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Structure of platinum adatom clusters on Pt(100): Experimental observations and embedded-atom-method calculations

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The structure of Pt adatom clusters on Pt(100) is observed to oscillate between chain- and island-type configurations as the number of adatoms is increased from three through six. Embedded-atom-method calculations are found to predict these results and show that lattice relaxations are a critical factor in causing this unusual series of structural transformations.

The structure assumed by adatom clusters on crystal planes reflects fundamental aspects of the adatom-adatom and adatom-surface interactions. Previous field-ion microscopy studies by other researchers[1,2] revealed the unusual phenomena that the initial structure of some platinum-group metal adatom clusters (Pt, Ir, Pd, and Ni) on W(110) are linear chains oriented in the close-packed ⟨111⟩ direction of the substrate surface. Two-dimensional island nuclei form only after a critical number of adatoms in the nucleus is exceeded. A subsequent study of the self-adsorption of Ir on Ir(100) yielded the interesting result that the initial formation of linear-chain nuclei can occur even in the case of homogeneous nucleation,[3] apparently due to repulsive configurations involving second near-neighbor adatoms.[4] With Ir on Ir(100), two-dimensional island nuclei become the stable configuration only for six or more adatoms. For five or fewer adatoms, a linear-chain nucleus oriented in the close-packed ⟨110⟩ surface direction is the most stable configuration.

The present experimental studies involve direct observation of Pt cluster nuclei on Pt(100) with the field-ion microscope. The theoretical calculations are based on the embedded-atom method (EAM).[5,6] On Pt(100), the Pt nuclei demonstrate a very interesting dependence upon the number of adatoms present in the nucleus. Specifically, the most stable nuclei structure oscillates between ⟨110⟩-oriented chains and island nuclei as the number of adatoms is increased from three through six. We also find that not only are the experimentally observed relative cluster stabilities predicted by the EAM, but that agreement between theory and experiment is achieved only if lattice relaxations are included in the calculations.

The experimental studies were conducted in an all-metal field-ion microscope capable of maintaining pressures below 1×10^{-10} Torr for two hours with only Ti gettering. The imaging gas was a mixture of ~80 at.% He and 20 at.% Ne at an absolute pressure of $\sim1\times10^{-3}$ Torr. Pt was deposited onto the emitter tip from Joule-heated Pt coils present in the vacuum system. The tip temperature was controlled by Joule heating of the Pt support loop on which the tip was mounted.

For three Pt adatoms on Pt(100), the linear-chain structure is the most stable. This configuration is always obtained upon heating dispersed adatoms to temperatures above those required for single adatom mobility, ~200 K. To demonstrate the metastable nature of the three adatom island, one can begin with the 2×2 adatom island of four adatoms shown in Fig. 2(b). If one of the corner adatoms is field evaporated at 77 K, the result is the island of three adatoms as shown in Fig. 1(a). Heating of this island to 200 K is sufficient to result in its reconfiguration into a linear chain, Fig. 1(b). This was the consistent result of five experiments. The metastable nature of the island configuration and the stable nature of the linear-chain configuration for three adatoms is clear from such experiments.

The most stable configuration for a nucleus comprised of four adatoms is the 2×2 adatom island. Following the deposition of four adatoms at 77 K and equilibration at low temperatures (~200 K), the nucleus is seen to be either the 2×2 island structure or, more often, a ⟨110⟩-oriented linear chain of four adatoms. An example of the linear-chain configuration is shown in Fig. 2(a). Heating this linear chain to temperatures of ~250 to ~280 K is seen to result in its reconfiguration into the 2×2 island, Fig. 2(b). This experiment was repeated three times. The reverse process of the 2×2 island reconfiguring into the linear chain is not observed up to temperatures of ~300 K where the island leaves the (100) plane.

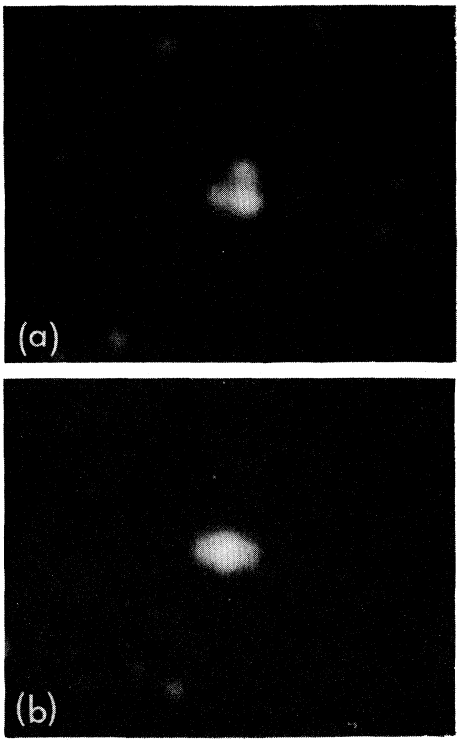

FIG. 1. A series of field-ion micrographs showing that the two-dimensional island of three adatoms is metastable, whereas the linear-chain configuration is stable. (a) An island of three adatoms. (b) The ⟨110⟩-oriented linear chain of three adatoms assumed by the island in (a) subsequent to heating at 200 K.

