Elementary displacement steps in the migration of tungsten diatomic clusters on the tungsten {110} plane

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Three elementary displacement steps of tungsten diatomic cluster migration on the W {110} plane have been identified. The relative frequencies of observing these displacement steps out of 597 observations at 299 ± 5 K are given. Several possible migration mechanisms which involve uncorrelated individual atomic jumps and which can qualitatively account for the three observed elementary cluster displacement steps are also discussed.

I. INTRODUCTION

On the W {110} plane, two $5d$ transition-metal adatoms usually combine to form a closely packed diatomic cluster aligned in the ⟨111⟩ direction.[1,2] The two atoms in a cluster can be marginally resolved in the field-ion microscope (FIM) if the tip radius is below ~200 Å. Judging from the expected resolution of the FIM and the image structure observed, the two atoms presumably sit at equivalent nearest-neighbor sites of the substrate lattice; the bond length will then be ~2.74 Å.

For single atoms on the W {110}, four sites of the substrate lattice, either because of symmetrical or geometrical consideration, are of particular interest.[3] These sites are the apex site A, the bridge site B, the lattice site C, and the surface site D, and they are shown in Fig. 1. The definitions of sites A, B, and C are obvious from the diagram. The surface site D corresponds to the location where an atom is at a closest possible distance to the surface plane when all the atoms are assumed to be spherical in shape.

Mappings of the locations of a single W adatom on the W {110} plane indicate that the W adatom sits most probably at a lattice site.[4] The adsorption sites of the two atoms in a diatomic cluster is difficult to pinpoint from the field-ion (FI) images. If the interaction between the two atoms is much smaller than their interaction with the substrate, one may assume that their adsorption sites are always the same as single adatoms. The cohesive energy between two W adatoms[1,3] on the W {110} is estimated to be only ~0.02 eV as compared to the several-eV binding energy of the atoms with the substrate. For simplicity, we will assume that the two W atoms in a diatomic cluster are located at lattice sites. A previous study, based on the symmetry of the atoms as seen in a double superposed image of a W_2 cluster at two positions, indicated that the atoms sat at surface sites.[5] However, a similar method, but based on the symmetry of the displacements of the center of mass of a Pt_2 cluster, concludes that the atoms sit most probably on lattice site.[6] Subsequently, a similar conclusion has been reached for atoms in W_2 cluster.[7] In a later section we will provide a new evidence which support the latter proposition. For our purpose here the precise site of adsorption is not critical to our discussion. As long as the energy barrier for jumps between two surface sites within a unit cell is small compared to jumps out of the unit cell, the two cases, lattice site and surface site adatom adsorption, are essentially equivalent. In this paper we will present an experimental observation of the detail steps of migration of diatomic W clusters on the W {110} plane.

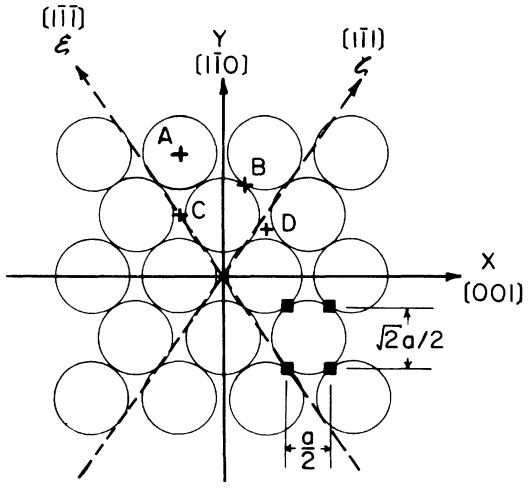

FIG. 1. Atomic structure of the W {110} plane. Four sites are of special interest. They are the apex sites A, the bridge sites B, the lattice site C, and the surface site D. Bridge sites from a rectangular lattice of $\frac{1}{2}a\hat{i} \times \frac{1}{2}\sqrt{2}a\hat{j}$ unit cell.

