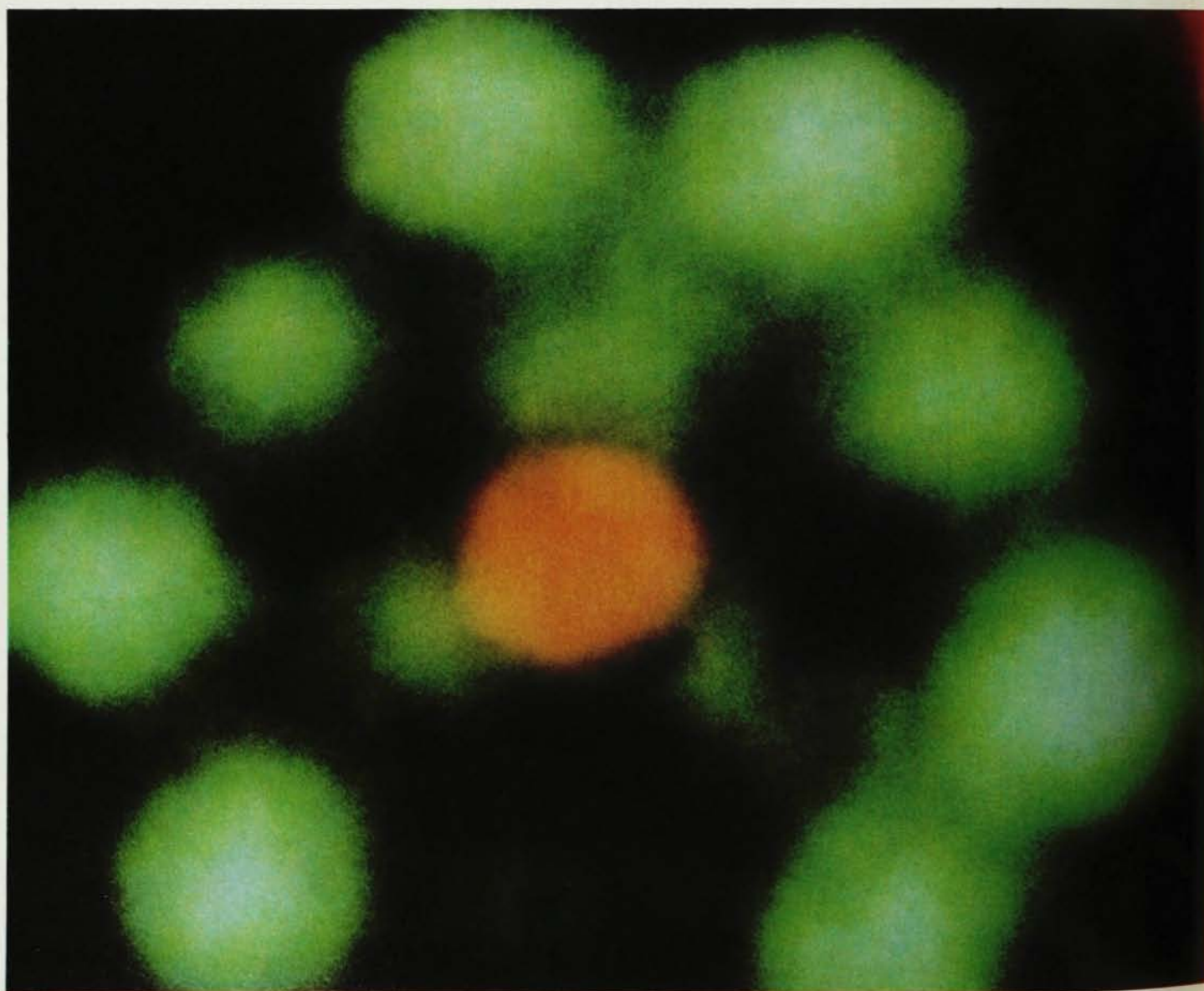


Wandering surface atoms and the field ion microscope

New insight into the atomic action that underlies the physical and chemical properties of surfaces is coming from time-sequence pictures of individual atoms on crystal planes.

Gert Ehrlich



Interest in information about individual atoms on crystal surfaces has been strong since the early 1930s. By then it had become clear that to understand technologically important surface phenomena such as crystal and thin-film growth, heterogeneous catalysis, sintering and surface oxidation, it was necessary to understand atomic processes at crystal surfaces. In response to this need for qualitative and quantitative knowledge physicists and chemists developed detailed models of atomic activity on crystal surfaces. However, for many decades there was no way to confront speculation with actual data on atomic behavior—that would require observations of individual atoms. No less a capability is now available (see figure 1) through the use of the field ion microscope. As we will see, observations of individual atoms have not only provided much interest-

ing information on surfaces but they have also become surprisingly routine.

