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Monte Carlo simulations of the interface layer in Pb/Cu(110); a tight-binding-model calculation

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Abstract. Monte Carlo simulations with energies computed via the tight-binding model are applied in studying the equilibrium properties of the interface layer in the system Pb/Cu(110). In a submonolayer range below 0.5 ML (ML \equiv monolayer), the model based on the coverage-dependent interactions reveals a lattice-gas random adsorption, an equilibrium adatom–substrate intermixing and formation of a centred $c(2 \times 2)$ phase. The process of intermixing is found to be coverage and temperature dependent. At high adatom concentration, 0.75–0.80 ML, as a result of very subtle competition between the strain energy and the energy gain due to mixing, the system forms a succession of commensurate unidimensional $p(n \times 1)$ structures. The results are in line with those recently obtained from scanning tunnelling microscopy and thermal energy atom scattering observations.

(Some figures in this article appear in colour in the electronic version; see www.iop.org)

1. Introduction

The very early stages in the formation of monatomic layers, structural phase transitions and order–disorder phenomena in adsorbed phases are of particular interest in fundamental surface science since in most cases the phases are considered as physical realizations of two-dimensional (2D) systems. The exotic ability to manipulate crystal surfaces at the atomic level and the experimental realization of superlattices with unique physical characteristics are additional motivations for the metal monatomic layers deposited on metal substrates to be widely studied. Due to the progress achieved in high-resolution diffraction techniques such as spot-profile-analysis low-energy electron diffraction (SPA-LEED), in thermal energy atom scattering (TEAS) and in scanning tunnelling microscopy (STM), many systems already studied in the early seventies are now being reconsidered. One of the most studied is obviously the case of Pb/Cu. The low melting point of lead, its chemical inertness and the lack of miscibility of the two metals are reasons for this choice. A large variety of structural phase transition on differently oriented copper substrates have been observed [1]: a succession of centred structures in the case of Pb/Cu(100) [2–5]; one centred and a series of quasi-unidimensional primitive structures for Pb/Cu(110) [6–9]; an incommensurate strongly compressed phase for Pb/Cu(111) [10]. On the other hand, this system became attractive in view of the surface alloying process taking place in a submonolayer range of coverages, although lead and copper are immiscible in the bulk solid state. The experimental observations of this phenomenon, occurring despite the large difference (37%) in ‘atomic diameters’ of Pb and Cu, is an additional motivation for the present study. Both STM and TEAS experiments of

Pb/Cu(100), Pb/Cu(110) and Pb/Cu(111) demonstrate that Pb atoms preferentially replace Cu atoms in the substrate lattice matrix, overcoming the strain energy of the topmost layer [1,5,11]. Recently it was shown that the large variety of ordered lead alloys on the (110) face of copper can be explained by the delicate competition between the strain energy and the energy gain due to mixing in the layer [14]. Thus surface alloying can be considered as an equilibrium state of the system Pb/Cu. This phenomenon was foreseen many years ago in the framework of a simple model of isomorphous substances taking into account only nearest-neighbour interactions [12, 13]. Unfortunately, a serious disadvantage of the model is the absence of an elastic strain energy contribution due to the difference in size of the atomic diameters of the adsorbate and substrate, despite its significance in the mixed-phase formation. At present, no general treatments of this phenomenon are available.

Computer simulation methods have proved to constitute a powerful tool for studying such types of phenomenon, acting as a bridge between analytical theory and experiment [16, 17]. Historically, lattice-gas models with adatoms allowed to reside only at specific lattice sites and pair potential approximations that express the total energy as a sum over pairwise interactions have been used [18–21]. These simplifications are introduced in order to facilitate the treatment of complex many-body systems chemisorbed or physisorbed on crystalline surfaces. However, lattice-gas models do not allow studies of structural changes in the adsorption system due to the incompatibility between the substrate and adsorbate. The pair potential approximation, although useful in many situations, has significant difficulty in correctly describing surface structure and relaxation properties, vacancy formation energies and alloy surfaces. Many-body potential schemes overcome to a great extent the shortcomings of the above models [22, 23]. A tight-binding (TB) method [26], used in this study, has been successful in computing the structures of defects, surfaces and interfaces of metals and alloys involving filled and nearly filled d bands and s, p-bonded metals such as Al and Pb. In this model, the total energy consists of a band energy for a tight-binding (TB) Hamiltonian plus a sum of pair interactions. The assumption for the TB potentials is that the band energy scales with the bandwidth, which is proportional to the second moment of the electronic density of states (DOS). In the TB model, the local second moment of the DOS can be represented in a pair functional form, where the energy of each atom is related to a function of a simple sum over its neighbours. This makes the TB model calculations nearly as fast as calculations with a simple pair potential. Thus, it is feasible to implement TB method computer simulations that include structural changes in the adsorbate layer, surface intermixing and atomic-scale relaxations.

In the present paper, we study the equilibrium properties of a three-dimensional (3D) continuum-space model of Pb on the Cu(110) substrate applying standard Monte Carlo (MC) sampling and TB energy calculations [15, 24]. We show that surface alloying is an equilibrium phenomenon even in the case of volume-immiscible systems. We also study the structure formation in a 0.75–0.80 ML range where a succession of unidimensional $p(n \times 1)$, $n = 4, 8, 13, 17, 5$, structures were experimentally observed. Including coverage-dependent interactions [24, 38] in the model, we obtained Pb/Cu(110) interface properties in close agreement with recent TEAS and STM experimental findings.