II. EXPERIMENTAL PROCEDURES AND RESULTS

Detail procedures of single-adatom FIM experiments are well established and can be found elsewhere.[2,8] We emphasize here that particular care was taken to ensure the vacuum condition of the FIM. The vacuum as read by an ionization gauge was always $\sim 2 \times 10^{-11}$ Torr, the x-ray limit of the gauge, even when the system was valved off from pumps. The residual gas is mostly helium since we use exclusively helium for imaging. The partial pressures of chemically reactive gases were too low to be detected. Two different methods were employed for depositing adatoms on field evaporated W surface planes. The first method used heating of a well degassed W coil as is generally done. The other method retained two atoms on a plane by carefully field evaporating the rest of the atoms in the top surface layer away. The latter method involved no generation of heat in the system after the system was valved off, thus no degassing of the system could occur. This method was, however, rather difficult since no matter whether dc or pulsed voltage was used for the field evaporation, the last bunch of atoms tended to field evaporate together. About one-half the data reported here use the latter method, and about one-half use the former, or the conventional, method. However, we detect no difference in the results obtained with the two methods. We use exclusively Vyco glass diffused helium for FI imagings. Once two atoms were retained or deposited on a W {110} plane, routine procedures of heating and imaging were followed. Each heating period was 60 sec. The heating temperature was 299 ± 5 K.

From the field-ion micrographs obtained, several distinct displacement steps of the diatomic cluster migration can be identified by using a color-comparator technique.[9] Figure 2 illustrates these observed steps, whereas in Fig. 3 the FIM images of corresponding migration steps are shown. Table I lists the number of times these steps were observed in a total of 597 heating periods. Because of the symmetry of the substrate surface structure, each displacement step of a diatomic cluster can occur in four directions, two from the cluster bond directions, and two from the displacement directions. Table I also lists the number of observations in the four directions for each specific displacement step. A bar in the symbols listed signifies the bond direction. The arrows show the "apparent" jump direction of the atoms. The word "apparent" indicates that images of the atoms are indistinguishable. Thus in reality we do not have the information of which atom displaces to which location. Such distinction may be possible if atoms of different species of a proper choice are used to form clusters.

Before we search for the mechanisms of migration of the diatomic cluster, we have to identify the elementary cluster displacement steps. If adatoms in a

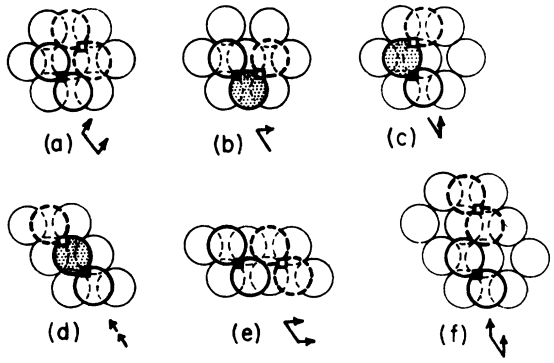

FIG. 2. (a) to (f) Six diatomic cluster displacement steps identified from field-ion micrographs. Symbols of such steps are also shown. Out of 597 heating periods, only in four cases, the displacements are too large to be identified by the color-superposition technique.

TABLE I. Frequencies of displacement steps observed in a total of 597 heating periods.

Displacement step observed	Frequency	Substep	Frequency
[1$\bar{1}$0] / [001]	48		9
			12
			14
			13
	64		13
			20
			15
			16
	47		13
			10
			11
			13
	3		1
			2
	2		1
			1
	1		1
Unidentified displacement	4		

