CENTENARY LECTURE

Field-ion Microscopy and the Electronic Structure of Metal Surfaces

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1 Introduction*

There is a fascination in the immediate encounter with the atom in field-ion microscopy, FIM. You look at the atom as an individuum, and maybe, it looks at you. No more is the atom merely a well established concept, so convincing by its billionth of a contribution to a dim diffraction spot, but it is there really to be seen, to be touched and moved. It is seen in its environment, with neighbours of like or different nature, its organisation within the geometry of steps, net-planes and crystal facets. Actually, the surface observed is not as dead as it appears in the micrograph (Figure 1), there is quite an activity. Gas atoms impinge, exchanging energy and making permanent or temporary bonds, electrons and ions tunnel busily in the appropriate directions, metal surfaces evaporate in the form of highly charged ions at rates unheard of before. Obviously, there is plenty of surface electronics involved.

Before the beginning of this decade field-ion microscopy had been firmly established,[1] and with the direct visualisation at the atomic level of lattice defects such as vacancies, interstitials, radiation damage, dislocations, slip bands and grain boundaries, its potential in metallography was obvious. Since the early sixties the technique came into wide use all over the world, starting with its acceptance by an enthusiastic group of investigators at Cambridge where the existing knowledge of metallurgists was immensely helpful to appreciate the power of the new research tool.[2]

As usual when the promise of a new technique is realised, technology almost takes over. But in spite of ultra-high vacuum gadgetry, computers, image intensifiers, data acquisition considering the taking of half a million photographs from one specimen, the basic imaging has not been changed since 1956 and the image quality has been improved only marginally. The main progress, other than in straightforward applications, has been in the gradual advancement of our

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* It does not appear necessary to present here all the field-ion micrographs that were shown in the lecture, as most of them have been published elsewhere. However, a number of literature references have been added to this written version.

[1] E. W. Müller, in 'Advances in Electronics and Electron Physics', vol. 13, Academic Press, New York, 1960, pp. 83-179.
[2] A. H. Cottrell, *J. Inst. Metals*, 1962, **90**, 449.

understanding of the image formation and in the art of image interpretation.

What I want to consider today is the challenge of field-ion microscopy to chemists and surface physicists. When we realise the uniquely extreme conditions at our specimen surfaces, and if we further see chemistry as basically dealing with electronic interaction and transition between neighbouring atoms, the potential relevance of our technique becomes obvious.

2 Field Ionisation

While the basic imaging process appeared simple, a radial projection of the locations of strong-field ionisation of the image gas, we soon had to learn a few significant details. Field ionisation is seen as tunnelling of an electron from the ground state of the image gas, usually helium. A surprise was the narrowness of the energy distribution of the ions as obtained by retarding potential analysis.[3] It indicates that the zone of ionisation probability is located closely above a protruding surface atom in a disc only 0·2 Å thick, that is one tenth of the diameter of the helium atom. Now, a WKB calculation of tunnelling probability out of the approaching gas atom does not give such a sharp localisation. This looks more like a pretty hard collision. Indeed, Boudreaux and Cutler[4] have successfully used rearrangement collision theory to obtain such narrow distribution widths. Alas, as all too often in quantum mechanics, results are obtained just for the hydrogen atom in front of a planar surface. Therein the experimentalist finds little consolation, so he turns again to looking more closely at his micrographs. Presumably, field ionisation reflects the local field strength, which is primarily determined by the degree of protrusion of the surface elements. This is measured quantitatively by Moore's computer model[5] which considers all surface atoms to be imaged whose centres are located within a spherical shell of thickness between 5 and 20% of the lattice parameter. Indeed a plot of atom dots computed for an f.c.c. (face-centred cubic) or b.c.c. (body-centred cubic) lattice resembles quite well a field-ion pattern, except that any chemical specificity is absent. In reality, micrographs[6] of b.c.c. tungsten, molybdenum, tantalum, and niobium, and iron are very different in regional brightness and emphasis of atoms at certain lattice sites, and so are the patterns of f.c.c. iridium, platinum, palladium, nickel, cobalt, gold, and copper as well as those of h.c.p. (hexagonal close-packed) rhenium, ruthenium, zirconium, cobalt, and beryllium. In comparing these photographs, we have to abstract from imperfect imaging of some metals due to their low lattice strength, which makes some metals difficult to handle. Today, high school students at science fairs produce quite acceptable field-ion micrographs of tungsten and iridium, while good images of the metals towards the end of my lists are still worth half an experimental thesis.

In the view of quantum mechanics,[4] field ionisation, or the electronic transi-

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[3] T. T. Tsong and E. W. Müller, *J. Chem. Phys.*, 1964, **41**, 3279.

[4] D. S. Boudreaux and P. H. Cutler, *Surface Sci.*, 1966, **5**, 230.

[5] A. J. W. Moore, *J. Phys. and Chem. Solids*, 1962, **23**, 907.

[6] E. W. Müller, *Science*, 1965, **149**, 591.

tion probability, is given by the overlap of the wave functions ψ_α of the surface atom with the wavefunction ψ_a of the image-gas atom:

$$P = \frac{4\pi^2}{h} N(E_\alpha) \, | < \psi_\alpha | V | \psi_a > |^2,$$

with h denoting Planck's constant, $N(E_\alpha)$ the density of surface states, and V the interaction potential. As I indicated, these parameters are not by themselves available for the situations encountered in field-ion microscopy, nor, for that matter, are the wavefunctions known for any surface. We simply have no theory of surface states. This situation is about as embarrassing as the lack of a theory of melting must be to the solid-state scientist. There is no doubt that the redistribution of electronic surface charge due to the assymmetry of the surface as well as due to its specific crystallographic topography[7] is of primary significance, and under the extreme conditions of field-ion microscopy operated at 500 Mv/cm. field strength, the charge redistribution is further modified. Gauss' law connects two-dimensional surface charge density with the strength of the external field, and field penetration into the depth of the surface needs to be considered to obtain the effective surface field responsible for the local image brightness of single atoms.[8,9]

