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Screening of shallow impurities in germanium within the local-density approximation

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We present here an *ab initio* study of the linear screening of shallow impurity potentials in Ge. This is done using large dielectric matrices calculated within the local-density approximation. The local-field and exchange-correlation effects are fully accounted for; the linear operator relevant to this problem is the so-called test-charge–electron inverse dielectric matrix. We find that the resulting electron polarization densities depend crucially on the position of impurities in the crystal and have only site symmetry. The intervalley scattering matrix elements due to screened impurity potentials are also investigated.

I. INTRODUCTION

Quantitative aspects of physical systems such as crystals with point defects have been extensively studied throughout the decades. Some of the achievements of the theory of defects are very relevant to the progress of solid-state physics. The very popular effective-mass approximation (EMA), for example,[1,2] has had great success in describing shallow electronic states due to Coulomb-like impurities in semiconductors. On the other hand, in the limit of strongly localized potentials, the Green's-function technique has been developing rapidly over the last few years, reaching the accuracy of the most modern methods used in the band-structure and total-energy calculations.[3]

The natural and common trend in theoretical descriptions of systems of electrons is to use an *ab initio* parameter-free approach. Such a unified approach is provided, for example, by the density-functional formalism. Within the local-density approximation (LDA) to this formalism an accurate description of localized defects in crystals is possible and several computational methods have been developed to deal with the electron in a periodic system with a point defect. Apart from the above-mentioned Green's-function approach let us mention here the supercell[4] or cluster[5] approaches. The localization in space of defect potentials and electronic states was a necessary condition to get convergent results and make these methods computationally applicable. In the case of shallow impurities however, with their bound electron states extending over many unit cells, the use of the above methods encounters serious technical problems and becomes questionable. There the EMA is still the most useful approach and except for the ground states of some shallow impurities gives an excellent quantitative description. Within the EMA one must solve a Schrödinger equation with an effective mass in the kinetic energy term and a Coulomb potential screened with the *macroscopic* dielectric constant of the crystal. The simplicity of this method becomes its drawback when we search for numerically accurate solutions for the ground state. This concerns especially the case of donors in multivalley semiconductors such as Si or Ge. Ground-state wave functions of shallow impurities have 1*s*-like character, being then sensitive to the real shape of impurity potential in the central-cell region. The deviation of the impurity potential from the macroscopically screened Coulomb potential in the neighborhood of the impurity is called "central-cell correction" and is different for different chemical species and for different impurity sites. This produces the chemical shift in the position of the electronic levels. It was also recognized that in the multivalley case the finite distance in $\mathbf{k}$ space between different valleys (comparable with the first-Brillouin-zone dimensions) implies the use of $\mathbf{q}$-dependent screening.[6] Such a $\mathbf{q}$-dependent screening is weaker than the macroscopic one (i.e., the one obtained using the dielectric constant throughout). This fact, together with the perturbative treatment of multivalley matrix elements of the effective impurity potential, causes the calculated ground state of shallow donors to be lower than that of the standard EMA solutions. These corrections to the EMA improve the agreement between theory and experiment. Improvements to the EMA to treat multivalley cases were developed recently.[7,8] In both of these references *bare* impurity potentials are screened with a static q-dependent dielectric function resulting in a spherical, site-independent screened potential. The site dependence of the resulting electronic structure was in those methods determined only by the interference of Bloch states of different valleys.

Given a bare impurity potential, the real shape of the screened one is given within the linear regime by the inverse dielectric operator $\epsilon^{-1}(\mathbf{r},\mathbf{r}')$. Equivalently the polarization charge around a *bare* impurity is obtained from the density response operator $\chi(\mathbf{r},\mathbf{r}')$. Both of these operators are nonlocal in space coordinates and in general *do not* depend only on the difference $\mathbf{r}-\mathbf{r}'$ between the two arguments as in the case of the homogeneous model semiconductor implicit in the use of a $\mathbf{q}$-dependent (diagonal) screening. As a consequence the resulting screened impurity potential and the polarization charge density depend on the position of the defect in the crystal. When working in Fourier space the response operators become matrices in the reciprocal-lattice vectors **G**, **G**′ and the problem of the site dependence of screening is contained in the off-diagonal elements of these matrices.[9]

The purpose of this paper is to study within the LDA scheme the microscopic response to the presence of Coulomb-like impurities in substitutional and interstitial positions in Ge. To this end we calculate a set of response matrices over a mesh of **q** points inside the first Brillouin zone and use them to screen Coulomb potentials in the interstitial tetrahedral and substitutional sites and/or the As pseudopotential at the substitutional position. When working in the LDA approximation the question of proper inclusion of exchange correlation in screening arises. The crucial role of exchange correlation in the evaluation of phonon frequencies in Ge was reported recently.[10] Here we revise this problem in a different context—the screening of impurity potentials.

Two groups have previously investigated a similar problem in a couple of papers which appeared a few years ago.[9,11] Car and Selloni[9] have constructed a model dielectric matrix (DM) fitted to the *ab initio* random-phase-approximation (RPA) calculation at the Γ point to study the effect of the off-diagonal terms in screening Coulomb impurities in Si. Mattausch *et al.*[11] used a first-principle approach to obtain response matrices and screened Coulomb potentials in diamond and Si. In their calculation based on the many-body technique in the derivation of response operators different kinds of assumptions and recipes were used[12] while the present work is the *exact* application of the LDA formalism. Nevertheless the qualitative conclusions are similar and our calculation shows trends in screening which are similar to those of Refs. 9 and 10. The only essential approximations we make in the present work are the use of local exchange correlation, of local pseudopotentials, and of a finite number of **q** points for Brillouin-zone (BZ) integration.

