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**A review of recent
theoretical developments
in the understanding of
the migration of helium
in metals and its interaction
with lattice defects**

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August 1976

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A REVIEW OF RECENT THEORETICAL DEVELOPMENTS IN THE
UNDERSTANDING OF THE MIGRATION OF HELIUM IN METALS
AND ITS INTERACTION WITH LATTICE DEFECTS

D.J. Reed*

ABSTRACT

Recent theoretical calculations of the properties of rare gases, and in particular Helium, in the common f.c.c. and b.c.c. metals, have been reviewed from the viewpoint of the worker concerned with the behaviour of rare gas in such radiation damage phenomena as surface blistering and void swelling. Particular attention has been paid to mechanisms by which Helium may migrate in a damaged metal lattice during irradiation and to the properties of small gas and vacancy clusters which may represent bubble or void nuclei. Initially the proposed rapid migration of interstitial Helium has been discussed together with the substitutional de-trapping mechanism, whereby thermally activated Helium jumps from a substitutional to an interstitial position. This has enabled a mechanism of substitutional Helium diffusion to be proposed which may proceed at temperatures below those of self-diffusion. The formation, binding, migration and dissociation energies of gas-vacancy clusters have been reviewed. The relevance of the predicted trend towards the optimum stability of clusters composed of equal numbers of gas atoms and vacancies has been discussed. The limited data available dealing with the binding of a Helium atom to a pure edge dislocation line has been presented together with comments on the possible nature of the interaction of Helium with the dislocation jog.

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1. Introduction

The role of rare gases, and, in particular, Helium, in such radiation damage phenomena as void swelling and surface blistering, has promoted a considerable interest in the fundamental behaviour of such gases in metals.

In the absence of definitive experimental data much of the behaviour of rare gases, and in particular, Helium must be deduced by recourse to theoretical models. The large capacity high speed computer has made possible the simulation of crystal processes using an atomic model of the crystal lattice. The technique has been to take up to a thousand or so mass points, representing atoms interacting with each other, and compute the equations of motion of each atom as the lattice is subjected to an external stimulus. The stimulus may take many forms. If one atom is suddenly given momentum a collision cascade may be modelled^{1,2}. If a foreign atom is injected into the set of atoms forming the lattice ion penetration may be simulated³. Similarly shock waves, thermal motions, magnetism and, in the present context most significantly, lattice defects and the behaviour of rare gas impurities can be studied⁴.

Recent years have seen the publication of a number of theoretical studies of the migration Helium in the common f.c.c. and b.c.c. metals. Such studies have been largely based on the type of atomistic calculation outlined above, and have followed in the tradition of lattice defect simulation. This communication sets out firstly to review briefly this type of theoretical study in the context of its development, so that it may be viewed in its correct perspective, and secondly to review the work from the standpoint of the worker concerned with the utilization of the results as a compliment to experimental studies.

With the origins of recent calculations in mind, some elements of the techniques employed will be elucidated by tracing briefly the development of the methods involved. In particular the limitations imposed by poorly defined interatomic potentials will be discussed, dealing then with attempts to provide more reliable interaction models. Aside from a superficial mention of such problems, a critical appraisal of the derivation applicability and limitations of the interaction potentials employed will not be attempted. The behaviour of the rare gases in simple substitutional and interstitial positions will be discussed together with the substitutional de-trapping mechanism proposed for Helium in which the gas atom jumps thermally from a substitutional to an interstitial position. Whilst the emphasis of this review is placed primarily on the results of atomistic calculations, because the experimental technique of thermal evolution spectrometry has proved to be a useful tool in the study of the migration of inert gases in metals, some mention of the nature of such work will be made, where a direct comparison of data is possible. This leads naturally to a discussion of theoretical studies, supported by some experimental investigations, of the nature of clusters of Helium atoms and vacancies, together with the interaction of Helium with an edge dislocation. Finally a brief mention will be made of some typical experimental investigations, but this will not deal with thermal evolution data in any detail since this work will be reviewed at a later date.

2. The Simulation of Lattice Defects

The type of computer model described has been used successfully to determine the properties of crystal lattice defects. It has been proposed⁴ that the configuration of various metastable defect states can be found in several ways. A fully dynamic model will produce a situation where the atomic configuration oscillates about the state in question. If, however, some artificial damping is introduced the condition will converge to the final configuration so minimising computer time. Without damping vibrational modes can be determined, but little use of this approach has been made⁴. Thermally induced migration of defects can, similarly, be studied in two ways, either by introducing thermal agitation and then counting the actual number of defect jumps, or by computing an energy barrier to a particular type of jump and then using a rate theory formula. In the same way the change in entropy at the top of the barrier may be found. The barrier described is found by moving the defect in a series of steps, computing at each stage the change in energy, until the maximum is defined. Such methods have more recently been applied to the migration of inert gas atoms in metals. In view of this the methods and results of some typical defect calculation, in this case from Johnson^{5,6}, will be briefly discussed.

In an early treatment Johnson⁵ used a spherical crystallite of 530 atoms surrounded by an elastic continuum. Using an interaction potential derived earlier for iron⁷ he calculated vacancy formation and migration energies together with eight stable interstitial configurations. The approach was to define an energy equation

$$E = \frac{1}{2} \sum_i \sum_j \Phi^{ij} + \sum_i \sum_k \Phi^{ik} + aK + bK^2 \quad (1)$$

where Φ^{ij} was the interaction potential between atoms i and j , the i sum was over all atoms in the crystallite, the j sum was over all atoms in the crystallite which interacted with the i^{th} atom. The term aK accounted for the work done against the forces holding the crystallite in equilibrium and the bK^2 term accounts for the energy stored in the elastic field. A value of E was computed for the crystallite when, for example, a vacancy was introduced or a lattice atom was moved to an interstitial configuration, thus enabling deduction of formation or migration energies. For example, the formation energy was defined by,

$$E^f = E - E_0 + E_s \quad (2)$$

where E was the new energy, E_0 was the perfect lattice energy,

$$E_0 = \frac{1}{2} \sum_i \sum_j \Phi_0^{ij} + \sum_i \sum_k \Phi_0^{ik} \quad (3)$$

and E_s the energy to place the defect on the surface,

$$E_s = \pm \frac{1}{2} \sum_j \Phi_0^{ij} \quad (4)$$

where the plus sign indicates vacancies and the minus interstitials. To find energy minima and saddle points the approximate vector positions of each atom were chosen near to the expected new configuration. The co-ordinates of each atom in turn were then varied until the force on each fell to zero. The process was iterated 10 or 20 times until the

additional contributions to the energy change were thought to be negligible.

Johnson's⁵ calculations illustrated the need for carefully determined interaction potentials. The potential developed for b.c.c. iron⁷ was adapted to f.c.c. nickel because it reproduced experimentally determined vacancy formation and migration energies. It is clear that a pre-requisite in calculations of this type is a reliable and wide ranging potential that reproduces known defect properties. Having established a working potential for nickel Johnson⁶ developed calculations of the properties of vacancy and interstitial clusters in an f.c.c. lattice. This work predicted the collapse of a 3-dimensional vacancy cluster when it reached about 180 vacancies. Migration mechanisms for di-vacancies and tri-vacancies were presented and Johnson⁶ concluded that all clusters moved with a migration energy higher than that of the di-vacancy. The calculations were at their most powerful when they were used to develop broad behavioural patterns and trends rather than to specify precise activation energies. It can be readily appreciated that the 'experiments' described, when developed to include rare gas impurities, could be a powerful tool in the study of void or bubble nucleation and growth.

3. The Choice of Interaction Potentials

The limitations introduced as a result of poorly defined interatomic potentials especially at large separations, of the order of lattice constants, have already been briefly mentioned. The development of the metal-metal, metal-gas potentials that have been used in the most recent atomistic calculations of the behaviour of rare gases in metals will now be briefly discussed. For a comprehensive review of empirical potentials and point defect calculations in metals, reference is best made to Johnson⁸.

Johnson⁹ has related methods of deriving empirical potentials to the lattice defect simulation problem. Potentials for Copper and Nickel were deduced from phonon dispersion curves and elastic moduli using an atomistic model of the lattice. In practice a simultaneous close fit could not be obtained using central forces. Johnson⁹ concluded that there was no unique way to determine the potential at separations not occurring in the perfect lattice. To deduce an empirical potential for Copper he therefore utilized vacancy data. Additionally, it was shown that the results of defect calculations were very sensitive to the interaction cut-off up to the second neighbour atom separation.

