

***Ab initio* study of ZnO (10 $\bar{1}$ 0) surface relaxation**

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Periodic Hartree-Fock total-energy calculations on two-dimensional slabs have been used to study the symmetry-conserving relaxation of the nonpolar (10 $\bar{1}$ 0) surface of ZnO. We find that it is energetically favorable for the Zn-O surface dimers to tilt slightly (by 2.3°) and move downwards towards the slab, and for the dimer bond to shorten significantly. Our results agree fairly well with those of a recent density-functional calculation, but disagree with empirical tight-binding theory which predicts surface bonds to shorten only slightly while the surface dimers undergo a large tilt (18°). The available experimental data lies between the *ab initio* and tight-binding results with large error bars. We have tested the effects of several refinements of our Hartree-Fock calculation, including improvements of the orbital basis set and precision tolerances, the use of thicker slabs in approximating the semi-infinite crystal, and post-self-consistent-field density-functional correlation corrections to the total energy. None of these refinements significantly changed our results. We discuss possible reasons for the disagreement between our results and those of tight-binding theory.

The ionic semiconductor ZnO, which normally crystallizes in the wurtzite structure, has a number of technological applications (catalysis, chemical sensors, etc.) in which its surface properties are important. Theoretical modeling is of great value in understanding the properties of such surfaces, especially where complex surface reconstruction, defects, or adsorbates are present, since experimental characterization of such surfaces can be difficult. First-principles theory is especially important since empirical theories contain phenomenological parameters that may be poorly known (or simply inapplicable) for complex surfaces (such as polar surfaces or surfaces with adsorbed species). However, any such theory must first pass the test of predicting realistic structures and properties for simple, well understood surfaces. For wurtzite-structure semiconductors, the clean nonpolar (10 $\bar{1}$ 0) surface is the simplest one to treat, and is the surface considered in this paper. [The unreconstructed polar (0001) and (000 $\bar{1}$) surfaces have higher symmetry but are difficult to treat theoretically since they are charged and may have metallic character; experimentally these surfaces are somewhat unstable and may be subject to very complex reconstruction and imperfect stoichiometry.]

Experimental and theoretical work on semiconductor surface reconstruction has recently been comprehensively reviewed by La Femina.¹ Experimentally, the nonpolar surfaces of many compound semiconductors undergo symmetry-conserving relaxations (as opposed to reconstructions that alter the surface periodicity or point symmetry) that take them from the truncated bulk geometry to one of lower free energy (we restrict ourselves here to the situation at zero temperature, so only the ground-state total energy actually concerns us). In particular the (10 $\bar{1}$ 0) surface of the wurtzite-structure II-VI semiconductors, shown schematically in Fig. 1, is believed to un-

dergo a symmetry-conserving relaxation characterized by four changes: bonds between adjacent anions and cations in the outermost layer shorten, these surface dimers tilt such that the anion is outermost, the dimer centers sink inwards towards the bulk and shift a short distance along the bulk *c* axis, and the second layer of atoms undergoes a very slight distortion that we shall neglect hereafter. This picture has been found to apply qualitatively to ZnO (Ref. 2) and CdSe (Refs. 3 and 4) by low-energy electron,^{2,3} (LEED) or positron⁴ diffraction. Empirical tight-binding (TB) total-energy calculations⁵ on surfaces of this type, which are parametrized to reproduce a few features of the experimental lattice and theoretical electronic structure of the bulk solid, predict that for all the II-VI wurtzite (10 $\bar{1}$ 0) surfaces the tilt angle of the surface dimers is approximately 18° and the bond lengths remain nearly constant. These results are in reasonable agreement with the experimental surface geometry of CdSe

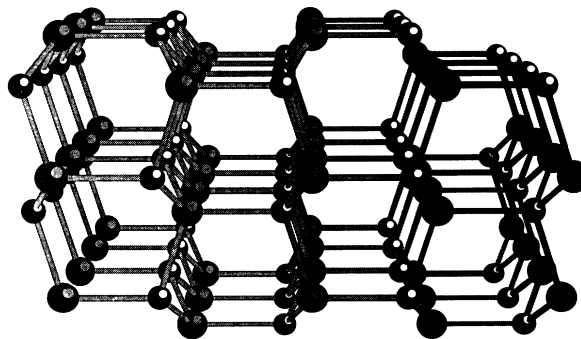


FIG. 1. Perspective view of the unrelaxed six-layer wurtzite slab. The (10 $\bar{1}$ 0) surface is at the top with the "surface dimers" seen from the side. The large spheres represent Zn atoms in the present case, while the small ones represent oxygen.