In order to advance in this complex situation, we may borrow some crutches from chemistry to arrive at a few practically useful concepts. A first hint of the action of surface charge redistribution was obtained from the effect of hydrogen promotion of field ionisation:[10] normally the field required for the ionisation of helium is 450 Mv/cm., but with a small quantity of hydrogen added a very bright and well resolved helium-ion image is obtained at only 2/3 of that field. This works with a number of metals and is of practical use as it permits imaging of metals with lower cohesion energy at a reduced mechanical field stress.[11] A reasonable explanation of this surprising effect is the charge transfer from the protruding metal atoms to adsorbed hydrogen atoms forming a hydride-like bond.[12] Only crystallographic regions where the interstices can spatially accommodate the 1·3 Å radius of the negative hydride ion are effective. Thereby, the local charge-density of the metal atoms at 300 Mv/cm. externally applied field is as large as it would be at 450 Mv/cm. without adsorbate.

Another case of regularly patterned charge redistribution occurs in the surface of ordered alloys. In the interpretation of images of ordered Pt–Co and Pt_3–Co given by Tsong and myself[13] the cobalt atom is invisible, so that certain planes develop a coarser structured super-lattice pattern, occasionally interrupted in its perfection by substituted atoms of the wrong kind.

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[7] R. Smoluchowski, *Phys. Rev.*, 1941, **60**, 661.

[8] E. W. Müller, *Surface Sci.*, 1964, **2**, 484.

[9] T. T. Tsong, *Surface Sci.*, 1968, **10**, 303.

[10] E. W. Müller, S. Nakamura, O. Nishikawa, and S. B. McLane, *J. Appl. Phys.*, 1965, **36**, 2496.

[11] O. Nishikawa and E. W. Müller, *Surface Sci.*, 1968, **12**, 247.

[12] E. W. Müller, *Surface Sci.*, 1967, **8**, 462.

[13] T. T. Tsong and E. W. Müller, *Appl. Phys. Letters*, 1966, **9**, 7; *J. Appl. Phys.*, 1967, **38**, pp. 545, 3531.

The effect of charge rearrangement on the imaging of a single surface-metal atom is best seen in the case of chemisorption, which, of course, displays a considerable variety of possibilities. Oxygen on tungsten and platinum were, as a matter of curiosity after our previous experience with field emission microscopy, the first systems studied,[1] and an investigation of the interaction of oxygen with tantalum followed.[14] The system of oxygen on tungsten has also more recently been studied by Anderson and his coworkers.[15] After exposure of the specimen to oxygen, with the field off and at low temperature, rapid desorption of bright spots is seen before best-image voltage condition is reached again, and imaging with neon at a reduced field also indicates early desorption of oxygen.[1] What remains is a heavily corroded surface, with many metal atoms removed from net-plane edges or shifted to adjacent sites. Numerous bright spots most likely represent not adsorbed oxygen atoms, but rather metal atoms which have assumed an excessive positive charge by the adsorption of an oxygen atom. However, with the adsorption of a small number of oxygen atoms, one finds that the brightness of a tungsten atom may also be reduced, thus indicating a multiplicity of possible situations depending upon the specific site or the degree of the formation of an oxide molecule.

With nitrogen, which is initially chemisorbed as a molecule, most of the adsorbate is also gone when the best image voltage is re-established, and at larger coverage, as well as at higher temperature, there is heavy corrosion of the metal substrate presumably following dissociation of nitrogen. Again, a small number of extra-bright spots remain, interpreted by one investigator,[16] as nitrogen molecules, and by others,[17] quite emphatically as tungsten atoms displaced to a proud position; I am inclined to accept the invisibility of the nitrogen atom. As can be concluded from positive or negative work-function changes in field-electron microscopy, depending upon the specific net plane, nitrogen may attract negative charge from the substrate. In FIM it reduces the field locally to suppress field ionisation. The extra-bright spots, in the view of charge rearrangement, represent tungsten atoms bonded to an invisible nitrogen atom, the latter draining electronic charge from one metal atom and thus increasing its field ionisation probability.

To the list of invisible adsorbates, hydrogen, oxygen and nitrogen, we may also add carbon. Evaporated onto a tungsten surface or added to the tip material in a carburising reaction it again gives the surface a mottled appearance by metal atoms and increasing their efficiency of field ionisation.

The resolution of FIM does not suffice to establish the exact location of the adsorbate with respect to the enhanced metal atom. All four species discussed are of small atomic size and are known to form interstitials in the matrix metals. So it may well be possible, as Anderson[15] suggests, that the adsorbate assumes a sub-surface position, into which it can move by utilising its adsorption energy

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[14] S. Nakamura and E. W. Müller, *J. Appl. Phys.*, 1965, **36**, 3634.

[15] J. S. Anderson, *Rec. Austral. Acad. Sci.*, 1967, **1**, 109.

[16] G. Ehrlich, *Discuss. Faraday Soc.*, 1968, **41**, 7.

[17] W. M. H. Sachtler and A. A. Holscher, *Discuss. Faraday Soc.*, 1966, **41**, 29.

against the weakened bond of the affected surface atom. Sometimes, for instance in the case of oxygen in tantalum,[14] the bright surface spots are indeed hard to distinguish from bulk interstitials exposed to the surface by field evaporation. Usually, however, the metal atom spots enhanced by adsorption are not quite as bright as those obtained from intrinsic interstitials; thus for the adsorbed atom I would prefer assuming a sideways attachment. This seems to be the only acceptable mechanism in the case of adsorbed carbon monoxide, which also produces bright spots and is known not to dissociate upon adsorption on tungsten.