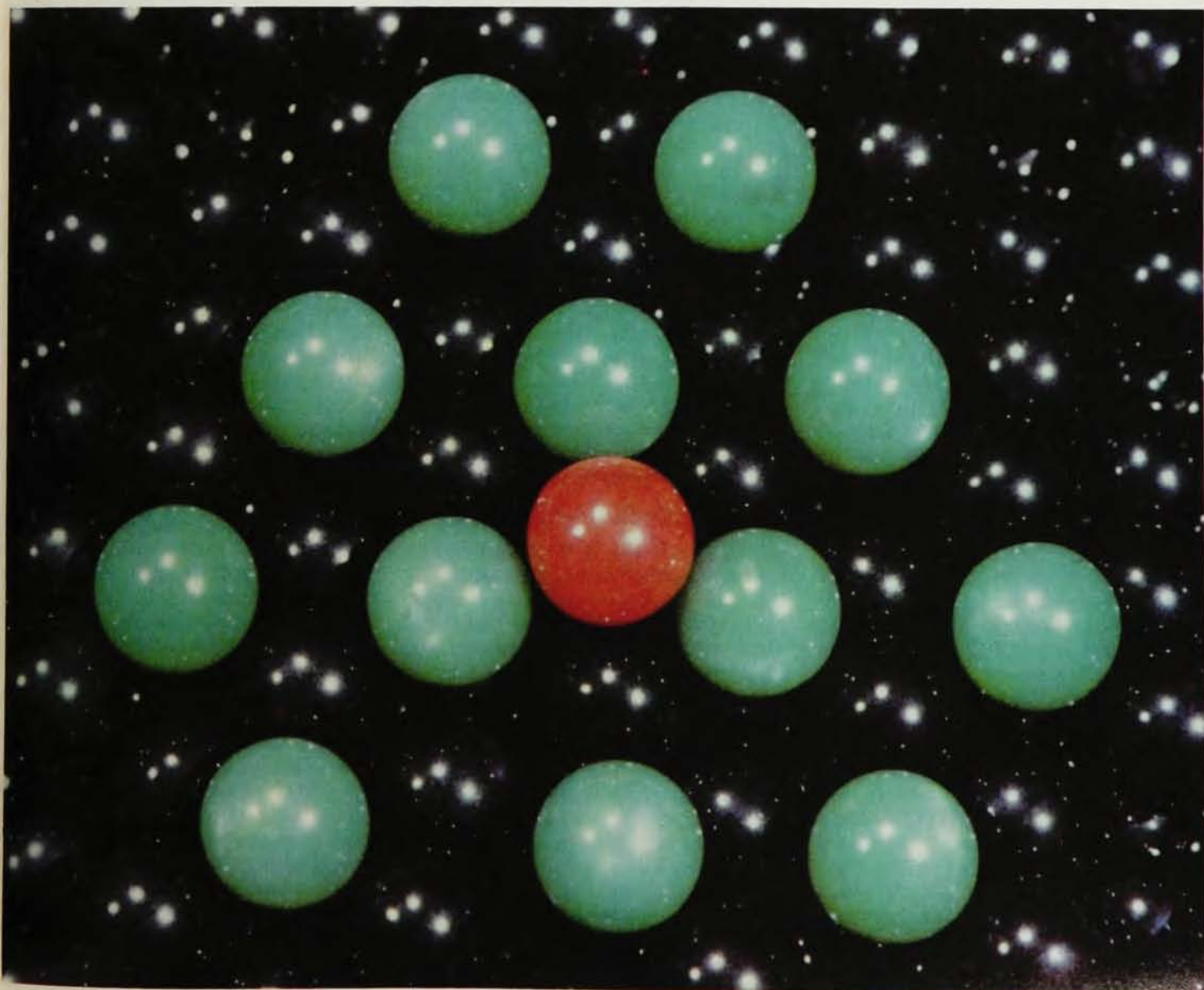
Over the last decade rapid progress was made in the physics and chemistry of surface layers through the systematic application of diffraction and spectroscopic methods, which have provided an extensive body of information about well-characterized monolayers on solids. In contrast, insights into the behavior of individual adsorbed atoms and their interactions on solids have been obtained only incidentally and occasionally. We are accustomed to thinking in terms of atomic models, and quantitative experimental information about atoms on solids therefore is clearly desirable: It is necessary for any systematic understanding of surface phenomena.

There is a great deal we may wish to know about atomic behavior at an interface. To appreciate this, consider the growth of a smooth crystal plane from a slightly supersaturated vapor. According to the classical model of W. K. Burton, Nicolas Cabrera and Charles Frank,¹ growth occurs in a sequence of steps. Atoms from the

vapor phase are adsorbed on the solid; these adsorbed atoms, or "adatoms," move about on the surface. If, in their random motion, adatoms encounter a lattice step, they are incorporated into it, causing the crystal to grow; otherwise, they reevaporate. At higher supersaturations and on highly perfect planes, we may also expect the formation of clusters through the interaction of several adatoms with each other, clusters that can serve as nuclei for subsequent formation of a new plane.

In any attempt to understand actual growth phenomena on the atomic level, we certainly have to know how the adatoms interact with the substrate. These interactions should be affected by the local atomic arrangement,

Image of a single atom of tungsten, in orange, adsorbed on the (111) plane of a tungsten crystal, in green, is the result of the superposition of two field ion microscope pictures. In the green picture, taken before the adatom was evaporated onto the surface, every atom in the outermost lattice layer is resolved. The atomic geometry is suggested by the model on the right. Figure 1





Hard-sphere model of a body-centered cubic lattice reveals a variety of atomic arrangements on different crystal planes. A single adsorbed atom residing on the surface is represented by the sphere on the (211) plane. Figure 2

which, as is apparent from the hard-sphere model in figure 2, varies significantly from one plane to the next. Beyond this qualitative realization we now confront a series of unknowns:

- ▶ Where on the surface are the adatoms bound?
- ▶ How do they move over the crystal?
- ▶ What are the kinetics and energetics of this diffusion?
- ▶ How do the atoms interact with each other?
- ▶ What are the consequences of these interactions?

To answer these simple but important questions, it is necessary to command techniques for preparing surfaces in a known state of perfection as well as for visualizing the individual adatoms. For metals and semiconductors, both of these capabilities are inherent in the field ion microscope,² invented by Erwin Müller in the 1950s. An image of the (111) plane of tungsten obtained with such a microscope is shown in figure 1; every lattice atom in the outermost layer is resolved. More than that, we readily detect a single tungsten atom evaporated onto the surface, and it is even possible to discern its position relative to that of the lattice atoms.

Through the consistent application of the field ion microscope to the study

of surface phenomena, much information has become available about individual adatoms. The technique has had a considerable impact on other fields as well, especially in metallurgical investigations³ of radiation damage and of alloys. My purpose is to sketch some of the applications to surface studies. I shall stress the unrivaled ability of this microscope to provide quantitative data about surface behavior on the atomic level. First, however, the instrument itself.

Field ion microscopy of surfaces

In principle the field ion microscope is exceedingly simple. Its components are shown schematically in figure 3. The sample, usually a single-crystal wire previously pointed by electrolytic methods, is spot welded onto a hairpin loop, which serves as a support. The sample and support are incorporated into an ultrahigh vacuum system in such a way that the tip can be cooled, preferably to 20 K and below. On applying a positive voltage high enough to raise the local field to roughly 5 volts per angstrom, protruding atoms at the surface are ionized and stripped off. We have here a procedure for preparing surfaces smooth on the atomic level. Even on the atomic level, the local field is highest at protuberances, and these

are therefore removed preferentially. The smooth surface produced in this way can now be imaged with a resolution approaching a lattice spacing by introducing an inert gas, typically helium or neon, at low pressure.

