Direct measurement of pair energies in adatom-adatom interactions on a metal surface

T. T. Tsong and R. Casanova
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802
(Received 18 November 1980; revised manuscript received 9 March 1981)

Pair energies in adatom-adatom interaction on the W{ 110 } plane were obtained for Re-Re, W-Re, Ir-Ir, and W-Ir pairs. Each set of pair energies was derived from an experimental pair distribution involving about 1000 field-ion-microscope observations with exactly two adatoms on a W{ 110 } plane, and a theoretical pair distribution calculated for two noninteracting atoms on a plane of similar shape and size. The Re-Re interaction exhibited an oscillatory tail beyond 10 Å. The amplitude was about 8 meV from the 10-Å range. A strong repulsive region existed near 5 Å. These results were completely different from existing data for Re-Re interaction on the W{ 112 } plane, strongly indicating a crystal plane dependence of the adatom-adatom interaction. Since, of all the adatom-adatom interactions examined theoretically so far, only the indirect interaction exhibited an oscillatory tail, we believe that our results confirm the existence of such an interaction and also give quantitatively reliable data on it. The W-Ir interaction also clearly showed an oscillatory tail. However, our data on W-Re and Ir-Ir interactions, while giving some indication of oscillatory tails, did not exhibit these tails clearly. From the pair distributions we also derived, for the first time, reliable values for the pair energy at the closest bond separation. They were 99.0 ± 0.7, 82.0 ± 2.5, and 53.2 ± 3.6 meV, respectively, for W-Re, Ir-Ir, and W-Ir pairs. This study represents one of those rare cases where atomic interactions over large distances have been obtained in solid-state and surface phenomena with a direct method.

I. INTRODUCTION

The force laws governing the interaction of two atoms adsorbed on a solid surface represent some of the most fundamental information in surface physics.[1] Such information is vital to an atomistic understanding of surface phenomena. Several effects have been considered theoretically in the past,[2] including a dipole interaction,[3] a weak van der Waals interaction,[4] an interaction due to a mutual elastic distortion of the substrate lattice by the adatoms,[5] an interaction arising from the substrate phonon field,[6] and an indirect interaction.[7–10] All the interactions, except the last one, give rise to weak pair energies monotonic in distance dependence. The indirect interaction arises from the fact that the wave functions of both adatoms can tunnel through narrow potential barriers to the metal and couple with propagating metal wave functions. The asymptotic form of the indirect interaction is oscillatory.

Adatom-adatom interactions can be studied directly by field-ion microscopy.[11] Macroscopic techniques can give only indirect information. Since the range of interaction is comparable to the distances between adatoms in macroscopic adsorption studies, the information derived reflects the potential of mean force rather than the pair interaction.[12] It is well known that it is a hopelessly difficult task to derive pair interaction from a potential of mean force unless the particle density is very low. In field-ion microscopy (FIM), pair interaction between two adatoms can be studied with exactly two adatoms on a plane.[11] Thus, pair energy as a function of distances can be measured directly.

A direct FIM observation of cluster formation and dissociation was reported by Bassett and Parsley[13] in 1969. From the dissociation temperature, they estimated binding energy of a few diatomic clusters. In 1971, Tsong observed the long-range interaction between diffusing atoms.[11,14] The cooperative walks of two to four adatoms in adjacent channels of the W{ 112 } plane were observed. A pair distribution at two separations was measured, and the pair energy difference at the two separations was calculated.[11] Tsong also reported that on the W{ 110 } plane, Re adatoms repelled each other[11] at around 5 Å. At greater distances, Re-Re interaction exhibited an oscillatory struc-

ture. This observation was later substantiated with a measurement of radial distributions with five Re adatoms on a W{ 110 } plane.[15] The potential of mean force that was derived, which should closely approximate the pair potential energy at low particle density of that FIM experiment, exhibited an oscillatory tail. The result, however, was questioned, since statistical fluctuations of the data were comparable to the amplitudes of the oscillation.[16] Also, experiments on Re-Re interaction on the W{ 112 } plane showed that the interaction was less than $\frac{1}{2}kT$, $\approx$ 15 meV, beyond 9 Å; no long-range oscillatory tail was observed.[17] Despite the uncertainties, the result has attracted considerable interest.[8-10]

Ever since we started an FIM study of the long-range force between adatoms, we have been continuing the study with various adatom pairs on the W{ 110 } plane, often with thousands of heating periods. Recently, we reported a study of pair interaction of Ir-Ir and W-Ir pairs on the W{ 110 } plane.[18] We present here a study of W-Re and Re-Re pairs on the W{ 110 } plane. Each pair distribution contains more than 1000 heating periods of observations. The W-Ir and Ir-Ir data were analyzed by assuming the substrate plane to be circular in shape. In this report, the new as well as the old data will be analyzed by accounting for the slightly elliptical shape of the substrate planes.

