

Order-Disorder Transition of Au and Pt (110) Surfaces: The Significance of Relaxations and Vibrations

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The embedded-atom method has been combined with Monte Carlo simulations to study the structure and order-disorder transformation of Au and Pt (110) surfaces. We find that the missing-row structure of Au disorders at 570 K, in close agreement with the experimental value of 650 K. For Pt, we predict a transformation at 750 K. Relaxations and vibrations are found to be essential for the accurate calculation of the critical temperature.

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The (110) surfaces of Au and Pt both reconstruct to a structure with 1×2 symmetry. A variety of experiments¹ and total energy calculations^{2,3} clearly indicate that the 1×2 structure of both metals is a missing-row geometry. Scanning tunneling micrographs of Au(110) reveal that the rows on the surface tend to be interrupted by steps, kinks, and larger (111) facets.⁴ Moreover, the missing-row structure of Au(110) has been observed in LEED experiments to disorder at 650 K.^{5,6} Short-range order, as determined by the 1×2 spot intensity and width, is seen to persist well above the critical temperature. Ion-scattering measurements also conclude that the surface atoms remain near lattice sites.⁷ The experimental observation of a similar transition for Pt(110) is not so clear. Salmerón and Somorjai⁸ reported that the 1×2 LEED spot intensity versus temperature showed features at 520, 720, 930, 990, and 1040 K. Above the last temperature, the 1×2 spot disappeared entirely. However, the authors expressed some concern about oxygen contamination. Campuzano, Lahee, and Jennings⁹ have investigated the fcc (110) phase transition as a physical realization of the 2D Ising model. In their traditional lattice-gas simulation, pair interactions between the "adatoms" were assumed and the qualitative behavior was compared to the experimentally observed behavior of Au(110). In the present work, we show that Monte Carlo simulations using energies computed via the embedded-atom method (EAM) show the occurrence of order-disorder transitions on Au and Pt (110). The critical temperatures are calculated and the nature of the ordering is investigated in detail.

The EAM has been described in detail in previous publications,¹⁰ and we will outline it briefly here. In this semiempirical scheme, the total energy of an arbitrary arrangement of atoms in a metallic environment is approximated by

$$E_{\text{tot}} = \sum_i F(\sum_{j \neq i} \rho^a(R_{ij})) + \frac{1}{2} \sum_{ij} \phi(R_{ij}).$$

The sums are over atoms, and F is the embedding energy of an atom in a metallic host characterized by a local electron density. This density is approximated by a su-

perposition of atomic electron densities, ρ^a , and R_{ij} is the distance between atoms i and j . In addition, there is an electrostatic, two-body interaction, ϕ .

The semiempirical functions required by the EAM have been determined previously by the fitting of bulk properties of the metal (lattice constant, cohesive energy, elastic constants, and dilute heats of alloying) and were used to predict point-defect properties as well as surface energies and relaxations of the unreconstructed low index surfaces. These functions are applied here without modification.

The EAM allows the incorporation of many-body interactions in a scheme whose computational effort scales with size like two-body interactions. Many-body interactions are quite important in the determination of the energetics of surfaces, as discussed in Ref. 3 and as is evident from the results to be presented here. These many-body interactions affect some of the bulk properties that are used as input to the semiempirical functions, and we therefore expect the EAM to contain a realistic estimate of surface properties.

We have found in previous calculations with the EAM that the missing-row structure is indeed lower in energy than the 1×1 structure for both Pt and Au (110) surfaces.³ Similar calculations for Ni and Cu showed that the unreconstructed surface structure was lower in energy in agreement with the observation that these surfaces do not reconstruct. For Pd and Ag, which also do not reconstruct, the calculations marginally favor the missing-row structure. Relaxed geometries for the missing-row structure were also computed and found to be in good agreement with the LEED and medium-energy ion-scattering results.

The present calculations determine the equilibrium structure as a function of temperature. Equilibrium Monte Carlo simulations were performed on a (110) slab, seven layers thick (with two surfaces), and periodic along the $[1\bar{1}0]$ and $[001]$ directions. The geometry chosen for the current calculations represents an 8×8 surface unit cell. A mesh of ideal sites was laid out over each surface, and an additional half monolayer of atoms

was spread out on each surface (these are defined as the *adatoms*). Three kinds of random jump were then executed in the Monte Carlo¹¹ simulations: (1) small jumps representing vibrational motion of substrate atoms and adatoms (this incorporates the contribution of vibrations and relaxations to the free energy), (2) jumps of the adatoms to unoccupied sites on the same surface, and (3) jumps of the adatoms to unoccupied sites on the opposite surface. With these jumps, an arbitrary arrangement of adatoms can anneal into a missing-row structure or disorder into a random array. In particular, the second and third types of jump help bring the system to equilibrium relatively rapidly, as opposed to waiting for atoms to migrate across a surface by only the first type of jump. Also, because the opposite faces can communicate, it is possible for the system to form two faces of 1×1 symmetry. (In Monte Carlo simulations on Ni, the missing-row structure very rapidly converts to a 1×1 structure while, at low temperatures, simulations of Au and Pt do the reverse.)

