

Rashba splitting and relativistic energy shifts in In/Si(111) nanowires

U. Gerstmann, N. J. Vollmers, A. Lücke, M. Babilon, and W. G. Schmidt

Lehrstuhl für Theoretische Physik, Universität Paderborn, 33098 Paderborn, Germany

(Received 25 October 2013; revised manuscript received 16 April 2014; published 30 April 2014)

A numerically efficient methodology that allows for relativistic calculations including spin-orbit coupling for spatially anisotropic potentials is employed to study the energetics and electronic properties of In/Si(111)(4×1)/(8×2) nanowires within density-functional theory. For the subtle total energy balance between the metallic In zigzag chain structure observed at room temperature and the insulating In hexagons that form below the critical temperature, scalar-relativistic corrections to the kinetic energy are clearly far more important than the spin-orbit coupling. On the other hand, a relativistic treatment including spin-orbit coupling is required to describe correctly the electronic band structure that shows a large, strongly anisotropic k -point-dependent spin splitting of the In-related states at the X point of the surface Brillouin zone. Suitably combined with the metal-insulator transition, the resulting quasi-1D Rashba effect may be used for spin filtering.

DOI: [10.1103/PhysRevB.89.165431](https://doi.org/10.1103/PhysRevB.89.165431)

PACS number(s): 68.35.Rh, 73.20.-r, 79.60.Dp

I. INTRODUCTION

The electronic properties of quasi-1D systems [1–5] are of both scientific interest and technological relevance, e.g., for atomic-scale interconnects or spin filters. The ordered array of In nanowires formed upon room temperature (RT) In monolayer deposition on Si(111) substrates and subsequent annealing is one of the most intensively investigated model systems in this context [4]. These nanowires show the interesting peculiarity of a temperature-dependent phase transition from the conducting RT phase to an insulating low temperature (LT) structure. Experiment and theory have established a structural model (top panel in Fig. 1) that is well accepted for the RT phase of the nanowire array [6–14]: each nanowire consists of two zigzag chains of In atoms within a (4×1) surface periodicity. The nanowires are separated by Si chains resembling the π -bonded chains of the clean Si(111)(2×1) surface. For temperatures below about 120 K, a charge-density wave (CDW) formation is observed; at this temperature, the In atoms slightly rearrange and—instead of zigzag chains within a (4×1) symmetry—a (8×2) surface periodicity is clearly observed with scanning tunneling microscopy [15–20]. This reversible temperature-induced phase transition leads to significant changes of the electronic properties. The RT (4×1) phase is a quasi-1D metal [21,22] characterized by electron transport attributed to In-related surface states [16,21,23,24]. In contrast, the CDW formation is accompanied by the opening of a fundamental energy gap of 0.1–0.3 eV [15–18,25]. The atomic structure of the low temperature (8×2) phase seemed elusive for a long time. Eventually, the Flores group suggested a structural model based on In hexagons in a (8×2) surface periodicity [26,27] (cf. Fig. 1) that accounts for the high-energy positron diffraction data [28,29] as well as the vibrational [11,30] and optical signatures [31] measured for the In nanowires at low temperatures and provides a plausible scenario for the (4×1)-(8×2) phase transition [30,32].

From a theoretical point of view, however, the understanding of the In nanowires is not satisfactory. The stability of the In hexagons depends critically on the treatment of the In 4d electrons and the exchange and correlation (XC) functional used to describe the many-particle interaction in density-functional theory (DFT). Stekolnikov *et al.* [33] find

the hexagon model to be favored over the zigzag chain by 3 meV per In atom, provided the calculations are performed within the local-density approximation (LDA) to the DFT and the In 4d electrons are frozen into the core. In contrast, calculations within the generalized-gradient approximation (GGA) or calculations that treat the In 4d states as valence electrons find the hexagons less favorable than the zigzag chains. According to Cho and Lee [34], the hexagons are not even metastable, i.e., the structure relaxes to restore ideal In zigzag chains. Very recently, Kim and Cho [35] used van der Waals (vdW) corrected hybrid DFT calculations to study the energetics of the In nanowires. While their GGA calculations favor the zigzag chains over the hexagon structure, they find that the vdW-corrected hybrid HSE functional [36] shifts the subtle energy balance, and the hexagon model is favored by about 6 meV. Obviously, the available theoretical studies show clearly that (i) the energy differences between the competing structures are very small and (ii) they depend critically on the numerical details as well as the physical approximations made in the calculations.

The extremely flat potential energy surface of the In/Si(111) nanowires in conjunction with the fact that a very small structural modification leads to a band gap opening calls for exploring the influence of relativistic effects on the energetic and electronic properties of this system. In fact, chains of spins were recently reported for 1D templated silicon surfaces stabilized by adsorbed gold atoms [5]. Large or even giant Rashba effects, i.e., k -point-dependent spin splittings of the bands due to the combination of spin-orbit (SO) coupling and the asymmetry of the potential in the direction perpendicular to the surface [37,38] are reported for 2D surface alloys such as Bi/Cu(111) [39] and Bi/Ag(111) [40–43]. Similar effects may be expected for In nanowires, and—if suitably combined with the metal-insulator transition of these wires—can possibly be exploited as spin filter [44]. The present study aims at clarifying the influence of relativistic effects, notably SO coupling, on the energetics and electronic properties of the In/Si(111) nanowires. In particular, we investigate in detail the Rashba splitting of the In-related surface bands which are responsible for the (4×1)-(8×2) phase transition. It will be shown that scalar-relativistic corrections have a sizable influence on the energy separation between In hexagon and

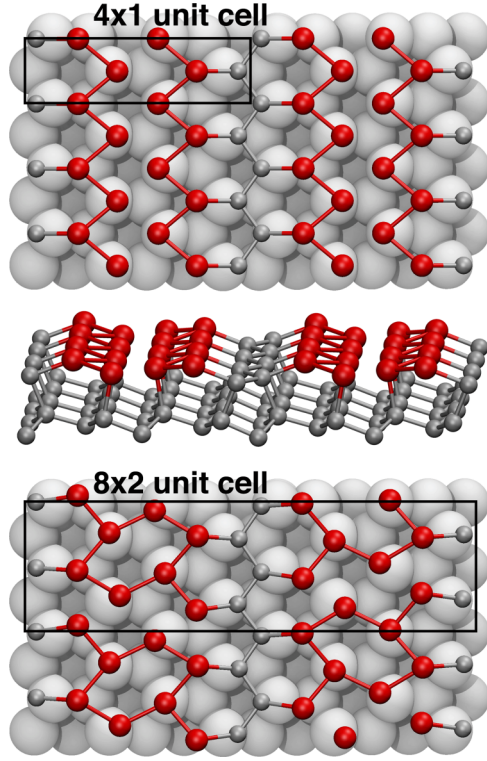


FIG. 1. (Color online) Schematic views of the ideal, unreconstructed zigzag chain structure (top and middle) and hexagon model of the reconstructed In/Si(111) nanowire array (bottom). Dark (red) balls indicate indium atoms.

zigzag chain structures and that a pronounced Rashba effect for In $5p$ derived surface bands shows up at the X point of the surface Brillouin zone (SBZ).

II. METHODOLOGY

The present calculations are based on density functional theory as implemented in the QUANTUM-ESPRESSO package [45]. We use a plane-wave basis and projector-augmented wave (PAW) pseudopotentials, i.e., the all-electron wave functions are replaced by smooth pseudo-wave-functions which allow, however, for the reconstruction of the all-electron information [46]. The In/Si(111) surfaces are simulated by repeated slabs containing the In nanowires adsorbed on the silicon substrate. The latter is modeled with three Si bilayers and the bottom layer is hydrogen saturated. Thereby, the equilibrium lattice constants calculated for the various functionals are used, which deviate from the measured value by -1% (LDA) [47], $+0.4\%$ (GGA PW91) [48], and $+0.6\%$ (GGA PBE) [49], respectively. The k -space integrations are performed using uniform meshes equivalent to 256 points in the (1×1) SBZ. The smearing scheme proposed by Marzari *et al.* [50] with an electronic temperature of 120 K is used to soften the occupation number discontinuities at the Fermi energy.

