Symmetric lattice distortions around deep-level impurities in semiconductors: Vacancy and substitutional Cu in silicon

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A model based on the electrostatic Hellmann-Feynman theorem and an empirical valence-force potential has been used to study breathing-mode distortions around the vacancy and substitutional Cu in silicon. The calculation of the forces driving the distortion is based on a self-consistent calculation of the charge-density perturbation. In both cases considered, we find an outward breathing-mode distortion of the lattice. By using a Kubic-harmonics expansion of the charge density, the structure of the forces can be examined. It is found that the outward breathing-mode distortion is caused mainly by the reduced charge anisotropy around the defect, which is a result of the defect-induced deficiency in the number of valence electrons. Distortion amplitudes and the spatial extension of the distortion fields are also calculated for the fully relaxed lattice.

I. INTRODUCTION

Over the past few years, substantial progress has been made in advancing the one-electron theory of deep-level impurities in semiconductors. This has mainly been accomplished by various developments of the Green's-function theory,[1-3] which has become a powerful and practical tool for solving the one-electron problem in the local-density approximation to a high degree of precision. Applications of the method to various systems have generated a great deal of information, and as a result, considerable insight into the electronic structure of deep-level impurities has been gained.

Because of the complexity of the deep-level problem from a theoretical point of view, only rather idealized situations have been considered. For instance, in almost all calculations performed so far, the distortion of the lattice due to defects has been neglected. Larkins and Stoneham[4] investigated lattice relaxations around the vacancy in diamond and silicon using the defect-molecule method of Coulson and Kearsley[5] and an empirical valence-force model. This relatively early calculation failed to give definite information about the relaxation around the silicon vacancy, however. The experimental information about impurity-induced lattice distortions in semiconductors is also very limited. Sometimes the local symmetry around the defect is deduced from, for instance, ESR measurements,[6] but the actual amount of distortion has to the best of our knowledge not yet been measured. Thus this very important aspect of the deep-level problem is still very much unexplored.

Among some of the few other calculations involving defect-induced lattice distortions,[7-11] the papers by Baraff *et al.*[8(a),8(b)] on the Anderson negative-U property of the silicon vacancy are particularly interesting. Some of the parameters of the model developed by these authors for the negative-U system were calculated within a valence-force model similar to that used by Larkins and Stoneham.[4] The direction and amplitude of the breathing-mode distortions, needed as input to their model, was not calcu-

lated, but assumed [in analogy with the silicon (111) surface] to be an outward distortion. As will be seen later, our calculation confirms the assumption of an outward breathing-mode distortion.

The main objectives of this study are the following: (i) to determine the *direction* of symmetry-conserving (breathing-mode) forces on the nearest neighbors to the defect, i.e., to determine whether inward or outward distortions are expected for a given impurity, (ii) to estimate the *amplitude* of breathing-mode distortions on atoms surrounding the defect and the spatial extension of the distortion fields, and (iii) to study the mechanism driving the distortion. This is made possible by investigating the forces caused by the defect on individual atoms. The approach used in this paper is very similar in spirit, but not in detail, to that used by Larkins and Stoneham. Our calculation of the forces caused by the defect is based on results of modern and very precise self-consistent Green's-function calculations. Results for the neutral vacancy and substitutional Cu in silicon will be presented.

II. MODEL FOR LATTICE DISTORTIONS AROUND DEFECTS

A. The electrostatic Hellmann-Feynman theorem

In the pseudopotential approximation, the quantum-mechanical force $\vec{F}_p$ acting on the pseudo*ion* at $\vec{R}_p$ is given by

$$\vec{F}_p = -\vec{\nabla}_p E(\{\vec{R}_\mu\}) , \tag{1}$$

where $E(\{\vec{R}_\mu\})$ denotes the total energy of the (pseudo) crystal for a particular ion configuration $\{\vec{R}_\mu\}$. Using the density-functional formalism[12] and the $X\alpha$ approximation[13] for the exchange-correlation potential, it is straightforward to show[14] that, if the ion at site $\vec{R}_p$ is described by a *local* pseudopotential $v(|\vec{r}-\vec{R}_p|)$, $\vec{F}_p$ is given by

$$\vec{F}_p = \int [-\vec{\nabla}_p v(\, | \, \vec{r} - \vec{R}_p \, | \,)] \rho(\vec{r}) d\vec{r}$$

$$+ \sum_{\mu \, (\neq p)} \frac{Z_p Z_\mu}{| \vec{R}_p - \vec{R}_\mu |^3} (\vec{R}_p - \vec{R}_\mu) \, . \tag{2}$$

Here $\rho(\vec{r})$ denotes the pseudo-charge-density and Z_μ is the valence of the ion at site $\vec{R}_\mu$. It has also been assumed that the ions are spherically symmetric and nonoverlapping.

