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Energy Minimization Calculations for Diamond (111) Surface Reconstructions

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Energy Minimization Calculations for Diamond (111) Surface Reconstructions

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1. Introduction

A remarkable variety of surface reconstructions occur on the (111) surfaces of the tetrahedral elements C, Si and Ge [1]. A possible common denominator may be the occurrence of a similar 2×1 reconstruction on all three elemental surfaces. While clear 2×1 LEED patterns are observed for Si and Ge (111) surfaces, LEED cannot distinguish between a true 2×2 or disordered domains of 2×1 for the diamond (111) surface [2]. However, the similarity of the angle-resolved photoemission (ARUPS) results for C [3], Si [4], and Ge [5] suggests that a common 2×1 structure may be responsible. The 2×1 structure disappears upon annealing for Si and Ge but appears upon annealing for C, indicating that it may be thermodynamically stable only for C. Thus the study of the diamond 2×2/2×1 surface is of particular interest.

The π-bonded chain model proposed by Pandey [6] has attracted much attention as a possible candidate for the 2×1 structure. Energy-minimization calculations identify the Pandey chain structure as the lowest in energy of those tested for Si [7] and Ge [8], and the calculated dispersion of the occupied surface bands is in good agreement with the ARUPS data [4-5]. Ion backscattering [9] and optical [10] measurements appear to support this identification. However, contrary indications from LEED [11] and, most recently, photoemission [12] experiments have insured a continued controversy over this assignment.

Less experimental work has been done on the diamond 2×2/2×1 surface [3,13-15]. A comparison of ARUPS results [3] with the calculated surface state dispersion provides indirect evidence for the Pandey π-bonded chain model [6,16], possibly with some dimerization along the chain [6]. However, discrepancies in the location and dispersion of the surface state persist, and the model remains controversial. The Haneman buckled model [17], the Seiwatz single chain model [18], and the Chadi π-bonded molecule model [19] are possible alternatives. No energy minimization calculations have previously been done for diamond.

Here, we report direct energy minimization calculations for these models. A first principles linear combination of atomic orbitals approach has been used to calculate total energies in the pseudopotential [20] and local density (LDA) [21] approximations. The method is a generalization of the approach of Chelikowsky and Louie [22] to cases for which interatomic charge transfer must be treated self-consistently [23]. The calculations have been carried out using a slab geometry with 12 (10) atomic layers for 1×1 (2×1) cases respectively.

2. Results

The energies of the various models are compared in Table I. We begin with the Haneman buckling model [17]. Buckling of the ideal 1×1 surface is found to raise the energy. A similar result has been found for Si and Ge [7,8]; if anything, such a buckling distortion should be even less likely in diamond because of the Coulomb repulsion associated with charge transfer into the highly localized carbon dangling bond.

We find the ideal Pandey model [6], defined as having all bulk bond lengths (except for graphite-length bonds along the surface chains), to have an energy slightly lower than that of the ideal 1×1 surface. As we shall see, it is also lower than that of any of the other unrelaxed models.

The Chadi π-bonded molecule model [19] was tested and found to be higher in energy than the unrelaxed Pandey chain model, even though the the tested geometry included relaxations as determined by Chadi using a tight-binding energy-minimization approach. Furthermore, the calculated surface state dispersion [16] is in very poor agreement with the ARUPS data [3]. Thus, we feel the model can be ruled out, and we have not tried to relax it further.

Finally, the unrelaxed. Seiwatz chain model is found to have a total energy 1.30 eV above the ideal 1×1. We also tested a "relaxed" geometry provided by Chadi [24], again based upon tight-binding energy-minimization; the energy was only reduced to 0.97 eV. Moreover, the position of the calculated surface bands [16] is in error by more than 2 eV. The model therefore appears untenable.

Thus the Pandey chain model is the only promising 2×1 model of those we considered. We have calculated the relaxations in some detail for this model. This was done by adjusting, one by one, the four surface-most bond lengths d_1 to d_4 in Fig. 1, minimizing the energy for each one while the others were held constant. The procedure was repeated a second time to allow each bond to relax in a more fully relaxed environment. Next, we minimized with respect to buckling of the surface chain ($\phi \neq 0$ in Fig 1). Finally, the geometry was relaxed further using a Keating force-constant model [25] to direct the relaxation of the subsurface atoms in the middle of the slab, and the LDA total energy was calculated again. The final total energy for this fully relaxed geometry was found to be -0.68 eV/surface-atom. By comparison, energy minimization for the 1×1 case was also carried out, and led to a relaxed geometry with an energy of -0.37 eV/surface-atom. Thus, the π-bonded chain model appears to be a very promising candidate for the stable surface.

