

SURFACE DIFFUSION OF TRANSITION METALS ON PLATINUM

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ABSTRACT

Single atom diffusion of platinum, gold, iridium and tungsten upon the (111), (113), (011) and (133) planes of a platinum surface has been studied in the field ion microscope. Owing to the very high adatom mobility on the Pt (111) plane and the relative immobility of tungsten adatoms within the experimental temperature range, it was not possible to obtain quantitative data for each adsorbate on all of the substrate planes. Data could not be obtained on the (100) plane owing to poor adatom visibility and substrate plane reconstruction.

Activation energies for surface diffusion were determined from the temperature dependence of the mean square atomic displacements. Their magnitudes for the respective platinum planes varied in the order:

$$\text{Pt (133)} > (011) > (113) > (111),$$

following a rough-smooth plane ordering; and for the respective adatoms in the order:

$$\text{W} > \text{Ir} > \text{Pt} > \text{Au},$$

following the variations in adsorbate cohesive energies.

The channelled (133), (113) and (110) planes were expected to exhibit one-dimensional adatom movement, while two-dimensional movement was anticipated on the relatively flat (111) plane. These expectations were fulfilled except for platinum and iridium diffusion on the (110) plane for which two-dimensional adatom motion was observed. Gold on the (110) plane exhibited solely one-dimensional movement.

Values for the activation energies were also obtained by calculation using a pair-wise interaction model with a modified Morse potential to describe the interaction between atoms. The calculations were found to correspond closely with experiment,

except for the (111) surface and in the cases of two-dimensional diffusion on the (110) plane.

Under high field conditions gold adatoms exhibited widespread imaging perturbations or suffered atomic displacements arising from polarisation of the gold adatom.

Palladium and nickel specimens were imaged but owing to difficulties in field evaporation well developed surfaces of nickel suitable as substrates for diffusion studies were not obtained.

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I. INTRODUCTION

Surface diffusion plays a vital role in a variety of important technological processes. Crystal growth, evaporation, sintering and the formation of films or epitaxial layers are good examples, each involving diffusion at the gas-solid interface as one important step. Study in this field is also of interest in its own right as a means of increasing the understanding of interatomic forces at surfaces, where the unsymmetrical environment of surface atoms introduces special problems.

1. Surface Diffusion

Surface diffusion can be defined as the mass transport over a surface resulting from the random, and usually thermally activated jumping of surface atoms. Most surfaces vary considerably in local atomic texture, and the overall diffusion process will consist of many different types of atomic jump occurring at different frequencies and reflecting the associated local surface structure. Between diffusion jumps the atom can be considered in equilibrium with the substrate and will consequently occupy a site of minimum energy. For diffusion to occur, the diffusing atom must possess sufficient energy to surmount the energy barriers in its paths between sites.

Considering a simple pair-bonding model, the interatomic bonding will be proportional to the number of nearest neighbours an atom possesses (the coordination number), thus the energy barrier to diffusion will depend upon the number of bonds broken as the atom moves from one site to another. Rough surfaces will possess an energy profile consisting of various energy minima at different levels separated by large energy barriers; thus in

general the rougher a surface is the higher will be the necessary activation energy for diffusion. In detail, the activation energies required for diffusion across atomic channels, planes or ledges will be quite different, and dependent not only upon the surface structure but also upon the diffusion direction being considered. The overall diffusion activation energy, as determined in mass transport experiments, will be effectively set by the diffusion event requiring the largest energy. This event in practice is that of diffusion over an atomic step from a recess or kink in a ledge of atoms to the next atomic plane. In reality many diffusion events of different sorts occur simultaneously and any estimation of the expected overall diffusion activation energy must consider interactions between atoms, together with possible correlated movements of large numbers of atoms.¹

This already complex picture of surface diffusion is further complicated in the case of adsorbate diffusion, when the adsorbate-adsorbate interaction will often be quite different to the adsorbate-substrate interaction and the potential energy profile of the surface will be consequently modified. Minimum energy sites may no longer be at substrate lattices sites for example.

2. Previous Diffusion Work

Surface diffusion studies have been reviewed recently by Rhead¹ and Gjostein². The work to date can be conveniently split up into three main areas of study, which presented in chronological order are: (i) tracer or surface impurity diffusion, (ii) surface mass transport, and (iii) field ion microscopy.

2.1. Tracer and Impurity Diffusion

In these experiments a small amount of tracer or impurity

element is deposited upon a particular chosen surface and its diffusion over the surface at a particular temperature is monitored.

The drawbacks to this technique are that an independent monitor of surface structure and cleanliness must be used, together with the fact that tracer losses due to evaporation or diffusion into the bulk are difficult to estimate satisfactorily. However careful experiments do enable diffusion data to be obtained for specific surface orientations.

2.2. Mass Transport

This technique involves direct monitoring of changes in surface structure due to diffusion. Observations have been made of diffusion effects upon grain boundary groove or void growth, scratch decay, facet growth, sintering and blunting of field emitters. Such topographical changes can be monitored by interference optical microscopy, laser diffraction from a sinusoidal scratch profile, or from the changes in shape of a field emitter tip in a field emission microscope (FEM). These mass transport measurements will involve all the different diffusion mechanisms described in Section 1, and hence theoretical problems are encountered in modelling the diffusion process. Serious experimental difficulties have also been encountered in obtaining the properly clean surfaces which are necessary for accurate results.

2.3. Field Ion Microscopy

Field Ion Microscopy,^{3,4} a technique first reported by Muller in 1955, represented a potential breakthrough in possibilities for diffusion studies, enabling routine observation of

individual atoms upon an atomically perfect clean surface.

The Field Ion Microscope (FIM) was developed from attempts to improve the resolution of the FEM, which operates by field emission of electrons in a vacuum from a pointed field emitter specimen, or tip, held at a negative potential relative to a phosphor imaging screen. The resolution of the FEM is in the range 2-3 nm which enables diffusion studies of specimen blunting or adsorbed layer diffusion over the tip surface.

The FIM operates with a tip in an ultra-clean inert gas. A positive potential is applied to the specimen, creating an ion current due to field ionisation, which impinges on a phosphor screen opposite the specimen thus forming an image. The important experimental facts from a diffusion point of view are: (i) atomic resolution of 0.2-0.3 nm is quite feasible with the specimen at cryogenic temperatures, and (ii) construction of atomically perfect surfaces in a variety of orientations suitable for diffusion studies is feasible using the technique of field evaporation.

Only using the FIM can measurement be made of the individual atomic jumps constituting a particular type of diffusion mechanism. At the normal FIM operating temperatures diffusion does not occur, which enables a precise control over diffusion by heating the specimen to a previously chosen temperature for a measured interval of time. This diffusion cycle is performed with the field removed, and once the tip is cool again the new atomic positions of the diffusing atoms will be "frozen in" suitable for photographic recording.

For reasons of imaging contrast in using the FIM, observations of diffusing atoms are most feasible upon flat, low Miller-index planes of atoms, although observations can be made of diffusion over the atomic step at the plane edges.

The first work to take full advantage of the FIM for diffusion studies was by Ehrlich and Hudda⁵ in 1966, who observed self-diffusion of tungsten atoms. This work was confirmed and extended to diffusion of six more transition elements upon tungsten by Bassett and Parsley⁶ in 1969. More recently in 1972 Ayrault and Ehrlich⁷ have studied the self-diffusion of rhodium. An important breakthrough was the realisation that atomic interactions were important which was noted by Bassett and Parsley⁶ and Tsong⁸, however the first quantitative measure of its importance was by Ayrault and Ehrlich⁹, who performed diffusion experiments with a single atom on a plane for comparison with multiple atom diffusion.

2.4. Summary of Field Ion Microscopy

To summarise, field ion microscopy has been used to study self-diffusion and adsorbate diffusion upon the (123), (110), (111) and (112) planes of tungsten¹⁰ (a body-centred-cubic metal), and self-diffusion of rhodium⁷ (a face-centred-cubic metal) on the (111), (113), (133), (110) and (100) planes. Some work has also been performed for diffusion upon iridium surfaces.¹¹

Some of the quantitative results available are presented in Table 1, where H is the activation energy required for diffusion to occur and D_0 is a frequency factor arising from the oscillatory nature of the diffusing atom's attempts to cross the energy barrier. Diagrams of some of the surfaces over which this diffusion has been measured are presented in Fig.1.

The simple broken-bond model, as described earlier, successfully predicts the one-dimensional diffusion as observed on the channelled BCC (112) and (321), and the FCC (113), (133) and (110) planes. Observations of two dimensional diffusion on the flat BCC

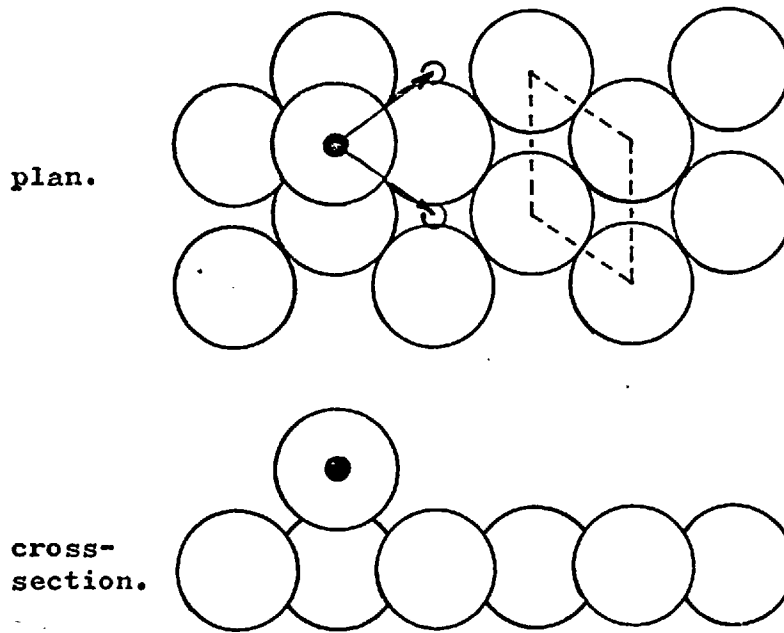
TABLE 1Surface Self-Diffusion DataSelf-Diffusion of Tungsten Atoms

Substrate Plane	Ehrlich and Hudda ⁵		Bassett and Parsley ⁶	
	D_0 ($\text{cm}^2 \text{sec}^{-1}$)	H (kcal mol^{-1})	D_0 ($\text{cm}^2 \text{sec}^{-1}$)	H (kcal mol^{-1})
(011)	2.6×10^{-3}	21.2 ± 1.1	2.1×10^{-3}	19.9
(211)	3.0×10^{-8}	12.3 ± 0.9	3.8×10^{-7}	13.0
(321)	3.7×10^{-4}	20.1 ± 1.8	1.2×10^{-3}	19.4
(211)	3.0×10^{-4}	17.5 ± 1.7	Single Atom Diffusion ⁹¹	

Self-Diffusion of Rhodium Atoms

Substrate Plane	Ehrlich and Ayrault ⁷	
	D_0 ($\text{cm}^2 \text{sec}^{-1}$)	H (kcal mol^{-1})
(111)	2×10^{-4}	3.6 ± 0.5
(113)	2×10^{-3}	12.4 ± 1.2
(110)	3×10^{-1}	13.9 ± 0.8
(133)	1×10^{-2}	14.8 ± 0.9
(100)	1×10^{-3}	20.0 ± 1.7

(a) BCC(110).



(b) FCC(110).

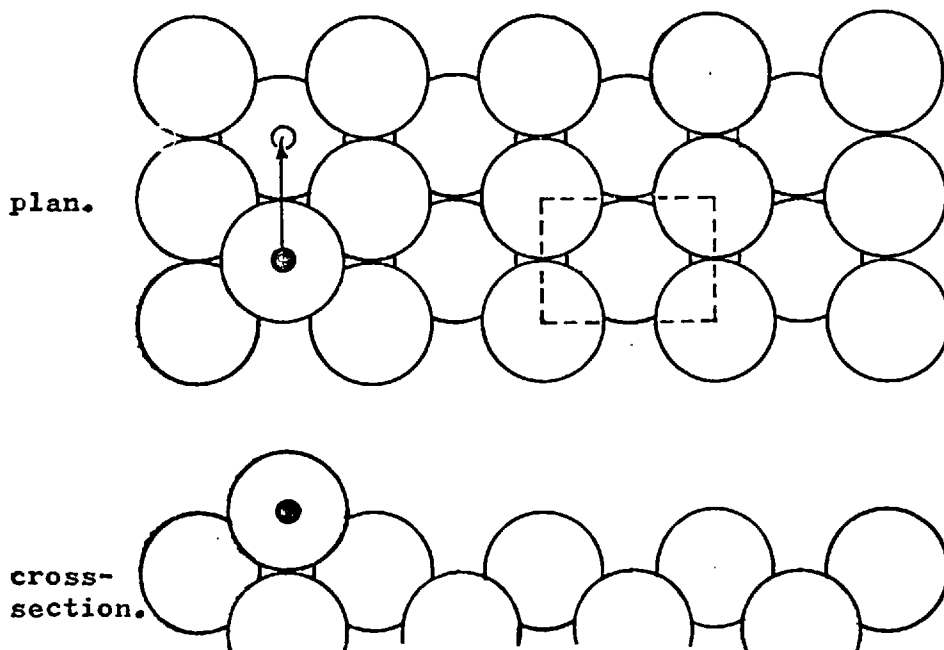
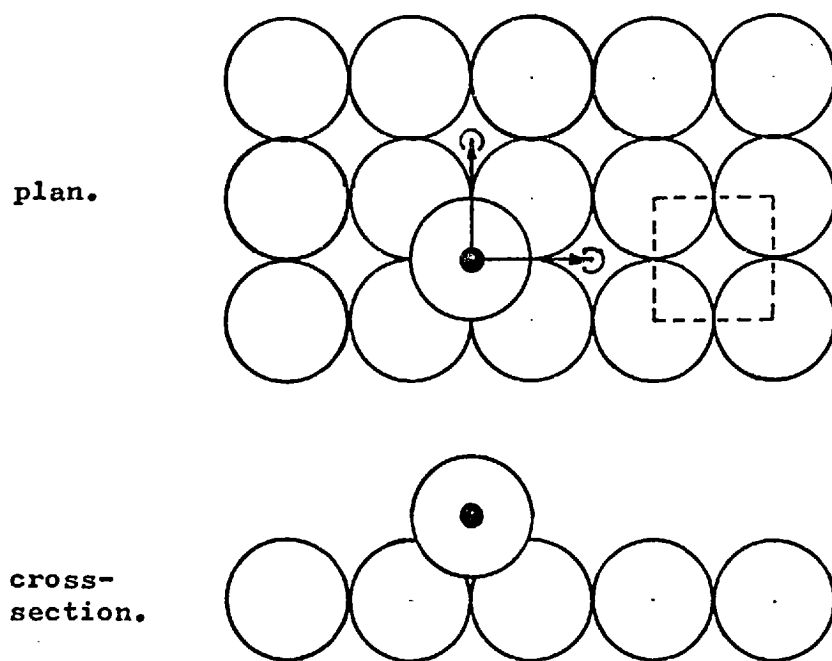


Fig.1. BCC and FCC Surface Structures.

(c) FCC(100).



(d) FCC(111).

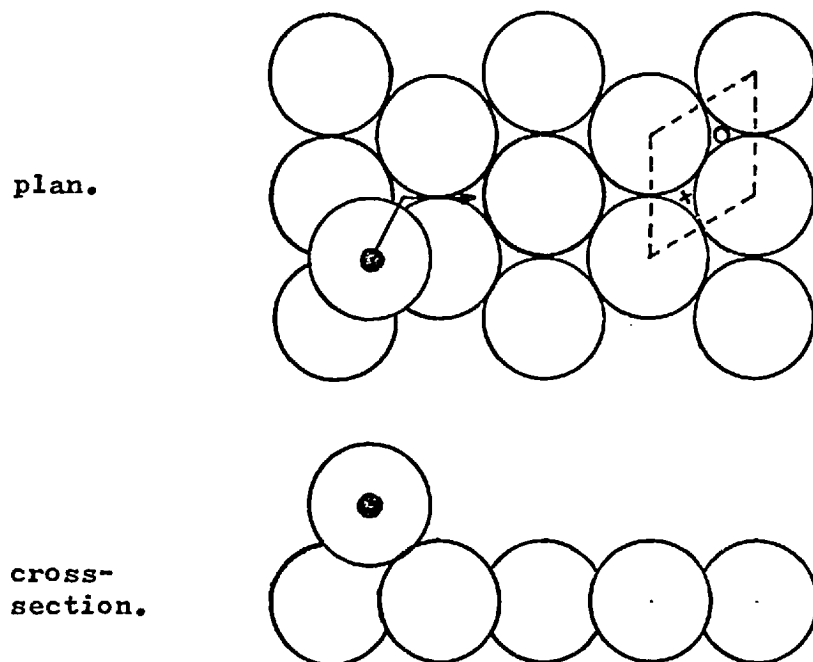
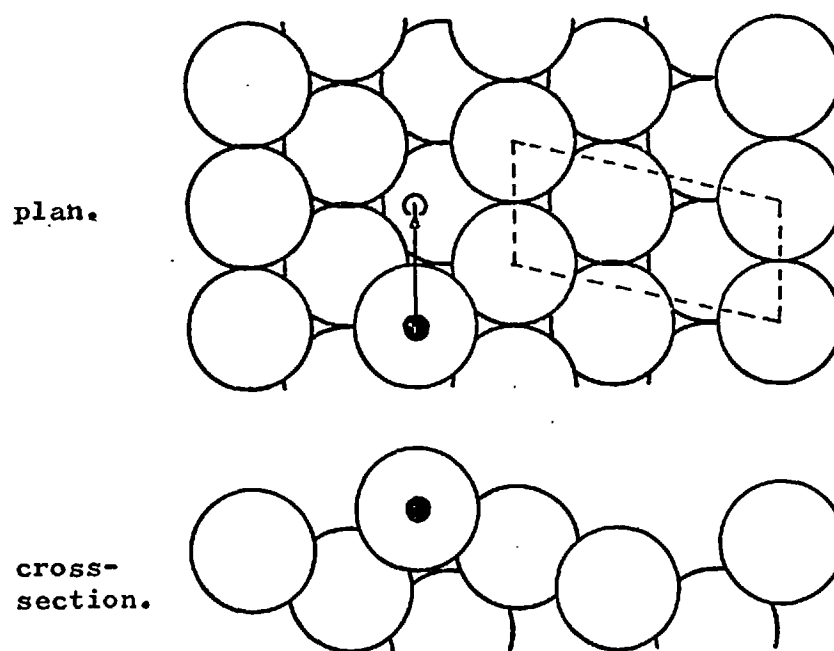


Fig.1. BCC and FCC Surface Structures,
(continued).

(e) FCC(133).



(f) FCC(113).

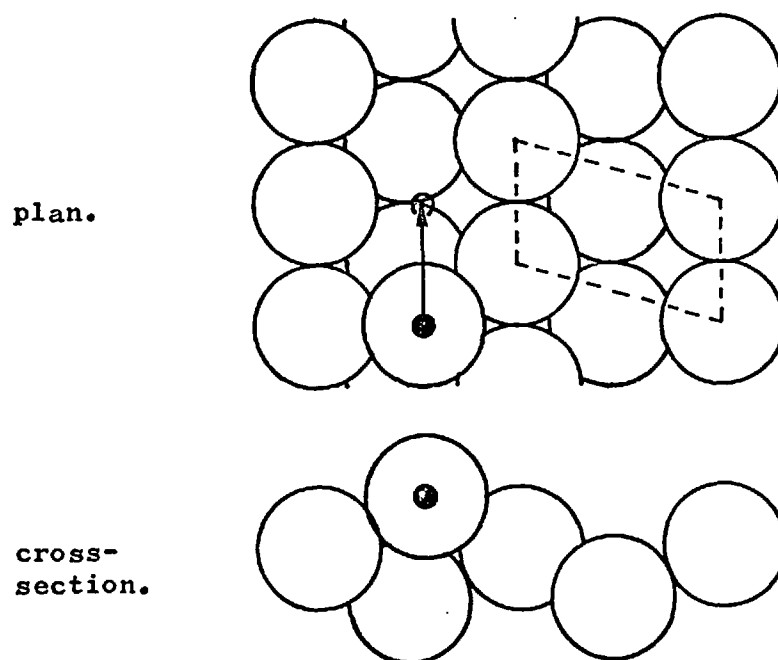


Fig.1. BCC and FCC Surface Structures,
(continued).

(110) and FCC (111) and (100) planes are also in accordance with expectations. The relative magnitudes of H within each packing scheme follows a straightforward rough-smooth plane variation with the important exception of the smooth tungsten (110) plane, where an anomalously high value of H has been measured. This anomaly has not been satisfactorily explained and may even be atypical of the BCC metals, as the only results available in this packing scheme are for tungsten.

3. Model Calculations

For successful model calculations to be made the physical process modelled must be well defined and theoretically tractable. An important feature of the FIM approach to diffusion is that one has selected out just such a process. In this case direct comparison of experimental results with calculations provides a critical test of the validity of the models used for the calculations and can thus be used to draw conclusions about the nature of bonding at the surface.

The simple broken-bond model outlined previously cannot be used to explain the detailed variation of H values with surface structure, nor the anomalous BCC (110) result.

Several more sophisticated calculations have been made of activation energies for diffusion with pair-bonding models using a variety of power-law variations or empirical potentials. The earliest studies used a modified broken-bond model with a sixth power variation with distance of an attractive potential^{12,13}. Subsequently Neustadter and Bacigalupi used a Lennard-Jones¹⁴ 6-12 potential to calculate the dependence of adsorption properties on surface structure for BCC surface planes¹⁵, and hence the energy barriers to diffusion. They followed this work in 1970 with

similar calculations for the FCC lattice¹⁶. In 1968 Wynblatt and Gjostein used an empirical Morse potential¹⁷ to calculate self-diffusion activation energies for copper¹⁸, an FCC metal, following this work in 1970 with equivalent calculations for tungsten¹⁹ as representative of the BCC metals. A very important advance made by Wynblatt and Gjostein was to minimize the total energy properly, by allowing atoms in the surface region to relax to new positions displaced from those of the bulk crystal lattice. More recently Ayrault and Ehrlich have performed calculations following the method of Wynblatt and Gjostein for rhodium⁹, and obtained fairly good agreement of experimental results with calculations, except for the (111) plane. Attempted detailed comparisons of the BCC results for tungsten with any available calculation scheme fail dismally with discrepancies of factors of two or more. However, it is worth noting that pairwise interatomic potentials calculated for bulk materials are scarcely likely to work very well at surfaces, where the sudden interruption of the bulk structure will create surface potentials not typical of the bulk. At present no proper quantum dynamical calculation methods are remotely near providing better answers than the quasi-static empirical calculation already employed.

Some model calculations have also been made for the case of foreign atom diffusion upon tungsten. The calculations by Neumann and Hirschwald²⁰ used as input data the self-diffusion results for tungsten, and by a simple relation of the adsorbate and substrate melting points successfully obtained relative activation energies for various metals on tungsten. More recently Halicioglu²¹ has used a Lennard-Jones potential to model copper adsorption on tungsten for various coverages. However to date no absolute calculations for foreign atom diffusion have been made.

4. The Present Work

One can now see that rather scanty information is available about atomic steps in surface diffusion. The analysis of calculations for which experimental information is available shows that the situation for rhodium (FCC) is fair, but for tungsten (BCC) calculations have not been successful.

Further diffusion work is clearly necessary on other FCC or BCC metals to widen our experimental information. To further explore the validity of empirical pairwise potentials there are two possible approaches: (i) studies of adsorbate effects upon diffusion, and (ii) diffusion involving large changes in coordination number (diffusion over steps). Method (i) is most tractable for FIM studies.

Bearing these considerations in mind, and with the hope of eventually studying metals of more technological importance, we have chosen to study diffusion of single atoms of the 5d-transition metals, namely tungsten, iridium, platinum and gold, upon the (111), (113), (133), (110) and (100) planes of platinum, a face-centred-cubic metal. Morse potential parameters for platinum were available from Ayrault²². This enabled calculations to be made similar to those of Wynblatt and Gjostein¹⁸, and Ayrault²², for comparison with the experimental data on platinum self-diffusion.

It was hoped to modify the above calculation procedure so that foreign adatom diffusion could be modelled for comparison with the experimental data.

4.1. Expectations

From previous studies of FCC metals²² one can anticipate that adatom mobility on platinum will be most rapid on the close-

packed (111) plane, followed by the (113), (110), (133) and (100) planes obeying a strict rough-smooth sequence. Considering simple binding energy differences, adatom dependent variations of mobility are expected in the descending order: gold, platinum, iridium, tungsten. Other general expectations are of one-dimensional adatom diffusion on the channelled (110), (113) and (133) planes, and two-dimensional movement on the relatively flat (100) and (111) planes.

To summarise, our experiments form an extended test for the validity of empirical pair-bonding calculations in the Pt-Pt, Pt-Au, Pt-Ir and Pt-W systems, coupled with an investigation of platinum surface plane structures over quite a wide temperature range.

II. THEORY

1. Theory of Field Ion Microscopy

1.1. Introduction

The basic microscope^{3,4}, as shown schematically in Fig.2, consists of a vacuum chamber containing a sharp pointed specimen, or tip, and filled with an ultra-clean inert gas. For imaging purposes the specimen is connected to a high positive potential, which produces a very high local electric field at the sharply curved tip surface. This field is sufficient to cause local field ionisation of the imaging gas, and hence produces an ion beam which impinges upon a phosphor viewing screen, where it forms an image. More sharply curved areas of the tip surface, such as isolated atoms or terraces of atoms, produce a locally higher contribution to the total ion current and a correspondingly brighter area on the screen. By cooling the specimen to below 100K and using imaging gas pressures of less than 10^{-3} torr it is possible to achieve a resolution of about 0.2 nm, which, combined with a magnification factor of several million enables atomic displacements of the order of a crystal lattice spacing to be observed. The specimen cooling has the added advantage of effectively immobilising any adatoms under study between diffusion heating cycles.

A thermally annealed tip presents quite a smooth end-form, but by raising the imaging voltage sufficiently above the best image voltage the process of field evaporation is initiated, which enables controlled removal of atoms from the specimen surface, producing many atomically perfect low Miller-index facets. Characteristic field evaporated end-forms of (111) and (100) oriented platinum tips are shown in Fig.3.

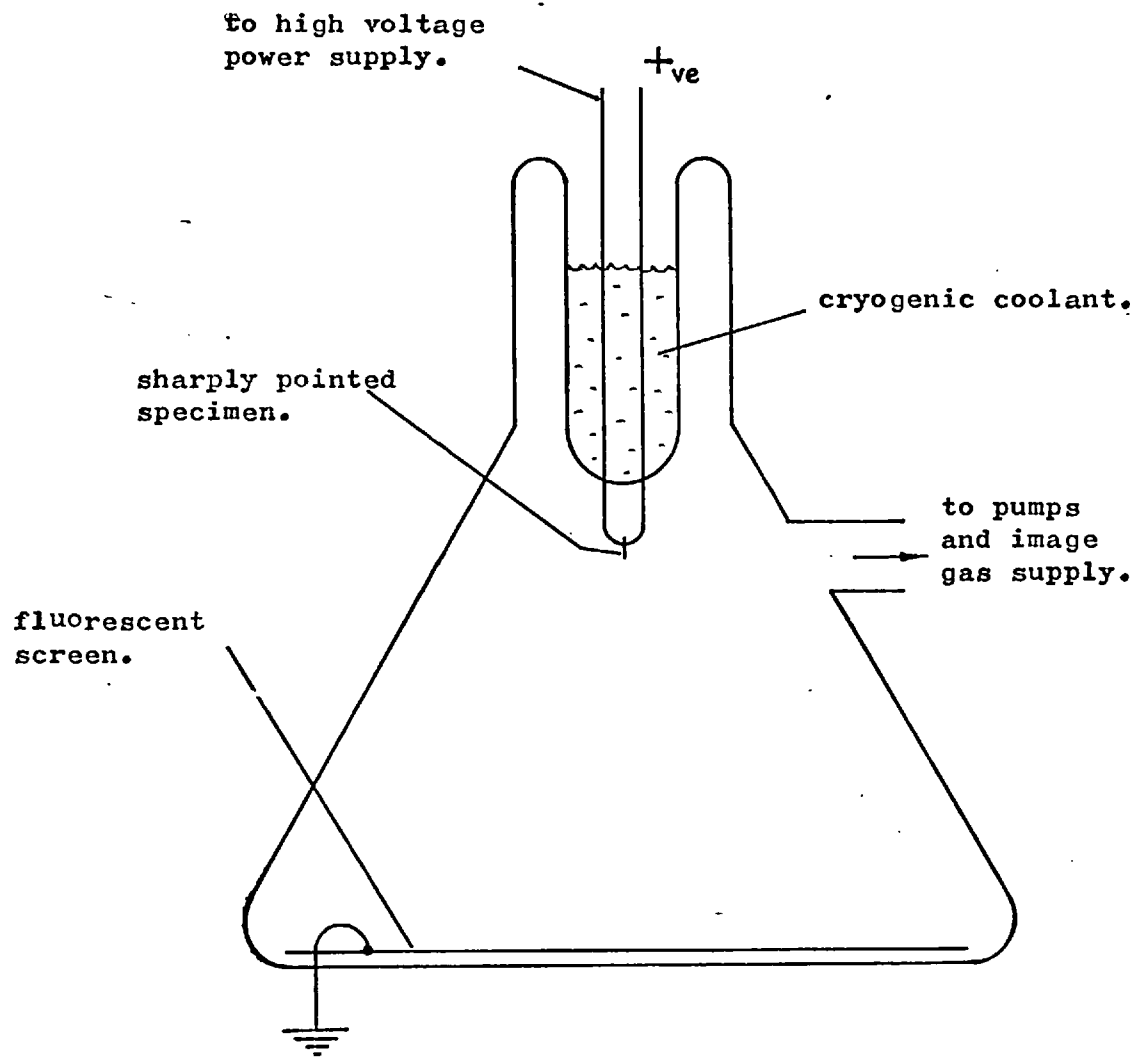
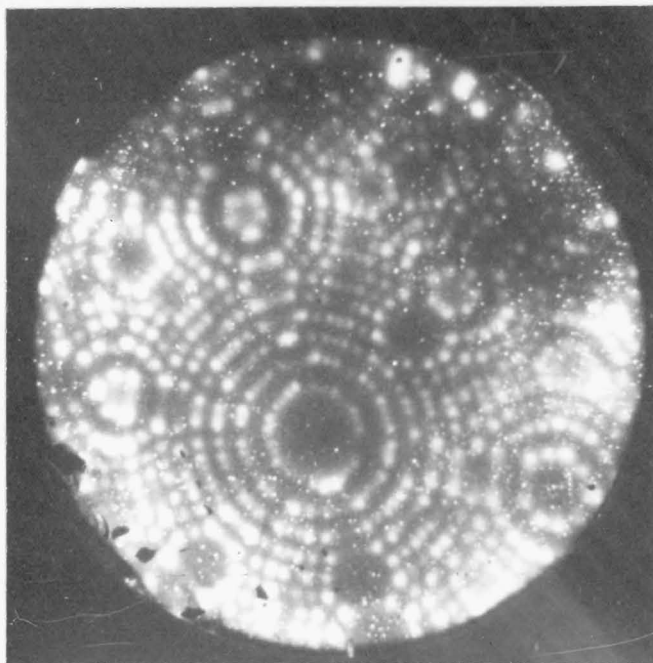


Fig.2. A Schematic Diagram of a Field Ion Microscope.

(a) (111) oriented Pt specimen.



(b) (100) oriented Pt specimen.