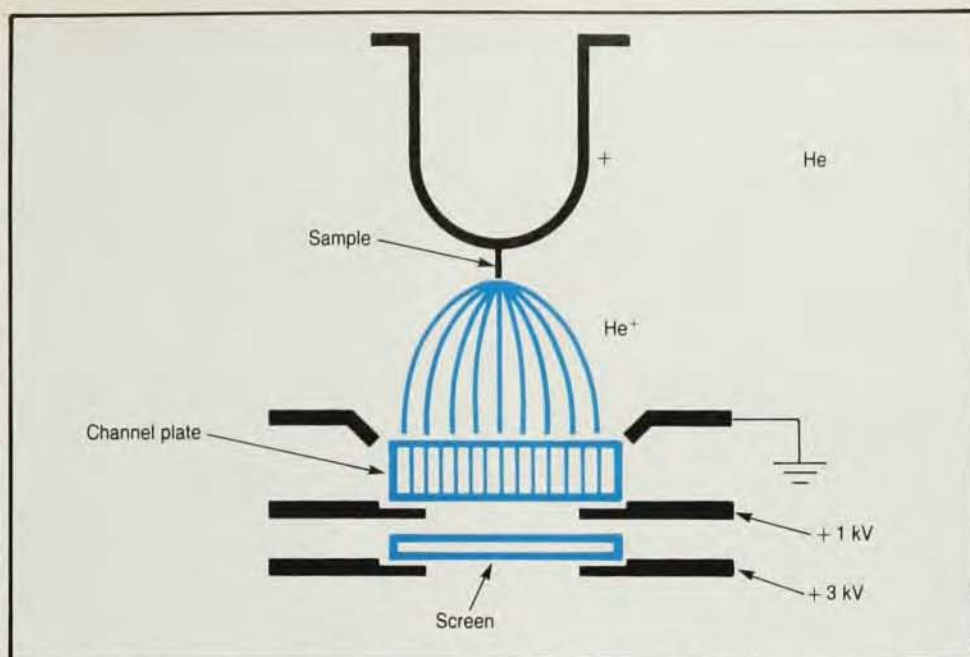
At the heart of the field ion microscope is the process of field ionization, which was already discussed by J. Robert Oppenheimer⁴ in the 1920s. He recognized that in a sufficiently high electric field (greater than 4 volts per angstrom with helium), electrons will tunnel through the distorted Coulomb barrier around an atom core, leaving behind a positively charged ion. At a metal surface, and especially at protrusions, field ionization is enhanced by the locally higher field and by overlap of the metal wave functions with those of the atom. Ionization at the surface thus occurs at a finite rate even when the rate is negligible in free space, and this makes it possible to depict protruding surface features. The ions of the image gas formed at the surface follow the field lines emanating from the sample and eventually impinge upon the detector. There they create a highly magnified map of the sites at which ionization takes place; the resolution is a few angstroms. A microchannel plate coupled to a fluorescent screen is the standard detector; it converts the ion picture into an electron image of higher intensity. With such amplification we can now image at lower fields by resorting to gases of lower ionization potential but greater mass than helium, gases for which the direct excitation efficiency of the phosphor would otherwise be too low. The fields of 2-4 volts per angstrom required for imaging are readily achieved by applying a few kilovolts to tips that have been properly sharpened to a diameter of a few hundred angstroms. A wide variety of materials, including metals as soft as gold and aluminum, have been examined in this way.

It is apparent from figure 1 that sometimes we can fully resolve the arrangement of the outermost layer of lattice atoms in the field ion microscope. In principle, then, direct examination should yield considerable information about the structure of surfaces. However, there are significant limitations. The field ion microscope does not provide information about absolute distances, such as is readily available from diffraction methods. Distances can be inferred, however, by looking at surface features of a known spacing. Only on surfaces with a spacing of at least 3 angstroms are lattice atoms easily resolved and even such planes must be small so that the field does not vary greatly over them. Despite these restrictions, field ion microscopy has provided interesting information about surface layers.

Individual vacancies were observed and studied long ago. More recently the arrangement of atoms in the surface layer of tungsten (100) has been examined. We know from studies of low energy electron diffraction that this plane does not have the ideal structure of a (100) layer in the bulk. The atomic arrangement of the surface unit cell is what is called $c(2 \times 2)$: It is as if every second atom in the layer had been displaced; lateral as well as vertical displacements have been proposed to account for the LEED data. Using the field ion microscope, Alan Melmed and coworkers⁵ have now found evidence for such rearrangement. Careful field evaporation at temperatures below 20 K produces what appears to be a perfect (100) plane. At elevated temperatures, however, field evaporation occurs not at the edges, where we expect the field to be the highest, but at the center of the plane. As this process continues, the vacancies left behind form a $c(2 \times 2)$ arrangement. Evidently the (100) plane of tungsten was not flat initially; it appears to be periodically dimpled in such a way as to make some of the interior atoms more susceptible to field evaporation.

For tungsten (100) this result is not unexpected—the rearrangement was recognized previously with low energy electron diffraction. Bill Graham and colleagues are continuing these investigations, however, searching for rearrangements in hitherto unsuspected cases. These studies provide a good illustration of the ability of the field ion microscope to provide information, albeit indirectly, about the atomic arrangement of surfaces.

The field ion microscope really comes into its own domain in visualizing and studying individual adatoms. One basic question about adatoms is: Where on a solid are they held? Inasmuch as we can locate lattice atoms in some planes by field ion microscopy, the lateral position of adatoms should also be recognizable by direct examination. This has been accomplished for tungsten and nickel atoms on the (111) plane of tungsten. Under the usual conditions it is difficult to simultaneously image both the adatom and the substrate with high resolution, but this problem has been overcome in two ways. The initial studies⁶ demonstrating that the primary binding site of a tungsten atom on (111) corresponds to a normal lattice position were done by sequential imaging: The adatom is photographed first; it is then stripped off and the substrate is imaged at high resolution, under optimal conditions. To identify the binding sites, the two images are superimposed, as was done to obtain figure 1. Peter Flahive and Graham⁶ used a more direct method of identification. They discovered that



Schematic diagram of a field ion microscope shows it to be an exceedingly simple instrument. In a high field, helium atoms at the sample's surface are ionized. The ions follow the diverging electric field lines from the sample to the detector, where they form a highly magnified image of the surface. Figure 3

when imaging at a reduced field, both the adatom and the immediately surrounding substrate atoms appear on the same photograph. As far as the lateral position is concerned, the sites for adatoms are those filled if growth of the lattice were to continue.

The field ion microscope does not provide much information about the location of adatoms in the direction perpendicular to the surface. Also, the position of an adatom identified in this way corresponds to the location in the high field necessary for imaging. This does not appear to be a major source of distortion, and so far the efforts with the field ion microscope are the only ones by any technique to establish the location of adatoms on their own lattice.

Behavior of individual adatoms

Our ability to see atoms on a solid opens up for study a range of interesting questions. One problem that has not been satisfactorily resolved, however, is the energy for removing adatoms from the surface. Information about how this energy varies with the atomic arrangement of the substrate would be important indeed. Attempts⁷ to deduce the binding strength of atoms on variously structured surfaces have relied on measurements of the electric field required to desorb the atoms. Such measurements are easy, but their interpretation rests upon quite detailed assumptions concerning the kinetic mechanism of field evaporation, assumptions that are probably not valid.

