Theoretical intrinsic lifetime limit of shallow donor states in silicon

Valeriy Tyuterev,* Jelena Sjakste, and Nathalie Vast
Ecole Polytechnique, Laboratoire des Solides Irradiés, CEA-DSM, CNRS, 91128 Palaiseau, France
(Received 31 March 2010; published 21 June 2010)

The intrinsic lifetime of the $2p_0$ shallow impurity state in silicon doped with P, As, Sb, or Bi has been computed by combining matrix elements of the electron-phonon coupling within the density-functional perturbation theory, with the envelope function approximation for the impurity wave functions. The theoretical lifetime due to the electronic interaction with intervalley phonons has been found to be 1.1 ns for P-doped silicon, and this theoretical limit is much longer than has been previously believed for the last five decades.

DOI: 10.1103/PhysRevB.81.245212 PACS number(s): 78.20.Bh, 71.15.Mb, 71.38.−k, 71.55.−i

I. INTRODUCTION

Shallow impurity centers in silicon have recently attracted a lot of attention in the context of the development of lasers in the terahertz range. Indeed, the difference in the intrinsic lifetime of different shallow impurity states allows for the population inversion at temperatures lower than 30 K. For example, in the case of Si doped with group V donors such as P or Sb, the $2p_0$ state turns out to be particularly long living and to be the lasing state. Therefore, the theoretical understanding and prediction of the lifetime of shallow impurity states in silicon is crucial for the improvement of terahertz lasers.[1–3]

However, the old and seemingly well-understood problem of the lifetime of shallow impurity states and of the linewidth of their Lyman spectral lines,[4,5] contains new challenges both theoretically and experimentally. The finite linewidth had been attributed to a lifetime effect caused by the electron-phonon coupling.[6] However, the assumption that all important inhomogeneous broadening mechanisms are minimized in earlier experimental works[4,5] has since proved to be inaccurate: the isotopic disorder has recently been recognized as an important source of inhomogeneous broadening (see, e.g., the first column of the Table I for Si:P).[7,10,14] Except for the case of resonant interactions between zone-center optical phonons and certain impurity states, as those occurring for bismuth donors,[15,16] the experimental intrinsic lifetime limit of shallow impurity states in isotopically pure silicon (due to the electron-phonon interaction) turns out to be much longer than previously believed.

In this work, we show that this actual limit of the intrinsic lifetime of the $2p_0$ state is still underevaluated by one order of magnitude. Even in the most recent experimental work on ^{28}Si:P, the observed width of the $2p_0$ state cannot be caused only by the electronic interaction with intervalley phonons. Indeed, the shallow impurity donor states are essentially combinations of conduction-band states close to the conduction-band minima (CBM or valleys). The electron is transferred from one equivalent minimum to another one via the emission of a short-wavelength (intervalley) phonon. In silicon, one distinguishes between f- and g-type intervalley transitions [Figs. 1(a) and 1(b)]. The energy differences between the impurity levels fix the frequencies of the phonons allowed in the transitions [Fig. 1(c)]. For the long-living $2p_0$ state of Si:P, Si:Sb, and Si:As, the lifetime is determined by transitions from the $2p_0$ to the $1s(E)$ and $1s(T_2)$ states, assisted by emissions of longitudinal-acoustic (LA) g-type phonons or transverse-acoustic (TA) f-type phonons, all other transitions being forbidden by the energy conservation law. We have computed the total transition rate of these electron-phonon processes. The importance of the electron-phonon coupling appears to have been largely overestimated in all previous calculations,[3,6,8,11] and the *ab initio* computation of the matrix elements turns out to be crucial in order to overcome the latter overestimation.

II. THEORY

The inverse lifetime of the $2p_0$ shallow impurity donor state in Si doped with group V donors has been computed with our approach for the calculation of the electron-phonon coupling constants in semiconductors,[17,18] based on the density-functional perturbation theory (DFPT).[19] Here it has been combined with the envelope function approximation which has proved successful in describing the shallow impurity states.[20] The shallow impurity wave function Ψ_μ can be expanded in the basis set of the conduction-band states with a Wannier representation,

TABLE I. Si:P. First column: full width at half maximum of the $2p_0$ infrared-absorption line of isotopically enhanced or natural silicon. Other columns: theoretical linewidth of the $2p_0$ spectral line due to the $2p_0 \rightarrow 1s(E,T_2)$ intervalley electron-phonon transitions, computed with *ab initio* electron-phonon coupling constants (second column) or with an effective deformation potential (previous works, third column).