2. The tight-binding model

The tight-binding model (TBM) has been shown to provide an appropriate way to account for the bulk interactions in the case of transition metals [26,27]. It has also been used to investigate properties of transition metal surfaces [26,28,29] and microclusters [31,32]. In the TBM, the atom–atom interactions are described as a combination of a short-range repulsive pair potential plus an effective-band term [27]. In this approach the total cohesive energy is written for an

atom i as

$$E_i = E_i^r + E_i^b. \quad (1)$$

E_i^r is the repulsive energy, given by

$$E_i^r = \sum_{j, r_{\alpha\beta} < r_c} A_{\alpha\beta} \exp \left[-p_{\alpha\beta} \left(\frac{r_{ij}}{r_{\alpha\beta}^0} - 1 \right) \right] \quad (2)$$

where α, β denote the chemical natures of the atoms, $r_{\alpha\alpha}$ is the first-neighbour distance of the pure metal and $r_{\alpha\beta}^0 = (r_{\alpha\alpha} + r_{\beta\beta})/2$ if $\alpha \neq \beta$, r_{ij} is the distance between atoms i and j , and r_c is the cut-off distance for the interaction. E_i^b is the band energy obtained in the form of the second-moment of the electron density of states, which is expressed as

$$E_i^b = - \sqrt{\sum_{j, r_{ij} < r_c} \xi_{\alpha\beta}^2 \left[-2q_{\alpha\beta} \left(\frac{r_{ij}}{r_{\alpha\beta}^0} - 1 \right) \right]} \quad (3)$$

where ξ is an effective hopping integral and q describes its dependence on the relative interatomic distance.

In the present paper the equilibrium properties of a 3D continuum-space model of Pb on the Cu(110) substrate were studied using canonical MC sampling [15] along with Verlet tables [25] of the neighbours of each of the particles which were updated after each set of ten MC steps. The summations in (2) and (3) are performed over all atoms within a sphere of radius three times the Cu nearest-neighbour (NN) distance. The contribution to the internal energy of adsorbate atoms placed at larger distances was found to be less than 5% and was not accounted for. Nevertheless, this cut-off was extended to five times the Cu NN distance for the structures in the higher-coverage range. The parameters A , p , q and ξ of the interaction potentials for Pb and Cu are given in [33]. Since Pb and Cu are miscible only at very high temperatures, i.e. in a liquid state, a precise tuning of the heteroatomic interaction parameters is problematic. Using the data from the literature [34], we estimate the appropriate values of the heats of dissolution at $T = 1400$ K of one impurity of Pb in Cu and vice versa as (Pb) 0.374 eV/atom and (Cu) 0.286 eV/atom. Using the arithmetic mean of the parameters for the pure metals, we obtain for Pb, 1.693 eV/atom and for Cu, 0.671 eV/atom. These values were obtained allowing the system to relax at $T = 0$ K. The calculated values of the heats of dissolution are far larger than the experimental ones, as could be anticipated taking in account the experimental conditions [34]. On the other hand, these values increase the tendency towards immiscibility in the volume, which gives support to using this choice of Pb–Cu interaction parameters, as does the reasonable behaviour of the Pb monolayer structure on Cu(100) obtained using similar TBM calculations [33].

We should point out that in our simulation model for the Pb/Cu(110) system the substrate atoms are not fixed at their ideal sites in the fcc (110) lattice. The atoms of the uppermost substrate layers are allowed to move in the same manner as adsorbed Pb atoms. Thus we could investigate the surface relaxation due to the presence of adsorbate atoms as well as possible atom exchanges between different layers. The latter process of surface alloying has recently been experimentally determined to occur not only for Pb/Cu(110) [11] but also for Pb/Cu(100) [5] and even in the case of the most closely packed system Pb/Cu(111) [35].

The fcc (110) lattice planes form rectangular lattices with lattice constants 1 and $\sqrt{2}$, where we choose a unit system in which the lattice constant $b/\sqrt{2}$ of the substrate is unity. The linear dimensions L_x and L_y are multiples of 1 and $\sqrt{2}$ respectively, so the influence of box size on the adsorbate's structure is kept to a minimum. The Z -axis is perpendicular to the planes, pointing from the surface ($Z = 0$ corresponds to the centres of the top-layer substrate atoms

fixed at their ideal sites in the fcc (110) lattice) into the adsorbate space. In our simulation, the lattice size $M = L_x \times L_y$, where $M = 14 \times 10$, 20×14 and 28×20 , has been used, with periodic boundary conditions. The MC simulations for the higher Pb coverage range of 0.75–0.80 ML were carried out with a larger number of atoms in the $(1\bar{1}0)$ direction in comparison to the (001) direction in order to include more $p(n \times 1)$ ($n = 4$ or 5) unit cells and the expected adlayer structures, and to keep the system to a reasonable size. The lattice size of $M = 20 \times 6$ was used for simulating 0.75–0.80 ML Pb coverage structures. As we have already noticed, since some surface relaxation of the copper lattice and exchange with Pb adatoms are expected, and since the interactions are rather extended, in the case of high coverages 0.75–0.80 ML, we allow Cu atoms in the two uppermost layers of the substrate to move. The inclusion of an additional Cu layer with Cu atoms allowed to relax does not produce any difference in the results, but substantially increases the computation time. For each simulation, 10^5 MC moves were attempted per atom. A single MC displacement consists in sequentially selecting a new atom position R_i in the simulation box and calculating the change in energy for the proposed move. MC events related to atom moves with energy changes of less than or equal to zero were automatically accepted. Displacements that cost an energy difference dE were accepted with probability $\exp(-dE/kT)$ (k : Boltzmann constant; T : temperature) by comparison with a random number. The maximal single displacement was considered temperature and species dependent, so an acceptance rate of 50% of trial states for each species was maintained during the run. The equilibrium state is established after the total system energy reaches its minimum and fluctuates around it. The coverage θ is defined as the ratio of the number of adsorbed atoms to the maximum number of substrate adsorption sites.

