Local-Field Effects in the Screening of Impurities in Silicon

R. Car
Laboratoire de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

and

Annabella Selloni
Laboratoire de Physique Théorique, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland
(Received 7 November 1978)

A model inverse dielectric matrix is used to calculate the electronic response to impurity potentials in silicon. We show that local-field effects are strong on the scale of interatomic distances and that they give rise to relevant quantitative effects on the binding energies and wave functions of both deep and shallow impurities.

The screening of shallow impurities in semiconductors[1] has generally been described either by a dielectric constant ϵ_0,[2] or by a dielectric function $\epsilon(q)$,[3] thus neglecting local-field (LF) effects due to the off-diagonal elements[4] of the dielectric response matrix (DM).

The off-diagonal elements of the DM in semiconductors, however, are not negligible.[5,6] Only if they are taken into account can the linear RPA screening be an excellent approximation to the full self-consistent response.[7]

In the present work, we investigate for the first time the importance of LF's in the impurity problem. For this purpose we propose a simple model which yields accurate results for the inverse static DM at all $\vec{q}$ vectors. We then apply the model to the screening of a pointlike impurity in silicon, and show how LF's account for the bond-charge polarization and for the site dependence of the screening and discuss their effects on the impurity binding energies and wave functions. We show that LF effects are strong on the scale of interatomic distances and thus are important in the description of deep impurity centers. The short-range details of the impurity potential are also important[1] for the ground state of shallow impurities, as shown experimentally by the chemical shifts, so that LF's cannot in principle be ignored even in this case.

The inverse DM at all $\vec{q}$ vectors is required in order to screen nonperiodic perturbations as the Coulomb potential considered here. In this case a model DM has to be used since accurate calculations need a great computational effort and have been performed, within RPA, in the $\vec{q}\to 0$ limit only.[5,6] A simple model without any adjustable parameter has been proposed by Johnson,[8] but we have found that it agrees poorly with the $\vec{q}\to 0$ DM calculated in Ref. 6 for silicon. On the other hand, the Sinha factorization *Ansatz* in its simplest form[9] does not provide a particularly convenient approximation for convalent materials, since it is strictly valid for tightly bound electrons only. We found, however, that a functional form similar to the Johnson model gives a fair interpolation of the known $\vec{q}\to 0$ results in silicon with two adjustable parameters only. Our model is

$$\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}') = f_d(\vec{q}+\vec{G})\,\delta_{\vec{G}\vec{G}'} + f_{od}(\vec{q}+\vec{G},\vec{q}+\vec{G}')(1-\delta_{\vec{G}\vec{G}'}), \tag{1}$$

$$f_{od}(\vec{q}+\vec{G},\vec{q}+\vec{G}') = \frac{A}{[1+B|(\vec{q}+\vec{G})\cdot(\vec{q}+\vec{G}')|]^2}\,\rho_v(\vec{G}-\vec{G}')\,\frac{(\vec{q}+\vec{G})\cdot(\vec{q}+\vec{G}')}{|\vec{q}+\vec{G}|^2}. \tag{2}$$

Since the off-diagonal elements of the DM in silicon are small with respect to the diagonal ones, an analytical expression for the inverse DM can be obtained by first-order perturbation theory

$$\epsilon^{-1}(\vec{q}+\vec{G},\vec{q}+\vec{G}') = \frac{1}{f_d(\vec{q}+\vec{G})}\left[\delta_{\vec{G}\vec{G}'} - \frac{f_{od}(\vec{q}+\vec{G},\vec{q}+\vec{G}')}{f_d(\vec{q}+\vec{G}')}(1-\delta_{\vec{G}\vec{G}'})\right]. \tag{3}$$