Γ (μeV)		
Expt.	This work	Prev. calc.
4 ± 1.5 (Ref. 7)[a]	0.5[c]	17 (Refs. 8 and 9)[d]
10 ± 1.5 (Refs. 7 and 10)[b]	0.6[d]	10 (Ref. 3)
21 ± 7.0 (Ref. 4)[b]		20 (Ref. 11)
		60 (Ref. 6)

[a]Isotopically pure ^{28}Si.
[b]Natural Si.
[c]Obtained with envelope function parameters from Ref. 12.
[d]Obtained with envelope function parameters from Ref. 13.

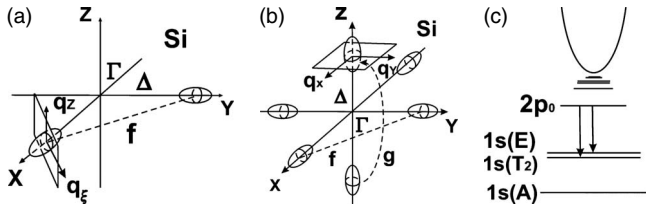

FIG. 1. Doped Si. Schemas (a) and (b): f- and g-type intervalley transitions (dashed lines) between the CBM. The planes perpendicular to the vectors linking the CBM are defined for further use in Fig. 2. Schema (c): shallow impurity energy levels below the CBM. The vertical arrows indicate the transitions studied in this work.

$$\Psi_\mu(\mathbf{r}) = \sum_{n,L} \Phi_\mu^n(\mathbf{R}_L) w_n(\mathbf{r} - \mathbf{R}_L), \tag{1}$$

where $w_n(\mathbf{r})$ are Wannier basis functions, $\Phi_\mu(\mathbf{R}_L)$ are the expansion coefficients, $\mathbf{R}_L$ are lattice vectors, and the μ index labels the localized impurity states (e.g., $2p_0$ and $1s$). We point out that a Wannier basis is used here for the clarity of the theoretical development and does not enter into the numerical application. In this work, the one-band approximation has been considered and the band index n is going to be omitted. In the envelope approximation,[21] the Fourier transform of Φ_μ reads

$$\Phi_\mu(\mathbf{R}_L) = \sum_{\boldsymbol{\kappa},s} \beta_s F_\mu^s(\boldsymbol{\kappa}) e^{i\mathbf{k}_s \mathbf{R}_L} e^{i\boldsymbol{\kappa}\mathbf{R}_L}, \tag{2}$$

where s labels the six equivalent CBM located at $\mathbf{k}_s$ in the reciprocal space and $F_\mu^s(\boldsymbol{\kappa})$ are the envelope functions in the Fourier space. The coefficients β_s guarantee that the impurity state has the proper symmetry.[22]

Using the well-known relationship between Wannier and Bloch bases, an electron-phonon matrix element between localized impurity states reduces to a linear combination of the electron-phonon matrix elements between Bloch states $\psi_\mathbf{k}$,

$$\langle \Psi_\mu | H_{el\text{-}ph} | \Psi_\nu \rangle = \sum_{ss'\boldsymbol{\kappa}\boldsymbol{\kappa}'} \beta_s^* \beta_{s'} F_\mu^{s*}(\boldsymbol{\kappa}) F_\nu^{s'}(\boldsymbol{\kappa}') \times \langle \psi_{\mathbf{k}_s+\boldsymbol{\kappa}} | H_{el\text{-}ph} | \psi_{\mathbf{k}_{s'}+\boldsymbol{\kappa}'} \rangle. \tag{3}$$