3. Lattice-gas formation and transition to the $c(2 \times 2)$ phase

According to experimental observations, the Pb atoms alloy in the outermost substrate Cu(110) layer at low coverages [1]. On the basis of some theoretical [40] and recent experimental findings, the atom exchange between the adsorbed layer and substrate is expected to be a reversible process [11, 37]. On increasing the coverage, the concentration of Pb atoms inside the Cu matrix reaches a maximum at about 0.3 ML. Diffraction TEAS experiments on this phenomenon suggest a first-order transition between the alloyed phase and pure $c(2 \times 2)$ structure [11]. Against the background of these experimental findings, we have performed MC simulations for the range of coverage 0.1–0.5 ML and temperatures between 250 K and 400 K. All simulations are done with a random initial configuration of Pb atoms adsorbed on a Cu(110) surface with a system size 10×14 . A typical snapshot of a randomly chosen configuration after equilibration of the system at 0.3 ML at 300 K is shown in figure 1. Pb atoms are randomly distributed on the Cu surface, forming a lattice gas. Additionally, some of the adatoms are incorporated at the usual Cu(110) lattice sites, expelling the appropriate Cu atoms. In the lattice-gas region, 0.1–0.4 ML, we observed the saturation of a number of alloyed Pb atoms at different temperatures at around 0.3 ML; see figure 2. It is evident that the adsorbate–surface intermixing is a temperature-activated process. The saturation behaviour of the group of alloyed adatoms can be related to the maximum amount of compression that may be endured by a Cu lattice. Let us recall the large difference of 37% in ‘atomic diameter’ of Pb and Cu. Obviously, an additional incorporation of adatoms inside the outermost substrate layer is not thermodynamically favourable, since the process is controlled by the competition between the strain energy and the energy gain due to mixing in the layer. This delicate energy balance may explain the slightly different behaviour of the relative number of exchanged Pb and Cu atoms at $T = 400$ K. Since the amount of strain built up in an adsorbate–substrate interface seems to decrease with increasing temperature [36], the saturation level shifts to lower

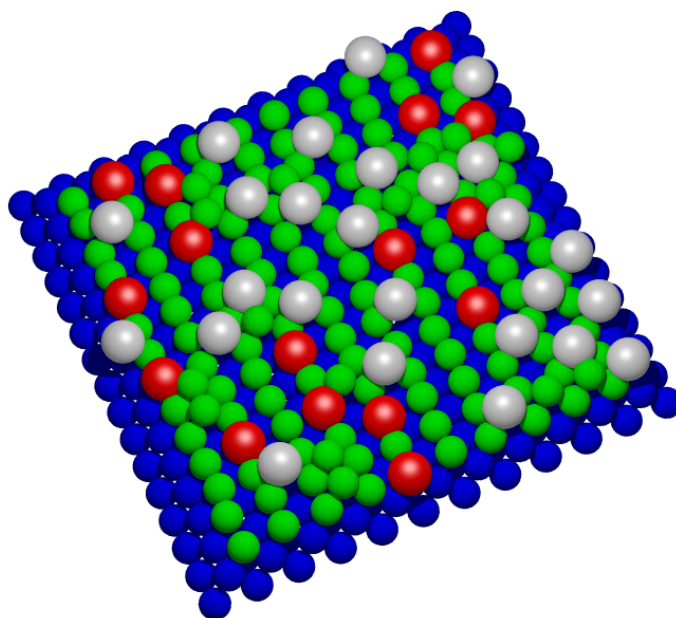


Figure 1. A snapshot of a randomly chosen configuration from the MC simulation of 0.3 ML of Pb (grey balls) on a (110) Cu surface (light green balls: the first Cu layer with the lattice dynamics included; blue balls: the second and third layers with fixed atoms at exact positions). $T = 300$ K. A lattice-gas random distribution of Pb atoms is seen as well as Pb–Cu interface mixing. Pb atoms embedded in the first substrate (red balls) layer exactly replace Cu atoms.