We fit f_d to the diagonal dielectric function calculated by Walter and Cohen,[10] and the constants A and B to the off-diagonal elements of the $q\to 0$ inverse DM calculated from the same pseudopotential band structure[6] (for Si we find $A=115.86$ a.u. and $B=1.07$ a.u.), $\rho_v(\vec{G})$ being the corresponding pseudocharge density. Our model, as does that of Johnson, satisfies the f-sum rules.[8] In the limit $\vec{q}+\vec{G},\vec{q}+\vec{G}'$) reproduces the values calculated in Ref 6 with an accuracy of better than 20% for the most important DM

elements. We remark that the accuracy of both the band structure and the RPA is expected to be of the same order.[6,11]

We study the site dependence of the screening by considering a point-charge (PC) potential in the substitution site $S \equiv (0, 0, 0)$ and in the interstitial empty tetrahedral site $I \equiv \frac{1}{4}a(\bar{1}, \bar{1}, \bar{1})$. With the choice of the origin at the impurity site, the screened potential corresponding to $V_{\text{ext}} = 4\pi Ze^2/q^2$ is

$$V(\vec{q}+\vec{G}) = \sum_{\vec{G}'} \epsilon^{-1}(\vec{q}+\vec{G}, \vec{q}+\vec{G}')\, V_{\text{ext}}(\vec{q}+\vec{G}), \qquad (4)$$

where ϵ^{-1} is given by Eq. (3) and the site dependence is contained in the charge density factor $\rho_v(G)$. By Fourier inverting Eq. (4) we calculate the screened potential $V(\vec{r})$, and through Poisson's equation we determine the induced charge density $\rho_{\text{ind}}(r)$.

As the point group of the crystal both in S and I cases is T_d, we develop $V(\vec{r})$ and $\rho_{\text{ind}}(\vec{r})$ in cubic harmonics $K_{l1}(\theta, \varphi)$ of Γ_1 symmetry, i.e.,

$$V(r, \theta, \varphi) = V_d(r) + V_0(r) + V_3(r, \theta, \varphi) + V_4(r, \theta, \varphi) + \cdots, \qquad (5)$$

where $V_d(r)$ is the potential screened by the diagonal part of ϵ^{-1} alone, and the terms $V_l(r, \theta, \varphi) \equiv V_l(r)K_{l1}(\theta, \varphi)$ are due to the local fields in the crystal. We have numerically verified that the contribution of the terms with $l > 4$ in the series (5) is negligibly small. The term $l = 0$ is the LF spherical correction to V_d so that $V_s = V_d + V_0$ is the spherical average of $V(\vec{r})$. The cubic terms $l = 3, 4$ determine the tetrahedral character of $V(\vec{r})$.

LF effects in the screened PC potential were calculated by including off-diagonal terms up to $(a/2\pi)(\vec{G} - \vec{G}') = (331)$ in the inverse DM. In Figs. 1(a) and 1(b) we show the ratio V_s/V_d and V/V_d along the $\langle 111 \rangle$ and the $\langle \bar{1}\bar{1}\bar{1} \rangle$ directions for the substitutional and the interstitial cases, respectively. In both cases the oscillations of V_s/V_d are as large as 0.3 and have a range of one bond length approximately but opposite phases. A cross section of the off-diagonal contribution to ρ_{ind} (i.e., $\rho_0 + \rho_3 + \rho_4$) in the $(1\bar{1}0)$ plane is shown in Figs. 2(a) and 2(b) for the cases S and I. Figure 2(a) shows the presence of localized dipoles on the four bonds departing from the S site, whereas in Fig. 2(b) the polarization charge appears only at distances of approximately one bond length from the impurity, i.e., in correspondence with the first-neighboring bonds.