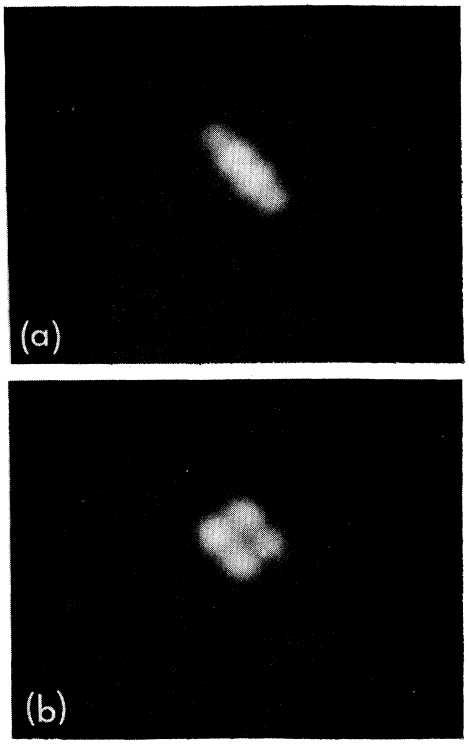

FIG. 2. A series of field-ion micrographs showing that the linear chain is metastable whereas the two-dimensional island configuration is stable for four adatoms. (a) A ⟨110⟩-oriented linear chain of four adatoms. (b) The two-dimensional island assumed by the chain in (a) subsequent to heating to 270 K.

Equilibrating five dispersed adatoms on the (100) plane at ~200 K resulted in the formation of either the chain or island configuration. However, due to the more frequent appearance of the chain, the island of five adatoms is more readily formed by the field evaporation of one corner atom from the 2×3 island of six adatoms, the result of which is shown in Fig. 3(a). The metastability of the five adatom island was evident in four experiments, where heating to temperatures of ~250 to ~270 K resulted in its reconfiguration into a linear chain, as shown in Fig. 3(b). Heating of five adatom linear chains resulted in their dissociation at temperatures of ~280 K. Reconfiguration of the chain into an island cluster was never observed.

Linear chains of six adatoms could be reliably formed by first forming the linear chain of five adatoms. After a sixth adatom was deposited on the plane, and following several heating cycles at a temperature of 200 K, the result was a linear chain of six adatoms, Fig. 4(a). This configuration was found to be metastable as heating to temperatures of ~260 to 280 K resulted in its reconfiguration into the 2×3 island shown in Fig. 4(b). Such reconfigurations were observed in three experiments. The 2×3 adatom island of six adatoms was stable up to temperatures of ~300 K, at which the adatoms left the plane. The chain configuration was never observed to reappear.

These experiments demonstrate that the stability of the chain and island configurations show an oscillatory dependence upon the number of atoms in the nucleus for three through six adatoms. We note, however, that the transitions from the metastable to the stable configurations for four, five, and six adatom clusters occur at temperatures sufficient to also lead to partial, or total, dissociation of the metastable configuration before the cluster assumes its most stable structure. Apparently, the energy barrier between the metastable and stable configurations is such that particular channels of reconfiguration lead to dissociation while others lead to the stable configuration. Accordingly, modeling the reconfiguration process could be very informative.

In addition to the above experiments, some observations were made of the seven adatom cluster comprised of one adatom bound to the 2×3 adatom island of six adatoms. At temperatures of ~260 K, the seventh adatom was seen to diffuse around the circumference of the 2×3 island. In 40 heating cycles, the adatom was observed to be bound to each of the eight corner positions of the 2×3 adatom island but never to one of the two adatoms in the middle of the long sides of the six adatom island. The seven adatom island was never seen to reconfigure into a chain configuration as was observed with lesser odd numbers of adatoms.