Three initial configurations were used: an ideal missing-row structure, a 1×1 structure, and a random structure. At each temperature, parallel runs were performed starting with each of these initial configurations and the simulations were run until the results were independent of the initial state. Thus we have observed the missing-row structure disorder above the critical temperature and also the disordered structure anneal into the missing-row structure below the critical temperature.

In order to quantify the ordering, the two-dimensional structure factor was computed. The structure factor is defined here by $S(\mathbf{k}) = \langle |\sum_j \exp(i\mathbf{k} \cdot \mathbf{R}_j)|^2 \rangle / N$. The sum is over adatoms, \mathbf{k} is the wave vector in reciprocal space, \mathbf{R}_j is the position of atom j , N is the number of adatoms, and the angular brackets denote an average over configurations. The structure factor was evaluated for $k_z = 0$ where the z direction is normal to the surface. While this quantity does not directly correspond to a specific measurement, the structure factor will have the same symmetry as the diffraction pattern. In addition,

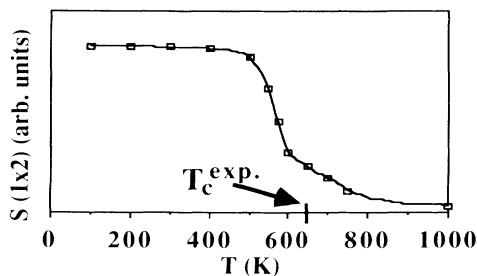


FIG. 1. The structure factor for the 1×2 structure as a function of temperature on Au(110). The theoretical critical temperature is 570 K, in excellent agreement with the experimental value of 650 K (Ref. 6).

the structure factor and the LEED intensity are measures of the ordering and should therefore have the same temperature dependence.

The resulting structure factor for Au evaluated at the 1×2 diffraction condition as a function of temperature is plotted in Fig. 1. The transition temperature (defined as the inflection point in the curve¹²) occurs at around 570 K.¹³ This is in excellent agreement with the experimental value of 650 K, *especially when we consider that only bulk data were used in determining the semiempirical functions*. In this sense, these calculations represent the first quantitatively realistic prediction of the order-disorder transformation of a surface reconstruction.

The 1×2 structure factor for Pt(110) has a temperature dependence very similar to that for the Au in Fig. 1, except that the predicted transition temperature is about 750 K. Because of the semiempirical nature of the EAM, one would expect reliability in predicting trends in properties from one metal to another closely related metal. Thus the prediction that the transition temperature for Pt is higher than that for Au is expected to be reliable. Furthermore, the remarkable agreement between the experiment and theory for the case of Au lends credence to the calculations for Pt. Perhaps the concerns expressed in Ref. 8 about oxygen contamination in the Pt(110) experiment are justified. Hopefully, future experiments to resolve this question will be performed.

The disorder of the surface is characterized in the current calculations by the second moment of the structure factor (i.e., the "spot width") in the vicinity of the wave vector for the 1×2 symmetry. In Fig. 2 we show the spot widths for Au(110), parallel and perpendicular to the rows, as functions of the temperature. The temperature dependence is very similar to that for the experimental LEED spot width, which is fairly constant below T_c and then increases rapidly with increasing temperature.⁶ The current theory shows, additionally, that the "spot" is not circular above T_c , but instead that the disorder per-

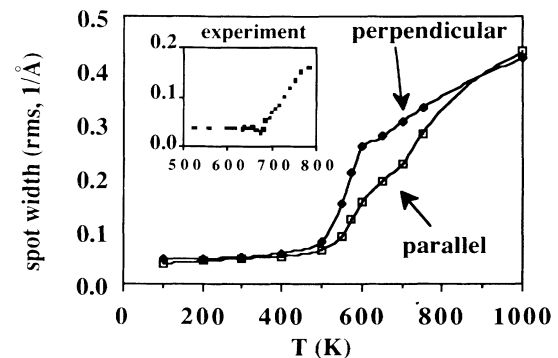


FIG. 2. The rms width of the structure factor around the 1×2 spot for Au(110), as a function of temperature. The width is shown for both the $[1\bar{1}0]$ (parallel) and $[001]$ (perpendicular) directions. Inset: Experimental values, from Ref. 6.

pendicular to the rows is stronger than that parallel. (The experimental data are available for a scan across the spot along only one direction; no discussion is made of any spot elongation.)

The picture that emerges from Figs. 1 and 2 is that below the critical temperature, the rows are generally long and coordinated, with some defects present. Well above the critical temperature short-range order persists in the form of short chains of atoms along the $[1\bar{1}0]$ direction with little coordination among the rows. This is confirmed by snapshots of individual configurations generated by the Monte Carlo simulations, as exemplified in Fig. 3.

