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SURFACE STRUCTURE, BONDING, AND DYNAMICS:  
THE UNIVERSALITY OF ZINCBLLENDE (110)  
POTENTIAL ENERGY SURFACES

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**MASTER**

**Surface Structure, Bonding, and Dynamics:  
The Universality of Zincblende (110) Potential Energy Surfaces**

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Abstract.

Using a tight-binding, total energy (TBTE) model we examine the hypothesis that the potential energy surfaces (PES) describing the (110) cleavage faces of the tetrahedrally coordinated, zincblende-structure compound semiconductors exhibit a common "universal" form if expressed in terms of suitably scaled parameters. TBTE calculations on both III-V and II-VI compounds reveal a linear scaling with bulk lattice constant of the geometric parameters of the reconstructed surfaces. This scaling is analogous to that found using low-energy, electron-diffraction surface-structure determination. The surface atomic force constants (found from a TBTE calculation) also scale monotonically with the lattice constant. Using TBTE models proposed previously for GaP, GaAs, GaSb, InP, InSb, and ZnSe, we find that the force constants scale as the inverse square of the bulk lattice constant. These results suggest that if distances are measured in units of the bulk lattice constant, the PES may be a universal function for the cleavage surfaces of zincblende-structure compound semiconductors, on average, with small fluctuations from this average occurring in individual materials.

## I. Introduction

Compound semiconductors which crystallize in the zincblende structure (e.g. ZnS, GaAs, InP, CdSe, and other III-V and II-VI materials) form charge neutral surfaces along their (110) cleavage planes. These surfaces relax as a result of the redistribution of surface dangling bond charge density and the accompanying rehybridization of the surface atomic orbitals. Moreover, these relaxations are characterized by large, nearly-bond-length conserving displacements of the surface atoms from their truncated bulk positions.<sup>1,2</sup> This is because the energy cost associated with a significant distortion of the local bond lengths is large compared to that of motion along a bond-length conserving path.

For many of these materials, the (110) surface atomic geometries have been determined quantitatively by low-energy, electron-diffraction (LEED) intensity analyses. In each case, the relaxed surface exhibits a large tilt of the first (surface) layer relative to bulk positions and a much smaller counter-tilt of second layer, with all bond lengths approximately equal to their bulk values.<sup>1,2</sup> An analysis of the displacements normal to the surface within the top layer, described by the parameter  $\Delta_{1\perp}$  (defined in Fig. 1), showed that  $\Delta_{1\perp}$  scaled with the bulk lattice constant,  $a_0$ , as would be expected for a bond-length conserving top-layer rotation.<sup>3</sup>

The scaling of  $\Delta_{1\perp}$  with  $a_0$  led to a re-examination of the entire body

of LEED data using a top-layer only, bond-length conserving rotation model for the relaxation.<sup>2</sup> This simple model leads to predicted intensities which fit the LEED intensity data nearly as well as those associated with the best-fit structures. Moreover, the resulting surface-layer tilt angles  $\omega$ , (defined in Fig. 1) are essentially independent of the material (i. e.,  $\omega = 29^\circ \pm 3^\circ$ ), as expected<sup>3</sup> from the linear scaling surface geometric parameters with  $a_0$ . The idea thus arose that the surface structure might be "universal" in that all of the surface structure parameters would scale linearly with  $a_0$ , even for the completely refined structure. (This linear scaling with  $a_0$ , was contained implicitly within tight-binding total energy [TBTE] structure calculations of III-V and II-VI compound surfaces, but not explicitly discussed.<sup>4,5</sup>) Subsequent TBTE structure calculations of both the  $(10\bar{1}0)$  and  $(11\bar{2}0)$  surfaces of various wurtzite-structure materials displayed a similar universal behavior: the surface relaxes through approximately bond-length conserving motions, and all of the surface structure parameters scale linearly with the bulk lattice constant (even the deviations from bond-length conserving displacements).<sup>6</sup> In each case, the relaxed surface geometry is determined primarily by the topology of the truncated bulk surface, which allows the cation to relax to  $sp^2$  hybridization via bond-length-conserving atomic displacements.<sup>1,2</sup>

Wang and Duke<sup>7</sup> extended the bond-length-conserving relaxation model to surface vibrations by interpreting an observed 10 meV "optical" surface phonon mode of the GaAs (110) surface<sup>8</sup> as a bond-length conserving libration of the surface layer. A small class of such surface modes is allowed due to the topology of the cleavage surfaces. A tight-binding total energy (TBTE), frozen-phonon calculation of the frequency of

such a libration reproduced the experimental value.<sup>7</sup> However, bond-charge slab model calculations<sup>9</sup> and TBTE, compressible-bond calculations<sup>10</sup> of the atomic dynamics of GaAs (110) have since shown that this class of bond-length-conserving modes do not figure prominently in the surface lattice dynamics of compressible lattices. Consequently, the relationship between the surface normal modes and surface topology is more complicated than that between the surface topology and equilibrium surface geometry.

The curvature of the potential energy surface, as a function of atomic displacements, determines the force constants for these displacements. In the limit of an incompressible lattice (i.e., a lattice which allows only bond-length conserving motions of the atoms), the potential energy is a function of two angular coordinates per layer (for changes of layer tilt and registration). Such a model has been demonstrated to be inadequate for a description of the surface normal modes.<sup>10</sup> Each atom has three degrees of freedom; consequently, to correctly describe the normal mode spectrum, the potential energy as a function of surface atom displacements in all directions (i. e., a "potential energy surface" [PES] which is a function of the surface-atom coordinates), must be constructed for the compressible lattice.