There are several reasons for choosing the W{ 110 } plane for adatom-adatom interaction studies. First, it is a very smooth plane with the largest-density-of-adsorption sites available on a W field-ion-emitter surface. The adatoms can assume a wide range of separations, from the closest possible bond distance to almost the diameter of the plane. No severe distance restrictions such as two adatoms on the adjacent channels of the W{ 112 } exist. Second, the W{ 110 } plane is known to be the least susceptible to contamination of all planes; thus, contamination problems can be minimized. Third, as the plane is comparatively smooth, wave-mechanical-interference effects of the indirect interaction are expected to show up more readily. The larger size of this plane also enables us to study the asymptotic behavior of the interaction. Since a large two-dimensional plane also contains a big area and a great number of adsorption sites, many observations have to be made for each pair distribution for the data to be statistically significant. Each of the pair distributions reported here contains about 1000 heating periods. The data are further subjected to statistical smoothings, as will be described later.

II. EXPERIMENTAL PROCEDURES

Detailed procedures of single-adatom field-ion-microscope experiments are already well established, and can be found elsewhere.[19] The unique advantage of FIM single-atom experiments has been the capability of processing a substrate plane to atomic perfection by field evaporation, and by controlling the number of adatoms participating in an experiment by repeated depositions and controlled field desorptions.[11]

In the present experiment, involving long hours of experimentation with two atoms on a plane, an extremely rigorous vacuum requirement was mandatory. After a specimen replacement, the system was always subjected to several cycles of baking and degassing. Each cycle consisted of about 20 hours of baking of the entire system at 250 °C, degassing of the Ti-sublimation pump during the baking, ion bombardments of the channel plate by pure helium field ions for several hours, degassing of the deposition source coil close to the melting point, extensive degassing of the ion gauge, and heating of the Vyco glass bulb to 500 °C. The vacuum, after almost one week of rigorous processing, was always about 2×10^{-11} Torr, the x-ray limit of the ion gauge, before the cold finger and the getter were cooled. Vyco-glass-diffused helium was exclusively used for the imagings. The diffusion temperature was 350 °C. Exactly two atoms, of either identical species or different species, were deposited on a well developed plane by repeated depositions from source coils and controlled field desorptions. A field-ion micrograph was taken after each heating period of 60 sec at 330 ± 5 K. No voltage was applied during the heatings; thus, adatoms assumed separations with no interference from the imaging field. The adatom positions were mapped out using lattice atom images as fiducial marks. The distance calibration was based on the smallest displacements observed in single W adatom diffusion at low temperatures, which was taken to be 2.74 Å, the nearest-neighbor distance of the substrate lattice.[20] This was based on all our available evidence that a W adatom sits on a lattice site on the W{ 110 } plane.[20,21] It was not evident, however, that other adatoms such as Ir and Re also sit on lattice sites. Since our data analysis took the averages of frequencies of observations over 3 ranges of 1 Å each, the exact site of adsorption had no significant effect.

Pair distributions were plotted as histograms with distance intervals of 1 Å each. Although when adatoms are separated by only a few Å the distance can

be determined with an accuracy of 1 Å, in general, this is not possible because of an intrinsic nonuniform magnification of the field-ion images. The 1 Å interval is only a convenient starting point for further statistical data smoothings, as will be discussed in the next section.

III. METHOD OF DATA ANALYSIS

The adatom-adatom pair interaction is defined as the difference in the potential energy of an adatom on the plane with and without the presence of another adatom on the plane. This definition assumes that the two adatoms occupy equivalent adsorption sites on the surface. All FIM observations indicate that the interaction between two metallic adatoms on a metal surface is very much weaker than the interaction of the adatoms with the substrate surface.[19,22] It is, therefore, reasonable to assume that the adatoms sit on equivalent sites, irrespective of their distance-dependent interaction. For W adatoms on the W{ 110 }, most available evidence shows that the adsorption site is the lattice site.[20,21] We will assume that adsorption sites for Ir and Re adatoms on the W{ 110 } are also lattice sites. Again, since our analysis is based on average frequencies of observations within distance intervals of 3 Å all questions concerning the exact site of the adsorption are unimportant.

When two adatoms are confined to a plane of reflective boundary, the thermodynamic equilibrium pair distribution, as obtained by repeated observations with two adatoms, depends not only on the pair interaction but also on the geometry of the plane. To derive the pair interaction, we must first find out the effect of the plane geometry and the discrete site adsorption on the pair distribution. The pair interaction, then, can be derived by comparing the experimentally measured pair distribution with a calculated pair distribution for two noninteracting atoms on a plane of the same size, shape, and structure.

When two adatoms are present on an elliptical plane of major axis a, the range of possible adatom separations is from r_0 to $2a$, where r_0 is the closest possible bond length between the two adatoms, which is about 2.74 Å, the nearest-neighbor distance of the substrate lattice. In an experimental measurement, the exact distance between two adatoms cannot be determined. The accuracy of distance measurements depends very much on the locations of the adatoms on the plane, and also on the distances. Since the number of experimental observations is also limited, a pair distribution is plotted in the form of a histogram with a distance interval of Δr.