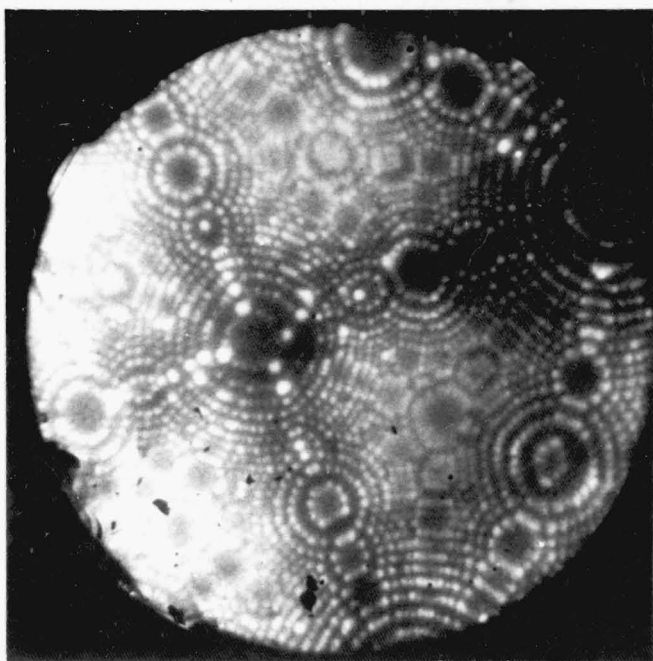
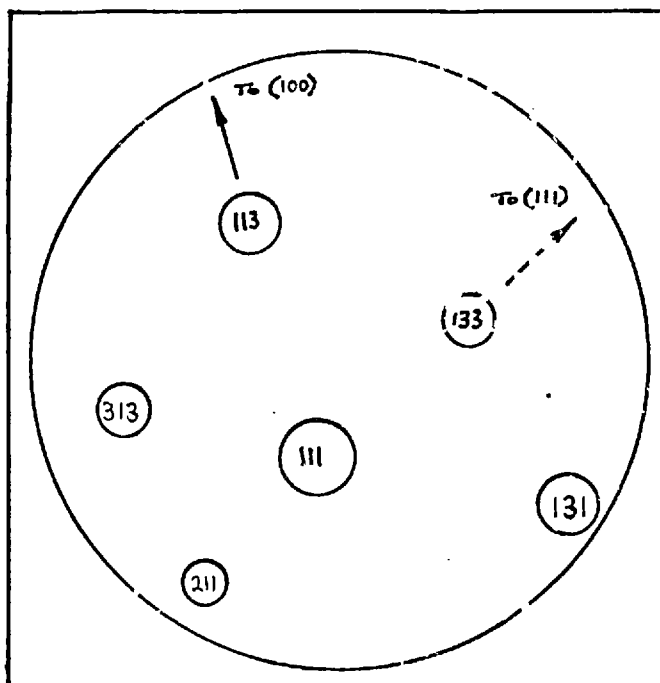
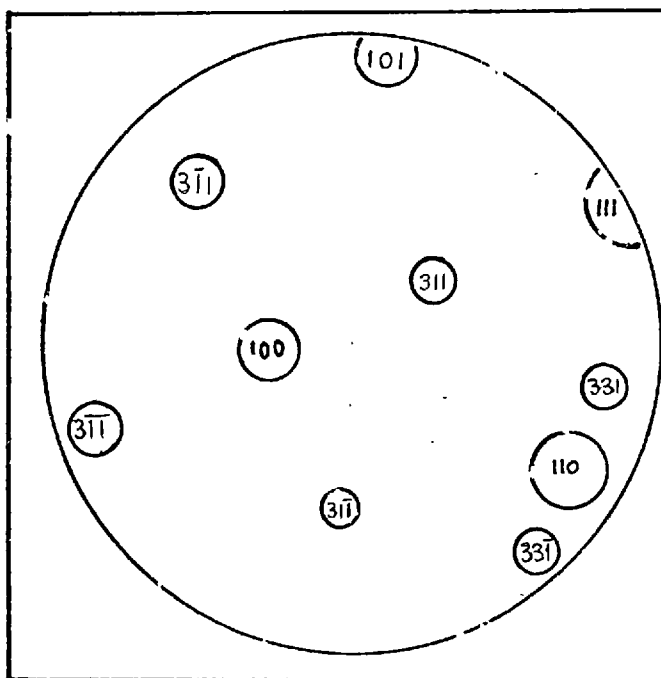


Fig.3. Characteristic Field Evaporated Platinum Surfaces.

(a) (111) oriented Pt specimen.



(b) (100) oriented Pt specimen.

KEY to Fig.3.

1.2. Field Ionisation

Any imaging gas atom which enters the high field region near the tip surface experiences a strongly attractive force due to induced dipole interactions with the strongly inhomogeneous field. Most theories of field ionisation assume that the gas atom performs a series of hops over the tip surface losing kinetic energy at each collision until it accommodates to the tip temperature and is ionised.

Ionisation occurs by electron tunnelling through the field deformed atomic potential well. As shown in Fig.4, ionisation can only occur once the electronic ground state is raised just above the metal Fermi level, thus the positive ion formed originates at or beyond a critical distance x_c from the specimen surface given by:

$$x_c = \frac{I - \phi}{F} \text{ nm} \quad (1)$$

where I is the gas ionisation potential, ϕ the metal work function and F the electric field.

Recent work by Tsong and Muller²³ has shown that imaged metal atoms are capped by an imaging gas atom trapped by the field-induced polarisation forces.

The unusual feature of field adsorption is the site of the adsorbate at the apex of the substrate atom in the direction of the local field, as shown in Fig.5, rather than the recessed location of ordinary physisorption or chemisorption which require the closest possible contact with several surface atoms. The significance of this apex location is that the imaging gas atom must be ionised by electron tunnelling through the adatom. It has been suggested²⁴ that the electron transfer through this transient molecule of highly polarised noble gas atoms results in an enhanced ionisation probability. However, the presence of the field

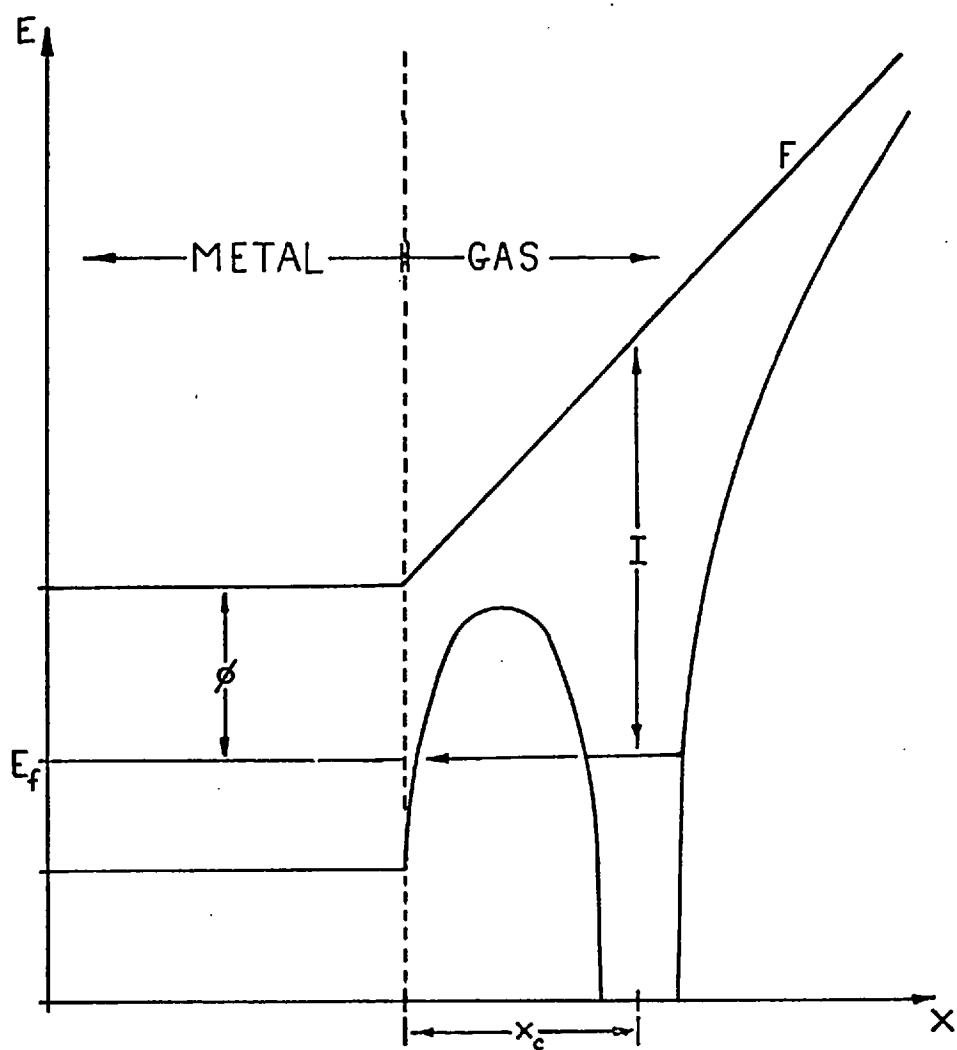


Fig.4. Electronic Potential Energy Diagram for Field Ionisation.

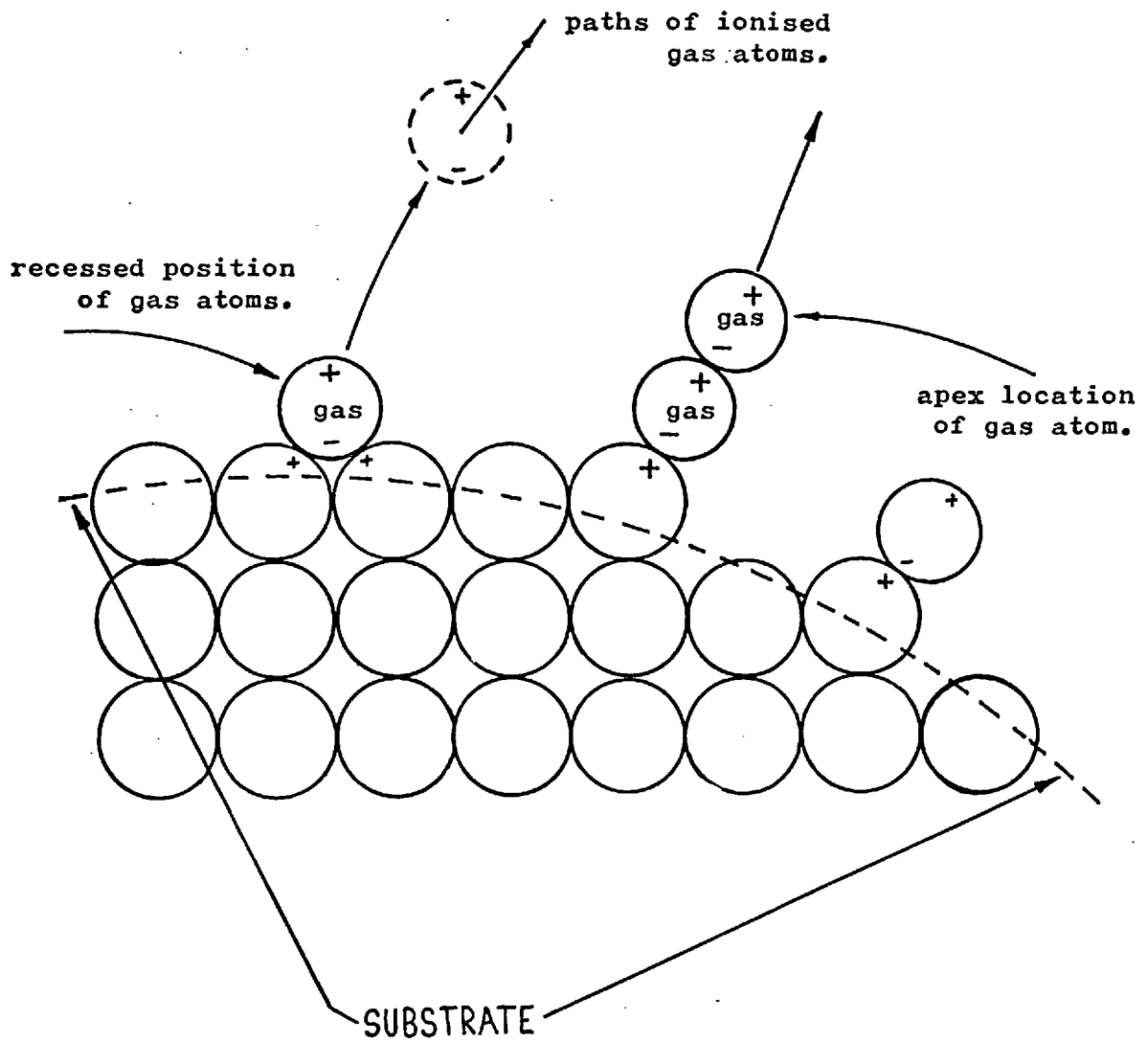


Fig.5. Field Adsorbed Positions of Gas Atoms.

adsorbed atom produces a locally deeper potential well, which is more likely to provide an ionisation site for the hopping gas atoms by reason of their increased "dwell time" at such a site. At this stage it is not quite clear whether gas supply or ionisation probability is the limiting factor determining the local field ionisation rate.

1.3. Imaging

Once ionisation has occurred, the gas ion travels outwards from the tip along an essentially radial trajectory. To a good approximation the image on the screen is a stereographic projection of the tip, with the radial divergence of the imaging beam determining the magnification M , given by:

$$M = \frac{D}{br} \quad (2)$$

where D is the tip-screen distance, r is the tip radius, and the field compression factor b is a constant of order 1.5-2 dependent upon the geometry of the microscope. M can easily be made several million.

The resolution of the FIM is limited by: (i) the beam broadening due to the radial divergence and scattering, (ii) the Heisenberg uncertainty in the spot size at the screen, and (iii) the initial tangential velocity of the ion leaving the surface. In the practical microscope imaging gas pressures used are kept low to reduce scattering and the third consideration becomes more important. One of the reasons for cooling the tip below 100K is to reduce translational ionic movement as much as possible. Tip cooling is also necessary to initiate adsorption of the imaging gas molecules to produce the enhanced imaging described in Section 1.2, and to immobilise adatoms between diffusion heating cycles.

The resolution d has been given by:⁴

$$d = \frac{6 * 10^{-2} T_r}{F} \text{ nm} \quad (3)$$

where T is the absolute temperature of the tip, and F is the field in volts nm^{-1} . Under normal operating conditions with liquid nitrogen cooling of the tip ($T = 77\text{K}$), d is in the order of 0.2-0.3 nm.

1.3.1. Imaging in the FEM Mode

Under operation in the FEM mode, as briefly described in Chapter I Section 2.3, the resolution is strongly limited by the high translational velocity of the imaging electrons. Tip cooling cannot be used to reduce this velocity as electrons obey a largely temperature independent Fermi-Dirac distribution of energies.

The current density J of emitted electrons is related to the field F by the Fowler-Nordheim equation²⁵:

$$J = 6.2 * 10^6 F^2 \frac{[E_f/\phi]^{\frac{1}{2}}}{[E_f + \phi]} \exp(-6.8 * 10^7 \frac{\phi^{\frac{3}{2}}}{F}) \text{ amp cm}^{-2} \quad (4)$$

where E_f is the metal Fermi level and ϕ the electronic work function. From this relation it can be seen that image contrast in the FEM mode is strongly dependent upon ϕ , making this technique a powerful tool for monitoring surface work function changes due to contamination.

1.4. Field Evaporation

Field evaporation²⁶, besides providing an excellent method for cleaning and tailoring the tip surface, subjects the specimen to the highest fields used in the FIM technique. As a consequence the specimen is subjected to large mechanical stresses which are a common cause of tip failure by fracture. Adatoms under study on

the surface may also be inadvertently removed at potentials at or below the substrate best image voltage.

The physical process of field evaporation can conveniently be split up into three steps: (i) initial ionisation of the metal atom, (ii) activation over a possible energy hump, and (iii) field evaporation of the ion. Step (i) ionisation, occurs at the intersection of the atomic and field distorted ionic potential curves; after this event the ion is either a) attracted back to, or b) repelled from, the metal surface. These two cases illustrate the two models commonly used to describe field evaporation.

a) The Schottky Hump Model, see Fig.6a. In this model, first proposed by Muller²⁷, the ionic potential at a distance x from the metal surface in an applied field F is given by:

$$V(x,F) = I_n - n\phi - \frac{ne^2}{4x} - nFex \quad (5)$$

where I_n is the sum over n ionisation potentials of the evaporating ion, e is the charge on the electron, and ϕ is the metal work function. Examination of this equation reveals a maximum in V (referred to as the Schottky, or image, hump) at a distance

$$x_h = (ne/4F)^{\frac{1}{2}} \quad (6)$$

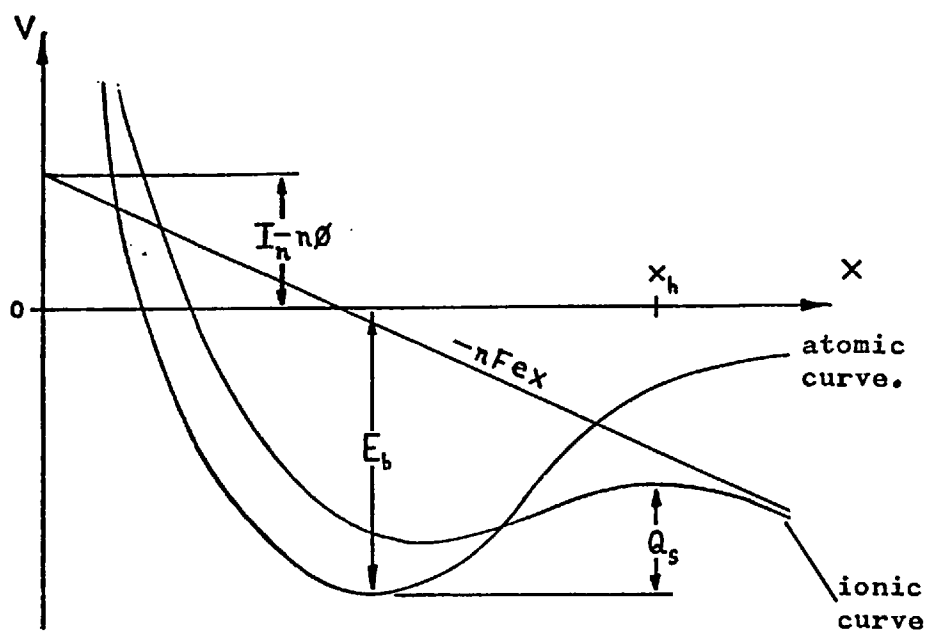
Substitution of this value back into equation (5) gives the height of the energy barrier the ion must surmount to field evaporate as:

$$Q_s = E_b + I_n - n\phi - (n^3e^3F)^{\frac{1}{2}} \quad (7)$$

where E_b is the binding energy of the atom. In this model Q_s determines the evaporation rate.

b) The Intersection Model, see Fig.6b. In this model, introduced by Gomer and Swanson²⁸, the evaporation rate is determined by the intersection of the ionic and atomic potential curves at a distance x_i from the surface. From substitution of x_i into equation (5) the activation energy for evaporation is given by:

(a) The Schottky Hump Model.



(b) The Intersection Model.

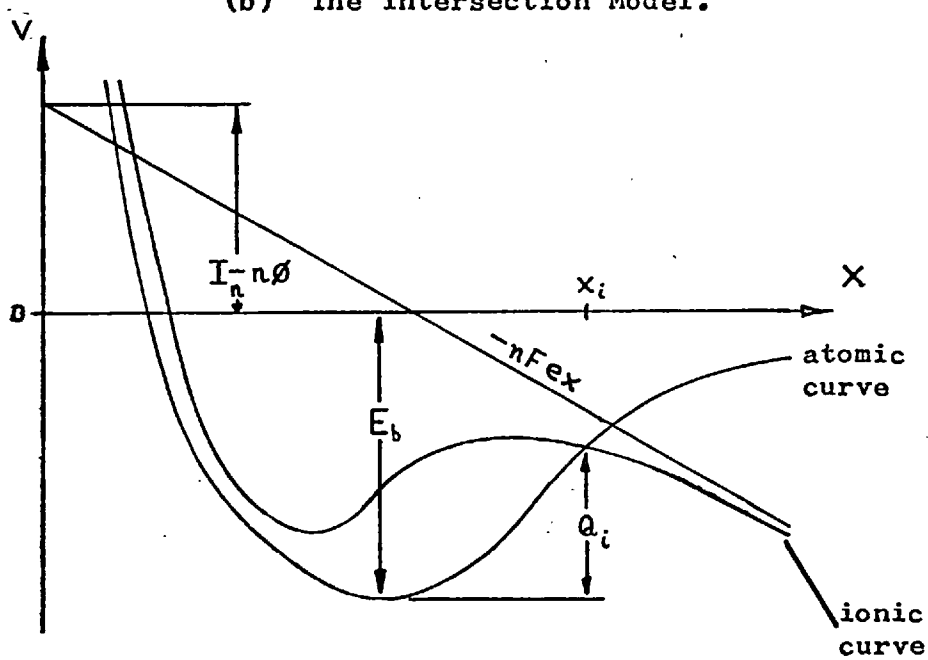


Fig.6. Models of Field Evaporation.

$$Q_i = E_b + I_n - n\phi - \frac{ne^2}{4x_i} - nFex_i \quad (8)$$

This equation can be further adjusted by the addition of correction terms to account for the difference in ionic and atomic polarisability²⁹, broadening of the ionic energy levels with associated energy shifts³⁰, and repulsive energy terms²⁹. However, without specific knowledge of the atomic surface potential the variation of the activation energy with field cannot be calculated, and these corrections become rather superfluous.

It is difficult to choose which model applies best to the physical situation. At the high fields necessary to field evaporate the refractory metal the Schottky hump is of the order of 0.1 nm from the metal surface, which is considerably less than an atomic radius, and hence has no real meaning in a classical sense. Furthermore, Tsong³¹ has shown that no image hump exists in field evaporation of the lower charged atomic states M^+ , M^{2+} and possibly M^{3+} . Neither model can successfully account for the evaporation of triply charged ions or the metal-gas ionic complexes which have been found in atom-probe studies³².

1.5. Field Effects

It is clearly important to know how a surface adatom under study may be affected by the intense electric fields necessary for imaging in the FIM.

According to Drechsler³³ the field can be considered to induce an electric dipole in the adatom thus increasing its effective binding energy with the surface by an amount

$$E_p = -mF - \frac{1}{2}pF^2 \quad (9)$$

where it is assumed that the field F is uniform, where m is the induced surface dipole, and p is the adatom polarisability.

Experimental measurements by Plummer and Rhodin³⁴ and others³⁵ indicate that m is about one tenth of pF for single metallic adatoms, thus equation (9) can be simplified to:

$$E_p = -\frac{1}{2}pF^2 \quad (10)$$

introducing tolerable errors. Utsugi and Gomer³⁶ have pointed out that the polarisability of an adatom at the saddle and trough positions of the surface potential may be different. The electric field at these positions may also be different. As a result, the effective barrier to diffusion with a field present is given by:

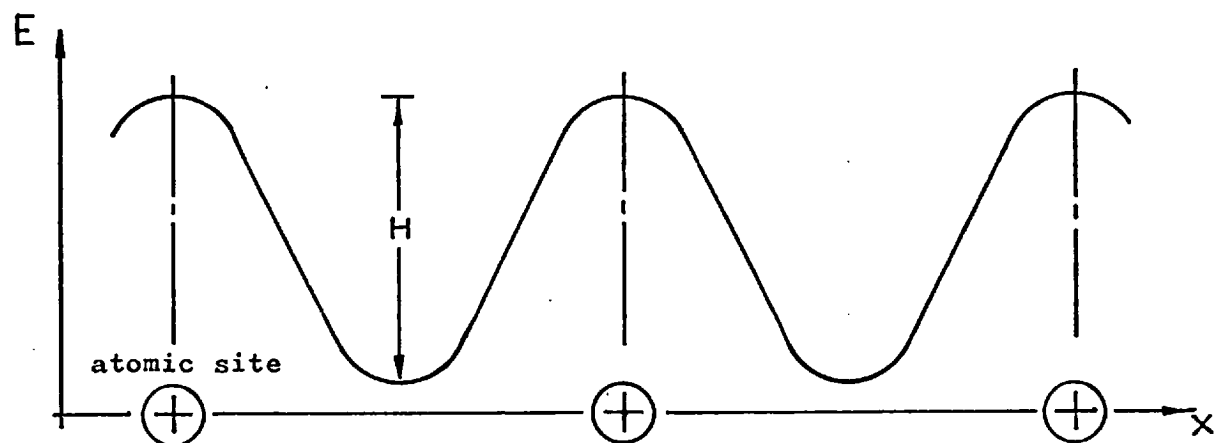
$$H_f = H - \frac{1}{2}(p_s F_s^2 - p_t F_t^2) \quad (11)$$

where the subscripts s and t refer to the saddle and trough sites respectively. Such field effects upon diffusion have been observed by Tsong et al^{37,38} who also noted a driving force toward the plane edges resulting from the gradual increase in local field. If the field reaches a certain critical value F_c , H_f will become zero, as has been observed by Utsugi and Gomer³⁶ for barium diffusion on tungsten. Further increase of the field results in a reversal of the normal surface potential energy profile, as shown in Fig.7, and the saddle site becomes the new site of minimum potential energy. Under these conditions the adatom may move to the new minimum energy site, initiated by momentum transfers from collisions with imaging gas atoms. An adatom in such a field stabilised site is likely to possess rather unusual imaging characteristics, protruding as it does considerably from the surface, with the consequent effects of local field distortion leading to locally enhanced magnification and image intensity.

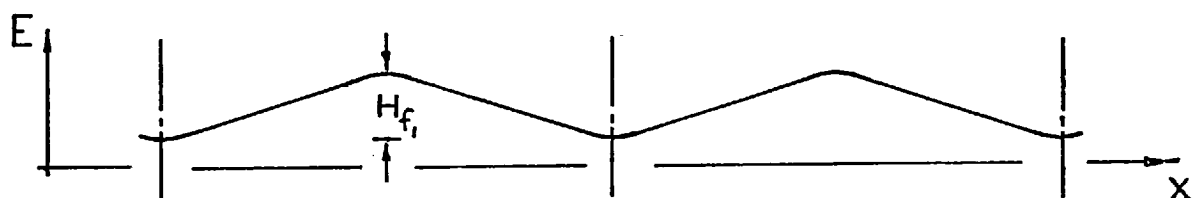
1.6. Choice of Imaging Gas

Observation of a stable surface in the FIM is only possible

(a) Normal Zero Field Potential.



(b) Low Field Inversion of Potential.



(c) High Field Inversion of Potential.

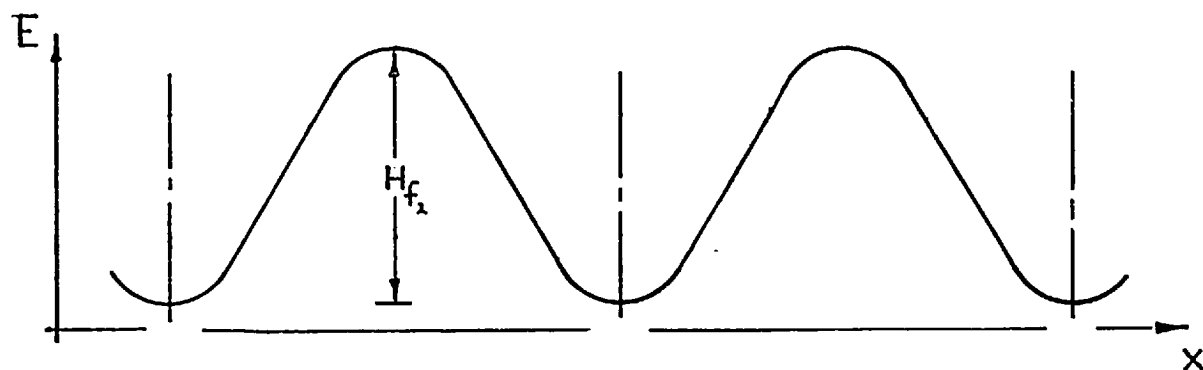


Fig.7. Potential Profiles at a Surface in Various Applied Fields.

if image formation by ionisation of the imaging gas occurs at fields below those required for field evaporation of the metal under study. The imaging gas should also not react chemically with the surface under study, thus only rare gases such as helium, neon and argon are suitable for consideration.

This work concerns the imaging of nickel, palladium and platinum in the FIM. Evaporation fields for these metals have been calculated by Southworth using a method developed by Brandon³⁹, and are presented along with the data for ionisation fields due to Muller⁴⁰, in Table 2. It can be seen that Ne and Ar can be expected to form stable images of the metals in question, although palladium and nickel can be expected to be only marginally stable for neon imaging. Hydrogen cannot be considered for diffusion studies, despite its lower imaging field (Table 2), due to its high reactivity with Pt, Pd and Ni, whilst argon and neon may induce lattice defects by atom bombardment during thermal accommodation. In this latter respect the neon ion is substantially lighter than the argon atom and should cause much less damage. For best use of field evaporation to clean the tip surface the highest field practicable is required, and for this reason neon was finally chosen as the imaging gas for use.

TABLE 2Metal Evaporation and Gas Ionisation Fields

Metal	Evaporation Field (V nm^{-1})	Ionisation Field (V nm^{-1})	Gas
		45	He
Pt	44		
Pd	37	37	Ne
Ni	35		
		23	Ar
		23	H ₂

2. Theory of Diffusion

2.1. Introduction to Diffusion

In common with earlier work⁵⁻⁷, the raw diffusion data from our experiments is in the form of intermittent observations of adatom location on a small atomically perfect plane bounded by an atomic step. Our primary interest is to obtain the size of the energy barrier to diffusion on the surface, and to this end the diffusion process must be considered in detail.

The diffusion coefficient D for one-dimensional diffusion is defined by the equation

$$J = -D(\partial c / \partial x) \quad (12)$$

otherwise known as Fick's 1st law. Here J is the flux of atoms passing through unit area in unit time, and c is the concentration of diffusing atoms per unit volume.

Let us consider the diffusion between two planes, designated 1 and 2, perpendicular to the x -axis and separated by a distance l . Let there be n_1 diffusing atoms per unit area in plane 1 and n_2 in plane 2. If each atom jumps an average of w times per second, then the net flux of atoms leaving plane 1 is $J_1 = n_1 w$, and similarly the flux of atoms leaving plane 2 is $J_2 = n_2 w$. Assuming that the diffusing atoms are equally likely to diffuse in either direction along the x -axis then on average only half of the atoms leaving planes 1 or 2 will contribute to the flux between them. Therefore, the flux of atoms diffusing from plane 1 to plane 2 is:

$$J = \frac{1}{2}J_1 - \frac{1}{2}J_2 \quad (13)$$

and by substituting for J_1 and J_2 ,

$$J = \frac{1}{2}w(n_1 - n_2) \quad (14)$$

The quantity $(n_1 - n_2)$ can be related to the concentrations c_1

and c_2 of diffusing atoms at the two planes by the equations

$$c_1 = n_1/l \text{ and } c_2 = n_2/l. \text{ Thus,}$$

$$J = \frac{1}{2}wl(c_1 - c_2) \quad (15)$$

In the small interval l , the concentration c will in practice have only changed slightly, therefore,

$$(c_1 - c_2) = -l \partial c / \partial x \quad (16)$$

and thus

$$J = -\frac{1}{2}wl^2 \partial c / \partial x \quad (17)$$

From comparison with Fick's 1st law, equation (12),

$$D = \frac{1}{2}wl^2 \quad (18)$$

This expression is valid for diffusion along one axis, that is one-dimensional diffusion. Thus l can now be identified as the distance between two adjacent atomic sites along the x direction.

The next necessary step is to calculate an expression for the jump frequency w . If the diffusion between two atomic sites is considered to be a reversible isothermal process at constant pressure, then the work done in moving the atom from the equilibrium to the saddle sites is equal to the change in Gibbs free energy in that region, ΔG , given by:

$$\Delta G = \Delta H' - T\Delta S \quad (19)$$

where $\Delta H'$ and ΔS are the changes in enthalpy and entropy respectively. The probability of an atom crossing this energy barrier in a given attempt is:

$$p = \exp(-\Delta G/RT) \quad (20)$$

where R is the gas constant. If the atom is oscillating such that it attempts to cross this barrier at a frequency v_0 then the jump frequency w is given by:

$$w = v_0 p = v_0 \exp(-\Delta G/RT) \quad (21)$$

and by substitution from equation (19):

$$w = v_o \exp(\Delta S/R) \cdot \exp(-\Delta H'/RT) \quad (22)$$

It is not absolutely clear what value should be assigned to v_o but by comparing equation (21) with the equivalent result in transition-state theory⁴¹ v_o can be identified as:

$$v_o = kT/h \quad (23)$$

where k and h are respectively Boltzmann's and Planck's constants. The relation for D (equation (18)) can now be written in full as:

$$D = \frac{v_o l^2}{2} \exp(\Delta S/R) \cdot \exp(-\Delta H'/RT) \quad (24)$$

Empirically it is found that D can be described by the equation

$$D = D_o \exp(-H/RT) \quad (25)$$

Comparing these two equations it can be seen that:

$$D_o = \frac{v_o l^2}{2} \exp(\Delta S/R) \quad (26)$$

which, for $S = 0$, can be approximated to:

$$D_o = \frac{v_o l^2}{2} \quad (27)$$

This relation has been used to estimate D_o where an empirical value was not available.

Available experimental data are mainly compatible with the approximation of $\Delta S = 0$ when interaction effects have been eliminated, and are tabulated in Table 3.

2.2. The Experimental Measurement of Diffusion.

The experimental observations are in the form of a sequence of adatom positions after a set of specimen heatings to a temperature T , for a time interval t . The theoretical expression for D ,

$$D = \frac{1}{2} w l^2 \quad (28)$$

TABLE 3Activation Entropies ΔS (cal mol⁻¹ K⁻¹)Diffusion on Tungsten

Surface	W^a	adatom W^b	Re^b	W^d
W(110)	$+2 \pm 4$	+1.1	+4.9	-
W(211)	-22 ± 4	-16.8	+3.1	-5.2 ± 5.3
W(321)	-4 ± 6	-1.1	-6.7	-7.5 ± 4.4

Self-Diffusion of Rhodium

Surface	Rh^c
Rh(111)	0 ± 8
Rh(311)	0 ± 6
Rh(110)	$+11 \pm 5$
Rh(331)	$+4 \pm 4$
Rh(100)	-1 ± 5

a-- Ehrlich and Hudda Ref.5.

b-- Bassett and Parsley Ref.6.

c-- Ayrault Ref.22.

d-- Graham and Ehrlich Ref.91

can be modified to the form

$$D = \frac{wt l^2}{2t} = \frac{Nl^2}{2t} \quad (29)$$

where $N = wt$ is the number of jumps made in time t , and the quantity Nl^2 corresponds to the mean square displacement of the adatom. This expression is only valid if successive atom jumps are uncorrelated and can be satisfied if w is kept small by making measurements at relatively low diffusion temperatures, when the diffusing atom has enough time to reach equilibrium at its new site before making another jump.