The paper is organized as follows. First (Sec. II) we define the different response operators which are basic in the LDA scheme. Following, Sec. III is devoted to the technical details of the calculation while in Sec. IV our results for the screening of different impurity potentials placed at the relevant impurity sites of Ge are discussed. In Sec. V we study the effect of the off-diagonal response on the intervalley scattering matrix elements. Our conclusions are drawn in Sec. VI.

II. THEORY

We want to summarize in this chapter the concepts and tools one uses when working with response operators with LDA scheme, as well as to derive some of the basic expressions to be used in this work. For a more extended and somewhat different account see Ref. 13.

Suppose a weak external (bare) potential V_{ext} is applied to the electron system described by the one-particle wave equation within the LDA formalism

$$\left[\frac{p^2}{2m}+V_I(\mathbf{r})+V_s(\mathbf{r})\right]\psi_i(\mathbf{r})=E_i\psi_i(\mathbf{r}) \ . \tag{1}$$

Here V_I is the electrostatic potential due to the ions and V_s is the self-consistent field

$$\begin{aligned}V_s(\mathbf{r})&=V_H(\mathbf{r})+V_{\text{xc}}(\mathbf{r})\\&=\int d\mathbf{r}'\frac{e^2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+V_{\text{xc}}(\mathbf{r}) \ .\end{aligned} \tag{2}$$

V_{ext} will polarize the electrons of the system giving rise to a change in the electron density $\delta\rho$ and to a change in the self-consistent field δV_s. Within linear regime we can write

$$\delta\rho=\chi V_{\text{ext}} \ , \tag{3}$$

$$\delta V_s=v_C\delta\rho+f_{\text{xc}}\delta\rho \ , \tag{4}$$

where χ is the density response operator, v_C is the Coulomb interaction and $f_{\text{xc}}=\delta V_{\text{xc}}/\delta\rho$ is the functional derivative of exchange-correlation potential taken at the unperturbed ground-state electron density $\rho_0(\mathbf{r})$. Here and in the following we are using shorthand notation for operator products in real space, corresponding to algebraic (matrix) products in reciprocal space.

Since ρ is derived from Eq. (1) we can also define the independent-particle polarizability operator χ_0 by

$$\delta\rho=\chi_0(V_{\text{ext}}+\delta V_s) \ . \tag{5}$$

It should be noticed that χ_0 (unlike χ) gives the response to the full change in self-consistent potential with exchange and correlation parts included. The inverse dielectric operator ϵ^{-1} gives by definition the *electrostatic* response to the *electrostatic* perturbation

$$V_{\text{ext}}+v_C\delta\rho=\epsilon^{-1}V_{\text{ext}} \ . \tag{6}$$

Equation (6) implies then the relation

$$\epsilon^{-1}=1+v_C\chi \ . \tag{7}$$

When working in the Hartree scheme [$V_{\text{xc}}=0$ in Eq. (2)], E_{RPA} can be defined

$$\epsilon_{\text{RPA}}=1-v_C\chi_0 \tag{8}$$

the inverse of which is the true electrostatic dielectric response at the Hartree level. The name RPA is also used in other schemes, e.g., LDA, when the dielectric operator is related to χ_0 through (8). In these cases however it loses the character of electrostatic response to the electrostatic perturbation. In order to find such a response one has to extract from δV only its electrostatic part. After some manipulations it is easy to derive the following expressions (Devreese *et al.* in Ref. 13):

$$\begin{aligned}\epsilon_{\text{LDA}}&=1-v_C\chi_0(1-f_{\text{xc}}\chi_0)^{-1}\\&\equiv 1-v_C(\chi_0^{-1}-f_{\text{xc}})^{-1} \ .\end{aligned} \tag{9}$$

Replacing $f_{\text{xc}}=0$ in (9) one obtains Eq. (8), i.e., the expression for ϵ_{RPA}. The dielectric response ϵ_{LDA} should be used in the interatomic-force or phonon calculations in crystals and in problems where the electrostatic interactions *only* are of importance. When the perturbed electronic levels are studied as the effect of V_{ext} one is interested in the *total* change in the self-consistent potential, i.e, together with exchange-correlation part. It is then useful to define, say, an *electronic* dielectric operator, which is a *different* kind of linear response

$$\epsilon_e = 1 - v_C \chi_0 - f_{xc} \chi_0 \ . \tag{10}$$

One should use ϵ_e when calculating electron-phonon interactions or impurity-induced electron states, for example.

It was pointed out recently[14] that exchange correlation [f_{xc} in Eq. (9)] plays a crucial role in the response matrices. Some elements of DM's and the dielectric band structure[15] of Ge differ more because of the effect of f_{xc} in (9) than because of different band-structure schemes. ϵ_{RPA} obtained from the Cohen-Bergstresser empirical scheme[16] is closer to the ϵ_{RPA} obtained from the self-consistent pseudopotential of Cohen and co-workers[17] than the ϵ_{RPA} to the ϵ_{LDA} within the same scheme of Cohen and co-workers. It was also found[10,14] that the role of f_{xc} is particularly crucial in phonon calculations: The frequencies of transverse-acoustic phonons become imaginary when obtained from RPA response, while the frequencies of all phonons are much closer to experiment if calculated from LDA response.