In our measurements, a was about 25 to 30 Å. Δr was taken to be 1 Å. The number of observations for each pair distribution was about 1000. The frequency of observation falling into a distance range of Δr was thus ~ 20. The expected statistical fluctuations were simply too large. The accuracy of the distance measurement for large separations was expected to be worse than 1 Å. We therefore used a standard method to smooth the experimental pair distribution. This method took the sum of the frequency of observation of the distance interval in question with those of the two nearest-neighbor intervals as the frequency of observation of this interval. Thus, energy states that were sharply defined spatially, but weak, may have escaped observation. Our method of analysis was therefore deliberately conservative, intended to avoid misinterpreting statistical fluctuations as spatially very sharply defined energy states. Although such states have been claimed to exist,[23] we believe that this is unlikely unless they are near an impurity atom which is present in the substrate surface or is adsorbed on the surface.[20]

The expected relative probability of observing atomic separations falling within r and $r + \Delta r$ for two noninteracting atoms is the product of the average density of adsorption sites in that distance range, and the probability of having an atomic separation falling in the same range on a structureless plane. A structureless plane means that an adatom can sit anywhere on the plane.

The average number of adsorption sites per unit area in the range between r and $r + \Delta r$ is proportional to the number of adsorption sites within an area enclosed by circles of radii r and $r + \Delta r$, $n(r)$, divided by r. $n(r)$ can be easily calculated from the structure of the substrate lattice, as has been shown in Fig. 1 in Ref. 18.

The relative probability of having an atomic separation falling within the range from r to $r + \Delta r$ on a structureless plane of elliptical shape is very difficult to solve analytically. However, it can be solved in a straightforward fashion using a numerical method which involves quadruple summations. As shown in Fig. 2, this method consists of dividing the entire area of the elliptic into small squares of the width $\Delta x = \Delta y$, and calculating all the distances from the center of each of the squares to that of the other squares. These distances are plotted in a histogram, and then normalized and smoothed. This function, shown in Fig. 3, can be called the pair

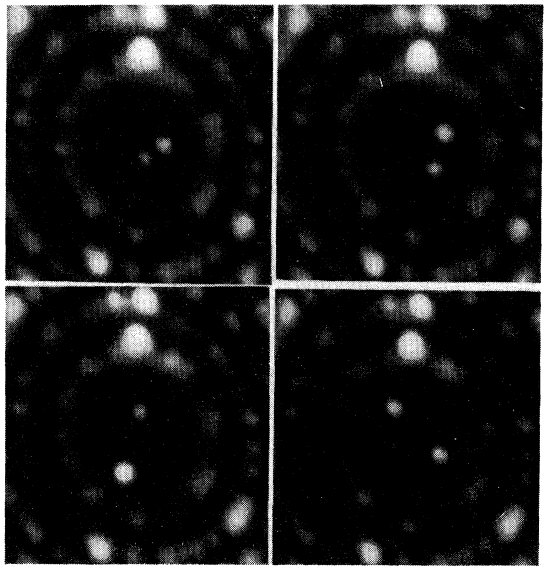

FIG. 1. Typical field-ion images showing two adatoms Ir and Ir at various locations on a W{ 110 } plane. When adatoms are near the plane edges, their image is greatly magnified; thus, accurate determination of atomic separation becomes difficult. The averaging procedures, as discussed in the text, are thus necessary.

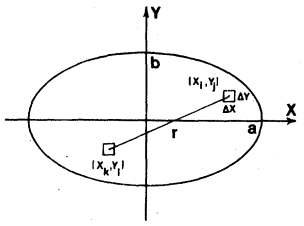

FIG. 2. Method of evaluating $F(r)$. The elliptic is divided into small squares of the width $\Delta x = \Delta y$. All the distances from the center of each square to all the other squares are calculated and plotted in a histogram. The distribution is then normalized and smoothed.

probability density function on an elliptical plane $F(r)$. The pair probability density function on a structureless circular plane can be partially solved analytically, and has been discussed by us earlier.[15,18] The present numerical method agrees with the previous result for a circular plane.

For two noninteracting atoms, the probability of observing a pair separation falling into a small distance interval of Δr about r is given by