In this paper we examine the relationship between surface topology, surface equilibrium atomic structure (location of PES minimum) and atomic force constants (curvature of the PES near its minimum) for the (110) cleavage faces of a variety of III-V and II-VI compound semiconductors. We use the same TBTE model which has successfully reproduced their equilibrium surface atomic geometries and surface state eigenvalue

spectra.<sup>1-4,6</sup> This method allows direct, tractable calculations of the surface interatomic force constants (rather than treating them as independent parameters) by relating them to the electronic structure and bulk elastic parameters. First, we provide a comprehensive, quantitative study of the incompressible-lattice limit by examining the effect of the bond-length conservation constraint on the equilibrium surface structure, and effective force constants for bond-length conserving surface vibrations. Next, we generalize the model to include lattice compression, and show that the concept of a universal-scaled force-constant matrix applies to the general case, although in a different form than in the incompressible-lattice limit.

Calculations of the (110) surfaces of the II-VI compound ZnSe, and III-V compounds GaAs, InP, GaP, GaSb and InSb yield four important results. In the incompressible-lattice limit, the displacements of the surface atoms from their truncated bulk positions scale linearly with bulk lattice constants, consistent with LEED results.<sup>2,3</sup> Moreover, the effective force constant for a bond-length-conserving tilt of the surface layer scales as the inverse fourth power of the lattice constant, so that a universal form of the PES is predicted in this limit. When the constraint of incompressibility is relaxed, both geometric and dynamic parameters still scale with the bulk lattice constant, although values for the various materials exhibit scatter around the trend curve. The force constants for atomic displacements now scale as the inverse square of the lattice constant, however, leading to a single, universal form of the force-constant matrix. Thus, this analysis predicts both a universal minimum and curvature of the PES for the (110) surface, with small deviations from the average characterizing individual materials.

We proceed by describing the TBTE model in Section II and its application to zincblende-structure (110) surfaces in Section III. Our scaling analysis is presented in Section IV, and we conclude with a synopsis.

## II. The Tight-Binding Total Energy Model

The tight-binding total energy (TBTE) model used herein was developed by Chadi,<sup>5</sup> Vogl et al.,<sup>11</sup> and Mailhiot et al.<sup>12</sup> The total energy is separated into a one-electron "band structure" contribution and an elastic contribution from each of the bonds:

$$E_{total} = E_{bs} + \sum_{ij} [U_1(ij) \epsilon_{ij} + U_2(ij) \epsilon_{ij}^2]. \quad (1)$$

$\epsilon_{ij}$  is the fractional change in the distance between near-neighbor atoms  $i$  and  $j$ .  $E_{bs}$  is the sum of the occupied eigenvalues of a one-electron, orthogonal, nearest-neighbor, Slater-Koster<sup>13</sup> Hamiltonian integrated over the reduced Brillouin zone. Electronic parameters in the Hamiltonian were chosen to fit bulk crystal structures, optical absorption and photoemission data, and are taken from previous studies.<sup>14</sup> The integration of eigenvalues over k-space for  $E_{bs}$  is accomplished via a quadrature scheme developed by Chadi and Cohen,<sup>15</sup> which approximates the integral as a sum of eigenvalues evaluated at a set of nodes, or "special" k-points. For the substances studied here, convergence is rapid. Use of a single node is adequate to fix energy differences to 0.5 meV per unit cell. This leads to an uncertainty in the calculated force constants of less than 5 percent. The



elastic parameters,  $U_1$  and  $U_2$ , are determined from bulk structure and moduli, and are also taken from previous work.<sup>14</sup>

It is useful at this point to define the various limits in which we examine the scaling relationships. Equation (1) shows that when  $U_2$  is very large, motions which compress bonds are energetically unfavorable. At the singular point where  $U_2$  is infinite, the lattice is rigorously incompressible and  $\epsilon$  is always zero. For this "incompressible lattice limit," atomic motion is only allowed along bond-length-conserving paths. We restrict our discussion of the incompressible lattice to motions which change layer tilts without changing layer registration. For large but finite  $U_2$  (i.e., a "large modulus limit"), bond compression, while energetically unfavorable, is nonetheless allowed. This limit is examined by setting  $U_2$  for each material to 99.0 eV per bond, an order of magnitude larger than typical empirically-fitted values. The compressible lattice is investigated by setting the various  $U_2$  to empirically fitted values.

These limits can be characterized by which term dominates the total-energy expression (Equation [1]). For an incompressible lattice  $\epsilon$ , and hence the strain contribution, always equal zero. Changes in the total energy are then due solely to changes in the band-structure energy as the positions of the various atoms are changed in such a fashion as to leave all bond lengths at their bulk value. In the large-modulus limit, changes in the total energy are dominated by changes in the repulsive strain term. Finally, for the compressible lattice both the band-structure and repulsive terms contribute to changes in the total energy.

### III. Zincblende (110) Surfaces

The zincblende structure is a face-centered cubic lattice with two atoms (one compound formula unit) per unit cell. Each atom is tetrahedrally coordinated. The (110) surface (Fig. 1) consists of parallel zigzag chains back-bonded to lower layers of similar chains.