In practice the adatom cannot perform a random walk, but encounters the plane boundaries where it is either reflected or adsorbed. Consequently the measured value of the mean square displacement $\langle r^2 \rangle$ is not equivalent to Nl^2 but somewhat smaller depending on the values of N and the plane size. Ehrlich⁴² has shown that the mean square displacement of atoms for one-dimensional diffusion along a channel of length a , for reflecting or adsorbing boundaries is given by:

$$\langle r^2 \rangle = Nl^2 \left(1 - (4/3a)(2Nl^2/\pi)^{1/2} \right) \quad (30)$$

A value of Nl^2 from $\langle r^2 \rangle$ can be obtained by iterative or graphical methods. The validity of this expression has been tested by Ayrault²² using a computer model of diffusion. For $Nl^2 < a^2/6$ a deviation of less than 1% from the true value of the mean square displacement was discovered. In our experiments the condition originally set by Ehrlich of $Nl^2 < a^2/10$ was always fulfilled.

2.3. The Treatment of Errors

The measured mean square displacement $\langle r^2 \rangle$ is obtained from a finite sampling set of size n upon an essentially infinite population of true mean square displacement $\langle r_*^2 \rangle$ where

$$\langle r_*^2 \rangle \sim \langle r^2 \rangle = \frac{1}{n} \sum_i r_i^2 \quad (31)$$

The best estimate of the true standard deviation s_* is the adjusted r.m.s. deviation s_n^{43} where

$$s_n^2 = \frac{1}{n-1} \sum_i (r_i^2 - \langle r^2 \rangle)^2 \quad (32)$$

The accuracy of $\langle r^2 \rangle$ as an estimate of $\langle r_*^2 \rangle$ is given by the standard error S , where

$$S = \frac{s_n}{\sqrt{n}} \quad (33)$$

s_n is itself an estimate and subject to error leading to the final expression for the standard error S_n on $\langle r^2 \rangle$ as:

$$S_n = \frac{s_n}{\sqrt{n}} \pm \frac{S_n}{\sqrt{n-2}} \quad (34)$$

A strictly more correct statistical analysis was used by Ehrlich and Hudda⁵ which involved calculation of the second and fourth moments of the population, M_2 and M_4 respectively, approximated by the sample moments m_2 and m_4 where

$$\text{Variance}(S_n^2) = \frac{1}{n(n-1)} (M_4(n-1) - M_2^2(n-3)) \quad (35)$$

This expression is also subject to errors and makes no appreciable difference to the analysis in practice. In this work the simpler analysis technique (equation (34)) has been used throughout.

After calculation of D following the method outlined the results were fitted to equation (25):

$$D = D_0 \exp(-H/RT) \quad (25)$$

and a linear regression analysis was performed regressing $\ln(D)$ upon $1/T$ weighting each point according to the inverse of its standard error. The calculated errors on the results come directly from the errors calculated for the gradient and intercept. Of course the statistical analysis can take no account of systematic temperature errors, but in this case the value obtained for H

remains unchanged, and D_0 is very slightly affected except for huge $1/T$ errors.

III. EXPERIMENTAL

1. The Apparatus

The practical realisation of the FIM for use in diffusion studies must be designed so that:

1. The surface after field evaporation can be maintained in a clean state for the duration of a normal experimental run.
2. The image is bright enough for fairly rapid photographic recording.
3. The microscope parts, and especially the specimen, can be simply and rapidly replaced.
4. A means for deposition of metal atoms on to the specimen is provided.
5. An accurate means exists for heating the specimen to a chosen temperature.

All of the above requirements can be fulfilled in a stainless steel FIM fitted with an image intensifying channel plate and operable under Ultra High Vacuum (UHV) conditions.

1.1. The FIM

The FIM used in this study (Fig.8) was designed by D.W. Bassett using stainless steel components manufactured by Vacuum Generators Ltd.

As shown schematically in Fig.9, the specimen was vertically mounted beneath a double dewar arrangement containing liquid nitrogen for cooling purposes, and surrounded by a cylindrical radiation shield pierced in two places to allow deposition on to the tip from the two metal evaporators. The specimen assembly was readily demountable for tip replacement purposes by means of a steel flange with a gold wire seal, used to avoid particles of



Fig.8. A Photograph of the Microscope Used.

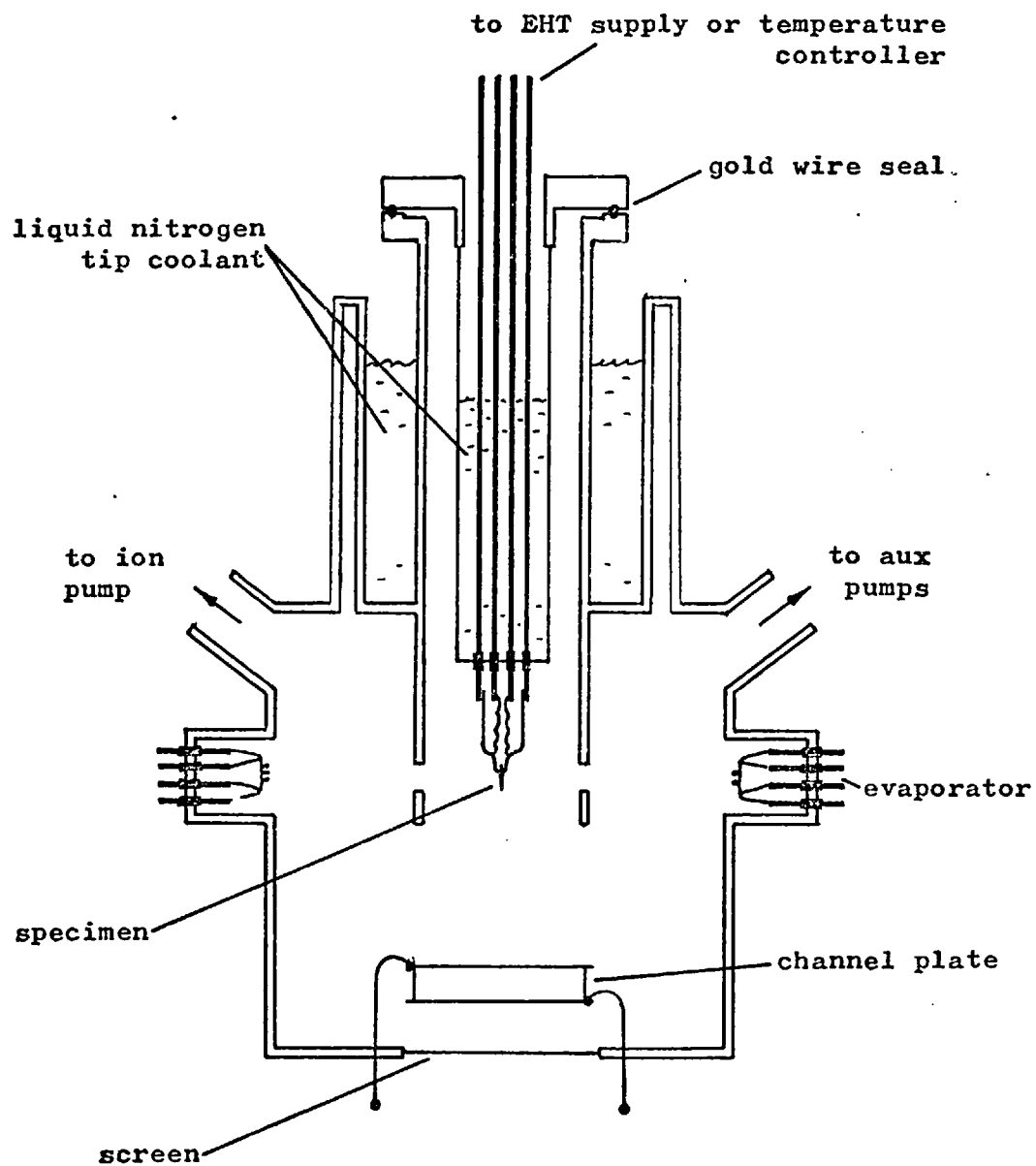


Fig.9. The Metal Field Ion Microscope.

copper oxide dropping into the microscope.

The evaporators consisted basically of resistively heated metal wires from which metal atoms could be evaporated on to the tip. Their exact construction differed somewhat for the various metals deposited and is detailed in Fig.10.

The chamber also contained a molybdenum film getter, an observation window and a Bayard-Alpert type vacuum gauge. Connection to the gas admission and vacuum lines was via metal valves; thus the entire microscope chamber was fully bakeable to 200°C .

1.2. The Pumping System

The UHV system comprised three main pumping lines, as shown in Fig.11. The microscope chamber could be evacuated by (i) the main mercury-in-glass diffusion pump line at a rate of about 1 Lsec^{-1} , and (ii) the 20 Lsec^{-1} magnetron sputter ion pump, whilst the gas handling and cleaning section was evacuated by a separate mercury diffusion pump line. Both of the diffusion pump lines were isolated from the other sections of the microscope by liquid nitrogen cooled vapour traps and rough pumped by the rotary pump, which was itself isolated by a cold trap containing a molecular sieve.

For specimen or evaporator replacement, the chamber could be isolated from the pumps by valves V_1 and V_2 , and directly backfilled with argon via valves V_3 and V_4 , thus reducing chamber contamination whilst the chamber was open to the atmosphere. Argon backfilling via the diffusion pump line was avoided because this route necessitates switching off the pumps and warming the traps with the inherent dangers of impurity blow back into the chamber.

Subsequent rough pumping of the chamber could be performed by the rotary pump through the molecular sieve by opening valve V_5 .

(a) Evaporator Construction for W or Ir Deposition.

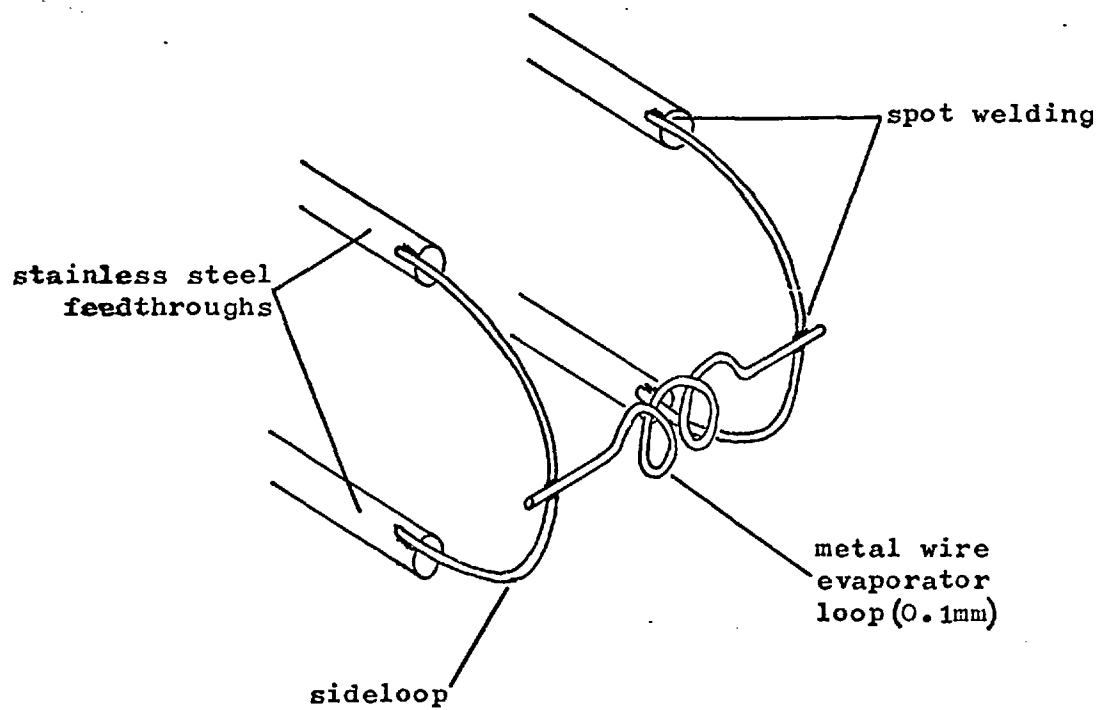
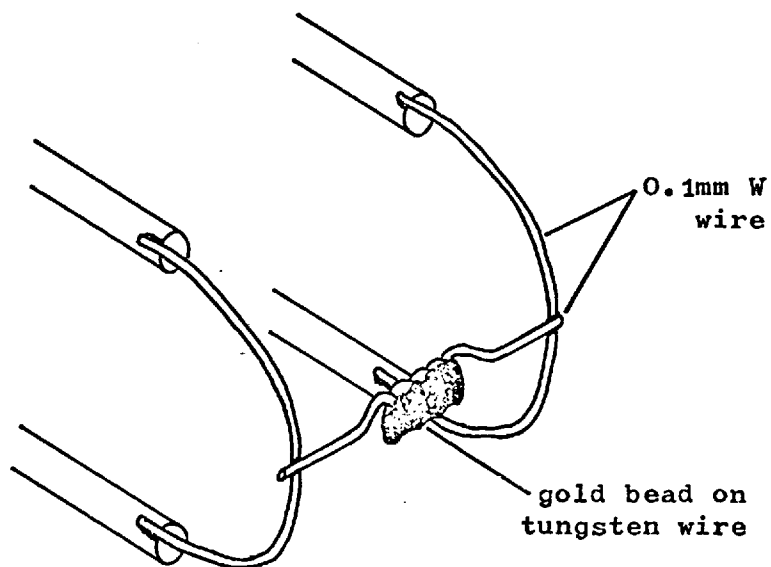


Fig.10. Details of Metal Evaporators.

(b) Gold Evaporator Construction.



(c) Platinum Evaporator Construction.

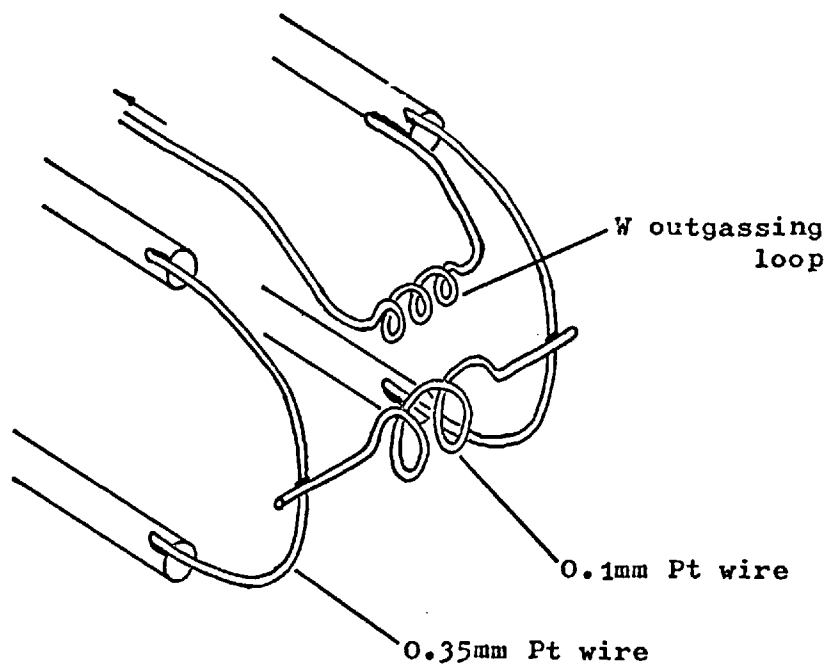


Fig.10. Details of Metal Evaporators,
(continued).

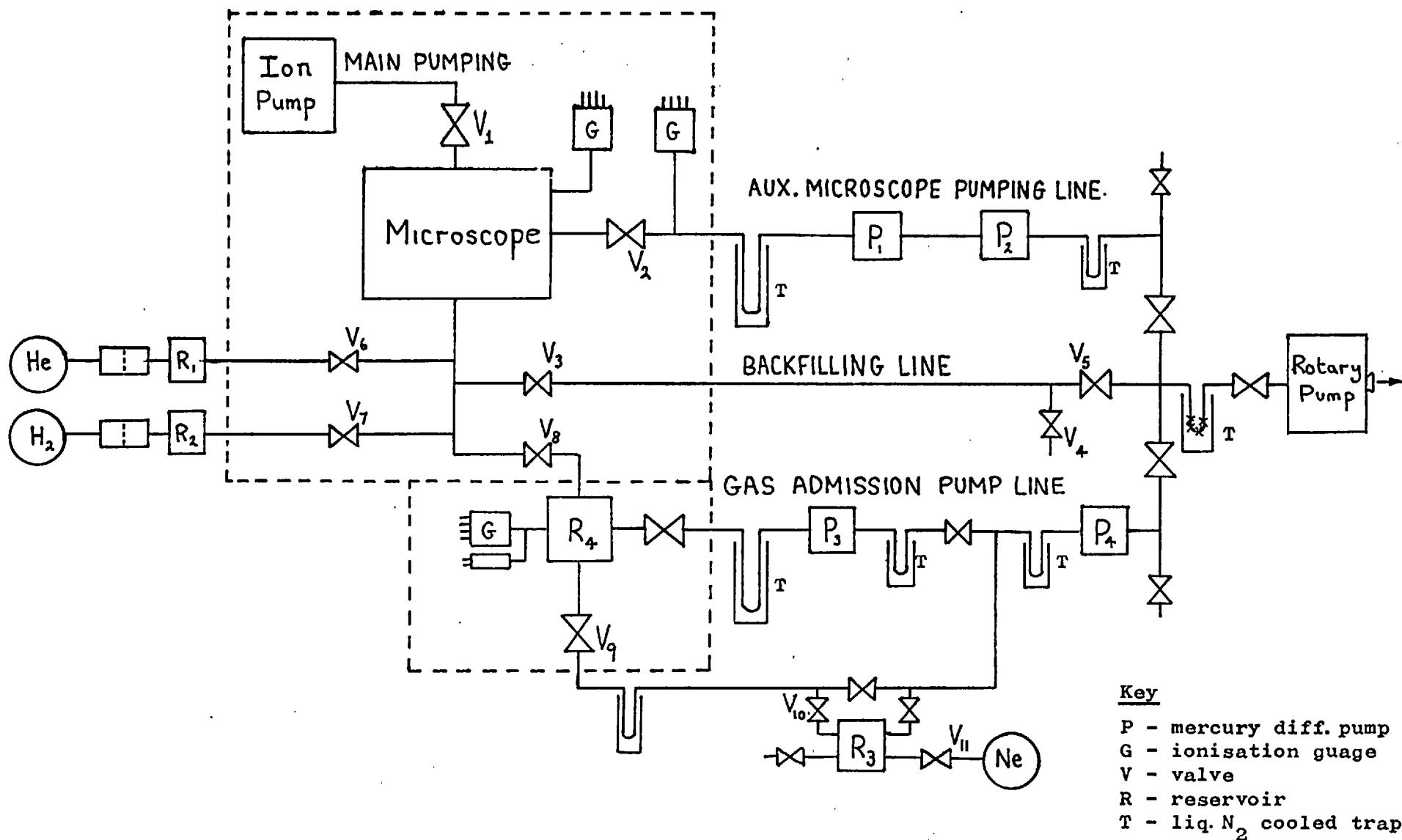


Fig.11. The Vacuum Pumping System.

The chamber was then pumped by the diffusion pump line until a pressure of less than 5×10^{-6} torr was reached when the pumping was augmented by opening valve V_1 to the ion pump. This precaution was taken to avoid the possibility at high gas pressures of the ion pump discharge propagating into the chamber and damaging the tip.

1.3. Gas Admission

This system can be further subdivided into two main sections: (i) the helium and hydrogen admittance systems, and (ii) the neon admittance system.

(i) Hydrogen and helium were purified by diffusion through electrically heated quartz membrane diffusers into reservoirs R_1 and R_2 . Their final admission to the microscope was controlled by valves V_6 and V_7 . The connecting tubing on the gas storage side of this sub-system was isolated from the pumps and had been evacuated prior to fracturing the break tip seals on the gas storage bulbs.

(ii) Neon imaging gas was not purified by diffusion but was processed by the main gas handling system. After this system had reached satisfactory vacuum conditions, neon was admitted via valve V_{11} into a small storage reservoir R_3 from the main storage bulb. A small pulse of this gas was then admitted through valve V_{10} , over the liquid nitrogen cooled trap, and a further reduced pressure of gas leaked into the UHV processed getter bulb R_4 via leak valve V_9 . A fresh molybdenum getter film was deposited in this bulb just prior to neon admission and cleaned the gas by adsorption of active contaminants on to the film. The gas was then ready for subsequent admission to the microscope through valve V_8 .

1.4. Ancillary Apparatus

The Brandenburg stabilised high voltage supply was connected via a potential divider to a digital voltmeter for accurate voltage measurement, and to the specimen via a $1000\text{M}\Omega$ current limiting resistor for field ion imaging purposes. A separate photomultiplier high voltage supply was used for field emission imaging.

A Vacuum Generators' ionisation guage controller was used for monitoring vacuum conditions via the Bayard-Alpert guages.

The microscope screen was normally observed via a mirror with the unaided dark-adapted eye or a telescope. For photographic recording the mirror could be swivelled out of the way. A 35mm camera was used at f2.8 with Kodak 103ag spectroscopic film. Exposure times ranged from 20 secs - 2 minutes, with a monitor of screen brightness being provided by a sensitive photomultiplier mounted near the camera lens.

For the purposes of specimen heating, the temperature controller was used. As shown in Fig.12 this consisted of a Kelvin bridge resistance measuring network which, connected through an operational amplifier controlled the power amplifier circuitry.

As shown in Fig.13, the specimen was spot welded on to a 14 thou Pt wire heating loop, with two additional 2 thou W leads for the purposes of resistance measurement. The four resulting leads were in turn spot welded to 1mm tungsten rods which were connected to the temperature controller via tungsten glass vacuum feed-throughs.

The temperature controller was calibrated assuming a linear resistivity characteristic for platinum in the range 77K - 500K. Two calibration points were taken, at liquid nitrogen temperature, and at room temperature respectively. At liquid nitrogen

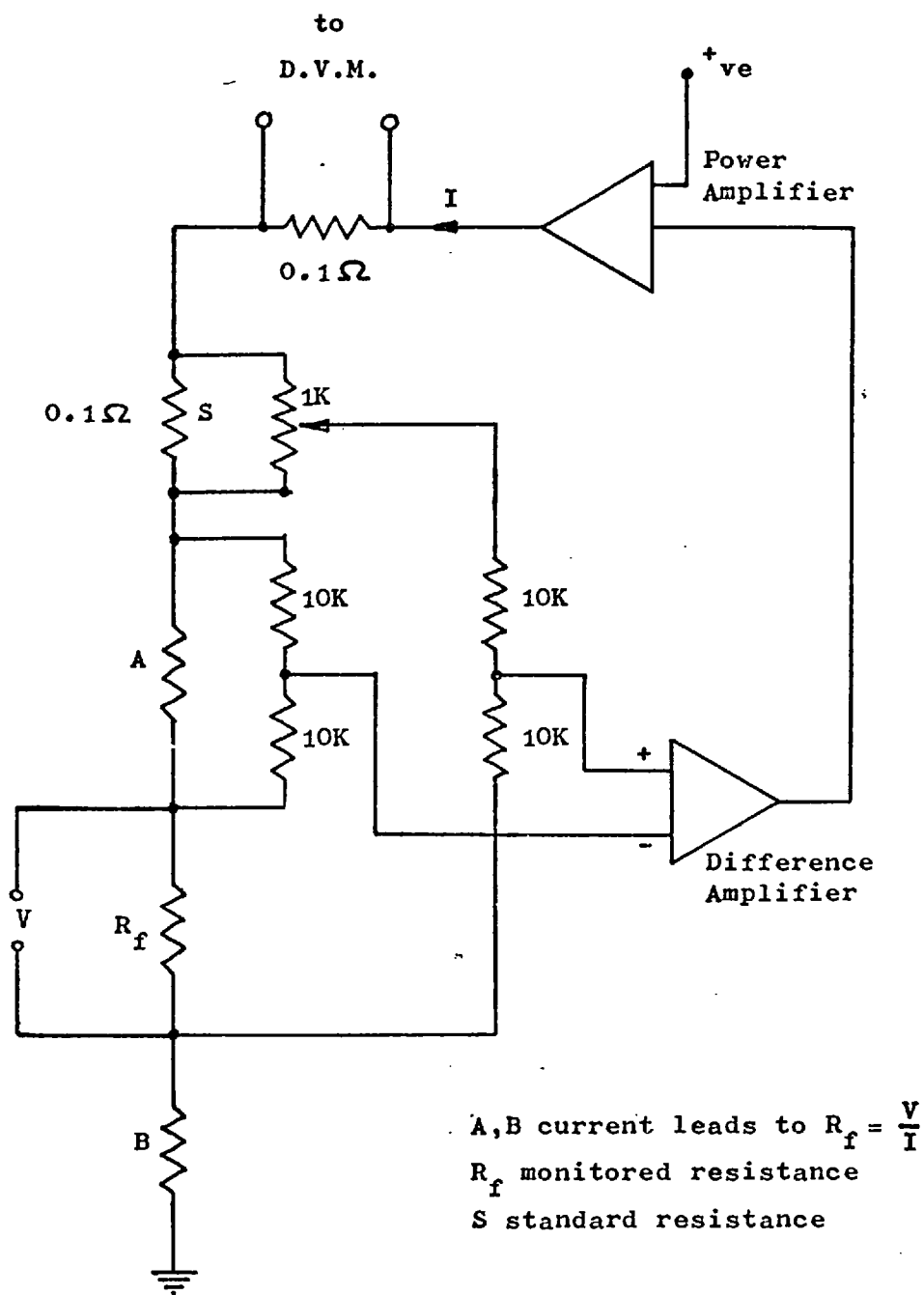


Fig.12. The Temperature Controller Circuitry.

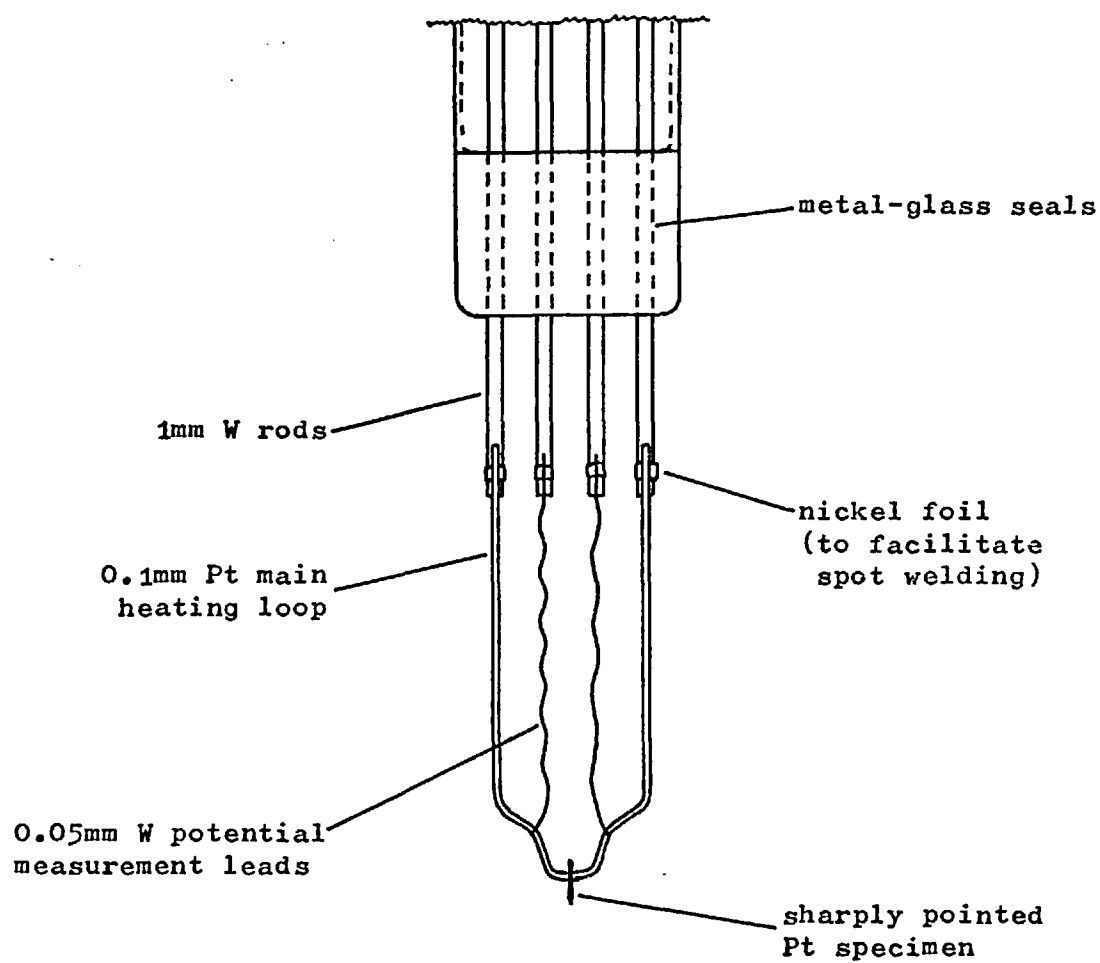


Fig.13. The Specimen Assembly.

temperature the chamber was evacuated and the specimen allowed three hours to reach thermal equilibrium. No measurable shifts were observed between calibrations performed at ambient temperatures of 290K to 310K in this case. The room temperature calibration was performed after the microscope had been left overnight.

Resistance measurement was by a current v. voltage plot using an X - Y plotter. As shown in Fig.14 the obtained temperature calibration line agrees very well with independent platinum temperature coefficient measurements.

2. Initial Specimen Preparation

In all cases specimens were prepared by electro-polishing whilst under observation by a conventional microscope. A final criterion of sharpness was made with the specimen removed from the electrolyte solution by observing the Fresnel fringes associated with the tip image.

2.1. Nickel

A solution of 1:1 H_2SO_4 (conc.): H_2O was used with +20V D.C. applied to the nickel wire. The wire was immersed 2mm until a waist was formed, then truncated at the waist, reimmersed 5mm or more and finally sharpened using 10-15V D.C. An alternative method for final sharpening was using a solution of 2:3:3 HCl (conc): H_2O :Glycerol.

2.2. Palladium

The same solution and voltage supply was used as for nickel. The wire was immersed 2mm until quite thin, then withdrawn until a violent reaction (sparking and fizzing) occurred near the

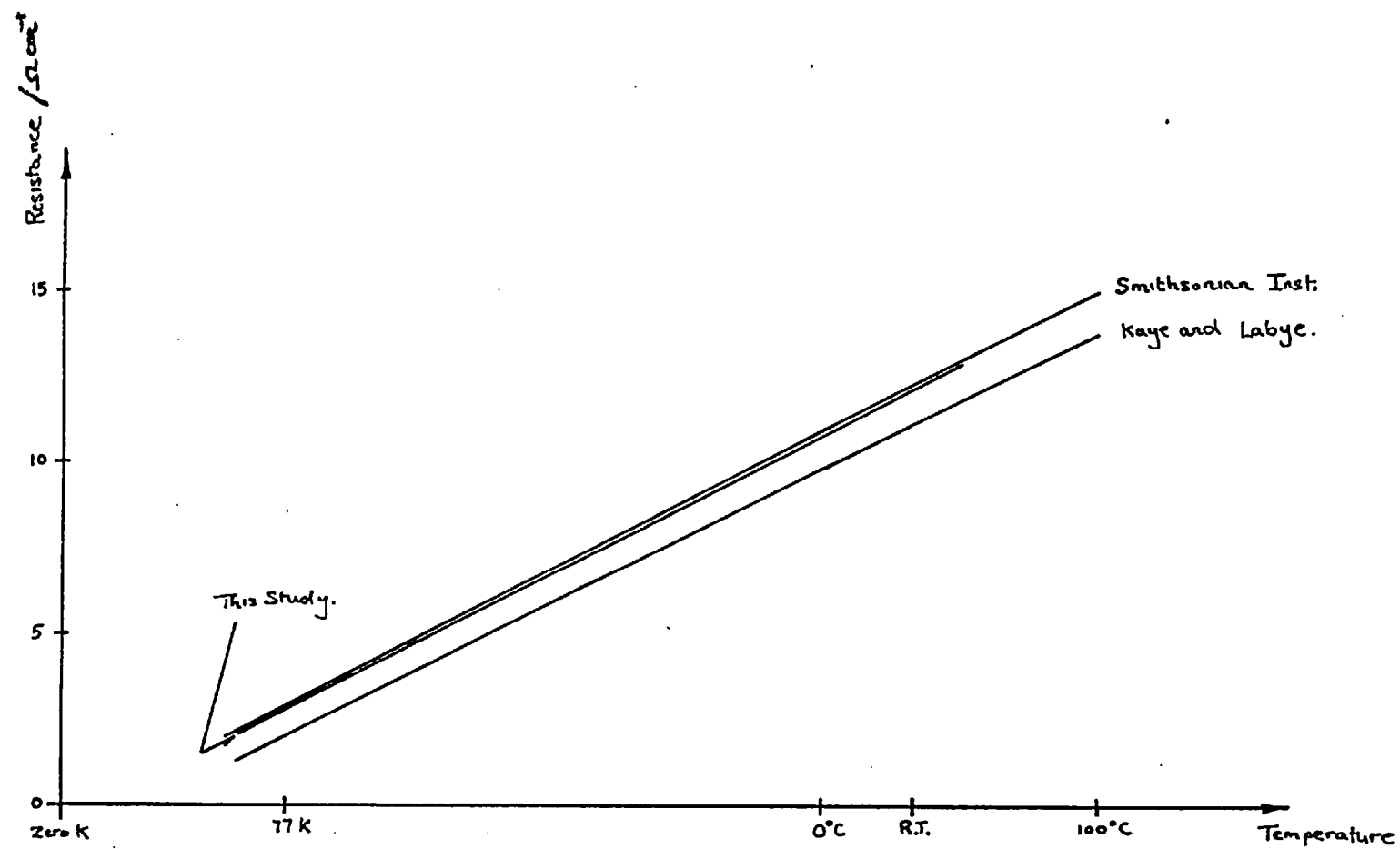


Fig.14. Platinum Resistance Measurements v Temperature.

solution surface which necked the wire. The wire was then reimmersed 5mm to finish off. Some difficulties were experienced in judging the amount of necking required to finally achieve a near parallel sided tip.