The field-ion microscopical image of intrinsic interstitials, be they self-interstitials or impurity atoms, is therefore of interest. Self-interstitials can be introduced by irradiation, and impurities may be added by ion implantation or by diffusion, all these processes being done either *in situ* or before forming the specimen tip, and they can be made to show at the surface by either field evaporation or thermally activated diffusion. The generally quite uniform appearance in the form of a single, bright atom spot, perfectly round even on a net-plane with a pronounced atom-row structure, led me to abandon my original interpretation[1] as a bulge on the distorted net-plane surface. In view of the concept of electronic charge redistribution I rather like to see the lattice atom above the sub-surface interstitial assume an enhanced field ionisation probability when it has to provide an additional electron for a bond to the interstitial underneath.

The interesting fact is that obviously only one surface atom is affected. (If there are di-interstitials, as can be produced[14] by starting with tantalum containing oxygen interstitials in a counted concentration of 8×10^{-3} and annealing the tip *in situ* at 375°K for 100 hr., there are two surface atoms involved.) The one-to-one relation indicates a strictly one-to-one, localised bond.

The concept of metal-surface atoms exhibiting localised bonds has recently been increasingly applied to the interpretation of results in chemisorption and catalysis. In this view, surface atoms have atomic or molecular orbitals partially or fully occupied by electrons and emerging in spatial directions approximately corresponding to those of the bonds in the bulk crystal.[18,19] These dangling orbitals may overlap those of ad-atoms to make the bonds. The mechanism of field ionisation as expressed by the matrix element of the wavefunctions and the interaction potential can now be refined by looking for effects of orbital directions.[20] Field ionisation will occur where the fully occupied orbitals of the image gas-atom can overlap with the extended, only partially occupied orbitals of the surface atom. Temporarily there is a molecule formed from the protruding surface-atom and the image-gas atom, which then quickly dissociates to release the image-gas ion.

Experimental evidence is seen in the distribution of regional brightness of field-ion patterns. There are abrupt changes of brightness across certain zones even within one net plane where the degree of protrusion, as measured in the

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[18] J. B. Goodenough, 'Magnetism and the Chemical Bond', Interscience, New York, 1963.
[19] G. C. Bond, *Discuss. Faraday Soc.*, 1966, **41**, 200.
[20] Z. Knor and E. W. Müller, *Surface Sci.*, 1968, **10**, 21.

thin-shell model, does not change at all. What does change, however, is the direction and number of nearest, next nearest, third, fourth, and so on, dangling bonds or, in other words, empty or only partially occupied orbitals extending into space. These change abruptly as we move across a crystallographic zone whose axis is parallel to the bond vector. The change in regional brightness, however, is not uniquely related to the geometrically determined broken bond pattern. Moore and Brandon[21] have recently mapped these geometrical zones for the b.c.c. and f.c.c. lattices. Comparison with micrographs of tungsten, tantalum, and molybdenum clearly shows that only some of the critical first- and fourth-neighbour zones affect the regional brightness pattern, and others do not (Figure 2). The chemical specificity within one lattice type, particularly pronounced in the b.c.c. lattice, but also seen in the f.c.c. metals platinum and iridium (Figures 3, 4), must enter by the distinct degree of occupation of those extended orbitals which are directed away from the surface, and possibly by their hybridization.

Further detailed analysis of micrographs will be necessary to unravel the intricacies of field ionisation through overlapping orbitals. Two features of the vicinity of the basal plane of the h.c.p. lattice as observed in rhenium, ruthenium, cobalt, and beryllium may be indicative. First, there is a six-fold symmetric alternation of net-plane edge brightness, making always one 60° sector invisible (Figures 5, 6). By comparison with the three-fold symmetry around the (111) poles of Pt one can conclude that it is the single nearest neighbour t_{2g} bond with a large component normal to the surface that contributes overwhelmingly to the ionization, while the more sideways protruding t_{2g} bonds at the alternate (0001) plane edges are ineffective for field ionisation (Figure 7). The other specific feature are the most conspicuous atoms of the $[11\bar{2}1]$ zone decorations. Presumably these are single atoms moved away from the net-plane edge to a metastable position where they obtain their extra binding energy sufficient to withstand the desorbing force of the nearly unshielded field exposure from a far-reaching rearrangement of their electronic configuration.[8] This results in an increased polarisability and the corresponding large bonding force $\frac{1}{2}\alpha F^2$. A close inspection of the shape of the decoration atom spots reveals that those leaning on a visible (0001) plane edge often are extended sideways by showing wings, while those atoms leaning on an invisible edge are round. Comparison with a ball model (Figure 7) in which the more outreaching t_{2g} orbitals are represented by rods, indicates that the first type of metastable atoms have two such orbitals, somewhat sideways directed, and the second type has only one dangling orbital normal to the surface. Similarly, one can occasionally observe sideways satellites on the [100] zone decoration atoms of tungsten. It thus appears that there is a real possibility of seeing directly individual extended orbitals by the field-ionisation process.

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[21] A. J. W. Moore and D. G. Brandon, *Phil. Mag.*, 1968, **17**, 679.

3 Field Evaporation

Next to field ionisation the effect of field evaporation is the most significant process in field-ion microscopy. Without it, we would not be capable of preparing surfaces with the high degree of geometrical perfection that alone makes the radial-projection principle work properly down to the atomic resolution. In this lecture there is not enough time for even a cursory review of all that is involved in this effect, and I shall confine myself to a very few points.