Fig. 1 contains a schematic depiction of a typical reconstruction of a zincblende-structure compound semiconductor (110) surface, and a definition of the independent surface structural parameters. The surface-layer tilt angle,  $\omega$ , of the reconstructed top layer relative to the ideal bulk surface is geometrically related to the displacements  $\Delta_{1x}$  and  $\Delta_{1y}$ ; a similar scaling with the bulk lattice constant  $a_0$  of these latter two parameters implies a similar tilt angle for each material.

We model the surface with a slab eight atomic layers thick. Periodic boundary conditions are imposed in all directions; in the  $z$  direction (normal to the surface) the period is much longer than the slab thickness. Slabs therefore do not interact. The total energy of the system is minimized by minimization of the Hellman-Feynman forces<sup>16</sup> on each atom, providing the equilibrium structure of the slab. Then, the top layer atoms are displaced by various amounts, while all other atoms are frozen in their equilibrium positions. The total energy (as a function of the positions of the two surface atoms) is fitted to a harmonic function (second order in the atomic displacements), providing the PES for small displacements of the surface atoms from equilibrium. The gradient of this surface in an appropriate coordinate system gives the various pairwise surface atom-atom force constants.<sup>10</sup> The periodic boundary conditions require that any

atomic displacement in a surface unit cell be mimicked in all other cells. The six-by-six matrix of force constants together with the atomic masses provide, within the limitations of the TBTE model, the equations of motion for surface vibrations at the center of the reduced surface Brillouin zone ( $\bar{\Gamma}$ ).

This method ignores long-range Coulomb interactions. It thus cannot, in general, provide high accuracy in phonon dispersion calculations. For example, the splitting of LO and TO modes in GaAs cannot be reproduced without such interactions.<sup>17</sup> The method can be extended to include long-range interactions.<sup>18</sup> Neglect of these interactions, however, is not expected to affect our purpose here: to demonstrate trends in the local force constants and their relationship with surface electronic properties, thus gaining insight into the common features of these materials.<sup>10</sup>

#### IV. Scaling

##### A. Surface Atomic Structure (Minima of the Surface PES)

Figures 2 and 3 illustrate the results of TBTE minimization structure calculations for the reconstruction parameters  $\Delta_{1\perp}$  and  $\Delta_{1y}$  (Fig. 1), respectively, under various constraints. In each graph a reconstruction parameter is plotted as a function of the bulk lattice constant  $a_0$ . Figs. 2 (a) and 3 (a) represent the large-modulus limit, for which bond-compressing displacements are allowed, but are energetically unfavorable. All of the other independent linear parameters from Fig. 1 have also been calculated, and each scales in the same way as  $\Delta_{1\perp}$  and  $\Delta_{1y}$ . The surface-tilt angles for the materials, found from the  $\Delta_{1\perp}$  and  $\Delta_{1y}$  values in Figs. 2 and 3, are

displayed in Table 1; the results agree quantitatively with the  $29 \pm 3$  degree result from the scaling of the LEED data.<sup>2,3</sup> These results reveal that in an average sense, the positions of the PES minima linearly scale with  $a_0$ .

When the  $U_2$  parameters are obtained empirically (lower panels, Figs. 2, 3), the lattice assumes its "normal" compressibility. Differences in the local repulsive potentials from one compound to another degrade the scaling relationship. There remains, however, a significant correlation among the various  $\Delta_{1\perp}$  and  $\Delta_{1\parallel}$ . (Once again, the other parameters from Fig. 1 scale in the same way.) Therefore the concept of a universal average PES minimum remains valid for compressible, as well as incompressible, lattices.

#### B. Surface Force Constants (Curvatures of the Surface PES)

As with the equilibrium surface atomic structure (specified by the PES minimum), the surface elastic force constants (specified by the curvature of the PES near its minimum) are determined by the surface electronic structure and interatomic repulsion potentials. It is reasonable, therefore, to ask if the force constants of the various materials have some analog to the universal structural scaling evident in Figs. 2 and 3. It is useful to approach this question by considering separately the band structure and elastic contributions to the total energy. The incompressible lattice is a convenient starting point because it illustrates the special case of bond-length conserving ("bond-bending") displacements that can exist for the zincblende-structure (110) surfaces by virtue of the surface topology. While these displacements do not exert a dominant effect on the

surface vibrational modes of the compressible lattice, they are of interest because their force constants differ fundamentally from those of "bond-stretching" displacements.

Suppose the surface layer of each material is moved from its equilibrium tilt angle  $\omega_r$  to a new tilt  $\omega$  along a bond-length conserving path. Because the structures are similar, the distance that a surface atom of the  $i^{\text{th}}$  material has been displaced is  $ca_{0i}(\omega - \omega_r)$ , where  $a_{0i}$  is the bulk lattice constant of the  $i^{\text{th}}$  material, and  $c$  is a dimensionless number which is constant for all materials. The curvature of the total energy as a function of  $a_{0i}\omega$  thus equals  $k_{BLCi}/c^2$ , where  $k_{BLCi}$  is the effective force constant for a displacement of the atoms along a bond-length conserving path. These curvatures are shown in Fig. 4 for the various materials. According to Fig. 4, if the atoms of each substance are displaced by the same distance from equilibrium in this direction, the various restoring forces will vary as  $a_0^{-4}$ .

