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(110) surface atomic structures of covalent and ionic semiconductors

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A total-energy-minimization approach is applied to the determination of the (110) surface atomic geometries of Si, Ge, GaAs, InP, InSb, ZnSe, and ZnTe. The accuracy of the model employed in the energy minimization was tested by comparing calculated values of bulk elastic coefficients and phonon frequencies to experimental data. Generally good agreement between the calculated and experimental results were obtained. The *relative* displacements of nearest-neighbor surface atoms, when scaled for differences in lattice constants, are found to be very similar for all the semiconductors studied. The displacements of individual atoms from unrelaxed bulk terminated positions are, however, appreciably different and ionicity dependent. The bond rotation or tilt angle at the surface which provides a *partial* characterization of surface relaxation is nearly constant varying only from 30° in Si to 25.6° in ZnSe. The reduction in total energy resulting from surface relaxation decreases from approximately -0.55 eV (per surface atom) in Si to -0.30 eV in ZnSe and ZnTe. Subsurface relaxations are generally found to make a very small (≈ 0.02 eV) contribution to the lowering of the total energy.

I. INTRODUCTION

Studies of low-energy-electron diffraction (LEED) spectra have shown[1] the surfaces of most semiconductors to be relaxed or reconstructed. While it is relatively easy to determine the space group symmetry of the surface unit cell through LEED measurements, it is more difficult to extract information on the exact positions of surface atoms. In the last few years analyses of LEED intensities have indicated that the rearrangements occurring at the surface involve large atomic displacements. These surface relaxations have been shown to greatly influence the electronic structure at the surface, causing shifts of up to $\simeq 1$ eV in surface states and resulting in metal-semiconductor transitions in some cases.[2-7] These results suggest that relatively large decreases in the total energy of the electron-ion system may be involved in surface relaxations and reconstructions of semiconductors. A reasonably accurate model for the dependence of the total energy on atomic coordinates would therefore be very useful in determining surface structure. Such a model is developed in this paper and utilized in the determination of the (110) surface structures of several semiconductors. An energy-minimization approach to structural properties of crystals[8-10] and surfaces[10-14] has also been used in several recent publications.

This paper is organized as follows: A model for the variation of the total energy with atomic displacements is developed in Sec. II and its accuracy in determining bulk structural properties is discussed. The application of the model to the (110) surfaces of Si, Ge, GaAs, InP, InSb, ZnSe, and ZnTe is discussed in Sec. III and the results of the calculations for surface atomic coordinates are given.

The main results of the surface calculations which are discussed in more detail in Sec. III are: (i) The bond rotation angle θ [as defined by Eq. (9)] at the surface is nearly constant with a value of about 27.5° ± 2° for all the semiconductors studied. (ii) The displacements of the surface anions (cations) in the direction normal to the surface decrease (increase) with increasing ionicity in agreement with LEED studies[2] of (110) GaAs and (10$\bar{1}$0) ZnO surfaces. The displacements of anions and cations are in opposite directions with the anions moving away from bulk atoms. (iii) The reduction in total energy results primarily from the relaxation of first layer (surface) atoms. The relaxation of the first subsurface layer lowers the energy by an amount which is more than an order of magnitude smaller than for the surface layer; relaxations of lower layers make even smaller contributions.

II. TOTAL ENERGY APPROACH TO BULK AND SURFACE STRUCTURAL PROPERTIES

A. Components of the total energy

It is important to note that in this work we are not interested in the value of the ground-state total energy. Our primary interest is to obtain a method by which *changes* in the total energy resulting from atomic motions can be calculated. For the bulk this allows a calculation of elastic coefficients and phonon frequencies. For the surface it enables us to determine whether a particular kind of relaxation increases or decreases the total energy and it therefore allows a determination of the surface structure.

The total energy E_{tot} of an electron-ion system can be expressed as

$$E_{\text{tot}} = E_{ee} + E_{ei} + E_{ii} , \tag{1}$$

where E_{ee}, E_{ei}, and E_{ii} denote the electron-electron, electron-ion, and ion-ion interaction energies. Equation (1) can be cast into a more suitable form by introducing the electronic band-structure energy E_{bs} defined as

$$E_{bs} = \sum_{\vec{k},n} E_n(\vec{k}) , \tag{2}$$

where the sum is over occupied single-particle states with wave vector k and band index n. Because of the double counting of electron-electron interactions in Eq. (2) we have

$$E_{bs} = E_{ei} + 2E_{ee} . \tag{3}$$

Using this in Eq. (1), E_{tot} can now be expressed as

$$E_{\text{tot}} = E_{bs} + U , \tag{4}$$

where

$$U \equiv E_{ii} - E_{ee} . \tag{5}$$

The advantage of Eq. (4) over Eq. (1) is that for two ions that are separated by a distance much larger than the Thomas-Fermi screening length the combined ion plus screening electron system is nearly neutral and U is close to zero. It may therefore be expected that to a good approximation this term can be described by a short-range force-constant model. In fact, as shown below, the variations in U with atomic displacements can be adequately accounted for by a two-parameter model. For the bulk the model predicts changes in U with atomic motions that are consistent with those obtained by Wendel and Martin,[8] who have used a detailed self-consistent pseudopotential approach in their calculations.