I had originally developed an image force theory[22] which subsequently has been justified and refined.[23,24] The removal of a surface atom over a diminishing barrier, Q, can be expressed by:

$$Q = \Lambda + I_n - n\phi + \tfrac{1}{2}\alpha F^2 - (n^3e^3F)^{1/2},$$

where Λ is the heat of vaporisation of the neutral atom, I_n its nth ionisation potential, ne its positive electronic charge, ϕ the work-function of the site, and α essentially the polarisability of the atom at its site. Way back in 1957, after having shown how one can deposit single metal atoms on the tip and observe their motion by surface diffusion, or their removal by field evaporation, I had suggested that it was only a matter of patience to carry out the experiments for measuring the activation energy of surface migration and the binding energy of atoms at individual sites.[25] These delicate but straightforward experiments have now been carried out in a series of skilful experiments by Ehrlich and Hudda[26] as well as by Plummer and Rhodin,[27] in the U.S., and most recently by Bassett and Parsley in London. Their most significant quantitative result is that surface binding cannot be described by adding up the pairwise interactions with nearest, next nearest, and so on neighbours, regardless whether Lennard–Jones or Morse potentials are used that are giving quite reliable results for the computation of the bulk cohesive energy of metal lattices. This deviation then results from the charge redistribution at the surface.

In our equation Q amounts only to one tenth or less of an ev in a low-temperature field evaporation experiment; the remaining, small barrier is either overcome by thermal activation, or, more probably, by ionic tunnelling.[28] The principal unknown factor in our equation is the polarisation term, which probably is larger than the 0·5 ev which Ehrlich and Plummer assume. Their results may also have to be reinterpreted in the light of new experimental facts about the unexpected magnitude of ionic charge coming from a novel modification of FIM, the atom-probe.

4 The Atom-probe FIM

Ever since the discovery of water and nitrogen corrosion of FIM specimens and the promotion of field evaporation by hydrogen and other gases,[1] I have been

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[22] E. W. Müller, *Phys. Rev.*, 1956, **102**, 618.
[23] R. Gomer and L. W. Swanson, *J. Chem. Phys.*, 1963, **39**, 2813.
[24] D. G. Brandon, *Surface Sci.*, 1965, **3**, 1.
[25] E. W. Müller, *Z. Elektrochem.*, 1957, **61**, 43.
[26] G. Ehrlich and F. G. Hudda, *J. Chem. Phys.*, 1966, **44**, 1039.
[27] E. W. Plummer and T. N. Rhodin, *J. Chem. Phys.*, 1968, **49**, 3479.
[28] T. T. Tsong, *Surface Sci.*, 1968, **10**, 102.

interested in chemically identifying the field evaporation products. Conventional mass spectroscopy[29] is marginal because of the noise problem with so few ions available from a field evaporating tip. So I came to a radical solution by pointing one atomic site of interest into a probe hole drilled in the screen, and running the field desorbed particle through a mass spectrometer equipped with a detector of single-ion sensitivity.[30] The noise problem is dealt with by a time correlation between the evaporation and the detection event. In our present device this is done conveniently by pulse evaporating the particle and by employing a time-of-flight mass analyser, as shown schematically in Figure 8. Of course, the atom-probe is a most powerful microanalytical tool, in fact one of ultimate sensitivity, as it needs only one atom for identification, but in the frame of this lecture I shall not dwell at this at all.

The first surprising result was the three- or four-fold positive charge carried by the field evaporation products from tungsten and molybdenum emitters.[30] A number of complex molecular ions such as WO_2^{3+}, $W_2O_3^{4+}$ were found, but most unexpected is the occurrence of three- and four-fold charged tungsten, tantalum, molybdenum, and rhenium and three- and two-fold charged iridium, platinum, rhodium, and beryllium.[31] We are using 2 or 20 nsec. square-wave desorption pulses, and find that the abundance of the higher charge species always increases with the pulse height, which affects the rate of field evaporation. In some cases we field evaporate as much as 10 atomic layers within two nanoseconds, which is a fantastic evaporation rate of 1 m./sec. We do not know the charges for conventional 'slow' field evaporation, but Brenner and McKinney[32] who have followed up our work by constructing a similar instrument with bell-shaped 10^{-7} sec. pulses and less mass resolution also obtain some W^{4+} and Ir^{3+} besides the more abundant triply and doubly charged ions. It is an open question whether the higher ionisation stages are due to intrinsic field evaporation with the high charge, or whether an additional electron is lost by field ionisation following the evaporation act.[1]

The operation of the atom probe is much facilitated if the image gas can be kept in the microscope during pulsing. This is no problem as a bright atom spot emits only about 10^4 helium ions/sec. at a chamber filling of $\frac{1}{2}$ mtorr, so that spurious gas ions at random times during the 5 or 10 μsec. gating of our detector scope are quite rare events.

In order to test our mass resolution we have recently concentrated on tip metals having one isotope mass only. Beryllium, cobalt, niobium, rhodium, tantalum, and gold are such metals with which we already have good experience in field ion microscopy. For instance with $^{103}Rh^{2+}$, appearing at $m/m = 51{\cdot}5$, we have about 1/2 mass unit reproducibility with the time uncertainty of ± 20 nsec.

If we now operate at 21 °K in the presence of helium as imaging gas, we quite often obtain peaks at 53·5 a.m.u., which only can indicate a doubly charged

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[29] D. F. Barofsky and E. W. Müller, *Surface Sci.*, 1968, **10**, 177.

[30] E. W. Müller, J. A. Panitz, and S. B. McLane, *Rev. Sci. Instr.*, 1968, **39**, 83.

[31] E. W. Müller, S. B. McLane, and J. A. Panitz, Proc. 4th European Regional Conf. Electron Microscopy, vol. 1, Rome, 1968, p. 135.