The origin of the result shown in Fig. 4 can be ascertained from an analytic argument based on a simplified tight-binding picture. Consider a set of slabs consisting of one slab each of GaAs, InSb, GaP, etc., with each slab constrained to have all bond lengths equal to the bulk values. Each slab has an arbitrarily imposed atomic structure, such that the structures of all the slabs, measured in units of their respective lattice constants, are identical. The set is then said to be composed of geometrically similar slabs. Since all bond lengths have bulk values, the strain contribution to the total energies of the slabs vanish; energy differences as a function of atomic displacements for each slab arise solely from direction cosines in the electronic Hamiltonians of the various materials. Moreover, when the slabs are geometrically similar, the direction cosines are identical from one

material to another.

Let the arbitrary structure imposed on the geometrically similar slabs be denoted by  $\alpha$ . We wish to compare the band-structure energies of the various slabs in this set. Harrison and co-workers have developed a universal electronic parameter set in which the off-diagonal Hamiltonian elements are given by  $v/d^2$ , where  $v$  is a constant for all materials and  $d$  is the bond length.<sup>19,20</sup> Using this parameter set, the electronic Hamiltonians for the various materials differ only in their diagonal elements, and in that their off-diagonal elements scale as the inverse square of the respective lattice constants. Furthermore, since the electronic structures of all the different materials are qualitatively similar,<sup>11,19</sup> each material has a comparable degree of  $sp$  hybridization from the diagonal elements of its electronic Hamiltonian. Moreover, each material has a similar density of states for its filled bands,<sup>19,20</sup> justifying a second-moment approximation<sup>21</sup> for the band structure energy of the various slabs. It can be shown that in this approximation, the band structure energies of the various slabs are proportional to the widths of their respective occupied bands. These widths are, in turn, proportional to the magnitudes of the off-diagonal elements,<sup>21</sup> and hence proportional to  $a_0^{-2}$ . For the set of slabs with structure  $\alpha$ , then, the total energy scales as  $a_0^{-2}$ . That is, for the  $i^{\text{th}}$  material,

$$E_i = b_\alpha a_0^{-2} \quad ,$$

where  $b_\alpha$  is a constant valid for all materials in structure  $\alpha$ . If the slabs are all moved to a new structure  $\beta$ , the energy cost is

$$\Delta E_i = b_\beta a_0^{-2} - b_\alpha a_0^{-2} = (b_\beta - b_\alpha) a_0^{-2} \quad . \quad (2)$$

In the limit of the incompressible lattice, all the slabs have identical equilibrium structures in units of the lattice constants (Table I, Figs. 2 and 3). We now chose  $\alpha$  to be this common equilibrium structure, with each slab having an identical equilibrium tilt  $\omega_r$ , and  $\beta$  to be the same structure except for a different surface layer tilt  $\omega$ . Equation (2) dictates that the energy costs associated with these tilts will scale as  $a_0^{-2}$ . If there is some regime near  $\omega_r$  in which the total energy is quadratic in the displacement  $ca_0(\omega_r - \omega)$ , that is,

$$\Delta E_i = (1/2)k_{BLCi}[ca_0(\omega - \omega_r)]^2, \quad (3)$$

then the effective force constant is given by

$$k_{BLCi} = 2\Delta E_i/[ca_0(\omega - \omega_r)]^2 \quad (4)$$

Equation (4), along with the  $a_0^{-2}$  scaling of  $\Delta E_i$ , immediately gives an  $a_0^{-4}$  scaling for  $k_{BLCi}$ .

Within the tight-binding model, deviations from this ideal behavior can be expected in a less approximate treatment. Such deviations occur in the results of Fig. 4, which were found using empirically fitted electronic parameters, and without the simplistic assumptions about the degree of hybridization and the densities of states in the argument given above. Further deviations, from effects such as ionicity<sup>18</sup>, would arise from a more complete model; however, we expect these to be small.

While the incompressible-lattice limit is useful in characterizing the electronic contribution to the surface dynamics, real lattices are compressible. In order to examine the independent elastic contributions to the force constants, we first consider the large modulus limit, in which changes in the total energy are dominated by changes in the repulsive term of Equation (1). Moreover, because each material has  $U_2$  set to 99.0

eV/bond, in a force constant calculation the contribution of the elastic term is the same magnitude for each substance. The force constant  $k_{x_1x_1}$  (for motion in the  $x$ -direction of atom 1 [the cation] of the surface unit cell), calculated in the large-modulus limit, is shown in the top panel of Fig. 5 as a function of the inverse square of the lattice constant. There is clearly a linear relationship between these values. Calculations of each of the 36 independent pairwise surface-atom Cartesian force constants produce similar scaling curves. It is interesting to note that this scaling relationship is qualitatively different from that of Fig. 4, since it reflects the dominance of the repulsive strain energy, as opposed to the band structure energy, in the total energy difference.

In the large-modulus limit, the diagonal elements of the force constant matrix are given by

$$k_{x_i} = 2 \Delta E_i / x_i^2, \quad (5)$$

where  $x_i$  is any Cartesian displacement. If the various materials all have displacements of  $x_i$  proportional to their lattice constants, the fractional changes in bond distances  $\epsilon_{ij}$  are independent of the lattice constants. Since the value of  $U_2$  is identical for each material,  $\Delta E_i$  is constant. This causes the force constant to scale inversely with  $a_0^2$ , as shown in the top panel of Fig. 5.

This large-modulus limit is unphysical, however, since for a compressible lattice the different repulsive potentials will vary with the respective bulk moduli. The experimental bulk moduli themselves, however, roughly scale with  $a_0$ .<sup>22</sup> This suggests that the surface atom force



constants might scale as some function of  $a_0$ , even for the compressible lattice.

