Recent Studies of
Point Defects in Metals
Selected Topics*

Allen N. Goland
Department of Physics
Brookhaven National Laboratory
Upton, New York USA

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2 cp.

Point Defects in Metal

Selected Topics

- I. Introduction.
- II. Statistical Thermodynamics of Point Defects in Equilibrium Concentration.
 - A. Formation and Binding Entropies and Enthalpies.
 - B. Inclusion of Impurities.
- III. Determination of Point Defect Parameters and Configurations.
 - A. Defect Concentrations.
 - B. Formation and Binding Energies.
 - C. Annealing Kinetics and Rate Theory for Point Defects.
 - D. Defect Sites and Configurations.
- IV. Point Defects and Elastic Property Changes.
 - A. Dislocation Damping and Pinning.
 - B. Bulk Effect.
 - C. Point Defect Relaxation.
- V. Point Defect Research in Radiation Damage and Technology.
 - A. Radiation-induced Point Defects.
 - B. Helium in Metals.
 - C. Void Nucleation and Growth in Metals.

I. INTRODUCTION

The term "point defect" is generally understood to apply to those small imperfections in a periodic structure which can be completely enclosed by a spherical surface. Beyond this surface, the influence of these imperfections is regarded as negligible. In most cases, the radius of such a sphere is assumed to extend only a few atomic spacings. However, we shall see later that in some recent experiments, it is actually the long-range part of the displacement field of the defect that furnishes us with information about defect symmetries. Point defects fall naturally into two categories: intrinsic and extrinsic. The former consists of vacancies, interstitials and small clusters of each. The latter consists of impurities, vacancy- or interstitial-impurity pairs, clusters of impurities, including those bound to intrinsic defects, and solute precipitates.

Unlike the dislocation, a concept that initially was greeted with skepticism by the metallurgy establishment, the concept of point defects is intuitively obvious and readily accepted by all. Thus, research into their properties has been flourishing vigorously for over 25 years. A major stimulus to this activity was, of course, provided by the nuclear power program in many industrialized nations. Now we have moved into a new phase of this effort in which breeder reactors and fusion reactors are severely challenging our ability to predict the behavior of point defects in metals at elevated temperatures under new conditions of stress and purity. In view of the relatively long history of point-defect investigations it is perhaps startling to realize that the past may only have been a prelude to our understanding of the properties and behavior of point defects in metals.

The accumulated literature on point defects is now so extensive¹ that it is possible to discern only the broad outlines of the whole field. Specialists have developed expertise in diverse aspects of the subject, and in many instances they use their own particular language. No place is this more evident than in the study of mechanical properties of metals. Ductility, creep, hardness, fracture, ductile-to-brittle transitions and related terms are the everyday language of physical metallurgists but not of solid-state physicists. Yet the underlying physical phenomena which control these properties are atomistic in nature, and they ultimately must be understood within this framework. It is therefore the purpose of these lectures to provide some details insofar as they have now been well-established. Emphasis will be placed upon some of the newer methods of investigation which yield information from data that is independent of those previously obtained from more traditional measurements.

The most extensive knowledge of point defects exists for the f.c.c. metals. These metals were available in highly-purified form many years ago, and once the trend toward research on f.c.c. metals began it became self-sustaining. It afforded many scientists an opportunity to compare and combine data from a variety of experiments on the same series of metals. Moreover, the complexity of the interpretations of data prompted additional experiments designed to unravel new complications. Technologically, interest in the f.c.c. metals was consistent with some of the needs of the nuclear power industry.

In recent years, an effort to accumulate comparable information for b.c.c. metals has begun. In these metals, the presence of impurities constitutes the first major obstacle to meaningful studies of intrinsic point defects. Gaseous impurities such as O, N, and H and as well the ever-present C are all present in the concentration range from 10-1000 ppm. They occupy interstitial sites or lattice sites; they interact with intrinsic defects so as to affect rate processes; they cluster and they form compounds (eg. carbides) some of which can in turn dissolve quantities of gaseous impurities.² To this list of impurities must now be added He which builds up to the same concentration range in fast fission reactors over a period of 1 to 2 years. Similar concentration buildups are anticipated in the first wall of a fusion reactor.³ Unless b.c.c. metals of high purity are produced, and this is not easy, there is faint possibility of studying intrinsic defects in them. A further complication is that some of these metals can dissolve O and N readily so that once purified they must be handled with extreme care. For instance, they should only be heated under ultra-high vacuum conditions so as to reduce the possibility of O or N adsorption during annealing.

Aside from the importance of radiation-damage studies, radiation has long been a major means of introducing point defects into metals.⁴ However, radiation is only one of several means available for creating point defects. The other two most common methods are quenching and cold working. Quenching freezes-in a concentration of vacancies characteristic of some effective quench temperature. If not performed with care, however, quenching can also introduce large concentrations of dislocations. Cold-working is employed alone or in conjunction with radiation. In any case, it produces a variety of defect structures which must be distinguished from one another by a combination of experiments. All three methods introduce nonequilibrium concentrations of

defects. However, this is generally necessary in order that there be present a high enough concentration of the defects we wish to study. Equilibrium measurements can yield information only about monovacancies and possibly divacancies because only they are present in sufficient concentrations at equilibrium to be studied with reasonable experimental sensitivity.

From the foregoing discussion we are led to the conclusion that point defects must be investigated by a combination of equilibrium and nonequilibrium measurements. The former can be helpful in sorting out those features of the latter that should be attributed to interstitials or complexes of interstitials and impurities.

The experiment most commonly performed is a measurement of the change in electrical resistivity during the course of isochronal or isothermal annealing. The technique is very sensitive and can be applied with high precision. However, the accuracy and interpretation of results are subject to uncertainties associated with our understanding of the factors which influence electrical resistivity and our simplified models of rate processes. Size-effect corrections, deviations from Matthiessen's rule, magnetoresistance effects, multiple scattering, and scattering from clusters of defects can affect the accuracy significantly. Several authors have pointed out the limitations on the usefulness of resistivity-recovery studies which are interpreted in terms of the equations of chemical rate theory.⁵ The primary virtue of these equations is the ease with which they can be manipulated analytically or by digital-computer computations. It is generally agreed that distinctions between different recovery models cannot be made uniquely when based solely upon recovery kinetics.⁶ However, rate equations have been used to describe diffusion-controlled reactions between defects in metals for so long that there is a tendency to overlook their deficiencies. Nevertheless, the theoretical justification for their

use is weak, and more attention is being given to diffusion theories⁽⁷⁾ and computer-simulation techniques.⁽⁸⁾

Of course, electrical-resistivity recovery is not uniquely subject to difficulties of interpretation. Any experiment which relies upon a measurement of the change in some physical property is subject to the uncertainties associated with the theories relating defects to that physical property. This fact has stimulated a continuing search for new methods which yield as directly as possible the relevant parameters that describe defects: atomic configuration, concentration, formation and migration energies (or enthalpies), binding energies and recombination volumes, for example. Fortunately, a number of powerful tools have been developed to satisfy this need, and we will review some of them later. Some of the parameters just mentioned arise naturally within the framework of the statistical thermodynamics of point defects and clusters, a subject which will also be treated subsequently. Following that discussion, we will turn our attention to certain experiments which provide information about defect parameters and configurations. In this category are simultaneous length-change and lattice-parameter measurements, field-ion microscopy, x-ray and neutron scattering and transmission experiments, positron-annihilation studies, relaxation effects and channeling. This list is not exhaustive, of course, but rather reflects a certain bias toward newer techniques as well as toward several of the older methods which are likely to retain their importance. Measurements of electrical-resistivity changes will be cited frequently in spite of earlier remarks about interpretational difficulties, because shortcomings notwithstanding, this method will continue to be a dominant one for studying point defects.

Coincident with the development of new experimental tools, the high-speed digital computer has made possible detailed investigations of lattice defect models. Both static and dynamic calculations have been performed, and while there may be some serious questions concerning the validity of quantitative results, even the qualitative information has furnished valuable insight into the physical properties of defects, their interactions and dynamic behavior in metals. Such studies are frequently referred to as "computer experiments" to convey the idea in one simple phrase. Results of some of these calculations will be discussed, whereas alternate methods employing pseudopotential theory will be developed by other lecturers. From among the many possible examples of point defects three have been selected for a detailed treatment: the self-interstitial in f.c.c. and b.c.c. metals, and He in metals. Space limitations will not permit a discussion of C in Fe or H in metals, two very important systems.

Discussion of the point defects just mentioned will lead naturally into a review of the relationship between point defects and mechanical-property changes. There are five identifiable effects, all detectable with varying degrees of sensitivity: dislocation pinning, bulk effects, polarization effects, relaxation effects and a fifth effect having to do with changes in the temperature dependence of the elastic constants. Dislocation pinning will be described more completely by Prof. Hirsch and others, and only a brief comment or two will be presented in these lectures on point defects.

Finally, the technological effects associated with point defects are many and varied. Some aspects of the subject will have been touched upon throughout this presentation, but a more detailed treatment will have to be postponed to another time. Radiation effects are a primary

topic because of their continuing importance to our nuclear power technology.^{8a} Radiation hardening, radiation enhancement of rate processes, and void formation and swelling are all manifestations of point-defect interactions in solids, and are under intensive study in many laboratories. Here, too, time and space limitations preclude a discussion of much of this work.

II. STATISTICAL THERMODYNAMICS OF DEFECTS IN EQUILIBRIUM CONCENTRATION

A. Formation and Binding Entropies and Enthalpies

At first thought it may seem perplexing that a crystal should contain temperature-dependent concentrations of intrinsic defects since the internal energy will be increased by the work done to create the defects. Nevertheless the total free energy of the system will be lowered because of the entropy of mixing. We may imagine that a vacancy is created by the removal of an atom from the crystal to infinity and its return to the surface. This requires a certain amount of work, E_F , the formation energy of a vacancy. In reality the vacancy is created when an atom at the surface jumps out to start a new surface and the vacancy then diffuses into the interior of the crystal. The thermodynamic driving force for vacancy formation is thus the change in free energy associated with the creation of n vacancies. Minimization of the free-energy change with respect to n will yield the equilibrium vacancy concentration, n_{eq} .

The free energy to which we refer is the Gibbs free energy $G_{1V}^F = H_{1V}^F - TS_{1V}^F$ which applies to a system whose volume may not be constant. H_{1V}^F represents the change in enthalpy (or the work done to create a vacancy), and S is the associated entropy change. The latter consists of the contribution from the change in lattice vibrational frequencies which accompanies the creation of a vacancy.⁽⁹⁾ The change in the Gibbs free energy when n vacancies are created is thus,

$$\Delta G = nG_{1V}^F - TS_{mix} \quad , \quad (1)$$

where S_{mix} is the entropy of mixing given by the number of ways in which

n vacancies can be arranged on N lattice sites. At any temperature T , the free energy will be a minimum for a certain concentration of vacancies determined by the balance between enthalpy and entropy terms in ΔG . We can calculate this equilibrium in the following manner:

The number of ways, ω , in which n defects can be arranged on N lattice sites is just given by the binomial coefficient. This automatically takes into account the possibility of counting the same defect twice or more. Thus,

$$\omega = N!/(N - n)! n! , \text{ and} \quad (2)$$

the configurational entropy S_{mix} is given by elementary statistical mechanics by the expression

$$S_{\text{mix}} = k \ln \omega = k \ln \{N!/(N - n)! n!\}, \quad (3)$$

where k is Boltzmann's constant. Using the well-known Stirling's approximation to $\ln(N!)$ for large N we obtain

$$S_{\text{mix}} \approx k_B [N \ln N - (N - n) \ln (N - n) - n \ln n] . \quad (4)$$

The equilibrium value of n is that which minimizes ΔG . Thus, from the condition that

$$\partial \Delta G / \partial n = 0 , \quad (5)$$

we may obtain n_{eq} .

We find that

$$G_{1V}^F - T \frac{\partial}{\partial n} S_{\text{mix}} = G_{1V}^F + kT \ln \left(\frac{n}{N-n} \right) = 0 . \quad (6)$$

This leads to the equilibrium condition

$$n/(N-n) = e^{-G_{1V}^F/kT} , \quad (7)$$

and if $n \ll N$, then the atomic fraction of any isolated defect is given by the expression

$$n/N = C = e^{-G/kT} = e^{S/k} e^{-H/kT} . \quad (8)$$

This atomic fraction is generally designated C_{1V} when it applies to monovacancies. The enthalpy of formation H_F is frequently replaced by the energy of formation, E_F , in discussions because the experiments are performed under conditions of constant pressure and volume.

We can use some simple arguments to estimate the value of E_F . Suppose that the crystal is bound only by central forces between atoms, and that electronic or atomic rearrangements around a vacancy are neglected. Then, the cohesive energy per atom E_c , is given by

$$E_c = -\frac{1}{2} \sum_k V(r_k) , \quad (9)$$

where k is the summation over all lattice atoms; $V(r)$ is the inter-atomic potential.

Suppose that E_∞ = the energy required to remove an atom from the crystal interior to infinity. Then

$$E_\infty = -\sum_k V(r_k) = 2E_c . \quad (10)$$

Recalling the thermodynamic cycle for creating a vacancy we may conclude that in this simplified model

$$E_F = E_\infty - E_C = E_C \quad (11)$$

When we include the changes in E_F arising from the relaxations which were neglected, then the true formation energy is approximately

$$E_F = E_C - E_R \quad (12)$$

where E_R represents the effect of including relaxation around the vacancy. For metals, the calculation of E_R is very difficult, and entails the following computations as major components:

1. Redistribution of electrons around the defect, a quantum mechanical calculation,
2. determination of the change in closed-shell repulsion energy - a short-range interaction more easily taken into account than 1), and
3. calculation of the change in crystal energy arising from distortion around a defect - this can be calculated with reasonable accuracy by means of large digital computers.

Theoretical estimates of E_F and experimental results indicate that for vacancies this quantity is of the order of 1 eV. Interstitial formation energies, on the other hand, are generally several electron volts. Provided that the entropies of formation are not excessively large, it is unlikely that equilibrium concentrations of interstitials are appreciable relative to those of vacancies. Confidence in this assumption is furnished by the absence of experimental evidence for

appreciable interstitial concentrations in those experiments capable of detecting their presence. On the other hand, it is possible that one or two other point-defect configurations will have formation energies and entropy factors similar to those governing vacancy concentrations. Many experiments have been analyzed on the basis that divacancies and trivacancies are present at high temperatures although there is little direct evidence for their existence.

Thermodynamic calculations similar to those for monovacancies can be performed for higher-order clusters of vacancies. Consider, for example, the divacancy in which two vacancies are bound together with a binding energy E_{2V}^B .

If the number of nearest neighbors in a lattice structure is z , then there are $zN/2$ adjacent pairs of lattice sites. Assuming only that divacancies are present, n_2 of them can be distributed in

$$\omega_2 (zN/2)! / [(zN/2 - n_2)! n_2!] \text{ ways.} \quad (13)$$

Following the same reasoning as for monovacancies we find that

$$n_2/N = C_{2V} = \frac{1}{2} z \exp(-G_{2V}^F/kT) \quad (14)$$

However, in this case the Gibbs free energy is

$$G_{2V}^F = H_{2V}^F - TS_{2V}^F \quad (15)$$

where the subscript is used to identify the divacancy. Defining an enthalpy and entropy of binding as before:

$$H_{2V}^B = 2H_{1V}^F - H_{2V}^F$$

and

$$\Delta S_{2V} = S_{2V}^F - 2S_{1V}^F$$

we find that

$$\begin{aligned} C_{2V} &= \frac{1}{2} z \exp\{-2(H_{1V}^F - TS_{1V}^F)/kT\} \exp\{(H_{2V}^B + T\Delta S_{2V})/kT\} \\ &= \frac{1}{2} z (C_{1V})^2 \exp(\Delta S_{2V}^B/k) \exp(H_{2V}^B/kT) . \end{aligned} \quad (16)$$

H_{2V}^B is commonly replaced by the binding energy E_{2V}^B , and the binding entropy is given as ΔS_{2V}^B . The same reasoning can be carried through for a cluster of m vacancies and leads to analogous expressions:

$$\begin{aligned} C_{mV} &= \frac{z}{2} \exp(-G_{mV}^F/kT) \\ \text{or} \quad C_{mV} &= \frac{z}{2} \exp(\Delta S_{mV}^B/k) \exp(H_{mV}^B/kT) (C_{1V})^m . \end{aligned} \quad (18)$$

The value of z which must be used is often difficult to determine. Defect calculations sometimes cannot clearly distinguish between different defect configurations, for example, between first-neighbor or second-neighbor divacancy configurations. In fact, the anisotropy of most crystal structures makes it likely that different orientations of defect configurations involving the same neighbors, will give rise to different entropy and enthalpy factors.

Up until this point we have assumed that formation enthalpies and energies are temperature independent. In fact there are good physical arguments why they cannot be and these have been reviewed recently by Seeger.⁽¹⁰⁾ They vary with temperature in such a way that the Gibbs

free energy of formation decreases with increasing temperature more rapidly than if the enthalpy and entropy were constants. Nevertheless, it is a fortuitous consequence of thermodynamics that the slope at each point on an Arrhenius plot of the defect concentration is equal to the enthalpy at that temperature. This greatly simplifies the interpretation of experimental results.

B. Inclusion of Impurities

As a final consideration within the framework of statistical thermodynamics, we may examine the all-important case of impurities. In particular, we need to examine the equilibrium between point defects and defect-impurity complexes. The general approach should be equally valid for a vacancy bound to an interstitial impurity atom as for an interstitial that is similarly bound as long as the pre-exponential configuration term and the entropy factor are correctly evaluated in each case. Consider once again the monovacancy case. If there is a positive binding energy between a vacancy and a solute atom, we may expect that a certain concentration of vacancies will be bound to solute atoms and another concentration will be unbound, the total equilibrium vacancy concentration being the sum of the two. Expressions for this total concentration become complicated for anything but dilute alloys and simple monovacancy-solute atom combinations. The most common model is that developed by Lomer⁽¹¹⁾ who assumed that binding only occurs when a vacancy occupies a nearest-neighbor site to a solute atom. We define the following quantities:

C_S^0 = concentration of solute atoms

z = coordination number of each impurity

C_{VS} = concentration of vacancy-solute pairs

G_{VS}^B = Gibbs free energy of binding.

Following the same reasoning we used earlier to calculate the entropy of mixing we find that

$$C_{VS} = \frac{zC_S^0 \exp\left(-\frac{G_{1V}^F - G_{VS}^B}{kT}\right)}{1 + z \exp\left(-\frac{G_{1V}^F - G_{VS}^B}{kT}\right)} \quad (19)$$

Because zC_S^0 sites cannot be counted as permissible sites for free vacancies, the equilibrium concentration of unbound vacancies is:

$$C_{1V} = [\exp(-G_{1V}^F/kT)](1 - zC_S^0) \quad (20)$$

When C_S^0 becomes large enough to correspond to about 10^{-3} atom fraction, then the assumption that the free vacancy concentration is unaffected by the vacancy-impurity pairs becomes poor. The correction to C_{1V} can become larger than one percent in such cases. When clustering occurs, additional complications arise and are probably responsible for the wide variations in vacancy-solute binding energies reported in the literature for a given alloy. ⁽¹²⁾

III. DETERMINATION OF DEFECT PARAMETERS AND CONFIGURATIONS

A. Concentrations

1. Equilibrium Concentrations

In the previous sections, we have pointed out that intrinsic interstitial concentrations are negligible compared to vacancy concentrations. However, the vacancy concentration is itself extremely low and rises only to 10^{-3} to 10^{-4} at the melting point. Thus, only measurements at high temperatures can be expected to yield results of high accuracy. An obvious quantity to be determined is C_v , the total number of vacant sites. Two methods have been used primarily: simultaneous length-change lattice-parameter measurements,⁽¹³⁾ and, in a few cases, field-ion microscopy.⁽¹⁴⁾ However, the field-ion microscopy results were based on rather poor statistics, and the instrument is used primarily for studies of the spatial distribution and configurations of defects, and impurity effects. We can return to a discussion of field-ion microscopy in a subsequent section. That leaves us free to discuss length-change lattice-parameter measurements.

The simultaneous determination of thermal expansion by lattice parameter and length-change measurements so far has provided the only unambiguous values of the total vacant site concentration in metals under thermal equilibrium conditions. Complications arise when the crystal structure is not cubic but these have been investigated and are understood.⁽¹⁵⁾ However, other difficulties associated with a nonrandom distribution of the sources and sinks for vacancies and interstitials can arise even in cubic crystals. Nevertheless these experiments have been performed by Simmons and Balluffi,⁽¹³⁾ Nowick and Feder,⁽¹⁶⁾ and others.⁽¹⁷⁾ Conceptually, the underlying physical idea is straightforward. We can imagine that a vacancy is

formed by the removal of an atom from the interior to the surface, as in our earlier discussion. This produces an increase in volume of one atomic volume, Ω , assuming the lattice is rigid. But the atoms around the vacant site relax, and this relaxation alters the change in volume by some amount Δv per vacancy.

Let us suppose that a sample contains N atoms and V vacant sites. To a good approximation, because $V \ll N$, the vacancy concentration $C_V = V/N$. The volume of the sample without relaxation would be $(N+V)\Omega$, but allowing relaxation it becomes $(N+V)\Omega + V\Delta v$. For the moment we say nothing about the sign of Δv . We expect that under the new conditions, there will also be a new atomic volume $(\Omega + \Delta\Omega)$ such that

$$(N+V)(\Omega + \Delta\Omega) = (N+V)\Omega + V(\Delta v), \quad (21)$$

which leads to

$$\Delta\Omega = C_V(\Delta v). \quad (22)$$

A measurement of the lattice parameter, a , by x-rays will detect this change in atomic volume since the lattice parameter and the atomic volume are related. Another way of visualizing the effect is associated with the fact that the lattice parameter is a statistical average of the spacing between atoms on lattice sites. The relaxation introduces a small change in this average. In a cubic crystal $\Delta a/a = \frac{1}{3}C_V(\Delta v/\Omega)$.

The original volume of the perfect crystal is $N\Omega = v$. When V vacancies are created and the lattice is permitted to relax, the new volume becomes $N\Omega + V(\Omega + \Delta v)$. This implies that the total volume change Δv_t is

$$\begin{aligned} \Delta v_t &= N\Omega + V(\Omega + \Delta v) - N\Omega \\ &= V(\Omega + \Delta v). \end{aligned} \quad (23)$$

Thus the fractional volume change is given by

$$\Delta v_c / v = C_v (1 + \Delta v / \Omega). \quad (24)$$

In terms of change in length

$$\Delta l / l = \frac{1}{3} C_v (1 + \Delta v / \Omega) \quad (25)$$

This is what we would observe if we measured the change in the length of a sample or in its density owing to the introduction of a concentration, C_v , of vacancies. Subtracting the expression for the fractional lattice-parameter change from that for the fractional length change we find that

$$\Delta l / l - \Delta a / a = 1/3 C_v \quad (26)$$

and we see immediately that there is the possibility of determining the concentration of vacant sites directly from simultaneous measurements on the same sample. Note that $C_v = \sum C_{mv}$. That is, the measurements do not tell us directly what the distribution of vacancies is among the many possible clusters. Moreover, the experiments only become sensitive to C_v at high temperatures where the concentration of vacant sites is high, and this is precisely the condition under which multiple vacancies are most likely to form. Therefore, analysis of the data to determine C_{1v} requires some additional knowledge or insight into the correct values of free energies and entropies of binding.

Experiments have been carried out on a number of metals to date including Al, Pb, Cu, Ag, Au, Li, Na, Mg, and Cd. Agreement for a particular metal among different experimenters is reasonably good, and reflects primarily different assumptions concerning multiple-vacancy properties. Table I taken from the recent review by Seeger⁽¹⁰⁾

summarizes the results, and Fig. 1 illustrates typical experimental data. The figure shows that the effect of thermal expansion upon the length and lattice parameter is much greater than the difference between the two. It is also clear that the difference rapidly decreases with decreasing temperature. This reinforces the point made earlier that the accuracy of the experiment is highest at temperatures close to the melting point.

It should be pointed out that throughout the preceding discussion, we have neglected the presence of interstitials. The thermodynamic arguments mentioned earlier are the basis for this approach. If the existence of an appreciable concentration of interstitials had been included in the development, then we would have arrived at an expression for $C_V - C_I$ which could become negative for the appropriate combination of concentration and relaxation about the defects. A negative result has never been observed experimentally, and while this is not conclusive evidence that interstitials are negligible, it is consistent with this assumption.

Several other methods have been applied to the study of equilibrium defect concentrations with varying degrees of success. Measurements of specific heat and electrical resistivity⁽¹⁸⁾ at high temperatures are beset with problems of subtraction of background for the perfect metal, extrapolation of data to high temperatures and anharmonicity. At present there is no new technique to use which promises to yield more reliable values of C_V than the length and lattice-parameter measurements. Newer experimental techniques, however, dictate that some of the latter experiments be repeated to furnish more accurate results.

Table 1. Equilibrium concentrations of vacancies in pure metals from the comparison of x-ray and dilatometric thermal expansion measurements. (Ref. 10)

Metal structure melting temp.	Ref.	Temperature range [K]	$10^4 C_v(T_m)$	$H_{\text{eff}}^v/\text{eV}$	S_{eff}^v/k	Remarks	Best values (see text)
Al f.c.c. $T_m = 933 \text{ K}$	41	843-929	≈ 3	—	—	Only X-ray measurements;	$H_{\text{iv}}^v = 0.66 \text{ eV}$
	55	693-923	9.4	0.76	2.4	{length measurements taken from literature}	$S_{\text{iv}}^v = 0.6 \text{ k}$
	56	823-923	11 ± 2	0.64 ± 0.12	1.4 ± 1.1		$H_{\text{iv}}^v = 0.23 \text{ eV}$
	57	$\approx T_m$	8.7 ± 1.2	—	—		$\Delta S_{\text{iv}} = 2.2 \text{ k}$
	58	753-926	8.6	0.71	1.76		
	59	767-911	9.6	0.81	3.12		
Pb f.c.c. $T_m = 600 \text{ K}$	60	293-573	—	—	—	no measurable effect; $C_v(573 \text{ K}) < 3 \cdot 10^{-4}$	$H_{\text{iv}}^v = 0.50 \text{ eV}$
	41	298-596	1.5	—	—		$S_{\text{iv}}^v = 0.6 \text{ k}$
	61	541-598	2	—	—		
	62	445-600	1.7	0.49	0.7		
Cu f.c.c. $T_m = 1356 \text{ K}$	63	1211-1348	2.0	1.06	0.5	H_{iv}^v based on assumptions $S_{\text{iv}}^v = 0.6 \text{ k}$, $G_{\text{iv}}^v(T_m) \approx 0.3 \text{ eV}$	$H_{\text{iv}}^v = 1.06 \text{ eV}$
Ag f.c.c. $T_m = 1233 \text{ K}$	64	1173-1229	1.7	> 0.92	> 0 (theory)	H_{iv}^v based on assumptions $S_{\text{iv}}^v = 0.6 \text{ k}$, $G_{\text{iv}}^v(T_m) \approx 0.4 \text{ eV}$	$H_{\text{iv}}^v = 0.99 \text{ eV}$
Au f.c.c. $T_m = 1336 \text{ K}$	65	1173-1330	7.2	0.87	0.4	H_{iv}^v based on assumptions $S_{\text{iv}}^v = 0.6 \text{ k}$, $G_{\text{iv}}^v(T_m) = 0.33 \text{ eV}$	$H_{\text{iv}}^v = 0.92 \text{ eV}$
Li b.c.c. $T_m = 454 \text{ K}$	66	338-449	4.4	0.34 ± 0.04	0.9 ± 0.8		
Na b.c.c. $T_m = 371 \text{ K}$	67	280-368	19.4	0.16	-2.0 ± 0.5	two different measurements, large scatter	
	68	280-368	16.6	0.12	-3.8 ± 1.0		
	69	300-370	7.5	0.42 ± 0.03	5.8 ± 1.1		
Mg h.c.p. $T_m = 923 \text{ K}$	70	680-923	7.2	0.58	0 ± 0.3		
Cd h.c.p. $T_m = 594 \text{ K}$	71	450-591	5.6	0.40 ± 0.02	0.3 ± 0.4	H_{iv}^v based on assumptions $S_{\text{iv}}^v = 0.5 \text{ k}$, $2C_{\text{iv}}(T_m) \ll C_{\text{iv}}(T_m)$	$H_{\text{iv}}^v = 0.41 \text{ eV}$

Fig. 1

Fig. 1 Changes in length l and lattice parameter a as a function of T for Al. (Ref. 13)

2. Nonequilibrium Concentrations

The preceding discussion dealt only with the equilibrium concentration of vacancies. There are some means of deducing values for the nonequilibrium concentrations of point defects introduced by quenching or electron irradiation. Cold work introduces point defects, also, but they are accompanied by such large concentrations of dislocations, that it is not feasible to extract point-defect concentrations from subsequent experiments. Quenching or electron irradiation when performed carefully produce only the simpler point defects.

The measurements of vacancy concentrations in quenched gold are based upon the observation⁽¹⁹⁾ that excess vacancies in that metal precipitate in the form of stacking-fault tetrahedra under certain reproducible conditions. Great care must be taken to uniformly heat the sample and to quench it without introducing dislocations. The technique, as developed by Siegel and his colleagues,⁽²⁰⁻²¹⁾ depends for its success upon the availability of high-purity gold and the careful employment of transmission electron microscopy/ (see Fig.2). Samples are quenched from temperatures between 800 and 930C, and subsequently nucleated at 60C and aged at 40C for varying amounts of time. Each sample is then examined under the electron microscope. The size distribution and number of tetrahedra are measured accurately, and the concentration of vacancies stored in the tetrahedra, $C_V^* = (a/4)N_S L_{RMS}^2$ is deduced. Here N_S is the density of stacking-fault tetrahedra, L_{RMS} , their root mean square edge length, and a , the lattice parameter. In samples aged for 25 hours at 40C, precipitation is found to have reached completion. The associated tetrahedron concentration, $C_T^*(\infty)$, should be related to the concentration of vacancies present at the quench temperature. There are again several uncertainties such as the relative concentration of mono-, di- and trivacancies, the rates of diffusion of these species, and the

Fig. 2

Fig. 2 An idealized representation of the initial and final states of the samples in the quenching experiment. The triangles represent schematically the distribution of tetrahedron average size and density in the samples. (Ref. 21)

Fig. 3

Fig. 3 Schematic diagram of a field ion microscope (FIM). (Ref. 25)

efficiency of the stacking faults as sinks for the vacancies. The latter quantity has been measured directly and found to lie between 0.6 and 0.7.⁽²²⁾ Other parameters have been deduced from self-consistent calculations which combine self-diffusion, quenching, and electrical-resistivity data. The equilibrium vacancy concentration finally calculated is in reasonably good agreement with the length change-lattice parameter results quoted earlier. Although the study of stacking-fault tetrahedra is not applicable to a large class of metals, it has been useful as an independent means of determining vacancy properties.