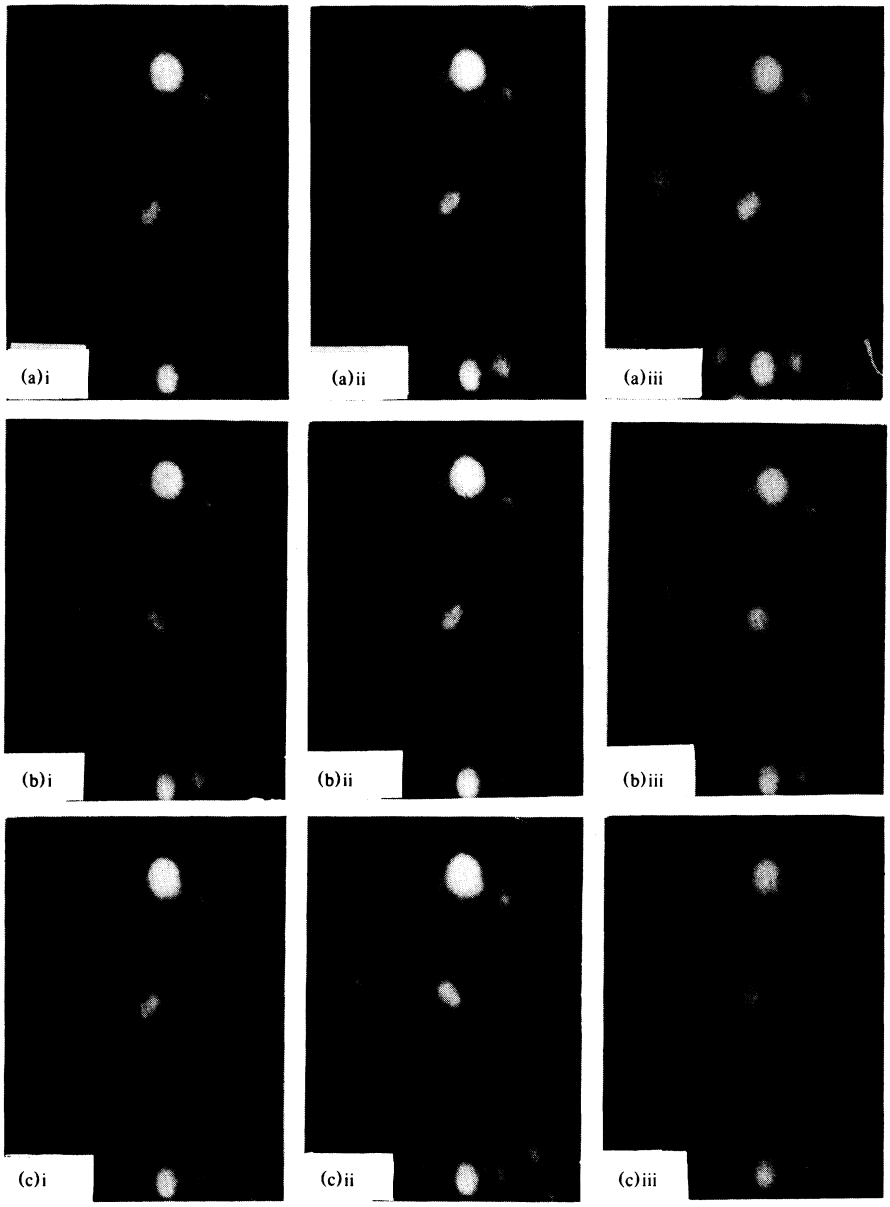

FIG. 3. Field-ion images observed which lead to the identification of the displacement steps shown in Figs. 2(a), 2(b), and 2(c). Images shown in iii are superpositions of images shown in i and ii.

diatomic cluster sit in lattice sites, or close to lattice sites as has been assumed, then from the symmetry of the lattice the center of mass (c.m.) of the cluster can sit only in a bridge site. During a migration the displacement vectors of the cluster c.m. form a rectangular lattice of $\frac{1}{2}a\hat{i} \times \frac{1}{2}\sqrt{2}a\hat{j}$ unit cell as shown in Fig. 1. The shortest possible displacements of the c.m. are $\frac{1}{2}a\hat{i}$ and $\frac{1}{2}\sqrt{2}a\hat{j}$. Any simple cluster displacement steps which lead to a displacement of either $\frac{1}{2}a\hat{i}$ or $\frac{1}{2}\sqrt{2}a\hat{j}$ are necessarily elementary displacement steps. Obviously the steps shown in Figs. 2(b) and 2(c) belong to this category. The question is whether the other displacement steps observed and shown in Fig. 2 are also elementary.