When the latter are calculated with our approach,[17,18] they contain the perturbation of the self-consistent crystal potential $\Delta W^{\mathbf{Q}\lambda}$, induced by the phonon of wave vector $\mathbf{Q}$, mode λ, and frequency $\omega_\mathbf{Q}^\lambda$. We have considered very low temperatures and have neglected the absorption processes. The momentum-conservation law for the emission of one phonon implies that $\boldsymbol{\kappa}' = \mathbf{k}_s - \mathbf{k}_{s'} + \boldsymbol{\kappa} + \mathbf{Q}$, where $\mathbf{Q}$ is meant to describe both normal and umklapp transitions. Furthermore, we use the fact that Fourier-transformed envelope functions $F_\mu^s(\boldsymbol{\kappa})$ in Eq. (3) are strongly localized near $\boldsymbol{\kappa}=\mathbf{0}$, and thus it is justified to use a mean point approximation at $\boldsymbol{\kappa}=\mathbf{0}$ in our electron-phonon matrix elements. It is then convenient to define the argument of the envelope function with a small vector, $\mathbf{q} = \mathbf{Q} + \mathbf{k}_s - \mathbf{k}_{s'}$.

The transition probability per unit of time at low temperature between two impurity energy levels E_μ and E_ν via the spontaneous emission of one phonon can be calculated by Fermi's golden rule,

$$P_{\mu\nu} = \sum_{\mathbf{q}ss'} \frac{\pi}{\rho\omega_\mathbf{Q}^\lambda} |\beta_s|^2 |\beta_{s'}|^2 |f_{\mu\nu}^{ss'}(\mathbf{q})|^2 (D_{\mathbf{k}_s,\mathbf{Q}}^\lambda)^2 \delta(E_\mu - E_\nu - \hbar\omega_\mathbf{Q}^\lambda), \tag{4}$$

where we have introduced the form-factor function,

$$f_{\mu\nu}^{ss'}(\mathbf{q}) = \sum_{\boldsymbol{\kappa}} F_\mu^{s*}(\boldsymbol{\kappa}) F_\nu^{s'}(\boldsymbol{\kappa} + \mathbf{q}), \tag{5}$$

and the intervalley deformation potential proportional to the modulus of the electron-phonon matrix element,[17]

$$D_{\mathbf{k}_s,\mathbf{Q}}^\lambda = \sqrt{\frac{2V\rho\omega_\mathbf{Q}^\lambda}{\hbar}} |\langle \psi_{\mathbf{k}_s} | \Delta W^{\mathbf{Q}\lambda} | \psi_{\mathbf{k}_s+\mathbf{Q}} \rangle|. \tag{6}$$

V is the crystal volume and ρ is the Si mass density.

Our Eq. (4) is completely general and is not limited to the allowed transitions for which $D_{\mathbf{k}_s,\mathbf{Q}} \neq 0$ at $\mathbf{q}=\mathbf{0}$, as in Refs. 8 and 16. The numerical implementation of Eq. (4) is possible only with a method able to provide a realistic $\mathbf{q}$ dependence (or, equivalently, $\mathbf{Q}$ dependence) of the intervalley deformation potential.[17,18] To obtain the total scattering rate Γ, the probabilities [Eq. (4)] for the transitions from the $2p_0$ state to the $1s(E)$ and $1s(T_2)$ states via both f-TA and g-LA phonons are added up. The inverse linewidth $\tau = \hbar/\Gamma$ yields the $2p_0$ lifetime.

III. RESULTS

We have described pure silicon within the density-functional theory (DFT) and the local-density approximation (LDA), with the pseudopotential of Ref. 23, a plane-wave basis set with a cutoff energy of 45 Ry and a Monkhorst-Pack grid of ten nonequivalent $\mathbf{k}$ points in the irreducible Brillouin zone (BZ). We have obtained an equilibrium lattice parameter a of 5.40 Å. The conduction band minima were at points equivalent to $\mathbf{k}_s = (0,0,k_0)\frac{2\pi}{a}$, with $k_0=0.84$ in our calculations and $k_0=0.85$ in the scientific literature.[24] The computed transverse and longitudinal effective masses of the lowest Δ valley were, respectively, $m_t=0.20m_0$ and $m_l=0.97m_0$, where m_0 is the electron mass, in complete agreement with the measured ones $m_t=0.19m_0$ and $m_l=0.98m_0$.[25] The impurity energies are not calculated within the DFT and the main drawback of the DFT-LDA, i.e., the underestimation of the band gap, plays no role in this study.