2.3. Platinum

A saturated solution of CaCl_2 in H_2O was used with 5V A.C. applied to the specimen. The 4 thou platinum wire used was supplied by Johnson-Matthey Ltd. as grade 1 wire. Impurities were largely palladium and iron, these constituting 20 p.p.m. of the bulk. The wire was cut-off as nearly square-ended as possible and immersed about 5mm for sharpening. Final sharpening was done with part of the Pt heating loop also immersed to reduce the current density at the tip. During the course of the experimental work on platinum described in this thesis the same piece of specimen wire was used throughout. Resharpening of the tip after failure by fracture or gas discharge was necessary on five occasions.

3. Pumping Down Procedures

After insertion of a newly prepared tip, the FIM chamber was pumped out as described in Section 1.2. to a pressure of 1×10^{-6} torr or less. In the absence of any leaks, the chamber was then baked out two or three times to achieve a background pressure of 6×10^{-10} torr or less.

Sources of contamination were:

1. the channel plate image intensifier,
2. the evaporator loops,
3. metal or glass surfaces near the evaporator loops,
4. the imaging gas,

5. the tip supports,
6. the chamber walls.

The channel plate (a 3" Bendix plate with 37μ channels) was a major source of contamination. After each bakeout this was outgassed by electron bombardment at 100eV for 2-8 hours. For this purpose electrons were supplied by thermionic emission from a tungsten filament and accelerated by a ring electrode at -100V relative to the filament.

During use of the microscope over two years the outgassing decreased substantially. The pressure rise due to electron bombarding at maximum plate gain after full outgassing was $\sim 2 \times 10^{-11}$ torr (measured on a backed off guage on 10^{-10} setting). During all experimental runs the screen brightness was some orders of magnitude lower than during this procedure, and the pressure rise due to turning up the channel plate was not measurable. Excessive outgassing was found to substantially reduce the plate gain, which could then be restored by baking the chamber again. For this reason extensive outgassing of the plate was avoided after the last bakeout.

The adsorbate metal vapour-source filaments (Fig.10), their side loops, and the molybdenum gettering filament were routinely outgassed for one hour before each experimental run. Outgassing from the glass surrounds to the evaporators was a problem, and the platinum evaporator was fitted with a separate tungsten heating filament to facilitate outgassing of the surround. Outgassing of the tungsten loop holding the gold bead was performed for several hours at just below the gold evaporation temperature.

The tungsten potential leads to the specimen were outgassed at red heat.

The gas handling and cleaning system was usually baked-out and processed to a pressure of 2×10^{-9} torr in the UHV section.

The gas cleaning getter filament was outgassed for one hour to reach this pressure, and the molybdenum getter film deposited when the glass getter bulb had cooled. Neon was immediately admitted to a pressure of about 10^{-2} torr as measured on the Pirani guage. However, this guage was only working for brief periods, and the usual method adopted was to admit neon until the ionisation guage controller tripped out on the 10^{-3} torr setting.

4. Final Specimen Preparation

4.1. Nickel and Palladium

The following methods were used for surface cleaning of nickel and palladium:

1. heating in vacuo,
2. ion bombardment in neon,
3. heating in hydrogen,
4. field evaporation,

and will be dealt with in turn.

Heating in vacuo was not a very successful surface cleaning technique because of the low melting points of nickel and palladium; thus tips were quickly blunted and made useless for field ion microscopy.

Ion bombardment⁴⁴ produces a clean surface but a very rough one. For this reason subsequent thermal annealing is required which was found to largely re-contaminate the tips by impurity diffusion.

Heating in hydrogen was performed to break down suspected oxide layers by the reaction.



This was found to be successful, but hydrogen is a very insidious

contaminant in a UHV system and for subsequent imaging attempts was found very difficult to eliminate.

Field evaporation was performed in hydrogen, neon and He/Ne mixtures. Evaporation in hydrogen provided a smooth surface but is not a suitable imaging gas for diffusion studies due to its high reactivity with the substrates. Neon or He/Ne gas mixtures produced tips with well developed (111) regions and surrounding areas, but extensive field evaporation was found to be fraught with danger for nickel. However, palladium surfaces could be prepared in a clean well-developed state by field evaporation in neon. Some of our difficulties in cleaning nickel surfaces may be attributable to the fact that much of this work was performed with a faulty high voltage supply which was found to be supplying a D.C. voltage chopped at 50Hz. This set up is similar to certain strain release experiments^{45,46} performed at 20K, but in our case subjected the high tension cables and specimen to very high respective electrical and mechanical stresses; leading to a high rate of tip and E.H.T. cable failure.

4.2. Platinum Tip Preparation

The specimen was first imaged by field emission to ascertain its general shape and symmetry. The tip was then heated at up to 500K in vacuo until a smooth image was produced. Neon was then admitted and the tip (at 77K) cautiously imaged using field ion microscopy. The specimen was heated briefly to about 400K, disconnected from the temperature controller, and while still warm field evaporated near the usual low temperature best image voltage. This process was continued until the FIM image exhibited good symmetry without any grain boundaries. Several cycles of heating, followed by field evaporation while cold were then performed to

reduce contamination diffusing down the shank of the tip. In extreme cases of contamination, ion bombardment in 10^{-6} torr neon was used to clean the tip surface. This technique⁴⁴ could also be used to resharpen tips below a certain radius. Platinum imaging was performed at 1.5-8 kV, tips being initially blunted by heating cycles to image at around 6kV.

5. Diffusion Experiments on Platinum

Before each experimental run the channel plate was briefly electron bombarded, and the evaporator filaments and the molybdenum getter flashed up to full current. No experiments were conducted if a measurable pressure rise of greater than 2×10^{-11} torr could be detected. During each run a check on gas cleanliness was made by leaving the tip at zero field for several minutes. The voltage was then gradually turned up whilst looking carefully for desorbing or scintillating spots. Typically no such spots were observed after leaving the tip for 30 minutes. A periodic check upon surface contamination by diffusion down the shank of the tip was made by FEM imaging of a freshly field evaporated surface. Successive heatings at up to 400K produced no visible contrast changes in the image. Using this microscope it was not possible to monitor the emission-voltage characteristic which provides a more accurate check on contamination.

These conditions having been met, the tip was subjected to heating cycles at a temperature 50 Kelvins above the chosen diffusion temperature, followed by field evaporation.

For diffusion experiments heatings of one minute were made in zero field, followed by a 30 second cooling period. The new adatom position was then photographically recorded. All results were obtained using a single adatom per plane, thus eliminating

adatom-adatom interaction effects. After 5-10 heating cycles the adatom was field-evaporated and a new diffusion plane produced. Whilst this process was time consuming, a higher standard of surface cleanliness could be met. This also formed a periodic check on the adatom desorption voltages at various positions on various planes.

Imaging of adatoms was always below the best image voltage to minimise desorption during exposures. Consequently, even with channel-plate amplification, the image required dark adapted viewing.

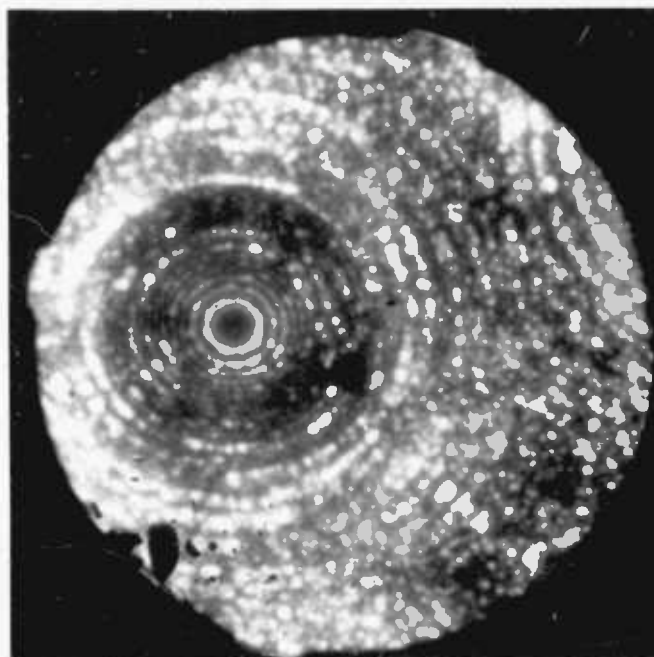
6. Imaging Characteristics

6.1. Nickel and Palladium

These metals were first imaged in the FIM by Muller⁴⁰, Very little subsequent work has been performed on palladium except in studies of binary alloys⁴⁷, while nickel has been imaged more extensively^{48,49}. Helium imaging of these metals at 20K, as performed by Muller, was found to induce dislocation networks due to the field stress, particularly in the (210) and (113) regions around the (111) plane. However, in the case of nickel, hydrogen-promoted field evaporation at a reduced field produced an image largely free from field induced artefacts. Boyes⁴⁹ has found that nickel at 20K can be field evaporated in neon without artefacts, while Rendulic⁴⁸ imaging at 77K with neon found initial hydrogen-promoted field evaporation necessary. It should be noted that at the higher imaging temperatures the metal yield stress will be reduced and artefacts such as slip more likely.

Field ion micrographs of nickel using neon and hydrogen imaging gases are presented in Fig.15. The hydrogen image was

(a) Hydrogen imaging gas.



(b) He/Ne imaging gas.

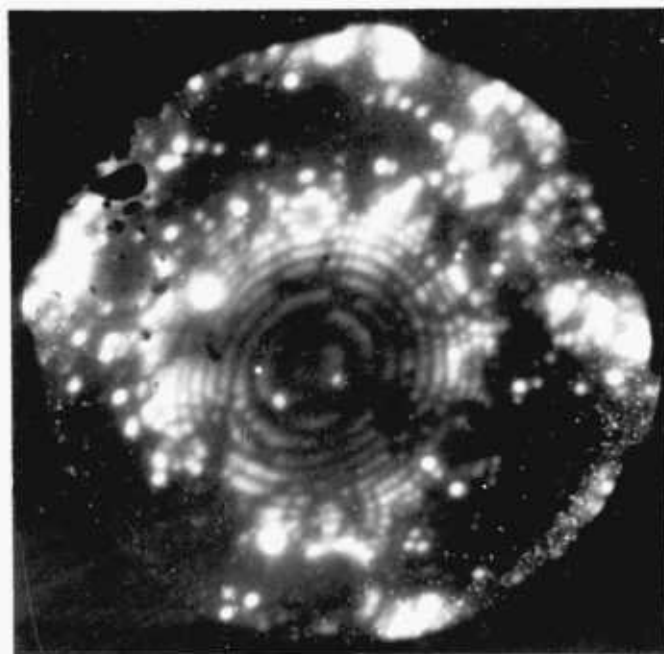


Fig.15. Field Ion Micrographs of Nickel.

taken while slow field evaporation was still occurring, which is the reason for the poor picture, but direct viewing revealed a smooth fairly well developed endform. The neon image shows better contrast and resolution around the (111) plane and surrounding regions, but exhibits marked disorder in an annular region about this. This may be an example of the field-induced dislocation networks noticed by Muller in helium images at 20K becoming important at our elevated tip temperatures for the reduced field stress involved in neon imaging. Another characteristic feature of nickel imaging was the way single bright atoms were observed to "steal" the image brightness from regions in their immediate vicinity. This effect was most marked when the bright atom formed part of a ring of atoms and the image intensity of the entire ring was markedly reduced, as has been observed by Ayrault²² with rhodium. Alternate light-dark contrast of consecutive (111) plane edge rings of atoms was also observed, every other ring imaging more brightly than the others.

A field ion micrograph of palladium is presented in Fig.16. As can be seen, this tip imaged at 77K with neon, showed no signs of field-induced dislocation networks and exhibits quite good image contrast and resolution with a well developed endform. Palladium was found to exhibit similar imaging characteristics to nickel, in that local "stealing" of image brightness by single atoms was observed, although to a less marked extent.

While both nickel and palladium were observed to be stable in neon imaging, field evaporation occurs at a voltage not far above the best image voltage for neon. Thus, stable imaging of single adatoms is rather difficult as these protruding atoms field desorb at even lower fields than the substrate. For this reason, combined with certain difficulties in hydrogen removal and tip

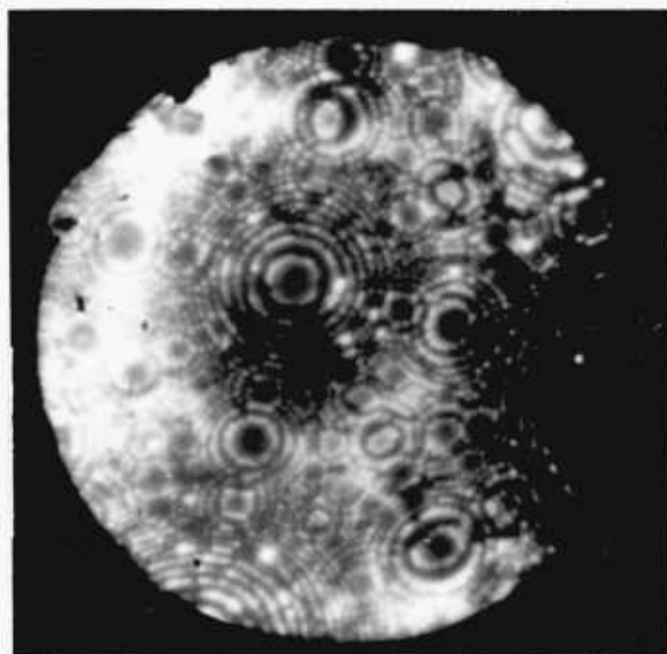


Fig.16. Field Ion Micrograph of Palladium.

cleaning, no diffusion experiments were performed on these metals.

6.2. Platinum Imaging

Platinum has been quite widely imaged in the FIM, largely for metallurgical investigations into dislocations⁴⁵, vacancy concentration^{45,46}, or radiation damage⁵⁰ for example. By far the most commonly reported technique is that of helium imaging at 20K^{40,45} although some work has been performed with neon imaging at 20K⁵¹ and at 77K⁵². The first reported FIM imaging of platinum was by Muller⁴⁰, who observed strain release by creep at room temperature, resulting in the gradual emergence of dislocations at the tip surface. This phenomenon was explained by assuming that whilst the tip was only elastically strained by the imaging field, some yield occurred further down in the shank. Thus, when the field was removed the tip found itself under stress from the yielded region below. A part of this strain could then be released by creep at room temperature.

The strain release effect has not been mentioned by other workers and was not observed in this study, however the purity of the platinum sample is of great importance in determining the mobility of dislocation (the more impurities the less mobile the dislocations) and may be the reason for these discrepancies in observation. Our work with neon imaging gas also subjects the tip to much reduced imaging stress than for helium.

The characteristic features of platinum imaging in helium at 20K are the cross-like zone decoration⁵³ of atoms leading from the (100) to the (113) planes, and the bright (120) regions. Our observations of imaging with neon at 77K show similar characteristics, as shown in Fig.17, and well developed low index planes suitable for adatom deposition could easily be constructed by

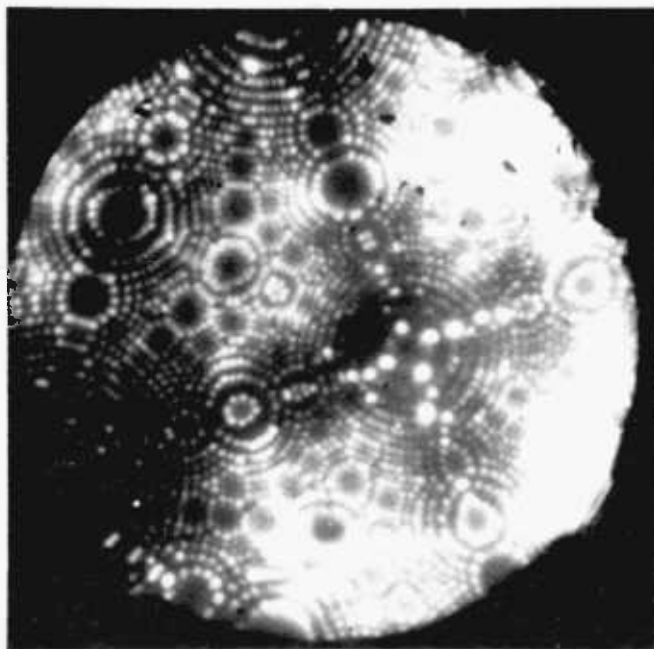


Fig.17. Field Ion Micrograph of Platinum.

field-evaporation.

6.3. The Imaging of Metal Adsorbates on Platinum

Before performing any diffusion studies it was necessary to establish the various adsorbate imaging characteristics and desorption voltages, as these factors determine the image interpretation and imaging voltages used.

The adsorbate metals imaged on platinum were tungsten, iridium, platinum and gold. Table 4 depicts typical adsorbate desorption voltages as a percentage of the platinum field-evaporation voltage. It should be noted, however, that adatom position on the plane in question could vary the desorption voltage as much as 10%, edge atoms desorbing at much lower fields due to local field variation across the plane. The desorption voltage of an adatom should depend upon the strength of the platinum-adsorbate bond. The relative strengths of these bonds can be roughly estimated from the sublimation energies of the adsorbate metals and this leads one to expect tungsten to be the adsorbate most difficult to remove, followed by iridium, platinum, and gold in that order. This is, in fact, the sequence observed.

Tungsten and iridium adatoms were found to be quite difficult to remove from the (111) or (100) planes of platinum. Some tungsten atoms on these planes could only be removed during fast field-evaporation of two or three substrate layers. In contrast, gold adatoms desorbed at very low voltages, far below the best image voltage of platinum for all the low index planes under study.

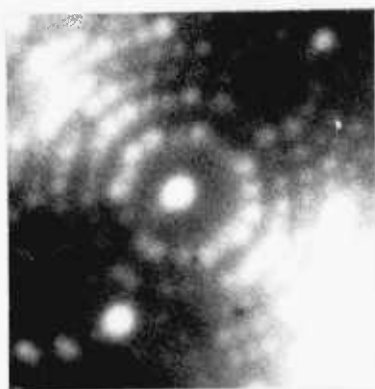
Imaging of tungsten, iridium and platinum adsorbates could be achieved quite routinely and some micrographs depicting these adatoms are shown in Fig.18. To achieve stable imaging of gold, very low imaging voltages were necessary at which the substrate

TABLE 4Adsorbate Desorption Voltages

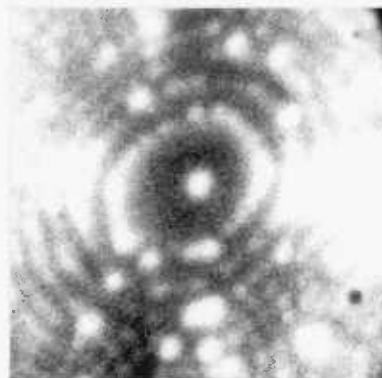
(as a percentage of the Pt field-evaporation voltage)

Platinum Substrate Plane	Adatom Type			
	Platinum	Iridium	Tungsten	Gold
(110)	80-90%	88%	99%	71%
(133)	87-92%	97%	100%	87%
(113)	98%	98%	100%	70%
(111) and {100}	100%	100%	100%	95%

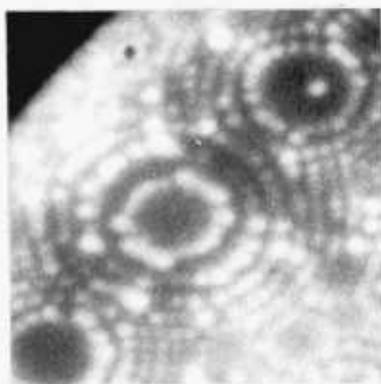
(a) Pt/Pt(113).



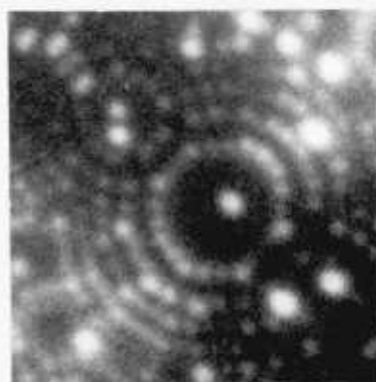
(b) Pt/Pt(110).



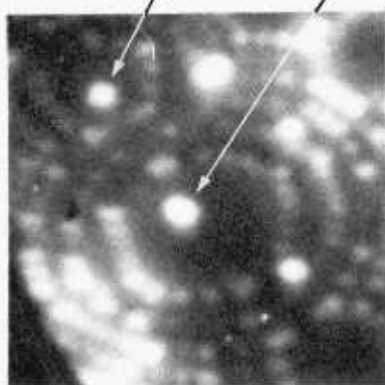
(c) Pt/Pt(133).



(d) Ir/Pt(113).



(e) Ir/Pt(133) and (110).



(f) W/Pt(111).

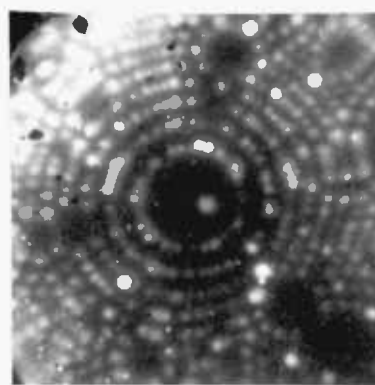


Fig.18. Single Adatoms of W,Ir and Pt on various Platinum Surfaces.

atoms were only just visible. For this reason gold imaging on the Pt (113) plane (Fig.19a) was considerably more difficult than on the brighter (110) and (133) planes as shown in Fig.19b.

However, for our purposes the important fact was that all of these atoms could be imaged on the various platinum planes with sufficient contrast to enable accurate measurement of atomic displacement.

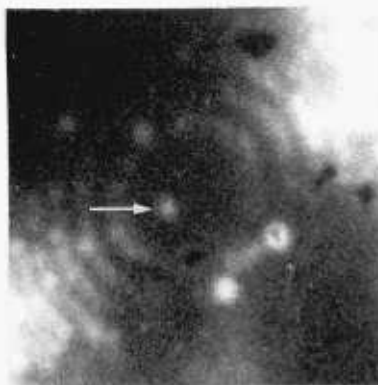
7. Imaging Perturbations

When imaging at voltages close to the adsorbate field-desorption voltage, certain metal adatoms were observed to undergo displacements relative to the substrate. Such perturbations were observed only with the foreign adatoms studied on platinum. In the case of gold this significantly limited the working voltage suitable for routine imaging.

Near their field desorption voltage gold adatoms were observed to "pop-up" as a prelude to desorption, the atom in this position increasing greatly in brightness and apparent size, as shown in Fig.20a. Subsequent reduction of the imaging voltage caused the atom to "pop-down" and image normally again, as shown in Fig.20b. This effect was observed routinely with gold on the Pt (113), (110) and (133) planes but not on the Pt (100) plane. The effect could be demonstrated cyclically on the Pt (113) and (110) planes with pop-up and pop-down occurring at 70% and 65% of the platinum field-evaporation voltage respectively. On the Pt (133) plane gold atoms popped up and desorbed almost immediately, preventing such observations.

Evidence that these phenomena involve a physical movement of the adatom and not an imaging promotion effect, can be seen in the fact that after one pop-up and down, an adatom was frequently

(a) Au/Pt(113).



(b) Au/Pt(110).

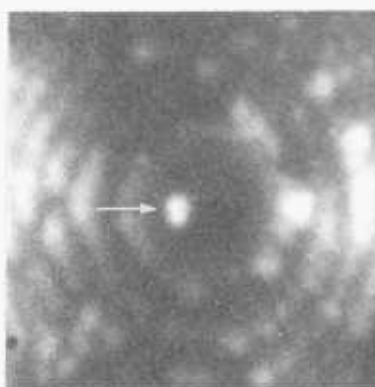
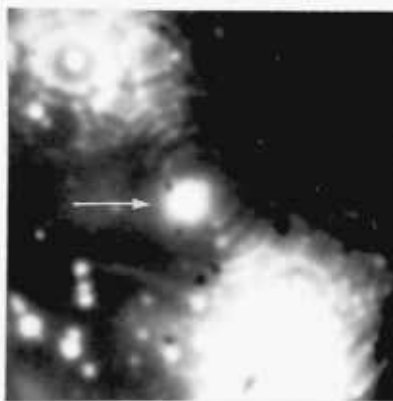


Fig.19. Imaging of Gold Adatoms.

(a) Gold adatom in "popped-up" position.



(b) Gold adatom imaging normally.

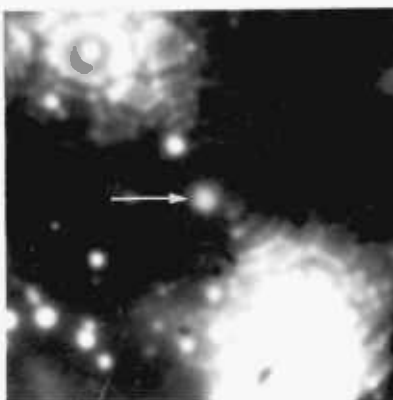


Fig.20. High Field Imaging Perturbations of Gold Adatoms on the Platinum (113) Surface.

observed to have moved to an atomic site in an adjacent row. Fig. 21 depicts such a sequence of gold cross-row movements on the Pt (113) plane. High field dissociation of a gold dimer on the Pt (113) plane was also observed on one occasion, as shown in Fig. 22.

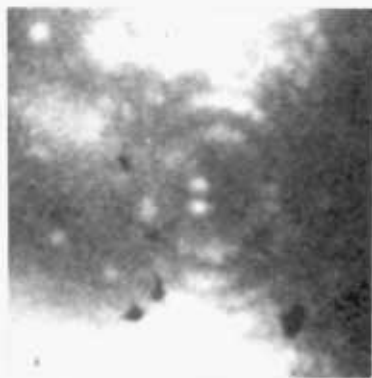
Another interesting effect sometimes occurred before pop-up. Gold adatoms were observed to glide down an atomic row as far as seven atomic diameters before popping up and desorbing, perhaps crossing a row before doing this. Atoms appeared to be propelled radially towards the plane edge, hence only fairly central adatoms were ever observed to move along rows.

These phenomena, occurring as they did in an effort to study diffusion, were originally found to be rather frustrating, but were eventually successfully utilised for the purposes of manoeuvring gold atoms off the plane edge leaving one remaining atom for diffusion studies.

High field imaging perturbations of other metal adatoms on platinum were seldom observed. As shown in Fig. 23, tungsten atoms exhibited pop-up on the Pt(110) plane in a similar fashion to gold, but no cross-row movements were ever observed. On two occasions iridium atoms were observed to move a distance of one atomic diameter along the Pt (113) plane row direction, and on one occasion an iridium dimer was dissociated in high field conditions on the Pt (100) plane, as shown in Fig. 24. In no cases were image perturbations observed for platinum adatoms.

A striking example of the influence of field effects was noticed with the imaging of retained nickel atoms on the Ni (111) plane. In this case, after field-evaporation of a (111) layer of atoms such that a small central island remained, atoms were observed to break away from the central island and move across towards the plane edge. These atoms would then normally field-

(a) Initial positions of gold adatoms.



(b) Cross-row movement of one adatom.



close-packed
direction

(c) Further cross-row motion.

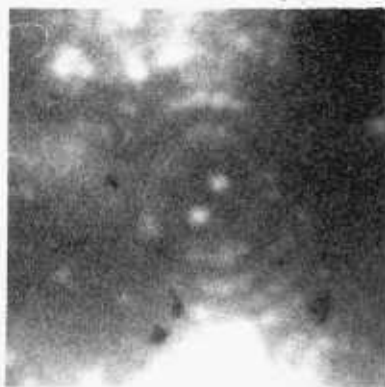
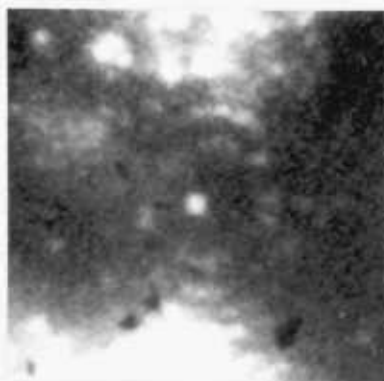
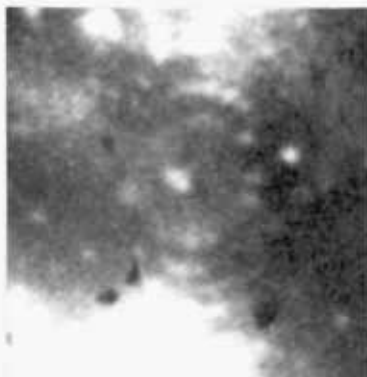


Fig.21. Cross-row movement of gold adatoms in high fields.

(a) Au dimer on the Pt(113) plane.



(b) Dissociated dimer.



(c) Two atoms moved further apart.

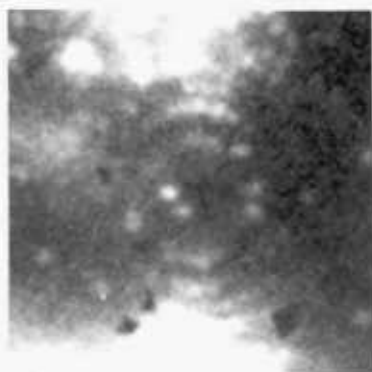
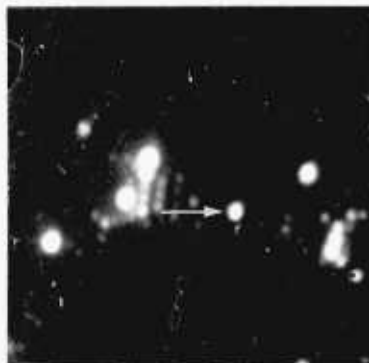


Fig.22. Dissociation of an Au Dimer Under High Field Conditions.

(a) Tungsten adatom in "popped-up" position.



(b) Tungsten adatom imaging normally.

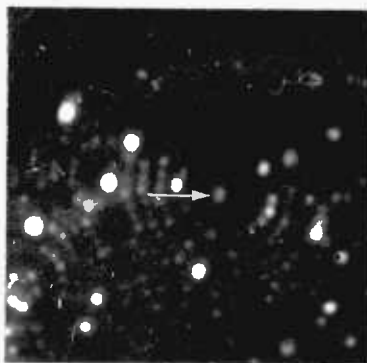
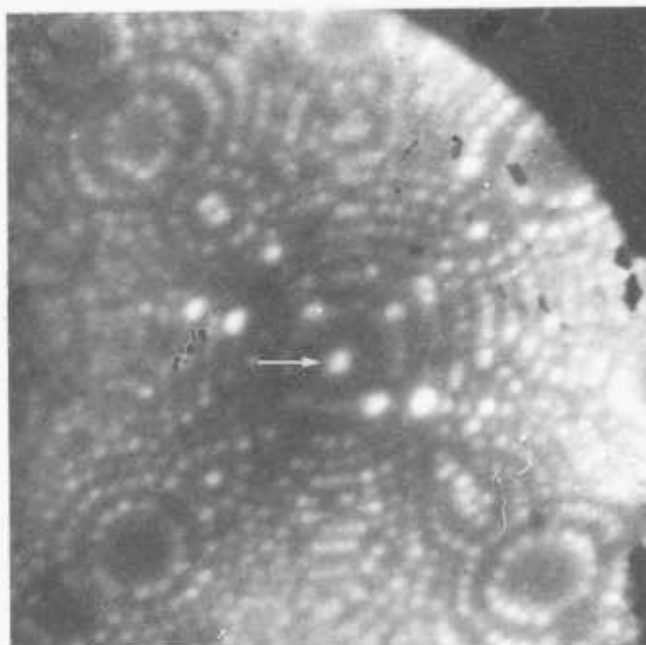


Fig.23. High Field Imaging Perturbations of Tungsten Adatoms on the Platinum (110) Surface.

(a) Ir dimer on the Pt(100) surface.



(b) Dissociated dimer.