(Refs. 3 and 4) while LEED (Ref. 2) gives a smaller tilt angle of 11.5° for the dimers on the ZnO surface, though with a large uncertainty (approximately $\pm 5^\circ$). To date there has been only one first-principles theoretical study⁶ of this surface, to which we will compare our present results below.

We have used *ab initio* periodic Hartree-Fock (HF) all-electron total-energy calculations to compute the equilibrium atomic geometry of the $(10\bar{1}0)$ surface of ZnO. The *ab initio* periodic Hartree-Fock linear-combination-of-atomic-orbitals program CRYSTAL (Ref. 7) employs linear combinations of Gaussian orbitals to construct a basis of localized atomic orbitals from which Bloch functions are constructed by a further linear combination. These functions are the basis in which the solid-state band-structure problem is solved. The Gaussian atomic-orbital set is the same one that was carefully optimized in a recent study⁸ of bulk ZnO using CRYSTAL. That basis set has here been taken over without change; as discussed below, reoptimizing the outer exponents on the surface atoms resulted in only very slight changes in the Gaussian exponents and total energy. Computational conditions were slightly less stringent than used in the earlier study⁸ but were adequate for the level of accuracy needed.

Our model of the semi-infinite solid bounded by the $(10\bar{1}0)$ surface is a slab that is periodic in two dimensions and is terminated on both top and bottom by the same physical $(10\bar{1}0)$ surface. This provides a tractable problem while avoiding the unphysical features of molecular or small cluster calculations (extra dangling bonds beyond those belonging to the surface in question, or artificial added hydrogens or other atoms to saturate those extra bonds) or three-dimensional repeated slab calculations (where, especially with plane-wave basis sets, much effort is required to make sure the vacuum gap is large enough to effectively isolate the layers without causing computational problems). However, we still have to make sure that the slab itself is thick enough that the interaction between the two surfaces has negligible effects on the properties of each surface. We, therefore, began our study with total-energy calculations of unreconstructed (truncated bulk) slabs containing two, four, and six atomic layers, respectively. (Each layer contains an equal number of Zn and O atoms.) The bulk geometry was that which minimized the total energy in our earlier study⁸ of bulk ZnO. We then determined the surface energy per surface atom by comparing the energies of the various slabs to the bulk total-energy calculated at the same level of precision. We find that the surface energy per surface atom is 0.82, 0.91, and 0.92 eV for the two-, four-, and six-layer slabs, respectively. We see that this energy appears to be already converging to its infinite-thickness limit at the four-layer thickness, at least within the numerical uncertainty of our calculation which we estimate at 0.02 eV per atom based on convergence tests⁸ on bulk ZnO. The four-layer slab, which we use hereafter, is the thinnest one that has distinct surface and interior atoms; since we are relaxing the positions of only the surface atoms, the interior atoms maintain the bulk periodicity in the directions parallel to the slab.