[32] S. S. Brenner and J. T. McKinney, *Appl. Phys. Letters*, 1968, **13**, 29.

rhodium–helium molecular ion. Triply charged ions of this type seem to occur more rarely. If we image with neon gas, there are some rare, about one in fifty, events which indicate rhodium–neon ionic molecules of various charges (Table 1). The quite surprising occurrence of these helium- and neon-metal molecular ions in field evaporation leads us back to the concept of field ionisation by overlapping orbitals of the surface atom and the gas atom. During the normal image process, the short lived noble-gas–metal molecule dissociates to release the image-gas ion. In field evaporation, the image-gas–metal molecule ion takes off as a unit. If its life time is more than 20 nsec., the time required to full acceleration, it will be recorded as a molecule ion with the appropriate mass. Particularly in the case of rhodium, field evaporating in neon, there are often an abundant number of random apparent masses observed. These UFO's or unidentified flying objects, are certainly not of extra-terrestrial origin, but are indicating a lifetime of the rhodium–neon-ion molecules of less than the acceleration period.

Table 1 *Field evaporation at* 21 °K *with image gas*

Rhodium in neon (5×10^{-5} to $5 \cdot 10^{-4}$ torr)		*Rhodium in helium* (4×10^{-6} torr)	
Rh^+	1	Rh^+	—
Rh^{2+}	40	Rh^{2+}	9
Rh^{3+}	7	Rh^{3+}	1
$^{20}Ne^+$	35	He^+	12
$^{22}Ne^+$	2	$RhHe^+$	1
$RhNe^+$	1	$RhHe^{2+}$	9
$RhNe^{2+}$	1	UFO	12
$RhNe^{3+}$	2		
$RhNe_2^+$	1		
$RhNe_2^{2+}$	1		
UFO	25 ($p > 10^{-4}$ torr)		

When these noble-gas–metal ion molecules appear, there are also individual He^+ and Ne^+ ions coming off the surface at 21 °K. This indicates the presence of adsorbed noble-gas atoms. The weakening of the metal bonds due to this adsorption suffices to explain the promotion of field evaporation by the impact with polarisation energy of the imaging-gas atoms,[33] so that we no longer need the never very convincing concept of an electron shower from the gas-atoms field ionised farther out in space.

There are, of course, more stable molecular ions produced by field evaporation of metals when chemically more active gases are adsorbed. Various oxide molecules were in fact the first species detected by the atom probe, and Table 2 lists the field evaporation products from a rhodium tip in the residual gas of 5×10^{-8} torr to which some hydrogen has been added. Nitrides and hydrides are abundant, as could have been expected from the long known promotion effect that these gases have on field evaporation of most metals.

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[33] O. Nishikawa and E. W. Müller, *J. Appl. Phys.*, 1964, **35**, 2806.

Table 2

Rhodium at 21 °K	*Residual gas plus* H_2, $p = 5 \times 10^{-7}$ torr
Rh^{2+}	37
Rh^{3+}	14
RhN^{2+}	4
RhN^{3+}	6
RhN_2^{2+}	1
RhN_2^{3+}	3
RhH_2^{2+}	7
H^+	34
N^{2+}	1
O^+	3
UFO	3

It appears that the atom-probe field-ion microscope will become a quite useful research tool for surface chemistry and physics as well as metallurgy, besides its promise to elucidate some of the still vexing problems of field-ion microscopy itself.[34] In a sense, this is a most satisfactory development of this branch of microscopy. We now can really deal much more intimately with the individual atoms which we encounter, since we know their names.

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[34] E. W. Müller and T. T. Tsong, 'Field Ion Microscopy', Elsevier, New York, 1969.