When the elastic parameters are determined empirically, both the repulsive and electronic terms contribute to changes in the total energy. Moreover, these contributions are of comparable magnitude. The various materials also exhibit differences in their local chemical environments and in their interatomic repulsive forces. The different substances therefore deviate from a simple scaling law. In an average sense (as for the surface atomic coordinates), however, the surface atomic force constants still exhibit an  $a_0^{-2}$  scaling, as shown in the lower panel of Fig. 5.

We infer from Fig. 5, and its analogs for the other independent force constants, that the force-constant matrix of each material is, on average, equal to a scalar multiple of a single, universal matrix. This universality of the PES indicates that, within the TBTE model, characteristics of the surface vibrational modes and frequencies of the various materials are determined primarily by the lattice constant and the atomic masses. Our analysis further suggests that similar scaling laws should be exhibited by bulk vibrational modes.

## V. Synopsis

The universality of geometric structures of (110) surfaces of zincblende-structure compound semiconductors has been established experimentally.<sup>2,3</sup> The geometric parameters which describe the surface reconstructions scale linearly with a single variable, the bulk lattice constant. These reconstructed geometries correspond to a minimum in the

potential energy surface (PES), which is a function of the atomic positions.

This structural universality is also predicted by our tight-binding total energy calculations for GaAs, GaP, InP, InSb and ZnSe. Agreement with a linear scaling of the surface geometric parameters in the lattice constant is rigorous in the incompressible-lattice limit, and approximate when bond lengths are allowed to vary.

The idea of universality can be applied to the local curvature about equilibrium, as well as the equilibrium position, of the PES. In the limit of an incompressible lattice, TBTE calculations show that the curvature scales as the inverse fourth power of the bulk lattice constant. When bond compressions are allowed, curvatures scale approximately as the inverse square of the lattice constant. This difference is due to the differing scalings of the electronic and strain contributions to the total energy.

These results imply that for each zincblende-structure compound surface the six-by-six matrix of atomic force constants is, on average, equal to a scalar multiple of a single universal matrix. Differences in modes and frequencies of surface vibrations among the various materials depend primarily on the lattice constants and atomic masses. Thus, the concept of a universal average PES, with distances measured in units of the lattice constant, is supported by our analyses of both the location of its minimum and the curvature about this minimum.

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## References

- <sup>1</sup>C. B. Duke, in *Reconstructions of Solid Surfaces*, edited by K. Christman and K. Heinz (Springer-Verlag, Berlin, 1991), in press.
- <sup>2</sup>C. B. Duke, in *Surface Properties of Electronic Materials*, edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1988), pp. 69 - 118.
- <sup>3</sup>C. B. Duke, *J. Vac. Sci. Tech. B* **1**, 732 (1983).
- <sup>4</sup>C. Mailhot, C. B. Duke and D. J. Chadi, *Surf. Sci.* **149**, 366 (1985).
- <sup>5</sup>D. J. Chadi, *Phys. Rev. Lett.* **41**, 1062 (1978); *Phys. Rev. B* **19**, 2074 (1979); *Vacuum* **33**, 613 (1983); *Phys. Rev. B* **29**, 785 (1984).
- <sup>6</sup>C. B. Duke and Y. R. Wang, *J. Vac. Sci. Tech. A* **6**, 692 (1988).
- <sup>7</sup>Y. R. Wang and C. B. Duke, *Surf. Sci.* **205**, L755 (1988).
- <sup>8</sup>U. Harten and J. P. Toennies, *Europhys. Lett.* **4**, 833 (1987).
- <sup>9</sup>P. Santini, L. Miglio, G. Benedek, U. Harten, P. Ruggerone and J. P. Toennies, *Phys. Rev. B* **42**, 11942 (1990).
- <sup>10</sup>T. J. Godin, John P. LaFemina and C. B. Duke, *J. Vac. Sci. Tech. B* **9**, 2282 (1991).
- <sup>11</sup>P. Vogl, Harold P. Hjalmarson and John. D. Dow, *J. Phys. Chem. Solids* **44**, 365 (1983).
- <sup>12</sup>C. Mailhot, C. B. Duke and D. J. Chadi, *J. Vac. Sci. Tech. A* **3**, 915 (1985).
- <sup>13</sup>J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954).
- <sup>14</sup>J. P. LaFemina, C. B. Duke and C. Mailhot, *J. Vac. Sci. Tech. B* **6**, 888 (1990); Y. R. Wang, C. B. Duke and C. Mailhot, *Surf. Sci. Lett.* **188**, L708 (1987).
- <sup>15</sup>D. J. Chadi and M. Cohen, *Phys. Rev. B* **8**, 5747 (1973).

- <sup>16</sup>R. Feynman, *Phys. Rev.* **5 6**, 340 (1939).
- <sup>17</sup>P. Brüesch, *Phonons: Theory and Experiments I* (New York, Springer, 1982), pp. 129 ff.
- <sup>18</sup>S. E. Toet and D. Lenstra, *Appl. Phys. A* **4 3**, 85 (1987).
- <sup>19</sup>Walter A. Harrison, *Electronic Structure and the Properties of Solids* (New York, Dover, 1989).
- <sup>20</sup>Sverre Froyen and Walter A. Harrison, *Phys. Rev. B* **2 0**, 2420 (1979).
- <sup>21</sup>D. G. Pettifor, in *Many-Atom Interactions in Solids*, edited by R. M. Nieminen, M. J. Puska and M. J. Manninen (Springer-Verlag, Berlin, 1990), p. 64.
- <sup>22</sup>J. A. Majewski and P. Vogl, *Phys. Rev. B* **3 5**, 9666 (1987).