It should be noted, however, that the factor of 2 multiplying E_{ee} in Eq. (3) is strictly valid when exchange and correlation effects are ignored. For example, for a $\rho^{1/3}$ statistical exchange-correlation model, the coefficient would be 4/3 for this component of electron-electron interaction energies. Since, as discussed below, the variations in U are determined by a semiempirical model, the exact value of the coefficient of E_{ee} in Eq. (3) does not affect the results obtained from the model.

B. Calculations of E_{bs} and U

To calculate E_{bs} for Si, Ge, GaAs, InP, InSb, ZnSe, and ZnTe the tight-binding method with the parameters shown in Table I were used. These were previously obtained[15-17] by fitting x-ray and ultraviolet photoemission valence-band spectra and optical gaps. Only interactions of s and p orbitals on nearest-neighbor atoms were considered. The Hamiltonian matrix elements depend explicitly on the nearest-neighbor atomic geometry. For example, consider the interaction between two p_x orbitals on two nearest-neighbor atoms, one at $(0,0,0)$, the other at $(x_1 x_2 x_3)$. If $x_2 = x_3 = 0$, then the magnitude of the interaction is equal to $V_{pp\sigma}$ (see Table I). However, if $x_1 = 0$, the interaction is equal to $V_{pp\pi}$. For the general case, denoting the direction cosines of the second atom with respect to the first atom by $(c_1 c_2 c_3)$, the interaction within the two-center approximation is given[18] by $c_1^2 V_{pp\sigma} + (c_2^2 + c_3^2) V_{pp\pi}$. The interaction parameters $V_{pp\sigma}$, $V_{pp\pi}$, etc., are assumed to depend only on nearest-neighbor distance. Our previous work[16] on the structural properties of crystalline semiconductors shows this to be a reasonable approximation.

Spin-orbit interactions were considered in both bulk and surface calculations[17,19] for InSb and ZnTe. For ZnTe the calculations showed the surface and bulk structural properties to be insensitive to spin-orbit interactions, and these were left out of the final calculations. For InSb spin-orbit interactions were included in all the calculations. This was done since the 0.25-eV bandgap of InSb is much smaller than the 0.82-eV spin-orbit splitting of the top valence bands at the Γ point

TABLE I. Tight-binding parameters used in the calculations. The subscripts 1 and 2 refer to anion and cation, respectively. The parameters Δ_i, $i=1,2$ correspond to the renormalized atomic spin-orbit splittings. Spin-orbit interactions were included only in the calculations for ZnTe and InSb.

	E_{s_1}	E_{p_1}	E_{s_2}	E_{p_2}	V_{ss}	V_{xx}	V_{xy}	$V_{s_1p_2}$	$V_{s_2p_1}$	Δ_1	Δ_2
Si (Refs. 15,16)	−4.03	3.17	−4.03	3.17	−8.13	3.17	7.51	5.88	5.88	···	···
Ge (Refs. 15,16)	−5.79	2.62	−5.79	2.62	−6.78	2.62	6.82	5.31	5.31	···	···
GaAs (Ref. 16)	−8.21	1.28	−3.19	3.47	−6.76	2.11	5.96	4.75	5.48	···	···
InP (Ref. 17)	−7.76	1.17	−1.98	3.87	−5.59	2.12	4.90	3.81	5.25	···	···
InSb (Ref. 17)	−8.22	0.76	−3.23	2.57	−5.43	1.71	4.46	3.93	4.76	0.97	0.39
ZnSe (Ref. 16)	−11.94	0.47	0.35	7.04	−6.16	1.81	5.49	3.26	6.0	···	···
ZnTe (this work)	−10.8	0.6	0.01	6.15	−5.35	1.92	5.07	3.77	5.80	1.10	0.07

of the zinc-blende Brillouin zone. Spin-orbit interactions do not seem to affect the surface structure of InSb very much, either. The calculated surface atomic coordinates are similar to those of the other semiconductors studied.

In this work we have used a d^{-2} dependence of the tight-binding parameters on nearest-neighbor distance d. This approximation leads to predictions of changes in E_{bs} with atomic motions that are in agreement with the self-consistent pseudopotential calculations of Ref. 8.

The variation of U with changes in atomic coordinates $\{\vec{r}_i\}$ is determined semiemprically in our model through the imposition of constraints on the total energy functional $E_{\text{tot}}(\{\vec{r}_i\})$. The most important constraint is that ΔE_{tot} should be at least quadratic in $\{\Delta\vec{r}_i\}$, i.e., there should be no linear terms in $\{\Delta\vec{r}_i\}$. We find that this can be accomplished by satisfying the single condition

$$\frac{dE_{\text{tot}}}{dV}=0 \tag{6}$$

at equilibrium *and* by assuming that the *linear* term in ΔU is given by

$$\Delta U=\sum_{i>j} U_1\epsilon_{ij}\,, \tag{7}$$

where ϵ_{ij} is the fractional change in the bond length between two nearest-neighbor atoms denoted by i and j. The value of U_1 was chosen such that ΔU exactly canceled the *linear* term in the variation of the band-structure energy E_{bs} with volume. With the choice of ΔU, in the form given by Eq. (7), ΔE has no linear terms in $\{\Delta\vec{r}_i\}$.