Many DFT total-energy calculations use pseudopotentials generated within the so-called scalar-relativistic approximation [51,52]. Thus, relativistic kinetic energy corrections are obtained in a well-defined manner, but spin-orbit coupling is

neglected. The modeling of the Rashba effect requires, however, a relativistic multi-component description of the wave functions including SO coupling. A spinor-based approach using full-relativistic pseudopotentials generated by solving Dirac's equation for free atoms [53,54] has been proposed by Dal Corso and implemented in DFT codes like QUANTUM ESPRESSO code [45]. It allows for an accurate description of relativistic effects including the Rashba splitting in periodic systems. It is, however, computationally demanding and for the relativistic calculation of complex structures with several hundred atoms often more approximative approach are used. Some DFT packages use a separable Kleinmann-Bylander SO implementations [55,56], where based on scalar-relativistic wave functions the SO coupling is taken into account in spherically averaged form {cf. Eq. (3) in Ref. [57]}.

The Foldy-Wouthuysen (FW) transformed [58,59] Dirac Hamiltonian

$$\hat{\mathcal{H}}_{\text{FW}} = \hat{I} \left[c^2 + \frac{(\hat{p} + \frac{1}{c} \vec{A})^2}{2} - \frac{\hat{p}^4}{8c^2} - \frac{1}{8c^2} \nabla \cdot \vec{E} + \varphi \right] - \hat{\sigma} \cdot \left[\frac{\mu_B}{2} \vec{B} + \frac{i}{8c^2} \nabla \times \vec{E} + \frac{1}{4c^2} \vec{E} \times \left(\hat{p} + \frac{1}{c} \vec{A} \right) \right] \quad (1)$$

is a suitable starting point to derive an efficient, but spatial anisotropies including gauge-invariant scheme. It determines the movements of electrons described by spinors in the presence of electromagnetic fields $\vec{E} = -\nabla\varphi$ and $\vec{B} = \nabla \times \vec{A}$. Here, $\hat{I}$ is the identity matrix, and $\hat{\sigma}$ denotes the vector of the Pauli spin matrices

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The first part in square brackets is diagonal in its action on a spinor and differs from the corresponding expression in Pauli theory by the relativistic rest mass, the kinetic energy correction, and the Darwin term. While the rest mass term can be eliminated by a suitable phase factor, the kinetic energy correction—in this form not well defined [60,61]—can be treated within the scalar-relativistic approximation [51,52]. The second part of $\mathcal{H}_{\text{FW}}$ acts on the spin degrees of freedom and includes in addition to the Zeeman term two terms that describe the SO coupling for the general case of time-dependent electromagnetic fields. In the absence of magnetic fields, they reduce to

$$\Delta \hat{\mathcal{H}}_{\text{SO}} = \frac{1}{4c^2} \hat{\sigma} \cdot (\nabla V(\vec{r}) \times \hat{p}), \quad (2)$$

i.e., the SO coupling term known as the second-order approximation [62] already contained in Pauli theory. As its derivation via the FW transformation is exact up to sixth order in $\frac{1}{c}$, it allows for an accurate modeling of the effects of spin-orbit coupling for not too heavy elements. If combined with scalar-relativistic pseudopotentials that account for relativistic kinetic energy corrections, a relativistic description of the electrons including both, relativistic kinetic energy and spin-orbit coupling is possible. In the following, we will refer to this type of calculations as Pauli-type theory. For heavy elements, a further improvement may be obtained by the so-called zero-order regular approximation (ZORA) [63,64], where the

Dirac Hamiltonian is expanded in terms of $E/(2c^2 - V)$ leading to a reduced gradient

$$\tilde{\nabla} V = \nabla \left[\frac{2c^2}{1 - V/(2c^2)} \right] = \frac{1}{(1 - \frac{V}{2c^2})^2} \cdot \nabla V, \quad (3)$$

which enters the SO Hamiltonian (2). Since close to the nuclei the potential behaves as $V \approx -\frac{Z}{r}$, the potential-dependent prefactor actually leads to a reduced gradient and by this to a reduced SO coupling. The Pauli-type as well as the ZORA-corrected form of the SO Hamiltonians provide an efficient two-component spinor description and allow for a direct comparison of scalar-relativistic and SO-including relativistic treatment, since the calculations on both levels of approximation can be performed using identical scalar-relativistic pseudopotentials.

We have implemented this scheme in the QUANTUM ESPRESSO package. Specifically, we exploit PAW pseudopotentials and account for SO coupling by applying a two-component version of Blöchl's PAW transformation [46]

$$\hat{T} = \hat{1} + \sum_{\mathbf{R},m} [|\phi_{\mathbf{R},m}\rangle - |\overline{\phi_{\mathbf{R},m}}\rangle] \langle p_{\mathbf{R},m}|$$

on $\Delta\hat{\mathcal{H}}_{\text{SO}}$ either from the Pauli form Eq. (2) or taking into account the reduced gradient of the effective potential within ZORA [see Eq. (3)]. The two-component projectors $|p_{\mathbf{R},m}\rangle$ are set up from scalar-relativistic components. They are used to reconstruct the all-electron spinors $|\psi_o\rangle = \hat{T}|\psi_o\rangle$ from the pseudospinors $|\psi_o\rangle$. The SO part of the relativistic all-electron Hamiltonian is then given by

$$\begin{aligned} \overline{\Delta\hat{\mathcal{H}}_{\text{SO}}} &= \hat{T}^+ \Delta\hat{\mathcal{H}}_{\text{SO}} \hat{T} = \frac{1}{4c^2} \left[\hat{\sigma} \cdot (\tilde{\nabla} V_{\text{ps}}(\vec{r}) \times \hat{p}) \right. \\ &\quad \left. + \sum_{\mathbf{R}} \sum_{n,m} \underbrace{|p_{\mathbf{R},n}\rangle f_{\mathbf{R},nm} \langle p_{\mathbf{R},m}|}_{=\hat{F}_{\mathbf{R}}^{\text{NL}}} \right], \quad (4) \end{aligned}$$

where the nonlocal second term $\sum_{\mathbf{R}} \hat{F}_{\mathbf{R}}^{\text{NL}}$ reconstructs the all-electron contribution to the SO coupling [65,66]. Thereby, the matrix elements are given by

$$\begin{aligned} f_{\mathbf{R},nm} &= \langle \phi_{\mathbf{R},n} | \hat{\sigma} \cdot \tilde{\nabla} \mathcal{V}_{\text{ac}}(r) \times \hat{p} | \phi_{\mathbf{R},m} \rangle \\ &\quad - \langle \overline{\phi_{\mathbf{R},n}} | \hat{\sigma} \cdot \tilde{\nabla} \overline{\mathcal{V}}_{\text{ps}}(r) \times \hat{p} | \overline{\phi_{\mathbf{R},m}} \rangle. \quad (5) \end{aligned}$$

while the all-electron potential $\mathcal{V}_{\text{ac}}(r)$ and both components of the spinor $|\phi_{\mathbf{R},m}\rangle$ come from a scalar-relativistic treatment of the spherically symmetric atomic problem, and $\overline{\mathcal{V}}_{\text{ps}}(r)$, $|\overline{\phi_{\mathbf{R},m}}\rangle$ are the corresponding pseudoquantities. The approach can be made computationally more efficient by exploiting that the overwhelming part of the SO coupling stems from the augmentation region. Therefore the second term in Eq. (5) and the first term in Eq. (4) are both small, nearly cancel each other, and one may approximate

$$\begin{aligned} \overline{\Delta\hat{\mathcal{H}}_{\text{SO}}} &= \frac{1}{4c^2} \sum_{\mathbf{R},n,m} |p_{\mathbf{R},n}\rangle \langle \phi_{\mathbf{R},n} | \frac{1}{r} \frac{\partial \mathcal{V}_{\text{ac}}(r)}{\partial r} \\ &\quad \times \hat{\sigma} \cdot \hat{L} | \phi_{\mathbf{R},m} \rangle \langle p_{\mathbf{R},m} |. \quad (6) \end{aligned}$$

In this *reconstruction-only* form, the SO coupling is accounted for simply by an additional contribution to the nonlocal part of the pseudopotential. This may be considered as a non-separable generalization of the separable Kleinman-Bylander approach [56], where the SO coupling is taken into account in spherically averaged form. The nonseparable representation in Eq. (6)—while providing an atomically centered expression as well—reproduces the results of the full-potential scheme Eq. (4) that fully accounts for spatial anisotropies of the potential. It thus allows, as we will show below, for an accurate description of the Rashba effect.

In order to assess how the approximations discussed above influence the numerical results, we performed a series of tests on well-characterized systems such as silicon bulk, the bismuth bilayer and 2D surface alloys. In case of bulk Si ($Z = 14$), we find irrespective of the details of the relativistic description a value of 48 meV for the asymmetric splitting of the light- and the two heavy-hole-like valence bands at the Γ point. This value reproduces exactly the valence band splitting calculated within the original, full-relativistic Dal Corso approach and is in fair agreement with experimental data of about 43 meV [67].