## Figure Captions

- Fig. 1. Schematic representation of a typical reconstruction of a (110) surface of a III-V or II-VI semiconductor, showing geometric parameters of the reconstructed surface.
- Fig. 2. Tight-binding total-energy (TBTE) predictions for the parameter  $\Delta_{1\perp}$  (Fig. 1) for (110) surfaces of GaP, GaAs, ZnSe, InP, GaSb and InSb, plotted as a function of lattice constant  $a_0$  for: (a) the large-modulus limit, and (b) the compressible lattice. The linear scaling relation implies a universal reconstruction. All quantities are expressed in units of Ångstroms.
- Fig. 3. Tight-binding total-energy (TBTE) predictions for the parameter  $\Delta_{1y}$  (Fig. 1) for (110) surfaces of GaP, GaAs, ZnSe, InP, GaSb and InSb, plotted as a function of lattice constant  $a_0$ . Panels (a) and (b) refer to the same cases as the corresponding panels of Fig. 2. All quantities are in expressed units of Ångstroms.
- Fig. 4. TBTE calculation of the force constants for bond-length conserving displacements of surface layer atoms.  $c$  is a dimensionless structural parameter, defined in the text, which is constant for all materials. Like the structure parameters, the force constant scales with the bulk lattice constant, in this case as  $a_0^{-4}$ . Units for force constants are Newtons/meter; for lattice constants, Ångstroms.
- Fig. 5. TBTE calculation of the force constants for a linear displacement of each surface cation in the  $x$  direction (parallel to the surface zigzag chains) for: (a) the large-modulus limit, and (b) the compressible lattice. Units for force constants are Newtons/meter; for lattice constants, Ångstroms.

Table I. Surface layer tilt angle  $\omega$ , of the relaxed (110) surfaces of various materials calculated with the TBTE model for incompressible and compressible lattice models.

	GaP	GaAs	ZnSe	InP	GaSb	InSb
$a_0$ (Å)	5.451	5.654	5.657	5.869	6.118	6.478
$\omega$ , (degrees) for:						
incompressible lattice	27.2	27.6	27.7	29.6	27.7	28.6
compressible lattice	28.9	29.4	29.9	32.1	28.9	29.8

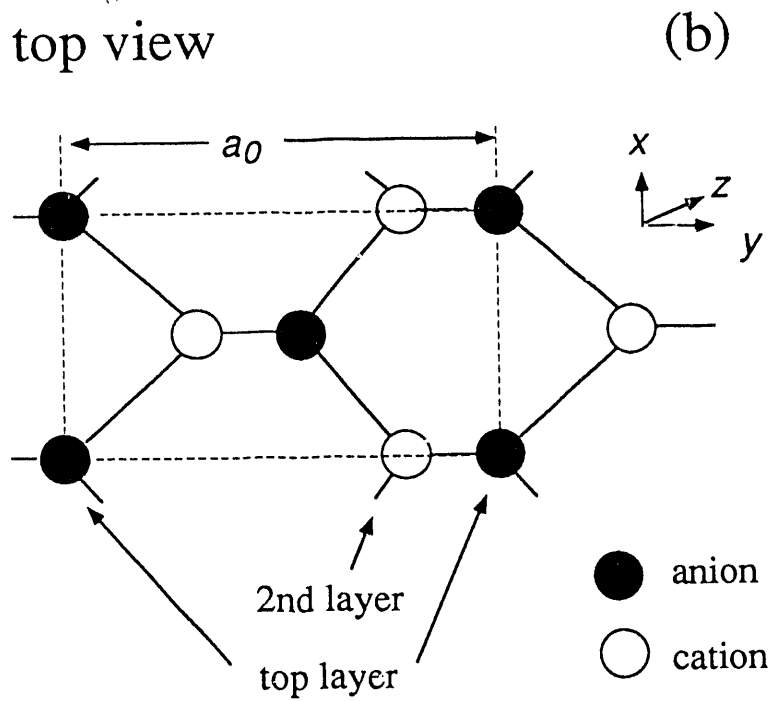
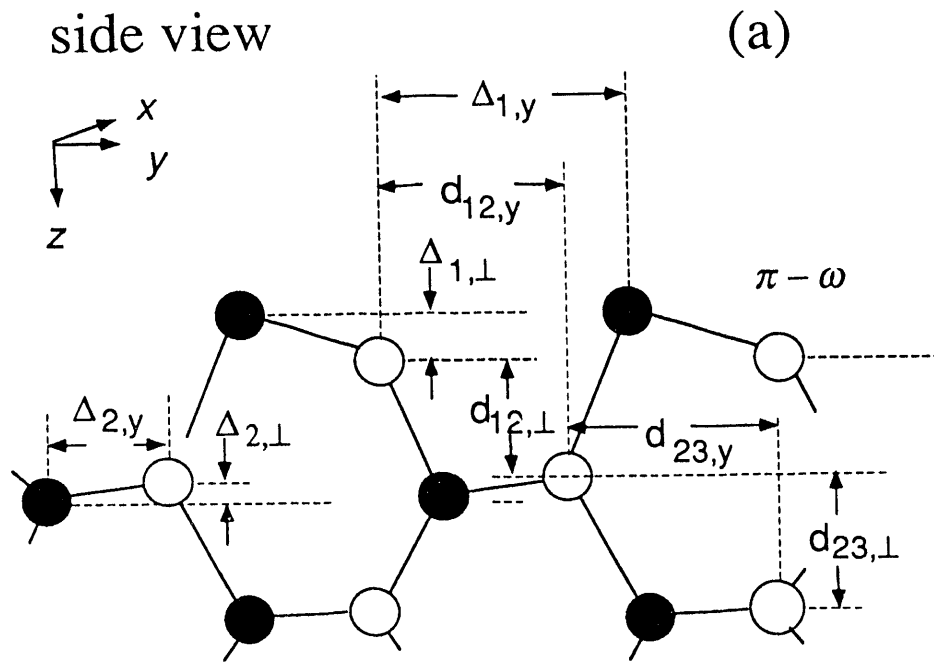