III. TECHNICAL DETAILS

For nonperiodic perturbation the polarization electron density has in general all Fourier components nonzero. One can write then

$$\delta\rho(\mathbf{r}) = \sum_{\mathbf{G}} \frac{\Omega_0}{(2\pi)^3} \int_{\mathrm{BZ}} d\mathbf{q}\, \delta\rho(\mathbf{q}+\mathbf{G}) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \ , \tag{11}$$

where $\delta\rho(\mathbf{q}+\mathbf{G})$ for each $\mathbf{q}$ and $\mathbf{G}$ is obtained from Eq. (3), which in Fourier space reads

$$\delta\rho(\mathbf{q}+\mathbf{G}) = \sum_{\mathbf{G}'} \chi(\mathbf{q}+\mathbf{G}, \mathbf{q}'+\mathbf{G}') V_{\mathrm{ext}}(\mathbf{q}+\mathbf{G}') \ . \tag{12}$$

We perform the integral in (11) numerically as a finite sum over a mesh of $\mathbf{q}$ points. We chose a mesh of 256 points in the first BZ which results from the (8,8,8) mesh of Monkhorst and Pack notations[18] which correspond to the 10 mean-value points in the irreducible part of the first BZ.[19] At each of these points we calculate the density-response matrix $\chi(\mathbf{q}+\mathbf{G}, \mathbf{q}+\mathbf{G}')$; the size of the matrices is determined by the cutoff of 10 Ry we are using for $|\mathbf{q}+\mathbf{G}|^2$.[20]

The successive steps are the following. First we evaluate the "perturbative" expression for $\chi_0(\mathbf{q}+\mathbf{G}, \mathbf{q}+\mathbf{G}')$

$$\chi_0(\mathbf{q}+\mathbf{G}, \mathbf{q}+\mathbf{G}') = -\frac{4}{(2\pi)^3} \sum_{v,c} \int_{\mathrm{BZ}} d\mathbf{k} \frac{\langle \mathbf{k}+\mathbf{q}c \,|\, e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \,|\, \mathbf{k}v \rangle \langle \mathbf{k}v \,|\, e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}} \,|\, \mathbf{k}+\mathbf{q}c \rangle}{E_c(\mathbf{k}+\mathbf{q}) - E_v(\mathbf{k})} \ . \tag{13}$$

Starting from χ_0 it is easy to obtain ϵ_{LDA} through (9), invert it and through (7) obtain χ. In the work of Mattausch *et al.*[11] χ_0 was calculated once at the Γ point only, the whole dependence on $\mathbf{q}$ being given by, the Coulomb v_C and the exchange integral only. Here χ_0 has the full $\mathbf{q}$ dependence. The finite mesh of $\mathbf{q}$ points for performing the integration in Eq. (11) could be the major reason for computational inaccuracies. The $1/q^2$ Coulomb singularity is cut off, for example, but this is not important since we want to study the charge polarization inside the central and neighboring cells only and we are not interested in the Coulomb tail.

The band structure underlying the evaluation of (13) is obtained from a self-consistent solution of the Kohn-Sham equations with the local ionic pseudopotentials of Ref. 17 and LDA the same as used in Ref. 21. A plane-wave basis set with cutoff of 12 Ry is built and the resulting Hamiltonian matrices are directly diagonalized without any approximating procedure. The local exchange-correlation potential used in the Kohn-Sham equations is, as in Ref. 21 given by

$$V_{xc}(\mathbf{r}) = -0.8\tfrac{3}{2} e^2 \left[\frac{3\rho(\mathbf{r})}{\pi} \right]^{1/3} \ . \tag{14}$$

In the evaluation of matrix elements in Eq. (13) we employed the fast-Fourier-transform technique, which significantly speeds up the procedure. The summation over all available conduction bands was performed in (13) and the integral over BZ was done using the (4,4,4) mesh of Monkhorst and Pack.[18]

IV. SCREENING OF IMPURITIES IN GERMANIUM

In Figs. 1 and 2 the electron polarization around Coulomb impurities of charge $+e$ in the interstitial and substitutional positions in Ge is shown along [111] and [100] directions. The choice of a pure Coulomb $1/r$ bare potential is unphysical in the substitutional case, but has been made in order to emphasize the main differences in the screening of interstitial versus substitutional impurities. On both these figures the effect of the diagonal and off-diagonal responses is shown separately. The solid and dotted lines correspond to LDA and RPA types of screening, respectively, as defined above. Near the origin some of the curves go beyond the scale of the figures. The maxima at the origin, outside the figure, are reached monotonically without further structure. Their actual values (in electrons per unit cell) are equal to 2.7, 17.1, -14.4 for the interstitial Coulomb impurity in the case of LDA response and total, diagonal, and off-diagonal contribution to screening, respectively; for the RPA response they are equal to 2.3, 13.6, -11.3. For the Coulomb impurity in the substitutional position these values are equal to 13.3, 17.1, -3.8 for LDA and 11.1, 13.6, -2.5 for RPA responses, respectively. The positions of nearest host atoms are shown by the arrows.