The phonon frequencies have been calculated within the DFPT, and the computed and experimental phonon-dispersion curves were in total agreement for Si.[19] It has been shown that the probability of presence of an electron in the lowest conduction bands, given by the modulus of the wave functions $\psi_{\mathbf{k}_s+\boldsymbol{\kappa}}$, is well described within the DFT-LDA.[26] Therefore, the electron-phonon matrix elements have been computed with the help of the wave functions obtained in DFT.

Two kinds of envelope functions F_μ^s have been used for the form-factor functions: those in the anisotropic form of

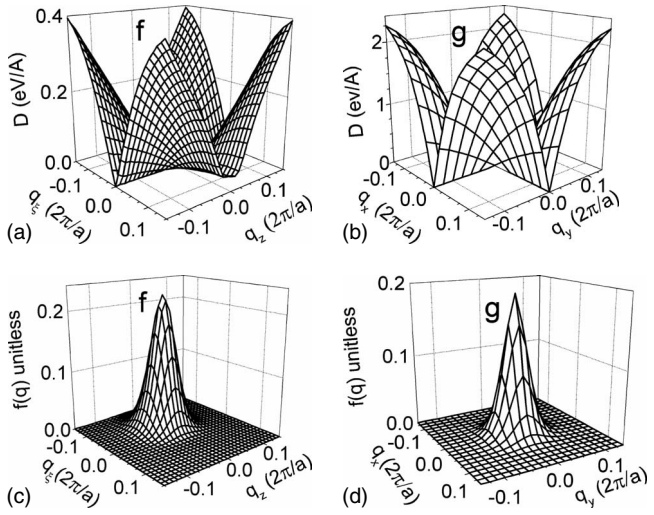

FIG. 2. Si:P. Left panels: f processes. Right panels: g processes. Upper panels: the deformation potential D (eV/Å) in planes defined as in Fig. 1(a) for f processes and Fig. 1(b) for g processes. Lower panels: the form-factor function $f^{2p_0\rightarrow 1s}(\mathbf{q})$ computed with the envelope functions of Ref. 12.

Ref. 12, with the parameters obtained therein with the variational method[27] and those with another set of parameters obtained from the asymptotic behavior of shallow impurity wave functions[13,28] and used in previous calculations.[8] The sum over $\mathbf{q}$ in Eq. (4) has been computed on a very fine uniform three-dimensional grid in $\mathbf{q}$ space with a step of $0.02\frac{2\pi}{a}$. It has been found to converge in a cube $\Omega_{\mathbf{q}}$ with an edge of 0.28 $\frac{2\pi}{a}$ centered at $\mathbf{q}=\mathbf{0}$.

The intervalley f-TA and g-LA deformation potentials have a very complicated $\mathbf{q}$ dependence in the vicinity of a symmetry-forbidden transition. We display in Figs. 2(a) and 2(b) the representative examples of their behavior in the selected planes of Figs. 1(a) and 1(b). When $\mathbf{q}=\mathbf{0}$, the intervalley transitions assisted by f-TA and g-LA phonons are forbidden by the symmetry selection rules and the deformation potential vanishes. This fact had already been pointed out in Ref. 30

However, not only are the f-TA and g-LA transitions between two minima not permitted but they are also forbidden along several high-symmetry directions in the Brillouin zone [Figs. 2(a) and 2(b)]. But this does not mean that the scattering by f-TA and g-LA phonons is impossible. As the modulus of $\mathbf{q}$ grows, or in other words, as $\mathbf{Q}$ goes away from high-symmetry directions, selection rules are lifted and the deformation potentials increase very rapidly (Fig. 2).

Yet, in order to obtain the total electron-phonon-scattering rate of Eq. (4), a sum including deformation potentials and the form-factor functions of Eq. (5) has to be computed. All form-factor functions used in this work have their maximum in the neighborhood of $\mathbf{q}=\mathbf{0}$, where the deformation potential vanishes, and are extremely localized. This has been illustrated in Figs. 2(c) and 2(d) for transitions between the $2p_0$ and $1s$ states of Si:P. Consequently, only a very tiny region $\Omega_{\mathbf{q}}$ of the Brillouin zone yields a nonzero contribution to the scattering rate.