$$p_0(r) = Cn(r)F(r)/r \ , \tag{1}$$

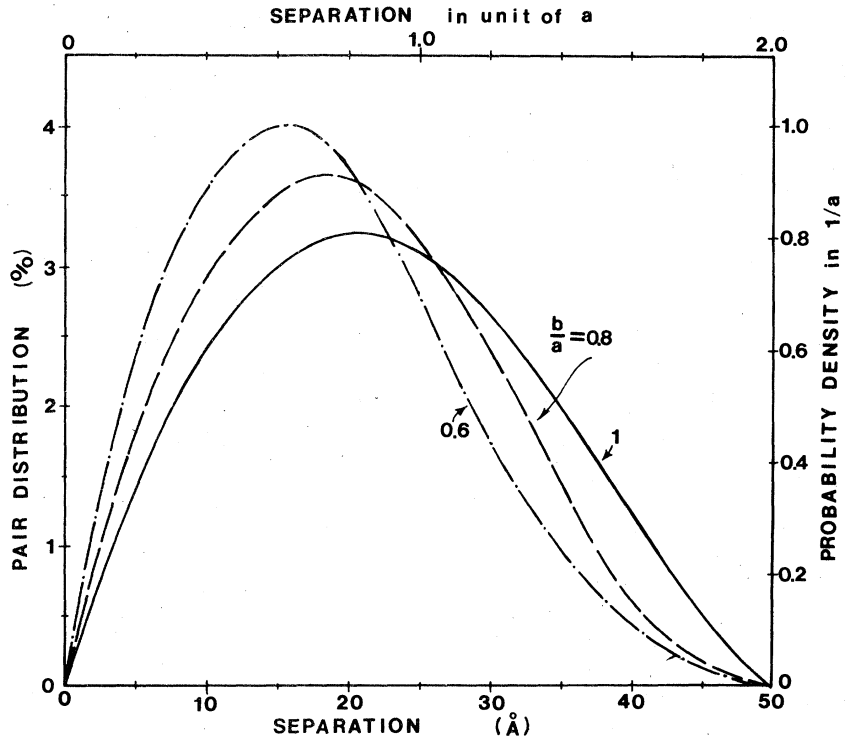

FIG. 3. Pair distributions for two noninteracting atoms on a structureless, elliptical plane. Left-hand side and lower scales are for planes with major axis $a = 25$ Å. Right-hand side and upper scales are for any plane of any size. The scales are now in reduced units.

where C is a normalization constant given by

$$C = \left[\sum_{i=0}^{2b/\Delta r} n(r_i) \frac{F(r_i)}{r_i} \right]^{-1} . \quad (2)$$

r_i is given by $(i + \frac{1}{2})\Delta r$. Figure 4 gives an example of the pair distributions on an elliptic of $a = 25$ Å, and $b = 15$, 20, and 25 Å.

The experimentally observed frequencies in various distance intervals $p_e(r)$ are related to each other by the pair energies $U(r)$ and the statistical weights $p_0(r)$

$$\frac{p_e(r_i)}{p_e(r_j)} = \frac{p_0(r_i)\exp[-U(r_i)/kT]}{p_0(r_j)\exp[-U(r_j)/kT]} . \quad (3)$$

Thus,

$$\frac{p_e(r_i)}{p_0(r_i)} = K \exp\left[-\frac{U(r_i)}{kT} \right] , \quad (4)$$

where K is an undetermined proportionality constant. The pair energy is given by

$$-U(r_i) = E_c(r_i)$$
$$= kT \ln[P_e(r_i)/P_0(r_i)] - kT \ln K . \quad (5)$$

$E_c(r)$ is the cohesive energy of the adatom-adatom interaction, defined simply as the negative value of the pair energy. An interaction energy is always relative, depending on the choice of a reference. The proportionality constant can be obtained by choosing a proper reference level. In our data analysis, we simply choose $K = 1$. This is equivalent to choosing $U(r \rightarrow \infty) = 0$ as in the conventional definition of the pair energy.

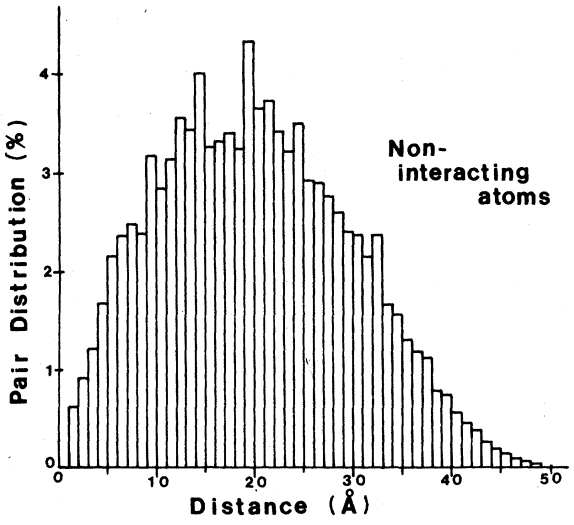

FIG. 4. Normalized theoretical pair distribution for two noninteracting atoms on an elliptical plane of $a = 25$ Å and $b = 20$ Å. The plane has the W{ 110 } structure; the same averaging procedures as in the experimental data analysis are used to derive this histogram.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Re-Re interaction on the W{ 110 }

Rhenium adatoms on the W{ 110 } plane exhibit high evaporation fields.[22] Accidental field evaporation of adatoms does not occur. Thus, the Re-Re pair was one of the earliest systems chosen for studying atomic interaction.[15] It was reported in 1972 by Tsong[11] that around room temperature, Re adatoms on the W{ 110 } plane repelled each other below ~ 5 Å. A weak binding state existed around 7 Å using a different distance calibration method as was used in the present study. However, heating to about 400 K resulted in an occasional observation of closely bound diatomic clusters which were found to be unstable with respect to migration. From these observations, it was concluded that Re-Re interaction exhibited at least two attractive regions and a repulsive region, indicating a possible oscillatory behavior.[11] A subsequent study of radial distributions with five Re adatoms on a W{ 110 } plane[15] indicated again that the adatoms did not form closely bonded diatomic clusters at 330 K. The potential of mean force derived exhibited a long-range oscillatory tail.[15] From dissociation time measurement of the closely bonded diatomic clusters, it was concluded that an attractive region existed around 3 Å with a cohesive energy of ~ 260 meV.