Recently, a method has been developed for deducing interstitial concentrations in metals irradiated at liquid-helium temperature by energetic electrons. The technique involves a combination of lattice-parameter and diffuse x-ray scattering measurements. The former is proportional to C_I , the latter to C_I^2 . This subject will be considered in more detail in a subsequent section where we will examine the current techniques for deducing point-defect configurations in metals. We simply note here that the x-ray methods have yielded for the first time a value of C_I .

The power of modern field-ion microscopy (FIM) as a tool for studying point defects has been growing through the application of sophisticated data-acquisition techniques. Figure 3 illustrates schematically the basic elements of a field ion microscope.

The field ion microscope represents the only effective method of imaging the crystal lattice on an atomic scale. In addition to possessing this unique feature, FIM is compatible with several highly-desirable experiments:

1. In situ irradiation can be performed.
2. Low temperature annealing phenomena can be followed up to about 120K.
3. The atomic configuration of various defects can be studied.
4. Field evaporation permits layer by layer examination of the sample.

At present, the method is not without its drawbacks, however, perhaps the major one being that it is limited to the class of metals which can withstand stresses of $\sim 10^{11}$ dynes cm^{-2} arising from the high potential required for imaging. Nevertheless a number of bcc metals, as well as gold, have been successfully studied.

Some objections have been raised that the high local stresses alter the configuration and mobility of the observed defects so that results are not typical of the bulk material. Moreover, ambiguities can arise in distinguishing self-interstitials from impurities. Additional work is required on the theory of image formation in the FIM, especially for clusters and extended defects.

All of these problems have been considered by the Cornell Group under Balluffi and Seidman.⁽¹⁴⁾ They have shown that through the introduction of image intensification and automated data processing it is possible to examine systematically the thousands of photographic frames that must be analyzed to achieve quantitative results. It seems reasonable to suggest that other facilities as sophisticated as the one at Cornell should be constructed; one can imagine such an apparatus attached to an electron or ion accelerator, for example. Positive identification of the defects migrating in the various recovery stages would settle many controversies. In that

regard, it would be very helpful if a high-temperature FIM could be developed so that isothermal as well as isochronal experiments could be conducted through stages III and IV. Figure 4 relates the resolution of the FIM to the tip radius for various temperatures.

The atom probe field ion microscope is essentially an FIM which is attached to a time-of-flight mass spectrometer.⁽²³⁾ In an atom probe the atoms on the surface of an FIM tip are viewed by means of an internal intensification system based on a channel plate multiplier. This instrument provides the unique capability of measuring the charge-to-mass ratio of a single pre-selected atom on the surface of an FIM tip. It is to be noted that even though one may only analyze pre-selected atoms which are imaged on the surface of an FIM tip, the technique of field evaporation allows one to examine the interior of a specimen. Thus, the use of the atom probe FIM in combination with the pulse-field evaporation technique⁽²⁴⁾ allows one to obtain the three-dimensional spatial distribution of a given impurity atom.

The ability to analyze chemically single atoms is the basic requirement for studying point defect-impurity atom interactions. Hence, the atom probe FIM should be valuable for studying the following problems:^{8a}

1. The determination of which specific impurity atoms bind to vacancies in either bcc, fcc or hcp metals.
2. The determination of which specific impurity atoms bind to self-interstitial atoms (SIA's) in either bcc, fcc, or hcp metals.
3. The determination of the critical number of impurity atoms required to stabilize a void in either fast-neutron or ion-irradiated metals.
4. The determination of the critical number of impurity atoms required to stabilize either an interstitial or a vacancy cluster in either electron-, fast-neutron, or ion-irradiated metals.

Fig. 4 Theoretical resolution for helium accommodated to various temperatures (upper curve, no accommodation). (Ref. 25)

5. The role of impurity atoms in defocussing focused replacement collision sequences in either neutron, electron or ion-irradiated metals.
6. The study of solute atom-solute atom clusters in dilute alloys.

In addition, the following problems involving the interaction of impurity atoms with dislocations and planar boundaries are solvable by the atom probe FIM technique.

1. The determination of which specific impurity atoms bind to dislocations in either fcc, bcc or hcp metals.
2. The determination of which specific impurity atoms bind to specific types of grain boundaries in either fcc, bcc or hcp metals. In principle it should be possible to measure a Gibbs adsorption isotherm by studying specimens which have been equilibrated at a series of different temperatures. Since it is also possible to simultaneously determine the atomic structure of a grain boundary while chemically analyzing the boundary one would thus obtain a correlation between specificity of binding and grain boundary structure.

As examples of the application of FIM to studies of point defect concentrations we cite the work of Seidman and coworkers on quenched platinum. Notice that we are once again considering a nonequilibrium concentration of defects. Most applications of FIM seem to be directed toward such studies; as pointed out earlier, equilibrium investigations suffer from poorer statistics because they must be conducted at very low temperatures in the microscope. Even in the case of quenched or irradiated specimens, the statistics are poor. In the platinum work 32,700 ft. of film were examined. In all 137 monovacancies and 9 divacancies were found in 593,800 sites in three as-quenched samples. In five samples which were partially annealed after quenching, 76 monovacancies were found in 321,000 sites. Another 319,600 sites were scanned to determine how many so-called artifact monovacancies were present. The electrical resistivity of the as-quenched specimens was measured also so that a value for the resistivity per defect could be deduced. The experimental results for platinum were as follows:

1. Vacant lattice sites are the predominant defect at 1700C in platinum. Monovacancies dominate; $C_{2V}/C_{1V} = 0.06 \pm 0.02$ after the quench. It must be remembered that the ratio of mono- to divacancies is not characteristic of the quench temperature, but of some lower temperature, T^* , at which diffusion becomes too slow to sustain quasiequilibrium conditions.
2. The total concentration of vacant sites following a 1700C quench depended upon the electropolishing treatment given the specimens. For two different treatments the values were $(2.15 \pm 0.59) \times 10^{-4}$ and $(2.64 \pm 0.14) \times 10^{-4}$.

3. From the relative loss of divacancies compared to monovacancies following a high-temperature electropolish it was deduced that the divacancy in platinum is more mobile than the monovacancy. This has been suggested by a number of investigations, but was directly observed by FIM.
4. The upper limit on resistivity per defect in platinum is $(5.75 \pm 0.30) \times 10^{-4} \text{ } \Omega\text{cm (at fr)}^{-1}$.

Other investigations of defect concentrations, configurations and mobilities have dealt with a variety of questions arising in connection with radiation-induced damage. Some of these will be mentioned subsequently in the appropriate context.

B. Formation and Binding Energies

1. Thermodynamics

Although we have formally introduced the correct thermodynamic terminology in discussing enthalpies of formation and binding, henceforth we shall refer to these quantities as the energy of formation and binding, respectively. This is consistent with the language found commonly in the literature on point defects. Under most circumstances, the PV term in the enthalpy is totally negligible, and this has led to the change in notation and terminology.

We have seen that the equilibrium concentration of clusters of m vacancies is

$$C_{mV} = g \exp(-G_{mV}^F/kT) = g \exp(\Delta S_{mV}^F/k) \exp(-E_{mV}^F/kT) \quad (27)$$

where g is a geometrical factor related to the periodic structure of the lattice and the model describing vacancy binding. Thus, with a knowledge of C_{mV} we can determine E_{mV}^F from a combination of the equation above and

the thermodynamic requirement that

$$\frac{\partial E_{mV}^F}{\partial T} = T \frac{\partial S_{nV}^F}{\partial T} \quad (28)$$

The resulting relation is that

$$E_{mV}^F(T) = k \frac{\partial \ln C_{mV}}{\partial (1/T)} \quad (29)$$

An Arrhenius plot of C_{mV} versus $1/T$ will yield the value of $E_{mV}^F(F)$ at T . Unfortunately there are no direct experimental determinations of C_{mV} , but only of $C_V = \Sigma m C_{mV}$. Clustering is inherently involved in the measurements of C_V , and supplementary information is required to separate the components of C_V . The shape of the Arrhenius plot furnishes some clues. Curvature will occur under two circumstances:

1. A significant concentration of clusters is present at the measurement temperature, or the quench temperature (in the case of non-equilibrium experiments);
2. Clusters are negligible but E_{IV}^F and S_{IV}^F are temperature dependent.

Balluffi et al⁽¹⁴⁾ and Nowick and Dienes⁽²⁷⁾ have examined these two possibilities, separately. Figures 5 and 6 taken from the former authors illustrate the consequences. Figure 5 illustrates the behavior of the Arrhenius plot when clusters are present, while Fig. 6 refers to the case when the formation energies and entropies are temperature dependent.

Fig. 5 Arrhenius plots of $\ln(AC_{1V})$ versus $1/T$ calculated for a monovacancy divacancy system in thermal equilibrium with the various vacancy parameters given, showing the variation of curvature and slope as the defect parameters are changed. The curves are presented using an arbitrary vertical scale for clarity. (Ref. 14)

Fig. 6 Arrhenius plots of $\ln(AC_{1V})$ versus $1/T$ calculated for a monovacancy system with a temperature dependent energy and entropy of formation with various values of the parameter B . The curves are presented using an arbitrary vertical scale for clarity. (Ref. 14)

The conclusions drawn from these considerations are:

1. The presence of large concentrations of defect clusters at high temperatures may introduce observable curvature into an Arrhenius plot of a measured physical property change. This is a sufficient condition, however, and not a necessary one. That is, the curvature may be unobservable, but the deduced value of the monovacancy formation energy may differ significantly from the correct value.
2. A temperature-dependent monovacancy formation energy is unlikely to produce a detectable curvature in an Arrhenius plot. Yet the value of E_{1V}^F derived from the average slope of the plot can vary by the order of 10 percent for physically reasonable variations in the temperature dependence.

There remains the question of how important these temperature dependences are in metals. Seeger and Mehrer⁽²⁸⁾ have reviewed the situation and have concluded that the effects are generally small. The temperature dependences of the energy and entropy are not independent but are related by the thermodynamic relation

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{1}{T} \left(\frac{\partial E}{\partial T} \right)_P . \quad (30)$$

At low temperatures the entropy must be temperature dependent where quantum statistical mechanics is applicable. At high temperatures where classical statistics are a good approximation, anharmonicity of the lattice vibrations, and thermal expansion introduce a positive temperature coefficient in the entropy. Thus, $\partial E_{1V}^F / \partial T > 0$, in general. Physical arguments^(27,28) lead to the conclusion that the variations in E_{1V}^F and S_{1V}^F are sufficiently small that they may be expressed by the relations:

$$E_{1V}^F(T) = E_{1V}^F(T_0) + \alpha_F k(T - T_0) ,$$

and

$$S_{1V}^F = S_{1V}^F(T_0) + \alpha_F k \ln(T/T_0) .$$

(31)

T_0 is a reference temperature which should be of the order of the Debye temperature and k is Boltzmann's constant in these expressions. (28-31)
Theoretical estimates by a number of authors arrive at the conclusion that for f.c.c. metals the temperature dependence of monovacancy formation energy is smaller than for more open lattices.

The foregoing thermodynamic arguments are equally valid for the energies and entropies of migration. However, it is expected that α_M , the coefficient in the expansion of these quantities, will be larger than α_F . Nowick and Dienes⁽²⁷⁾ have suggested that the sum of $\alpha_F + \alpha_M$ is not larger than k . This would imply that α_F is a fraction of α_M . Calculations by Flynn⁽³²⁾ lead to just this conclusion for monatomic crystals. He finds that the temperature dependence of the monovacancy formation energy should be about one-third that of the corresponding migration energy.

We see from the preceding discussion that high-temperature equilibrium measurements are subject to some uncertainties arising from the temperature dependence of E_{IV}^F and S_{IV}^F . Nevertheless, these effects are likely to be small compared to uncertainties in binding energies and entropies.

Techniques other than that of simultaneous length and lattice parameter measurements suffer from additional drawbacks. As mentioned earlier, high-temperature specific heat⁽¹⁸⁾ and electrical resistivity^(18,33) measurements are subject to largely unknown background corrections owing to lattice anharmonicities and phonon scattering. Recently, a new method of determining monovacancy properties has been developing, and it holds out the promise of providing useful information derived from measurements in a temperature range where some of the preceding difficulties are absent. The method is based upon the properties of positron annihilation in metals. Although several reviews have recently appeared,⁽³⁴⁻³⁸⁾ the subject is sufficiently new that it

probably warrants discussion in reasonable detail here. The field is still in its infancy, and is therefore subject to further evaluation. At present, its application to point defects is focussed on studies of vacancy formation energies, vacancy-solute binding energies, and those large clusters of vacancies known as voids. In addition, a number of experiments have been performed on deformed metals and on metals undergoing cyclic stress. The experimental evidence is that the positron-annihilation process is altered when the positron annihilates in regions of imperfect solid. In order to understand why the positron is sensitive to defects and how positron experiments are performed, we need to begin with some background discussion.

2. Positron Annihilation Applied to Vacancy Studies

Because the positron was the first antiparticle to be discovered, it is not surprising that the fundamentals of positron physics are by now well documented. Modern quantum electrodynamics is capable of providing an explanation for all of the observed properties of the annihilation process wherein a positron and an electron are replaced in the final state by n photons ($n = 1, 2, 3 \dots$). In the decade of the fifties, perhaps due to the renewed interest in positrons aroused by quantum electrodynamics, studies of the annihilation process in solids began in earnest. Reviews of subsequent work are readily available in the open (39-44) literature. We will concentrate here only on recent developments in the application of positron annihilation to studies of imperfect solids. In particular, we will consider the present status of this field as it applies to metallic solids.

Being conjugate particles, the electron and positron have opposite parity so that the intrinsic parity of the annihilating pair must be odd. Thus the two states 1S_0 and 3S_1 both have odd parity. Considering the parity of the n-photon states which result from the annihilation process, one finds that when $J = 0$ and $n = 2$, states of even or odd parity are allowed. Therefore the 1S_0 state can decay into 2 photons each of energy mc^2 (≈ 511 keV). On the other hand, when $J = 1$ annihilation into 2 photons is forbidden. Therefore, the 3S_1 state cannot decay into 2 photons, but must decay into 3 or more. One-photon annihilation can occur, but it is essentially a three-body event, and the probability of its occurrence relative to that of two-photon annihilation is $\leq 7 \times 10^{-5}$.⁽⁴⁵⁾ Thus, although in principle, one-quantum annihilation could furnish information about electron-electron correlations in solids, in practice it has not become a useful effect.

Experimental measurements of lifetimes in gases lead to the discovery that a positron and an electron can form a bound state. This is positronium, Ps, which is a hydrogen-like system with an energy level scheme analogous to that of hydrogen, but with a reduced mass of $m/2$ instead of m where m is the electron mass. Thus the energy levels of Ps are given by the relation,

$$E_n = -\frac{me^4}{4\hbar^2 n^2} \quad (32)$$

The Ps ionization potential is $\frac{1}{2}Ry$ (≈ 6.8 eV), and positronium exists in a 1S_0 or 3S_1 1S state. The lifetime of the singlet (para) 1S_0 state is 1.25×10^{-10} sec whereas that of the triplet (ortho) 3S_1 state is 1.4×10^{-7} sec. The spin averaged lifetime $\approx 5 \times 10^{-10}$ sec. The ratio of the number of two-photon events to three-photon events is determined by the respective annihilation rates and statistical weights:

$$\frac{\text{2-photon annihilation rate}}{\text{3(3-photon annihilation rate)}} = \frac{1}{3} (1115) \approx 372.$$

Positron Sources

A search of the periodic table reveals that there are very few usable positron sources. A usable positron source in the present context is one that can be produced easily by neutron capture or through a charged-particle reaction, and that has a reasonably long half-life. A measure of the latter criterion is, of course, the ratio of the half-life to the duration of an experiment. Using these two criteria, one finds that the sources listed in Table II are of experimental value.

Table II. Positron Sources

Isotope	Half-life	Means of Production	End-point Energy
^{22}Na	2.58 y	$^{25}\text{Mg}(p, \alpha)^{22}\text{Na}$	0.54 MeV
^{65}Zn	245 d	$^{64}\text{Z}(n, \gamma)^{65}\text{Zn}$	0.33 MeV
^{64}Cu	12.8 h	$^{63}\text{Cu}(n, \gamma)^{64}\text{Cu}$	0.66 MeV
^{58}Co	71 d	$^{58}\text{Ni}(n, p)^{58}\text{Co}$, $^{65}\text{Mn}(\alpha, n)^{58}\text{Co}$	0.48 MeV
^{55}Co	18.2 h	$^{58}\text{Ni}(p, \alpha)^{55}\text{Co}$, $^{56}\text{Fe}(p, 2n)^{55}\text{Co}$	1.50 MeV
^{68}Ga	68 m	$^{66}\text{Zn}(\alpha, 2n)^{68}\text{Ga}$ ^{68}Ga ^{68}Ga 275d	1.90 MeV
^{57}Ni	36 h	$^{56}\text{Fe}(^3\text{He}, 2n)^{57}\text{Ni}$	0.85 MeV
^{90}Nb	14.7 h	$^{90}\text{Zr}(p, n)^{90}\text{Nb}$, $^{90}\text{Zr}(d, 2n)^{90}\text{Nb}$	1.50 MeV
^{44}Sc	3.9 h	$^{45}\text{Sc}(p, 2n)^{44}\text{Sc}$ ^{44}Ti ^{44}Sc 487	1.47 MeV

Typical source strengths used in experiments range from the order of μCi to a few mCi .

The most frequently used member of this group is ^{22}Na ; it is readily available albeit expensive. Its long half-life makes it ideal for all of the typical positron annihilation experiments. A less expensive alternative is ^{58}Co which can be produced in a nuclear reactor. ^{68}Ge and ^{44}Sc sources are coming into use for Doppler broadening experiments because they are daughter products of isotopes with long half-lives.

Note that the end-point energies of the positrons emitted from the sources listed in Table II are all greater than several tenths of an MeV. As they enter a metal, then, the positrons are moving rapidly, and one must ask how they lose their energy. The relevant questions are: how much time does a positron require to reach thermal energies, and how does this time, τ_T , compare with the lifetime against annihilation?

These questions were first investigated analytically by Lee-Whiting.⁽⁴⁶⁾ His calculation predated the modern many-body techniques and neglected all correlations. Carbotte and Arora⁽⁴⁷⁾ re-examined the process using standard propagator formalism. Considering only positron-electron interactions, they assumed that the positron loses energy only

through the creation of electron-hole pairs. The rate of energy loss is then given by the imaginary part of the positron self-energy operator. We note that Carbotte and Arora only calculated the energy-loss rate for low-energy positrons ($E_t \gtrsim 5$ eV), and thereby neglected plasmon creation. In fact, plasmon creation is the dominant mode of energy loss in the kilovolt region.

Carbotte and Arora found that most of the thermalization time occurs toward the end of the positron range. They also noted that the thermalization time increases with increasing electron density. This is because screening increases with electron density, and the stronger the screening the weaker the coupling of the positron to the electronic system.

For positron energies $\leq \sim 0.1$ eV, they obtained an expression identical to Lee-Whiting's when the Thomas-Fermi screening length for the electron gas is used as the screening parameter in Lee-Whiting's formula. Their more exact treatment reveals that at room temperature τ_T for Na and Al are much shorter than the lifetime for annihilation. In fact this is true for Na throughout the temperature range from 110K to 600K. However, for Al, $\tau_T > \tau_{\text{Annih.}}$ at 110K. Thus thermalization is not complete in this case. On the other hand, Carbotte and Arora pointed out that the time required for a positron to fall to an energy of ~ 0.1 eV is very short compared to typical lifetimes. Therefore, they assert, it is generally a good assumption that the positron momentum is negligible at the instant of annihilation.

Recently, consideration has been given to effects of the positron-phonon interaction in metals by Mikeska.⁽⁴⁸⁾ He has investigated the role of this interaction in the thermalization process as well as its effect upon the positron effective mass. His treatment considers positrons in thermal equilibrium with the electrons and phonons. He finds that although the phonon contribution to the effective mass is

negligible, for thermal energies the phonon contribution to the momentum distribution of the positrons can become much larger than the electron contribution. The rate of energy loss due to phonon emission at $T = 0$ is

$$R_{ph}(p)_{T=0} = \frac{\eta\pi}{k_F} C^2 p^3, \quad (33)$$

where C is the velocity of sound, k_F is the wave vector at the Fermi energy, p is the momentum of the positron, and η measures the strength of the positron-phonon interaction and is of order unity.

The rate of energy loss to electrons at low energies according to Carbotte and Arora is

$$R_{elec.-hole\ pairs} = \frac{1}{105} \frac{\pi}{k_F} \frac{p^6}{m^2 k_F}. \quad (34)$$

Comparing Eq. 2 and Eq. 3, Mikeska observed that in the case of sodium, for example, $R_{ph} > R_{eh}$ for $p^2/2m <$ an energy corresponding to $230^\circ K$.

Moreover, he found that the positron momentum distribution is not Boltzmann-like. If one identifies the 2nd moment of the momentum distribution with the observed minimum temperature of the positron, then for the Mikeska distribution function

$$\left\langle \frac{p^2}{2m} \right\rangle \approx 1.8 \left(\frac{3}{2} kT \right). \quad (35)$$

Therefore the mean energy of the positron is larger than that predicted on the basis of a Boltzmann distribution.

It turns out theoretically that the positron effective mass is nearly equal to unity, but an apparent effective mass closer to two has been deduced experimentally on the incorrect assumption that the

positron momentum is described by a Boltzmann distribution. Thus, Mikeska's results apparently explain most of the discrepancy between the theoretical effective mass derived neglecting positron-phonon interactions, and that deduced from the observed thermal smearing of the experimental momentum distribution.

Charge Density Enhancement

A natural quantity to investigate in studying positron annihilation in metals is the annihilation rate, or its reciprocal, the lifetime. In metals one expects that this quantity will provide information about the electron density at the positron. Generally, in this field, electron density is described in terms of a dimensionless parameter r_s , the radius of the sphere which contains just one electron. Thus, if n is the number of valence electrons per cm^3 then

$$n = \left[\frac{4}{3} \pi a_0^3 r_s^3 \right]^{-1} \quad (36)$$

where a_0 is the radius of the first Bohr orbit.

From Sommerfeld's free electron theory one finds that

$$\lambda_{\text{Somm.}} = 12 r_s^{-3} \times 10^9 \text{ sec}^{-1}.$$

This result predicts a rather strong variation of lifetime with electron density. However, such a dependence is not observed. In fact, the variation of annihilation rate with r_s is found to be rather small; most metals exhibit lifetimes of about $1.5\text{--}2.0 \times 10^{-10}$ sec. The reason for the failure of the Sommerfeld theory is the strong Coulomb interaction between the electrons and the positron. Thus, it is not the average electron density that is important, but rather the electron density at the positron position. Calculations taking into account this fact have been performed by several authors. (49-51) One

example is the work of Sjölander and Stott⁽⁵¹⁾ in which a new method for handling screening effects is used to account for the strong electron-electron correlations. The electron distribution is given in terms of the positron-electron static pair-correlation function $g^{+-}(r)$. Figure 7 taken from their paper illustrates the effect of the strong positron-electron attractive potential. The figure clearly shows that a positron in a metal becomes surrounded by its own polarization cloud. The total induced charge is unity however, so that total charge neutrality is preserved. The annihilation rates calculated on the basis of this theory are in good agreement with experiments in aluminum and in the alkali metals, except for cesium which corresponds to an r_s of about 5.7. The results become unrealistic beyond an r_s of about 5.

At present, there is no reason to believe that positronium is formed in metals. If it were, a so-far unobserved long lifetime should arise from 3S_1 annihilation. Or else, a rapid triplet-singlet conversion could give rise to an unobserved lifetime equal to four times the 1S_0 lifetime, i.e., 5×10^{-10} sec. The primary reason given for the absence of positronium is that a positronium-like bound state cannot form at normal metallic electron densities, but only at densities such that $r_s \geq 8.6$.⁽⁵²⁾ For real metals $1.8 \leq r_s \leq 5.5$.

Since the two antiparticles disappear during an encounter, all information about the event is carried away by the photons. We have noted earlier that two-quantum annihilation is most common, and it is the event most often studied in metals.

Basically there are three types of measurements commonly performed.

Fig. 7 The static pair correlation function according to Sjölander and Stott (full line) and using linear response theory (broken line). (Ref. 31)

Fig. 8 Schematic diagram of a typical 2-photon angular correlation experiment.

One is a measurement of the positron lifetime, another is the Doppler broadening of the annihilation line, and the third is a measurement of the angular correlation of two-photon annihilation radiation.

Suppose that $\Gamma^2(p)dp$ is the probability per unit time that annihilation into two photons whose total momentum lies between p and $p+dp$ takes place. Then it has been shown⁽⁵³⁾ that if the electron is in a state ψ_i , and the positron in state ψ_t ,

$$\Gamma_i^{2Y}(p)dp = \frac{a^3}{4\pi^2} \left| \int \psi_i(r) \psi_t(r) e^{ip \cdot r} dr \right|^2 dp, \quad (37)$$

where atomic units have been used and the atomic unit of time is 2.42×10^{-17} sec. The annihilation rate into any total momentum then must be,

$$\Gamma_i^{2Y} = \int \Gamma_i^{2Y}(p) dp = \frac{a^3}{4\pi^2} \iint \psi_i(r) \psi_t(r) e^{ip \cdot r} dr dp. \quad (38)$$

By Parseval's theorem this becomes

$$\Gamma_i^{2Y} = 2\pi a^3 \int |\psi_i(r) \psi_t(r)|^2 dr = 2\pi a^3 \int |\psi_i(r)|^2 |\psi_t(r)|^2 dr, \quad (39)$$

the partial annihilation rate, λ_i . Summing over all occupied electron states we obtain the total annihilation rate, the reciprocal of which is the lifetime of the positron:

$$\tau^{-1} = \sum_{\text{occ. } i} \Gamma_i^{2Y}. \quad (40)$$

Now let us consider a typical angular-correlation experiment. The sample and positron source are located, as shown in Figure 8 midway

between a pair of photon detectors. Generally a linear slit is placed in front of each detector and the sample-detector distance is made long enough so that the angular resolution is between 0.5 and 1.0 mrad. Appropriate lead shielding is placed around the source so that the detectors see only photons created in the sample.

If the annihilating pair were at rest in the center-of-mass system, then the two quanta would be emitted precisely in opposite directions in the laboratory system. We have concluded in our earlier discussion of thermalization that for most purposes one may assume that the positron is thermalized and, hence, it is essentially at rest. The annihilating electron, however, is not. Therefore, the center of mass of the annihilating pair is in motion, and the two photon directions deviate slightly from 180° relative to one another in the laboratory system. This slight deviation is what gives rise to the demand for high angular resolution. In practice one arm of the instrument shown in Figure 8 is held stationary while the other is moved in small angular increments in the z direction, for example. In order to obtain sufficient sensitivity with the available positron sources, one employs large-volume detectors whose long dimension is parallel to the collimating slits. Thus, the detectors are insensitive to the x and y components of momentum, and the experiment determines only one component, say p_z . From the figure we see that to a good approximation for the small angular range under consideration (roughly 0-50 mrad) $p_z = mc\theta$ ($= c\theta$ in atomic units). In terms of the expressions given in the previous section the rate of annihilation into the momentum region between $p_z = c\theta$ and $c(\theta+d\theta)$ becomes, (54)

$$N_z(\theta) = \sum_i c \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Gamma_i(p_x, p_y, c\theta) dp_x dp_y \quad (41)$$

and the area under the angular correlation curve is

$$\int_{-\pi}^{+\pi} N_z(\theta) d\theta = \sum_i c \int_{-\pi}^{+\pi} \Gamma_i(p_x, p_y, c\theta) dp_x dp_y d\theta \quad , \quad (42)$$

a quantity proportional to the total annihilation rate.

Of course, in practice, the area under the actual measured angular-correlation curve is just equal to the total number of coincidence counts collected. But if the normalization factor were known this area could be converted into an annihilation rate or a total lifetime.

If one calculates electron wave functions for the electrons in various shells of an atom or for valence electrons, and if one also knows the positron wavefunction, then it is possible to generate a theoretical angular-distribution curve. This can be normalized to a measured distribution, and one then can make some assessment of the relative contribution which electrons in different states make to the observed annihilation process. An example of the method applied to aluminum is shown in Figure 9 taken from the work of Berko and Plaskett (Fig. 12, Ref. 54). The theoretical curves, shown as solid lines, have been normalized to the experimental counting rate at 0°. The open circles are the experimental points. The parabolic curve corresponds to the angular distribution arising from annihilation with the three valence electrons, while the other curve represents the contribution from l-shell electrons. This illustrates the high-momentum contribution to the angular distribution which are assumed to come from core annihilations.

Considering annihilation in a gas of free electrons, it is easy to see how the parabolic valence-electron distribution in Figure 10 comes about. We know that the momentum of the photons comes from the electrons since the positron is essentially at rest. The electron momenta are distributed uniformly throughout a sphere whose radius is the Fermi momentum. The conventional method of measuring an angular distribution corresponds to taking a slice through the sphere at a

Fig. 9 Angular distribution for aluminum. The points are experimental data for the [111] direction in aluminum, and the solid curve is a theoretical one normalized to the experimental counting rate at 0°. (Ref. 54)

Fig. 10 A slice through the Fermi surface for a free-electron gas showing how the parabolic angular distribution arises.

transverse momentum $k_z = mc\theta$. The area of this slice as shown in Figure 10 is going to be proportional to the rate of annihilation into the angular region θ to $\theta + d\theta$. But this area is proportional to $k_F^2 - k_z^2$, and so the expected distribution for a Fermi gas is an inverted parabola. Many metals exhibit this form of low-momentum distribution (aluminum, for example in Figure 9). Consequently one usually speaks of this portion of an angular-distribution curve as the valence or conduction-electron part. We shall learn shortly that it has become common practice to resolve a measured distribution into a parabolic and a Gaussian part for the purposes of analysis. This is an approximation that is valid for some solids but it assumes, among other things, that the valence electrons make no contribution to the high-momentum tail of the angular-correlation distribution.

We noted in the preceding section that the detectors used in angular-correlation experiments are insensitive to the component of electron momentum lying along the direction of the emitted photons. This component gives rise to the usual Doppler broadening of the annihilation photon at 511 keV. If E_0 is the rest energy of the electron, then the broadening ΔE is given by the relation

$$\Delta E/E_0 = (v_{c.m.})_x/c$$

Assuming that the positron is at rest, we find that the velocity of the center of mass, $v_{c.m.}$, equals $\frac{1}{2} v_e$, the electron velocity.

Thus,

$$\Delta E/E_0 = \frac{1}{2} (v_e)_x/c \quad (43)$$

or

$$\Delta E = (p_x/2m_0 c) E_0, \text{ where } p_x \text{ has its usual meaning.}$$

If the medium is isotropic with respect to the annihilation process, then all momentum components are equivalent. This means that p_x is equivalent to $p_z = m_0 c \theta$ as determined in the usual angular-correlation experiment.

Thus,

$$\Delta E = (m_0 c \theta / 2 m_0 c) E_0 = \frac{1}{2} E_0 \theta = 255.5 \theta \text{ eV}, \quad (44)$$

where θ is in milliradians and ΔE in electron volts. So we see that a one milliradian angular resolution corresponds to a Doppler broadening of 255.5 eV, and in principle, the two experimental techniques can furnish the same information. If the instrumental resolution is unfolded from the Doppler-broadened annihilation peak, then the electron momentum distribution will be recovered.