A more critical test is given by the single Bi(111) bilayer, which is built up by heavy atoms ($Z = 83$). It is structurally reminiscent of graphene, but it is not perfectly flat. The bonds between neighboring Bi atoms, enclose an angle of 96.5° and, consequently, neighboring Bi atoms are situated in two different sublayers separated by $1.67 \text{ \AA}$ [68,69]. Relativistic effects have indeed a dramatic influence on the electronic band structure of this system, as shown in Fig. 2. The outcome of scalar-relativistic calculations that disregard SO coupling deviate strongly from the full-relativistic results. The splitting of the three uppermost valence bands at the Γ point, for example, amounts to only 0.3 eV, more than 2 eV smaller than the full-relativistic value. Moreover, in the scalar-relativistic approximation a wrong dispersion and band crossings around the K point are obtained.

Taking the SO coupling via the Pauli-type SO Hamiltonian Eq. (2) into account, we actually obtain the correct dispersion of the valence bands, but the splitting at the Γ point is now overestimated by about 30%. The ZORA Hamiltonian with a reduced gradient is necessary to shift the Bi valence bands closer to the full-relativistic reference, cf. Fig. 2. The use of a reconstruction-only or the full-potential scheme, however, has no influence onto the band structure: within a numerical accuracy of 0.1 meV the one-particle band energies obtained via the *reconstruction-only* approach [Eq. (6)] agree with the prediction of the full scheme using $\Delta\hat{\mathcal{H}}_{\text{SO}}$ according Eq. (4).

Finally, we evaluate the reliability of these schemes with respect to the description of the Rashba effect. Although the Bi(111) bilayer features strong SO coupling, its inversion symmetry suppresses the Rashba splitting. The inversion symmetry is lost, however, at surfaces. The Bi(111) surface [70] and in particular Bi-related surface alloys on noble metal substrates like Bi/Cu(111) [39] and Bi/Ag(111) [40–42] show prototypical Rashba effects at the Γ point of the SBZ. Here, surface alloying leads to an enhancement of the surface potential gradient and, by this, dramatically increases the Rashba effect [39]. As shown in Table I, the methodology proposed here allows for an excellent reproduction of this effect. For Bi/Cu(111), both the ZORA-corrected as well as

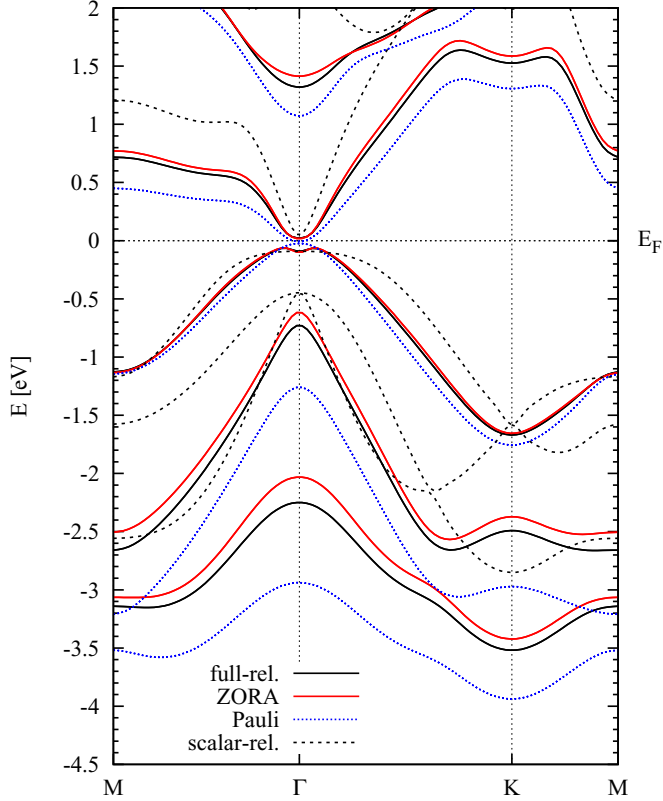


FIG. 2. (Color online) Band structure of a single Bi bilayer calculated in scalar-relativistic approximation, the full-relativistic approach [53,54] and the present implementations of Pauli and ZORA-type SO Hamiltonians, where the relativistic band structure is reconstructed from scalar-relativistic pseudopotentials. For all calculations, the PBE functional has been used.

the Pauli-type calculations are in very good agreement with the experimental data and with former theoretical work (see also Table I). A similar degree of agreement is obtained in case of the Bi/Ag(111) alloy, provided the ZORA-type of SO-including Hamiltonian is used.

This holds true for both methods, for the full-potential approach [Eq. (4)] as well as for the approximative *reconstruction-only* scheme [Eq. (6)]. While both approaches lead to virtually identical results, the latter approximation leads to a substantial reduction of the computational costs. Moreover, it provides an atomically resolved SO coupling analysis on the fly. As will be shown below, this is very helpful for gaining physical insight into the microscopic origin of SO coupling related effects. The methodology proposed here is applicable to norm-conserving as well as ultrasoft pseudopotentials. In the following, for the investigation of In/Si(111) nanowires, we use norm-conserving pseudopotentials and perform relativistic calculations based on the ZORA Hamiltonian.

III. RESULTS AND DISCUSSION

Obviously, the accurate description of SO coupling in the In nanowires requires the correct description of the In electrons. Bulk indium shows a structural peculiarity in the sense that it deviates from the close-packed structure usually formed by

TABLE I. Rashba splitting of Bi-related surface alloys (Γ point). The Rashba energy of the split states E_R calculated for different levels of relativistic approximation, the corresponding momentum offset Δk and the Rashba parameter $\alpha_R = 2E_R/\Delta k = \frac{\hbar^2 \Delta k}{m^*}$ are given and compared with experimental and theoretical data available in literature.

system [Ref.]		E_R [meV]	Δk [$\text{\AA}^{-1}$]	α_R [$\text{eV \AA}$]
Bi/Cu(111) surf. alloy	Exp. [39]	13	0.032	0.82
	DFT [39]	9	0.028	0.62
	full-relativistic (Dal Corso)	14.5	0.032	0.89
	ZORA, Eq. (4)	12.7	0.027	0.94
	ZORA, Eq. (6)	12.7	0.027	0.94
	Pauli, Eq. (4)	13.3	0.028	0.95
	Pauli, Eq. (6)	13.3	0.028	0.95
Bi/Ag(111) surf. alloy	Exp. [40]	200	0.13	3.05
	DFT [40]	145	0.10	2.90
	full-relativistic (Dal Corso)	144	0.082	3.63
	ZORA, Eq. (4)	145	0.085	3.38
	ZORA, Eq. (6)	145	0.085	3.38
	Pauli, Eq. (4)	168	0.100	3.37
	Pauli, Eq. (6)	168	0.100	3.37

metallic elements. Its body-centered tetragonal unit cell, with lattice parameters a and c , contains the two equivalent atoms at the corners and the center of the cell. The In bulk total energy in dependence on the c/a ratio exhibits a double-well behavior with two minima and a local maximum exactly at the c/a ratio of the ideal face-centered cubic (fcc) structure [71,72]. The stabilizing energy of the ground-state structure with respect to the fcc structure is rather small, below 2 meV per atom. We generated a series of scalar-relativistic and nonrelativistic In pseudopotentials within the LDA and the GGA, where the In 4d electrons were either frozen into the core, included as valence electrons, or partially considered by using a nonlinear core correction to the XC energy [73]. It turns out that the double-well feature of the total energy requires either the inclusion of the In 4d states as valence states, or at least their consideration by means of a nonlinear core correction.

In order to exclude the technical treatment of the In 4d electrons as a possible source for inaccuracies, the nanowire calculations presented here fully include the In 4d states. Using norm-conserving pseudopotentials this requires an energy cutoff of 680 eV for the plane-wave basis. It renders the relativistic calculations computationally rather expensive, given the comparatively large 136 atom supercell required to model the nanowire hexagon structure within a (8×2) unit cell. In such cases the *reconstruction-only* scheme proposed above is particularly helpful, as it reduces the computational costs in comparison to the standard implementation by about one order of magnitude.