As a step towards understanding the fundamental interactions which drive such an unusual series of transformations in the fundamental structure of the Pt nuclei, we have used the EAM to calculate the relative stability of the Pt adatom chain and island configurations on the

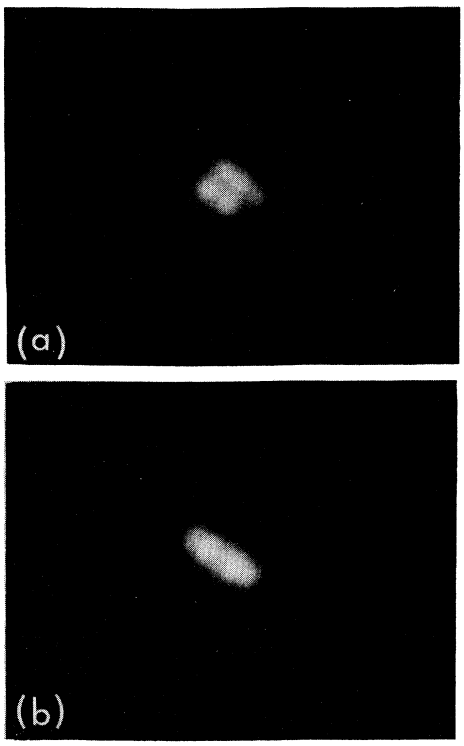

FIG. 3. A series of field-ion micrographs showing that the two-dimensional island of five adatoms is metastable and that the ⟨110⟩-oriented linear chain of five adatoms is stable. (a) An island of five adatoms. (b) The linear chain of five adatoms assumed by the island in (a) subsequent to heating at 260 K.

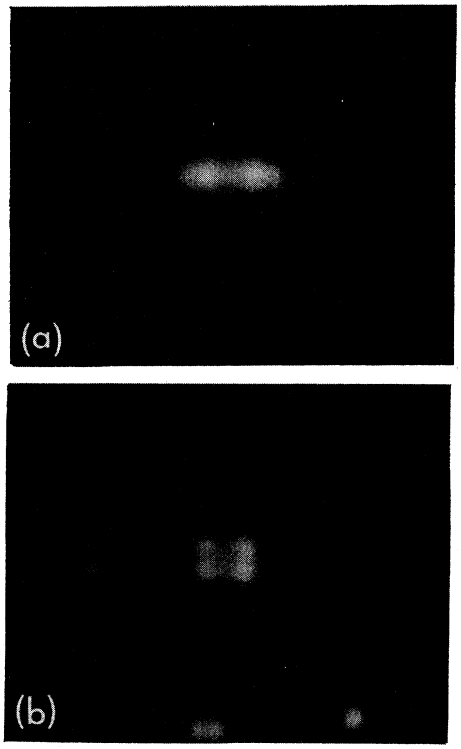

FIG. 4. A series of field-ion micrographs showing that for six adatoms, the ⟨110⟩-oriented linear chain is metastable, whereas the two-dimensional island is stable. (a) A linear chain of six adatoms. (b) The island of six adatoms assumed by the chain in (a) subsequent to heating to 270 K.

Pt(100) plane. In the EAM approach, the total energy of a metal is looked upon as the sum of two terms: (i) the energy to embed an atom into the local-electron density provided by the surrounding atoms; and (ii) the energy associated with pairwise electrostatic interactions. These terms are determined empirically by fitting to various known bulk properties of the metal under consideration which has been previously done for Pt.[6] The calculations performed here involve taking differences between the total energies of systems (substrate and adatoms) having different configurations, and/or numbers, of adatoms. For example, the difference in energy between a three-dimensional "slab" of Pt having a bare (100) surface E_s and the same slab having a Pt atom adsorbed on the (100) surface is the binding energy of Pt on Pt(100), E_0. Similarly, the nearest-neighbor pair interaction between two Pt adatoms on Pt(100) is the energy of the slab having two Pt adatoms in nearest-neighbor positions on the (100) surface minus (E_s+2E_0). In this way various pair and N-body interactions can be extracted from the total-energy calculations. It is very interesting that the calculations of the relative cluster stabilities using the EAM agree with the experimental observations, and that this agreement is achieved only if lattice relaxations are allowed for in the calculations. The importance of lattice relaxations can be seen by first calculating the relative stability of the chain and island configurations when both the adatoms and substrate are allowed to relax. In this case the experimentally observed oscillating chain and island stability is predicted: (i) for three adatoms the chain is of lower energy than the island by 159 meV; (ii) for four the island is lower in energy than the chain by 52 meV; (iii) for five the chain is lower in energy than the island by 32 meV; and (iv) for six adatoms the island is lower in energy than the chain by 240 meV. In addition, the seven adatom island with the seventh adatom bonded to one of the eight corner positions of the 2×3 island was calculated to be of lower energy than both the chain of seven adatoms, and the seven adatom island with the seventh adatom bonded to one of the two central adatoms on the long side of the 2×3 island, by 170 and 87 meV, respectively. (Actually, a corner position on a short side of the 2×3 island lowers the island energy relative to bonding to a corner position on a long side by 3 meV. The aforementioned energy differences of 170 and 87 meV refer to the case of bonding to the short side.) In contrast, if the substrate is frozen at its calculated "adsorbate free" equilibrium geometry, and not allowed to relax subsequent to the deposition of the adatoms, the island configurations are always more stable than the chain configurations. In this unrelaxed case, the islands of three, four, five, and six adatoms are lower in energy than their associated chain configurations by 1, 438, 462, and 915 meV, respectively.