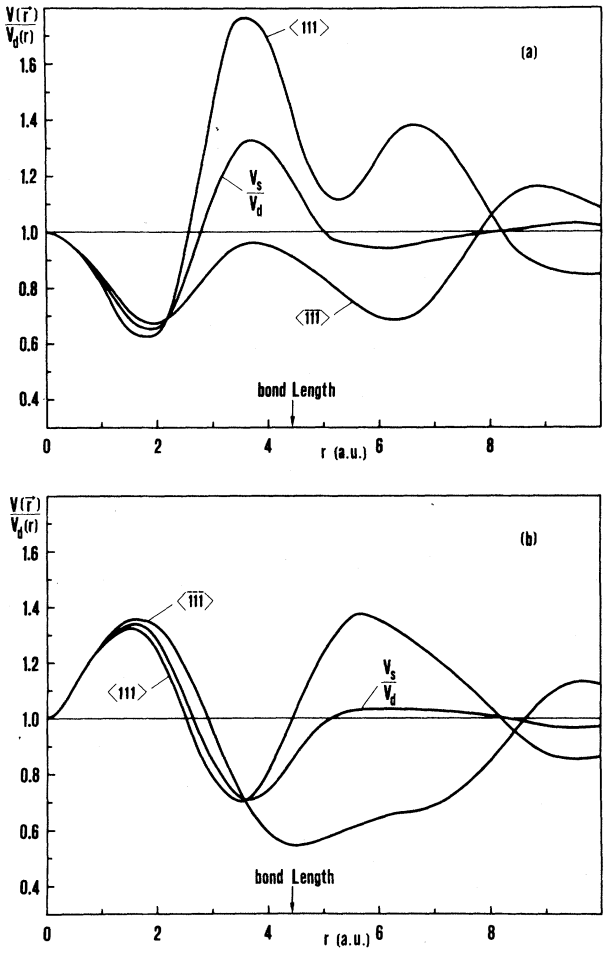

FIG. 1. Deviations of the screened potential V and of the spherical screened potential V_s from the diagonal screened potential V_d. (a) Substitutional impurity; (b) interstitial impurity.

These results are in agreement with the picture that the polarizable charge in silicon is localized on the bonds.[12]

In order to obtain an understanding of the influence of LF on the energies and wave functions of impurities, we consider a spherical model where the bound particle is characterized by a scalar mass m and the fully screened potential $V(\vec{r})$ is replaced by its spherical average $V_s(r)$.

Our results for the binding energy E_B of the single- and the double-charged impurities are shown in Fig. 3. Within this simplified model the donor (for Si we assume $m_e \sim 0.2$) binding energy for both $Z = 1$ and $Z = 2$ is unaffected by LF corrections, whereas using the heavy-hole mass ($m_h \sim 0.5$), E_B is reduced by ~10% for the $Z = 1$ and by ~50% for the $Z = 2$ acceptor. Assuming

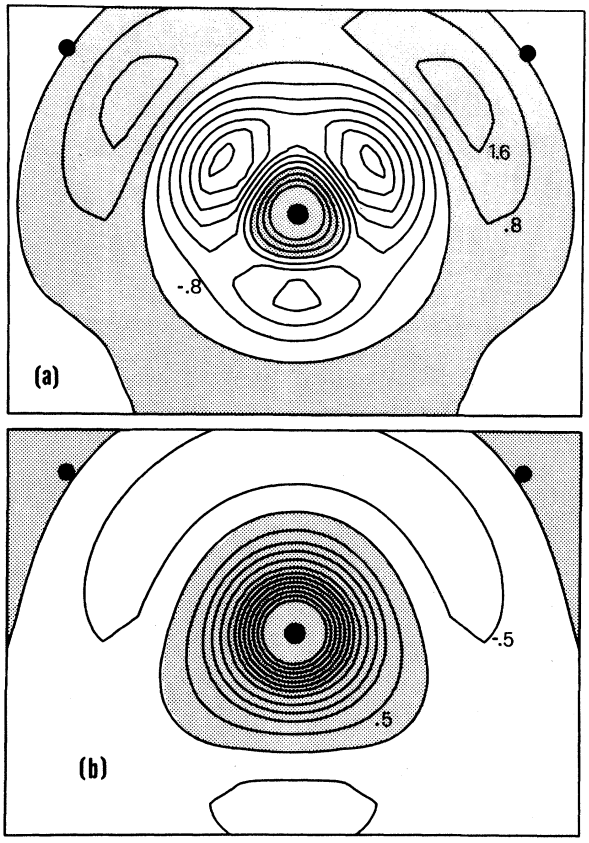

FIG. 2. Nondiagonal contribution to the polarization charge ρ_{ind} on the $(1\bar{1}0)$ plane. The units are electrons/cell. Shaded areas indicate positive charge. (a) Substituttional impurity; (b) interstitial impurity.