This result is usually referred to as the electrostatic Hellmann-Feynman theorem. It is valid both in the all-electron case[14] and in the pseudopotential case.[15] It formally requires, however, that the charge density is constructed from the true *eigenfunctions* to the one-particle Schrödinger equation.[14] In practical applications, this requirement is hardly ever met, and the general experience has been that the forces predicted by Eq. (2) can be very inaccurate unless the charge density is obtained to very high precision.[16] Studying the literature, however, it seems as if this experience is mainly based on calculations of the force on the *nucleus* in an all-electron picture: A small polarization of the core electrons often leads to a large change in the electric field at the nucleus compared to a situation where the charge density of the core electrons is regarded as spherically symmetric.[17] Consequently, if the polarization of the core is neglected, it may lead to a large error in the calculated force acting on the nucleus. As was pointed out by Harris et al,[18] the accuracy of the force predicted by the electrostatic Hellmann-Feynman theorem depends critically on whether the frozen-core approximation (i.e., retaining the spherically symmetric atomic core) is done *before or after* the gradient of the total energy is calculated. If the frozen-core approximation is done after the gradient of the total energy is calculated, the actual polarization of the core is neglected and the force on the nucleus may be grossly inaccurate. If, however, the order of operations is reversed, one is actually requiring stationarity of the energy functional with respect to the valence charge density alone when deriving the one-particle Schrödinger equation, and the error in the force due to the deviation of the core density from its atomic (frozen-core) form is eliminated. Differentiating this (modified) energy functional with respect to the nuclear coordinates corresponds then to calculating the gradient under a rigid shift of the nucleus plus corresponding core, i.e., one has effectively the force acting on the spherically symmetric *ion*. It was demonstrated in Ref. 18 that the force acting on the ion as a whole is much less sensitive to errors in the (valence) charge density than is the force acting on the nucleus alone due to all electrons (core plus valence). Since the pseudopotential approach basically adopts the idea of making the frozen-core approximation in the energy functional, i.e., before the gradient of the total energy is taken, we feel that Eq. (2) gives realistic values of the force if $v(\vec{r})$ is taken to be an (ionic) pseudopotential. This conclusion is also supported by a rather recent successful calculation of phonon frequencies using the Hellmann-Feynman theorem in the context of pseudopotentials.[19]

B. Forces due to defects

Consider an isolated point defect at $\vec{R}_0$. We will limit ourselves to substitutional defects, but the generalization to interstitial defects is trivial. If we denote by ΔZ the difference in ionic charge between the impurity atom and the host atom it replaces, the ionic charge Z_μ at an arbitrary lattice point $\vec{R}_\mu$ is given by

$$Z_\mu = Z_\mu^0 + \Delta Z \, \delta_{\mu,0} \, , \tag{3}$$

where Z_μ^0 is the valence of the host (pseudo) atoms. Furthermore, it is convenient to write

$$\rho(\vec{r},\vec{Q}) = \rho^0(\vec{r},\vec{Q}) + \Delta\rho(\vec{r},\vec{Q}) \, , \tag{4}$$

where ρ^0 is the charge density of the host crystal and $\Delta\rho$ the change in charge density due to the presence of the defect. In Eq. (4) we have indicated that the various quantities depend on the relative positions of the N atoms in the crystal through the $3(N-1)$-dimensional vector

$$\vec{Q} = (\vec{R}_1, \vec{R}_2, \dots, \vec{R}_{N-1}) \, . \tag{5}$$

Inserting Eqs. (3) and (4) into Eq. (2) gives

$$\vec{F}_p(\vec{Q}) = \vec{F}_p^0(\vec{Q}) + \Delta\vec{F}_p(\vec{Q}) \, , \tag{6}$$

where $\vec{F}_p^0(\vec{Q})$ is the force acting on the pth ion when no impurities are present and $\Delta\vec{F}_p(\vec{Q})$ is the extra force on the pth host ion due to the presence of the impurity. $\vec{F}_p^0(\vec{Q})$ is given by Eq. (2) with zero superscripts on ρ and Z, and $\Delta\vec{F}_p(\vec{Q})$ is given by

$$\Delta\vec{F}_p(\vec{Q}) = \int [-\vec{\nabla}_p v(\, | \, \vec{r} - \vec{R}_p \, | \,)] \Delta\rho(\vec{r},\vec{Q}) d\vec{r} \, ,$$

$$+ \frac{\Delta Z \, Z_p^0}{| \vec{R}_p - \vec{R}_0 |^3} (\vec{R}_p - \vec{R}_0) \, . \tag{7}$$

At the atomic equilibrium positions $\{\vec{R}_\mu^0\}$ of the host crystal we have $\vec{F}_p^0(\vec{Q}^0) = 0$, where $\vec{Q}^0$ is defined in complete analogy with Eq. (5). Thus in this case, $\vec{F}_p(\vec{Q}^0) = \Delta\vec{F}_p(\vec{Q}^0)$ and the forces acting on the ions in the undistorted lattice configuration, and therefore their expected direction of motion, can be determined quite easily once $\Delta\rho(\vec{r},\vec{Q}^0)$ is known.

C. Estimate of the relaxed atomic positions

To calculate the distorted equilibrium positions of all atoms in the crystal containing the defect, one has to find the vector $\vec{Q} = \vec{Q}^*$ for which $\vec{F}_p(\vec{Q}^*) = 0$ for all p [Eq. (6)]. In practice, this approach requires that we calculate $\vec{F}_p(\vec{Q})$ for different lattice configurations $\vec{Q}_i$ until we find the vector $\vec{Q}_i = \vec{Q}^*$ which makes all $\vec{F}_p(\vec{Q}) = 0$, i.e., one is required to make a fully self-consistent calculation for each trial vector $\vec{Q}_i$. Unless $\vec{\mu}^* = \vec{Q}^* - \vec{Q}^0$ is *known* to be confined to the first few neighbors of the impurity, this task is formidable and a simpler approach is called for. To get a simple, and yet realistic, estimate of the magnitude of the distortion, we will make the following two approximations:

(i) In Eq. (4) we approximate the *impurity-induced*

change in charge density $\Delta\rho(\vec{r},\vec{Q})$ with $\Delta\rho(\vec{r},\vec{Q}^0)$, i.e., we set

$$\rho(\vec{r},\vec{Q}) \simeq \rho^0(\vec{r},\vec{Q}) + \Delta\rho(\vec{r},\vec{Q}^0) , \quad (8)$$

while keeping the full $\vec{Q}$ dependence in ρ^0. When inserted in Eq. (2) this gives [cf. Eq. (6)]

$$\vec{F}_p(\vec{Q}) \simeq \vec{F}_p^0(\vec{Q}) + \Delta\vec{F}_p(\vec{Q}^0) , \quad (9)$$

where

$$\Delta\vec{F}_p(\vec{Q}^0) = \int [-\vec{\nabla}_p v(|\vec{r}-\vec{R}_p|)] \Delta\rho(\vec{r},\vec{Q}^0) d\vec{r}$$