The step shown in Fig. 2(a) produces a c.m. displacement of $\frac{1}{2}a\hat{i} + \frac{1}{2}\sqrt{2}a\hat{j}$, therefore may be achieved by two successive elementary displacements $\frac{1}{2}a\hat{i}$ and $\frac{1}{2}\sqrt{2}a\hat{j}$. This successive occurrence of two elementary displacement steps is illustrated in Fig. 4(a). The probability of observing a $\frac{1}{2}\sqrt{2}a\hat{j}$ c.m. dis-

placement for the cluster is $p_{\uparrow}=47/597$. The probability of observing a $\frac{1}{2}a\hat{i}$ c.m. displacement of the cluster is $p_{\rightarrow}=64/597$. The probability of observing a displacement step shown in Fig. 2(a), if it is produced by two successive elementary steps as shown in Fig. 4(a), is $\sim 4\times 2(\frac{1}{4}p_{\uparrow})(\frac{1}{4}p_{\rightarrow})=\frac{1}{2}(p_{\uparrow}p_{\rightarrow})$ $=2.5/597$. The factor 4 comes from the two possible jump directions and the two possible bond directions. $(\frac{1}{4}p_{\uparrow})$ $(\frac{1}{4}p_{\rightarrow})$ is the probability of observing a successive occurrence of two elementary displacement steps. The factor two comes from two possible equivalent steps as shown in Fig. 4(a). The experimentally observed probability for the displacement step shown in Fig. 2(a), 48/597, is much too large to be accounted for by the successive occurrence of two elementary displacement steps. Thus we must conclude that the observed step shown in Fig. 2(a) is itself an elementary displacement step.

The probabilities of observing the displacement steps shown in Figs. 2(d), 2(e), and 2(f), if they occur by two successive elementary displacement steps, should be given, respectively, by $\sim 4\times 2(\frac{1}{4}p_{\uparrow})(\frac{1}{4}p_{\rightarrow})$ $=2.5/597$, $\sim 4(\frac{1}{4}p_{\rightarrow})(\frac{1}{4}p_{\rightarrow})=\frac{1}{4}p_{\rightarrow}^{2}=1.7/597$, and $\sim 4(\frac{1}{4}p_{\uparrow})(\frac{1}{4}p_{\uparrow})=\frac{1}{4}p_{\uparrow}^{2}=0.9/597$. These values agree within statistical fluctuations with the experimentally observed values of 3/597, 2/597, and 1/597, respectively. These observed displacement steps thus cannot be established to be elementary displacement steps. Each of them is most probably a successive occurrence of two elementary displacement steps of Figs. 2(b) and 2(c). In any case, the frequencies of observing the displacement steps of Figs. 2(d), 2(e), and 2(f) are very much smaller than those of observing the displacement steps of Figs. 2(a), 2(b), and 2(c). Thus even if they are partly elementary, they are relatively rare events. As listed in Table I, we have also observed four displacement steps which are not readily identified by the technique used. All of them result in an orientation change of the cluster.

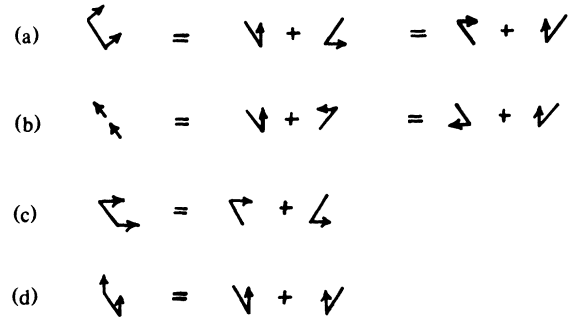

FIG. 4. (a) to (d): Symbolic equations showing equivalent displacement steps.

III. DISCUSSIONS

In deriving information concerning the migration mechanisms of a tungsten diatomic cluster on the W {110}, one has to recognize that no intermediate bond structure has ever been observed. The cluster is very stable at 299 K without observation of a single dissociation in 597 heating periods of 60 sec each. Reorientations occur very frequently; 115 out of a total of 169 displacement steps observed result in a change of the cluster orientation. This represents a 68%, or about a two-thirds probability of observing an orientation change. Whatever the migration mechanisms are, those which can lead to the observed elementary displacement steps shown in Figs. 2(a), 2(b), and 2(c) should be the dominant ones.

