der due to the shear. The static structure factor is broadening and becoming more like that of a gas. In a gas the particles have a greater variation in separation. Measurements on the trailing edge ($k_y = 0$, $k_z < 0$) indicate similar results consistent with the general theoretical forms discussed.

Colloidal suspensions of highly charged particles have again[12,13] served as a model soft-sphere fluid and provided a means of studying model fluids, as well as real colloids. The position of the maximum intensity in $\mathcal{S}(\vec{k})$ along lines of constant θ is given by a simple distortion model for the pair correlation function and can be used to measure the relaxation time τ_a. A harmonic model illustrates similar ellipsoidal symmetry with a variation in the maximum amplitude of $g(\vec{r})$ as a function of θ. A similar variation is noted in intensity on the Debye-Scherrer rings as a function of θ as seen in Fig. 2; however, a more sophisticated model is needed to explain these observations quantitatively.

This work was supported in part by a grant from the Research Corporation.

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Evidence for Nonmonotonic Long-Range Interactions between Adsorbed Atoms

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(Received 3 December 1979)

The distribution function of the distance between a mobile and an immobile atom on a single-crystal surface has been measured for various temperatures, resulting in the first experimental demonstration of nonmonotonic long-range interactions. With W as the immobile atom and Pd as the mobile atom, at least two well-defined bond distances, 3.2 and 11 Å, are observed; with Re replacing W, at least one well-defined bond distance, 5.0 Å, and a strong anisotropy are seen. Additional bound states are indicated at larger distances.

PACS numbers: 68.20.+t, 73.20.Hb

The interaction between adsorbed atoms is one of the fundamental problems of surface physics. A considerable theoretical effort has been made, in particular during the past ten years, to obtain an understanding of these interactions (for a review, see Einstein[1]). Experiment, likewise, has been successful, for example, in measuring binding energies between dimers (for reviews, see Bassett and Tice,[2] Kellogg, Tsong, and Coulan,[3] Ehrlich,[4] and Tsong and Cowan[5]). The experimental confirmation of one of the major predictions of the theory, that of long-range oscillatory interactions, however, has been elusive. An apparently successful attempt at such a confirmation by field-ion microscopy (FIM), with Re atoms on a W(110) surface,[6] was later shown to be inconclusive for Re on W(110),[2] W(112), and W(123) (Ref. 7) surfaces. The only well-founded results indicating an "abnormal" distance dependence of the adatom interactions are limited to short distances: The (internal) binding energy of a Re dimer on W(112) with the smallest adatom distance (4.48 Å) is smaller than that with the next largest distance (5.25 Å) (100± 50 vs 165± 50 meV).[8] For distances $R > 7$ Å the two atoms behaved like independent particles.[7]

These negative results are not surprising because the predicted oscillatory interactions decrease rapidly with increasing distance. If they are to be demonstrated, dipole-dipole interactions and direct electronic interactions caused by overlap of the wave functions of the two atoms must be weak. This condition was fulfilled in the previous work.[2,5-7] However, a second condition was not fulfilled—the activation energy for surface diffusion must be small. Low diffusion temperatures T_{dif} can then be used resulting in small kT_{dif} values which allows the measurement of small interaction energies $E_i \gtrsim kT_{\mathrm{dif}}$. A third condition is that data collection and evaluation must be very efficient and accurate.

The last two conditions lead to the following choice: One atom should be mobile at the temperature at which the closely bound state dissociates at an acceptable rate, while the other should be immobile. The immobile atom gives a very dependable reference point for the measurement of the pair distribution function. Inspection of the literature, e.g., Fig. 3 in Ref. 2, leads to the choice of Re and W as immobile atoms and of Ni, Pd, or Pt as mobile atoms. This choice at the same time fulfills the first condition: The dipole moments of the adatoms are small,[9] and the close-spaced bond can be expected to be weak based on the dependence of the M_2 bond strength on the kind of metal (denoted as M) atom under study. Because an earlier study was concerned with Pd,[10] the pairs W-Pd and Re-Pd were chosen.