We also calculated several pair interactions in the fully relaxed (unrelaxed) case described above: (i) the nearest-neighbor pair is attractive by 336 meV (299

meV); (ii) the second near-neighbor pair is repulsive by 121 meV (59 meV), and; (iii) the third near-neighbor pair is repulsive by 44 meV (3 meV). Given the pair interactions, and the energies of the cluster configurations, various N-body interactions can be extracted in the relaxed case. The most important were (i) the four-body interaction of four adatoms in the 2×2 island which is attractive by 163 meV, and (ii) the three-body interaction of three adatoms in the close-packed triangle which is repulsive by 66 meV. The corresponding values for the unrelaxed case were a four-body interaction that was repulsive by 22 meV and a three-body interaction that was attractive by 76 meV. For reference, the single adatom binding energy in the relaxed and unrelaxed systems was calculated to be 5.23 and 5.01 eV, respectively.

From the interactions calculated in the fully relaxed systems above one can rationalize the oscillatory stability of the chain and island configurations observed experimentally. The relatively large repulsive second-neighbor pair and triangular-triplet interactions tend to drive the formation of linear-chain nuclei; however, in addition to nearest-neighbor interactions, the surprisingly large four-body interaction of the 2×2 island helps to stabilize the island relative to the chain configuration for four, six, and more adatoms.

Although a detailed, theoretical understanding of the origin of such interactions is still lacking, it has been shown that the nonmonotonic nature of the interaction energies between adatoms as a function of separation can be due to a through-the-metal electronic interaction.[7,8] Here, the attractive or repulsive nature of the N-body interactions arises from the coupling of the adatoms wave functions through the surface. If the wave functions are in phase, the interaction will be attractive; whereas, if they are out of phase, a repulsive interaction results. Thus, the sign of the interactions will be a function of separation distance and direction on the surface. Nonmonotonic interactions may also result from lattice distortions due to the adsorption of adatoms. Further theoretical understanding is clearly required if the structural transitions in the adatom nuclei are to be understood.

The excellent agreement between theory and experiment regarding the structure of Pt adatom nuclei on Pt(100) allows for some fundamental understanding of adsorbate interactions on surfaces. The most noteworthy, in a general sense, is that the EAM calculations predict the experimentally observed relative chain and island stabilities only if the adatoms and substrate are allowed to fully relax indicating that such effects can play a critical role in determining the effective adatom-adatom interactions.

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[1]D. W. Bassett, in *Surface Mobilities on Solid Materials,* edited by V. T. Binh (Pergamon, New York, 1963).

[2]H. W. Fink and G. Ehrlich, Surf. Sci. **110**, L611 (1981).

[3]P. R. Schwoebel and G. L. Kellogg, Phys. Rev. Lett. **61**, 578 (1988).

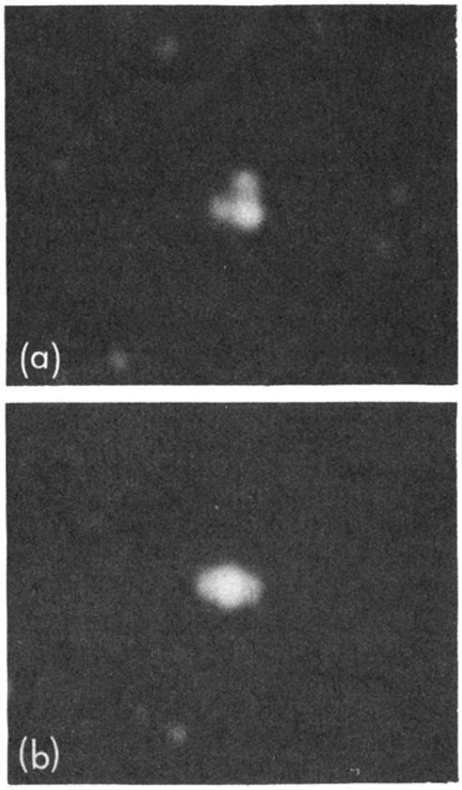
[4]P. R. Schwoebel and Peter J. Feibelman, Surf. Sci. (to be published).