The properties of adatoms on the surface have proved much more amenable to examination in the field ion

microscope. Diffusion of atoms on a crystal⁸ is of special interest, but for understanding crystal growth and for a rational picture of surface behavior. In the simplest view of this phenomenon, we can think of an adatom being occasionally excited out of its binding site into an adjacent site a distance λ away. If jumps in one direction occur at the rate α , and an adatom loses all sense of its previous history prior to making another jump, then the mean square displacement along one coordinate during a time interval τ is just

$$\langle \Delta x^2 \rangle = 2\alpha\tau\lambda^2$$

From Einstein's relation $\langle \Delta x^2 \rangle = 2D\tau$, it follows that the diffusivity D , the parameter most useful in describing diffusion, is $\alpha\lambda^2$. The energy barrier V_m that the atoms must overcome in order to move can then be deduced from the temperature dependence of the diffusivity. Thus observations of atomic motion should provide information about more than just the dynamics of diffusion: the moving atom serves as a probe that responds to V_m , the effective potential parallel to the surface.

How can we measure diffusion? This is most simply done by examining the location of an adatom just prior to and after diffusion. Figure 4 shows the location of a single rhenium atom as it diffuses over the (211) plane of tungsten during 30-second intervals at 339 K. If we measure the displacement during each diffusion interval, square this distance and then average the results of many such determinations we arrive at the diffusivity D . The diffusivity is not affected by the high field required for

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imaging. While the adatom moves, there is no voltage applied to the sample. Imaging is done only when the temperature has dropped to about 20 K, and it is easy to verify that under these conditions there is no significant displacement by the field. Thus our measurements probe diffusion in an ordinary thermal environment.

There are at least two experimental problems in carrying out such a program. The first is to measure the absolute distance between equilibrium locations. The second is more subtle. So far we have assumed that the adatom executes a random walk. On the typical specimen used for field ion microscopy the largest planes are at most 100 Å in diameter. Whenever an adatom encounters an edge, its immediate environment is different from that on an infinite plane; furthermore, some correlation enters the jump process as the atom is either reflected or permanently bound to the edge on striking the boundary. The formalism has been adapted to account for such effects, however, and it is feasible to deduce the jump rate from observations on quite small planes. Distance measurements also turn out to be straightforward even though the field ion microscope provides no absolute indication of length. The adatom itself, in moving over the surface, maps out the available binding sites. If the surface spacing has been determined by some other technique, the distance between binding sites is readily derived by lining up the field ion images, not in their chronological sequence, but so as to show the atoms in adjacent binding sites. If there are sufficient data in a diffusion sequence, this procedure makes it quite straightforward to describe distances in terms of the spacing between sites. On the (211) plane of tungsten it turns out that the number of binding sites found in observations of diffusion is in good accord with the number of lattice sites deduced from the dimensions of that plane. In fact, direct imaging experiments⁶ have revealed that adatom sites on (211) correspond to the normal lattice sites. Such detail is intrinsically interesting but not necessary for deriving values of the diffusivity.

These techniques have provided considerable information about the movement of metals atoms on metals. Much of this information deals with atomic behavior on tungsten, a body-centered-cubic refractory metal, which is especially easy to work with. If atomic motion on a solid were similar to that of a marble rolling on a surface, we might expect a smooth plane such as the (110) to show the highest mobility, with slower motion on rougher surfaces such as the (100) and (211) surfaces modeled in figure 2. It turns out that atomic

behavior on tungsten is not that simple. As is apparent from the table,⁸ there is rather little difference in the barrier to movement of atoms on planes that differ in structure as much as (110), (211) and (321) the three surfaces that have been most intensively examined. Estimates of the barriers based on the assumption of pairwise additive interactions fail to give even a qualitatively correct view of atomic behavior on tungsten. Despite that, the dynamics of atomic motion appear to be simple.

A marble rolling over a surface would follow the lines of close-packed surface atoms. We might expect atoms also to diffuse preferentially along the channels evident on the planes such as (211) and (321). This is precisely what has been found in all experiments on these two planes. Diffusion of a variety of metal atoms—tungsten, rhenium, tantalum, rhodium, iridium, molybdenum—always occurs along the channels, never across them.

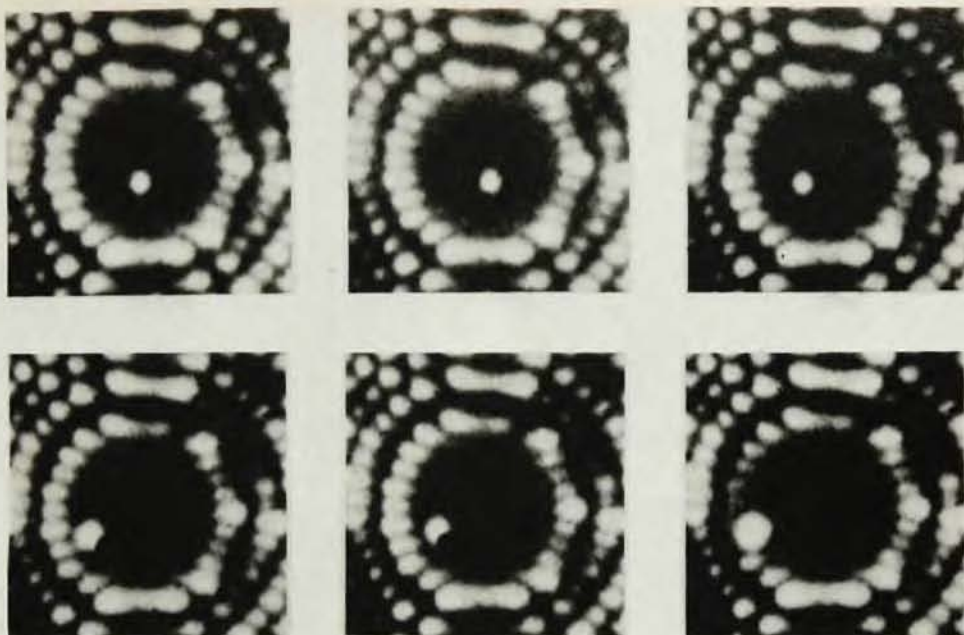
More quantitatively, if we write the jump rate α in the usual way, as the product of an attempt frequency α_0 and a Boltzmann term involving the barrier height V_m , then the diffusion coefficient can be represented as a function of the temperature by

$$D = D_0 \exp(-V_m/kT) \quad (1)$$

$$D_0 \equiv \alpha_0 \lambda^2$$

In our simple picture of atomic motion by uncorrelated jumps between adjacent sites, the prefactor D_0 should be on the order of magnitude of 10^{-3} cm²/sec: We expect α_0 to be roughly comparable to the Debye frequency, that is 10^{12} Hz, and lattice spacings on a surface are typically 3 Å. Values of D_0 from experiment are endowed with considerable error, as it is primarily the barrier that affects the magnitude of the diffusivity. Nevertheless, the prefactors derived from observations are in reasonable accord with our simple model.