The quadratic terms in the expansion of ΔE_{tot} as a function $\{\Delta\vec{r}_i\}$ are related to harmonic restoring forces which can be experimentally determined from measurements on elastic coefficients and phonon frequencies. To obtain these restoring forces, it is necessary to include in Eq. (7) the second-order changes in ΔU. One component of the second-order terms which has been included in the calculations is the radial one, i.e., we take

$$\Delta U=\sum_{i>j}(U_1\epsilon_{ij}+U_2\epsilon_{ij}^2)\,, \tag{8a}$$

$$\Delta E_{\text{tot}}=\Delta E_{bs}+\Delta U\,. \tag{8b}$$

For a d^{-2} dependence of the tight-binding parameters on the nearest-neighbor distance d, the values of U_1 and U_2 used in the calculations are shown in Table II.

Without using any additional parameters the above model for ΔE_{tot} predicts the correct angular restoring forces. The elastic coefficients C_{11}-C_{12} and C_{44} and the zone-boundary transverse acoustic (TA) phonon mode at X are all related to angular restoring forces and can be calculated directly from the variation of E_{tot} with the appropriate atomic displacements. The calculated and experimental values of these quantities for several semiconductors are compared in Table III. The agreement between the two, except for the TA (X) mode which involves long-range forces,[8] is sufficiently close so that no additional force-constant parameters were used. To test the adequacy of the model we have also calculated the transverse-optical (TO) mode at Γ. The changes in bond lengths and bond angles are first order in the atomic displacements for this mode. The calculated and experimental values of the TO frequencies for several semiconductors as shown in Table III agree to within a few per cent.

In general there are other three-body terms such as those proportional to $\epsilon_{ij}\epsilon_{ik}$ that need to be included to describe the dependence of ΔE_{tot} and ΔU on atomic displacements. For simplicity, these extra terms have been ignored in this work. The coefficient of the $\epsilon_{ij}\epsilon_{ik}$-type terms is of the same sign as and approximately 12% of the ϵ_{ij}^2 terms. The inclusion of these extra terms results in a value of U_2 close to that used in this paper. For all the materials studied here we find that the values of U_2 should be increased uniformly by 20% in order to obtain the correct values for the bulk modulii which tend to be underestimated in the present model.[19b] This does not affect the surface calculations very much because U_2 is still sufficiently large so that it tends to allow only small changes in bond lengths at the surface.

The combination of ion-ion and electron-electron interactions represented by the energy term U in Eqs. (4) and (5) is often ignored in many calculations and the approximation $E_{\text{tot}}\simeq E_{bs}$ is used. Our calculations indicate that it is important to take into account, in both bulk and surface calculations, at least the short-range nature of U in the

TABLE II. Parameters U_1 and U_2 (in eV) for use in Eq. (8).

	Si	Ge	GaAs	InP	InSb	ZnSe	ZnTe
U_1 (eV)	−23.50	−20.10	−35.91	−15.00	−13.87	−14.34	−14.12
U_2 (eV)	53.35	47.52	44.80	43.32	39.00	36.67	37.34

TABLE III. Values of some bulk elastic coefficients and phonon frequencies calculated from E_{tot} as compared to their experimental values (given in parenthesis).

	Si	Ge	GaAs	InP	InSb	ZnSe	ZnTe
$C_{11} - C_{12}$	10.12	7.27	6.22	4.34	3.04	3.21	2.76
(10^{11} erg/cm^3)	(10.18)	(8.02)	(6.49)	(4.46)	(3.03)	(3.22)	(3.06)
C_{44}	8.95	7.37	6.17	4.65	3.36	3.33	2.88
(10^{11} erg/cm^3)	(7.96)	(6.71)	(5.92)	(4.60)	(3.02)	(4.41)	(3.12)
TA (X)	6.52	3.14	3.02	3.18	1.76	2.30	2.02
(10^{12} Hz)	(4.49)	(2.39)	(2.39)	(2.05)		(2.10)	
TO (Γ)	15.5	8.97	8.42	10.19	5.61	6.25	5.76
(10^{12} Hz)	(15.6)	(9.1)	(8.1)	(9.1)	(5.37)	(6.21)	(5.31)

model for E_{tot}. The surface structures determined when U is included or excluded from the calculation are not the same, i.e., the minimum of E_{tot} does not, in general, coincide with that of E_{bs}. In our previous work[16] on angular restoring forces in semiconductors, the linear term in the variation of U with ϵ_{ij} was included implicitly in the calculations, i.e., both U_1 *and* the variations of the tight-binding parameters with ϵ_{ij} were set equal to zero, thereby satisfying Eq. (6). In addition, only lattice distortions resulting in second-order changes in bond lengths were considered in these calculations,[16] so that the contribution of the $U_2\epsilon_{ij}^2$ term in Eq. (8) would be negligible, justifying the neglect of U_2. The results for the elastic coefficients and the TA (X) mode calculated here and previously are therefore very similar, as expected.

