Direct Mapping of Adatom-Adatom Interactions

Fumiya Watanabe and Gert Ehrlich
Coordinated Science Laboratory and Department of Materials Science, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
(Received 15 July 1988)

The dependence of pair interactions at a metal surface upon interatomic distance as well as orientation has for the first time been explored by mapping out the two-dimensional distribution function for two metal atoms at equilibrium on W(110). Observations with the field-ion microscope have been made for the pairs Re-Pd, W-Pd, and Ir-Ir. For all these, interactions are highly anisotropic, with repulsion along $[1\bar{1}0]$ and [001], but long-range oscillatory attraction along $[1\bar{1}1]$. This anisotropy is consistent with elastic calculations; the observed decay of attractions is not.

PACS numbers: 68.35.Md, 61.45.+s, 68.55.Rt, 82.65.Dp

Despite the current interest in the growth and stability of chemisorbed overlayers and crystals, rather little is known about the interactions between adatoms which are responsible for cohesion in surface layers. There has been considerable theoretical activity in this field,[1-12] but the experimental information available is limited.[13] Some idea about the strength and range of atomic interactions at surfaces has been obtained by fitting phase diagrams of adsorbed layers, observed in LEED studies, with lattice-gas models in which the interactions are included as adjustable parameters.[14-16] This essentially macroscopic approach has been supplemented by observations of the radial distribution function for individual adatoms,[17-21] using the field-ion microscope.[22] Both theory and experiment have emphasized the dependence of pair interactions upon the interatomic separation. Some time ago, however, Einstein and Schrieffer[2] as well as Stoneham[4] recognized that interactions should be anisotropic, and preliminary experiments on W(110) indicate there may indeed be a significant dependence of the interaction energy upon the orientation of the atom pair on the surface.[23] In order to establish the functional dependence of two-atom energies upon interatomic distance *and* pair orientation, we have carried out an extensive two-dimensional mapping of interactions between metal atoms on W(110), the first such determinations on any surface.

The direct determination of interactions between adatoms is, in principle, straightforward. For a system at equilibrium at a temperature T, the probability $P(\mathbf{R})$ of finding two adatoms on a surface separated from each other by the vector $\mathbf{R}$ is given by

$$P(\mathbf{R}) = CP_0(\mathbf{R})\exp[-W(\mathbf{R})/kT]. \quad (1)$$

Here $P_0(\mathbf{R})$ is a geometrical factor, equal to the probability of finding two noninteracting adatoms at the separation $\mathbf{R}$, $W(\mathbf{R})$ is the potential of mean force acting between the two adatoms, or equivalently, the free energy of interaction at $\mathbf{R}$, and C is a temperature-dependent normalization term. To measure the interaction $W(\mathbf{R})$ we deposit two atoms on a W(110) surface in a field-ion microscope, equilibrate long enough in the absence of applied fields so that the atoms sample a wide variety of different configurations on the surface, and then cool the specimen to observe the location of the adatoms. For W(110), the structure of the substrate is not revealed in the field-ion microscope, but the adatoms are clearly imaged. By repeated observation of the adatoms after equilibration, a grid of the binding sites present on the surface can be mapped out, as in Fig. 1, and it is then an easy matter to assign coordinates to each adatom position.

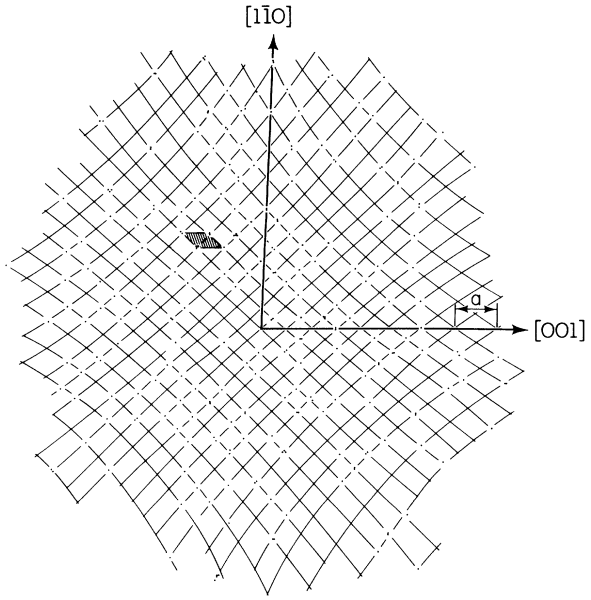

FIG. 1. Map of atom sites on W(110), obtained by repeated observation of iridium atoms after diffusion at $T=375$ K. Reproducibility is indicated by multiple observations at same site. Grid lines are drawn along close-packed directions connect points at which atoms are located. The surface unit cell is shaded in grey.