At this stage it is worth remarking upon the temperature range in which diffusion is observed. Mean square displacements of less than 1 Å² per second can be readily detected and measured quantitatively. Diffusion of this order of magnitude occurs on tungsten at temperatures corresponding to considerably less than $1/10$ of the melting point. At these temperatures there is no net transfer of tungsten over the surface. Such transfer is a much more complicated process than the movement of atoms on a perfect plane. It involves removal of atoms from lattice steps, a process that does not take place until much higher temperatures and occurs over an energy barrier greater than 3 electron volts. Studies of individual atomic motion have focused pri-



Time-lapse photographs of a single atom of rhenium trace its migration over the surface. The adatom was imaged at about 20 K after being allowed to diffuse during 30-second intervals at 339 K. Here we are looking down on a needlepoint of tungsten, which is, in effect, a stack of smaller and smaller crystal planes (in this case, (211) planes). The smooth plane at the tip appears dark and only the lattice atoms at the circular edges of the stacked planes, and the single adatom, form images. The (111) plane is to the left; the (100) plane, to the right. Figure 4

marily upon phenomena on perfect planes at low temperatures. Nevertheless, some interesting observations have been made of diffusion at plane edges and also of the disordering of lattice steps as atoms move out onto the terraces at higher temperatures.⁹ So far there are few quantitative data available, and such work is difficult possibly because of problems from migration of contaminants to the area under study.

Atomic jumps

The motion of atoms on tungsten at the low temperatures at which most of the available work has been done appears to conform to the simple notions that lead us to equation 1. It should be evident, however, that the apparent agreement of the experimental prefactors with values from a simple jump model does not constitute proof that diffusion does indeed occur by atoms

jumping only between adjacent sites. To test this model rigorously it is necessary to examine the distribution of distances covered by a diffusing atom, not just the second moment of this distribution, which suffices to define the diffusivity. Consider an atom that diffuses by jumps two atom spacings long. For time intervals so short that only a few jumps are possible, the distribution of distances of such an atom will be different from the distribution of an atom that jumps to nearest neighbor sites only, even though the mean square displacement is precisely the same for both—atom number one, for example, will never be found one spacing away from the origin.

We can deduce the nature of the jump process from a quantitative analysis of the distances covered by a diffusing atom.⁸ If diffusion does indeed occur by jumps to nearest neighbor sites only, at a rate α , then the probabil-

Self-diffusion of single metal atoms

		Diffusion prefactor D_0 (cm ² /sec)	Energy barrier V_m (electron volts)	
			Experimental	Calculated
Tungsten	(110)	3×10^{-3}	.92 ± .05	.52
	(211)	3×10^{-4}	.76 ± .07	.42
	(321)	4×10^{-4}	.87 ± .08	.51
Rhodium	(111)	2×10^{-4}	.16 ± .02	.04
	(311)	2×10^{-3}	.54 ± .05	.43
	(110)	3×10^{-1}	.60 ± .03	.48
	(331)	1×10^{-2}	.64 ± .04	.60
	(100)	1×10^{-3}	.88 ± .07	.70

From reference 8

From reference 8

ity that the atom will be at a distance x from the origin after a time τ is just

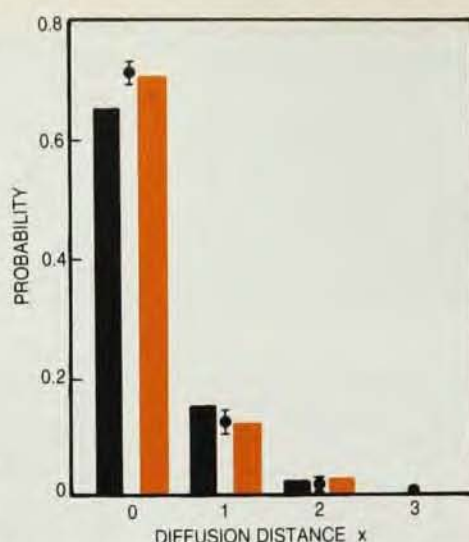
$$p_x(\tau) = e^{-2\alpha\tau} I_x(2\alpha\tau)$$

where I_x is the modified Bessel function of order x . If the motion is more complicated, and jumps to second nearest neighbor sites are also possible at a rate β , then the probability becomes

$$p_x(\tau) = e^{-2(\alpha+\beta)\tau} \times \sum_{j=-\infty}^{+\infty} I_j(2\beta\tau) I_{x-2j}(2\alpha\tau)$$

All that is necessary now is to establish by experiment which expression better represents the distance distribution actually observed for a diffusing atom. A start has been made toward this goal. The distribution of tungsten atoms on the (211) plane of tungsten, shown in figure 5, fits reasonably well with diffusion by nearest-neighbor jumps only. However, a better representation is obtained if jumps to second-nearest neighbors are also allowed, as long as these only occur at a rate approximately $1/10$ that of nearest neighbor jumps. At low temperatures at least the simplest model of surface diffusion seems to account adequately for the phenomena observed on the (211) plane—only occasionally are there jumps longer than a single spacing.