The relaxed chain geometry is shown in Fig. 1 and Table II, where the corresponding results for Si and Ge [7,8] are shown for comparison. Several interesting trends emerge. The relaxations of the surface chain bonds and others in the surface layer are similar for the three elements. Surprisingly, the subsurface interlayer bond d_4 was found to lengthen by a large amount, ~8%, in diamond. This can be understood as being due to the highly directional nature of the bonding in C; the bond angle strains in the subsurface layer weaken this bond, thereby lengthening it. The tilting of the chain clearly increases from C to Si to Ge. The greater stiffness of bond angle restoring forces in C may be responsible. Finally, the total energy compared to the unrelaxed 1×1 is lowest for C, although it should be remembered that the scale of bonding energies is larger for C.

Dimerization of the relaxed chain geometry was tested. The k-point sample was carefully chosen to resolve any Peierls band splitting at the JK zone boundary. Table I shows that the energy rises monotonically with the dimerization parameter. We have also tried smaller and larger dimerizations than those shown in Table I, including a model proposed by Chadi [24] in which a radically large dimerization occurs. In all cases the dimerization energy was found to be positive. We conclude that dimerization does not occur.

In Fig. 2 we show the calculated surface band structure in the gap region for the relaxed chain model. The dispersion of the occupied surface band along ΓJ has been greatly reduced from that of Pandey [6], who found a difference of $\gtrsim 3$ eV between $E(\Gamma)$ and $E(\mathrm{J})$. This was already reduced to ~2.3 eV in our previous calculation on the ideal structure [16], and has now been reduced further to ~1.7 eV due to relaxations. The dispersion is thus in good agreement with experiment without the need for dimerization. The calculated band is too high by a rigid shift of ~1 eV, but this is also true (by ~0.3 eV and ~ 0.8 eV respectively) for Si and Ge [7,8].

Finally, Fig. 3 shows the charge density for the chain geometry. It is evident from the total charge density in Fig. 3(a) that the bond charge is somewhat reduced along the weakened bond d_4. The charge density in the occupied surface band is shown in Fig. 3(b), clearly indicating the highly-localized dangling-bond nature of this state. The dangling bonds can be seen to be nearly verical, so that the π-interactions are expected to be strong.

3. Discussion

The driving force for the reconstruction is the presence of an energetically unfavorable dangling bond containing an unpaired electron on each surface atom. The reconstruction models attempt to pair electrons via charge transfer or π-bonding, but must pay a price in Coulomb repulsion or elastic strain. Our total energy calculations indicate that the costs outweigh the gains in all cases except the π-bonded chain model.

Both the π-bonding and elastic energies are evidently larger for the π-bonded model for C, compared with those for Si and Ge. π-bonding is more common in carbon chemistry, which would suggest stronger π-bonding in C. The elastic energies are also expected to be larger, because the principal strains are due to bond bending, and the bond-angle force constants are relatively larger in C [25]. Energy minimization calculations for Si indicate [7] that the ideal Pandey chain model is already at -0.22 eV with respect to the ideal 1×1, while relaxations only lower this to -0.36 eV; for C the corresponding numbers are -0.05 eV and -0.68 eV respectively. Thus consideration of relaxations is even more important for C than for Si or Ge.

The idea that the π-bonded chain might dimerize [6] was natural, given the need to reduce the dispersion of the occupied surface band and open a gap, and the analogy to polyacetylene. As we showed in the previous section, however, the dispersion has been corrected without the need for dimerization. Moreover, the analogy with $(\mathrm{CH})_x$ is only approximate; the elastic restoring forces must be stronger here because of the subsurface bonding, and the π-interactions are weaker here because the dangling bonds are not entirely parallel.