The method of performing these experiments is to use a high-resolution Ge(Li) detector as part of an energy spectrometer. The instrumental resolution function $f(E, E')$, is determined by least-squares fitting of a multiparameter analytical expression to the shape of an unbroadened line from a known decay scheme at an energy conveniently near 511 keV. If the true energy distribution in the Doppler-broadened line is $N(E)$ then the convolution function

$$g(E) = \int N(E') f(E, E') dE' \quad (45)$$

can be calculated and compared with the experimental data point by point using least-squares analysis. This procedure yields the true distribution $N(E)$. Difficulties in obtaining a good fit arise from the determination of the resolution function, and from problems associated with the deconvolution of the experimental peak.

The limiting experimental factor at present is the FWHM of the Ge(Li) detector. The best available detector has a FWHM of about 1.1 keV; this corresponds to an angular resolution of about 4 mrad, not very good by comparison with angular-correlation instruments. The FWHM of these detectors is given by,

$$\text{FWHM} = 2.36\sigma(E\epsilon)^{1/2} \quad (46)$$

where σ is the statistical width, E the energy of the photon, ϵ the energy required to produce a charge pair, and F is a characteristic of the charge-pair creation process called the Fano factor. It is a measure of the fraction of the total number of electron-hole pairs created that is statistically independent. If the FWHM were smaller then there would be real promise for this method as an alternative to angular correlation measurements. For defect studies, only changes in the lineshape have been used, and the possibility of competing with angular-correlation experiments remains unexploited.

The method has one distinct advantage. It requires only one detector and no coincidence circuitry. Data can be collected rapidly and the statistics are, therefore, very good. Stabilized electronics are essential, however. A table prepared by Rama Reddy and Carrigan⁽⁴⁵⁾ comparing angular correlation and Doppler broadening methods is reproduced here as Table III.

The measured lifetimes of positrons in metals are all around 0.2 nsec. There are now commercially available electronic components that can be assembled to measure such short times. They operate near the limit of their capability, however, and great care is required to achieve reproducible results.

Table III. Comparison of 2-Photon Angular Correlation and Doppler-Broadening Techniques (Ref. 45).

Feature	Conventional 2-photon angular correlation	Doppler broadening
1) Basic measurement	angular correlation	line broadening
2) Resolution	very good; 0.5 mrad typical (4 mrad/1 keV) No convenient calibration in this method	not very good yet, best FWHM $\sim$ 1.1 keV at present
3) Electronic circuitry	fast coincidence	linear pulse analysis
4) Measured parameter	transverse pair momentum	longitudinal pair momentum
5) Applicability	a) useful for 2- γ decay only b) desired portion of curve can be scanned at will c) slow counting rate in "tail"	a) useful for 1,2,3 photon decay b) entire energy spec- trum obtained at once c) may be better for "tail" data because counting rate is high
6) Sample constraints	a problem - limits angu- lar resolution, count- ing rate, etc.	no problem in working with high pressures, variable temperatures, electric and magnetic fields, etc.
7) Data acquisition rate	slow	about 10 times faster with weaker sources than for angular-cor- relation method.

The standard method of measuring lifetimes employs delayed-coincidence counting, and a typical system is shown in the block diagram of Fig. 11. The system includes a time-to-amplitude converter by means of which the elapsed time between the emission of the positron and its annihilation in the sample is converted to a proportional pulse which is stored in a multichannel analyzer. The distribution of time intervals, and therefore pulse heights, is an exponential whose decay time is the mean life, τ , provided that the natural delay is long compared to the slope of the prompt resolution curve. The time resolution is determined by measuring the pulse-height distribution from a source that emits two coincident gamma rays, for example ^{60}Co . The typical spectra would appear as in Fig. 12. The lifetime equals the difference in the centroids of the two curves shown in Fig. 12. Newton^{54a} has shown that it also can be determined from the slope of the tail of the delayed coincidence spectrum. However, generally the analysis is performed by computer fitting of a sum of exponentials to that part of the delayed curve corresponding to large positive delays. The prompt resolution curve is often approximated by a Gaussian and folded with the exponentials in a least-squares calculation. In the case of metals, it is generally assumed that the delayed curve consists of only two exponentials. One exponential corresponds to the desired lifetime while the other is of weak intensity ($\sim 2-5\%$) and arises from annihilation within the source. The latter usually yields a lifetime of ~ 0.5 nsec.

The use of delayed-coincidence circuitry requires that care be taken to achieve good electronic stability. The major problem arises from the so-called "walk" effect in fast-pulse spectrometry. Walk arises because pulses of the same rise time but different amplitude cross the zero-level discriminator at slightly different times. Thus,

Fig. 11 Block diagram of slow-fast delayed coincidence method for time spectroscopy of annihilation photons.

Fig. 12 Typical appearance of prompt and delayed spectra obtained by the delayed coincidence technique depicted in Fig. 11.
(Ref. 54a)

the timing has an inherent error in it. Methods have been devised for reducing this effect and are now in common use. The stability of the electronic system is both temperature and humidity sensitive. It is essential that the experiments be conducted in an area where good control over these ambient conditions exists. Recent developments in integrated circuitry may reduce the problem, for small IC chips lend themselves to temperature regulation through the use of cooling devices such as thermoelectric coolers.

The positron literature has grown rapidly with applications to point defects as well as to extended defects introduced by deformation or cyclic fatiguing. We will discuss the general principles upon which the defect studies are based. Detailed reviews are available for those who wish to delve more deeply into the subject.^(34-38,55) It seems likely that positron-annihilation experiments will take their place beside length-lattice parameter measurements as a new means of studying point defects in equilibrium. We shall see later that nonequilibrium experiments are also meaningful.

(56)

In 1967 MacKenzie, Khoo, McDonald, and McKee reported that the positron lifetime showed a reversible increase with increasing temperature which they suggested might be caused by thermally induced vacancies. Their results were explained in terms of Brandt's "trapping model" by Bergersen and Stott and independently by Connors and West. The theory which they developed is based on two simple assumptions: The first assumption is that the annihilation lifetime of a positron trapped in a monovacancy, τ_V , is longer than the lifetime of a positron in the lattice, τ_L , because the electron density is lower in a vacancy than in the lattice. The second assumption is that positrons become trapped at a rate $\mu_{1V}c_{1V}$ which is proportional to the monovacancy concentration c_{1V} . Here μ_{1V} is the specific positron trapping rate which is defined as the positron trapping rate per unit vacancy concentration.

If $n_L(t)$ and $n_{1V}(t)$ are the fraction of free and trapped positrons, respectively, as a function of time we can write a set of simple equations for their time rate of change

$$\begin{aligned} dn_L(t)/dt &= -n_L(t)/\tau_L - \mu_{1V}^c(T)n_L(t) \quad , \\ dn_{1V}(t)/dt &= -n_{1V}(t)/\tau_{1V} + \mu_{1V}^c(T)n_L(t) \quad . \end{aligned} \quad (47)$$

That is, the change in the fraction of positrons in the lattice per unit time is determined by the fraction lost through annihilation and the fraction lost through trapping; and the change in the fraction of positrons trapped in vacancies per unit time is given by the fraction lost through annihilation plus the fraction gained through trapping. If we assume that initially no positrons are trapped we have for the observed rate of annihilation as a function of time and temperature

$$\begin{aligned} P(t,T) &= (d/dt) [n_L(t) + n_{1V}(t)] \\ &= \frac{\tau_L \mu_{1V}^c(T)}{[\tau_{1V} - \tau_L + \tau_{1V} \mu_{1V}^c(T)]} e^{-t/\tau_{1V}} \\ &\quad + \frac{(\tau_{1V} - \tau_L) [1/\tau_L + \mu_{1V}^c(T)]}{[\tau_{1V} - \tau_L + \tau_{1V} \mu_{1V}^c(T)]} e^{-[1/\tau_L + \mu_{1V}^c(T)]t} \quad . \end{aligned} \quad (48)$$

This is a sum of two exponential components whose decay rates and intensities depend on τ_L , τ_{1V} , and $\mu_{1V}^c(T)$.

The solution can be expressed in terms of the mean positron lifetime defined as $\bar{\tau}(T) = \int_{-\infty}^{\infty} tP(t,T)dt$. Substituting $P(t,T)$, from above we obtain

$$\bar{\tau}(T) = \tau_L \left(\frac{1 + \tau_{1V} \mu_{1V}^c(T)}{1 + \tau_L \mu_{1V}^c(T)} \right) \quad . \quad (49)$$

We see that at low temperature when $\mu_{1V}^c(T)$ is small compared to $1/\tau_{1V}$ and $1/\tau_L$, $\bar{\tau}$ approaches τ_L , the lifetime of positrons in the lattice. Similarly

at high temperatures when $\mu_{1V}c_{1V}(T)$ is large, $\bar{\tau}$ approaches τ_{1V} , the lifetime in the vacancy. At intermediate temperatures $\bar{\tau}$ takes some value between the two extremes. This is qualitatively the experimentally observed behavior as seen in Fig.13. By inverting the equation for $\bar{\tau}$ we obtain the concentration of vacancies

$$c_{1V}(T) = \frac{\bar{\tau}(T) - \tau_L}{\mu_{1V}\tau_L[\tau_{1V} - \bar{\tau}(T)]} \quad (50)$$

To deduce the monovacancy formation energy from positron-lifetime experiments we can make use of the foregoing equation in the following way: First we can make measurements at low temperatures, where there is little trapping to obtain τ_L ; next we can make measurements at high temperatures, where most of the positrons are trapped, to obtain τ_{1V} ; and finally, we can make measurements at intermediate temperatures to obtain $\bar{\tau}(T)$. From the slope of a semilogarithmic plot of the quantity $[\bar{\tau}(T) - \tau_L]/[\tau_{1V} - \bar{\tau}(T)]$ as a function of $1/kT$ we should obtain the monovacancy formation energy E_{1V}^F .

The foregoing procedure for obtaining the monovacancy formation energy is based upon several assumptions, some of which require further examination:

1. Those which are quite reasonable and which are supported by experimental evidence:
 - (a) Positrons become trapped in vacancy-type defects.
 - (b) The lifetime of a trapped positron is different from the lifetime of a positron drifting freely through the lattice. ^(57-59, 60)
2. Those which require further investigation:
 - (a) The specific positron trapping rate, μ_{1V} , is a constant independent of temperature. ⁽³⁴⁻³⁸⁾
 - (b) No detrapping of positrons occurs, i.e., that once a positron is trapped it stays trapped until annihilation. ^{(34-38) (61, 62)}

3. Those which are often made in this type of analysis but which are incorrect:

- (a) The mean lifetime $\bar{\tau}$ may be obtained by fitting the data with a single exponential component.
- (b) The lifetime in the lattice, τ_L , may be obtained by fitting data from low temperatures.
- (c) The lifetime in the vacancy trap τ_{1V} , may be obtained by fitting data from high temperatures.

In addition there are errors associated with commonly used methods of taking the instrumental resolution into account when extracting lifetimes from real experimental data. The assumption that the lifetime in the trap, τ_{1V} , can be obtained by a fit to the high-temperature lifetime data is at best an approximation. Even at the melting point, typically only 95 percent of the positrons are trapped. Although the assumption that τ_L can be obtained from low-temperature measurements seems at first reasonable, Fig. 14 gives evidence that this is not correct. The flattening off of this graph at low temperatures suggests that the trapping rate κ_{1V} is not purely exponential in $1/kT$, but rather has the form

$$\kappa_{1V} = \kappa_{1V}^0 e^{\frac{S_{1V}^F}{k}} e^{-\frac{E_{1V}^F}{kT}} + \kappa_D \quad (51)$$

where κ_D represents the presence of temperature-independent defect traps. We can interpret these temperature-independent defect traps as being associated with dislocations, although they may be some other type of temperature-independent traps such as might exist on the surface of the metal. It is known from work on deformed metals that positrons are

Fig. 13 Mean lifetime, $\bar{\tau}$, of positrons in aluminum versus temperature at which measurements were performed.

Fig. 14 Arrhenius plot of trapping rate versus $1/kT$ showing flattening off at low temperatures. (Ref. 65)

sensitive to dislocations, ^(61,63,64) and it is also known that although annealing near the melting point can reduce the dislocation density, the positrons may be sensitive to those dislocations which remain in the samples even after they were annealed. Therefore τ_L cannot be obtained from a single-exponential fit to low-temperature data.

In order to eliminate the assumptions concerning τ_L and τ_{1V} an extension of the trapping model which allows for the presence of several types of defect traps has been developed. ⁽⁶⁵⁾ The trapping rate for each type of trap is taken as

$$\kappa_j(T) = \nu_j c_j(T) = \nu_j e^{S_j^F/k} e^{-E_j^F/kT}, \quad (52)$$

where $j = 1 \dots m$ denotes the defect type,

$\kappa_j(T)$ = the trapping rate,

ν_j = the specific trapping rate,

$c_j(T)$ = the concentration of defects, and

S_j^F and E_j^F are the defect formation entropy and energy, respectively.

With the trapping rates defined in this way the temperature-independent term may be represented by setting $E_j^F = 0$, for one particular value of j .

Assuming that a positron in trap type j has an annihilation rate $\lambda_j (= \tau_j^{-1})$, we write the rate equations for $n_L(t)$, the fraction of free positrons, and $n_j(t)$, the fraction of positrons trapped in defect type j in the form:

$$\begin{aligned} dn_L(t)/dt &= -\lambda_L n_L(t) - \sum_{j=1}^m \kappa_j(T) n_L(t) \quad , \\ dn_j(t)/dt &= -\lambda_j n_j(t) + \kappa_j(T) n_L(t) \quad . \end{aligned} \quad (53)$$

This set of differential equations can be solved for the time distribution of the annihilations

$$P(t, T) = -d \left(n_L(t) + \sum_{j=1}^n n_j(t) \right) / dt \quad (54)$$

$$= \sum_{j=1}^n \frac{\lambda_j \kappa_j(T)}{s - \lambda_j} e^{-\lambda_j t} + s \left[1 - \sum_{j=1}^n \frac{\kappa_j(T)}{s - \lambda_j} \right] e^{-st}$$

where

$$s = \lambda_L + \sum_{j=1}^n \kappa_j(T)$$

This is a sum of exponential terms, one term for each defect type j with decay rate equal to the annihilation rate λ_j , plus one additional term with a decay rate which is a function of both the annihilation rate in the perfect lattice and the trapping rates $\kappa_j(T)$. A theoretical justification for these equations based upon Waite's theory of diffusion-limited reactions has recently been published by Frank and Seeger. (66) They have shown that the foregoing model is valid provided that the trapping process is not diffusion-limited and that escape from traps is very improbable.

Most of the applications to defects have employed the simple two-state trapping model which leads directly to expressions for the mono-vacancy formation energy in terms of measured characteristics of the annihilation process. For example, if any annihilation characteristic, F , is a linear function of the positron states, j , such that,

$$\bar{F} = \sum_j F_j n_j / \sum_j n_j,$$

where n_j has the same meaning as in Eqs. (53) and (54),

then $F = F_F P_1 + F_T P_2$, in the two-state model

where P_1 and P_2 are probabilities of annihilation from free or trapped states, respectively. F may be the mean positron lifetime or the normalized peak height of an angular-correlation distribution.

In the two-state model

$$P_1 = \frac{\lambda_1}{\lambda_1 + \mu C_{1V}} \quad (55)$$

$$P_2 = 1 - P_1 = \frac{\mu C_{1V}}{\lambda_1 + \mu C_{1V}} .$$

Solving for the vacancy concentration we obtain

$$C_{1V} = \frac{\lambda_1}{\mu} \left(\frac{F - F_f}{F_t - F} \right), \text{ or } \ln \left(\frac{F - F_f}{F_t - F} \right) = - \frac{E_{1V}^F}{kT} + \text{const.} \quad (56)$$

An Arrhenius plot thereby provides a value for E_{1V}^F . The trapping model is generally applied to angular correlation data in this manner. (67)

A similar analysis of lifetime data can be performed. From the expressions for the intensities I_1 and I_2 , associated with annihilation from each of the two possible positron states we deduce that,

$$\ln \frac{I_2}{I_1} = \ln \frac{\mu C_{1V}}{\lambda_1 - \lambda_2} = - \frac{E_{1V}^F}{kT} + \text{const.} \quad (57)$$

Once more an Arrhenius plot yields the monovacancy formation energy. Other methods of analyzing lifetime have also been employed. Often, the measured time spectrum is deconvoluted by using the known resolution function of the spectrometer, and the unfolded spectrum is fitted to a sum of exponential decay functions. Alternatively, the shift of the centroid of the time spectrum relative to its value for no trapping is measured directly. (68) Then, from the trapping model,

$$\Delta\tau = \frac{1}{\lambda_2 - \lambda_1} \left(\frac{\mu C_{1V}}{\mu_1 + \mu C_{1V}} \right),$$

leading again to a determination of the formation energy.

By now formation energies have been determined in a number of metals and alloys by one or more positron annihilation experiments. Table IV lists some of the values of E_{1V}^F deduced from the data. It is important to point out that the trapping effect saturates at a temperature well below that at which the divacancy concentration is important. Thus, the positron technique has a definite advantage over the length-lattice parameter method. In fact, it should be regarded as complementary to the latter experiments. Taken together, they provide a means of separating divacancy contributions at high temperatures.

Recently, the positron experiments have been extended to include measurements in dilute alloys.⁽⁶⁹⁻⁷¹⁾ Most experiments have been performed on aluminum alloys, because a wide range of impurities is soluble in this metal, and because numerous quenching and ageing experiments have yielded a range of binding energies for a given impurity. According to the simple Lomer model, vacancies in these alloys are either free or bound to impurity atoms. From a comparison between annihilation characteristics in a pure metal and its alloy, it has been possible to determine E_{VS}^B . For the few cases reported, the binding energy is smaller than that deduced from other kinds of data. However, the positron experiments are not without their deficiencies too. Effects of impurities on the trapping parameters such as the specific trapping rate and the lifetime in the traps are unknown. Further investigations will be required before binding energies can be determined routinely.

Table IV Values of vacancy formation energy, trapping rate and capture cross section of vacancies for positrons in several metals. (Ref. 55)

Metal	ϵ_v (eV)	νA (sec ⁻¹)	$\sigma \times 10^{16}$ (cm ²)
Al	0.66 ± 0.04	1.2×10^{15}	14.7
Cd	0.39 ± 0.04	1.9×10^{14}	2.9
Pb	0.50 ± 0.03	6.2×10^{14}	13.7
In	0.55 ± 0.02	1.5×10^{17}	25.5
Zn	0.54 ± 0.02	3.6×10^{15}	3.6

The general question of positron behavior near vacancies, internal voids and surfaces has been under theoretical investigation, too. Hodges and Stott⁽⁷²⁾ have taken into account the positron zero-point energy, positron-electron correlation energy and surface dipole barrier in deriving the positron potential shown in Fig. 15. Their primary concern was to develop a theory of the positron work function, ϕ_p . However, they concluded that their treatment of the metal surface problem corresponded to an earlier discussion by Hodges,⁷³ of positron trapping at vacancies. The analogy of the vacancy with the surface problem was made by setting the vacancy trapping well depth, V_t , equal to the sum of E_0 , the zero-point energy and D , the surface dipole barrier. The results were in good agreement with Hodges' earlier calculations⁷³ which showed that well depths in many metals are several tenths of a Rydberg. The binding energy ϵ_b , defined as the depth of the positron ground state energy band in the metal, varies from a few hundredths of a Rydberg for Li to a few tenths for Al (see Table V).

In addition to the existence of bound states for positrons in vacant sites, there is the question of detrapping. Seeger³⁶ has suggested that the escape rate of positrons will be of the order of magnitude

$kT \exp(-\tau_{1V}/kT)/h$, where h is Planck's constant. If detrapping is to be unimportant, then the escape rate must be much smaller than the annihilation rate in traps. This implies that

$$\epsilon_b \gg kT \ln (kT\tau_{1V}/h) .$$

On the basis of this prediction, we would find that

Fig. 15 Positron potential in a solid and at a distance x from its surface. The dashed curve represents the Hartree potential of ions and valence electrons. The full curve shows the positron pseudopotential inside the metal and the electron-positron correlation and image potentials outside. The dotted curve shows the potential acting on positronium outside the metal. (Ref. 72)

Table V Values of the vacancy trapping well depth, V_t , and the binding energy, E_b , calculated in the Hartree self-consistent approximation (A) and with the electron correlation effect taken into account (B). (After Hodges and Stott.)

Metal	A		B	
	V_t (in Ry)	ϵ_b	V_t (in Ry)	ϵ_b
Li	0.32	0.05	0.22	0.01
Na	0.27	0.06	0.17	0.01
K	0.22	0.07	0.12	0.01
Rb	0.21	0.08	0.10	0.01
Cs	0.19	0.07	0.09	0.01
Mg	0.50	0.18	0.33	0.07
Zn	0.60	0.19	0.43	0.08
Cd	0.50	0.17	0.34	0.06
Kg	0.40	0.11	0.24	0.02
Al	0.72	0.28	0.52	0.15
Ga	0.57	0.20	0.38	0.08
In	0.55	0.22	0.36	0.10
Tl	0.47	0.17	0.30	0.06
Sn	0.56	0.24	0.38	0.10
Pb	0.52	0.22	0.33	0.09

for alkali metals ϵ_b must exceed about 0.15 eV and it should be greater than about 0.75 eV in the noble metals. The trapping properties of vacancies in the various metals will depend upon such parameters as the electronic structure of the metals, relaxation around vacancies and valence. The apparent absence of trapping in some metals may be attributed to the absence of a bound state or to detrapping. Perhaps, in some cases vacancies are weak traps but multiple vacancies are not. Quantitative studies are warranted, and it is likely that in the next few years details about the electronic structure of defects will be forthcoming from positron studies,

Specific studies of mechanical-property changes in metals have been conducted by various workers. These have been described in the reviews by Goland,³⁴ Dekhtyar⁵⁵ and West.³⁷ Recently, Lynn et al.⁷⁴ have performed careful lifetime measurements on deformed and cyclically-stressed metals. They coupled these measurements to an analysis of x-ray line broadening as a means of determining dislocation densities. In pure nickel and Ni-66.5%Co, they observed that the positron lifetime increased rapidly during plastic fatigue cycling; it leveled off at a value of ~ 230 psec as compared to an initial value of 140 psec. in the alloy. This saturation was more rapid than that which occurred for the x-ray particle size, but they concluded that positron-lifetime measurements could be used as a nondestructive method for estimating dislocation densities. The mean lifetime $\bar{\tau}$ saturated at a dislocation density of about 10^{10} cm^{-2} in the alloy. Further studies of this kind will be required in order to put the technique on a firm basis. It may be that some other characteristic of annihilation such as the lineshape of the 511-keV gamma ray will prove to be a more sensitive and useful measure of plastic deformation.

C. Annealing Kinetics and Rate Theory

1. Introduction

We have been considering ways to determine "directly" the formation and binding energies of defects; now we turn our attention to the activation energies of thermally-activated processes. Methods of deducing these quantities from annealing experiments are fully described in the literature,⁶ and need not be covered in great detail here. Perhaps it will be most instructive to consider some of the shortcomings of rate theory in order to gain further appreciation for the importance of new, more direct, experimental techniques, advances in the theory of diffusion, and methods of data analysis.

Defects can be introduced in detectable quantities by cold work, quenching or by irradiation. Then their properties are deduced from subsequent annealing experiments. By this means it is possible to learn something about defect migration energies, interactions between defects and between defects and solute atoms. In spite of the many careful efforts which have been expended on attempts to identify defect species, there are still a number of controversies, and a realistic view might be that conclusions drawn from annealing data can be specious.

We have said that radiation is one way to introduce a nonequilibrium concentration of defects into a solid. There is always a driving force tending to reduce such an excess concentration, and this leads to annealing of the defects in the solid. The annealing process will be governed by some diffusion process characterized by an activation energy for migration of the defects. In a complex annealing process involving several steps we cannot say in advance which is the rate-controlling step. The excess defects disappear from the crystal by migrating to sinks or by recombining with other defects. During these processes trapping at defects or at impurities may

play a dominant role. In general, the formalism of chemical-rate theory encompassing the law of mass action has been used to investigate the kinetic problems that can arise. This amounts to making two assumptions about the reacting species:

- a. the interaction between species must be short range, and
- b. the defect concentrations are low.

Actually, for a charged defect the interaction goes as $\sim \cos(r/r_0)/r^3$ and is not really so short range. Also, investigation has shown that the presence of the configurational entropy term in the free energy makes it difficult to speak of defect binding energies in alloys whenever the solute concentration is $>1\%$. Usually in what follows the configurational entropy term is neglected, as is commonly done. When the concentration of impurities, i_s , is sufficiently low, then if there is a positive binding energy, E_{VS}^B , between vacancies and impurities, the total vacancy concentration, C_{1V}^t , is:

$$C_{1V}^t \approx e^{-E_{1V}^F/kT} [1 - Zi_s + Zi_s e^{E_{VS}^B/kT}] , \quad \frac{N_{i_s}}{N} \ll 1. \quad (59)$$

This result is just the sum of the bound vacancy and free vacancy concentrations. It must be modified to include at least solute pair interactions at higher concentrations of solute. For instance, it would not be valid when $C_{\text{solute}} > C_{1V}^{\text{equilib.}}$.

2. Annealing of Nonequilibrium Concentrations of Defects

The variety of possible annealing processes that can be postulated is so large that we cannot hope to consider them all here. Moreover, only a few of them are tractable in the sense that they can be solved in closed form for the defect concentrations as a function of time. Therefore, we will consider only a few of the simpler cases, and simply mention some of the other possibilities:

a. Random diffusion to fixed sinks:

This is the simplest process that can be envisioned. The solution can be obtained from classical diffusion theory for various sinks using appropriate boundary conditions. There are transient solutions and a long-time solution, and the importance of the former depends upon the initial distribution of defects and sinks. In general, a simple exponential fits most experimental data that obey first-order kinetics and one can write:

$$dn/dt = -Kn, \text{ with } K = \alpha D. \quad (60)$$

n is the defect concentration at time t , α depends upon the sink geometry, and D is the diffusion coefficient. Thus, $n = n_0 e^{-Kt}$. (The traps are assumed unsaturable). Calculations can be performed to determine α in cases where the external surface is the only sink, or where various internal surfaces act as sinks: ⁶

	Sphere	Rectangular Parallelopiped	Infinite Cylinder
Migration to external surfaces	$\alpha = \pi^2/R^2$	$\alpha = \pi^2(1/A^2+1/B^2+1/C^2)$	$\alpha = X_1^2/R^2$
	<u>Random Distribution of Spherical Sinks</u>	<u>Random Distribution of Dislocations</u>	
Migration to internal sinks	$4\pi r_0 N_0$	$2\pi N_0 / \ln(r_1/r_0)$	

For this simple case it is possible to calculate the mean number of jumps, $\bar{j}$, that a defect makes before finding a sink. ⁶ For a random distribution of sinks $\bar{j}$ can be calculated by a random-walk computation. Suppose that the lattice has coordination number Z , and that each jump is only to a nearest neighbor with probability $1/Z$. Then random-walk theory states that for a large number of jumps j , the average number of distinct sites visited, S_j , is

$$S_j = b_j.$$

So b can be thought of as the probability of a jump to a fresh site. Suppose $P(j)$ is the probability of survival after j jumps and suppose that c is the sink concentration. Then the probability of finding a sink at a fresh site is just c . The probability $P(j)$ will obey the equation:

$$dP(j) = P(j)bcdj$$

or

$$P(j) = e^{-bcj} .$$

(61)

The value of $\bar{j}$ can now be calculated:

$$\bar{j} = \int_0^{\infty} bcj e^{-bcj} dj = 1/bc .$$

$$\bar{j} = 1.345 (1/c) , \text{ f.c.c.}$$

For the common metals : $\bar{j} = 1.393 (1/c) , \text{ b.c.c. .}$

Thus the average number of jumps to annihilation at a sink is approximately equal to the reciprocal of the atomic fraction of sinks. It has been assumed here that each defect occupies only one lattice site so in some cases the approximation can be poor. Nevertheless it yields a physically reasonable estimate of $\bar{j}$.

b. Recombination of Vacancies and Interstitials

There is often the possibility that two types of defects co-exist in the lattice, and that they disappear by recombination. For example, we know that radiation can produce vacancies and interstitials, and that these are very likely to recombine.

i. Random recombination

Assume a concentration of C_{1V} vacancies and C_1 interstitials. Let the jump frequency be v_1 for the interstitial, the faster moving of the two defects. Let Z be the number of sites adjacent to the vacancy from which an interstitial can jump "into" a vacancy. Suppose i' is the probability that an interstitial is on a site; then

$$dC_{1V}/dt = -Zv_1C_{1V}i' \quad (62)$$

Suppose that $i' = C_1$, that is, the interstitials are randomly distributed and the random distribution is maintained by the diffusion process. We know that

$$C_{1V}^0 - C_{1V} = C_1^0 - C_1 \quad , \text{ so}$$

$$dC_{1V}/dt = Zv_1C_{1V}(C_1^0 - C_{1V}^0 + C_{1V}) \quad , \text{ bimolecular recombination.}$$

Note that we have not assumed that $C_{1V}^0 = C_1^0$, that is, equal initial concentrations. If we do,

$$dC_{1V}/dt = -Zv_1C_{1V}^2 \quad , \text{ a second-order rate equation.} \quad (63)$$

$$\text{Then } 1/C_{1V} - 1/C_{1V}^0 = Zv_1t.$$

Even if $i' \neq C_1$, the long-time behavior of the solution obeys bimolecular kinetics.

ii. Non-uniform initial distribution

Radiation produces many close pairs which annihilate with one another from close-neighbor positions. The annealing rate depends only upon the concentration of either defect and we again have a first-order

process with exponential decay. In this case, $K = Zv_1$ in the expression $C_{1V} = C_{1V}^0 e^{-Kt}$.

Generally, a mobile interstitial either recombines with its nearest neighbor or it diffuses away to annihilate with some other vacancy as described by the bimolecular equation. It has been asked: what fraction of interstitials escape their neighboring vacancy after a long time? If C_i^0 interstitials are located at a distance r_i from a vacancy of radius r_0 , and if the interstitials migrate at random then to a good approximation

$$\frac{C_i}{C_i^0} = 1 - \frac{r_0}{r_i}.$$

At the low concentrations typical of most experiments, the equation suggests that only a small percentage of defects anneal by correlated recombination if they are initially distributed at random. Thus, the interstitial usually visits the vicinity of several vacancies before recombination, and the assumption leading to bimolecular kinetics is quite reasonable. The experiments of Wollenberger *et al.*⁷⁵ and computer calculations^{76,77} give some quantitative indication of the critical recombination radii.

c. Migration of Vacancies to Sinks of Variable Concentration

This is a model that is a slight modification of random diffusion to fixed sinks. For example, sinks may form from vacancies that cluster, and then they may alter their dimensions. An example that has been worked out considers sinks of sessile dislocation rings alone and in combination with fixed sinks. The kinetic scheme is $C_{1V} \xrightarrow{K_3}$ variable sinks, and the differential equation describing the process is $dC_{1V}/dt = -K_3 C_{1V}$ where the rate constant $K_3 = f(C_{1V})$. The results take an especially

simple form when only the variable sinks are present:

$$C_{1V} = C_{1V}^0 [\cosh(1/2\beta t)]^{-2} \quad \text{where } \beta = \pi (K_3/n_v) \sqrt{N_s} C_{1V}^0. \quad (64)$$

N_s is the initial concentration of sessile dislocation nuclei, and n_v , the atomic fraction of sessile dislocation sinks.