In the surface structure calculations discussed below, the bond lengths at the surface were not constrained to remain fixed. We have therefore tested the adequacy of the harmonic expansion in Eq. (9). For Si the coefficient U_3 of ϵ_{ij}^3 can be obtained from the results of Keating[20] and also from the recent self-consistent pseudopotential calculations of Wendel and Martin.[8] The value of U_3 obtained in this way is found to be about -166 eV. This indicates for $|\epsilon_{ij}| \simeq 0.05$, the cubic term is only about 15% of the quadratic term. In general, the effect of the cubic term is even smaller since both bond-length contractions and expansions occur at the surface and $|\epsilon_{ij}|$ is usually smaller than 0.05. The cubic term results in corrections of 0.02 Å in the relaxations of surface atoms and was not included in the (110) surface calculations.

C. Application to surface structure

For all the surfaces considered in this paper the electronic configuration, after surface relaxation, is such that all bands are either completely filled or empty. Since the total electronic charge distribution at the surface is not greatly different than the bulk, the electron-electron interaction energy at the surface is expected to be similar to that in the bulk. In the surface structure calculations all parameters were assumed to be the same at the surface as in the bulk. In previous calculations[7] this approximation has been shown to lead a surface band structure in agreement with experiment.

The surface state calculations were started on a six-layer slab periodic in two dimensions and extended to a 12-layer slab when subsurface relaxations were also taken into account. To obtain E_{bs} the energies of all occupied states, whether bulk or surface derived, were summed. The calculations show that $|\Delta E_{bs}|$ arising from surface relaxation is insensitive to the number of layers used, increasing by 0.02 eV or less when the number of layers is increased from 8 to 12. A small number of special points in the Brillouin zone were found to give convergent results for ΔE_{bs}, especially for the nonmetallic ionic surfaces. For Si and Ge the surface is metallic in the absence of surface relaxation, and a larger number of points need to be used in determining the Fermi energy and the change in E_{bs} with relaxation. The calculated values of ΔE_{tot} for these two compounds are not as accurate as those for the zinc-blende materials. This does not, however, affect the accuracy of the calculated surface structures. Surface relaxation makes the surface semiconducting, making the calculations similar to those for zinc-blende materials. The relaxed surface coordinates are determined by finding the minimum of E_{tot}, and the exact value of ΔE_{tot} does not affect the results.

III. (110) SURFACE RELAXATION

A. General discussion

The most important feature of (110) surface relaxation is the outward (away from bulk atoms) and inward motions of the two atoms in the two-dimensional unit cell (see Fig. 1). Occupied surface states near the valence-band maximum are

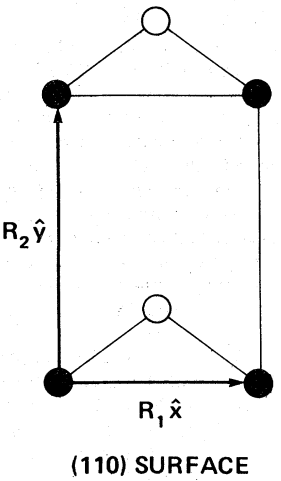

FIG. 1. Two-dimensional unit cell for the (110) surface of zinc-blende structure crystals.

associated primarily with the outwardly relaxed atoms, which for zinc-blende compounds corresponds to the anions. Similarly empty surface states near the conduction-band minimum arise primarily from the inwardly relaxed cations. For the Group IV semiconductors we will refer to the raised and lowered atoms by anions and cations, even though the same species of atoms are involved.

The tilt angle θ of the relaxed anion-cation bonds at the surface gives a partial but useful description of (110) surface relaxation. This angle is zero for the unrelaxed surface since all atoms lie in the same plane. Taking the x and y directions to be as in Fig. 1 and the z direction to be normal to the surface, θ is defined by

$$\theta = |\tan^{-1} z_{12}/y_{12}| , \tag{9}$$

where y_{12} and z_{12} are the differences in the y and z coordinates of nearest-neighbor atoms at the surface. Analyses of LEED spectra[1] indicate that the displacements of the surface atoms are in the y and z directions only. In the unrelaxed configuration, $|y_{12}|$ is equal to $\frac{1}{4}a$, where a is the cubic lattice constant. The effect of relaxation is to increase $|z_{12}|$ and to decrease $|y_{12}|$. The angle θ defined through Eq. (9) is valid even when bond-lengths at the surface are not constant.

