SAND2000-0731J

For Physical Review Letters, 3/13/00

Formation and diffusion of S-decorated clusters on Cu(111)

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Because of their strong internal bonding, S-decorated Cu trimers are a likely agent of S-enhanced Cu transport between islands on Cu(111). According to ab-initio calculations, excellent healing of dangling Cu valence results in an ad-Cu_3S_3 *formation energy of only ~0.28 eV, compared to 0.79 eV for a self-adsorbed Cu atom, and a diffusion barrier* ≤ 0.35 *eV.*

The power of low concentrations of foreign atoms to affect growth morphology has persuaded surface scientists to devote a decade's work to "surfactant-directed" self-assembly of ultra-thin films.[1] But effects of impurities *not deposited purposely* may be as important as surfactants', and also merit serious study.

Time-resolved scanning-tunneling microscopy (STM) reveals, e.g., that Cu mounds on thick Cu(111) films decay two to three orders of magnitude faster when S, a common impurity, is adsorbed.[2] To understand how the S acts, I ask what Cu_nS_m clusters form more readily on Cu(111) than a Cu adatom, and diffuse easily. A systematic *ab-initio* search reveals that the smallest such cluster is ad-Cu_3S_3 (see Fig. 1). Its formation energy is ~0.5 eV lower than a Cu adatom's, and, corresponding to tight internal bonding, its diffusion barrier is ≤ 0.35 eV.

This result shows that S can be a "skyhook," weakening the bonds of Cu adatoms to the rest of the substrate and promoting their transport. An effect of this kind has been proposed for H on metals (M), through formation of HM dimers,[3] but how *divalent* S might act as a "skyhook" has not been known till now.

Because close-packing means better coordinated first-layer atoms, self-adsorption costs more energy on closer-packed surfaces. Cu/Cu(111) obeys this rule. The present Density Functional Theory[4] (DFT) calculations, based on the Generalized Gradient Approximation[5] (GGA), say that 0.79 eV is needed to form a Cu adatom on Cu(111). The same logic that predicts this large E_{form}(ad-Cu) suggests that the self-diffusion barrier on Cu(111), E_{diff}(ad-Cu), should be small. The present finding, E_{diff}(ad-Cu) ≈ 57 meV, again agrees.

These results constrain ideas of how S promotes Cu-transport at 300K. E.g, since little can be gained by lowering a barrier close to $2k_BT$ (=51.7 meV), *S must act by increasing the concentration of diffusing adspecies*. However, S does not act by reducing the *barrier* to dissociating Cu atoms from island edges onto terraces. On geometric grounds, this barrier must be close to E_{form}(ad-Cu) + E_{diff}(ad-Cu) = 0.85 eV (expt.[6] = 0.78 ± 0.04 eV), i.e., again only ~57 meV larger than the minimum needed to produce an ad-Cu on a terrace.

S impurities must therefore promote island-decay by forming tightly bound, and correspondingly plentiful Cu_nS_m ad-species that diffuse easily.[7] This, however, raises a general issue: *What complex with a divalent impurity can significantly enhance metal adatom transport?* For S/Cu(111), I show that *ad-Cu_3S_3* is a good candidate.

Results reported here were obtained with the VASP[8-10] total-energy code, its ultrasoft pseudopotentials (USP's),[11] and the Perdew-Wang '91 GGA.[5] I compute adsorption energies using 6- to 8-layer slabs to represent Cu(111), fixing the lower three slab-layer atoms at bulk relative positions and relaxing the rest till forces are <0.03 eV/Å. I set the slab lattice parameter to the bulk GGA value for a 60-point sample of the irreducible 1/48th of the Brillouin Zone (BZ), namely 3.64 Å (exp't. = 3.61 Å). To accelerate electronic relaxation, I use Methfessel and Paxton's Fermi-level smearing method (width = 0.3 eV).[12]

USP's produce converged total energies with modest basis size. E.g., a 17.2 Ry plane-wave cutoff produces total energies accurate to a few tens of meV, adequate for preliminary cluster-formation energies. For a refined value of $E_{form}(Cu_3S_3)$, needed because this energy affects the ad-Cu concentration exponentially, I increase the cutoff 25% to 21.5 Ry. I also increase the width of the vacuum region from 3 to 5 times the bulk (111)-layer spacing, allowing cancellation of the unphysical dipole fields introduced because only upper slab surfaces are relaxed.[13]

The formation energy of an adsorbed Cu-S complex equals E_{form} for the cluster without its S's, minus the maximum energy adsorbed S's can gain in attaching to it. Thus the energy of the weakest bound ad-S's is needed. I estimate it as the binding energy, E_B(ad-S) ≈ 5.42 eV, of a S adatom isolated in a large supercell.