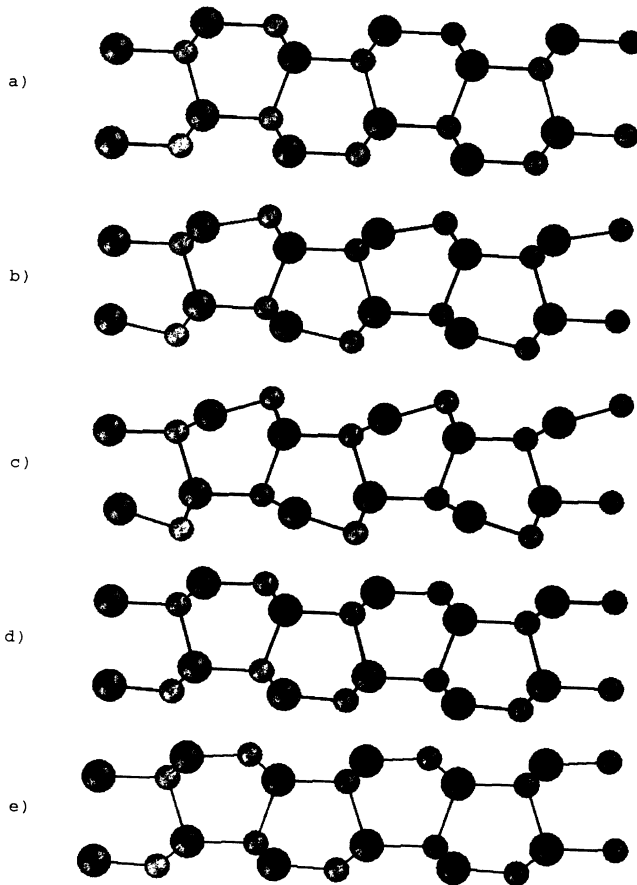


FIG. 2. Side view of four-layer slabs for four surface relaxation models: (a) unreaxed, (b) experimental relaxation (at the midpoint of the range of uncertainty quoted in Ref. 4), (c) tight-binding theory results of Ref. 7, (d) present Hartree-Fock results for a general (not bond-length-conserving) relaxation. The large spheres represent Zn, the small oxygen.

A perspective view of the unreaxed $(10\bar{1}0)$ surface is shown in Fig. 1, and a side view in Fig. 2(a). The translational lattice constants of the slab are the uniaxial c and the basal plane a of the bulk wurtzite structure, with values $c = 5.241$ Å and $a = 3.290$ Å taken from the Hartree-Fock optimized bulk structure⁸ of ZnO.⁹ Relaxation of the surface is expected to conserve the symmetry of the slab, which corresponds to a subgroup of the full symmetry group $P6_3mc$ of the bulk wurtzite structure. For the $(10\bar{1}0)$ surface with $4n$ layers (where n is an integer) this subgroup is the two-sided plane group corresponding to the space group $P2_1ma$ with translations perpendicular to the plane of the slab deleted. [For $4n - 2$ layers the plane group corresponds to $P2_1mn$, while for the slab terminated by the polar (0001) and $(000\bar{1})$ surfaces the plane group corresponds to $P3m1$ for any thickness.¹⁰] It should be noted that in our notation the conventional (0001) or z axis of the bulk structure becomes the x axis in the $(10\bar{1}0)$ slab geometry while the new z axis is taken perpendicular to the slab and the y axes lies in the plane of the slab along the $(1\bar{1}20)$ direction perpendicular to x and z . Figure 2(b) is a side view of the exper-

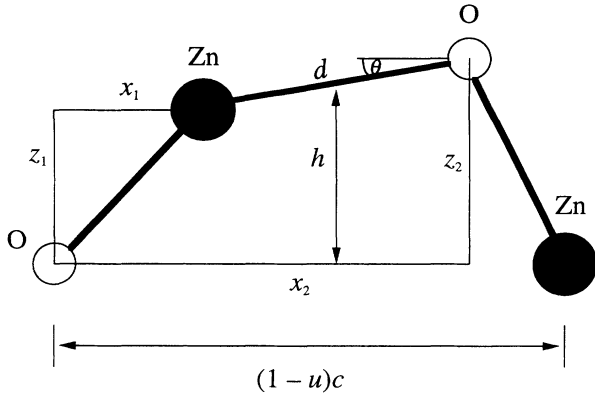


FIG. 3. Details of surface coordinate definitions and related quantities.

imental relaxed surface² while Fig. 3 shows in detail the coordinates we use to describe the surface relaxation, with the relations between these and other commonly used coordinates shown in Table I.

We began our structure optimization in the rigid bond-length model, in which nearest-neighbor distances remain constant, as suggested by the TB studies.⁵ In this approximation there is only one free coordinate for relaxation of the surface layer which we take to be the tilt angle θ , so that only a limited number of energy points needed to be computed. After minimizing the energy with respect to the tilt angle, we found that the surface dimers tilt by an angle of only 2.58° (positive angles signify that the anion, in this case oxygen, is furthest out from the slab). Also, the surface energy per surface atom was reduced by only 0.02 eV. This prediction of a nearly unrelaxed surface in our constant-bond-length calculation suggests that the conservation of tetrahedral bond lengths is too severe a constraint to capture the essentials of the structural relaxation in this system.