Thus, our calculated linewidth of the $2p_0$ spectral line in Si:P is 0.5 μeV or 0.6 μeV (Table I, second column). Our value of Γ is the only one which does not contradict experimental data for isotopically enhanced Si (Table I, first column), at variance with all other theoretical values (Table I, third column). We predict that the electronic interaction with intervalley phonons has been largely overestimated in the interpretation of experiments. On the contrary, our value of Γ is lower by one order of magnitude than the most recent experimental value for the full width at half maximum of the $2p_0$ state in ^{28}Si.[7]

TABLE II. Theoretical lifetime of the $2p_0$ state in Si doped with P, As, Sb, or Bi due to transitions from $2p_0$ to $1s(E,T_2)$ states obtained with envelope parameters from Ref. 12. The separate lifetimes of f-TA and g-LA processes are also given. Experimental data (Ref. 29) have been measured in natural Si.

Lifetime (ns)	Si:P	Si:As	Si:Sb	Si:Bi
τ	1.1	1.8	1.3	2.4
τ_f	2.2	3.2	2.4	4.5
τ_g	2.1	4.1	3.0	5.2
Expt.	0.205	0.105		

The theoretical lifetimes of the $2p_0$ state in Si doped with P, As, Sb, or Bi lie between 1.1 and 2.4 ns (Table II). Both f and g processes are contributing to the lifetime. We point out that experimental inverse lifetimes in isotopically enhanced silicon are available only for phosphorus impurities and that resonant intravalley interactions in Si:Bi are known to considerably reduce the lifetime of the $2p_0$ state.[15,16] The value of the lifetime of the $2p_0$ state measured in pump/probe transient absorption experiments[29] is, respectively, 0.205 ns and 0.105 ns in natural Si:P and natural Si:As. It is much smaller than our corresponding theoretical lifetime in isotopically pure silicon.

From the results of the Table II, several conclusions can be drawn: our theoretical results support the outcomes of Refs. 7, 10, and 14 that anterior experimental works[4,5] contained unrecognized sources of inhomogeneous broadening. The width measured in Ref. 4 should be attributed to the isotopic disorder rather than to the electronic coupling to intervalley phonons, even though the latter is expected to be increased by the lift of the selection rules induced by the isotopic disorder. The role of the isotopic disorder should also be recognized in the performance of the terahertz lasers mentioned in the introduction.

IV. DISCUSSION AND CONCLUSION

Our results show that even in the latest experiment about ^{28}Si,[7] the width of the $2p_0$ spectral line cannot be interpreted as uniquely due to electron-phonon intervalley transitions, as has been done in the scientific literature so far. Although effects beyond the electron-one phonon interaction cannot be excluded, we estimate that their importance is small. A theoretical treatment of the effects of higher order processes involving two and three phonons is, however, beyond the scope of the paper. On the experimental side, the authors of

Ref. 7 were measuring inhomogeneous widths. The latter may be affected by strain fluctuations or other mechanisms. For instance, the samples of Ref. 7 have been mentioned to be chemically less pure than those in which the doping had been obtained by nuclear transmutation.[4] Furthermore, despite its improvement, the instrumental resolution is still three times larger than our theoretical expectation for the linewidth (Table I). On the other hand, the authors of Ref. 29 were measuring homogeneous broadenings (lifetimes) but in samples with isotopic disorder. At this point in time, we stress the difference with our theoretical values (Table II). An experiment like the one of Ref. 29 should be performed in an isotopically pure sample of Si:P, where we expect the lifetime to be five times longer. If such is the case, the difference could then be attributed to the isotopic disorder.