The experimental work we have presented so far has all been done on tungsten. This fact immediately leads to the question: Are the results on this body-centered cubic metal representative of diffusion phenomena on metals in general or are they peculiar to this one material? A fair amount is known about self-diffusion of rhodium atoms on different planes of rhodium, a face-centered cubic metal. The barrier to atomic motion varies dramatically from one plane to the next (see table). On the (111) plane, which in the face-centered cubic lattice is close-packed, diffusion is rapid at cryogenic temperatures; on the rougher (100) plane, motion only becomes important at room temperature. These wide variations are in accord with our qualitative expectations. In fact, pairwise two-body interactions seem to give a semi-quantitative account of the energetics of diffusion on rhodium. Of special interest are the directional effects observed.⁸ The (110) or (311), and (331) planes of the face-centered cubic lattice are structurally much like the (211) and (321) planes of the body-centered cubic lattice, with channels running along the surface. From our experience with tungsten we expect preferential diffusion along these channels. That is precisely what is observed. For rhodium, at least, the energetics and kinetics of individual atom motion seem simple



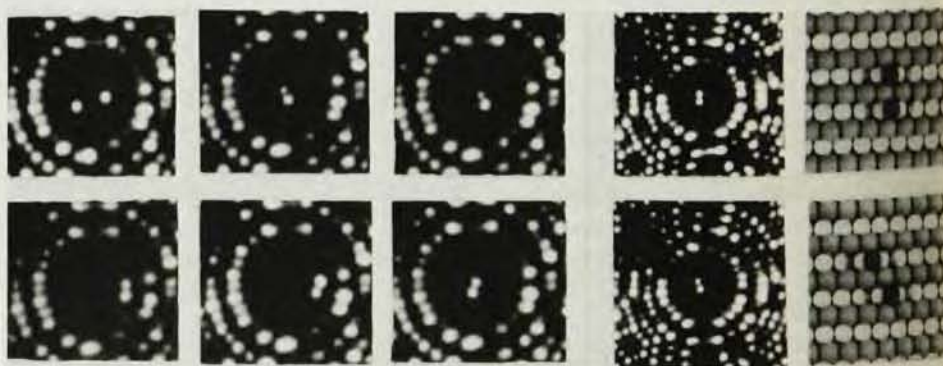
Distribution of displacements for tungsten adatoms on the (211) surface of a tungsten crystal after making, on the average, half a jump. Points give results of experiment. Heights of black bars represent distribution predicted for atoms making single jumps only. Colored bars represent predicted distribution for atoms making 10 single jumps for every double jump. The experiments are fit best by the latter assumption. Figure 5

indeed.

Unfortunately this is not generally true. Other face-centered cubic substrates have been explored recently. For platinum and iridium atoms on platinum, David Bassett¹⁰ has found a variation in the barrier to diffusion on different planes fairly similar to what is seen on rhodium. However, there is a startling effect on the (110) plane—diffusion occurs rapidly across as well as along the surface channels. Cross-channel motion is even more pronounced on the (110) plane of iridium. We must consider two different possibilities in any attempt to understand this unexpected behavior: jumps over the channel wall, or else an exchange of the adatom with a lattice atom in the channel wall. Here we note that both the platinum and iridium (110) planes are rearranged, so that the repeat dis-

tance of the surface grid at right angles to the close-packed [110] rows is twice the normal. This could leave the [110] rows less firmly bound and more susceptible to fluctuations, so that jumps across the channels might be more attractive than one would think at first sight.

A clear distinction between the two mechanisms is possible. Suppose we deposit a foreign adatom, say tungsten, on a (110) plane of platinum or iridium. If cross-channel motion occurs by jumps over the channel walls, then it is a tungsten atom that appears in an adjacent channel after cross-channel diffusion. If an exchange mechanism dominates, however, then after a cross-channel event a lattice atom will be present in the adjacent channel. All that is required to distinguish these possibilities is a technique that allows us to determine the location and chemical identity of a single adatom. This can be readily done in Müller's "atom probe,"¹² which is a combination of a field ion microscope and a time-of-flight mass spectrometer. John Wrigley¹¹ in our laboratory has used this device to examine the behavior of tungsten atoms on the (110) plane of iridium. We can readily distinguish iridium and tungsten atoms that have been evaporated onto an iridium surface maintained at a temperature low enough so that no motion is possible. When a tungsten atom is evaporated onto a (110) surface that is then warmed until cross-channel motion occurs, the atom that appears in the adjoining channel is clearly iridium. Furthermore, atom-by-atom probing of the lattice after the adatom is removed has established the presence of tungsten in the surface layer. These studies demonstrate that at least in this system cross-channel diffusion occurs by an exchange mechanism, in which an adatom takes the place of a lattice atom. Again it must be stressed that this is a phenomenon that occurs at room temperature, where there is otherwise no perceptible thermal disordering of the surface.



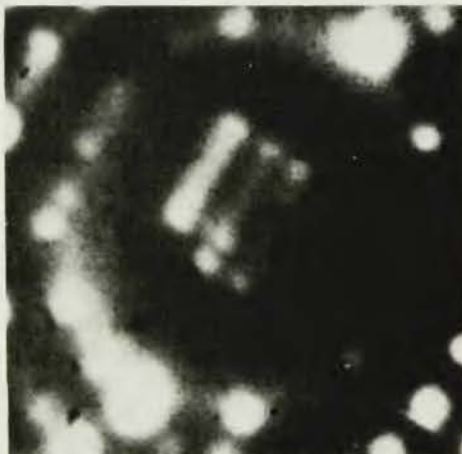
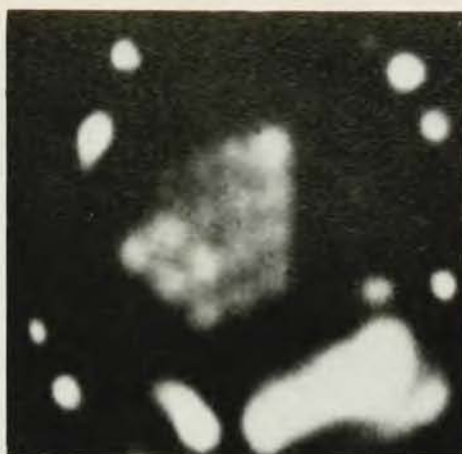
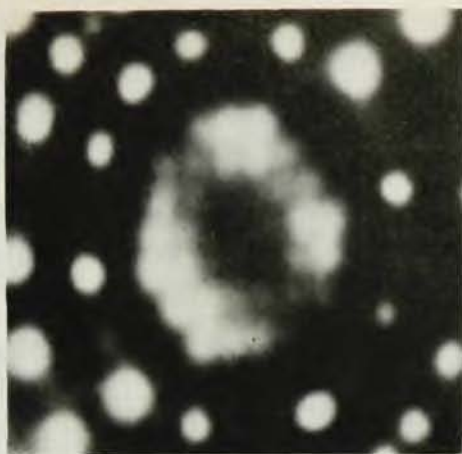
Field ion micrographs of a rhenium dimer on the (211) surface of tungsten depict its formation and migration during 3 sec intervals at 375 K. The two basic configurations, straight or 0, and slanted or 1, are shown at the right both in field ion micrographs and models. Rhenium dimers on a tungsten (211) surface are surprisingly mobile. Figure 6

Precisely why there is cross-channel diffusion on the (110) plane of iridium and platinum but not on rhodium is not clear at the moment. It is tempting to correlate the difference in behavior with the absence of restructuring on rhodium's (110) surface. Recently, however, researchers¹² at the University of Pennsylvania have observed cross-channel motion of single nickel adatoms on the (110) plane of nickel, even though there is no indication of any lateral rearrangement of this surface. Obviously we still have much to learn, but observations with the field ion microscope have already provided surprisingly detailed insights into the motion of single metal atoms on metals. Such observations need not be limited to metals—we have examined semiconductor adatoms by the same methods.