Accordingly, we have recalculated the minimum-energy geometry for a general relaxation of the outer layers (top and bottom) of our four-layer slab. This involved self-consistently optimizing four coordinates (x_{Zn} , x_{O} , z_{Zn} , and z_{O}) requiring altogether around 40 self-consistent-field (SCF) calculations. We performed line minimizations on each coordinate in turn, going back to the first and continuing the process until a stable geometry was reached. The final values were $x_{\text{Zn}}=0.707$ Å, $x_{\text{O}}=2.581$ Å, $z_{\text{Zn}}=0.691$ Å, and $z_{\text{O}}=0.766$ Å corresponding to the geometry shown in Fig. 2(d). The tilt angle of the surface ZnO dimer changes very little under this full relaxation; we now find the angle to be 2.31°. However, the surface bonds shorten from a bulk value of 2.021 to a relaxed value of 1.876 Å, and the geometric center of the bond moves towards the center of the slab by 0.221 Å reflecting the shortening of both surface and “backbonds” (the latter term meaning the bonds between surface atoms and the next layer). The bond centers are predicted to shift only a short distance parallel to the slab, in agreement with experiment.⁸ The energy cost of creating the surface is reduced to 0.72 eV per surface atom, which is 0.19 eV per atom less than for the unrelaxed surface.¹¹ Recent tight-binding studies⁵ have given quite different results, with only slight changes in bond lengths and a large surface dimer tilt ($\sim 18^\circ$) and consequently a large shift along the c axis (see Table II). The TB results have been interpreted¹ as a change in the surface cation coordination from tetrahedral sp^3 to approximately planar sp^2 hybridization, accompanied by charge transfer to the surface anion which adopts a distorted p^3 configuration. Our results are in closer accord with a qualitative description in which a double bond forms between the surface anion and cation.

In view of the difference between our results and the TB⁵ predictions, it is important to look for possible sources of error in our calculation. One such source is

TABLE I. Coordinate definitions and related quantities for the wurtzite (10 $\bar{1}$ 0) surface, and their values for an unrelaxed surface in terms of bulk lattice parameters. The first column of definitions are the ones used in the present work and are shown in Fig. 3. The second column of definitions are those used in Ref. 5.

Coordinate definitions			
$x_1 = x_{\text{Zn}}$		$d_{121} = z_1$	
$x_2 = x_{\text{O}}$		$\Delta_{11} = z_2 - z_1$	
$z_1 = z_{\text{Zn}}$		$d_{12y} = x_1 + uc$	
$z_2 = z_{\text{O}}$		$\Delta_{1y} = c - (x_2 - x_1)$	
Related quantities			
surface bond length $d = [(x_2 - x_1)^2 + (z_2 - z_1)^2]^{1/2} = [\Delta_{11}^2 + (c - \Delta_{1y})^2]^{1/2}$			
dimer rotation angle $\theta = \arctan \left[\frac{z_2 - z_1}{x_2 - x_1} \right] = \arctan \left[\frac{\Delta_{11}}{c - \Delta_{1y}} \right]$			
dimer midpoint height $h = \frac{z_1 + z_2}{2} = d_{121} + \frac{\Delta_{11}}{2}$			
dimer midpoint lateral position $x = \frac{x_1 + x_2}{2}$			
Unrelaxed values			
$x_1 = c(\frac{1}{2} - u)$		$d_{121} = a/(2\sqrt{3})$	$d = uc$
$x_2 = c/2$		$\Delta_{11} = 0$	$\theta = 0$
$z_1 = a/(2\sqrt{3})$		$d_{12y} = c/2$	$h = a/(2\sqrt{3})$
$z_2 = a/(2\sqrt{3})$		$\Delta_{1y} = (1 - u)c$	$x = (1 - u)c/2$