More recently, Johnson and Wilson¹⁰ have provided interatomic potentials for a range of b.c.c. and f.c.c. metals. In this work a non-central interaction was employed for the f.c.c. metals, of the type previously used by Wilson and Johnson for calculations in LiH¹¹. The potential was cut off at first neighbour distance. In the b.c.c. metals a central force interaction was used up to second neighbour distance. The primary character of both types of potentials was determined by a fit to elastic constants. Parameters in the f.c.c. potential that could not be deduced in this way were derived by trial and error until the model reproduced known vacancy formation and migration energies. Potentials for Cu, Ni, Ag, Pd, Au, V, Fe, Mo, Ta and W have been calculated. The ability of some of these potentials to reproduce phonon dispersion data was then tested. Convincingly close agreement was obtained for Cu, Ni, Fe, W, without adjustment of the fit to elastic constants. Mo gave quite a good fit but V and Ta were poor. Bearing in mind that Johnson's potentials reproduce known defect data acceptably and that they were based firmly

on an empirical fit to elastic and phonon data, it may be concluded that they are perhaps the most reliable metal-metal potentials available for use in the following atomistic modelling of rare gas migration.

The basis of metal-gas and gas-gas potentials developed by Wilson and Bisson¹², used in atomistic calculations of the behaviour of Helium in metals¹³, will now be discussed briefly. A modification of a method which was attributed to Wedepohl¹⁴, was employed as an alternative to the complete set of potentials for $Z = 2$ to $Z = 105$, of the Born-Mayer form, published by Abrahamson¹⁵. Wedepohl compared potentials derived using four electron density distributions, quantum mechanical¹⁶, Thomas-Fermi¹⁷, Thomas-Fermi-Dirac, and those derived from X-ray scattering measurements¹⁹. The total energy of interaction E between the charge distributions expressed as the sum of E_{nn} , nuclear-nuclear, E_{ee} , electron-electron, E_{en} , electron-nuclear, E_k , kinetic and E_a the exchange energy.

$$E = E_{ee} + E_{nn} + E_{en} + E_k + E_a \quad (5)$$

Wilson and Bisson calculated each term as follows,

E_{nn} from a simple coulomb interaction.

E_{ee} by calculating the interaction between elementary shells and then integrating analytically over the distance between centres, using charge distributions derived from Hartree-Fock-Slater radial wave functions^{20,21}.

E_{en} from consideration of Gauss's law.

E_k and E_a were examined at length by Wilson and Bisson¹² and the reader is referred there for a comprehensive discussion where Wilson has used a number of approaches proposed by Slater et al.²² to estimate the exchange term. He concludes by choosing the most versatile close fit to data derived from molecular beam scattering experiments.

Using a number of existing Copper-Copper potentials Wilson and Bisson¹² then calculated activation energies for interstitial Helium migration of 0.62, 0.71, 0.45, 0.54 and 0.49 eV. This represented a firm case for placing confidence in the ensuing extensive calculations of Helium migration in metals having demonstrated a relative insensitivity to the potential employed.

4. The Properties of Single Gas Atoms in Substitutional and Interstitial Positions

The majority of theoretical treatments of rare gases in metals have, until recently, been limited to macroscopic considerations²³. Apart from the work of Norgett and Lidiard²⁴ with alkali halides and that of Wilson and Johnson¹¹ with Lithium Hydride, little atomistic work remains, with the exception of early studies by Rimmer and Cottrell²⁵, dealing with all the rare gases in Copper, Anderman and Gehman²⁶ dealing with Xenon in Copper and Harrison et al.²⁷ dealing with all the gases in Tungsten. More recently there has, however, been some attention paid to the atomistic behaviour of rare gases and in particular Helium in metals, stimulated by interest in reactor cladding problems.

The early work of Rimmer and Cottrell²⁵ is summarised in Table 1. The calculations gave configurational energies of rare gas atoms in interstitial and substitutional sites.

TABLE 1
Estimated Energies of Solution of Inert Gases in Copper
(Rimmer and Cottrell²⁵)

Solution	Energy	He	Ne	Ar ₍₁₎	Ar ₍₂₎	Kr ₍₁₎	Kr ₍₂₎	Xe ₍₁₎	Xe ₍₂₎
Interstitial Gas	Strain	1.7	3.4	10.6	7.7	14.9	10.8	24.5	17.5
	Electronic	0.8	1.2	3.0	2.3	4.6	3.0	6.5	4.9
	Total E _i	2.5	4.6	13.6	10.0	19.5	13.8	31.0	22.0
Substitutional Gas	Strain	0.0	0.3	2.2	1.7	3.8	2.7	7.8	5.7
	Electronic	0.0	0.1	0.7	0.5	1.4	0.8	2.4	1.0
	Vacancy	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Total E _s	1.0	1.4	3.9	3.2	6.2	4.5	11.2	8.2
Add self interstitial formation energy to give gas-copper replacement energy E _D		4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
		5.5	5.9	8.4	7.7	10.7	9.0	15.7	12.7

The formation energy of each type of site was found from the sum of strain and electronic energies (when in an interstitial position) plus the vacancy formation energy (when in a substitutional position). It can be seen in Table 1 that the rare gas always preferred a substitutional site if vacancies were available. The larger gas species possessed sufficient interstitial configurational energy, however, to generate a Frenkel defect, (compare E_i with E_D, where E_D came from E_s by adding the self-interstitial formation energy). Krypton and Xenon were clearly able to move easily from an interstitial position by forming a Frenkel defect. Helium was equally clearly not able to do so. In view of the approximate nature of the potentials involved no firm conclusion could be made about Neon and Argon. In experimental terms this meant that if Helium was injected into a crystal lattice at energies below that required to cause lattice displacements, it would reside interstitially or diffuse out of the lattice, depending on its migration energy, unless it was trapped in pre-existing damage.

The properties of rare gases in interstitial positions in Tungsten have been investigated more recently by Harrison et al.²⁷ using a theoretical atomistic model. The potentials employed were composed of Morse, Born-Mayer and matched cubic functions. A small crystallite of 250 atoms, at absolute zero, was employed which was oriented with a (010) surface. Few claims were made about the absolute accuracy of their results, which aimed to illustrate more general behavioural trends. Equilibrium positions for Argon were studied in most detail, but the work was extended to the other rare gases. Helium and Neon were found to be most stable close to the centre of the octahedral void, formed by any four face atoms and the body centred atom above and below the plane. The results suggested that Argon, Krypton, Xenon and Tungsten would form a split interstitial configuration, consistent with the calculations of Erginsoy et al.³ for Tungsten interstitials.

The general trend was that as the mass of the gas increased its stable position moved from the centre of the octahedral void to a split configuration shared with the Tungsten, former body centred, atom. The split interstitial configuration, however, may have been expected to anneal at low temperatures $< 150\text{K}$ when a vacancy would be generated which would act as a gas or a Tungsten trap. It may have been argued, therefore, that at room temperature, when interstitial mobility exists, gas atoms which occupied the split interstitial configuration, shared with a Tungsten atom, possessed sufficient energy to move from a split interstitial position to a substitutional position by effectively generating a Frenkel pair. Argon, Krypton and Xenon may have been expected to behave in this way whereas Helium and Neon may not. This compares well with Rimmer and Cottrell's predictions for f.c.c. copper.

Dealing more specifically with Helium, Wilson and Johnson¹³ have published calculations based on the metal-metal potentials derived by Johnson and Wilson¹⁰ and the gas-metal potentials already described¹². A model of interstitial Helium migration and of simple Helium vacancy interactions was presented. Two independent methods of defect calculations have been employed. In the first a symmetrical shell of atoms distributed about the defect configuration was moved to an estimated minimum and the energy change noted. It was then held while the next shell was released. The result was obtained after about six successively smaller iterations usually ending with a final shell shift of about 10^{-3} of a half lattice constant. Approximately 200 atoms and a final shift of the size mentioned, was sufficient to define the total energy change to within 0.01 eV.

In the second method all the atoms involved were allowed to move simultaneously. The forces on each atom were computed and then the relaxed co-ordinates after a time Δt , so giving the energy change. The forces at the new co-ordinates were then computed and the process repeated as many times as necessary to obtain zero force conditions. This usually amounted to a hundred steps or so. Since non-central forces were not included in method two, and since a test comparison between the methods showed little ultimate difference, other than in superior computing speeds, method one was used for f.c.c. metals and method two for b.c.c.