We have also used the EAM-Monte Carlo simulations to investigate the ways in which this system is unlike a lattice-gas simulation of a 2D Ising model, as examined, for example, in Ref. 9. We have identified two differences which do not affect the qualitative nature of the transformation but which do strongly affect the value of the calculated critical temperature. These differences are as follows: (1) The adatom-adatom interactions are more complex than assumed in Ref. 9, and (2) the lattice-gas simulations ignore lattice vibrations and relaxations.

The adatom-adatom interactions can be estimated by the placement of two or three atoms in various arrangements on ideal sites on a $\text{Au}(110)\text{-}1\times 1$ surface. These interactions are displayed in column a of Table I. Campuzano, Lahee, and Jennings⁹ considered only $[1\bar{1}0]$ and $[001]$ pair interactions, which we find to be important. However, additional interactions involving diagonal pairs and linear trios are also important. The existence of these interactions forbids an analytical solution of the 2D Ising model, and so we have performed a numerical solution of the lattice-gas model using the interactions de-

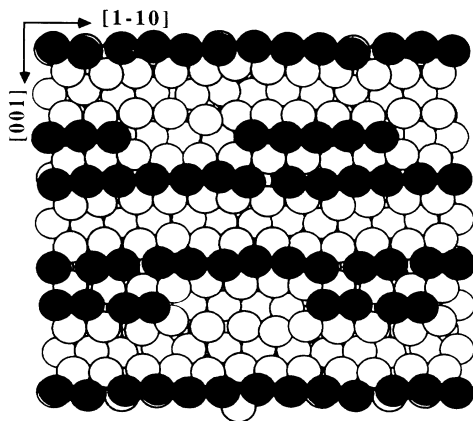


FIG. 3. Snapshot of a randomly chosen configuration from the Monte Carlo simulation of the $\text{Au}(110)$ surface showing behavior typical of a temperature slightly above the critical temperature. All atoms are Au atoms, with the adatoms darkened for illustration.

scribed in Table I, column a. The critical temperature is calculated to be 1090 K (compared to 570 K).¹⁴

The difference in T_c between the simulations using Table I, column a, and the EAM-Monte Carlo simulations illustrates the role of relaxations and vibrations since these effects are not included in the lattice-gas model but are in the EAM-Monte Carlo simulations. The snapshot of Fig. 3 shows that the atoms in the EAM-Monte Carlo simulations do indeed move off of ideal lattice sites. These vibrations and relaxations contribute to the free-energy difference between the ordered and disordered states.

The relaxations affect the enthalpy by modifying the effective interactions in a largely temperature-independent way. We have estimated the effects of the relaxations by considering pair and trio interactions with complete relaxation of the substrate and adatoms. The relaxed, effective adatom-adatom interactions are given in column b of Table I. The change in the interactions is significant, particularly for the $[1\bar{1}0]$ pair. The performance of lattice-gas simulations with use of these effective interactions reduces the critical temperature to about 850 K. Thus the relaxations account for about half of the difference between lattice-gas and EAM-Monte Carlo simulations.

The vibrations affect the entropy, introducing a temperature dependence into the effective interactions. We have estimated the vibrational effects by calculating the vibrational free energy in the harmonic approximation¹⁵ as a function of temperature. We find that the vibrational entropy difference is constant for temperatures above 300 K, and favors breaking up chains of atoms, thus lowering the critical temperature. By defining the effective interactions in terms of the free energy (making the interactions temperature dependent), we have calculated the effective interactions at 800 K. The results are shown in column c of Table I. The calculated critical temperature of the lattice gas with these interactions is about 700 K.

In summary, the calculations predict the critical temperature in excellent agreement with experiments on Au and provide stimulus for further measurements on Pt.

TABLE I. Significant effective pair and trio interactions, in electronvolts, for Au adatoms on $\text{Au}(110)\text{-}1\times 1$ computed from the EAM. The interactions are calculated by our constraining all atoms to ideal sites (column a), allowing relaxation (column b), and including the free energy of vibrations at 800 K (column c).

Configuration	a	b	c
Nearest $[1\bar{1}0]$ pair	-0.446	-0.281	-0.204
Nearest $[001]$ pair	+0.003	+0.013	-0.004
Nearest $[1\bar{1}2]$ pair	+0.022	+0.025	+0.022
Linear $[1\bar{1}0]$ trio	+0.039	+0.019	-0.002

We also see that relaxation and vibration contributions to the critical temperature are significant. Approximations to the effective interactions of pairs and trios to mimic these effects can significantly improve the quantitative calculation of critical temperatures by lattice-gas simulations.

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¹³The calculated transition temperature depends weakly on the size of the cell. To test this finite-size effect, we have performed a series of lattice-gas simulations with two- and three-body interactions determined to mimic the full EAM calculations. A single lattice of size 40×40 had a critical temperature within 2%–3% of that for two 8×8 cells which can communicate (analogous to the two surfaces of our slab).

¹⁴EAM–Monte Carlo simulations *without* relaxations show a critical temperature of 1050 K, in good agreement with the corresponding lattice-gas simulation.

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