The diagonal contributions on both figures are, as it should be, the same and this fact reflects the site independence of the impurity potentials screened with a dielectric *function* only. The real shape of the electron polarization density is determined from the balance between the diagonal and off-diagonal contributions. This balance results in a strong cancellation at the origin: while the diagonal response tends to push more screening charge closer and closer to the positively charged impurity, the off-diagonal response has an opposite effect—it prevents too many electrons from coming close to the impurity. The diagonal screening is almost structureless and spherical, having about the extent of the central cell. The whole complexity of the structure of the screening charge is determined by the off-diagonal response. It is then evident that the detailed shape of the impurity potentials in the central cell is very much different from that obtained with the dielectric *function* only. We can expect that the off-diagonal part in screening has a significant effect on the ground electron states in the presence of the impurity.

There is a qualitative difference in the polarization charge behavior between the interstitial and subsitutional cases. For the interstitial impurity, the electron polarization density takes much smaller values near the origin than in the substitutional case. This means that screening is much more effective for substitutional impurities, as it should be, since there the impurity is surrounded by the high electron density of four nearest bonds, while the interstitial impurity is placed in a region of low electron density. The most prominent feature of Figs. 1 and 2 is the polarization of bonds near the impurities. This polarization is completely due to the off-diagonal contribution to screening. It can be seen in Figs. 1 and 2 that the effect of exchange and correlation in screening of impurities in Ge is quantitatively less important than the effect of the off-diagonal screening. The values of the polarization charge densities are smaller and the induced structures (e.g., polarization of bonds) are weaker if calculated with RPA response, but the overall shape of the electronic screening remains the same. A much greater effect is brought about by the local fields than by exchange correlation in response. This is in agreement with the findings of Mattausch *et al.*,[11] whose results concerning silicon are similar to ours while the results for screening in diamond indicate greater dependence on the exchange in that case.

In order to study the effectiveness of screening we have calculated the *total* polarization charge contained in a sphere of radius R around the impurity. The results are presented in Fig. 3 for the case of the LDA type of response and the Coulomb impurities in the interstitial tetrahedral and substitutional positions. The contributions coming from the diagonal and off-diagonal elements of density-response matrices are also shown. The arrows indicate the distances from the impurity to the successive shells of atoms. The *wavy* structure of the polarization charge is again brought about by the local fields. The almost structureless diagonal contribution should go in principle for large R to the limit determined by the *macroscopic* electronic dielectric constant ϵ_∞ according to the relation

$$Z^* \xrightarrow[R\to\infty]{} 1-\frac{1}{\epsilon_\infty}\,, \tag{15}$$

where Z^*e is the screening charge inside the sphere of radius R. The value of ϵ_∞ yielded by (15) and Fig. 3 is

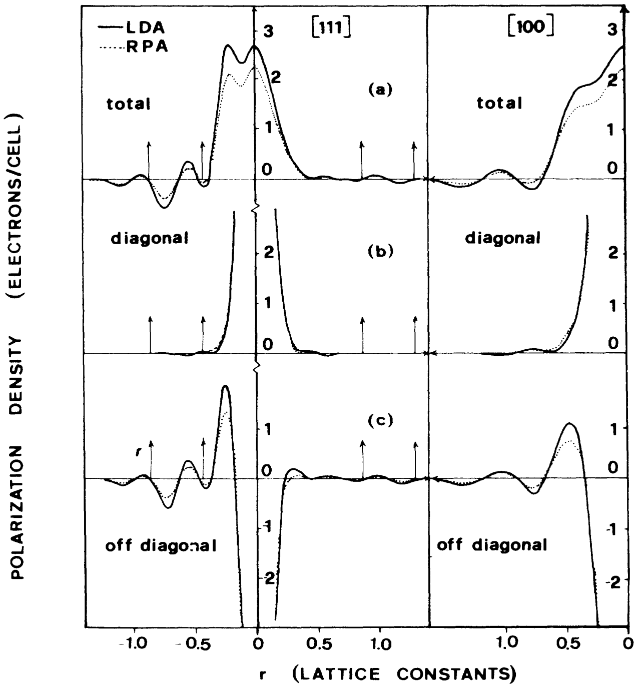

FIG. 1. Induced electron polarization density (in electrons per cell) due to a positive $+e$ point charge in the interstitial tetrahedral position in Ge along the [111] direction (left part of the figure) and [100] direction (right part); the results of the total (a), diagonal (b) and off-diagonal (c) contributions to screening are shown separately. Solid lines correspond to the LDA type of response, dotted line corresponds to the RPA type. The nearest atoms shown by arrows.