To obtain E_{form} for the pure ad-cluster, I consider Cu(111) slabs, L layers thick, with N atoms per supercell in each layer. Imagine removing a layer from *n* such slabs and distributing their Cu atoms as clusters of *n* ad-Cu's, one to a supercell, on N slabs, each L-1 layers thick. The original slabs thus lose one "bulk" layer each, for sufficiently large L, and each of the N, (L-1)-layer slabs gains an *n*-cluster per cell. For large L and N, this costs $N \times E_{form}(n\text{-cluster})$. Thus,

$$E_{form}(n\text{-cluster}) = E_{ad}(N,L-1) - E_{cln}(N,L-1) - n\,[E_{slab}(N,L) - E_{slab}(N,L-1)]/N\,, \quad (1)$$

where $E_{ad}(N,L-1)$ and $E_{cln}(N,L-1)$ are the energies/supercell of an L-1 layer slab with one ad-Cu on it, per supercell, or clean. In Eq. 1, the last term is the energy needed to remove "bulk" Cu-atoms, while $E_{ad}(N,L-1) - E_{cln}(N,L-1)$ is what they gain by adsorbing as *n*-clusters on slabs. With all contributions to Eq. 1 computed using the same supercell and BZ sample, error cancellation should be good.[14]

Cu adatoms - Values of E_{form}(ad-Cu) and E_{diff}(ad-Cu) (see Table I) are derived from total energies of 12 atom/layer, $3 \times 2\sqrt{3}$ supercells -- large enough that inter-adatom interactions should be small. Based on convergence studies of Cu step- and kink-formation,[15] I sample the surface BZ with a 6×6 grid of k-vectors, equally spaced in the x- and in the y-directions.

To place bounds on quantum size effects (QSE), I evaluate E_{form}(ad-Cu) and E_{diff}(ad-Cu) for 6-, 7- and 8-layer films. To avoid confusing basis-convergence error with QSE, I use the high plane-wave cutoff of 21.5 Ry. The results (without dipole correction) show QSE of ~10 meV, and also that formation and diffusion energetics are well-converged on a 6-layer (111) slab. With the lower plane-wave cutoff, 17.2 Ry, E_{diff}(ad-Cu) is 53, 36 and 52 meV for 6, 7 and 8 layer slabs. The apparent QSE is a non-convergence artifact.

Cu adatoms prefer *fcc* to *hcp* 3-fold sites on the 6-layer slab, but only by 7 meV (cf. Table I). Correspondingly, the ad-Cu diffusion barrier lies almost equidistant from the 3-fold hollows at a twofold bridge. To an excellent approximation, E_{diff}(ad-Cu) is thus the difference in energies for an ad-Cu in an *fcc* hollow and at the symmetric bridge. The computed sum, E_{form}(ad-Cu) + E_{diff}(ad-Cu) = 0.85 eV, compares well with the value, 0.78 ± 0.04 eV, obtained from STM observations of Cu island decay rates.[6] Effective Medium Theory calculations by Stoltze yield 0.71 eV and 53 meV for E_{form}(ad-Cu) and E_{diff}(ad-Cu),[16] in relatively good agreement with the best *ab-initio* results, 0.79 eV and 57 meV.

Cu-S ad-dimers - If ad-CuS is the plentiful species that accounts for S-enhanced Cu transport,[2] at a minimum ad-Cu and ad-S must attract each other. But they do not. A S adatom *loses* 1.08 eV binding energy in approaching the ad-Cu closely, and forming a Cu-S dimer with the S beside the Cu (cf. Table II) *costs* 1.87 eV.[17]

Presumably because the S cannot conveniently form two bonds, repulsion of the same magnitude also inhibits formation of an ad-CuS with the Cu-end down. But even in the S-end down configuration, where S and Cu valence requirements *can* be satisfied, the dimer formation energy (with the CuS in an fcc hollow) is 1.26 eV, compared to E_{form}(ad-Cu)=0.79 eV. Thus, the Cu-S adcluster responsible for enhanced Cu-island decay contains more than one Cu atom.