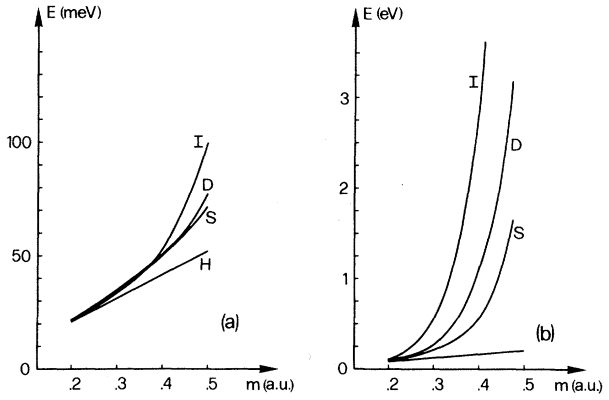

FIG. 3. Ground-state binding energy vs bound-particle mass for (a) $Z=1$ and (b) $Z=2$. Traces include S for substituttional, I for interstitital, D for diagonal approximation, and H for hydrogenic model $V_{\mathrm{H}}(r)=Z/\epsilon_0 r$.

that in a realistic acceptor calculation these corrections would roughly be of the same magnitude, the correction for $Z=1$ should improve the agreement of the PC binding energy, $E_B \simeq 80$ meV,[13] with the experimental data for the isocoric impurity Al ($E_B = 68$ meV). In the case of double acceptors, our results show the relevance of LF effects for deep impurities, though the present effective-mass model has only indicative value. The influence of LF on the impurity wave functions is even larger than that on the binding energies as shown for instance by the site dependence of the ground-state electron density at the impurity site for donors ($|\Phi(0)|_I^2/|\Phi(0)|_S^2 = 1.17$ for $Z=1$, and 2.52 for $Z=2$).

The spherical model discussed so far systematically underestimates donor binding energies. For the $Z=1$ and the $Z=2$ cases, it gives $E_{B1} = 21$ meV and $E_{B2} = 101$ meV, respectively, as compared to the experimental values $E_{B1} = 45.5$ meV and $E_{B2} = 613.6$ meV for the isocoric P and S^+ impurities.[1] In a realistic theory, band-structure effects and intervalley mixing, including umklapp contributions,[14] should be taken into account. In this case the short-range components of the impurity potential, and thus also LF effects, become more important. An accurate variational one-band multivalley calculation using the PC potential gives $E_B = 55$ meV for the substitutional donor when only umklapp effects are included, whereas $E_B = 45$ meV is obtained when both umklapp and LF contributions are taken into account due to the ~20% reduction of the intervalley matrix elements produced by LF's. In view of the uncertainties in the DM, in the band structure, and in the variational calculation, this result does not mean perfect agreement between theory and experiment, but rather it should be considered as a test of the quantitative importance of LF's even in the shallow-donor case. The details of this calculation will be reported elsewhere.[15] The reduction of E_B would be even more pronounced for double donors. In this case Pantelides and Sah,[16] neglecting LF's, found $E_B = 1085$ meV for the PC model, i.e., a value significantly larger than the experimental value for the isocoric impurity. In the case of the interstitial donor the umklapp contributions give rise to a deep level[17] in agreement with experiment.[18] LF's significantly enhance this effect,[15] by increasing the intervalley matrix elements up to 40%, as a consequence of the less-efficient screening at small distances for the interstitial site.

