}^+ center. This change in the lattice distortion goes in the expected direction: The filling of the deep (antibonding) level yields a contribution to the force which is repulsive between the impurity atom and its nearest neighbors. However, this influence of the occupation of the deep level on the lattice distortion is found to be very small, i.e., 0.01 Å. This comes about because the deep-level wave function is vacancylike,⁸ i.e., it is largely built from p orbitals at the four neighboring P atoms. A change in the occupation of this deep level yields therefore a change in the defect-induced charge density which is roughly symmetric along the $\langle 111 \rangle$ directions with respect to each of the four P atoms. As a consequence the change of the lattice relaxation upon ionization is very small.

Similar calculations have been performed for the single donors C_{Ga} and Si_{Ga} in GaP.⁸ These results support the above-discussed interpretations: Also for these systems we find an inward lattice relaxation which changes only by very little upon ionization.

In conclusion, we have developed a parameter-free approach which allows us to calculate the lattice distortion around simple defects in semiconductors. The calculations demonstrate that the proposed method is efficient, computationally simple, and fast. The results have brought insight into the mechanisms which determine the

lattice relaxation for neutral and charged defects.

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⁷An alternative way would be to determine the equilibrium distortion from the minimum of the total energy. This, however, involves a more elaborate calculation, because the total energy contains *explicitly* the corrections due to many electron interactions.

⁸A detailed description of the theory and its application to GaP:C_{Ga}, :Ge_{Ga}, and :Si_{Ga} will be published elsewhere.

⁹R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).

¹⁰It is well known from molecular calculations that a basis set $\{\varphi_\alpha\}$ which is appropriate for electronic structure calculations is usually not sufficiently complete for a calculation of the force. However, the inclusion of the functions $d\varphi_\alpha/dq$ in the basis set implies that the calculated force comes to close agreement with the slope of the total energy [see H. Nakatsuji, K. Kanda, and T. Yonezawa, *Chem. Phys. Lett.*

75, 340 (1980)]. For *s-p*-bonded impurities studied in the present paper we have therefore included also *d* and *f*₀ basis functions (see also Ref. 8). Furthermore, it is worth noting that pseudopotential force calculations do not suffer from core polarization effects since the differentiation of the Hamiltonian is performed after the frozen-core approximation is made [see J. Harris, R. O. Jones, and J. E. Müller, *J. Chem. Phys.* **75**, 3904 (1981)].

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¹⁸The use of local pseudopotentials, which give a reasonable bulk charge density, is appropriate for the host ions. This can be understood in particular at the undistorted geometry: Here the electronic contribution to F^0 (which depends very sensitively on the host crystal restoring forces) vanishes by symmetry. Therefore the only way these potentials enter our force is through their ability to provide a good description of the change in the electronic structure induced by the defect. This ability was well established previously (Ref. 11).

¹⁹The Coulombic tail that is present in the potential of the transition-state calculation was included by perturbation theory.

Calculated Structural Phase Transitions in the Alkaline Earth Metals

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The local-density approximation and the linear muffin-tin orbital method have been used within the atomic-sphere approximation to calculate structural energy differences for all the alkaline earth metals at zero temperature. At ordinary pressure the calculations predict the crystal structure sequence hcp→fcc→bcc as a function of atomic number. As a function of pressure they predict the structure sequence fcc→bcc→hcp. The structural transitions and the onset of superconductivity under pressure are correlated with the *d* occupation number.

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The crystal structures of the elemental metals tend to occur in certain sequences, both as a function of atomic number and as a function of

pressure. Most celebrated in this respect are the hcp→Sm-type→dhcp→fcc and the hcp→bcc→hcp→fcc sequences observed in the rare-earth