Clean and S-decorated Cu dimers - One expects Cu's adsorbed on Cu(111) to attract, and indeed (Table III) Cu-Cu attraction lowers E_{form}(ad-Cu_2) by 0.27 eV. But does attaching S atoms to such a dimer reduce its E_{form} by *another* 0.53 eV, to make S-decorated Cu-dimers more plentiful than Cu monomers? At least for the most obvious S-decorations of Cu addimers, the answer is no (cf. Table II). Placing a single S on the side of the dimer, where it is 4-coordinated (the "A-type" side), lowers the formation energy by 0.04 eV. Adding another, on the other side of the dimer lowers it 0.19 eV more, not enough to compensate the cost of the second ad-Cu.

Other geometries, e.g., Cu's decorating a S-addimer, or S's and Cu's alternating to form a flat tetramer, seem unfavorable. The former would require S's to be nearest neighbors even while S_2 dissociates on Cu(111). The latter is unlikely because, as noted above, an ad-S beside an ad-Cu is a repulsive configuration. The search for a low energy Cu-S complex thus moves to still larger clusters.

Clean and S-decorated Cu trimers - S-decorated trimers (cf. Fig. 1) are big enough that using $3 \times 2\sqrt{3}$ supercells to compute their formation energies is a concern. To quantify the interaction of clusters in neighboring cells, I compute trimer formation energies in both $3 \times 2\sqrt{3}$ and $4 \times 2\sqrt{3}$ supercells. The difference is small for the pure trimer (0.02 eV) but considerable (0.07 eV) for the ad-Cu_3S_3.

On a per adatom basis, forming Cu ad-trimers should cost less than dimers, because each ad-Cu has *two* ad-Cu neighbors, not just one. Counting bonds, with a Cu-Cu bond strength of 0.27eV (see above), one expects E_{form}(ad-Cu_3)≈1.59 eV, i.e., about triple the monomer formation energy, 2.4 eV, minus 3×0.27 eV.

Direct calculations confirm this logic. The energy needed to form a trimer, with the three Cu adatoms in neighboring fcc hollows bounded by (100)- or "A-type" microfacets, is ~1.7 eV. If the trimer is rotated 60°, so that its sides are (111)- or "B-type" microfacets, its E_{form} is 0.02 meV less (cf. Table III).[18]

Though bond-counting predicts E_{form}(ad-Cu_3) rather well, a similar approach *greatly* underestimates how much S-decoration reduces it. Rather than by 0.1 to 0.2 eV per added S-atom, as S+Cu-dimer results would suggest, decorating a Cu trimer with three S atoms reduces the formation energy of the complex by 0.47 eV/S-atom,[19] for a trimer bounded by A-type microfacets. *Forming S-decorated Cu trimers thus costs only 0.28 eV, much less than Cu monomers!*

In Fig. 2, to provide insight, I compare d-band local densities of states (d-LDOS's) of a Cu atom of an ad-Cu_3S_3, a nearby, uncovered surface-layer Cu and a third-layer ("bulk") Cu atom. Note that bonding with S shifts the d-LDOS of the trimer-Cu well below the uncovered surface Cu atom's.[20] Indeed, the healing of the trimer's dangling bonds is so good that the centroid of its d-LDOS is virtually the same as that of the third-layer, "bulk" Cu.

Diffusion of S-decorated Cu trimers - Given that creating a Cu_3S_3 ad-complex costs just 0.28 eV, and the related fact that S-decoration lifts the Cu adatoms ~0.14 Å higher above the nearest surface Cu's, the cluster diffusion barrier should be low. A plausible diffusion path involves moving each Cu from its initial hollow, say an *fcc* site,[21] (along the arrow in Fig. 1) over a neighboring bridge to an adjacent *hcp* hollow, the three S atoms following more or less rigidly. A lower bound for the barrier along this path is the energy difference between the initial and final configurations of the decorated trimer, or (see Fig. 1) between S-decorated trimers with A- vs. B-type sides.

This bound is significant, because S atoms have an affinity for Cu's arranged in a square.[22] In the present case, the affinity amounts to an energetic preference of ~0.33 eV for an A-sided trimer. It remains to learn if the B-trimer represents a transition geometry or a metastable state, and if the latter, whether the minimum barrier is much bigger than 0.33 eV.