In conclusion, the above discussion points out that the relevance of LF's goes along with that of

the short-range details of the impurity potential. A more refined theory should contain both a better impurity potential[1] and a better description of the screening. The authors wish to thank Dr. M. Altarelli, Dr. A. Baldereschi, Dr. K. Maschke, and Dr. E. Tosatti for helpful discussions. One of us (A.S.) is partially supported by Landis and Gyr AG, Zug, Switzerland.

[1]See, for instance, F. Bassani, G. Iadonisi, and B. Preziosi, Rep. Progr. Phys. 37, 1099 (1974); S. T. Pantelides, Rev. Mod. Phys. 50, 797 (1978).

[2]W. Kohn, in *Solid State Physics*, edited by E. Ehrenreich, F. Setiz, and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 257.

[3]J. Hermanson, Phys. Rev. 150, 660 (1966).

[4]S. L. Adler, Phys. Rev. 126, 413 (1962); N. Wiser, Phys. Rev. 129, 62 (1963).

[5]S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. Lett. 34, 155 (1975).

[6]A. Baldereschi and E. Tosatti, Phys. Rev. B 17, 4710 (1978).

[7]A. Baldereschi and K. Maschke, in *Proceedings of the International Conference on Lattice Dynamics, Paris, 1977*, edited by M. Balkansky (Flammarion, Paris, 1977).

[8]D. L. Johnson, Phys. Rev. B 9, 4475 (1974).

[9]S. K. Sinha, R. P. Gupta, and D. L. Price, Phys. Rev. B 9, 2564, 2573 (1974).

[10]J. P. Walter and M. L. Cohen, Phys. Rev. B 2, 1821 (1970).

[11]J. A. Van Vechten and R. M. Martin, Phys. Rev. Lett. 28, 446 (1972).

[12]J. C. Phillips, Phys. Rev. 166, 832 (1968).

[13]A. Baldereschi and N. O. Lipari, private communication; the value reported here was obtained using the same $\epsilon(q)$ (Ref. 10) which is used in the present paper.

[14]K. Shindo and H. Nara, J. Phys. Soc. Jpn. 40, 1640 (1976); M. Alterelli, W. Y. Hsu, and R. Sabatini, J. Phys. C 10, L605 (1977).

[15]M. Altarelli, R. Car, and A. Selloni, to be published.

[16]S. T. Pantelides and C. T. Sah, Phys. Rev. B 10, 621 (1974).

[17]M. Altarelli and W. Y. Hsu, private communication, and to be published.

[18]See, for instance, J. H. Brewer, K. M. Crowe, F. M. Gygax, and A. Schenck, in *Muon Physics*, edited by V. W. Hughes and C. S. Wu (Academic, New York, 1975), Vol. III, p. 4.

Light Scattering and Pair-Correlation Functions in Fluids with Nonuniform Velocity Fields

Jonathan Machta and Irwin Oppenheim

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

and

Itamar Procaccia

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel [a]

(Received 22 January 1979)

We study fluctuations in a fluid with a stationary, linear shear. We find that the pair-correlation function gains a long-ranged part. The Brillouin components of scattered light are enhanced or reduced compared to equilibrium depending on the scattering angle. The Landau-Placzek ratio no longer holds and the total scattering intensity is k dependent. We suggest a simple light-scattering experiment to test our predictions. The new features are explained by the differential attenuation of sound modes.

Fluctuations in fluids with nonuniform velocity fields are of great current interest, in the context of the hierarchy of hydrodynamic instabilities[1,2] and the transition to turbulence.[3] In this Letter we report some results of a theoretical investigation of hydrodynamic fluctuations in systems with stable nonuniform velocity field, and we argue that the existence of a dissipative momentum flux is accompanied by the appearance of a long-ranged part in the pair-correlation function as well as interesting and measurable new effects in the spectrum of light scattering.

The method of calculating the correlation functions in the presence of a velocity field is based on our statistical-mechanical theory of nonequilibrium stationary states. The theory was presented in great detail in Refs. 4–6 and a shortened version was outlined in a previous Letter.[7] We do not repeat the derivations here, and simply remind the reader that the main result of the