TABLE II. Values of top layer surface coordinates and related quantities for various experimental and theoretical cases. The rows labeled "Bulk" are for the unrelaxed surface, while the others are for various models of the surface relaxation as described in the text. The abbreviations "Expt", "Corr," and "CB" refer to experiment, post-SCF correlation calculations, and constant bond lengths, respectively. The columns for Δd and Δh refer to deviations from the unrelaxed values appropriate to each model.

	x_1 (Å)	x_2 (Å)	z_1 (Å)	z_2 (Å)	$d(\text{Zn-O})$ (Å)	Δd (%)	θ	Δh (Å)	Δx (Å)
Bulk expt ^a	0.613	2.605	0.938	0.938	1.992	0.0	0.0°	0.0	0.0
Bulk HF ^b	0.600	2.621	0.950	0.950	2.021	0.0	0.0°	0.0	0.0
Bulk HF+corr ^c	0.584	2.551	0.924	0.924	1.967	0.0	0.0°	0.0	0.0
Surf. expt ^d	0.62	2.59	0.54	0.94	2.010	+0.9	11.5°±5°	-0.123	-0.004
TB ^e	0.98	2.82	0.53	1.10	1.926	-3.3	17.2°	-0.198	0.291
HF(CB) ^c	0.672	2.691	0.900	0.990	2.021	0.0	2.58°	-0.005	0.071
HF ^c	0.707	2.581	0.691	0.766	1.876	-7.2	2.31°	-0.221	0.034
HF+corr ^c	0.683	2.521	0.678	0.758	1.839	-6.5	2.48°	-0.206	0.035
LDA ^f	0.534	2.365	0.623	0.738	1.835	-7.9	3.59°	-0.258	-0.160

^aReference 8.

^bReference 7.

^cPresent work.

^dReference 2.

^eReference 5.

^fReference 6.

our use of an orbital basis set that was optimized for the bulk solid only. To examine this point, we have reoptimized the outermost Gaussian exponents on the surface atoms in our four-layer slab, leaving the basis on the interior atoms unchanged and holding the geometry fixed at the minimum-energy configuration found earlier. We find that the exponents change very little: from 0.24 to 0.23 a.u.⁻² for the outer shell on the O atom and from 0.15 to 0.14 a.u.⁻² on the outermost shell of the Zn atom. These changes are much too small to cause a significant change in the equilibrium geometry, though they are in the expected direction; the surface atoms become slightly more diffuse, since they do not have another layer of atoms above them to "compress" them. We have also found that the addition of a polarization function of d symmetry to our O orbital basis caused only very small changes in the surface geometry.

The only remaining major approximation in our calculation is the use of standard Hartree-Fock theory itself, i.e., the neglect of electron correlation. To address the question of the effect of correlation on the equilibrium geometry of the 10 $\bar{1}$ 0 surface of ZnO we undertook to recalculate the geometry using post-SCF density-functional correlation corrections to the total energy.¹² We employed a correlation-only functional (since exchange was already included at the HF level) derived from the generalized gradient approximation.¹³ First, we recalculated the equilibrium structure of bulk wurtzite ZnO with correlation included in the total energy, since it is important that the lattice constants in the plane of the slab and the geometry of the inner layers should correspond to the equilibrium structure at the same level of theory that we use to treat the surface relaxation (otherwise the surface may try to distort in unphysical ways to compensate for having the wrong periodicity, etc.). We obtained $a=3.203$ Å, $c=5.102$ Å (the internal coordinate u was assumed not to change from its HF value of 0.386). Then we proceeded to reoptimize the surface geometry, start-

ing from a suitably scaled version of the previous HF energy minimum. A stable equilibrium geometry was found after about 20 SCF *a posteriori* correlation corrected calculations in which the surface dimers were tilted by 2.48° and the surface bonds were 1.839 Å in length versus 1.967 Å in the unrelaxed case. At our calculation level of accuracy, these results for the surface relaxation are essentially identical to those of the uncorrected HF theory.