Turning to other theoretical results, we stress that the fact that f-TA and g-LA intervalley transitions are forbidden by symmetry has been neglected so far.[3,8] All transitions have been treated as allowed ones, with a constant *effective* deformation potential (third column of the Table I). This approach had proved to be successful in modeling transport properties of Si with $D^f_{eff}=0.3$ eV/Å for f processes and $D^g_{eff}=0.8$ eV/Å for g transitions.[25]

But there is a fundamental difference between transport properties and transitions between shallow impurity levels. In the former problem, the intervalley scattering between the CBM reduces the electronic mobility in Si doped with electrons. The chemical potential lies close to the bottom of the conduction band, and the distribution of electrons around the chemical potential can be described by a function extended in a rather wide region of the reciprocal space. Considering Figs. 2(a) and 2(b), this means that the electronic distribution "probes" the large values of the deformation potential as well as the small ones close to $\mathbf{q}=\mathbf{0}$. For instance, the mean values of our *ab initio* deformation potentials averaged in the above-defined volume $\Omega_{\mathbf{q}}$ are $D^f_{av}=0.2$ eV/Å for f-TA processes and $D^g_{av}=1.2$ eV/Å for g-LA transitions, respectively, close to the values of the effective potential used in the simulation of transport properties and reported above.

In the case of the shallow impurity levels, on the contrary, the form-factor functions f are very strongly localized around $\mathbf{q}=\mathbf{0}$ [Figs. 2(c) and 2(d)] so that the values of the deformation potential which contribute to the transition rate are much smaller than the effective values for the transport properties. Thus, it is not astonishing that the approach of Refs. 3 and 8 unrealistically overestimated the importance of the electron-phonon coupling. This contribution to the mobility of the electron-intervalley phonon scattering should be strongly dependent on the chemical potential. However, in the mobility of Si, this effect is masked owing to the much higher scattering rates that arise from the ionized impurities,[30] from the high-energy phonons,[30] and from the plasmons.[31]

In conclusion, we have calculated the intrinsic lifetime of shallow impurity states in silicon by combining the *ab initio* matrix elements of the electron-phonon coupling, with the envelope function approximation for the impurity states. The computed lifetime turns out to be much longer than has been thought for the last 50 years and suggests that the value of the linewidth actually observed in the infrared experiment on isotopically enhanced silicon is due not only to the electronic interaction with intervalley phonons. Our theoretical upper limit for the intrinsic lifetime of shallow impurity states provides a new challenge for the understanding of fundamental processes in silicon.

ACKNOWLEDGMENTS

Results have been obtained with the (modified) QUANTUM ESPRESSO package (Refs. 19 and 32). The authors acknowledge discussions with P. Giannozzi, A. Polian, and I. Timrov, support from the ANR (project PNANO ACCATTONE), and computer time granted by CEA/DSM (project p93), GENCI (project 2210), and IRSC of Tomsk State University. V.T. acknowledges support from the Ecole Polytechnique (postes d'accueil) and CNRS (poste rouge), from the Russian Foundation of Basic Research (Grant No. 08-02-00640-a) and from a Russian Federation President's Grant (No. SS-871.2008.2). Lastly, we thank M. Cardona and M.L.W. Thewalt, who have drawn our attention to Ref. 29.

*Permanent address: Tomsk State Pedagogical University, 634061 Kievskaya 60, Tomsk, Russia.

[1] S. G. Pavlov, R. K. Zhukavin, E. E. Orlova, V. N. Shastin, A. V. Kirsanov, H.-W. Hübers, K. Auen, and H. Riemann, Phys. Rev. Lett. **84**, 5220 (2000).

[2] S. G. Pavlov, H.-W. Hübers, J. N. Hovenier, T. O. Klaassen, D. A. Carder, P. J. Phillips, B. Redlich, H. Riemann, R. K. Zhukavin, and V. N. Shastin, Phys. Rev. Lett. **96**, 037404 (2006).

[3] R. K. Zhukavin, V. V. Tsyplenkov, K. A. Kovalevsky, V. N. Shastin, S. G. Pavlov, U. Böttger, H. W. Hübers, H. Riemann, N. V. Abrosimov, and N. Nötzel, Appl. Phys. Lett. **90**, 051101 (2007).

[4] C. Jagannath, Z. W. Grabowski, and A. K. Ramdas, Phys. Rev. B **23**, 2082 (1981).