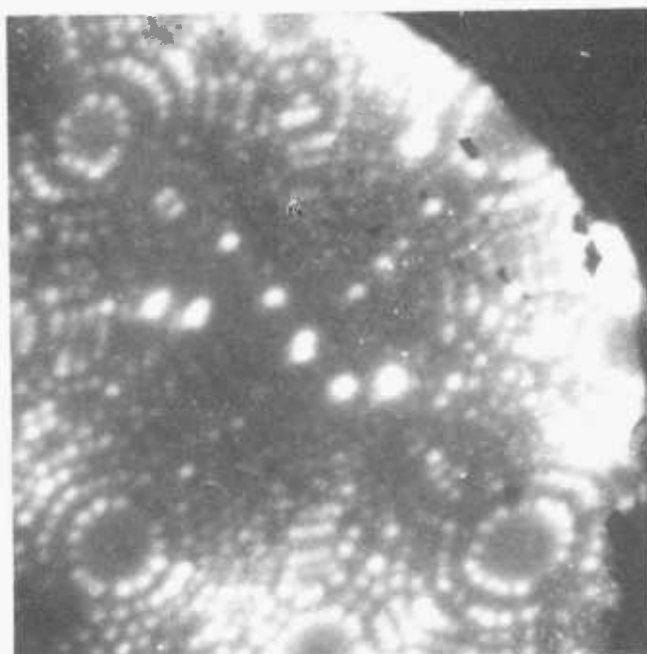


Fig.24. Dissociation of an Ir Dimer Under High Field Conditions.

evaporate after undergoing several reflections at the plane edge. These observations on nickel may have been influenced by other factors, such as the presence of hydrogen in the imaging gas, but the directionality of the atomic movement towards the (111) plane edge were quite unmistakeable.

Field effects upon imaging have been reported by other workers. Bassett and Parsley⁵⁴ noted pop-up of iridium atoms on the tungsten (211) plane and (111) steps, while Plummer and Rhodin⁵⁵ noted similar effects with platinum and gold on tungsten. Other curious imaging phenomena have been observed, such as image spot scintillation due to hydrogen⁵⁶ or neon⁵⁷ promoted imaging and the as yet unexplained haloes associated with the images of some retained atoms on the Ir (100) plane.⁵⁸

'Pop-up' can be qualitatively explained as being due to a high-field potential profile inversion as described in Chapter II. The observations on gold and tungsten indicate that these atoms can be sufficiently polarised by the field such that they occupy a saddle-type site on or near the row edge between two channels of atoms.

Considering equation (11), Chapter II Section 1.5,

$$H_f = H - \frac{1}{2}(p_s F_s^2 - p_t F_t^2) \quad (11)$$

it is apparent that the critical field necessary for H_f to become zero is not only dependent upon the adatom polarisabilities but also upon the energy barrier H . Thus, adatom pop-up or similar field dependent perturbations are most likely to be expected with the more weakly bound or more polarisable adatoms. Calculations by Thorhallson et al⁵⁹ of free atom polarisabilities and experimental results from Tsong et al^{37,38} with adatoms on tungsten indicate that of W, Ir, Pt and Au atoms, tungsten should be the most polarisable. As mentioned earlier in Section 6.3, gold adatoms

should be the most weakly bound. These considerations single out tungsten and gold as likely candidates for field dependent image perturbation effects, which was the case as observed experimentally.

The observations of a radial atomic driving force can be qualitatively explained by the field enhancement toward the plane edges leading to a slight potential gradient for polarised adatoms in that direction. Such a force has also been observed by Tsong et al³⁷ with 5d transition metal adatom diffusion on the W (110) plane.

IV. MEASUREMENTS OF ADATOM DIFFUSION ON PLATINUM

Following the methods outlined in Chapters II and III, the diffusion of Pt, Ir, Au, and W adsorbates was examined on various platinum planes. Preliminary experimental work showed that qualitative data was obtainable only on the channelled surfaces, namely the Pt (110), (113) and (133) planes. However qualitative observations on these planes, and on the Pt (111) and (100) planes enable some more general features to be pointed out.

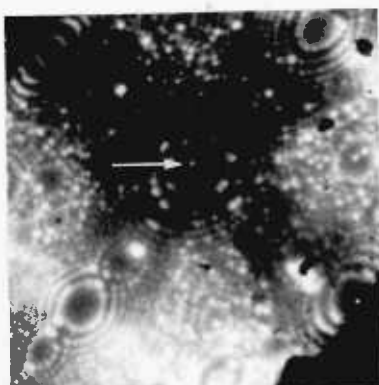
1. Qualitative Observations of Diffusion

On the Pt (111) plane, diffusion was found to occur at temperatures of 100K or less, where the temperature controller was not sufficiently sensitive for accurate work. Tungsten was the only adsorbate studied on this plane to exhibit reasonable mobility for measurement purposes and diffused at around 100K, while even at 77K, a platinum atom was observed to have moved in a sequence of 30 minute observations. Gold and iridium displayed similarly high mobilities.

On the Pt (100) plane, observations could not be made at sufficiently high temperatures to study diffusion accurately because of problems with substrate rearrangements or the diffusion of contaminants from the tip shank. Single platinum atoms (Fig.25a) were impossible to relocate after a heating to around 360K because of this contamination and faceting (or reconstruction) confusing the situation. As shown in Fig.25b, adatom visibility on this plane was also rather poor due to the four nearest Pt zone-decoration atoms "stealing" the image brightness from the surrounding regions.

As a more general guide to the different mobilities of

(a) Pt/Pt(100).



(b) Poor image contrast on the Pt(100) plane.

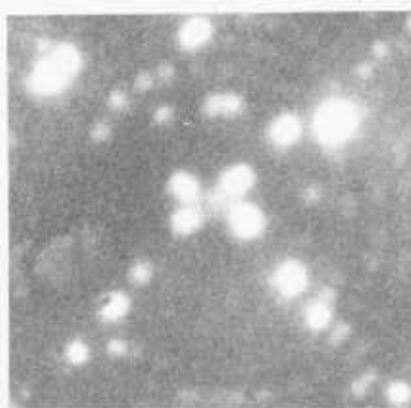


Fig.25. Imaging on the Pt(100) Plane.

adatoms on platinum Table 5 gives the temperatures at which adatom mobility was just detectable (taken as $10^{-17} \text{ cm}^2 \text{ sec}^{-1}$)⁶. Only upper or lower temperature limits can be provided for diffusion on the Pt (100) and (111) planes for the reasons described above. Tungsten adatoms were found to be immobile on all but the Pt (111) planes, and for this reason a lower temperature limit is given in these cases.

Large variations in mobility were observed attributable to adatom type on the one hand and surface structure on the other. Considering surface effects upon mobility, the Pt (111) plane allowed most movement followed by the (113), (110), (133) and (100) planes, in order of decreasing mobility. Comparing adatom types, W was least mobile followed by Ir, Pt and Au in that order, this sequence paralleling the adatom sublimation energy variations.

Barring certain anomalies, to be discussed later, the general character of platinum self-diffusion is in accord with the findings of Ayrault²² for rhodium self-diffusion. The general surface properties are also paralleled for gold and iridium adatoms, once allowance has been made in scale for the rather different adatom-substrate bonding expected in these cases.

1.1. Anomalous Diffusion

From simple structure considerations and prior FCC work²², as outlined in Chapter I, the channelled planes (the (110), (113), and (133)) were expected to exhibit one-dimensional adatom movement, while two-dimensional diffusion was anticipated on the relatively flat (100) and (111) planes.

These expectations were fulfilled, except in the cases of iridium and platinum diffusion on the Pt (110) plane for which two-dimensional adatom motion was routinely observed, as shown in

TABLE 5

Temperatures for which $D = 1 \times 10^{-17} \text{ cm}^2 \text{ sec}^{-1}$.

Platinum Substrate Plane	A d a t o m T y p e			
	Platinum	Iridium	Gold	Tungsten
(111)	<100	<100	<100	~105
(113)	243	263	174	>340
(110)	279	282	223	>340
(133)	312	-	-	>340
(100)	>340	>340	>340	>340

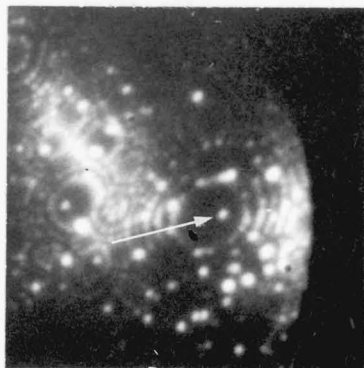
(all temperatures in Kelvins)

Fig.26. Gold on the Pt (110) plane exhibited solely one-dimensional movement. If this is purely a surface effect, then these results define a transition temperature for onset of two-dimensional motion within the range 235-265K. LEED (Low Energy Electron Diffraction) experiments by Bonzel and Ku⁶⁰ and others^{61,62} indicate reconstructions of the Pt (110) plane to a (2*1) surface at slightly higher temperatures. The exact structure of this (2*1) rearrangement is not clear, but some possible surface models have been suggested⁶⁰⁻⁶² and some are presented in Fig.27.

A close examination of Pt (110) planes before and after heating to temperatures sufficient to produce two-dimensional motion yielded no definite results about possible plane reconstructions. Contamination was suspected and looked for, but no good evidence was found to suggest its presence. No statistically significant variations in adatom mobility at the start or finish of experimental runs were observed. In fact "cross-row" movement occurred slightly more often during the first heating cycle. A two-dimensional analysis of atomic diffusion sites visited reveals a pattern of largely diagonally oriented starting and finishing sites for diffusion. In the absence of more detailed information about these atomic jumps no definite conclusion about a possibly rearranged Pt (110) surface can be reached, but these observations are certainly compatible with surface models, as shown in Fig.27, or similar, where the original row structure of the (110) plane is now completely changed.

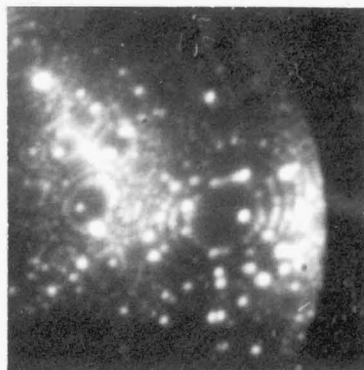
If surface rearrangement of the Pt (110) plane is occurring sufficient to cause the observed two-dimensional movements, some sort of surface irregularities or buckling will be present. This is likely to cause unusual adatom imaging effects if some atomic sites are rather more recessed or raised than average. However, no

(a) Initial adatom position.



arrow parallel
to close-packed
direction.

(b) After heating to 290K.



(c) After further heating to 290K.

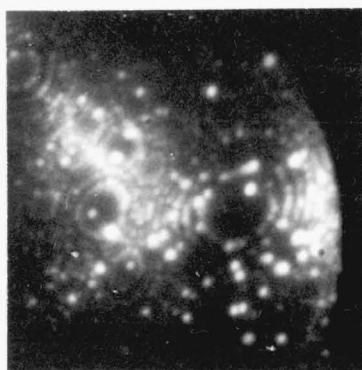
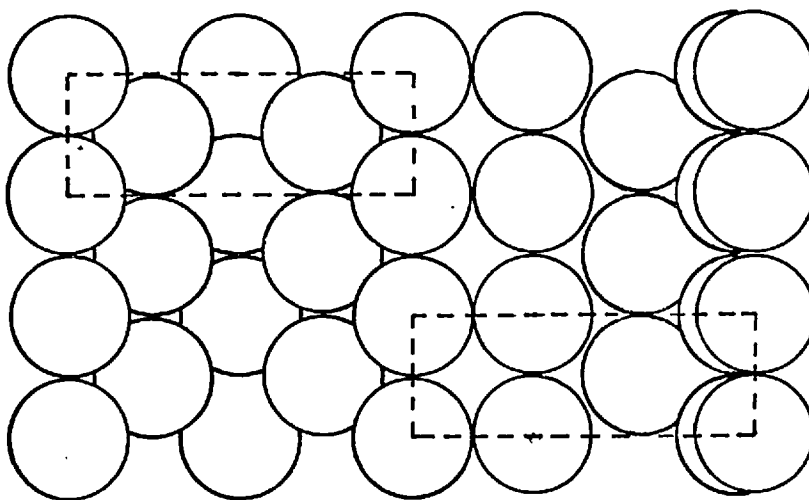


Fig.26. Two-dimensional Diffusion on the Pt(110) Plane.

- (a) Two possible (2x1) reconstructions of the Pt(110) suggested by Ducross and Merrill.⁶¹



- (b) A (4x2) rearrangement of the Pt(110) suggested by Tucker.⁶²

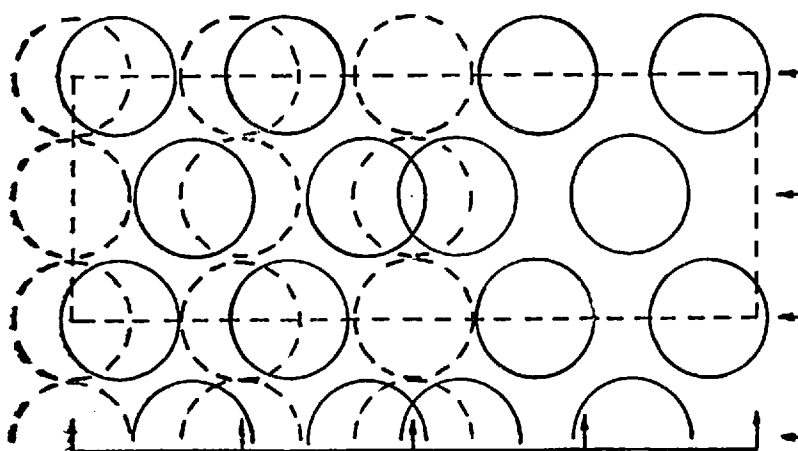


Fig.27. Rearranged Pt(110) Surfaces.

irregular imaging of platinum or iridium on the Pt (110) plane was observed. This may of course only indicate a symmetrical rearrangement leading to a distribution of identical atomic sites. Also surface buckling, if present, is likely to bias the chosen adatom sites towards more recessed sites with higher binding energies; thus a randomly moving adatom is not a very good sampler of the surface configuration in this case.

1.2. Dimers and Adatom-Adatom Interactions

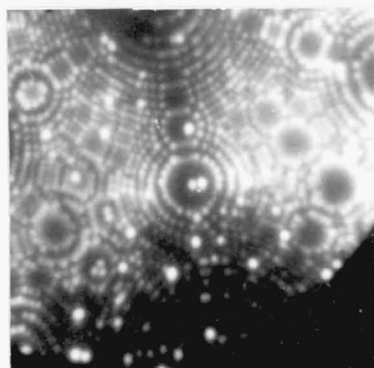
This diffusion study has avoided adatom-adatom interactions by making measurements upon single diffusing adatoms. However, some qualitative observations were made upon multiple adatoms on various planes. As expected from previous studies^{8,63,64} dimers or multiple clusters of adatoms were observed to be less mobile than single atoms. In some cases pairs of atoms separated by one or two atomic radii were observed to form quite stable configurations at normal diffusion temperatures. Some examples of stable dimers or pairs of atoms are shown in Fig.28.

Some observations of stable square arrays of Ir, Pt and Au atoms were also made on the Pt (100) plane, as shown in Fig.29. In all cases these arrays of atoms formed in line with the (100) close packed directions after a few heatings sufficient to initiate diffusion.

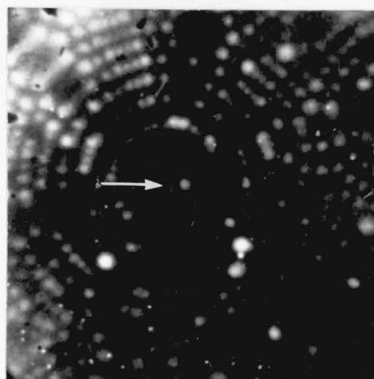
Quantitative observations were made of multiple (two or three) platinum atoms on the Pt (113) plane and show a mobility reduced by a factor of about fifteen relative to the corresponding single atom measurements.

These observations stress the necessity for performing initial diffusion experiments using only single adatoms.

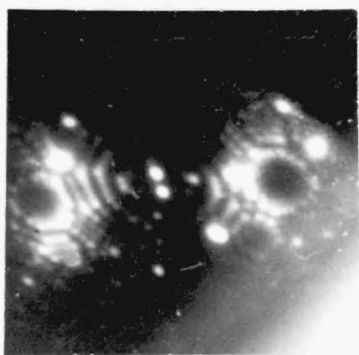
(a) Pt/Pt(113).



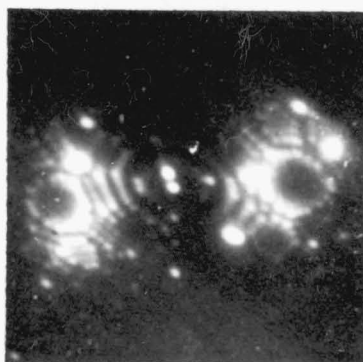
(b) W/Pt(111).



(c).



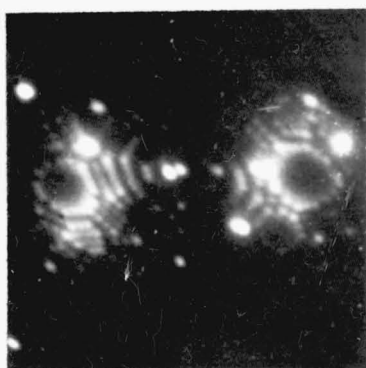
(d).



(c) - (f):

Pt/Pt(113) with successive heatings to 260K.

(e).



(f).

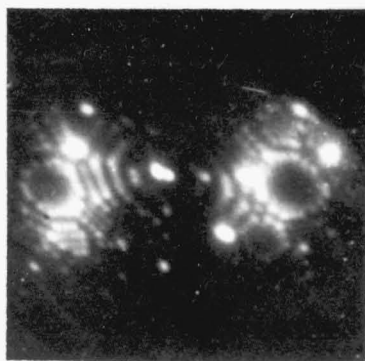
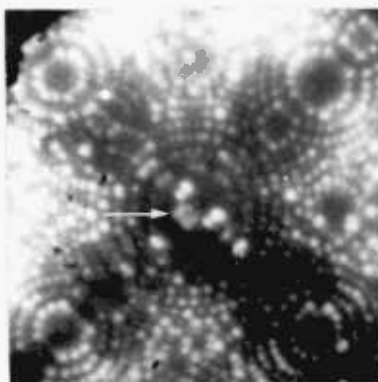
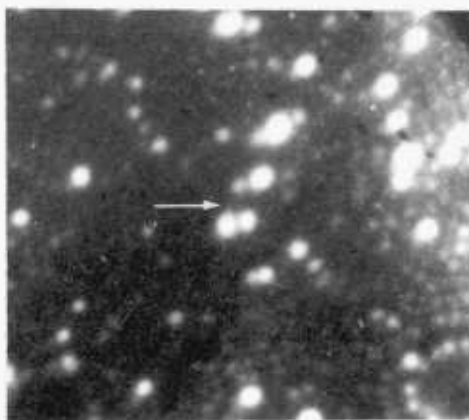


Fig.28. Interactions Between Pairs of Adatoms.

(a) Square cluster of Pt adatoms on the Pt(100) plane.



(b) Four Ir adatoms on the Pt(100) plane.



(c) Square cluster formed by heating to 320K.

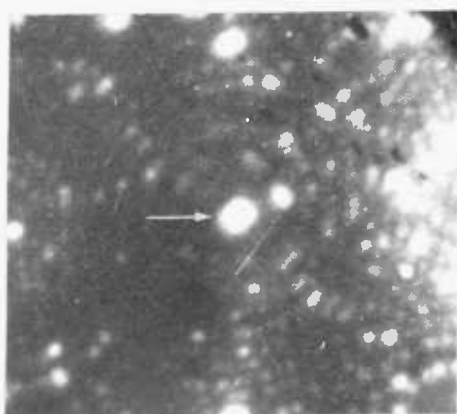
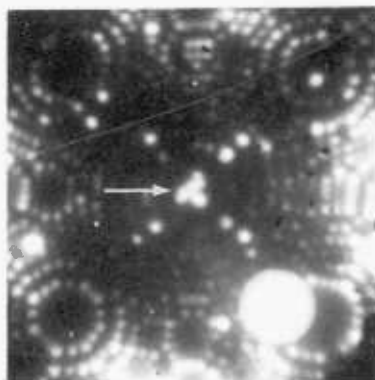
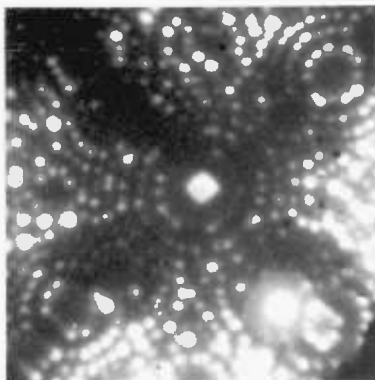


Fig.29. Adatom Clusters on the Pt(100) Plane.

(d) Cluster of several Au atoms on the Pt(100) plane.



(e) Square cluster formed by heating to 320K.



(f) Faceted surface formed by heating to 450K.

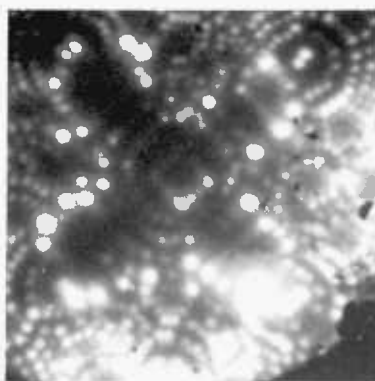


Fig.29. Adatom Clusters on the Pt(100) Plane,
(continued).

2. Quantitative Results

2.1. The Calibration of Micrographs

For a truly quantitative analysis of diffusion an accurate method was required for the measurement of adatom positions. Measurement was made directly from prints, using a superimposed clear acetate sheet. By choosing suitable fiduciary marks atomic positions could be measured to within 15% of an atomic diameter or better.

Three independent methods were used to scale the measurements correctly:

(i) By counting the number n , of atomic ledges of height h , between two crystallographic planes at θ degrees relative to one another, and hence calculating the tip radius r from the relation:

$$r = \frac{nh}{1 - \cos\theta} \quad (36)$$

(ii) By measurement of the smallest atomic displacement and integral multiples of it, assuming a smallest movement along channelled plane rows of 0.2775nm (the effective platinum atomic diameter).

(iii) By measurement of the known atomic row separations on the plane concerned (only possible on the (113) and (133) planes).

These calibration methods were found to agree quite closely and in any case sufficiently to allow integral numbers of the unit jump distance to be identified.

In the case of two-dimensional motion on the (110) plane the unit jump distance could not be certainly identified because of possible substrate rearrangements of an unknown nature. Method (i) was used in this case, and comparisons made with measurements

on the adjacent (133) plane. Similar methods were used for calibration on the (111) plane.

2.2. Diffusion Calculations and Results

From the measured atomic displacements $\langle r^2 \rangle$ was calculated, and hence D , following the method outlined in Chapter II. Using a linear regression program the results were fitted to:

$$D = D_0 \exp(-H/RT) \quad (25)$$

in an Arrhenius plot of $\ln(D)$ versus $1/T$. In this plot equation (25) can be rewritten as:

$$\ln(D) = \ln(D_0) - H/RT \quad (37)$$

where $\ln(D_0)$ is the intercept and $-H/R$ the gradient.

For comparison a weighted gradient fit was calculated using an additional theoretical point $(\ln(D_0), 0)$ calculated from the relation:

$$D_0(\text{calc}) = \frac{1}{2} \frac{kTl^2}{h} \quad (27)$$

The Arrhenius plots of the experimental data, together with the two lines of best fit are presented in Figs.30a-30d. As can be seen, the plots for W/Pt (111) and Ir/Pt (113) exhibit quite high scatter. Consequently only the weighted gradient fits are presented here. For two-dimensional motion on the (110) plane (Pt/Pt (110) and Ir/Pt (110)) the results were analysed by taking components of displacements parallel (r_x), and perpendicular (r_y), to the expected row direction. The corresponding values for the diffusion coefficients in the two directions, D_x and D_y , can be related to the two-dimensional diffusion coefficient D_{xy} by the relation:

$$D_{xy} = (D_x + D_y)/2 \quad (38)$$

However, this two-dimensional treatment obscures the slight

(a) Platinum Adatom Diffusion Data.

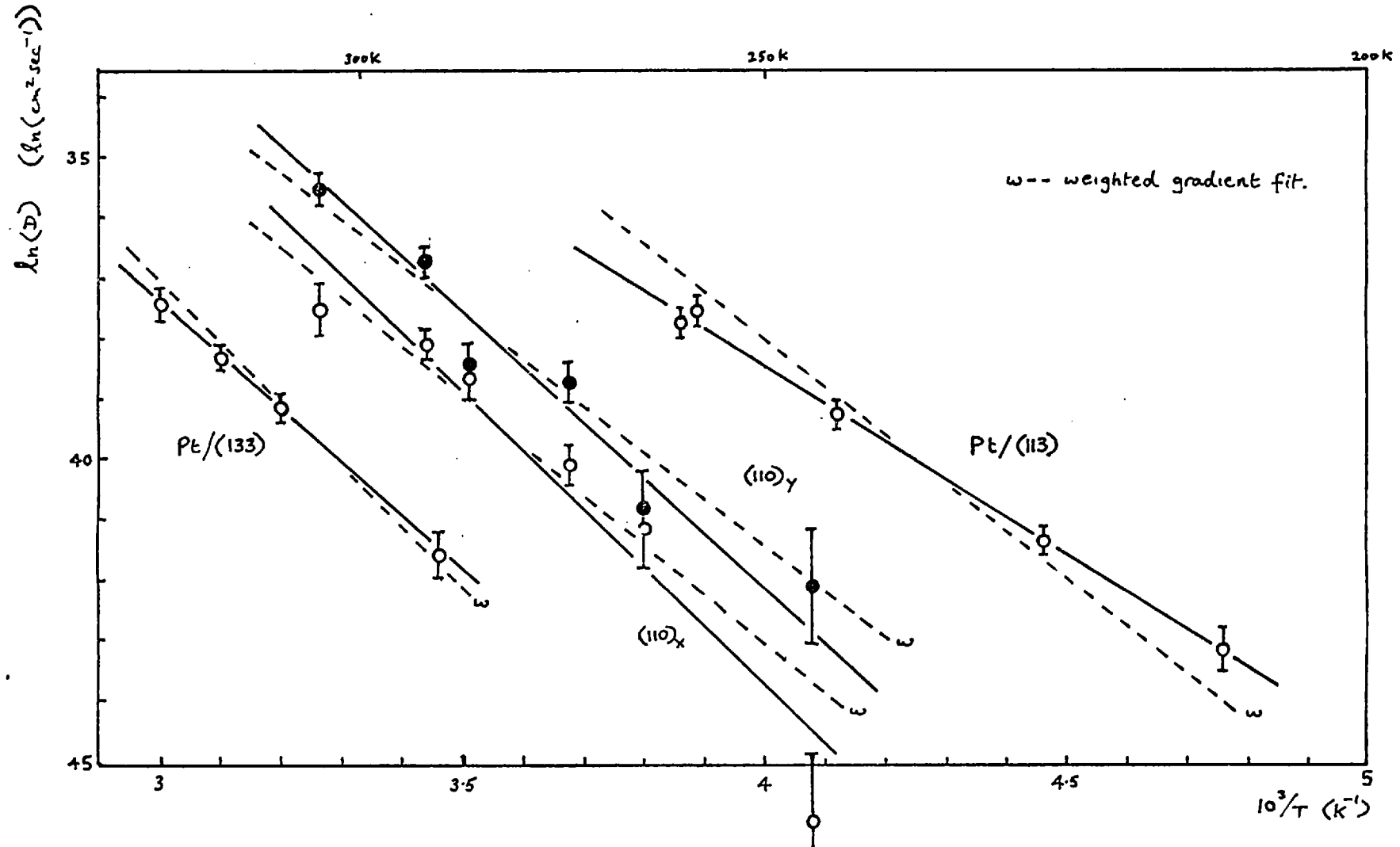


Fig.30. The Temperature Dependence of Adatom Diffusion.

(b) Gold Adatom Diffusion Data.

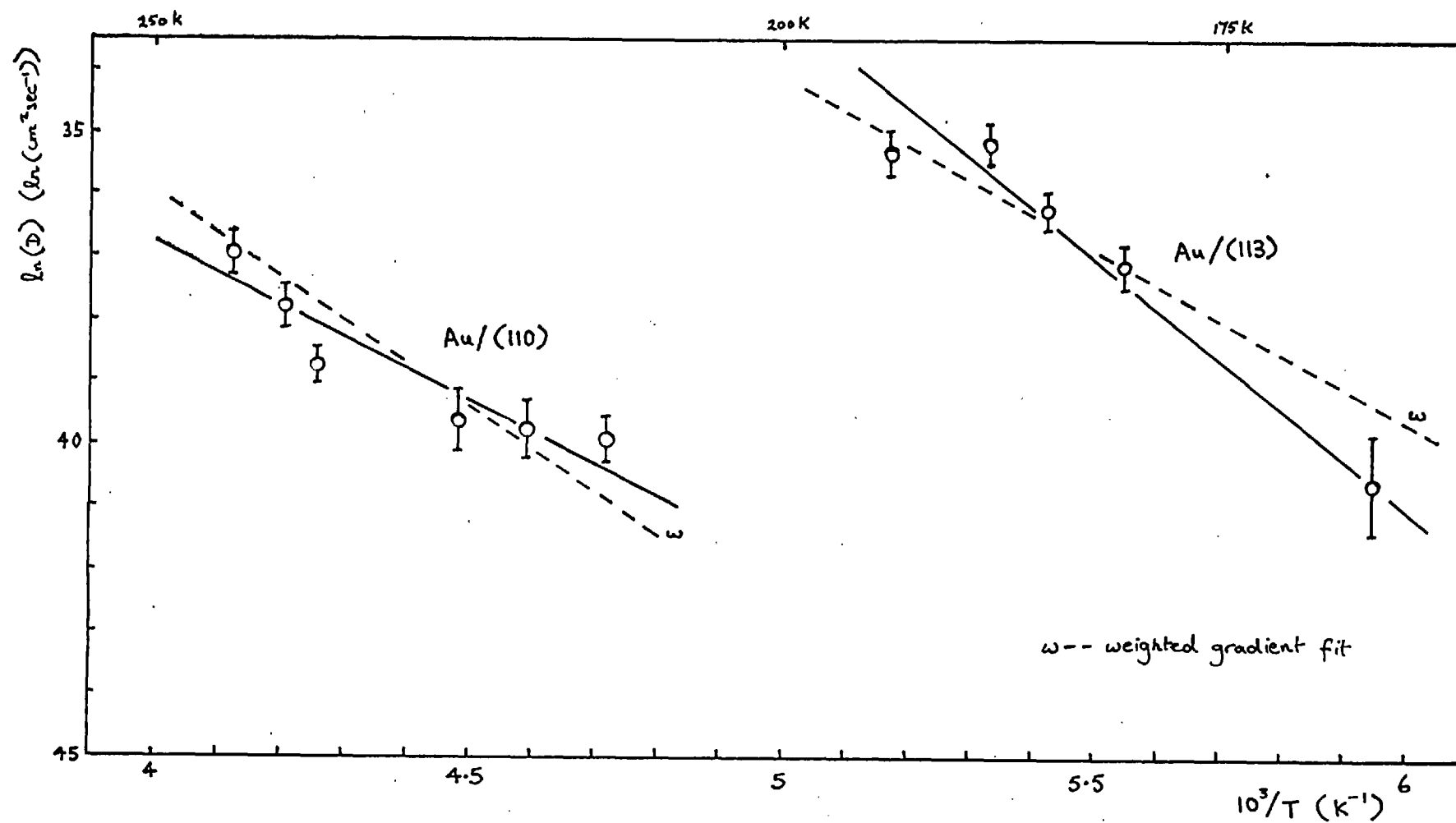


Fig.30. The Temperature Dependence of Adatom Diffusion,
(continued).

(c) Iridium Adatom Diffusion Data.