Applying Jónsson's Nudged Elastic Band (NEB) method[23] with two replicas of the S-decorated trimer along the path between A-trimer in *fcc*- and B-trimer in *hcp*-hollows, I find a transition state close to the B-trimer geometry and a barrier of 0.35 eV. Thus $E_{form}(Cu_3S_3)+E_{diff}(Cu_3S_3)\approx0.63$ eV, *which is 0.22eV lower than the similar sum for a Cu adatom.*

Assuming "diffusion-limited" Cu-island decay,[24] the decay-*rate* scales with the concentration of Cu-carrying adspecies times their diffusion constant. This product is proportional to $D_0(\text{ad-Cu})\exp\{-[E_{form}(\text{ad-Cu})+E_{diff}(\text{ad-Cu})]/kT\}$, for Cu-adatom transport, and to $D_0(Cu_3S_3)\theta_S{}^3\exp\{-[E_{form}(Cu_3S_3)+E_{diff}(Cu_3S_3)]/kT\}$, for Cu_3S_3 clusters, where θ_S is the ad-S concentration and the D_0's are diffusion prefactors.[25] The S-induced speedup is proportional to the latter divided by the former. With a calculated $E_B(\text{ad-S}) \approx 5.42$ eV, the Cu_3S_3-mediated decay rate $\approx 5000\ \theta_S{}^3 \times D_0(Cu_3S_3)/D_0(\text{ad-Cu})$ that for clean Cu(111). This result makes it plausible that Cu_3S_3 clusters account for the speedup seen in Ref. 2. Whether they *really* do depends on the D_0's and other uncertainties in the calculations.

Clean and S-decorated Cu tetramers - The advantages of additional Cu-Cu bonds and S-decoration persist beyond Cu-trimers. To form ad-Cu_4S_4, e.g., requires only ~0.48 eV.[26] However, since barriers to concerted diffusion of Cu_nS_n clusters likely rise with n, Cu-transport via S-decorated tetramers, pentamers, etc. should be less facile than via Cu_3S_3, yet another subject for further study.

Caveat; discussion - A undying issue in DFT total energy studies of 300K phenomena is that k_BT is near the accuracy of the results. Here, e.g., $E_{form}(Cu_3S_3)$ includes the $3E_B(\text{ad-S})$ given up by three isolated S atoms when they attach to the cluster. An error of only 20 meV in E_B(ad-S) thus produces an order of magnitude change in exp(-E_{form}/k_BT). This difficulty together with others noted above makes it hard to predict the S-induced speedup of mound decay quantitatively. Quench experiments allowing observation of Cu_3S_3 on terraces would make more elaborate theoretical and experimental effort worthwhile.[7]

Acknowledgments - I thank N. C. Bartelt and B. S. Swartzentruber for many helpful discussions. VASP was developed at the T. U. Wien. This work supported by the U. S. Department of Energy under Contract No. DE-AC04-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U. S. Department of Energy.

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17. This is not an unusual effect. For the case of Al and S on Al(100), see P. J. Feibelman, Phys. Rev. **B38**, 12133 (1988).

18. This result is consistent with computations (see Ref. 15), saying that forming a B-type step costs less than an A.

19. This value corresponds to the $4 \times 2\sqrt{3}$ supercell.

20. The centroid of the surface-layer Cu d-LDOS is -2.10 eV on *perfect* Cu(111). The large difference between this value and those of the uncovered Cu's in the $4 \times 2\sqrt{3}$ cell reflects slow decay of LDOS perturbations with distance from a defect.

21. Only a slight difference is expected if the A-trimer starts with Cu's in *hcp* hollows.

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25. $\theta_S{}^3$ represents the entropy loss when lattice-gas S adatoms attach to a trimer.

26. The Cu's of the ad-Cu_4S_4 form a parallelogram with two Cu's roughly in 3-fold hollows and two in bridge-sites. A fifth S atop ad-Cu_4S_4 is unhelpful, with E_{form}(ad-Cu_4S_5) ≈ 1.17eV.

Figure captions -

1. Cu_3S_3 ad-clusters on Cu(111), in the $4 \times 2\sqrt{3}$ supercell indicated by the dotted rectangle. The inset cluster is displaced by the distance between *fcc* and *hcp* hollows, in the direction indicated by the arrow. As a result, the S-atoms that cover it are on (111)-microfacets, rather than the (100)-microfacets of the undisplaced clusters. This change of S-adsorption geometry is the main source of the 0.35 eV Cu_3S_3 diffusion barrier.

2. Gaussian-smeared d-band LDOS's for one of the Cu's of a S-decorated trimer, for an uncovered surface Cu in a $4 \times 2\sqrt{3}$ cell containing an ad-Cu_3S_3, as in Fig. 1, and for a third layer, effectively "bulk" Cu of the same slab. The Fermi energy is at 0.0 eV. Centroids of the d-LDOS's are indicated by vertical lines at the bottom of the plot.