These methods were used to calculate the formation energies, relative to the perfect lattice, of Helium in various interstitial positions. The results are summarised in Figures 1 and 2, and Tables 2 and 3. The interstitial migration energy was calculated in each case by taking the difference between the lowest two interstitial configurations and is shown in each table. It is perhaps unwise to place too much emphasis on the value of $E_{\text{He},i}^{\text{M}}$, other than as a rough estimate, since the figures were a small difference between large quantities which may have been significantly in error. Generally, the interstitial migration energy in f.c.c. metals was ~ 0.2 eV value whereas in the f.c.c. metals values were less consistent ranging from 0.08 eV to 1.74 eV.

In a similar way the formation energy of Helium in an existing vacancy has been calculated for f.c.c. and b.c.c. metals. These results are presented in Table 4, column one. In order to relate these quantities to absolute formation energies, account had to be taken of the technique employed. The relative vacancy formation energy (wrt the perfect lattice) was found by allowing the lattice to relax and computing the energy shift

TABLE 2

Formation Energies of Helium in Various Interstitial Positions in b.c.c. Metals¹³. Also shown are the Helium Interstitial Migration Energies

	V	Fe	Mo	Ta	W
1 0 1	4.61	5.36	4.91	4.23	5.47
$\frac{1}{2}$ 0 1	4.74	5.53	5.14	4.22	5.71
0 0 1	4.61	5.36	4.91	4.23	5.47*
$\frac{3}{4}$ $\frac{1}{4}$ 1	4.90	5.76	5.55	4.60	6.19
$\frac{1}{2}$ $\frac{1}{2}$ 1	5.38	6.28	6.52	5.04	7.35
$\frac{1}{4}$ $\frac{3}{4}$ 1	4.90	5.76	5.55	4.60	6.19
$\frac{3}{4}$ $\frac{1}{4}$ $\frac{3}{4}$	5.02	5.80	5.67	4.62	6.32
$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$	5.18	6.16	6.57	5.15	7.44
$\frac{1}{4}$ $\frac{3}{4}$ $\frac{1}{4}$	5.02	5.79	5.66	4.61	6.32
E_{Hei}^M	0.13	0.17	0.23	~0.00	0.24

* Symmetrical interstitial positions producing the same formation energy

TABLE 3

Formation and Activation Energies of Helium in Various Interstitial Positions in f.c.c. Metals¹³. Also shown are the Helium Interstitial Migration Energies

	Ni	Cu	Pd	Au
1 0 0	4.6	2.03	3.68	1.53
$\frac{1}{2}$ $\frac{1}{2}$ 0	4.52	2.60	5.42	2.39
$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$	5.39	2.96	5.43	2.60
E_{Hei}^M	0.08	0.57	1.74	0.86

TABLE 4

Formation Energy of Helium in Interstitial Positions and in Pre-existing Vacancies¹³. Also shown are the Simple Substitutional De-trapping Energies ΔE_1 and the Mapped Minimum De-trapping Threshold Energies ΔE_2

	$E_{\text{He,v}}^F$	$E_{\text{He,i}}^F$	E_1	E_2
Cu	0.15	2.03	1.88	1.84
Ni	1.36	4.52	3.16	-
Pd	0.52	3.68	3.16	-
Au	0.0	1.53	1.53	-
Fe	1.61	5.36	3.75	3.98
Mo	1.04	4.91	3.81	4.19
W	1.05	5.47	4.42	4.75
V	1.65	4.61	2.96	3.20
Ta	0.93	4.23	3.30	3.44

after the removal of a lattice atom. This did not take into account the energy needed to place the removed atom on the surface. Johnson and Wilson⁹ computed this value, which they call the unrelaxed vacancy formation energy. The sum of this value and the formation energy of the vacancy relative to the perfect lattice gave the absolute vacancy formation energy. Table 4 shows the formation energy relative to the empty vacancy. To express this relative to the perfect lattice it is necessary to add the vacancy formation energy relative to the perfect lattice. To further convert to an absolute formation energy, the unrelaxed vacancy energy described must be added as well. Since, in Table 4, the vacancy remains after the Helium has left, it is convenient to express the change, relative to the vacancy. The difference between columns one and two gives a value for substitutional Helium de-trapping. This is shown in column three. In some cases Wilson and Johnson have computed the actual dissociation path by a series of different attempt mechanisms, so defining the minimum threshold for Helium de-trapping. These results are shown in column four of Table 4 and compare well with the simple results shown in column three. As a result most of the calculations which followed employed the simpler approach of calculating the energy difference between states rather than mapping the minimum energy path. The nature of additional checks and tests employed by Wilson and Johnson leave a convincingly reliable picture which is probably the best to date within the level of accuracy claimed.

In a more detailed study of helium diffusion in Copper and Tungsten, Wilson and Bisson²⁸ have carefully examined the mechanisms of Helium migration using methods similar to those already described except that a larger number of atoms (665) were allowed to relax. The approach was to calculate the energy needed to move Helium from a substitutional to an interstitial position by mapping interstitial energy contours as shown in Figures 3 and 4. In this way, all stable interstitial positions could be found. The energy difference between the two lowest energy positions gave an interstitial migration energy of 0.45 eV and 0.24 eV for Copper and Tungsten respectively compared with 0.57 eV and 0.24 eV calculated earlier¹². At the same time, the substitutional de-trapping energy was found from the better mapping method. Values of 2.15 eV and 4.69 eV were obtained for Copper and Tungsten for the actual threshold compared with 1.84 and 4.75 eV obtained from previous calculations¹³.

Wilson and Bisson²⁸ also presented a plausible, though relatively speculative, model for combined Helium and vacancy migration. Setting Helium in an interstitial position, the effective vacancy migration energy was calculated as a copper atom was moved to the original vacancy so leaving the Helium atom to fall into the vacancy left behind. Under these conditions it was found that the vacancy migration energy was reduced from 0.98 eV (calculated) to 0.53 eV for Copper, whereas for Tungsten it was not significantly shifted from the computed 1.41 eV. (This value is far removed from the experimental 3.1 eV²⁹ which Wilson and Bisson attribute to an experimental impurity effect.)

5. The Properties of Multiple Gas Atom and Vacancy Clusters

Some stimulus to the theoretical study of the properties of small clusters of Helium and vacancies has been derived from experimental observations of the migration of Helium in metals. Such observations have been made using the technique of thermal evolution spectrometry³⁰. In this method gas ions are implanted into the target metal at energies

from a few eV to a few MeV. By careful choice of the implant energy, dose, temperature and target pre-damage, deductions can often be made about the nature of rare-gas diffusion. The analysis is carried out during a usually linear, post-bombardment annealing schedule, where the target is heated at rates of from a few degrees per second up to typically 40 K/sec. The approach is to monitor the rate of release of the implanted species. Generally the release occurs in a number of stages, each displaying an evolution rate maximum. Several analytical methods have been employed in order to relate the temperature of an evolution rate maximum to the activation energy of the mechanism responsible. Release has been assumed to proceed, in cases where the implanted gas resides within a few layers of the surface, by a single jump mechanism³⁰. Alternatively a multi-step diffusion system has been adopted for cases where the implanted species lie far into the bulk of the target^{31,32}.

In practice the release of implanted gas observed is rarely as simple as would be predicted by the mechanisms described in the previous section, but often consists of many unresolved release rate maxima³³. One interpretation of such data is that mechanisms which are a result of other than the simple combination of a gas atom and a vacancy or simple interstitial diffusion are responsible for the observed release.

Wilson and Bisson³⁴ have examined the properties of Helium in a Copper di-vacancy. The minimum energy configuration of a Helium atom in a di-vacancy made up of vacancies at (000) and (101) was found to be 0.13 eV, the same as that for a single vacancy²⁸. The Helium was located then at (0.01, 0.0, 0.01) and could migrate between vacancies with an energy of 0.26 eV. More significantly the di-vacancy migration energy when containing a Helium atom was found to be 0.74 eV compared with 0.47 eV when empty which agrees reasonably with experimental values from Wright and Evans³⁵. An occupied di-vacancy migration energy of 0.74 eV and interstitial Helium migration of 0.55 eV¹³ begins to show how unresolved evolution rate spectra could be built up.

Dealing specifically with the interpretation of thermal evolution data, Wilson and Bisson³⁶ have recently presented a study of six thermal re-emission stages of low doses of Helium injected into pre-existing vacancies in a Tungsten single crystal, based on the results of work undertaken by Kornelsen^{37,38}. It has previously been reported by Erents et al.³⁹ and later by Kornelsen³⁷ that Helium could be trapped in Tungsten due to the presence of pre-existing damage, whilst if Helium ions were incident onto a perfect crystal at energies which were too low to produce lattice displacements, then the Helium would not be trapped. This behaviour is shown in Figure 5 from Kornelsen³⁸, where, without 5 keV Krypton pre-damage, virtually no Helium trapping occurs. Two factors must be taken into account when comparing pre-damaged and non-pre-damaged Helium trapping:-

1. does low energy Helium penetrate the lattice?
2. does Helium trapping occur?