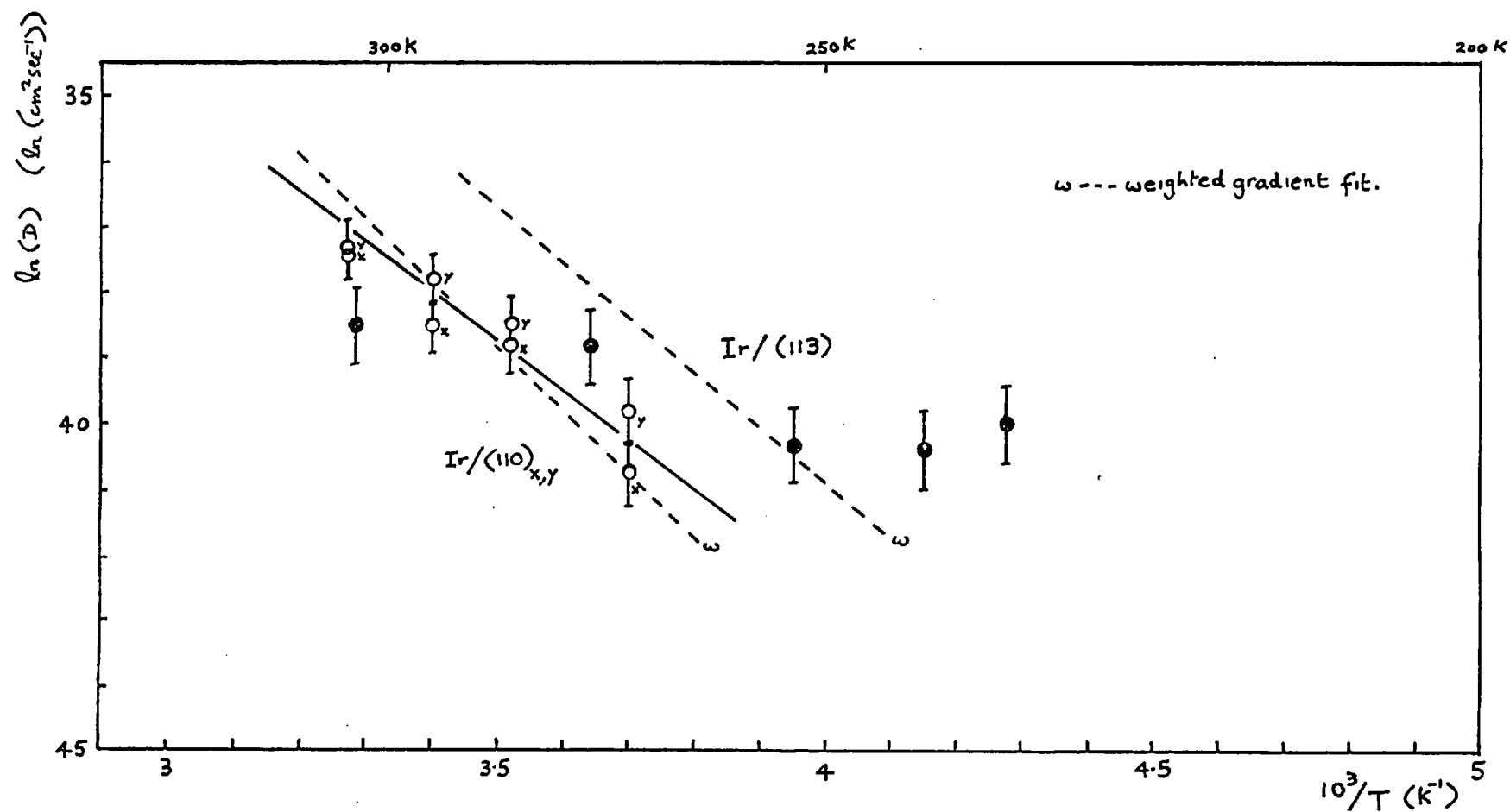


Fig.30. The Temperature Dependence of Adatom Diffusion, (continued).

(d) Tungsten Adatom Diffusion Data.

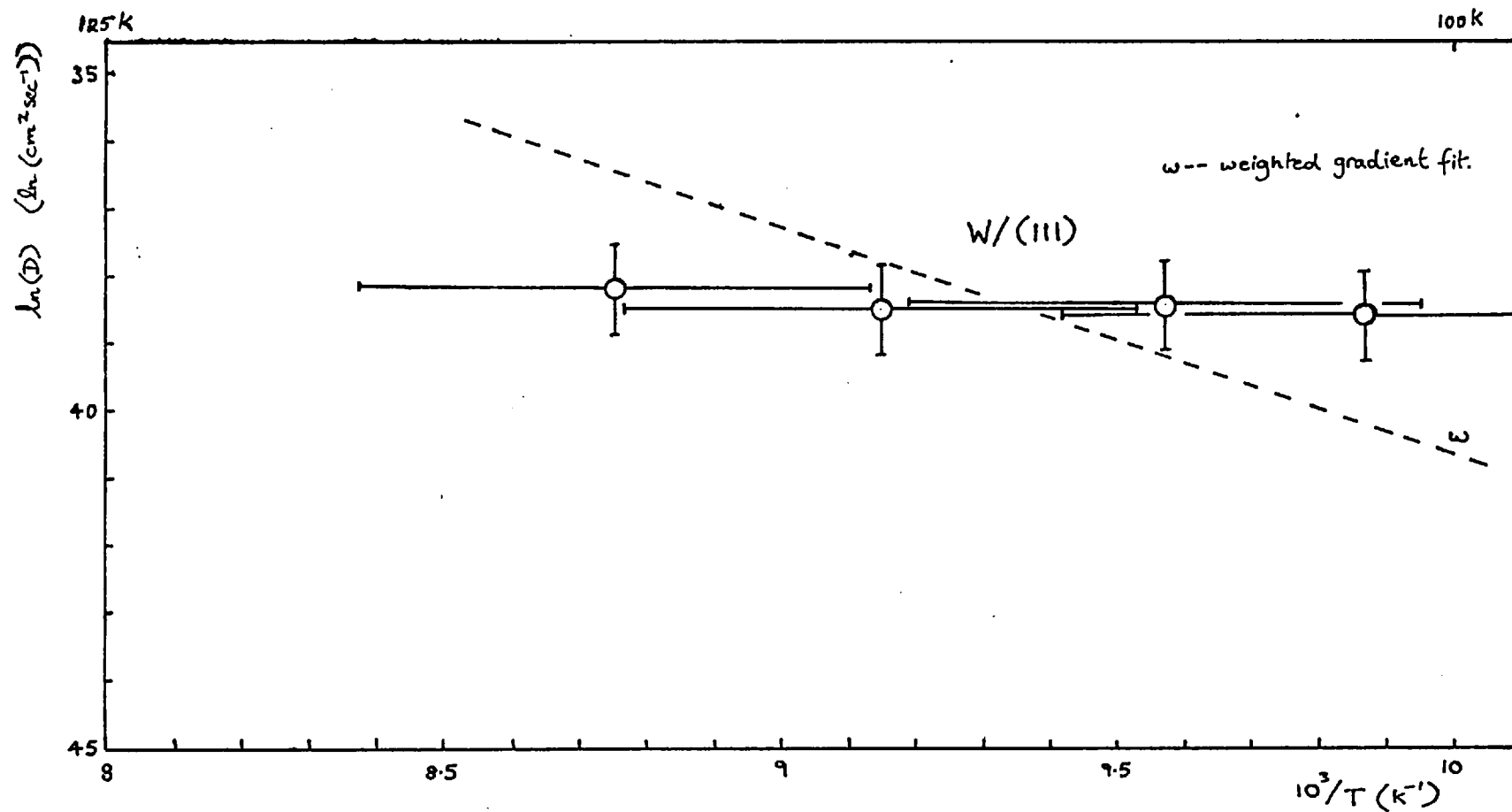


Fig.30. The Temperature Dependence of Adatom Diffusion,
(continued).

anisotropy of these results and was therefore not used.

As described above, two lines of best fit were calculated for each set of data. Thus in each case two estimates were obtained of the activation energy H . In the absence of any criteria for choosing either set of data, and following standard statistical methods, the best estimate of H is given by the relation:

$$H = \frac{1}{2}(H_{\text{exp}} + H_w) \pm \frac{1}{2}(H_{\text{exp}} - H_w) \quad (39)$$

where the suffixes exp, and w, refer respectively to the simple experimental, and weighted results. These resultant values of H are presented in Table 6. The experimental values of D_0 are presented in Table 7, and can be compared with the theoretical estimates $D_0(\text{calc})$. Large errors are involved in obtaining the experimental D_0 values due to the rather long extrapolation required for the intercept value. Consequently small errors in gradient (and in H) result in order of magnitude errors in D_0 .

2.3. Temperature Errors

The temperature controller calibration procedure has already been outlined in Chapter III, Section 1.4.

The portion of the platinum heating loop (Fig.13) used for temperature measurement was assumed to be at uniform temperature and in thermal equilibrium with the specimen tip. Possible sources of error are: (i) incident infra-red radiation heating the tip, (ii) errors due to the finite heating up time, and (iii) non-uniform heating of the resistance section.

(i) Incident radiation was kept to a minimum by conscientious topping up of the liquid nitrogen level in the dewar cooling the radiation shield. Errors here are assessed as negligible because they have not significantly affected the initial temperature calibration.

TABLE 6Activation Energies for Surface Diffusion

(from experiment)

Platinum Substrate Plane	A d a t o m T y p e			
	Platinum	Gold	Iridium	Tungsten
(111)	3 ± 2	-	-	7 ± 2
(113)	14 ± 1.8	12 ± 1	17.2 ± 2	-
(133)	$20 \pm .6$	-	-	-
(110) _x Along Channels	$19 \pm .4$	12.5 ± 2	16.8 ± 1.6	-
(110) _y Across Channels	$18 \pm .4$	0	16.8 ± 1.6	-

(all energies in kcal mol⁻¹)

TABLE 7

Pre-exponentials for Diffusion on Platinum

Platinum Substrate	A d a t o m T y p e					
	Platinum		Iridium		Gold	
Plane	calc.	exp.	calc.	exp.	calc.	exp.
(113)	2.0×10^{-3}	1.6×10^{-6}	2.1×10^{-3}	-	1.4×10^{-3}	2.6×10^{-1}
(110)	2.2×10^{-3}	4.6×10^{-3}	2.2×10^{-3}	6.0×10^{-6}	1.8×10^{-3}	2.2×10^{-7}
(133)	2.5×10^{-3}	4.1×10^{-4}	-	-	-	-

($\text{cm}^2 \text{sec}^{-1}$)

(ii) Upon switching on the heating controller the platinum loop takes a finite time to reach the required temperature. Observations of the swiftly changing current and voltage during this period indicate that the set resistance is achieved within 5 seconds.

(iii) The heating loop was long compared to the resistance section thus avoiding resistance measurements in the non-uniform temperature areas.

Considering the heating process as a dynamic one, and assuming that no thermal oscillations occur, the middle of the heating loop will rise in temperature most quickly followed by the rest of the loop (within the boundary conditions of 77K at the loop ends). After less than 5 seconds the set temperature is reached and any transient thermal gradients should gradually dissipate as the loop achieves final thermal equilibrium. During this period the heating current may be expected to drift slightly. Drifts of 0.2% were observed, and are evidence that transient thermal effects have a negligible effect on tip temperature. Furthermore no evidence for any thermal oscillations was ever observed.

From the various considerations above the temperature errors can be estimated as $\pm 2\text{K}$. Consequently the typical errors in $1/T$ are quite negligible in comparison with errors in $\ln(D)$, justifying this assumption in the regression analysis.

In the case of the measurements of tungsten diffusion on the Pt (111) plane occurring at around 100K, some difficulties were experienced in accurate temperature measurement. At these low temperatures the platinum loop resistance is extremely low and the corresponding out-of-balance signal to the Kelvin bridge very small. It was also suspected that incident radiation may have been rather more important here. For these reasons a temperature error of $\pm 8\text{K}$ has been applied in this case.

V. MODEL CALCULATIONS FOR ADATOM DIFFUSION

From the observations of diffusion described in Chapter IV, values are now available of the energy barriers to diffusion for a variety of adatom/substrate-plane systems. As stated earlier, one aim of doing these experiments was to come to an understanding of the forces at a surface. To this end the procedure adopted was to select a particular interatomic potential and calculate the expected energy barriers to diffusion. These calculated values can then be compared with experiment and the validity of the chosen potential determined. For our purposes a pairwise additive interaction model was chosen using an empirical Morse potential to describe the interaction between pairs of atoms.

The system under consideration, as shown schematically in Fig.31, can be regarded as consisting of a bulk crystal, a surface region, and a diffusing adatom. The bulk region is considered as fixed, with the surface region consisting of a few surface planes in relaxed positions upon it. The adatom in question is placed centrally on the top surface layer. At any stage of diffusion the bulk, surface and adatom must all be in equilibrium within certain constraints imposed by the small finite time taken for the adatom to jump from one equilibrium site to another.

The basic computational approach adopted follows the method of Wynblatt and Gjostein¹⁸ (W & G) in which the calculations are split up into four discrete sections. These four sections are:

PROGRAM 1. Relaxation of the surface layers without an adatom present.

PROGRAM 2. Calculation of the energy barrier ΔE_d to adatom diffusion with the lattice fixed at its relaxed positions from program 1.

PROGRAM 3. Calculation of the adatom relaxation energy ΔE_e at the

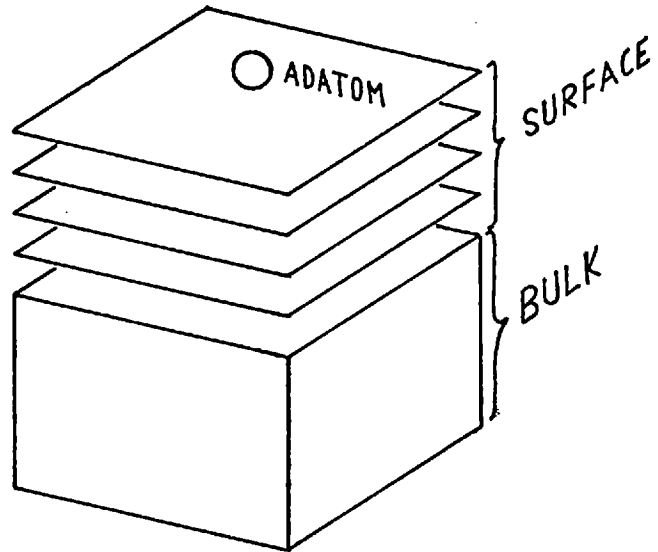


Fig.31. Schematic Diagram of the Adatom-Surface Model.

equilibrium site.

PROGRAM 4. Calculation of the adatom relaxation energy ΔE_s at the saddle point.

As shown in Fig.32, the energy barrier to diffusion ΔE is then given by:

$$\Delta E = \Delta E_d + \Delta E_e - \Delta E_s \quad (40)$$

The four programs used to calculate these quantities for self-diffusion were based on Fortran programs given by Ayrault²² with certain modifications to enable running on the college CDC 6600/6400 system. However for the purposes of modelling foreign adatom diffusion or diffusion across a (111) step, to be described in detail later, it was necessary to rewrite some of the calculation procedures in programs 2, 3 and 4.

1. The Calculation Procedure

Following the formulation of Girifalco and Weizer⁶⁵ the interatomic potential was given by:

$$\phi_{ij} = D \exp(-2\alpha(r_{ij} - r_0)) - 2\exp(-\alpha(r_{ij} - r_0)) \quad (41)$$

where D , α and r_0 are constants and ϕ_{ij} is the potential acting between two atoms separated by a distance r_{ij} . Values of D , α and r_0 were taken from calculations made by Ayrault²², based on the values of bulk properties extrapolated to zero K. The resultant potentials for Rh, Au, Pt, Ir and W are presented in Fig.33. From equation (41) the total energy of a given atom is given by:

$$\phi = \frac{1}{2} \sum_{ij} \phi_{ij} \quad (42)$$

where the factor of $\frac{1}{2}$ arises from the fact that all interactions are counted twice in the summation. An atom at equilibrium satisfies the equations:

$$\frac{\partial \phi}{\partial x} = \frac{\partial \phi}{\partial y} = \frac{\partial \phi}{\partial z} = 0 \quad (43)$$

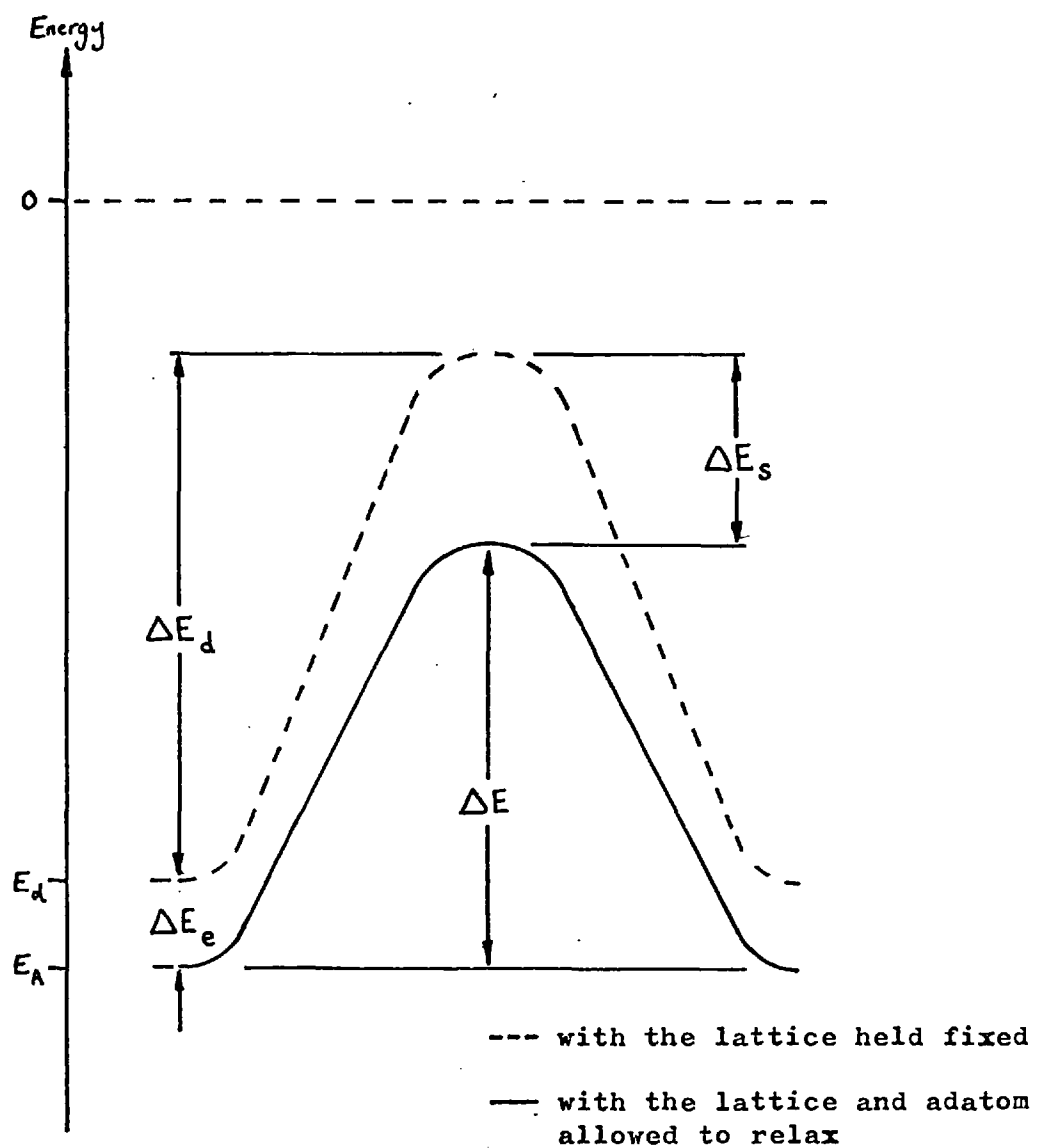


Fig.32. Schematic Potential Energy Diagram for Surface Diffusion.

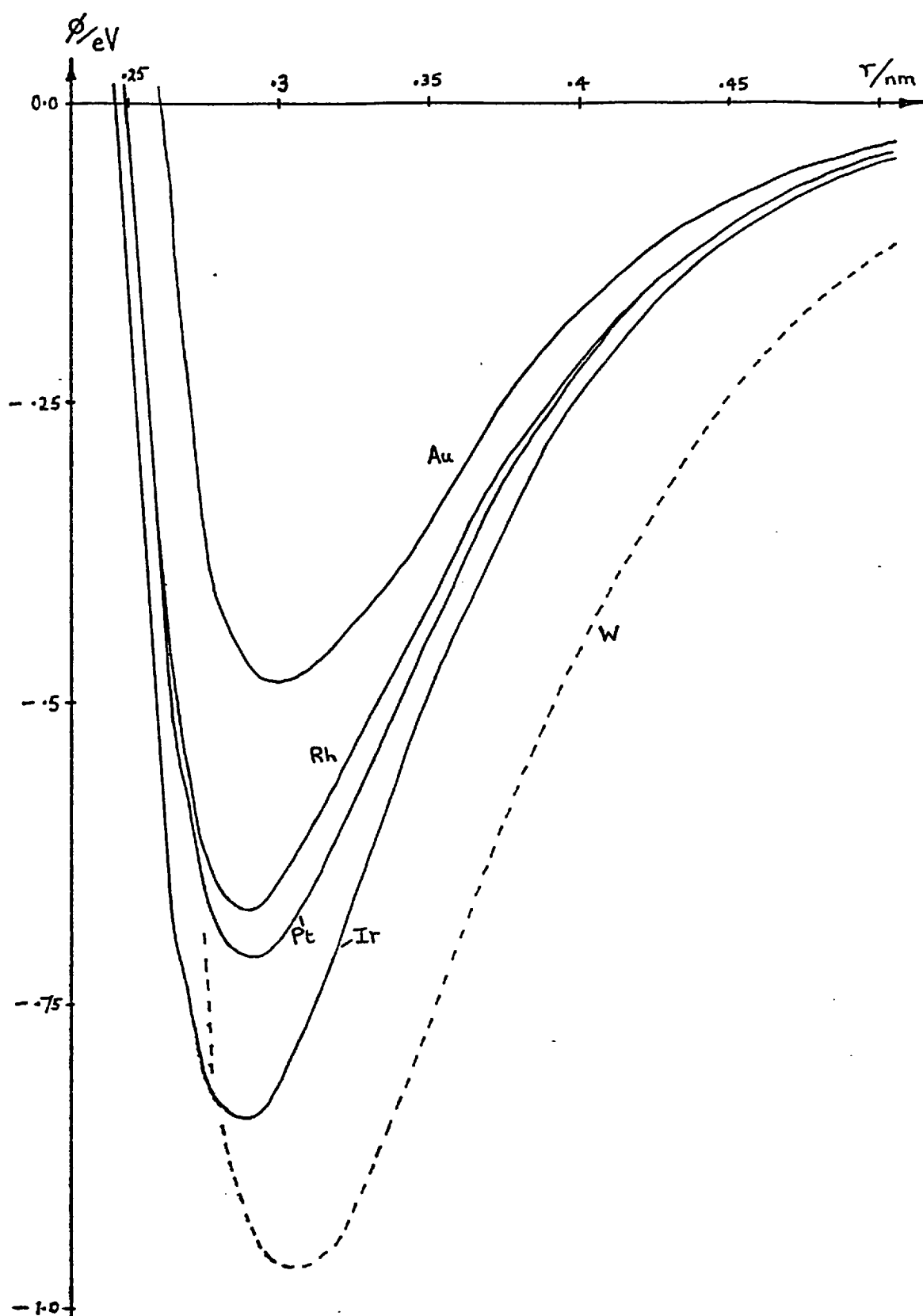


Fig.33. Morse Potential Curves.

which can be solved in an iterative manner using a 1st order Taylor series expansion, giving three equations of the form:

$$-\frac{\partial \phi}{\partial x} = \frac{\partial^2 \phi}{\partial x^2} \Delta x + \frac{\partial^2 \phi}{\partial y^2} \Delta y + \frac{\partial^2 \phi}{\partial z^2} \Delta z \quad (44)$$

$$\begin{aligned} x &= x_0 \\ y &= y_0 \\ z &= z_0 \end{aligned}$$

which can be written in matrix form:

$$\begin{bmatrix} \frac{\partial^2 \phi}{\partial x^2} & \frac{\partial^2 \phi}{\partial y \partial x} & \frac{\partial^2 \phi}{\partial z \partial x} \\ \frac{\partial^2 \phi}{\partial x \partial y} & \frac{\partial^2 \phi}{\partial y^2} & \frac{\partial^2 \phi}{\partial z \partial y} \\ \frac{\partial^2 \phi}{\partial x \partial z} & \frac{\partial^2 \phi}{\partial y \partial z} & \frac{\partial^2 \phi}{\partial z^2} \end{bmatrix} \begin{bmatrix} \Delta x \\ \Delta y \\ \Delta z \end{bmatrix} = - \begin{bmatrix} \frac{\partial \phi}{\partial x} \\ \frac{\partial \phi}{\partial y} \\ \frac{\partial \phi}{\partial z} \end{bmatrix} \quad (45)$$

$$\begin{aligned} x &= x_0 \\ y &= y_0 \\ z &= z_0 \end{aligned}$$

Solving for Δx , Δy and Δz gives a new starting point after the first iteration at $x_1 = x + \Delta x$; $y_1 = y + \Delta y$; $z_1 = z + \Delta z$. Successive iterations were used to give x_n , y_n and z_n to the required accuracy, 10^{-3} lattice parameters. Owing to finite computer limitations a lattice cube of $10 \times 10 \times 10$ unit cells was used as a starting point for all calculations. To create the required surface the cube was cut in a suitable orientation through a central atom. To avoid possible complications caused by meeting the edges of the cube the individual energy for each atom was calculated by taking components inside a $6 \times 6 \times 6$ unit cell cube centred around it. The detailed calculation processes involved in the four programs can now be considered.

1.1. Calculation of Surface Relaxations (Program 1)

In this program the top four or six lattice planes were

allowed to relax. To monitor the state of relaxation of the surface layers a net energy was calculated of central atoms in each plane ignoring in-plane interactions. After each successive relaxation of the surface layers the new net energy was calculated and relaxation continued until the energy change on relaxation was less than 10^{-6} eV. A flow diagram of this process is shown in Fig.34. The calculated relaxation distances, as a fraction of the bulk interplanar spacing, are presented in Table 8 and formed the starting point for the diffusion calculations.

1.2. Adatom Diffusion with the Substrate Held Fixed (Program 2)

This is the first of three computational stages (Sections 1.2, 1.3 and 1.4) in evaluation of the final adatom migration energy. After relaxing the surface planes as described in Section 1, the adatom was moved incrementally in a straight line between adjacent equilibrium sites situated centrally on the top plane. The energy of the adatom was then computed for each position at and between the sites, giving the magnitude of the energy barrier ΔE_d . A flow diagram of this process is shown in Fig.35.

1.3. The Equilibrium Relaxation Energy (Program 3)

Again starting with the relaxed surface from Program 1, the adatom was placed on a central equilibrium site and the adatom and substrate allowed to relax. The adatom in diffusing spends most of its time at the equilibrium site thus the lattice was completely relaxed about the adatom to a radius of about seven nearest neighbours. This limitation involves an inaccuracy of less than 10^{-2} eV in the energy calculation but saves considerably in computing time due to the iterative nature of the relaxation process. A flow diagram is presented in Fig.36.

TABLE 8

Calculated Platinum Surface Relaxations

Plane No. from Surface	Platinum Surface Plane				
	(111)	(100)	(110)	(113)	(133)
1	2.0%	5.36%	3.84%	9.85%	8.66%
2	0.16%	0.84%	0.52%	4.55%	13.0 %
3	0.005%	0.11%	0.24%	0.83%	-3.85%
4	0.018%	-0.01%	0.003%	0.7 %	4.14%
5	0.012%	-0.02%	0.02%	0.01%	-0.62%
6	0.005%	-0.011%	-0.004%	0.075%	0.12%

(as a percentage of the normal plane separation)

1.4. The Saddle Point Relaxation Energy (Program 4)

In this case the adatom was initially situated at a saddle point and the adatom-substrate system allowed to relax. The diffusive event occurs quickly, thus the elastic disturbance in the substrate can only travel a short distance in the time taken for the jump. To mimic this dynamic event the substrate was allowed to relax for only a small radius about the adatom. Using the kinetic criterion of Wynblatt and Gjostein¹⁸ the inverse of the Debye frequency (V_D) of the adatom was taken as representative of the speed of the jump. The elastic wave was assumed to travel at a speed of

$$u = \sqrt{\frac{B}{\rho}} \quad (46)$$

where B and ρ are the bulk modulus and density respectively. Combining these two assumptions gives the distance r travelled by the elastic wave in time $1/V_D$ as

$$r = \frac{1}{V_D} \sqrt{\frac{B}{\rho}} \quad (47)$$

this relation was used to calculate the allowed radius of substrate relaxation.

By its nature the saddle point position of the adatom is one of unstable equilibrium and the adatom without constraints would simply relax into the equilibrium site about which the relaxation radius was centred. These problems are avoided in the W & G approach by centring the relaxation radius about the saddle point and by first calculating a complete set of iterative relaxations prior to relaxing the system en bloc. The details of this process are shown in Fig.37.

Section 1, and sub-sections, has described the basic method used previously by W & G/Ayrault in adatom migration self-diffusion calculations. As stated earlier, it was felt that it would

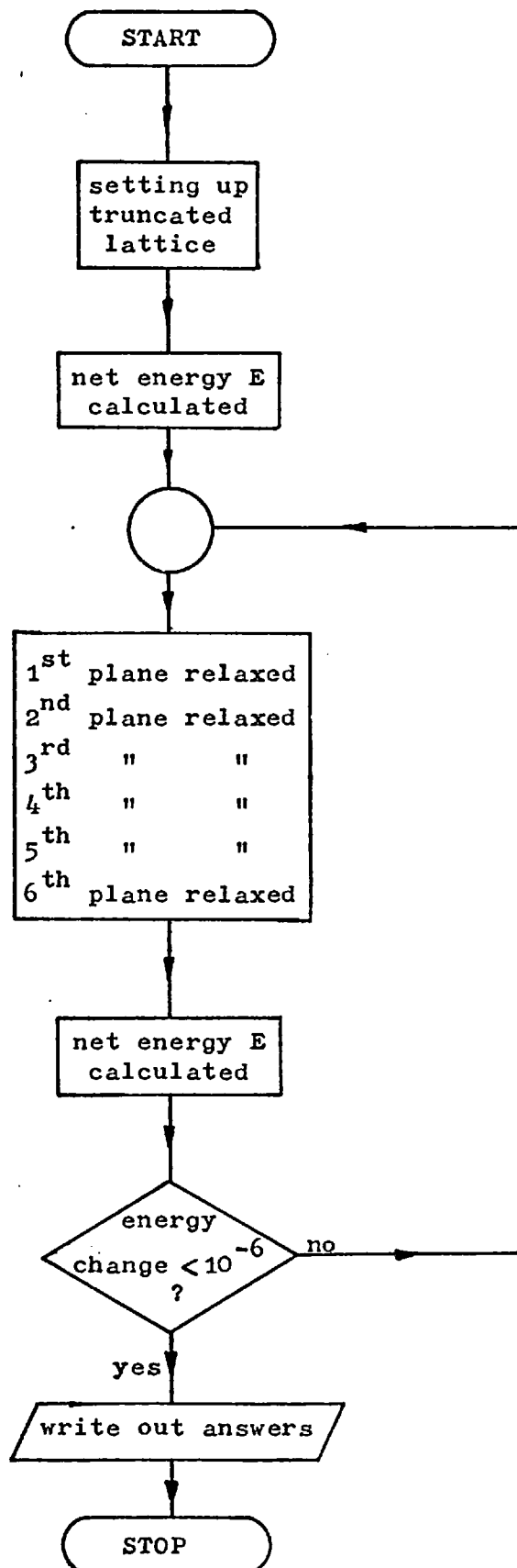


Fig.34. A Flow Diagram of Program 1. (Surface Relaxation).

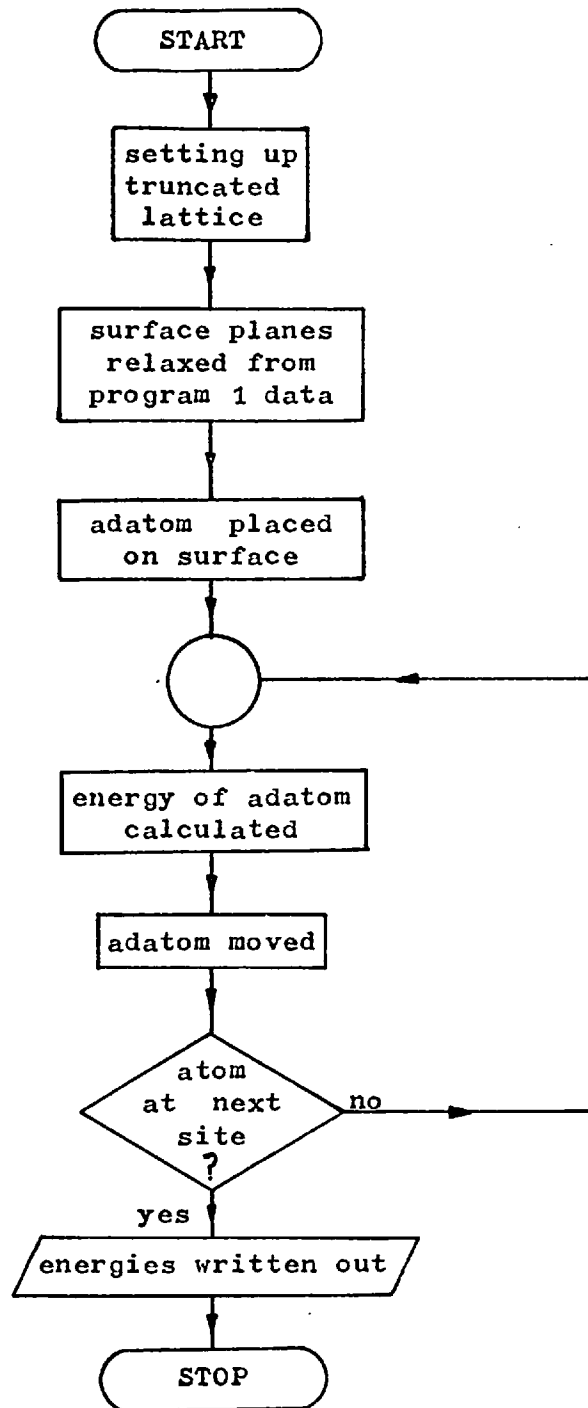


Fig.35. A Flow Diagram of Program 2.