After completing the calculations described above we learned of the calculation⁶ of Schröer, Krüger, and Pollmann to which we now compare our results. That calculation employed the local-density approximation (LDA) of density-functional theory with norm-conserving pseudopotentials. As in our work a Gaussian basis set was used, and the Zn 3*d* states were included as valence-band states. The results⁶ are in very good overall agreement with ours. The surface dimer tilt angle works out to 3.59°, somewhat larger than our value but still much smaller than the TB result,⁵ and there is again a large surface and backbond contraction (see Δd and Δh in Table II). The only significant disagreement with our results is the prediction of a fairly large shift (0.160 Å) of the surface dimer center along the c axis towards the nearest second-layer oxygen atom. This shift, however, is still much smaller than that predicted by TB theory,⁵ and is in the opposite direction.

Since our disagreement with the surface relaxation predicted by recent TB theory⁵ is stable against refinements in our calculation and is supported by the results of Ref. 6, we believe a reassessment of TB theory applicability to ZnO may be needed. We begin by noting that the TB method is entirely phenomenological and in the case of ZnO (Ref. 5) has been parametrized using data on the bulk wurtzite phase only. There is no guarantee that this data will accurately characterize states of atomic coordination differing greatly from bulk wurtzite, including surface atoms and high pressure phases. Indeed the TB

model of Ref. 5 fails to predict¹⁴ the phase transition from wurtzite to rocksalt which occurs in ZnO at approximately 9 GPa according to experiment,¹⁵ while *ab initio* HF theory predicts the transition pressure very accurately.⁸ Moreover, some predictions of TB theory depend strongly on rather arbitrary assumptions about the distance dependence of the interaction matrix elements and the choice of which interactions to include or exclude from the model. For example, when next-nearest-neighbor matrix elements are included but the Zn 4*p* states are not, TB theory gives predictions for the effect of ZnO surface relaxation on the surface electronic states¹⁶ that disagree with those in Ref. 5, while other authors¹⁷ find it important to include Zn 3*d* states in their model. Finally, electronic TB fitting parameters like the valence-band width and optical band gap are useful when an empirical surface band structure is desired, but may not be relevant in total-energy calculations since excitation energies of real solids are not simply eigenvalue differences but contain complex many-body effects (orbital relaxation, self-energy, etc.) For all these reasons we are inclined to have more confidence in the *ab initio* results for ZnO, despite the success of TB theory for more covalent solids.

At this point it is natural to examine the experimental results in detail. The structure determination of Ref. 2 appears to be the best to date but still suffers from large uncertainties. In addition to whatever uncertainties of a purely experimental nature may be present in the LEED spectra, their interpretation in terms of atomic positions depends on a model theory involving many approximations. The scattering potential felt by incident electrons is assumed to be constant in interstitial regions and to be spherically symmetric inside spheres surrounding the nuclei, and the form of the model potential inside the spheres is taken from atomic calculations rather than self-consistent bulk solid-state (much less surface) calculations. Even ignoring all these concerns the estimated uncertainty in the vertical displacements² was large ($z_{\text{O}} - z_{\text{Zn}} = 0.4 \pm 0.2$ Å). The experimental geometry is slightly closer to the TB geometry than to our *ab initio* results, but in view of the large experimental uncertainties, it is not possible to choose one theory over the other on the basis of experiments done on ZnO to date.

On the other hand, there is solid evidence for large sur-

face dimer rotations at the (110) nonpolar surface of zinc-blende semiconductors such as GaAs (Ref. 18) and ZnTe (Ref. 19) as well as the (10 $\bar{1}$ 0) surface of wurtzite CdSe,^{3,4} in reasonable agreement with TB calculations.¹ We believe, however, that this evidence²⁰ does not invalidate the results of our calculations on ZnO. There are many instances in which semiconductors with first-row anions have different properties than isoelectronic compounds with heavier anions; in particular, they often adopt different crystal structures, for example the wurtzite structure in nitrides versus zinc blende in other III-V compounds, or the rocksalt structure in CdO. Different behavior in surface relaxation is, therefore, also plausible. Such behavior would result from greater ionicity and cation-anion size mismatch with first-row anions, and differences in electronic structure due to the lack of *p* orbitals in the anion cores. For other, more covalent semiconductors, we would expect TB and *ab initio* results to be in better agreement. Clearly, it would be helpful to perform HF calculations on surfaces such as ZnS and GaAs(110), and to obtain more accurate experimental measurements of the (10 $\bar{1}$ 0) surface structure of ZnO.