The evidence of Figure 5 and references 37, 38 and 39 establish the latter point which necessarily verifies the first. This showed that at room temperatures Helium was mobile in Tungsten and readily diffused out of the crystal if traps were not present; behaviour consistent with that predicted by Wilson and Johnson¹³ and Wilson and Bisson²⁸. The assumption was made here and in what follows that the simple vacancy was the predominant trapping centre.

It is convenient at this point to introduce a gas-vacancy reaction notation based on molecular dissociation of the type

where A and B are the constituent elements and Q the thermal activation energy. The notation is fully explained in Table 5.

TABLE 5
Gas-Vacancy Reaction Notation

H_e	one interstitial Helium atom
He_n	n interstitial Helium atoms
V	one host lattice vacancy
V_m	m host lattice vacancies
V_2^I	first neighbour di-vacancy
V_2^{II}	second neighbour di-vacancy
HeV	one Helium atom in a vacancy (substitutional occupancy)
Ne, Ar, Kr	other impurity rare gas atoms
$HeNeV_2^I$	mixed substitutional occupancy of a di-vacancy
Example of a thermal activated dissociation of Helium in a di-vacancy at a temperature T^0K :-	
$He_2V_2^I \xrightarrow{T^0K} He + HeV_2^I$	
$E_1 + Q \longrightarrow E_2 + E_3$	
where Q_{eV} is the activation energy and E_{eV} is the computed configurational energy relative to the perfect lattice.	

Kornelsen³⁸ measured the variation of the gas released in each of six stages which comprise the typical spectra of Figure 6. It was observed that the variation in the quantities of gas in each stage varied as a function of the incident dose, the square of the incident dose or the cube of the incident dose as shown in Figure 7. It was argued that this was consistent with a site being occupied by one, two or three gas atoms respectively. Kornelsen thus suggested that gas may be trapped in combination with the simple vacancy, the di-vacancy or with a vacancy associated with a second neighbour substitutional Krypton atom. The model proposed is summarised in column one of Table 6.

In their analysis of the typical re-emission spectrum shown in Figure 6 Wilson and Bisson³⁶ have calculated the activation energies of the reactions proposed by Kornelsen. With the exception of He-He potentials provided by Beck⁴⁰, the interaction potentials were those previously described^{10,12,13}. A summary of the activation energies and reactions proposed is given in Table 6 column two. Here all the formation energies are given relative

TABLE 6

A Comparison of Experimental and Theoretical Data Dealing with the Interaction of Helium
with Defects in a Tungsten Crystal

Experimental Reactions Proposed by Kornelsen (ref. 38)	Theoretical Reactions from Wilson and Bisson (Ref. 36)	Theoretical Reactions from Caspers et al. (ref. 41)
E $\text{He}_4 \xrightarrow[2.41 \text{ eV}]{950^\circ \text{K}} \text{He} + \text{He}_3^{\text{V}}$	$\text{He}_4 \rightarrow \text{He} + \text{He}_3^{\text{V}}$ $12.81 + 2.50 = 5.44 + 9.87$	$\text{He}_4 \rightarrow \text{He} + \text{He}_3^{\text{V}}$ $13.69 + 2.94 = 5.91 + 10.43 + 0.29^{*1}$
F $\text{He}_3 \xrightarrow[2.88 \text{ eV}]{1120^\circ \text{K}} \text{He} + \text{He}_2^{\text{V}}$	$\text{He}_3 \rightarrow \text{He} + \text{He}_2^{\text{V}}$ $9.87 + 2.52 = 5.44 + 6.95$	$\text{He}_3 \rightarrow \text{He} + \text{He}_2^{\text{V}}$ $10.43 + 3.02 = 5.91 + 7.25 + 0.29$
G $\text{He}_2 \xrightarrow[3.14 \text{ eV}]{1220^\circ \text{K}} \text{He} + \text{HeV}$	$\text{He}_2 \rightarrow \text{He} + \text{HeV}$ $6.95 + 2.89 = 5.44 + 4.40$	$\text{He}_2 \rightarrow \text{He} + \text{HeV}$ $7.25 + 3.43 = 5.91 + 4.48 + 0.29$
H' $\text{HeKrV}_{22}^{\text{II}} \xrightarrow[3.84 \text{ eV}]{1480^\circ \text{K}} \text{He} + \text{KrV}_{22}^{\text{II}}$ $\text{HeV}_{22}^{\text{II}} \xrightarrow[< 4.05 \text{ eV}]{< 1560^\circ \text{K}} \text{V} + \text{HeV}$	$\text{HeKrV}_{22} \rightarrow \text{He} + \text{KrV}_{22}^{\text{I}}$ $13.72 + 4.40 = 5.44 + 12.88$	
H $\text{HeV} \xrightarrow[4.05 \text{ eV}]{1560^\circ \text{K}} \text{He} + \text{V}$	$\text{HeV} \rightarrow \text{He} + \text{V}$ $4.40 + 4.39 = 5.44 + 3.35$ $\text{He}_2^{\text{I}} \text{V}_{22} \rightarrow \text{He} + \text{HeV}_{22}^{\text{II}}$ $8.38 + 4.42 = 5.44 + 7.36$ $\text{HeV}_{22}^{\text{II}} \rightarrow \text{He} + \text{V}_{22}^{\text{I}}$ $7.36 + 4.38 = 5.44 + 6.30$	$\text{HeV} \rightarrow \text{He} + \text{V}$ $4.48 + 5.07 = 5.91 + 3.35 + 0.29$ $\text{He}_2^{\text{I}} \text{V}_{22} \rightarrow \text{He} + \text{HeV}_{22}^{\text{I}}$ $8.89 + 5.27 = 5.91 + 7.56 + 0.29$ $\text{HeV}_{22}^{\text{I}} \rightarrow \text{HeV} + \text{V}$ $7.56 + 1.67 = 4.48 + 3.35 + 1.40^{*2}$
J $\text{He}_2^{\text{I}} \text{V}_{22} \xrightarrow[4.8 \text{ eV}]{1850^\circ \text{K}} 2\text{He} + 2\text{V}$		
K $\text{He}_n \text{V}_3 \xrightarrow[5.8 \text{ eV}]{\sim 2200^\circ \text{K}} \text{H}_{n-1} + \text{He}$		

*1 He migration energy

*2 V migration energy

to the perfect lattice, e.g. the unit HeV is made up of 1.05 eV formation energy relative to a single vacancy and 3.35 vacancy formation energy relative to the perfect lattice. In the case of peak H' Wilson and Bisson show that the first neighbour structure $\text{HeKrV}_2^{\text{I}}$ is more strongly bound by 0.93 eV than the structure $\text{HeKrV}_2^{\text{II}}$ suggested by Kornelsen³⁸. Similarly, in the case of peak I the first neighbour configuration $\text{He}_2\text{V}_2^{\text{I}}$ is preferable, but only by an inconclusive 0.02 eV. Notice in column two of Table 6 that Wilson and Bisson proposed a reversion to the more stable second neighbour structure HeV_2^{II} when $\text{He}_2\text{V}_2^{\text{I}}$ loses a Helium atom. However, the unit HeV_2^{II} will then spontaneously dissociate.

Peaks EFG, H show reasonable agreement between predicted and experimental activation energies. All of these peaks involve reactions of the type,

In addition, Wilson and Bisson³⁶ have calculated activation energies for reactions for n equal to 5 and 6 of 2.31 and 2.52 eV respectively. The value of 2.52 at n = 6 is either in error or an anomalously stable configuration is produced which will spontaneously emit four Helium atoms, corresponding to n = 3, 4, 5, 6 reactions, when activated with 2.52 eV. The n = 7 case gave 1.03 eV consistent with the saturation of the octahedral symmetry of the single vacancy. Wilson and Bisson³⁶ have suggested that up to 30 Helium atoms could be accommodated in association with the vacancy.

It is instructive to note that Wilson and Bisson do not discuss the mobility of their proposed configurations. This highlights a conceptual problem that will be discussed shortly. Some clusters, e.g. $\text{He}_2\text{V}_2^{\text{I}}$, may have a calculated migration energy which is much lower than the helium dissociation energy. Because of this it might be expected that clusters will migrate to a fixed sink rather than dissociate; a further stumbling block in the interpretation of thermal re-emission data.