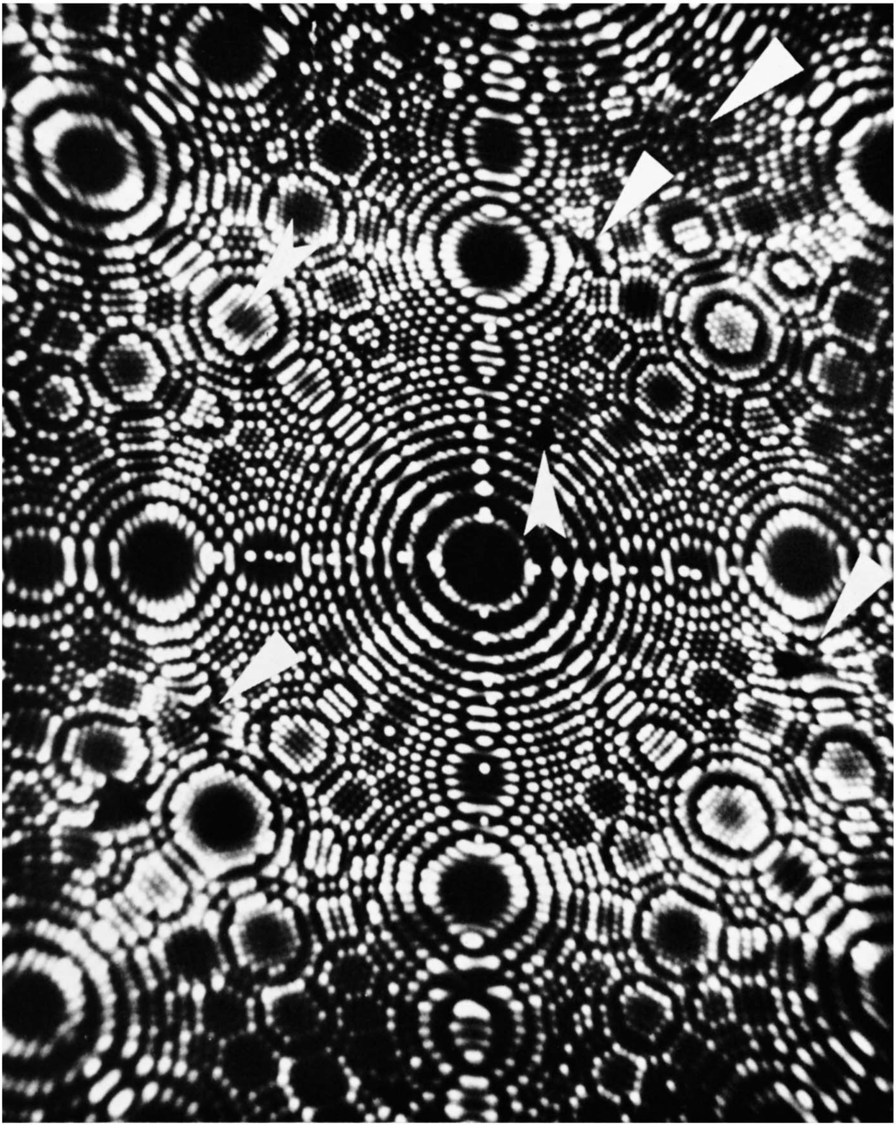

Figure 1 *Field-ion micrograph of an iridium tip as seen through the window of the atom-probe* FIM. *A vacancy and dislocations are marked by slanted arrows. The probe hole is at the vertical arrow point*

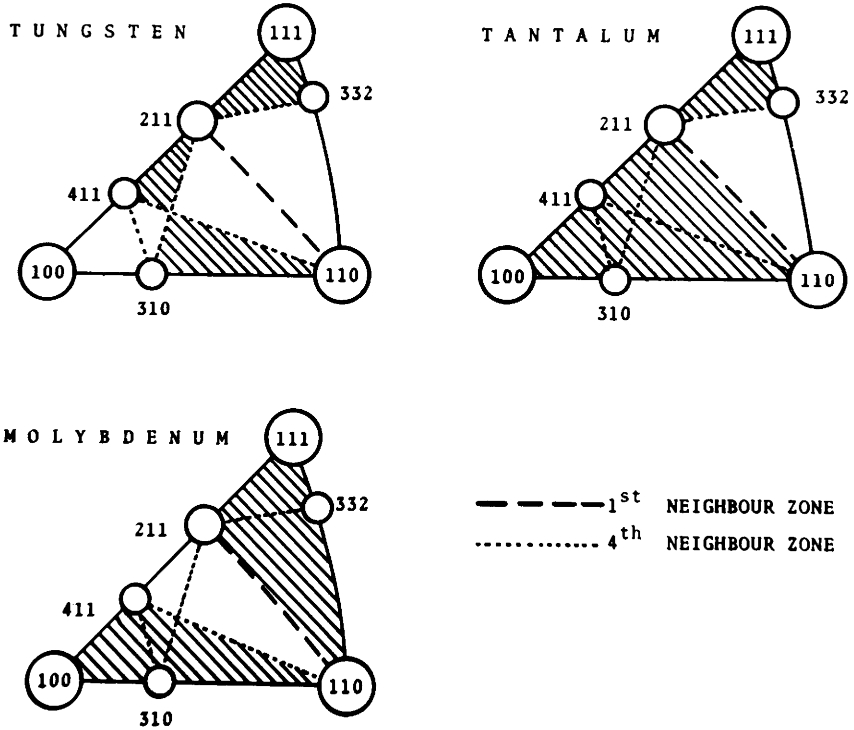

Figure 2 *Critical zones of broken* 1st *and* 4th *neighbour bonds in the* b.c.c. *crystallographic triangle, and regions of increased brightness* (*hatched*) *in* W, Ta, *and* Mo *micrographs*