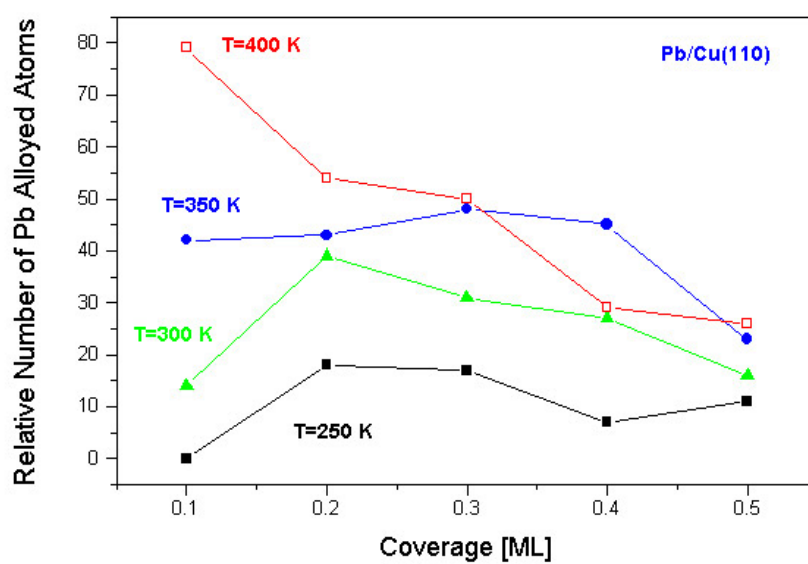


Figure 2. The relative number of alloyed Pb atoms versus coverage and temperature. The maximum amount of Pb atoms inside the Cu topmost layer is at about 0.3 ML.

coverages. We point out that if we use the bulk parameters in the interaction potentials, the system cannot generate the experimentally observed emerging $c(2 \times 2)$ structure at ~ 0.4 ML coverage and even at its saturation coverage of 0.5 ML. It has been shown that using coverage-dependent interaction potentials it is possible to obtain a stable $c(2 \times 2)$ Pb structure on a Cu(110) surface [24]. The order–disorder transition that the $c(2 \times 2)$ phase undergoes was studied in detail [24] in the framework of the same TB model as is presented here. Depending on the kinds of defects, this transition was found to be ‘first order’ or of the continuous Ising type [39, 41, 42]. Thus it was shown that appropriate modification of the hopping integral ξ leads to critical behaviour very close to the experimental findings. The important influence of the defects on the temperature stability of this structure was revealed in connection with the atomic interaction dependence upon the local environment. Using the same correction in the Pb–Pb-atom interaction potential, i.e. decreasing the value of the hopping integral ξ in the band-energy term (3), by 25% of the value appropriate for the bulk Pb crystal [24], we could observe at around 0.4 ML slight demixing and formation of the first islands of the $c(2 \times 2)$ Pb phase.

Figure 3 shows the Pb structure at 0.5 ML. Most of the substrate is covered with Pb atoms arranged in a $c(2 \times 2)$ lattice, although the presence of disordered areas can be observed. Analyses of these defect regions indicate that they appear in sub-areas on the substrate where initially Pb atoms are more loosely packed than is appropriate for 0.5 ML. This occurs because of the initial random distribution of adatoms in the simulations. It leads to adlayer starting configurations with higher (or lower) Pb concentration than is expected for a uniform structure. Obviously the simple correction of the Pb–Pb interaction based on the intuitive idea that stronger bonding of adatoms to the nearest surface atoms may weaken their own interactions

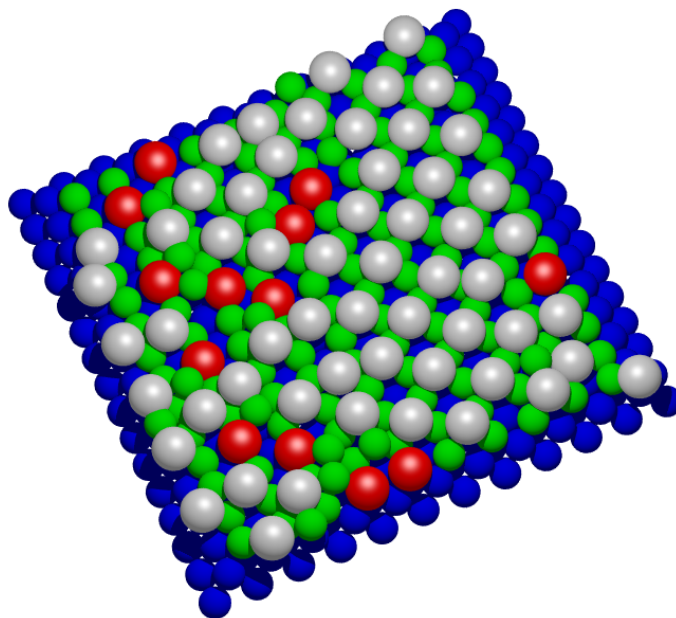


Figure 3. A snapshot of a randomly chosen configuration from the MC simulation of 0.5 ML of Pb (grey balls) on a (110) Cu surface (light green balls: the first Cu layer with the lattice dynamics included; blue balls: the second and third layers with fixed atoms at exact positions). $T = 300$ K. A $c(2 \times 2)$ structure and Pb atoms still in exchange positions (red balls) are seen.

hardly reflects a versatile configuration situation. Nevertheless, MC results correlate with recent TEAS data where the first diffraction peaks originating from the $c(2 \times 2)$ structure appear at about 0.4 ML coverage [11], and at 0.5 ML the system forms $c(2 \times 2)$ structure with an equilibrium distribution of about 10% alloyed Pb atoms.

4. Commensurate $p(4 \times 1)$ and $p(5 \times 1)$ phases

The final issue to be addressed in present work is that of the stability and mechanism by which the $p(n \times 1)$ quasi-unidimensional Pb structures form on the Cu(110) surface in the Pb 0.75–0.80 ML coverage range. Although it has recently been revealed [1, 9] that the periodic exchange of $\langle 001 \rangle$ Cu atomic rows with Pb atoms in the $\langle 1\bar{1}0 \rangle$ direction occurred, a full understanding of the structure formation and the mobility of the adatoms would be valuable.