$$+ \frac{\Delta Z\, Z_p^0}{|\vec{R}_p - \vec{R}_0|^3}(\vec{R}_p - \vec{R}_0) , \quad (10)$$

which differs from Eq. (7) only in that $\Delta\rho(\vec{r},\vec{Q})$ is replaced by $\Delta\rho(\vec{r},\vec{Q}^0)$. This approximation clearly corresponds to the assumption that the change in charge density *due to the presence of the defect* is independent of the lattice distortion within the range of distortions being considered. To avoid misinterpretation of the notation $\Delta\vec{F}_p(\vec{Q}^0)$ in Eq. (10), it should be emphasized that the impurity-induced force $\Delta\vec{F}_p(\vec{Q}^0)$ driving the distortion of the host ion at $\vec{R}_p$ is *not* a constant force, independent of the displacement. It still depends on the single-position vector $\vec{R}_p$, both through the argument in the pseudopotential and through the ion-ion interaction term [the last term in Eq. (10)].

(ii) To simplify the evaluation of the quantities in Eq. (6) further, we use

$$\vec{F}_p^0(\vec{Q}) = -\vec{\nabla}_p \Phi^{\text{def}}(\vec{Q}) , \quad (11)$$

where $\Phi^{\text{def}}(\vec{Q})$ is the deformation potential of the host crystal. Several deformation potentials for bulk silicon can be found in the literature (see, for instance, Refs. 20 and 21). We have chosen to work with a potential that gives a good overall fit to experimental phonon spectra.[22,23] Its explicit form is[4,23]

$$\Phi^{\text{def}}(\vec{Q}) = \sum_{i=0}^{N-1} \Phi_i \quad (12a)$$

with

$$\Phi_i = \frac{1}{4}F_r \sum_{j=1}^{4} (\Delta r_{ij})^2$$

$$+ \sum_{j=1}^{3} \sum_{k=j+1}^{4} [\frac{1}{2}r_0^2 F_\theta(\Delta\theta_{jik})^2 + f_{rr}\Delta r_{ij}\Delta r_{ik}$$

$$+ r_0 f_{r\theta}(\Delta r_{ij} + \Delta r_{ik})\Delta\theta_{jik}] . \quad (12b)$$

Φ_i is the potential energy contribution associated with each atom in the lattice, Δr_{ij} denotes the change in bond length between nearest-neighbor atoms i and j from the equilibrium value r_0, and $\Delta\theta_{jik}$ is the change in bond angle between atoms j, i, and k where i is the atom at the apex. For silicon the values of the force constants are[4] $F_r = 9.2697$ eV/$\mathring{A}^2$, $F_\theta = 0.1838$ eV/$\mathring{A}^2$, $f_{rr} = 0.1684$

eV/$\mathring{A}^2$, $f_{r\theta} = 0.2495$ eV/$\mathring{A}^2$, and $r_0 = 4.4447$ a.u. Since the valence potential in Eq. (12) reproduces the overall structure in the experimental phonon spectra,[24] this potential has essentially the same status in phonon dispersion calculations as the empirical pseudopotentials[25] in electronic band-structure calculations.

In summary, when approximations (i) and (ii) are made, the force exerted on the pth host ion is given by

$$\vec{F}_p(\vec{Q}) = \Delta\vec{F}_p(\vec{Q}^0) - \vec{\nabla}_p \Phi^{\text{def}}(\vec{Q}) , \quad (13)$$

where $\Delta\vec{F}_p(\vec{Q}^0)$ (which is *not* independent of $\vec{R}_p$) and $\Phi^{\text{def}}(\vec{Q})$ are given in Eqs. (10) and (12), respectively. In what follows, $\Delta\vec{F}_p$ will be referred to as the Hellmann-Feynman force. Apart from the approximations contained in Φ^{def}, the basic approximation is that the change in charge density induced by the motion of the atoms from their equilibrium positions is unaffected by the presence of the impurity.

III. CALCULATION OF FORCES AND EQUILIBRIUM POSITIONS

The relaxation model described in the preceding section has been applied to the vacancy and substitutional Cu in silicon. The unrelaxed $(\vec{Q}=\vec{Q}^0)$ electronic structure of both defects has been studied in detail with the quasiband crystal-field (QBCF) method,[3] and here we will only quote those results which are relevant for the discussions in the present paper.

A. The charge density and symmetry of forces

Both for the silicon vacancy and for Si:Cu, a sixfold-degenerate gap state (including spin degeneracy) of t_2 symmetry in the T_d point symmetry group is introduced when no lattice relaxation is allowed to occur $(\vec{Q}=\vec{Q}^0)$. For the silicon vacancy, the gap state is occupied by two electrons and for Si:Cu by three electrons, all states of lower energy (the perturbed valence bands) being completely filled. We can split up the total charge density $\rho(\vec{r})$ in the $\vec{Q}=\vec{Q}^0$ configuration into two parts: one describing the contribution to the charge density from the perturbed valence bands $\rho_{\text{VB}}(\vec{r})$ and the other describing the contribution from the gap state $\rho_{\text{gap}}(\vec{r})$,

$$\rho(\vec{r}) = \rho_{\text{VB}}(\vec{r}) + \rho_{\text{gap}}(\vec{r}) . \quad (14)$$