If fixed sinks are simultaneously present, the solution is much more cumbersome. One finds the concentration of vacancies absorbed by sessile loops, and fixed sinks, C_{1V}^V and C_{1V}^F , respectively, as well as C_{1V} , the free vacancy concentration.

$$C_{1V}^F = \frac{2C_{1V}^0(1-e^{-Kt})}{1 + \sqrt{1 + 2\gamma C_{1V}^0} - (1 - \sqrt{1 + 2\gamma C_{1V}^0})e^{-Kt}} \quad (65)$$

$$C_{1V}^V = 1/2\gamma (C_{1V}^F)^2, \quad C_{1V} = C_{1V}^0 - C_{1V}^F - C_{1V}^V, \quad \text{where}$$

$K = \alpha\lambda^2(K_3/n_v)\sqrt{1 + 2\gamma C_{1V}^0}$, $\gamma = 1/2\pi^2 N_s/(\alpha\lambda^2)^2$. The equations apply if divacancies are the mobile species by replacing C_{1V} by C_{2V} , and N_s by $N_s/2$. This is true for the simpler case, too. The annealing curves are very sensitive to the presence of a small fixed sink concentration as illustrated by the examples shown in Fig. 16.

Fig. 16 Representative annealing curves from the Kimura *et al.* theory. Curves 1 and 2: variable sink decay for two different sessile dislocation concentrations, 1.2×10^{-8} and 5×10^{-8} , respectively. Curves 3 and 4: simultaneous decay to variable and fixed sinks; fixed sink concentrations of $\alpha = 10^9$ and $\alpha = 10^{10}$ added to curves 1 and 2 respectively. Curve 5: a typical curve for vacancy - divacancy mechanism shown for comparison. (Ref. 6)

In some cases there is a short delay time and an inflection point. These occur if $N_s C_{1V}^0 / \alpha^2 > 2 \times 10^{-31}$ where $\alpha^2 \approx$ number of dislocation lines/cm². As α increases (say, by cold working the sample), the annealing process accelerates, the delay disappearing.

d. Other Annealing Processes

The preceding processes are the only simple ones we will discuss. Many others have been considered.⁷⁸ They usually involve a set of coupled nonlinear differential equations whose solutions can only be approximated analytically or solved numerically on digital or analog computers. Usually, the results are complex and cannot be simply described so that they are beyond the scope of these lectures.

3. Analysis of Annealing Curves

In performing an annealing experiment the goal is to separate the various kinetic processes we have just discussed. This is not always possible, and as we shall see later it can often happen that we think we have isolated one process when in reality we have not. Fortunately, in many instances a single activated process can be separated from others occurring at different temperatures. Then several methods of analysis are open to us under rather weak restrictions. Suppose p is some physical property, say the electrical resistivity. Then for a single activated process with a constant activation energy

$$dp/dt = -K_0 f(p) \exp[-BE_{eff}] \quad (66)$$

where K_0 is some rate constant and

$f(p)$ allows for the interaction of defect species and changes in the sink structure. E_{eff} can also be a function of p and T in the most general situation.

But suppose that E_{eff} is independent of p and T . Then the following methods of analysis may be used:

a. Arrhenius Plot (or cross-cut method)

$$\int_{p_0}^p dp/f(p) = -K_0 t \exp[-\beta E_{\text{eff}}] = -K_0 \Theta \quad (67)$$

Suppose we perform a series of isothermal annealing experiments at temperature $T_1, T_2, \dots$

The results will look like those shown in Fig. 17.

If we draw a line parallel to the abscissa at some arbitrary level where p has decreased to p_1 we can read the times t_1, t_2, t_3 at which this decrease has occurred. But the left-hand side of the equation is a constant because it is just $\int_{p_0}^{p_1} \frac{dp}{f(p)}$ in each case. Thus,

$$\ln t_1 = \beta E_{\text{eff}} + \ln \Theta - \frac{1}{K_0} \int_{p_0}^{p_1} dp/f(p) \quad (68)$$

and a plot of $\ln t_1$ vs. $1/T$ (or $\beta = \frac{1}{kT}$) yields E_{eff} : If we make another cut at p_2 the only change should be in the $\int_{p_0}^{p_1}$ so all straight lines should be parallel to one another. If they are not, the assumption of a single, constant energy process is invalid. Note, when $f(p) = p$ we are dealing with a simple first-order reaction such as annealing

Fig. 17 Illustration of the cross-cut method for determining activation energies from isothermal annealing data. (Ref. 6)

to fixed sinks. Then

$$p = p_0 \exp[-K_0 \exp\{-\beta E_{\text{eff}}\}t] \quad (69)$$

and the isothermals are exponentials but their slopes are temperature dependent.

b. Constant Rate of Heating

Often, a simple technique of sample heating is used in which the sample is heated at a constant rate α and the physical property p is measured more or less continuously. Because the annealing is thermally activated there will be a narrow temperature range over which dp/dt increases rapidly and then decreases to zero. This is the range over which the defect anneals out by migration to sinks or by some recombination.

Suppose $T = \alpha t$ where α is constant and t is the elapsed time of heating. Then,

$$\frac{dp}{dt} = \frac{dp}{d\beta} \frac{d\beta}{dt} = -\alpha k_B \beta^2 \frac{dp}{d\beta} \quad (\beta = 1/k_B T)$$

$$\text{so} \quad \int_{p_0}^p \frac{dp}{f(p)} = -\frac{K_0}{\alpha k_B} \int_{\infty(T=0)}^{\beta} \frac{\exp(-\beta E_{\text{eff}})}{\beta^2} d\beta \quad (70)$$

In any experiment the range ∞, β is such that $\beta E_{\text{eff}} \gg 1$ so we can integrate by parts and keep the leading term in the expansion in $(\beta E_{\text{eff}})^{-1}$. This gives

$$\int_{p_0}^p \frac{dp}{f(p)} \approx -\frac{K_0}{\alpha k_B} \frac{\exp(-\beta E_{\text{eff}})}{\beta^2 E_{\text{eff}}} \quad (71)$$

Now suppose the experiment is conducted twice at different heating rates, α_1 and α_2 , until p decays to the same fraction of p_0 . This will occur at the two temperatures β_1 and β_2 , and the left-hand side of the equation above will have the same value. Thus,

$$\alpha_2 \beta_2^2 / \alpha_1 \beta_1^2 = \exp[(\beta_1 - \beta_2) E_{\text{eff}}]$$

or

$$E_{\text{eff}} = \frac{1}{\beta_1 - \beta_2} \ln \left(\frac{\alpha_2 \beta_2^2}{\alpha_1 \beta_1^2} \right) \quad (72)$$

Again, if $f(p) = p$, then

$$p = p_0 \exp \left\{ - \frac{K_0}{\alpha k_B} \frac{\exp(-\beta E_{\text{eff}})}{\beta^2 E_{\text{eff}}} \right\} \quad (73)$$

If E_{eff} is a function of p and T , then several other methods may be more appropriate.

c. Meechan-Brinkman Method = simultaneous analysis of isochronal and isothermal curves

Often the constant-heating method is replaced by a method in which the sample is heated at successively higher temperatures for equal time intervals, the temperature intervals being small. This method, isochronal annealing, approximates the constant-heating technique when the temperature steps are small. The value of p is plotted as a function of T_i (or β_i), the temperature during the i^{th} pulse.

Suppose the time interval chosen is Δt . Then recalling the function

$\Theta = t \exp[-\beta_1 E_{\text{eff}}]$ that we defined earlier, we can write

$$\Delta\Theta = \Delta t \exp[-\beta_1 E_{\text{eff}}] . \quad (74)$$

Now the change in p during this heating pulse is $p_{i-1} - p_i$, and on an isothermal heating curve at some annealing temperature T_a (or β_a) the same change in p can be associated with the elapsed time

$$\Delta\tau_i = \tau_i - \tau_{i-1} .$$

Then, $\Delta\Theta = \Delta\tau_i \exp(-\beta_a E_{\text{eff}})$. Thus we can write $\Delta t \exp[-\beta_1 E_{\text{eff}}] =$

$\Delta\tau_i \exp(-\beta_a E_{\text{eff}})$, or

$$E_{\text{eff}} = \frac{1}{\beta_a - \beta_1} \ln \left(\frac{\Delta\tau_i}{\Delta t} \right) . \quad (75)$$

Since β_a can be held fixed and Δt is a constant, one can plot $\ln \Delta\tau_i$ against β_1 to obtain E_{eff} . If E_{eff} thus derived is not constant then more than one process has been thermally activated.

d. Ratio-of-slopes Method

One final technique should be mentioned. We note from the original equation for dp/dt that if the temperature is suddenly changed from T_1 to T_2 , the slope, dp/dt , must change discontinuously in such a way that

$$\begin{aligned} \frac{(dp/dt)_{T_1}}{(dp/dt)_{T_2}} &= -K_o f(p) \exp[-\beta_1 E_{\text{eff}}] / -K_o f(p) \exp[-\beta_2 E_{\text{eff}}] \\ &= \exp[-(\beta_1 - \beta_2) E_{\text{eff}}], \text{ i.e., } \ln \left[\frac{(dp/dT)_{T_1}}{(dp/dT)_{T_2}} \right] = (\beta_2 - \beta_1) E_{\text{eff}} . \end{aligned} \quad (76)$$

In principle, this method is very simple, but it is rather difficult in practice to measure the two slopes at the same instant in time. Thus the method gives some average in the p, t plane at a point T . The experimental difficulties inherent in data acquisition in any of the methods described above have been reduced greatly in recent years through the introduction of automatic data-acquisition equipment. It is possible, for example, to nearly continuously sample a set of measuring devices by programming a digital voltmeter and clock. Current, potential differences and time can be sequentially measured and recorded on paper tape, magnetic tape or paper. By interfacing the data-acquisition system to a small computer it is also possible to continuously reduce the data and produce a nearly real-time graphical display. In view of this increased sophistication in data taking and reduction, it is important to bear in mind that certain simplifying assumptions underlie the methods of data analysis and that these may not be valid in a particular case. In the next two sections we will examine these assumptions.

4. The General Chemical Rate Equation

We have noted that often a single activated process is governed by the simple equation

$$dp/dt = -K_0 f(p) \exp[-\beta E_{\text{eff}}] \quad (77)$$

If $f(p) = p^\gamma$ then the equation is known as a chemical rate equation. We have seen examples when $\gamma = 1$ (diffusion to fixed sinks) and $\gamma = 2$ (recombination of initially equal concentrations of two defects).

We have seen how E_{eff} can be determined, and if it is known, how we can determine the order of the reaction, γ , from a constant-heating curve, for

$$-\frac{dp}{dT} = \frac{K_0}{\alpha} p^2 \exp[-\beta E_{eff}] ,$$

$$\text{so that } \beta E_{eff} + \ln \left(-\frac{dp}{dT} \right) = \ln \frac{K_0}{\alpha} + \gamma \ln p. \quad (78)$$

We can plot the left hand side against $\ln p$ and obtain γ from the slope. But suppose that the derived value of γ is very large or non-integer. Then we do not know how to interpret our results, and such is often the case. This brings us to the subject of difficulties in the interpretation of Reaction Kinetics.

5. Difficulties in the Interpretation of Reaction Kinetics

a. Unequal Initial Concentrations of Reactants

Recall that for annealing by recombination when the two defect types are initially present in equal concentrations, $\gamma = 2$ and $1/C_{IV}$ at. Thus, if we assume that the physical property we are measuring, p , is proportional to C_{IV} we expect that if we obtain a linear graph we will find $\gamma = 2$ by the analysis in the last section. However, Nihoul and Stals⁷⁹ and Fujita and Damask⁸⁰ have shown that if the concentrations of reactants are initially unequal this expectation is unwarranted. In fact in this case $1 \leq \gamma \leq \infty$. Typical results obtained are shown in Fig. 18. Let us call the atomic fractions of the two reactants n_1 , and n_2 , and their initial values n_1^0 and n_2^0 . The reaction we are discussing as an example is :

Nihoul and Stals⁷⁹ performed the most general calculation for this reaction and found:

$$\gamma = 1 + \frac{C_r}{C_r + f - 1} + \frac{1}{2A^2(1+\gamma/A^2)[(1+\gamma/A^2)^{1/2} - 1](C_r + f - 1)}, \text{ where} \quad (79)$$

Fig. 19 Theoretical curve showing reciprocal of concentration of defects c versus time. Linearity of curve would suggest second-order process, whereas in model used order ranges from 1.5 to 5. This illustrates difficulties which can arise in diffusion-controlled processes. (Ref. 79)

$$C_r = n_1/n_1^0, \quad \text{if } n_1 < n_2 \quad \left| \quad f = n_1^0/n_2^0, \quad \text{if } n_1^0 > n_2^0 \right.$$

$$= n_2/n_2^0, \quad \text{if } n_1 > n_2 \quad \left| \quad = n_2^0/n_1^0, \quad \text{if } n_1^0 < n_2^0 \right.$$

$$A = 4r_0^3 C, \quad r_0 = \text{a capture radius (parameter of the calculation)}$$

$$y = [1/(f-1)] \ln [(C_r + f - 1)/C_r f].$$

Only if $r_0 \ll a$ (lattice constant) and $n_2^0 = n_1^0$ does $\gamma = 2$.

Fujita and Damask⁸⁰ have simulated an experimental decay curve under somewhat more restrictive conditions, but they obtain curves of n_1/n_1^0 vs. t for different starting conditions n_2^0/n_1^0 as shown in Fig. 19. The corresponding order of the reaction was derived from these curves and is shown in Fig. 20, too. Thus other information is needed in order to substantiate any interpretation of reaction kinetics derived by these methods.

b. Variable Activation Energy

The activation energy of even a single activated process can vary as the annealing proceeds. A simple example can be treated to show the possible consequences of such a situation. Suppose⁶

$$E_{\text{eff}} = E_0 - \alpha n,$$

where n is the number of defects present.

Then the chemical rate equation becomes $dn/dt = -K_0 n \exp(-E_0/kT) \exp(\alpha n/kT)$.

Formal integration yields

$$\int_{n_0}^n \frac{e^{-\alpha n/kT}}{n \gamma} dn = -K_0 t e^{-E_0/kT}. \quad (80)$$

Fig. 19 Bimolecular decay for unequal initial concentration of reactants. (Ref. 80)

For a fixed value of n as in the cross-cut method we can write

$$t = K'e^{+E_o/kT} e^{-\alpha n/kT} \quad \text{where } K' \text{ will be a constant determined}$$

by γ .

Then $\ln t = \ln K' + (E_o - \alpha n)/kT$, and a plot of $\ln t$ against $1/T$ will yield $E_{\text{eff}} = E_o - \alpha n$ for the chosen n . But for another cross cut at a new $n = n'$, a different value of $E_{\text{eff}} = E_o - \alpha n'$ will be found. The general equation above can be numerically integrated for γ integer to yield a series of curves from which we would see that an increasing γ is qualitatively similar to an E_{eff} that increases with decreasing n . It is thus possible to fit an annealing curve of fixed γ and variable E_{eff} with a constant E_{eff} and a different, higher and probably non-integral γ .

c. Complex Simultaneous Annealing

Johnson^{81,82} has shown just how complex an annealing process can become by considering the annealing of excess vacancies in a metal including cluster formation and annealing to sinks. Clusters of up to seven vacancies were specifically treated by reaction theory and larger clusters were treated in an approximate fashion. Johnson assumed that monovacancies are immobile at temperatures where small clusters can migrate. This simplified the calculation and permitted a closer study of cluster behavior. Migration was assumed to be a divacancy mechanism and the simulated electrical resistivity was taken as a linear function of cluster concentration. A great number of parameters were used in these computer calculations and the results were generally complex and dependent upon the binding energy of the divacancy. Typical results are shown in Fig. 20 where a plot of quenched-in resistivity versus time in minutes has been plotted. After an initial transient, the curves are linear, suggesting a first-order effect. However,

Fig. 20 Isothermal runs at 425 and 450K. Two stages are apparent, an initial rapid annealing followed by a slower annealing stage with first-order kinetics. The primary effect of the latter is a decrease in the single-vacancy concentration. (Ref. 81)

the activation energy deduced from the computer experiments did not correspond to any one of the single processes included in the calculation by Johnson. In fact, the annealing curve represented the combined annealing of mono-, di-, tri- and clusters of vacancies. It seems, then, that reliance upon annealing kinetics alone can lead to physically unrealistic models of the defects. March and Rousseau have recently discussed some of the typical interactions between point defects in metals.⁸³ In the next section we will investigate some of the methods now available for determining the configuration of a point defect. With this information, it may be possible to sort out the behavior of annealing data.

D. Defect Sites and Configurations

There has been a growing realization that much of the effort expended over the past twenty-five years to identify defect configurations has yielded inconclusive results. The primary reason is that these characteristics have been deduced from observed changes in physical properties and from studies of annealing kinetics. From such investigations it is possible to construct self-consistent, but not necessarily unique, models of defects. Consequently, there is a continuing demand for new techniques which directly provide information about defect type, configuration and location. There are several of these methods which have now achieved prominence, and we will examine a few of them here. The three most noteworthy are x-ray and neutron scattering, FIM and channeling. These have enabled us to study nonequilibrium concentrations of intrinsic defects or impurities deliberately added to the host crystal. We have briefly mentioned FIM previously in connection with equilibrium concentrations, but we will return to it if time permits.

1. X-ray and Neutron Scattering Methods

The presence of defects in a lattice creates a strain field that produces changes in the physical properties as well as in the volume and the lattice constant as we have already seen. The defects and their associated displacement fields also effect the scattering of x-rays and neutrons, and these effects manifest themselves experimentally in several ways:

1. the lattice parameter will change owing to relaxation of the atoms surrounding the defects,
2. the intensity of the Bragg reflections will be reduced because the static displacements are analogous to the thermally-induced displacements whose mean square magnitude determine the Debye-Waller factor,
3. diffuse scattering will arise from a random distribution of defects and their displacement field, and
4. the presence of defects in an otherwise very perfect crystal can alter the anomalous transmission in a way that is related to the size and type of defect.

a. Diffuse Scattering

The diffuse scattering from simple defects was treated by Eckstein,⁸⁴ Huang, Cochran and Kartha and Borie.⁸⁵⁻⁸⁷ Subsequently Krivogla⁸⁸ and his colleagues published a series of papers which treated the whole field of scattering from imperfect crystals. This research is summarized in a recent book by Krivogla⁸⁸. During this period only a few quantitative experiments were performed. There are several reasons for the dearth of research:

1. if point defects are to be studied, then in many cases of interest the experiments must be performed at low temperatures to immobilize them. Moreover, they must be present in a concentration greater than $\sim 10^{-19}$ cm⁻³ to be effective in producing observable effects,

2. if clusters form, the diffuse intensity will grow but it will also move in closer to the Bragg reflections. Therefore, extremely good crystals having small mosaic spread must be used together with a high-resolution monochromator,
3. background corrections are difficult because the standard sample used for comparison may contain defects, also, and,
4. general lack of familiarity with the research of Krivoglaz probably slowed progress.

In the last few years however, a renewed interest has developed on the part of theorists and experimentalists. It has been shown theoretically by Dederichs⁸⁹ and Trinkaus⁹⁰ that symmetry properties of defects can be deduced from the diffuse scattering close to the Bragg reflections. Keating and Goland^{91,92} have studied the techniques for calculating diffuse scattering over large regions of reciprocal space by means of high-speed computers. Larson and Young⁹³ have used a variety of x-ray methods to deduce defect properties, and a particularly vigorous group of experimentalists is at work in Germany on this subject. This includes Erhart and Schilling,⁹⁴ Peisl and his coworkers,^{95,96} and Schmatz and his collaborators.⁹⁷ The timeliness of the field was reflected in the size of a recent meeting.⁹⁸

Several theoretical treatments of diffuse scattering from point defects and defect clusters^{84-92,99,100,101} exist. They are all essentially the same. Assuming a statistical (random) distribution of defects, low defect concentrations and linear superposition of strain fields, the diffuse scattering intensity is given by the expression

$$S_{\text{diff}} = C |F(\underline{k})|^2, \quad (81)$$

$$\text{where } F(\underline{k}) = f_k^D + f_k \sum_n e^{i\underline{k} \cdot \underline{R}^n} (e^{i\underline{k} \cdot \underline{t}^n} - 1).$$

The quantity $\underline{k}$ is the scattering vector; $\underline{R}^n$ is the position vector of the n^{th} atom in the homogeneously expanded lattice, $\underline{t}^n$ is the static displacement of atom n due to the defect taken as the origin. The defect concentration as an atom fraction is C and f_k is the atomic scattering factor, whereas f^D is the scattering factor of the defect. If we confine our investigation to the vicinity of the Bragg reflection we can write $\underline{k} = \underline{h} + \underline{q}$ where $\underline{h}$ is a reciprocal lattice vector. The defect structure factor $F(\underline{k})$ then becomes

$$F(\underline{k}) = f_k^D + f_k \sum_n e^{i\underline{q} \cdot \underline{R}^n} (e^{i\underline{k} \cdot \underline{t}^n} - 1), \quad (82)$$

and we see that the diffuse scattering consists of three parts, scattering from the defect itself, scattering from the displacement field around the defect, and an interference term which is the product of the first two terms. The third term is often referred to as the size effect term. The defect scattering factor is given by different expressions depending upon the kind of point defect it is:

$$f_k^D = \begin{cases} f_k^I \exp(i \cdot \underline{k} \cdot \underline{R}^n), & \text{interstitial impurity} \\ f_k^I - f_k, & \text{substitutional impurity} \\ -f_k, & \text{vacancy} \\ f_h (2 \cos \underline{k} \cdot \underline{R}^I - 1), & \text{split interstitial.} \end{cases} \quad (83)$$

R is the interstitial position relative to the center of the defect, and f_k^I is the scattering factor of the impurity.

The long-range part of the displacement field of the defects determines the intensities in the vicinity of the Bragg reflections, the Huang scattering. In this small q limit the exponential in the expression for the diffuse scattering can be expanded and k may be replaced by h . Then, following Dederichs¹⁰² and Ehrhart and Schilling,⁹⁴

$$S_{\text{diff}}(\underline{k}) = S_{\text{Huang}}(\underline{k}) + S_{\text{anti}}(\underline{k}), \text{ where}$$

$$S_{\text{Huang}}(\underline{k}) = C f_k^2 |\underline{h} \cdot \underline{\tilde{t}}(\underline{q})|^2, \text{ and} \quad (84)$$

$$S_{\text{anti}}(\underline{k}) = 2 C f_h^2 \cdot \eta(\underline{h}) [\underline{h} \cdot \underline{\tilde{t}}(\underline{q})]$$

$$\text{with } \eta(\underline{h}) = \sum_n (1 - \cosh \underline{h} \cdot \underline{\tilde{t}}^n) - R(f_h^D / f_h).$$

We see that the Huang scattering is related to the Fourier transform of the displacement field, $\underline{\tilde{t}}(\underline{q})$. Since the displacement field always has inversion symmetry [$\underline{t}(\underline{r}) = -\underline{t}(-\underline{r})$], its Fourier transform does, too. This means that the Huang scattering also has inversion symmetry about the Bragg reflection, $S(\underline{h} + \underline{q}) = S(\underline{h} - \underline{q})$. This would imply that there is a nodal plane through the reciprocal lattice point. However, the foregoing development applies to the case when only one kind of defect configuration is present. Generally, anisotropic defects are present in all equivalent orientations and an averaging must be performed. For reasons of symmetry there may still be a nodal surface in the intensity pattern. However, it may be reduced to a line or it may vanish completely. The calculations of

Keating and Goland for Fe-C martensite and ferrite show this effect clearly.¹⁰³

The key to calculation of S_{Huang} is the evaluation of $\tilde{t}(q)$. This can be accomplished by direct evaluation using an analytical expression for $t(R^n)$. However, another approach is generally used which is more elegant. This approach involves the lattice Green function and is essentially derived from the concepts of lattice statics.¹⁰⁴ In matrix notation, it can be shown that the atomic displacements are related to the forces on the atoms by the expression

$$\underline{t} = \underline{G} \underline{F} \quad (85)$$

where G is the static Green function for the imperfect lattice, and F is the force on an atom when it is on a lattice site. An equivalent expression is

$$\underline{t} = \underline{G}_0 \underline{F}^* \quad (86)$$

where G_0 is the static Green function for the perfect lattice and F^* is the force on the atoms in their displaced positions (see Bullough and Tewary¹⁰⁴). This is exactly the concept introduced by Kanzaki,¹⁰⁰ and F^* is the Kanzaki force. We may think of F^* as that arrangement of forces which produces the same displacements at large distances as the defect. For large distances lattice statics goes over to elastic continuum theory and it can then be shown that¹⁰²

$$\tilde{t}_i(q) = \frac{1}{qv_c} \sum_{j,l} g_{ij}(\kappa) \kappa_l p_{jl}, \quad \kappa = q/q, \quad \kappa^2 = 1. \quad (87)$$

In this expression V_c is the volume of a unit cell, $g_{ij}(\kappa)$ is the inverse of the tensor $\sum_{k,l} C_{ikjl} \frac{\kappa_k \kappa_l}{k^2}$ and P_{jl} is the first moment of the Kanzaki forces, the so-called dipole tensor. The tensor above is just the inverse of the long-wavelength limit of the dynamical matrix where C_{ikjl} are the elastic constants. Thus, the Fourier transform of $\underline{t}$ can be determined from phonon dispersion curves and an evaluation of the dipole tensor. We have

$$S_{\text{Huang}}(\underline{k}) = C f_{\underline{h}}^2 \left(\frac{h}{q}\right)^2 \left| \frac{1}{V_c} \sum_{i,j,l} h_i g_{ij}(\underline{k}) \kappa_l P_{jl} \right|^2. \quad (88)$$

Note that $S_{\text{Huang}}(\underline{k})$ is proportional to the square of the dipole tensor which is much larger for interstitials than for vacancies. A general conclusion is that Huang scattering from interstitials is about twenty times greater than that from vacancies.⁹⁴

The expression above must be averaged over all equivalent orientations in a lattice. This averaging has been carried out for cubic crystals by Trinkaus.⁹⁰ The result is that

$$S_{\text{Huang}}(\underline{k}) = C f_{\underline{h}}^2 \left(\frac{h}{q}\right)^2 [\gamma^{(1)} \pi^{(1)} + \gamma^{(2)} \pi^{(2)} + \gamma^{(3)} \pi^{(3)}], \quad (89)$$

where the γ 's are factors which depend upon the elastic constants and on the directions of $\underline{h}$ and $\underline{q}$. The quantities $\pi^{(i)}$ are functions of the dipole force tensor-components:

$$\begin{aligned} \pi^{(1)} &= \left(\frac{1}{3} \sum_i P_{ii}\right)^2, \\ \pi^{(2)} &= \frac{1}{6} \sum_{i>j} (P_{ii} - P_{jj})^2, \text{ and} \\ \pi^{(3)} &= \frac{2}{3} \sum_{i>j} P_{ij}^2. \end{aligned} \quad (90)$$

The lattice parameter change is determined by $\pi^{(1)}$:

$$\Delta a/a = C \frac{\sqrt{\pi^{(1)}/3}}{V_C(C_{11} + 2C_{12})} \quad (91)$$

As pointed out earlier, averaging over all equivalent orientations eliminates the general occurrences of nodal planes. However, certain combinations of the $\gamma^{(1)}$'s and $\pi^{(1)}$'s can still give rise to nodal planes or lines. Tables VI and VII taken from Ehrhart and Schilling⁹⁴ show how by looking in different directions around high symmetry directions it is possible to determine defect orientations and $\pi^{(1)}$ values. An important point to note is that $S_{\text{Huang}}(\underline{k})$ contains the product $C(\text{trace } P_{ij})^2$ whereas $\Delta a/a$ is proportional to $C(\text{trace } P_{ij})$. Therefore, a combination of both measurements will yield a value for C. This is the only means of determining the absolute concentration of Frenkel pairs in an irradiated solid.

It has also been pointed out that to a first approximation when clustering occurs

$$S_{\text{Huang}}^{\text{cluster}} \sim CN S_{\text{Huang}}^{\text{interstitial}},$$

where N is the number of interstitials per cluster.

If the scattering from the defect itself is not too large so that η_h is always positive then the sign of S_{anti} will give the sign of the long-range part of the displacement field. For a center of dilatation (eg. an interstitial) $S(\underline{k})$ is larger for $\underline{q} \cdot \underline{h} > 0$ than for $\underline{q} \cdot \underline{h} < 0$.

Ehrhart, Schilling and Schlagheck^{94,105} have applied this theory to measurements on electron-irradiated Al and Cu. Thin single crystals were electron-irradiated at liquid-helium temperature and transferred to an x-ray diffractometer while being maintained at that temperature.

Table VI Parameters $\pi^{(2)}$ and $\pi^{(3)}$ for point defects of different symmetry and planes P and lines L of zero diffuse scattering around the reflections of type (h00), (hh0), and hhh). (Ref 94)

Defect symmetry and Symmetry axis	Reflection				
	$\pi^{(2)}$	$\pi^{(3)}$	(h00)	(hh0)	(hhh)
Cubic	0	0	$P \perp \{100\}$	$P \perp \{110\}$	Surface $\perp \{111\}$
Tetragonal (100)	+	0	$P \perp \{100\}$	$L \parallel \{001\}$	...
Trigonal. (111)	0	+	...	$L \parallel \{110\}$	...
Orthorhombic (110)	+	+		...	...

Table VII Experimental and theoretical values of the parameters $\pi^{(2)}/\pi^{(1)}$ and $\pi^{(3)}/\pi^{(1)}$ describing the deviation of the strain field from cubicity. The theoretical values for the various single-interstitial configurations pertain to the model calculations for Cu. (Ref. 94)

Experimental values			Theoretical values for												
Single interstitial	Di-interstitials	Interstitial clusters $n \approx 10$	Single force dipoles in direction			Single interstitials in configuration							Interstitial loops		
			(100)	(111)	(110)	O	T	H_O	H_T	H_C	C	On {111} planes with $\bar{b} = \frac{1}{2}a(111)$	On {110} planes with $\bar{b} = \frac{1}{2}a(110)$		
$\pi^{(2)}/\pi^{(1)}$	$6\frac{1}{2} \times 10^{-3}$	$9(\pm 3) \times 10^{-3}$	$0.02(\pm \frac{1}{2}, \frac{1}{10})$	1	0	$\frac{1}{2}$	0	0	0.002	0	0.007	0.012	0	0.012	0.012
$\pi^{(3)}/\pi^{(1)}$	$0\frac{1}{2} \times 10^{-3}$	$0.012(\pm 0.002)$	$0.05(\pm 0.02)$	0	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0	0.04	0.16	0.23	0.046	0.053	0.035

Huang scattering was measured for various accessible reflections and q directions, and the results were compared with theory. Wire samples for resistivity measurements were irradiated simultaneously. The various possible interstitial configurations shown in Fig. 21 are denoted by:

O = octahedral position

T = tetrahedral position

C = crowdion

H_O , H_T , H_C = dumbbell configurations with $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ axes, respectively.