Table Captions -

1. Cu adatom formation and diffusion barrier energies on L-layer Cu(111) slabs.

2. Clean- and S-decorated-cluster formation energies, E_{form}, on a 6-layer, Cu(111) slab. N_S and N_{Cu} are the numbers of S and Cu adatoms in each cluster. For Cu dimers and trimers I indicate the face that the S atoms decorate. The "B" cases correspond to Cu's in hcp hollows. In all other cases the Cu's occupy fcc sites. When the dipole correction (see text) is included, the vacuum width used is ~5 bulk Cu(111) layer spacings. Otherwise it is ~3 of them. Supercell width and PW cutoff are self-explanatory. Values of E_{form} in bold face are "best" values for the various cluster types. For the Cu monomer plus one S adatom, the three E_{form} values are for S down, Cu down and S-beside-Cu configurations.

3. Pure Cu cluster formation energies on 6-layer Cu(111).

Table 1:

L	adatom site	E_{form}	E_{diff}
6	*fcc*	0.80eV	58meV
6	*hcp*	0.81eV	
7	*fcc*	0.78eV	58meV
8	*fcc*	0.79eV	57meV

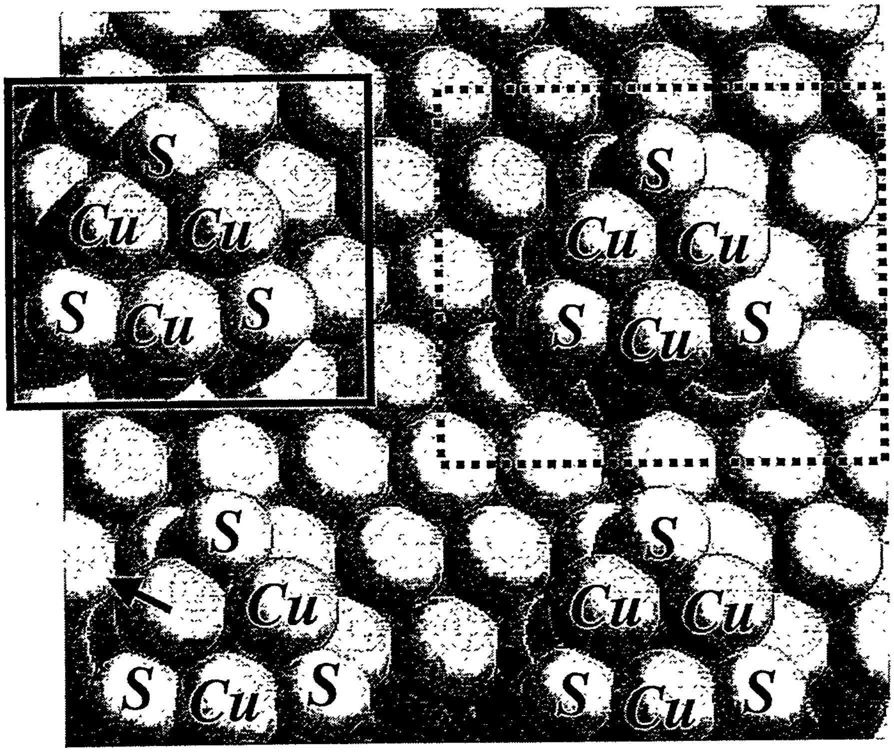
Table 2:

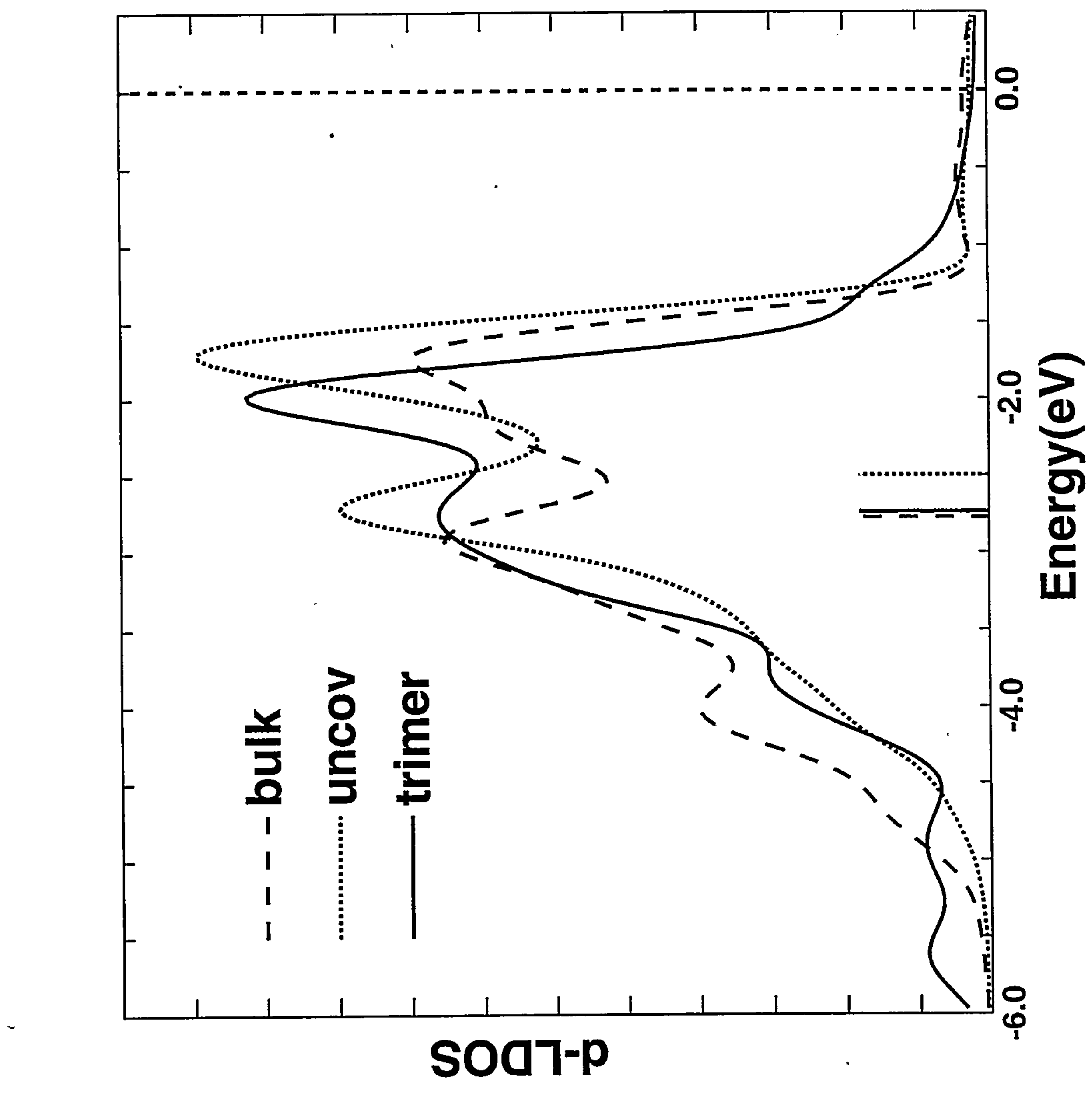
N_S	N_{Cu}	face	dipole corr.	supercell	PW cutoff	E_{form}(eV)
0	1		no	$3\times 2\sqrt{3}$	17.2	0.80
0	1		yes	$3\times 2\sqrt{3}$	21.5	**0.79**
1	1		no	$3\times 2\sqrt{3}$	17.2	**1.26**, 1.87, 1.87
1	2	A	no	$3\times 2\sqrt{3}$	17.2	1.29
2	2		no	$3\times 2\sqrt{3}$	17.2	**1.06**
0	3	A	yes	$4\times 2\sqrt{3}$	17.2	1.66
3	3	A	yes	$4\times 2\sqrt{3}$	17.2	0.34
3	3	B	yes	$4\times 2\sqrt{3}$	17.2	0.68
0	3	A	yes	$4\times 2\sqrt{3}$	21.5	1.69
3	3	A	yes	$4\times 2\sqrt{3}$	21.5	**0.28**
3	3	B	yes	$4\times 2\sqrt{3}$	21.5	0.62
4	4		no	$4\times 2\sqrt{3}$	17.2	**0.48**
5	4		no	$4\times 2\sqrt{3}$	17.2	1.09

Table 3:

cluster	supercell	E_{form}(ad-Cu_n)
monomer	$3 \times 2\sqrt{3}$	0.80 eV
dimer	$3 \times 2\sqrt{3}$	1.33 eV
A-trimer	$3 \times 2\sqrt{3}$	1.68 eV
A-trimer	$4 \times 2\sqrt{3}$	1.66 eV
B-trimer	$3 \times 2\sqrt{3}$	1.66 eV

Fig. 1





bulk
uncov
trimer
d-LDOS
Energy(eV)
-6.0
-4.0
-2.0
0.0