The MC structures of 0.75 and 0.80 ML Pb coverages were obtained starting from two different initial configurations: (i) with all Pb atoms homogeneously distributed on the Cu(110) surface: model I; and (ii) with a configuration proposed by Nagl *et al* [9], with Pb atoms substituted every fourth and fifth (001) Cu row along the $\langle 1\bar{1}0 \rangle$ direction for 0.75 and 0.80 ML Pb coverages, respectively, and with expelled Cu atoms randomly distributed over the adsorbate: model II. Since the main features at the two Pb coverages are similar, in the following we concentrate on the results obtained at 0.80 ML Pb coverage.

The final configuration of the Pb layer at coverage 0.80 ML starting from model I reveals a (5×2) structure, where the Pb $\langle 001 \rangle$ neighbouring rows are displaced slightly with respect to one another in the $\langle 1\bar{1}0 \rangle$ direction and a pseudo-hexagonal structure is formed. Similar behaviour is observed for the 0.75 ML Pb coverage, where a $p(8 \times 1)$ structure develops. In these adsorbate structures the number of closely placed nearest-neighbour (NN) atoms increases. Starting with the model-I Pb layer configuration, no Pb–Cu atom exchange events were observed using the bulk parameters of the interaction potentials.

Figure 4 (dashed curve) shows the pair distribution functions (PDF) in the X – Y plane of

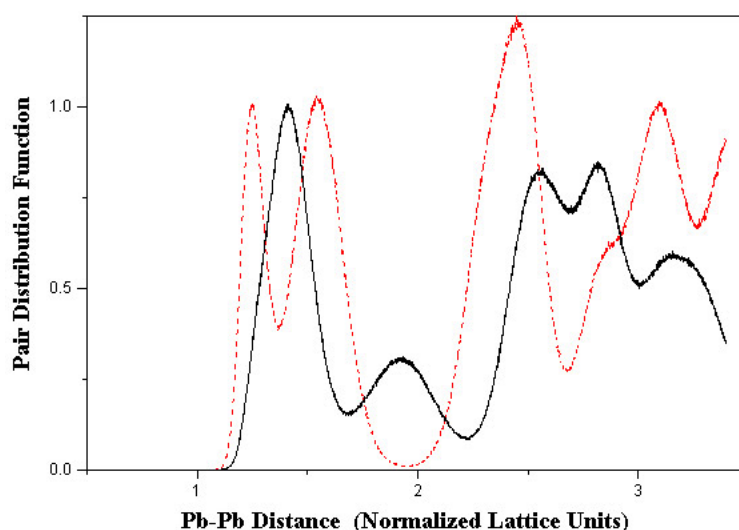
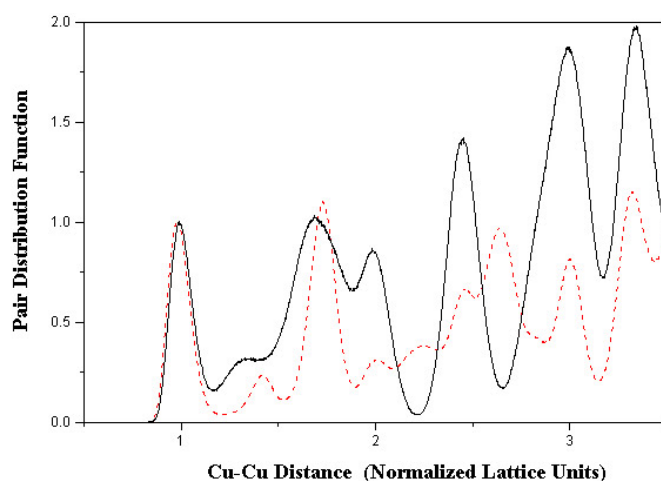


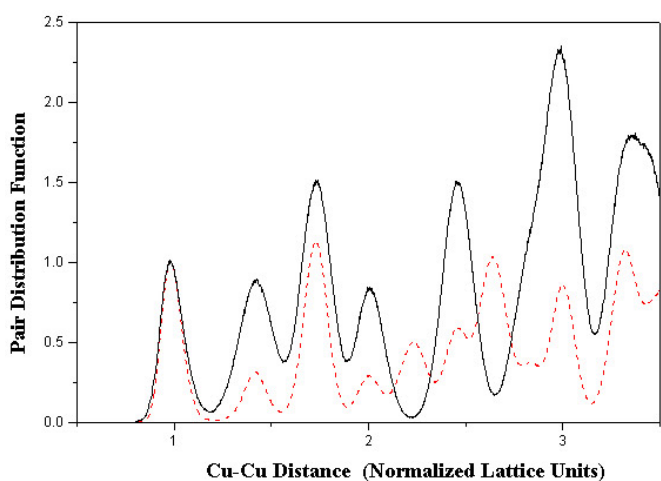
Figure 4. The pair distribution function of Pb atoms for 0.80 ML coverage on a (110) Cu surface in two models: I: with adatoms distributed on the substrate surface (dashed line); and II: with Pb atoms regularly exchanged for Cu atoms (solid line).

the adlayer. The position of first peak, corresponding initially to the first-neighbour distance in the Pb layer, is on average at 1.24, slightly less than the value for bulk Pb, which is 1.367 in units of the Cu NN distance. The position of the second peak is at 1.54; this value is relatively large compared to the Pb NN bulk distance but is also far from the substrate-imposed $\sqrt{2}$ NN distance in the $\langle 001 \rangle$ direction.