The field-ion microscope was equipped with movable Pd and W or Re evaporators which allowed us to deposit Pd, W, or Re at normal incidence onto the (110) surface. Thus chemical potential gradients across the (110) plane due to coverage gradients as they occur upon the usual evaporation from the side are avoided; therefore, no external driving force must be taken into account in our diffusion experiments. The sequence of FIM images shown in Fig. 1 illustrates various steps of a typical experiment. First a (110) plane with the desired diameter—about 40 Å in Fig. 1—is prepared by field evaporation. Then W or Re atoms are deposited onto the tip and subsequently removed all but one by successive controlled field desorption [Fig. 1(a)]. Usually this atom is close to the center of the plane because of the decrease of the field from the edge to the center of the plane. This procedure was repeated with Pd, resulting in a single Pd atom in addition to the W or Re atom [Fig. 1(b)]. Figure 1(c) shows the surface after a 40-sec anneal at 178 K without electric field. This closely bound dimer occurs in four distinct configurations, two of which can be seen in Figs. 1(c) and 1(d). In a small fraction of all anneals the dimer dissociates apparently [Fig. 1(e)] but recombines with high probability to the closely bound configuration [Fig. 1(f)]. Distances were measured with an improved mapping technique[10] of the centers of the image disks of the atoms.

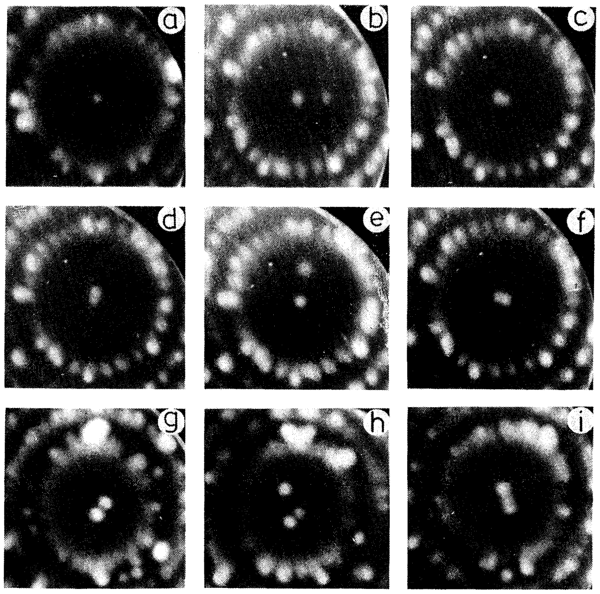

FIG. 1. Typical FIM images taken at 80 K of (a)-(f) W-Pd, (g) Re-Pd atom paris, and (h), (i) trimers on W(110). See text for explanation.

For the system W-Pd quantitative experiments were performed under the following sets of conditions [annealing temperature, annealing time, and diameter d of the (110) plane]: 162 K, 60 s, 50 Å; 178 K, 40 s, 40 Å; and 240 K, 30 s, 70 Å. In the absence of the W atom these conditions would give rms Pd-atom displacements $\langle r^2\rangle^{1/2} \equiv \bar{r}$ of 7, 19, and 2000 Å, respectively, based on the diffusion parameters $E_{\mathrm{dif}} = 0.50$ eV and $D_0 = 7\times10^{-4}$ cm^2 s^{-1}.[11] A comparison of the $\bar{r}$ and d values shows that the influence of the (110) plane boundary should be quite different in the three cases so that edge effects can be excluded if the three conditions lead to the same deviation from a statistical distance distribution function. A representative distance distribution function $N(r)$ is shown in Fig. 2 together with a map of

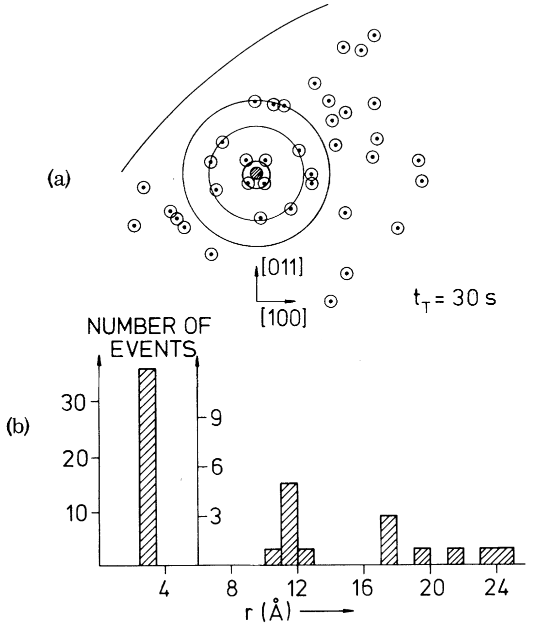

FIG. 2. Results of diffusion experiment with the W-Pd atom pair at 240 K. (a) Distribution of Pd atoms obtained from superposition of FIM images after various diffusion steps. For clarity, only part of the data is shown. The line in the upper left indicates the boundary of the (110) plane which causes the somewhat asymmetric distribution. (b) Histogram of W-Pd distances. Note change of scale.