At first, GGA calculations using the PW91 and the PBE XC functional as well as scalar-relativistic pseudopotentials are used to determine the In nanowire structure and energy without consideration of SO coupling effects, see Table II. The (8×2) hexagon model does not even represent a metastable minimum on the potential energy surface calculated within the PBE approximation. A large number of starting configurations were probed, but the structural relaxation always resulted in

TABLE II. Total energies (in meV, per In atom) of the (8×2) hexagon structure of the In nanowire with respect to the (4×1) zigzag chains. Thereby nonrelativistic and scalar-relativistic pseudopotentials, respectively, were used. The latter were also used in conjunction with a relativistic ZORA description including spin-orbit coupling (see text).

method	energy [meV/(In atoms)]
GGA-PW91 scalar-rel.	+4.87
GGA-PBE scalar-rel.	not stable
LDA nonrel.	-10.45
LDA scalar-rel.	-7.14
LDA ZORA	-7.38

the (4×1) zigzag chain model. In case of PW91 calculations we succeeded in identifying a metastable (8×2) reconstructed hexagon model. However, it is 5 meV per In atom less stable than the zigzag chain model. These problems to describe the (8×2) ground state of the In nanowire within the GGA corroborate earlier findings of Stekolnikov and co-workers [33] as well as Cho and Lee [34].

Therefore we turn to the local-density approximation (LDA) in the following. The use of nonrelativistic pseudopotentials results in a stable hexagon model that is by 10 meV lower in energy than the ideal zigzag chain structure, see Table II. Direct experimental data on the relative stability of the two nanowire structures are not available. However, from the measured phase transition temperature and the entropy contributions for the two phases calculated in Ref. [30], one expects an energy difference of about 6 meV between the two phases, about half the value obtained without consideration of any relativistic effect. If the latter are partially included in the total-energy calculations by using scalar-relativistic pseudopotentials, one obtains indeed a smaller stabilization energy for the hexagon model, 7 meV.

Recently, antiferromagnetically coupled spin chains were found stable for Au nanowire stabilized Si surface templates [5]. Therefore we probed a variety of antiferromagnetic and ferromagnetic spin configurations using the same scalar-relativistic pseudopotentials as before within the local-spin density approximation (LSDA). It turns out that the lowest energies are achieved for configurations where both the total as well as the local magnetization vanish. This agrees with earlier LSDA calculations by Bechstedt's group [14]. In their work, it was concluded that "spin-density waves and surface magnetism do not play an important role in the self-assembly of the In chains on a Si(111) substrate." This statement also holds when SO coupling—not investigated in Ref. [14]—is included in the calculations. Despite the vanishing magnetization density within the In chain structure, the SO coupling influences the energy difference between the two phases, but only in a slight way, stabilizing the In hexagon structure with respect to the In zigzag chains by 0.24 meV per In atom, see Table II.

Despite these rather small SO-induced changes in the total energy, interesting modifications of the band structure occur, see Fig. 3. Again, similar to the case of Bi(111) bilayers, we obtain virtually identical results for the two alternative schemes [Eq. (4) versus Eq. (6)], with deviations below

0.1 meV. First we discuss the SO splitting of orbital-degenerate bands: the largest energy splittings for the occupied bands are found at the Γ point. They occur for the Si related states, which are energetically degenerate with the valence-band maximum (VBM) of silicon bulk (shaded in grey in Fig. 3). With a value of 43 and 39 meV [for the (4×1) and the (8×2) phase, respectively] the valence band splitting of silicon bulk material is reproduced. For the conduction bands, the largest SO splitting is found at the X point of the SBZ boundary, where the direct gap of the insulating low-temperature phase is located. In case of the (4×1) RT phase, a SO related energy splitting of about 65 meV is observed for formerly two-fold orbital degenerate bands around 1.3 eV above the bulk Si valence-band maximum (VBM), see Fig. 3. For the (8×2) phase, a similar splitting is found 1.2 eV above the VBM. Here the energy splitting is less pronounced, 28 meV.

Besides these energy shifts, considerable spin-dependent k shifts of formerly spin-only-degenerate bands are obtained around the X point. The Rashba effect is most pronounced for the four In-related surface states S_1 , S_2 , S_3 , and S_4 . It is of comparable strength for the LT (8×2) and the RT (4×1) phases. Obviously, the break of the inversion symmetry of the In wires by the Si substrate is sufficient for the occurrence of the Rashba effect. Further symmetry breaks, related, e.g., to structural modifications accompanying the charge-density wave formation in the hexagon structure, are not required, but do affect the details of the resulting Rashba splitting; while the S_i bands are electron-like for the (4×1) phase, i.e., have positive, albeit anisotropic effective masses, the situation is more complicated for the (8×2) phase. In this case, the electron or holelike character of the surface states depends on the direction and results in a very anisotropic and complicated spin splitting in k space, see left part of Fig. 3.

In Fig. 3, also the influence of the SO coupling on the quantum conductance is shown, calculated from the solution of the scattering problem as implemented in the PWCOND modul of the QUANTUM ESPRESSO package [45]. Energy splits of formerly orbital-degenerate bands give rise to an additional fine-structure in the quantum conductance. Since the quantum conductance for the periodical In wires reflect the number of conductivity channels as given by the number of bands for a given energy, Rashba splittings do not alter the total quantum conductivity, but give rise to small differences in the spin-polarized quantities.

The Rashba parameters that describe the SO coupling at the X point for both phases of the In nanowire system are compiled in Table III. The comparison with the values for a variety of systems typically discussed in the context of the Rashba effect (cf. Tables I and III) shows that the splitting calculated here for the In/Si(111) nanowires is more than one order of magnitude larger than for indium containing InGaAs/InAlAs heterostructures [74,75]. In fact, with E_R values up to 11 meV, the Rashba splitting at the In/Si(111) (8×2) surface becomes comparable to that of the Bi(111) surface. The Rashba parameter $\alpha_R = 1.047$ is in between the values of Bi/Cu(111) [39] and Bi/Ag(111) [40–42], i.e., textbook examples for Rashba splitting (cf. Table I). In these surface alloys, every third noble metal atom in the surface is replaced by Bi. The Bi atoms are thus isotropically distributed and separated by a hexagonal arrangement of Cu or Ag atoms.