Our surface band structure of Fig. 2 is nominally metallic, whereas experiments do indicate an insulating surface with a gap [14]. In the absence of dimerization, antiferromagnetic ordering could open a gap along the JK zone boundary and lower the occupied surface bands [26,27]. This would tend to improve the agreement with the ARUPS data, and we think it likely that some such antiferromagnetic ordering occurs.

The discrepancy in the location of the occupied surface band, which is calculated to be ~1 eV higher than indicated by the ARUPS data [3], may partly be due to antiferromagnetic ordering. It may also partly be explained by the experimental difficulty in locating the Fermi level precisely [3]. Finally, it should be remembered that the LDA eigenvalues have no physical meaning as electron removal energies; the measured removal energy contains an electron-hole correlation which is not correctly included in LDA. Qualitatively, a correction for this effect would lower the theoretical occupied surface band, improving the agreement with experiment.

4. Summary

We have calculated the total energy of several proposed 2x1 reconstruction models for the C(111) surface. The *undimerized* Pandey π-bonded chain model is found to have the lowest energy, ~ 0.3 eV lower than that of a relaxed 1x1 structure. The dispersion of the calculated surface band is found to be in good agreement with experiment, without the need for dimerization. The other models appear implausible on the basis of total energy and surface state dispersion. Unfortunately, the relative paucity of experimental information on the diamond (111) 2x2/2x1 surface makes our identification tentative at present; we hope to stimulate further experimental work in this area.

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Table I. Calculated total energies of diamond (111) 1×1 and 2×1 surface reconstruction models.

Surface model	Energy (eV/surface-atom)
Ideal 1×1	0.00
Buckled[a] ($\Delta z = \pm 0.26$Å)	0.35
Chadi π-bonded molecule[b]	0.28
Seiwatz single chain[c]	1.30
Ideal Pandey π-bonded chain[d]	-0.05
Relaxed 1×1	-0.37
Relaxed Pandey π-bonded chain	-0.68
ΔE_{tot}, ±2% dimerization	+0.01
ΔE_{tot}, ±4% dimerization	+0.04
ΔE_{tot}, ±6% dimerization	+0.09

[a] Ref. [17].
[b] Ref. [19].
[c] Ref. [18].
[d] Ref. [6].

Table II. Relaxed geometries of π-bonded chain model for several elements. See Fig. 1 for definition of parameters.

	C	Si[a]	Ge[b]
Δd_1	-4%	-5%	-5%
Δd_2	1%	-1%	-1%
Δd_2	1%	-3%	-3%
Δd_3	1%	0%	0%
Δd_4	8%	2%	0%
ϕ	3°	9°	13°
E_{tot} (eV)	-0.68	-0.36	-0.34

[a] Ref. [7].

[b] Ref. [8].

Figure 1. Side view of Pandey π-bonded chain model, with definition of parameters used to describe relaxed geometry in Table II.

Figure 2. Calculated surface bands (solid lines) and resonances (dashed lines) for fully relaxed Pandey chain model. The bulk projected band structure (shaded) and the experimental ARUPS data of Ref. [3] (black dots) are shown for comparison.

Figure 3. Charge density contour plots in a plane perpendicular to the chain. Atom positions are indicated by filled circles; only half are in the plane of the plot. (a) Total charge density. (b) Charge density of the occupied surface band in the gap.