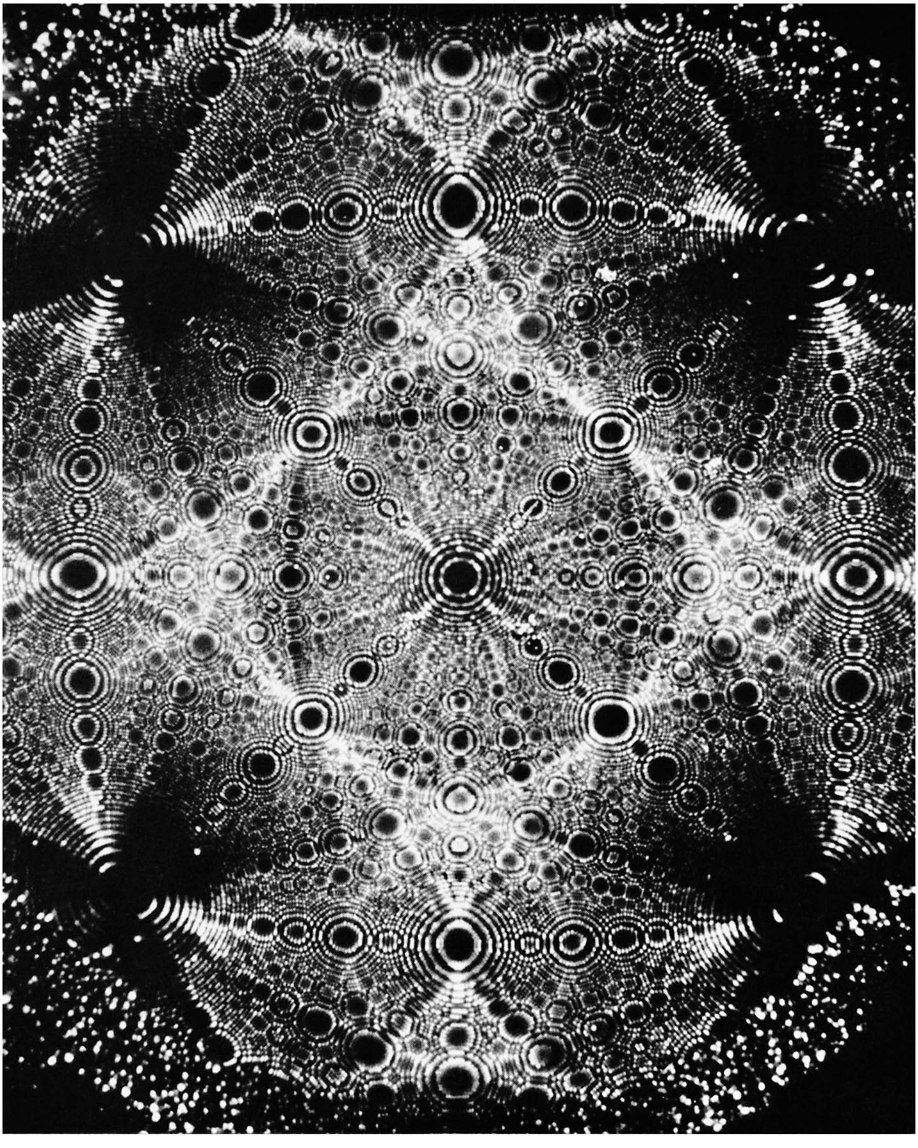

Figure 3 *Regional brightness of a large radius* Pt *tip*

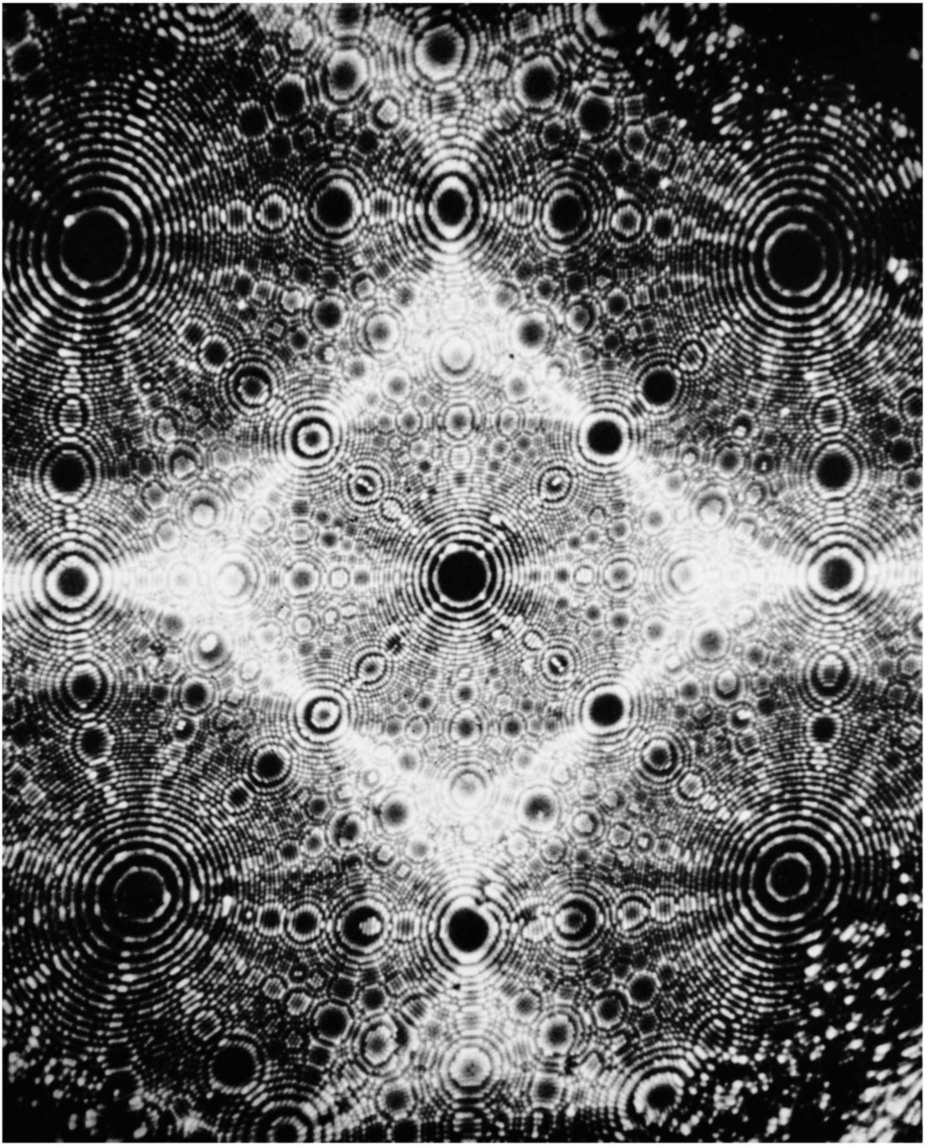

Figure 4 *Regional brightness of an* Ir *tip*

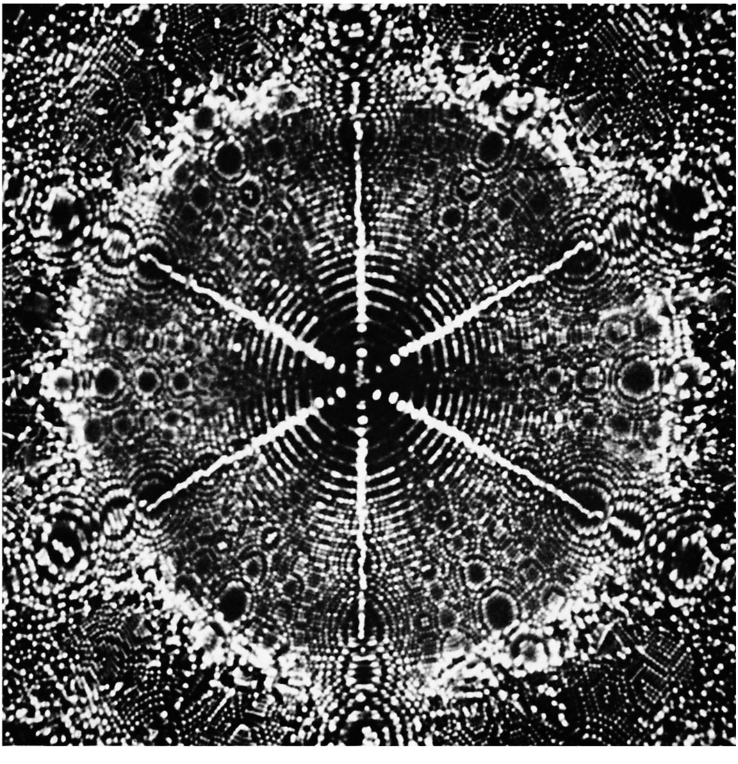

Figure 5 *Basal plane and vicinity of* h.c.p. *rhenium*

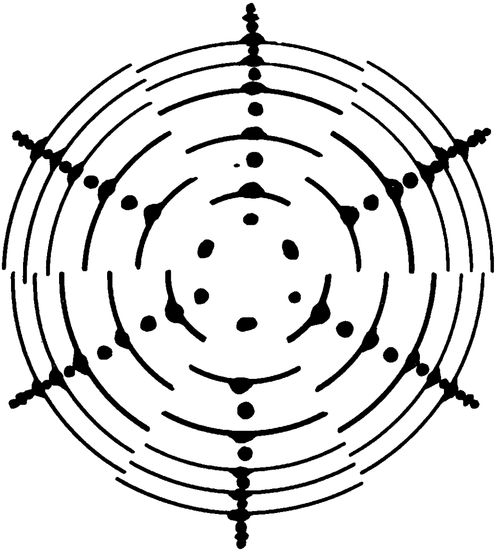

Figure 6 *Schematic diagram of alternating* (0001) *plane edges of* Re, *and the shape of zone decoration atoms*