The PDFs of substrate layers allowed to relax show a drastic difference; see figure 5(a). The PDF of the first relaxed Cu layer shows a bulk-like ordering. However, in the PDF of the surface Cu layer there is observed a shift of the second, third and fourth peaks to smaller distances, and their overlap indicates that the degree of long-range order in the surface Cu layer



(a)



(b)

Figure 5. (a) The pair distribution function of the upper two copper layers for model I with adatoms over the Cu(110) surface. The layer on the hard Cu(110) surface: dashed line; and the uppermost Cu layer: solid line. (b) The pair distribution function of the upper two copper layers for model II with a proportion of the surface Cu atoms exchanged with adatoms. The layer on the hard Cu(110) surface: dashed line; and the uppermost Cu layer: solid line.

substantially decreases. The analysis of the adsorbate substrate atom bonding shows that Pb atoms tend to avoid the bridge-site position of the Cu surface atoms, i.e. the position with the lowest coordination of the adlayer structure. This indicates that the effect of the driving force for the appearance of the observed adsorbate structures is to increase the number of NN bonds even at the expense of increasing strain in the layers. As can be expected, a higher energy of adatoms in the underlying substrate tries to bind as many adatoms as possible, while the large mismatch and relatively densely packed Pb atoms at higher coverages oppose the formation of a pseudomorphic adlayer. Surprisingly, adlayer ordering imposed a drastic substrate surface rearrangement and a 2D liquid-like surface Cu layer formed.

Our calculations for model II turned out to be unstable using bulk interaction parameters. It appears that the expelled Cu atoms tend to re-exchange with the nearby Pb atoms either in the adlayer or already built into the Cu surface lattice. This is contrary to experimental observation [1, 9], which shows that the substituted Cu atoms either diffuse to steps or form islands. However, the adsorbate structure behaves stably in the areas where no Cu-exchange atoms are disposed. This indicates that the interaction of expelled Cu atoms with neighbour atoms may be not the same as at the regular lattice site positions. We can argue that the Pb adlayer partly screened out the interaction of the expelled Cu atoms with the native substrate atoms. Additionally, the Pb atoms have rather strong bonds to the nearest underlying surface atoms, which in turn may weaken the energy of the bonding with any additional Cu atom on top of the adsorbate. Similar behaviour has been observed for other substrate–adsorbate systems [30]. The presumed configuration variation of the interaction potentials, as discussed above in the case of the simulation of adlayer structure at lower coverages, can be introduced by modifying the values of the hopping integrals, ξ , of the Cu–Cu and consequently Cu–Pb interaction potentials, equation (1), of the expelled Cu atoms. In addition, we used bulk parameters for these atoms if they became close to each other, in order to promote Cu-island formation over the Pb layer. With these corrections to the interaction potentials, MC simulation shows stable $p(4 \times 1)$ and $p(5 \times 1)$ structures for coverages of 0.75 and 0.80 ML, respectively; see figure 6. It is also seen that expelled Cu atoms formed clusters on an adlayer. We would like to note that modified interaction potentials are used only for Cu atoms on top of the Pb adlayer and if there are no other expelled Cu atoms in the neighbourhood up to second-nearest

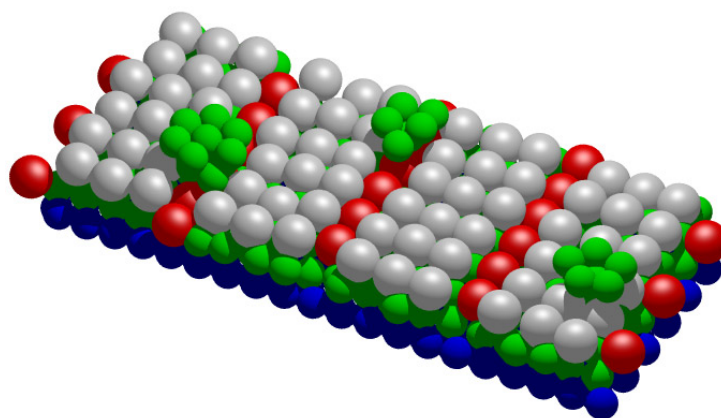


Figure 6. A snapshot of a randomly chosen configuration from the MC simulation of the 0.8 ML of Pb (grey balls) on the (110) Cu surface. The $p(5 \times 1)$ structure with Pb atoms (red balls) substituted every fifth (001) Cu row along the (110) direction is clearly seen.

neighbours. Thus, even a two-Cu-atom cluster leads to switching on of the bulk interaction potentials again. Modified potentials are used only during the equilibration procedure, since the Cu atoms quickly form relatively large islands with no free Cu atoms on the Pb adlayer as shown in figure 6—i.e. Cu-atom configurations where the original potentials are employed. Our empirical approach is not justified by strong physical arguments. However, our intention is not to develop optimal configuration-dependent potentials, but rather to indicate possible trends of their behaviour. Using density functional calculations, Fu *et al* [45] have shown that at a (100) surface in W (bcc), the large amount of local screening manifests itself in the fact that only interactions between adjacent layers are important in determining atomic relaxation. This surprising result indicates the relatively low influence of second-nearest neighbours even for bcc metals where the ratio between first- and second-nearest-neighbour distances is lower in comparison to that for fcc metals. The above result gives some support to the procedure that we used here, in diminishing second-neighbour, third-neighbour, ... interactions. Tan *et al* [46] have recently shown in Monte Carlo simulations using generalized Lennard-Jones potentials that after appropriate initial distribution of Pb adatoms on a Cu(100) surface, a stable structure reproducing the experimental results could be obtained.