Two distinct mechanisms of atomic jumping process may be considered. One involves a simultaneous jump of the two atoms. The other involves uncorrelated jumps of individual atoms, thus the bond stretches during a displacement step of the cluster.[10] If the diatomic cluster migration is achieved exclusively by the simultaneous-jump mechanism, then reorientation of the cluster cannot be expected. Such mechanism requires an angular momentum for the cluster to change its orientation during the jump which is absent prior to the jump. Since as much as two-thirds of cluster displacements result in an orientation change, the simultaneous jump mechanism cannot be a dominant one, certainly cannot be an exclusive one.

We now consider the bond-stretching mechanism. For single W atom diffusion on the W {110}, the diffusion coefficient along the $[1\bar{1}0]$ direction was found to be about twice larger than that along the [001] direction.[3] This anisotropy in the diffusion coefficient is consistent with the assumption that atomic jumps occur exclusively along the $\langle 111\rangle$ surface channels. An investigation of the two-dimensional displacement distribution function of a W atom on a W {110} plane confirms that assumption.[7,11] In the diatomic cluster diffusion, due to the presence of adatom-adatom interaction, the potential energy profile of an adatom is effectively modified. Thus there is no reason why the jumps of the individual atoms in a diatomic cluster has to be exclusively along the $\langle 111\rangle$ surface channels. We will consider here mechanisms which can produce an elementary displacement step of the cluster with less than two jumps of single atoms.

Let us consider first two-jumps mechanisms with jumping directions along the $\langle 111\rangle$. This particular mode of migration mechanisms has been discussed earlier.[7] As shown in Figs. 5(a), 5(b), and 5(c), when the bond direction of a diatomic cluster is along the $[1\bar{1}\bar{1}]$ direction, or the ξ axis, a jump along one of the $\langle 111\rangle$ surface channels by either one of the two atoms will result in three intermediate bond

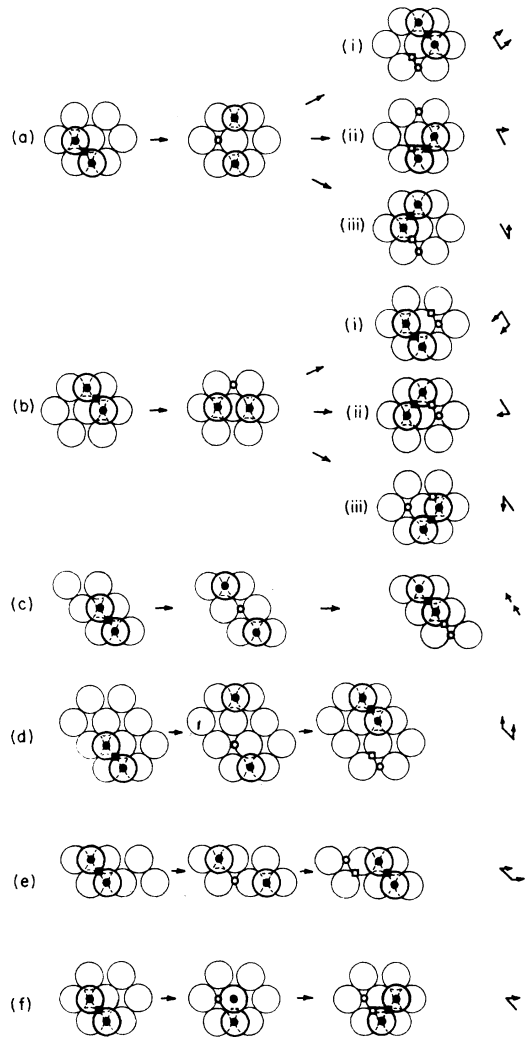

FIG. 5. (a), (b), and (c): Two-jumps mechanisms of cluster migration with jumps along ⟨111⟩ surface channels. (a) A $[1\bar{1}0]$ intermediate bond direction, (b) a [001] intermediate bond direction, and (c) a $[1\bar{1}\bar{1}]$ intermediate bond direction. (d) and (e) Two-jump mechanisms of cluster migration with jumps along, respectively, the $[1\bar{1}0]$ and the [001] directions. (f) One-jump mechanism with jumping direction in the [001].