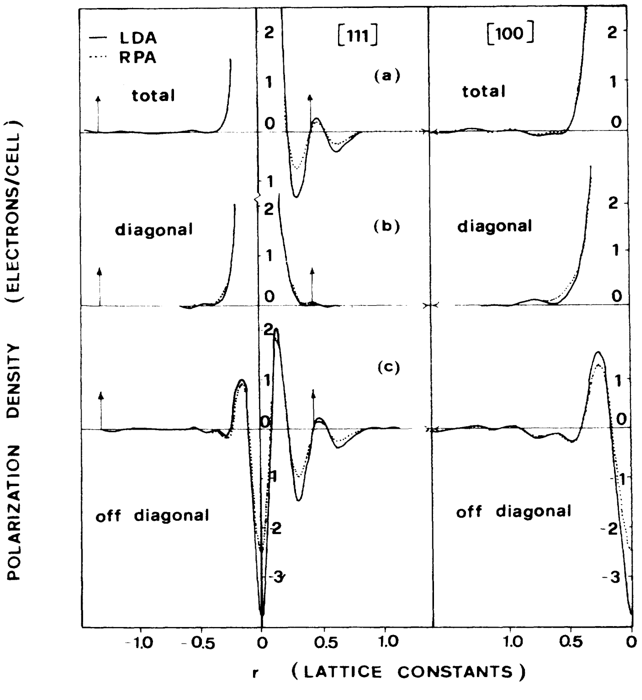

FIG. 2. Induced electron polarization density (in electrons per cell) due to the $+e$ point charge in the substitutional position in Ge. Same as in Fig. 1.

about 14.3. Its very good agreement with experiment is rather surprising and seems accidental; ϵ_∞ should in fact be calculated from the $\mathbf{q}\rightarrow 0$ limit of response matrices which corresponds to the screening of the constant electric field, while the polarization charge of Figs. 1–3 was obtained from the response matrices evaluated at the finite mesh of q points, each distant from 0. ϵ_∞ obtained from $\mathbf{q}\rightarrow 0$ limit is equal to 22.4 and this is mainly caused by the simple, local pseudopotential which together with $X\alpha$ type of exchange correlation gives too small gaps. Kunc and Resta obtained in Ref. 21 with the same pseudopotential but different approach the value 19.08 for ϵ_∞. We are, however, interested in this work mostly in the microscopic screening, where the macroscopic constant plays a minor role.

It is proved in Fig. 3 that the screening in the substitutional case is more effective: The first peak in the total polarization charge is situated in the distance of about the half of the bond length, while in the interstitial case this distance is of about one bond length. This is because the off-diagonal contribution to screening for the substitutional impurity almost entirely adds to the diagonal contribution, while in the case of interstitial impurity these contributions have opposite sign.

In Figs. 4 and 5 we analyze the polarization electron density in the (110) plane around the Coulomb impurity

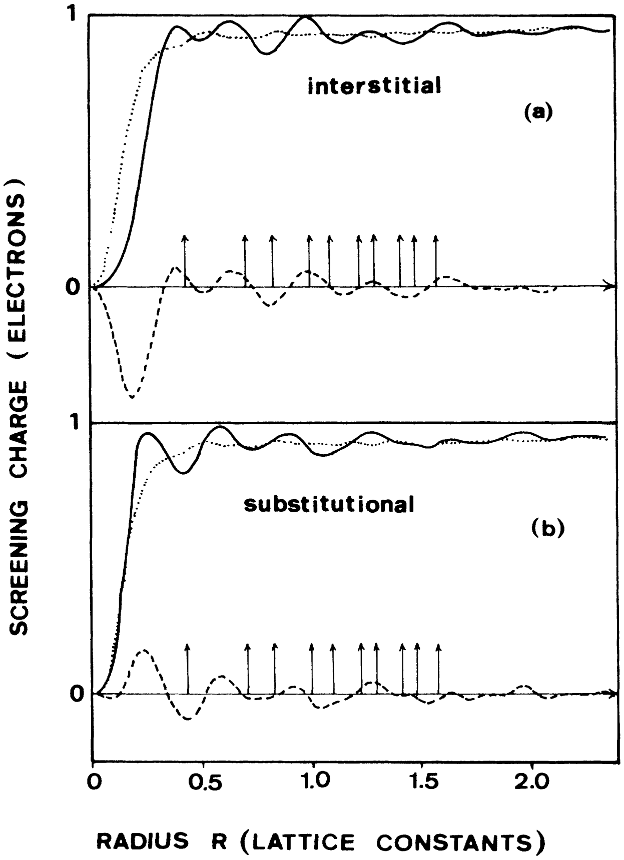

FIG. 3. The negative of the total induced charge inside the sphere of radius R around the $+e$ point charges in the interstitial tetrahedral position (a) in Ge and the substitutional (b) position. Solid lines—total, dotted lines—diagonal, dashed lines—off-diagonal contributions to screening. Arrows indicate the distances to a few nearest shells of atoms.