In the present investigation, we have carried out a similar experiment with Re adatoms on the W{ 110 }, but with exactly two adatoms on a plane. The heating temperature was 330 ± 5 K. Each heating period was 60 sec. Figure 5 shows a normalized experimental pair distribution obtained from 1045 observations. Not even once was a bond separation below 6 Å observed. If there is no strong repulsive force existing below 6 Å, one expects a frequency of more than 30 for observing a bond length below 6 Å.

When the pair distribution was compared to the theoretical pair distribution of a circular plane of diameter 50 Å published recently,[18] a pair energy shown in Fig. 6 was obtained. The statistical errors were calculated by using $\pm \sqrt{N}$ as the uncertainty in observation of N events. The pair energy shows a

small-amplitude oscillatory tail superimposed on a slowly varying attractive potential. The oscillatory tail, while very small (with an amplitude of only $\sim$ 8 meV), is clearly visible and cannot be taken as statistical fluctuation. The slowly varying attractive potential is similar to what has also been recently observed in Ir-Ir and W-Ir interactions.[18] It was speculated that this could be due to adatom — plane-edge interaction. However, when the pair distribution for two noninteracting particles on an elliptical plane of eccentricity 0.8 was used for comparing with the experimental data, a pair energy as shown in Fig. 7 was obtained. The small oscillation was then more clearly visible, while the shallow attractive potential had disappeared. We can therefore conclude that the slow attractive potentials observed earlier for Ir-Ir and W-Ir interactions are artifacts of approximating the real elliptically shaped W{ 110 } planes with a circular plane. This point will be discussed further. The results of this study, therefore, confirm qualitatively the earlier results on a potential of mean force.[15] The present result, however, is the first quantitatively reliable pair energy for the Re-Re interaction on the W{ 110 } plane.

Earlier observations[11,15] indicate that the closely bonded ($\sim$ 2.74 Å) Re diatomic cluster can be formed by heating the surface to $\sim$ 400 K. We have attempted to obtain more reliable data for the cluster formation in this study, but have not been successful. In one experiment with two Re atoms on a W{ 110 } plane, not a single closely bonded Re diatomic cluster was formed in 20 heating periods of two minutes each at 390 K, plus 15 heating periods of three minutes each at 390 K, plus 20 heating periods of two minutes each at 400 K. In another experiment with two Re atoms at 410 K, in one case a bonded cluster was observed after 29 heating periods of one minute each, in another case after 21 periods, and in two cases after 15 periods. In all four cases, the cluster dissociated within one heating period. These results, combined with the 1045 heating periods at 330 K without observing a single closely bonded diatomic cluster, seem to indicate that the very high repulsive potential existing around 5 Å prevents the limiting amount of data available to represent a true thermodynamic equilibrium condition in the distance range below 5 Å. However, if this is the reason, why was the closely bonded Re diatomic cluster never seen at 330 K in as many as 1045 heating periods? It should also be noted that the cluster is very unstable, having an average lifetime of less than 30 sec at 410 K. One may suspect that the formation of the diatomic cluster is caused by an impurity atom coming from the tip shank, which becomes mobile at around 400 K. Currently, the situation is too uncertain to reach a conclusion on the formation of the closely bonded Re-Re clusters. Thus, while the present observation is consistent with the earlier ones, we will not estimate the cohesive energy at the closest bond by a dissociation rate measurement as has been done previously.[15] Such a method can at best give an order-of-magnitude estimate of the pair energy, but

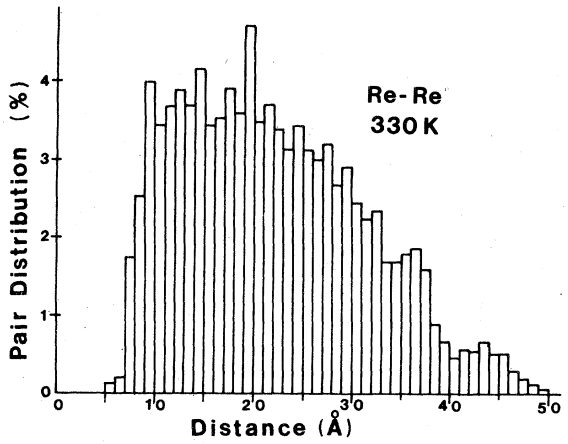

FIG. 5. Normalized experimental pair distribution obtained from 1045 observations with two Re adatoms on the W{ 110 } plane at 330 K.

