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Self-consistent calculation of the internal strain parameter of silicon

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We have extended our total-energy computation method, based on the density-functional formalism in the local-density approximation and written in terms of the Wannier functions of the semiconductor, to include distorted crystals. In this way the internal strain parameter ξ of silicon can be calculated in a self-consistent fashion. The result $\xi=0.86$ is consistent with the recently reported experimental value (0.73 ± 0.03).

The knowledge of the elastic constants of a crystal is not enough to infer the positions of the atoms in a crystal submitted to stress if the crystal has a basis formed by more than one atom. These additional degrees of freedom are characterized by internal-strain parameters. Anastassakis and Cardona[1] have studied the number of independent internal-strain parameters and its relation with the $k=0$ optical phonons. Silicon has only one internal-strain parameter which was introduced and defined for the first time by Kleinman.[2] It has been directly measured by means of x-ray diffraction in crystals submitted to an uniaxial stress in the [111] direction.[3,4] Even though the analysis of the data is difficult, it seems now that the value of the internal-strain parameter ξ is 0.73 ± 0.03 for silicon, somewhat larger than earlier reports (0.62 ± 0.04).[3] On the theoretical side it is interesting to calculate ξ because the state of the art in total-energy calculations based on the density-functional formalism in the local-density approximation allows the obtainment of the ground-state properties of semiconductors with a high degree of precision. In this way the equilibrium lattice constant, the cohesive energy, and the bulk modulus have been computed for silicon by several authors.[5] All the results that can be found in the literature agree with each other.

We report here on a self-consistent calculation of the internal-strain parameter ξ for silicon. The computation is a slight extension of our previous work. Specifically, we have adapted the computer program which was used for the calculation of the cohesive energy of different kinds of stacking faults in silicon.[6] A supercell containing six silicon atoms and with the shape of a right hexagonal prism was chosen. The total energy for this supercell was minimized as a function of the lattice constant. We found the minimum energy -3.81011 hartree for a lattice constant $a=10.37$ bohr. To study the deformed crystal we only need to strain the supercell in a homogeneous way. The strain tensor for a uniaxial stress in the [111] direction has the form

$$\underline{\epsilon}=\begin{pmatrix}\epsilon_1 & \epsilon_2 & \epsilon_2\\ \epsilon_2 & \epsilon_1 & \epsilon_2\\ \epsilon_2 & \epsilon_2 & \epsilon_1\end{pmatrix},$$

where ϵ_1 defines a pure hydrostatic volume change and ϵ_2 defines a pure trigonal deformation. The distances along the [111] direction are modified by a factor $1+\epsilon_1+2\epsilon_2$, whereas the distances in the (111) plane are modified by a factor $1+\epsilon_1-\epsilon_2$. The positions of the ions in the strained supercell are given by

$$\vec{R}_1'=(\underline{I}+\underline{\epsilon})\vec{R}_1\ ,$$

$$\vec{R}_2'=(\underline{I}+\underline{\epsilon})\vec{R}_2-\tfrac{1}{2}a\xi\epsilon_2\begin{pmatrix}1\\1\\1\end{pmatrix}\ ,$$

where $\vec{R}_1$ and $\vec{R}_2$ give the positions of the ions in the unstrained supercell, a is the fcc lattice constant, and ξ is the internal-strain parameter. The indexes 1 and 2 label the two interpenetrated fcc sublattices which form the diamond lattice. The resulting bond lengths are

$$l_{111}=\frac{a\sqrt{3}}{4}[1+\epsilon_1+2(1-\xi)\epsilon_2]\ ,$$

$$l_{\bar{1}\bar{1}1}=l_{\bar{1}1\bar{1}}=l_{1\bar{1}\bar{1}}=\frac{a\sqrt{3}}{4}[1+\epsilon_1-\tfrac{2}{3}(1-\xi)\epsilon_2]\ ,$$

where the direction of the bond is explicitly given.

We have done three sets of calculations for the determination of the internal-strain parameter.