In theoretical work very similar to that of Wilson and Bisson, Caspers et al.⁴¹ have independently derived similar results based on an analysis of Kornelsen's³⁹ evolution rate spectra. The formation energies of various helium and vacancy configurations have been computed together with the dissociation energies of the various cluster considered. It should be pointed out that an additional quantity, the migration energy of the most mobile reaction product, was included in the equation to ensure genuine product separation. There are some slight differences in formation energies which may be attributable to slight differences in potentials and crystallite boundary conditions, but otherwise the correlation between all three sets of data is striking.

In addition to the results described Caspers et al.⁴¹ have also calculated the formation and migration energies of a wide range of Helium and multiple vacancy configurations. This data is summarised in Table 7 with the two stable configurations of the cluster He_3V shown in Figure 8. An examination of these results begins to show how closely atomistic calculations of this type have to be studied before serious interpretation of evolution rate spectra can be made. Even then it is clear that the process is by no means straightforward. It is possible for an existing Helium-vacancy cluster to change state in four ways:-

1. it may lose a Helium atom,
2. it may lose a vacancy,
3. it may migrate to a fixed sink or a free surface,
4. it may combine with another cluster.

TABLE 7

Activation Energies for the Dissociation and Migration
of He V Clusters in Tungsten (Caspers et al.⁴¹)
n-m

Cluster	Formation	Loss of He	Loss of V	Migration
He	5.91			0.29
V	3.35			1.40
HeV	4.48	5.07		5.07
He ₂ V	7.25	3.43		>5 *5
He ₃ V	10.43	3.02		>5
He ₃ V *1	10.73	2.73		>5
He ₄ V	13.69	2.94		>5
V ₂ ^I	6.65			1.6
HeV ₂ ^I	7.56	5.29	1.67	1.6 *4
He ₂ V ₂ ^I	8.49	5.27	3.51	3.7
He ₃ V ₂ ^I	10.35	4.34	4.83	4.0
V ₂ ^{II}	6.31			1.6
HeV ₂ ^{II}	7.47	5.04	1.76	1.6 *4
He ₂ V ₂ ^{II}	8.61	5.06	3.39	3.6
He ₃ V ₂ ^{II}	11.04	3.77	1.14	3.9
V ₃ *2	9.48		I *3 II	~1.4
HeV ₃	10.21	5.47	2.10 2.01	~1.4
He ₂ V ₃	11.18	5.23	2.06 2.18	~1.4
He ₃ V ₃	12.42	5.24	2.68 3.37	~2.7

*1 *3 Alternative table configurations

* Most stable configuration chosen⁴²

* Assumed to be di-vacancy migration energy

* Limiting migration step removal of last He

Additionally it may change state by a combination of any number of any of these processes. The complication is that the experimental technique most readily available, i.e. thermal re-emission, provides implicit data. The ideas here are best qualified by example and reference to Table 7.

e.g. 1 He₃V will lose all its Helium before migrating or losing a vacancy, so giving release.

- e.g. 2 $\text{He}_3\text{V}_2^{\text{I}}$ will migrate at 4.0 eV before it loses a vacancy at 4.83 eV or a Helium atom at 4.34 eV and may give release at the surface.
- e.g. 3 $\text{He}_2\text{V}_2^{\text{I}}$ (used to explain Kornelsen's peak I at 4.37 eV) will lose a vacancy at 3.51 eV before it migrates at 3.7 eV or loses Helium at 5.27 eV, and so give release as He_2V at 3.43 eV.
- e.g. 4 If during annealing the reaction

$$4.48 + 3.35 \rightarrow 7.56 + 0.27 \text{ eV}$$

occurs when vacancies are mobile at 1.4 eV the unit HeV_2^{I} is formed which could activate release when mobile at 1.6 eV.

It is clear that with data available for all combinations of up to three Helium atoms in three vacancies, the number of ways of explaining release maxima is becoming unmanageable.

It is worth noting at this stage that some interesting trends are developing in the higher order clusters, e.g. He_3V_3 . For both di-vacancy and tri-vacancy clusters, adding more Helium tends to immobilise the structure and inhibit vacancy loss. The energy to remove one of several Helium atoms is tending to be a constant high value in the larger clusters. The inference is that in a cluster of the type He_nV_m where n, m , there is less possibility of migration or Helium or vacancy loss. It would perhaps be worthwhile examining the properties of larger vacancy clusters containing Helium to find the optimum stable values of n and m . Using the data in Table 7, it seems that the cluster $\text{He}_3\text{V}_2^{\text{I}}$ is most stable (except HeV), with a migration energy of 4.0 eV a vacancy dissociation energy of 4.83 eV and a Helium dissociation energy of 4.34 eV. This, in the absence of calculations for larger clusters is not a conclusive result, but it serves as an illustration. A similar concept is embodied in work by Russell⁴³ of a radically different nature. Using a thermodynamic treatment Russell calculated the free energy change in forming a void described by He_nV_m . It was found that the free energy tended to increase with n and m until a saddle point was reached at $n = 6$ and $m = 11$, thereafter decreasing for values of n of the order of m . The most stable clusters were found to be composed of gas atoms and vacancies in roughly this ratio, with clusters larger than six gas atoms and eleven vacancies free to grow by vacancy and gas atom acquisition. It is encouraging to see a trend similar to that suggested by the computer calculations described earlier in that there was a critical agglomerate of a few vacancies and Helium atoms which, if exceeded, gave rise to a stable void. The direct application of such a result to the nucleation problem does not readily follow since the effect of irradiation and so interstitial supersaturation cannot be included⁴⁴.

As a consequence of the relative success of the atomistic approach of Wilson and Bisson³⁶ and Caspers et al.⁴¹, in interpreting experimental thermal evolution data from Kornelsen for the Helium-Tungsten system^{37,38}, Caspers et al.^{45,46} and Fastenau et al.^{47,48} have adopted a similar approach to the Helium-Molybdenum system which interfaces with some experimental work from Van Veen et al.⁴⁹. The Delft group^{41,45-49} have employed metal-metal potentials due to Johnson and Wilson¹⁰, gas-metal potentials from Wilson and Johnson and gas-gas potentials from Abrahamson⁵⁰. The choice of gas-gas potential differs from

that made by Wilson and Johnson¹³ for Molybdenum, where the potentials discussed earlier, from Wilson and Bisson¹² were employed. This again differs from the choice made for Tungsten where Wilson and Bisson³⁶ used potentials ascribed to Beck⁴⁰.

Initially Caspers et al.^{45,46} have examined interstitial clustering of Helium on a (110) plane in Molybdenum. A binding energy of 0.25 eV was calculated between two Helium atoms. The binding energy of the third through to the eighth Helium atom added was found to be 0.5, 0.6, 0.4, 0.6, 1.0, 0.9 eV respectively. Stacking the Helium with unit lattice spacing gave a mean binding of 0.55 eV. However, using half-lattice stacking gave 0.91 eV. This suggested the possibility of interstitial Helium platelets in Molybdenum stable at room temperature.

Caspers et al.⁴⁶ have also examined the He-Mo interstitial binding energy which at 0.7 eV is much larger than the He-He binding of ~ 0.25 eV. This raises three important questions.

1. To what extent can self-interstitials nucleate Helium clusters and vice versa?
2. What is the He-Mo interstitial loop binding energy?
3. To what extent can mixed He-Mo interstitial loops be found and how bound will they be?

When considering the possibility of forming an interstitial gas cluster the effect of the remaining defect species, the vacancy, must be considered. Were the Helium interstitial to act as a self-interstitial, cluster formation could be visualised. However, the vacancy can accommodate several Helium atoms (e.g. six atoms each bound by 2.52 eV in a Tungsten vacancy³⁶, with the possibility of seven or more bound by ~ 1 eV³⁶). This reduces the possibility of cluster formation correspondingly. In gas-release studies where Helium has been implanted at high energies, e.g. Erents and McCracken³² where immobile vacancy concentrations were high, significant trapping in the form of interstitial gas clusters may not be expected. In low energy studies, e.g. Kornelsen³⁸, surface image forces may be expected to sweep clusters from the sample, in the same way that self-interstitial loops are lost.