For aluminum it was possible to conclude that configurations C, H_T and H_C could be ruled out. H_O appeared to be most probable, but because of experimental errors C and T could not be eliminated. The volume change per Frenkel defect was found to be $\Delta V = 1.9 \pm 0.2$ atomic volumes and the resistivity per atomic percent Frenkel defects,

$\rho_F = 3.9 \pm 0.7 \mu\Omega\text{cm}$. The corresponding results for copper were again that H_O is favored, but O, and T are not ruled out; ΔV per interstitial is 1.45 atomic volumes, ΔV per vacancy is -0.4 atomic volumes and ρ_F per Frenkel pair is $2.0 \mu\Omega\text{cm}$.

It must be remembered that the nature of the Huang scattering is such that it yields the symmetry of the long-range part of the displacement field. The near-neighbor configuration of a defect, on the other hand, governs the diffuse intensity far away from the Bragg reflections. Experiments in this regime have been undertaken by H.G. Haubold¹⁰⁶ and should provide independent evidence of defect configurations.

Diffuse scattering experiments have been performed on annealed specimens as well, and yield information on interstitial clustering in Al at various stages in the annealing process. Corresponding observations of $\Delta\rho/\rho$ and $\Delta a/a$ raise interesting questions about the mechanism of cluster

$$O: \begin{pmatrix} P_{11} & 0 & 0 \\ 0 & P_{11} & 0 \\ 0 & 0 & P_{11} \end{pmatrix}$$

$$T: \begin{pmatrix} P_{11} & 0 & 0 \\ 0 & P_{11} & 0 \\ 0 & 0 & P_{11} \end{pmatrix}$$

$$C: \begin{pmatrix} P_{11} & P_{12} & 0 \\ P_{12} & P_{11} & 0 \\ 0 & 0 & P_{33} \end{pmatrix}$$

$$H_O: \begin{pmatrix} P_{11} & 0 & 0 \\ 0 & P_{22} & 0 \\ 0 & 0 & P_{22} \end{pmatrix}$$

$$H_T: \begin{pmatrix} P_{11} & P_{12} & P_{12} \\ P_{12} & P_{11} & P_{12} \\ P_{12} & P_{12} & P_{11} \end{pmatrix}$$

$$H_C: \begin{pmatrix} P_{11} & P_{12} & 0 \\ P_{12} & P_{11} & 0 \\ 0 & 0 & P_{33} \end{pmatrix}$$

Fig. 21 Various interstitial configurations in a face-centered cubic lattice. O = octahedral positron, T = tetrahedral position, C = crowdion, H_O , H_T , H_C = dumbbell configurations with $\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ axes, respectively. (Ref. 94)

formation and the resistivity contribution per interstitial in clusters or loops as compared with that of individual interstitials.

These techniques are not confined to metals, having been applied to KBr,⁹⁵ nor to radiation-induced defects, having been recently applied to the study of oxygen in Nb.¹⁰⁷

b. Dynamical Diffraction

We shall see shortly that channeling has been successfully applied to the determination of lattice-atom positions in crystals. However, it should be noted that the energetic particles in the incident beam can produce radiation damage along their paths. It has been found that in several cases¹⁰⁸ the foreign atoms under investigation have interacted with the defects produced and assumed new positions in the lattice. Therefore, it is of interest to consider alternate means of determining foreign-atom positions in crystals. One method which has not received the attention it deserves relies upon the dynamical diffraction of x rays (or neutrons). Batterman and Cole¹⁰⁹ have described this phenomenon in great detail, and Batterman¹¹⁰ has demonstrated its applicability to impurity location.

According to two-beam dynamical theory, when an incident x-ray beam is Bragg reflected from a perfect crystal, standing wave fields are excited which have nodes or antinodes at the host lattice sites. On the low-angle side of the Bragg reflection the primary and diffracted rays form a wave field that creates a node at the atom sites, and hence cause a decrease in absorption by the atoms. On the high-angle side, conversely, the intensity of the field is enhanced at the atom sites as an antinode coincides with them. The nodal and antinodal surfaces are parallel to the reflection planes and have the same spacing. If a foreign atom occupies a lattice site, then as an antinode forms at that site, the fluorescence

yield from the atom will increase. If the foreign atom occupies an interstitial position the yield will increase in a different angular region as the crystal is rotated. Thus, by taking advantage of the movement of standing waves in a known way through the lattice, it becomes possible to locate solute atoms. One limitation of the method is that primary extinction can dominate the angular yield of the fluorescent radiation. However, if the foreign atoms lie within a distance from the surface which is less than the extinction length for the particular reflection, then extinction effects become unimportant. Batterman¹¹⁰ demonstrated the feasibility of impurity location using As in Si. Recently, Golovchenko, Batterman and Brown,¹¹¹ have shown that the extinction effects can indeed be made negligible by controlling the depth distribution of the foreign atoms. They diffused As in Si at 1100C to create a distribution which effectively ended at about 0.4 μ m below the surface according to backscattering measurements. A double-crystal spectrometer in which the sample was the second crystal was employed as shown in Fig. 22. Detector D1 was used to monitor the Bragg reflection while D2 detected the fluorescence yield from the sample. The measured As fluorescence yield is shown as the points in Fig. 23. The solid curve represents the yield calculated on the assumption that the As atoms occupy substitutional sites in the [220] planes. The yield is assumed to be proportional to the absorption at depth z given by dynamical theory, and is determined by convoluting this absorption function with the empirically determined depth distribution of the As and the reflectivity curve for the first crystal. The dotted curve in the inset corresponds to the result which would have been obtained if the As atoms occupied positions between the planes.

Fig. 22 Schematic illustration of experimental setup for dynamical diffraction experiment. (Ref. 111)

Fig. 23 Data points showing experimental As(K_{α}) fluorescence x ray yields in detector D_2 as crystal 2 is scanned through the Bragg condition. Solid curve is from theoretical calculation. The sketch in the inset contrasts the different results expected for impurities directly between planes (dotted curves) and impurities in the planes (solid line). (Ref. 111)

If such data are obtained for several reflections it should be possible to pinpoint atom locations. The method requires reasonably perfect crystals, but so do channeling experiments. It may be extended to the use of neutrons in those cases where a capture event results in the emission of detectable radiation. Moreover, it circumvents the problem of radiation damage being produced during the experiment.

2. Channeling - Foreign Atom Location

When a collimated beam is incident upon a single crystal and aligned with a low-index axis, all particles which enter the surface within a distance $r_{\min}$, the critical distance of closest approach, of the axial "strings" of atoms are scattered through angles $>\psi_c$. The angle $\psi_c \sim E^{-1/2}$ is the so-called critical angle for channeling. The remainder of the incident particles are aligned in an axial channel. The minimum yield of particles emerging exactly parallel to a crystal axis is given by

$$\chi = \pi d N r_{\min}^2, \quad (92)$$

where N is the number of atoms per unit volume, and d is the atomic spacing along the axis. If $\psi_c \sim 1^\circ$, then $\chi \sim 1-10\%$. The important point about the aligned beam is that the particles in it cannot participate in processes that require close approach, for example nuclear reactions, inner-shell x-ray emission, and large-angle scattering. The latter occurs if a particle comes within $10^{-4} - 10^{-5} \text{ \AA}$ of a nucleus. But the "excluded zone" for channeled particles has a radius of $\sim 0.1 - 0.2 \text{ \AA}$. The aligned particles can thus detect displacements from the perfectly aligned atomic rows. Under favorable conditions this sensitivity makes it possible to locate impurity atom sites in a crystal. Several complications arise such as the phenomenon of flux peaking,^{108,112,113} and atomic positions which are neither pure interstitial nor pure vacancy. Nevertheless, in many cases accurate results can be obtained from purely

geometrical considerations. The basic principles of atom location are simple:

When a foreign atom is on a site whose location is forbidden to a channeled particle then attenuation of events requiring close collisions with the atom will occur, just as it does for the atom strings comprising the channel "walls". On the other hand, if the foreign atom is in an allowed region for the aligned beam it will not exhibit a decrease in yield for a characteristic process. Generally, although the yield from nuclear reactions or of inner-shell x rays can be used, the technique most commonly used is that of Rutherford backscattering. Data can be taken along several low-index directions in order to unambiguously determine the defect location. Figure 24 illustrates this approach for a fictitious two-dimensional lattice.¹⁰⁸ We will discuss the attenuation of yield of back-scattered particles for the three foreign atom sites ●, x and □, i.e. substitutional, interstitial but along a specific row, and interstitial both directions. We can prepare a chart to learn what to expect:

Directional Effect (i.e., attenuation of backscattering)			
	●	x	□
<01>	Yes	50%	No
<11>	Yes	No	Yes

The Rutherford back-scattering technique works very well when the impurity atom is heavier than the host. Then by means of accurate energy analysis it is possible to pick out the impurity peak and study its angular yield. Limitations of the method are imposed by lack of crystal perfection, uncertainty in the depth from which the back-scattered particles originate, multiple scattering, complicated flux

LOCATION OF FOREIGN ATOMS BY CHANNELING

TWO-DIMENSIONAL MODEL

Fig. 24 Two-dimensional schematic illustrating the principles of foreign-atom channeling experiments. (Refs. 108, 114)

distributions and local crystal symmetry.

A typical experimental arrangement is shown in Figs 25 and 26).¹¹⁴ By means of accurate energy discrimination it is possible to relate the loss ΔE to a certain depth t (with uncertainty Δt) by using the known energy resolution of the experimental apparatus. The depth t is defined by the relationship between E and the stopping power, and by the kinematics of the scattering process. The normal yield at t from Δt is:

$$y_n(t)\Delta t \left\{ \frac{d\sigma}{d\Omega} \right\}_{\text{Rutherford}} \Omega \Delta t, \quad (93)$$

where Ω is the solid angle subtended by the detector.

A recent example of the power of this technique was shown in the work of Swanson et al¹¹⁵ who identified Al-Mn split interstitials in irradiated Al-0.09% Mn crystals. Initially, triangulation measurements indicated that >96% of the Mn atoms were substitutional. Following irradiation with 0.3- or 1-MeV He^+ ions the $\langle 110 \rangle$ minimum yield for Mn drastically increased compared to the increase for Al (see Fig 27). Partial shadowing of the Mn atoms occurred in several axial and planar directions. Taken together the data suggest that the Mn has a $\langle 100 \rangle$ displacement. Swanson et al. conclude that the evidence confirms that the Mn atoms are displaced $\sim 1.3\text{\AA}$ in $\langle 100 \rangle$, and are believed to be one half of an Al-Mn split interstitial. The defect is thought to form during the migration of a radiation-produced interstitial. Annealing experiments verified that the Mn was indeed present as a simple defect. This is apparently the first time that an interstitial-impurity split interstitial has been found. It illustrates the importance of the technique.

Fig. 25 Typical arrangements for channeling measurements using Rutherford scattering or nuclear reactions. The position of the detector is arbitrary. The angles θ and ϕ correspond to goniometer motions available to vary the crystal orientation relative to the incident beam direction. Other types of detectors and incident beams are often used. (Ref. 114)

Fig. 26 A typical energy spectrum for the scattering yield of helium ions ($E_0 \sim 1$ MeV) from an amorphous silicon target containing a heavy impurity atom (antimony) implanted to a depth of approximately $0.1 \mu\text{m}$ beneath the crystal surface. (Ref. 108)

Fig. 27 Angular dependence of the normalized yield of backscattered He^+ ions (incident energy 1 MeV) from Al and Mn atoms in an Al-0.09 at.% Mn crystal after irradiation at 65K with $\sim 10^{16}$ 0.3-MeV He^+ ions/cm². The yield is plotted as a function of the angle from the [110] direction near the $(1\bar{1}2)$ plane. The backscattering yield was measured from a depth of 1000 Å (for Mn this was an average from 500-1500 Å or twelve channels). Note that the angular dependence of the energy loss of the He^+ ions is not nearly sufficient to cause an observable peak in Mn yield. (Ref. 115)

3. Lattice Models of Defects

In order to treat theoretically the complex behavior of point defects it is necessary to approximate the complicated many-body problem by some set of interatomic forces which are derived from experiments and theory (pseudopotentials, for example). Calculations of the energies of point defects in metals is most commonly performed by defining the lattice energy as a function of the position of all of the atoms in the lattice. Often the interaction is assumed to be describable in terms of pairwise forces between the atoms, and the interatomic potential is generally chosen to match physical properties of the solid, for example, the elastic constants. The form of the potential is governed somewhat by the nature of the calculations, and by the number of parameters which it is desired to fit.

The calculations are performed by means of high-speed large-memory digital computers. Even so, in order to limit the time and cost of these computations, a finite crystallite must be defined and boundary conditions chosen so as to simulate the response of the rest of the solid. With this scheme, formation and migration energies, and equilibrium configurations have been determined. The energy equation is evaluated in a region of the lattice dictated by the symmetry of the problem. The formation energy of a defect is given by the difference in energy between the crystallite with and without the defect. To determine a migration energy, it becomes necessary to map out the energy surface in order to find the saddle-points between two stable configurations. The migration energy is defined as the energy difference between the lowest-energy saddle-point configuration and the configuration with the defect at one of the stable sites.

The history of this field has been reviewed by Johnson¹¹⁶ recently, and it is also collected in the report of a colloquium on Interatomic Potentials and Simulation of Lattice Defects.¹¹⁷ Several viewpoints regarding the method of choosing potentials are expressed in the colloquium report. Johnson has divided the choices into semi-empirical, empirical and pseudopotentials. Most calculations to date have been performed with potentials which fall into one of the first two classes. However, increased effort to apply pseudopotential theory to defect problems¹¹⁷ has begun to yield results. Each approach to the determination of a potential seems to have shortcomings, and all of them might be regarded as providing only semi-quantitative information about the relative energies of various defect configurations. This fact underscores the importance of experimental determinations of defect energies and configurations as a means of evaluating the relative merits of empirical potentials.

There is another method by which the defect state can be investigated. It does not require that the explicit form of the potential energy function be known, but rather its derivatives. The method was introduced by Matsubara⁹⁹ and later Kanzaki¹⁰⁰ and is sometimes called the "Kanzaki Method". More often it is referred to as the method of lattice statics by virtue of its relationship to the theory of lattice dynamics. It has been widely applied by Hardy and Flocken¹¹⁸ and discussed by Bullough and Tewary¹⁰⁴ in connection with their Green function formalism. The appealing feature of the method of lattice statics is that it replaces the interatomic potential by the perfect crystal dynamical matrix whose elements, in turn, can be derived from phonon-dispersion data. However, some notion of the equilibrium defect configuration must be available because the Fourier transform of the force

array corresponding to a particular defect configuration must be calculated. These forces, which nowadays are called "Kanzaki forces" may be thought of as that set of forces which produces in the perfect lattice the same distortion as the defect would produce. The calculations in the lattice-statics formalism are carried out in Fourier-transform space, i.e. in the reciprocal lattice. Therefore, the transform of the defect displacement field is obtained directly. Thus lattice statics is especially well-suited to diffuse-scattering calculations.

The principles of the method are rather straightforward. They arise from the fact that the potential energy, U , of a distorted lattice can be expanded in terms of the interaction of a defect with the host atoms and displacements of the atoms from their lattice sites owing to the presence of the defect. In the harmonic approximation to lattice dynamics,

$$U = U_0 + \sum_l \psi(|r_l + u_l|) + \frac{1}{2} \sum_{ll'} \sum_{\alpha\beta} u_{\alpha}^l \phi_{\alpha\beta}^{ll'} u_{\beta}^{l'} \quad (94)$$

where ψ is an effective pairwise potential, r_l is the position of the l^{th} atom taking the origin on the defect site, u_l is the displacement of the atom at r_l , and α, β refer to Cartesian components of the displacements. The quantity $\phi_{\alpha\beta}^{ll'}$ is the dynamical matrix, i.e. the force constant matrix for the perfect lattice. Equilibrium is defined by minimizing U with respect to the displacements. The result may be written as

$$F_{\alpha}^l = \sum_{l'\beta} \sum_{\alpha\beta} \phi_{\alpha\beta}^{ll'} u_{\beta}^{l'} \quad (95)$$

The calculations are performed in a periodic superlattice of defects. Therefore if the displacements are expanded in normal coordinates, the complete set of distinct wavevectors q is contained within the first Brillouin zone. We have

$$u^{\ell} = \frac{1}{N} \sum_q Q^q \exp[iq \cdot \underline{r}^{\ell}] \quad (96)$$

After a certain amount of algebraic manipulation we find that the Fourier transforms of the real space forces and the dynamical matrix, given respectively by the expressions,

$$F_{\alpha}^q = \sum_{\ell} F_{\alpha}^{\ell} \exp(-iq \cdot \underline{r}^{\ell}) \text{ and} \quad (97)$$

$$V_{\alpha\beta}^{-q} = \sum_{\ell, \ell'} \phi_{\alpha\beta}^{\ell\ell'} \exp(iq \cdot \underline{r}^{\ell'}) \quad (98)$$

are related by the relation

$$F_{\alpha}^q = \sum_{\beta, q} V_{\alpha\beta}^{-q} Q_{\beta}^q \quad (99)$$

so that

$$Q_{\beta}^q = \left[\sum_{\alpha} V_{\alpha\beta}^{-q} \right]^{-1} F_{\alpha}^q \quad (100)$$

Here, too, the problem involves numerical evaluations which are best performed by a large computer. The elements of the force-constant matrix can be determined from phonon-dispersion data. In fairness to advocates of the direct-space approach using empirical potentials, it should be noted here that knowledge of the phonon frequencies alone is not sufficient to uniquely determine a set of force constants.¹¹⁹ In fact an infinite number of sets give the same frequencies. The polarization properties of the

phonons must be known also in order to remove the ambiguity, but they are seldom deduced. Johnson¹¹⁶ has already pointed out that for copper two different potentials yield good agreement with the measured dispersion curves.

Whereas the foregoing discussion dealt with calculations of static defect configurations, other lattice models have been set up to provide insight into the dynamic behavior of defects. The calculations of Gibson et al.⁷⁶ represent the earliest attempt to simulate defect dynamics, and many other programs have subsequently been based upon the essential features of that early investigation. A recent study of this type has been reported by Scholz and Lehmann⁷⁷ in which the stability and vibrational behavior of point defects in copper were examined. Of particular interest to us are their results on the structure and dynamic behavior of vacancies, interstitials and Frenkel pairs.

Scholz and Lehmann's research confirmed many of the results reported earlier by Gibson et al. For example, the relaxation of atomic shells about a vacancy exhibits the typical outward relaxation of the shell of 2nd nearest neighbors; the stable interstitial configuration in Cu is the dumbbell-shaped split interstitial oriented along a $\langle 100 \rangle$ direction, and spontaneous recombination occurs within a region of instability comprising 74 sites surrounding an interstitial. In the (100) plane the location of the unstable sites agree with those found by Gibson et al.⁷⁶ as shown in Fig. 28 .

The dynamic behavior of the defects proved very interesting. Investigation of vacancy motion furnished no surprises, however. The easiest way for a vacancy to form is to allow one of its neighbors to jump into it along the line connecting the two sites. A rather broad minimum exists around this direction, but then the threshold energy rises rapidly. The behavior of the interstitial was investigated in two energy transfer regimes:

Fig. 28 Location of unstable sites for interstitial-vacancy pairs in the (100) plane of Cu. (Ref. 76)

- 1) small energy transfer where only vibrational states could be excited,
- and 2) larger transfers in which the interstitial can migrate.

1. Small Energy Transfers

From symmetry properties of the lattice Scholz and Lehmann deduced the vibrational modes of the dumbbell configuration as given in Table VIII. The frequencies ω_1' were calculated with the dumbbell in a rigid cage for comparison with the computer calculations, ω_1 . The latter were higher with the exception of ω_3 in which the center of mass oscillates parallel to the dumbbell axis. A number of trial cases were run and it was discovered that the axial mode (1) was always excited along with other modes. The axial mode has a high frequency as expected and its amplitude is only slowly attenuated. Mode 3, vibration of the center of mass, is much slower and is rapidly attenuated. Generally a high-frequency mode is found to superimpose upon a low-frequency vibration which is rapidly attenuated. As predicted, the mode frequencies (except mode 3) are localized since the neighboring atoms vibrate out of phase with the dumbbell atoms.

Mode 3 is a resonance mode and in a subsequent investigation, Dederichs, Lehmann and Scholz¹²⁰ discovered another resonance mode which was initially unexpected. This mode is a libration like mode 2 in Table VIII. In both cases, a high-frequency, nearly undamped localized mode, is superimposed as before. Dederichs et al. have furnished a qualitative explanation for their observations in terms of two force constants, $f_{||}$, important for displacements parallel to the dumbbell axis, and $f_{\perp}$, for displacements perpendicular to that direction. They state that in the neighborhood of the dumbbell the lattice is so highly compressed that $f_{\perp}$, which would be negligible in a perfect lattice, cannot be neglected. Moreover, because of the strong repulsive forces between atoms, $f_{\perp}$ is always negative. For vibrations which do not emphasize parallel displacements, and hence the

Table VIII

Vibrational modes of the dumbbell. The frequencies ω'_i are values from an analytical treatment; the frequencies ω_i are computer results. (The maximum frequency is $\omega_m = 4.2 \times 10^{13} \text{ sec}^{-1}$; the time unit is $t_0 = 3.27 \times 10^{-15} \text{ sec.}$)

Mode no.	Mode	Degeneracy	$\frac{\omega'_i}{10^{13} \text{ sec}}$	$\frac{\omega'_i}{\omega_m}$	$\frac{T}{t_0} = \frac{2\pi}{\omega_i t_0}$	$\frac{\omega_i}{\omega_m}$	$\frac{ \omega_i - \omega'_i }{\omega_i}$
1		1	5.5	1.30	33	1.37	5%
2		2	3.6	0.85	37	1.25	32%
3		1	1.8	0.42	≈ 300	≈ 0.15	$> 100\%$
4		2	4.1	0.97	38	1.21	20%

f_1 , the f_2 become important. They lower the frequency and are the source of resonance modes.

The physical significance of these modes in terms of observed mechanical properties of metals was pointed out by Dederichs et al.¹²⁰

Two effects come to mind:

1. The large thermal displacements which may accompany resonance modes can lead to diffusion of dumbbells, perhaps by a combination of a jump and a 90° rotation.
- ii. The presence of the libration mode implies that the interstitial is easily polarized by an external applied shear stress. This should give rise to an observed softening of the lattice. In fact, large negative changes of the elastic shear constants in irradiated metals have been reported.¹²¹
2. Larger Energy Transfers
We shall discuss the effect of defects on mechanical properties in

the next section. At present, the dynamics of interstitial motion are not fully explored. It appears from the computer studies that interstitial rotation is always accompanied by a jump to a new site. In addition the threshold energy for this motion is dependent upon the presence or absence of a nearby vacancy. Much remains to be examined in detail not the least of which is the dependence of results upon the choice of potentials. Drittler et al.¹²² have conducted an independent investigation of some Frenkel-pair annihilations using a similar model but a Morse potential. The question of recombination volumes is especially interesting because it has become possible to determine them experimentally from damage production-rate measurements as shown by Wollenberger and his colleagues.⁷⁵

IV. POINT DEFECTS AND ELASTIC PROPERTY CHANGES

Point defects can produce changes in the elastic properties of a metal by means of several different processes. These have been described by a number of authors including Holder et al.^{121,123} and Townsend et al.¹²⁴ Taking into account effects which have recently been recognized there are five phenomena:

1. dislocation pinning in which point defects act as pinning points along the dislocation, and alter the decrement and the dynamic Young's modulus,
2. bulk effects arising from local changes in elastic properties near a defect and long-range effects of the elastic strain,
3. relaxation effects which take place when the defect is thermally induced to reorient under an applied strain,
4. polarization effects, as described by Pistorius and Ludwig¹²⁵ and Dederichs et al.¹²⁰ which occur if the defect is highly polarizable in an external stress, and ,
5. thermal excitation of defect resonance modes which induces a temperature dependence in the elastic-constant changes caused by the presence of the defects.

It is rather difficult to sort out the various causes of mechanical property changes as they may all occur in a given experiment. In fact, it may be impossible to observe effects associated with point defects unless the dislocations are pinned first so that they do not contribute to the internal friction and modulus defect. Once the dislocation effects have been suppressed, then the two most familiar point-defect phenomena can be observed. The first is a change in the modulus for large defect concentrations. This is called the "bulk effect", and we shall say more about it shortly. The second effect is called stress-induced reordering,

and it is manifested as a peak in the logarithmic decrement versus temperature curve. It is not always possible to know unequivocally whether a modulus defect is a bulk effect or is related to a defect causing a peak in the logarithmic decrement, i.e. a relaxation effect. It is helpful in such studies to simultaneously follow the behavior of another physical property during annealing. Electrical resistivity is the best candidate and has been employed in some studies involving elastic-constant measurements on irradiated metals.

The fact that point defects can migrate to dislocations and alter the dynamic response of the latter to an external stress has played an important role in mechanical-properties studies. However, it is not clear after all these years of investigation whether the results have fulfilled the original promise of the research. Hence, we will not review this aspect of the field in detail. In all likelihood it will be dealt with by other lecturers so that we only mention it below for the sake of completeness.

A. Dislocation Damping and Pinning

We will be discussing the anelastic effects associated directly with point defects. However we cannot overlook the indirect effect of dislocations for they are always present, initially as an undesirable background. In fact, there are many dynamic-loss phenomena connected with point-defect dislocation interactions under a time-dependent applied stress. An entire course could be devoted to the subject of dislocations and their mechanical behavior as related to internal friction in metals. Let us consider the most successful model of dislocation damping that explains reasonably well the internal friction associated with dislocation motion. This is the Koehler-Granato-Lücke theory based upon a string model of a dislocation. 126,127

In this model the dislocations are assumed to be pinned by defects or nodes so that we can speak of an average dislocation length, ℓ . The dislocation is then endowed with all of the properties of a string so that the mathematical formalism for the equation of motion of the dislocation under an applied time-dependent stress is:

$$M \frac{\partial^2 y}{\partial t^2} + B \frac{\partial y}{\partial t} - T \frac{\partial^2 y}{\partial x^2} = \sigma_0 b e^{-i\omega t} \quad (101)$$

M = effective mass per unit length of the dislocation = $\pi \rho b^2$,

B = a viscous damping coefficient,

T = effective line tension of the dislocation (responsible for the restoring force), and

b = magnitude of the Burgers vector.

The boundary conditions are that $y(0,t) = y(\ell,t) = 0$.

It is seldom necessary to calculate the exact solution to the string equation. The natural frequency of the string is $\omega = \pi c/\ell$, where c is the velocity of sound and ℓ , the average dislocation length. For $c \sim 10^5$ cm/sec and ℓ , typically $\sim 10^{-3}$ cm, $\omega \sim 10^8$ Hz. This is a frequency well beyond that at which internal-friction experiments are normally conducted. Thus, the inertial term may be neglected in most cases. The remainder of the terms are physically reasonable to consider. Provided that we are performing measurements in the small stress range so that the internal friction is amplitude independent, we should find, according to KGL theory that

$$\delta = k_{\delta} \frac{\pi E b^2}{T^2} \omega B \Lambda \ell^4, \text{ and}$$

(102)

$$\Delta E/E = k_E \frac{E b^2}{2T} \Lambda \ell^2,$$

where Λ is the total dislocation length per unit volume; E is the dynamic Young's modulus, and k_{δ} and k_E depend upon the choice of functions used to describe the distribution of dislocation lengths. The important features of the two equations are the dependence of δ upon ℓ^4 and of $\Delta E/E$ on ℓ^2 , and the dependence of δ on ω as well. The experimental situation with regard to these two dependences is as follows:¹²⁸

1. Frequency Dependence: $\delta \propto \omega$

At low frequencies (<30-40 kHz), δ is independent of ω and in some experiments it has been found that δ actually increases with decreasing ω . On the other hand in the MHz range $\delta \propto \omega$ as predicted.

2. Length Dependence: $\delta \propto \ell^4$, $\Delta E/E \propto \ell^2$.

In order to avoid assumptions about the number of pinning points along a dislocation one commonly plots δ vs $(\Delta E/E)^2$. This should be a linear plot, but generally it is not found to be so experimentally.

In the comparison of theory with experiment, radiation has played a major role for a number of reasons:

- a) The point defects created by radiation can act as new pinning points upon arrival at dislocation lines,
- b) the concentration of new primary points can be controlled by the choice of irradiation conditions,
- c) the new point-defect pinners simply add to the concentration of pre-existing pinners under appropriate conditions,

- d) the only factor affected by the addition of point defects to dislocations is the average dislocation loop length, ℓ , and, finally,
- e) in the absence of any complications such as impurity trapping, and diffusion along dislocations ("pipe diffusion"), the way in which ℓ is affected is assumed to be given by the relation $\ell = \ell_0 / (1+n)$, where n is the number of new pinners added to a dislocation of initial length ℓ_0 . This requires that n be large, and incidentally, this condition is not met in some of the most interesting recent experiments.

The foregoing is the framework within which studies of point-defect related internal friction have been conducted. In spite of the discrepancies between the KGL theory and experiment, the field has been under intensive investigation for many years and there is every reason to believe that it will continue to be extremely active.

B. Bulk Effect

The effect of point defects upon all of the elastic constants, has been considered by Zener,¹²⁹ Dienes,¹³⁰ Nabarro,¹³¹ Townsend et al.¹²⁴ Melngailis,¹³² and Holder and Granato.¹³³ Reviewing these efforts, we conclude that the theory of elastic defect effects is in rather poor shape, and experimentally, the contribution from dislocations will tend to obscure the results. With the availability of low dislocation-density crystals, the experimental problems have eased somewhat. However, uncertainty still surrounds the expected elastic constant changes.

The early calculations by Dienes¹³⁰ suggested a positive bulk effect of ~ 10 percent per atomic percent of interstitials, and a negative effect of about one percent per atomic percent of vacancies. Townsend et al.¹²⁴ draw similar conclusions from calculations based upon isotropic elasticity theory, and Holder and Granato arrive at about the same values from thermodynamic arguments. Experimental results are not much more encouraging and are summarized in Table IX and X taken from a recent paper by Rehn et al.¹²¹ These table summarize results for elastic constant changes induced by radiation of various types. Radiation has played an important role throughout these studies for it offers a means of introducing sufficient intrinsic-type defects to be observable and controllable.