Extensive measurements of the equilibrium distribution have been done for the pair Re-Pd on W(110). This system was chosen as the rhenium atom remains fixed in place for temperatures at which palladium is quite mobile, greatly simplifying the analysis.[18] To minimize boundary effects in our experiments, a rhenium atom is deposited at the center of the (110) plane, which is typically ≈ 70 Å in diameter. A single palladium atom is then evaporated onto the surface, and is allowed to equilibrate for 20 sec at 205 K. Under these conditions, the rms displacement of the palladium atom exceeds 40 Å; that is, the excursions of the Pd adatom between observations are comparable to the radius of the plane under study, guarantying a thorough sampling of energetically different configurations. Equilibration is done in the absence of applied fields and conditions therefore correspond to an ordinary thermal ensemble. In all measurements imaging potentials are applied only after the surface has cooled close to 20 K; from repeated viewing of the adatoms, without heating, we know that the act of observation does not disturb the location of an adatom in any significant way. The distribution of Pd around a central Re atom, observed in 1600 such measurements, is shown in Fig. 2.

Two following features of the distribution are striking: (1) the extended range (> 8 Å) over which the frequency of Pd sightings deviates from the limiting values at long distances and (2) the pronounced effect of pair orientation, which changes not only the magnitude but also the sign of the interaction energy.

At the site closest to the Re adatom along the [001] direction, that is at the second-nearest-neighbor position (2,0), and also along the [1$\bar{1}$0] direction, at the third-nearest-neighbor position (0,2), no Pd atom is observed. In contrast, along the close-packed direction [1$\bar{1}$1] the frequency of atom sightings is far higher at (1,1), the site adjacent to the rhenium atom, than anywhere else, and it continues high beyond. The absence of atoms on second- and third-nearest-neighbor sites is *not* an artifact of the method of observation: These sites can occasionally be occupied by depositing palladium onto a cold W(110) with a rhenium adatom on it. The configurations so formed are stable under repeated observation, provided the surface is too cold for adatoms to move, but disappear upon heating to 200 K. We have also been able to show, by Monte Carlo simulations combined with observations of diffusion at low temperatures, that the observed distribution corresponds closely to that established at the equilibration temperature; redistribution of adatoms during cool down is insignificant.

Quantitative values for the interaction $W(\mathbf{R})$ are plotted in Fig. 3. These are derived from the observed distribution using Eq. (1), on the assumption that at sites more than ≈ 11 Å from the central rhenium atom, interactions have decayed to a negligible value. We estimate repulsive interactions of at least 45 meV for the sites, primarily along [1$\bar{1}$0] and [001], at which no Pd adatoms are observed. Along [1$\bar{1}$1], however, along the close-packed rows of substrate atoms, interactions are attractive. At (1,1), the nearest-neighbor site to the central rhenium atom, the interaction amounts to -35

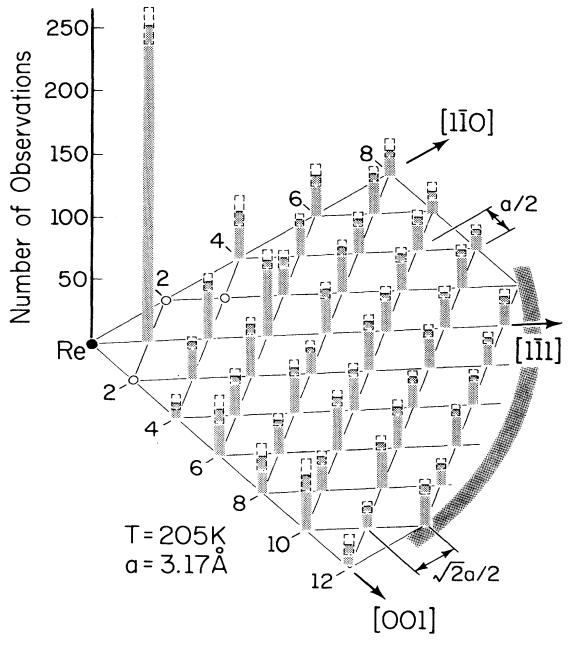

FIG. 2. Distribution of a single palladium atom around a rhenium atom centrally located on W(110), after equilibration for 20 sec at 205 K. All observations are mapped into the first quadrant. Broken lines indicate estimated standard deviation, shading gives limit beyond which edge effects may enter.