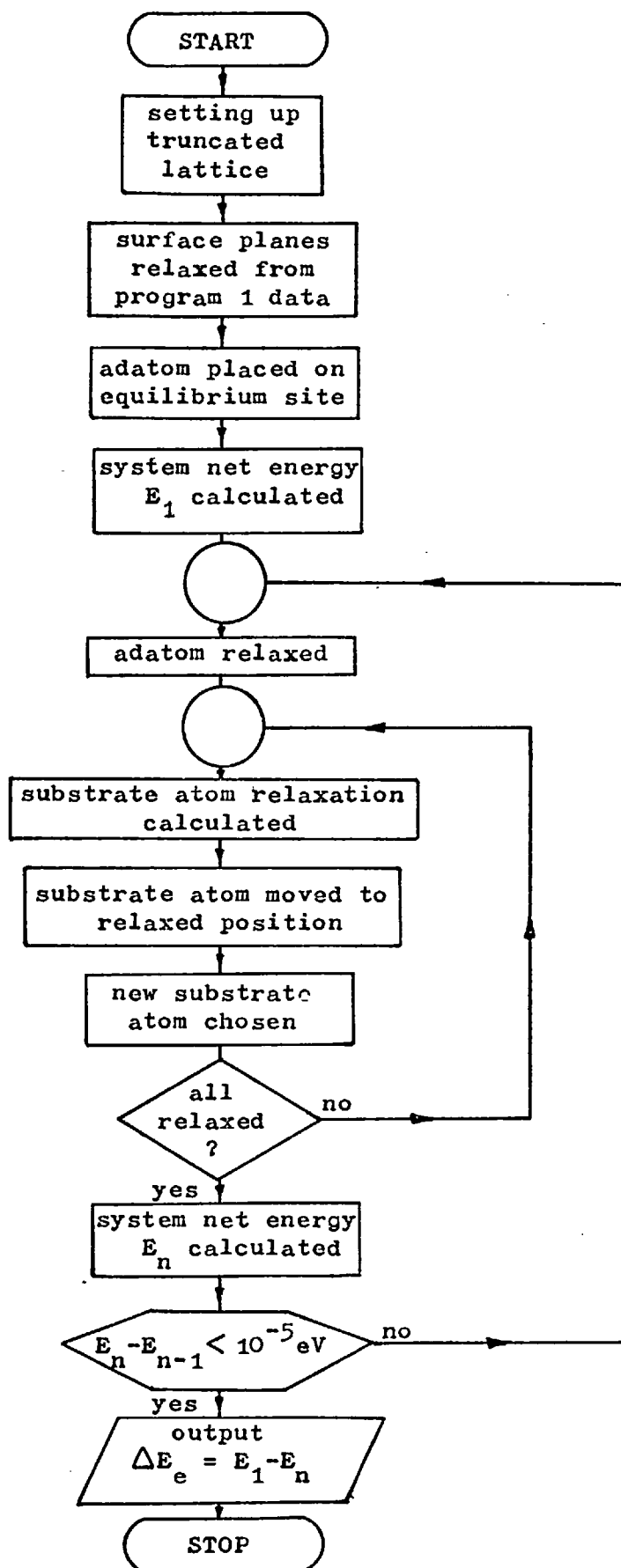


Fig.36. A Flow Diagram of Program 3.

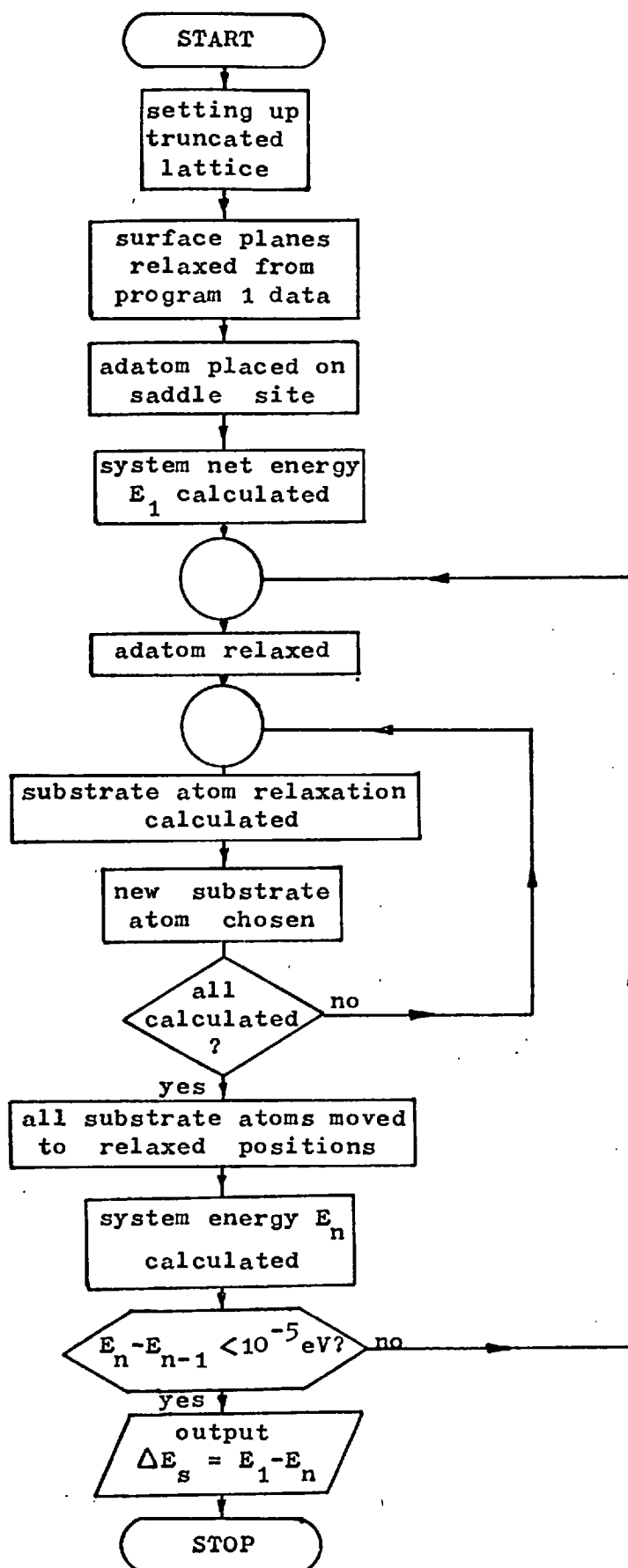


Fig.37. A Flow Diagram of Program 4.

be useful to extend these calculations to the more general case of an adatom of different type to the substrate and also for diffusion across an atomic step. These two cases will be discussed separately.

2. Foreign Adatom Diffusion

The physical picture is now changed to that of a foreign adatom upon the substrate and allowances must be made for this. Quite clearly any interactions involving the adatom must now use a different interaction potential from substrate-substrate interactions. Moreover the close proximity of an adatom of rather different bonding properties may change the interaction between substrate atoms (second order effects). In practice the adatom potential will be screened so that the effective pair potential should differ from that for a pair of substrate atoms only for immediate neighbours of the adatom. In calculations for foreign adatoms it is therefore assumed that interactions of the adatom with substrate atoms beyond some cut-off distance x can still be represented by the substrate pair potential, while for the remaining close neighbours a new potential is used. Some sort of mean potential between the two elements concerned is required because a new Morse potential cannot be calculated which is an empirical fit to experimental data, as this data is not available.

Consider atoms A and B, with Morse potentials describing them ϕ_{AA} and ϕ_{BB} respectively where

$$\phi_{AA} = D_A \exp(-2\alpha_A(r - r_A)) - 2\exp(-\alpha_A(r - r_A)) \quad (48)$$

and similarly for ϕ_{BB} . Where the Morse potential parameters α_A , r_A and D_A correspond to α , r and D in equation (41). The mean potential ϕ_{AB} will be defined as

$$\phi_{AB} = \frac{\phi_{AA} + \phi_{BB}}{2} \quad (49)$$

and $\phi(A,B)$ as

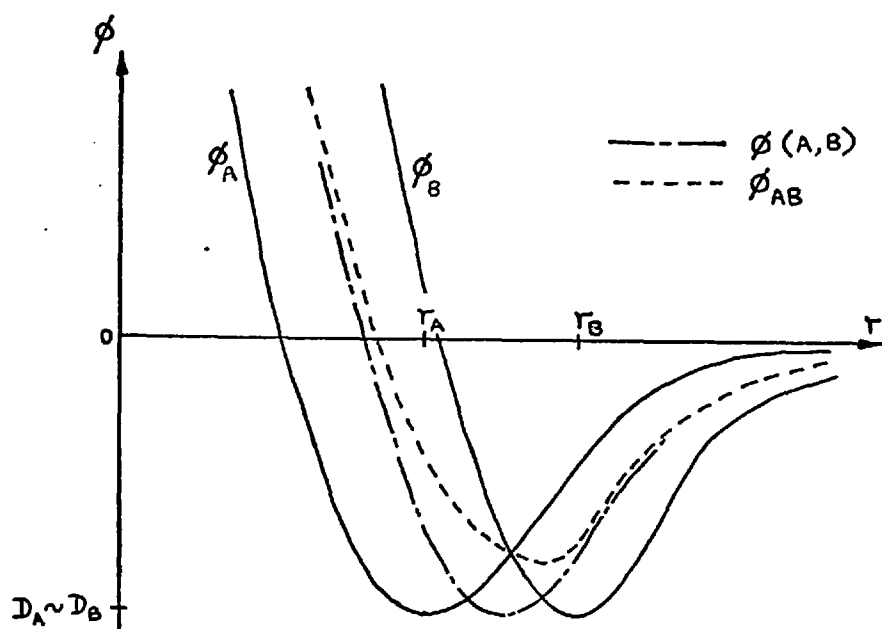
$$\phi(A,B) = D_{AB} \exp(-2\alpha_{AB}(r - r_{AB}) - 2\exp(\alpha_{AB}(r - r_{AB})) \quad (50)$$

where $\alpha_{AB} = (\alpha_A + \alpha_B)/2$; $r_{AB} = (r_A + r_B)/2$; and $D_{AB} = (D_A + D_B)/2$.

Potential $\phi(A,B)$ whilst being very similar to ϕ_{AB} , has some quite important deviations in cases where the individual Morse parameters of the two atoms concerned are very different. It should be noted that $\phi_{AB} = \phi(A,B)$ for $\alpha_A = \alpha_B$ and $r_A = r_B$; the D_A and D_B values not affecting this relationship. The effects upon the Morse potential of varying α , r and D are important. α is a shape determining constant, r_0 determines the position of the energy minimum at $r = r_0$ and D is a scaling or normalisation constant equivalent to the dissociation energy of a pair of atoms. Fig.38 illustrates two extreme cases of pairs of Morse potentials and their combinations ϕ_{AB} and $\phi(A,B)$. As can be seen $\phi(A,B)$ is qualitatively speaking a better potential to represent the likely interaction forces, whilst ϕ_{AB} suffers from drawbacks in the case of r_A and r_B being rather different. In the case of $r_B \gg r_A$, $D_A = D_B$ and $\alpha_A = \alpha_B$ (Fig.38a), ϕ_{AB} yields a potential which if interpreted as a Morse potential has an effective r_{AB} value of $\sim r_B$ and an effective D_{AB} less than D_A or D_B . These results seem rather unlikely, and the combination of a weak cohesive energy D with a large r_0 would in all likelihood lead to spuriously large relaxations of the adatom. For these reasons $\phi(A,B)$ has been used in all calculations involving the adatom potential.

In all cases the experimental situation chosen has been that involving very similar Morse potentials, as shown in Fig.38b. The adatoms primarily chosen for calculations: rhodium, gold and iridium, all have very similar Morse parameters compared to the platinum substrate. The values of α agree to within 0.7% and r_0

(a) $r_B \gg r_A$, $D_A \sim D_B$, $\alpha_A \sim \alpha_B$.



(b) $r_B \sim r_A$, $D_B \gg D_A$, $\alpha_A \sim \alpha_B$.

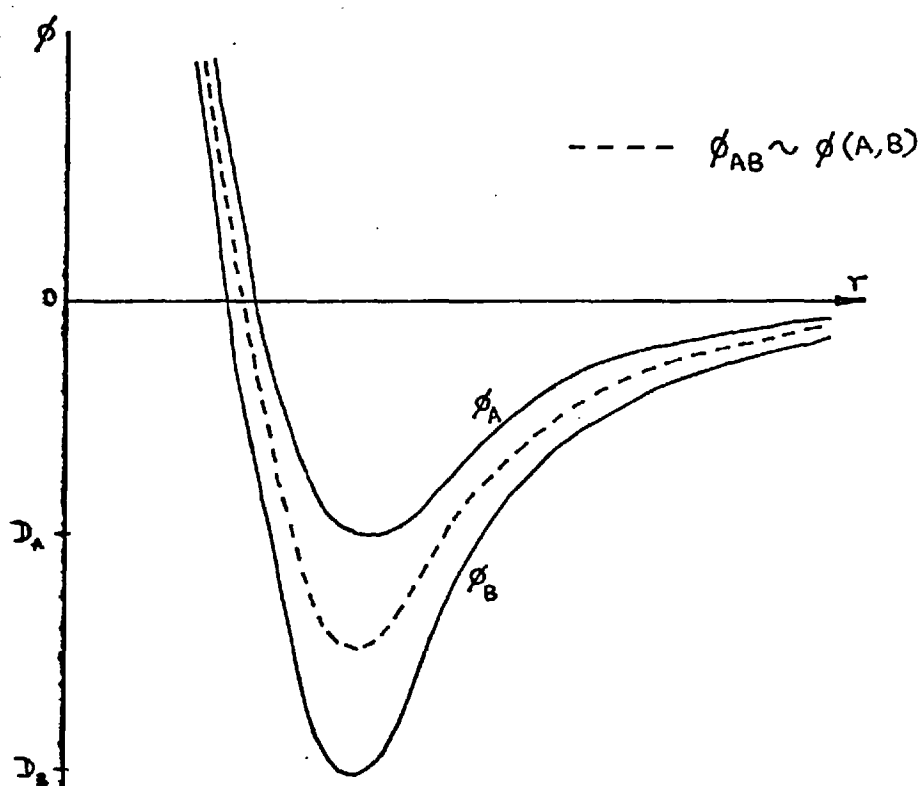


Fig.38. Various Mean Morse Potentials.

to within 3.5% of the Pt values respectively (see Table 9). The chief difference between the potentials is one of scaling factors, the values of D however, only varying up to 30% from the Pt value. In the worst case, Au on Pt, $\phi_{AB} = \phi(A,B)$ to within 1% for the r values sampled by neighbouring atoms.

The potential screening radius was set at the saddle point relaxation radius. In all energy calculations involving the adatom-substrate interaction over distances larger than this the substrate potential was used.

A screened averaged parameter Morse potential is now available for the adatom. Second order effects, as mentioned previously, were not considered, being rather difficult to estimate, but some calculations were made using the mean potential to describe the interaction between substrate atoms within a small radius of the adatom to give a maximum likely value of this effect.

In calculating the saddle relaxation energy a new value of the allowed relaxation radius is required, because the adatom has a different Debye frequency associated with it due to its modified binding energy with the substrate. The mean Debye temperature of the adatom, and substrate was taken as representative of the speed of the diffusive jump. The speed of propagation of the elastic disturbance in the substrate was considered unaffected by the adatom.

At this stage the theoretical model proposed takes account of different bonding strengths, atomic sizes, potential shapes, and diffusive jump speeds.

3. Diffusion Across an Atomic Step

A Pt {111} step was chosen for this calculation, alternatively a {100} step would be suitable, the {100} and {111}

TABLE 9

Program Input Parameters

Metal	Morse Parameters			Lattice Parameter	Mean
	(nm ⁻¹)	D (eV)	r ₀ (nm)		Relaxation Radius
				A (nm)	r _{rel} (nm)
Pt	16.047	0.7102	0.2897	0.38804	0.625
Ir	16.260	0.8435	0.2864	0.38313	0.625
Au	16.166	0.4826	0.3004	0.40614	0.784
Rh	15.423	0.6674	0.2875	0.38044	0.496
W	13.850	0.9710	0.3053	0.31609	0.625

planes being the most closely packed planes for the FCC materials.

Initial relaxation of the surface was achieved with a (13, 15, 15) plane, which produces a straight atomic step between two (111) surfaces, the step crossing the centre of the plane, as shown in Fig.39. The initial and final diffusion sites were chosen by hand and the latter three programs modified to input the information. Diffusion in both directions was modelled, and as expected the potential barrier to diffusion was asymmetric, the adatom energy at the terrace site having a lower value than at the plane edge. The saddle relaxation energy calculation now assumes a greater importance making the value of the relaxation radius quite an important variable. Difficulties were encountered in properly relaxing the adatom due to the asymmetry of the step edge site. It is not strictly correct to relax the adatom perpendicular to the (13,15,15) surface, but if this was not done problems in matrix inversion or relaxation down the step were encountered. To compensate for these factors and to test the dependence of the energy barrier upon the relaxation radius some calculations were also made with a relaxation radius double that of usual.

The programs were written so that a foreign adatom could be diffused across the step. Our main interest in this calculation was to estimate the potential at the plane edge, relative to the plane centre, leading to an estimate of the likelihood of reflections at this edge.

4. Theoretical Results and Discussions

4.1. Diffusion Over Low-Index Planes

The activation energies ΔE for the various adatoms and platinum surfaces are presented in Table 10. The individual

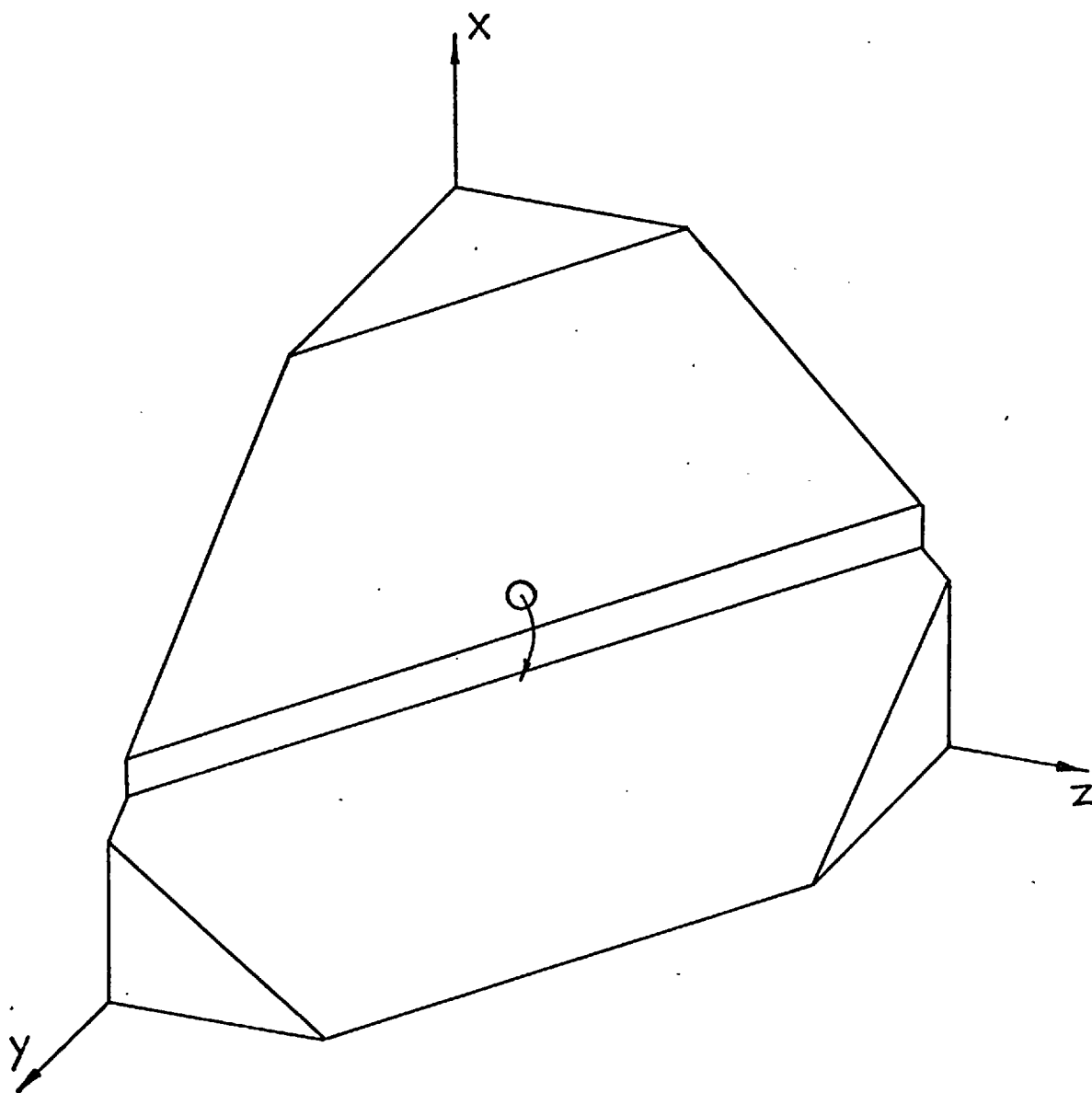


Fig.39. The (111) Step used in Calculations.

components forming ΔE , namely ΔE_d , ΔE_e and ΔE_s are presented in Table 11. The activation energies are also plotted as a function of adatom type and surface structure, as shown in Fig.40, enabling salient features to be more readily picked out. As can be seen, the activation energies for the various surface planes vary generally in the order:

$$\Delta E \text{ for } (100) > (133) > (110) > (113) > (111);$$

and for the various adatoms in the order:

$$\Delta E \text{ for Ir} > \text{Pt} > \text{Rh} > \text{Au}.$$

These variations are as anticipated from the discussion in Chapter I. However, certain discrepancies in this ordering can be noted in the adatom dependence of ΔE for the (133) and (110) planes where:

$$\Delta E \text{ for Rh} > \text{Ir} > \text{Pt} > \text{Au};$$

and also in the substrate dependence of ΔE for the rhodium and gold adatoms where:

$$\Delta E \text{ for } (133) \geq (100) \geq (110) > (113).$$

In the latter case both the (133) and (110) results are rather larger than would be expected from a simple scaling down of the platinum self-diffusion results. These apparent anomalies can be explained by a consideration of the allowed relaxation radii at the saddle point, and the effects of adatom size relative to the substrate structure.

The FCC (133) and (110) planes (see Fig.1), are both fairly loosely packed with widely spaced rows of close-packed atoms forming diffusion channels for an adatom. Relaxations of the channel-wall atoms in the plane of the surface, thus widening the diffusion channel, would be expected to reduce the magnitude of the potential barrier to diffusion. Some of the calculated adatom and substrate atom displacements associated with such relaxations for the channelled (133), (011) and (113) planes are presented in Table 12.

TABLE 10

Calculated Activation Energies for
Surface Diffusion on Platinum

Platinum Substrate	A d a t o m T y p e			
	Plane	Platinum	Iridium	Rhodium Gold
	(100)	18.8	20.6	18.6 15.6
	(133)	17.8	18.7	20.3 15.7
	(110)	14.8	15.1	18.5 13.2
	(113)	11.5	12.7	11.1 9.5
				Tungsten
	(111)	1.5	1.5	1.9 1.4

(all energies in kcal mol⁻¹)

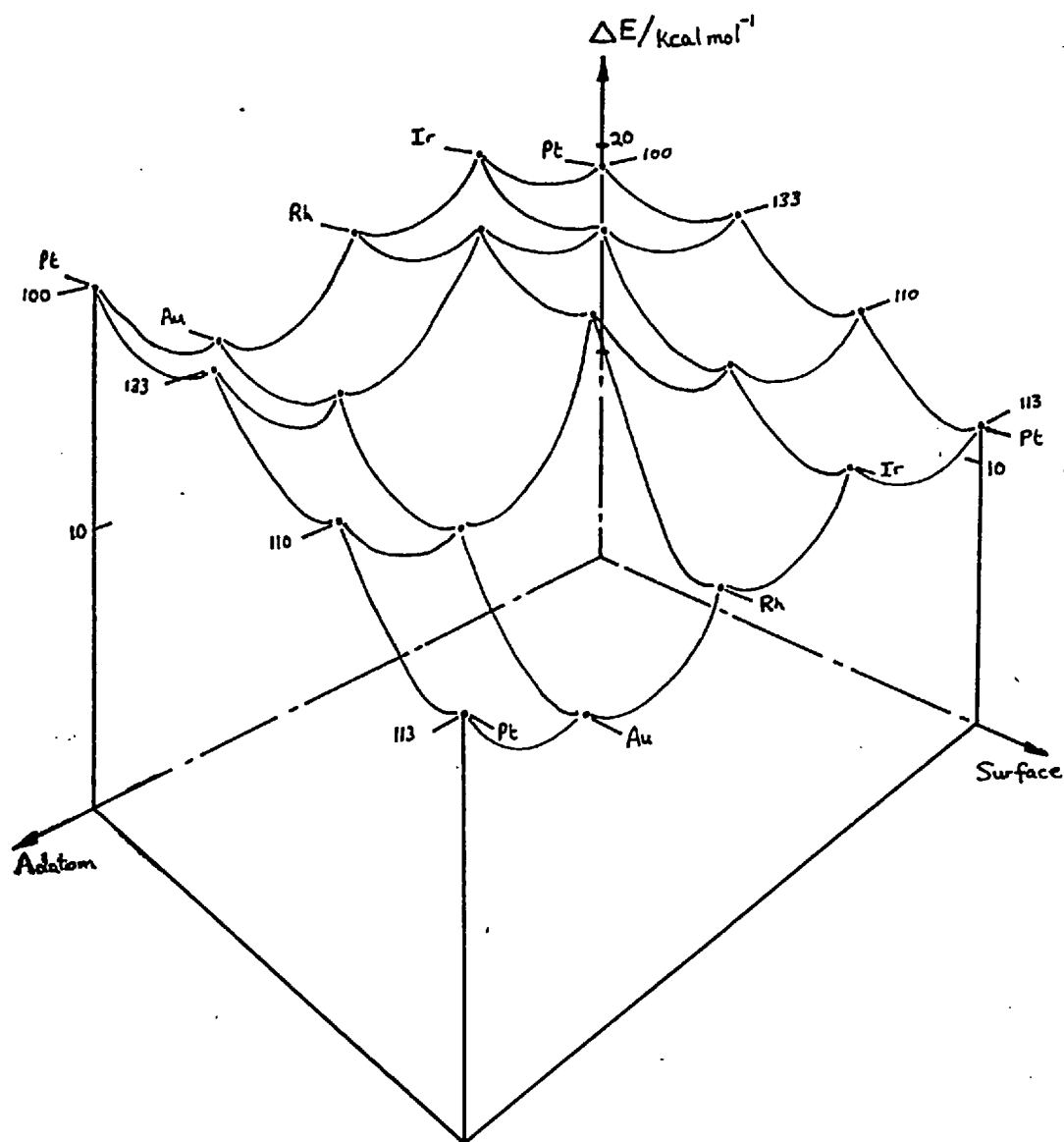


Fig.40. The Calculated Activation Energies, (as a function of surface and adatom type).

TABLE 11Calculated Relaxation Energies

P l a t i n u m A d a t o m					
Energy	Pt(111)	Pt(100)	Pt(110)	Pt(113)	Pt(133)
ΔE_d	5.8	77.5	63.9	74.1	86.6
ΔE_e	2.8	6.1	5.4	8.5	10.8
ΔE_s	7.0	64.8	54.5	71.2	79.6
I r i d i u m A d a t o m					
ΔE_d	6.1	81.6	67.3	78.1	91.3
ΔE_e	2.7	5.4	4.9	8.1	10.3
ΔE_s	8.0	66.3	57.1	73.5	82.9
R h o d i u m A d a t o m					
ΔE_d	5.0	67.6	55.7	64.5	75.2
ΔE_e	1.9	4.3	3.5	6.2	8.0
ΔE_s	5.0	53.4	40.7	59.6	62.9
Tungsten A d a t o m					
G o l d A d a t o m					
ΔE_d	7.0	80.1	66.1	76.5	89.3
ΔE_e	5.6	10.0	9.0	12.7	16.2
ΔE_s	11.24	74.6	61.8	79.8	89.8

(all energies in Kcal mol⁻¹)

TABLE 12

Calculated Relaxation Distances from Lattice Points
for the Channelled Planes

Displacements from lattice points before (bracketed) and after relaxation are measured normal to the plane (Δz) and in the plane (Δx). Saddle site displacements measured relative to the mid-point of the line joining two adjacent lattice sites.

		A d a t o m T y p e									
Platinum	1 st	Platinum		Iridium		Gold		Rhodium			
Surface	Layer	EQ.	SADDLE	EQ.	SADDLE	EQ.	SADDLE	EQ.	SADDLE		
(110) Δz	11	(17)8	(54)5	(14)5	(52)-1	(26)22	(62)22	(14)6	(51)12		
Channel Widening	- -		600		650						
(113) Δz	12	(17)11	(39)28	(15)8	(37)25	(26)23	(45)40	(14)9	(36)27		
Δx	8	(13)17	(43)39	(13)17	(44)39	(13)18	(43)40	(13)15	(43)40		
(133) Δz	8	(23)11	(61)15	(20)8	(59)10	(32)25	(68)34	(20)8	(58)24		
Δx	13	(13)14	(21)13	(12)13	(22)11	(16)18	(25)20	(12)13	(22)15		

(all displacements in pm)

It is apparent that relaxations are of least importance for the (113) plane for which the rows of close-packed atoms forming the diffusion channels are rather more embedded in the surface and consequently less free to move than for either the (133) or (011) planes. For the latter two planes lateral displacements of channel wall atoms allow the adatom at the saddle point to relax down into the channel. The energy change associated with this relaxation (see Table 11) is found to be comparable with the final activation energies. Relaxation of the channel walls in the calculation procedure is thus significantly reducing the activation energy for diffusion in the manner described by Ehrlich and Kirk⁶⁶. It is clear that omitting substrate relaxations about the adatom at the saddle point would result in the activation energies for diffusion on the (011) and (133) planes being higher than for diffusion on the (100) plane, as found by Tick and Witt⁶⁷.

The apparent anomalies in the calculated activation energies noted earlier, can now be interpreted in the light of these relaxation effects. The high activation energies for rhodium diffusion on the Pt (011) and (133) planes, can be attributed to the relatively small relaxation radius allowed for the Rh/Pt case compared with the other adsorbates (see Table 9). The small relaxation radius means that the (011) and (133) channel walls cannot widen sufficiently to allow facile passage of the rhodium adatom. To check this, the calculations were repeated using a larger relaxation radius similar to that of platinum. The activation energy obtained was lower by a factor of 25%, which demonstrates an unusually high sensitivity of the calculation procedure to the relaxation radius. For gold diffusion on the Pt (011) and (133) planes the calculated activation energies were also high relative to the other planes. In this case the relaxation radius is large

and channel wall relaxations are presumably mainly restricted by energy considerations. However, the gold adatom is large compared to the other adsorbates and the channel walls do not relax sufficiently to allow facile diffusion of the gold adatom. In complete contrast, channel widening allows relatively easy passage of the comparatively small iridium atom. Consequently, the activation energies for iridium diffusion along the channels of the (011) and (133) planes are lower in relation to those for platinum than the binding energies would suggest.

Despite the above-mentioned adatom size effects upon activation energies, the adsorption energies at the equilibrium site E_A , as shown in Table 13, follow almost exactly the ratios of the cohesive energies D_{AB} of the mean potentials assumed for the adatom-substrate interactions. (Here the adsorption energy (see Fig. 32) is defined as $E_A = E_d + \Delta E_e$, where E_d is the energy calculated for the unrelaxed atom at the equilibrium site in Program 2). The dependence of the adsorption energy upon D_{AB} indicates that the relaxations at the equilibrium site were sufficient to optimise the adatom nearest-neighbour distances very closely to the minimum interaction distance r_{AB} of the mean potential. It would thus appear that atomic size effects of up to 5% are unimportant at the equilibrium site where they are fully adjusted for by adatom-substrate relaxations.