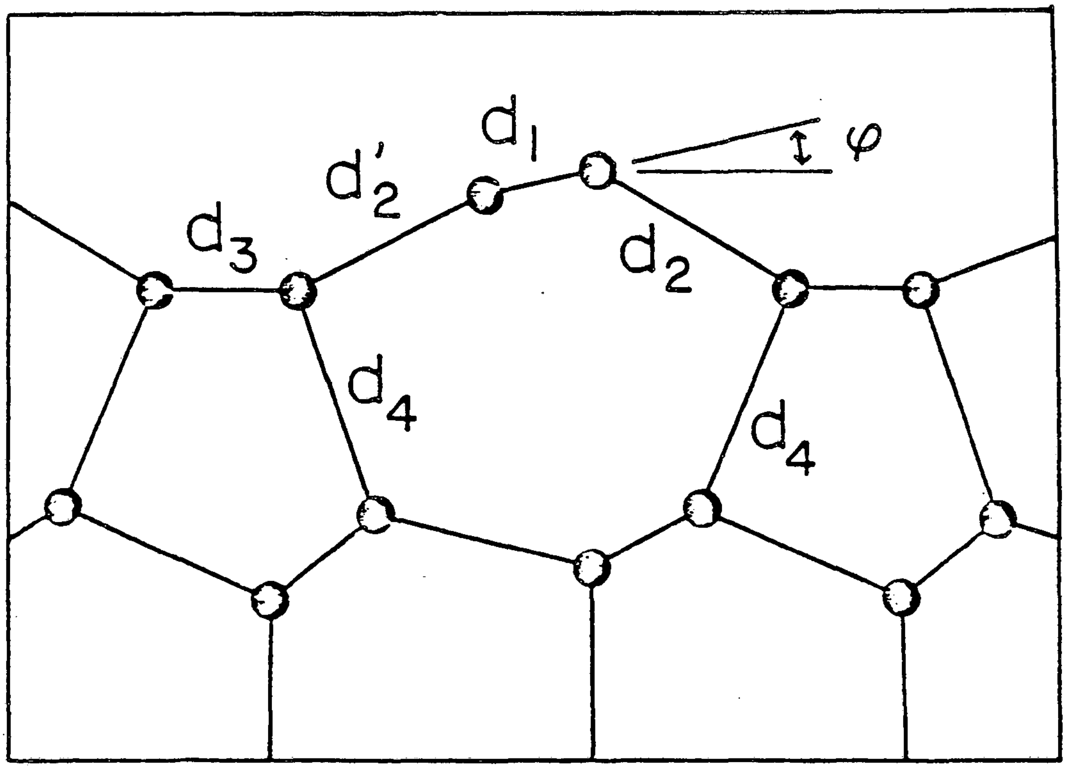
d_1
d_2'
φ
d_3
d_2
d_4
d_4

Fig. 1

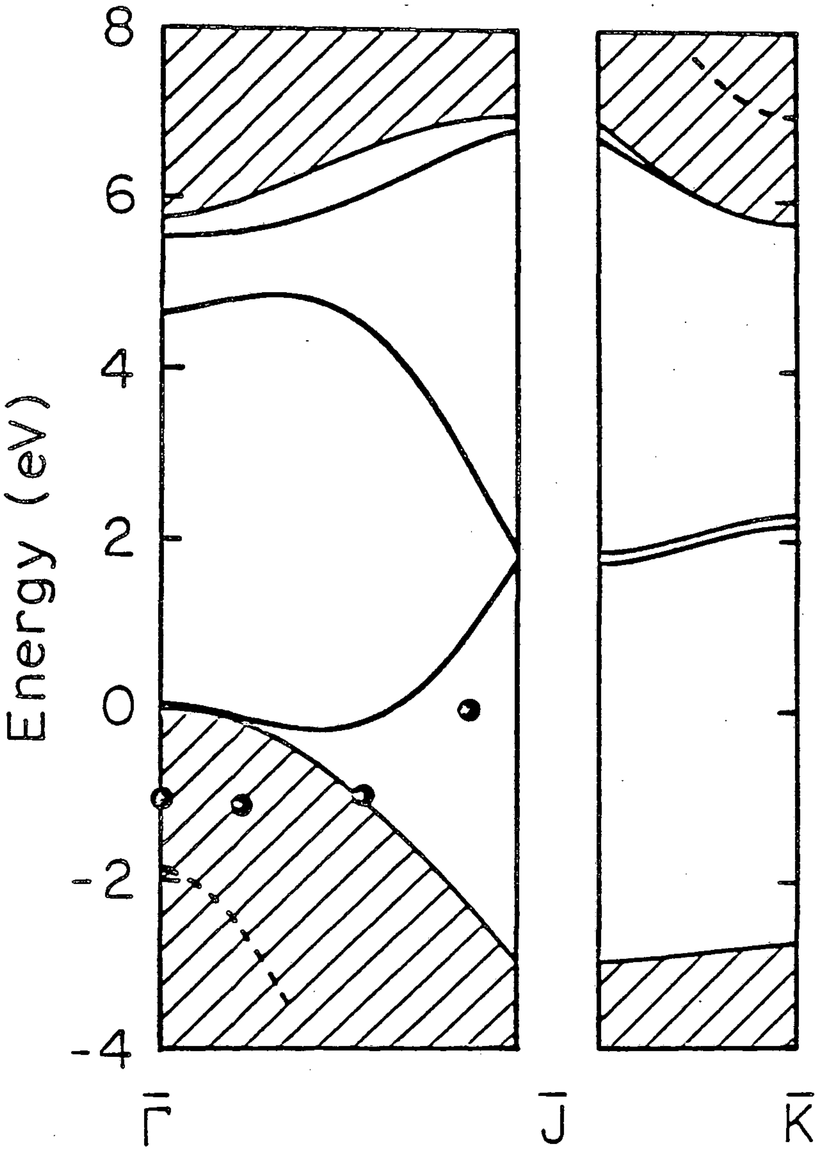