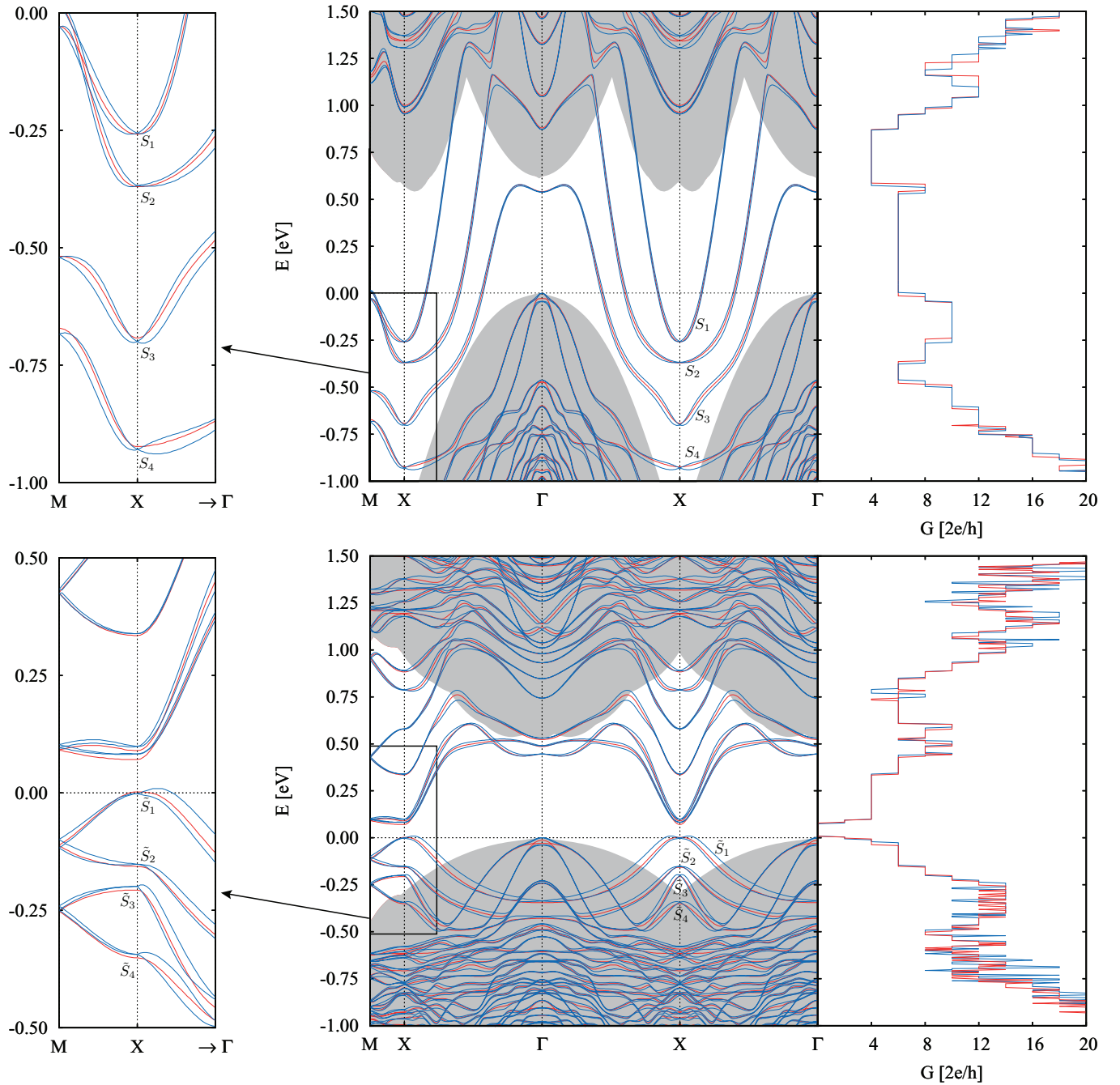


FIG. 3. (Color online) Scalar-relativistic (red/dark) and full-relativistic (blue/light) band structures calculated for the conducting In/Si(111)(4×1) and the insulating (8×2) phase (top and bottom, respectively). The corresponding quantum conductance along the In chains is also given (right). Note that the Brillouin zones for the two structures differ by a factor of two both in k_x and k_y direction. Here x and y denote the direction parallel and perpendicular to the nanowire, respectively. Hence, the band structure of the (8×2) phase contains four times as many bands.

Noble metal surfaces show Rashba-split surface states, with the amount of splitting typically related to the atomic SO coupling strength λ of their p orbitals (cf. Tables III and IV). The surface alloying with outward relaxing Bi atoms leads to an enhancement of the surface potential gradient and, by this, dramatically increases the Rashba effect, as discussed in Ref. [39].

The situation is similar for In/Si(111) nanowires. While the Rashba effect is below the detection limit for ideal Si(111)

surfaces, it is enhanced by more than two orders of magnitude by In atoms decorating the surface. The In nanowires are separated by Si surface atoms which gives rise to a structural anisotropy. Compared to the surface Si atoms, the outer and inner atoms of the In zigzag double chain are 0.7 and 0.3 Å above the surface plane, respectively, see also Fig. 4. This structural peculiarity gives rise to anisotropically enhanced components of the surface potential gradient. The In surface bands are energetically well separated from the Si bulk bands

TABLE III. Calculated spin-orbit splitting at the X point for the In-related surface bands of In/Si(111) nanowires compared with literature data and calculations for other reference systems (Γ point). The Rashba energy of the split states E_R , the momentum offset Δk and the Rashba parameter $\alpha_R = 2E_R/\Delta k = \frac{\hbar^2 \Delta k}{m^*}$ are given.

system [Ref.]	E_R [meV]	Δk [$\text{\AA}^{-1}$]	α_R [eV $\text{\AA}$]
InGaAs/InAlAs [74,75]	<1	0.028	0.07
Cu(111) surface [76]	≈ 0	≈ 0	≈ 0
Ag(111) surface [77]	<0.2	0.004	0.03
Au(111) surface [78,79]	2.1	0.012	0.33
Bi(111) surface [70]	14	0.05	0.56
In/Si(111) (4×1): $S_1(\parallel k_x)$	1.2	0.009	0.267
$S_1(\parallel k_y)$	3.0	0.020	0.300
$S_2(\parallel k_x)$	1.6	0.022	0.145
$S_2(\parallel k_y)$	2.8	0.020	0.280
(S_1, S_2 average)			(0.248)
$S_3(\parallel k_x)$	3.4	0.013	0.523
$S_3(\parallel k_y)$	2.0	0.010	0.400
$S_4(\parallel k_x)$	9.0	0.044	0.409
$S_4(\parallel k_y)$	1.3	0.007	0.371
(S_3, S_4 average)			(0.426)
In/Si(111) (8×2): $\tilde{S}_1(\parallel k_x)$	11.0	0.021	1.047
$\tilde{S}_1(\parallel k_y)$	<0.05	<0.005	...
$\tilde{S}_2(\parallel k_x)$	<0.1	<0.001	...
$\tilde{S}_2(\parallel k_y)$	1.5	0.017	0.176
$\tilde{S}_3(\parallel k_x)$	3.6	0.007	1.028
$\tilde{S}_3(\parallel k_y)$	<0.05	<0.005	...
$\tilde{S}_4(\parallel k_x)$	3.4	0.011	0.618
$\tilde{S}_4(\parallel k_y)$	<0.05	<0.005	...

at the X point of the SBZ, where hybridization plays only a minor role. As a consequence, the In $5p$ -related states at the X point (cf. Fig. 4) are mainly localized within the topmost surface layers. The contributions at the In atoms show roughly an atomiclike behavior with recognizable p_x , p_y , p_z contributions, which are exposed to the surface potential gradient. The p_x and p_y orbitals couple with the available spin degrees of freedom, causing a Rashba splitting. Its detailed origin can be understood by analyzing the orientation of the In $5p$ orbitals. Substituting $\vec{p} = \hbar \vec{k}$ in Eq. (2) and assuming an effective potential gradient along z as well as effective masses m_x^* and m_y^* that enter the Rashba parameter $(\alpha_R)_i = \frac{\hbar \Delta k}{m_i^*}$ one

TABLE IV. Atomic SO coupling strength λ [Ry] for relevant atoms and selected p orbitals. Given are values calculated via $\lambda(Z) = \frac{1}{4c^2} Z^4 [n^3 l(l + \frac{1}{2})(l + 1)]^{-1}$ from perturbation theory and derived from experimental ionization energies [80,81].

atom	Z	orbital	λ_{pert}	orbital	λ_{pert}	$\lambda_{\text{exp.}}$
Si	14	$2p$	0.021	$3p$	0.006	0.01
Cu	29	$2p$	0.393	$3p$	0.116	0.15
Ag	47	$2p$	2.708	$4p$	0.339	0.27
In	49	$2p$	3.199	$5p$	0.204	0.18
Au	79	$2p$	21.617	$5p$	1.383	0.83
Bi	83	$2p$	26.339	$6p$	0.976	1.25

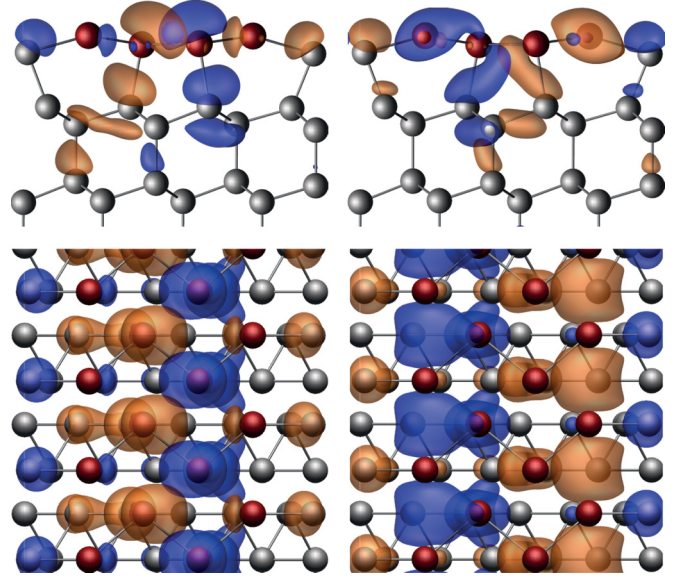


FIG. 4. (Color online) (4×1) phase of the In/Si(111) nanowire: the orbital character of the In-related bands S_1, S_2 (left: light, dark) and S_3, S_4 (right: light, dark) at the X point is indicated.

obtains the spin-orbit Hamiltonian in k space:

$$\Delta \hat{H}_{\text{SO}}(\vec{k}) = (\alpha_R)_y \cdot \hat{\sigma}_x k_y - (\alpha_R)_x \cdot \hat{\sigma}_y k_x. \quad (7)$$

Since $\vec{k} = \vec{p}/\hbar = \frac{\nabla}{i}$, the orientation of the p orbitals in real space determines the orientation of the respective k_i related contribution to the Rashba effect.