For a purely rotational type of relaxation which does not involve any bond length changes, θ completely determines the surface relaxation when only surface (and not subsurface) relaxation is considered. For the general case, however, θ gives only a partial description of surface relaxation. This can be easily seen from Eq. (9); for example, a uniform displacement of surface atoms along y or z leaves θ unchanged. The energy-minimization calculations indicate that θ varies in the narrow range of 25.5°–30° for all the semiconductors studied. The calculated relaxations are not purely "rotational" characterized by constant nearest-neighbor distance. Bond-length changes, even though small, have a large effect on the transverse displacements of the atoms. The variations in bond lengths tend to *reduce* the transverse (i.e., along y) motions of *both* anions and cations at the surface as compared to that expected from a purely rotational relaxation. In Table IV we compare the relaxed coordinates of (110) ZnSe for a rotational relaxation characterized by $\theta = 25.6°$ and that obtained from the energy-minimization procedure which is also characterized by $\theta = 25.6°$ but which, in addition, involves bond-length changes.

It is useful to study the purely rotational relaxations in more detail. Taking GaAs as a prototypical material, these types of relaxations are equivalent to a decrease of the Ga-As-Ga angle in Fig. 2 from $2\theta_0$ to $2\theta_0 - \varphi$ and an increase of the As-Ga-As angle from $2\theta_0$ to $2\theta_0 + \varphi'$, where $2\theta_0$ is the ideal tetrahedral angle of 109.47° (the angles θ_0 and θ are completely unrelated). The constraint of constant bond lengths implies that φ and φ' are not independent of each other. The relation between the two is given by

$$\cos(2\theta_0 - \varphi + \varphi') - \sqrt{3}\cos(\theta_0 - \varphi') = \sqrt{3}\cos(\theta_0 - \varphi) - \tfrac{7}{3} . \tag{10}$$

Therefore, for a given value of φ the angle φ' can be determined numerically from the above equation. In addition, from the new coordinates of the atoms obtained using the values of φ and φ' the tilt angle θ as defined by Eq. (9) can also be determined. In Table V the values of φ' and θ for φ ranging from 10° to 20° are given. The corre-

TABLE IV. Comparison of the surface atomic structure of ZnSe for two relaxations characterized by a bond-rotation angle θ of 25.6°. The structure determined from energy minimization involves bond-length relaxations, whereas in the purely rotational relaxation all bond lengths are kept constant. The displacements shown are in Å.

ZnSe:	θ	Δy_a	Δy_c	Δz_a	Δz_c
Energy minimization	25.6°	0.184	0.374	0.036	−0.55
Rotational relaxation	25.6°	0.316	0.456	0.190	−0.42

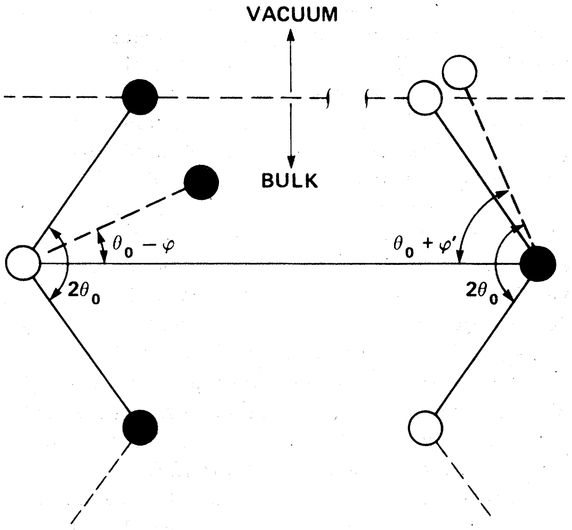

FIG. 2. Side view of a (110) surface showing atomic motions involved in a purely rotational relaxation. Relaxed atomic positions are showed by dashed lines. The angles φ and φ' are not independent and the relation between the two is given in Eq. (10) and in Table V.

sponding displacements from unrelaxed positions of of the surface anions and cations are also shown.

B. Results

The calculated atomic displacements for the first three layers at the surface, ΔE_{tot} (in eV per surface atom) and θ for Si, Ge, GaAs, InP, ZnSe, ZnTe, and InSb are shown in Table VI. The relaxations of the atoms are in the same sense as for purely rotational relaxations. Some noteworthy features of the results are:

(i) (110) surface relaxations are accompanied by large changes in the total energy. In the III-V semiconductors ΔE_{tot} varies from about -0.51 eV per surface atom in GaAs to about -0.30 eV in ZnSe and ZnTe (see Table VI). The large value of ΔE_{tot} in GaAs is consistent with the results of Goddard *et al.*[12] They have considered the (110) surface relaxation through the use of clusters, and find a ΔE_{tot} of approximately -0.65 eV per surface atom. For Si and Ge the corresponding energy lowering is approximately -0.55 eV per surface atom. As noted above, the values of ΔE_{tot} for Si and Ge were not determined as accurately as for the heterpolar materials. The surface atomic coordinates are determined by finding the minimum of E_{tot} and are unaffected by the uncertainties in the value of E_{tot} for the unrelaxed structure. The values of ΔE_{tot} for Si, Ge, GaAs, InP, and ZnSe are fitted almost exactly by the relation

$$\Delta E_{\text{tot}} = -0.55(1 - f_i^2) \text{ eV/surface atom}, \qquad (11)$$

where f_i is the Phillips[21]–Van Vechten[22] ionicity parameter. The values of ΔE_{tot} for InSb and ZnTe are both within 0.1 eV of those obtained from Eq. (11). The large spin-orbit splittings in the latter two compounds, which were taken into account in obtaining the tight-binding parameters, may have affected the results for ΔE_{tot}.