Fig. 2

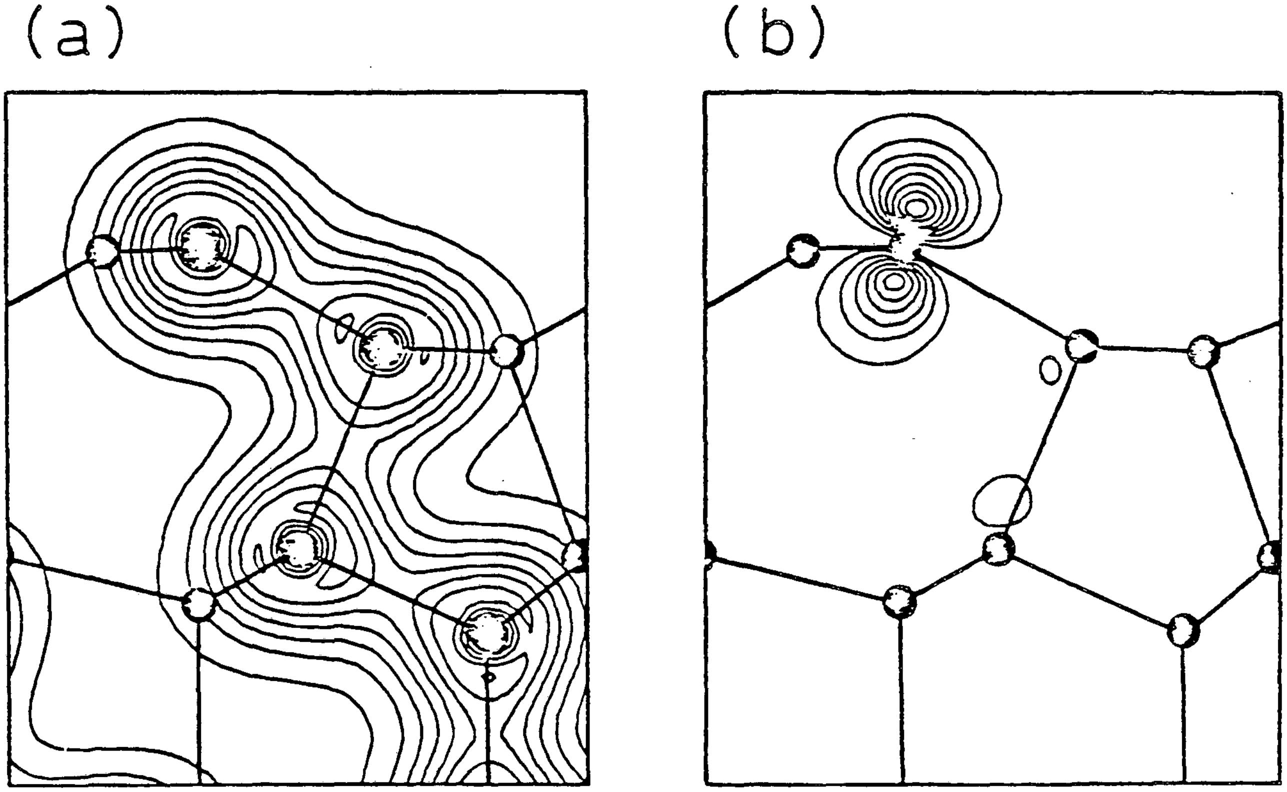

Fig. 3

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