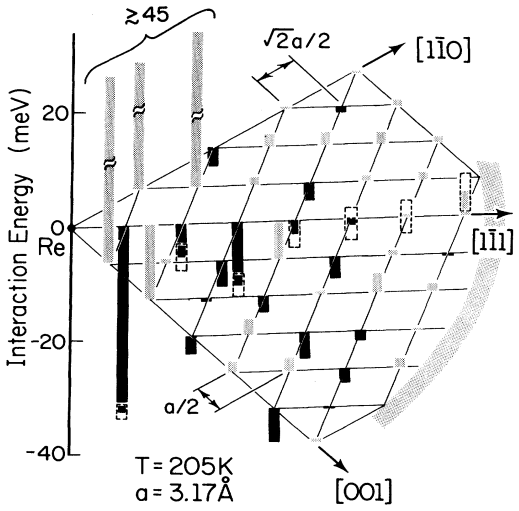

FIG. 3. Interaction energy $W(\mathbf{R})$ for Re-Pd on W(110), derived from the pair distribution function using Eq. (1). Attractive interactions in black, repulsions in grey. To reduce clutter, only selected standard errors are shown.

meV. Its magnitude diminishes with distance, but not monotonically, and even when the palladium atom moves along [1$\bar{1}$1] to the site at (3,3), the attraction still amounts to $\approx$ 12 meV.

The strong angular anisotropy and the long range of atomic interactions is not limited to Re-Pd. We have observed qualitatively similar effects in studies on W-Pd, and they are also evident in the interactions between two identical iridium adatoms, shown in Fig. 4. For the two iridium atoms, however, there are some important quantitative differences from the behavior observed for heteropairs. As is clear in Fig. 4, interactions between two Ir adatoms at the nearest-neighbor site, (1,1), are highly repulsive. Only at larger separations do interactions along [1$\bar{1}$1] become strongly attractive, as they are in the heteropairs already examined. It is also clear that the repulsions at sites adjacent to an Ir atom along [1$\bar{1}$0] and [001] are not as effective as in Re-Pd. Nevertheless, the general pattern of long-range anisotropic interactions is repeated.

The alternation between repulsion and attraction as the orientation of the atom pair on the surface is changed is expected if the substrate lattice is strained by the presence of an adatom[4]: that is, for indirect lattice interactions. Tungsten is elastically isotropic, but Kappus[6] has pointed out that pair interactions will nevertheless be anisotropic if the interactions between a single adatom and the lattice are anisotropic. If the forces between a single adatom and the lattice are repulsive along [001] and attractive along [1$\bar{1}$0], then elastic interactions between the strain fields around the individual adatoms will lead to attraction between adatoms in the [1$\bar{1}$1] direction, and repulsion along [001] and [1$\bar{1}$0].

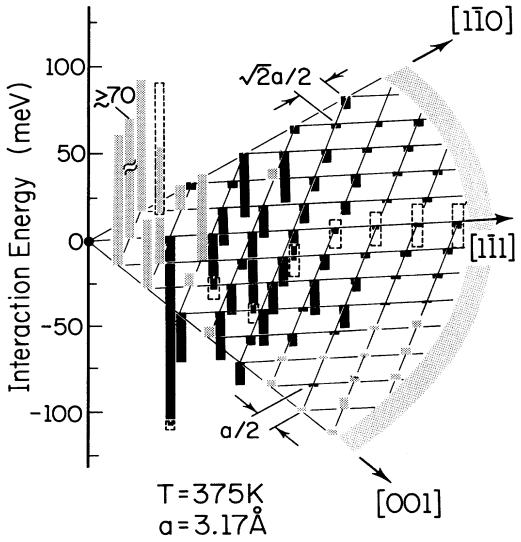

FIG. 4. Interaction energy between two iridium adatoms on W(110), derived from 1776 observations after 15-sec equilibration at 375 K.

This is the pattern observed in all the systems thus far examined on W(110). However, the elastic estimates predict a $1/R^3$ radial dependence for interactions in a given direction, rather than the oscillatory behavior actually observed along [1$\bar{1}$1] both for heteropairs and for two iridium atoms. For indirect electron interactions, Einstein and Schrieffer[2] found pronounced anisotropies even on a (100) cubium surface, and extensions of the theoretical estimates[9,10] for W(110) will certainly be of interest.