TABLE V. Variation in surface atomic coordination from unrelaxed positions for rotational relaxations in which bond lengths are kept fixed. The tilt angle θ is a measure of the rotation of surface anion-cation bonds and is obtained from Eq. (9). The relaxations can be regarded as resulting from two separate (but not independent) rotational displacements through the angles φ and φ' of the surface cations and anions, respectively (see Fig. 2). The displacements along y are in units of $\frac{1}{4}a$ and those along z are in units of $a/2\sqrt{2}$, where a is the cubic lattice constant. The angles φ, φ', and θ are in degrees.

φ	φ'	θ	Δy_a (Δy_c)	Δz_a (Δz_c)
10.0	7.1	17.9	0.182 (0.230)	0.080 (−0.138)
12.0	7.9	21.3	0.204 (0.272)	0.088 (−0.169)
14.0	8.5	24.7	0.220 (0.312)	0.094 (−0.201)
16.0	9.0	28.0	0.234 (0.351)	0.098 (−0.234)
18.0	9.3	31.4	0.241 (0.388)	0.101 (−0.267)
20.0	9.4	34.8	0.244 (0.423)	0.102 (−0.302)

(ii) The normal (to the surface) displacements of the surface anions are, on the average, a decreasing function of ionicity. This result is consistent with LEED studies[2] of GaAs (110) and ZnO (10$\bar{1}$0) surfaces. In units of the interlayer spacing $a/2\sqrt{2}$, where a is the cubic lattice constant, Δz_c ranges from 0.12 in Si to 0.09 in GaAs to 0.03 in ZnTe and 0.02 in ZnSe. There is relatively much less variation in the normal displacements Δz_c of the surface cations. For Si and group III-V semiconductors, Δz_c, in the same units as above is in the range -0.22 to -0.24. For the II-VI materials ZnSe and ZnTe, Δz_c is about -0.28. The negative values of Δz_c denote a relaxation toward bulk atoms. For purely rotational relaxations different trends for Δz_a and Δz_c would be expected i.e., the results shown in Table V indicate that for bond rotation angles θ ranging from about 18° to 35° the normal displacements of the anions are fairly constant, whereas the displacements of the cations vary by a factor of nearly 2.

(iii) The bond-rotation angle θ at the surface is nearly constant for all the semiconductors studied. This angle is found to vary between 25.6° in ZnSe to about 27.3° in GaAs and 30° in Si. The values of θ and the surface atomic coordinates of GaAs are in good agreement (see Table VII) with the LEED determined structures of Mark *et al.*[23] ($\theta \simeq 26.4°$). The displacements of Ga and As surface atoms

TABLE VI. Surface atomic relaxations from unrelaxed positions as determined from the energy-minimization procedure. The y and z displacements are in units of $\frac{1}{4}a$ and $a/2\sqrt{2}$, where a is the cubic lattice constant; z is normal to the surface, and the x and y directions are shown in Fig. 1. The superscripts a and c refer to anion and cation, respectively. The subscript 1 refers to the surface layer, 2 to the subsurface layer, etc.

	ΔE_{tot}	θ	Δy_1^a (Δy_1^c)	Δz_1^a (Δz_1^c)	Δz_2^a (Δz_2^c)	Δz_3^a (Δz_3^c)
Si	≈−0.55	30°	0.13 (0.24)	0.12 (−0.245)	−0.05 (0.025)	0.02 (−0.02)
Ge	≈−0.55	29.4°	0.13 (0.24)	0.12 (−0.235)	−0.05 (0.025)	0.02 (−0.02)
GaAs	−0.51	27.3°	0.13 (0.245)	0.093 (−0.23)	−0.03 (0.035)	0.01 (−0.02)
InP	−0.40	26.5°	0.15 (0.27)	0.085 (−0.225)	−0.02 (0.035)	0.01 (−0.02)
InSb	−0.39	25.7°	0.13 (0.245)	0.082 (−0.22)	−0.03 (0.035)	0.01 (−0.02)
ZnSe	−0.30	25.6°	0.13 (0.265)	0.018 (−0.275)	−0.025 (0.06)	0.02 (−0.02)
ZnTe	−0.30	27.5°	0.075 (0.225)	0.031 (−0.282)	−0.04 (0.053)	0.01 (−0.02)

relative to one another are also in excellent agreement with the LEED determined results of Tong *et al.*[24] ($\theta = 27°$). The atomic displacements for the 34.8° rotational relaxation model[25] and the reductions in ΔE_{tot} for the various surface relaxations are also shown in Table VII. The electronic structures calculated[7] for the ≈27° relaxed surfaces are in good agreement with photoemission measurements.[26-29] Therefore, at least for GaAs, the results of different probes of the surface structural and electronic properties all seem to be consistent with each other.