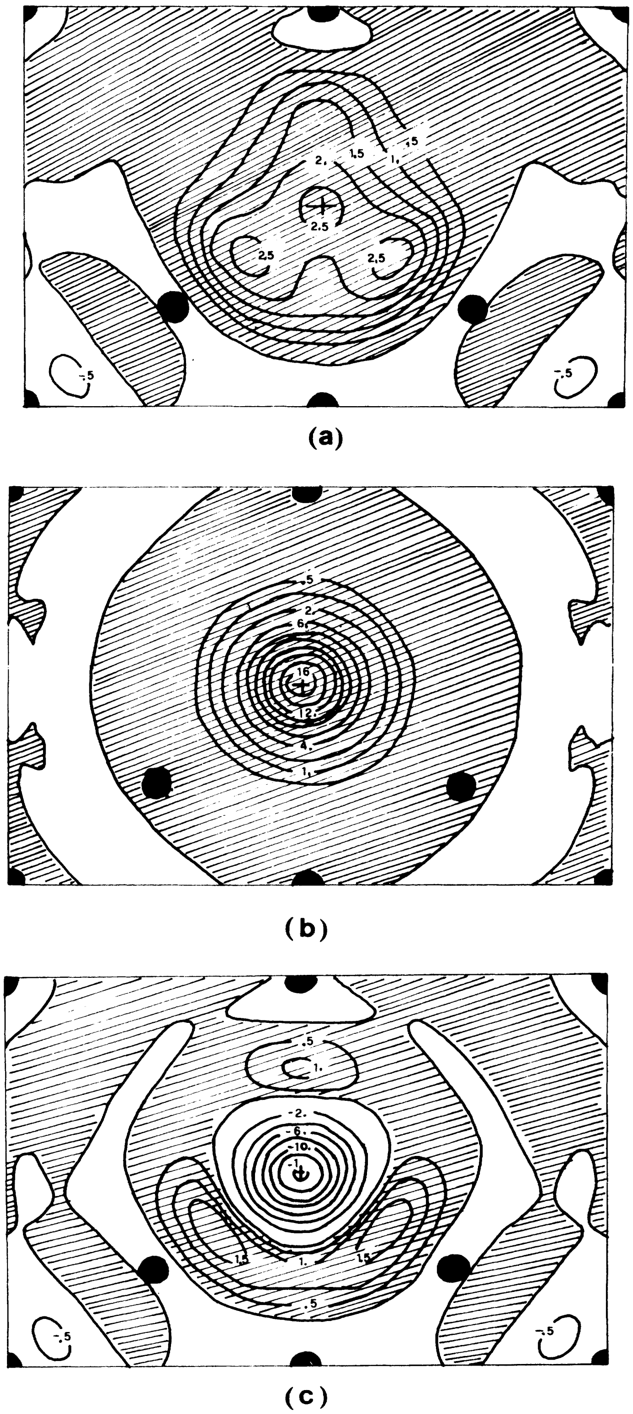

FIG. 4. Polarization of electrons in $(1\bar{1}0)$ plane (in electrons per cell) around the $+e$ point charge in the interstitial tetrahedral position in Ge; (a) full, (b) diagonal, (c) off-diagonal screening. Black dots indicate atoms, the cross shows the position of the impurity. Shaded areas indicative positive electron density.

at the interstitial and an arsenic at the substitutional position. As the perturbing impurity potential in the letter case we use the difference between the As and host ionic pseudopotentials.[17] The contour plots show again the contributions coming from the diagonal and off-diagonal screening and it is seen very clearly now that the local-field effects are mostly responsible for the details of the structure of the polarization electron density.

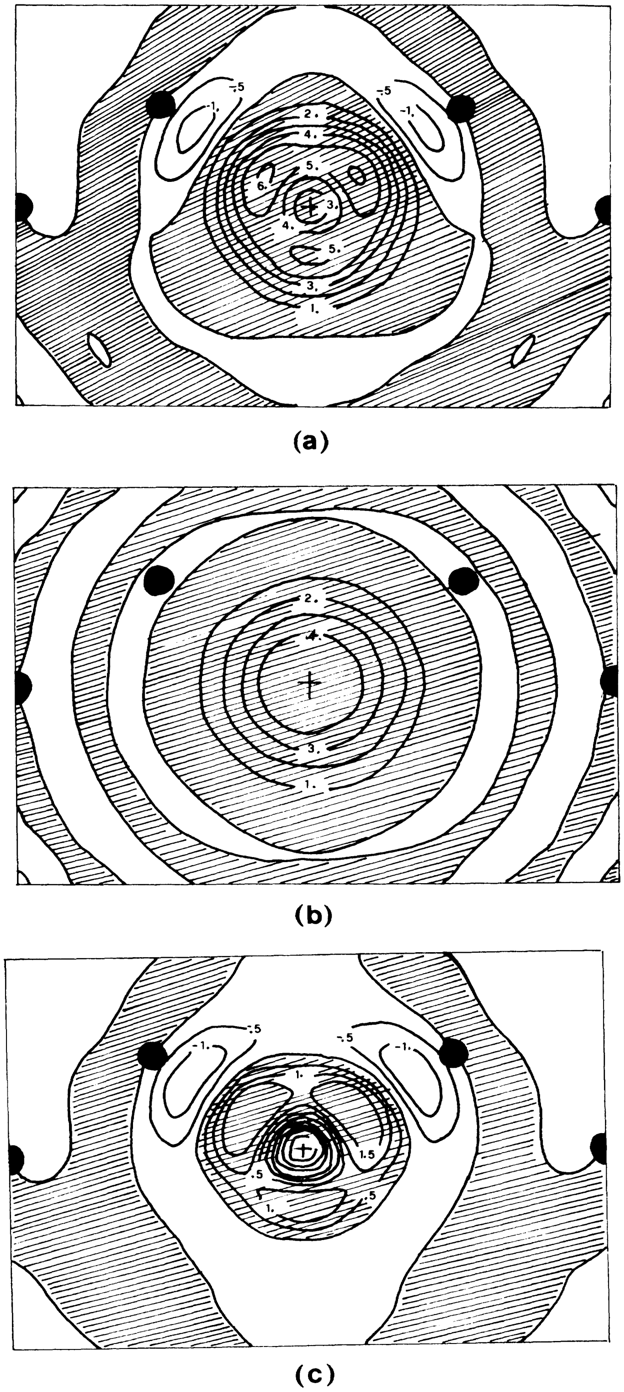

FIG. 5. Polarization of electrons in $(1\bar{1}0)$ plane (in electrons per cell) around the substitutional As in Ge. The *bare* impurity potential is the difference between As and host atomic pseudopotentials. Symbols as in Fig. 4.