Adatom clustering

If we are ever to establish a bridge between the behavior of individual adatoms and the properties of monolayers we will have to understand what happens when adatoms interact with each other. Interesting things occur when more than one atom is deposited on a crystal plane. If the surface temperature is high enough for diffusion, the adatoms often cluster together. These events have been examined quite closely on the (211) plane of tungsten.¹³ Figure 6, for example, shows a dimer formed from two rhenium atoms in adjacent channels. At low temperatures the dimer exists in two states, which we shall label as straight and staggered, or equivalently, by the lateral separation of the adatoms, as 0 and 1. Surprisingly enough, the dimers are quite mobile. In fact, they diffuse rapidly at temperatures at which a single rhenium atom is immobile. This increased mobility could be important in surface transport—but how does it come about?

By examining the dimers at low temperatures at which movement during one observational interval is infrequent, the elementary mechanism of diffusion has been identified. Diffusion occurs through the motion of one atom at a time. Migration takes place in two distinct steps: the transformation of a straight into a staggered conformation, followed by the return to a straight dimer. Both rates have been measured quantitatively. For atoms in the dimer, the attempt frequency is not much different from that of an isolated adatom. However, the barrier opposing the transformation of the straight into the staggered configuration is significantly smaller than for the reverse process. Both are smaller than the barrier to motion of an isolated rhenium adatom. In other words, interactions between the two atoms reduce the barrier for jumping in the



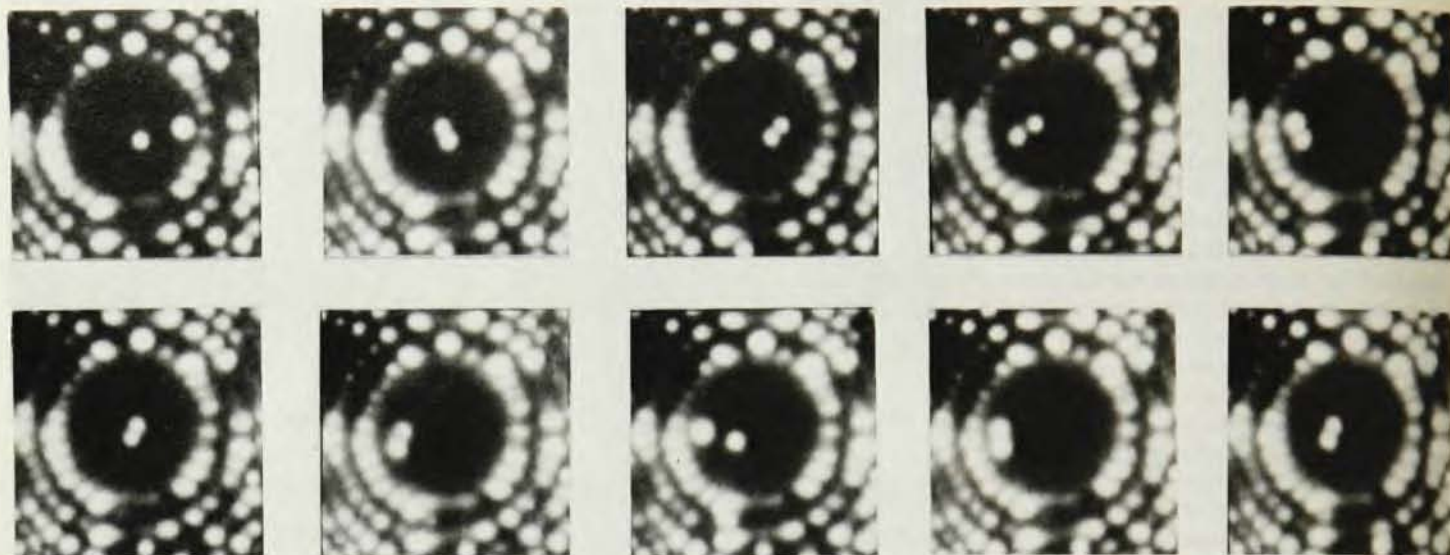
Images of large clusters of adatoms on the (110) plane of tungsten show the beginning of a new atomic layer. Shown in these photographs taken by H.-W. Fink, are large clusters of palladium and iridium adatoms (top), and platinum and silicon adatoms (bottom). These adlayers are not densely packed and the symmetry of the atomic arrangement is not the same for all. Individual atoms in the adlayers are so widely spaced that they can be resolved; the (110) substrate surface, in contrast, is densely packed and appears dark and featureless. Figure 7

dimer. When yet a third atom is added in a channel adjacent to the dimer, the rate processes become much more complicated. A total of nine distinct steps now contribute to diffusion. These have not yet been examined in detail. Contrary to what might be expected from extrapolation, however, rhenium trimers move no more rapidly than rhenium dimers. Obviously there is more work to be done here.

This type of behavior is not general for clusters—it is specific to rhenium atoms in adjacent channels. Cluster properties turn out to be significantly affected both by the chemical nature of the constituent adatoms and their arrangement on the surface. Contrary to the results for rhenium dimers, cross-channel dimers of iridium on the tungsten (211) plane, for example, diffuse much more slowly than single iridium atoms. Evidently the distance dependence of the effective potential between iridium atoms in adjacent channels is different from that between rhenium atoms; it does not bring about a lowering of the barrier to atomic jumps in the dimer. Another intriguing fact is that two rhenium atoms in the same channel behave quite differently than

two rhenium atoms in adjacent channels. An in-channel rhenium dimer must overcome a barrier much higher than that confronting a single rhenium atom, so motion only occurs at elevated temperatures. Addition of a third rhenium atom into the same channel stops diffusion, at least at temperatures readily accessible. On one and the same substrate surface, cluster properties are thus immediately affected by the geometry of the cluster.