(i) $\epsilon_1 = 0$ and $\epsilon_2 = -0.02$. In this case the volume change vanishes as a result of a 4% compression in the [111] direction and a 2% expansion in the (111) planes.

(ii) $\epsilon_1 = \epsilon_2 = -\frac{1}{3}(0.04)$. In this case the volume is diminished 4% as a result of a 4% contraction in the [111] direction, whereas the distances in the (111) planes remain unchanged.

(iii) $\epsilon_1 = \epsilon_2 = \frac{1}{3}(0.04)$. In this case the volume is increased 4% as a result of a 4% stretching in the [111] direction, whereas the distances in the (111) planes do not change.

Once the strained supercell (or, equivalently, crystal) is defined we proceed to a minimization of the total energy as a function of ξ. For each value of ξ a fully self-consistent computation is done. All the details are as in our previous work.[6] (This means ionic pseudopotential, actual local-density approximation for the exchange-correlation potential, use of the Wannier functions to achieve self-consistency between electronic charge and total potential and convergence criteria). It is worthwhile to mention only that with the deformation a change of the reciprocal superlattice vectors takes place. In particular, this fact modifies the Brillouin zone (BZ). Nevertheless, in the selected supercell geometry, the shape of the BZ remains unchanged allowing the usual integration over it. In other words, only the height-width ratio of the right hexagonal prism changes and the new set of special points needed for the BZ integration can easily be recalculated.

The results of the first calculation are shown in Table I and Fig. 1. In Table I the total energy per atom as a function of ξ is compiled. The minimum of the energy curve occurs for $\xi_i = 0.816$. This minimum is obtained after a fit of the tabulated values by a parabola. The same procedure is used to determine ξ_{ii} and ξ_{iii} from Table II (see below). The fit by a polynomial of higher degree modifies slightly ($<5\%$) the previous values. Figure 1 shows the valence electronic charge for the ionic configuration which minimizes the energy, i.e., for $\xi_{\text{i}} = 0.816$. The lengths of the bonds are $l_{111} = 0.9924\ l_0$ and $l_{\bar{1}\bar{1}1} = l_{\bar{1}1\bar{1}} = l_{1\bar{1}\bar{1}} = 1.0025\ l_0$, being l_0 the equilibrium bond length. The [111] direction coincides with the y axis of the figure. The most striking feature is that in spite of the minor contraction of the (111) bond, the charge has been removed from the three other bonds and accumulated on the (111) bond in order to reduce the energetic cost of the deformation. We re-

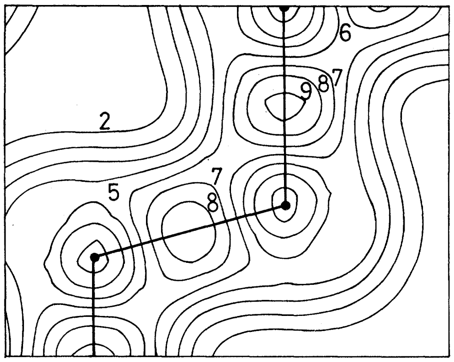

FIG. 1. Self-consistent electronic charge density for a silicon crystal compressed 4% in the [111] direction and expanded 2% in the (111) plane in order to keep the volume constant. The electronic charge is shown for $\xi = 0.816$ (the value of the internal-strain parameter that minimizes the total energy). The unit is the number of electrons per ion (the average value of the electronic charge is 4 in this unit) and the [111] direction coincides with the y-axis direction.

TABLE I. Total energy per atom for a silicon crystal compressed 4% in the [111] direction and expanded 2% in the (111) plane in order to keep the volume constant. The total energy per atom is shown as a function of the internal-strain parameter ξ. The value of ξ that minimizes the energy is 0.816.