Since the perturbed valence bands are fully occupied, $\rho_{\text{VB}}(\vec{r})$ is of a_1 symmetry (i.e., totally symmetric under operations in the group T_d, cf. Unsöld's theorem), whereas $\rho_{\text{gap}}(\vec{r})$, because of the partial occupancy of the gap state, may be of lower symmetry. In a situation like this, the general procedure in self-consistent calculations on the unrelaxed system is to occupy each of the three partner functions of the t_2 bound state by equal amounts to produce a charge-density distribution invariant under T_d.[8(b),26] This is equivalent to projecting out the a_1-symmetric part of $\rho(\vec{r})$ using the projection operator technique of group theory.[27] (This procedure is quite analogous to that widely used in self-consistent atomic structure calculations,[28] where the charge density is spherically symmetrized, i.e.,

the $l=0$ component is projected out, for atoms including those having incompletely filled shells of electrons). It is the a_1-symmetric part of $\rho(\vec{r})$ [or $\Delta\rho(\vec{r})$] which is driving the symmetry-conserving breathing-mode distortion, while it is the residual (and nonunique) terms of lower symmetry which are responsible for Jahn-Teller distortions,[29] which are superimposed on the breathing-mode distortion. For a full description of lattice distortions around defects, one must, of course, treat Jahn-Teller distortions as well as breathing-mode distortions. The latter appear to be particularly important, however, because they are most likely present for any point defect, in contrast to Jahn-Teller distortions, and are therefore always of interest. For instance, the chalcogen impurities in silicon introduce a_1 states into the gap,[30] so that only symmetry-conserving distortions and *no* Jahn-Teller distortions are expected. Furthermore, there is experimental evidence from spin-resonance measurements that the $3d$-transition atom impurities Cr, Mn, and Fe in silicon show no Jahn-Teller distortions, so that again a model for breathing-mode distortions only is appropriate. For the silicon vacancy, and probably also for substitutional Cu in silicon, Jahn-Teller effects are certainly not negligible [see, for instance, Ref. 8(b) and references therein]. Nevertheless, symmetry-conserving distortions in these systems are both important and instructive to study, and in this paper we will confine ourselves to such distortions only. The work on extending

the model to include also the more difficult Jahn-Teller distortions is in progress.

B. Computational aspects

Next we describe briefly an effective method for finding the distorted equilibrium configuration. Let M denote the number of atoms that are allowed to relax, and introduce the $3M$-dimensional column vector $\vec{\mu}=\vec{Q}-\vec{Q}^0$. With the definition $\vec{\Gamma}_p(\vec{\mu})=\vec{F}_p(\vec{Q})$ we also introduce the column vector $\vec{\Gamma}(\vec{\mu})=(\vec{\Gamma}_1(\vec{\mu}),\vec{\Gamma}_2(\vec{\mu}),\ldots,\vec{\Gamma}_M(\vec{\mu}))^T$, where T denotes the transpose of the vector. The problem of finding the distorted equilibrium configuration $\vec{Q}^*$ is then transformed into that of finding the $3M$-dimensional vector $\vec{\mu}^*$ for which $\vec{\Gamma}(\vec{\mu}^*)=0$. With these definitions, the problem of finding the configuration $\vec{Q}^*=\vec{\mu}^*+\vec{Q}^0$ is formally the same as that discussed in Ref. 31 in a different context, and can be solved iteratively. Thus, in analogy with Ref. 31, the distortion $\vec{\mu}^{(i+1)}$ in the $(i+1)$th iteration is assumed to be related to the distortion $\vec{\mu}^{(i)}$ in the ith iteration through

$$\vec{\mu}^{(i+1)}=\vec{\mu}^{(i)}-G^{(i)}\vec{\Gamma}(\vec{\mu}^{(i)}),\tag{15}$$

where $G^{(i)}$ is the inverse of the Jacobian matrix $J^{(i)}$, $(G^{(i)})^{-1}=J^{(i)}=\partial\vec{\Gamma}(\vec{\mu}^{(i)})/\partial\vec{\mu}^{(i)}$. The matrix $G^{(i)}$ is updated from one iteration [the $(i-1)$th] to the next (the ith) according to the formula

$$G^{(i)}=G^{(i-1)}+\frac{\{\vec{\mu}^{(i-1)}-\vec{\mu}^{(i)}-G^{(i-1)}[\vec{\Gamma}(\vec{\mu}^{(i-1)})-\vec{\Gamma}(\vec{\mu}^{(i)})]\}[\vec{\Gamma}(\vec{\mu}^{(i-1)})-\vec{\Gamma}(\vec{\mu}^{(i)})]^T}{|\vec{\Gamma}(\vec{\mu}^{(i-1)})-\vec{\Gamma}(\vec{\mu}^{(i)})|^2}.\tag{16}$$

In contrast to Ref. 31, we have chosen to update the inverse of the Jacobian matrix rather than the Jacobian matrix itself to avoid inverting the $3M\times3M$-dimensional matrix J in each iteration. With this minor difference in mind, the derivation of these expressions parallels that of Ref. 31.

To start the iteration procedure, we need an initial guess for $G^{(1)}$. This can be obtained, for instance, by *imposing* a given lattice distortion $\vec{\mu}^{(1)}$ and calculate the corresponding force vector $\vec{\Gamma}$. A method very similar in spirit to that used here has been applied previously[32] to calculate the relaxation due to defects in the alkaline earth fluorides. The method is quite general and was, for instance, also used to obtain electronic self-consistency in the QBCF method.[3]

IV. RESULTS AND DISCUSSIONS

The charge-density perturbation $\Delta\rho(\vec{r},\vec{Q}^0)$ needed as input to the present model calculation was generated with the very accurate self-consistent QBCF method.[3] The QBCF calculation was based on the (local) host-crystal pseudopotential $v(\vec{r})$ used in Ref. 33 with exchange coefficient $\alpha=1.0$, and therefore the calculation of the Hellmann-Feynman forces is based on the same pseudopotential. The Cu impurity was represented by a first-

principles nonlocal pseudopotential,[34] where both the atomic $3d$ and $4s$ electrons were treated as valence electrons.