directions, namely, $[1\bar{1}0]$, [001], and $[1\bar{1}\bar{1}]$. Another jump along one of the ⟨111⟩ surface channels by either one of the atoms will return the cluster to its original bond length. We have omitted in Figs. 5(a), 5(b), and 5(c) those mechanisms leading to no net displacement of the cluster center of mass. Of the seven mechanisms shown, three of them lead to a displacement of the c.m. either in ζ or ξ directions, two of them in x direction, and two of them in y direction. The former three produce also an orientation change of the cluster, whereas no change in the orientation occurs from the latter four mechanisms.

Let us denote the rate of transition via [001] intermediate bond state by ν_1, via $[1\bar{1}0]$ intermediate state by ν_2, and via $[1\bar{1}\bar{1}]$ intermediate state by ν_3. The observed elementary displacement step of the cluster as shown in Fig. 2(a) can be achieved by mechanisms shown in Figs. 5(a)(i) and 5(b)(i), thus the step occurs with a rate of $\frac{1}{3}(\nu_1+\nu_2)$. Similarily, the observed cluster elementary displacement steps shown in Figs. 2(b) and 2(c) can be achieved, respectively, by the mechanisms shown in Figs. 5(a)(ii) and 5(b)(ii), and by those shown in Figs. 5(a)(iii) and 5(b)(iii) with the same rate of again $\frac{1}{3}(\nu_1+\nu_2)$.

If the diatomic cluster migration occurs exclusively by the mechanism described, two jumps along the ⟨111⟩, then the frequencies of observing the elementary cluster displacement steps shown in Figs. 2(a), 2(b), and 2(c) should be equal. Table I indeed shows that the frequencies of observing 2(a) and 2(c) steps are nearly the same, 48 in one case and 47 in the other case. However the frequency of observing 2(b) step, 64, is considerably larger than the other two cluster displacement steps. Let us consider other possible mechanisms of cluster migration.

Figures 5(d) and 5(e) show two two-jump mechanisms where an atom jumps over the apex of a substrate surface atom either in the y or the x direction, and then followed by the other atom. These two mechanisms will give the observed cluster displacement steps shown in Figs. 2(f) and 2(e), respectively, and will produce no change in the orientation of the cluster. Since these two observed cluster displacement steps can also be produced by two successive elementary cluster displacement steps as has been discussed, there is no definitive proof that such mechanisms indeed occur. In any case the frequencies of observing cluster displacement steps of Figs. 2(e) and 2(f) are so much smaller, even if the mechanisms of Figs. 5(d) and 5(e) do occur at all, they are relatively rare events.

Let us now consider mechanisms involving a jump of only one of the two atoms. The jump may either be in x direction, or in y direction. Figure 5(f) shows the case with a jump in the x direction. The exact path of the jump is not known. For our discussion here it is not critical. As one can recognize easily, the one-jump mechanism in x direction produces the observed elementary cluster displacement step shown in Fig. 2(b), thus has exactly the same effect as the two-jump mechanisms shown in Figs. 5(a)(ii) and 5(b)(ii). If this one-jump mechanism occurs, the frequency of observing cluster displacement step of Fig. 2(b) will be larger than that of observing cluster displacement step of either Fig. 2(a) or 2(c). Since this seems to be the case, this mechanisms may indeed occur. One may also expect to have a similar mechanism with an atom jumping in the y direction. From the lattice structure, however, one can intui-