Cluster motion has also been studied on other planes of tungsten,¹⁴ primarily on (110), the most closely packed plane of this lattice. On this surface there is only a slight difference in the energy of motion of tungsten dimers and single tungsten adatoms. Bassett examined larger clusters and found that mobility diminishes with cluster size. The barrier to diffusion of an isolated atom amounts to 0.67 eV. For Pt₂ it is also 0.67 eV, but it increases to 0.78 eV and 0.87 eV for Pt₃ and Pt₄ respectively. However, just as on the (211) plane, diffusion takes place by jumps of individual atoms. This was confirmed recently for tungsten dimers on a tungsten (110) plane.¹⁴ The behavior of clusters on this surface is



Pictures of a cross-channel rhenium dimer reveal that dissociation is quite frequent at higher temperatures. This field ion microscope sequence shows the dimer's behavior at a temperature of 392 K. Figure 8

rather different from that on the tungsten (211) plane and it appears that the nature of the substrate markedly affects cluster properties.

Work of this sort is not necessarily limited to clusters of a few atoms. When more and more atoms are placed on one plane they eventually form a new crystal layer. We can depict such overlayers with atomic resolution, as in figure 7. Hans-Werner Fink has found that the atomic arrangement here may not correspond to close packing. This is evident in figure 7, for example, from the fairly open packing of the iridium adlayer, which consists of 16 clearly resolved atoms. There has not yet been a systematic exploration of the properties of these clusters. Enough has already been done, however, to indicate that significant information about them is accessible through direct observation in the field ion microscope.

Interactions in clusters

The properties of clusters on a surface, and ultimately of monolayers, depend upon the interactions among adatoms and between adatoms and the substrate. Observations of clusters can in turn reveal much about these interactions. This is most readily illustrated by considering a channeled plane such as tungsten (211), on which adatoms are constrained to move in one dimension. If two atoms are present in separate channels, then the probability of finding the atoms in an equilibrium distribution a lateral distance R apart is given by

$$P_R = C(2 - \delta_{R0})(L - R) \exp(-F_R/kT)$$

Here L is the number of sites in a channel, F_R is the free energy change (a negative quantity) on bringing two atoms from infinity to the separation

R , and C is a normalization constant. From the frequency with which the atoms are observed at a given separation, one can in principle deduce the free energy, and from the temperature dependence of the distance distribution, the internal energy of interaction.

For rhenium cross-channel dimers we have gained a fair amount of information in this way.¹³ The probability of finding dimers in the staggered compared to the straight configuration follows from the preceding equation as

$$P_1/P_0 = [2(L-1)/L] e^{-(F_1-F_0)/kT}$$

This ratio plotted against $1/T$ yields an energy difference of 60 meV between the two states. At more elevated temperatures the two atoms of the dimer occasionally part company, as illustrated by the sequence in figure 8. The probability P_d that a dimer is dissociated as compared with being in state 1 is

$$P_d/P_1 = [(L-2)/2] e^{F_1/kT}$$

From the temperature dependence of this ratio, the difference in energy between two rhenium atoms in the staggered configuration and dissociated from each other turns out to be 160 meV.

Three things are worth noting about these studies. Equilibration of the system is done in the absence of applied fields, and thus we measure the energetics in an ordinary thermal ensemble. The effective interaction energy for two rhenium atoms is found in this way to be nonmonotonic in the atomic separation: Attractions are stronger in the staggered than in the straight configuration. It is this distance dependence that is responsible for the low barrier to

the diffusion of rhenium dimers. The third point of interest is the magnitude of the dissociation energy: It is very small, comparable to the cohesive energy of atoms in rare gas crystals. In spite of this the dimers are stable even above room temperature because of entropy effects. There is only a small increase in entropy on dissociation, inasmuch as the number of configurations accessible to the separated atoms is limited by the finite size of the plane, and this stabilizes the bound state.

The distance distribution for a system in equilibrium can also provide information on interactions at longer distances. When two atoms are separated from each other by an intervening empty channel, interactions become negligible. The distance distribution for tungsten adatoms arranged in this way on the (211) plane of tungsten has been measured and found to conform well to that of noninteracting entities.¹⁵ On the (211) plane at room temperature, interactions at distances greater than 9 Å thus appear to be less than kT .

Considerable but less quantitative work has been done to characterize atomic interactions on tungsten (110), the most densely packed plane of the body-centered cubic lattice. Observations of the kinetics of dissociation at one temperature¹⁶ have provided estimates of the dissociation energy of various dimers on this plane. In the sixth row of the periodic table, the dissociation energy diminishes from 0.62 eV for Ta₂ to 0.32 eV for W₂; interactions between rhenium adatoms appear repulsive at close distances. There should also be interactions at longer distances. Theory predicts oscillations in the potential, and several attempts have been made to isolate

these by observing the distribution of metal atoms on the (110) plane.¹⁵ Early endeavors of this sort were done with many atoms on a plane. The first of these studies suggested oscillations, but they were artifacts produced by inadequate experimentation. Later, more careful examination failed to reveal oscillations of any sort.

Just recently Fink¹⁵ reported the first proper experiments to explore interactions between two atoms on the (110) plane of tungsten. He came up with an ingenious way of measuring the spatial distribution function of adatoms. In these experiments he deposited two chemically different atoms on a (110) plane. One of the atoms is immobile around room temperature, while the other is able to diffuse rapidly at lower temperatures. In this way Fink determined the distribution of palladium around rhenium and also around tungsten. In separate experiments, in which the palladium atom was allowed to wander over the surface by itself, the binding sites available to it were mapped out to provide a reliable distance scale. The measurements for the palladium-tungsten adatom pair suggest that interatomic distances of 3.2 Å and 11 Å are favored, but that the region between these separations is shunned by palladium atoms. It appears that the effective potential between a palladium and a tungsten adatom has at least two dips in it, with the minimum at 3.2 Å approximately 30 meV deeper than that at 11 Å. This is the first indication of nonmonotonic long-range behavior on this plane. Such behavior does not appear limited to this particular pair of atoms. Recent measurements¹⁷ of the distance distribution for tungsten-iridium pairs also show two minima, the second of which is at 11 Å, roughly 30 meV above the first.

The details of these atomic interactions are yet to be fully explored, and in trying to account for cluster properties it will be especially important to establish the contribution of many-body interactions to cohesion. It is clear, however, that interesting information is already being obtained about atomic forces on solids. That is also the general impression I would like to convey about the field as a whole. Most surprising perhaps is how routine the observation of individual atoms has become. The studies surveyed here should provide convincing evidence of this and of the power of the techniques. By direct observation it is now possible to establish both the dynamic and equilibrium properties of metal and semiconductor adatoms and of clusters on solids. Up to this point the work has been largely exploratory, aimed at defining the limits of the

techniques. Systematic examination of different and more complicated systems will help delineate trends, and should eventually establish a quantitative link between the properties of individual adatoms and those of monolayers.

* * *

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