(iv) The relaxations obtained from the energy-minimization procedure involve bond-length variations at the surface. The variations are largest for ZnSe (with $\epsilon_{ij} \simeq -7\%$) and ZnTe (with $\epsilon_{ij} \simeq -6\%$). The bonds affected most are the ones between surface anions and subsurface cations. There are only minor changes (≤1.5%) in the surface anion-cation bond lengths. For the III-V semiconductors all bond-length changes are calculated to be less than 3%. The main effect of the bond-length changes is to reduce the transverse motions of the surface anions and cations from the one expected for purely rotational relaxations.

(v) The relaxation of atoms on the surface layer makes the largest (≥90%) contribution to the reduction in E_{tot}. The relaxation of each subsequent layer below the surface reduces E_{tot} by approximately an order of magnitude less than the layer immediately above it. This is not surprising, since the atomic relaxations are largest at the surface and these are damped very quickly as one goes toward bulk atoms.

C. Accuracy of calculations

There are two separate questions that can be asked regarding the accuracy of the surface structure calculations. The first concerns the accuracy of the energy-minimization procedure in predicting the "real" surface geometry. This can only be answered by comparing the calculated surface geometries against those determined from various surface sensitive measurements such as LEED, photoemission, and surface EXAFS. At present the most thoroughly studied III-V surface is that of (110) GaAs. The calculated (110) surface atomic and electronic structures of GaAs for structures characterized by $\theta \approx 27°$ are consistent with LEED[23-25] and photoemission measurements,[26-29] respectively. Future LEED and photoemission work on other semiconductors should allow for more extensive tests of the calculated surface

TABLE VII. Atomic displacements in Å from unrelaxed positions for the (110) surface of GaAs as compared to LEED determined structures. The calculated ΔE_{tot} are in eV per surface atom. In previous work (Refs. 7 and 26) the surface structure of Ref. 23 has been referred to as the "bond-relaxation" model.

	GaAs			
	Present work	Ref. 23	Ref. 24	Ref. 25
θ	27.3°	26.4°	27.1°	34.8°
ΔE_{tot}	−0.51	−0.39	−0.46	−0.42
Δy_1^a (Δy_1^c)	0.19 (0.35)	⋯	0.32 (0.48)	0.34 (0.60)
Δz_1^a (Δz_1^c)	0.19 (−0.46)	0.20 (−0.50)	0.10 (−0.55)	0.20 (−0.60)
Δz_2^a (Δz_2^c)	−0.06 (0.07)	−0.05 (0.05)	⋯	⋯
Δz_3^a (Δz_3^c)	0.02 (−0.04)	0.025 (−0.025)	⋯	⋯

structures.

Assuming that the model used for the total energy is accurate, the *sensitivity* of the energy-minimization procedure in separating different surface geometries differing only slightly in their $E_{\rm tot}$ needs to be analyzed also. One has to ask whether a few hundredths of an eV difference in $E_{\rm tot}$ for two different structures has any significance? To answer this question it is useful to consider first the application of the total energy procedure in determining bulk structural properties. Consider, for example, atomic displacements characteristic of a $\vec{k}=0$ TO phonon mode in GaAs. For a relative displacement of 0.045 Å of the two basis atoms along the (100) direction we find an increase in $E_{\rm tot}$ of 0.011 eV. This value for $\Delta E_{\rm tot}$ can also be inferred from the measured TO(Γ) phonon frequency. In determining bulk atomic positions through an energy-minimization procedure this *increase* of 0.01 eV in $E_{\rm tot}$ with atomic displacements, although small, is significant and can be calculated with sufficient accuracy. For the surface calculations, in order to give a better description of the sensitivity of the energy-minimization procedure in discriminating between different structural models, it is convenient to consider the six different *rotational relaxation* models shown in Table V. We will consider the change in $\Delta E_{\rm tot}$ for GaAs resulting from these relaxations. The first relaxation characterized by $\theta = 17.9°$ gives a $\Delta E_{\rm tot}$ of -0.46 eV (per surface atom), which is 0.05 eV *higher* than the value of -0.51 eV obtained through energy minimization. The calculations show that close to $\theta = 17.9°$, $\Delta F_{\rm tot}$ decreases at the rate of approximately 0.01 eV per surface atom for each 2° change in θ. Since there are two surface atoms in the surface unit cell, $\Delta E_{\rm tot}$ for the two atoms is changing at the rate of $\simeq 0.01$ eV per degree, which is an appreciable rate of decrease for $\Delta E_{\rm tot}$. Using a quadratic interpolation between the calculated values of E for the various values of θ in Table V, we find that the minimum of $E_{\rm tot}$ for the rotationally relaxed surfaces occurs for $\theta \simeq 23.4°$. At this angle the interpolated value of $\Delta E_{\rm tot}$ is nearly -0.48 eV. Near $\theta \simeq 23.4°$, $\Delta E_{\rm tot}$ is quadratic in $\Delta\theta$ and varies very slowly with changes in θ. The energy-minimization procedure is sufficiently sensitive, however, that *rotational-relaxation models* characterized by θ as small as 18° or as large as 35° can be ruled out. It should be emphasized again at this point that the surface structures determined via the energy-minimization approach and shown in Table VI are not rotational in character since bond-lengths are not constrained to remain fixed in these calculations. The atomic displacements are, however, in the same sense as in rotational relaxations.