For the (4×1) phase, the Rashba splittings calculated for the specific bands can indeed be understood by analyzing the orientation and populations of the p orbitals (see Fig. 4 and Table V). The upper surface bands S_1 and S_2 are mainly localized at the inner In atoms where they correspond to p orbitals oriented along the surface normal (cf. Fig. 4). Hence these orbitals with predominately p_z character do not couple with the available spin degrees of freedom and do not contribute to an in-plane spin splitting. Only minor admixture of p_x can be found. As a result, comparatively small splittings along k_x are obtained. Besides the dominating p_z contributions, however, a smaller but still considerable contribution to the S_1 and S_2 bands originates from the p_y orbitals of the outer In atoms, oriented perpendicular to the

TABLE V. Decomposition of the In $5p$ surface bands into p_x , p_y , p_z contributions for the (8×2) hexagon structure and the (4×1) zigzag chains of the In nanowire.

phase	band	$(E_R)_x$	$(E_R)_y$	p_x	p_y	p_z
(4×1)	S_1	1.2	3.0	2.83	9.86	19.69
	S_2	1.6	2.8	1.24	5.61	18.52
	S_3	3.4	2.0	20.18	8.96	4.64
	S_4	9.0	1.3	20.40	7.20	9.61
(8×2)	$\tilde{S}_1$	11.0	0.1	23.99	5.86	4.98
	$\tilde{S}_2$	0.1	1.5	26.78	1.33	6.57
	$\tilde{S}_3$	3.6	0.1	28.23	2.42	4.38
	$\tilde{S}_4$	3.4	0.1	26.02	1.56	2.58

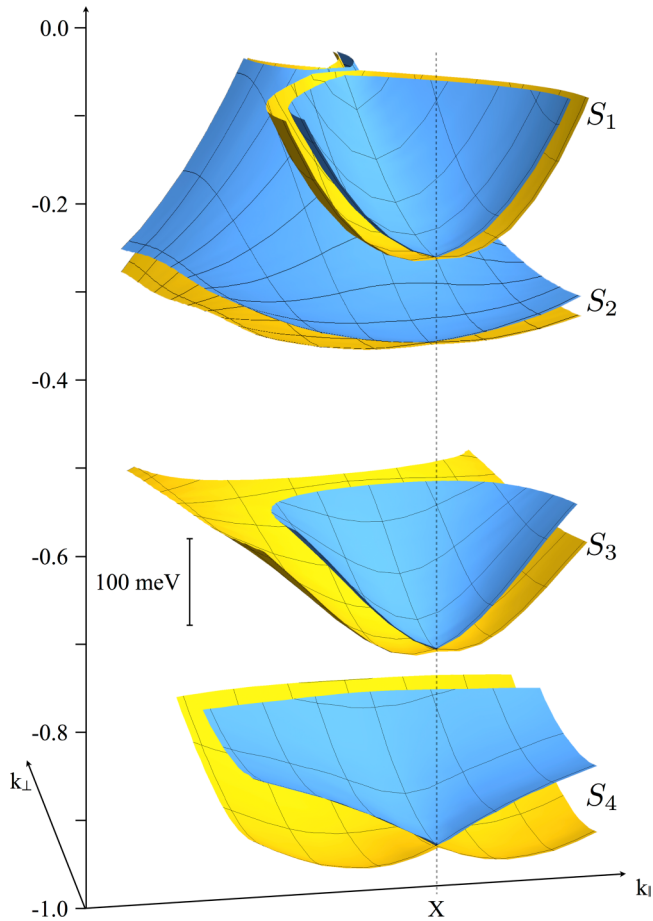


FIG. 5. (Color online) Calculated energy dispersion $E(k_{\parallel}, k_{\perp})$ of the surface states S_1 , S_2 , S_3 , and S_4 of In/Si(111)(4 $\times$ 1) around the X point. The two spin channels are indicated by different (dark/light) colors.

surface normal, towards the inner In atoms. It is instructive to note that the Rashba splittings along k_y are fully determined by the p_y components of the outer In atoms which show the largest outward relaxation. Restricting the SO coupling to these atoms exclusively, the full Rashba splitting of the S_1 and S_2 bands is already reproduced. This holds also in case of S_3 and S_4 . Both bands, the S_3 and in particular the S_4 band are localized predominantly at the outer In atoms, which show a large outward relaxation. This outward relaxation allows a reorientation of the p orbitals along the In nanowires. The resulting p_x orbitals provide one of the main ingredients of the conducting (4 $\times$ 1) phase as (i) they provide the conductivity channel along the wire direction and (ii) they can easily couple with the available spin degrees of freedom as well as with the surface potential gradient resulting in large Rashba parameters along k_x , see also Table III. In case of the S_3 band, the resulting Rashba effect is only slightly larger than in k_y direction. Together with the parabolic band shape, the resulting quasi-isotropy is responsible for the 2D character of the Rashba splitting (cf. Fig. 5). The S_4 band, however, predominantly arising from p_x orbitals at the outer In atoms (see Fig. 4) results in a large $(E_R)_x$ value and, thus, in a much more anisotropic Rashba effect. Its shape (see Figs. 3 and 5) is reminiscent of a typical quasi-1D electron liquid [82].

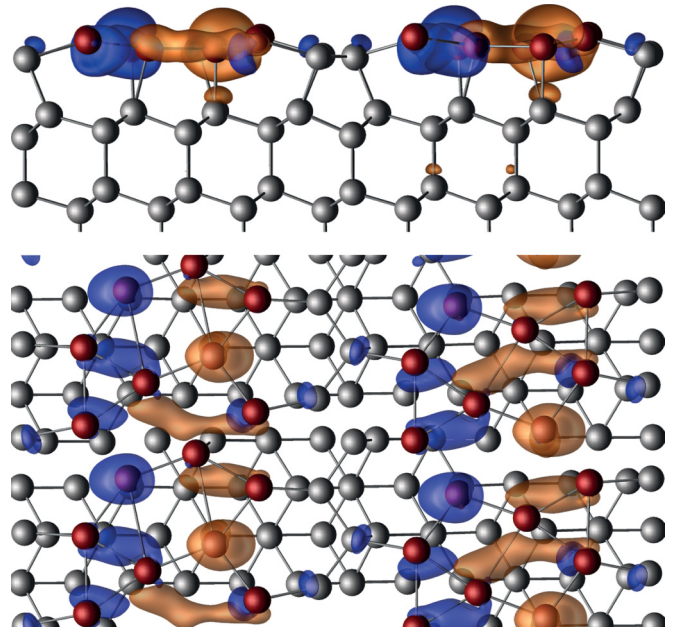


FIG. 6. (Color online) (8 $\times$ 2) phase of the In/Si(111) nanowire; the orbital character of the In-related bands $\tilde{S}_1$, $\tilde{S}_2$ (top: light, dark) at the X point is indicated.

The situation becomes more complicated in the case of the (8 $\times$ 2) phase, where the four In-related surface bands split into 16 bands. Half of them can be found above and below the Fermi level, respectively. It is this splitting of the former conducting surface bands that makes the (8 $\times$ 2) hexagon structure (semi-)insulating. In the following, we focus our discussion onto the four hole-like bands $\tilde{S}_1$, $\tilde{S}_2$, $\tilde{S}_3$, and $\tilde{S}_4$ close to the Fermi level; for these bands the p orbital contributions are found similar to the S_3 and S_4 bands of the (4 $\times$ 1) phase (cf. Table V and Fig. 6). Consequently, similar Rashba splittings should be expected. For the $\tilde{S}_1$ and $\tilde{S}_3$, $\tilde{S}_4$ bands the Rashba splittings in k_x direction indeed correspond to those of the metallic (4 $\times$ 1) phase. But perpendicular to the In double chains (along k_y) the splittings are almost vanishing. In other words, the anisotropy of the Rashba effect becomes much more pronounced. Furthermore, the $\tilde{S}_2$ band shows the peculiarity that its Rashba effect cannot be explained by the population of the p orbitals alone since the anisotropy is inverted, i.e., the p_y orbitals with the smallest population corresponds to a comparatively large Rashba splitting in k_y direction, while the dominating p_x channel does not find a counterpart in the Rashba splitting: along k_x the Rashba effect is even vanishing. Note that a more detailed projection of the density of states onto inequivalent, individual In atoms does not give further information. For the (8 $\times$ 2) hexagon structure, the inner and outer In atoms contribute within 3% in the same way to the values given in Table V. An explanation for the unusual Rashba effect for the $\tilde{S}_2$ band can be found by using the *reconstruction-only* approach and performing calculations in which the SO coupling is selectively taken into account for a given subset of In atoms. If we restrict the SO coupling to the inner or outer In atoms alone, we obtain within numerical accuracy the same band dispersion, but for the k_x direction of the $\tilde{S}_2$ band and the k_y direction of the $\tilde{S}_1$, $\tilde{S}_3$, $\tilde{S}_4$ bands the two subsets yield reversed spin polarizations. Hence their