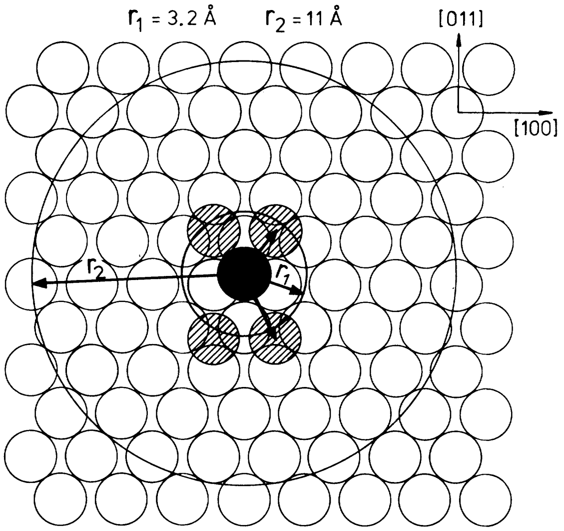

FIG. 3. Preferred Pd adsorption sites in the environment of a W atom on a W(110) surface. Only r_1 and r_2 are shown; r_{11} and r_{12} are indicated by arrows.

some of the observed Pd-atom locations. 110 annealing steps were made of which none left the Pd atom untouched and 63 lead to a statistical distribution for $r > 19$ Å because of the large $\bar{r}$ and kT at 240 K. For $r < 19$ Å distinct deviations from a statistical distribution (see, e.g., Refs. 2, 5, and 7) are seen: The closely bound state already mentioned at $r_1 = 3.2$ Å and another preferred distance at $r_2 = 11$ Å, separated by a distance range in which the Pd atom is never observed (Fig. 3). A possible third preferred distance is seen at $r_3 = 18$ Å. Although it does not occur frequently enough in Fig. 2 as to consider it significant, it is also a clearly preferred distance at the lowest temperature (162 K).

The energy difference between the two bound states r_1 and r_2 can be obtained if the assumption is made that the distributions are not determined by kinetic limitations but represent the equilibrium situation with state occupations determined by the Boltzmann factor weighted with the numbers n_1 and n_2 of the available states r_1 and r_2. The relative frequency W_i of the two states is then $W_2/W_1 = (n_2/n_1)\exp[-(E_2-E_1)/kT]$. In the case of completely isotropic forces all sites with $r_2 \pm \Delta r$ are equivalent so that $n_2 = 20-30$ depending on the r_2 uncertainty Δr; in the case of extreme anisotropy, e.g., bound states only in $\langle 111 \rangle$ directions, $n_2 = 4 = n_1$. The second case gives the upper limits $E_2 - E_1 = \Delta E = 28$, 31, and 30.5 meV for the three experimental conditions, with an average value of 30 ± 2 meV. A comparison of this value with $kT_{\mathrm{dif}} = 14$, 15, and 21 meV, respectively, shows how delicate these experiments are.

Figure 3 shows schematically the observed dimer states. For the r_2 state only the center distance is shown from which mean deviations of ± 1 Å occur. The four r_1 configurations are drawn asymmetrically as clearly evidenced by experiment: The frequency distribution of the r_1 distances has two maxima r_{11} and r_{12} with $r_{11}:r_{12} = 1:1.3$. If all atoms are in surface sites as assumed in Fig. 3, then theoretically $r_{11} = 2.74$ Å, $r_{12} = 3.71$ Å, and $r_{11}:r_{12} = 1:1.35$. Of the four surface sites available below the W atom in Fig. 3, only the indicated ones (r_{12}) are occupied. They are observed 2.8 times more frequently than the upper (r_{11}) sites.

For Re-Pd dimers an even weaker bond for the close-spaced dimer is expected on the basis of theory[12] and experiment[2-6,8] for M_2 dimers. Therefore, it should be easier to observe dimers with larger interatomic distances, and a smaller number of annealing steps should be necessary to reveal the preferred distances. Experiment confirms this expectation as shown in Fig. 4 which is based on 51 diffusion steps of 30-s duration at approximately 250 K on a 45-Å-diam (110) plane. A distance of 5 Å [Fig. 1(g)] is clearly preferred; another one of 8 Å is less pronounced. This second distance is frequently seen in trimers together with the 5-Å distance [Fig. 1(h)]. Distances below 5 Å are never observed in dimers but can be obtained with sufficient activation in trimers [Fig. 1(i)]. Observations with trimers and larger clusters will be reported and discussed in detail elsewhere.[13]