In the surface structure calculations a large number of surface coordinates were tested in determining the structure with the lowest energy. The variations of $E_{\rm tot}$ were required to be quadratic in the atomic displacements for the final relaxed structures. Atomic displacements by ± 0.02 Å about their equilibrium positions result in small (< 0.01 eV) variations in $E_{\rm tot}$. The small energies associated with typical phonon modes suggest that at finite temperatures the phonon contribution to the total energy should be included in the calculations and the Debye-Waller factors need to be taken into account in measurements of atomic positions. The possibility of using the method to calculate surface phonon modes and the surface Debye temperature are under study at present.

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[1] For a recent review see C. B. Duke, Crit. Rev. Solid State Mater. Sci. 8, 69 (1978), and references therein; C. B. Duke, J. Vac. Sci. Technol. 14, 870 (1977).

[2] C. B. Duke, A. R. Lubinsky, B. W. Lee, and P. Mark, J. Vac. Sci. Technol. 13, 761 (1976).

[3] J. A. Appelbaum and D. R. Hamann, Phys. Rev. B 12, 1410 (1975).

[4] M. Schlüter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B 12, 4200 (1975).

[5] K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. 34, 1450 (1975); K. C. Pandey, J. L. Freeouf, and D. E. Eastman, J. Vac. Sci. Technol. 14, 904 (1977).

[6] E. J. Mele and J. D. Joannopoulos, Surf. Sci. 66, 38 (1977); Phys Rev. B 17, 1816 (1978).

[7] D. J. Chadi, J. Vac. Sci. Technol. 15, 631 (1978); 15, 1244 (1978); Phys. Rev. B 18, 1800 (1978).

[8] H. Wendel and R. M. Martin, Phys. Rev. Lett. 40, 950 (1978); Phys. Rev. B (to be published).

[9] D. W. Bullett, J. Phys. C 8, 2707 (1975); Philos. Mag. 32, 1063 (1975).

[10] J. Ihm and M. L. Cohen, Solid State Commun. (to be published).

[11] W. A. Harrison, Surf. Sci. 55, 1 (1976); D. J. Miller and D. Haneman (unpublished).

[12] A. Redondo, W. A. Goddard, T. C. McGill, and G. T. Surratt, Solid State Commun. 20, 733 (1976); W. A.

Goddard, J. J. Barton, A. Redondo, and T. C. McGill, J. Vac. Sci. Technol. 15, 1274 (1978).

[13] D. J. Chadi, Phys. Rev. Lett. 41, 1062 (1978).

[14] J. A. Appelbaum and D. R. Hamann, Surf. Sci. 74, 21 (1978).

[15] D. J. Chadi and M. L. Cohen, Phys. Status Solidi B 68, 405 (1975).

[16] R. M. Martin and D. J. Chadi, *Proceedings of the Thirteenth International Conference on the Physics of Semiconductors, Rome, 1976*, edited by F. G. Fumi (North-Holland, Amsterdam, 1977); D. J. Chadi and R. M. Martin, Solid State Commun. 19, 643 (1976).

[17] D. J. Chadi, Phys. Rev. B 16, 790 (1977).

[18] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

[19] (a) When the parameters of Ref. 17 were used but spin-orbit interactions were ignored the atomic *p* energies of the anion and cation were increased by $\Delta_0/3$, where Δ_0 is the spin-orbit splitting at Γ. This results in keeping the direct gaps at Γ unchanged. (b) The calculated values of the bulk moduli were incorrectly given in Ref. 13.

[19b] The calculated values of the bulk value were incorrectly given in Ref. 13.

[20] P. N. Keating, Phys. Rev. 149, 674 (1966).

[21] J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970).

[22] J. A. Van Vechten, Phys. Rev. 182, 891 (1969).

[23] P. Mark, A. Kahn, E. So, and C. B. Duke, Bull. Am. Phys. Soc. 23, 400 (1978); A. Kahn, E. So, P. Mark, and C. B. Duke, J. Vac. Sci. Technol. 15, 580 (1978).

[24] S. Y. Tong, A. R. Lubinsky, B. J. Mrstik, and M. A. Van Hove, Phys. Rev. B 17, 3303 (1978).

[25] A. R. Lubinsky, C. B. Duke, B. W. Lee, and P. Mark, Phys. Rev. Lett. 236, 1058 (1976); C. B. Duke, A. R. Lubinsky, B. W. Lee, and P. Mark, J. Vac. Sci. Technol. 13, 761 (1976).

[26] A. Huijser, J. van Laar, and T. L. van Rooy, Phys. Lett. A 65, 337 (1978).

[27] G. P. Williams, R. J. Smith, and G. J. Lapeyre, J. Vac. Sci. Technol. 15, 1249 (1978).

[28] W. E. Spicer *et al.*, J. Vac. Sci. Technol. 13, 780 (1976).

[29] W. Gudat and D. E. Eastman, J. Vac. Sci. Technol. 13, 831 (1976).