A. The structure of the driving forces

Because of the central role played by the charge density in the present formulation of the problem, we shall, in order to better understand the origin of the forces driving the distortions, first investigate the charge density of the perfect silicon host crystal. In Fig. 1 we show the lowest radial l components $\rho_l^0(r)$ of the self-consistent host-crystal charge density $\rho^0(\vec{r})\equiv\rho^0(\vec{r},\vec{Q}^0)$ in a Kubic-harmonics expansion around a Si atom. The l components are formally defined through the series expansion

$$\rho^0(\vec{r})=\sum_l \rho_l^0(r)K_l^{a_1}(\hat{r}).\tag{17}$$

$K_l^{a_1}(\hat{r})$ is the normalized Kubic harmonic of order l (i.e., symmetrized linear combination of spherical harmonics of angular momentum quantum number l) transforming according to the totally symmetric a_1 representation in the group T_d, while $\hat{r}$ denotes the direction of $\vec{r}$ and $r=|\vec{r}|$. In the group T_d, $K_l^{a_1}(\hat{r})$ is zero for $l=1,2$, and 5. Within the nearest-neighbor distance, the amplitude of the radial l components $\rho_l^0(r)$ decreases rather rapidly with increasing l. Hence, since the $l=0$ term is spherically symmetric,
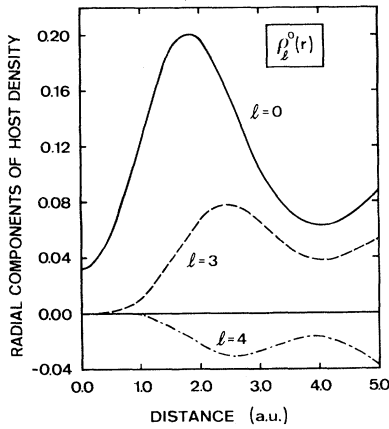
FIG. 1. Three lowest nonzero radial l components of the self-consistent pseudo-charge-density for silicon in a totally symmetric (a_1) Kubic-harmonics expansion around a silicon atom.
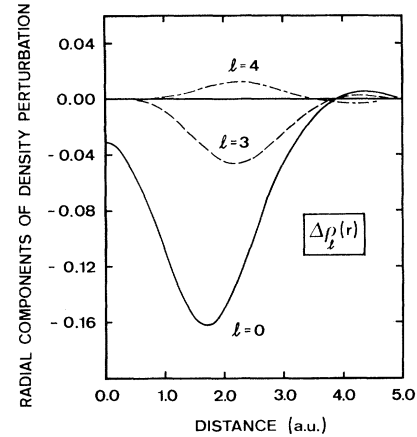

FIG. 2. Three lowest nonzero radial l components of the self-consistent change $\Delta\rho(\vec{r})$ in charge density for the silicon vacancy in an a_1 Kubic-harmonics expansion.

the $l = 3$ term in Eq. (17) is the lowest and single most important term describing the formation of covalent bonds (cf. Fig. 1), while higher terms keep adding to the spatial anisotropy of the charge density until the covalent bonds are fully reproduced.

As to the self-consistent change in the charge density $\Delta\rho(\vec{r}) \equiv \Delta\rho(\vec{r},\vec{Q}^0)$ caused by the defect in the undistorted lattice, we make a similar expansion in terms of Kubic harmonics around the defect center. For $l \geq 6$ the radial components $\Delta\rho_l(r)$ are found to be small and have only a very small effect on the forces. Using the explicit expressions for the a_1 Kubic harmonics in Cartesian coordinates, we therefore have to a very good approximation

$$\Delta\rho(\vec{r}) = \Delta\rho_0(r)\left[\frac{1}{4\pi}\right]^{1/2} + \Delta\rho_3(r)\left[\frac{105}{4\pi}\right]^{1/2}\frac{xyz}{r^3}$$

$$+ \Delta\rho_4(r)\left[\frac{21}{16\pi}\right]^{1/2}\frac{1}{r^4}$$

$$\times [x^4 + y^4 + z^4 - 3(x^2y^2 + x^2z^2 + y^2z^2)] . \quad (18)$$

In Figs. 2 and 3 we show the three lowest l components of $\Delta\rho(\vec{r})$ for the vacancy and substitutional Cu in silicon, respectively. A comparison between Figs. 1 and 2 reveals that the major effect of the vacancy on the charge distribution is to dig a rather structureless spherically symmetric $(l = 0)$ hole around the atomic site, *accompanied by a reduction in the spatial anisotropy of the host charge density* through the $l = 3$ and 4 terms in Eq. (18). This feature should be kept in mind when we analyze Fig. 4, which shows the x component $\Delta F^x_{p=1}$ of the Hellmann-Feynman force acting on a nearest-neighbor Si atom $(p = 1)$ as a function of its distance $|\vec{R}_1 - \vec{R}_0|$ from the vacancy site. The orientation of the coordinate system is such that the nearest-neighbor Si atom is at $\vec{R}^0_1 = \frac{1}{4}a(1,1,1)$, where a is the silicon lattice constant, so that by symmetry $\Delta F^x_1 = \Delta F^y_1 = \Delta F^z_1$. Moreover, the signs

are chosen such that a positive force component is pointing away from the defect site (outward). The figure shows the contribution to ΔF^x_1 from the $l = 0$, 3, and 4 components of $\Delta\rho(\vec{r})$ together with their sum (total).[35]

First of all, we observe that at the *undistorted* position $\vec{R}^0_1$, ΔF^x_1 is positive and therefore an *outward* breathing-mode distortion of the nearest-neighbor atoms around the vacancy is expected. An outward breathing-mode distortion was *assumed* in the paper by Baraff et al.[8(b)] on the negative-U property of the silicon vacancy and is thus
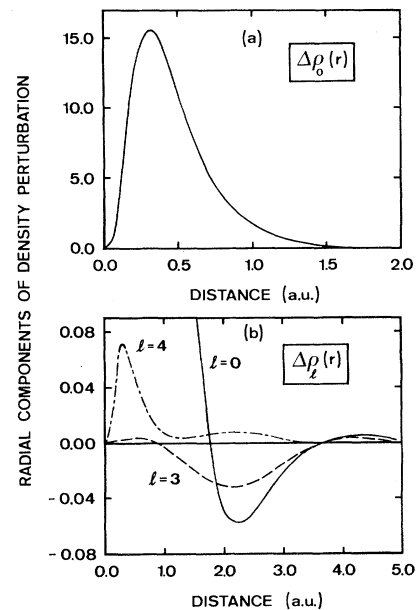