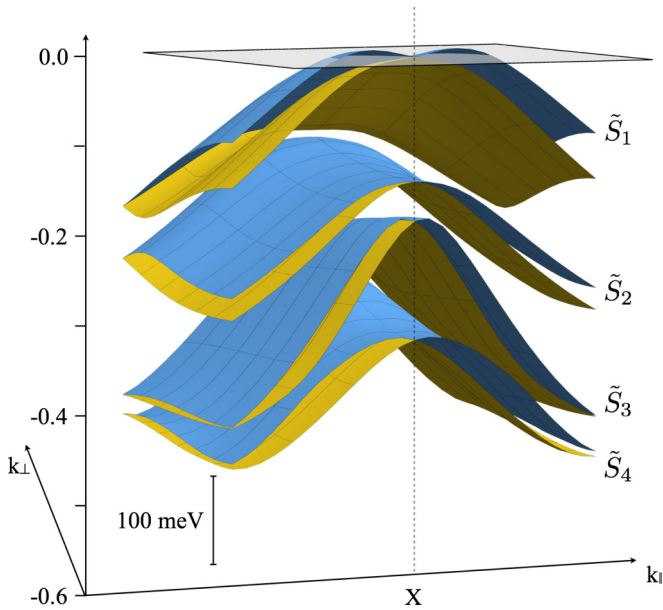


FIG. 7. (Color online) Calculated energy dispersion $E(k_{\parallel}, k_{\perp})$ of the holelike surface states of the quasi 1D In/Si(111) nanowire in the (8×2) phase. The two spin channels are indicated by different (dark/light) colors. About 40 meV below the top of $\tilde{S}_1$ is the valence band maximum (VBM) of the Si substrate, indicated by a horizontal plane.

superposition leads to a cancellation of the spin-dependent splittings. The dependence of this destructive superposition on the band and in particular on the orientation in k space gives rise to the unusual and extremely anisotropic Rashba effects. Thereby the $\tilde{S}_1$ valence band is unique in respect to its position to the Fermi level as it defines the top of the valence bands 30 meV above the VBM of the silicon substrate (cf. Figs. 3 and 7). As a consequence, the Rashba-split $\tilde{S}_1$ bands are energetically not protected by the substrate and can be easily depopulated by applying voltage or external magnetic fields.

IV. SUMMARY

First-principles calculations on the influence of relativistic effects on the energy and band structure of Si(111)-stabilized In nanowires were performed. Thereby a spinor approach was used, where, in order to include spin-orbit coupling for spatially anisotropic potentials, the SO coupling enters in nonseparable form the nonlocal parts of scalar-relativistic pseudopotentials. This approach was found to be as accurate as previous implementations with respect to the calculation of

SO-related phenomena like the Rashba effect, but at the same time sufficiently efficient to be applicable to investigate the complex nanowire structure.

Nonrelativistic LDA calculations for the In/Si(111) nanowire structure favor the formation of In hexagon structures arranged in a (8×2) surface symmetry. However, compared to the measured phase transition temperature and previously calculated entropy terms, the energy gain due to the hexagon formation seems overestimated. This changes as soon as kinetic relativistic effects are taken into account via the scalar-relativistic approximation. Spin-orbit coupling, in contrast, little affects the energetics of the system. It leads, however, to considerable SO splitting related changes of the In-related surface bands throughout the surface Brillouin zone. Thereby, the SO-related vertical energy shifts in the band structure are comparatively small. The largest shifts of about 70 meV are found for conduction band states 1.3 eV above the Fermi level at the X point.

More pronounced, however, are Rashba splittings, which for both phases occur at the X point in a broad energy range within about one eV below the Fermi level. Mainly the In nanowire-related surface bands are affected. The surprisingly large effect and its band-dependent anisotropy is explained by analyzing the orientation and population of the involved In $5p$ orbitals. For the conducting (4×1) phase, the Rashba effect is predominantly determined by the outer, strongly outward relaxing In atoms. Thereby the strength of the Rashba splittings in k_x and k_y direction is related to in-plane oriented In p_x and p_y orbitals resulting in band-dependent anisotropies. The inner and outer In atoms of the (8×2) hexagon structure give rise to contributions of the same order of magnitude, but depending on the direction in k space with parallel or opposite spin polarization. Their superposition, thus, leads to an increase or a cancellation of the spin-dependent splittings, i.e., to strongly anisotropic Rashba splittings. The resulting 1D Rashba effect is not protected by the silicon substrate and may be used for spin filtering controlled by external fields. The present system is interesting in this context as (i) it is Si-based and (ii) shows a temperature-induced metal-insulator transition that allows for combining the Rashba effect with variable conductivity channels.

ACKNOWLEDGMENT

We are grateful to Andrea Dal Corso for helpful discussions. The numerical calculations were done using grants of computer time from the Paderborn Center for Parallel Computing (PC²) and the Höchstleistungs-Rechenzentrum Stuttgart (HLRS). The Deutsche Forschungsgemeinschaft (DFG) is acknowledged for financial support.

- [1] F. J. Himpsel, K. N. Altman, R. Bennewitz, J. N. Crain, A. Kirakosian, J. L. Lin, and J. L. McChesney, *J. Phys.: Condens. Matter* **13**, 11097 (2001).
- [2] C. Blumenstein, J. Schäfer, S. Mietke, S. Meyer, A. Dollinger, M. Lochner, X. Y. Cui, L. Patthey, R. Matzdorf, and R. Claessen, *Nat. Phys.* **7**, 776 (2011).
- [3] J. Aulbach, J. Schäfer, S. C. Erwin, S. Meyer, C. Loho, J. Settlein, and R. Claessen, *Phys. Rev. Lett.* **111**, 137203 (2013).
- [4] P. C. Snijders and H. H. Weitering, *Rev. Mod. Phys.* **82**, 307 (2010).
- [5] St. C. Erwin and F. J. Himpsel, *Nat. Commun.* **1**, 1 (2010).
- [6] O. Bunk, G. Falkenberg, J. H. Zeysing, L. Lottermoser, R. L. Johnson, M. Nielsen, F. Berg-Rasmussen, J. Baker, and R. Feidenhans'l, *Phys. Rev. B* **59**, 12228 (1999).
- [7] J.-H. Cho, D.-H. Oh, K. S. Kim, and L. Kleinman, *Phys. Rev. B* **64**, 235302 (2001).