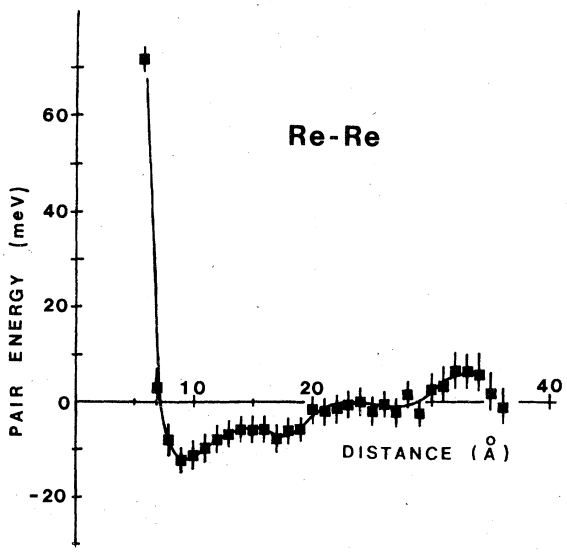

FIG. 6. Pair energies derived for Re-Re interaction. The W{ 110 } planes are approximated by circular planes of radius 25 Å. The slowly varying potential could be misinterpreted as a repulsive interaction between the adatoms and the plane edges.

no accuracy can be achieved. For some atomic pairs, this information can be obtained accurately by pair distribution measurements, as will be evident from further discussions.

It is appropriate to point out here that our results are different from those derived from cooperative-walk studies of two Re adatoms in adjacent channels of the W{ 112 } plane.[17,24] Studies on this plane indicate an attractive potential at about 5.2 Å, and that the interaction beyond 7 Å is small. Our results on W{ 110 } definitely did not find an attractive potential around 5 Å, but rather a repulsive potential (see Fig. 7). We must conclude that adatom-adatom interaction is specific not only to metals but also to crystal planes. Such specificity has in the past not been emphasized either in experimental studies or in theoretical studies. There are also many other evidences of the crystal plane specificity of atomic interactions. The closely bonded diatomic clusters Re_2 and W_2 on the W{ 110 } dissociate readily around 400 K. W_2 on the W{ 110 } is very mobile around 400 K, and is unstable. On the W{ 112 } plane, when two Re atoms or two W atoms form a closely bonded diatomic cluster within an atomic channel, the cluster is very stable and is immobile around 400 K. Only when the temperature is raised to beyond 500 K can such clusters be dissociated. At this temperature, the small W{ 112 } plane also starts to dissolve by losing atoms from the plane edges.

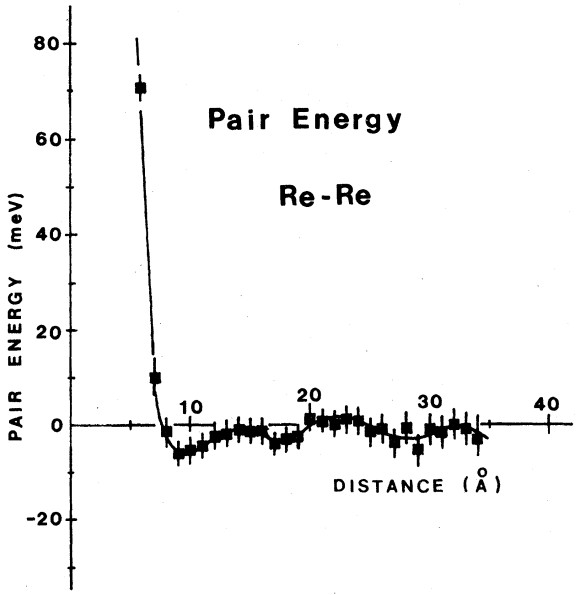

FIG. 7. Pair energies for Re-Re interaction derived by using a realistic plane shape, with elliptics of $a = 25$ Å and $b = 20$ Å.

B. W-Re interaction on the W{ 110 }

In Re-Re interactions, not a single closely bonded diatomic cluster was found in more than 1045 heating periods of 60 sec each at 330 K. This was not the case with W-Re, Ir-Ir, and W-Ir pairs. For the W-Re pair, out of 1111 heating periods, as many as 332 times the atoms were found to be in the closest bonded diatomic cluster form. The interatomic distance was 2.74 ± 0.50 Å. The first nearest-neighbor distance of the substrate lattice was 2.74 Å. The uncertainty was that expected from FIM distance measurement in this distance range, estimated from single-atom mappings as discussed earlier.[11,20] The closely bonded diatomic cluster is metastable with respect to diffusion. Of the 332 observations, 47 times they were found to be dissociated within one heating period, and 33,21,11, 4,5,2,2,0,2,0,1 times, respectively, within 2 to 12 heating periods. The average lifetime at 330 K is thus approximately 48.5 sec.

The experimental pair distribution obtained at 330 K from these 1111 observations is shown in Fig. 8. The frequency in each Å interval is the average of the frequencies of three-neighbor intervals as described earlier, except for the frequency in the 2—3 Å range. In this latter case, there were enough statistics within an interval, and there was no large uncertainty in determining the atomic separations. In Fig. 9, the pair distribution derived from Eq. (5) is given. From the pair energy, a few significant features can be drawn. A strong binding state existed at a distance of 3 Å; the bond strength was