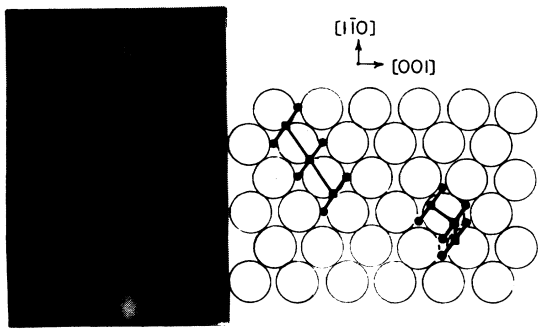

FIG. 6. If two atoms of a diatomic cluster sit in two nearest-neighbor lattice sites or close to them, then the center of mass is located at a bridge site. Two successive elementary displacement steps of the cluster in the same direction will form two displacements of the c.m. in the same direction with the same magnitude as can be seen also from the field-ion micrograph. If atoms sit in surface sites, then the displacements of the c.m. show a kink as seen in the diagram; the magnitudes are also different.

tively see that such a process probably will not differ very much from the two-jump mechanism with [1$\bar{1}$0] intermediate bond state since the path of the jump is expected to pass close to a lattice site unless the atom jumps vary far away from the surface plane. Such a jump is highly improbable from energy consideration. The one-jump mechanism is therefore favored to occur with a jump in the x direction. This is in fact consistent with the experimental result. While the elementary displacement steps of Figs. 2(a) and 2(c) occur with the same frequency as expected from the two-jump mechanisms, the frequency of observing the elementary displacement step of Fig. 2(b) seems larger, unexpected from the two-jump mechanisms alone. The one-jump mechanism can help account for this observation. One must, of course, realize that a much larger amount of data are needed to establish whether the one-jump mechanism really occurs, and if occurs, with what relative frequency.

Finally, we will also present here supporting evidence that two adatoms of a diatomic cluster sit at two neighboring lattice sites. In eight cases where a cluster aligned in the ζ (or ξ) direction, and which makes two successive displacements in the ζ (or ξ) direction, seven of them have the three locations of the center-of-mass lineup in the ξ (or ζ) direction with equal spacings as shown in Fig. 6. Thus the seven cases are consistent with the assumption that atoms sit in or close to lattice sites with the c.m. located at bridge sites. In one case, the two displacements seem to point in slightly different directions, but have the same magnitude. This may simply be due to the accuracy of the color superposition technique. However, in all eight cases, the magnitude of the displacements all fall within $\sim \pm 10\%$ of each other, which indicates that the color superposition technique, when used carefully, can give an accuracy of the displacement to within ± 0.3 Å. Such accuracy however can be expected only for tips of very small radius, ~ 200 Å or less. A previous study[2] ascertains that even though the resolution of the FIM, as defined by the shortest distance between two atoms which can be resolved, is about 3 Å, the accuracy of determining the position of an adatom in the FIM is better than 0.5 Å is further confirmed.

IV. SUMMARY

Using a color-comparison technique, three elementary displacement steps for the diatomic W cluster migration on the W {110} plane have been identified from the field-ion images. Frequencies of observing these steps are given and are compared with some possible migration mechanisms of the diatomic cluster. The mechanisms based on two uncorrelated single atomic jumps along the ⟨111⟩ surface channels plus a mechanism involving one single atomic jump in the [001] direction can qualitatively account for the observed elementary displacement steps. A much larger amount of data are needed to establish the relative frequencies of the occurrence of various mechanisms of migration. These frequencies are directly related to the adatom-adatom interaction on the plane. Although the elementary displacement steps are established only for tungsten diatomic cluster, we expect a similar behavior on the W {110} for other diatomic clusters with a comparable bond length. One would like to see whether at higher temperatures, the elementary displacement steps are the same. The difficulty of heating at a higher temperature, even if only 10 or 20 K higher, is that it often results in large displacements which are difficult to identify. Thus temperature dependence of the frequencies of observing various elementary displacement steps is difficult to obtain. Such difficulty, however, can be overcome by pulsed-laser heatings.[12] Further investigations of the high-temperature behavior should be most interesting.