FIG. 3. (a) The $l = 0$ component of the self-consistent change $\Delta\rho(\vec{r})$ in charge density for Si:Cu in an a_1 Kubic-harmonics expansion. (b) An enlarged view of the three lowest nonzero radial l components of $\Delta\rho(\vec{r})$.
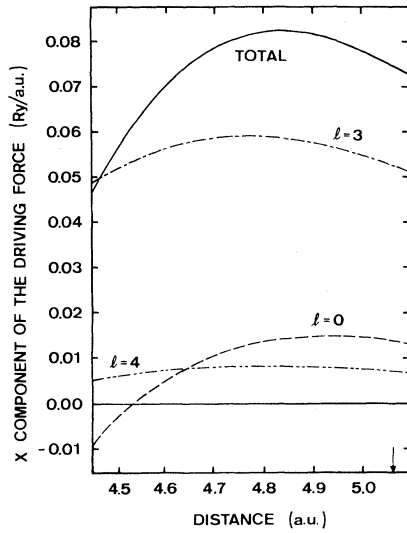
FIG. 4. x component ΔF_1^x of the Hellmann-Feynman force $\Delta \vec{F}_1(\vec{Q}^0)$ [Eq. (10)] on the nearest-neighbor host atom in the $\langle 111 \rangle$ direction ($p = 1$) for the silicon vacancy (solid line), as a function of the distance from the vacancy center. Owing to symmetry, $\Delta F_1^x = \Delta F_1^y = \Delta F_1^z$. Also shown are the individual contributions to ΔF_1^x from the $l = 0, 3$, and 4 components of the change in charge density. For the $l = 0$ component, the spherically symmetric ion-ion force term [the last term in Eq. (10)] has been added to the Hellmann-Feynman force integral [the first term in Eq. (10)] to give an *effective* $l = 0$ contribution to the force. The curves start at 4.445 a.u., which is the distance between the vacancy and the nearest-neighbor atom in the undistorted lattice. The arrow shows the fully relaxed nearest-neighbor equilibrium distance.

FIG. 5. Same as Fig. 4 but for Si:Cu.

confirmed by this calculation. Speculations by Van Vechten[36] also led to the same result. Note that the approximations made in Sec. II C do not affect the results obtained at the undistorted lattice positions. Next we observe that the single most important component in $\Delta \rho(\vec{r})$ driving the outward distortion at $\vec{R}_1^0$ is the $l = 3$ term, with some help from $l = 4$, and that this also appears to be the case away from $\vec{R}_1^0$. We therefore conclude that *the outward distortion of the nearest-neighbor atoms to the vacancy is mainly caused by the reduced anisotropy of the local charge density around the vacancy.* Since the integral of the anisotropic part of $\Delta \rho(\vec{r})$ equals zero when integrated over a sphere containing $\Delta \rho(\vec{r})$, this part of $\Delta \rho(\vec{r})$ does not contain any net charge, which means that it is the reduction in covalent bonding (weakening of bonds) rather than the actual removal or addition of equal amounts of electronic and ionic charge in itself that drives the outward distortion.

Turning now to Si:Cu we find on comparison between Figs. 1 and 3 that there is again a reduction in the spatial anisotropy of the charge density, although somewhat less than for the vacancy, while the spherically symmetric part of $\Delta \rho(\vec{r})$ is quite different from the vacancy and has some extra structure. It should be noted, however, that the
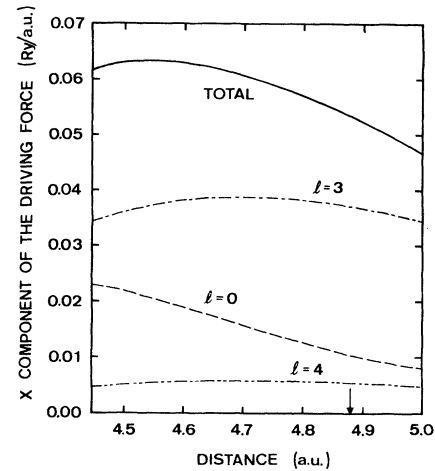
huge peak in $\Delta \rho_0(r)$ is largely cancelled by the change in ionic charge already at around 2.0 a.u. [the dip in $\Delta \rho_0(r)$ removes around 0.5 electrons] so the effect on the neighboring atoms is not at all that dramatic. The somewhat smaller reduction in the anisotropic part of the charge density for Cu compared to the vacancy is understandable: Regarding for a moment the Cu $3d$ electrons as being part of an inert core, the introduction of the Cu atom effectively corresponds to removing three valence electrons (first taking out four valence electrons to create the vacancy and then putting one valence electron, the atomic $4s$, back) while the vacancy removes four valence electrons. The ratio 3:4 is very close to the ratio between the minimum values of $\Delta \rho_3$ for Cu and for the vacancy (~ 0.73). In fact, it was found in Ref. 3 that a sphere centered at the defect site and with a radius equal to the nearest-neighbor distance in silicon (the central-cell sphere) contains six valence electrons for the vacancy and, after substracting ten $3d$ electrons, seven valence electrons for Si:Cu, whereas the central-cell sphere contains approximately ten valence electrons in the perfect silicon crystal. Thus the "extra" Cu electron, which apparently is confined to the central-cell region, partially heals the broken bonds and therefore the reduction in anisotropy of the charge density due to the Cu impurity is smaller than for the vacancy.