The behaviour of Helium in a simple vacancy in Molybdenum has been investigated by Caspers et al.⁴⁵ and Fastenau et al.⁴⁸. The binding of up to three atoms in a single vacancy has been calculated. A summary of the data is contained in Table 8 together with similar calculations from Wilson and Johnson^{10,13} and single vacancy data from Fastenau et al.⁴⁷. The results of thermal desorption experiments from van Veen et al.⁴⁹ are also included for comparison. A measure of correlation has been obtained for the detrapping of Helium as one of a tri-mer, one of a di-mer or present singly in a vacancy. The technique used here was identical to that employed by Kornelsen^{37,38}, for the Helium-Tungsten system, except that Krypton was used as a damaging irradiation prior to 250 eV Helium injection.

In addition, van Veen et al.⁴⁹ have examined the trapping of Helium in the simple vacancy, as a function of the temperature to which the pre-damaging Krypton irradiation was annealed. It was observed that a reduction in the quantity of gas released from vacancies containing one Helium atom occurred following annealing to progressively higher

TABLE 8

A Comparison of Experimental⁺ and Theoretical Values of Formation, Migration and Binding Energies for Occupied and Unoccupied Vacancies in Molybdenum

Ref.	H _e		V		HeV		He ₂ V		He ₃ V	
	E _f	E _m	E _f	E _m	E _f	E _{B,He}	E _F	E _{B,He}	E _F	E _{B,He}
45	4.97	0.3			4.29	4.2	6.70	2.9	9.45	2.6
47			3.23	1.29						
48					4.30		6.71			
10				1.26						
13	4.91	0.23				4.19				
49 ⁺						3.0		2.5		2.3

temperatures. This effect in the temperature range 400–500 K was attributed to the gradual reduction in the quantity of vacancies left after the initial damaging irradiation. This was essentially a reduction analogous to Stage III resistivity recovery usually centred on ~ 520 K. This technique proved to be a useful tool in the investigation of vacancy loss. Some controversy surrounds the mechanism of vacancy loss in Stage III. It has been proposed that, on the one hand, the migration of vacancies were responsible^{51–57}, whilst on the other, that the migration of meta-stable interstitials, or interstitials which become de-trapped, were responsible^{54–56}. Recently, Evans and Eldrup⁵⁷ and Eldrup et al.⁵⁸ have used simultaneously techniques of positron annihilation and resistivity recovery with subsequent transmission electron microscopy, in a further study of Stage III recovery. In particular it was observed that an 80% recovery of the induced resistivity occurred in the range 150 to 300 C. At the same time a large increase in the long positron lifetime was observed (195–400 ps). Since it had been established that such a lifetime was sensitive to the presence of vacancies and vacancy clusters, it was shown that the observed increase could be explained by the formation of vacancy clusters. This necessarily required vacancy migration in Stage III, which ultimately gave rise to observable voids on further annealing with a further increase in lifetime.

In the type of study employed by van Veen et al.⁴⁹ the surface becomes a convenient interstitial sink. This leads to a marked enhancement of the vacancy concentration near the surface compared with deeper regions. Rothman et al.⁵⁹ have examined this effect by solving the appropriate rate equations in a model 1 μ m thick silver foil. Provided that steady state conditions are not achieved, a reasonable assumption in most cases, up to half an order of magnitude increase over the bulk in the vacancy concentration just beneath the surface was found to be possible. In other words the larger portion of the vacancies remaining after irradiation did not have corresponding interstitials left in the bulk, however, trapped. Since the foil employed by Rothman et al.⁵⁹ can be considered as semi-infinite, compared with the present application, the concept still holds good here. Bearing in mind that the incoming and thermalised interstitial Helium will tend to encounter the vacancy rich zone first, the annihilation of vacancies, manifesting a reduced level of gas trapping, was more reasonably ascribed to vacancy loss by migration rather than to

loss by recombination with mobile interstitials which were not present in sufficient quantities, having been lost to the surface during irradiation.

Fastenau et al.⁴⁶ have also calculated some properties of di-vacancies and tri-vacancies containing Helium atoms in Molybdenum. Typical values of formation and binding energies of the di-vacancy in various configurations are shown in Table 9. The first and second neighbour configurations of (000) and ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) had a slight positive binding which was enhanced by the presence of gas. More distant neighbours often had a slight negative binding. The single Helium atom contained in first and second neighbour configurations exhibited a low migration energy consistent with Wilson and Bisson's work in Copper³⁴ discussed earlier. For large vacancy separation this value predictably increased dramatically. Curiously, Fastenau et al.⁴⁸ have not discussed di-vacancy migration. Typical values of formation and binding energies for the occupied and unoccupied tri-vacancy are shown, for various configurations, in Table 10. Typical values of migration energies are shown in Table 11. Here again the presence of gas tends to improve the binding of the cluster giving stable clusters at room temperature. This work has outlined a mechanism of gas-vacancy clustering where gas and vacancies are moved via an unoccupied di-vacancy and then stabilised by meeting a vacancy occupied or otherwise.

TABLE 9
Vacancy Pair Formation and Binding Energies in Molybdenum
(Fastenau et al.^{47,48})

Coordinates	V.V		HeV.V		HeV.V			He ₂ V.V	HeV.HeV	
	E _F	E _B	E _F	E _B	E _F	E _B	E _m He			
000 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	6.44	0.02	7.28	0.25	7.28	0.25	0.09	unstable reverting to →	8.16	0.44
000 100	6.02	0.44	7.11	0.42	7.11	0.42	0.85		8.18	0.42
000 101	6.51	-0.05	7.56	-0.03	7.56	-0.03	3.20	9.96 -0.02	8.61	-0.61
000 111	6.50	-0.04	7.55	-0.02	7.55	-0.02	-	9.92 0.02	-	-
000 200	6.49	-0.07	7.58	-0.05	7.58	-0.05	-	9.99 -0.05	-	-

TABLE 10
Trivacancy Formation and Binding Energies in Molybdenum
(Fastenau et al.^{47,48})

Coordinates	V ₃		HeV.V ₂		(HeV) ₂ V	
	E _F	E _B	E _F	E _B	E _F	E _B
000 $\bar{1}00$ 100	8.83	0.86	9.93	0.83	-	-
000 001 100	8.85	0.84	9.92	0.84	-	-
000 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ $\bar{1}\frac{1}{2}\frac{1}{2}$	9.13	0.56	9.85	0.98	10.73	1.10
000 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ $\bar{1}00$	9.19	0.54	-	-	10.96	0.87
000 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ $\bar{1}\bar{1}\bar{1}$	-	-	-	-	11.31	0.52

TABLE 11

Helium Filled Tri-vacancy Migration Energies in Molybdenum

Defect	Coordinates	Em →	Coordinates	Em ←
HeV.V ₂	000 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ $\bar{1}\frac{1}{2}\frac{1}{2}$	1.3	000 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ 001	1.08
(HeV) ₂ V	000 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ $\bar{1}\frac{1}{2}\frac{1}{2}$	1.3	000 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ $\bar{1}\frac{1}{2}\frac{1}{2}$	1.3
HeV.V ₂	000 100 200	1.51	000 $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ 200	0.76

Using potentials employed in earlier work on the Helium-Copper system, Wilson et al.²⁸ have examined the binding energy of the n^{th} Helium atom in a cluster of n interstitial atoms and the binding of the n^{th} Helium and the m^{th} vacancy in a cluster He_nV_m . The data is summarised in Table 12. The binding of the n^{th} Helium in an interstitial cluster was found to be typically small, with the sixth atom not bound at all. The binding of the n^{th} Helium atom in a vacancy cluster tended to decrease as a function of the number of atoms therein. Alternatively the binding of a vacancy tended to increase with Helium content. The most stable cluster therefore was that which had the highest simultaneous binding energy for a vacancy and a Helium atom. It can be seen in Table 12 that clusters where $n \approx m$ fulfil this requirement with a vacancy binding of approximately 1.27 eV and a Helium binding of approximately 1.84 eV. This means that such clusters are stable at about 0.4 of the melting temperature, T_m , a convenient mid-point in the characteristic 0.3 to 0.5 T_m void swelling region. The formation of clusters where $n \approx m$ represents the most efficient nucleation path for voids since, at 0.4 T_m , loss of vacancies and Helium does not occur. At slightly higher temperature some vacancy loss may be expected which has to be compensated by additional vacancy arrival. Alternatively this means that the rate of nucleation is reduced. It is interesting to compare this result with a radically different approach to nucleation from Russell and Hall⁶¹. Here the optimum arrival ratio for vacancies and gas atoms at the void was found to be one to one with the nucleation path being displaced from the origin in gas-vacancy space by eight vacancies and described roughly by $n = m - 8$.