ACKNOWLEDGMENTS

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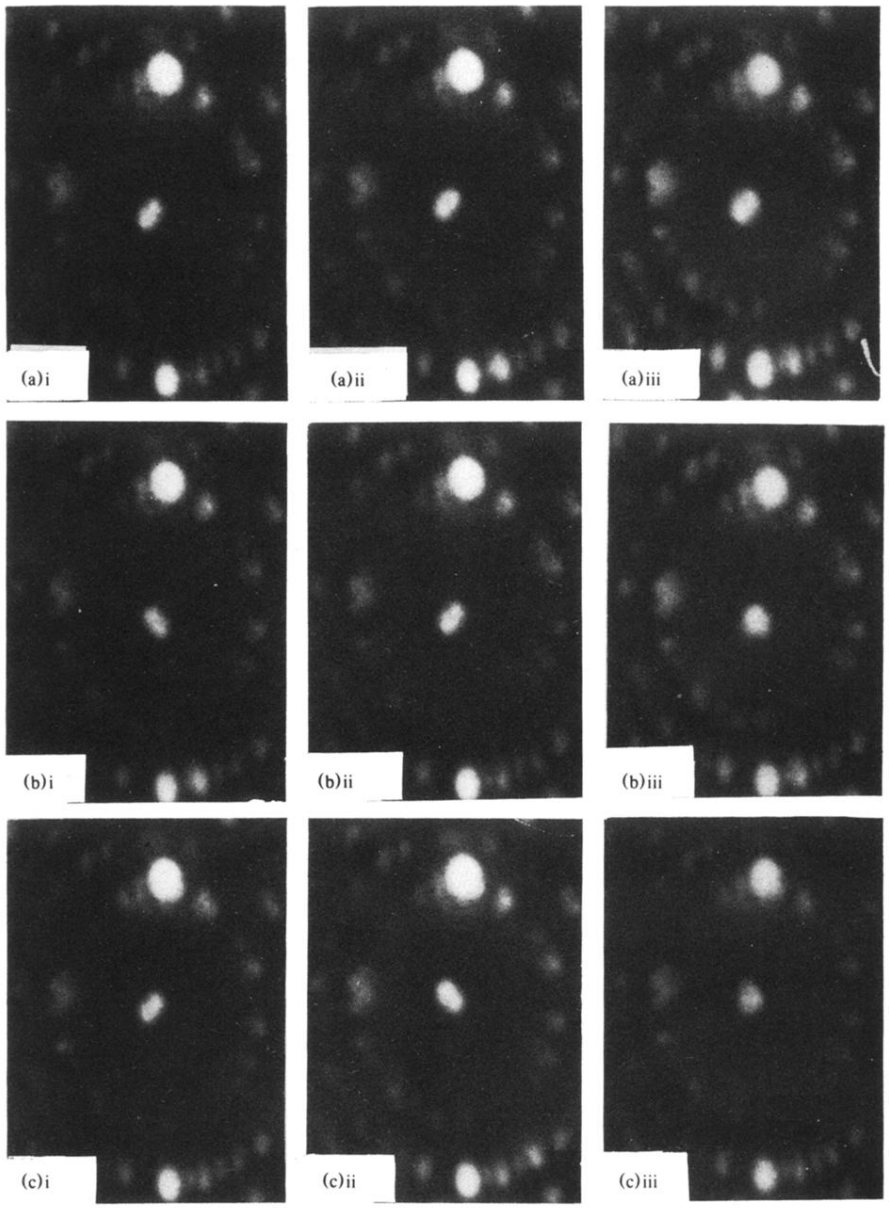

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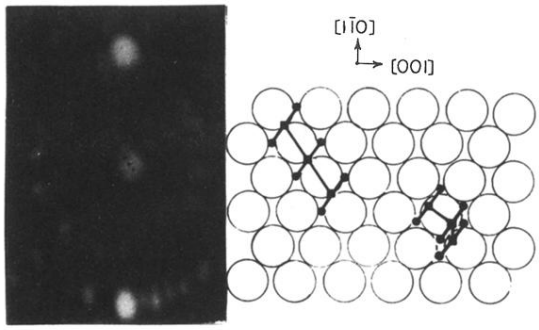

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