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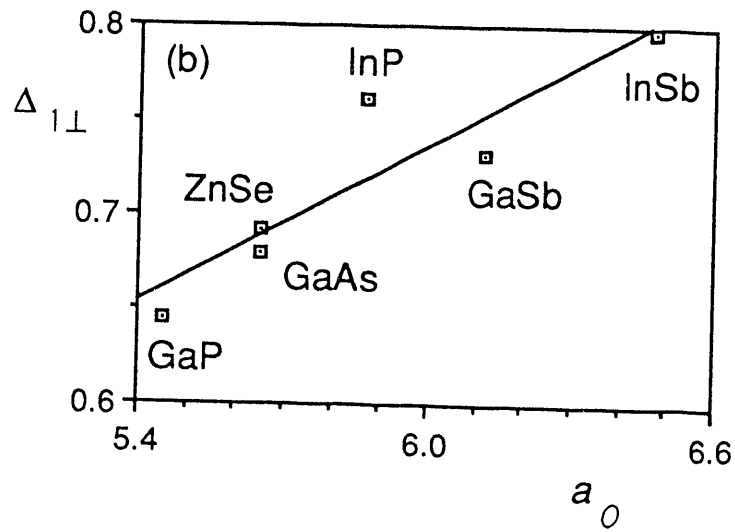
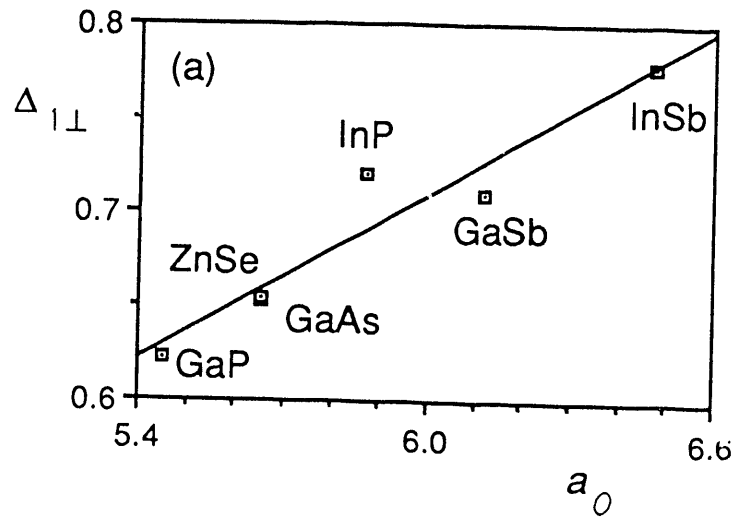


Fig. 2 T.J. Godin, J.P. LaFemina, C.B. Duke, J. Vac. Sci. Tech. A.



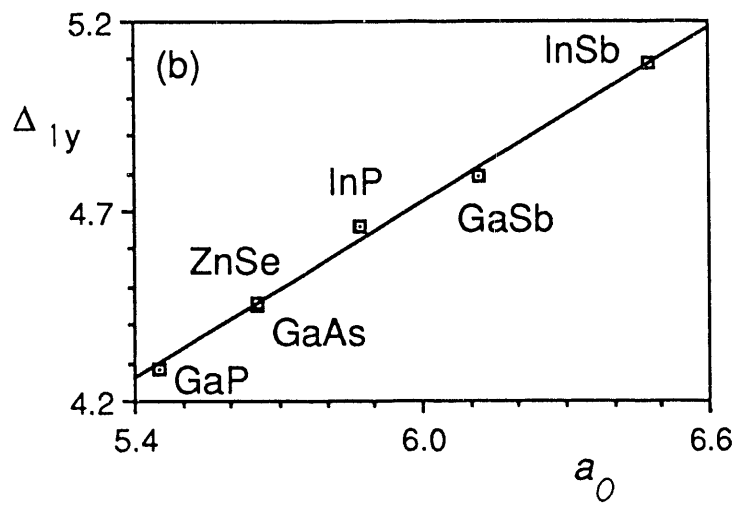
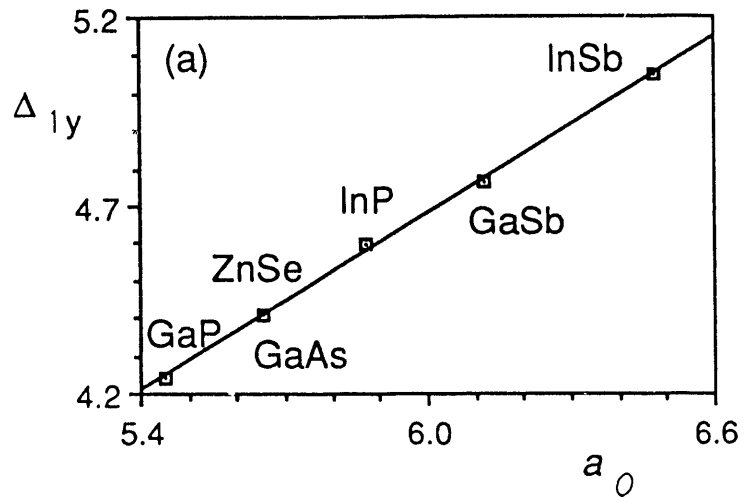