Recently the interaction of a free self-interstitial with a singly occupied vacancy has been considered as a Helium resolution mechanism during irradiation^{62,63}. Wilson and Bisson⁶² have reported calculations in Copper of the type already described. They concluded that a first neighbour self-interstitial was able to displace substitutional Helium leaving it as a free-interstitial. The larger rare gases were, however, able to resist the displacement. Using data already discussed, the required Helium de-trapping energies¹³ of 1.88 eV in Cu, 3.16 eV in Ni and 1.53 eV in Silver, can be seen to be smaller than the energy produced by interstitial vacancy recombination¹⁰ typically 3.81 eV, 4.18 eV and 4.15 eV respectively. In order to test more fully the proposed displacement reaction Guinan and Stuart⁶³ have investigated the implications of the static calculations by recourse to a dynamic model using identical potentials^{10,36}. Simulation was carried out using 1500 atoms in dynamic equilibrium. The authors concluded that there was no barrier to recombination. A spontaneous Frenkel pair recombination volume of atomic volumes was found to

TABLE 12

Binding Energies of the n^{th} Helium Atom and the m^{th} Vacancy to a Cluster He_nV_m in Copper, after Wilson et al.⁶⁰
 (Figures in parenthesis, added here for completeness, are based on an interstitial formation energy for Helium of 2.03 eV⁶⁰.)

$\text{He}_n \backslash \text{V}_m$	0	1	2	3	4	5	6	7	8	9	10
0	- -	- -	0.08 -	0.18 -	0.08 -	0.18 -	0.02 -	- -	- -	- -	- -
1	- -	1.84 (1.84)	0.79 (3.87)	0.57 (5.90)	0.66 (7.93)	0.60 (9.96)	0.86 (11.99)	0.25 (14.02)	0.24 (16.05)	0.20 (18.08)	0.20 (20.11)
2	- 0.22	1.84 0.22	1.84 1.27	1.09 1.79	0.66 1.79	0.85 2.04	0.90 2.08	0.75 2.58	0.85 3.19	0.67 3.66	0.85 4.31
3	- 0.45	1.84 0.45	1.84 0.45	1.84 1.20	1.25 1.79	0.89 1.83	0.99 1.92	0.69 1.86	0.78 1.79	0.98 2.10	0.70 1.95
4	- 0.58	1.97 0.71	1.84 0.71	1.73 0.60	1.93 1.28	1.25 1.64	1.13 1.78	1.12 2.21	1.10 2.53	0.65 2.20	0.82 2.32

differ little from the case when Helium was absent. The effective self-interstitial capture volume was found to be 250 atomic volumes, roughly similar to the volume in which correlated Frenkel pair recombination occurs. The mechanism is a major contributor to Helium re-solution and could dramatically control void nucleation rates.

A much neglected Helium trapping site, the edge dislocation, has recently been examined by de Hosson et al.⁶⁴. Again Molybdenum and Tungsten have been chosen as model materials in an atomistic approach similar to those described earlier. The binding of Helium to a pure edge dislocation perpendicular to the (112) plane with a Burgers vector of $\frac{1}{2}$ [111] in that plane has been calculated. A static model of 3000 atoms has been employed equilibrated using potentials derived by Wilson and Bisson^{10,13}. Using the now familiar relaxation technique the formation energy of a dislocation with and without a Helium atom has been calculated. The difference in these quantities was taken as the formation energy of a Helium atom on an existing dislocation. The results are shown in Table 13. In addition, formation energies for Helium in an interstitial position and in

TABLE 13

Formation, Binding, Dissociation and Migration Energies of Helium on a $\frac{1}{2}$ [111], (110) edge Dislocation in Molybdenum Compared with the Single Vacancy and in an Interstitial Position (de Hosson et al.⁶⁴)

	Tungsten	Molybdenum
$E_{He,D}^F, \text{eV}$	3.93	3.42
$E_{He,I}^F$	5.46	4.97
$E_{He,D}^B$	1.53	1.55
$E_{He,V}^B$	4.0	3.8
$E_{He,D}^{\text{Diss}}$	1.93	1.95
$E_{He,V}^{\text{Diss}}$	4.4	4.2
$E_{He,I}^M$	0.4	0.4
$E_{He,D}^M$	0.3 - 0.4	

a vacancy have been included. Curiously the formation energy of a Helium atom in an existing vacancy differs considerably from that reported by Caspers et al.⁴¹ which was discussed earlier, but compares more favourably with calculations from Wilson and Bisson³⁶. It can be seen in Table 13 that the Helium atom is bound nearly twice as strongly in a vacancy than it is on an edge dislocation. In addition, de Hosson et al.⁶⁴ have calculated the migration energy along the edge dislocation in a (112) direction. At 0.3-0.4 eV this does not differ appreciably from the bulk value. This gives the possibility of pipe diffusion

along the perfect edge described. Whilst therefore the edge acts as a trap with respect to perfect crystal the gas still retains considerable mobility along the dislocation core.

In practice the edge dislocation possesses discontinuities⁶⁵. One may expect kinks in the glide plane and more importantly jogs formed by adding a semi-infinite row of atoms to the edge so forming a step. This dramatically increases the formation energy of the dislocation⁶⁵. If a self-interstitial becomes bound to a pure edge then the formation energy of the system increases by what may be thought of as the formation energy of two jogs. If, however, a self-interstitial falls into a jog then the energy of the dislocation remains unchanged⁶⁵. The binding energy may be thought of as equal to the formation energy of the self-interstitial. In much the same way it can be argued that a Helium atom encountering a jog will occupy the site with virtually no formation energy and so be bound by an energy roughly equivalent to the interstitial formation energy. It is reasonable to argue, therefore, that Helium will be tightly bound in a jog and stable against thermal de-trapping. One may at least expect a stronger binding than the gas atom would experience if bound on a pure edge. The jogged dislocation, a physically more realistic case, so becomes a powerful gas trap. It has a large capture cross-section with quasi-trapping in the core along which the gas is free to migrate until it encounters the jog. In the case of an interstitial loop one may loosely think of it as containing a high density of jogs and at least crudely approximate behaviour to that postulated for the jogged dislocation. The frequent observation of bubbles formed on dislocations and interstitial loops in many ways substantiates the argument advanced above.

6. Some Experimental Investigations

For completeness and as an illustration of the usefulness of the atomistic analysis of the properties of Helium in Tungsten recent lattice location studies of Picraux and Vook⁶⁶ will be briefly discussed. 500 keV deuterons were used as a probe. By injecting this specie parallel to a $\langle 100 \rangle$ channel, implanted ^3He was located by observing products from the $^3\text{He}(d,p)^4\text{He}$ reaction, previously used for ^3He profiling⁶⁷. The reaction has documented cross-sections⁶⁸ enabling quantitative measurement of ^3He concentrations. To summarise, for various doses of 10^{15} and 10^{14} of 60 keV and 200 keV ^3He , Picraux and Vook observed four flux peaks symmetrically distributed about a narrow minimum in an angular scan of the probe beam through a $\langle 100 \rangle$ channel. The flux peaks were still observed when the ^3He was implanted at 735 K (462°C). The peaks were associated with location of three ^3He atoms, set in an equilateral configuration on a (100) plane. This amounts to Helium in two semi-interstitial positions about any $\langle 100 \rangle$ atomic row such that any channel contains two different pairs of two Helium atoms. This assignment was based on and correlated with the theoretical predictions of Bisson and Wilson⁶⁹. Bisson and Wilson have also calculated the configuration of two Helium atoms in a vacancy. Picraux and Vook⁶⁶ comment that such a configuration may be present in a lesser concentration in which case it would be unresolved against the maxima derived from the triple occupancy structure described. These results indicate that the singly, doubly and triply occupied vacancy are the predominant Helium trapping site, a result consistent with Kornelsen's³⁸ observations described earlier.