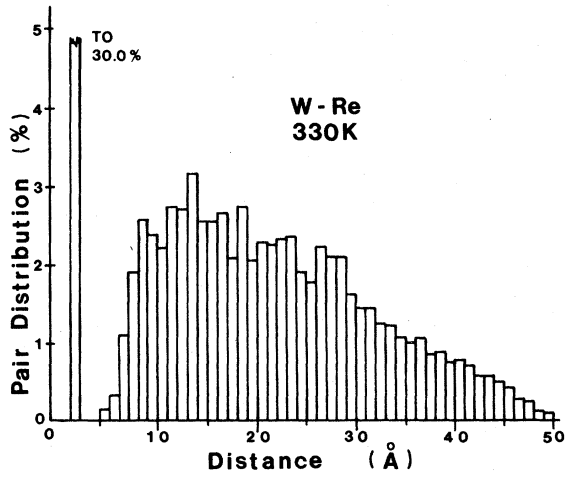

FIG. 8. Normalized experimental pair distribution obtained from 1111 observations with one Re and one W adatoms on the W{ 110 } plane at 330 K.

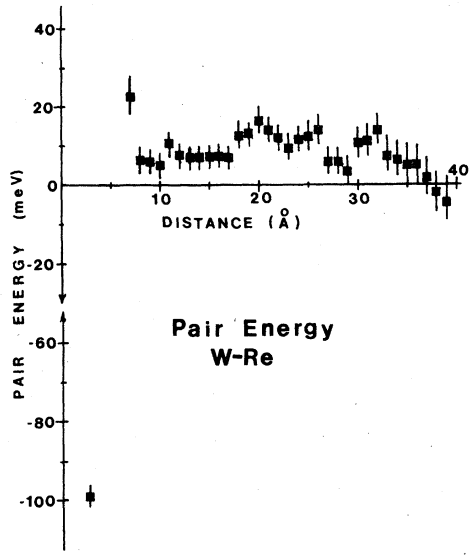

FIG. 9. Pair energies derived for W-Re interaction using a realistic plane shape.

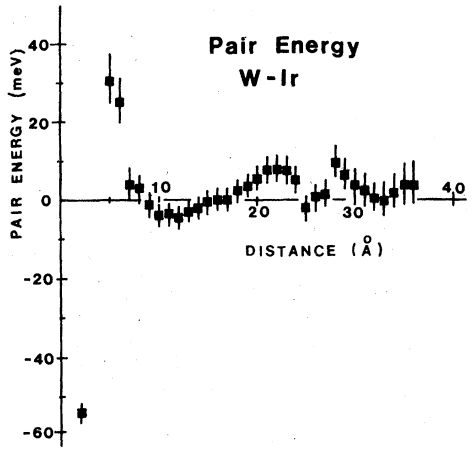

FIG. 10. Pair energies derived for W-Ir interaction using a realistic plane shape. The experimental pair distribution has been published by us in Fig. 9(b) of Ref. 18. It is from 947 observations.

99.0 ± 0.7 meV. Between 3 and 6 Å, there was a repulsive region with a repulsive potential energy of more than ~ 50 meV. Our limited number of observations does not permit us to give a reliable estimate of this repulsive energy. Beyond this distance range, the interaction may be oscillatory. However, the amplitude is too small to be clearly seen in our data.

C. W-Ir and Ir-Ir interactions on the W{ 110 }

We have recently reported a study of W-Ir and Ir-Ir interactions on the W{ 110 } plane.[18] The data analysis was based on approximating the W{ 110 } planes to be circular in shape. Since, in the present study, we were able to analyze data based on a realistic elliptical shape of the W{ 110 } plane, the previous data were reanalyzed, and the pair energies of the W-Ir and Ir-Ir pairs are shown, respectively, in Figs. 10 and 11. Figure 10 is a result of 947 observations at 330 K, and Fig. 11 is from 610 observations. As explained in the last paragraph, no averaging of the frequencies of observations is really necessary or justified for closest bond separations; thus, in the present analysis no such procedure was adopted as had been done in the previous report.[18]

The significant improvement in the present analysis is that the slowly varying potential as found in the previous report for both W-Ir and Ir-Ir pairs, which was speculated to be adatom-plane edge interaction, has now disappeared. The oscillatory behaviors of the W-Ir and the Ir-Ir are now even more recognizable. The cohesive energy at the closest bond distance is no longer unnecessarily dampened by the artificial averaging process. The averaging process, however, is still needed for all other distance intervals, since statistics for other intervals are still limited and the accuracy of distance determination for large separations is still poor.

For the W-Ir pair, the closest bond was 2.74 ± 0.50 Å. Cohesive energy at this distance was found to be 58.2 ± 3.6 meV. For the Ir-Ir pair, as explained in great detail in the previous report, the closest bond was 5.5 ± 0.5 Å. The cohesive energy

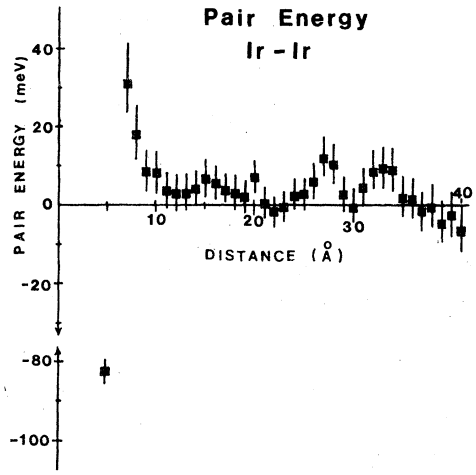

FIG. 11. Pair energies derived for Ir-Ir interaction using a realistic plane shape. The experimental pair distribution, obtained from 610 observations, has been published by us in Fig. 6(c) of Ref. 18.

at this distance was then calculated to be 82.0 ± 2.5 meV.