A detailed analysis of the distance and azimuthal distribution of the smallest dimer distance (5 Å) leads to the conclusion—illustrated in Fig. 4—that the Pd atoms are preferentially found in one of four azimuthally equivalent sites (a, indicated by full circles) although six other sites (b and c, indicated by triangles and squares, respectively) have exactly the same distance (5.03 Å) from the Re atom (n_a:n_b:n_c = 10:1:0). This indicates that there is a nontrivial azimuthal anisotropy superimposed on the radial distribution: The ⟨111⟩ directions are apparently preferred bonding directions, not only in closely bound dimers (WPd, M_2) but also in dimers with larger interatomic distances.

It is impossible at present to make a quantitative comparison between our experimental results and the theory of indirect electronic interactions for several reasons. First, there are no quantitative calculations for a system which is close enough to those investigated here. The most closely related work is that of Burke[12] on M_2 dimers on bcc M(110) surfaces. However, heteronuclear molecules are not treated in this work, and even for homonuclear dimers the calculated bond energies are much higher than the measured ones. Nevertheless, this work predicts the correct trends. Secondly, there is another interaction between adatoms, the elastic interaction,[14,15] which is important in our case. This interaction results from the superposition of the strain fields which the two atoms cause in the substrate. It is comparable in range to indirect electronic and dipole-dipole interactions and is expected to be significant here because W and Re are very strongly bound to the substrate causing considerable elastic strain. Although the resulting interactions are repulsive for identical adatoms on an elastically isotropic substrate they can be attractive for different adatoms.[14] Recently it was shown[16] that the interaction can be attractive in certain directions, even for identical atoms, if the force dipole tensor, which creates the surface stress, is sufficiently anisotropic.

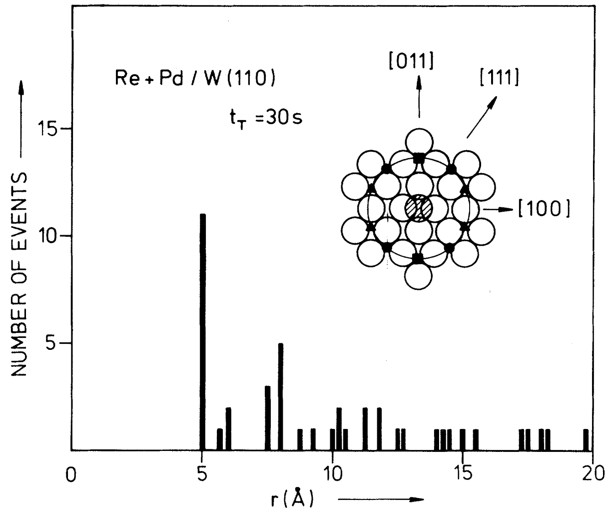

FIG. 4. Results of diffusion experiment with Re-Pd atom pair at approximately 250 K. (A temporary instability in the feedback system of the temperature control caused T variations of ± 10 K.)

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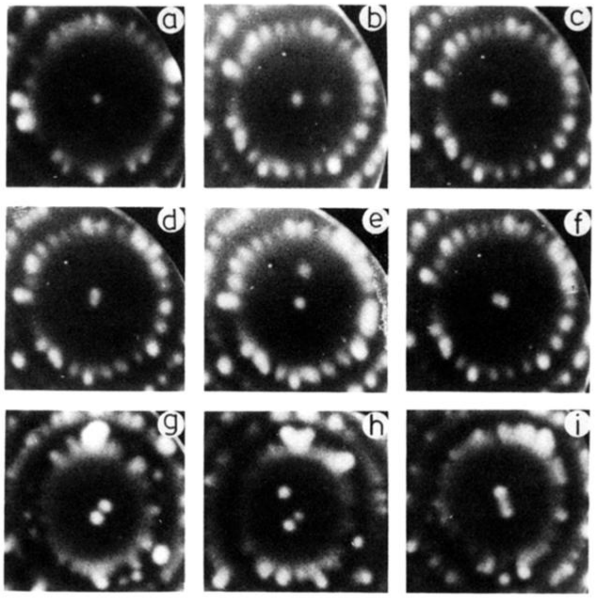

FIG. 1. Typical FIM images taken at 80 K of (a)-(f) W-Pd, (g) Re-Pd atom paris, and (h), (i) trimers on W(110). See text for explanation.