Finally a group of studies utilising precision X-ray measurement of changes in lattice parameter in b.c.c. and f.c.c. metals after Helium injection will be briefly

discussed. Early work of Russell and Hastings⁷⁰ apparently identifies Helium in interstitial positions in a Copper-1% Boron neutron irradiated alloy. The conclusion was based on the observation that the lattice parameter showed an approximately 0.01% increase after a build up of 0.012 atomic % of Helium from the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction. The rather speculative assumption was that this was caused by interstitial Helium. In later work Hastings and Russell⁷¹ have observed a concentration dependence in this effect. They reported the lattice parameter initially increasing in proportion to the Helium concentration up to 0.08 to 0.1% when precipitation to form bubbles was observed during irradiation at 75-100°C. In view of the fact that the concentrations of Helium in both cases reported was high, even at 0.01 atomic %, and that in Copper there is vacancy mobility at the irradiation temperature, using a migration energy of 0.91 eV⁷², it seems highly probable that complex clusters may have been formed which then gave rise to the observed lattice dilation. Additional doubt is cast by later work from Vela, Hardy and Russell⁷³ on Cu-0.01 wt.% ^{10}B examined on the transmission microscope after neutron bombardment. Two separate spherical shells of interstitial loops were observed surrounding a small Boron particle. The inner being associated with the lower energy ^7Li reaction product whilst the outer was justifiably associated with the higher energy ^4He product, particularly so since bubbles were observed on annealing in the outer shell. The presence of such a dense dislocation structure suggests that the observed lattice dilation might more easily be interpreted in terms of such radiation damage and its annealing behaviour.

In similar X-ray measurements of the changes in lattice parameter of aluminium, Cost and Johnson⁷⁴ reported a reduction in the lattice parameter, after cyclotron injection of 50 atomic parts per million (ppm) or 0.005% of Helium, which they attributed to substitutional occupancy. However, in contrast to Russell and Hastings, Cost and Johnson⁷⁴ note that the decrease is much less than theoretically predicted by single Helium vacancy occupancy. They have consequently proposed that multiple occupancy may be the dominant configuration which is consistent with the observations of Picraux and Vook⁶⁶ reported earlier for b.c.c. Tungsten. Later work from Johnson and Cost⁷⁵ for Niobium has reached a similar conclusion based on lattice parameter measurements of Niobium where again an unusually small decrease was observed.

The inference that follows from the experimental work discussed is that great care must be exercised in interpreting experimental data for cases where the Helium concentration is high, particularly when there is vacancy mobility. This allows the possibility of multiple occupancy of single or multiple defects which can greatly change the simplistic interpretation of data.

A markedly different behaviour has been reported for Argon in Silver, Gold, Aluminium and Lead, which are all f.c.c. materials. Tucker and Norton⁷⁶ observed an almost negligible change in the lattice parameter when up to 2% Argon was loaded into the lattice. This was far from the predicted 0.6% increase. Tucker and Norton wisely place little weight on their observations other than to conclude that gross re-ordering may well occur giving rise to small bubble nuclei.

A conclusion that does follow from the work just described⁷⁰⁻⁷⁶ is that rare-gas behaviour must be interpreted in relation to and not separate from what may be gross lattice damage.

7. Conclusions

The development of more reliable interatomic potentials has enabled a more tenable atomistic approach to the diffusion of rare gases in some common metals to be realised. Whilst some agreement has been obtained with limited experimental data in materials like Tungsten³⁸ and Molybdenum⁴⁹ it is probably safe only to place weight on the general trends predicted for other materials. This is particularly so for the common f.c.c. metals. This guarded approach in no way detracts from the usefulness of the work that has been described above, but avoids stretching the data beyond the limits specified by the authors. In particular, a number of valuable mechanisms have been indicated and the relative importance and magnitude of each has been identified.

In the first instance substantial evidence has been accumulated which strongly suggests that Helium has a low value of activation energy for interstitial diffusion. Values were found to lie around 0.5 eV indicating substantial mobility at room temperature. Perhaps more surprisingly Helium was found to have a high interstitial formation energy compared with that which may be intuitively expected. Values typically were found to lie between 1.5 and 4.5 eV, which approached the 3-4 eV for the self-interstitial in some f.c.c. materials. The same trend was found in the common b.c.c. metals. The implication was that Helium was not the inobtrusive impurity it was often thought to be, a view further substantiated by calculated formation energies of Helium in an existing vacancy of typically 1 eV.

Perhaps a more surprising phenomenon was the proposed Helium de-trapping mechanism, where the gas jumps from a substitutional to an interstitial position. In the interstitial position the gas was then free to diffuse until encountering another vacancy. Experimental evidence has been shown to substantiate largely this behaviour. Typical values of the thermal de-trapping energy were found to lie between the activation energy for vacancy motion and the self-diffusion energy. Were the gas to diffuse as a substitutional impurity its diffusion constant would be represented by⁷⁷,

$$D_s = 2\lambda^2 v_o \exp\{-Q/kT\} \quad (6)$$

where Q is the activation energy for self-diffusion, λ the jump distance, and v_o the vibrational frequency constant. If, however, the gas atom moves from vacancy to vacancy, its jump distance is best represented by the distance between available vacancies, i.e. $\lambda C_v^{-1/3}$ together with a vibration frequency controlled by the Helium de-trapping energy. The time spent in a vacancy $v_o^{-1} \exp\{E_{He}^D/kT\}$ is large compared with the time that the gas spends in an interstitial position before encountering a vacancy, $v_o^{-1} C_v^{-1} \exp\{E_{He}^I/kT\}$, provided that C_v is sufficiently large. Typically, at temperatures where thermal de-trapping can occur it is required that $C_v \gg 10^{-10}$, a condition readily fulfilled under thermal conditions. The Helium diffusion constant can now be approximated by

$$D_d = \frac{v_o \lambda^2}{6} C_v^{-2/3} \exp\{-E_{He}^D/kT\} \quad (7)$$

Since $E_{He}^D < Q$ and $C_v^{-2/3} \gg 1$, then $12D_d \gg D_s$.

The occupied di-vacancy³⁴ has been proposed as a specie which is highly mobile and

capable of transporting Helium at room temperature via a substitutional mechanism. It has also been shown that the di-vacancy is easily dissociated⁴⁸ which indicates that gas transported via the di-vacancy is moving via an enhanced diffusion mechanism where Helium in a vacancy collects a vacancy, migrates and dissociates leaving a Helium atom in a vacancy.

Multiple levels of vacancy occupancy have been shown to occur. Again, some experimental support was available. It was shown that the binding of the n^{th} Helium was generally weaker than the $(n-1)^{\text{th}}$.

The properties of clusters of the type He_nV_m have been examined and it was shown that for large m or large n the cluster was likely to emit a vacancy or a Helium atom respectively with a small binding energy. Optimum stability was shown to occur when $n \approx m$. Data for Copper indicated stable binding up to $0.4 T_m$.

The binding of Helium to a pure edge dislocation was shown to be somewhat less than that to a single vacancy. It has been argued that the trapping encountered in practice would be to a dislocation jog. In that case the binding energy would tend to approach the high values of interstitial formation energy discussed earlier. The effect of the lesser binding to pure edge was to enhance the capture cross-section of the deeper jog site.

Finally the important exchange reaction between a self-interstitial and a substitutional Helium atom was shown to exhibit no barrier to this spontaneous gas displacement mechanism.

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AERE - R 8419 Fig. 1
Some interstitial positions proposed by Wilson and Johnson⁽¹³⁾ for helium in an f.c.c. lattice.

AERE - R 8419 Fig. 2
Some interstitial positions proposed by Wilson and Johnson for helium in a b.c.c. lattice.

AERE - R 8419 Fig. 3

Helium energy contours in an (001) plane in copper calculated by Wilson and Bisson⁽²⁸⁾. The contour spacing was 0.2 eV with energies given relative to a vacancy at the origin. The half lattice constant was r_0 .

AERE - R 8419 Fig. 5

The general effect of heavy ion prebombardment, and so the presence of lattice disorder, on the trapping of helium incident at sub-threshold energies onto a tungsten single crystal. Shown is the thermal release of $2.4 \times 10^{13} \text{ cm}^{-2}$ of 250 eV He^+ , (a) with no predamage and (b) with predamage by $2.4 \times 10^{11} \text{ cm}^{-2}$ of 5 keV Kr^+ . (Kornelson⁽³⁸⁾).

AERE - R 8419 Fig. 6

A helium desorption spectrum for a pre-damaging bombardment of $8 \times 10^{11} \text{ cm}^2$ of 5 keV Kr^+ and a probe dose of $8 \times 10^{12} \text{ cm}^2$ of 250 eV He^+ . Also shown, as dashed curves, are the six theoretical desorption transients proposed by Kornelson⁽³⁸⁾ as the constituents of the spectrum.

AERE - R 8419 Fig. 7

The number of helium atoms released in each of the peaks shown in Fig. 6 as a function of the helium probe dose. The broken lines are drawn with slopes of 1, 2 and 3 as indicated (Kornelsen⁽³⁸⁾).

AERE - R 8419 Fig. 8

Two stable configurations of three helium atoms in a vacancy in tungsten calculated by Caspers et al.⁽⁴¹⁾.