V. SUMMARIES

The pair interactions of Re-Re, W-Re, Ir-Ir, and W-Ir pairs on the W{ 110 } plane were derived by measurements of the pair distributions with two atoms on a W field-ion emitter plane. The planes developed by field evaporation were elliptical in shape, with a major axis of about 25 Å, and a minor axis of about 20 Å. All of the adatoms selected migrated quite freely around 330 K. The plane edges were also reflective. Thus pair distributions could be derived by repeated observations. Each pair distribution consisted of about 1000 observations.

Three of the pairs, W-Re, Ir-Ir, and W-Ir, showed a relatively strong (50—100 meV) cohesive energy at the closest bond separations. Re-Re and W-Ir pairs showed oscillatory tails clearly in the interactions, while for the W-Re and Ir-Ir pairs, the oscillation was too small to be established within our limited accuracy and the amount of data. From the pair distributions, we were also able to derive for the first time accurate values of the cohesive energy at the closest bond for W-Re, Ir-Ir, and W-Ir diatomic clusters.The results are summarized in Table I. Such information in previous studies has been estimated from a dissociation rate measurement with little accuracy.

An important question from this measurement is what effects are responsible for the observed adatom-adatom interactions. Several effects have been discussed in the past, as mentioned in Sec. I. The dipole-dipole interaction is given by $625\mu_a\mu_b/R^3$ meV when the dipole moments μ_a and μ_b are expressed in debye and the distance R is expressed in Å. Using adatom dipole moments given by Kellogg and Tsong,[25] we obtained values of the repulsive potential energies at the closest separations for three pairs. These values are also listed in Table I. As can be seen, the dipole-dipole interaction for 5*d* transition-metal adatoms on the W{ 110 } was simply too small to account for the repulsive force observed for all adatom pairs in our experiment. Since all the interactions showed, to some extent, oscillatory tails, it is possible that the repulsive regions were just part of the indirect adatom-adatom interaction. Unfortunately, reliable values for the repulsive energy could not be derived from this experiment.

TABLE I. Cohesive energy at closest bond distance.

Adatoms	Bond distance	Bond strength	Dipole repulsive potential energy at the closest bond
Re-Re	2.5—3.5 Å	?	0.35 meV
W-Re	2.5—3.5 Å	99.0 ± 0.7 meV	0.61 meV
Ir-Ir	5—6 Å	82.0 ± 2.5 meV	~ 0
W-Ir	2.5—3.5 Å	53.2 ± 3.6 meV	~ 0

Our Re-Re result on the W{ 110 } plane was quite different from that obtained for Re-Re adatoms on the W{ 112 } plane.[24] Since both results are quantitatively reliable, we conclude that the distance dependence of adatom-adatom interactions is specific to crystal planes. Theoretical studies so far have ignored such dependence. Now that reliable data are available for adatom-adatom interaction, further theoretical studies will be most beneficial in an atomistic understanding of surface phenomena. From the experimental side, we intend to widen the range of adatom pairs and substrate surfaces, and also to collect a larger amount of data to improve the accuracy.

ACKNOWLEDGMENTS

The authors acknowledge the support of this work by NSF Grant No. DMR-7904862. R. Casanova acknowledges the support of a fellowship from Universidad de los Andes, Merida, Venezuela.

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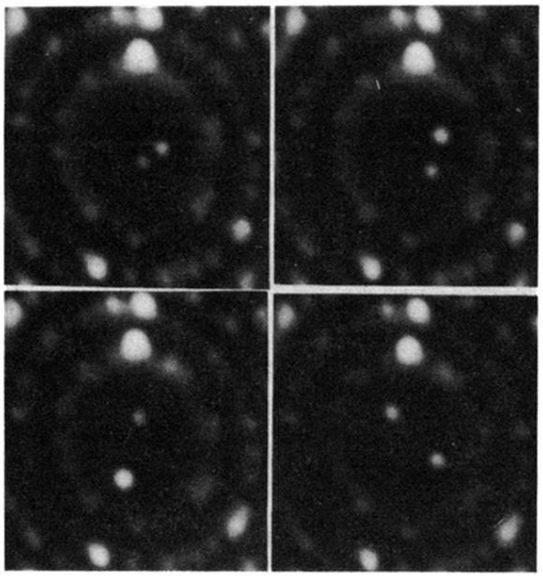

FIG. 1. Typical field-ion images showing two adatoms Ir and Ir at various locations on a W{ 110 } plane. When adatoms are near the plane edges, their image is greatly magnified; thus, accurate determination of atomic separation becomes difficult. The averaging procedures, as discussed in the text, are thus necessary.