ξ	E_{tot} (a.u.)
0	−3.80624
0.48	−3.80735
0.79	−3.80757
1.00	−3.80751

TABLE II. Total energy per atom for a silicon crystal expanded 4% in the [111] direction $[\epsilon_1 = \epsilon_2 = \frac{1}{3}(0.04)]$, or compressed 4% in the [111] direction $[\epsilon_1 = \epsilon_2 = -\frac{1}{3}(0.04)]$. The total energy per atom is shown as a function of the internal-strain partameter ξ. The values of ξ that minimize the energy are $\xi_{\text{iii}} = 0.99$ for the expanded crystal and $\xi_{\text{ii}} = 0.785$ for the compressed crystal.

	ξ	E_{tot} (a.u.)
$\epsilon_1 = \epsilon_2 = \frac{1}{3}(0.04)$	0.006	−3.80767
	0.797	−3.80834
	1.191	−3.80836
	1.585	−3.80814
$\epsilon_1 = \epsilon_2 = -\frac{1}{3}(0.04)$	0.348	−3.80776
	0.704	−3.80792
	1.060	−3.80786

mark that the sign of this charge transfer from the stretched bonds region into the compressed bond region coincides with the result found by Maschke and Baldereschi[7] for a different ion configuration (the distortion produced by a Γ'_{25} optical phonon).

The internal-strain parameter which minimizes the energy in the compressed crystal is $\xi_{\rm ii}=0.785$, whereas in the expanded crystal the lowest energy is obtained for $\xi_{\rm iii}=0.99$ (see Table II). These values show a pronounced dependence of the internal-strain parameter on the crystal volume. Assuming a linear dependence of ξ on the volume variation, a least-squares fit to the three results yields

$$\xi=0.86+2.56(\Delta V/V) \ .$$

The dimensionless parameter that gives the dependence of ξ on the volume variation is

$$\frac{1}{\xi}\frac{d\xi}{d\ln V}=2.97 \ .$$

This result indicates that the angular forces lose importance with respect to the central forces as the volume increases. In this manner ξ approaches 1 (only central forces) as the volume increases.[8] Nevertheless, the numerical value for $(1/\xi)(d\xi/d\ln V)$ has to be taken carefully since it is strongly influenced by the value $\xi_{\rm iii}=0.99$ obtained for an extremely flat parabola (see Table II).

Our final result for the internal-strain parameter is $\xi=0.86$ (in absence of pressure). It supports the recently reported experimental value 0.73 ± 0.03 (Ref. 4) as opposed to earlier experimental determinations (0.62 ± 0.04).[3] A quite recently reported calculation by Harmon, Weber, and Hamann[5] gives for the same parameter a value 0.61. It may be concluded that, in spite of the overall agreement between theory and experiment, a definite theoretical value of ξ is hard to obtain because of the very slight dependence of the total energy on the internal strain parameter.

As a by-product of the present effort we obtain a value for the elastic stiffness constant C_{44}. Paradoxically, the authors that have done self-consistent computation of the total energy have paid little attention to the elastic constants of semiconductors. They can be only indirectly inferred from the phonon dispersion relations published very recently by Kunc and Martin[9] for Ge and GaAs and by Yin and Cohen[9] for Si.

The change in energy density corresponding to a uniaxial deformation in the [111] direction with $\epsilon_1=0$ is

$$\Delta U=6C_{44}\epsilon_2^2 \ .$$

Substituting the values corresponding to $\epsilon_2=-0.02$ we get $C_{44}=1.21\times10^{12}$ dyn cm^{-2}, which is 50% in error with respect to the experimental value $C_{44}=0.796\times10^{12}$ dyn cm^{-2}.[10] The origin of our difficulties is the poor convergence of the ion-electron contribution to the total energy as a function of the number of $\vec{g}$ vectors, if a hard-core ion potential is used. This point was extensively discussed in Ref. 6. This difficulty arises in the evaluation of C_{44} but not in the evaluation of ξ because of the need in the first case of an accurate energy difference between the strained and the unstrained crystals. The converged value for this difference is beyond our present computational facilities and therefore a converged estimate for C_{44}. Nevertheless, only the position of the minimum in the energy curve is needed for the obtainment of ξ and this position is supposed to depend weakly on the number of $\vec{g}$ vectors taken into account.

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