The PDF of the Pb layer in model II (see figure 4, solid curve) is completely different to that of model I. This indicates that adatoms on Cu surfaces adopt a fcc (110) Pb-like order, with NN distances of 1.42 and 1.93, 1.367 and 1.933 being the bulk values, in the $\langle 1\bar{1}0 \rangle$ and $\langle 001 \rangle$ directions, respectively. Thus, the first peak in the PDF reflecting the NN distance shows 5% dilation. In fact, the projection of Pb-atom positions onto the hard substrate surface indicates more than 6% NN compression. These observations indicate a strong vertical modulation of Pb-atom positions on the Cu surface that has also been observed experimentally [9]. The Pb atoms on the Cu surface again avoid bridge-site positions. The PDFs of the relaxed Cu layers also show a clear change of adsorbate–substrate bonding in comparison with the results of model I. While there is no difference in the first-Cu-layer ordering in both models, the order of the Cu surface layer is obviously restored in model II, with Pb–Cu exchange included; see figure 5(b). Our results show a rather subtle interplay of the adsorbate–adsorbate and adsorbate–substrate interaction and the atom configuration dependences. It appears that the most important reason for the structures obtained in the present study is that Pb atoms tend to occupy positions on the substrate with as many neighbour atoms—and at as small distances—as possible. This leads in model I to a disordering of the surface Cu layer, although the Cu–Cu interaction is far stronger than the Pb–Pb bonding. It is interesting to note that models proposed so far [6–8, 43, 44] for the Pb overlayers in a higher-coverage range include Pb atoms placed at bridge-site positions and assume a coherent surface Cu layer, clearly at variance with the behaviour observed in our calculations. The STM experiments have established unambiguously the formation of the exchange $p(n \times 1)$ Pb structures. As we described above, in model II, the periodic (001)-row Cu–Pb exchange may be favoured due to the gain in energy engendered by decreasing the strain built up in the adsorbate–substrate system. This is realized, first, in the Cu surface layer, bringing the remaining Cu atoms at coherent positions to the underlying substrate layer and, second, in the adlayer, by effectively increasing the space available to the adatoms for accommodation on the ordered surface. It may be argued that the experimentally observed succession of $p(n \times 1)$ ($n = 4, 8, 13, 17, 5$) structures, over a 0.75–0.80 ML range, expressed the limit of accommodation of n adatoms on a surface layer that still preserves its coherency with the underlying substrate. Finally, we note that the configuration-dependent interaction potentials used in model II reveal structures similar to those observed experimentally. However, the stability of the structures of model-I calculations imply a very subtle atom–atom configuration interaction dependence that seems to be difficult to follow with our model simulations. As in the case of Pb coverage 0.5 ML [24], it also indicates that

the Pb-atom bonding to the Cu surface and resulting structures may be highly sensitive to any defects that influenced the potential fields surrounding interacting atoms.

5. Summary

In the present study, we described the interface layer behaviour of the system Pb/Cu(110) using a tight-binding many-body potential. We have shown that appropriate modification of the bulk value of the hopping integral ξ in a band-energy term (3) that describes the overlapping of tight-binding wave functions of neighbour atoms leads to system behaviour in fairly good agreement with the experimental findings. The modifications suggested do not develop optimal configuration-dependent potentials; they indicate rather the possible trends of their behaviour. Monte Carlo simulations based on coverage- or configuration-dependent interactions have revealed some important features of 2D Pb layers adsorbed on Cu(110) substrates:

- (i) Formation of a disordered lattice gas at lower coverages (less than 0.4 ML) accompanied by partial Pb–Cu atom exchange. The maximum number of Pb atoms incorporated is temperature dependent but is observed to be always around 0.3 ML coverage. This corresponds to the maximum compression of the outermost Cu lattice layer.
- (ii) Demixing that takes place with increasing coverage and the formation of Pb islands with $c(2 \times 2)$ structure. At 0.5 ML, the $c(2 \times 2)$ phase nearly covers the substrate, but some Pb atoms remain in exchange positions.
- (iii) Formation of stable commensurate $p(4 \times 1)$ and $p(5 \times 1)$ phases at 0.75 and 0.8 ML coverages. In the simulation model with non-alloyed adatoms, adlayer order is accompanied with disordering of the underlying surface Cu layer.

Finally we would like to point out that both centred $c(2 \times 2)$ and commensurate quasi-unidimensional $p(n \times 1)$ phases are formed as a result of very subtle competition between the strain energy and the energy gain due to mixing. This process controls the phase equilibrium and the structure of the 2D layer.