V. INTERVALLEY SCATTERING MATRIX ELEMENTS

The essential problem in calculating the shallow donor states and energies in semiconductors having several equivalent conduction band minima is the treatment of the intervalley interactions. The inclusion of these interactions can change dramatically the character of EMA (intravalley) solutions and it was shown[7,8] that the shallow-deep instability can occur for strong intervalley couplings. It was also proved that two factors are important in the calculation of intervalley scattering matrix elements: the dispersive screening of impurity potential[6] and the microscopic (G-dependent) form of the overlapping Bloch functions from different valleys.[22]

Altarelli *et al.*[7] define a dimensionless renormalization factor λ_{ij} through the relation

$$\langle \mathbf{k}_i^0 | V_{\rm imp}^{\rm scr} | \mathbf{k}_j^0 \rangle = \lambda_{ij} \frac{4\pi e^2}{\epsilon(\mathbf{k}_i^0-\mathbf{k}_j^0)\,|\mathbf{k}_i^0-\mathbf{k}_j^0|^2} \; . \qquad (16)$$

Here $\mathbf{k}_i^0$, $\mathbf{k}_j^0$ in the matrix element stand for the Bloch functions of the bottoms of valleys at $\mathbf{k}_i^0$ and $\mathbf{k}_j^0$, respectively. The authors of Ref. 7 claim that the values of λ_{ij} for i,j much smaller than 1 determine the shallow nature of donors, while whenever λ_{ij} is close to 1 or larger, one could expect the formation of deep states. They predict shallow substitutional and deep interstitial donors in Si and shallow ones in Ge. The deep character of the ground state due to the interstitial proton in Ge would be however caused by the additional, higher minima on Δ direction. Resca and Resta,[8] on the other hand, predict deep states due to Coulomb potential for both substitutional and interstitial donors in Si.

There is general agreement on the fact that progress in the theoretical description of donors in multivalley semiconductors necessarily must include the detailed behavior of Bloch function over the Brillouin zone and not only use their periodic parts fixed at the band minima. Our aim here is not to improve upon this line, we want rather to revise the accuracy of the calculation of Altarelli *et al.* of multivalley scattering matrix elements taking into account the site dependence of screened Coulomb potential. In both alternative approaches of Refs. 7 and 8 the bare Coulomb potential is screened with the diagonal q-dependent dielectric function, which results in the spherical site-independent impurity potential. We ask the question what are the effects of local fields and exchange correlation on the intervalley scattering matrix elements, Eq. (16). A similar question was addressed in Ref. 23, where a model dielectric matrix was used to build λ_{ij} renormalization factors for the absolute conduction-band minima in Si and the additional, higher minima on the Δ direction in Ge. A model dielectric matrix used in Ref. 23 has been obtained from the fitting to the RPA *ab initio* calculation at Γ point only and does not contain much of the complexities of many-body effects provided by the exchange and correlation in screening. Moreover, in contrast to Ref. 23, we consider here the absolute minima of conduction band of Ge located at L points.

For the bare Coulomb potential the renormalization factors λ_{ij} can be expressed in terms of the inverse dielectric matrix and the periodic parts of Bloch functions $u_{\mathbf{k}_i}, u_{\mathbf{k}_j}$ as:

$$\lambda_{ij}=\sum_{\mathbf{G}} c(\mathbf{k}_i,\mathbf{k}_j,\mathbf{G}) \left\{ \frac{\epsilon^{-1}(\Delta\mathbf{k}_{ij}+\mathbf{G},\Delta\mathbf{k}_{ij}+\mathbf{G})}{\epsilon^{-1}(\Delta\mathbf{k}_{ij},\Delta\mathbf{k}_{ij})} \frac{|\Delta\mathbf{k}_{ij}|^2}{|\Delta\mathbf{k}_{ij}+\mathbf{G}|^2} + \sum_{\substack{\mathbf{G},\mathbf{G}' \\ (\mathbf{G}\neq\mathbf{G}')}} \frac{\epsilon^{-1}(\Delta\mathbf{k}_{ij}+\mathbf{G},\Delta\mathbf{k}_{ij}+\mathbf{G}')}{\epsilon^{-1}(\Delta\mathbf{k}_{ij},\Delta\mathbf{k}_{ij})} \frac{|\Delta\mathbf{k}_{ij}|^2}{|\Delta\mathbf{k}_{ij}+\mathbf{G}'|^2} \right\}, \qquad (17)$$

where $\Delta\mathbf{k}_{ij}=\mathbf{k}_i-\mathbf{k}_j$ and $c(\mathbf{k}_i,\mathbf{k}_j,\mathbf{G})$ is given by

$$u^*_{\mathbf{k}_i}(\mathbf{r})u_{\mathbf{k}_j}(\mathbf{r})=\sum_{\mathbf{G}} c(\mathbf{k}_i,\mathbf{k}_j,\mathbf{G})e^{i\mathbf{G}\cdot\mathbf{r}} . \qquad (18)$$