Despite individual differences, the unifying theme of all our observations on W(110) is that attraction dominates two-atom interactions along the close-packed [1$\bar{1}$1] direction, whereas repulsion is favored along [1$\bar{1}$0] and [001]. For iridium, these findings are in keeping with previous studies,[24,25] which indicate that chains of several iridium atoms on W(110) are preferentially oriented along [1$\bar{1}$1]. However, it also appears that the detailed information on pair energies that is now attainable cannot be simply applied to larger clusters. Preliminary measurements suggest that two-atom interactions do *not* account for the stability of Ir_3 trimers, and that many-atom effects[1] play a significant role in the cohesion of iridium clusters, as they do in other systems.[21]

This work was supported by the National Science Foundation under Grant No. DMR 87-22519.

[1]For reviews of early work, see T. L. Einstein, CRC Crit. Rev. Solid State Mater. Sci. **1**, 261 (1978); T. L. Einstein, Surf. Sci. **84**, L497 (1979); J. P. Muscat and D. M. Newns, Prog. Surf. Sci. **9**, 1 (1978); M. C. Desjonquères, J. Phys. (Paris), Colloq. **41**, C3-243 (1980).

[2]T. L. Einstein and J. R. Schrieffer, Phys. Rev. B **7**, 3629 (1973).

[3]K. H. Lau and W. Kohn, Surf. Sci. **65**, 607 (1977).

[4]A. M. Stoneham, Solid State Commun. **24**, 425 (1977).

[5]W. Kappus, Z. Phys. B **29**, 239 (1978).

[6]W. Kappus, Z. Phys. B **38**, 263 (1980).

[7]W. Kappus, Z. Phys. B **45**, 113 (1981).

[8]W. Kappus, Surf. Sci. **115**, L147 (1982).

[9]J. P. Bourdin, M. C. Desjonquères, D. Spanjaard, and J. Friedel, Surf. Sci. **157**, L345 (1985).

[10]H. Dreyssé, D. Tomanek, and K. H. Bennemann, Surf. Sci. **173**, 538 (1986).

[11]J. P. Bourdin, M. C. Desjonquères, D. Spanjaard, and G. Tréglia, Surf. Sci. **181**, L183 (1987).

[12]D. J. Feibelman, Phys. Rev. Lett. **58**, 2766 (1987).

[13]E. Bauer, in *The Chemical Physics of Solid Surfacs and Heterogeneous Catalysis,* edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1984), Vol. 3, Part B, Chap. 1.

[14]L. D. Roelofs, in *Chemistry and Physics of Solid Surfaces, IV,* edited by R. Vanselow and R. Howe (Springer-Verlag, Berlin, 1982), Chap. 10.

[15]A review has recently been given by E. Bauer, in *Structure and Dynamics of Surfaces II,* edited by W. Schommers and P. von Blanckenhagen, Topics in Current Physics Vol. 43 (Springer-Verlag, Berlin, 1987), Chap. 4.

[16]D. P. Landau, in *Applications of the Monte Carlo Method,*

edited by K. Binder (Springer-Verlag, Berlin, 1987), 2nd ed., Chap. 3.

[17]Field-ion microscopic studies of clusters have been surveyed by D. W. Bassett, in *Surface Mobilities on Solid Materials,* edited by V. T. Binh (Plenum, New York, 1983), p. 83.

[18]H.-W. Fink, K. Faulian, and E. Bauer, Phys. Rev. Lett. **44**, 1008 (1960).

[19]R. Casanova and T. T. Tsong, Phys. Rev. B **22**, 5590 (1980).

[20]T. T. Tsong and R. Casanova, Phys. Rev. B **24**, 3063 (1981).

[21]H.-W. Fink and G. Ehrlich, J. Chem. Phys. **81**, 4657 (1984).

[22]The technique is described by E. W. Müller and T. T. Tsong, *Field Ion Microscopy, Principles and Applications* (Elsevier, New York, 1969); J. A. Panitz, J. Phys. E **15**, 1281 (1982).

[23]H.-W. Fink, Ph.D. thesis, Technical University of Munich, 1982 (unpublished).

[24]D. R. Tice and D. W. Bassett, Thin Solid Films **20**, S37 (1974).

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