Some of the experimental discrepancies in Tables IX and X may be attributed to differences in the nature of the defects introduced by the various types of radiation used. The effects are different for the various elastic constants, too. However, the range of results is too great to be explained away on these grounds. Recent theoretical results at Jülich have explained many puzzling features of the results in terms of the resonance modes of split interstitials discussed earlier.^{77,120}

C. Point Defect Relaxation

Point defects can produce in a crystal a property called by Zener "anelasticity", a form of imperfect elasticity.¹³⁴ Formally, the concept of anelasticity is embodied in a generalization of Hooke's Law, $\epsilon = J\sigma$ which takes the form:

$$J_R \sigma + \tau_\sigma J_u \dot{\sigma} = \epsilon + \tau_v \dot{\epsilon} \quad (103)$$

Table IX A brief description of the reported measurements of
irradiation induced changes in the elastic modulus of
various materials other than copper. (Ref 121)

	$\frac{d \ln C}{dy}$	Material	Radiation Type	Radiation Temperature (K)	Measurement Temperature (K)	Simultaneous Resistivity	Measurement Frequency (Hz)
Gerlich <u>et al.</u> ^a	Few percent decrease for all 3 constants	LiF	Reactor Neutrons	300	300	No	10^7
Muss and Townsend ^b	-0.44	W	13.7 Mev Deuterons	300	300	No	10^3 - 10^4
DiCarlo and Townsend ^c	-(0.2-1)	W	13 Mev Deuterons	78-90	78	No	10^3 - 10^4
DiCarlo <u>et al.</u> ^d	-11	W	2.5 Mev Electrons	≤ 20	≤ 20	Yes	600
Townsend <u>et al.</u> ^e		W	10 Mev Protons	< 15	4.2	No	$5-20 \times 10^2$
Hillairt <u>et al.</u> ^f	Large decrease	Mg	Reactor Neutrons	80	80	No	--
Likhter and Kikoin ^g	No effect on bulk modulus	Mg Al	Reactor Neutrons	300	300	No	--
Folweiler and Brontzen ^h	-10	Al	Quench (only vacancies)	Quench from 800	300	No	10^5

Table continued

	$\frac{d\ln C}{dy}$	Material	Radiation Type	Radiation Temperature (K)	Measurement Temperature (K)	Simultaneous Resistivity	Measurement Frequency (Hz)
Ehrensperger et al. ⁱ	-47 -67	Al Pt	Reactor Neutrons	4	4	Yes	50-300
Chountas et al. ^j	-39 $\pm$ 9	Ag	Reactor Neutrons	25	10	Yes	44 140
Soulie et al. ^k	-70	Ni	2 Mev Electrons	11-21	11-21	Yes	350

^aReference 14.

^bD. R. Muss and J. R. Townsend, J. Appl. Phys. 33, 1804 (1962).

^cJ. A. DiCarlo and J. R. Townsend, Acta. Met. 14, 1715 (1966).

^dJ. A. DiCarlo, C. L. Snead, and A. N. Goland, Bull. Am. Phys. Soc. series II, 13, 381 (1968).

^eReference 8

^fJ. Hillairet, E. Bonjour, and J. P. Poirier, Journal de Physique 7, C2-31 (1971).

^gA. I. Likhter and A. I. Kikoin, J. Exptl. and Theoret. Phys. (U.S.S.R) 32, 945 (1957).

^hR. C. Folweiler and F. R. Brotzen, Acta. Met. 7, 716 (1959).

ⁱReference 41.

^jK. Chountas, W. Donitz, K. Papathanassopoulos and G. Vogl. Phys. Stat. Sol. 53, 219 (1972).

^kJ. C. Soulie, J. Lauzier, and C. Minier, Rad. Effects 19, 63 (1973).

^aD. Gerlich, J. Holder, and A. Granato, Phys. Rev. 181, 1220 (1969).

Table continued

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Soulie et al. ^k	-70	Ni	2 Mev Electrons	11-21	11-21	Yes	350

^aReference 14.^bD. R. Muss and J. R. Townsend, J. Appl. Phys. 33, 1804 (1962).^cJ. A. DiCarlo and J. R. Townsend, Acta. Met. 14, 1715 (1966).^dJ. A. DiCarlo, C. L. Snead, and A. N. Goland, Bull. Am. Phys. Soc. series II, 13, 381 (1968).^eReference 8^fJ. Hillairet, E. Bonjour, and J. P. Poirier, Journal de Physique 7, C2-31 (1971).^gA.I. Likhter and A. I. Kikoin, J. Exptl. and Theoret. Phys. (U.S.S.R) 32, 945 (1957).^hR. C. Folweiler and F. R. Brotzen, Acta. Met. 7, 716 (1959).ⁱReference 41.^jK. Chountas, W. Donitz, K. Papathanassopoulos and G. Vogl. Phys. Stat. Sol. 53, 219 (1972).^kJ. C. Soulie, J. Lauzier, and C. Minier, Rad. Effects 19, 63 (1973).

Table X A brief description of the reported measurements of
irradiation induced changes in the elastic modulus
of copper. (Ref. 121)

	$\frac{d\ln C}{dy}$	Material	Radiation Type	Radiation Temperature (K)	Measurement Temperature (K)	Simultaneous Resistivity	Measurement Frequency (Hz)
Present Experiment	$C_{11} -4.8$ $C_{44} -15.8$ $C' -18.1$	Cu	Thermal Neutrons	<4	3.6	Yes	10^7
Dieckamp and Sosin ^a	-140 ± 50	Cu	1 Mev Electrons	78-206 (gradient)	78	No	500
Roth and Naundorf ^b	-75 ± 20	Cu	3 Mev Electrons	120	78	Yes	2.5×10^3
Thompson et al. ^c	none (< 1)	Cu	Reactor Neutrons	21	21	No	10^4
Konig et al. ^d	-130	Cu	5.3 Mev Alpha particles	-30	4	No	10^2
Okuda and Nakanii ^e	~ 80	Cu	Reactor Neutrons	<15	4	No	4×10^2
Wenzl et al. ^f	-39	Cu	Reactor Neutrons	4	4	Yes	50-300
Townsend et al. ^g	-13 ± 3	Cu	10 Mev Protons	<15	4.2	No	$5-20 \times 10^2$

^aReference 2

^dReference 12

^gReference 8

^bReference 40

^eReference 44

^cReference 3

^fReference 41

The references in the footnotes can be found in Ref. 121: L. E. Rehn, et al.,
Phys. Rev. 10B, 349 (1974).

This generalization still retains two important restrictions on the property of the solid:

1. linearity of response, that is, doubling the stress will double the strain, and
2. uniqueness of response, that is, a unique equilibrium state corresponds to every instantaneous applied stress. When the stress is removed, the strain returns eventually to zero, although there will be a relaxation time associated with this process.

Generally, in studies of point defects one is most interested in a dynamic experiment in which the applied stress has a sinusoidal time dependence:

$$\sigma = \sigma_0 \exp(i\omega t).$$

The detection of point defects by the application of such a stress depends upon the ability of the stress to change the free energy associated with the presence of the defects. This can occur if the defects produce a local strain field whose symmetry is lower than that of the lattice; the defects are then called "asymmetric defects". Under these conditions, when the external stress is applied, defect lattice positions that were energetically equivalent under zero-stress conditions split in energy. The result is a redistribution of the defect population among the available positions provided that the temperature is high enough for the defects to be mobile. This phenomenon is called "stress-induced ordering". For an alternating applied stress, the energies of the various positions are dependent upon the time so that the excess defect population always will tend to reorient toward the orientation with the lowest instantaneous energy. However, the defects cannot reorient instantaneously, but instead will exhibit a finite

relaxation time, τ , associated with their motion. Thus, stress-induced defect reorientation will be out of phase with the applied stress, giving rise to energy losses and the so-called "internal friction". We can see formally how this comes about from the generalized equation for the standard anelastic solid given earlier. We noted that the applied stress can be represented as $\sigma = \sigma_0 \exp(i\omega t)$. We also have concluded that there will be a phase lag in the associated strain because the defects require time to move. Thus, we can write:

$$\epsilon = \epsilon_0 \exp(i\omega t - i\phi) = (\epsilon_1 - i\epsilon_2) \exp(i\omega t). \quad (104)$$

From this expression and the generalized Equation (103) we can develop the expression for the so called "decrement". Substituting into the generalized equation, we find that

$$\epsilon = J \sigma = (J_1 - iJ_2) \sigma, \quad (105)$$

where

$$J_1 = J_U + \frac{\delta J}{1 + \omega^2 \tau^2} \quad \text{and} \quad J_2 = \delta J \frac{\omega \tau}{1 + \omega^2 \tau^2},$$

with $\delta J = J_R - J_U$.

We note also that $\tan \phi = \epsilon_2 / \epsilon_1 = J_2 / J_1$.

Zener and others have shown that when $\delta J / J_U$ is small, as it usually is in any of the experiments we are interested in, then

$$\tan \phi = \frac{\Delta \omega \tau}{1 + (\omega \tau)^2}, \quad (106)$$

to a good approximation, where $\Delta = \delta J / J_U$ is known as the relaxation strength, and τ is the relaxation time for the asymmetric defects to reorient. The quantity $\tan \phi$ is generally called the decrement, δ , because it can be shown that

$$\delta = \pi \tan \phi = \Delta W / 2W, \quad (107)$$

where W is the total vibrational energy associated with the maximum elastic strain energy, and ΔW is the energy loss per cycle. Thus we have the relation

$$\delta = \pi \Delta \frac{\omega \tau}{1 + (\omega \tau)^2} . \quad (108)$$

Notice that if we plot δ versus $\omega \tau$ we have a maximum when $\omega \tau = 1$, i.e., when $\tau^{-1} = \omega$, the frequency of the applied stress.

In order to experimentally trace out this curve over the entire frequency spectrum we would need very special apparatus and experimental design. However, recall that the motion of the defects is thermally activated, i.e.,

$$\tau = \tau_0 \exp(E_R/kT) , \quad (109)$$

so that $\omega \tau = \omega \tau_0 \exp(E_R/kT)$ and $\ln \omega \tau = \ln \omega \tau_0 + (E_R/k)1/T$. Therefore, since $\ln \omega \tau$ is a linear function of T^{-1} one can just as well plot δ versus T^{-1} as against $\ln \omega \tau$. Also as T increases, τ will decrease, so that the time required for reorientation will decrease.

Because stress-induced ordering depends upon the symmetry of the defect, it is possible to learn something about the symmetry by means of an internal-friction experiment. Suppose that in a strain-free lattice a defect can assume any one of n energetically equivalent positions. These

positions will differ in the orientation of their strain fields relative to axes fixed in the crystal. The total atomic fraction of defects is thus,

$$C = \sum_{p=1}^n C_p, \text{ and} \quad (110)$$

when $\epsilon = 0$, $C_p = C_{p+1}$, $p = 1 \dots n-1$.

The total crystal strain tensor is then composed of elements

$$\epsilon_{ij} = \sum_{p=1}^n \lambda_{ij}^{(p)} C_p, \quad (111)$$

where $\lambda_{ij}^{(p)}$ is the ij^{th} component of a 3×3 elastic strain tensor associated with the defects in the p^{th} orientation. $\lambda_{ij}^{(p)}$ can be diagonalized yielding the diagonal components $\lambda_1, \lambda_2, \lambda_3$ independent of p , and these represent the three principle strains of the defect along three mutually perpendicular axes. So the asymmetric defect can be specified by the crystallographic directions of its three principle strain axes. For example, the "split-interstitial" that we have discussed earlier has the three principal directions: $\langle 110 \rangle$, $\langle \bar{1}\bar{1}0 \rangle$ and $\langle 001 \rangle$.

We have seen that the magnitude of the internal friction is related to Δ , the relaxation strength. Nowick and Heller¹³⁵ have investigated theoretically the expression for Δ in the presence of point defects in cubic crystals. They found that

$$\Delta \sim \frac{C}{T} \psi^{[hkl]},$$

$\psi^{[hkl]}$ is a quantity dependent upon the applied stress direction, and upon the degree of anisotropy of the defect strain field. As an example, we can consider the lower symmetry defects of the type: tetragonal, trigonal or orthorhombic in cubic crystals. Then we find the following results in the b.c.c. lattice:

Asymmetric Defects in a Cubic Lattice

Defect symmetry	<u>tetragonal</u>	<u>trigonal</u>	<u>orthorhombic</u>
Principal Strain directions			
(λ_1)	$\langle 100 \rangle$	$\langle 111 \rangle$	$\langle 110 \rangle$
(λ_2)	$\langle 010 \rangle$	$\langle 1\bar{1}0 \rangle$	$\langle 1\bar{1}0 \rangle$
(λ_3)	$\langle 001 \rangle$	$\langle 11\bar{2} \rangle$	$\langle 001 \rangle$
Symmetry relations	$\lambda_2 = \lambda_3$	$\lambda_2 = \lambda_3$	---
No. of orientations	3	4	6
Relaxation strength (ψ) vs. stress direction $[hkl]$			
$[100]$	$2(\lambda_1 - \lambda_2)^2$	0	$2\left(\frac{\lambda_1 + \lambda_2}{2} - \lambda_3\right)^2$
$[111]$	0	$\frac{4}{3}(\lambda_1 - \lambda_2)^2$	$(\lambda_1 - \lambda_2)^2$
bcc interstitial configurations			
(single atom)	octahedral, tetrahedral	activated-crowdion	
(split)	$\langle 100 \rangle$	$\langle 111 \rangle$	$\langle 110 \rangle$

Thus, if we compare the observed dependence of Δ on stress direction in a single crystal, with the theoretical dependence for different defect configurations, we can determine experimentally the defect geometry.

Two examples of the observation of intrinsic point defects illustrate the power of the relaxation technique. The two cases represent relaxation in Cu, an f.c.c. metal and in W, a b.c.c. metal. In each case, the point defects were created by irradiation at or near liquid-helium temperature. The copper single crystals were exposed to 8.9-MeV protons, whereas the tungsten single crystals were irradiated by 2.5-MeV electrons. The mechanical vibrations of the samples were detected by a piezoelectric method or an f.m. detection technique. In either case, the frequency of the sample could be measured as a function of integrated flux. The logarithmic decrement, δ , was determined by counting the number of cycles which the decaying oscillating voltage completed between two preset voltage levels or by measurement of the decaying signal as recorded on a photograph taken from an oscilloscope. The envelope of the decaying signal is an exponential from which δ can be deduced.

Nielsen and Townsend found that upon annealing their Cu samples after irradiation, an internal friction peak appeared at 10K in polycrystalline samples and in a single crystal oriented with its axis along the $\langle 111 \rangle$ (see Figs. 29-30). direction. The peak failed to appear in measurements on a $\langle 100 \rangle$ -oriented crystal. By measuring the internal friction and resonant frequency for the fundamental and first overtone modes of the sample, Nielsen and Townsend were able to show that the observed internal-friction peak was related to a thermally-activated process, (see Figs. 31,32).

Recalling that the peak maximum occurs when $\omega \tau_0 \exp(E_R/kT) = 1$ we see that measurement of peak temperature as a function of applied frequency yields E_R and τ_0 . Thus,

$$\ln \omega = -(E_R/k)(1/T) - \ln \tau_0, \quad (112)$$

so that the slope of an Arrhenius plot yields E_R and the intercept gives

Fig. 29 The variation of δ and f_r with temperature in the temperature range from 5 to 16 K of a $\langle 111 \rangle$ - oriented single crystal copper sample. (Ref. 136)

FIG. 30 The temperature variation of δ and f_y after subtracting the background in the temperature range from 5 to 16 K of a $\langle 111 \rangle$ -oriented single crystal copper sample. (Ref. 136)

Fig. 11 A comparison of Δ and f_r in the temperature range 5 to 60 K of a $\langle 100 \rangle$ - oriented single crystal copper sample after irradiation and after annealing to 55 K. (Ref. 136)

Fig. 32 The linear variation of $\ln(2\pi f_r)$ vs. $1/T_{\max}$ for all samples having an anelastic process around 10 K. (Sample numbers are shown near data points.) (Ref. 136)

a characteristic frequency. Nielsen and Townsend found $E_R = 0.015 \pm 0.002$ eV and $\log_{10} 2\pi\tau_0 = -11 \pm 1$. They were fortunate in that the peak did not anneal as it was being detected. Therefore its shape and position could be well defined. Above about 25K peak annealing began as indicated by a reduction in peak height. This is the temperature at which interstitial-vacancy close pairs are believed to anneal (Stages I_b and I_c) with activation energies for migration of ~ 0.090 eV. It was found that the behavior of the decrement and the modulus defect was consistent with the concepts of anelasticity. Therefore, the symmetry arguments mentioned earlier were applicable. The absence of a peak for the $\langle 100 \rangle$ -oriented crystal can only occur if the defect axis has a $\langle 111 \rangle$ orientation, ie, trigonal symmetry. The anisotropy factor, $\Delta\lambda$, deduced from modulus-defect data was found to be $0.15 \pm .04$.

More recently, measurements of elastic-constant changes following low-temperature neutron irradiation of Cu single crystals have been reported by Holder et al.¹²³ and Rehn et al.¹²¹ They used a pulse-echo technique which allowed them to observe the bulk modulus, C_{44} and $C' = (C_{11} - C_{12})/2$ separately in one of the most complete experiments of its kind. The irradiations were performed with thermal neutrons to ensure that only simple defects were created. We note that they also observed a sharp dispersion in C_{44} which is characteristic of a relaxation process. The orientation dependence of the effect agreed with the Nielsen-Townsend measurements. The temperature at which the sharp change in C_{44} occurred (18K) was consistent with the temperature shift expected on the basis of the difference in applied-stress frequencies.

Holder et al. went further than Nielsen and Townsend in trying to identify the configuration of the defect responsible for the relaxation effect. They concluded first that the defect must correspond to substage I_c in Cu because of its annealing behavior. Furthermore, correcting for differences in estimated defect concentrations, they achieve excellent agreement with Nielsen and Townsend if the shape factor $\Delta\lambda = |\lambda_1 - \lambda_2| = 0.5$. Finally, by symmetry arguments they conclude that it is not a vacancy-interstitial complex which relaxes, but only the interstitial member of the pair which reorients. The most probable configuration of the split interstitial is proposed as that shown in Fig. 33. It satisfies all the necessary criteria and is consistent with other known experiments.

Experiments similar to those performed by Nielsen and Townsend were carried out on single crystals of W by DiCarlo et al.¹³⁷ using 2.5-MeV electrons. Electrical resistivity, dynamic Young's modulus and internal friction were all measured following irradiations at $\sim 20K$. After irradiation a prominent but transient internal-friction peak was observed at 30K as shown in Figs. 34, 35, and a prominent resistivity recovery peak was observed at the same temperature which is believed to be that of a major close-pair recovery substage (Fig. 36). Determination of the defect symmetry from single-crystal data was more difficult than in the case of copper because the same peak was observed in $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ -oriented crystals. Therefore, conclusions had to be drawn from the relative relaxation strengths for different crystal orientations. Di Carlo et al. concluded that the defect responsible for the 30K relaxation probably had orthorhombic symmetry, its maximum distortion lying along $\langle 110 \rangle$. Their conclusions regarding the exact configuration of the defect were more tenuous,

Fig. 33 Most probable configuration of stage I_c defect deduced from elastic-constant data. Four of the 24 equivalent sites for the center of mass of the interstitial are marked with a small cross. The equivalent position into which the split-interstitial relaxes is shown by a dotted outline. (Ref. 123)

Fig. 34 The logarithmic decrement versus temperature results for the preirradiation and anneal runs on a [100] single crystal of tungsten which was previously subjected to heavy dislocation-pinning irradiations. (Ref. 137)

Fig. 35 The logarithmic decrement versus temperature results for the preirradiation and anneal runs on a [100] and a [110] single crystal. Both samples were subjected to identical irradiation and annealing treatments. (Ref. 137)

Fig. 36 The derivative of the isochronal resistivity - recovery curve
for a polycrystalline sample of tungsten. (Ref. 137)

but they believed that the relaxation could be attributed to the interstitial partner in a close pair.

It is interesting to recall that in the computer simulations of defects in Cu by Scholz and Lehmann⁷⁷ they observed that an isolated interstitial never rotated without an accompanying translational motion. The experiments just described suggest that if a nearby vacancy is present, the split interstitial may rotate about its center of mass into an equivalent position without undergoing simultaneous translation.

V. POINT DEFECT MODELS FROM RADIATION RESEARCH AND TECHNOLOGY

A. Radiation Damage

In the introduction to these lectures and throughout the succeeding sections it has been evident that radiation plays a key role in the study of point defects. In particular, irradiations with energetic electrons (0.1-3.0 MeV) are the best means for introducing simple vacancy and interstitial pairs. Irradiations at or near 4K followed by annealing experiments have been performed for many years in this field. From resistivity recovery data, well-defined annealing stages were established for many metals. A typical example of these results is shown in Fig. 37 taken from the work by Sonnenberg and Schilling¹³⁸ on platinum. Resistivity recovery was measured following introduction of about 50 ppm of Frenkel defects by irradiation with 3-MeV electrons at a sample temperature of 4.5K. Substages I_A - I_E of the major close-pair recovery state I are clearly visible as are stages II and III. In some metals a stage IV and V are also observed, and in others stage I is not so well defined. The original proposal by Corbett, Smith, and Walker¹³⁹ that substage I_A , I_B , and I_C represent the recombination of close pairs by various mechanisms has withstood the test of time, and it is regarded as well established. The general model for state I is illustrated schematically in Fig. 38.¹⁴⁰ The relevant parameters which characterize the dynamics of the defect motion, annihilation or trapping, are r_p , r_i , r_v , and r_t . These quantities represent, respectively, the primary separation radius when a Frenkel pair is created, the interaction radius for interstitial-interstitial (di-interstitial) formation, the interaction radius for interstitial-vacancy mutual annihilation and the interaction radius for interstitial

Fig. 37 Isochronal recovery of pure Pt irradiated at 4.5K with 3-MeV electrons to $\Delta\rho_0 = 56 \text{ n}\Omega\text{cm}$ (equivalent to about 50 ppm Frenkel defects). (Ref. 140)

Fig. 38 Schematic view of the reactions of freely migrating interstitials in stages I_D and I_E . *, interstitial, □, vacancy.
 (Ref. 140)

trapping, at an impurity or some other trap. Values for these quantities can be obtained by comparing drift diffusion theory to resistivity damage rate and isochronal annealing data.^{141,142} Stages I_A through I_C are believed to arise from recombinations of interstitials with their own vacancies by single jump processes. Stage I_D is attributed to correlated recombination of interstitials with their own vacancies, following a random walk process. The probability that an interstitial performs a random walk and then recombines with its own vacancy is taken as $f_{\text{corr}} = r_v/r_p$. The probability that the interstitial escapes its own vacancy is $(1-f_{\text{corr}})$. This escape accounts for the occurrence of stage I_E , uncorrelated recovery. This stage is well defined in samples of low intrinsic defect density and high purity. As the defect density increases the distance to any vacancy becomes about equal to r_p so stage I_E begins to merge with I_D . If the impurity concentration increases, impurity trapping begins to dominate and again stage I_E is suppressed.

Wollenberger and his associates^{75,142} have shown how damage-rate measurements well above stage I, using electrical resistivity as a property proportional to defect concentration, can yield information about the reaction parameters relating to stage I. At 80K where the measurements are taken during irradiation, the remaining interstitials must be trapped in order to survive. Then the rate of increase of the radiation-induced defect concentration with flux, $dc/d\phi$ is given by the expression:

$$\left(\frac{dc}{d\phi} \right)_{80K} = \sigma'_d (1-f_{\text{corr}}) \left(\frac{r_t c_t}{r_t c_t + r_v c} \right). \quad (113)$$

The quantity σ'_d is the probability of free interstitial creation, $(1-f_{\text{corr}})$ has been defined earlier, and the last factor is the fraction of interstitials which is trapped by the impurities that are present in concentration c_t .

From the slope and intercept of $(dc/d\phi)_{4K}/(dc/d\phi)_{80K}$, f_{corr} and $(r_v/r_t)c_t$ can be found. The results as shown below are in good agreement with those deduced from Stage I annealing data:

	Pt	Cu	Al
r_p/r_v	1.5	1.5	1.4
r_i/r_v	1.4	~ 1	~ 2
r_v/a (a = lattice constant)	~ 6	~ 5	~ 5

The region of instability as determined by the computer simulations mentioned in an earlier section is consistent with these experimental results.^{76,77} Also, the probability of close-pair or correlated recovery in these metals, r_v/r_p , exceeds 66 percent. This accounts for the large proportion of resistivity recovery in stages I_A through I_D .

In our discussion of diffuse scattering it was pointed out that the diffuse intensity should be proportional to the cluster size when clusters form out of a dilute solution of randomly-distributed interstitials. This phenomenon appears to be occurring at the end of stage I and through stage II in copper and aluminum as seen by Schilling and his colleagues. Their analysis indicates that the cluster size is about ten interstitials, but the details of the clustering mechanism are not clearly understood as yet. Moreover, while the cluster size is growing the electrical resistivity recovery continues, suggesting that the resistivity of a cluster is smaller than that of an equal number of isolated interstitials. More work will be needed in this temperature region to define the process by which clusters grow, and

to identify interstitial-impurity complexes.

The most controversial stage at present remains stage III which is variously attributed to vacancies or interstitials. The evidence from the diffuse scattering experiments in stage I favors the vacancy interpretation for stage III, but inconsistencies still exist in this model. Perhaps positrons which, as we have learned, are sensitive to vacancies but not to interstitials will be most useful in studies of stage III.

Stages IV and V, when they exist, are most probably manifestations of vacancy-impurity, vacancy-vacancy and vacancy-dislocation interactions. Transmission electron microscopy and x-ray scattering techniques can be applied to investigations of these stages.

It has taken many years of effort by some very ingenious people to reach the present degree of sophistication with regard to simple point defects. Now as a result of the continuing worldwide energy crisis, the role of nuclear power has become even more evident than before. Those who have been investigating point defects and their interactions at low temperatures are being asked to solve problems arising from defect production at high temperatures. The tools which have been developed already will undoubtedly play an important part in solving these problems. As an example of the kind of problem that has been encountered, Fig. 39 illustrates what happens to the mechanical properties of annealed type-304 stainless steel following neutron irradiation at elevated temperatures.¹⁴³ We see that this alloy completely loses its ductility after prolonged neutron irradiation.

Fig. 39 Total creep elongation and rupture life as a function of fast neutron fluence for annealed type 304 stainless steel tested at 550 C and 35,000 psi. (Ref. 143)

It has been known for a long time that radiation affects the mechanical properties of metals, generally making them harder and more brittle, and raising the ductile to brittle transition temperature. The general models for describing these phenomena involve the interaction of radiation-produced defects with dislocations to explain radiation embrittlement and hardening. Yet the mass of complex data that exists has still not been sorted out.

It is not only intrinsic defects which play an important part in determining the mechanical properties of metals as illustrated in Fig. 40.^{144,145} This shows the effect of neutron irradiation on a series of steels from which the trace impurities Cu and P have been removed. Comparison of the top part of the slide with the bottom shows that when the two trace elements have been removed the steel is no longer sensitive to radiation in at least this one aspect. Further work is needed to confirm these results.

Removing impurities however is not the solution to all problems because under long-term exposure to neutrons, metals accumulate appreciable quantities of transmutation products, including gaseous impurities such as H and He. At high temperatures in bcc metals, at least, H is probably not a serious problem because it has such a low activation energy for motion that it can diffuse rapidly out of the host metal. Helium is a different matter, however, as it remains in the solid where it can cluster and form small gas bubbles. In the next section, we will discuss some of the recent work which provides information about helium in metals and its effects upon mechanical properties.¹⁴⁶

Fig. 40 Comparison of radiation embrittlement (as measured by Charpy - V notch 5.2 kg/cm² transition temperature) of steels with varying amounts of residual phosphorus and copper. (Refs. 144, 145)

The most surprising observation associated with point defects in high neutron fluxes at high temperatures was the discovery of void formation and its relationship to macroscopic swelling.¹⁴⁷ It had been a widely-held belief that nothing unusual would happen during a long-term high-temperature irradiation because of rapid recombination or migration of defects to sinks. This proved to be an oversimplification of defect dynamics, and it is now believed that a slight bias for interstitial capture by sinks such as dislocations leads to a condition of vacancy supersaturation which in turn permits vacancy cluster formation and growth. Figure 41 illustrates the swelling phenomenon in a series of aluminum alloys.¹⁴⁸ This phenomenon occurs in most metals under prolonged neutron irradiation at temperatures between 0.3 and 0.5 of their melting point. General agreement exists that the growth phenomenon is caused by the buildup of an excess concentration of vacancies. However, the mechanism of vacancy cluster nucleation is still not fully understood. An even more curious phenomenon - the ordered void superlattice - has proved to be a serious challenge to theorists. Semiquantitative agreement with theory has been achieved but the predictions based upon elastic anisotropy are not in full accord with experiment. The mechanisms of void nucleation are probably complex and not unique. It is believed, for example, that nucleation is associated with helium atoms acting as impurity traps for vacancies.

These problems will all be compounded in proposed fusion reactors where neutron energies and fluxes will be higher. In fact, projected fluxes are so high and possess such a significant component of neutron flux between 8 and 14 MeV that they cannot be found for testing purposes

Fig. 41 Density change, $-\Delta\rho/\rho$, as a function of fluence in aluminum and several of its alloys irradiated at about 50C. (Ref. 148)

among present-day neutron sources. As an example of the situation, Fig. 42 compares the calculated first-wall flux in a fusion reactor with that in an existing fission reactor. The lower half of the figure compares the normalized recoil probability distribution in niobium arising from the two spectra.¹⁴⁹ The added component of high-energy recoils is the other new feature beside gas production in fusion reactor technology.

Our problem at present is to determine anticipated helium production rates in various proposed simulation sources, and to find the appropriate parameters to describe radiation-damage processes. Heretofore, the parameter "displacements per atom" has been used, but it is obvious that dpa's do not give information about cluster sizes, cluster spatial distributions, the number of freely migrating vacancies arising from displacement cascades, etc.