Because of the similarities between the two cases, it is now not very surprising that an outward breathing-mode distortion is found also for Si:Cu (Fig. 5). Again the decrease in covalent bonding around the defect helps to push the neighboring atoms out, although this mechanism is not as dominant in this case as for the vacancy. This is partly due to the presence of the extra valence electron around Cu, and partly due to the fact that the effective force caused by the spherically symmetric part of $\Delta \rho(\vec{r})$ has changed. Still, however, it is the anisotropic part of $\Delta \rho(\vec{r})$ which gives rise to the largest force.

B. Relaxation of the lattice

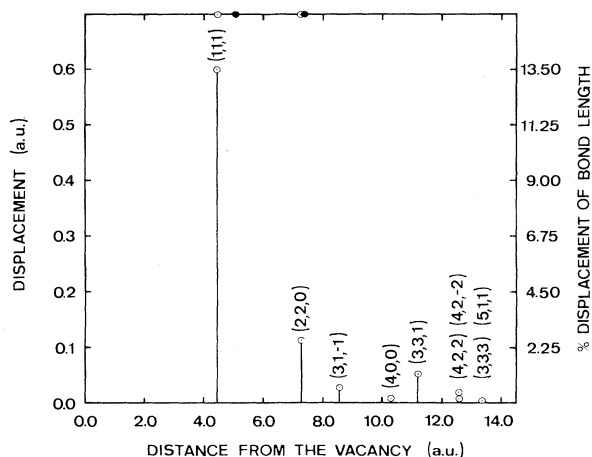When the lattice is allowed to relax freely to absorb the forces exerted on the nearest neighbors to the defect, we

FIG. 6. Radial displacement $|\vec{R}_p| - |\vec{R}_p^{\,0}|$ of atoms around the silicon vacancy vs their distance from the vacancy center in the undistorted lattice. The numbers in parenthesis label the various shells of atoms. Note that all atoms in a given shell have the same displacement in a breathing-mode distortion. On the upper scale, the radial positions of the host atoms in the undistorted (open circle) and fully relaxed (solid circle) lattice are indicated for the atoms in the two shells closest to the vacancy.

obtain the distortion pattern shown in Fig. 6 for the vacancy and in Fig. 7 for Si:Cu.[37] The two cases differ only in the amplitude of the distortion, with a larger distortion around the vacancy than around the Cu impurity; otherwise they are nearly identical in structure. The outward displacement of the four nearest-neighbor atoms is for the vacancy 0.6 a.u. (13.5% of the undistorted bond length) and for Si:Cu 0.45 a.u. (10% of the bond length).[38] In both cases, the Hellmann-Feynman force $\Delta\vec{F}_p$ acting on the other shells of atoms is vanishingly small and these shells have moved away from the defect only because of the outward relaxation of the (1,1,1) shell. [The contribution to $\Delta\vec{F}_p$ from $\Delta\rho_0(r)$ is eventually cancelled by the ion-ion interaction term in Eq. (10), but the contribution from the anisotropic components in $\Delta\rho(\vec{r})$ have no cancelling counterpart in the Hellmann-Feynman force formula and may therefore in principle be of long range. These forces, however, turn out to be negligible on all shells of atoms except the first.]

From Figs. 6 and 7 it is clear that the amplitude of the distortion decreases rather rapidly with increasing distance to the shell and stays less than around 1% of the bond length beyond the second shell. The large displacement of the (3,3,1) shell relative to some shells closer to the defect [e.g., the (3,1,−1) shell] merely reflects the anisotropic crystal structure.

The reason for the around 20% larger distortion around the vacancy (when comparing distortion amplitudes of the nearest neighbors) can be found in Figs. 4 and 5. These figures show that at the *distorted* equilibrium positions of the nearest neighbors, the effective $l = 0$ contribution to the Hellmann-Feynman force is almost the same in both
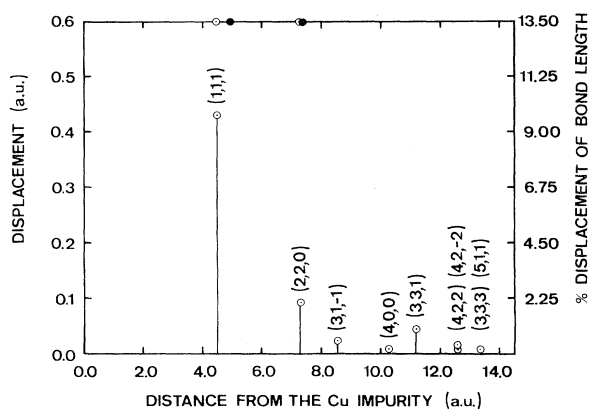

FIG. 7. Same as Fig. 6 but for Si:Cu.

cases and that the larger force caused by the vacancy is mainly due to the larger $l = 3$ contribution. Our model therefore suggests that the smaller displacement around the Cu impurity is mainly due to the extra valence electron for Cu in the central-cell sphere. According to this argument, and assuming that the *effective* $l = 0$ contribution to the Hellmann-Feynman force does not change too much, one would expect a decreasing outward breathing-mode distortion as one moves to the immediate right in the Periodic Table from Cu to Ge.

Finally, we examine how sensitive the displaced equilibrium positions of the inner-shell atoms are to the relaxation of the outer shells. Allowing only the four nearest neighbors in the (1,1,1) shell to relax, we find that for Si:Cu the error in the radial displacement of the nearest neighbors is 8%, whereas if all shells except the (1,1,1) and (2,2,0) shells are kept fixed, the same error is only 1.6%, while the error in the much smaller radial displacement of the (2,2,0) shell is 28%. This result may be of value in more elaborate calculations on lattice relaxation using for instance the self-consistent Green's-function method[1−3] throughout, without any of the approximations made in Sec. II C.