4.2. Diffusion Over an Atomic Step

The calculated energy barrier for a platinum atom crossing a (111) step is presented in Fig. 41. As can be seen, the barrier is quite dependent upon the relaxation radius. However in general, the calculated activation energy for crossing the step in the plane-terrace direction is significantly higher than the (111)

TABLE 13Calculated Adsorption Energies

Platinum Substrate	A d a t o m T y p e			
	Plane	Platinum	Iridium	Rhodium Gold
(113)		117	127	114 98
(133)		116	127	114 98
(110)		110	120	108 92
(100)		90	108	89 90
				Tungsten
(111)		84	91	78 110

(all energies in kcal mol⁻¹)

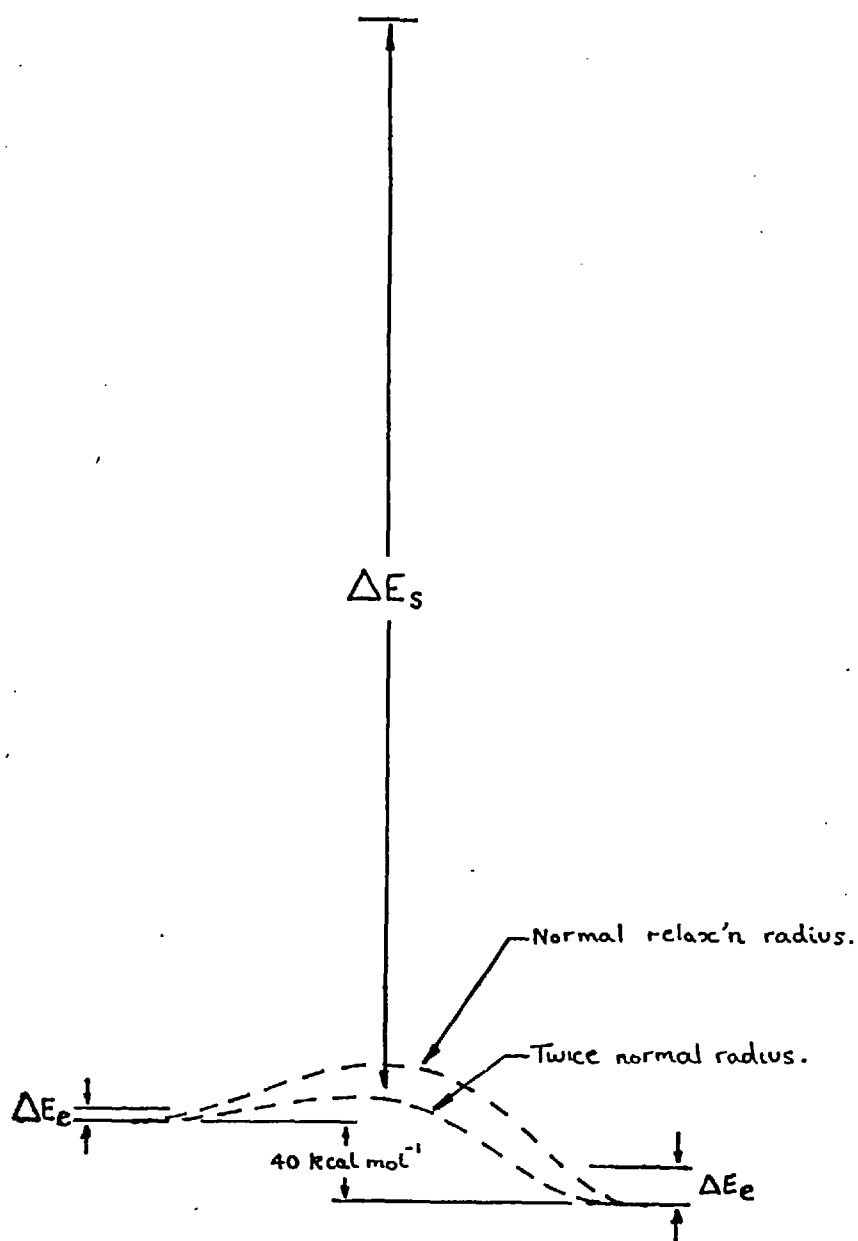


Fig. 41. The Calculated Energy Barrier to Diffusion for a Pt Ad-atom Crossing a (111) step.

activation energy on the plane, predicting a reflecting barrier of large proportions. For all relaxation radii the difference in energy between the plane site and the step site was found to be 39 kcal mol⁻¹. This energy represents the limiting case for a very large relaxation radius and sets a lower limit for the activation energy for diffusion in the terrace-plane direction.

VI. DISCUSSION

In the preceding chapters we have described the results of the experimental and theoretical studies of adatom diffusion on platinum surfaces. The experiments show, in agreement with the studies of rhodium by Ayrault²², that the activation energies for diffusion on the surface of a face-centred-cubic metal vary in the order $(100) > (133) > (110) > (113) > (111)$. In addition we find that the activation energies for different adsorbates on a given plane vary in the same manner as the expected binding energies of these adsorbates. The calculations yield results showing similar features to the experimental results, as also noted by Ayrault²² for rhodium. Direct comparison of the calculated and experimental results provides an indication of both the relative importance of the various factors that can influence adatom diffusion, and the weaknesses of the adopted calculation procedure.

The calculated and experimental activation energies for adatom diffusion are compared in Table 14 and Fig. 42. The calculations are in reasonable agreement with the experimental results and correctly predict the ordering of the activation energies with respect to the various adatom species and substrate planes. However, the magnitude of all calculated values are up to 25% lower than experiment, except in the case of the Pt(111) plane where the calculations grossly underestimate the activation energies indicated by the diffusion temperatures. These discrepancies are very similar to those found by Ayrault and appear characteristic of the calculation procedure. However, since the error is reasonably constant it appears that the most important factors determining the magnitude of the activation energy are being adequately described by the calculation.

TABLE 14

Activation Energies for Surface Diffusion
from Calculation and Experiment

Platinum		Adsorbate Type					
Substrate		Platinum		Iridium		Gold	
Plane		calc.	exp.	calc.	exp.	calc.	exp.
(113)		11.5	14 ± 1.8	12.7	17.2 ± 2	9.5	12 ± 1
(110) _x		14.8	19 ± .4	15.1	16.8 ± 1.6	13.2	12.5 ± 2
Along 'Channels'							
(110) _y		45	18 ± .4	-	16.8 ± 1.6	-	0
Across 'Channels'							
(133)		17.8	20 ± .6		-		-

(all energies in kcal mol⁻¹)

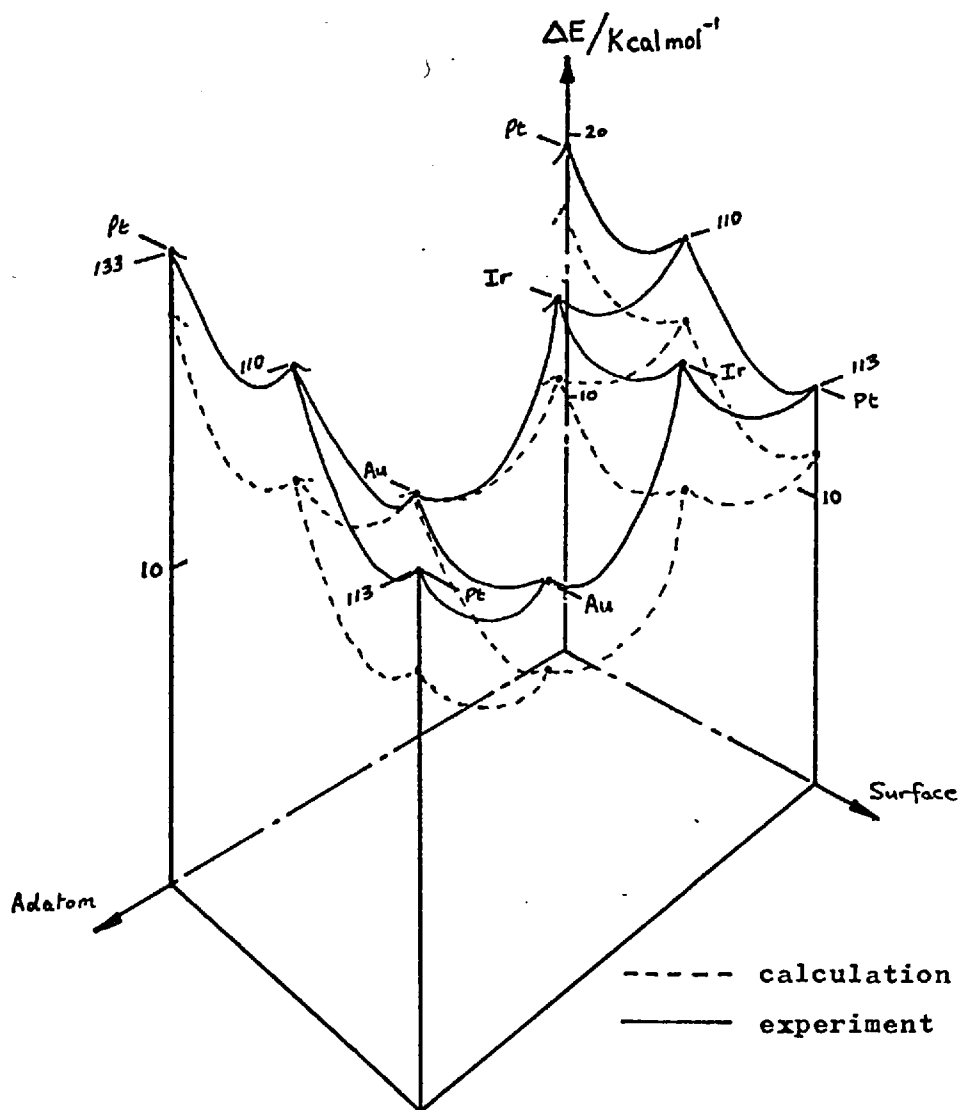


Fig.42. Comparison of Calculated and Experimental Activation Energies for Diffusion on Platinum.

1. The Effects of Surface Structure on Activation Energy

Both experiment and calculation agree in the ordering of the activation energies for adatom diffusion for the various planes. Clearly the major factor underlying this variation is the change in the number of nearest-neighbour bonds to the adatom between the adsorption site and the saddle site. This leads to the general increase in activation energy with increasing surface roughness as indicated in Chapter I. However, comparisons of the present calculations with those of Tick and Witt⁶⁷ indicate that the surface relaxation effects, as discussed in Chapter V, must be an essential feature of adatom diffusion that can modify the ordering of the activation energies. In contrast to the present calculations, Tick and Witt found that for adatom diffusion on a fixed lattice the activation energies should be in the order $(110) > (100) > (111)$ for an FCC metal substrate. That this order is not found experimentally is clear evidence that local adatom-substrate relaxation, and particularly channel-widening for the (133) and (011) planes does indeed occur.

The good agreement between our calculations and experiment in respect of the ordering and relative magnitudes of the activation energies suggest that relaxation effects are satisfactorily described for platinum adatoms. This is interesting because the calculation procedure probably does not in fact give a very satisfactory general description of surface relaxation. The calculations (see Table 8) show the first surface layer to be relaxed outwards by some 2-10% of the normal interplanar spacing, as discussed in more detail below, whereas LEED structural studies⁶⁸⁻⁷⁰ indicate much smaller expansions or even contractions for comparable surfaces of other FCC metals. However, when the adatom is present on the surface the outward relaxation of the top layer is

greatly reduced in the adatom vicinity for both the equilibrium and saddle site positions. This feature of the calculation thus does not greatly influence the resultant activation energy. The relaxations that are of most importance in determining the activation energy are those occurring within the surface plane as a result of adding the adatom to the surface. Good examples of this, as discussed earlier, are the channel-widening effects on the (011) and (133) surfaces. These lateral relaxations will not be significantly dependent on the inward-directed surface forces which determine the net outward relaxation of each surface layer, and may be more correctly described by a pair-bonding approach provided that a suitable relaxation radius can be chosen. However, the sensitivity of the rhodium diffusion calculations to the relaxation radius on the (133) and (110) planes indicate the possible pitfalls inherent in this approach and indicate a need for further experimental work to test the validity of the chosen model. Different values of the relaxation radius would certainly result in a different sensitivity of adatom diffusion to surface structure, which should be most apparent for the (133) and (011) planes. If relaxation is restricted, diffusion on these planes should become more difficult in comparison to the other planes, as noted for the rhodium calculations. For unrestricted relaxation, the activation energy ordering should revert to the same variation as for platinum self-diffusion.

2. Two-Dimensional Diffusion on Platinum

The observed two-dimensional diffusion of iridium and platinum adatoms on the Pt (110) plane would not be expected considering the channelled structure of this plane. Certainly inter-channel diffusion over intervening close-packed rows of atoms

would involve a much larger change in adatom coordination number than for along-channel diffusion and consequently a much higher activation energy. These effects are reflected in the calculations which predict a much higher activation energy for diffusion across than along the channels, see Table 14. From the complete failure of the calculation procedure to model cross-row diffusion it seems reasonable to assume that the mechanism for this diffusion is different from that considered.

While possible impurity effects cannot be absolutely discounted, it is difficult to see how an impurity atom or atoms could facilitate cross-row diffusion while still allowing along-channel diffusion to occur with a reasonable activation energy. However, the thermally induced rearrangement of the Pt (011) surface noted in various LEED studies⁶⁰⁻⁶², as mentioned in Chapter IV, suggests an alternative explanation. Whilst the precise nature of the (2*1) reconstructed surface is not known, the models that have been suggested^{61,62} (see Fig.27) involve lateral displacements of surface atoms and some surface buckling. Such displacements may be creating gaps in the channelled structure sufficient to allow facile cross-row diffusion. Another possibility suggested by Bassett⁷¹ is that a vacancy could be formed in the channel wall adjacent to the adatom caused by a lateral displacement of a substrate atom. This vacancy could then be filled by either a surface atom or by the adatom. In the latter case substitution of the adatom by the substrate atom would have occurred. In view of the very similar diffusion characteristics found for Ir and Pt adatoms on the Pt (011) surface such substitution could readily have escaped detection. Both the diffusion mechanisms suggested above are compatible with the strictly one-dimensional diffusion of gold on this plane. At the lower temperatures involved in this diffusion the thermally dependent displacements of

channel wall atoms would be significantly reduced.

It is interesting to note that two-dimensional adatom diffusion has also been observed on the iridium (011) surface.¹¹ This two-dimensional diffusion may well be accounted for by similar mechanisms to those suggested for platinum as LEED studies have also noted a (2*1) rearrangement for this surface⁷².

It is unfortunate that diffusion data could not be obtained for the Pt (100) surface since several workers⁷³⁻⁷⁵ have established the existence of a (5*1) rearranged structure for this plane. Studies of gold⁷⁶ and iridium⁷⁷ (100) surfaces seem to confirm this finding. Auger Electron Spectroscopy (AES) indicates that both the (5*1) overlayer on the Pt (100) and the (2*1) structure for the (110) are typical of the clean surface. For the (100) surface these overlayers are hexagonal close-packed arrays of atoms similar to the (111) surface but buckled by typically ± 0.04 nm. Such a close-packed structure could be expected to greatly facilitate diffusion leading to an anomalously low activation energy for this plane.

In view of these widespread rearrangements of clean FCC surfaces further study of diffusion on the Pt, Ir and other FCC (110) and (100) surfaces is clearly desirable to test for the possibility of anomalous activation energies.

3. Diffusion Across a Step

Melmed⁷⁸ has obtained an activation energy of 29.7 ± 3 kcal mol⁻¹ for Pt surface self-diffusion by measuring the thermal blunting of emitter tips in the FEM. This figure is effectively set by the barrier to diffusion across an atomic step and can therefore be compared with our calculated value of at least 39 kcal mol⁻¹ for diffusion across a (111) step (large relaxation

radius). This is a large discrepancy between calculation and experiment which cannot be removed even by the use of a grossly large relaxation radius in the calculation procedure. It would appear then that the assumption of pairwise-additive bonding may be breaking down for the large changes in atomic coordination number involved in atomic movement over a step.

4. The Effect of Adsorbate Binding Energy and Size on the Activation Energy for Diffusion

From elementary considerations it is to be expected that in the absence of other more chemically specific factors adatom binding energy and size should be the factors chiefly responsible for differences in adsorbate diffusion behaviour on a given surface. The chief difference between the adsorbates studied is that of binding energy, which for gold and iridium is respectively 50% less and 10% more than the corresponding platinum value. The adatoms also exhibit small size differences, the gold and iridium atoms being respectively 5% larger and 1% smaller than platinum. From the influence of these factors on the calculation procedure it is apparent that these small atomic size effects should be largely, but not entirely minimised by substrate relaxations. The chief factor influencing the measured activation energies should therefore be the effective binding energy acting between the adsorbate atom and substrate atoms. However, small adatom size effects should be evident for the (110) and (133) surfaces, where the calculated activation energies for gold and iridium diffusion are respectively a little larger and a little smaller than would be expected if the values scaled solely in proportion to D_{AB} . Unfortunately the measured activation energies are not sufficiently accurate to establish whether such effects occur. Nevertheless, the

agreement between the calculations and experiment is sufficiently good to suggest that the mean parameter potential adequately describes the chief factors influencing adatom diffusion, namely the adatom-substrate binding and local substrate relaxations. Further diffusion studies are clearly desirable to test for the effects of large atomic size differences on the channelled planes.

5. The Adequacy of the Pairwise Interaction Potential

The preceding sections have shown that there is a good measure of agreement between calculation and experiment, however there are discrepancies and to identify their likely origins the calculation procedure must be discussed in more detail.

5.1. Choice of a Potential

In our calculations a central, pairwise-additive interaction between atoms has been used, the interatomic force being derived from bulk properties and depending only upon atomic separation. This choice can be criticised on several grounds. Firstly, atomic forces are in general neither purely central nor pairwise-additive⁷⁹; secondly, the application of a potential derived from bulk parameters is of doubtful validity; and thirdly, no allowance is made for the directionality of atomic bonding. Despite these deficiencies, a pair-potential model does at least provide a tractable theoretical means of taking into account adatom types and surface structures. However, it is essential that the chosen potential can satisfactorily model a real surface and calculations of surface relaxations represent one test of this.

Pair-potential calculations by their nature always predict a generally outward relaxation of the surface because, as shown in Fig.43, in the bulk crystal the net repulsive force exerted upon

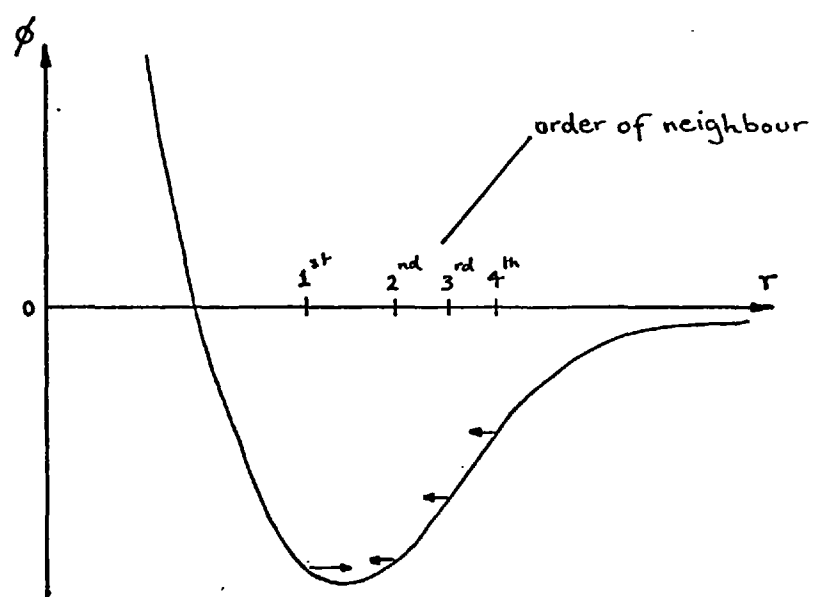


Fig.43. The Attractive and Repulsive Forces Exerted by an Atom upon its nearest neighbours.

an atom by its nearest neighbours is balanced by the attraction of its next nearest neighbours, and so on. Upon exposing a surface, each surface atom is subject to a net repulsive force due to the removal of slightly less than half of the neighbouring atoms, and consequently relaxes outwards. This effect is shown in the results of a number of calculations with a wide variety of pair-potentials. Some of the results applicable to the FCC (100) surface are presented in Table 15 for comparison with our calculations of platinum and copper (100) relaxations. Tick and Witt⁶⁷ used a Lennard-Jones potential of the form

$$\phi(r) = -\frac{A}{r^4} + \frac{B}{r^7} \quad (51)$$

while as in the present work, Jackson⁸⁰ and W & G¹⁸ used the empirical Morse potentials (Equation 41) introduced by Girifalco and Weizer⁶⁵. As is to be expected, our calculations tally very closely with those of W & G. Jackson noted similar relaxations. In comparison, Tick and Witt⁶⁷ calculated very large relaxations.

In general, the magnitudes of the surface plane displacements decrease very rapidly with distance into the bulk, and are quite negligible at the sixth plane from the surface. Allowing a finite number of planes to relax introduces a boundary effect at the artificially created bulk-surface interface. This can introduce a certain amount of "overshoot" in the relaxation of the inner surface plane possibly leading to a small spurious contraction here⁶⁷. In our calculations this effect was checked upon by comparing calculations with four and six relaxing planes, and was found to amount to less than 0.1% of the interplanar spacing. Only in the case of the Pt (133) surface were larger contractions of inner planes found, and these can be attributed to instabilities inherent in the calculation procedure.

It is interesting to note that quite different results

TABLE 15

FCC(100) Relaxations Obtained from
Various Calculation Schemes

Calculations by:	Surface	Plane No. from Surface		
		1 st	2 nd	3 rd
Wynblatt and Gjostein	Cu(100)	13%	3%	1%
Jackson	Cu(100)	10%	2.5%	0.75%
Tick and Witt	Cu(100)	75%	60%	50%
Present Work	Cu(100)	13%	3%	1%
Present Work	Pt(100)	5%	1%	0.1%

(as a percentage of the normal plane separation)

have been obtained in calculations using non-central forces.

Johnson and White⁸¹ used an empirical pair-potential with a volume dependent energy term to maintain equilibrium. The calculated relaxations in this case are small compared to the central force models and can be outward or inward depending upon the parameters chosen. There is in fact no general requirement that the surface planes should relax only outwards and recently Finnis and Heine⁸² have discussed a mechanism for contraction of the interlayer spacing at metal surfaces. Finnis and Heine consider the consequences of the smoothing of the electron gas at the surface.⁸³ They define surface Wigner-Seitz cells, which are polyhedral cells surrounding each atom and each containing its quota of electron gas. The electron distribution is then assumed to relax to a perfectly flat surface and, as shown in Fig.44, this brings the electrostatic centre of each cell nearer the bulk. As a consequence surface ions experience an attractive force towards the bulk, and relax inwards. First order calculations assuming a constant electron density lead to 4.6, 16 and 1.6% contractions of the (100), (110) and (111) surfaces for aluminium, respectively. This effect, leading to contractions of the surface interlayer spacing, should occur for any FCC metal since it is solely a result of structure.

Unfortunately there is no critical test for the calculated platinum relaxations, but LEED data is available on surface relaxations of other FCC metals. For nickel, Marcus et al⁶⁸ found a 5% contraction of the (110) surface, while for the (100) surface relaxations were less than $\pm 2.5\%$. This latter result has also been independently confirmed⁶⁹. Martin and Somorjai⁷⁰ suggest a 15% contraction of the aluminium (110) surface with no relaxation for the (111) surface. From a comparison of these experimental results with the theoretical models discussed earlier, it is apparent that none of the calculations of surface relaxations are

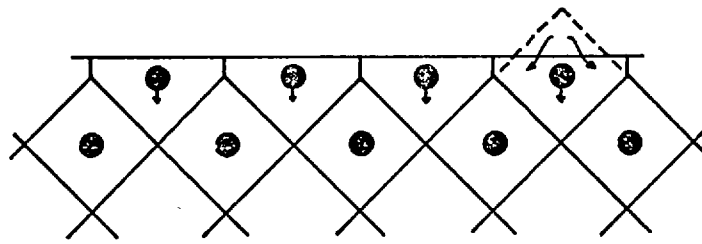


Fig.44. Surface Wigner-Seitz Cells.

very satisfactory. The Lennard-Jones potential used by Tick and Witt⁶⁷ is clearly very unrealistic and its use for metals is questionable⁸⁴. Equally, calculations of inward relaxations due to the surface Madelung force are not by themselves useful.⁸⁵ The Morse potential used here lies between these extremes but clearly can be improved upon. Modification of the potential to include volume-dependent energy terms, as in the work of Johnson and White⁸¹, represents one possible approach for future improvements but it seems questionable whether any potential fitted only to bulk properties can ever be entirely satisfactory.

To summarise, calculations based on the use of a Morse-potential show small outward relaxations for platinum surfaces. The evidence from other FCC metals suggests that these relaxations may be too large, and possibly even in the wrong direction for Pt (110). However, the Morse-potential is reasonably satisfactory for diffusion calculations and it can be concluded that it is an adequate compromise between the requirements of computational tractability and a completely realistic description of interatomic bonding.

5.2. The Choice of Surface Structure

As discussed in relation to the two-dimensional character of adsorbate diffusion on the Pt (011) plane, the possibility exists that this surface does not have the structure that would be anticipated by taking a section through the bulk crystal. Instead the surface may rearrange to some more stable form. The calculation procedure adopted cannot model such surface rearrangements directly because no account is taken of thermal vibrations of the crystal lattice, which presumably must reach some critical magnitude in order to make available enough energy for the surface

reconstruction. If the structure of the reconstructed surface were known empirically in some detail, the surface could be modelled by initially placing the atoms in the correct positions and then allowing any further relaxations to occur. This calculation procedure would certainly be no more unrealistic than placing the atoms initially at bulk lattice sites for the FCC or BCC packing schemes, as is done at present, which is after all only following empirical data about which crystal lattice to apply.

5.3. The Static Lattice Approximation

The computer model takes a fixed relaxed lattice as the starting point for calculations and uses parameters extrapolated to zero K for reasons of self-consistency. The real situation is one of dynamic diffusion occurring over a vibrating lattice at 300K, and these vibrational effects can be expected to modify the diffusion barrier.

The quasi-static approximation used in our calculations, in common with those of W & G¹⁸ has been, as described earlier, to allow relaxation of substrate atoms within a small radius of the diffusing atom held artificially at the saddle point. Clearly, this approximation is unlikely to model dynamic substrate relaxations very accurately, but the use of available bulk parameters to calculate a relaxation radius does at least provide a physically meaningful cut-off point for relaxation, in contrast with more arbitrary procedures. For example Ehrlich and Kirk⁶⁶ allowed only the adatom and its two nearest neighbours to relax while Neustadter and Bacigalupi¹⁵, and Tick and Witt⁶⁷ used a fixed relaxed lattice. These models do not correctly predict the ordering of mobilities on the FCC planes.

However, the calculation procedure adopted does not allow

for the vibrations of substrate atoms which at our typical diffusion temperatures are three to four times the zero point displacements⁸⁶. The mean positions of the vibrating lattice atoms also forms a somewhat more relaxed configuration than at zero K. Some idea of the relative importance of surface vibrations for the various FCC surfaces can be gained from measurements of surface Debye frequencies, ν_D (surface). Experimental^{87,88} and theoretical^{89,90} studies of surface Debye frequencies have found reduced values by factors of 50-70% of the bulk. This can be attributed to the rather looser binding at the surface than in the bulk. Of more interest, studies of the channelled planes note anisotropies of ν_D (surface) parallel and perpendicular to the close-packed direction. Taking the FCC (110) plane for example, Clarke et al⁹⁰ calculated ν_D (surface) giving:

$$\nu_D(\text{surface}) \quad [110] \simeq [001] < [\bar{1}\bar{1}0] < \nu_D(\text{bulk})$$

in the respective directions (see Fig.45). These calculations were confirmed by experimental evidence from Macrae⁸⁸. These results indicate that vibrational effects upon diffusion should be most important for the channelled (110) and (133) planes where, as discussed earlier, substrate atoms are most free to move into the path of the diffusing atom.

Generally speaking, if the substrate vibrations are at a similar or higher frequency than the diffusion jump frequency, atomic movements will impede diffusion to some extent, taking the analogy of electrical resistance increase with temperature. The small underestimates compared with experiment of the calculated magnitudes of the activation energies for the (110) and (133) planes can thus be attributed in part to substrate vibrations impeding diffusion. This should also hold to a somewhat lesser extent for the (113) plane.

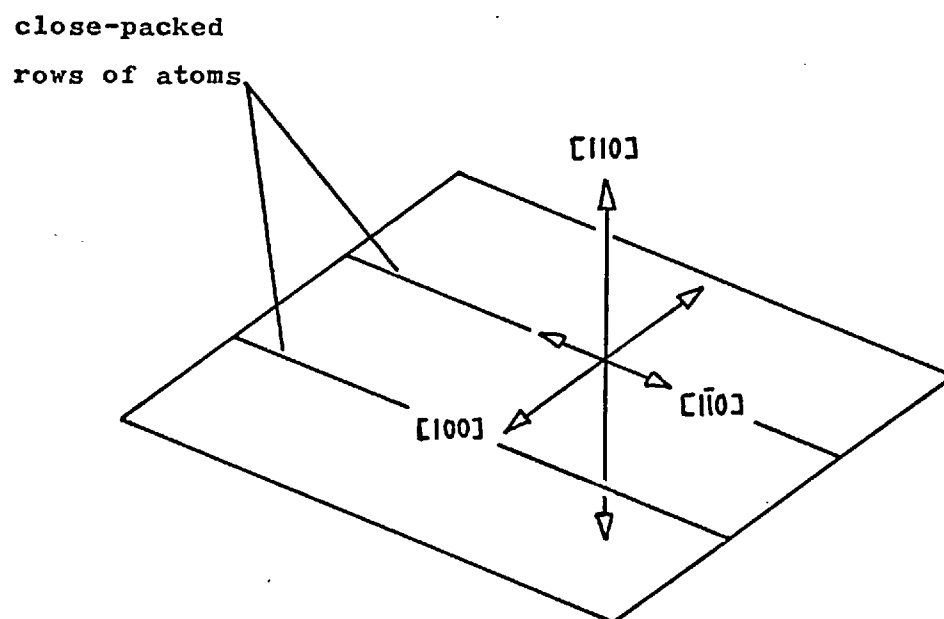


Fig.45. Crystallographic Directions Relative to the FCC(110) Plane.

The close-packed (111) plane does not exhibit large surface vibrations and the large discrepancies observed here cannot be explained satisfactorily by lattice vibrations. However, diffusion over the (111) surface is characterised by an extremely low activation energy and the approximations inherent in the calculation procedure can be expected to show up most here. The calculation procedure for the (111) plane does also involve some special difficulties. The diffusion path between two equilibrium or lattice sites is kinked and passes through an intermediate metastable fault site. For calculation purposes the potential barrier for diffusion was taken as the energy barrier existing between the lattice site and fault site. This barrier is rather asymmetric and introduces some calculation difficulties in properly relaxing the surface and adatom in a symmetrical fashion, as discussed by W & G.

5.4. Foreign Adatom Diffusion Calculations

The foreign adatom diffusion calculations pose some different problems to the self-diffusion case. Among these is the choice of a suitable screening radius for use with the mean-parameter potential. It seems reasonable to use a mean potential to describe the interaction of a particular adatom-substrate atom pair provided that the adatom can directly "see" the particular substrate atom and is not blocked by a nearer substrate atom. This simple-minded analysis defines a screening radius of one half to possibly one and a half lattice parameters. For the saddle point calculation a screening radius larger than the relaxation radius is not physically meaningful. Thus for consistency, the relaxation radius of one to one and a half lattice parameters was chosen to estimate the mean-potential screening radius. For the

adatoms chosen the calculations were not critically dependent upon this radius and errors due to this choice seem unlikely. It should be noted that the choice of any cut-off type screening radius, as used here, introduces a small potential step in the adatom substrate potential. For very different adatoms a large potential step would exist and could possibly lead to oscillations of the iterative calculation procedure in the case of an atom sampling the step.

The calculation of the relaxation radius was also made using mean bulk parameters, in this case to estimate a suitable Debye frequency. This is probably the best approximation that can be made in the absence of any better information. Adatoms with a very different Debye frequency to the substrate might well exhibit behaviour more characteristic of the substrate in view of the large numbers of substrate atoms. Such an effect would be very important for an adatom of very different characteristics such as rhodium on platinum where the calculations are very sensitive to the relaxation radius.

6. Conclusions

The diffusion behaviour found for platinum is essentially similar to that found for rhodium²² and the behaviour of the FCC metals can now be considered "well established". There remains however, a need for definitive measurements of activation energies for displacements taking atoms out of sites at steps for which the changes in adatom bonding are much larger than those studied here.

From the comparison of calculation and experiment it is apparent that with the exception of the (111) surface, and two-dimensional diffusion on the Pt (110) plane, the chosen pair-wise interaction model is valid for self-diffusion of platinum

involving small changes in coordination number. Furthermore, the diffusion of adatoms of different type is quite successfully modelled by the screened mean parameter potential including the effects of channel wall relaxations for the bad atomic fit case of gold diffusion on the Pt (110) surface. However, doubts remain about the general applicability of this model associated with the lack of any surface specific force contributions.

Considering the lack of success of model calculations for the BCC metal tungsten, it would be interesting to see how well this model would work for BCC/FCC metal diffusion, for example Mo/Pt.

With slight modifications, the calculation procedure could be used to model the diffusion of dimers or polyatomic clusters. Taking the diffusion of a dimer for example, some information about the diffusion mechanism could be obtained by comparing the measured activation energy with those calculated by moving: (a) one constituent atom at a time, or (b) both atoms simultaneously.

Further experimental work is also desirable to study diffusion, as described above, and to assess the generality of two-dimensional diffusion on the FCC (110) plane. Here studies with gold or iridium substrates would be of chief importance. Studies of rhodium diffusion on the platinum (011) and (133) surfaces would also be of interest to test the validity of the calculation procedure for these cases of high sensitivity to the allowed relaxation radius at the saddle point.

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