The problem can be summarized in the simple Equation (114):

$$G(E) = \int \sigma(E)K(E,T)g(T)dT . \quad (114)$$

The generalized damage parameter, $G(E)$, is a measure of the damage caused by an incident neutron of energy, E . The neutron has an interaction cross section $\sigma(E)$ with a given material, and it transfers kinetic energy, T , to the recoiling nucleus with a probability $K(E,T)$. The quantity $g(T)$ holds the secret of success. It is the function that relates recoil energy to observable radiation effects. At present it is generally replaced by the damage energy, i.e. the kinetic energy available for elastic collision, and through a simple model it can be converted to dpa. Table XI is a comparison of relevant results for niobium in different neutron spectra. It illustrates the wide range

Fig. 42 Comparison of the primary-atom recoil energy spectrum, $P(T)$, for Nb in a fission spectrum (EBR-II, row 7), and in a fusion first-wall spectrum (Benchmark). The neutron spectra are shown in the upper portion of the figure. (Ref. 149)

Table XI Neutron spectrum averaged cross sections for Nb. (Ref. 149)

Spectrum	$(\sigma_{n,\alpha})$ barn	$(E_D(\text{elastic}))$ 10^4 barn-eV	$(E_D(\text{nonelastic}))$ 10^4 barn-eV	$(E_D(\text{total}))$ 10^4 barn-eV	$(E_D(\text{total}))$ $T_0 = 10^5$ eV 10^4 barn-eV
Benchmark	2.2×10^{-3}	3.25 (34%)	6.41 (66%)	9.66	6.29 (65%)
LLI.	1.4×10^{-3}	2.73 (40%)	4.11 (60%)	6.84	3.88 (57%)
PTMAG	1.8×10^{-4}	1.91 (65%)	1.05 (35%)	2.96	0.67 (23%)
ORMAG	1.1×10^{-7}	0.238(99.2%)	0.002(0.8%)	0.24	4×10^{-4} (0.1%)
"14 MeV"	9.2×10^{-3}	4.60 (17%)	23.0 (83%)	27.6	24.8 (90%)
24 MeV Be(d,n)	4.0×10^{-3}	3.87 (20%)	15.6 (80%)	19.5	13.8 (71%)
19 MeV Li(d,n)	2.6×10^{-3}	4.27 (25%)	12.8 (75%)	17.1	10.3 (60%)
BLIP II	3.0×10^{-4}	2.03 (57%)	1.52 (43%)	3.55	1.23 (35%)
LAMPF	2.2×10^{-4}	2.66 (67%)	1.32 (33%)	3.98	0.97 (24%)
^{235}U	5.5×10^{-5}	4.44 (59%)	3.03 (41%)	7.47	0.77 (10%)
EBR II-2	1.4×10^{-5}	3.26 (80%)	0.84 (20%)	4.10	0.18 (4.4%)
EBR II-7	5.7×10^{-6}	2.49 (87%)	0.36 (13%)	2.85	0.07 (2.4%)

of results for the spectrum-averaged (n,α) cross section, and the damage-energy cross section to be expected in different neutron sources. We will have to use all of the knowledge about the dynamics of point-defect behavior which we have developed over the years in order to arrive at a good damage parameter to guide us in simulation studies.

B. Helium in Metals

Concern over the behavior of gases in metals grew swiftly as plans for nuclear power reactors were developed in the late fifties and the early sixties. Swelling of reactor fuel elements, often culminating in fracture was anticipated as a potential hazard and a limitation on component lifetime. One important source of the swelling is the precipitation and subsequent growth of bubbles containing inert gas, primarily helium. These impurities are products of the transmutations occurring during operation of a reactor. In general, inert gases have low solubilities in metals, but during the lifetime of a fuel element the concentration of insoluble gas may far exceed the solubility limit. This limit is only of the order of a few ppm. Two more recent developments in the nuclear power program have increased the technological importance of understanding the behavior of helium in metals. First, the discovery that voids are created in fuel cladding following long exposure to energetic neutrons at elevated temperatures has given rise to investigations of the role played by helium in void nucleation. Swelling caused by voids is the most serious materials problem associated with fast breeder reactors and if helium is involved it is vital that its effects be understood. Second, the increased importance attached to fusion power as an ultimate replacement for fission power, has given rise to detailed analyses of potential materials problems in controlled thermonuclear reactors. Once more it has become evident that gaseous transmutation products will abound.

The magnitude of the problem in fission reactors can be seen by examining Fig. 43 taken from a summary by McElroy and Farrar.¹⁵⁰

The figure shows a set of helium production curves for stainless steels exposed to several relevant neutron spectra. The curves are extrapolated to 10^{24} neutrons/cm² from data which end at $\sim 10^{23}$ neutrons/cm², and may be somewhat incorrect for the last decade of fluence. We see that typical helium concentrations will be around 150 ppm in LMFBR's after an exposure of 10^{24} neutrons/cm². Fewer data are available for the bcc metals under consideration as structural materials in fusion reactors. However neutronics calculations have been performed on typical blanket structures containing niobium¹⁵¹ and the results are given in Table XII. We find that here, too, a helium concentration well in excess of the solubility limit will be attained within one year from startup.

By virtue of the chronological order in which the problems arose, more investigations have been reported for fcc metals, eg. aluminum, copper and stainless steels, than for bcc metals. Nevertheless, the impetus furnished by CTR demands has fostered several recent studies in bcc metals. It is interesting to observe that several new techniques have become available since the early research and we will see how they furnish additional information as we begin to consider what is known about helium in metals.

Before turning to the more basic aspects of helium-metal research we should examine some examples of the effects of helium on the mechanical properties of metals. Two examples suffice. Figure 44 illustrates the phenomenon of helium embrittlement in a vanadium alloy.¹⁴⁶ Helium was injected into the specimens as 44-MeV alpha particles to an estimated concentration of ~ 25 ppm. Tensile tests were then conducted on unirradiated and

Fig. 43 Helium production in stainless steel for different reactor spectra. *Major elements only. Helium produced by nuclear reactions with Fe, Ni, and Cr only. (Ref. 150)

Table XII Transmutation reactions in potential CTR first-wall materials at 0.53 MW/m² wall loading. (Ref 151).

		Net Production Rate atomic ppm/MW/m ² /year	After 20 years	
			at.% Change	% Change of Original Composition
316 SS	Fe	-1220	-1.2	-2.0
	Cr	+ 24	+0.024	+0.13
	Ni	- 177	-0.18	-1.3
	Mn	+ 1160	+1.2	+58
	V	+ 177	+0.18	+80
	Ti	+ 45	+0.045	+390
	H	637	6370 ^a	NA
Nb-1 Zr	He	279	2790 ^a	NA
	Nb	-1490	-1.5	-1.5
	Zr	+1470	+1.5	+150
	Y	+ 11.7	+0.012	NA
	H	114	1140 ^a	NA
	He	36.2	362 ^a	NA
V-20 Ti	V	- 162	-0.16	-0.2
	Cr	+ 99	+0.099	+260
	Ti	+ 53	+0.053	+ 0.27
	Sc	+ 9.1	+0.0091	NA
	H	219	2190 ^a	NA
	He	71.8	718 ^a	NA

^aat ppm

NA Not applicable

Fig. 44 Effect of helium on the tensile ductility of V-15 wt % Cr-t wt % Ti.
(Ref. 146)

irradiated specimens in a vacuum of 10^{-6} Torr. The reduction of elongation in the helium-injected sample is caused by a sharp reduction in the uniform elongation, defined as the elongation to maximum load, and a nearly total disappearance of the strain after the maximum load. The reduction in area at fracture was measured as a function of test temperature and it sharply decreased above 700C. These results demonstrate that helium produces a loss in ductility leading to a decrease in the ability of the vanadium alloy to plastically deform. The second example illustrates the effect of the presence of helium close to the surface of a metal at elevated temperatures. Figure 45 is a series of SEM micrographs taken by Bauer and Thomas.¹⁵² It reveals that depending upon the temperature at which helium is injected into the niobium sample, it will cause flaking, blistering or the formation of holes on the surface. The nature of the surface effects depends upon the mobility of the helium atoms as well as vacancies, and upon the mechanism of helium bubble growth.

In order to fashion a complete picture of the processes involved in helium-metal interactions, studies should begin with a characterization of individual helium atoms in the lattice and progress to the formation of bubbles and voids. We can assemble this information from the work of a number of groups. Recent computer calculations by Wilson and Bisson¹⁵³ and Wilson and Johnson¹⁵⁴ give us data on formation and migration energies of helium in metals. Channeling studies by Picraux and Vook¹⁵⁵ on He in W provide experimental confirmation of the location of the gas atoms in a bcc lattice. Lattice parameter and internal friction measurements by Cost and Johnson¹⁵⁶ furnish additional experimental evidence about the location of helium in fcc and bcc metals. Re-emission studies as a function of temperature, dose rate, annealing, etc. are providing

HELIUM IMPLANTATION OF NIOBIUM

100μ
400°C → 4×10^{18}

10μ
1000°C → 4×10^{18}

100μ
500°C → 4×10^{18}

10μ
1200°C → 2×10^{18}

new insight into the behavior of helium. Such studies are being performed by Bauer and Thomas¹⁵² and by Kornelson.¹⁵⁷ Recently it has been demonstrated that positron-annihilation lifetimes are also sensitive to helium in aluminum.¹⁵⁸ The theory of bubble formation was developed some years ago by Barnes, Mazey, Nelson and others.¹⁵⁹ However, the new question of void formation in the presence of insoluble gases has only recently been addressed.¹⁶⁰ We will review these investigations as an example of the experimental and theoretical tools that can be employed to learn about the behavior of an extrinsic point defect in a metal.

Wilson and his colleagues have employed an approximate quantum mechanical method^{153,154} for calculating interatomic potentials which appears to be an improvement upon earlier fitting procedures. Using this approach they have determined helium atom-metal atom interactions calculated the configurations of helium atoms in Cu, Ni, Ag, Pd, Fe, Mo, V, W and Ta.¹⁵⁴ The calculations require high-speed digital computers and are lengthy and rather time consuming even when the symmetry properties of the lattice are invoked. Two methods of computation were investigated. Each involves calculation of the force on the atoms surrounding a particular defect configuration, relaxation of the atoms shell by shell or simultaneously, calculation of the energy of the new lattice configuration relative to the perfect lattice, and iteration until a zero-force condition is met. In each case a finite number of atoms was relaxed, and the minimum energy could be fixed to within ~ 0.01 eV. Figure 46 shows the interstitial positions for He atoms in fcc and bcc lattices. Table XIII taken from Wilson and Johnson's work¹⁵⁴ gives numerical results for fcc metals. The formation energy is the work necessary to bring a He atom from infinity to the site listed in the table. The activation energy is the energy required to move a He atom over the saddle point to a new stable position. Table XIV lists

a. f.c.c.

b. b.c.c.

Fig. 46 Symmetrical interstitial positions for a helium atom in metal lattice (a) in fcc; (b) in bcc. The $(1,0,1)$ and $(0,0,1)$ configurations are identical. (Ref. 154)

Table XIII Formation energies, in eV, for helium atoms in interstitial positions in fcc metals. Activation energies are given in the last column. The numbers in parentheses are the first-nearest neighbor displacement parameters, p , in units of the half lattice constant. (Ref. 154)

Solid	He (1, 0, 0)	He ($\frac{1}{2}$, $\frac{1}{2}$, 0)	He ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)	Activation Energy, eV
Ni	4.60 (-.121)	4.52 (-.246)	5.39 (-.092)	0.08
Cu	2.03 (-.069)	2.60 (-.215)	2.96 (-.074)	0.57
Pd	3.68 (-.071)	5.42 (-.182)	5.43 (-.062)	1.74
Ag	1.53 (-.052)	2.39 (-.200)	2.60 (-.058)	0.86

Table XIV Formation energies, in eV, of helium atoms in interstitial positions in bcc materials. The origin is taken as a normal lattice atom. (Ref. 154)

Coordinates of Helium Atom	Vanadium	Iron	Molybdenum	Tantalum	Tungsten
1, 0, 1	4.61	5.36	4.91	4.23	5.47
0.5, 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
0.75, 0.25, 1	4.90	5.76	5.55	4.60	6.19
0.5, 0.5, 1	5.38	6.28	6.52	5.04	7.35
0.25, 0.75, 1	4.90	5.76	5.55	4.60	6.19
0.75, 0.25, 0.75	5.02	5.80	5.67	4.62	6.32
0.50, 0.50, 0.50	5.18	6.16	6.56	5.15	7.44
0.25, 0.75, 0.25	5.02	5.79	5.66	4.61	6.32
Activation Energy	0.13	0.17	0.23	~0.0	0.24

the corresponding properties for He in bcc metals. The activation energies for migration, given on the bottom line, were calculated on the assumption that the saddle point is the tetrahedral (1/2, 0, 1) position.

Most of the experimental results suggest that helium becomes substitutional and is associated with one or more vacant sites. Wilson and Johnson also calculated the substitutional detrapping energies defined roughly as the difference between the formation energies in an interstitial and in a vacancy. Table XV gives these energies for fcc and bcc lattices, and they suggest that He will remain immobile in vacancies until rather high temperatures. Wilson and Bisson conclude that interstitial He atoms would diffuse rapidly through the W lattice. However, He atoms in single or multiple vacancies would be very stable. They have performed calculations for 2-He + V and 3-He + V defect configurations with the impurity atoms sharing a substitutional site; both configurations are stable. Kornelson¹⁵⁷ has published other experimental evidence that these kinds of complexes exist, and we shall review his results shortly.

Several different kinds of experiments have given recent support to the results of the computer calculations. Picraux and Vook¹⁵⁵ have employed the ^3He (d,p) ^4He reaction together with Rutherford backscattering to investigate the location of He in W single crystals. 60 keV $^3\text{He}^+$ ions were implanted at 296K to a fluence of 1×10^{15} He atoms/cm². The projected range of the $^3\text{He}^+$ is $\sim 1100\text{\AA}$ and the local concentration near the end of the range is $\sim 5 \times 10^{19}$ atoms/cm³. The nuclear reaction products were detected, and simultaneously the backscattered yield from the W crystals was observed from a depth corresponding to the range of the implanted impurity. Figure 47 shows the results of $\langle 100 \rangle$ axial channeling measurements on the ^3He -implanted W crystals. The angular scans remained essentially

Table XV Substitutional detrapping energies in fcc and bcc metals.

Values in parentheses are the relative energies of a helium atom in a vacancy and in an interstitial position. (Ref. 154)

	Formation Energy, in eV, of a He Atom in a Vacancy	Formation Energy, in eV, of a He Interstitial	Substitutional Detrapping (Popout) Energy, in eV
Cu	0.15	2.03	(1.88)
Ni	1.36	4.52	(3.16)
Pd	0.52	3.68	(3.16)
Ag	0.0	1.53	(1.53)
Fe	1.61	5.36	3.98 (3.75)
Mo	1.04	4.91	4.19 (3.87)
W	1.05	5.47	4.75 (4.42)
V	1.65	4.61	3.20 (2.96)
Ta	0.93	4.23	3.44 (3.30)

Fig. 47 Axial <100> angular scans using 500 keV D analysis beam for W implanted with ^3He under conditions indicated at top of curves. (Ref. 155)

unchanged for different implant energies and temperatures, and different analysis temperatures. By contrast with similar scans for D in W as found in the same study (see Fig. 48), the results for He are complicated. They indicate that the location of He in the lattice is neither a simple interstitial nor substitutional site. The satellite peaks suggest that the helium is displaced from the center of the channel. Using channeling theory it is possible to relate the measured flux-peak positions to corresponding He displacements toward specific crystallographic directions. Table XVI shows $\langle 100 \rangle$ channeling patterns which would arise from the 2-He + V and 3-He + V configurations predicted by Wilson and Bisson. The calculated patterns tend to support the 3-He + V configuration, but the sensitivity of the experiment does not permit elimination of the 2He + V defect. The surprising fact is that no substitutional helium was observed although several vacancies are formed per incident ion. This observation remains unexplained but may be related to dynamic effects during the displacement process and the high mobility of He atoms.

Other strong evidence related to He behavior in metals comes from re-emission¹⁵² and thermal desorption studies, especially on the bcc metals. In the re-emission studies 300-keV He ions were injected into samples of V, Nb and Mo held at temperatures between 400 and 1200°C. Bauer and Thomas report that re-emission characteristics can be separated into three temperature regimes:

- 1) 400-700°C, high-dose; re-emission is low and surface flaking dominates,
- 2) 700-1000°C high-dose; re-emission is high but no prominent surface features are seen although swelling occurs. This is the region in which voids are generally formed, but the He does not appear to enhance void densities,

Fig. 48 Angular scan through the <100> axis for W with $3 \times 10^{15}/\text{cm}^2$, 30 keV D implant at 296K using a 750 keV ³He analysis beam: O corresponds to backscattered yield from W and Δ corresponds to proton nuclear reaction yield from D. (Ref. 155)

Table XVI Predicted $\langle 100 \rangle$ channeling structure for the calculated He locations. (Ref. 155)

	Proj. Disp. from $\langle 100 \rangle$	Rel. Prob.	ψ_m
<p>(2 He + V)</p> <p>0.67 $\langle 100 \rangle$</p>	0	2/6	dip
	0.81 Å	4/6	0.24°
<p>(3 He + V)</p> <p>0.67 $\rightarrow$ 0.89 $\langle 100 \rangle$</p>	0	1/9	dip
	0.30 Å	2/9	0.81° + dip
	0.82 Å	2/9	0.23°
	0.87 Å	2/9	0.20°
	0.98 Å	2/9	0.16°

3. 1000-1200C, high-dose, re-emission is high and blisters and holes form at the surface.

The explanation for most of these observations is given in terms of He trapping at vacancies. By means of scanning electron microscopy fine bubble formation can be detected at the low temperatures, followed by void formation at intermediate temperatures. At high temperatures, He becomes mobile and large bubbles form. The formation of these gas-filled defects is thought to be responsible for the surface changes observed over the entire temperature range.

A very detailed study of He desorption performed by Kornelson¹⁵⁷ has provided substantial, albeit indirect, evidence of He-vacancy configurations in W. The lattice defects are introduced by bombardment with 5-keV heavy ions whereas the helium is injected at 250 eV. Figure 49 illustrates the effect of heavy-ion bombardment on subsequent He desorption. The same peaks occurred for all doses, angles of incidence and energies used and are taken to be characteristic of bulk defects in tungsten. The desorption spectrum could be fitted by a sum of first-order desorption transients corresponding to discrete binding energies. In general, six states were sufficient to fit the data. By investigating the population of desorption peaks as a function of incident dose Kornelson was able to argue for the formation of multiple He-vacancy configurations. The total number of helium atoms trapped was always proportional to injected dose implying that trapping occurred at a fixed number of sites whose trapping cross sections were independent of trap occupancy. Adding these facts to the initial assumption of discrete binding energies, Kornelson concluded that the evidence overwhelmingly favors point defects as the traps for helium in W. Annealing of the crystal between damage and injection bombardments was also very revealing. Figure 50 shows the population of individual peaks as a function of damage anneal

Fig. 49 Helium desorption spectrum for a damaging bombardment of $8 \times 10^{11}/\text{cm}^2$ 5 keV Kr^+ and injection of $8 \times 10^{12}/\text{cm}^2$ 250 eV He^+ . Dashed curves indicate theoretical desorption transients (assuming first-order kinetics and a rate constant $\sim 10^{13}$) from which the spectrum could be formed. (Ref. 157)

Fig. 50 Populations of individual peaks as a function of damage anneal temperature. Damage and injection parameters were the same as in Fig. 49. (Ref. 157)

temperature. At 700K several prominent peaks decrease sharply, while at 1000K three new peaks become prominent. If all processes are first-order, the 700K stage corresponds to an activation energy of 1.77 eV, the 1000K stage to 3.37 eV. Kornelson has developed a systematic picture of He-vacancy defects which is consistent with his observations:

Other peaks are thought to involve combinations of He, vacancies and the damaging ion (eg. Kr) because the peaks are mass dependent and at least one of them grows at 700K while other low-temperature peaks are diminishing. Finally, high-dose experiments cause the growth of new desorption peaks provided that the injection temperature does not exceed $\sim 1100\text{K}$. The associated binding energies are higher than those correlated with the low-dose peaks. Kornelson proposes that irreversible changes take place which represent the onset of bubble formation. If these experiments can be correlated with others, they will constitute an important new approach to the study of gases in metals.

In view of the variety of He + V configurations that appear to exist in metals, it would seem likely that an internal-friction peak associated with one or more of them should be observable. Johnson and Cost¹⁵⁶ investigated this possibility in Nb injected with 46 MeV alpha particles. The only peaks observed over the temperature range from -150 to 800C could be identified as the oxygen Snoek peak and the nitrogen cold-work peak. It is unclear why no identifiable peaks could be observed. This would imply

that the He defect site in niobium has the same symmetry as the lattice. A large reduction in lattice parameter was observed in Nb containing ~ 100 ppm He. The fractional change in $\Delta a/a_0$ was followed during successive isochronal anneals at 100°C intervals and was observed to increase by nearly 180 ppm between room temperature and 500°C . However $\Delta a/a_0$ did not return to zero above 1500°C although emission measurements indicate that most of the helium has escaped from the specimen by that temperature. The large initial decrease in lattice parameter is puzzling in view of other data we have cited. Wilson and Johnson have shown that several He-V configurations are stable other than the simple one, and the channeling data suggest that 3He-V or 2He-V defects are common. The He is thus partly interstitial. In fact these configurations lead to a predicted lattice parameter decrease which is $1/30$ the observed value. The observed value is also three times that predicted by Vegard's law. Nevertheless it is consistent with data for aluminum¹⁶¹ under similar experimental conditions. Evidence indicates that in copper, helium is interstitial, but once again $\Delta a/a$ per atom percent He is several times larger than would be predicted from simple interstitial site occupancy. The tentative conclusion which Johnson and Cost reach is that at $\sim 200^\circ\text{C}$ where most of the lattice parameter recovery occurs, a complex helium defect forms which does not affect the lattice parameter, and which remains stable to $\sim 800^\circ\text{C}$. At higher temperatures significant gas release begins and bubbles begin to coalesce into sizes large enough to become visible by TEM.

It seems evident that experiments which furnish insight into the behavior of helium before it forms visible bubbles in metals are needed. A new candidate in this category appears to be positron annihilation. Recent work at Brookhaven¹⁵⁸ on helium-injected aluminum reveals a strong

dependence of positron lifetime on the state of He in the lattice. The samples were irradiated at a temperature of $\sim 2000^\circ\text{C}$ to a fluence corresponding to 3ppm atomic concentration of He. The lifetime of positrons in the samples was then measured at room temperature after successive isochronal anneals in 25°C steps to 625°C . Analysis of the data in terms of the trapping model indicated that the trapping rate was initially high and decreased monotonically with increasing annealing temperature. The lifetime in the trap initially increased, reaching a peak at $\sim 400^\circ\text{C}$ and then decreasing rapidly to the initial value. TEM of the fully annealed sample revealed the presence of a very low density of voids whereas none were initially observable. These results suggest that the early stages of He migration and coalescence can be monitored for very low solute concentrations. Further work needs to be performed as a function of the important variables, temperature and concentration before the preliminary results can be understood.

C. Void Nucleation and Growth in Metals

While the mechanism of bubble growth, migration and coalescence and the equilibrium shape of bubbles is reasonably well understood,¹⁵⁹ the role of He in void formation is still unclear. Experiments seem to indicate that He can strongly affect void density and size, but not necessarily the macroscopic swelling. Recent theoretical work¹⁶² has attempted to define the parameters and environmental conditions of importance in this field. Wiedersich and Katz Bullough, Perrin and Brailsford, Russell and others have developed the kinetics of void nucleation in its general form, and have considered several special cases which can be treated analytically.

All of the preceding research has not been performed for purely academic reasons. It originates in the need to determine the nature of the helium defects which are believed to affect void nucleation rates. We now know that voids can form in the absence of helium as shown by high-voltage microscopy. However, we also know that helium is present in irradiated reactor materials. The theories of void nucleation and growth differ somewhat from one another, but they all start from the same underlying assumptions:

1. voids develop on nuclei which may be gas bubbles, or vacancy clusters, and.
2. another sink exists and/or is created in the solid by irradiation, and this sink has a slight preference for interstitials. In other words, vacancy supersaturation can occur.

Bullough and his coworkers^{163,164} have developed a general rate theory of void growth and have assumed that the swelling is directly proportional to the increase in volume occupied by voids. The general swelling rate is given by the net vacancy flux into the voids and is the solution of the equation:

$$\frac{dS}{d\Delta} = \frac{4\pi r_v C_v}{K} [D_v c_v - D_i c_i - D_v \bar{c}_v] , \quad (115)$$

where $\Delta = Kt$ = total dose in displacements per atom. C_v is the concentration of spherical voids of radius r_v , D_i and D_v are the diffusion coefficients of the steady-state vacancy and interstitial fractional concentrations, c_v , and c_i , respectively. The quantity $\bar{c}_v$ is the equilibrium vacancy concentration immediately adjacent to the void, taking into account that the void can emit vacancies. The swelling rate is assumed to arise from two distinct sources:

1. the slight interstitial-dislocation bias, and
2. thermal emission of vacancies from all sinks.

Gas generation is considered to be continuous and essential; otherwise, Brailsford and Bullough¹⁶³ find that swelling cuts off rapidly. Thus, in their model helium plays a crucial role. They argue that if no gas atoms are present in a vacancy cluster, it will collapse to form a dislocation loop. Even if the cluster were to become large enough to be energetically favorable, it would disappear because of the high probability of vacancy emission. Only the internal gas atoms can stabilize the three-dimensional configuration against collapse or disappearance.

The theory of void growth has been developed in great detail and we can only refer the reader to the literature.¹⁶²

However, we will complete our discussion of the influence of helium on void nucleation. Two theoretical approaches have been taken. Wiedersich and Katz¹⁶⁵ have assumed that the helium atoms are immobile, and have viewed void nucleation as the sum of a set of independent nucleation processes on clusters of all sizes. The total nucleation rate is then the sum of the separate nucleation rates for homogeneous nucleation on each cluster size. The concentration of gas clusters containing z atoms is taken as

$$C_z = C_1^{(z+1)/2},$$

the geometric mean between a random distribution, (C_1^z) , and a distribution consisting of equal concentrations regardless of size. Wiedersich and Katz have calculated void nucleation rates versus the vacancy supersaturation ratio, S for various temperatures, gas-cluster atom fractions,

and ratios of arrival rates of interstitials and vacancies at voids

β_i/β_v . Figures 51, 52, and 53 illustrate the results for $\beta_i/\beta_v = 0.98$.

Several general conclusions can be drawn:

1. Nucleation rates increase with increasing temperature at fixed supersaturation, S .
2. Nucleation rates decrease with increasing temperature for a fixed displacement rate. This obviously occurs because other thermally-activated sources of vacancies increase the equilibrium vacancy concentration relative to the radiation-induced steady-state concentration so that S decreases.
3. At low temperatures ($\sim 400^\circ\text{C}$) homogeneous nucleation (No gas, $z=0$) probably dominates.
4. The higher the temperature and the lower the defect production rate, the larger are the gas clusters required as nucleation centers.
5. At low enough temperatures, and high enough displacement rates, homogeneous nucleation predominates.

This implies that simulation of void production by means of accelerator-based experiments must be performed under carefully arranged conditions. Otherwise the results may not correspond to reactor conditions.

6. If conditions are right, spontaneous conversion of gas clusters to voids can occur as seen in Fig. 52.

Russell and Hall¹⁶⁶ have carried the theory one step further by allowing the gaseous impurities to be mobile. This corresponds to the physical situation at the higher temperatures. The formalism employed by these two men is somewhat different than that of Wiedersich and Katz, but we need only quote the new results obtained by Russell and Hall:

Fig. 51 Rates of void-nucleation on clusters of one to four gas atoms and homogeneous void-nucleation rates (no gas) as functions of vacancy supersaturation at 400 C. The assumed concentrations of the gas clusters are indicated as atom fractions. (Ref. 162)

Fig. 52 Rates of void-nucleation on clusters of one to four gas atoms and homogeneous void-nucleation rates (no gas) as functions of vacancy supersaturation at 600C. The assumed concentrations of the gas clusters are indicated as atom fractions. The supersaturation range in reactors falls below the supersaturation shown. (Ref. 162)

Fig. 53 Relation between gas-cluster size and the minimum vacancy supersaturation to remove the barrier to void nucleation at several temperatures. (Ref. 162)

- a. The void nucleation rate can be expressed in simple analytical form if the impurity atoms are either immobile or highly mobile relative to the vacancies.
- b. Impurities, including gaseous atoms, can appreciably enhance the void nucleation rate.
- c. Inert gases which are highly mobile may increase the nucleation rate by many orders of magnitude, depending upon the gas concentration.

The experimental verification of these detailed theories is not yet complete. Moreover, it has been complicated further by the observation of ordered void lattices.^{167,168} Until these are completely understood we cannot say that we know everything about void production in metals. However, it does appear that we have developed a rather good understanding of the role which helium plays in determining an important radiation-related property of metals.

References

Introduction

1. See, for example, J. Phys. F 3, (1973) for reviews and references.
2. D. E. Weaver, Lawrence Livermore Laboratory Report UCRL-51182, October 25, 1972.
3. Fusion Reactor First-Wall Materials, AEC Report WASH-1206, Jan. 1972.
4. G. J. Dienes and G. H. Vineyard, Radiation Effects in Solids, Interscience Publishers, Inc., New York 1957.
5. See, for example, W. Frank in Defects in Refractory Metals, Eds. R. de Batist, J. Nihoul and L. Stals (S.Ck./CEN Mol) 1972 p. 199.
6. See, for example, A. C. Damask and G. J. Dienes, Point Defects in Metals, Gordon and Breach, Science Publishers, Inc., New York, 1963.
7. See, eg., F. S. Ham, J. Phys. Chem. Solids 6, 335 (1958).
8. See, for example, O. Krisement, Phys. Kon. Mat. 1, 326 (1963); J. R. Beeler, Jr., Phys. Rev. 134, A1396 (1964); H. Mehrer, Z. fur Naturf 24a, 358, 367 (1969).
- 8a. Critical Questions in Fundamental Radiation Effects Research, U.S.A.E.C. Report WASH 1240-73 April 1973.

Statistical Thermodynamics of Defects in Equilibrium

9. G. H. Vineyard, J. Phys. Chem. Solids 3, 121 (1957).
10. A. Seeger, Cryst. Lattice Defects 4, 221 (1973).
11. W. M. Lomer, Vacancies and Other Point Defects in Metals and Alloys, (Inst. of Metals, London) 1958, p. 79.
12. See, for example, N. H. March and J. S. Rousseau, Cryst. Lattice Defects 2, 1 (1971).
13. R. O. Simmons and R. W. Balluffi, Phys. Rev. 119, 600 (1960) and subsequent references by the same authors.
14. R. W. Balluffi, K. H. Lie, D. N. Seidman and R. W. Siegel, Vacancies and Interstitials in Metals, Eds. A. Seeger, et al. (North-Holland Publ. Co., Amsterdam) 1970, p. 125; D. N. Seidman, J. Phys. F. 3, 393 (1973).

15. A. S. Nowick and R. Feder, Phys. Rev. B5, 1238 (1972).
16. R. Feder and A. S. Nowick, Phys. Rev. B5, 1244 (1972),
and references therein.
17. See references in Ref. 10.
18. See reviews by Ya. A. Kraftmakher and P. G. Strelkov, and
M. Hoch in Vacancies and Interstitials in Metals, Eds. A. Seeger,
et al. (North-Holland Publ. Co., Amsterdam) 1970, p. 59 ff, and
p. 81 ff.
19. M. Meshii, Lattice Defects in Quenched Metals, Eds. R.M.J. Cotterill,
M. Doyama, J. J. Jackson and M. Meshii (New York Academic Press)
1965, p. 77.
20. R. W. Siegel, Phil. Mag. 13, 337 (1966).
21. R. W. Siegel, K. C. Jain, T. Schober, R. W. Balluffi and L. E. Thomas
Cryst. Lattice Defects 1, 31 (1969).
22. R. W. Siegel, R. W. Balluffi and L. E. Thomas, Acta Met. 16, 7 (1968).
23. For example, see E. W. Müller, J. A. Panitz and S. B. McLane, R.S.I.
39, 83 (1968); S. S. Brenner and J. T. McKinney, Appl. Phys. Lett. 13,
29 (1968); E. W. Müller, Ber. der Bunsengesellschaft für Physik Chem.
75, 979 (1971).
24. S. H. Robertson and D. N. Seidman, J. Sci. Inst. 1, 1244 (1968).
25. See, for example, E. W. Müller and T. T. Tsong, Field Ion Microscopy,
(Elsevier Publ. Co., New York) 1969.
26. K. M. Bowkett and D. A. Smith, Field-Ion Microscopy (North-Holland,
Amsterdam) 1970.
27. A. S. Nowick and G. J. Dienes, Phys. Stat. Sol. 24, 461 (1967).
28. A. Seeger and H. Mehrer, Vacancies and Interstitials in Metals,
(North-Holland Publ. Co., Amsterdam) 1970 p. 1
29. L. M. Levinson and F.R.N. Nabarro, Acta Met. 15, 785 (1967).
30. L. A. Girifalco, Scripta Met. 1, 5 (1967).