Fig. 3 T.J. Godin, J.P. LaFemina, C.B. Duke, J. Vac. Sci. Tech. A.

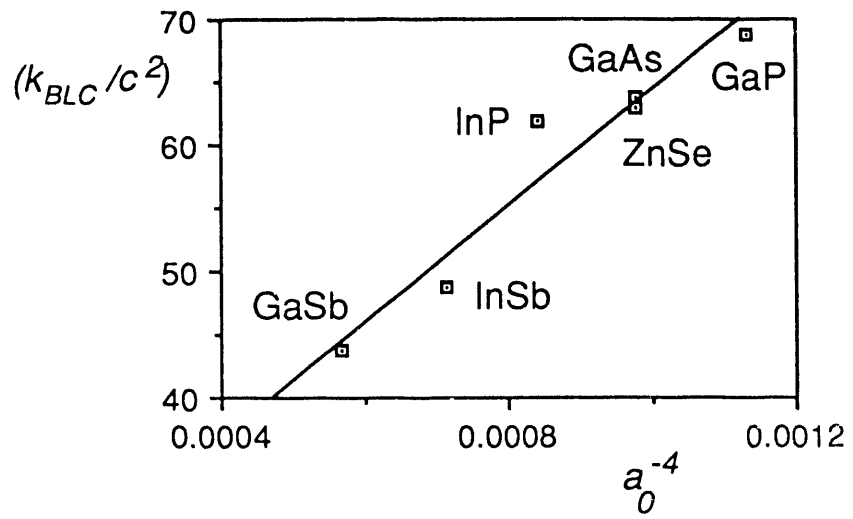


Fig. 4 T.J. Godin, J.P. LaFemina, C.B. Duke, J. Vac. Sci. Tech. A.

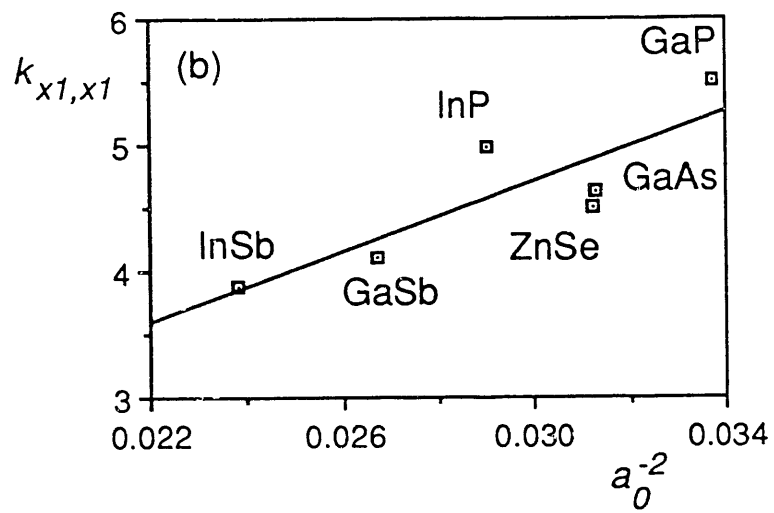
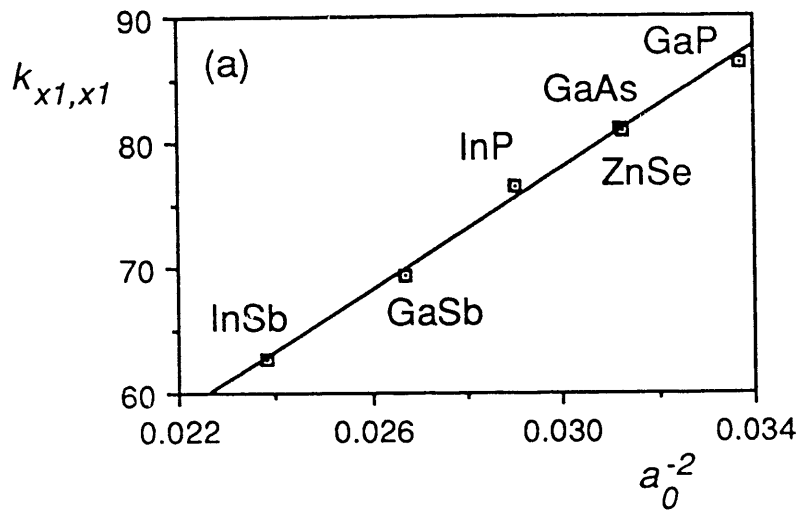


Fig. 5 T.J. Godin, J.P. LaFemina, C.B. Duke, J. Vac. Sci. Tech. A.

**END**