- [8] J. Nakamura, S. Watanabe, and M. Aono, *Phys. Rev. B* **63**, 193307 (2001).
- [9] R. H. Miwa and G. P. Srivastava, *Surf. Sci.* **473**, 123 (2001).
- [10] S. Wang, W. Lu, W. G. Schmidt, and J. Bernholc, *Phys. Rev. B* **68**, 035329 (2003).
- [11] K. Fleischer, S. Chandola, N. Esser, W. Richter, and J. F. McGilp, *Phys. Rev. B* **67**, 235318 (2003).
- [12] J.-H. Cho, J.-Y. Lee, and L. Kleinman, *Phys. Rev. B* **71**, 081310(R) (2005).
- [13] S.-F. Tsay, *Phys. Rev. B* **71**, 035207 (2005).
- [14] X. Lopez-Lozano, A. Krivosheeva, A. A. Stekolnikov, L. Meza-Montes, C. Noguez, J. Furthmüller, and F. Bechstedt, *Phys. Rev. B* **73**, 035430 (2006).
- [15] H. W. Yeom, S. Takeda, E. Rotenberg, I. Matsuda, K. Horikoshi, J. Schaefer, C. M. Lee, S. D. Kevan, T. Ohta, T. Nagao *et al.*, *Phys. Rev. Lett.* **82**, 4898 (1999).
- [16] T. Tanikawa, I. Matsuda, T. Kanagawa, and S. Hasegawa, *Phys. Rev. Lett.* **93**, 016801 (2004).
- [17] J. R. Ahn, J. H. Byun, H. Koh, E. Rotenberg, S. D. Kevan, and H. W. Yeom, *Phys. Rev. Lett.* **93**, 106401 (2004).
- [18] S. J. Park, H. W. Yeom, S. H. Min, D. H. Park, and I. W. Lyo, *Phys. Rev. Lett.* **93**, 106402 (2004).
- [19] J. Guo, G. Lee, and E. W. Plummer, *Phys. Rev. Lett.* **95**, 046102 (2005).
- [20] S. J. Park, H. W. Yeom, J. R. Ahn, and I. W. Lyo, *Phys. Rev. Lett.* **95**, 126102 (2005).
- [21] T. Kanagawa, R. Hobara, I. Matsuda, T. Tanikawa, A. Natori, and S. Hasegawa, *Phys. Rev. Lett.* **91**, 036805 (2003).
- [22] S. Wippermann, N. Koch, and W. G. Schmidt, *Phys. Rev. Lett.* **100**, 106802 (2008).
- [23] T. Uchihashi and U. Ramsperger, *Appl. Phys. Lett.* **80**, 4169 (2002).
- [24] W. G. Schmidt, S. Wippermann, S. Sanna, M. Babilon, N. J. Vollmers, and U. Gerstmann, *Phys. Stat. Sol. (B)* **249**, 343 (2012).
- [25] Y. J. Sun, S. Agario, S. Souma, K. Sugawara, Y. Tago, T. Sato, and T. Takahashi, *Phys. Rev. B* **77**, 125115 (2008).
- [26] C. Gonzalez, J. Ortega, and F. Flores, *New J. Phys.* **7**, 100 (2005).
- [27] C. Gonzalez, F. Flores, and J. Ortega, *Phys. Rev. Lett.* **96**, 136101 (2006).
- [28] M. Hashimoto, Y. Fukaya, A. Kawasuso, and A. Ichimiya, *Appl. Surf. Sci.* **254**, 7733 (2008).
- [29] Y. Fukaya, M. Hashimoto, A. Kawasuso, and A. Ichimiya, *Surf. Sci.* **602**, 2448 (2008).
- [30] S. Wippermann and W. G. Schmidt, *Phys. Rev. Lett.* **105**, 126102 (2010).
- [31] S. Chandola, K. Hinrichs, M. Gensch, N. Esser, S. Wippermann, W. G. Schmidt, F. Bechstedt, K. Fleischer, and J. F. McGilp, *Phys. Rev. Lett.* **102**, 226805 (2009).
- [32] S. Wall, B. Krenzer, S. Wippermann, S. Sanna, F. Klasing, A. Hanisch-Blicharski, M. Kammler, W. G. Schmidt, and M. Horn-von Hoegen, *Phys. Rev. Lett.* **109**, 186101 (2012).
- [33] A. A. Stekolnikov, K. Seino, F. Bechstedt, S. Wippermann, W. G. Schmidt, A. Calzolari, and M. Buongiorno Nardelli, *Phys. Rev. Lett.* **98**, 026105 (2007).
- [34] J.-H. Cho and J.-Y. Lee, *Phys. Rev. B* **76**, 033405 (2007).
- [35] H.-J. Kim and J.-H. Cho, *Phys. Rev. Lett.* **110**, 116801 (2013).
- [36] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003).
- [37] E. I. Rashba, *Fiz. Tverd. Tela (Leningrad)* **2**, 1224 (1960) [*Sov. Phys. Solid State* **2**, 1109 (1960)].
- [38] Y. A. Bychkov and E. I. Rashba, *J. Phys. C* **17**, 6039 (1984).
- [39] H. Bentmann, F. Forster, G. Bihlmeyer, E. V. Chulkov, L. Moreschini, M. Grioni, and F. Reinert, *Europhys. Lett.* **87**, 37003 (2009).
- [40] C. R. Ast, J. Henk, A. Ernst, L. Moreschini, M. C. Falub, D. Pacilé, P. Bruno, K. Kern, and M. Grioni, *Phys. Rev. Lett.* **98**, 186807 (2007).
- [41] L. El-Kareh, P. Sessi, T. Bathon, and M. Bode, *Phys. Rev. Lett.* **110**, 176803 (2013).
- [42] G. Bian, X. Wang, T. Miller, and T.-C. Chiang, *Phys. Rev. B* **88**, 085427 (2013).
- [43] I. Gierz, F. Meier, J. H. Dil, K. Kern, and Ch. R. Ast, *Phys. Rev. B* **83**, 195122 (2011).
- [44] M. Governale, D. Boese, U. Zülicke, and C. Schroll, *Phys. Rev. B* **65**, 140403 (2002).
- [45] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo *et al.*, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- [46] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [47] D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- [48] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- [49] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [50] N. Marzari, D. Vanderbilt, A. De Vita, and M. C. Payne, *Phys. Rev. Lett.* **82**, 3296 (1999).
- [51] D. D. Koelling and B. N. Harmon, *J. Phys. C* **10**, 3107 (1977).
- [52] T. Takeda, *Z. Phys. B* **32**, 43 (1978).
- [53] A. Dal Corso and A. MoscaConte, *Phys. Rev. B* **71**, 115106 (2005).
- [54] A. DalCorso, *Phys. Rev. B* **82**, 075116 (2010).
- [55] P. Blonski and J. Hafner, *Phys. Rev. B* **79**, 224418 (2009).
- [56] L. Kleinman, *Phys. Rev. B* **21**, 2630 (1980).
- [57] Y.-S. Kim, K. Hummer, and G. Kresse, *Phys. Rev. B* **80**, 035203 (2009).
- [58] L. L. Foldy and S. A. Wouthuysen, *Phys. Rev.* **78**, 29 (1950).
- [59] J. D. Bjorken and S. D. Drell, *Relativistic Quantum Mechanics* (McGraw-Hill, New York, 1965).
- [60] W. Kutzelnigg, *Chem. Phys.* **225**, 203 (1997).
- [61] W. Liu and D. Peng, *J. Chem. Phys.* **131**, 031104 (2009).
- [62] R. J. Elliot, *Phys. Rev.* **96**, 266 (1954).
- [63] E. van Lenthe, E. J. Baerends, and J. G. Snijders, *J. Chem. Phys.* **99**, 4597 (1993).
- [64] E. van Lenthe, J. G. Snijders, and E. J. Baerends, *J. Chem. Phys.* **105**, 6505 (1996).
- [65] C. J. Pickard and F. Mauri, *Phys. Rev. Lett.* **88**, 086403 (2002).
- [66] D. Ceresoli, U. Gerstmann, A. P. Seitsonen, and F. Mauri, *Phys. Rev. B* **81**, 060409 (2010).
- [67] Z. Yu, Y. X. Huang, and S. C. Shen, *Phys. Rev. B* **39**, 6287 (1989).
- [68] T. Hirahara, G. Bihlmayer, Y. Sakamoto, M. Yamada, H. Miyazaki, S. I. Kimura, S. Blügel, and S. Hasegawa, *Phys. Rev. Lett.* **107**, 166801 (2011).
- [69] Yu. M. Koroteev, G. Bihlmayer, E. V. Chulkov, and S. Blügel, *Phys. Rev. B* **77**, 045428 (2008).

- [70] Y. M. Koroteev, G. Bihlmayer, J. E. Gayone, E. V. Chulkov, S. Blügel, P. M. Echenique, and P. Hofmann, *Phys. Rev. Lett.* **93**, 046403 (2004).
- [71] U. Häussermann, S. I. Simak, R. Ahuja, B. Johansson, and S. Lidin, *Angew. Chem. Int. Ed.* **38**, 2017 (1999).
- [72] S. I. Simak, U. Häussermann, R. Ahuja, S. Lidin, and B. Johansson, *Phys. Rev. Lett.* **85**, 142 (2000).
- [73] S. G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26**, 1738 (1982).
- [74] J. Nitta, T. Akazaki, H. Takayanagi, and T. Enoki, *Phys. Rev. Lett.* **78**, 1335 (1997).
- [75] D. Grundler, *Phys. Rev. Lett.* **84**, 6074 (2000).
- [76] I. Gierz, B. Stadtmüller, J. Vuorinen, M. Lindroos, F. Meier, J. H. Dil, K. Kern, and C. R. Ast, *Phys. Rev. B* **81**, 245430 (2010).
- [77] D. Popović, F. Reinert, S. Hüfner, V. G. Grigoryan, M. Springborg, H. Cercellier, Y. Fagot-Revurat, B. Kierren, and D. Malterre, *Phys. Rev. B* **72**, 045419 (2005).
- [78] S. LaShell, B. A. McDougall, and E. Jensen, *Phys. Rev. Lett.* **77**, 3419 (1996).
- [79] H. Cercellier, C. Didiot, Y. Fagot-Revurat, B. Kierren, L. Moreau, D. Malterre, and F. Reinert, *Phys. Rev. B* **73**, 195413 (2006).
- [80] M. Vijayakumar and M. S. Gopinathan, *J. Mol. Struct. (Theochem)* **361**, 15 (1996).
- [81] K. Wittel and R. Manne, *Theor. Chim. Acta (Berlin)* **33**, 347 (1974).
- [82] A. V. Moroz, K. V. Samokhin, and C. H. W. Barnes, *Phys. Rev. B* **62**, 16900 (2000).