V. SUMMARY AND COMMENTS

We have presented a model for studying lattice relaxation around point defects in semiconductors, based on the electrostatic Hellmann-Feynman theorem and an empirical valence-force potential. By applying this model to the vacancy and substitutional Cu in silicon in a study of breathing-mode distortions the following was found: (i) In the undistorted lattice, each nearest-neighbor atom to the defect is acted on by an *outward* force, moving the atoms away from the defect along the direction of $\vec{R}_N - \vec{R}_0$, where $\vec{R}_N$ and $\vec{R}_0$ are the position vectors for a nearest-neighbor atom and the point defect, respectively. This result is thus valid both for the vacancy, confirming earlier speculations[8,36] as to the direction of the breathing-mode distortion, as well as for Cu, and is not affected by the approximations made in Sec. II C (i.e., replacing $\Delta\rho(\vec{r},\vec{Q})$ with $\Delta\rho(\vec{r},\vec{Q}^{\,0})$ in the Hellmann-Feynman force integral

and using an empirical valence-force potential for the host). (ii) In the fully relaxed equilibrium configuration, the outward displacement of the four nearest-neighbor atoms is estimated to be 0.6 a.u. (13.5% of the bond length) for the vacancy and 0.45 a.u. (10% of the bond length) for Si:Cu. The displacement of the next-nearest neighbors is in both cases only around $\frac{1}{5}$ of the displacement of the first shell. It was also found that the displacement of the nearest neighbors is surprisingly insensitive to whether the other shells are allowed to relax or not. (iii) Insight into the mechanism behind the outward distortion could be gained and a simple picture emerged: It was found that the reduction in the anisotropic part of the charge-density caused by the defect gives rise to a strong force acting in the outward direction away from the defect. Since a strongly anisotropic charge density in the neighborhood of each atom is the fingerprint of covalent bonding, we thus arrived at the simple picture that it is the weakening of the bonds caused by the defect-induced deficiency in the number of valence electrons that mainly drives the outward distortion, especially for the silicon vacancy. (iv) According to this picture, the larger equilibrium distortion of the surrounding lattice caused by the vacancy ($\simeq 20\%$ difference when comparing distortion amplitudes of the four nearest neighbors) could be explained by the presence of the extra valence electron around the

Cu atom, which is trying to heal the broken bonds.

Finally, a few words about some possible weaknesses of the calculation. We wish to emphasize that the approximations made in Sec. II C rightly can be questioned, since we have made no attempts to justify them. The only reason for making the approximations is of course that they permit a substantial simplification of an otherwise computationally very demanding problem. Note, however, that the lowest-order terms omitted in $\Delta\rho(\vec{r},\vec{Q})$ are of the form $(\vec{R}-\vec{R}^0)\cdot\vec{\nabla}_p(\Delta\rho(\vec{r},\vec{Q})$ and that the error in the driving forces due to the omitted terms goes to zero as the distortion becomes small. The approximations thus give us an opportunity to obtain in a simple way a first-order estimate of the amplitude of the relaxation around an impurity, which is an essentially unexplored quantity for the deep impurity problem. Since the approximations may mainly affect the amplitude of the distortion, we do not expect the main conclusions concerning the outward direction of the distortion and the physical mechanism driving the distortion (Sec. IV A) to be affected by them.

ACKNOWLEDGMENT

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to the Hellmann-Feynman force integral [the first term on the right-hand side of Eq. (10)] to give an *effective* $l = 0$ contribution to the force.

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[37]In Ref. 8(b) it was indicated that the valence-force potential parameters used in Ref. 4, which are the same as those used in the present paper (Sec. II C), give unrealistic results for the displacements of atoms. We wish to point out that this is not so. In Refs. 8(b) and 20, effective force constants for the breathing-mode distortion around the silicon vacancy were calculated in a simple model: The vacancy at site i was simulated by removing from Eq. (12) all bond-stretching terms involving atom i (case I), or all bond-stretching *and* bond-bending forces involving atom i (case II). Note that in this model it is not clear which case describes the vacancy better. By applying a force F_b on the four atoms surrounding the vacancy defined in this way, and then calculate the fully relaxed distortion Q_b of the four nearest neighbors, the effective force constant k_b, defined as $k_b = F_b / Q_b$, was calculated. Using the valence-force parameters of Ref. 8(b) (see Table I of Ref. 20), we obtain in case I, $k_b = 8.42$ eV/$\mathring{A}^2$ and in case II, $k_b = 6.38$ eV/$\mathring{A}^2$, i.e., the average value of k_b is 7.40 eV/$\mathring{A}^2$. This is very close to the value of k_b presented in Ref. 8(b) (7.47 eV/$\mathring{A}^2$). With the parameters quoted in Sec. II C we find $k_b = 8.01$ eV/$\mathring{A}^2$ (case I) and $k_b = 5.65$ eV/$\mathring{A}^2$ (case II), i.e., the average $k_b = 6.83$ eV/$\mathring{A}^2$. This result is in disagreement with the value $k_b \simeq 3.8$ eV/$\mathring{A}^2$ that can be deduced from Ref. 4 and which therefore was quoted in Refs. 8(b) and 20. Furthermore, we find that k_b scales roughly with F_θ. This is also in line with the findings of Refs. 8(b) and 20, whereas $k_b \simeq 3.8$ eV/$\mathring{A}^2$ does not seem to satisfy this rule. We therefore conclude that the parameters of Ref. 4 do in fact lead to results in close agreement with those obtainable with the parameters of Ref. 8(b). This conclusion is further strengthened by the fact that the parameters used in Ref. 4 are close to those of Ref. 8(b) (see Table I of Ref. 20).

[38]The sensitivity of these results to changes in $\Delta\rho(\vec{r})$ has been investigated and was found to be small: When the various l components of $\Delta\rho(\vec{r})$ are cut off at the nodes appearing between around 3 and 4 a.u. (see Figs. 2 and 3) and $\Delta\rho(\vec{r})$ is renormalized, we find that the relaxed atomic displacements of the four nearest neighbors change by only a couple of percent.