To evaluate Eq. (17) we use a full inverse dielectric matrix obtained within the first-principles approach as described in Sec. III. The proper inclusion of exchange and correlation implies the insertion in (17) of the electronic dielectric matrix (10). In order to study the influence of exchange and correlation we use in (17) also the RPA dielectric matrix. There are four conduction band minima in Ge located at the equivalent L points and for some of them $\Delta\mathbf{k}_{ij}$ is equal to $\mathbf{k}_x=(2\pi/a)(1,0,0)$. We evaluate λ_{ij} corresponding to $\mathbf{k}_x$, the other being equal by symmetry. The dielectric matrix at $\mathbf{k}_x$ is obtained within the same formalism and technical details as described in Sec. III. The results are given in Table I.

Comparing the values of λ_{ij} calculated within the different approximations we can analyze the relative importance of various factors: Bloch functions overlap Fourier coefficients $c(\mathbf{k}_i,\mathbf{k}_j,\mathbf{G})$, local-field effects, or exchange correlation in screening. As far as L minima only are concerned it results that the substitutional Coulomb impurity bonds stronger to the electrons than to the interstitial ones. In this former case λ_{ij} are mostly determined by the diagonal response, the off-diagonal one being much weaker does not change significantly the value of λ_{ij} which remains always greater than 1. The role of local fields grows up in the interstitial case. There both parts of summations in (17) are of the same order and of the same sign. The opposite sign of local-field effects in the substitutional and interstitial cases corresponds well with Fig. 3. In the former case the off-diagonal elements of the dielectric matrix are responsible for the part of electron transfer towards the impurity near the origin, which increases the effectiveness of screening and lowers the bonding properties of the impurity. It is just the opposite in the interstitial case. The off-diagonal part of the DM weakens the effectiveness of screening, which results in the increasing of value of λ_{ij}. Once could think then that the interstitial impurity bonds more strongly, opposite to the conclusions of Table I. This is not true (at least within the present approach), since the diagonal contribution to λ_{ij} in the substitutional case is much stronger. This contribution results mainly from the overlap of Bloch functions of different valleys.

The effect of exchange and correlation does not seem to be essential. It reduces by about half only the off-diagonal parts of λ_{ij}, the dominant diagonal ones remaining almost unchanged.

Finally we want to stress that the conclusions of this section are only qualitative and refer however to a theoretical treatment whose validity is not, at present, completely assessed. The proper theory of donor states cannot be based on the perturbative treatment of intervalley scattering on the top of EMA solutions. It should take into account the variation of Bloch functions outside the bottom of valleys as well as the other valence or conduction bands if necessary to the description of deeper states. Here we wanted primarily to study again the role of various kinds of screening and the above results could be relevant in the case of weakly-bonding (pseudo)potentials.

TABLE I. λ_{ij} renormalization factors for the absolute minima at L points of the conduction band of Ge for the screened $+e$ point charge at the substitutional and interstitial tetrahedral positions. The results of test-charge–electron [Eq. (10)] and RPA as well as full, diagonal, and off-diagonal types of screening shown separately.

Types of screening		Substitutional	Interstitial
RPA	Diagonal	2.37	0.69
	Off diagonal	−0.50	0.60
	Full	1.87	1.29
Test charge −electron	Diagonal	2.41	0.70
	Off diagonal	−0.27	0.36
	Full	2.14	1.06

VI. CONCLUSIONS

We have studied the site dependence of screening of impurity potentials in Ge. This dependence is contained in the off-diagonal elements of response matrices. We have calculated a number of response matrices within the LDA scheme and applied them to obtain the electron polarization density for various impurities. This density has a complex structure of tetrahedral symmetry in the central cell as visualized in Figs. 1–5. The strong cancellation between the diagonal and off-diagonal contributions to screening occurs at the impurity site and both these contributions are important to build up properly the polarization charge in the vicinity of defect. The details of the screening structure characteristic of a given position of impurity, such as, for example, the formation of dipoles along the nearest bonds or electronic charge displaced outside the bond region towards the interstitial impurity, are due to local-field effects. The screening of impurities is more effective in the substitutional case than in the interstitial one: More screening charge is displaced towards to defect. In both cases however the quantitatively significant deviations from the uniform (diagonal) screening are almost entirely contained in the central cell.

The effect of the exchange-correlation contribution to the response operators, so essential in lattice dynamics of Ge, seems to have less importance in the screening of the defect potentials. Exchange and correlation do not produce great changes in the shape of polarization charge (see Figs. 1 and 2). One should remember however that for the proper evaluation of the shallow impurity ground-state energy—a very small quantity—the corrections brought about by exchange and correlations could turn out to be non-negligible.

Here we do not combine the resulting screened impurity potential with any existing method to calculate one-electron impurity states. We have only analyzed which effect the local-fields and exchange correlation would produce in the calculation of the intervalley scattering matrix elements in Ge. Our conclusions are that for substitutional impurities these effects are minor ones, while for the interstitial defects they are greater. One could expect that these effects play a significant role in the formation of the ground state of (especially interstitial) weakly and intermediately bounding potentials. We believe also that our results can be useful in the construction of a proper theory of shallow-deep instabilities of defects in semiconductors.

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