31. A. Seeger and D. Schumacher, *Mat. Sci. Eng.* 2, 31 (1967).
32. C. P. Flynn, *Phys. Rev.* 171, 682 (1968).
33. A. Ascoli, G. Guarini and G. T. Queriolo, *Cryst. Lattice Defects* 1, 159 (1970).
34. A. N. Goland, *Proc. of NATO Advanced Study Institute, Istanbul 1971*,
BNL Report 50336.
35. A. Seeger, *J. Metal Phys.* 3, 248 (1973).
36. A. Seeger, *Cryst. Lattice Defects* 4, 221 (1973).
37. R. N. West, *Adv. in Phys.* 22, 263 (1973).
38. M. Doyama and R. R. Hasiguti, *Cryst. Lattice Defects* (1974).
39. S. DeBenedetti, R. E. Bell and M. Deutsch, in Beta- and Gamma-Ray Spectroscopy, K. Siegbahn, Ed., (Interscience Publishers, N.Y.)
1955, p. 672.
40. R. Ferrell, *Rev. Mod. Phys.* 28, 308 (1956).
41. P. R. Wallace, in Solid State Physics, F. Seitz and D. Turnbull, Eds.
Vol. 10 (Academic Press, N.Y.) 1960, p. 1.
42. A. T. Stewart, in Proc. Int'l. Conf. on Positron Annihilation,
A. T. Stewart and L. O. Roellig, Eds. (Academic Press, N.Y.) 1967, p. 17.
43. M. Deutsch and S. Berko in Alpha-, Beta- and Gamma-Ray Spectroscopy,
K. Siegbahn, ed., Vol. II (North-Holland Publ. Co., Amsterdam) 1965, p. 1583.
44. C. K. Majumdar, in Theory of Condensed Matter, (Int'l. Atomic Energy
Agency, Vienna) 1968, p. 829.
45. K. Rama Reddy and R. A. Carrigan, Jr., *Nuovo Cim.* 66B, 105 (1970).
46. G. E. Lee-Whiting, *Phys. Rev.* 97, 1157 (1955).
47. J. P. Carbotte and H. Arora, *Can. J. Phys.* 45, 387 (1967).
48. H. J. Mikeska, *Z. f. Phys.* 232, 159 (1970).
49. J. P. Carbotte, *Phys. Rev.* 155, 197 (1967).
50. B. Bergersen in Soft X-Ray Band Spectra, D. J. Fabian, Ed.
(Academic Press, London) 1968.

51. A. Sjölander and M. J. Stott, Sol. Stat. Comm. 8, 1881 (1970).
52. A. Held and S. Kahana, Can. J. Phys. 42, 1908 (1964).
53. S. de Benedetti, C. Cowan, W. Konneker and H. Primakoff,
Phys. Rev. 77, 208 (1950).
54. S. Berko and J. S. Plaskett, Phys. Rev. 112, 1877 (1958).
- 54a. T. D. Newton, Phys. Rev. 78, 490 (1950).
55. I. Ya. Dekhtyar, Czech. J. Phys. 12B, 1503 (1968);
Physics Reports 9C, 245 (1974).
56. I. K. MacKenzie, T. L. Khoo, A. B. MacDonald and B.T.A. McKee,
Phys. Rev. Lett. 19, 946 (1967).
57. W. Brandt, in Proc. Int'l. Conf. on Positron Annihilation,
A. T. Stewart and L. O. Roelleg, eds., (Academic Press, N.Y.)
1967, p. 180.
58. B. Bergersen and M. J. Stott, Sol. St. Comm 7, 1203 (1969).
59. D. C. Connors and R. N. West, Phys. Letters 30A, 24 (1969).
60. I. K. MacKenzie, T. W. Craig, and B.T.A. McKee, Phys. Lett. 36A,
227 (1971).
61. P. Hautojärvi, A. Tamminen and P. Jouho, Phys. Rev. Lett. 24, 459 (1970).
62. A. N. Goland and T. M. Hall, Phys. Lett. 45A, 397 (1973).
63. R.H.J. Cotterill, K. Petersen, G. Trumpy and J. Triff, J. Phys. F 2,
459 (1972).
64. (a) P. Hautojärvi, Sol. St. Comm. 11, 1049 (1972).
(b) J. W. Martin and R. Paetsch, J. Phys. F. 3, 997 (1972).
65. T. M. Hall, C. L. Snead, Jr., and A. N. Goland, Phys. Rev. B
(to be published).
66. W. Frank and A. Seeger, Appl. Phys. 3, 61 (1974).
67. B.T.A. McKee, W. Triftshäuser and A. T. Stewart, Phys. Rev. Lett. 28,
358 (1972).
68. D. Knapton and B.T.A. McKee, Proc. Second Int'l. Conf. on Positron
Annihilation, Kingston, Canada, 1971 (unpublished).

69. C. L. Snead, Jr., T. M. Hall, and A. N. Goland, Phys. Rev. Lett 29, 62 (1972).
70. N. K. Dave, B.T.A. McKee, A. T. Stewart and G. M. Hood, Conf. on Point Defects and Their Aggregates in Metals, U. of Sussex, England 1972 (unpublished).
71. M. Doyama, S. Tanigawa, K. Kuribayashi and S. Nanao, Cryst. Lattice Defects 4, 255 (1973).
72. C. H. Hodges and M. J. Stott, Sol. St. Comm. 12, 1154 (1973).
73. C. H. Hodges, Phys. Rev. Letters 28, 284 (1970).
74. K. G. Lynn, C. M. Wan, R. W. Ure, and J. G. Byrne, Phys. Stat. Solids 22a, 731 (1974).
75. H. Wollenberger, Vacancies and Interstitials in Metals (North Holland, Amsterdam 1972) p. 215; D. E. Becker, F. Dworschak and H. Wollenberger, Phys. Stat. Solidi 476, 171 (1971).
76. J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. 120, 1229 (1960).
77. A. Scholz and C. Lehmann, Phys. Rev. 6B, 813 (1972).

Annealing Kinetics and Rate Theory

78. L. Stals, Defects in Refractory Metals, Eds. R. deBatist, J. Nihoul and L. Stals (SCK/CEN, Mol. Belgium 1972) p. 171
P. Streda, Cryst. Latt. Defects 1, 229 (1970).
79. J. Nihoul and L. Stals, Phys. Stat. Sol. 17, 295 (1966).
80. F. E. Fujita and A. C. Damask, Acta Met. 12, 331 (1964).
81. R. A. Johnson, Defects and Defect Clusters in B.C.C. Metals and Their Alloys, Ed. R. J. Arsenault (Nat'l. Bureau of Standards) 1973, p. 565.
82. R. A. Johnson, Phys. Rev. 174, 684 (1968).
83. N. H. March and J. S. Rousseau, Cryst. Lat. Defects 2, 1 (1971).

Diffuse Scattering

84. H. Eckstein, Phys. Rev. 68, 120 (1945).
85. K. Huang, Proc. Roy. Soc. A190, 102 (1947).
86. W. Cochran and G. Kartha, Acta Cryst. 9, 944 (1956).
87. B. S. Borie, Acta Cryst. 10, 89 (1957); 12, 280 (1959).
88. M. A. Krivoglaz, Theory of X-Ray and Neutron Scattering by Real Crystals (Plenum Press, N.Y.) 1969.
89. P. H. Dederichs, Phys. Rev. B4, 1041 (1971).
90. H. Trinkaus, Phys. Stat. Sol. 51b, 307 (1972).
91. D. T. Keating and A. N. Goland, Phys. Rev. 4B, 1816 (1971);
Phys. Rev. (to be published, 1974).
92. D. T. Keating and A. N. Goland, Acta Cryst. A27, 134 (1971).
93. B. C. Larson and F. H. Young, Jr., Acta Cryst. A28, Suppl. S155,
(1972); International Conf. on Radiation Induced Voids in Metals,
Eds. J. W. Corbett and L. C. Ianniello, Albany, N.Y. 1971, NITS
1972, p. 672.
94. P. Ehrhart and W. Schilling, Phys. Rev. 8B, 2604 (1973).
95. H. Lohstötter, H. Spalt and H. Peisl, Phys. Rev. Lett. 29, 224 (1972).
96. H. Spalt, H. Lohstötter and H. Peisl, Phys. Stat. Sol. 56(b), 469 (1973).
97. W. Schmatz, T. Springer, J. Schelten, and K. Ibel, J. Appl. Cryst. 7,
96 (1974) and references therein.
98. Proceedings of the International Discussion Meeting on Lattice
Distortions and Atomic Arrangements, KFA-Julich, 1974. (to be
published, J. Appl. Cryst.).
99. T. Matsubara, J. Phys. Soc., Japan 7, 270 (1952).
100. H. Kanzaki, J. Phys. Chem. Sol. 2, 24, 107 (1957).
101. D. T. Keating, J. Phys. Chem. Solids 29, 771 (1968); 32, 2693 (1971).

102. P. H. Dederichs, J. Phys. F3, 471 (1973).
103. D. T. Keating and A. N. Goland, J. Phys. Chem. Solids 29, 785 (1968).
104. R. Bullough and V. K. Tewary, Interatomic Potentials and Simulation of Lattice Defects, Eds., P. C. Gehlen, J. R. Beeler, Jr., and R. I. Jaffee (Plenum Press, N. Y.) 1972, p. 155.
105. P. Ehrhart and U. Schlagheck (to be published).
106. H. G. Haubold and W. Schilling (to be published).
107. P. Wombacher, Jülich Report, Jü1-942-FF, 1972.

Dynamical Diffraction and Channeling

108. See, for example, the review by J. A. Davies in Channeling,
Ed. D. V. Morgan, John Wiley & Sons, New York, 1973.
109. B. W. Batterman and H. Cole, Rev. Mod. Phys. 36, 681 (1964).
110. B. W. Batterman, Phys. Rev. Lett. 22, 703 (1969).
111. J. Golovchenko, B. W. Batterman, and W. L. Brown, Phys. Rev. B,
(to be published).
112. B. Domeij, G. Fladda, and N.G.E. Johansson, Rad. Effects 6,
155 (1970).
113. J. U. Andersen, O. Andreason, J. A. Davies, and E. Uggerhøj,
Rad. Eff. 7, 25 (1971).
114. See the review by W. M. Gibson, Interaction of Energetic Charged
Particles with Solids, Ed., A. N. Goland, Brookhaven National
Laboratory Report, BNL 50336 (1973).
115. M. L. Swanson, M. Maury, and A. F. Quenneville, Phys. Rev. Lett
31, 1057 (1973).

Dynamical Diffraction and Lattice Models

116. R. A. Johnson, J. Phys. F 3, 295 (1973).
117. Interatomic Potentials and Simulation of Lattice Defects,
(Eds., P. C. Gehlen, J. R. Beeler, Jr., and R. I. Jaffee,
Plenum Press, N.Y.) 1972.
118. J. R. Hardy and J. W. Flocken, Phys. Rev. 175, 919 (1968);
1B, 2472 (1970).
119. W. Cochran, Acta Cryst. A27, 556 (1971).
120. P. H. Dederichs, C. Lehmann and A. Scholz, Phys. Rev. Lett. 31,
1130 (1973).
121. A summary is given in a recent paper by L. E. Rehn, J. Holder,
A. V. Granato, R. R. Coltman, and F. W. Young, Jr., Phys. Rev.
10B, 349 (1974).

Lattice Models

122. K. Dittler, H. J. Lahann, and H. Wollenberger,
Rad. Effects 2, 51 (1969).
123. J. Holder, A. V. Granato, and L. E. Rehn, Phys. Rev. 10B, (1974).
124. J. R. Townsend, J. A. DiCarlo, R. L. Nielsen, and D. Stabell,
Acta Met. 17, 425 (1969).
125. M. Pistorius and W. Ludwig, Jll. Conf. 2 (Vol. 2) 558 (1968).
126. J. S. Koehler, in Imperfections in Nearly Perfect Crystals,
(Eds., W. Shockley, et al.) Wiley and Sons, New York 1952, Chap. 7.
127. A. Granato and K. Lücke, J. Appl. Phys. 27, 583, 789 (1956).
128. See, H. M. Simpson and A. Sosin, Phys. Rev. 5B, 1382 (1972);
H. M. Simpson, A. Sosin, and D. F. Johnson, *ibid*, p. 1393.
129. C. Zener, Acta Cryst. 2, 163 (1949).
130. G. J. Dienes, Phys. Rev. 86, 228 (1952); Phys. Rev. 87, 666 (1952).
131. F.R.N. Nabarro, Phys. Rev. 87, 665 (1952).
132. J. Melngalis, Phys. Stat. Sol. 16, 247 (1966).
133. J. Holder and A. V. Granato, Phys. Rev. 182, 729 (1969).
134. See, A. S. Nowick and B. S. Berry, Anelastic Relaxation in Crystalline Solids, Academic Press, New York 1972.
135. A. S. Nowick and W. R. Heller, Advan. Phys. 12, 251 (1963); 14,
101 (1965).
136. R. L. Nielsen and J. R. Townsend, Phys. Rev. Letters 21, 1749 (1968);
Ph.D. Thesis, R. L. Nielsen, Univ. of Pittsburgh, 1969.
137. J. A. DiCarlo, C. L. Snead, Jr., and A. N. Goland, Phys. Rev. 178,
1059 (1969).
138. K. Sonnenberg, W. Schilling, K. Mika, and K. Dettmann, Rad. Eff. 16,
65 (1972).

139. J. W. Corbett, R. B. Smith, and R. M. Walker, Phys. Rev. 114, 1452, 1460 (1959).
140. K. Sonnenberg and W. Schilling, J. Phys. F3, 322 (1973).
141. K. Dettmann, G. Leibfried, and K. Schroeder (to be published).
142. A. Kraut, F. Dworschak, and H. Wollenberger, Phys. Stat. Solidi 44b, 805 (1971); D. Becker, F. Dworschak, A. Krout and H. Wollenberger (to be published).
143. J. O. Stiegler in Critical Questions in Fundamental Radiation Effects Research, U.S.A.E.C. Report, WASH 1240-73 April 1973.
144. U. Potapous and J. R. Hawthorne, Nucl. Appl. 6, 27 (1969).
145. T. C. Reuther and K. M. Zwilsky, in Proceedings of Kyoto International Conference, 25-26 October 1971.
146. A. T. Santhanam, A. Taylor and S. D. Harkness, Defects and Defect Clusters in B.C.C. Metals and Their Alloys, Ed. R. J. Arsenault, N.B.S. 1973, p. 302.
147. C. Cawthorne and E. J. Fulton, Nature 216, 515 (1967).
148. A. Jostons, E. L. Long, Jr., J. E. Furguson, and K. Farrell (to be published).
149. D. M. Parkin, H. Berry, and A. N. Goland, Trans. Amer. Nucl. Soc., (to be published).

Helium in Metals

150. W. N. McElroy and H. Farrar IV, Radiation-Induced Voids in Metals, Eds., J. W. Corbett and L. C. Ianniello, U.S.A.E.C. 1972.
151. G. L. Kulcinski, Trans. Amer. Nucl. Soc. 17, (1974).
152. W. Bauer and G. Thomas, Defects and Defect Clusters in B.C.C. Metals and Their Alloys. Ed., R. J. Arsenault, NBS, 1973, p. 255.
153. W. D. Wilson and C. L. Bisson, Phys. Rev. 3B, 3984 (1971).
154. W. D. Wilson and R. Johnson, Interatomic Potentials and Simulation of Lattice Defects, Eds., P. C. Gehlen, J. R. Beeler, Jr., and R. I. Jaffee (Plenum Press, N. Y.) 1972.
155. S. T. Picraux and F. Vook, Proc. International Conf. on Applications of Ion Beams to Metals (Plenum Press, N. Y.) 1974.
156. D. L. Johnson and J. R. Cost, Defects and Defect Clusters in B.C.C. Metals and Their Alloys, Ed., R. J. Arsenault NBS. 1973, p. 279.
157. E. V. Kornelson, Rad. Effects 13, 227 (1972).
158. C. L. Snead, Jr., T. M. Hall, and A. N. Goland, Bull. Amer. Phys. Soc. 18, 394 (1973).
159. See references in R. S. Nelson, D. J. Mazey, and R. S. Barnes, Phil Mag. 11, 91 (1965).
160. See papers in Refs. 150, 152.
161. J. R. Cost and D. L. Johnson, J. Nucl. Mat. 36, 230 (1970).
162. See papers in Ref. 156 (NBS Conf.).
163. A. D. Brailsford and R. Bullough, J. Nucl. Materials 44, 121 (1972).
164. A. D. Brailsford and R. Bullough, AERE Harwell Report T.P. 527 (1973).
165. H. Wiedersich and J. L. Katz, Ref. 162, p. 530.
166. K. C. Russell and D. H. Hall, Ref. 162, p. 565.
167. F. W. Wiffen, Ref. 150, p. 386.
168. G. L. Kulcinski, J. L. Brimhall, and H. E. Kissinger, Ref. 150, p. 449.

Table Captions

Table I	Equilibrium concentrations of vacancies in pure metals from the comparison of x-ray and dilatometric thermal expansion measurements. (Ref. 10)
Table II	Positron sources.
Table III	Comparison of 2-photon angular correlation and Doppler-broadening techniques. (Ref. 45)
Table IV	Values of vacancy formation energy, trapping rate and capture cross section of vacancies for positrons in several metals. (Ref. 55)
Table V	Values of the vacancy trapping well depth, V_t , and the binding energy, E_b , calculated in the Hartree self-consistent approximation (A) and with the electron correlation effect taken into account (B). (After Hodges and Stott.)
Table VI	Parameters $\pi^{(2)}$ and $\pi^{(3)}$ for point defects of different symmetry and planes P and lines L of zero diffuse scattering around the reflections of type (h00), (hh0), and hhh). (Ref 94)
Table VII	Experimental and theoretical values of the parameters $\pi^{(2)}/\pi^{(1)}$ and $\pi^{(3)}/\pi^{(1)}$ describing the deviation of the strain field from cubicity. The theoretical values for the various single-interstitial configurations pertain to the model calculations for Cu. (Ref. 94)
Table VIII	Vibrational modes of the dumbbell. The frequencies ω'_1 are values from an analytical treatment; the frequencies ω_1 are computer results. (The maximum frequency is $\omega_m = 4.2 \times 10^{13} \text{ sec}^{-1}$; the time unit is $t_0 = 3.27 \times 10^{-15} \text{ sec.}$) (Ref. 77)

Table IX	A brief description of the reported measurements of irradiation induced changes in the elastic modulus of various materials other than copper. (Ref 121)
Table X	A brief description of the reported measurements of irradiation induced changes in the elastic modulus of copper. (Ref. 121)
Table XI	Neutron spectrum averaged cross sections for Nb. (Ref 149)
Table XII	Transmutation reactions in potential CTR first-wall materials at 0.53 MW/m^2 wall loading. (Ref 151).
Table XIII	Formation energies, in eV, for helium atoms in interstitial positions in fcc metals. Activation energies are given in the last column. The numbers in parentheses are the first-nearest neighbor displacement parameters, p , in units of the half lattice constant. (Ref. 154)
Table XIV	Formation energies, in eV, of helium atoms in interstitial positions in bcc materials. The origin is taken as a normal lattice atom. (Ref. 154)
Table XV	Substitutional detrapping energies in fcc and bcc metals. Values in parentheses are the relative energies of a helium atom in a vacancy and in an interstitial position. (Ref. 154)
Table XVI	Predicted <100> channeling structure for the calculated He locations. (Ref. 155)

Figure Captions

- Fig. 1 Changes in length l and lattice parameter a as a function of T for Al. (Ref. 13)
- Fig. 2 An idealized representation of the initial and final states of the samples in the quenching experiment. The triangles represent schematically the distribution of tetrahedron average size and density in the samples. (Ref. 21)
- Fig. 3 Schematic diagram of a field ion microscope (FIM). (Ref. 25)
- Fig. 4 Theoretical resolution for helium accommodated to various temperatures (upper curve, no accommodation). (Ref. 25)
- Fig. 5 Arrhenius plots of $\ln(\langle AC_{1V} \rangle)$ versus $1/T$ calculated for a mono-vacancy di-vacancy system in thermal equilibrium with the various vacancy parameters given, showing the variation of curvature and slope as the defect parameters are changed. The curves are presented using an arbitrary vertical scale for clarity. (Ref. 14)
- Fig. 6 Arrhenius plots of $\ln \langle AC_{1V} \rangle$ versus $1/T$ calculated for a mono-vacancy system with a temperature dependent energy and entropy of formation with various values of the parameter B . The curves are presented using an arbitrary vertical scale for clarity. (Ref. 14)
- Fig. 7 The static pair correlation function according to Sjölander and Stott (full line) and using linear response theory (broken line). (Ref. 51)
- Fig. 8 Schematic diagram of a typical 2-photon angular correlation experiment.

- Fig. 9 Angular distribution for aluminum. The points are experimental data for the [111] direction in aluminum, and the solid curve is a theoretical one normalized to the experimental counting rate at 0° . (Ref. 54)
- Fig. 10 A slice through the Fermi surface for a free-electron gas showing how the parabolic angular distribution arises.
- Fig. 11 Block diagram of slow-fast delayed coincidence method for time spectroscopy of annihilation photons.
- Fig. 12 Typical appearance of prompt and delayed spectra obtained by the delayed coincidence technique depicted in Fig. 11. (Ref. 54a)
- Fig. 13 Mean lifetime, $\bar{\tau}$, of positrons in aluminum versus temperature at which measurements were performed.
- Fig. 14 Arrhenius plot of trapping rate versus $1/kT$ showing flattening off at low temperatures. (Ref. 65)
- Fig. 15 Positron potential in a solid and at a distance x from its surface. The dashed curve represents the Hartree potential of ions and valence electrons. The full curve shows the positron pseudopotential inside the metal and the electron-positron correlation and image potentials outside. The dotted curve shows the potential acting on positronium outside the metal. (Ref. 72)
- Fig. 16 Representative annealing curves from the Kimura et al. theory. Curves 1 and 2: variable sink decay for two different sessile dislocation concentrations, 1.2×10^{-8} and 5×10^{-8} , respectively. Curves 3 and 4: simultaneous decay to variable and fixed sinks; fixed sink concentrations of $\alpha \approx 10^9$ and $\alpha \approx 10^{10}$ added to curves 1 and 2 respectively. Curve 5: a typical curve for vacancy - divacancy mechanism shown for comparison. (Ref. 6)

- Fig. 17 Illustration of the cross-cut method for determining activation energies from isothermal annealing data. (Ref. 6)
- Fig. 18 Theoretical curve showing reciprocal of concentration of defects c versus time. Linearity of curve would suggest second-order process, whereas in model used order ranges from 1.5 to 5. This illustrates difficulties which can arise in diffusion-controlled processes. (Ref. 79)
- Fig. 19 Bimolecular decay for unequal initial concentration of reactants. (Ref. 80)
- Fig. 20 Isothermal runs at 425 and 450°K. Two stages are apparent, an initial rapid annealing followed by a slower annealing stage with first-order kinetics. The primary effect of the latter is a decrease in the single-vacancy concentration. (Ref. 81)
- Fig. 21 Various possible interstitial configurations in a face-centered cubic lattice. O = octahedral positron, T = tetrahedral position, C = crowdion, H_O , H_T , H_C = dumbbell configurations with $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ axes, respectively. (Ref. 94)
- Fig. 22 Schematic illustration of experimental setup for dynamical diffraction experiment. (Ref. 111)
- Fig. 23 Data points showing experimental $As(K_\alpha)$ fluorescence x ray yields in detector D_2 as crystal 2 is scanned through the Bragg condition. Solid curve is from theoretical calculation. The sketch in the inset contrasts the different results expected for impurities directly between planes (dotted curves) and impurities in the planes (solid line). (Ref. 111)

- Fig. 24 Two-dimensional schematic illustrating the principles of foreign-atom channeling experiments. (Refs. 108, 114)
- Fig. 25 Typical arrangements for channeling measurements using Rutherford scattering or nuclear reactions. The position of the detector is arbitrary. The angles θ and ϕ correspond to goniometer motions available to vary the crystal orientation relative to the incident beam direction. Other types of detectors and incident beams are often used. (Ref. 114)
- Fig. 26 A typical energy spectrum for the scattering yield of helium ions ($E_0 \sim 1$ MeV) from an amorphous silicon target containing a heavy impurity atom (antimony) implanted to a depth of approximately 0-1 μm beneath the crystal surface. (Ref. 108)
- Fig. 27 Angular dependence of the normalized yield of backscattered He^+ ions (incident energy 1 MeV) from Al and Mn atoms in an Al-0.09 at.% Mn crystal after irradiation at 65°K with $\sim 10^{16}$ 0.3-MeV He^+ ions/cm². The yield is plotted as a function of the angle from the [110] direction near the (112) plane. The backscattering yield was measured from a depth of 1000 Å (for Mn this was an average from 500-1500 Å or twelve channels). Note that the angular dependence of the energy loss of the He^+ ions is not nearly sufficient to cause an observable peak in Mn yield. (Ref. 115)
- Fig. 28 Location of unstable sites for interstitial-vacancy pairs in the (100) plane of Cu. (Ref. 76)
- Fig. 29 The variation of δ and f_r with temperature in the temperature range from 5 to 16 K of a $\langle 111 \rangle$ - oriented single crystal copper sample. (Ref. 136)

- Fig. 30 The temperature variation of δ and f_r after subtracting the background in the temperature range from 5 to 16 K of a $\langle 111 \rangle$ - oriented single crystal copper sample. (Ref. 136)
- Fig. 31 A comparison of δ and f_r in the temperature range 5 to 60 K of a $\langle 100 \rangle$ - oriented single crystal copper sample after irradiation and after annealing to 55 K. (Ref. 136)
- Fig. 32 The linear variation of $\ln(2\pi f_r)$ vs. $1/T_{\max}$ for all samples having an anelastic process around 10 K. (Sample numbers are shown near data points.) (Ref. 136)
- Fig. 33 Most probable configuration of stage I_c defect deduced from elastic-constant data. Four of the 24 equivalent sites for the center of mass of the interstitial are marked with a small cross. The equivalent position into which the split-interstitial relaxes is shown by a dotted outline. (Ref. 123)
- Fig. 34 The logarithmic decrement versus temperature results for the preirradiation and anneal runs on a $[100]$ single crystal of tungsten which was previously subjected to heavy dislocation-pinning irradiations. (Ref. 137)
- Fig. 35 The logarithmic decrement versus temperature results for the preirradiation and anneal runs on a $[100]$ and a $[110]$ single crystal. Both samples were subjected to identical irradiation and annealing treatments. (Ref. 137)
- Fig. 36 The derivative of the isochronal resistivity - recovery curve for a polycrystalline sample of tungsten. (Ref. 137)
- Fig. 37 Isochronal recovery of pure Pt irradiated at 4.5K with 3-MeV electrons to $\Delta\rho_0 = 56 \text{ n}\Omega\text{cm}$ (equivalent to about 50 ppm Frenkel defects). (Ref. 140)

- Fig. 38 Schematic view of the reactions of freely migrating interstitials in stages I_D and I_E . *, interstitial, $\square$, vacancy. (Ref. 140)
- Fig. 39 Total creep elongation and rupture life as a function of fast neutron fluence for annealed type 304 stainless steel tested at 550 C and 35,000 psi. (Ref. 143)
- Fig. 40 Comparison of radiation embrittlement (as measured by Charpy - V notch 5.2 kg/cm² transition temperature) of steels with varying amounts of residual phosphorus and copper. (Refs. 144, 145)
- Fig. 41 Density change, $-\Delta\rho/\rho$, as a function of fluence in aluminum and several of its alloys irradiated at about 50C. (Ref. 148)
- Fig. 42 Comparison of the primary-atom recoil energy spectrum, $P(T)$, for Nb in a fission spectrum (EBR-II, row 7), and in a fusion first-wall spectrum (Benchmark). The neutron spectra are shown in the upper portion of the figure. (Ref. 149)
- Fig. 43 Helium production in stainless steel for different reactor spectra. *Major elements only. Helium produced by nuclear reactions with Fe, Ni, and Cr only. (Ref. 150)
- Fig. 44 Effect of helium on the tensile ductility of V-15 wt % Cr-t wt % Ti. (Ref. 146)
- Fig. 45 SEM micrographs of Nb surface following injection of helium at indicated temperatures. (Ref. 152)
- Fig. 46 Symmetrical interstitial positions for a helium atom in metal lattice (a) in fcc; (b) in bcc. The (1,0,1) and (0,0,1) configurations are identical. (Ref. 154)

- Fig. 47 Axial $\langle 100 \rangle$ angular scans using 500 keV D analysis beam for W implanted with ^3He under conditions indicated at top of curves. (Ref. 155)
- Fig. 48 Angular scan through the $\langle 100 \rangle$ axis for W with $3 \times 10^{15}/\text{cm}^2$, 30 keV D implant at 296K using a 750 keV ^3He analysis beam: 0 corresponds to backscattered yield from W and Δ corresponds to proton nuclear reaction yield from D. (Ref. 155)
- Fig. 49 Helium desorption spectrum for a damaging bombardment of $8 \times 10^{11}/\text{cm}^2$ 5 keV Kr^+ and injection of $8 \times 10^{12}/\text{cm}^2$ 250 eV He^+ . Dashed curves indicate theoretical desorption transients (assuming first order kinetics and a rate constant $\sim 10^{13}$) from which the spectrum could be formed. (Ref. 157)
- Fig. 50 Populations of individual peaks as a function of damage anneal temperature. Damage and injection parameters were the same as in Fig. 49. (Ref. 157)
- Fig. 51 Rates of void-nucleation on clusters of one to four gas atoms and homogeneous void-nucleation rates (no gas) as functions of vacancy supersaturation at 400 C. The assumed concentrations of the gas clusters are indicated as atom fractions. (Ref. 162)
- Fig. 52 Rates of void-nucleation on clusters of one to four gas atoms and homogeneous void-nucleation rates (no gas) as functions of vacancy supersaturation at 600 C. The assumed concentrations of the gas clusters are indicated as atom fractions. The supersaturation range in reactors falls below the supersaturation shown. (Ref. 162)
- Fig. 53 Relation between gas-cluster size and the minimum vacancy supersaturation to remove the barrier to void nucleation at several temperatures. (Ref. 162)