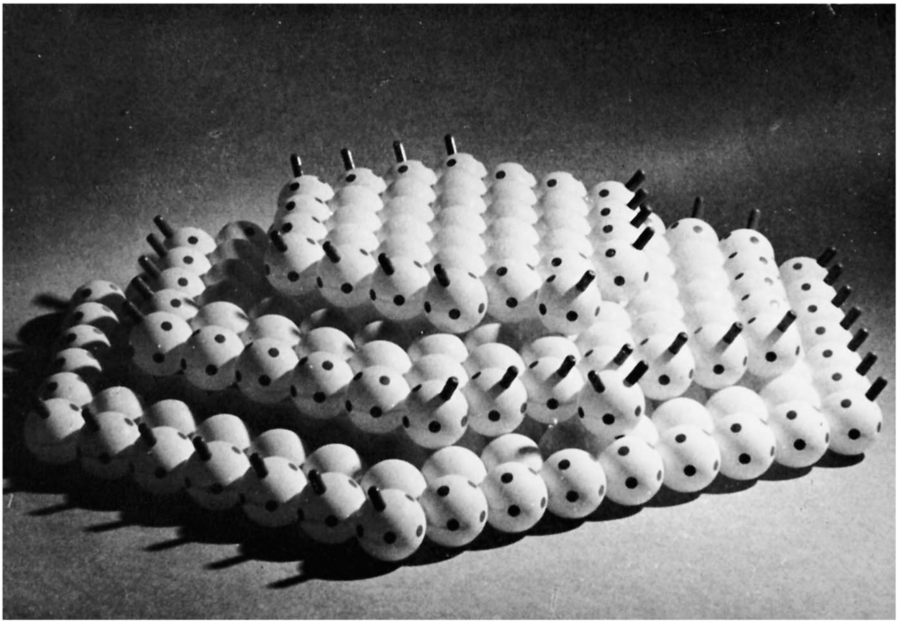

Figure 7 *Ball model of the three top* (0001) *planes of an* h.c.p. *crystal, showing extended orbitals that are effective for field ionisation. There are two* [1121] *zone decoration atoms leaning on a visible and an invisible lattice step*

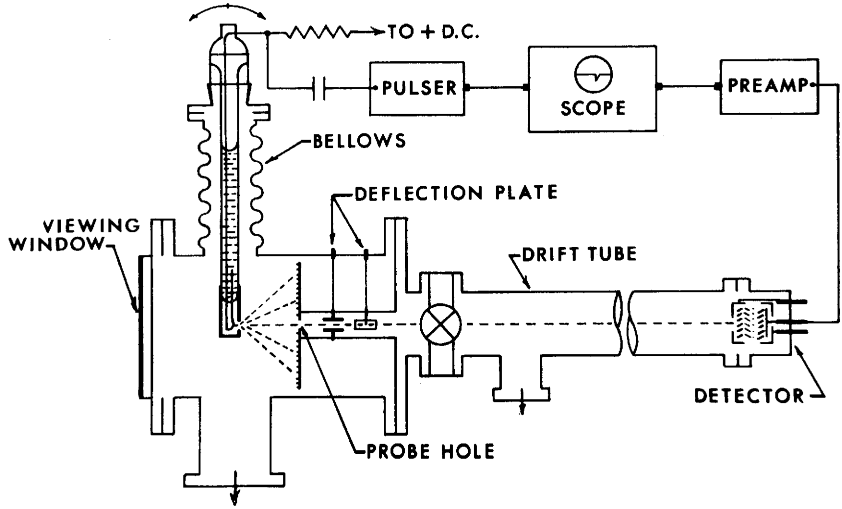

Figure 8 *Schematic diagram of the atom-probe* FIM