In conclusion, *ab initio* periodic HF theory predicts a relaxation of the (10 $\bar{1}$ 0) surface of wurtzite ZnO which is characterized mainly by a shortening of surface bonds, in contrast to the large bond-length-conserving surface dimer tilt predicted by tight-binding theory.⁵ The HF result is stable against various refinements of the calculation and is supported by recent density-functional work.⁶ Experimental data² does not clearly favor either model at this time. New experimental work on this surface is called for, and perhaps also the application of other theoretical approaches. Periodic HF treatments of thicker slabs (to allow multilayer relaxation) and of other, experimentally better characterized semiconductor surfaces would also be helpful.

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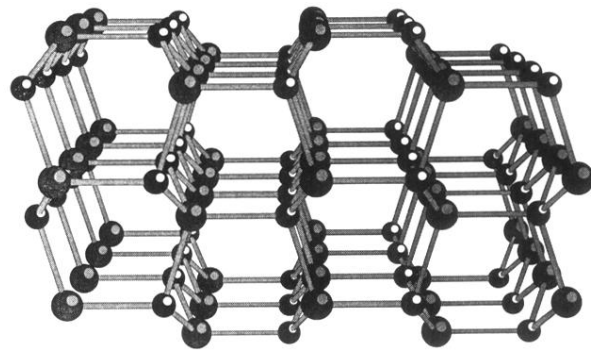


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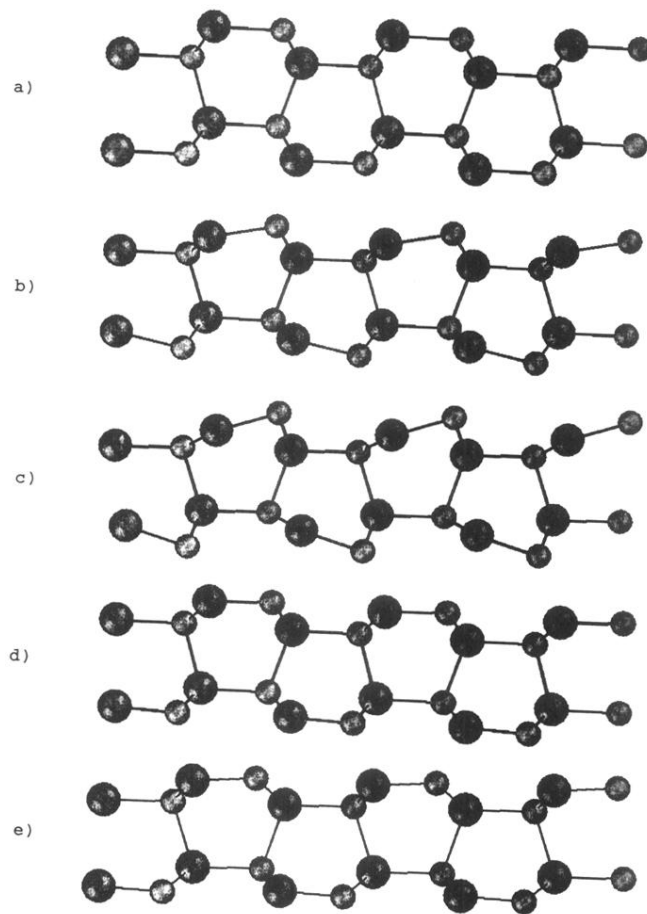


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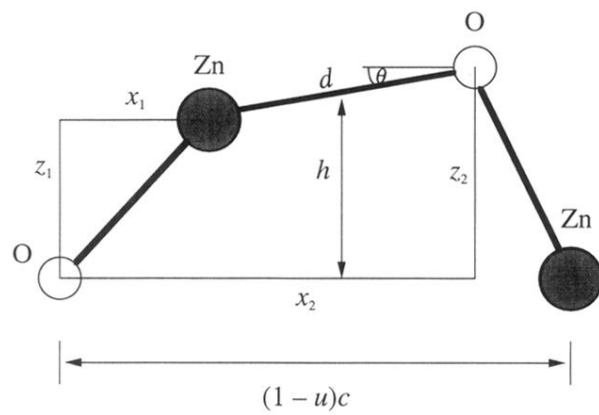


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