[5] A. Ramdas and S. Rodriguez, Rep. Prog. Phys. **44**, 1297 (1981).

[6] E. Kane, Phys. Rev. **119**, 40 (1960).

[7] D. Karaiskaj, J. A. H. Stotz, T. Meyer, M. L. W. Thewalt, and M. Cardona, Phys. Rev. Lett. **90**, 186402 (2003).

[8] V. V. Tsyplenkov, E. V. Demidov, K. A. Kovalevsky, and V. N. Shastin, Semiconductors **42**, 1016 (2008).

[9] In Ref. 8, the total linewidth of $2p_0$ spectral line due to electron-phonon scattering is not given, so we deduced it from Figs. 2 and 3 therein.

[10] M. Steger, A. Yang, D. Karaiskaj, M. L. W. Thewalt, E. E. Haller, J. W. Ager III, M. Cardona, H. Riemann, N. V. Abrosimov, A. V. Gusev, A. D. Bulanov, A. K. Kaliteevskii, O. N.Godisov, P. Becker, and H.-J. Pohl, Phys. Rev. B **79**, 205210 (2009).

[11] R. Barrie and K. Nishikawa, Can. J. Phys. **41**, 1823 (1963).

[12] T. Ning and C. Sah, Phys. Rev. B **4**, 3468 (1971).
[13] B. Shklovskii and A. Efros, *Electronic Properties of Doped Semiconductors* (Springer-Verlag, New York, 1984).
[14] M. Cardona and M. Thewalt, Rev. Mod. Phys. **77**, 1173 (2005).
[15] N. Butler, P. Fischer, and A. Ramdas, Phys. Rev. B **12**, 3200 (1975), and references therein.
[16] S. Rodriguez and T. Schultz, Phys. Rev. **178**, 1252 (1969).
[17] J. Sjakste, V. Tyuterev, and N. Vast, Phys. Rev. B **74**, 235216 (2006).
[18] J. Sjakste, N. Vast, and V. Tyuterev, Phys. Rev. Lett. **99**, 236405 (2007).
[19] S. Baroni, S. de Gironcoli, A. D. Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).
[20] W. Kohn and J. Luttinger, Phys. Rev. **98**, 915 (1955).
[21] P. Yu and M. Cardona, *Fundamentals of Semiconductors*, 3rd ed. (Springer-Verlag, Berlin, New York, 2001).
[22] G. E. Pikus and G. I. Bir, *Symmetry and Strain Induced Effects in Semiconductors* (Wiley, New York, 1974).
[23] P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991).
[24] *Semiconductors: Physics of Group IV Elements and III-V Compounds*, Landolt-Börnstein, New Series, Group III Vol. 17, Pt. A, edited by O. Madelung, H. Weiss, and M. Schulz (Springer-Verlag, Berlin, 1982).
[25] C. Jacoboni and L. Reggiani, Rev. Mod. Phys. **55**, 645 (1983).
[26] F. Bruneval, N. Vast, and L. Reining, Phys. Rev. B **74**, 045102 (2006).
[27] In our work, the parameters were taken in angstrom instead of atomic unit, to correct the misprint in Ref. 12.
[28] $a^2=\frac{\hbar^2}{2m_eE}$ and $b^2=\frac{\hbar^2}{2m_hE}$, where a and b are envelope function parameters and E is the energy level with respect to the bottom of conduction band. The impurity energy levels E where taken from Ref. 33.
[29] N. Q. Vihn, P. T. Greenland, K. Litvinenko, B. Redlich, A. F. G. van der Meer, S. A. Lynch, M. Warner, A. M. Stoneham, G. Aeppli, D. J. Paul, C. R. Pidgeon, and B. N. Murdin, Proc. Natl. Acad. Sci. U.S.A. **105**, 10649 (2008).
[30] D. Ferry, Phys. Rev. B **14**, 1605 (1976).
[31] M. V. Fischetti, Phys. Rev. B **44**, 5527 (1991).
[32] S. Baroni *et al.* (unpublished), http://www.pwscf.org
[33] A. J. Mayur, M. D. Sciacca, A. K. Ramdas, and S. R. Rodriguez, Phys. Rev. B **48**, 10893 (1993).