References

- [1] Mutaftschiev B 1996 *Proc. EWSSW'96: Thin Films and Phase Transitions on Surfaces (Pamporovo, Bulgaria, Feb. 1996)* ed M Michailov (Sofia: Coral Press, Bulgarian Academy of Sciences) p 13
- [2] Sanchez A and Ferrer S 1989 *Phys. Rev. B* **39** 5778
- [3] Li W, Lin J S, Karimi M and Vidali G 1991 *J. Vac. Sci. Technol. A* **9** 1707
- [4] Hosler W and Moritz W 1986 *Surf. Sci.* **175** 63
- [5] Nagl C, Platzgummer E, Haller O, Schmid M and Varga P 1995 *Surf. Sci.* **331+333** 831
- [6] Henrion J and Rhead G 1972 *Surf. Sci.* **29** 20
- [7] Liang K S, D'Amico K, Lee C H and Shen E Y 1990 *Phys. Rev. Lett.* **65** 3025
- [8] de Beauvais C, Rouxel D, Mutaftschiev B and Bigeard B 1992 *Surf. Sci.* **272** 73
- [9] Nagl C, Pinczolits M, Schmid M, Varga P and Robinson I K 1995 *Phys. Rev. B* **52** 16796
- [10] Meyer G, Michailov M and Henzler M 1988 *Surf. Sci.* **202** 125
- [11] de Beauvais C, Rouxel D, Michailov M and Mutaftschiev B 1995 *Surf. Sci.* **324** 1
- [12] Dunning W J 1963 *J. Phys. Chem.* **67** 2023
- [13] Mutaftschiev B 1965 *Adsorption et Croissance Cristalline* (Paris: CNRS Press) p 231
- [14] Rosenblatt T and Mutaftschiev B 1999 submitted
- [15] Binder K 1987 *Application of the Monte Carlo Method in Statistical Physics* 2nd edn, ed K Binder (Berlin: Springer)
- [16] Binder K 1979 *Monte Carlo Methods in Statistical Physics* (Berlin: Springer)
- [17] Binder K and Landau D P 1989 *Molecule–Surface Interactions (Advances in Chemical Physics vol 76)* ed P Lawley (New York: Wiley) p 91

- [17] Landau D P 1984 *Application of the Monte Carlo Methods in Statistical Physics (Springer Topics in Current Physics vol 36)* ed K Binder (Berlin: Springer) p 84
- [18] Roelofs L D 1982 *Chemistry and Physics of Solid Surfaces IV (Springer Series in Chemical Physics vol 20)* ed R Vanselow and R Howe (Berlin: Springer) p 219
- [19] King T S and Donnelly R G 1984 *Surf. Sci.* **141** 417
- [20] Baskes M I and Melius C F 1979 *Phys. Rev. B* **20** 3197
- [21] Williams F L and Nason D 1974 *Surf. Sci.* **45** 377
- [22] Folies S M, Baskes M I and Daw M S 1986 *Phys. Rev. B* **33** 7983
- [23] Carlsson A E 1990 *Solid State Physics* vol 43, ed H Ehrenreich, F Seitz and D Turnbull (New York: Academic)
- [24] Georgiev N and Michailov M 1998 *Phys. Rev. B* **58** 13 895
- [25] Verlet L 1967 *Phys. Rev. B* **159** 98
- [26] Rosato V, Guillopé M and Legrand B 1989 *Phil. Mag.* **59** 321
- [27] Cleri F and Rosato V 1993 *Phys. Rev. B* **48** 22
- [28] Mottet C, Tréglia G and Legrand B 1993 *Phys. Rev. B* **46** 16 018
- [29] Guillopé M and Legrand B 1989 *Surf. Sci.* **251** 577
- [30] Liem S Y, Kresse G and Clarke J H R 1998 *Surf. Sci.* **415** 194
- [31] Tománek D, Mukherjee S and Bennemann K H 1983 *Phys. Rev. B* **28** 655
- [32] Diep H T, Sawada S and Sagano S 1989 *Phys. Rev. B* **39** 9252
- [33] Gómez L and Diep H T 1995 *Phys. Rev. Lett.* **74** 1807
- [34] Rosenblatt T 1996 *PhD Thesis* Université Pierre et Marie Curie, Paris
- [35] Nagl C, Haller O, Platzgummer E, Schmid M and Varga P 1994 *Surf. Sci.* **321** 237
- [36] Feng K A and Henzler M 1993 *Mod. Phys. Lett. B* **7** 711
- [37] Nagl C, Schmid M and Varga P 1996 *Surf. Sci.* **369** 159
- [38] Tonchev V and Michailov M 1995 *Bulg. Chem. Commun.* **28** 57
- [39] Michailov M, de Beauvais C, Rouxel D and Mutaftschiev B 1996 *Proc. EWSSW'96: Thin Films and Phase Transitions on Surfaces (Pamporovo, Bulgaria, Feb. 1996)* ed M Michailov (Sofia: Coral Press, Bulgarian Academy of Sciences) p 205
- [40] Mutaftschiev B and Bonissant A 1973 *Surf. Sci.* **34** 649
- [41] Michailov M, de Beauvais C and Rouxel D 1994 *Bulg. Chem. Commun.* **27** 67
- [42] Roelofs L D 1982 *Appl. Surf. Sci.* **11+12** 425
- [43] Sepulveda A and Rhead G E 1977 *Surf. Sci.* **66** 436
- [44] Brenan S, Fuoss P H and Eisenberg P 1992 *The Structure of Surfaces (Springer Series in Surface Science)* ed M A van Hove and S Y Tong (Springer: Berlin)
- [45] Fu C L, Ohnishi S, Wimmer E and Freeman A J 1984 *Phys. Rev. Lett.* **53** 675
- [46] Tan S, Ghazali A and Levy J-C S 1997 *Surf. Sci.* **377-379** 15