[5]M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).

[6]S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).

[7]T. B. Grimley, Proc. Phys. Soc. **90**, 751 (1967).

[8]T. L. Einstein, CRC Crit. Rev. Solid State Phys. Mater. Sci. **7**, 261 (1978).



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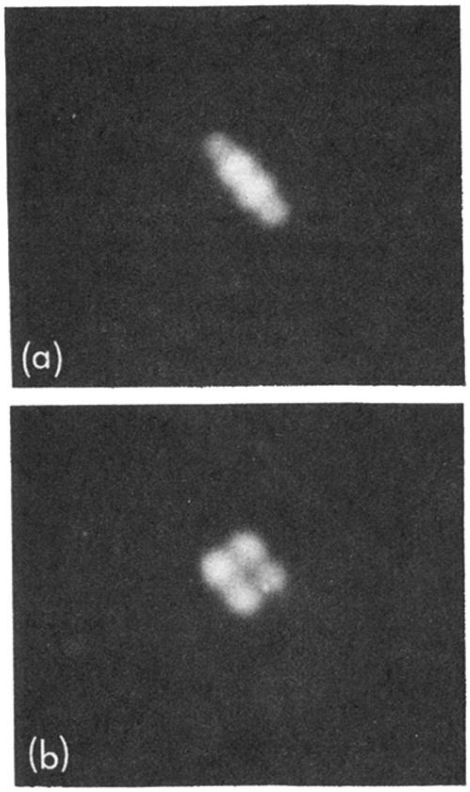

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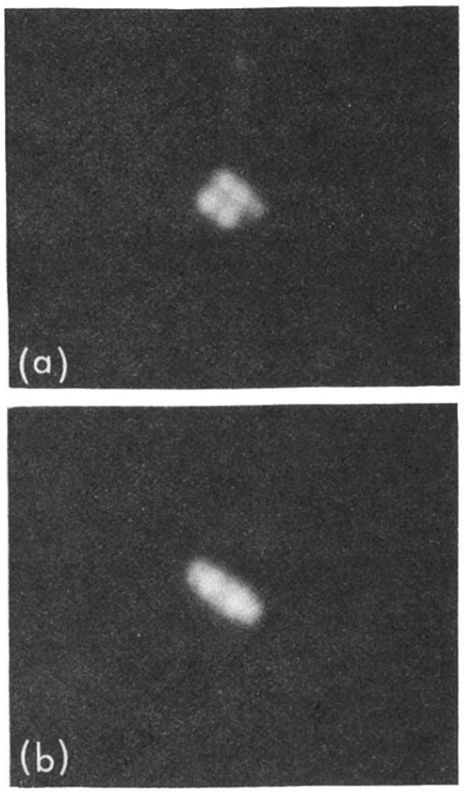

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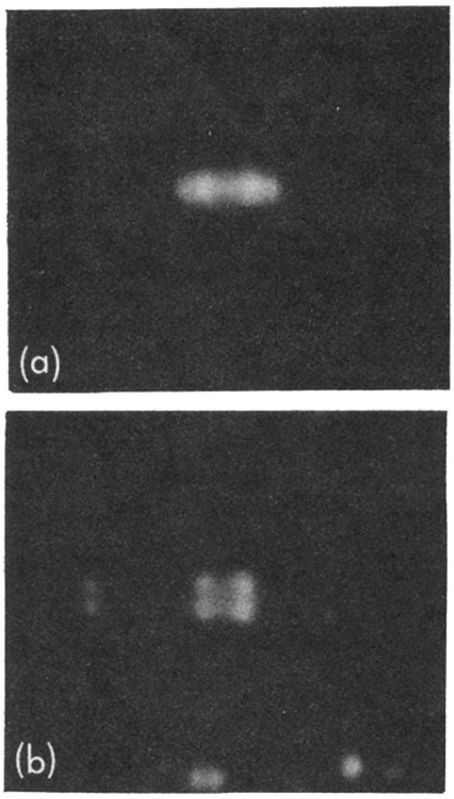

FIG. 4. A series of field-ion micrographs showing that for six adatoms, the ⟨110⟩-oriented linear chain is metastable, whereas the two-dimensional island is stable. (a) A linear chain of six adatoms. (b) The island of six adatoms assumed by the chain in (a) subsequent to heating to 270 K.